70-23,005

RUSSO, Peter Joseph, 1943-
SYNTHESES AND REACTIONS OF σ-SILYL-π-CYCLOPENTADIENYL TRICARBONYL DERIVATIVES OF CHROMIUM MOLYBDENUM, AND TUNGSTEN AND SYNTHESES AND REACTIONS OF SILYL DERIVATIVES OF CYCLOPENTADIENE AND METHYLCYCLOPENTADIENE.

The University of Oklahoma, Ph.D., 1970
Chemistry, inorganic

University Microfilms, A XEROX Company, Ann Arbor, Michigan

THE UNIVERSITY OF OKLAHOMA

GRADUATE COLLEGE

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and

SYNTHESES AND REACTIONS OF SILYL DERIVATIVES OF CYCLOPENTADIENE AND METHYLCYCLOPENTADIENE

A DISSERTATION

SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

BY

PETER JOSEPH RUSSO

Norman, Oklahoma

1970

SYNTHESES AND REACTIONS OF σ-SILYL-π-CYCLOPENTADIENYL TRICARBONYL DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

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SYNTHESES AND REACTIONS OF SILYL DERIVATIVES OF CYCLOPENTADIENE AND METHYLCYCLOPENTADIENE

APPROVED BY

Arnulf P. Hagen
Betty L. Pollak
Murphy
Stanley C. Neely

DISSERTATION COMMITTEE

IN MEMORIAM

Peter Ernest Russo M.D. 1904-1963

Peter Ernest Russo was born in Cortelone, Italy and became a pioneer in his early teens when he left his motherland and journied to the United States of America to begin a new life. His early education was received from the parochial schools of Cleveland, Ohio; he was graduated from Western Reserve University in 1926 with a B.A. degree. In 1930 he received his M.D. from St. Louis University. For ten years, 1931 to 1941, he engaged in general practice at St. John's Hospital of Cleveland. Radiology became his speciality and once again he became a pioneer to start a new life in Oklahoma City at University Hospital in 1941. He founded the Oklahoma City Radiological Society which was to eventually grow to five physicians. His honors were: President-Elect of the Oklahoma State Medical Association at the time of his death; Vice-President of the Radiological Society of North America in 1956; President of the Rocky Mountain Radiological Society in 1961; President of the Southwestern Chapter of the American Society of Nuclear Medicine in 1959-60; a member of the Radiological Society of North America; a member of the British Institute of Radiology; a Diplomat of the American Board of Radiology; author of thirty papers published in his speciality; Chairman and Professor Emeritus of the Department of Radiology of the University of Oklahoma Medical Center.

It is true that Peter Ernest Russo was a father, a physician, a teacher, a scholar, an artist, and a sportsman. His total person, radiant with a multitude of self-acquired virtues and principles, rose above the average for he was an uncommon man, and his way of life remained unique, an examplar of a meaningful, enriched, and devoted life. And it is true that Peter Ernest Russo patterned his life after another uncommon man, for he acknowledged his life as a mission to heal the sick, to comfort those in distress, and to kindle love in the hearts he touched. Seldom is there a man who practices meticulously what he preaches, who is honest without sacrifice, who is wise without pomp, who is critical without sarcascism, who accepts others without arrogance. And seldom is there a man who is humble with sensitivity, who helps others with pleasure, who speaks with kindness, and who advises with depth and understanding. And seldom is there a happy man. Peter Ernest Russo was most assuredly this rare and singular individual. His merits, quality of character, and works speak honestly of him. And these live in those who knew him and were close to him.

As the author and son gives his fullest esteem to his father, I am grateful and happy.

ACKNOWLEDGEMENTS

This research was initially funded by NASA grant number NGL 37-003-026; support was continued from the Petroleum Research Fund administered by the American Chemical Society during the author's terminal year of research at the University of Oklahoma.

The author thanks:

Dr. A. P. Hagen for his assistance in interpreting spectral data, practical as well as theoretical contributions throughout this manuscript and letters of recommendation.

Mr. Ron Stermer for his expert glass blowing.

Dr. Pat Flanigan (Continental Oil, Ponca City, Oklahoma) for running the initial low temperature n.m.r. samples of $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$.

Mr. J. D. Hoover for his drawings and sketches contained in this manuscript.

Earnestly and *most* *sincerely*, the author acknowledges the following persons who helped make this degree possible, a group to whom the author feels most indebted and now wishes to gratefully thank:

Mrs. P. E. Russo (Western Reserve D.D.S.) for her financial support throughout the author's academic career.

Mrs. Odilia Harvey (Randolph Macon B.A.) and Mrs. Elydreth Horton (University of Oklahoma B.A.) for their sisterly advice and encouragement.

Mrs. Petrina Browning (Oklahoma State University B.A.), twin sister, for her natural abilities, competitive spirit, and unfaltering stamina.

Mr. Gerald DeJon (University of Oklahoma M.S.) and Mrs. Gerald DeJon (University of Oklahoma B.A.) for being the author's second set of parents who taught true discipline, a sincere concern for others, and self-respect magnificiently.

Dr. Lynn Harrison, Dr. Hubert Anderson, Dr. Elmer Ridgeway, Dr. Ace Lile, and Dr. James Amspacher, their wives, and their families for their warm friendship and gracious kindness.

Mr. Lance Rentzel (University of Oklahoma B.S.) for his desire to succeed, the utilization of his natural abilities and talents, and his attitude of self-confidence.

Mr. Richard Marble (Harvard University M.S.) for his expert, precise, and enlightening method of instruction.

Mrs. Gilbert Tuck (University of Massachusetts B.S.) for her criticism and critical analysis of people and situations.

Mr. Burrage Warner (Harvard University A.B., M.Ed.) for his understanding and kind words.

Members of Alpha Epsilon Phi Sorority and Beta Theta Pi Fraternity for their friendship.

Miss Margee Blanchard for typing this dissertation and for her patience, strength, and love.

And numerous others for their assistance and moral support.

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CHAPTER I

INTRODUCTION

The primary goal of this research problem was to synthesize an organometallic compound containing a silicon-chromium linkage; extension of the research problem to include chromium's congeners, molybdenum and tungsten, was pursued in order that the silicon linkage to all three Group VI b transition metals could be studied. The first organometallic compounds of Group VI b linked chromium, molybdenum, and tungsten to the first element in Group IV, carbon. With the exception of silicon, the remaining Group IV (Ge, Sn, Pb) elements were linked much later to all three Group VI b metals.

Since no silicon-chromium linkage had been prepared in the form of an organometallic compound until this research problem was proposed, this dissertation in physical-inorganic synthetic chemistry now provides the missing silicon-chromium linkage.

The importance of the research problem lies in the comparison of the chemistries of silicon and carbon, since the presence of energetically available "3d" orbitals in silicon causes the chemistry of silicon to differ from the chemistry of carbon. Studies carried out by other workers on silicon bonded to transition metals have resulted in several interesting theories regarding the nature of silicon-transition metal bond. It is therefore of particular interest to examine the physical, spectroscopic, and chemical properties of analogous silicon and carbon compounds in order to determine how these elements are similar to, or different from, each other. Rationalization of the similarities and differences between similar silicon and carbon organometallic derivatives is therefore expected to enhance the understanding of factors (electronegativity, atomic size, octet behavior) which cause the properties of these elements and their compound analogues to change. For this reason, the novel compounds, $H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)$; (M=Cr, Mo, W)--the silicon analogues of $H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)$--were synthesized.

The research problem was extended further to the study of cyclopentadiene and its derivatives due to the discovery of $C_5H_5SiH_3$, the silicon analogue of methyl-cyclopentadiene ($C_5H_5CH_3$). As a consequence, the study of analogous silicon and carbon derivatives of cyclopentadiene was pursued in the light of investigating the chemistry of silicon and carbon in a non-metallic, unsaturated environment.

In summary, Chapter III (Exp. II-A) of this dissertation describes the study of the new, silyl organometallic derivatives of chromium, molybdenum, and tungsten, and Chapter III (Exp. II-B) describes the study of the new silyl derivatives of cyclopentadiene and methylcyclopentadiene. Whereas, Chapter II (Exp. I-C) relates the preliminary syntheses of several known organometallic compounds of Group VI b and the miscellaneous syntheses of known organometallic compounds of other transition metals and silicon derivatives of cyclopentadiene and methylcyclopentadiene.

(A)

Silicon-Organometallics

The organometallic chemistry of chromium, molybdenum, and tungsten had its early beginning in the middle 1950's both in Germany and in the United States. In particular, the principle works of E. O. Fischer [1] at the University of Munich and T. S. Piper and G. Wilkinson [2] at Harvard University describe the initial study of the formation of compounds containing carbonyl and a five-membered cyclopentadienyl ring bonded co-ordinate covalently to a Group VI b transition metal.

E. O. Fischer and co-workers prepared such organometallic compounds which took the form of either (1) alkali-metal salts prepared by heating an alkali cyclopentadienide salt in N,N-dimethylformamide with a Group VI b metal hexacarbonyl according to the equations:

$$K[C_5H_5] + Cr(CO)_6 \rightarrow K[Cr(CO)_3(\pi\text{-}C_5H_5)] + 3CO \qquad (1)$$

$$Na[C_5H_5] + Mo(CO)_6 \rightarrow Na[Mo(CO)_3(\pi\text{-}C_5H_5)] + 3CO \qquad (2)$$

$$Li[C_5H_5] + W(CO)_6 \rightarrow Li[W(CO)_3(\pi\text{-}C_5H_5)] + 3CO \qquad (3)$$

or (2) a metal hydride prepared through the reaction of an appropriate alkali-metal salt with acetic acid according to the equation,

$$M'[M''(CO)_3(\pi\text{-}C_5H_5)] + H_3CCOOH \rightarrow H\text{-}M''(CO)_3(\pi\text{-}C_5H_5) + H_3CCOO^-M'^+ \qquad (4)$$

where M'=K, Na, Li; M''=Cr, Mo, W; or (3) a methyl-metal derivative prepared by the reaction of the hydride of tungsten with diazomethane according to the equation:

$$H\text{-}W(CO)_3(\pi\text{-}C_5H_5) + CH_2N_2 \rightarrow H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5) + N_2 \qquad (5)$$

Thus Fischer and co-workers were most successful in transforming the hexacarbonyls of Group VI b metals into reactive intermediate species, since the yellow alkali-metal salts were air-sensitive and quite reactive in solution.

About the same time, Piper and Wilkinson reported another method of preparing the methyl-metal derivatives, viz.,

$$Na[M(CO)_3(\pi\text{-}C_5H_5)] + H_3CI \rightarrow H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5) + NaI \qquad (6)$$

All three methyl-metal derivatives readily sublimed in high vacuum at 60° in yields of 1-3% for chromium, 4% for molybdenum, and 80% for tungsten, and their thermal stabilities decreased from tungsten to chromium. Due to thermal instability, the methyl-chromium derivative was identified by infrared analysis only.

Another interest of Piper and Wilkinson[3] which proved to be most significant was their synthesis of the <u>first</u> compound containing a <u>transition metal</u> linked to <u>silicon</u>. The desired product was prepared in the form of a trimethylsilyl derivative by reaction of the sodium-iron salt with trimethylchlorosilane according to the equation:

$$Na[Fe(CO)_2(\pi\text{-}C_5H_5)] + (CH_3)_3SiCl \rightarrow (CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5) + NaCl \qquad (7)$$

This trimethylsilyl-iron derivative was air-sensitive but melted without decomposition. However, the words of Piper and Wilkinson[4], "...There would now seem to be no reason, in principle, why alkyl and aryl derivatives of other transition metals as V, Co, Ni cannot be made provided that other stabilizing groups e.g. C_5H_5, CO, or NO, are present in the molecules. The possibilities and also the possibility of forming compounds with bonds from the metal to elements such as P, Si, O etc., by the reaction of suitable halides with sodium salts, as above, are currently being investigated." never materialized at that time in the specific case of the Si-metal linkages of Group VI b since no further reports appeared on the subject.

About ten years after the initial success of Fischer and co-workers and Piper and Wilkinson, Patil and Graham[5] attempted to synthesize compounds containing a Group VI b transition metal linked to silicon following the method of Piper and Wilkinson (Eq 7), viz.,

$$2Na[M(CO)_3(\pi\text{-}C_5H_5)] + 2(CH_3)_3SiCl \rightarrow [M(CO)_3(\pi\text{-}C_5H_5)]_2 + ((CH_3)_3Si)_2 + 2NaCl \qquad (8)$$

But their results were dimerization of the starting materials. However, following the known method of Chalk and Harrod[6], Jetz and Graham reported[7] the synthesis of the <u>first</u> compound containing a <u>silicon-molybdenum</u> linkage in the form of a trichlorosilyl derivative by the reaction of bis[tricarbonyl-π-cyclopentadienylmolybdenum] with trichlorosilane at elevated temperatures according to the equation:

$$[Mo(CO)_3(\pi\text{-}C_5H_5)]_2 + 2HSiCl_3 \rightarrow 2Cl_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + H_2 \qquad (9)$$

This trichlorosilyl-molybdenum derivative melted without decomposition at 150°. It should be noted that under similar conditions, this researcher performed Eq (9) with chromium, but the dimer of chromium failed to give a positive reaction with $HSiCl_3$ at 110° thus excluding this method as a possible way to obtain a trichlorosilyl-chromium derivative.

The initial interest of Jetz and Graham in using the cyclopentadienyl group as a ligand appears to have been diverted in favor of the six-membered benzene ring in pursuing the organometallic chemistry of chromium, since they have also reported[8] the synthesis of a trichlorosilyl hydride derivative of chromium by a photochemical modification of the method of Chalk and Harrod, viz.,

$$(\pi\text{-}C_6H_6)Cr(CO)_3 + HSiCl_3 \xrightarrow{u.v.} Cl_3Si\text{-}CrH(CO)_2(\pi\text{-}C_6H_6) + CO \qquad (10)$$

Also, Lappert and co-workers[9] have reported the preparation of the trimethylsilyl derivatives of molybdenum and tungsten by the reaction of the appropriate metal hydride with N-dimethyltrimethylsilylamine in tetrahydrofuran according to the equation:

$$H\text{-}M(CO)_3(\pi\text{-}C_5H_5) + (CH_3)_3Si\text{-}N(CH_3)_2 \rightarrow (CH_3)_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5) + HN(CH_3)_2 \qquad (11)$$

The desired products were yellow colored and sublimed <u>in vacuo</u> at 100° with some decomposition. No trimethylsilyl-chromium derivative was mentioned at that time; in fact, from all previous indications it appeared that either (1) it was impossible to prepare a trimethyl- or trichlorosilyl-chromium derivative in the presence of the cyclopentadienyl group as a coordinating ligand because of the proposed silicon-metal bond thermal stability trend Si-Mn<Si-Fe<Si-Co [5,9] ; or (2) the methods of preparation used successfully in the past for silicon-molybdenum and tungsten derivatives appeared to be inapplicable to chromium because of chromium's sensitivity to temperature and the type of substituent on the silicon atom.

Consequently, a solution to the chromium problem, i.e., the inability of organometallic chemists to form a silicon-chromium linkage in the presence of the bonding cyclopentadienyl ligand, was attempted in the summer of 1968. It was decided to prepare such a linkage by abandoning earlier methods of preparation in favor of a novel, synthetic scheme; Chapter III (Exp. II-A) is devoted to the complete description of this new synthetic technique, but a brief summary is now presented to give an overall picture of the necessary synthetic features.

First, it was decided to change the environment around silicon so that its chemical surroundings resembled that of carbon in methyl bromide (H_3CBr). The desired silicon starting material (H_3SiBr) was obtained in a two step process which involved replacement of chlorine by hydrogen through hydrogenation of phenyltrichlorosilane followed by protonic cleavage of the Si-C bond and bromination of the H_3Si group according to the equations:

$$4C_6H_5SiCl_3 + 3LiAlH_4 \rightarrow 4C_6H_5\text{-}SiH_3 + 3LiCl + 3AlCl_3 \qquad (12)$$

$$C_6H_5\text{-}SiH_3 + HBr \xrightarrow[-78°]{} H_3SiBr + C_6H_6 \qquad (13)$$

Second, other workers in this area had preference toward sodium metal either by itself or in a mercury amalgam; it was decided to use pure potassium metal which Fischer had also used.

Third, after several attempts to find an appropriate solvent, 1,2-dimethoxyethane (b.p. 84°) was selected as a suitable solvent which could be easily handled in high vacuum chemistry.

Fourth, upon the formation of an appropriate potassium-metal salt of Group VI b, e.g.,

$$K + C_5H_6 \rightarrow K[C_5H_5] + 1/2\,H_2 \qquad (14)$$

$$K[C_5H_5] + M(CO)_6 \rightarrow K[M(CO)_3(\pi\text{-}C_5H_5)] + 3CO \qquad (15)$$

it was decided to <u>isolate</u> the potassium-metal salt by removal of the solvent by ordinary distillation under an inert atmosphere; the salt was dried thoroughly by heating at 60° to remove any unreacted metal hexacarbonyl.

Fifth, when the salt was considered dry and free of any $M(CO)_6$, it was then reacted with silyl bromide *in vacuo* at room temperature:

$$K[M(CO)_3(\pi\text{-}C_5H_5)] + H_3SiBr \rightarrow H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5) + KBr \qquad (16)$$

The results of Eq (16)--the formation of the new, σ-silyl-π-cyclopentadienyl tricarbonyl derivatives of chromium, molybdenum, and tungsten--comprise Chapter III (Exp. II-A-1, 2, 3) of this manuscript.

The only other H_3Si-metal compound to have been prepared containing the bonding cyclopentadienyl group is $H_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ and has been reported by Amberger, Mühlhofer, and Stern.[10] Using oppositely charged species employed by this researcher, their synthesis employed 1,2-dimethoxyethane as the solvent and differed from Eq (16) since the following reaction (13% yield of $H_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$) was performed at -40°:

$$(\pi\text{-}C_5H_5)Fe(CO)_2Br + KSiH_3 \rightarrow H_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5) + KBr \qquad (17)$$

A few reactions of organometallic compounds of molybdenum have been studied. (1) bond cleavage reactions occur according to the equations;

$$H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + CCl_4 \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_3Cl + HCCl_3 \qquad (18)$$

$$H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + H_3CI \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_3I + CH_4 \qquad (19)$$

$$Hg[Mo(CO)_3(\pi\text{-}C_5H_5)] + I_2 \rightarrow 2(\pi\text{-}C_5H_5)Mo(CO)_3I + Hg \qquad (20)$$

affording organo-halide derivatives of molybdenum.[2] (2) replacement of the Mo-Mg bond by the Mo-Hg bond[11] according to the equation:

$$(\pi\text{-}C_5H_5)(CO)_3Mo\text{-}MgBr + HgCl_2 \rightarrow (\pi\text{-}C_5H_5)(CO)_3Mo\text{-}HgCl + MgClBr \qquad (21)$$

(3) carbonyl insertion reactions with trisubstituted phosphorus ligands according to the equation,

$$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + L \rightarrow H_3C(CO)Mo(CO)_2L(\pi\text{-}C_5H_5) \qquad (22)$$

affording acyl complexes [12,13]; similar reaction occurs for $H_3C\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$, viz.,

$$H_3C\text{-}Fe(CO)_2(\pi\text{-}C_5H_5) + PR_3 \rightarrow H_3C(CO)Fe(CO)(PR_3)(\pi\text{-}C_5H_5) \qquad (23)$$

where $R=CH_3$, C_6H_5, OCH_3.[14,15] The following reaction, i.e.,

$$(H_3C)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5) + PR_3 \xrightarrow{u.v.} (H_3C)_3Si\text{-}Fe(CO)(PR_3)(\pi\text{-}C_5H_5) + CO \qquad (24)$$

indicates that "...the silicon-iron bond is so stabilized by d_π-d_π bonding that it cannot be broken by a carbonyl ligand..." [16] (4) substitution and unsymmetrical cleavage reactions of $[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$ with substituted phosphines have also been studied.[17,18,19] Similar reactions have been studied with other types of molybdenum derivatives.[20,21,22]

The relatively few number of organometallic compounds containing the Si-transition metal linkage are listed along with some of the carbon analogues in table 1.

ORGANOMETALLIC R_3Si-M AND R_3C-M BONDS

R=alkyl, aryl, halo; Cp=π-C_5H_5; Ph=C_6H_5

Carbon-Metal	ref	ref	Silicon-Metal
H_3C-Cr(NO)$_2$Cp	23		
H_3C-Cr(CO)$_3$Cp	2		H_3Si-Cr(CO)$_3$Cp
		9	$(CH_3)_3Si$-Mo(CO)$_3$Cp
F_3C-Mo(CO)$_3$Cp	31	7	Cl_3Si-Mo(CO)$_3$Cp
H_3C-Mo(CO)$_3$Cp	4		H_3Si-Mo(CO)$_3$Cp
		3	$(CH_3)_3Si$-W(CO)$_3$Cp
H_3C-W(CO)$_3$Cp	2		H_3Si-W(CO)$_3$Cp
		3	$(CH_3)_3Si$-Fe(CO)$_2$Cp
		5	Ph_3Si-Fe(CO)$_2$Cp
F_3C-Fe(CO)$_2$Cp	31	7,36	Cl_3Si-Fe(CO)$_2$Cp
H_3C-Fe(CO)$_2$Cp	24	10	H_3Si-Fe(CO)$_2$Cp
F_3C-Ni(CO)Cp	30	7	Cl_3Si-Ni(CO)Cp
H_3C-Ni(CO)Cp	30		
		39	$(Cl_3Si)_2$-Co(CO)Cp

Table 1

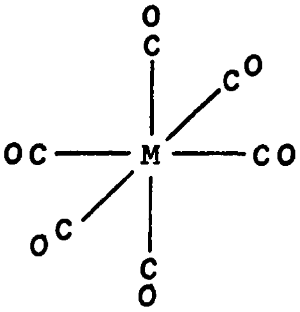
		41	$(CH_3)_3Si\text{-}Mn(CO)_5$
		29	$Ph_3Si\text{-}Mn(CO)_5$
$F_3C\text{-}Mn(CO)_5$	28		
$H_3C\text{-}Mn(CO)_5$	25,26	35	$H_3Si\text{-}Mn(CO)_5$
		34	$(Cl_3Si)_2\text{-}Fe(CO)_4$
		37	$(H_3Si)_2\text{-}Fe(CO)_4$
		37	$H_3Si\text{-}FeH(CO)_4$
		6	$R_3Si\text{-}Co(CO)_4$; R=Ph, Cl
$F_3C\text{-}Co(CO)_4$	28	33	$F_3Si\text{-}Co(CO)_4$
$H_3C\text{-}Co(CO)_4$	27	32	$H_3Si\text{-}Co(CO)_4$
		38	$(CH_3)_3Si\text{-}Co(CO)_4$
		40	$CH_3H_2Si\text{-}Co(CO)_4$
		40	$CH_3F_2Si\text{-}Co(CO)_4$

$(Cl_3Si)_2CrH(CO)_2(\pi\text{-}C_6H_6)$

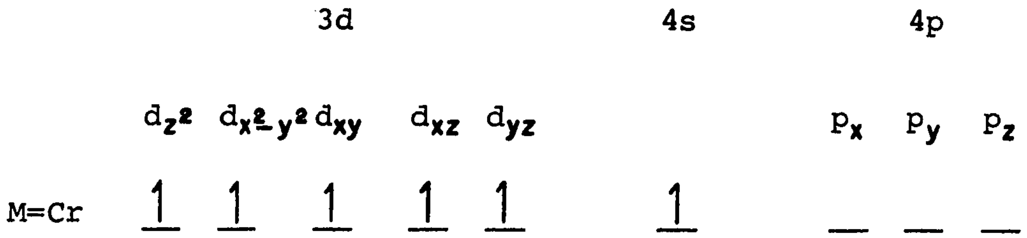
8

Table 1 cont.

This synthetic chemistry of Group VI b organometallic derivatives originates with the hexacarbonyls of chromium, molybdenum and tungsten.[42] Here the hexacoordinate transition metal is pictured[43] as occupying the center of an octahedron with four carbonyl ligands occupying the four corners of a square in the plane of the metal with the other two carbonyl ligands one lying above and the other below this plane. A picture of $M(CO)_6$ where M=Cr, Mo, W is shown below.

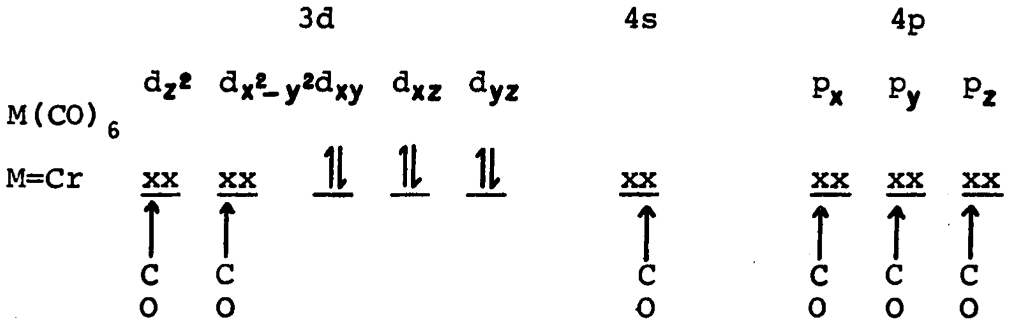


The uniqueness of such a compound is recognized when its chemical properties are investigated, or when one understands the electronic structure of the molecule. To be specific, this octahedral arrangement containing six carbonyls as ligands bonded co-ordinate covalently to the metal means that each carbonyl ligand donates two electrons for a total of twelve electrons (for six carbonyl ligands) shared with the central metal atom. The peculiar feature about the metal atom which differentiates it from other elements outside the transition metal family in the periodic table is that such an electron donation by ligands to the metal can and does occur due to the presence of vacant or unoccupied "d" orbitals of the metal. The electronic configuration of the free chromium (isolated atom) atom in its zero valency state without the presence of ligands is shown below:



The notation for this electron configuration of the free chromium atom is $3d^5 4s^1$; similarly, the notation for the free molybdenum and tungsten atoms are $4d^5 5s^1$ and $5d^5 6s^1$ respectively.

The next illustration represents the transition metal chromium, still in its zero valency state, coordinated to six carbonyl ligands as in $M(CO)_6$ with each carbonyl ligand donating a pair of electrons to the metal's vacant "d" orbital.

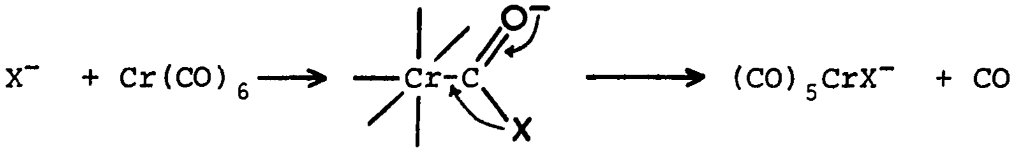


It is therefore assumed that the metal makes available to the six carbonyl ligands its $3d_{z^2}$, $3d_{x^2-y^2}$, 4s, $4p_x$, $4p_y$, and $4p_z$ orbitals; and linear combinations of these metal orbitals with the ligands' orbitals form twelve molecular orbitals (six bonding and six antibonding) in which the twelve ligand electrons are placed in the six bonding molecular orbitals to give a stable electronic arrangement in the molecule. The linear combinations of of molecular orbitals have been given elsewhere.[44,45,46,47,48]

Caulton and Fenske[49] have performed M.O. calculations on $Cr(CO)_6$ to determine electron charge density in the internuclear carbon-oxygen region and have suggested that carbon can therefore be susceptible to nucleophilic attack in which an acyl halide derivative is postulated as an intermediate.

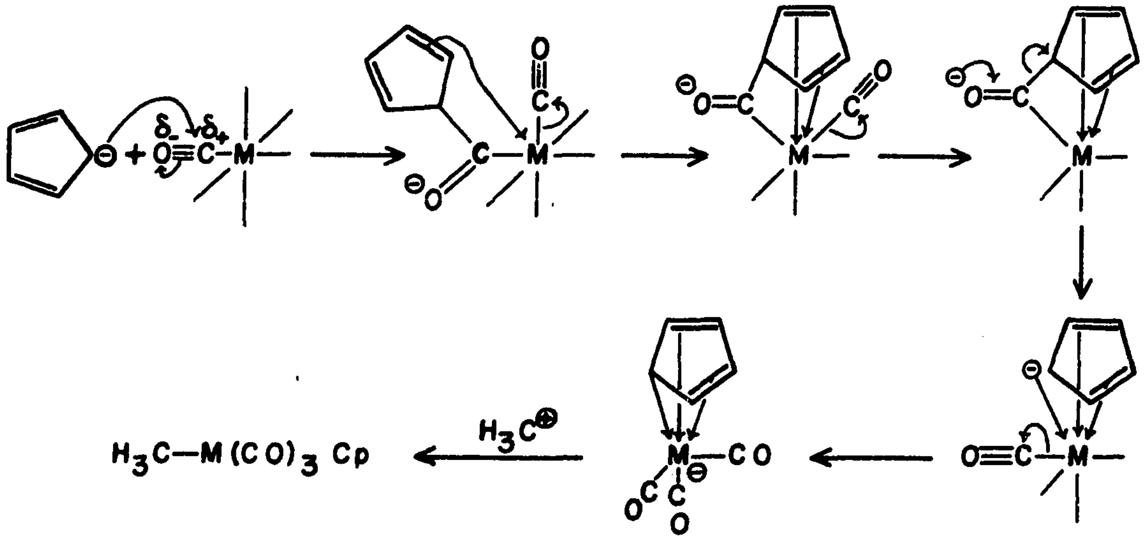
Thus, the formation of $K[M(CO)_3(\pi\text{-}C_5H_5)]$ from $M(CO)_6$ is an interesting mechanism to propose, since three carbonyls have been replaced by the six-electron donating ligand $C_5H_5^-$ where one hydrogen atom has been removed from the saturated (sp^3 hybridized) carbon atom in C_5H_6 leaving a pair of electrons at this carbon position. $C_5H_5^-$ has been ascribed aromatic properties[43,50,51] and can be pictured in an analogous way with benzene, i.e.,[110]

Following the proposed nucleophilic attack mechanism of Caulton and Fenske, in which the postulated acyl halide derivative of $Cr(CO)_6$ could react to form the pentacarbonyl halide according to the equation



(25)

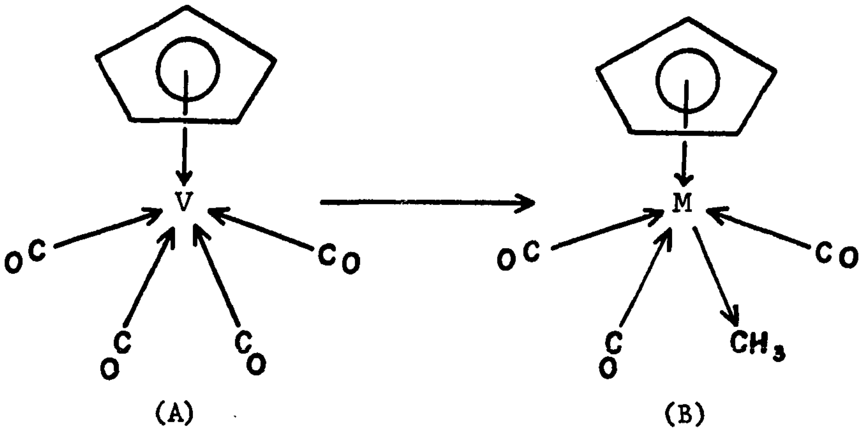
by an internal displacement, the nucleophilic attack by $C_5H_5^-$ on the metal carbonyl $M(CO)_6$ can be proposed as follows:



(26)

(27)

The compound $H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ can then be assumed to have a structure similar to the organometallic molybdenum chloride, $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$[52], in which the molybdenum atom is sandwiched between the cyclopentadienyl group above and by the three carbonyls and the chloride below. When the chloride atom is replaced by H_3C, the methyl group is assumed to reside on the same side as the carbonyls. An easier transformation to the methyl-metal specie can be made by considering the locally symmetric compound $(\pi\text{-}C_5H_5)V(CO)_4$ which is isoelectronic with $(\pi\text{-}C_5H_5)Cr(CO)_3CH_3$; it can now be imagined that when $(\pi\text{-}C_5H_5)V(CO)_4$ is replaced by $(\pi\text{-}C_5H_5)Cr(CO)_3CH_3$ one of the carbonyls is replaced by the methyl group as shown pictorially below:



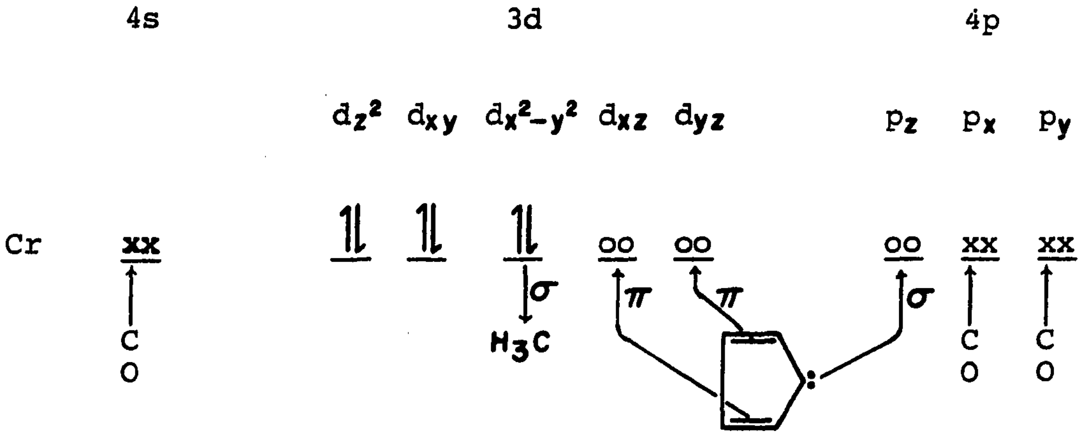
(28)

Structure (A) has local C_5 symmetry above and local C_4 symmetry below, but Structure (B) has local C_5 symmetry above and no local symmetry below. When nearly C_4 symmetry is assumed below, the following orbitals for the $C_5H_5^-$ group and a transition metal have been assigned to the irreducible representations under the appropriate symmetry:[45,53]

$$C_5H_5 \xrightarrow{C_5} \begin{cases} A_1 \\ E_1 \\ E_2 \end{cases}$$

$$\begin{tikzcd}
 & C_5 \begin{cases} A_1 - (s), (p_z, d_{z^2}) \\ E_1 - \quad (p_x, p_y), (d_{xz}, d_{yz}) \\ E_2 - \quad\quad (d_{xy}, d_{x^2-y^2}) \end{cases} \\
\text{transition metal} \arrow[ur] \arrow[dr] & \\
 & C_4 \begin{cases} A_1 - (s), (p_z), \quad (d_{z^2}) \\ B_1 - \quad\quad (d_{x^2-y^2}, d_{xy}) \\ E_1 - \quad (p_x, p_y), (d_{xz}, d_{yz}) \end{cases}
\end{tikzcd}$$

Due to the complex situation of assigning symmetry orbitals participating in the chemical bonding of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, a simplification is made by displaying the electron configuration for $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and is shown below:



The positions of the ligands' electrons have been shown in the labeled orbitals only to illustrate the most likely orbitals used in the structure; and the methyl-metal ($H_3C \leftarrow M$) linkage has been proposed as a pure sigma co-ordinate covalent bond from chromium to carbon. Upon resolving the carbonyl region (using cyclohexane as the solvent), King and Houk[54] have been able to perform force constant calculations on the methyl-metal derivatives of molybdenum and tungsten whose structures are based on the above Structure (B).

(B)

Silicon-Cyclopentadienes

Methylcyclopentadiene ($C_5H_5CH_3$) has been known for several years as a naturally occurring petroleum fraction (100-200°)[55], has antiknock characteristics[56], and is used in aircraft fuels.[57] The organometallic chemistry of $C_5H_5CH_3$ involves the anion $C_5H_4CH_3$ as a six-electron donating ligand in compounds such as $[Mo(CO)_3(\pi\text{-}C_5H_4CH_3)]_2$[58] and $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$.[59] Substituted alkyl ferrocences are also known.[60,61]

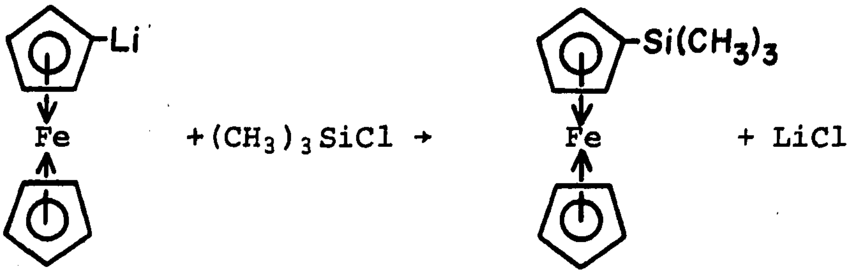
Alkyl and halo substituted silyl derivatives of cyclopentadiene and methylcyclopentadiene have been prepared with a trimethylsilyl[62] or trichlorosilyl[63] group attached to the C_5H_5 or $C_5H_4CH_3$ moiety according to the equations,

$$Na[C_5H_5] + R_3SiCl \rightarrow C_5H_5SiR_3 + NaCl \qquad (29)$$

$$Na[C_5H_4CH_3] + R_3'SiCl \rightarrow C_5H_4(CH_3)(SiR_3') + NaCl \qquad (30)$$

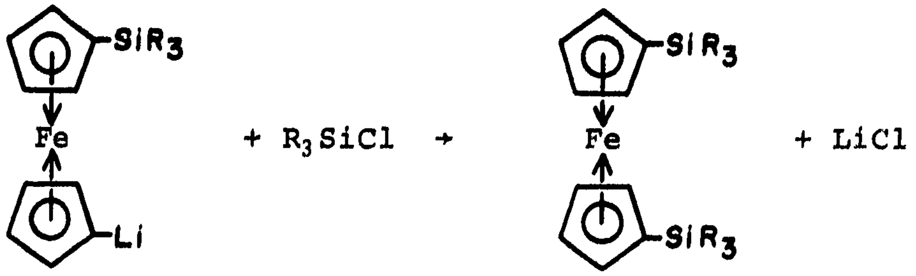
where $R=CH_3$, Cl; $R'=CH_3$.

The synthesis of a metalated ferrocence derivative has been reported[64] to occur according to the equation:



(31)

Disubstituted silyl ferrocences[65,66,67,68] have been prepared in a similar manner, i.e.,



(32)

While the chemistry of the Si-C bond is well documented [69,70,71], some reactions of the silicon-carbon linkage occur through (1) Diels-Alder Addition [72]; (2) cleavage by protonic reageants-HX; (X=Cl, Br, I)[73]; (3) cleavage by free halogens-X_2; (X=Cl, Br, I)[74,75]; and (4) cleavage by sodium-potassium alloy-Na/K.[76]

Desilylation (Si-C rupture) can be caused by a sodium-potassium alloy, since the Si-C bond can be weakened by the presence of bulky groups on silicon and carbon; and the product should be capable of resonance stabilization, viz.,[76]

$$C_6H_5C(CH_3)_2Si(C_6H_5)_3 + Na/K \rightarrow C_6H_5C(CH_3)_2K + (C_6H_5)_3SiK \qquad (33)$$

The reaction of phenylsilane with sodium-potassium alloy in diethyl ether occurs according to the overall equation

$$9C_6H_5SiH_3 + Na/K \rightarrow (C_6H_5)_2SiH_2 + (C_6H_5)_3SiH + (C_6H_5)_4Si + 6KSiH_3 + 6KH \qquad (34)$$

which is proposed to proceed through the following mechanism:[77]

$$6C_6H_5SiH_3 + 6Na/K \rightarrow 6KSiH_3 + 6C_6H_5K \qquad (35)$$

$$C_6H_5SiH_3 + C_6H_5K \rightarrow (C_6H_5)_2SiH_2 + KH \qquad (36)$$

$$C_6H_5SiH_3 + 2C_6H_5K \rightarrow (C_6H_5)_3SiH + 2KH \qquad (37)$$

$$C_6H_5SiH_3 + 3C_6H_5K \rightarrow (C_6H_5)_4Si + 3KH \qquad (38)$$

But at -70°, it has also been reported[78] that $C_6H_5SiH_3$ reacts with Na/K forming $[C_6H_5-C_6H_5]^{=}$.

In going from the six-membered ring to the five-membered cyclopentadienyl system, it has been reported[79] that sodium metal dispersed in tetrahydrofuran does not rupture the $(CH_3)_3Si-C$ bond, viz.,

$$C_5H_5-Si(CH_3)_3 + Na \rightarrow Na[C_5H_4Si(CH_3)_3] + \tfrac{1}{2}H_2 \qquad (39)$$

For this case the above sodium salt was not isolated but instead used as an intermediate specie.

At the time this research problem was proposed, one[67] organometallic compound containing the $C_5H_4SiH_3$ group as an electron donating ligand had been prepared. Chapter III (Exp. II-B) describes the attempts of such a novel ligand.

Initially, the primary goal of the original research problem concerned the syntheses of compounds containing

H_3Si-metal linkages of Group VI b. But in the early stages of this problem the new compound, $C_5H_5SiH_3$, was discovered, and thereafter the research problem was extended to the syntheses and characterization of silyl derivatives of cyclopentadiene and methylcyclopentadiene. Furthermore similarities and differences in the chemistry of silicon and carbon could then be studied in these carbocyclic diene systems.

The manner in which $C_5H_5SiH_3$ was discovered will now be briefly described noting that even though $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ and $C_5H_5SiH_3$ were synthesized simultaneously, $C_5H_5SiH_3$ was characterized first due to its ease of volatilization. Recalling that in the synthesis of a particular potassium-metal salt ($K[M(CO)_3(\pi-C_5H_5)]$) of Group VI b, the purity of the salt depends not only on the particular starting material in excess but also on the boiling point of the solvent. While the importance of these two factors was not realized until later, the literature [2,5] recommended using sodium and C_5H_6 in excess and THF (b.p. 65°) as the solvent in the specific preparation of $Na[Mo(CO)_3(\pi-C_5H_5)]$. Thus, for the reaction of $Na[C_5H_5]$ with $Mo(CO)_6$ in refluxing THF under an inert atmosphere, viz.,

$$Na[C_5H_5] + Mo(CO)_6 \rightarrow Na[Mo(CO)_3(\pi-C_5H_5)] + 3CO \qquad (40)$$

the desired sodium-molybdenum salt was by no means of high purity because of excess, unreacted $Na[C_5H_5]$ present. Since this method was used in the early stages of the research problem ($K[C_5H_5]$ was used in place of $Na[C_5H_5]$) $K[C_5H_5]$ contaminated the supposedly pure salt, $K[Mo(CO)_3(\pi\text{-}C_5H_5)]$. When H_3SiBr was then combined with $K[Mo(CO)_3(\pi\text{-}C_5H_5)]$, the following reactions occurred:

$$K[C_5H_5] + H_3SiBr \rightarrow KBr + C_5H_5SiH_3 \tag{41}$$

$$K[Mo(CO)_3(\pi\text{-}C_5H_5)] + H_3SiBr \rightarrow KBr + H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) \tag{42}$$

Both reactions proved to be important since two new compounds were synthesized simultaneously and could be easily separated <u>in vacuo</u>.

As a further note, this researcher must call attention to another method of preparing $Na[Mo(CO)_3(\pi\text{-}C_5H_5)]$ [80,81], whereby the dimeric specie of molybdenum reacts with sodium amalgam (sodium metal dissolved in mercury) in an etheral solvent at room temperature according to the equation:

$$[Mo(CO)_3(\pi\text{-}C_5H_5)]_2 + 2Na/Hg \rightarrow 2Na[Mo(CO)_3(\pi\text{-}C_5H_5)] \tag{43}$$

Since $[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$ is commercially available in high purity or prepared in lower purity in the common laboratory method, i.e., [85]

$$2Mo(CO)_6 + (C_5H_6)_2 \xrightarrow{135°} [Mo(CO)_3(\pi\text{-}C_5H_5)]_2 + 6CO + H_2 \tag{44}$$

the contaminant Na[C_5H_5] is totally absent. Eq (41) and Eq (42) therefore proved to be the most important of all the reactions performed in this research since they form the bases for all other subsequent reactions.

CHAPTER II

EXPERIMENTAL (I)

(A) TECHNIQUE AND INSTRUMENTATION

1. Vacuum System: The vacuum system (Figure 1) was constructed of borosilicate (Pyrex 7740) glass and equipped with precision ground glass or Teflon [Fischer and Porter #795-005-0004] stopcocks. Stopcocks up to 4mm and ground joints up to ₮ 45/50 were lubricated with Kel F and Apiezon N. The system was evacuated using a Welch Duo-Seal vacuum pump. Usually the vacuum system was evacuated to 10^{-3}-10^{-5} (1 torr = 1 mm Hg) before handling a material; i.e., each time a piece of apparatus was attached to the vacuum system, the line and the apparatus were evacuated before handling a material.

2. Pressure Measurement: Pressure measurements below atmospheric pressure were made using a mercury manometer. The pressure was read with a meter stick calibrated in millimeters and could be read to approximately ±0.3 mm.

3. Temperature Measurements: Low temperature measurements were made using a pentane in glass thermometer which was accurate to approximately ±2°. When a higher accuracy was desired, an iron-constantan thermocouple was standardized against a fixed junction at 0° connected to a Leeds and Northrup potentiometer (model 8690).

VACUUM SYSTEM

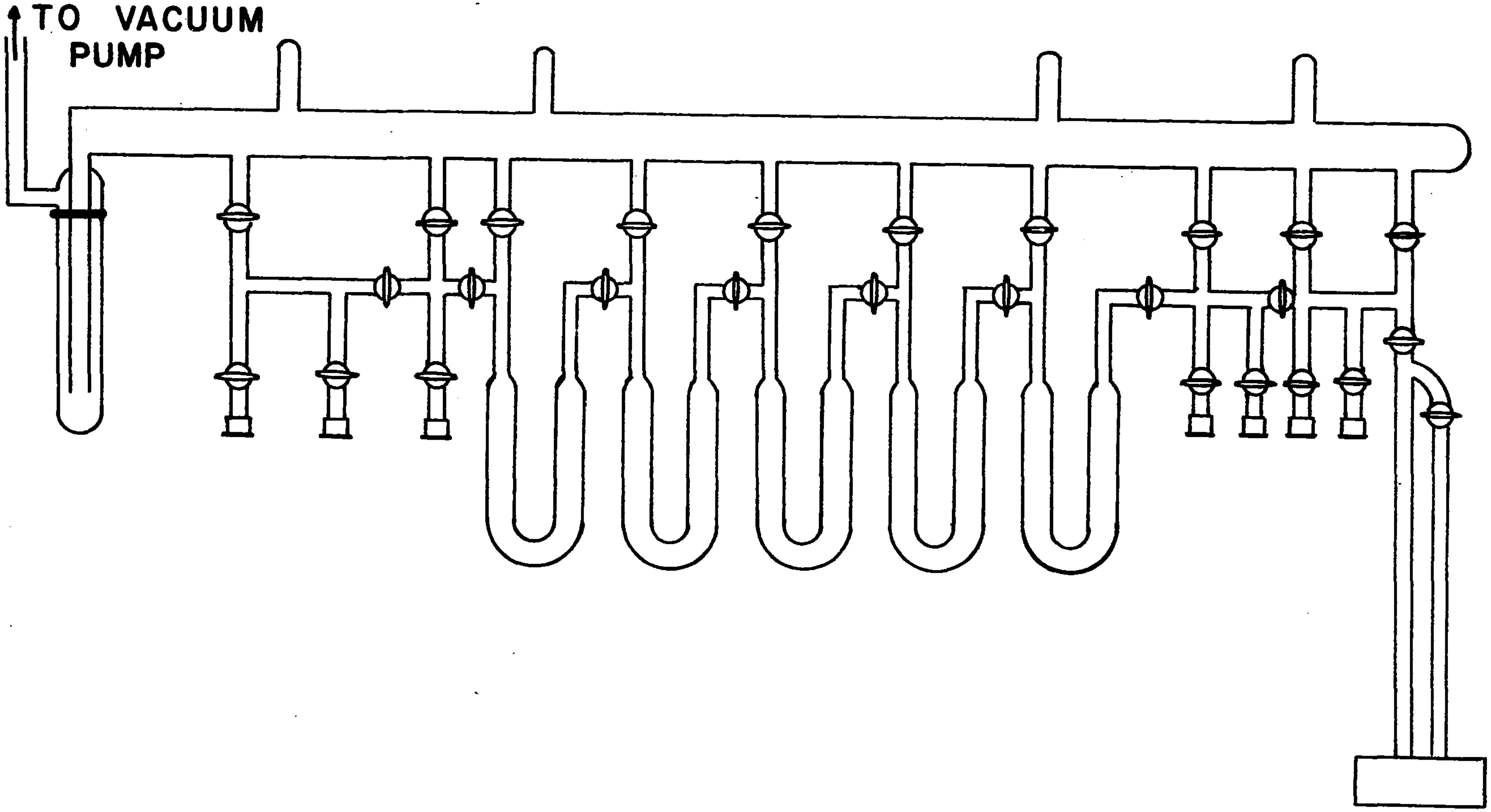


FIGURE 1

Room temperature measurements for molecular weight determinations were made with a thermometer which could be read to ±0.1° suspended from the vacuum system.

4. Production of Low Temperatures: Liquid nitrogen in Dewar flasks was used to maintain temperatures at -196°. Temperatures below ambient were maintained by the use of "slush" baths made by partially freezing appropriate (Table 2) solvents and then allowing the frozen material to melt.

Temperatures near the sublimation point of CO_2 (-78°) were obtained as a mixture of acetone and crushed "dry ice".

5. Separation of Volatile Materials: Mixtures of volatile materials were separated by fractional condensation in, or distillations from, traps maintained at low temperatures. The notation that will be used to facilitate descriptions of the various separations is as follows:

$$\mathrm{RT}\sim\underset{F(A)}{-96^\circ}\sim-\underline{196}^\circ \qquad \text{(n times)} \quad (1)$$

$$\downarrow$$

$$(-78^\circ \text{ and RT})\sim\underset{F(B)}{-130^\circ}\sim\underset{F(C)}{-196^\circ} \qquad \text{(n times)} \quad (2)$$

Line (1) means that a mixture was allowed to warm to room temperature (RT) from -196° without applying any external heat and without pumping; as soon as all of the volatile material had distilled from the trap at RT, the stopcocks on the traps were closed. In special circumstances distillations were carried out with pumping. In such instances this is specifically stated. The symbol "∿" signifies that the

LOW TEMPERATURE BATH[a]

0°	ice slush
-22°	CCl_4
-40°	orthochlorotoluene
-60°	chloroform
-78°[b]	dry ice-acetone
-96°	toluene
-126°	methylcyclohexane
-130°	n-pentane
-140°	methylcyclopentane
-150°	50-50 mixture of methylcyclopentane and iso-pentane
-160°	iso-pentane (2-methyl butane)

a:a slush.

b:crushed dry ice.

Table 2

material was distilling from a trap at one temperature to a trap at another temperature. In the above illustration, the material was passed through a trap held at -96° and then condensed in a trap held at -196°. A vertical arrow indicates that a new distillation scheme was employed. In line (2) of the above scheme, "(-78° and RT)" means that the trap was surrounded by a -78° bath for a certain period of time and then was warmed to room temperature. A capital letter signifies a fraction which was later examined. If no capital letter is present under a certain trap, this signifies that either the fraction in that trap was not examined or that there was no material in the trap.

The "n times" signifies the following operations upon the underlined trap, Fraction A or F(A):

$$\overset{\mathrm{F(A)}}{\mathrm{RT}}\sim-\underline{96}^\circ\sim-196^\circ \qquad (n=1)$$

$$\downarrow$$

$$\mathrm{RT}\sim-\underline{96}^\circ\sim-196^\circ \qquad (n=2)$$

$$\downarrow$$

$$\mathrm{RT}\sim\underset{\mathrm{F(A)}}{-96^\circ}\sim\underset{\mathrm{F(B)}}{-196^\circ} \qquad (n=3)$$

The process ends when n is reached, that is when no more material collects in the -196° trap. The process is then continued with F(B) until no additional material is found in the -96° trap.

F(B)
RT∿-96°∿-196°
↓
RT∿-96°∿-196°
↓
RT∿-96°∿-196°
↓ ↓
F(A) F(B)

Fractions with the same capital letter are combined.

6. Molecular Weight Measurement: The molecular weight determinations of volatile compounds were carried out using the method of Dumas. In such determinations the gas was assumed to follow the ideal gas equation as the pressure did not exceed 0.5 atmospheres. Therefore, the weight of the gas at a known temperature, pressure, and volume permitted the calculation of the molecular weight from the equation of state for a perfect gas:

$$PV = nRT = \frac{g}{M}RT$$

or

$$M = \frac{g}{P}\left(\frac{RT}{V}\right)76$$

where M = Molecular weight (mol. wgt.) in grams
g = Weight of gas in grams
P = Pressure in centimeters of mercury
R = Gas constant 82.1 $\frac{\text{ml-atm}}{\text{°K mole}}$
T = Temperature in °K
V = Volume in milliliters

7. Melting Point Measurement: Melting points were determined by means of a low temperature bath using the iron-constantan thermocouple when the compound had a low melting point.

Melting points of solid materials which melted above room temperature were obtained by means of melting point tubes filled with a nitrogen atmosphere and sealed with an oxygen torch.

8. Commercial Analysis: The analyses of new compounds were performed by Schwarzkopf Micro-Analytical Laboratories, Woodside, New York. These samples were transported for analysis in evacuated glass ampules.

9. Criteria of Purity: The purity of compounds obtained in this research was checked by the following procedures:

a. Molecular weight: so that the error in the difference between the calculated and experimental value did not exceed 1% of the calculated value.

b. Infrared spectrum: to agree with published spectrum or to a spectrum previously determined in this laboratory on the pure material.

c. Analyses: performed on all new compounds. In the case of new volatile materials and known solid compounds, values to within 1% of the theoretical percentages were considered acceptable. New solid compounds were analyzed as described in the previous section.

Values to within 1-2% of the theoretical percentages were considered acceptable.

d. Nuclear magnetic resonance spectrum: agreement with the expected ratio of the area under the resonance signals, and the position of the chemical shifts, and the nature of the fine structure observed in the signals.

10. Handling of Air-Sensitive Non-volatile Materials: For materials involving the use of an inert atmosphere, a polyethylene glove bag was filled with dry, deoxygenated nitrogen gas drawn from a liquid nitrogen tank. The phrase "in the dry bag" will imply that the above procedure was employed to prepare analysis samples, infrared Nujol mulls, n.m.r. tubes and/or fill glass pressure reactors. The dry bag was also used to perform certain reactions requiring a nitrogen atomsphere such as the preparation of $K[C_5H_5]$ in monoglyme. The thick-walled borosilicate (Pyrex) glass reactor is shown in Figure 19 and described in Appendix B.

11. Purity of Reageants, Volatile Products, and Solvents: Certain reageants and all volatile products of reactions were purified in the vacuum line by the distillation schemes described either in the appendix or in a particular experimental section. Identification was confirmed by an infrared spectrum consistent with the literature values and/or by a molecular weight determination. Solvents were purified by distillation over appropriate drying agents.

(B) SPECTROSCOPIC EQUIPMENT AND TECHNIQUES

1. Infrared Absorption Spectra: Infrared absorption spectra were obtained for volatile materials by enclosing a particular gaseous sample in a hollow borosilicate cell (10 cm path length, 3.3 cm diameter) fitted with KBr windows (4.0 cm diameter x 0.8 cm thick) which were sealed on with Glyptal resin.

Absorption spectra were obtained in the 2.5-15μ region using either a Beckman IR-8 or a Beckman IR-10 spectrometer. The spectra were calibrated with a polystyrene film.

2. Nuclear Magnetic Resonance Spectra: Proton nuclear magnetic resonance spectra were obtained from a Varian Associates A-60 or a Varian Associates HA-100 spectrometer which was operated at a fixed frequency of 60MHz or 100MHz.

Spectra were obtained at room temperature, unless otherwise noted, on spinning samples contained in sealed, evacuated (5 mm o.d.) borosilicate (Pyrex) glass tubes.

Peak areas were measured using an electronic integrator [one Hertz (abb. Hz) is equal to one cycle$\cdot$sec^{-1}].

(C) PRELIMINARY SYNTHESES

(1) SYNTHESIS OF $Cr(CO)_6$ AT ATMOSPHERIC PRESSURE

(a) Preparation of $CrCl_3$ [82]

Freshly distilled $SOCl_2$ (125 ml) was added to 25.5 gm (0.957 mol) of $CrCl_3 \cdot 6H_2O$ (bright green; previously dried in a desicator over $CaSO_4$ for three days). Then the mixture was refluxed under a nitrogen atmosphere, and the heating was continued for three to six hours until the green solution changed to a purple solution. After removal of excess $SOCl_2$ by ordinary distillation at 78°, the purple residue was dried first by means of a vacuum pump connected to a -78° dry ice-acetone trap, and then dried further in a vacuum oven at 140° for eight hours. 18.6 gm (0.117 mol) of anhydrous $CrCl_3$ (purple) were obtained in 12.2% yield based on the amount of $CrCl_3 \cdot 6H_2O$ initially employed.

(b) Preparation of Phenyl Magnesium Bromide [83]

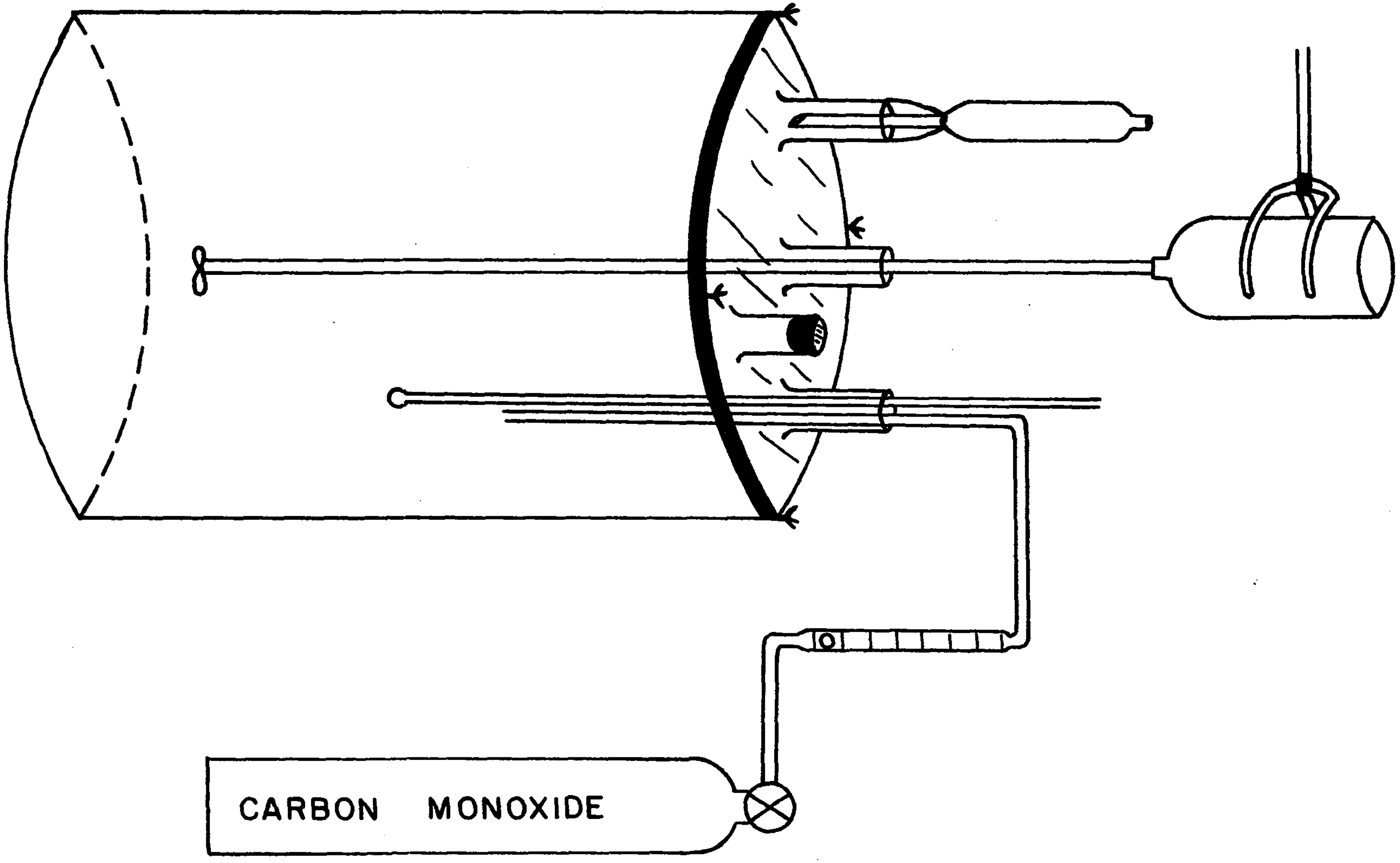
Magnesium metal turnings (18.2 gm, 0.758 mol) were placed in the bottom of a 1000 ml two-necked round-bottom flask fitted with a long reflux condenser and a dropping funnel. Moisture was removed from the apparatus by gently warming and flushing with dry nitrogen. 100 ml of anhydrous diethyl ether were added to the Mg turnings, and 90 ml of phenyl bromide were placed in the dropping funnel and added dropwise to the etheral solution. After ten to fifteen minutes, a brown coloration appeared, and the remainder of the C_6H_5Br, approximately 70 ml, was added to the reaction mixture. The use of an ice-bath was necessary to keep the reaction from becoming too vigorous. The resulting dark brown solution was refluxed for thirty minutes to react all the C_6H_5Br; with a small amount of Mg turnings remaining in the flask, the reaction was considered complete.

(c) Preparation of $Cr(CO)_6$ [84] (Figure 2)

Approximately 300 ml of the previously prepared Grignard Reageant (assumed to be 2.4N in C_6H_5MgBr) was added to a suspension of 22.1 gm (0.139 mol) of $CrCl_3$ (previously prepared in (a)) in about 700 ml of anhydrous diethyl ether cooled to -78°. The C_6H_5MgBr solution was added over a period of an hour while the reaction mixture was stirred mechanically at 1000 rpm. After addition of C_6H_5MgBr, the resulting solution was colorless; then carbon monoxide was introduced into the solution by means of a glass tube (7 mm o.d.) submerged beneath the liquid level. The flow of CO - 18.5 ml/min - was controlled by a flow meter. Stirring was increased to 15,000 rpm. As the cold bath was permitted to warm from -78°, the mixture changed color. At -40° a light brown solution appeared; at -30° a brown solution appeared; and at -15° to -10°

$Cr(CO)_6$ PREPARATION APPARATUS

FIGURE 2



a reddish brown solution appeared. CO was introduced at -1° for thirty minutes more; the resulting black reaction mixture was quenched by adding 35 ml of 6N H_2SO_4 and 100 gm of ice. Then the product was steam distilled. The ether layer which separated from the water was dried over $CaSO_4$ and removed through a fractionating column at 32° after filtration. Colorless crystals appeared in the bottom of the distilling flask along with a brown residue. Pure colorless crystals were obtained by filtering, washing with cold ether, and sucking the product dry by means of a water aspirator. 1.60 gm (0.072 mol) of $Cr(CO)_6$ were isolated in 5.22% yield based on the amount of $CrCl_3$ initially employed.

(2) SYNTHESIS OF $[M(CO)_3(\pi\text{-}C_5H_5)]_2$ [85]
M=Cr, Mo

The appropriate metal carbonyl (2.50 gm, 0.113 mol Cr; 0.0947 mol Mo) was added to 20 ml of dicyclopentadiene contained in a 100 ml ₮ 14/30 single-necked flask fitted with a reflux condenser; after flushing with dry nitrogen, the flask was heated to 134° by means of an oil bath equipped with a magnetic stirring bar and a heating coil connected to a variac. The initial colorless solution changed rapidly to a dark green solution in the chromium case or to a dark red-purple in the molybdenum case. After three to four hours of refluxing, the reaction mixture of $[M(CO)_3(\pi\text{-}C_5H_5)]_2$ was allowed to cool slowly to room temperature under a nitrogen atmosphere; much unreacted carbonyl was visible around the neck of the flask. After the reaction mixture was filtered, the residue was washed four times with 50 ml portions of pentane, sucked dry by means of a water aspirator, and placed in the bottom of a conventional sublimer. Upon evacuation, the bottom of the sublimer was heated to 60°, and the cold finger was cooled to 0° by a salt-ice water slush. Unreacted carbonyl was collected by the cold finger after four to six hours, leaving the desired dimer product in the bottom of the sublimer. 1.50 gm (0.0372 mol Cr; 0.0306 Mo) of dimer were recovered in 33.2% and 32.3% yields respectively based on the amount of the carbonyl compound initially employed.

(3) SYNTHESIS (LARGE SCALE IN THF) OF $K[C_5H_5]$ [85,86]

Potassium metal (23.5 gm, 0.601 mol), cut into small chunks, was placed in a 1000 ml three-necked round-bottom flask equipped with a pressure equalized dropping funnel, a condenser, and a mechanical motor stirrer; the condenser and funnel were fitted with nitrogen inlet valves. 400 ml of dry, nitrogen saturated tetrahydrofuran (freshly distilled over lithium aluminum hydride) were added to the flask, and the contents of the flask were heated to the boiling point of THF (65°) by means of a heating mantle connected to a variac. At this temperature the potassium metal melted, and vigorous stirring converted the potassium chunks to potassium sand. 55.0 ml (0.707 mol) of freshly cracked cyclopentadiene (diluted with 50 ml of dry nitrogen saturated THF) were placed in the dropping funnel and added dropwise to the potassium sand solution over a period of an hour. After all the potassium had dissolved, excess THF was distilled from the dark red solution of $K[C_5H_5]$; the desired product was dried by removing the remaining THF by means of a vacuum pump connected to a -78° dry ice-acetone trap. Pure white crystals of $K[C_5H_5]$ were obtained in nearly quantitative yield. After filling with nitrogen, the flask containing the product was stoppered in order to prevent extensive air oxidation.

(4) SYNTHESIS (LARGE SCALE IN DIGLYME) OF $K[M(CO)_3(\pi\text{-}C_5H_5)]$ [5,87]
M=Cr

Potassium metal (23.5 gm, 0.601 mol), cut into small chunks, was placed in a 1000 ml three-necked flask equipped with a reflux condenser, a mechanical stirrer, and a pressure-equalized dropping funnel; the tops of the funnel and condenser were fitted with nitrogen inlet valves. After flushing the apparatus with dry nitrogen, about 300 ml of dry diglyme (distilled over calcium hydride, redistilled under partial vacuum over potassium metal, and then redistilled under partial vacuum over $LiAlH_4$) were added to the flask; 60.0 ml (0.732 mol) of freshly cracked cyclopentadiene were placed in the dropping funnel and diluted with 50 ml of dry diglyme; the solution was heated to 65° where the potassium metal melted, and vigorous stirring converted the chunks to sand. Heating was discontinued, and the cyclopentadiene solution was added dropwise to the potassium sand while vigorous stirring continued; a vigorous reaction was evidenced by the evolution of gas and liberation of heat. After complete addition of the cyclopentadiene, a dull reddish-pink solution resulted; stirring was continued for four hours to ensure complete reaction of all the potassium metal.

25.0 gm (0.113 mol) of $Cr(CO)_6$ were added to the diglyme solution of $K[C_5H_5]$; after heating to gentle reflux (160°) for eight to twelve hours, a yellow-brown solution of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ resulted. This solution was cooled under nitrogen to room temperature; the necks of the flask were stoppered; and the flask was stored in a cool place in the dark for use in making the mercury and methyl derivatives of chromium.

(5) SYNTHESIS (LARGE SCALE IN THF) OF $K[M(CO)_3(\pi\text{-}C_5H_5)]$ [5,87] M=Mo

Potassium metal (23.5 gm, 0.601 mol), cut up into small chunks, was placed in a 1000 ml three-necked flask equipped with a reflux condenser, a mechanical stirrer, and a pressure-equalized dropping funnel, with the tops of the funnel and condenser fitted with nitrogen inlet valves. After flushing the apparatus with dry nitrogen, about

300 ml of dry THF (distilled over $LiAlH_4$) were added to the flask; 60.0 ml (0.732 mol) of freshly cracked cyclopentadiene were placed in the dropping funnel and diluted with 50 ml of THF; the solution was heated to the boiling point of the solvent (65°) where the potassium metal melted and vigorous stirring converted the chunks to sand. Heating was discontinued, and the cyclopentadiene was added dropwise to the potassium sand while the vigorous stirring continued; a vigorous reaction was evidenced by the evolution of gas and liberation of heat. After complete addition of the cyclopentadiene, a reddish-pink solution resulted; stirring was continued for four hours to ensure complete reaction of all the potassium metal.

Molybdenum hexacarbonyl (24.5 gm, 0.0910 mol) was added to the THF solution of $K[C_5H_5]$; after heating for six to eight hours at total reflux (65°), an orange-yellow solution of $K[Mo(CO)_3(\pi-C_5H_5)]$ resulted. This solution was cooled under nitrogen to room temperature; the necks of the flask were stoppered; and the flask was stored in a cool place in the dark for use in making the mercury and methyl derivatives of molybdenum.

(6) SYNTHESIS OF $Hg[M(CO)_3(\pi-C_5H_5)]_2$ [87]
M=Cr, Mo

About 100 ml of a 0.4 molar (2 gm in 200 ml) distilled water solution of $Hg(CN)_2$ were added to 35 ml of the $K[M(CO)_3(\pi-C_5H_5)]$ solution (3.95 mmol Cr; 3.18 mmol Mo) as prepared in parts (4) and (5) above. A voluminous yellow precipitate appeared immediately; after thirty minutes, the settled precipitate was filtered by suction from a water aspirator, washed with two 50 ml portions of water, and sucked dry. To obtain a pure crystalline product, the crude material was dissolved in 50 ml of boiling dry acetone and filtered again. Upon removal of the remaining solvent, 2.00 gm (3.31 mmol Cr; 2.89 mmol Mo) of bright yellow, air-stable crystals were obtained in 83.8% and 90.9% yields respectively based on the amount of $K[M(CO)_3(\pi\text{-}C_5H_5)]$ initially employed. The chromium derivative remained bright yellow indefinitely at room temperature while the molybdenum derivative turned yellow-green after several days. Infrared spectrum of $Hg[Cr(CO)_3(\pi\text{-}C_5H_5)]_2$ was consistent with the literature values.[88]

(7) SYNTHESIS OF $H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ [2,89]

M=Cr, Mo

About 10 ml (3.09 mmol) of methyl iodide were added to 5 ml of the $K[M(CO)_3(\pi\text{-}C_5H_5)]$ solution as prepared in parts (4) and (5) above. The reaction mixture was stirred at room temperature for several hours, after which the resulting yellow solution was poured into 100 ml of water, and the product was extracted with 20 ml of anhydrous diethyl ether; excess methyl iodide and ether were removed upon evacuation of the sublimer. The bottom of the sublimer was heated to 65°, and the cold finger cooled to 0° by means of a salt-ice water slush. A yellow sublimate was collected on the cold probe. In the dry bag, the product was scraped from the probe, placed in a bottle filled with nitrogen, and then stored in a freezer. The chromium derivative decomposed rapidly in air, but the molybdenum derivative was quite air stable for periods of several hours.

(8) SYNTHESIS OF $H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)$
M=Cr, Mo, W

In the dry bag, 1 gm of $K[M(CO)_3(\pi\text{-}C_5H_5)]$; (M=Cr, Mo, W) was placed into the bottom of the vacuum sublimer shown in figure 20 ; and from the vacuum line, 10 ml of anhydrous diethyl ether (degassed) and 5 ml of methyl iodide were condensed into the bottom of the vacuum sublimer at -78°. Upon warming to room temperature, the solution was stirred magnetically for several hours; excess methyl iodide and ether were removed by vacuum condensation in a -78° trap. The bottom of the sublimer was heated to 60° while the cold finger was cooled to liquid nitrogen temperature, -196°. A yellow sublimate was collected by the cold finger.

The sublimer was disconnected from the vacuum line and placed in a dry bag filled with nitrogen. The sublimer stopcock was opened filling the sublimer with nitrogen, and the bottom of the sublimer was separated from the cold finger. The yellow residue was removed from the probe by scraping with a razor blade. The sample was stored in a bottle which was enclosed in a plastic bag and then placed in a freezer. The infrared and n.m.r. spectra are shown in figures 3, 4, and 5 and are consistent with the literature values.[2,90]

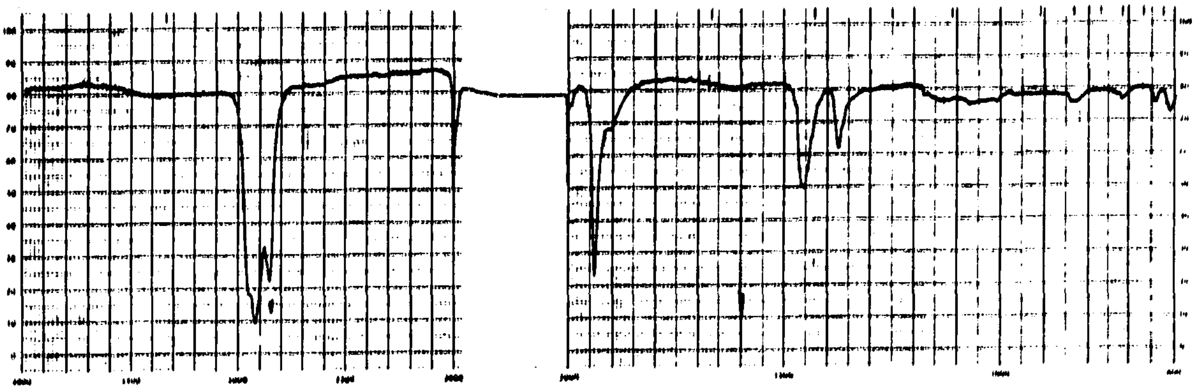
(9) SYNTHESIS OF $H\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ [1,2]
M=Cr, Mo, W

In the dry bag, 3.0 gm of $K[M(CO)_3(\pi\text{-}C_5H_5)]$; (M=Cr, Mo, W) were placed into the bottom of the vacuum sublimer shown in figure 20; and from the vacuum line, 25 ml of anhydrous diethyl ether (degassed) and 2.5 ml of anhydrous HBr were condensed into the bottom of the vacuum sublimer at -78°. A bright yellow solution resulted immediately; upon warming to 0° and then to room temperature, a yellow-brown residue resulted. Magnetic stirring was applied at room temperature for fifteen minutes. Excess HBr and Et_2O were removed by means of a water aspirator; the dark yellow-brown residue was further dried by pumping through a -78° dry ice-acetone bath connected to a vacuum pump. The cold finger of the sublimer was then filled with liquid nitrogen, while the bottom of the sublimer containing the residue was heated to 55°-60°. A bright yellow sublimate collected on the cold finger.

After the liquid nitrogen evaporated, and the sublimer reached room temperature (no more moisture

IR, NMR SPECTRA OF $H_3C-Cr(CO)_3Cp$

IR



NMR

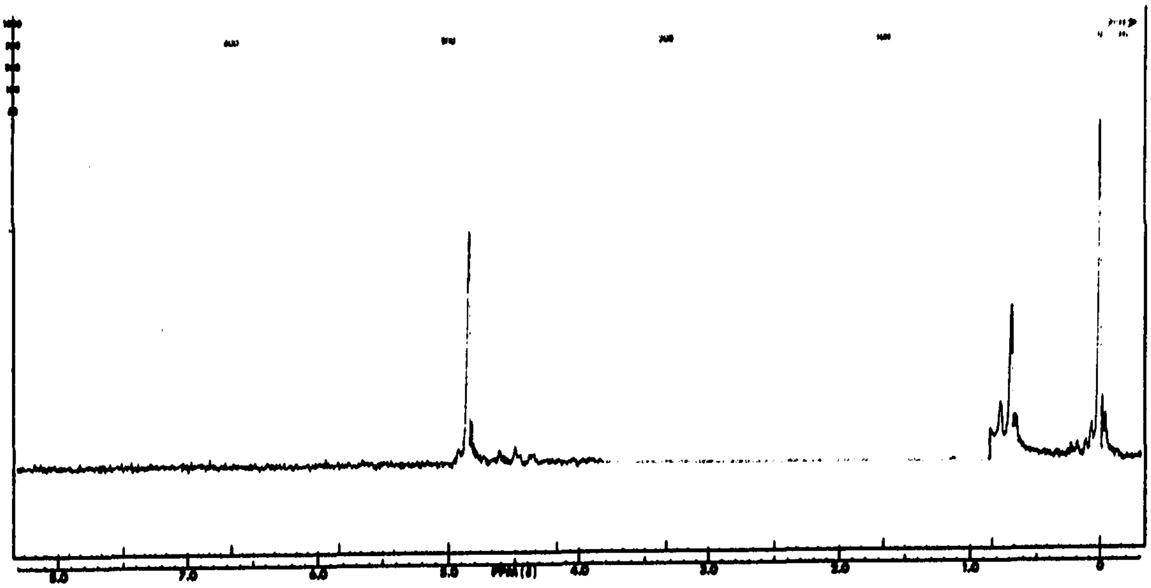
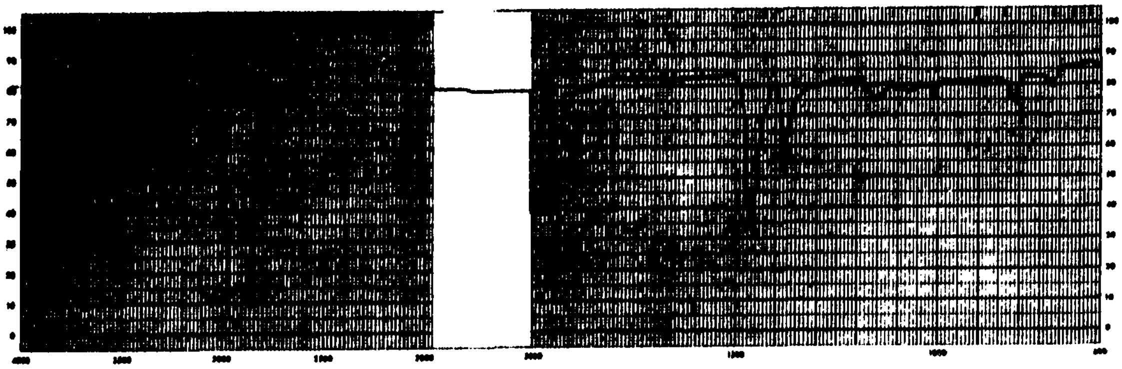


FIGURE 3

IR, NMR SPECTRA OF $H_3C\text{-}Mo(CO)_3Cp$

IR



NMR

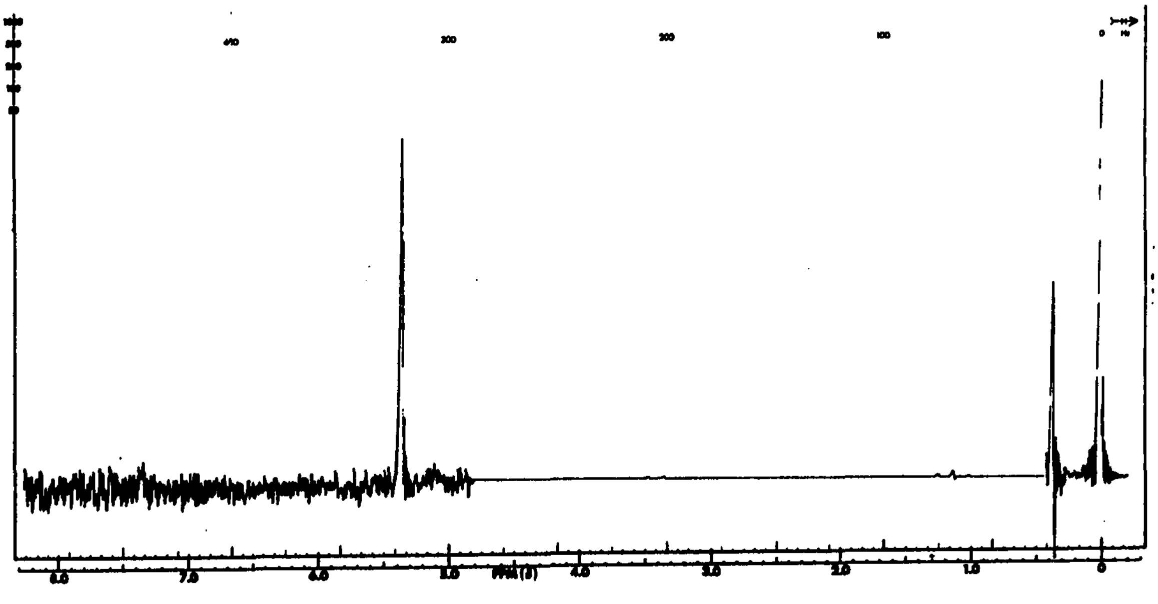
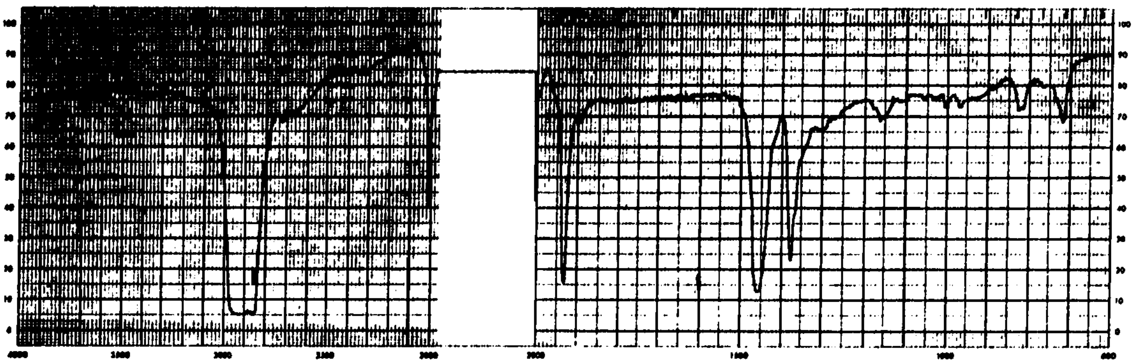


FIGURE 4

IR, NMR SPECTRA OF $H_3C\text{-}W(CO)_3Cp$

IR



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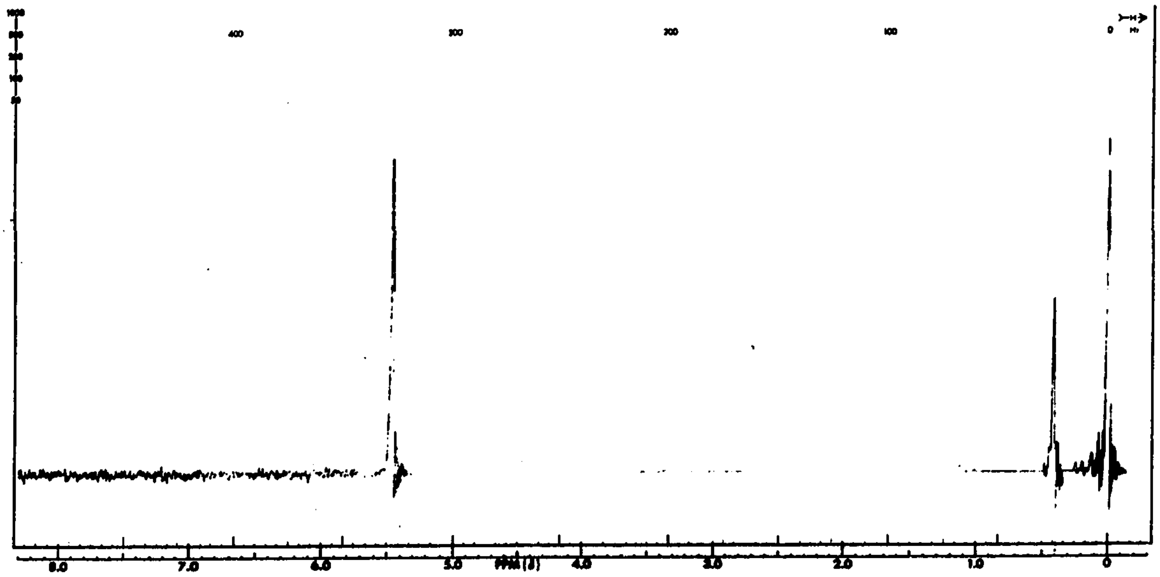


FIGURE 5

condensed onto it), the sublimer was placed in the dry bag. The stopcock to the sublimer was opened filling the sublimer with nitrogen, and the bottom of the sublimer was separated from the cold finger. The yellow crystals were removed from the cold finger by scraping with a razor blade. Infrared samples and nuclear magnetic resonance samples were immediately prepared in the dry bag, since thermal stability observations (decolorizations) were heeded. The infrared and n.m.r. spectra are shown in figures 6, 7, 8, and are consistent with the literature values.[2,90]

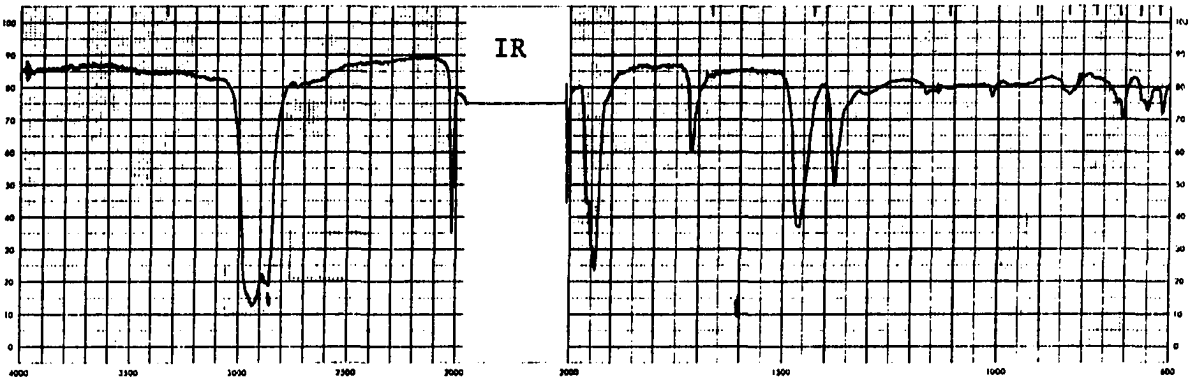
(D) MISCELLANEOUS SYNTHESES

(1) SYNTHESIS OF $[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$ [85,87]

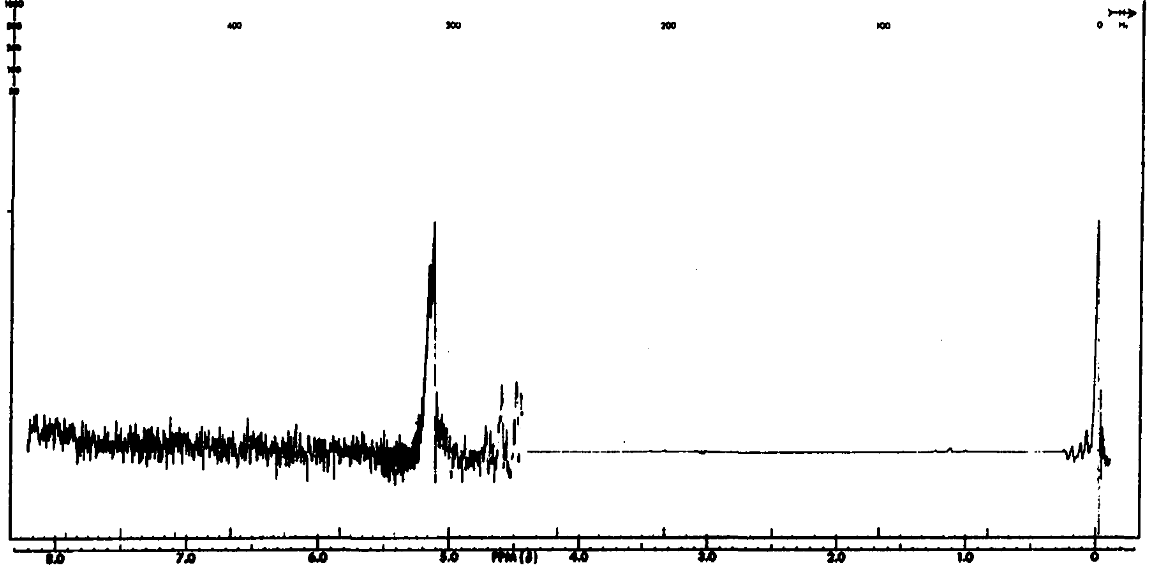
Iron pentacarbonyl (15 ml, 2.15 gm, 0.11 mol) was added to 100 ml of dicyclopentadiene contained in a 500 ml 𝕊 14/30 single-necked flask. After flushing with dry nitrogen, the reaction mixture was heated to 150° by means of an oil bath equipped with a magnetic stirring bar and a heating coil connected to a variac. When no yellow fumes of $Fe(CO)_5$ were visible in the condenser, after about four hours, the resulting dark red solution was slowly cooled under nitrogen to room temperature. Then the solution was filtered in air, and the residue was washed four times with 20 ml portions of dry pentane. The dark red residue was removed from the filter and dried overnight in a vacuum oven at 60°. 10.1 gm (0.0284 mol)

IR, NMR SPECTRA OF H-Cr(CO)$_3$Cp

IR



NMR(RT)



NMR(-40°)

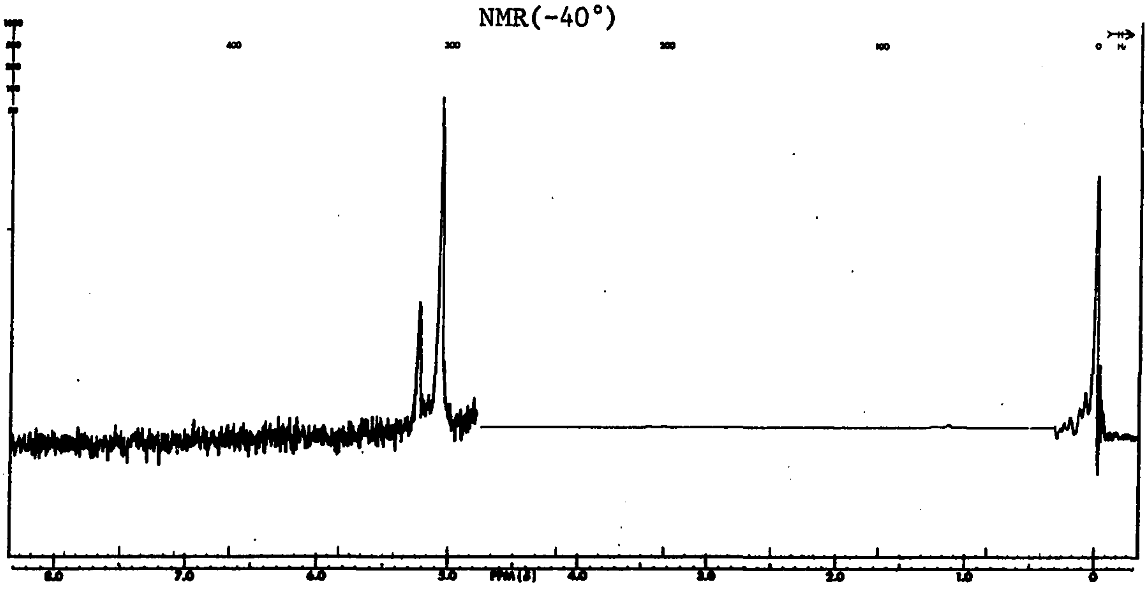
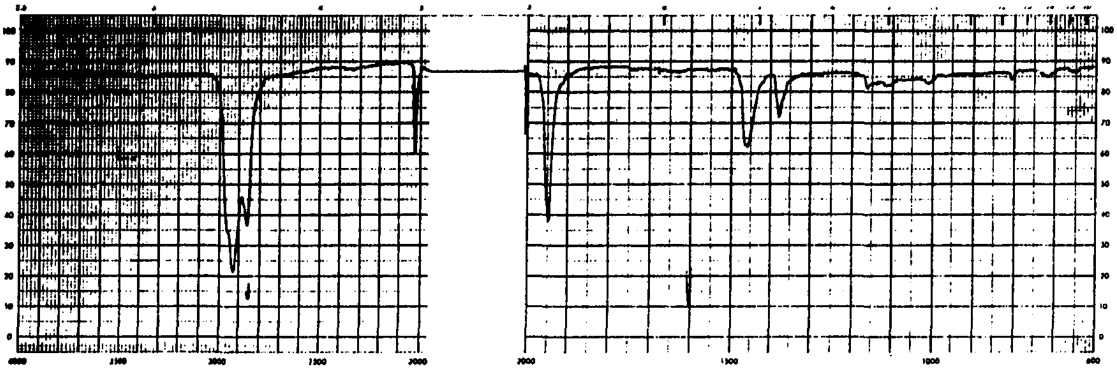


FIGURE 6

IR, NMR SPECTRA OF H-Mo(CO)$_3$Cp

IR



NMR

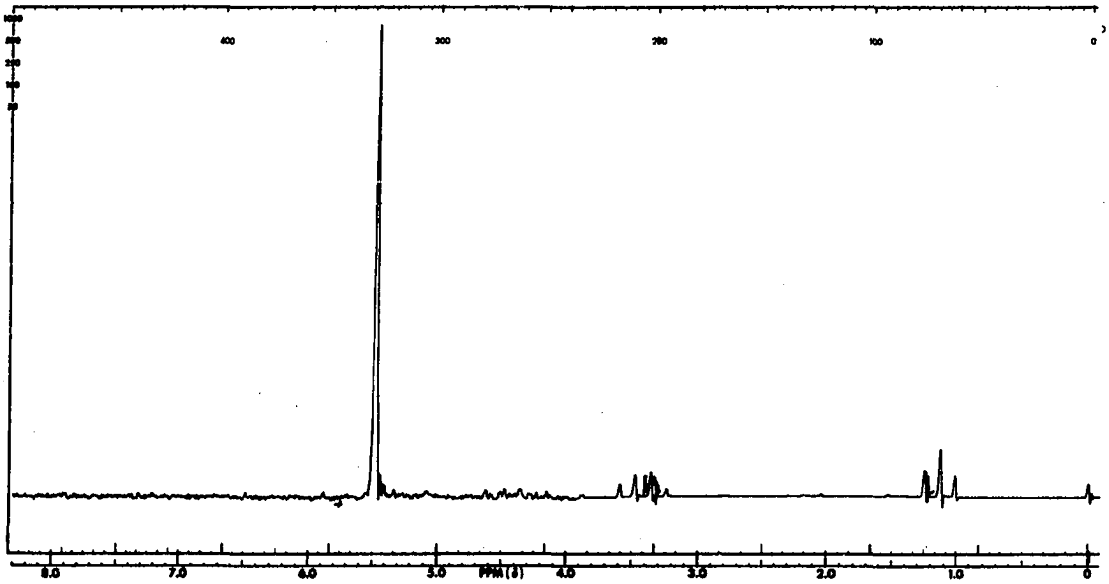
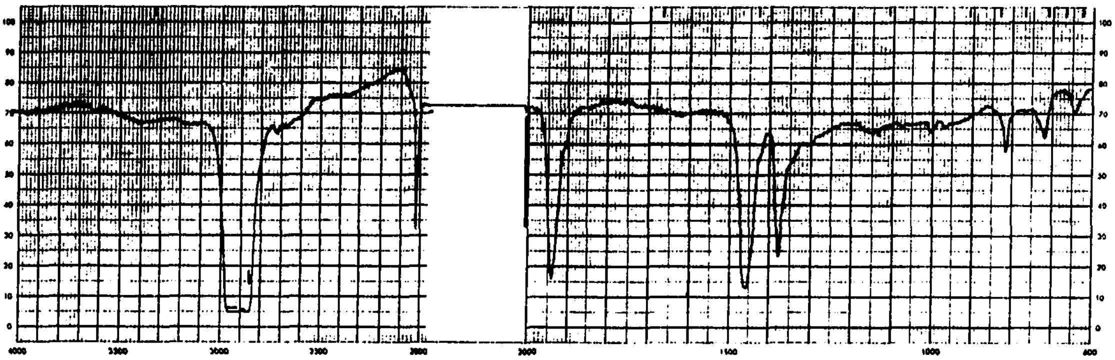


FIGURE 7

IR, NMR SPECTRA OF H-W$(CO)_3$Cp

IR



NMR

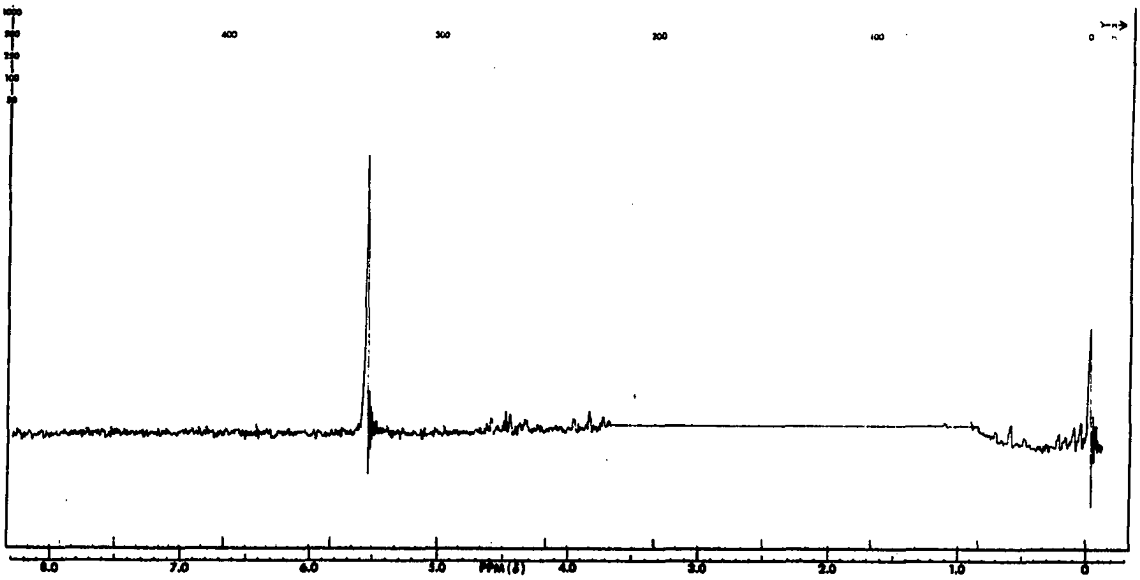


FIGURE 8

of dimer were obtained in 25% yield based on the amount of the $Fe(CO)_5$ initially employed. The infrared spectrum was consistent with the literature values.[85,92]

(2) SYNTHESIS OF $Ni(\pi\text{-}C_5H_5)_2$ [82]

(a) Preparation of $[Ni(NH_3)_6]Cl_2$

Nickel chloride hexahydrate (30.0 gm, 0.126 mol) was dissolved in about 60 ml of distilled water contained in a 250 ml ₷ 24/40 single-necked flask which was then heated to 60°. Approximately 100 ml of concentrated NH_4OH were poured gradually into the green solution of $NiCl_2 \cdot 6H_2O$ which was then stirred magnetically for several hours. The resulting blue solution was cooled slowly to room temperature and then to 0° by salt-ice water slush; this cooled solution was filtered, and the residue which collected on the filter was washed with ice water, cold ethanol, and cold diethyl ether. The blue residue was dried in air by means of a water aspirator. 14.4 gm (0.0620 mol) of $Ni(NH_3)_6Cl_2$ were prepared in 49.0% yield based on the amount of $NiCl_2 \cdot 6H_2O$ initially employed.

(b) Preparation of $K[C_5H_5]$

In the dry bag, 3.90 gm (0.0100 mol) of potassium metal, cut up into small pieces, were added to a 250 ml ₷ 24/40 single-necked round-bottom flask containing about 100 ml of dry tetrahydrofuran (distilled over $LiAlH_4$) and 12.0 gm (0.180 mol) of cyclopentadiene. The resulting deep red solution was stirred magnetically for an hour.

(c) Preparation of Ni(π-C_5H_5)$_2$

Ni(NH_3)$_6$$Cl_2$ (24.7 gm, 0.107 mol) was added to the THF solution of K[C_5H_5]. The reaction mixture was stirred at 40° for half an hour and then heated to a strong reflux (65°) for three hours. Excess THF was distilled from the dark green solution. The residue remaining in the bottom of the flask was dried by suction from a vacuum pump connected to a -78° dry ice-acetone trap.

In the dry bag, the green-brown residue was removed from the flask and placed in the vacuum line sublimer. The bottom of the sublimer was heated to 80° while the cold finger was cooled to liquid nitrogen temperature,-196°. Bright green crystals were collected by the cold finger along with a brown residue. A second sublimation produced 2.40 gm (0.0127 mol) of pure green nicklocene, Ni(π-C_5H_5)$_2$, in 11.8% yield based on the amount of the Ni(NH_3)$_6$$Cl_2$ initially employed.

(3) SYNTHESIS OF Co(CO)$_2$(π-C_5H_5) [85,87,171]

In the dry bag, 1.71 gm of $Co_2(CO)_8$ (stored in a freezer) were placed in the bottom of a 25 ml $\mathbf{\$}$ 14/30 round-bottom flask which was previously filled with dry nitrogen. A small sized magnetic stirring bar was also placed in the flask; a male to male adapter (14/30 to 12/30) was fitted (using stopcock grease) to the flask which was subsequently removed from the dry bag. Then the flask was connected to the vacuum line, cooled to 0° (to prevent sublimation of $Co_2(CO)_8$) and evacuated. Approximately 5 ml of C_5H_6 were condensed into the flask at -78° since no reaction took place at this cold temperature. The flask was next frozen to -196° by replacing the -78° dry ice-acetone bath with a liquid nitrogen bath. Then the manometer on the vacuum line was filled with carbon monoxide gas; the stopcock to the flask was opened so that CO entered the flask from the manometer. More CO was added so that the flask was pressurized at about 1 atmosphere. After the -196° liquid nitrogen bath was removed, and the contents of the flask warmed slowly to room temperature, a salt-ice water slush was placed around the flask, and a u.v. light was turned on shortly thereafter. After sixteen hours, the u.v. light was turned off, the ice water bath was replenished, and a dark red liquid was observed in the bottom of the flask.

The flask was disconnected from the vacuum line, placed in the dry bag, and the contents of the flask were filtered; a small amount of diethyl ether (saturated with nitrogen) was used to rinse the flask clean. The flask containing the filtrate was removed from the dry bag and connected to a micro-distillation apparatus. Excess ether was distilled off at 43° at atmospheric pressure.

The product, distilled under a reduced pressure of 0.1 mm Hg at 35°, was a dark orange-red liquid which was purified on the vacuum line as follows:

$$\underset{\text{F(A)}}{\text{RT}\sim 0^\circ}\sim -63^\circ\sim -196^\circ \qquad (n=4)$$

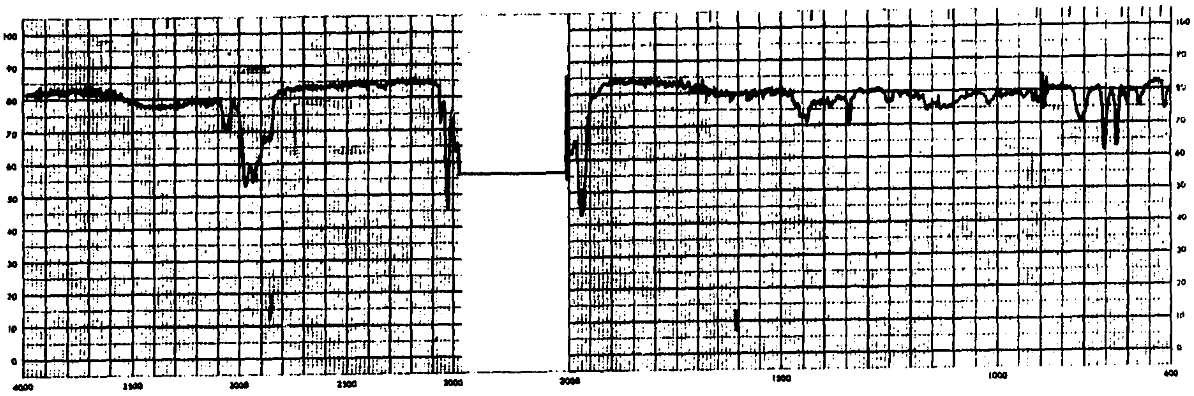
Fraction (A) contained pure $Co(CO)_2(\pi\text{-}C_5H_5)$ produced in 49.1% yield based on the amount of $Co_2(CO)_8$ (850 mgm, 4.72 mmol) initially employed. The infrared spectrum of the pure liquid and an n.m.r. spectrum taken in CS_2 are shown in figure 9 and are consistent with the literature values.[92,171,85]

(4) SYNTHESIS OF $C_5H_5Si(CH_3)_3$ [93]

In the dry bag, 2.0 gm (0.050 mol) of potassium metal, cut up into small pieces, were added to 50 ml of diethyl ether (saturated with nitrogen) and 6.0 ml (0.096 mol) cyclopentadiene contained in a 250 ml ₮ 24/40 single-necked round-bottom flask; after the last piece of potassium was added, the solution was stirred magnetically for one hour. 5.45 gm (0.0500 mol) of $(CH_3)_3SiCl$ were added to the etheral solution of $K[C_5H_5]$. The characteristic pink solution changed to a white solution immediately after the addition of the trimethylchlorosilane. The resulting solution was filtered in the dry bag, and the residue was washed twice with 25 ml portions of ether; the supernatant

IR, NMR SPECTRA OF $Co(CO)_2Cp$

IR



NMR

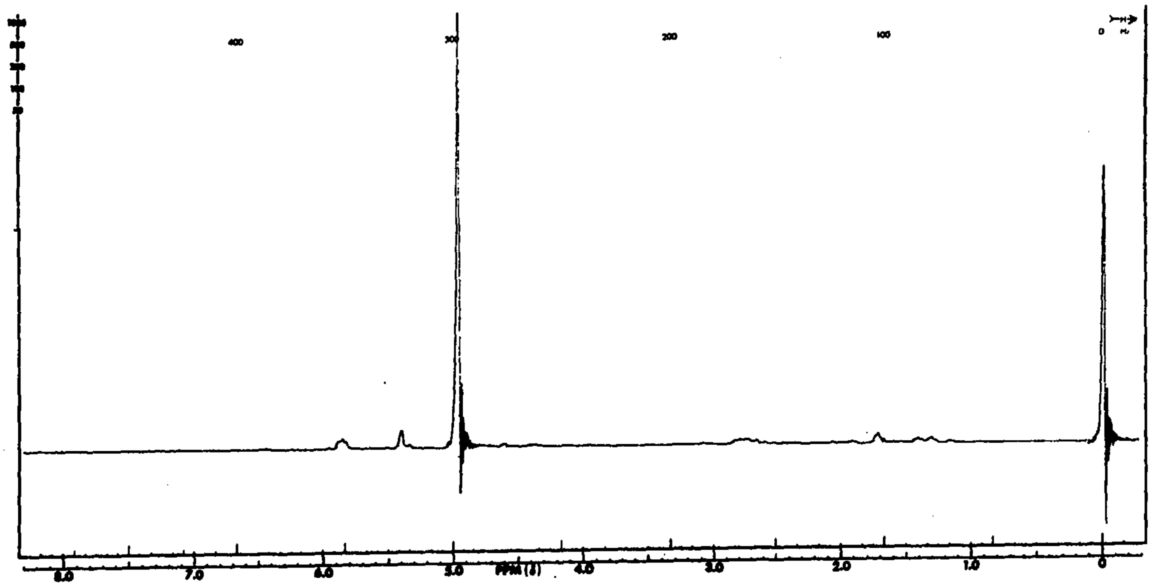


FIGURE 9

IR DATA OF $Co(CO)_2(\pi\text{-}C_5H_5)$-neat

Absorption	Intensity	Assignment[a]
3051	m	Cp
2964	s	
2935	s	
2055	w	
2020	s	-CO
1991	w	-CO
1966	s	
805	m	Cp
750	m	
721	m	

a:Ref. 92, 171.

Table 3

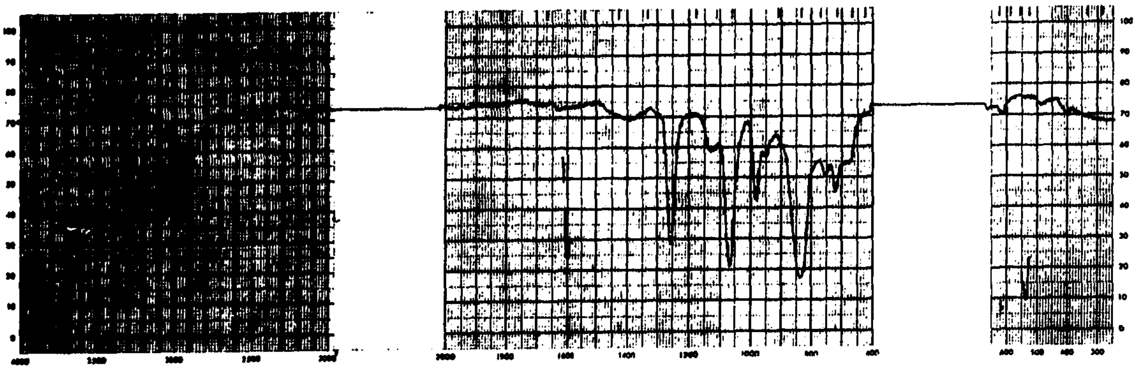
liquid was transferred to a take-off tube. The remaining ether was removed by vacuum condensation in a -78° dry ice-acetone trap. A yellow liquid remained in the take-off tube; purification of the crude product at 55°/(2 cm Hg) yielded a colorless, air-stable liquid. Its infrared and n.m.r. spectra are shown in figure 10 and are consistent with the literature values.[92,172,93]

(5) SYNTHESIS OF $C_5H_4(Si(CH_3)_3)(CH_3)$[175]

In the dry bag, 2.0 gm (0.050 mol) of potassium metal, cut up into small pieces, were added to 50 ml of diethyl ether (saturated with nitrogen) and 6.0 ml of methylcyclopentadiene contained in a 250 ml ₮ 24/40 single-necked round-bottom flask; after the last piece of potassium had been added, the resulting pink solution was stirred magnetically for one hour. 5.45 gm (0.0500 mol) of $(CH_3)_3SiCl$ were added to the etheral solution of $K[C_5H_4CH_3]$. The characteristic pink solution changed to a white solution immediately after the addition of the trimethylchlorosilane. The resulting solution was filtered in the dry bag, and the residue was washed twice with 25 ml portions of ether; the supernatant liquid was transferred to a take-off tube. The remaining ether was removed by vacuum condensation in a -78° dry ice-acetone trap. A yellow liquid remained in the take-off tube; purification of the crude product at 55°/(1 cm Hg) yielded a colorless, air-stable liquid.

IR, NMR SPECTRA OF $C_5H_5Si(CH_3)_3$

IR



NMR

FIGURE 10

IR DATA OF $C_5H_5Si(CH_3)_3$

Absorption	Intensity	Assignment[a]
3090	m	Cp
2965	s	
2900	m	
1255	vs	$Si-CH_3$[b]
1130	w	
1067	vs	Cp
982	s	
950	w	
835	vs	Cp
755	w	
720	m	

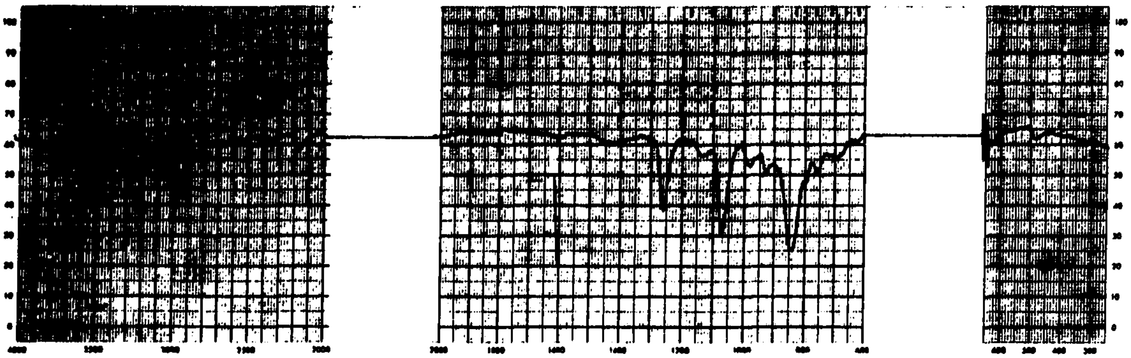
a:Ref. 92, 172.

b:Ref. 129, 130, 203.

TABLE 4

IR, NMR SPECTRA OF $C_5H_4(CH_3)Si(CH_3)_3$

IR



NMR

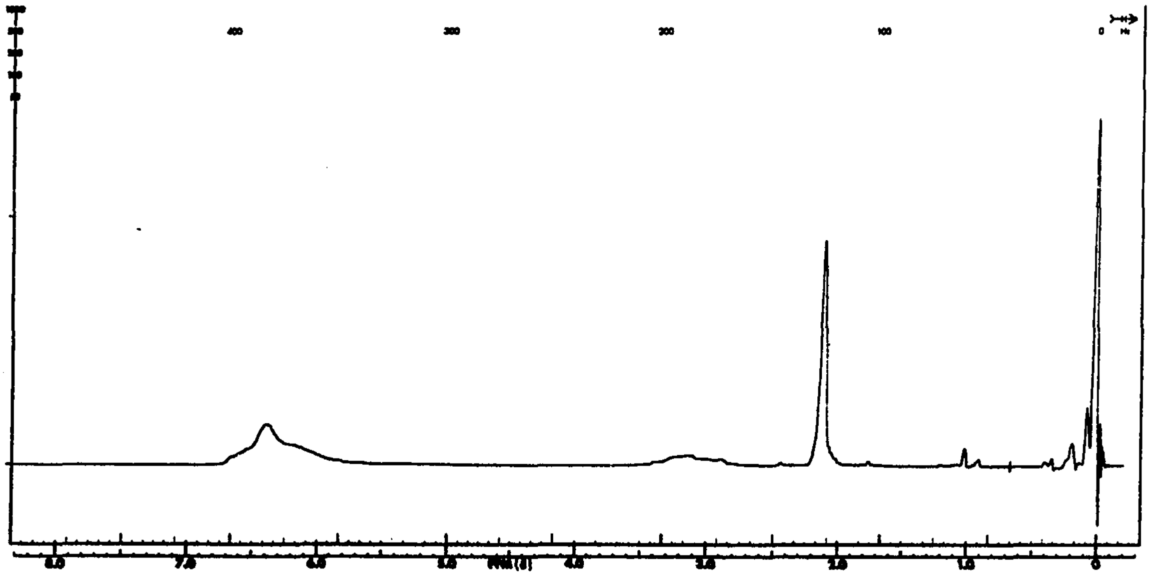


FIGURE 11

IR DATA OF $C_5H_4(CH_3)Si(CH_3)_3$

Absorption	Intensity	Assignment [a]
3085	w	Cp
2965	s	
1255	vs	$Si-CH_3$[b]
1062	vs	
980	w	
930	w	
844	vs	Cp
800	w	
760	w	

a:Ref. 109.

b:Ref. 129, 130, 203.

TABLE 5

Its infrared and n.m.r. spectra are shown in figure 11 and are consistent with the literature values.[94]

(E) SYNTHESIS OF H_3SiBr

(a) Preparation of $C_6H_5SiH_3$[95] (Figure 12)

Approximately 250 ml of anhydrous diethyl ether were refluxed over 7.50 gm (0.198 mol) of $LiAlH_4$ for twelve days; about 100 ml of this etheral solution were placed in the bottom of a sealed $ 45/50 female glass-ground joint containing a magnetic stirring bar and fitted with a water condenser, a dropping funnel and a nitrogen inlet valve. After flushing the apparatus with dry nitrogen, 44.5 gm (35.0 ml, 0.210 mol) of phenyltrichlorosilane, diluted with an equal volume of anhydrous Et_2O, were added dropwise to the etheral solution while magnetic stirring continued. Fumes and a white precipitate initiated the reaction. After all the $C_6H_5SiCl_3$ was added, the resulting gray-white mixture was refluxed for three hours at 45° by means of an oil bath. Excess diethyl ether was distilled off. The crude product was vacuum distilled at 60°/(10 mm Hg) and collected in a receiver flask, cooled to -78° by a dry ice-acetone bath. Purification of the product was performed by distillation at atmospheric pressure producing 16.5 gm (0.149 mol) of $C_6H_5SiH_3$ (b.p. 118°)[96] in 70.8% yield based on the amount of $C_6H_5SiCl_3$ initially

MICRODISTILLATION APPARATUS

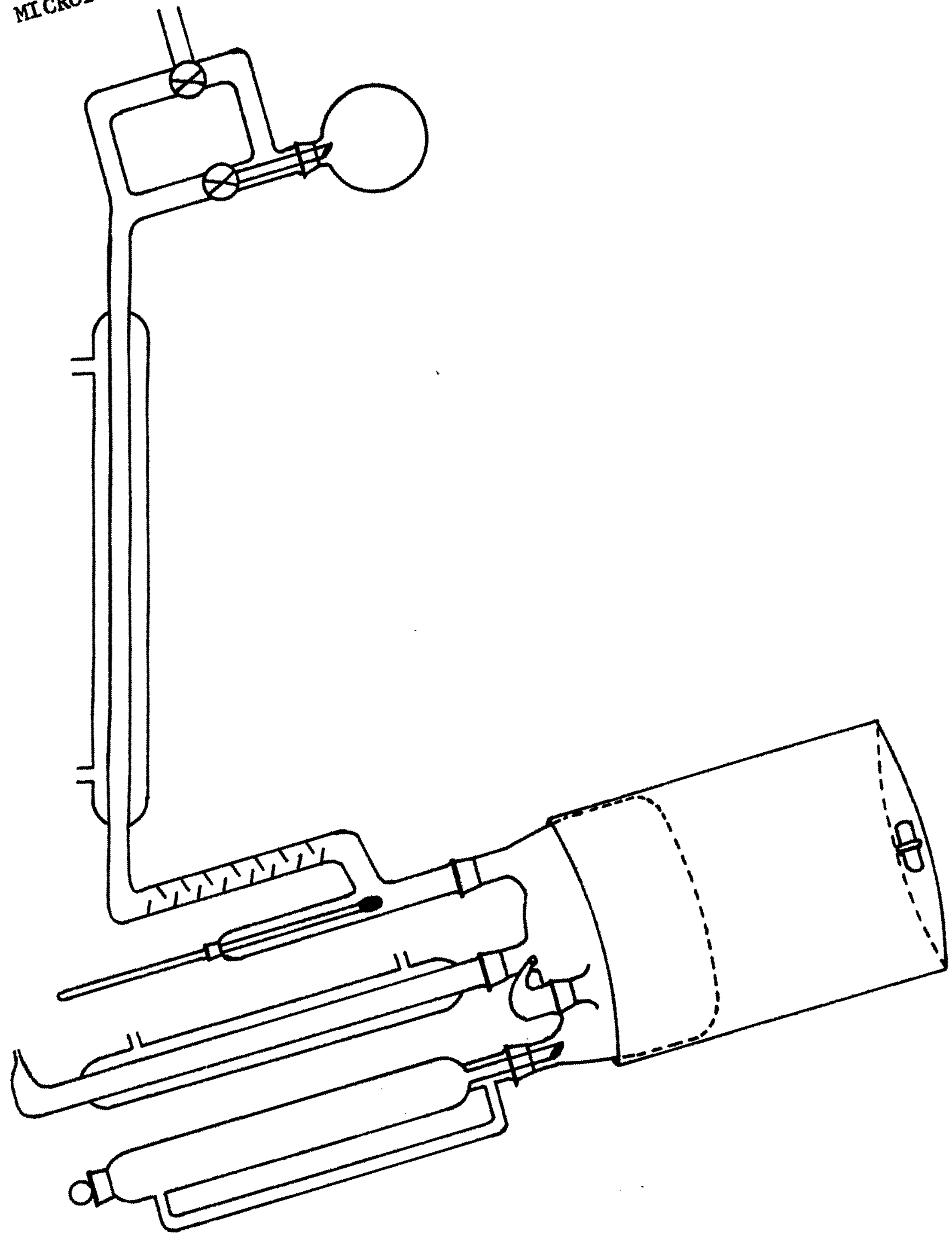
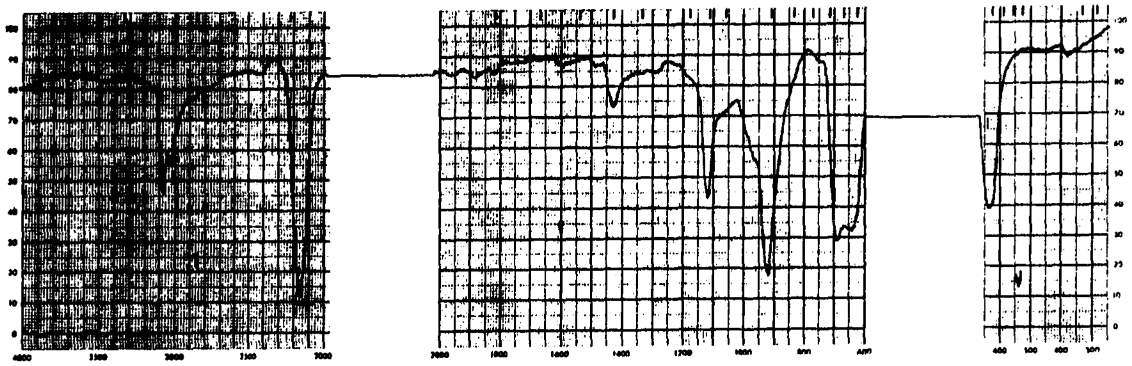


FIGURE 12

IR, NMR SPECTRA OF $C_6H_5SiH_3$

IR



NMR

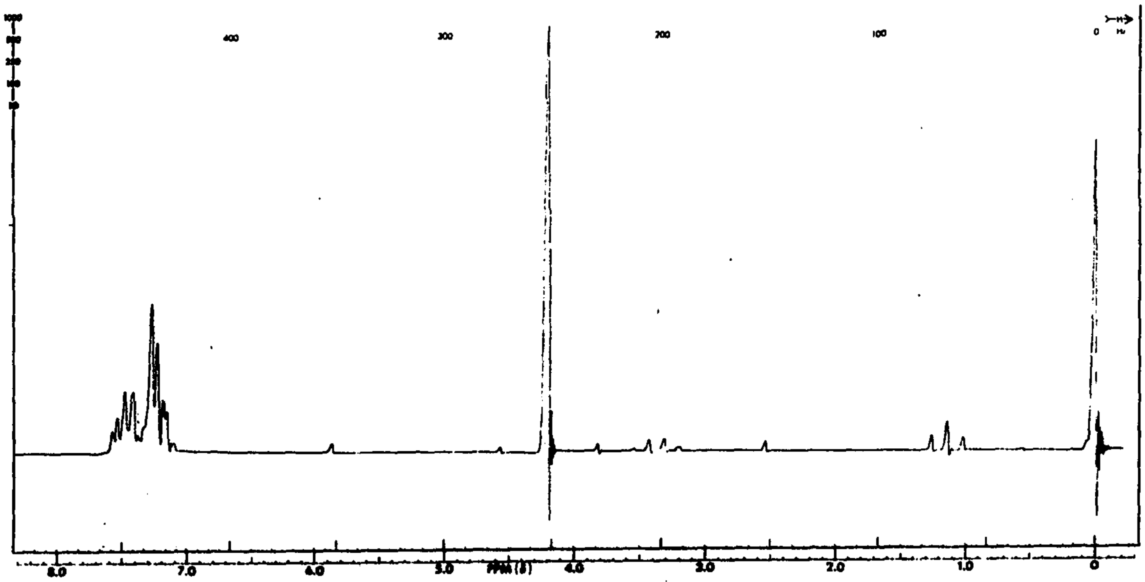


FIGURE 13

employed. The infrared (gas phase) and n.m.r. spectra of $C_6H_5SiH_3$ are shown in figure 13; J(^{29}Si-H) = 200 cps.[70]

(b) Preparation and Purification of H_3SiBr[95]

Anhydrous HBr (27.0 gm, 0.234 mol) was added to the 16.5 gm (0.149 mol) of $C_6H_5SiH_3$ (contained in a standard purex take-off tube). The HBr was condensed into the tube at -78°. This reaction mixture was stored at this temperature for sixteen days.

Purification of H_3SiBr was performed as follows (see figure 14):

After sitting about two weeks at -78°, the take-off tube, still held at -78°, was connected to the vacuum line and degassed twice. The material volatile at -78° (HBr and H_3SiBr) was condensed in two -196° traps connected in series, with occasional pumping. This slow distillation process was continued for about four hours, at which time the stopcock to the take-off tube was closed.

The material collected in the -196° traps was combined, warmed to -78°, and passed through -78°, -96°, -126°, and -196° traps, all in series. Impure H_3SiBr collected in the -96° and the -126° traps which were combined and distilled again through -96°, -126°, and -196° traps, all in series. The materials (F(A), F(B)) collected in the -96° and -126° traps were combined and distilled repeatedly in this manner until only a small ring was seen in the -196° trap. The material collected in the -196°

PURIFICATION SCHEME FOR H_3SiBr

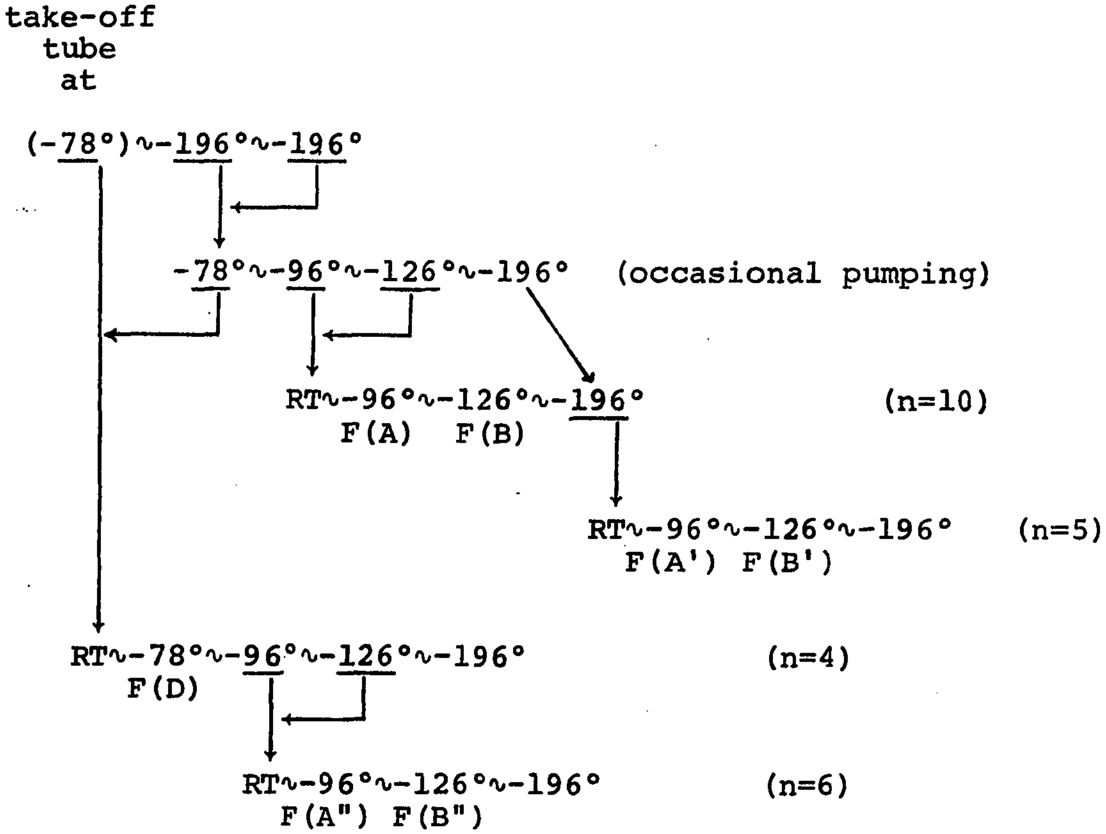


FIGURE 14

trap was transferred to another trap after each of the above distillations. Fractions (A) and (B) were stored at -196° in a take-off tube.

The material (F(C)) from the combined -196° traps was passed through -96°, -126°, and -196° traps, all in series. The material collected in the -196° trap was distilled repeatedly in this manner until only a small ring was seen in the -196° trap. Fractions (A') and (B') were stored at -196° in a take-off tube.

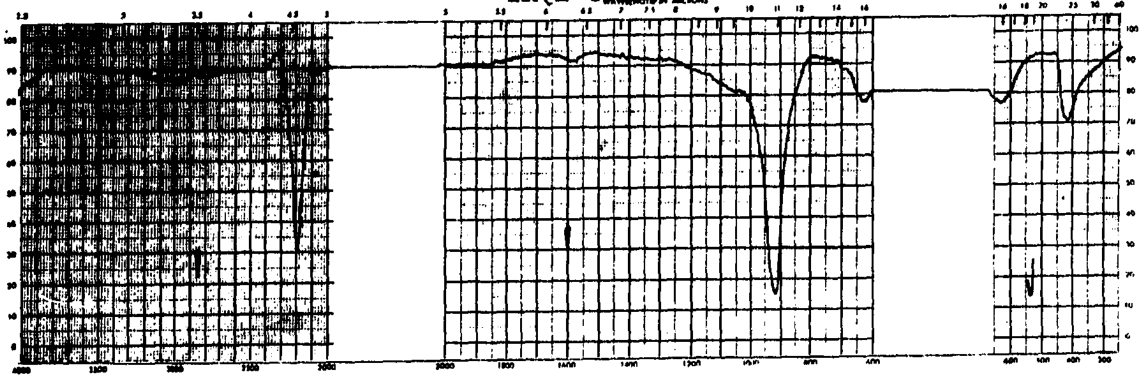
The remaining material in the reaction take-off tube was passed through -78°, -96°, -126°, and -196° traps, all in series. The material (F(D)) collected in the -78° trap was distilled repeatedly in this manner until a small ring appeared in the -196° trap whose material was transferred to another trap after each distillation.

The material collected in the -96° and -126° traps was combined and passed through -96°, -126°, and -196° traps. The material collected in the -96° and -126° traps were combined and distilled repeatedly in this manner until only a small ring appeared in the -196° trap whose material was transferred to another trap after each distillation. Fractions (A", B") were stored at -196° in a take-off tube.

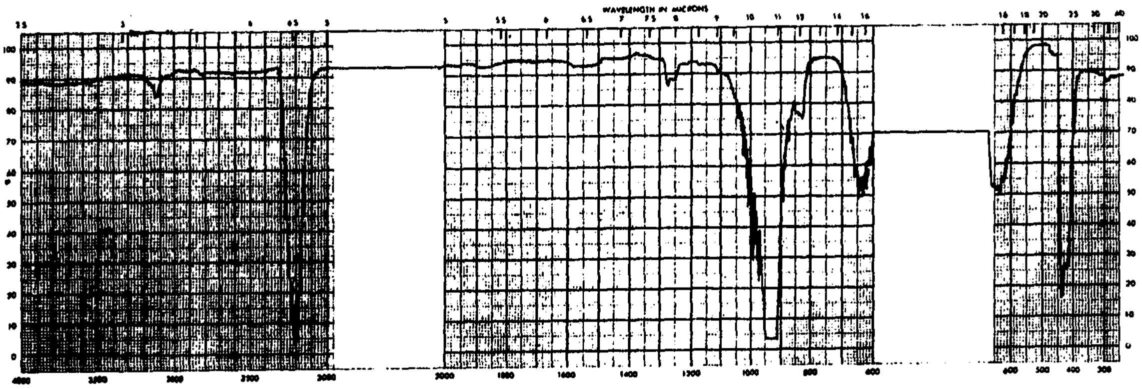
Finally, Fractions (A, B), (A', B'), and (A", B") were all combined to give 14.3 gm (0.129 mol) of H_3SiBr produced in 84.5% yield based on the amount of

IR, NMR SPECTRA OF H_3SiBr

IR(1 torr)



IR(3 torr)



NMR

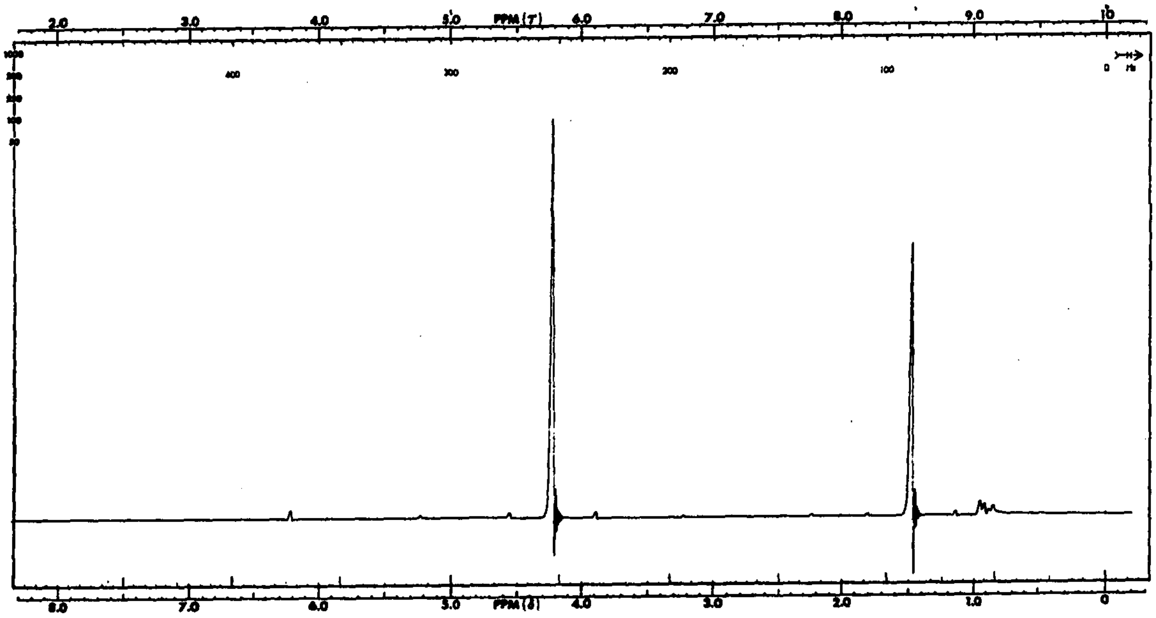


FIGURE 15

C_6H_6 (11.8 gm, 0.109 mol) produced and the amount of $C_6H_5SiH_3$ (13.9 gm, 0.129 mol) consumed. The infrared spectrum (various gas pressures) and the n.m.r. spectrum (taken in cyclohexane used as the internal standard) of H_3SiBr are shown in figure 15 and are consistent with the literature values; $J(^{29}Si\text{-}H) = 239$ cps in agreement with the literature value.[98,99]

It should be noted that H_3SiBr was always stored at -196° in a take-off tube which could be connected to the vacuum line and a certain amount of H_3SiBr removed. Caution should be used at all times when handling H_3SiBr due to its violent reaction with atmospheric oxygen.

(F)

(1) SYNTHESIS OF PENTYL ETHYL ETHER

In the dry bag, 48.5 gm (2.12 mol) of sodium metal, cut up into small pieces, were placed in the bottom of a 2000 ml $ 24/40 single-necked round-bottom flask. After removing the flask from the dry bag, the flask was filled with about 600 ml of cyclohexane and fitted with a condenser. Then 130 ml (102 gm, 2.20 mol) of ethyl alcohol were added dropwise to the heated solution (60°) of sodium metal in cyclohexane over a period of twenty-four hours. A white solution resulted. 242 gm (1.60 mol) of n-amyl bromide were added dropwise to the sodium ethoxide solution in cyclohexane over an extended period, thirty-six hours. An initial blue solution resulted, but a final brown-yellow solution resulted after stirring at 60° (ten hours). The solution was filtered, and the white residue remaining in the flask was washed twice with 50 ml portions of cyclohexane and filtered.

Excess cyclohexane was distilled off at 84°; at 104° a fraction was collected; at 118° a fraction was collected assumed to be n-amyl ether. The product was produced in 51.3% yield based on the amount of the n-amyl bromide initially employed.

(2) SYNTHESIS OF n-BUTYL PROPYL ETHER

In the dry bag, 60.1 gm (1.00 mol) of n-propanol were placed in a 1000 ml ₸ 24/40 single-necked round-bottom flask fitted with a reflux condenser, containing about 300 ml of cyclohexane. 23.0 gm (1.00 mol) of sodium metal, cut up into pieces, were added to the solution with stirring; as the sodium metal dissolved, reaction was evidenced by the evolution of gas and liberation of heat.

184 gm (1.00 mol) of n-BuI were added to the reaction mixture which still contained pieces of sodium metal. The pale yellow solution changed to a blue-milky white solution after stirring for twelve hours. The solution was cooled to room temperature, filtered, and the white residue remaining in the flask was washed twice with 100 ml portions of cyclohexane. Excess cyclohexane was distilled off at 82°; at 96° a fraction was collected; at 117° a fraction

was collected assumed to be n-butyl propyl ether. The product was produced in 41.8% yield based on the amount of the n-BuI initially employed.

The above ethers and dioxane failed to dissolve the potassium salt, $K[C_5H_5]$, and were subsequently discarded as appropriate synthetic solvents.

CHAPTER III

EXPERIMENTAL (II)

(A) SYNTHESES AND REACTIONS OF σ-SILYL-π-CYCLOPENTADIENYL TRICARBONYL DERIVATIVES OF CHROMIUM, MOLYBDENUM, AND TUNGSTEN

(1) SYNTHESIS OF $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$

Summary: It was found that the new compound, $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, could be synthesized in 38.1% yield based on the amount of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ initially employed by the reaction of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ with gaseous H_3SiBr, at an ideal gas pressure of 6.37 atm, after thirty minutes at room temperature according to the equation:

$$K[Cr(CO)_3(\pi\text{-}C_5H_5)] + H_3SiBr \rightarrow KBr + H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$$

(a) Preparation of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$

In the dry bag (Figure 17), 125 ml of monoglyme (1,2-dimethoxyethane; freshly distilled over $LiAlH_4$ and saturated with dry nitrogen) were placed in a 250 ml $\mathfrak{T}$ 24/40 single-necked round-bottom flask. 6.5 ml (0.076 mol) of cyclopentadiene (stored at -78°) were added to the flask along with a magnetic stirring bar. 2.00 gm (0.0511 mol) of potassium metal, cut up into small pieces, were added piecewise to the stirred monoglyme solution of C_5H_6 so that the potassium metal dissolved smoothly. After all the potassium had dissolved, the resulting solution changed from clear to yellow upon addition of the first few pieces of potassium, and finally to light pink with the addition of the last piece of potassium.

Transferring the wine-red monoglyme solution of $K[C_5H_5]$ to a closed ₮ 45/50 female glass ground joint (Figure 18), 11.5 gm (0.0523 mol) of $Cr(CO)_6$ were added to the monoglyme solution. Fitting the female receiver with a condenser, the monoglyme solution of $K[C_5H_5]$ containing $Cr(CO)_6$ was removed from the dry bag, and the receiver was clamped to a ring stand. A CO atmosphere blanketed the reaction mixture and was provided by means of a long glass tube extending the length of the condenser. After stirring magnetically for one hour at room temperature, the reaction mixture was heated slowly to 70° and then to 86° (vigorous refluxing of the solvent) for sixteen hours. Refluxing was discontinued with some of the metal carbonyl collecting on the sides of the receiver and in the condenser. $Cr(CO)_6$ was not removed from the sides of the receiver due to the construction of the apparatus. Excess solvent was distilled from the receiver after removal of the CO portal and condenser. The desired product was obtained by removing the remaining solvent on the vacuum line (Figure 1) by condensing the remainder of the solvent in a -78° dry ice-acetone trap. The potassium salt kept at room temperature was further purified by condensing any volatile material in a -196°

IR SPECTRUM OF K[Cr(CO)$_3$Cp]

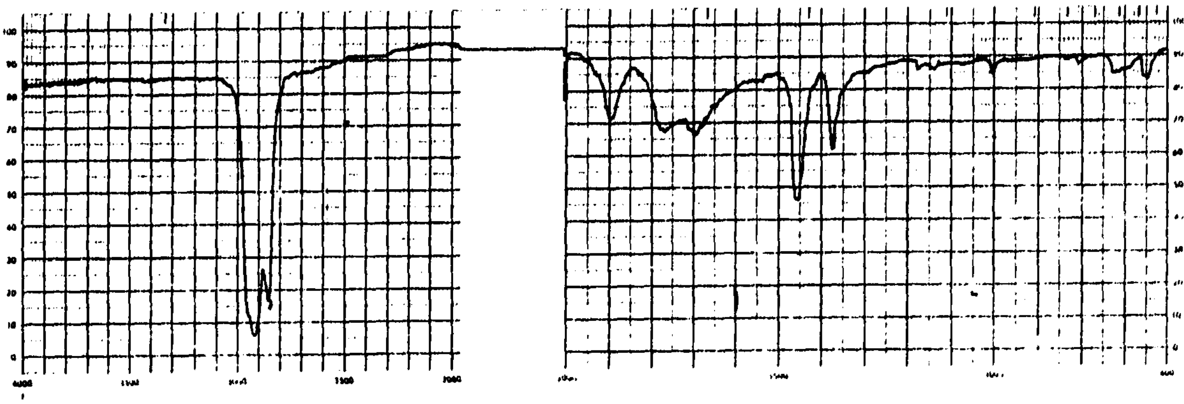


FIGURE 16

IR DATA OF K[Cr(CO)$_3$(π-C$_5$H$_5$)]

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	1900	s	-CO [a]
	1771	s	-CO [a]
	1698	s	-CO [a]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	1005	w	Cp[b]
	810	w	Cp[b]
Nujol	728	w	
	650	w	

a:Ref. 19, 92, 162, 165.

b:Ref. 109.

TABLE 6

GLOVE OR DRY BAG

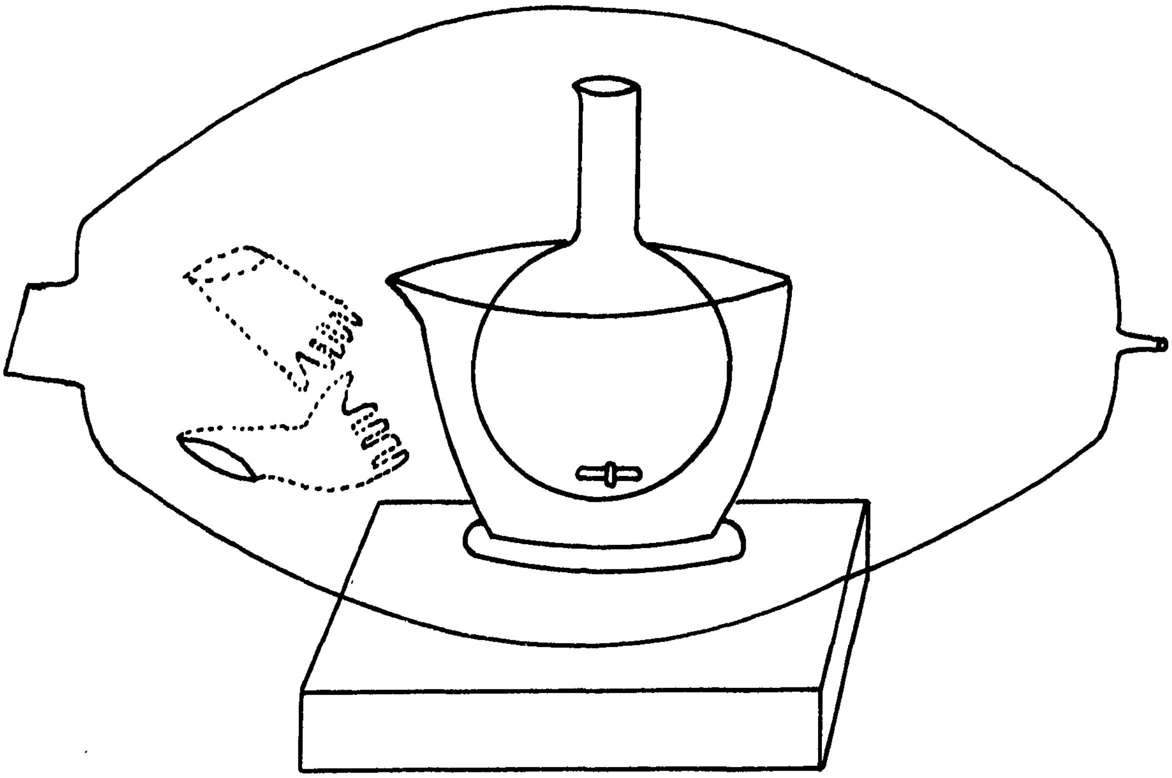


FIGURE 17

K[M(CO)$_3$Cp] PREPARATION APPARATUS

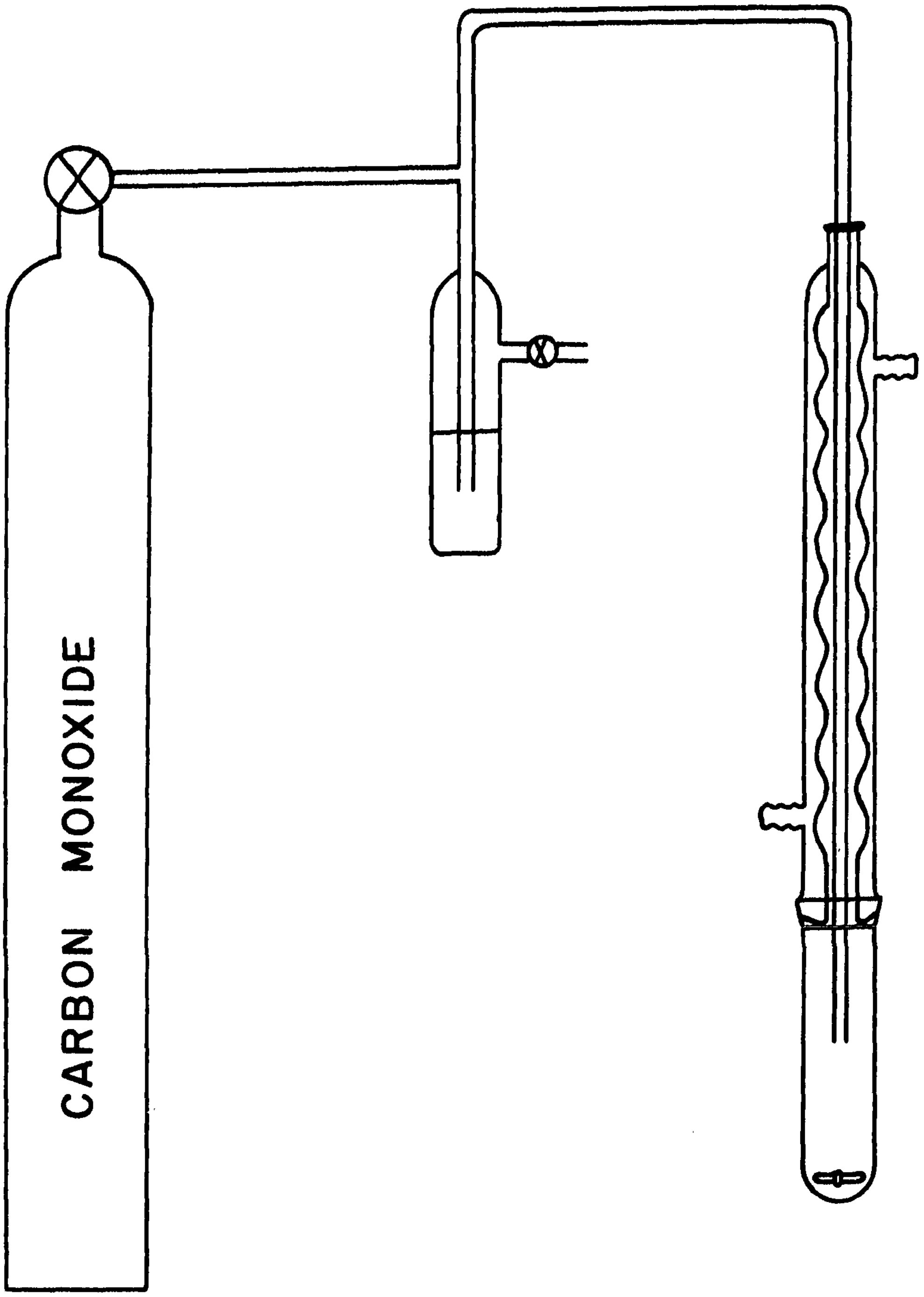


FIGURE 18

trap open to the pump, until no additional metal carbonyl was observed to collect in the -196° trap. The infrared spectrum of $K[Cr(CO)_3(\pi-C_5H_5)]$ is shown in figure 16.

(b) Preparation of $H_3Si-Cr(CO)_3(\pi-C_5H_5)$

In the dry bag, 926.2 mgm (3.856 mmol) of impure $K[Cr(CO)_3(\pi-C_5H_5)]$, as prepared in part (a), were placed in a glass pressure reactor (Figure 19) which was subsequently removed from the dry bag, connected to the vacuum line, and evacuated. 648.1 mgm (5.839 mmol) of H_3SiBr were condensed into the reactor at -196°; upon warming to room temperature, the reactor was disconnected from the vacuum line and laid at an inclination such that the silyl bromide liquified at or near the teflon stopcock without contacting the solid residue. As the reactor came to room temperature an orange coloration and brown residue appeared with the liberation of heat. After sitting for thirty minutes at room temperature, a yellow-brown coloration resulted.

The reactor was connected to the vacuum line sublimer (Figure 20) and cooled to -196°. 4.1 mgm of a non-condensible gas were pumped away, assumed to be a mixture of H_2 and CO. Warming the reactor to -78°, 235.9 mgm (2.125 mmol) of H_3SiBr were recovered (identified by gas phase infrared spectrum[98]); warming the reactor to room temperature, 33.4 mgm (0.151 mmol) of $Cr(CO)_6$

GLASS PRESSURE REACTOR

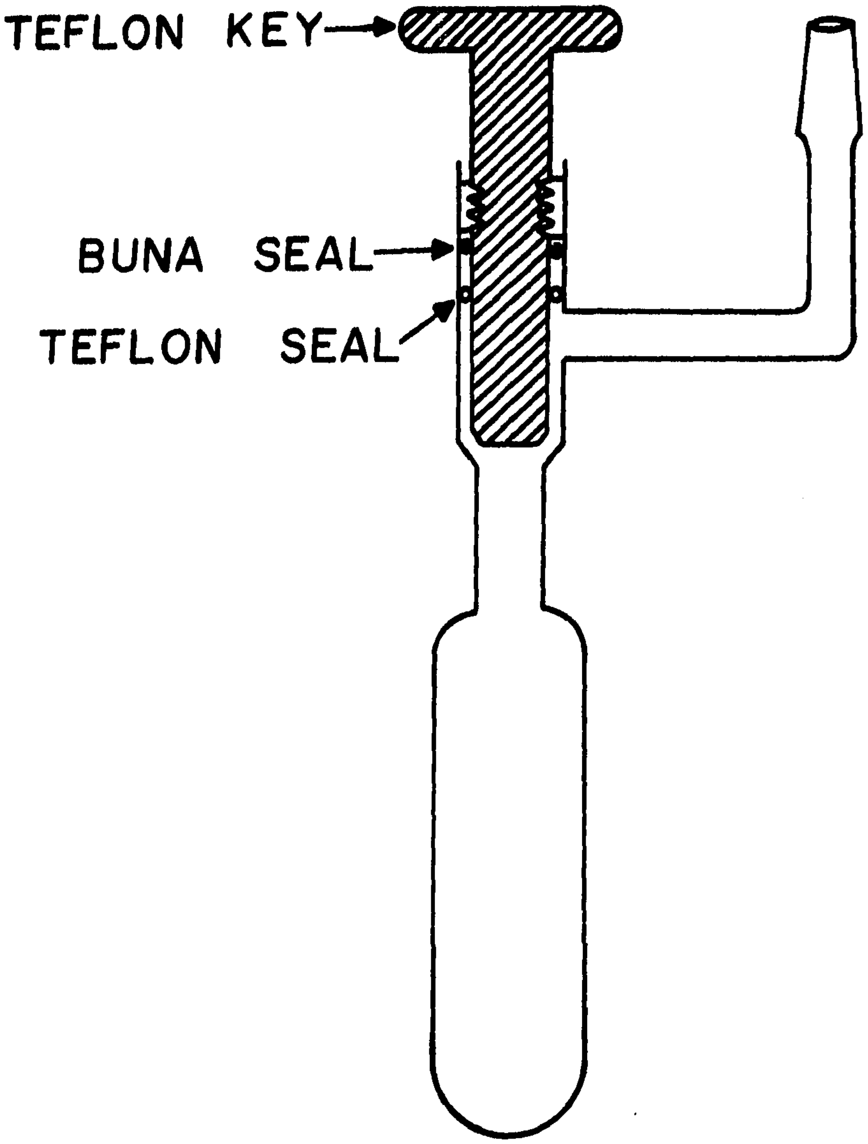


FIGURE 19

VACUUM LINE SUBLIMER

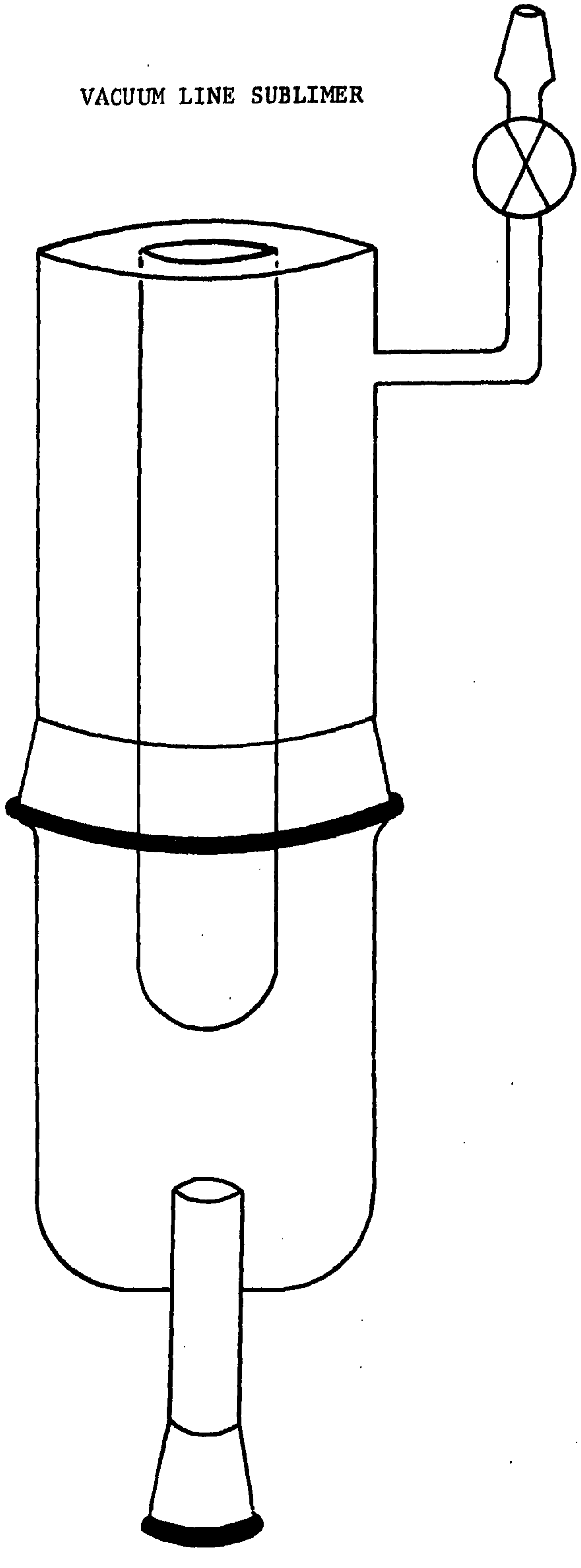


FIGURE 20

(identified by gas phase infrared spectrum[100]) were removed from the reactor and collected by the cold finger which was cooled to -196°; and 341.2 mgm (1.469 mmol) of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ were produced by the reaction in 38.11% yield based on the amount of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ initially employed. This product was removed from the reactor by heating the reactor to 75° by means of a hot water bath; bright yellow crystals sublimed into the neck of the reactor. The vacuum line sublimer was disconnected from the vacuum line, placed in the dry bag, and filled with dry nitrogen. The reactor was separated from the sublimer, and the yellow crystals were removed from the neck of the reactor by scraping the walls with a thinly-filed spatula. Small amounts of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ were used to prepare an analysis sample, a melting point capillary, a Nujol mull, and an n.m.r. sample. Other syntheses furnished additional $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ for various reactions described in part (d).

(c) Identification and Characterization

1. Analysis of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, approximately 10-30 mgm of material were placed in a 5 mm (o.d.) tube containing a $\mathfrak{T}$ 12/30 male joint. The tube was removed from the dry bag, evacuated on the vacuum line, and sealed with an oxygen torch. The following results were obtained:

Found: C - 40.60%; H - 3.49%; Si - 10.50%

Calculated: C - 41.37%; H - 3.47%; Si - 12.09%

2. Melting Point of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, a small amount of material (two or three small pieces) was placed in a capillary tube filled with deoxygenized nitrogen gas. A cork was placed in the flared mouth of the tube; after removing the tube from the dry bag, the tube was sealed by gently heating a portion of the tube near to the cork. Duplicate determinations were performed, the second one taken as the melting point. The melting point of 129-131° (uncorrected) was recorded for the compound $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$.

3. Infrared Spectrum of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: The infrared spectrum of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ was determined in the solid state in Nujol. In the dry bag, a drop of Nujol was placed on one of the KBr salt plates; a small amount of material was put on the drop of oil, and then the other KBr plate was placed over the drop, forming an air tight seal between both KBr plates. The infrared spectrum is shown in figure 22, and the principle absorptions are given in table 7.

4. Nuclear Magnetic Resonance of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, approximately 30 mgm of sample were placed in the bottom of a nitrogen-filled n.m.r. tube containing a ⊊ 12/30 male joint (Figure 21). The tube was fitted to an adapter, removed from the dry bag, and

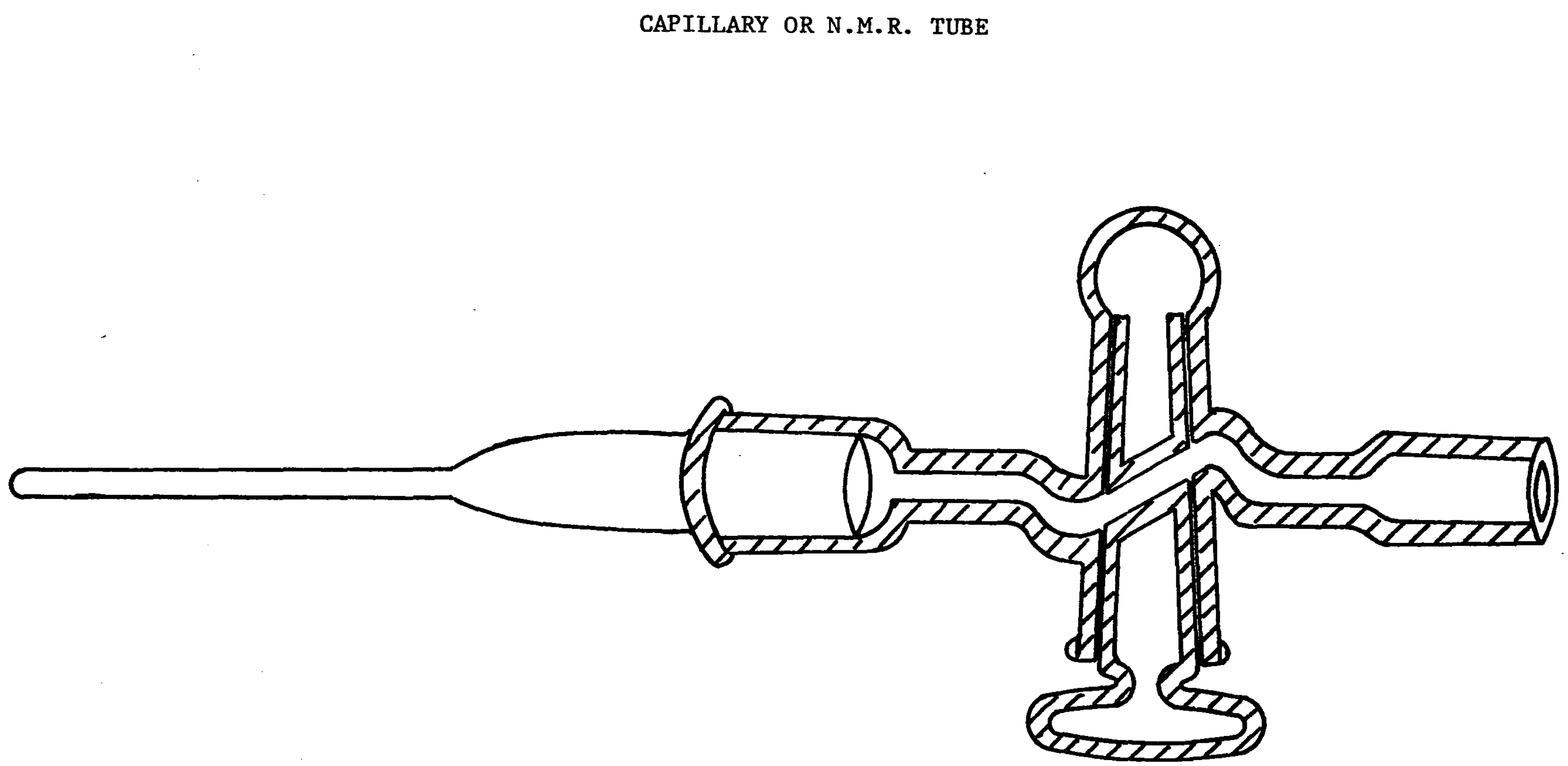
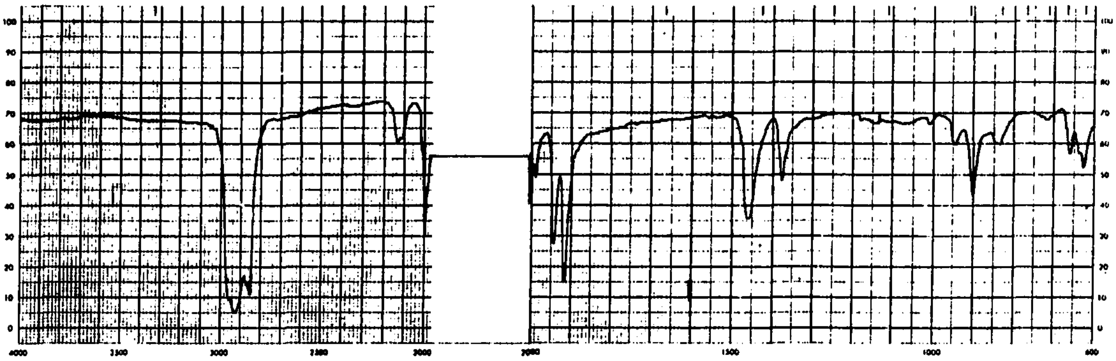


FIGURE 21

IR, NMR SPECTRA OF $H_3Si-Cr(CO)_3Cp$

IR



NMR

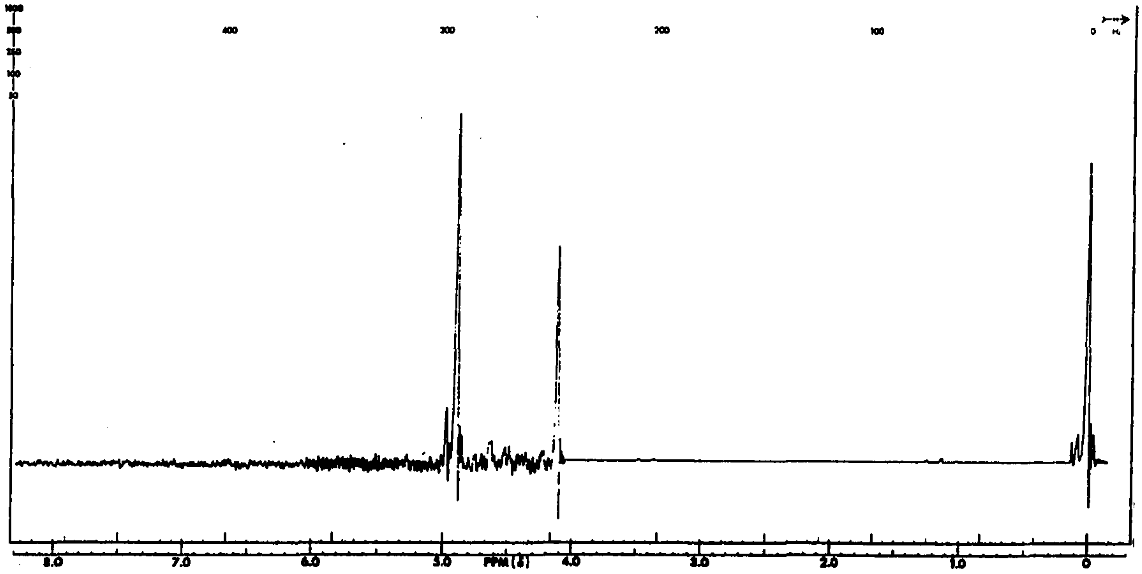


FIGURE 22

IR DATA OF $H_3Si-Cr(CO)_3(\pi-C_5H_5)$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2105(Sh)		
	2032	m	Si-H [a]
	2105(Sh)		
	1999	vs	-CO[b]
	1990(Sh)		
	1943	vs	-CO[b]
	1918	vs	-CO[b]
Nujol	1459	vs	
Nujol	1375	vs	
Nujol	1160	w	
	945	w	
	900	s	SiH_3 def.vib.[a]
	835	w	Cp [c]
Nujol	717	w	
	600	w	
	628	w	

a:Ref. 203.

b:Ref. 19, 54.

c:Ref. 92, 109

TABLE 7

evacuated on the vacuum line. A small amount of $Si(CH_3)_4$ (TMS) and approximately 4 cm of anhydrous diethyl ether (degassed twice) were condensed into the n.m.r. tube at -196°. Then the tube was sealed by heating a portion of the tube below the joint with an oxygen torch. The sample tube was stored at -196°. Before it was to be placed in the n.m.r. sample holder, the sample was allowed to warm to room temperature, and moisture removed by wiping with a paper towel. The n.m.r. spectrum is shown in figure 22 and the chemical shifts for the silyl hydrogens and the ring (Cp) hydrogens are given below:

Chemical Shift - δ from $Si(CH_3)_4$[a]

$Cp(C_5H_5)$	SiH_3
4.89	4.12

a:taken in diethyl with $Si(CH_3)_4$ as the internal standard

5. Thermal Stability of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ decolorized rapidly (several minutes) in an inert atmosphere at room temperature; since the silicon analysis never obtained a constant value after three attempts, it appears that $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ is the least thermally stable of the three derivatives, $H_3Si\text{-}Cr$, $H_3Si\text{-}Mo$, and $H_3Si\text{-}W$. However, $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ could be stored at -20° indefinitely.

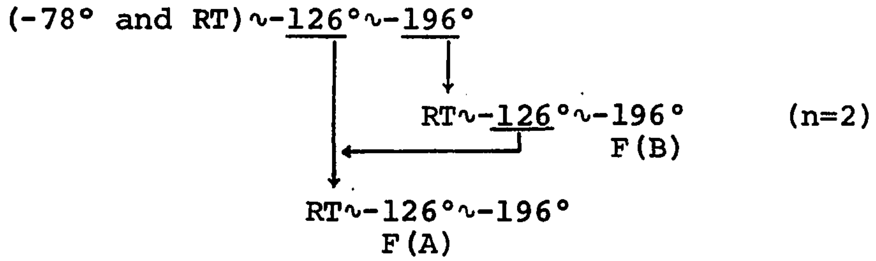
(d) Reactions of $H_3Si-Cr(CO)_3(\pi-C_5H_5)$

1. Reaction of $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ with HCl

Summary: It was found that cleavage of the silyl-chromium linkage occurred when $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ and HCl, at an ideal gas pressure of 1.52 atm, were combined for several hours at room temperature according to the equation:

$$H_3Si-Cr(CO)_3(\pi-C_5H_5) + HCl \rightarrow H-Cr(CO)_3(\pi-C_5H_5) + H_3SiCl$$

In the dry bag, 51.9 mgm (0.223 mmol) of $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ (light green) were placed in a reactor; and from the vacuum line, 50.9 mgm (1.40 mmol) of HCl were condensed into the reactor at -196°. Upon warming to room temperature and standing for three hours, a bright yellow residue resulted. The reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:



4.7 mgm were lost by the reactor.

The following materials were identified:

HCl: Fraction (B) [40.2 mgm, 1.11 mmol; 79.0% recovery based on the amount of HCl initially employed; some of this material was lost in transfer; identified by infrared spectrum identical to that observed for pure HCl[101]].

H_3SiCl: Fraction (A) [13.5 mgm, 0.203 mmol; 90.9% yield based on the amount of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ initially employed; identified by infrared spectrum identical to that observed for pure H_3SiCl [98]].

$H\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: Bright yellow solid [44.5 mgm, 0.220 mmol; identified by infrared spectrum previously observed for pure $H\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$].

---

2. Reaction of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ with $N(CH_3)_3$

Summary: It was found that a 1.00:0.92 trimethylamine adduct formation occurred when $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)+N(CH_3)_3 \rightarrow [(CH_3)_3N,SiH_3]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-$$

In the dry bag, 112.4 mgm (0.4841 mmol) of

$H_3Si{-}Cr(CO)_3(\pi{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 414.2 mgm (7.007 mmol) of $N(CH_3)_3$ were condensed in the reactor at -196°. Upon warming to 0° a yellow-green solution and a yellow solid were observed to form immediately. After thirteen hours at 0° the reactor was cooled to -196°, and no non-condensible gas was observed. Then the reactor was warmed to 0°, and excess $N(CH_3)_3$ was removed from the reactor by condensation in a trap held at -196°. The reactor gained 14.2 mgm (0.240 mmol) of $N(CH_3)_3$. Excess $N(CH_3)_3$ was once again condensed back in the reactor (cooled to -196°) which was then allowed to warm to room temperature. After sitting several days at ambient temperature the reactor with excess $N(CH_3)_3$ always removed at 0° before each weighing gained the following amounts of $N(CH_3)_3$: 18.1 mgm (0.306 mmol) after one day; 20.1 mgm (0.340 mmol) after two days; 25.3 mgm (0.428 mmol) after three days; and 26.3 mgm (0.445 mmol) after four days. The volatile materials removed from the reactor held at 0° were separated as follows:

(0°)∿-196°
↓
RT∿-96°∿-196° (n=2)
F(A) F(B)

[26.3 mgm (0.445 mmol) of $N(CH_3)_3$ were gained by the reactor].

The following materials were identified:

$N(CH_3)_3$: Fractions (A) and (B) [373.4 mgm, 6.317 mmol; 90.15% recovery based on the amount of $N(CH_3)_3$ initially employed; mol. wgt. calc.-59.11, found-59.06: 0.08%; confirmed by infrared spectrum identical to that observed for pure $N(CH_3)_3$[101]].

$[(CH_3)_3N,SiH\ ]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-$: Yellow solid [138.7 mgm, gross composition of $H_3Si\text{-}Cr:N(CH_3)_3$ was 0.4841:0.4449 or 1.00:0.92]. The infrared spectrum of this trimethylamine adduct (m.p. 84-89°) is shown in figure 23.

---

3. Reaction of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that a 1.00:1.26 dimethylamine adduct formation occurred when $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and $HN(CH_3)_2$ were combined for several days at room temperature according to the equation:

$$H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)+HN(CH_3)_2\rightarrow[H(CH_3)_2N,SiH_3]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-$$

In the dry bag, 96.8 mgm (0.419 mmol) of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 507.1 mgm (11.25 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to room temperature, slight bubbling occurred and dissolution of the yellow solid occurred forming a yellow-

IR SPECTRUM OF $[Me_3N,SiH_3]^+[Cr(CO)_3Cp]^-$

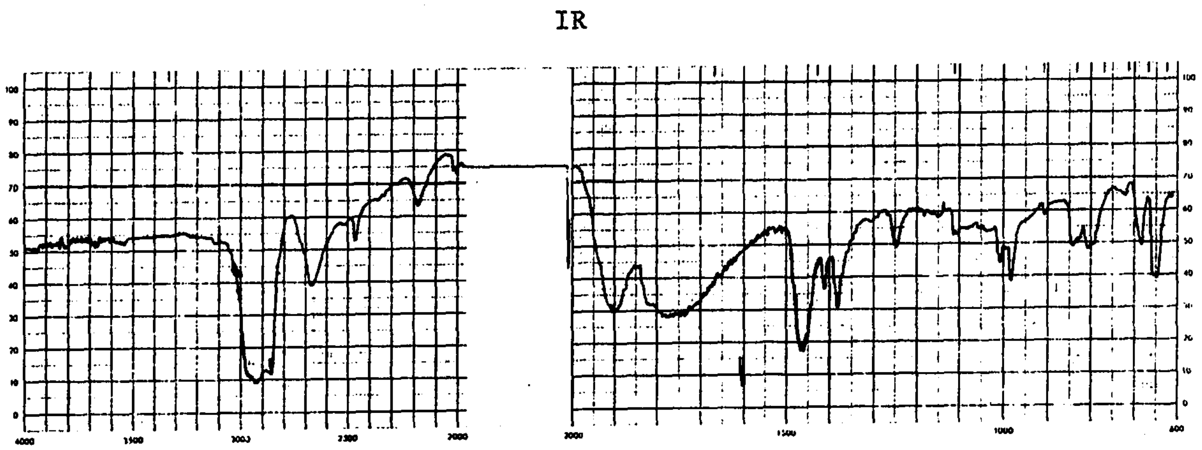


FIGURE 23

IR DATA OF $[(CH_3)_3N,SiH_3]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2660	m	
	2450	m	
	2170	w	Si-H[a]
	2010	w	
	1900	ms	-CO[b]
	1840	m	-CO[b]
	1750	m	-CO[b]
Nujol	1459	vs	
	1405	m	$N(CH_3)_3$[c]
Nujol	1375	vs	
	1240	m	$N(CH_3)_3$[c]
Nujol	1160	w	
	1003	m	Cp[d], $N(CH_3)_3$[c]
	978	m	SiH_3 def.vib.[a]
	835	m	$N(CH_3)_3$[c]
	800	m	
Nujol	717	w	
	680	m	
	642	s	

a:Ref. 203.

b:Ref. 19, 92, 162

c:App. F, Table 45; Ref. 101.

d:Ref. 109

TABLE 8

brown solution. After sitting at room temperature for three days, the reactor was cooled to -196°, and a small amount of non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$\underset{F(A)}{RT \sim -96°} \sim -130° \sim -196°$$

24.1 mgm (0.526 mmol) of $HN(CH_3)_2$ were gained by the reactor.

The following materials were identified:

$\underline{HN(CH_3)_2}$: Fraction (A) [483.4 mgm, 10.72 mmol; 95.33% yield based on the amount of $HN(CH_3)_2$ initially employed; identified by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

$\underline{[H(CH_3)_2N,SiH_3]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-}$: Yellow-brown solid [120.9 mgm, 0.4360 mmol; gross composition of $H_3Si\text{-}Cr:HN(CH_3)_2$ was 0.4190:0.5350 or 0.11:1.28]. The infrared spectrum of this dimethylamine adduct is shown in figure 24.

---

4. Reaction of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ with PF_5

Summary: It was found that a complex mixture resulted when $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and PF_5, at an ideal

IR SPECTRUM OF $[HMe_2N,SiH_3]^+[Cr(CO)_3Cp]^-$

IR

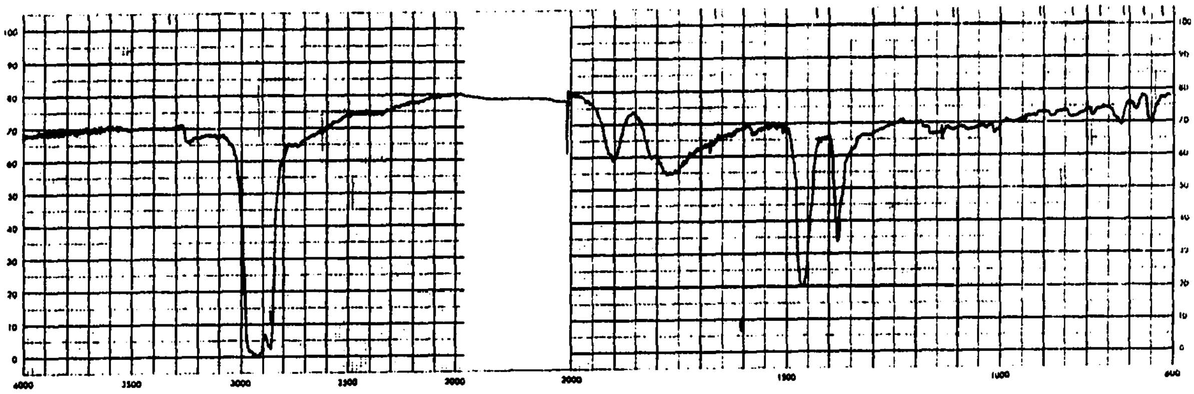


FIGURE 24

IR DATA OF $[(CH_3)_2NH,SiH_3]^+[Cr(CO)_3(\pi-C_5H_5)]^-$

	Absorption	Intensity	Assignment[a]
	3250	w	
Nujol	2920	vs	
Nujol	2852	vs	
	1900	m	-CO
	1820	m	-CO
	1775	m	-CO
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
Nujol	717	w	
	650	w	

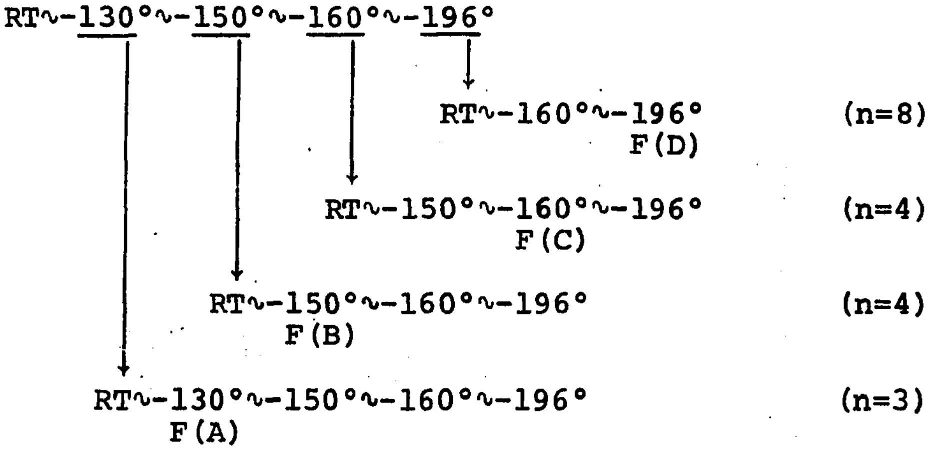
a:Ref. 19, 162.

TABLE 9

gas pressure of 3.80 atm, were combined for several days at room temperature according to the equation:

$$H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5) + PF_5 \rightarrow \begin{array}{l}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array} + HSiF_3 + PF_3$$

In the dry bag, 158.9 mgm (0.6843 mmol) of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 438.6 mgm (3.482 mmol) of PF_5 were condensed into the reactor at -196°. Upon warming to room temperature, a dark residue appeared immediately. After sitting for three days, the reactor was cooled to -196°, and a small amount of non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:



49.3 mgm were gained by the reactor.

The following materials were identified:

$\underline{PF_3}$: Fraction (D) [67.4 mgm, 0.766 mmol; 22.3% yield based on the amount of PF_5 initially employed; mol. wgt. calc.-87.97, found-87.61: 0.41%; confirmed by infrared spectrum identical to that observed for pure PF_3 [104]].

$\underline{SiF_4}$ and $\underline{HSiF_3}$: Fraction (C) [37.4 mgm; identified by infrared spectrum identical to that observed for a mixture of SiF_4 and $HSiF_3$ [105]].

$\underline{PF_5}$: Fraction (B) [50.2 mgm, 0.398 mmol; 11.4% recovery based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure PF_5 [104]].

$\underline{OPF_3}$: Fraction (A) [50.2 mgm, 0.483 mmol; 13.9% yield based on the amount of PF_5 initially employed; mol. wgt. calc.-103.97, found-104.6: 0.61%; confirmed by infrared spectrum identical to that observed for pure OPF_3 [104]].

complex mixture: Dark green solid [208.2 mgm; assumed to be a mixture of several poly-flourinated species]. No infrared spectrum (in Nujol) or n.m.r. spectrum (in deuterated acetone) were observed.

5. Reaction of $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ with H_2O

Summary: It was found that a trace of SiH_4 was formed when $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ and H_2O were combined for twelve hours at RT.

In a preliminary experiment, 35.9 mgm (0.155 mmol) of $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ and about one half milliliter of H_2O were combined in a glass pressure reactor. After sitting twelve hours at room temperature, the reactor was cooled to -196°, and a small amount of non-condensible gas was removed. The reactor was allowed to warm to -78°, and some volatile material was condensed in a -196° trap. Then the reactor was warmed to 0°, and no volatile material was condensed in the -196° trap. The volatile material collected in the -196° trap was purified as follows:

$$\mathrm{RT}\sim-78°\sim\underset{\mathrm{F(A)}}{-196°}$$

Fraction (A) contained SiH_4 identified by its infrared spectrum.[102]

(e) Reactions of $H_3C-Cr(CO)_3(\pi-C_5H_5)$

1. Reaction of $H_3C-Cr(CO)_3(\pi-C_5H_5)$ with HCl

Summary: It was found that a complex solid mixture resulted when $H_3C-Cr(CO)_3(\pi-C_5H_5)$ and HCl, at an ideal gas pressure of 4.15 atm, were combined for three days at room temperature according to the equation:

$$H_3C-Cr(CO)_3(\pi-C_5H_5) + HCl \rightarrow \begin{array}{l}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array}$$

In the dry bag, 315.9 mgm (1.462 mmol) of $H_3C-Cr(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 138.7 mgm (3.804 mmol) of HCl were condensed into the reactor at -196°. Upon warming to room temperature, a dark blue residue appeared immediately. The reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$RT \sim -126° \sim \underset{F(A)}{-196°} \qquad (n=2)$$

22.6 mgm were gained by the reactor.

The following materials were identified:

HCl: Fraction (A) [38.5 mgm, 1.06 mmol; 27.8% recovery based on the amount of HCl initially employed;

identified by infrared spectrum identical to that observed for pure HCl [101]].

complex mixture: Dark blue-green solid [293.3 mgm]. No infrared spectrum (in Nujol) or n.m.r. spectrum (in deuterated acetone) were observed. The solid formed a dark blue solution in deuterated acetone.

---

2. Reaction of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ with $N(CH_3)_3$

Summary: It was found that no reaction occurred when $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5) + N(CH_3)_3 \rightarrow \text{N.R.}$$

In the dry bag, 14.9 mgm (0.0689 mmol) of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 382.0 mgm (6.463 mmol) of $N(CH_3)_3$ were condensed into the reactor at -196°. Upon warming to room temperature, an orange liquid appeared which turned brown after three days. The reactor was cooled to -196°, and no non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

RT∿-78°∿-96°∿-126°∿-196°
↓
RT∿-96°∿-126°∿-196°
F(A) F(B)

0.5 mgm were gained by the reactor.

The following materials were identified:

$N(CH_3)_3$: Fractions (A) and (B) [377.4 mgm, 6.385 mmol; 98.79% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$: Bright yellow solid [15.3 mgm, 0.708 mmol; 103% recovery based on the amount of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ initially employed; identified by infrared spectrum identical to that observed for pure $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ [2]].

---

3. Reaction of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that the new compound, $[(CH_3)_3NH]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-$, was formed when $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and $HN(CH_3)_2$ were combined for thirty minutes at 0° according to the equation:

$H_3C-Cr(CO)_3(\pi-C_5H_5)+HN(CH_3)_2 \rightarrow [(CH_3)_3NH]^+[Cr(CO)_3(\pi-C_5H_5)]^-$

In the dry bag, 26.7 mgm (0.123 mmol) of $H_3C-Cr(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 1091.4 mgm (24.210 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to -78°, a light yellow solution appeared; warming further to 0°, a bright orange solution appeared. After sitting for thirty minutes at 0°, the reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:

$$0°\sim-130°\sim\underset{F(A)}{-196°}$$

5.5 mgm (0.12 mmol) of $HN(CH_3)_2$ were gained by the reactor.

The following materials were identified:

<u>$HN(CH_3)_2$</u>: Fraction (A) [1085.9 mgm, 24.088 mmol; 99.450% recovery based on the amount of $HN(CH_3)_2$ initially employed; identified by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

<u>$[(CH_3)_3NH]^+[Cr(CO)_3(\pi-C_5H_5)]^-$</u>: Bright orange-red solid [32.2 mgm, 0.123 mmol]. $[(CH_3)_3NH]^+[Cr(CO)_3(\pi-C_5H_5)]^-$ (gross composition of $H_3C-Cr:HN(CH_3)_2$ was 0.123:0.120)

IR SPECTRUM OF $[Me_3NH]^+[Cr(CO)_3Cp]^-$

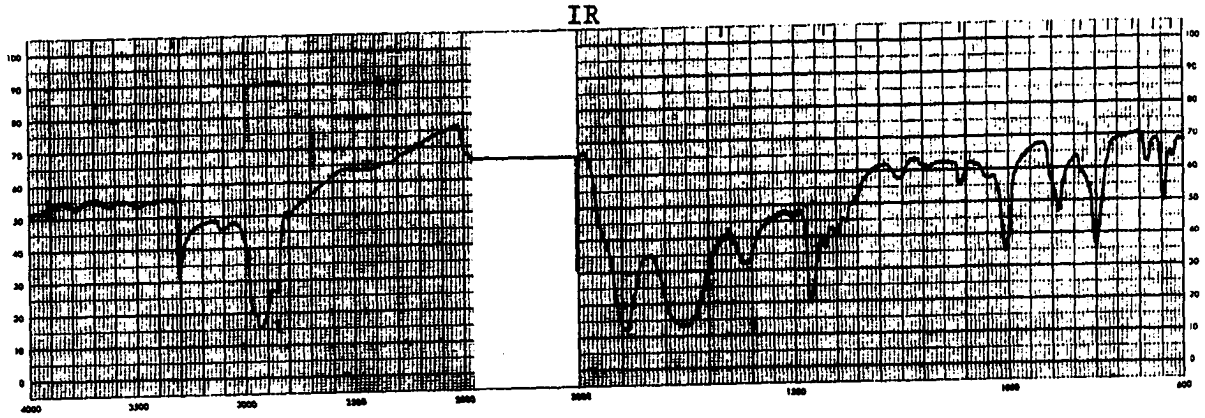


FIGURE 25

IR DATA OF $[(CH_3)_3NH]^+[Cr(CO)_3(\pi-C_5H_5)]^-$

	Absorption	Intensity	Assignment
	3308	s	
Nujol	2920	vs	
Nujol	2852	vs	
	1887	vs	-CO [a]
	1760	vs	-CO [a]
	1615	m	-CO [a]
Nujol	1459	s	
	1430	s	Cp[b] , $N(CH_3)_3$ [c]
Nujol	1375	s	
Nujol	1160	w	
	1010	s	Cp[b] , $N(CH_3)_3$ [c]
	886	s	
	800	s	Cp[b] , $N(CH_3)_3$ [c]
Nujol	717	w	
	685	m	
	674	s	

a:Ref. 19, 162.

b:Ref. 109.

c: App. G, Table 46; Ref. 204, 205.

TABLE 10

rapidly decomposed at room temperature, but could be stored successfully at -78° for several weeks. Its infrared spectrum is shown in figure 25.

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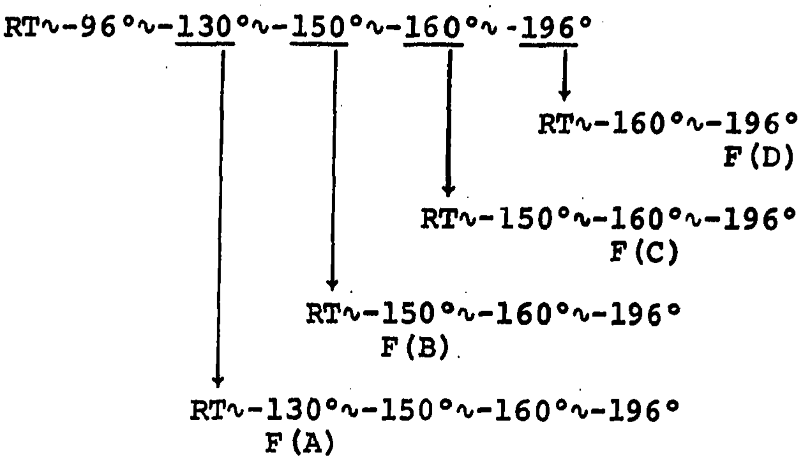
4. Reaction of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ with PF_5

Summary: It was found that a complex solid mixture occurred when $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and PF_5, at an ideal gas pressure of 2.96 atm, were combined for several days at room temperature according to the equation:

$$H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5) + PF_5 \rightarrow \begin{array}{l}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array}$$

In the dry bag, 97.4 mgm (0.451 mmol) of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 341.8 mgm (2.713 mmol) of PF_5 were condensed into the reactor at -196°. Upon warming to room temperature, the yellow solid changed instantly to a dark green solid. After sitting for four days, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:



(n=6)

59.7 mgm (0.474 mmol) of PF_5 were gained by the reactor.

The following materials were identified:

PF_3: Fraction (D) [a trace amount observed in the infrared spectrum].

SiF_4: Fraction (C) [55.2 mgm, 0.530 mmol; 19.5% yield based on the amount of PF_5 initially employed; mol. wgt. calc.-104.08, found-108.56: 4.30% confirmed by infrared spectrum identical to that observed for pure SiF_4 [105]].

OPF_3: Fraction (B) [37.4 mgm, 0.360 mmol; 13.3% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure OPF_3 [104]].

PF_5: Fraction (A) [a trace amount observed in the infrared spectrum].

complex mixture: Dark green solid [157.1 mgm]. No infrared spectrum (in Nujol) or n.m.r. (in deuterated acetone) were observed.

(2) SYNTHESIS OF $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$

Summary: It was found that the new compound, $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$, could be synthesized in 41.0% yield based on the amount of $K[Mo(CO)_3(\pi\text{-}C_5H_5)]$ initially employed by the reaction of $K[Mo(CO)_3(\pi\text{-}C_5H_5)]$ with gaseous H_3SiBr, at an ideal gas pressure of 9.18 atm, after thirty minutes at room temperature according to the equation:

$$K[Mo(CO)_3(\pi\text{-}C_5H_5)] + H_3SiBr \rightarrow KBr + H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$$

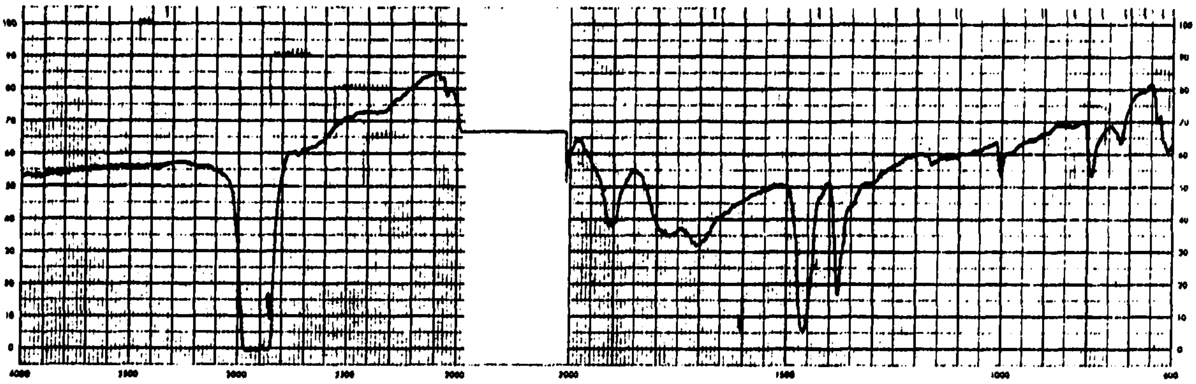
(a) Preparation of $K[Mo(CO)_3(\pi\text{-}C_5H_5)]$

In the dry bag (Figure 17), 125 ml of monoglyme (1,2-dimethoxyethane; freshly distilled over $LiAlH_4$ and saturated with dry nitrogen) were placed in a 250 ml, $\mathsf{\overline{S}}$ 24/40 single-necked round-bottom flask. 6.5 ml (0.076 mol) of cyclopentadiene (stored at -78°) were added to the flask along with a magnetic stirring bar. 2.00 gm (0.0511 mol) of potassium metal, cut up into small pieces, were added piecewise to the stirred monoglyme solution of C_5H_6 so that the potassium metal dissolved smoothly. After all the potassium had dissolved, the resulting solution changed from clear to yellow upon addition of the first few pieces of potassium, and finally to light pink with the addition of the last piece of potassium.

Transferring the wine-red monoglyme solution of $K[C_5H_5]$ to a closed ₸ 45/50 female glass ground joint (Figure 18), 13.5 gm (0.0513 mol) of $Mo(CO)_6$ were added to the monoglyme solution. Fitting the female receiver with a condenser, the monoglyme solution of $K[C_5H_5]$ containing $Mo(CO)_6$ was removed from the dry bag, and the receiver was clamped to a ring stand. A CO atmosphere blanketed the reaction mixture and was provided by means of a long glass tube extending the length of the condenser. After stirring magnetically for one hour at room temperature, the reaction mixture was heated slowly to 70° and then to 86° (vigorous refluxing of the) solvent) for sixteen hours. Refluxing was discontinued with some of the metal carbonyl collecting on the sides of the receiver and in the condenser. $Mo(CO)_6$ was not removed from the sides of the receiver due to the construction of the apparatus. Excess solvent was distilled from the receiver after removal of the CO portal and condenser. The desired product was obtained by removing the remaining solvent on the vacuum line (Figure 1) by condensing the remainder of the solvent in a -78° dry ice-acetone trap. The potassium salt kept at room temperature was further purified by condensing any volatile material into a -196° trap open to the pump, until no additional metal carbonyl was observed

IR, NMR SPECTRA OF K[Mo(CO)$_3$Cp]

IR



NMR

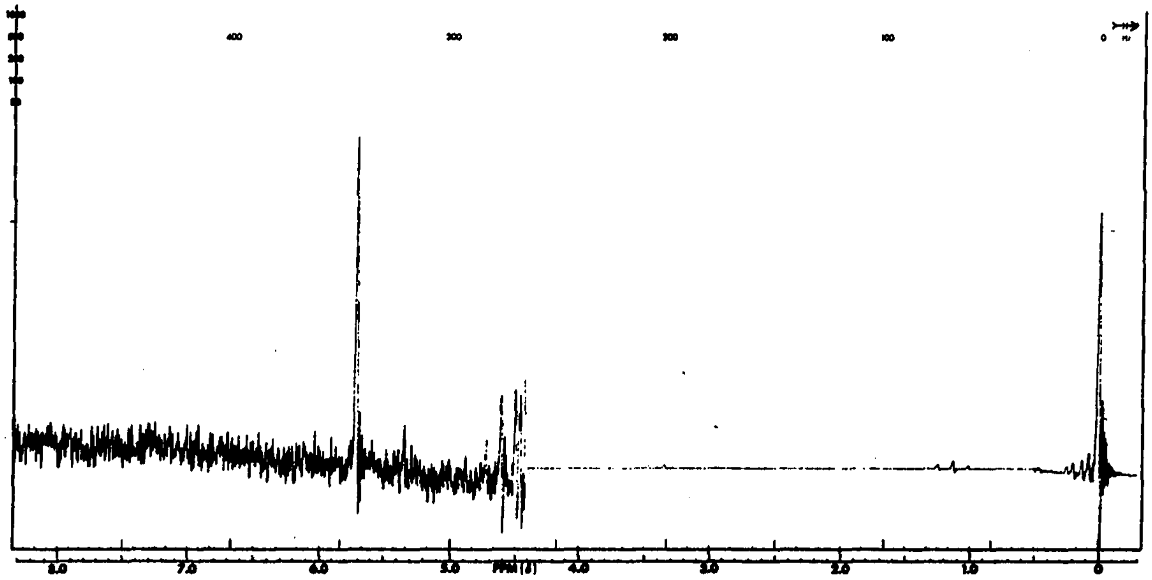


FIGURE 26

IR DATA OF K[Mo(CO)$_3$(π-C$_5$H$_5$)]

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2850	vs	
	2075(Sh)		
	2040(Sh)		
	1902	s	-CO [a]
	1765	s	-CO [a]
	1695	s	-CO [a]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	1000	m	Cp[b]
	789	m	Cp[b]
Nujol	718	w	
	632	w	
	608	w	

a:Ref. 19, 92, 162, 165.

b:Ref. 109.

TABLE 11

to collect in the -196° trap. The infrared spectrum and the n.m.r. spectrum of the salt are shown in figure 26.

(b) Preparation of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$

In the dry bag, 2482.0 mgm (8.7348 mmol) of impure $K[Mo(CO)_3(\pi-C_5H_5)]$, as prepared in part (a), were placed in a glass pressure reactor (Figure 19) which was subsequently removed from the dry bag, connected to the vacuum line, and evacuated. 933.1 mgm (8.406 mmol) of H_3SiBr were condensed into the reactor at -196°; upon warming to room temperature, the reactor was disconnected from the vacuum line and laid at an inclination such that the silyl bromide liquified at or near the teflon stopcock without contacting the solid residue. As the reactor came to room temperature an orange coloration and brown residue appeared with the liberation of heat. After sitting for thirty minutes at room temperature, a yellow-brown coloration resulted.

The reactor was connected to the vacuum line sublimer (Figure 20) and cooled to -196°. 0.4 mgm of a non-condensible gas were pumped away, assumed to be a mixture of H_2 and CO. Warming the reactor to -78°, 49.4 mgm (0.445 mmol) of H_3SiBr were recovered (identified by gas phase infrared spectrum [98]); warming the reactor to room temperature, 253.2 mgm (0.9510 mmol) of $Mo(CO)_6$ (identified by gas phase infrared spectrum [100]) were removed from the reactor and collected by the cold finger which was cooled to

-196°; and 988.8 mgm (3.580 mmol) of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ were produced by the reaction in 40.99% yield based on the amount of $K[Mo(CO)_3(\pi-C_5H_5)]$ initially employed. This product was removed from the reactor by heating the reactor to 75-80° by means of a hot water bath; light yellow crystals sublimed into the neck of the reactor. The vacuum line sublimer was disconnected from the vacuum line, placed in the dry bag, and filled with dry nitrogen. The reactor was separated from the sublimer, and the yellow crystals were removed from the neck of the reactor by scraping the walls with a thinly-filed spatula. Small amounts of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ were used to prepare an analysis sample, a melting point capillary, a Nujol mull, and an n.m.r. sample. Other syntheses furnished additional $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ for various reactions described in part (d).

(c) Identification and Characterization

1. Analysis of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$: In the dry bag, approximately 10-30 mgm of material were placed in a 5 mm (o.d.) tube containing a ₸ 12/30 male joint. The tube was removed from the dry bag, evacuated on the vacuum line, and sealed with an oxygen torch. The following results were obtained:

Found: C - 34.02%; H - 3.23%; Si - 10.25%
Calculated: C - 34.79%; H - 2.91%; Si - 10.17%

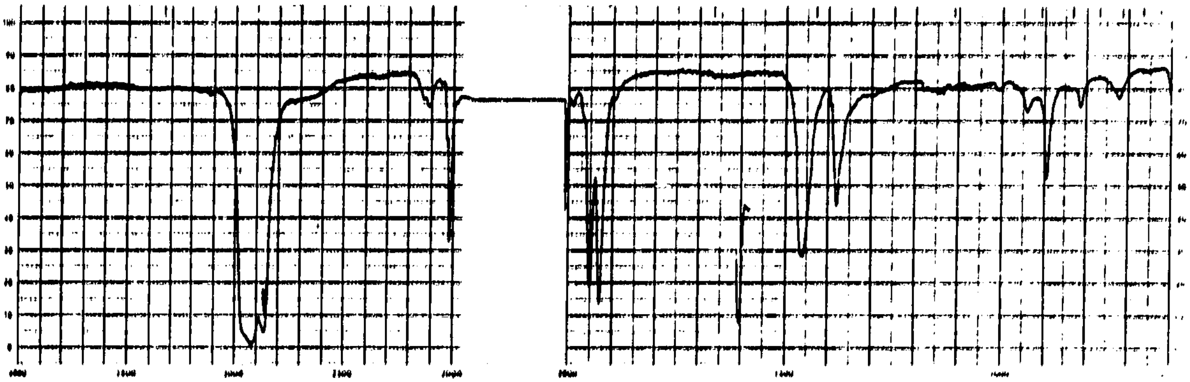
2. Melting Point of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, a small amount of material (two or three small pieces) was placed in a capillary tube filled with deoxygenized nitrogen gas. A cork was placed in the flared mouth of the tube; after removing the tube from the dry bag, the tube was sealed by gently heating a portion of the tube near to the cork. Duplicate determinations were performed, the second one taken as the melting point. The melting point of 94-96° (uncorrected) was recorded for the compound $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$.

3. Infrared Spectrum of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$: The infrared spectrum of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ was determined in the solid state in Nujol. In the dry bag, a drop of Nujol was placed on one of the KBr salt plates: a small amount of material was put on the drop of oil, and then the other KBr plate was placed over the drop, forming an air tight seal between both KBr plates. The infrared spectrum is shown in figure 27 , and the principle absorptions are given in table 12.

4. Nuclear Magnetic Resonance of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, approximately 30 mgm of sample were placed in the bottom of a nitrogen-filled n.m.r. tube containing a ₸ 12/30 male joint (Figure 21). The tube was fitted to an adapter, removed from the dry bag, and evacuated on the vacuum line. A small amount of $Si(CH_3)_4$ (TMS)

IR, NMR SPECTRA OF $H_3Si-Mo(CO)_3Cp$

IR



NMR

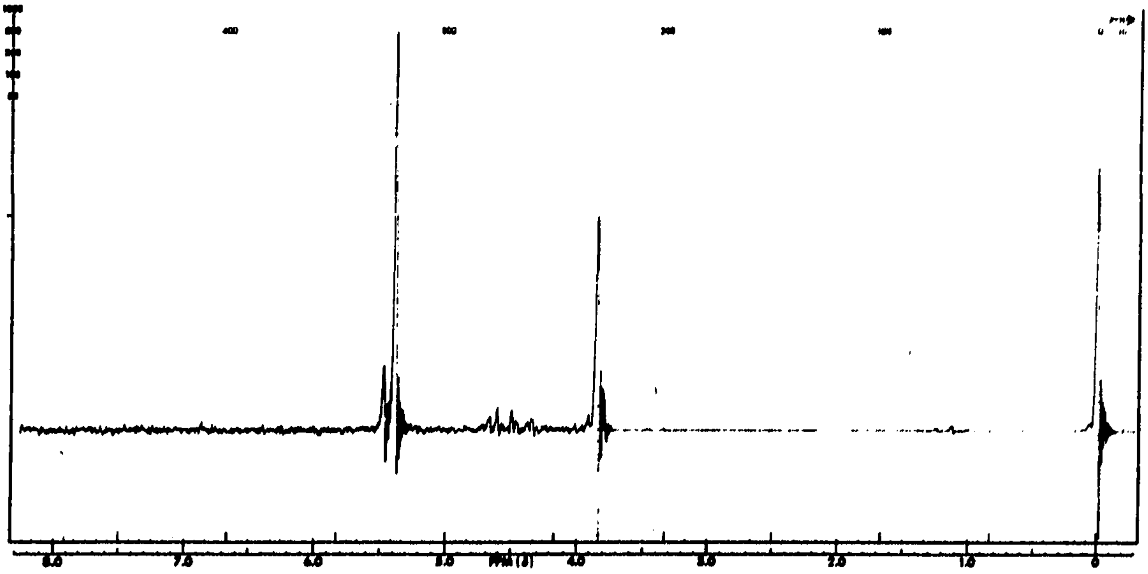


FIGURE 27

IR DATA OF $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2135(Sh)		
	2100	w	Si-H [a]
	2010(Sh)		
	2005	vs	-CO [b]
	1948	vs	-CO [b]
	1925	vs	-CO [b]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	1005	w	
	935	m	
	890	s	SiH_3 def.vib. [a]
	805	m	Cp [c]
Nujol	715	w	

a:Ref. 203.

b:Ref. 19, 54.

c:Ref. 109.

TABLE 12

and approximately 4 cm of anhydrous diethyl ether (degassed twice) were condensed into the n.m.r. tube at -196°. Then the tube was sealed by heating a portion of the tube below the joint with an oxygen torch. The sample tube was stored at -196° until it was to be placed in the n.m.r. sample holder; the sample was allowed to warm to room temperature, and moisture was removed by wiping with a paper towel. The n.m.r. spectrum is shown in figure 27, and the chemical shifts for the silyl hydrogens and the ring (Cp) hydrogens are given below:

Chemical Shift - δ from $Si(CH_3)_4^a$

$Cp(C_5H_5^-)$	SiH_3
5.35	3.85

a: taken in diethyl ether with $Si(CH_3)_4$ as the internal standard

5. Thermal Stability of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$:

Summary: It was found that no thermal decomposition occurred when $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ was heated *in vacuo* at 160° for forty-five minutes.

In the dry bag, 276.3 mgm (1.001 mmol) of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor which was subsequently removed from the dry bag, and evacuated on the vacuum line. Then the reactor was placed in an oil bath preheated to 162°, the oil level coming to within three inches of the teflon stopcock. After thirty seconds, the yellow solid melted and a dark liquid appeared which either seemed to boil or bubble as if a gas were being produced. After sitting forty-five minutes in the 162° heat, the oil bath was removed, allowing the reactor to cool slowly to room temperature. A colorless liquid and a white film were observed to condense on the inside walls of the reactor as it cooled. Once at room temperature, the reactor was cooled to -196°, and a small amount of non-condensible gas (2.4 mgm) was removed. Then the reactor was allowed to warm slowly to room temperature with the stopcock to the reactor open to a -196° trap. After five minutes at ambient temperature, a slight white ring was observed in the -196° trap. After closing the stopcock to the reactor, the -196° trap was removed, and the volatile material collected in this trap was allowed to enter an infrared cell. The resulting gas-phase infrared spectrum revealed a trace amount of SiH_4. No other volatile material was observed.

The reddish-brown solid residue (273.9 mgm, 0.9919 mmol) was removed from the reactor in the dry bag, and an analysis tube and Nujol mull were prepared. The infrared spectrum was identical to that observed for pure $H_3Si-Mo(CO)_3(\pi-C_5H_5)$; three strong -CO absorptions were observed at 2006, 1948, and 1935 cm^{-1} and a medium Si-H absorption at 2103 cm^{-1}. The commercial analysis which confirmed the identity of the solid as $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ is as follows:

Found: C - 25.5%; H - 2.38%

Calculated: C - 24.7%; H - 1.59%

From the above observations, it was concluded that no thermal decomposition of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ resulted when $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ was heated 66° above its melting point for nearly an hour. Also from commercial analysis, it was observed that $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ was more stable than $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$; however, it was difficult to determine whether $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ was more or less stable than $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$.

(d) Reactions of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$

1. Reaction of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with HCl

Summary: It was found that cleavage of the silyl-molybdenum linkage occurred when $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and HCl, at an ideal gas pressure of 0.87 atm, were combined for several hours at room temperature according to the equation:

$$H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + H_3SiCl$$

In the dry bag, 91.1 mgm (0.330 mmol) of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 30.1 mgm (0.830 mmol) of HCl were condensed into the reactor at -196°. Upon warming to room temperature and standing for six hours, a bright yellow residue resulted. The reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:

$$\begin{array}{ll} \text{RT}\sim\underline{-126^\circ}\sim-196^\circ & \\ \quad\quad\downarrow & \\ \quad\quad\text{RT}\sim-126^\circ\sim-196^\circ & \qquad\qquad (n=3) \\ \quad\quad\quad\quad\ \ \text{F(A)}\quad\ \ \text{F(B)} & \end{array}$$

3.3 mgm were lost by the reactor.

The following materials were identified:

HCl: Fraction (B) [13.0 mgm, 0.356 mmol; 43.2% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

H_3SiCl: Fraction (A) [7.0 mgm, 0.11 mmol; 32% yield based on the amount of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ initially employed; some of this material was lost in transfer; identified by infrared spectrum identical to that observed for pure H_3SiCl [98]].

$H-Mo(CO)_3(\pi-C_5H_5)$: Yellow solid [82.4 mgm, 0.335 mmol; identified by infrared spectrum identical to that observed for pure $H-Mo(CO)_3(\pi-C_5H_5)$ [2,90]].

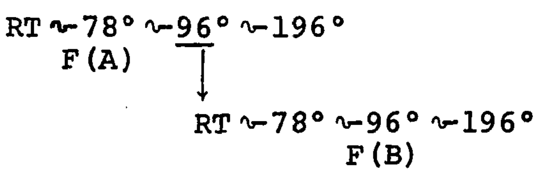
---

2. Reaction of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ with $N(CH_3)_3$

Summary: It was found that a 1.00:1.09 trimethylamine adduct formation occurred when $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$H_3Si-Mo(CO)_3(\pi-C_5H_5)+N(CH_3)_3 \rightarrow [(CH_3)_3N,SiH_3]^+[Mo(CO)_3(\pi-C_5H_5)]^-$$

In the dry bag, 186.3 mgm (0.6746 mmol) of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 129.0 mgm (2.182 mmol) of $N(CH_3)_3$ were condensed into the reactor at -196°. Upon warming to room temperature and sitting for three days, a bright yellow residue resulted. The reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:



43.8 mgm (0.741 mmol) of $N(CH_3)_3$ were gained by the reactor.

The following materials were identified:

$N(CH_3)_3$: Fractions (A) and (B) [85.1 mgm, 1.44 mmol; 66.0% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$[(CH_3)_3N,SiH_3]^+[Mo(CO)_3(\pi-C_5H_5)]^-$: Yellow solid [230.1 mgm; gross composition of H_3Si-Mo:$N(CH_3)_3$ was 0.6746:0.7409 or 1.00:1.09]. The infrared spectrum of this trimethylamine adduct is shown in figure 28.

---

3. Reaction of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that a 1.00:1.64 dimethylamine adduct formation occurred when $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ and $HN(CH_3)_2$ were combined for several days at room temperature according to the equation:

$$H_3Si-Mo(CO)_3(\pi-C_5H_5)+HN(CH_3)_2 \rightarrow [H(CH_3)_2N,SiH_3]^+[Mo(CO)_3(\pi-C_5H_5)]^-$$

In the dry bag, 126.6 mgm (0.4584 mmol) of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 81.7 mgm (1.81 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to room temperature, a vigorous bubbling occurred and

IR SPECTRUM OF $[Me_3N,SiH_3]^+[Mo(CO)_3Cp]^-$

IR

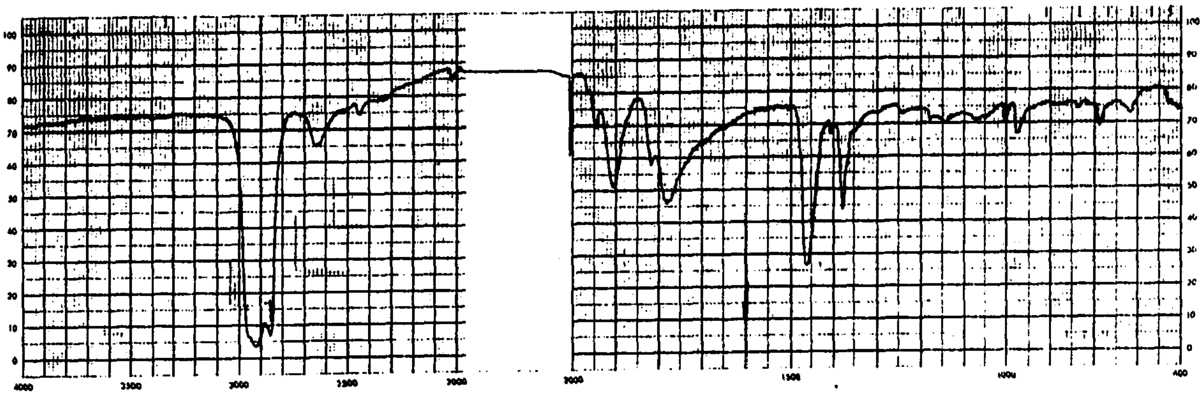


FIGURE 28

IR DATA OF $[(CH_3)_3N,SiH_3]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^-$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2640	w	
	2450	w	
	2175	w	Si-H[a]
	2010	w	
	1947	w	
	1903	s	-CO[b]
	1819	s	-CO[b]
	1780	s	-CO[b]
Nujol	1459	w	
	1406	w	$N(CH_3)_3$[c]
Nujol	1375	s	
Nujol	1160	w	
	1001	m	Cp[d], $N(CH_3)_3$[c]
	975	m	SiH_3 def.vib.[a]
	790	m	$N(CH_3)_3$[c]
Nujol	718	w	

a:Ref. 203.

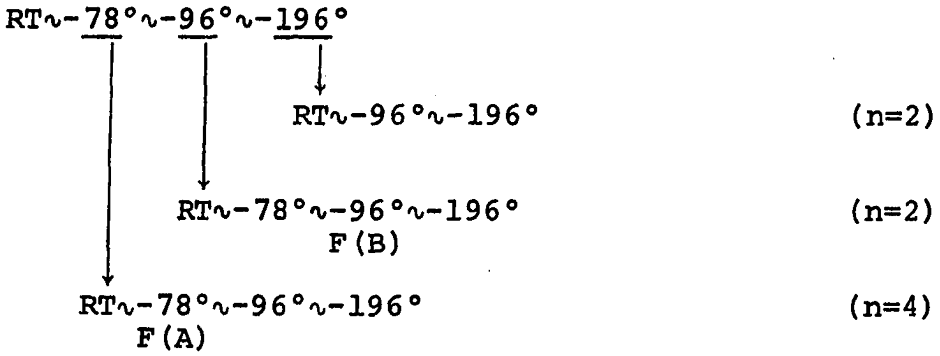
b:Ref. 19, 162.

c:App. F, Table 45; Ref. 101.

d:Ref. 109.

TABLE 13

dissolution of the yellow solid occurred forming a yellow-brown solution. After sitting at room temperature for three days, the reactor was cooled to -196°, and a small amount of non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:



33.9 mgm (0.752 mmol) of $HN(CH_3)_2$ were gained by the reactor.

The following materials were identified:

$\underline{HN(CH_3)_2}$: Fractions (A) and (B) [47.8 mgm, 1.06 mmol; 55.2% recovery based on the amount of $HN(CH_3)_2$ initially employed; mol. wgt. calc.-45.08, found-45.59: 1.13%; confirmed by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

$\underline{[H(CH_3)_2N,SiH_3]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^-}$: Yellow-white solid [160.5 mgm; gross composition of $H_3Si\text{-}Mo{:}HN(CH_3)_2$ was 0.4584:0.7520 or 1.00:1.64]. The infrared spectrum of this dimethylamine adduct is shown in figure 29.

IR SPECTRUM OF $[HMe_2N,SiH_3]^+[Mo(CO)_3Cp]^-$

IR

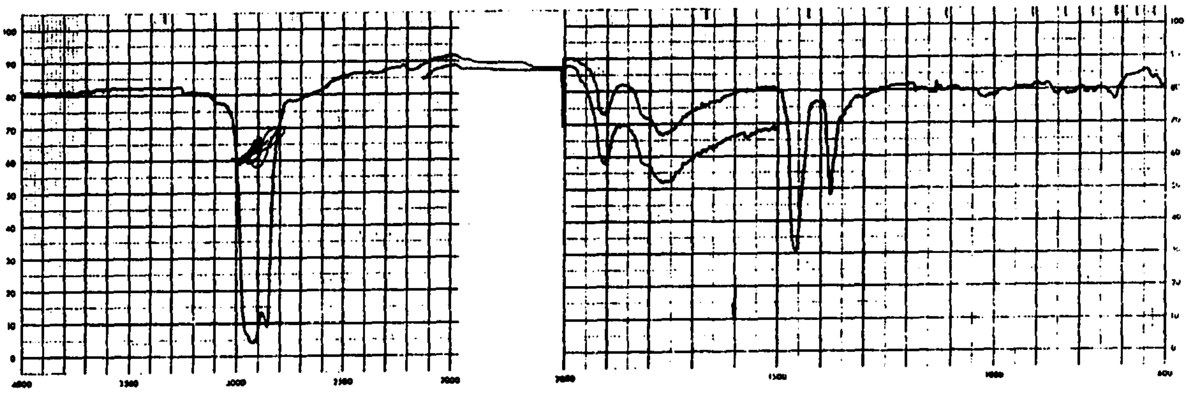


FIGURE 29

IR DATA OF $[H(CH_3)_2N,SiH_3]^+[Mo(CO)_3(\pi-C_5H_5)]^-$

	Absorption	Intensity	Assignment [a]
Nujol	2920	vs	
Nujol	2852	vs	
	1908	s	-CO
	1840	m	-CO
	1770	s	-CO
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
Nujol	717	w	

a:Ref. 19, 162.

TABLE 14

4. Reaction of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that the dimethylamine adduct decomposed at 70° according to the equation:

$$[H(CH_3)_2N,SiH_3]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^- \rightarrow H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + H_3Si\text{-}N(CH_3)_2$$

In the dry bag, 212.2 mgm (0.7684 mmol) of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 40.7 mgm (0.903 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to room temperature, and sitting for eight hours, a yellow residue appeared. The reactor was cooled to -196°, and a non-condensible gas was removed. The reactor was warmed to room temperature and then to 70° for thirty minutes. The volatile materials removed from the reactor were separated as follows:

$$\underset{}{RT} \sim \underset{F(A)}{-78°} \sim \underset{F(B)}{-96°} \sim \underset{F(C)}{-196°}$$

The following materials were identified:

$HN(CH_3)_2$: Fractions (B) and (C) [identified by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

$H_3Si\text{-}N(CH_3)_2$: Fraction (A) [identified by infrared spectrum identical to that observed for pure $H_3Si\text{-}N(CH_3)_2$ [103]].

$H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$: Yellow-pink solid [sublimed into the neck of the reactor assumed to be $H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$].

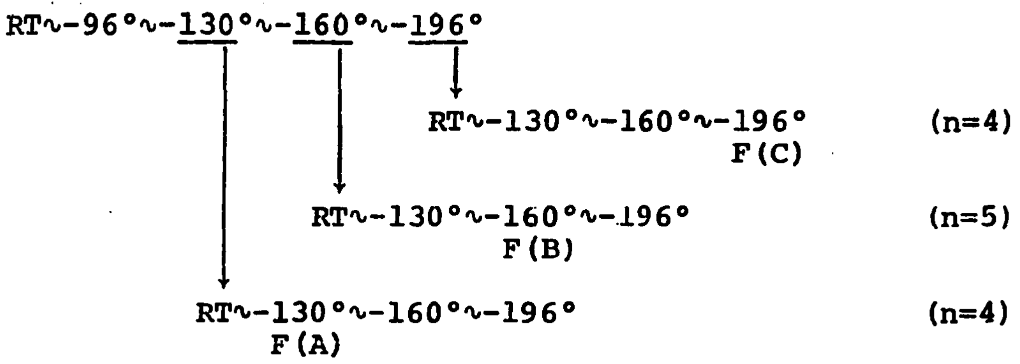
---

5. Reaction of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with PF_5

Summary: It was found that a complex solid mixture resulted when $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and PF_5, at an ideal gas pressure of 2.06 atm, were combined for several days at room temperature according to the equation:

$$H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + PF_5 \rightarrow \begin{array}{c}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array} + H_3SiF + PF_3$$

In the dry bag, 121.3 mgm (0.4392 mmol) of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 237.2 mgm (1.883 mmol) of PF_5 were condensed into the reactor at -196°. Upon warming to room temperature, and sitting for four days a purple residue appeared. The reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:



49.1 mgm were gained by the reactor.

The following materials were identified:

$\underline{PF_3}$: Fraction (C) [44.8 mgm, 0.509 mmol; 27.0% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure PF_3 [104]].

$\underline{SiF_4}$ and $\underline{PF_5}$: Fraction (B) [66.4 mgm, identified by infrared spectrum identical to that observed for a mixture of SiF_4 and PF_5[104,105]].

$\underline{OPF_3}$: Fraction (A) [54.5 mgm, 0.524 mmol; 27.8% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure OPF_3 [104]].

complex mixture: Dark red-purple solid [170.9 mgm] An n.m.r. spectrum (in deuterated acetone) showed a strong peak at 6.03δ assumed to be due to $[Mo(CO)_3(\pi\text{-}C_5H_5)]F$; a filtered diethyl ether solution showed a strong peak at 5.72δ assumed to be due to a polyflourinated specie.

6. Reaction of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with H_2O

Summary: It was found that a trace amount of SiH_4 formed when $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and H_2O were combined at 0°.

In the dry bag, 89.0 mgm (0.322 mmol) of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 182.6 mgm (1.013 mmol) of H_2O were condensed into the reactor at -196°. The reactor was allowed to warm to 0°. After sitting for twelve hours, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor at 0° were separated as follows:

$$\underset{F(A)}{0^\circ \sim -196^\circ}$$

4.5 mgm (0.25 mmol) of H_2O were gained by the reactor.

The following materials were identified:

SiH_4: Fraction (A) [a trace amount seen in the infrared spectrum].

solid residue: Pink-white solid [93.5 mgm].

(e) Reactions of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$

1. Reaction of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with HCl

Summary: It was found that cleavage of the methyl-molybdenum linkage occurred when $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and HCl, at an ideal gas pressure of 8.29 atm, were combined for several days at room temperature according to the equation:

$$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow (\pi\text{-}C_5H_5)Mo(CO)_3Cl + CH_4$$

In the dry bag, 100.5 mgm (0.3864 mmol) of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 276.8 mgm (7.592 mmol) of HCl were condensed into the reactor at -196°. Upon warming to room temperature, an orange-red liquid appeared immediately. After sitting for two days, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$\text{RT} \sim -130° \sim \underset{\text{F(A)}}{-196°}$$

9.5 mgm were gained by the reactor.

The following materials were identified:

HCl: Fraction (A) [267.1 mgm, 7.326 mmol; 96.50% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

$(\pi\text{-}C_5H_5)Mo(CO)_3Cl$: Orange-red solid [110.2 mgm, 0.3929 mmol; identified by infrared spectrum identical to that observed for pure $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$ [2,92]]. An n.m.r. spectrum (in deuterated acetone) shown in figure 30, shows a strong singlet at 5.88δ. [106] The infrared and n.m.r. spectra are shown in figure 30.

---

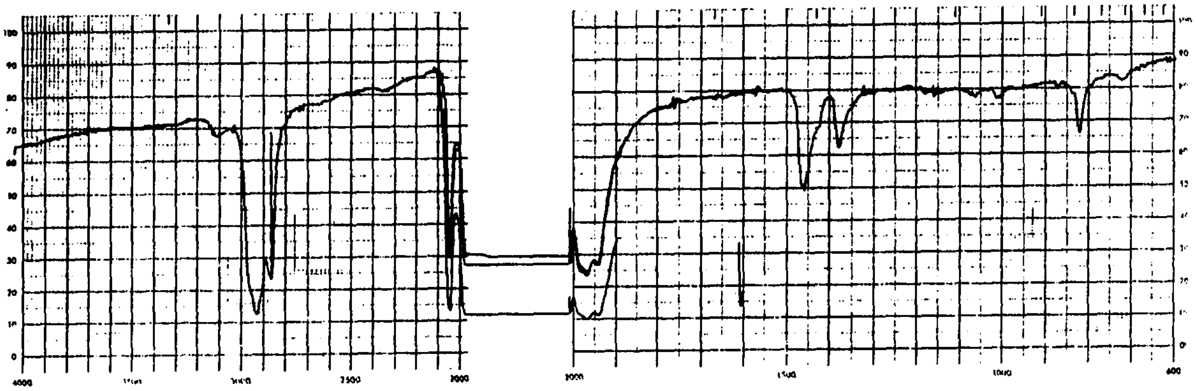
2. Reaction of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with $N(CH_3)_3$

Summary: It was found that no reaction occurred when $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + N(CH_3)_3 \rightarrow \text{N.R.}$$

In the dry bag, 201.8 mgm (0.7755 mmol) of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 1867.0 mgm (31.585 mmol) of $N(CH_3)_3$ were condensed into the reactor at -196°. Upon warming to room temperature, the yellow solid dissolved forming a bright yellow solution. After sitting for three days, the reactor was cooled to -196°, and no non-condensible

IR, NMR SPECTRA OF $CpMo(CO)_3Cl$


IR

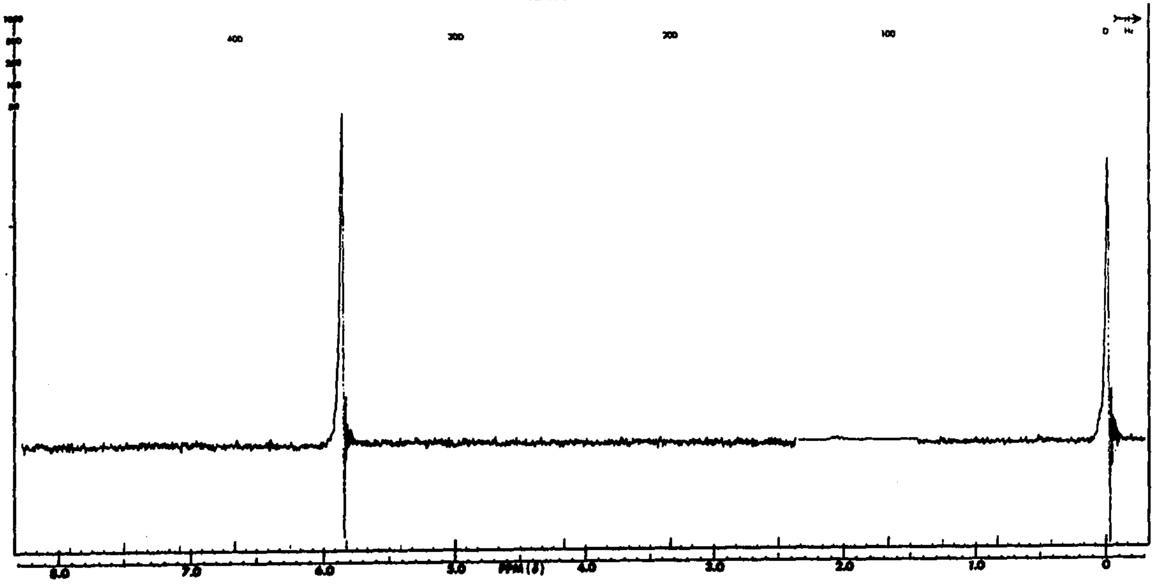

NMR

FIGURE 30

IR DATA OF $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2039	vs	-CO [a]
	1985	vs	-CO [a]
	1938	s	-CO [a]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	816	m	Cp [b]
	717	w	

a:Ref. 2, 92.

b:Ref. 109

TABLE 15

gas was removed. The volatile materials removed from the reactor were separated as follows:

RT∿-130°∿-196°
F(A)

0.5 mgm were gained by the reactor.

The following materials were identified:

$N(CH_3)_3$: Fraction (A) [1866.4 mgm, 31.575 mmol; 99.970% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$: Yellow solid [202.3 mgm, 0.7778 mmol; 100.3% recovery based on the amount of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ initially employed; identified by infrared spectrum identical to that observed for pure $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ [2]].

---

3. Reaction of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that a dimethylamine adduct formation occurred when $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and $HN(CH_3)_2$ were combined for one hour at 0° according to the equation:

$$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)+HN(CH_3)_2 \rightarrow [(CH_3)_3NH]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^-$$

In the dry bag, 182.8 mgm (0.7028 mmol) of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 853.6 mgm (18.94 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to -78°, a light yellow solution appeared; warming further to 0°, a bright orange-yellow solution appeared with complete dissolution of the yellow solid. After sitting for one hour at 0°, the reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:

$$\underset{F(A)}{0°\sim-130°}\sim-196°$$

7.1 mgm were gained by the reactor.

The following materials were identified:

<u>$HN(CH_3)_2$</u>: Fraction (A) [846.5 mgm, 18.78 mmol; 99.17% recovery based on the amount of $HN(CH_3)_2$ initially employed; identified by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

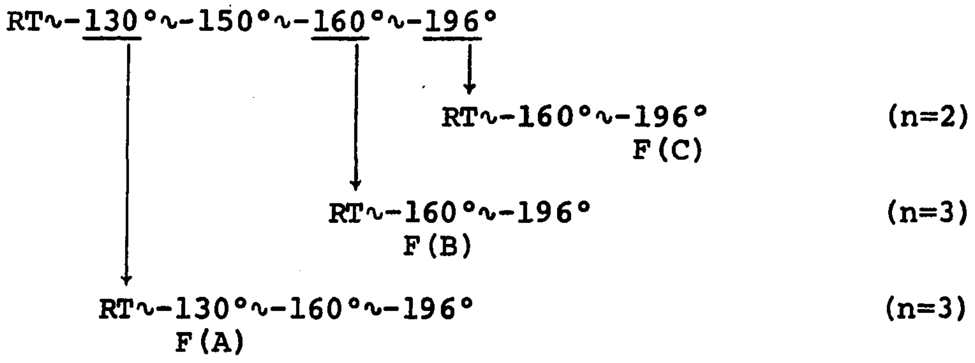
<u>$[(CH_3)_3NH]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^-$</u>: Bright orange-red solid [189.9 mgm, gross composition of $H_3C\text{-}Mo:HN(CH_3)_2$ was 0.703:0.160 or 1.00:0.227] decomposed rapidly at 25° liberating CO (identified by infrared spectrum) and forming a black residue.

4. Reaction of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with PF_5

Summary: It was found that a complex solid mixture occurred when $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and PF_5, at an ideal gas pressure of 1.04 atm, were combined for several days at room temperature according to the equation:

$$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + PF_5 \rightarrow \begin{array}{l}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array}$$

In the dry bag, 47.0 mgm (0.181 mmol) of $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 120.4 mgm (0.9559 mmol) of PF_5 were condensed into the reactor at -196°. Upon warming to room temperature and sitting for several minutes, the yellow solid changed slowly to a light red-purple solid. After sitting for four days, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:



15.1 mgm were gained by the reactor.

The following materials were identified:

PF_3: Fraction (C) [a trace amount seen in the infrared spectrum].

SiF_4: Fraction (B) [45.0 mgm, 0.432 mmol; 45.2% yield based on the amount of PF_5 initially employed; mol. wgt. calc.-104.08, found-102.69: 1.33%; confirmed by infrared spectrum identical to that observed for pure SiF_4 [105]].

OPF_3: Fraction (A) [91.0 mgm, 0.875 mmol; 91.6% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure OPF_3 [104]].

complex mixture: Purple solid [62.1 mgm] An n.m.r. spectrum (in deuterated acetone) showed a strong peak at 6.00δ assumed to be due to $[Mo(CO)_3(\pi\text{-}C_5H_5)]F$; and a weak singlet at 5.87δ assumed to be due to a polyflourinated specie.

---

(3) SYNTHESIS OF $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$

Summary: It was found that the new compound, $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$, could be synthesized in 20.8% yield based on the amount of $K[W(CO)_3(\pi\text{-}C_5H_5)]$ initially employed by the reaction of $K[W(CO)_3(\pi\text{-}C_5H_5)]$ with gaseous H_3SiBr, at an ideal gas pressure of 6.05 atm, after thirty minutes at room temperature according to the equation:

$$K[W(CO)_3(\pi\text{-}C_5H_5)] + H_3SiBr \rightarrow KBr + H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$$

(a) Preparation of $K[W(CO)_3(\pi\text{-}C_5H_5)]$

In the dry bag (Figure 17), 125 ml of monoglyme (1,2-dimethoxyethane; freshly distilled over $LiAlH_4$ and saturated with dry nitrogen) were placed in a 250 ml $\$$ 24/40 single-necked round-bottom flask. 6.5 ml (0.076 mol) of cyclopentadiene (stored at -78°) were added to the flask along with a magnetic stirring bar. 2.00 gm (0.0511 mol) of potassium metal, cut up into small pieces, were added piecewise to the stirred monoglyme solution of C_5H_6 so that the potassium metal dissolved smoothly. After all the potassium had dissolved, the resulting solution changed from clear to yellow upon addition of the first few pieces of potassium, and finally to light pink with the addition of the last piece of potassium.

Transferring the wine-red monoglyme solution of $K[C_5H_5]$ to a closed $\$$ 45/50 female glass ground joint

(Figure 18), 18.0 gm (0.0513 mol) of $W(CO)_6$ were added to the monoglyme solution. Fitting the female receiver with a condenser, the monoglyme solution of $K[C_5H_5]$ containing $W(CO)_6$ was removed from the dry bag, and the receiver was clamped to a ring stand. A CO atmosphere blanketed the reaction mixture and was provided by means of a long glass tube extending the length of the condenser. After stirring magnetically for one hour at room temperature, the reaction mixture was heated slowly to 70° and then to 86° (vigorous refluxing of the solvent) for sixteen hours. Refluxing was discontinued with some of the metal carbonyl collecting on the sides of the receiver and in the condenser. $W(CO)_6$ was not removed from the sides of the receiver due to the construction of the apparatus. Excess solvent was distilled from the receiver after removal of the CO portal and condenser. The desired product was obtained by removing the remaining solvent on the vacuum line (Figure 1) by condensing the remainder of the solvent in a -78° dry ice-acetone trap. The potassium salt kept at room temperature was further purified by condensing any volatile material in a -196° trap open to the pump until no additional metal carbonyl was observed to collect in the -196° trap. The infrared spectrum of $K[W(CO)_3(\pi\text{-}C_5H_5)]$ is shown in figure 31.

(b) Preparation of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$

In the dry bag, 1734.6 mgm (4.6605 mmol) of impure $K[W(CO)_3(\pi\text{-}C_5H_5)]$, as prepared in part (a), were placed

IR SPECTRUM OF K[W(CO)$_3$Cp]

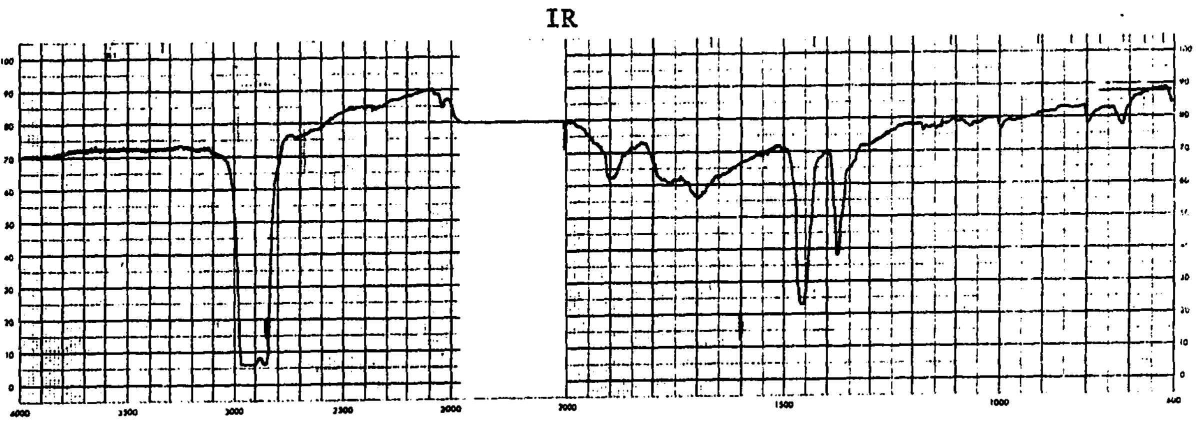


FIGURE 31

IR DATA OF $K[W(CO)_3(\pi\text{-}C_5H_5)]$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2078(Sh)		
	2048(Sh)		
	1898	s	-CO [a]
	1762	s	-CO [a]
	1696	s	-CO [a]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	998	w	Cp [b]
	799	w	Cp [b]
Nujol	718	w	

a:Ref. 19, 92, 162, 165.

b:Ref. 109.

TABLE 16

in a glass pressure reactor (Figure 19) which was subsequently removed from the dry bag, connected to the vacuum line and evacuated. 615.4 mgm (5.544 mmol) of H_3SiBr were condensed into the reactor at -196°; upon warming to room temperature, the reactor was disconnected from the vacuum line and laid at an inclination such that the silyl bromide liquified at or near the teflon stopcock without contacting the solid residue. As the reactor came to room temperature an orange coloration and brown residue appeared with the liberation of heat. After sitting for thirty minutes at room temperature, a yellow-brown coloration resulted.

The reactor was connected to the vacuum line sublimer (Figure 20) and cooled to -196°. 0.9 mgm of a non-condensible gas were pumped away, assumed to be a mixture of H_2 and CO. Warming the reactor to -78°, 83.8 mgm (0.755 mmol) of H_3SiBr were recovered (identified by gas phase infrared spectrum [98]); warming the reactor to room temperature and then to 50°, 50.5 mgm (0.428 mmol) of $W(CO)_6$ (identified by gas phase infrared spectrum [100]) were removed from the reactor and collected by the cold finger which was cooled to -196°; and 352.3 mgm (0.9763 mmol) of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were produced by the reaction in 20.76% yield based on the amount of $K[W(CO)_3(\pi\text{-}C_5H_5)]$ initially employed. This product was removed from the reactor by heating the reactor to 80°-90° by means of a hot water bath; white-yellow crystals sublimed into the neck of the reactor. The vacuum line sublimer was disconnected from the vacuum line, placed in the dry bag, and filled with dry nitrogen. The reactor was separated from the sublimer, and the yellow crystals were removed from the neck of the reactor by scraping the walls with a thinly-filed spatula. Small amounts of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were used to prepare an analysis sample, a melting point capillary, a Nujol mull, and an n.m.r. sample. Other syntheses furnished additional $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ for various reactions described in part (d).

(c) Identification and Characterization

1. Analysis of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, approximately 10-30 mgm of material were placed in a 5 mm (o.d.) tube containing a $\mathbb{S}$ 12/30 male joint. The tube was removed from the dry bag, evacuated on the vacuum line, and sealed with an oxygen torch. The following results were obtained:

Found: C - 26.59%; H - 2.28%; Si - 7.91%
Calculated: C - 26.39%; H - 2.15%; Si - 7.71%

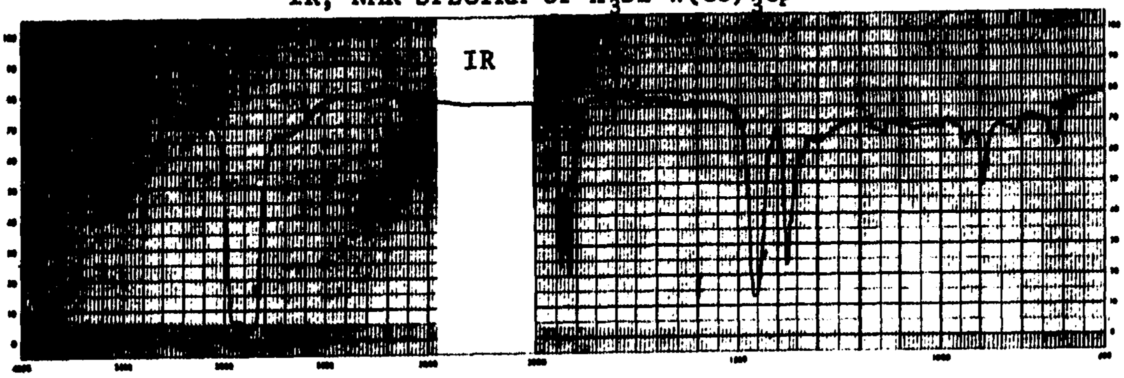
2. Melting Point of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, a small amount of material (two or three small pieces) was placed in a capillary tube filled with deoxygenized nitrogen gas. A cork was placed in the

flared mouth of the tube; after removing the tube from the dry bag, the tube was sealed by gently heating a portion of the tube near to the cork. Duplicate determinations were performed, the second one taken as the melting point. The melting point of 110-112° (uncorrected) was recorded for the compound $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$.

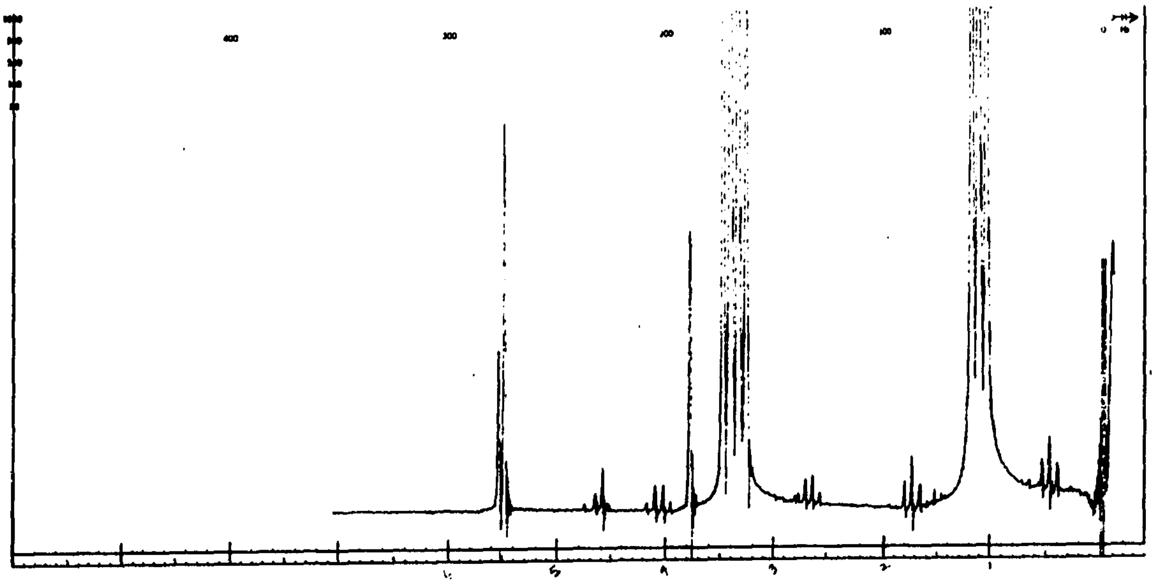
3. Infrared Spectrum of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$: The infrared spectrum of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ was determined in the solid state in Nujol. In the dry bag, a drop of Nujol was placed on one of the KBr salt plates a small amount of material was put on the drop of oil, and then the other KBr plate was placed over the drop, forming an air tight seal between both KBr plates. The infrared spectrum is shown in figure 32 , and the principle absorptions are given in table 17.

4. Nuclear Magnetic Resonance of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$: In the dry bag, approximately 30 mgm of sample were placed in the bottom of a nitrogen-filled n.m.r. tube containing a $ 12/30 male joint (Figure 21). The tube was fitted to an adapter, removed from the dry bag, and evacuated on the vacuum line. A small amount of $Si(CH_3)_4$ (TMS) and approximately 4 cm of anhydrous diethyl ether (degassed twice) were condensed into the n.m.r. tube at -196°. Then the tube was sealed by heating a portion of the tube below the joint with an oxygen torch. The sample tube was stored at -196° until it was to be placed in the n.m.r. sample

IR, NMR SPECTRA OF $H_3Si-W(CO)_3Cp$



NMR(HA-100)



NMR(A-60)

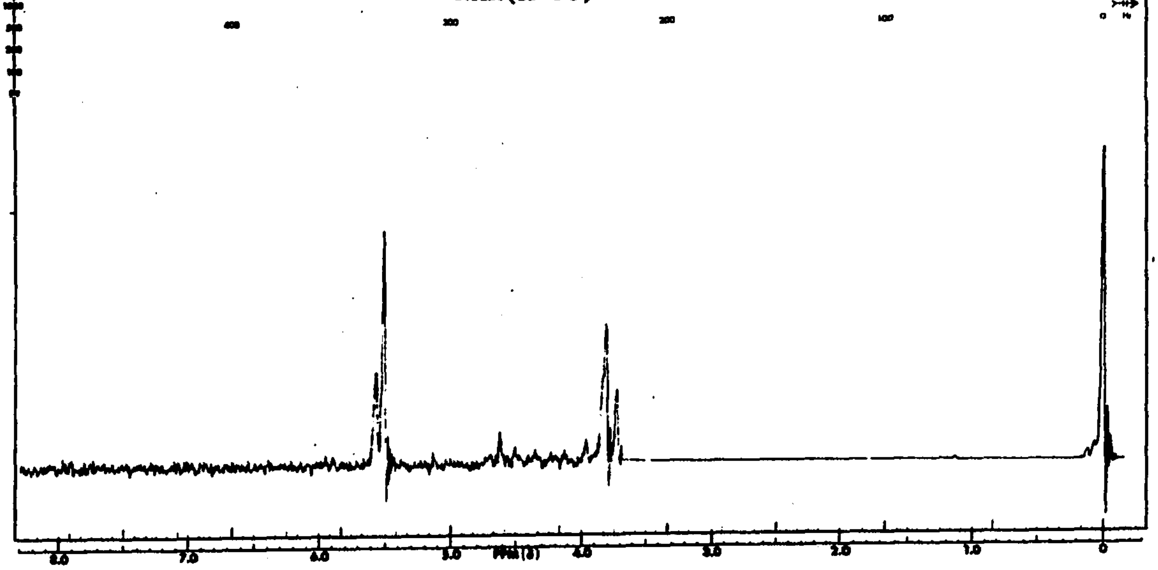


FIGURE 32

IR DATA OF $H_3Si-W(CO)_3(\pi-C_5H_5)$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2130 (Sh)		
	2100	w	Si-H [a]
	2018 (Sh)		
	2005	vs	-CO [b]
	1940	vs	-CO [b]
	1931	vs	-CO [b]
Nujol	1459	s	
Nujol	1357	s	
Nujol	1160	w	
	935	w	
	895	m	SiH_3 def.vib.[a]
	815	w	Cp [c]
Nujol	715	w	

a:Ref. 203

b:Ref. 19, 54.

c:Ref. 109.

TABLE 17

holder; the sample was allowed to warm to room temperature, and moisture was removed by wiping with a paper towel. The n.m.r. spectrum is shown in figure 32, and the chemical shifts for the silyl hydrogens and the ring (Cp) hydrogens are given below:

Chemical Shift - δ from $Si(CH_3)_4^a$	
$Cp(C_5H_5^-)$	SiH_3
5.50	3.82

a:taken in diethyl ether with $Si(CH_3)_4$ as the internal standard

5. Thermal Stability of H_3Si-$W(CO)_3(\pi$-$C_5H_5)$:

A non-condensible gas and a black-brown residue were the products of complete thermal decomposition of H_3Si-$W(CO)_3(\pi$-$C_5H_5)$ at a temperature above 200°. Also from commercial analysis, it was observed that H_3Si-$W(CO)_3(\pi$-$C_5H_5)$ was more stable than H_3Si-$Cr(CO)_3(\pi$-$C_5H_5)$; however, it was difficult to determine whether H_3Si-$W(CO)_3(\pi$-$C_5H_5)$ was more or less stable than H_3Si-$Mo(CO)_3(\pi$-$C_5H_5)$.

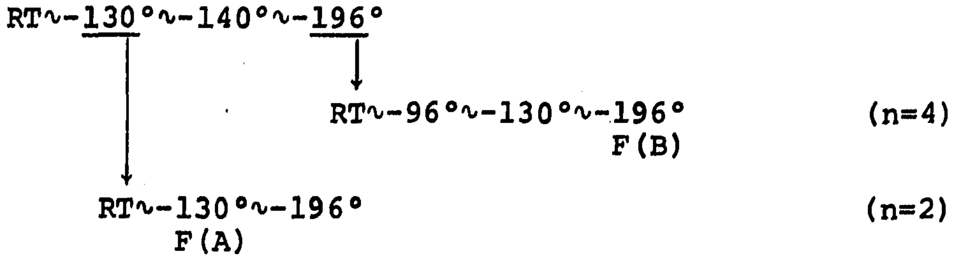
(d) Reactions of H_3Si-$W(CO)_3(\pi$-$C_5H_5)$

1. Reaction of H_3Si-$W(CO)_3(\pi$-$C_5H_5)$ with HCl

Summary: It was found that cleavage of the silyl-tungsten linkage occurred when H_3Si-$W(CO)_3(\pi$-$C_5H_5)$ and HCl, at an ideal gas pressure of 3.99 atm, were combined for several days at room temperature according to the equation:

$$H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow H\text{-}W(CO)_3(\pi\text{-}C_5H_5) + H_3SiCl$$

In the dry bag, 109.9 mgm (0.2993 mmol) of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 133.3 mgm (3.656 mmol) of HCl were condensed into the reactor at -196°. Upon warming to room temperature and sitting for three days, a bright yellow residue resulted. The reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:



2.0 mgm were gained by the reactor.

The following materials were identified:

HCl: Fraction (B) [111.3 mgm, 3.053 mmol; 83.5% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

<u>H_3SiCl and H_2SiCl_2</u>: Fraction (A) [20.0 mgm; identified by infrared spectrum identical to that expected for a mixture of H_3SiCl [98] and H_2SiCl_2 [122]].

<u>$H-W(CO)_3(\pi-C_5H_5)$</u>: Yellow solid [110.1 mgm; identified by infrared spectrum identical to that observed for pure $H-W(CO)_3(\pi-C_5H_5)$ [2,90]].

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2. <u>Reaction of $H_3Si-W(CO)_3(\pi-C_5H_5)$ with $N(CH_3)_3$</u>

<u>Summary</u>: It was found that a 1.00:0.63 trimethylamine adduct formation occurred when $H_3Si-W(CO)_3(\pi-C_5H_5)$ and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$H_3Si-W(CO)_3(\pi-C_5H_5)+N(CH_3)_3 \rightarrow [(CH_3)_3N,SiH_3]^+[W(CO)_3(\pi-C_5H_5)]^-$$

In the dry bag, 131.8 mgm (0.3619 mmol) of $H_3Si-W(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 327.3 mgm (5.537 mmol) of $N(CH_3)_3$ were condensed into the reactor at -196°. Upon warming to room temperature and sitting for three days a bright yellow residue resulted. The reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor were separated as follows:

RT∿-126°∿-196° (n=2)
F(A)

13.4 mgm (0.227 mmol) of $N(CH_3)_3$ were gained by the reactor.

The following materials were identified:

$\underline{N(CH_3)_3}$: Fraction (A) [311.7 mgm, 5.273 mmol; 95.23% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$\underline{[(CH_3)_3N,SiH_3]^+[W(CO)_3(\pi-C_5H_5)]^-}$: Gold-yellow solid [145.2 mgm, 0.3430 mmol; gross composition of $H_3Si-W:N(CH_3)_3$ was 0.3169:0.2267 or 1.00:0.63]. The infrared spectrum of this trimethylamine adduct was not exactly identical to that observed for the Cr and Mo trimethylamine adducts (Figure 43, p. 281), since low frequency CO absorptions below 1900 cm^{-1} were not observed.

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3. Reaction of $H_3Si-W(CO)_3(\pi-C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that a 1.00:2.06 dimethylamine adduct formation occurred when $H_3Si-W(CO)_3(\pi-C_5H_5)$ and $HN(CH_3)_2$ were combined for several days at room temperature according to the equation:

$$H_3Si-W(CO)_3(\pi-C_5H_5)+HN(CH_3)_2 \rightarrow [H(CH_3)_2N,SiH_3]^+[W(CO)_3(\pi-C_5H_5)]^-$$

IR DATA OF $[(CH_3)_3N,SiH_3]^+[W(CO)_3(\pi-C_5H_5)]^-$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2008	s	
	2002	s	-CO [a]
	1938	s	-CO [a]
	1920	s	-CO [a]
Nujol	1459	s	
	1400	w	$N(CH_3)_3$ [b]
Nujol	1375	s	
Nujol	1160	w	
	1000	w	Cp[c], $N(CH_3)_3$ [b]
	996	w	$N(CH_3)_3$ [b]
	915	w	SiH_3 def.vib.[a]
Nujol	718	w	

a:Ref. 19, 162.

b:App. F, Table 45. Ref. 101.

c:Ref. 109.

TABLE 18

In the dry bag, 116.9 mgm (0.3210 mmol) of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 520.9 mgm (11.56 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to room temperature, a vigorous bubbling occurred, and dissolution of the yellow solid occurred forming a yellow-brown solution. After sitting at room temperature for three days, the reactor was cooled to -196°, and no non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$\begin{array}{c} \text{RT} \sim -78^\circ \sim -96^\circ \sim -130^\circ \sim -196^\circ \\ \quad\quad F(A)\quad F(B)\quad\quad F(C) \end{array}$$

29.8 mgm (0.661 mmol) of $HN(CH_3)_2$ were gained by the reactor.

The following materials were identified:

$\underline{HN(CH_3)_2}$: Fractions (A), (B), and (C) [491.1 mgm, 10.89 mmol; 94.28% recovery based on the amount of $HN(CH_3)_2$ initially employed; identified by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

$\underline{[H(CH_3)_2N,SiH_3]^+[W(CO)_3(\pi\text{-}C_5H_5)]^-}$: White-gray solid [144.5 mgm, 0.3531 mmol; gross composition of $H_3Si\text{-}W{:}HN(CH_3)_2$ was 0.3210:0.6610 or 1.00:2.06].

IR DATA OF $[H(CH_3)_2N,SiH_3]^+[W(CO)_3(\pi\text{-}C_5H_5)]^-$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2026	w	
	1967	w	
	1906	m	-CO [a]
	1765	m	-CO [a]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1150	w	
	972	m	
	721	s	Cp [b]

a:Ref. 19, 162.

b:Ref. 109.

TABLE 19

IR DATA OF $[H(CH_3)_2N,SiH_3]^+[W(CO)_3(\pi\text{-}C_5H_5)]^-$

	Absorption	Intensity	Assignment
Nujol	2920	vs	
Nujol	2852	vs	
	2026	w	
	1967	w	
	1906	m	-CO [a]
	1765	m	-CO [a]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1150	w	
	972	m	
	721	s	Cp [b]

a:Ref. 19, 162.

b:Ref. 109.

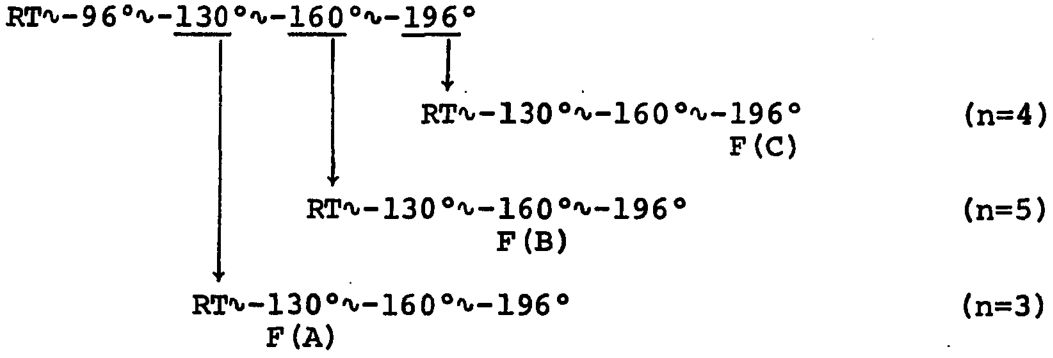
TABLE 19

4. Reaction of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ with PF_5

Summary: It was found that a complex solid mixture resulted when $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ and PF_5, at an ideal gas pressure of 7.36 atm, were combined for several days at room temperature according to the equation:

$$H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5) + PF_5 \rightarrow \begin{matrix}\text{complex}\\ \text{solid}\\ \text{mixture}\end{matrix} + H_3SiF + PF_3$$

In the dry bag, 169.1 mgm (0.4643 mmol) of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 849.2 mgm (6.741 mmol) of PF_5 were condensed into the reactor at -196°. Upon warming to room temperature a purple residue appeared. After sitting for four days, the reactor was cooled to -196°, and a noncondensible gas was removed. The volatile materials removed from the reactor were separated as follows:



11.4 mgm were gained by the reactor.

The following materials were identified:

$\underline{PF_3}$: Fraction (C) [60.8 mgm, 0.691 mmol; 10.2% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure PF_3 [104]].

$\underline{SiF_4}$: Fraction (B) [30.1 mgm, 0.289 mmol; 4.29% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure SiF_4 [105]].

$\underline{H_3SiF}$: Fraction (B) [a trace amount seen in the infrared spectrum].

$\underline{OPF_3}$ and $\underline{PF_5}$: Fraction (A) [186.1 mgm; identified by infrared spectrum identical to that observed for a mixture of OPF_3 and PF_5 [104]].

complex mixture: Red-purple solid [180.5 mgm]

An n.m.r. spectrum (in deuterated acetone) showed a strong singlet at 5.98δ assumed to be due to $[W(CO)_3(\pi\text{-}C_5H_5)]F$; and a strong singlet at 5.72δ assumed to be due to a polyflourinated specie.

(e) Reactions of $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$

1. Reaction of $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ with HCl

Summary: It was found that cleavage of the methyl-tungsten linkage occurred when $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ and HCl, at an ideal gas pressure of 5.38 atm, were combined for several days at room temperature according to the equation:

$$H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow (\pi\text{-}C_5H_5)W(CO)_3Cl + CH_4$$

In the dry bag, 111.9 mgm (0.3073 mmol) of $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 179.7 mgm (4.929 mmol) of HCl were condensed into the reactor at -196°. Upon warming to room temperature, an orange-red liquid appeared immediately. After sitting for four days, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$\text{RT}\sim\text{-}96°\sim\text{-}130°\sim\underset{\text{F(A)}}{\text{-}196°}$$

6.8 mgm were gained by the reactor.

The following materials were identified:

HCl: Fraction (A) [171.2 mgm, 4.696 mmol; 95.27% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

$(\pi-C_5H_5)W(CO)_3Cl$: Bright orange solid [118.7 mgm, 0.3221 mmol; 104.8% yield based on the amount of $H_3C-W(CO)_3(\pi-C_5H_5)$ initially employed; commercial analysis gave the following values, found: C - 25.32%, H - 1.26%, Cl - 9.70%; calculated: C - 23.56%, H - 1.51%, Cl - 9.94%]. $(\pi-C_5H_5)W(CO)_3Cl$ melted at 144° with decomposition. An n.m.r. spectrum (in deuterated acetone) shown in figure 33, shows a strong singlet at 6.00δ. Its infrared spectrum is also shown in figure 33.

---

2. Reaction of $H_3C-W(CO)_3(\pi-C_5H_5)$ with $N(CH_3)_3$

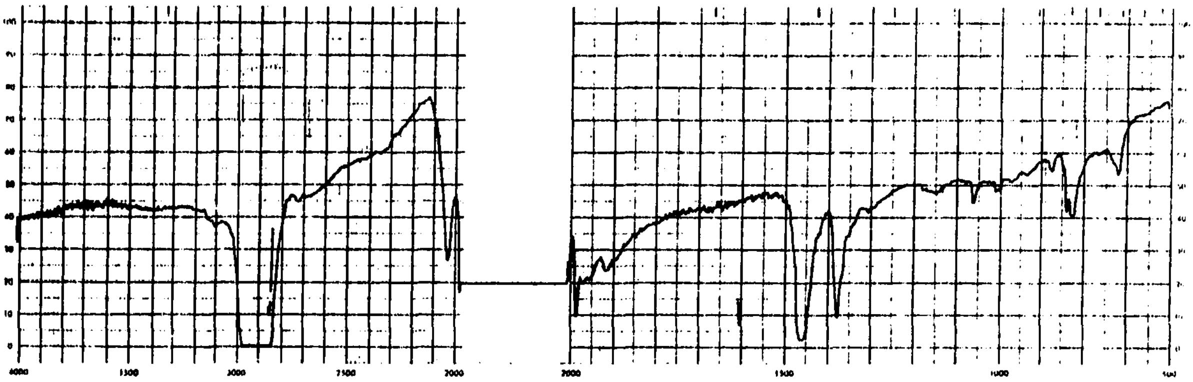
Summary: It was found that no reaction occurred when $H_3C-W(CO)_3(\pi-C_5H_5)$ and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$H_3C-W(CO)_3(\pi-C_5H_5) + N(CH_3)_3 \rightarrow \text{N.R.}$$

In the dry bag, 107.7 mgm (0.3094 mmol) of $H_3C-W(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 1290.4 mgm (21.830 mmol) of $N(CH_3)_3$

IR, NMR SPECTRA OF $CpW(CO)_3Cl$

IR



NMR

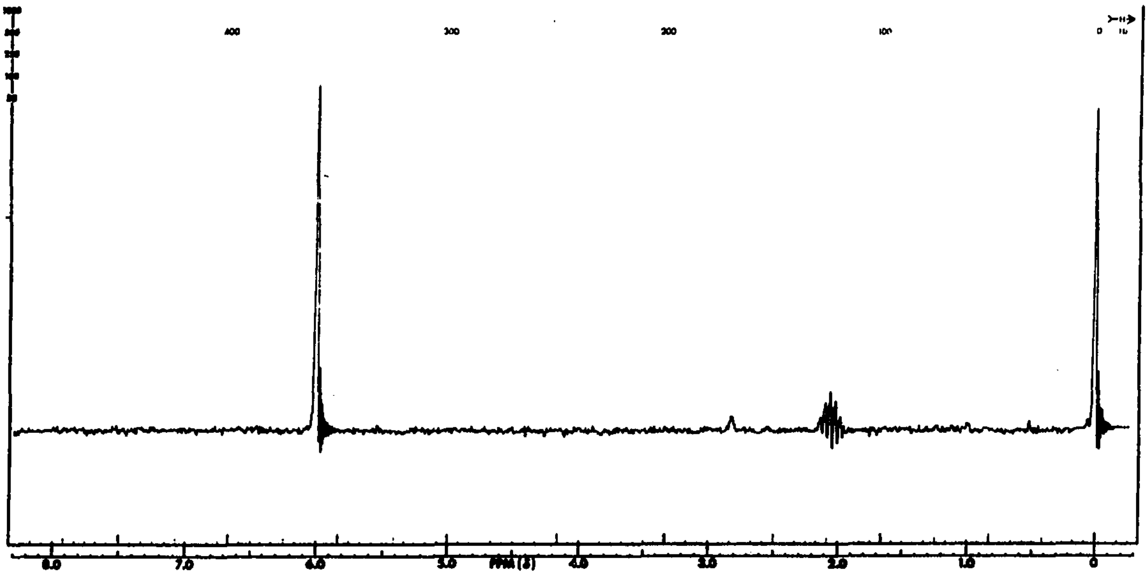


FIGURE 33

IR DATA OF $(\pi\text{-}C_5H_5)W(CO)_3Cl$

	Absorption	Intensity	Assignment
	3102	w	Cp [a]
Nujol	2920	vs	
Nujol	2852	vs	
	2036	vs	-CO [b]
	1986	vs	-CO [b]
	1915	s	-CO [b]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	1063	w	
	1012	w	Cp [a]
	1002	w	
	875	w	
	840	s	
	825	s	Cp [a]
Nujol	720	w	

a:Ref. 109.

b:Ref. 92.

TABLE 20

were condensed into the reactor at -196°. Upon warming to room temperature, the yellow solid dissolved forming a bright yellow solution. After sitting for five days, the reactor was cooled to -196°, and no non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$\underset{}{\mathrm{RT}}\sim\underset{F(A)}{-96^\circ}\sim\underset{F(B)}{-126^\circ}\sim -196^\circ$$

1.2 mgm were lost by the reactor.

The following materials were identified:

$\underline{N(CH_3)_3}$: Fractions (A) and (B) [1289.8 mgm, 21.820 mmol; 99.951% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$\underline{H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)}$: Yellow solid [106.5 mgm, 0.3059 mmol; 98.87% recovery based on the amount of $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ initially employed; identified by infrared spectrum identical to that observed for pure $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ [2]].

---

3. Reaction of $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ with $HN(CH_3)_2$

Summary: It was found that no reaction took place when $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ and $HN(CH_3)_2$ were combined for several days at room temperature according to the equation:

$$H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5) + HN(CH_3)_2 \rightarrow N.R.$$

In the dry bag, 32.0 mgm (0.0919 mmol) of $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ were placed in a reactor; and from the vacuum line, 158.7 mgm (3.520 mmol) of $HN(CH_3)_2$ were condensed into the reactor at -196°. Upon warming to room temperature, a yellow solution resulted with complete dissolution of the solid. After sitting for five days, the reactor was cooled to -196°, and no non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:

$$\begin{array}{c} RT \sim -96° \sim -130° \sim -196° \\ \quad F(A) \qquad F(B) \end{array}$$

2.0 mgm were lost by the reactor.

The following materials were identified:

$HN(CH_3)_2$: Fractions (A) and (B) [158.5 mgm, 3.516 mmol; 99.87% recovery based on the amount of $HN(CH_3)_2$ initially employed; identified by infrared spectrum identical to that observed for pure $HN(CH_3)_2$ [101]].

$H_3C-W(CO)_3(\pi-C_5H_5)$: Yellow-brown solid [30.0 mgm, 0.0862 mmol; 93.8% recovery based on the amount of $H_3C-W(CO)_3(\pi-C_5H_5)$ initially employed; identified by infrared spectrum identical to that observed for pure $H_3C-W(CO)_3(\pi-C_5H_5)$ [2]].

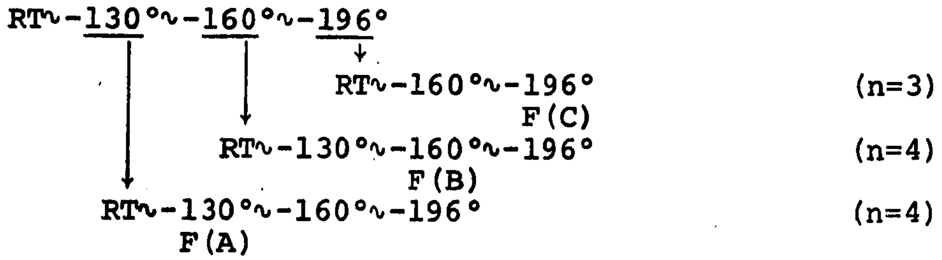
---

4. Reaction of $H_3C-W(CO)_3(\pi-C_5H_5)$ with PF_5

Summary: It was found that a complex solid mixture occurred when $H_3C-W(CO)_3(\pi-C_5H_5)$ and PF_5, at an ideal gas pressure of 1.10 atm, were combined for several days at room temperature according to the equation:

$$H_3C-W(CO)_3(\pi-C_5H_5) + PF_5 \rightarrow \begin{array}{l}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array}$$

In the dry bag, 29.0 mgm (0.0833 mmol) of $H_3C-W(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, 126.4 mgm (1.003 mmol) of PF_5 were condensed into the reactor at -196°. Upon warming to room temperature and sitting for sixteen hours, the yellow solid changed slowly to a light yellow-purple solid After sitting for four days, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor were separated as follows:



The following materials were identified:

$\underline{PF_3}$: Fraction (C) [5.2 mgm, 0.059 mmol; 5.7% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure PF_3 [104]].

$\underline{SiF_4}$: Fraction (B) [63.7 mgm, 0.612 mmol; 61.0% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure SiF_4 [105]].

$\underline{OPF_3}$: Fraction (A) [113.6 mgm, 1.093 mmol; 108.9% yield based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure OPF_3 [104]].

complex mixture: Purple-red solid [35.5 mgm]. An n.m.r. spectrum (in deuterated acetone) showed a strong singlet at 5.99δ assumed to be due to $[W(CO)_3(\pi\text{-}C_5H_5)]F$, and a strong singlet at 5.76δ assumed to be due to a polyflourinated specie.

(B) SYNTHESES AND REACTIONS OF SILYL DERIVATIVES OF CYCLOPENTADIENE AND METHYLCYCLOPENTADIENE

(1) SYNTHESIS OF THE NEW COMPOUND: $C_5H_5SiH_3$

<u>Summary</u>: It was found that the new compound, $C_5H_5SiH_3$, could be synthesized in 90% yield based on the amount of $K[C_5H_5]$ employed when dry $K[C_5H_5]$ and H_3SiBr were combined at -78° for one hour according to the equation:

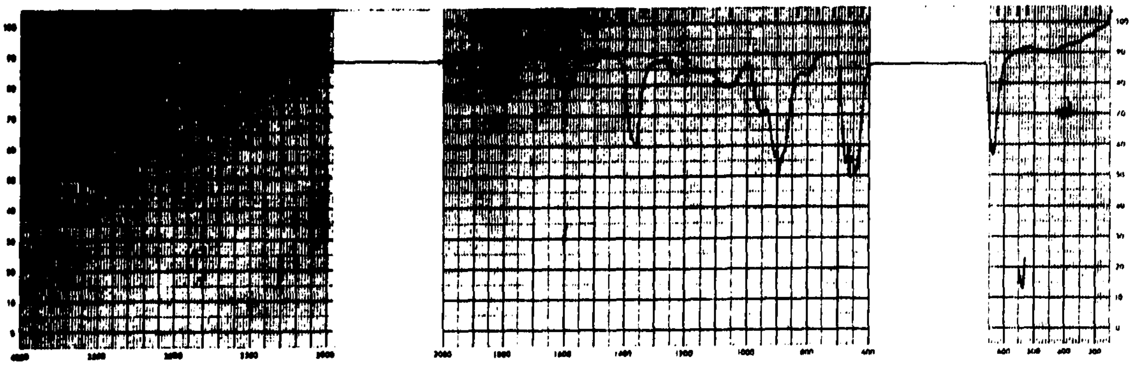
$$K[C_5H_5] + H_3SiBr \rightarrow KBr + C_5H_5SiH_3$$

(a) <u>Preparation of $K[C_5H_5]$</u>

In the dry bag, 419.9 mgm (10.74 mmol) of potassium metal, cut up into small pieces, were placed in a reactor; and from the vacuum line, 821.6 mgm (12.43 mmol) of cyclopentadiene (stored at -78°; infrared spectrum [107] and n.m.r. spectrum [2,108] shown in figure 34) and approximately 15 ml of diethyl ether (degassed twice) were condensed in the reactor cooled to -196°. The reactor was warmed to -78° by means of a dry ice-acetone bath and held at this temperature during the reaction. Initially, the reaction was evidenced by the evolution of gas bubbles; and within fifteen minutes, a white residue settled to the bottom of the reactor. After twelve hours, a complete reaction of all the potassium occurred, since the reactor was allowed to warm to room temperature intermittently and

IR, NMR SPECTRA OF C_5H_6

IR



NMR

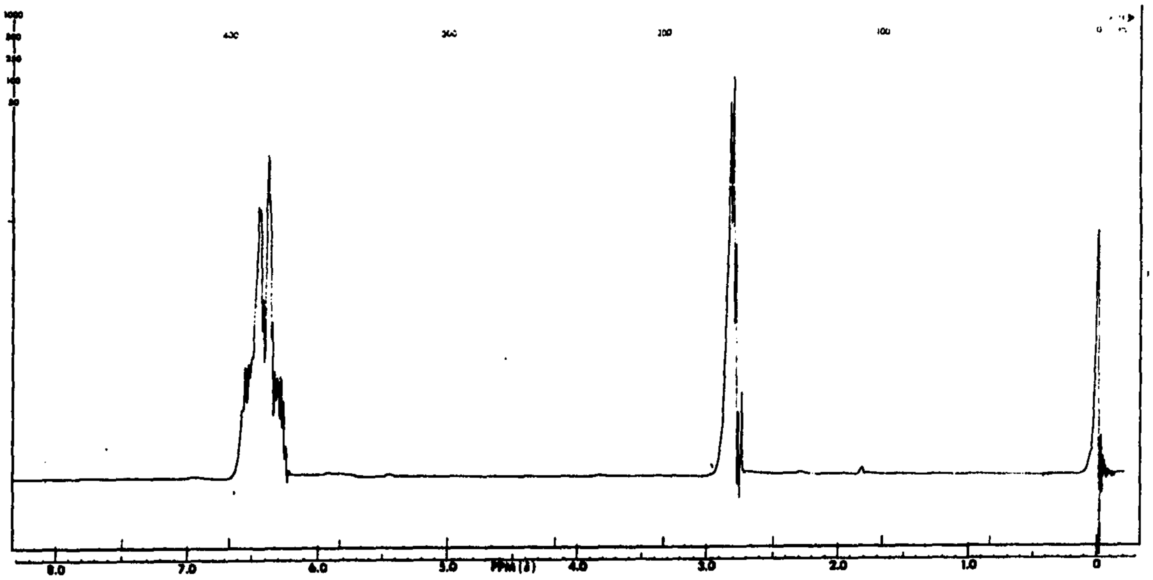


FIGURE 34

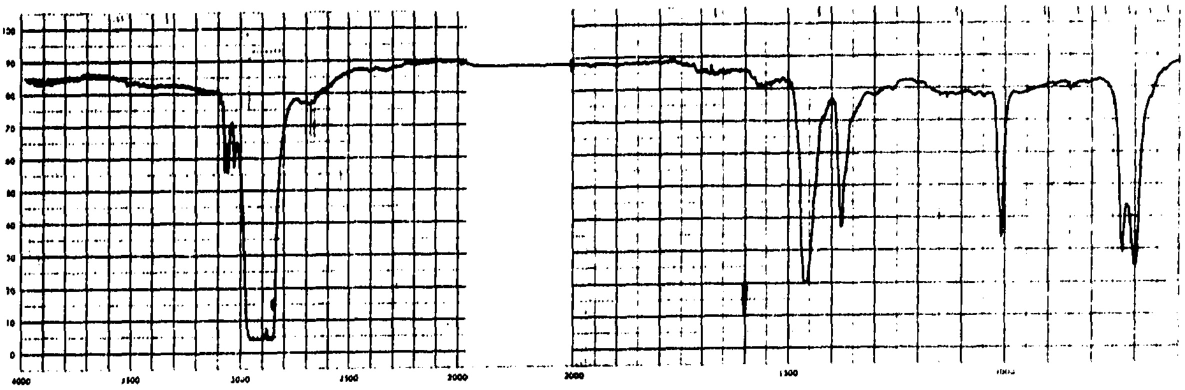
shaken. Then the reactor was cooled to -196°, and a non-condensible gas (assumed to be H_2) was pumped away; ether and excess cyclopentadiene were removed from the reactor warmed to -30° by means of a p-chlorotoluene bath by slowly condensing the volatile materials in a -78° dry ice-acetone trap. The resulting white solid in the reactor was dried thoroughly by warming the reactor to room temperature and then to 60° in order to drive off any adhering volatile material which was collected in a -196° trap open to the pump. Drying was considered complete after four hours. 1089.1 mgm (10.448 mmol) of $K[C_5H_5]$ were produced. The infrared spectrum (taken in Nujol)[109] and the n.m.r. spectrum (taken in diethyl ether) of $K[C_5H_5]$ are shown in figure 35 ; and the n.m.r. spectrum is consistent with that observed for pure $Na[C_5H_5]$.[111,118]

(b) Preparation of $C_5H_5SiH_3$

Silyl bromide (2356.6 mgm, 21.227 mmol) was condensed in the reactor containing $K[C_5H_5]$ previously prepared in part (a). Upon warming from -196° to -78°, a yellow-brown residue appeared instantly. After one hour, the reactor was again cooled to -196°, and no non-condensible gas was removed. Then the reactor was allowed to warm slowly to room temperature, and the volatile materials removed from the reactor were separated as follows:

IR, NMR SPECTRA OF K[C_5H_5]

IR



NMR

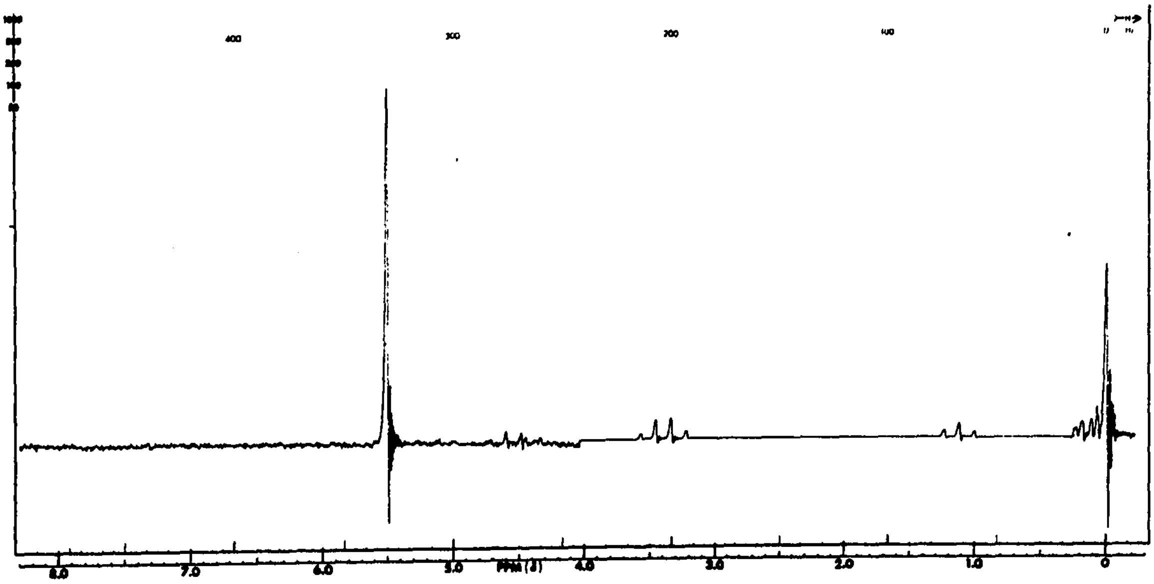


FIGURE 35

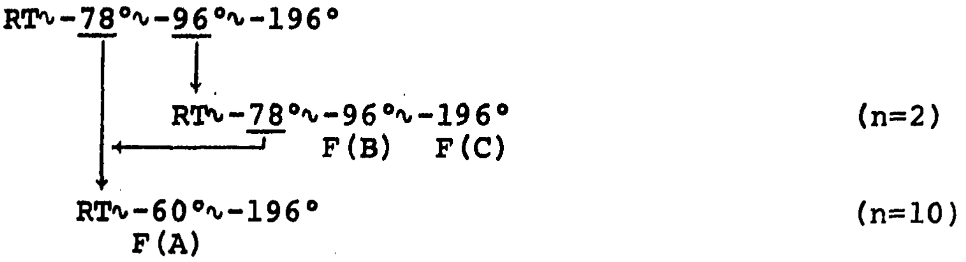
IR DATA OF K[C_5H_5]

	Absorption	Intensity	Assignment [b]
	3074 [a]	s	Cp
	3058 [a]	s	Cp
	3030 [a]	s	Cp
Nujol	2920	vs	
Nujol	2858	vs	
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	1008	vs	Cp
	730	vs	Cp
	700	vs	Cp

a:identical to frequencies observed in halocarbon 25-5S grease.

b:Ref. 109, 110.

TABLE 21



340.4 mgm (3.066 mmol) of H_3SiBr were gained by the reactor.

The following materials were identified:

$\underline{SiH_4}$: Fraction (C) [a trace amount observed in the infrared spectrum].

$\underline{H_3SiBr}$: Fraction (B) [1178.7 mgm, 10.617 mmol; 50.020% recovery based on the amount of H_3SiBr initially employed; identified by infrared spectrum identical to that observed for pure H_3SiBr [98]].

$\underline{C_5H_5SiH_3}$: Fraction (A) [909.2 mgm, 9.450 mmol; 89.01% yield based on the amount of $K[C_5H_5]$ initially employed; mol. wgt. calc.-96.21, found-96.47: 0.47%]. $C_5H_5SiH_3$ is a colorless, air stable liquid whose odor is similar to that of $C_6H_5SiH_3$.

(c) Identification and Characterization

1. *Commercial Analysis of* $\underline{C_5H_5SiH_3}$: From the vacuum line, 50 mgm of sample were condensed in an analysis tube cooled to -196°; the tube was sealed by fusing a portion of the tube below the 12/30 joint connecting the

tube to the vacuum line. The sample was stored in a freezer until sent for analysis. The following values were obtained:

Found: C - 62.70%; H - 8.62%; Si - 28.81%

Calculated: C - 62.42%; H - 8.38%; Si - 29.19%

2. Melting Point of $C_5H_5SiH_3$: From the vacuum line, approximately one half centimeter of sample was condensed in a 5 mm n.m.r. tube cooled to -196°. At first a methylcyclohexane bath cooled to -115° surrounded the n.m.r. tube and was allowed to warm slowly to -98°. An iron-constantan thermocouple, connected to a Leeds-Northrup potentiometer referenced at 0°, was placed in the bath along with a pentane thermometer. At -98°, the methylcyclohexane bath was replaced by a -96° (toluene) bath. The temperature at which half the material had melted was recorded as the melting point. Duplicate determinations yielded the melting point range of -94° to -96°.

3. Boiling Point of $C_5H_5SiH_3$: Approximately 5 ml of sample were placed in a micro-distillation apparatus. The sample was heated by means of an oil bath and distilled under a nitrogen atmosphere. The boiling point range of $C_5H_5SiH_3$ was found to be 59° to 61° at a barometric pressure of 737.5 mmHg measured at 22.5°.

4. Density of $C_5H_5SiH_3$: A preweighed (also preheated in an oven) one milliliter volumetric flask was filled to the mark with a sample of $C_5H_5SiH_3$. The volumetric flask was then weighed. The density of $C_5H_5SiH_3$ was calculated to be 0.8211 gm/ml at 25.5°.

5. Index of Refraction of $C_5H_5SiH_3$: Two drops of sample were placed on the polished quartz surface of the refractometer standardized against acetone at 25.5°. The index of refraction of $C_5H_5SiH_3$ was observed to be 1.4750 at 25.5° using the sodium D line.

6. Vapor Pressure of $C_5H_5SiH_3$: Attempts to obtain consistent plots of log P vs 1/T failed due to condensation above 0°; but the equation of state obtained from one plot of log P vs 1/T is as follows: $\log P(\text{mm}) = -1063/T + 5.711$; b(extra.) = 100.4°; $\Delta H_v = 0.23$ kcal/mole.

7. Infrared Spectrum of $C_5H_5SiH_3$: The infrared spectrum of $C_5H_5SiH_3$ determined in the gas phase at 1 to 2 torr is shown in figure 36 and the principle absorptions are given in table 22.

8. Nuclear Magnetic Resonance of $C_5H_5SiH_3$: From the vacuum line, a neat liquid sample of $C_5H_5SiH_3$ was condensed in a 5 mm n.m.r. tube cooled to -196°. After addition of a small amount of $Si(CH_3)_4$, the tube (still cooled to -196°) was sealed with an oxygen torch by

heating a small portion of the tube below the 12/30 joint. The sample tube was stored at -196° until placed in the n.m.r. tube holder. The n.m.r. spectrum of a neat sample of $C_5H_5SiH_3$ is shown in figure 36, and the chemical shifts observed at room temperature are as follows:

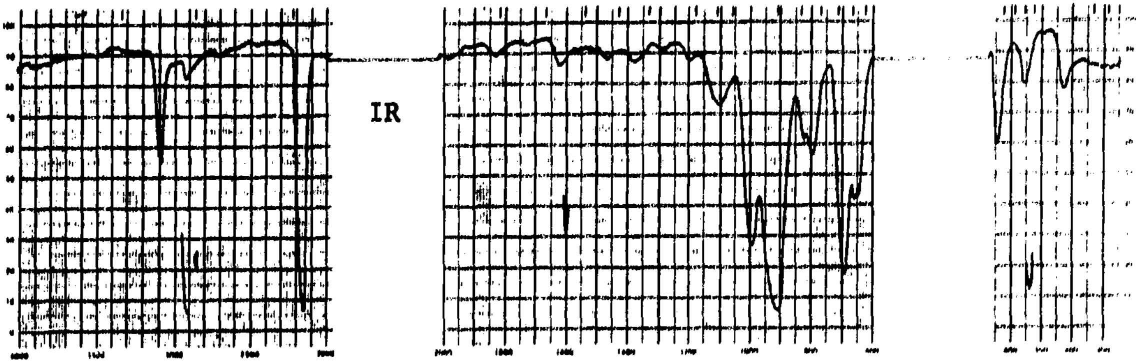
Group		Chemical Shift-δ
methylene proton	(complex)	2.83
$-SiH_3$	(singlet)	3.50
vinyl protons	(broad)	6.23

A dilute sample (50:50 mixture) of $C_5H_5SiH_3$ in CCl_4 was also prepared in a similar manner. The n.m.r. spectrum of a dilute sample of $C_5H_5SiH_3$ is shown in figure 36, and the chemical shifts observed at room temperature are as follows:

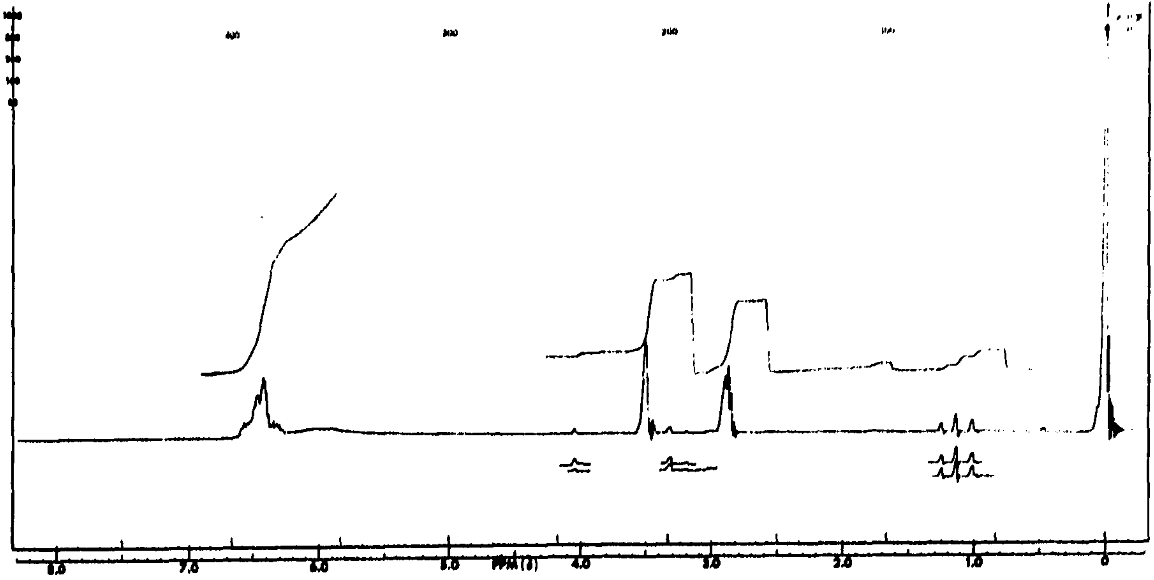
Group		Chemical Shift-δ
methylene proton	(triplet)	2.87
$-SiH_3$	(singlet)	3.50
vinyl protons	(complex)	6.43

A temperature-dependent n.m.r. study was carried out to determine the preferred stereochemical configuration of $C_5H_5SiH_3$. A detailed analysis of the results are given in Chapter V, section B.

IR, NMR (RT) SPECTRA OF $C_5H_5SiH_3$



NMR (dilute)



NMR (neat)

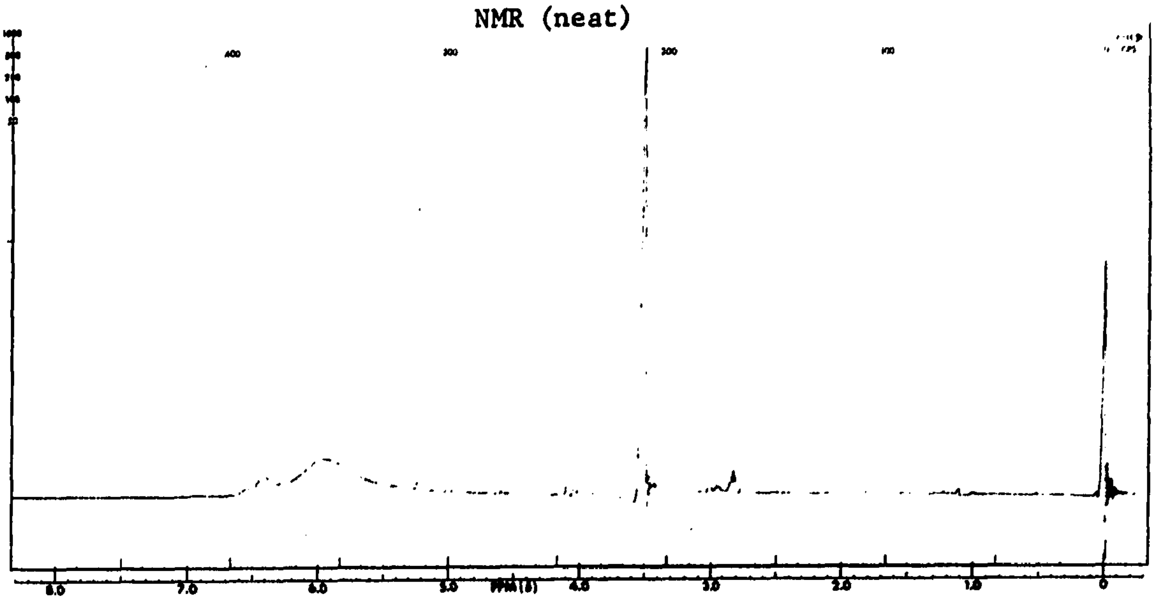


FIGURE 36

IR DATA OF $C_5H_5SiH_3$

Absorption	Intensity	Assignment
3100	m	Cp [a]
2930	vs	
2895		
2152	vs	Si-H [b]
1370	w	
1110	m	
999	s	Cp [a]
920	vs	SiH_3 def.vib. [b]
823	m	
793	m	
697	vs	Cp [a]
655	s	
645	s	
550	w	
425	m	Si-C [c]

a:Ref. 109.

b:Ref. 98.

c:Ref. 92.

TABLE 22

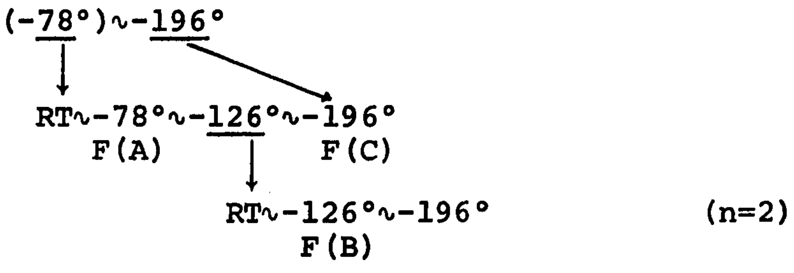
(d) Reactions of $C_5H_5SiH_3$

1. Reaction of $C_5H_5SiH_3$ with HCl at -78°

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_5SiH_3$ and HCl were combined for several hours at -78° according to the equation:

$$C_5H_5SiH_3 + HCl \rightarrow C_5H_6 + H_3SiCl$$

From the vacuum line, 380.9 mgm (3.959 mmol) of $C_5H_5SiH_3$ and 173.9 mgm (4.770 mmol) of HCl were condensed in a reactor cooled to -196°; upon warming the reactor to -78°, a clear liquid resulted. After two hours at -78°, excess HCl was removed by condensing the volatile material in a -196° trap; then the reactor was allowed to warm to room temperature while collecting the remaining volatile materials in -78°, -126°, and -196° traps, all in series. The material collected in the -126° trap was distilled several times, i.e.,



The following materials were identified:

HCl: Fraction (C) [13.7 mgm, 0.376 mmol; 7.88% recovery based on the amount of HCl initially employed; mol. wgt. calc.-36.46, found-36.61: 0.41%; confirmed by infrared spectrum identical to that observed for pure HCl [101]].

$\underline{H_3SiCl}$: Fraction (B) [214.8 mgm, 3.227 mmol; 81.52% yield based on the amount of $C_5H_5SiH_3$ initially employed; mol. wgt. calc.-66.65, found-67.84: 1.92%; confirmed by infrared spectrum identical to that observed for pure H_3SiCl [98]].

$\underline{C_5H_5SiH_3}$ and $\underline{C_5H_6}$: Fraction (A) [identified by infrared spectrum identical to that expected for a mixture of $C_5H_5SiH_3$ and C_5H_6].

$\underline{[C_5H_5SiH_3]_2}$: Colorless non-volatile liquid [37.3 mgm] assumed to be $[C_5H_5SiH_3]_2$ by infrared spectrum nearly identical to that observed for $[C_5H_6]_2$ with the addition of a strong absorption at 2140 cm^{-1} due to Si-H stretch.

---

2. Reaction of $C_5H_5SiH_3$ with HCl

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_5SiH_3$ and HCl, at an ideal gas pressure of 21.97 atm, were combined for one hour at room temperature according to the equation:

$$C_5H_5SiH_3 + HCl \rightarrow C_5H_6 + H_3SiCl$$

From the vacuum line, 558.2 mgm (5.802 mmol) of $C_5H_5SiH_3$ and 733.6 mgm (20.12 mmol) of HCl were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for one hour, a dark blue liquid resulted. Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to -126°; a wine-red liquid was observed as excess HCl was removed by condensing the volatile material in a -196° trap. As the reactor was warmed to -78°, a dark solution appeared and some volatile material was removed by collecting it in -126° and -196° traps, both in series. As the reactor was allowed to warm to room temperature, the remaining volatile material was collected in -78° and -196° traps, both in series; i.e.,

(-196°)
↓
(-126°)∿-196°
F(C)
↓
(-78°)∿-126°∿-196°
F(B)
↓
RT∿-78°∿-196°
F(A)

The following materials were identified:

HCl: Fraction (C) [25.6 mgm, 7.02 mmol; 3.49% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

H_3SiCl: Fraction (B) [301.6 mgm, 4.531 mmol; 78.10% yield based on the amount of $C_5H_5SiH_3$ initially employed; identified by infrared spectrum identical to that observed for pure H_3SiCl [98]].

$C_5H_5SiH_3$ and C_5H_6: Fraction (A) [identified by infrared spectrum identical to that expected for a mixture of $C_5H_5SiH_3$ and C_5H_6].

complex mixture: Green non-volatile liquid [446.4 mgm] The infrared spectrum of this viscous liquid resembled the spectrum of the viscous liquid produced by the reaction at -78°.

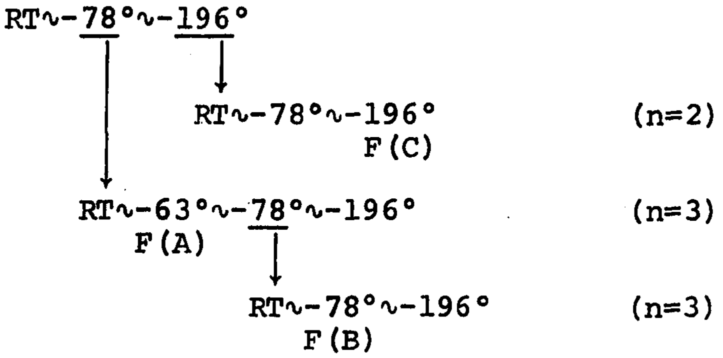
---

3. Reaction of $C_5H_5SiH_3$ with $N(CH_3)_3$

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_5SiH_3$ and $N(CH_3)_3$ were combined for several hours at room temperature according to the equation:

$$C_5H_5SiH_3 + N(CH_3)_3 \rightarrow C_5H_5CH_3 + H_3Si\text{-}N(CH_3)_2$$

From the vacuum line, 432.2 mgm (4.492 mmol) of $C_5H_5SiH_3$ and 997.8 mgm (16.88 mmol) of $N(CH_3)_3$ were condensed in a reactor cooled to -196°. Upon warming the reactor to room temperature and standing for several hours, trace amounts of a white solid appeared. After several days at ambient temperature, a very small amount of white fluffy crystals settled out of solution. Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

<u>$N(CH_3)_3$</u>: Fraction (C) [452.0 mgm, 7.647 mmol; 45.30% yield based on the amount of $N(CH_3)_3$ initially employed; mol. wgt. calc.-59.11, found-60.60: 2.51%; confirmed by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$H_3Si\text{-}N(CH_3)_2$: Fraction (B) [63.6 mgm, 0.846 mmol; 18.83% yield based on the amount of C_5H_5SiH initially employed; mol. wgt. calc.-75.18, found-75.23: 0.05%;[112] confirmed by infrared spectrum identical to that observed for pure $H_3Si\text{-}N(CH_3)_2$ [103]].

$C_5H_5SiH_3$: Fraction (A) [219.6 mgm, 2.282 mmol; 50.81% recovery based on the amount of $C_5H_5SiH_3$ initially employed; identified by infrared spectrum identical to that observed previously for pure $C_5H_5SiH_3$].

residue: Colorless non-volatile liquid [44.7 mgm].

4. Reaction of $C_5H_5SiH_3$ with Potassium in Diethyl Ether

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_5SiH_3$ and potassium metal were combined in diethyl ether at -78° according to the equation:

$$2C_5H_5SiH_3 + K + \text{"}3H\text{"} \rightarrow K[C_5H_5] + C_5H_6 + 2SiH_4$$

In the dry bag, 498.9 mgm (12.76 mmol) of potassium metal, cut up into very small pieces, were placed in a reactor; and from the vacuum line, 1365.3 mgm (14.191 mmol) of $C_5H_5SiH_3$ and about 10 ml of diethyl ether (distilled over $LiAlH_4$; degassed twice) were condensed in the reactor cooled to -196°. The reactor was warmed to and held at -78° by means of a dry ice-acetone bath during the reaction. Initially, slow evolution of gas bubbles was observed; and after twelve hours, a white residue settled on the bottom of the reactor, covering some of the unreacted pieces of potassium. The reactor was shaken intermittently to react more potassium. Then the reactor was cooled to -196°, and a very small amount of non-condensible gas was removed. The reactor was warmed to -30° by means of a o-chlorotoluene bath, and excess $C_5H_5SiH_3$ and ether were removed by slow condensation in a -78° dry ice-acetone trap. After four hours, the reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:

$$\begin{array}{ccccccc} RT & \sim & -96° & \sim & -130° & \sim & -196° \\ & & F(A) & & & & F(B) \end{array}$$

642.7 mgm were gained by the reactor.

The following materials were identified:

$\underline{SiH_4}$: Fraction (B) [251.9 mgm, 7.842 mmol; 55.30% yield based on the amount of $C_5H_5SiH_3$ initially employed; mol. wgt. calc.-32.12, found-32.17: 1.83%; confirmed by infrared spectrum identical to that observed for pure SiH_4 [102]].

$\underline{C_5H_6}$, $\underline{C_5H_5SiH_3}$, and $\underline{Et_2O}$: Fraction (A) [identified by infrared spectrum identical to that expected for a mixture of C_5H_6, $C_5H_5SiH_3$, and Et_2O].

$\underline{K[C_5H_5]}$: Gray-white solid [1221.5 mgm, 11.720 mmol; 91.840% yield based on the amount of potassium initially employed; identified by infrared spectrum identical to that observed previously for pure $K[C_5H_5]$; confirmed by n.m.r. spectrum identical to that observed previously for pure $K[C_5H_5]$].

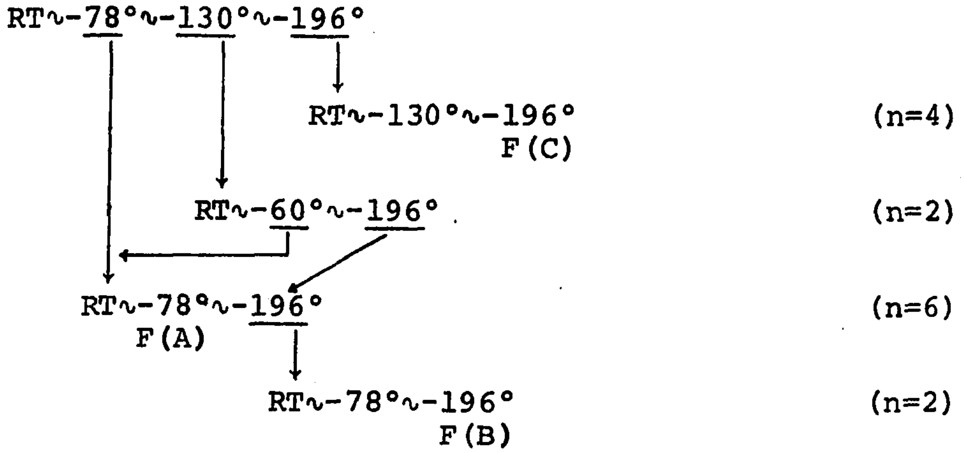
---

5. Reaction of $C_5H_5SiH_3$ with Potassium Metal in 1,2-dimethoxyethane

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_5SiH_3$ and potassium metal were combined at room temperature using 1,2DME as the solvent according to the equation:

$$2C_5H_5SiH_3 + K + \text{"3H"} \rightarrow K[C_5H_5] + C_5H_6 + 2SiH_4$$

In the dry bag, 135.5 mgm (3.455 mmol) of potassium metal, cut up into very small pieces, were placed in a reactor; and from the vacuum line, 558.5 mgm (5.805 mmol) of $C_5H_5SiH_3$ and 677.1 mgm (7.513 mmol) of 1,2DME (monoglyme: distilled over $LiAlH_4$; redistilled over potassium metal and degassed twice) were condensed into the reactor at -196°. As the reactor began to warm slowly to room temperature, a dark blue solution appeared instantly; evolution of gas bubbles could also be observed. After five minutes at ambient temperature, a dark pink solution resulted, and a white residue settled to the bottom of the reactor. After twelve hours, the reactor was cooled to -196°, and a very small amount of non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



489.7 mgm (5.090 mmol) of $C_5H_5SiH_3$ were gained by the reactor.

The following materials were identified:

$\underline{SiH_4}$: Fraction (C) [31.0 mgm, 0.965 mmol; 1.66% yield based on the amount of $C_5H_5SiH_3$ initially employed; identified by infrared spectrum identical to that observed for pure SiH_4[102]].

$\underline{C_5H_6}$ and $\underline{C_5H_5SiH_3}$: Fraction (B) [72.6 mgm; identified by infrared spectrum identical to that observed for a mixture of C_5H_6 and $C_5H_5SiH_3$].

1,2DME: Fraction (A) [618.3 mgm, 6.861 mmol; 91.32% recovery based on the amount of 1,2DME initially employed; identified by infrared spectrum identical to that previously observed for pure 1,2DME [113]].

complex mixture: Red-brown non-volatile solid-liquid residue [635.2 mgm]. An infrared spectrum showed absorptions due to $K[C_5H_5]$ and possibly $[C_5H_5SiH_3]_2$.

---

6. Attempted Synthesis of $C_5H_4(SiH_3)_2$

Summary: It was found that $C_5H_4(SiH_3)_2$ could not be synthesized from the reaction of H_3SiBr with the solid product from the interaction of $C_5H_5SiH_3$ with potassium in diethyl ether at -78°.

In the dry bag, 418.6 mgm (10.70 mmol) of potassium metal, cut up into small pieces, were placed in a reactor; and from the vacuum line, 1314.5 mgm (13.660 mmol) of $C_5H_5SiH_3$ and 841.8 mgm of diethyl ether (degassed twice) were condensed in the reactor cooled to -196°. Upon warming the reactor to -78° by means of a dry ice-acetone bath, reaction was evidenced by the evolution of gas bubbles; and within fifteen minutes, a white solid settled to the bottom of the reactor. After complete reaction of all the potassium metal (intermittently warming to room temperature and shaking), the reactor was cooled to -196°, and a non-condensible gas was removed. Then the reactor was warmed to -30° by means of a o-chlorotoluene bath, and SiH_4, excess $C_5H_5SiH_3$ and ether were removed by slow condensation in a -78° dry ice-acetone trap. After four hours, the reactor was warmed to room temperature, and the white residue in the reactor was dried further by heating the reactor to 60° and collecting any volatile material in a -196° trap open to the pump. The residue (1072.8 mgm, 10.292 mmol) assumed to be $K[C_5H_5]$ was considered dry after six hours.

From the vacuum line, silyl bromide (719.2 mgm, 6.478 mmol) was condensed in the reactor containing the white residue. Upon warming the reactor from -196° to room temperature, a yellow-brown residue resulted. After fifteen minutes, the volatile materials were removed from the reactor and separated as follows:

$$\mathrm{RT}\sim-\underline{78^\circ}\sim-96^\circ\sim-196^\circ \qquad (n=2)$$
$$\downarrow$$
$$\mathrm{RT}\sim-\underline{60^\circ}\sim-78^\circ\sim\underset{\mathrm{F(B)}}{-196^\circ} \qquad (n=3)$$
$$\downarrow$$
$$\mathrm{RT}\sim-30^\circ\sim\underset{\mathrm{F(A)}}{-60^\circ}\sim-196^\circ \qquad (n=4)$$

97.8 mgm (0.881 mmol) of H_3SiBr were gained by the reactor.

The following materials were identified:

H_3SiBr: Fraction (B) [195.2 mgm, 1.758 mmol; 27.14% recovery based on the amount of H_3SiBr initially employed; identified by infrared spectrum identical to that observed for pure H_3SiBr [98]].

$C_5H_5SiH_3$: Fraction (A) [426.2 mgm, 44.30 mmol; 43.00% yield based on the amount of $K[C_5H_5]$ initially employed assuming complete reaction of potassium; identified by infrared spectrum identical to that observed previously for pure $C_5H_5SiH_3$; confirmed by n.m.r. spectrum (taken at -50°) identical to that observed previously for neat $C_5H_5SiH_3$ (taken at -50°)].

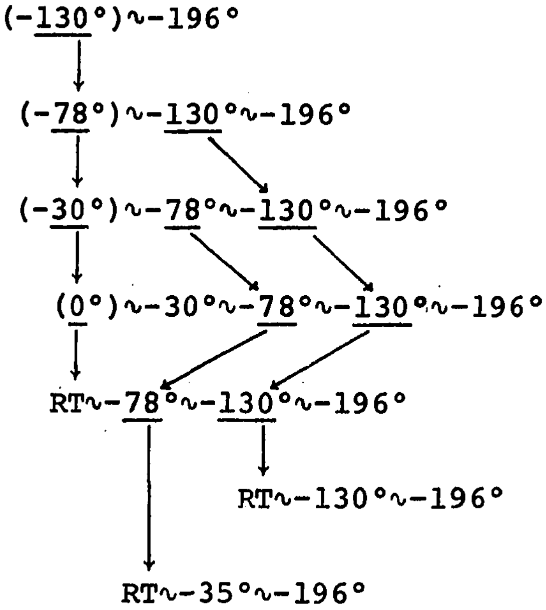
It should be noted that of the H_3Si groups employed in the silyl bromide reaction (6.478 mmol), Fractions (A) and (B) accounted for the recovery of 95.52% of these groups. This recovery represents a loss of only 30 mgm of SiH_3 and is within the limits of the experiment and supports the assertion that the solid residue used as the reactant with silyl bromide did not contain any silicon-carbon linkages.

7. Reaction of $C_5H_5SiH_3$ with $Co_2(CO)_8$ at -30°

Summary: It was found that cleavage of the Si-Co bond occurred when $C_5H_5SiH_3$ and $Co_2(CO)_8$ were combined under a CO atmosphere of 1 atm of pressure at -30° according to the equation:

$$C_5H_5SiH_3 + Co_2(CO)_8 \rightarrow \begin{array}{l}\text{complex}\\ \text{solid}\\ \text{mixture}\end{array} + HCo(CO)_4 + H_3SiCo(CO)_4$$

In the dry bag, 421.7 mgm (1.233 mmol) of $Co_2(CO)_8$ (stored in a freezer) were placed in a reactor which was subsequently removed from the dry bag, connected to the vacuum line; cooling to 0° by means of an ice slush to prevent sublimation of $Co_2(CO)_8$, the reactor was then evacuated. From the vacuum line, 748.1 mgm (7.776 mmol) of $C_5H_5SiH_3$ were condensed in the reactor cooled to -78°, since no reaction took place at this temperature. Then the reactor was warmed to -30° by means of a p-chlorotoluene bath. Slow evolution of gas bubbles was observed which became rapid as the reactor was intermittently warmed to room temperature and shaken. After twelve hours, the bath temperature was +5°. Then the reactor was cooled to -196°, and a non-condensible gas was removed; the reactor was warmed to room temperature slowly, and the volatile materials removed from the reactor were separated as follows:



(n=4)

187.8 mgm (1.952 mmol) of $C_5H_5SiH_3$ were gained by the reactor.

The following materials were identified:

$\underline{H_2}$ and $\underline{CO}$: Non-condensible gas [mol. wgt. found-13.73; assumed to be a mixture of H_2 and CO].

$\underline{C_5H_5SiH_3}$ and $\underline{H_3SiCo(CO)_4}$: Fraction (B) [520.2 mgm; identified by infrared spectrum identical to that expected for a mixture of $C_5H_5SiH_3$ and $H_3SiCo(CO)_4$].[114]

$\underline{C_5H_6}$: Fraction (B) [a trace amount seen in the infrared spectrum].

$\underline{HCo(CO)_4}$: Fraction (A) [26.3 mgm, 0.153 mmol; 7.45% yield based on the amount of $Co_2(CO)_8$ initially employed; mol. wgt. calc.-172.0, found-169.4:

1.52%; confirmed by infrared spectrum identical to that observed for pure $HCo(CO)_4$ 115].

complex mixture: Dark red non-volatile liquid [619.5 mgm] An infrared spectrum showed absorptions due to $Co_2(CO)_8$.

---

8. Reaction of $C_5H_5SiH_3$ with $Mo(CO)_6$

Summary: It was found that cleavage of the Si-C bond did not occur when $C_5H_5SiH_3$ and $Mo(CO)_6$ were combined together at 125° for several days according to the equation:

$$2C_5H_5SiH_3 + 2Mo(CO)_6 \rightarrow [Mo(CO)_3(\pi\text{-}C_5H_5SiH_3)]_2 + 6CO$$

$Mo(CO)_6$ (1009.0 mgm, 3.8220 mmol) was placed in a reactor; and from the vacuum line, 1274.8 mgm (13.250 mmol) of $C_5H_5SiH_3$ were condensed in the reactor cooled to -78°. Upon warming to room temperature, gas bubbles were observed to form slowly; gas evolution ceased after six hours. Then the reactor was placed in an oil bath and heated at 125°. Gas bubbles and a light pink solution were observed after twelve hours. After five days the reactor was removed from the oil bath, allowed to cool to ambient temperature, and then cooled to -196°. A non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile material removed from the reactor (held at 0°) was separated as follows:

$$0^\circ\sim-78^\circ\sim-196^\circ$$
$$\mathrm{F(A)}$$

297.9 mgm (3.096 mmol) of $C_5H_5SiH_3$ were gained by the reactor.

The following materials were identified:

$C_5H_5SiH_3$: Fraction (A) [129.3 mgm, 1.344 mmol; 10.14% recovery based on the amount of $C_5H_5SiH_3$ initially employed; identified by infrared spectrum identical to that observed previously for pure $C_5H_5SiH_3$].

$Mo(CO)_6$: White crystals [290.3 mgm, 1.100 mmol; 28.77% recovery based on the amount of $Mo(CO)_6$ initially employed; identified by infrared spectrum identical to that observed for pure $Mo(CO)_6$ [100]].

$[Mo(CO)_3(\pi-C_5H_5SiH_3)]_2$: White solid [small amount]. After removal of excess $C_5H_5SiH_3$ and $Mo(CO)_6$ from the reactor at 75°, a brown-yellow non-volatile liquid and a white residue remained in the reactor. Hexane dissolved the liquid but not the solid; this solution was filtered, and the residue was washed several times with 5 ml portions of hexane. The principle absorptions of the infrared spectrum (taken in Nujol) are given in table 23.

IR DATA OF $[Mo(CO)_3(\pi\text{-}C_5H_4SiH_3)]_2$

	Absorption	Intensity	Assignment
	3138		Cp [a]
Nujol	2920	vs	
Nujol	2852	vs	
	2138	s	Si-H [b]
	2110	s	Si-H [b]
	2037(Sh)		
	2004	s	-CO [c]
	1948	s	-CO [c]
	1908(Sh)		
	1897	s	-CO [c]
Nujol	1459	s	
Nujol	1375	s	
Nujol	1152	w	
	1023	w	
	948	s	SiH_3 def.vib.[b]
	937	s	SiH_3 def.vib.[b]
	875	w	
	832	w	
	809	vs	
Nujol	715	w	

a:Ref. 109. b:Ref. 203.

c:Ref. 58, 88.

TABLE 23

(e) Physical Characterization of Isomeric $C_5H_5CH_3$

1. Melting Point of $C_5H_5CH_3$: From the vacuum line, approximately one half centimeter of sample was condensed in a 5 mm n.m.r. tube cooled to -196°. At first a methylcyclohexane bath cooled to -115° surrounded the n.m.r. tube and was allowed to warm slowly to -98°. An iron-constantan thermocouple, connected to a Leeds-Northrup potentiometer referenced at 0°, was placed in the bath along with a pentane thermometer. At -98°, the methylcyclohexane bath was replaced by a -96° (toluene) bath. The temperature at which half the material had melted was recorded as the melting point. Duplicate determinations yielded the melting point to be -98°.

2. Boiling Point of $C_5H_5CH_3$: Approximately 5 ml of sample were placed in a micro-distillation apparatus. The sample was heated by means of an oil bath and distilled under a nitrogen atmosphere. The boiling point range of $C_5H_5CH_3$ was found to be 73°-75°, compared to the literature range of 65°-73°.[116]

3. Density of $C_5H_5CH_3$: A preweighed (also preheated in an oven) one milliliter volumetric flask was filled to the mark with a sample of $C_5H_5CH_3$. The volumetric flask was then weighed. The density of $C_5H_5CH_3$ was calculated to be 0.8005 gm/ml at 25.5°, compared to the literature value of 0.8040 gm/ml at 20.0°.[116]

4. Index of Refraction of $C_5H_5CH_3$: Two drops of sample were placed on the polished quartz surface of refractometer standardized against acetone at 25.5°. The index of refraction of $C_5H_5CH_3$ was observed to be 1.4486 at 25.5° using the sodium D line, compared to the literature value of 1.4510 at 20.0° using the sodium D line.[116]

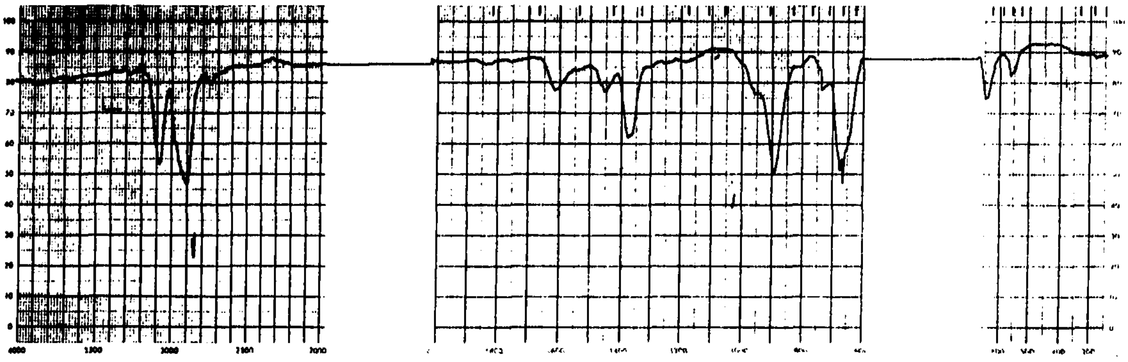
5. Vapor Pressure of $C_5H_5CH_3$: Two milliliters of sample were placed in a short take-off tube. An iron-constantan thermocouple was placed in a -60° (chloroform) bath which was allowed to warm slowly from -45° to +4°. A plot of log P vs 1/T gave the following equation of state: log P(mm) = -1462/T + 7.0984; b(extra.) = 73.2°; ΔH_v = 0.32kcal/mole.

6. Infrared Spectrum of $C_5H_5CH_3$: The infrared spectrum of $C_5H_5CH_3$ in the gas phase was identical to that observed for a mixture of 1,2 isomers and is shown in figure 37.[107]

7. Nuclear Magnetic Resonance of $C_5H_5CH_3$: From the vacuum line, a neat liquid sample of $C_5H_5CH_3$ was condensed in a 5 mm n.m.r. tube cooled to -196°. After addition of a small amount of $Si(CH_3)_4$, the tube (still cooled to -196°) was sealed with an oxygen torch by heating a small portion of the tube below the 12/30 joint. The sample tube was stored at -196° until placed in the n.m.r. tube holder. The n.m.r. spectrum of $C_5H_5CH_3$ is shown in figure 37 . The chemical shifts observed at room temperature were identical to those observed for a

IR, NMR SPECTRA OF $C_5H_5CH_3$

IR



NMR

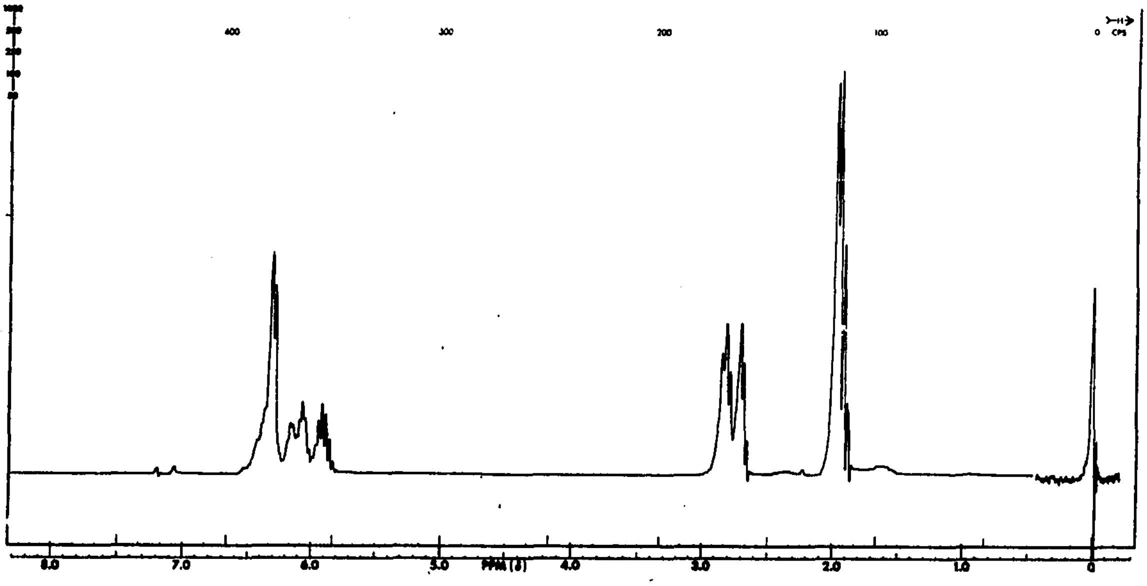


FIGURE 37

mixture of 1,2 isomers of methylcyclopentadiene and are shown in figure 37.[117]

(f) Reactions of $C_5H_5CH_3$

1. Reaction of $C_5H_5CH_3$ with HCl at -78°

Summary: It was found that a black tar occurred when $C_5H_5CH_3$ and HCl, at an ideal gas pressure of 5.72 atm, were combined for thirty minutes at -78° according to the equation:

$$C_5H_5CH_3 + HCl \rightarrow \text{black tar polymers} + \text{chlorination products}$$

From the vacuum line, 518.4 mgm (6.469 mmol) of $C_5H_5CH_3$ and 325.4 mgm (8.925 mmol) of HCl were condensed in a reactor cooled to -196°. A yellow coloration appeared immediately at this temperature. Upon warming the reactor to -78°, a black residue resulted. After sitting one half hour, the volatile materials were removed from the reactor at -78° and then at room temperature and were separated as follows:

$$\text{RT} \sim -130° \sim \underset{F(A)}{-196°}$$

The following materials were identified:

HCl: Fraction (A) [191.3 mgm, 5.245 mmol; 58.79% recovery based on the amount of HCl initially employed;

mol. wgt. calc.-36.46, found-36.76: 0.82%; confirmed by infrared spectrum identical to that observed for pure HCl [101]].

residue: Black tar [652.5 mgm]. 1,2 addition and polymerization were assumed to have taken place.[50]

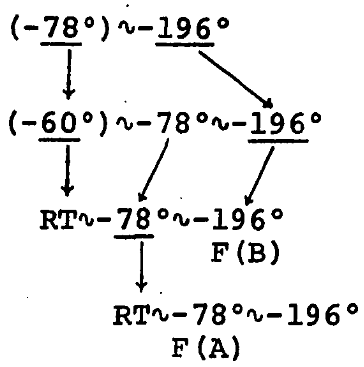
---

2. Reaction of $C_5H_5CH_3$ with $N(CH_3)_3$

Summary: It was found that no reaction occurred when $C_5H_5CH_3$ and $N(CH_3)_3$ were combined for several hours at room temperature according to the equation:

$$C_5H_5CH_3 + N(CH_3)_3 \rightarrow N.R.$$

From the vacuum line, 552.1 mgm (6.890 mmol) of $C_5H_5CH_3$ and 997.4 mgm (16.87 mmol) of $N(CH_3)_3$ were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for several hours, no visible reaction was observed. Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed slowly to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

$N(CH_3)_3$: Fraction (B) [mol. wgt. calc.-59.11, found-59.67: 0.09%; confirmed by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$C_5H_5CH_3$: Fraction (A) [545.7 mgm, 6.811 mmol; 98.8% recovery based on the amount of $C_5H_5CH_3$ initially employed; identified by infrared spectrum identical to that observed for pure $C_5H_5CH_3$ [107]].

---

3. Reaction of $C_5H_5CH_3$ with K at -78° in diethyl ether

Summary: It was found that $K[C_5H_4CH_3]$ could be synthesized in 95.18% yield based on the amount of potassium metal employed according to the equation:

$$C_5H_5CH_3 + K \rightarrow K[C_5H_4CH_3] + 1/2 H_2$$

For the experimental details see the following section under the synthesis of the new compound $C_5H_4(SiH_3)(CH_3)$.

4. Reaction of $C_5H_5CH_3$ with $Co_2(CO)_8$ at 0°

Summary: It was found that the new compound, $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$, could be synthesized at 0° in 47.2% yield based on the amount of $Co_2(CO)_8$ employed according to the equation:

$$2C_5H_5CH_3 + Co_2(CO)_8 \xrightarrow{u.v.} 2Co(CO)_2(\pi\text{-}C_5H_4CH_3) + 4CO + H_2$$

In the dry bag, 827.7 mgm (2.241 mmol) of $Co_2(CO)_8$ were placed in a reactor; and from the vacuum line, 540.8 mgm (6.749 mmol) of $C_5H_5CH_3$ were condensed in the reactor cooled to -78°. A u.v. light was then turned on and upon warming the reactor to 0° by means of an ice slush, slow evolution of gas bubbles and a dark solution were observed. After twelve hours, the reactor was cooled to -196°, and a non-condensible gas was removed. Then the reactor was warmed to room temperature; gas evolution commenced again but subsided until CO pressure stopped decomposition of the product. The red liquid in the reactor was dissolved in 10 ml of nitrogen-saturated hexane and placed on a chromatograph column containing alumina. After a yellow elutant was collected, an orange-red liquid was then eluted with hexane from the column. Excess hexane was removed under a reduced pressure of 10 mmHg, $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$, an orange-red liquid (550.0 mgm, 5.667 mmol) was produced in 47.20% yield based on the amount of $Co_2(CO)_8$ initially employed.

A melting point determination following the method previously described recorded a melting point range of -38° to -39° for $Co(CO)_2(\pi-C_5H_4CH_3)$. An infrared spectrum taken in CCl_4 showed the following absorptions: ν(C-H): 2920 cm^{-1}; ν(-CO): 2005 and 1960 cm^{-1}. The infrared spectrum of the pure liquid taken between two KBr plates is shown in figure 38, and the principle absorptions are listed in table 24. An n.m.r. spectrum relative to cyclohexane (taken in CS_2) showed the following peaks: CH_3 (singlet) at 1.95δ; vinyl protons (two weak broad peaks) at 4.98δ and 4.82δ. The n.m.r. spectrum of $Co(CO)_2(\pi-C_5H_4CH_3)$ relative to $Si(CH_3)_4$ (taken in CS_2) is shown in figure 38, and the chemical shifts are as follows:

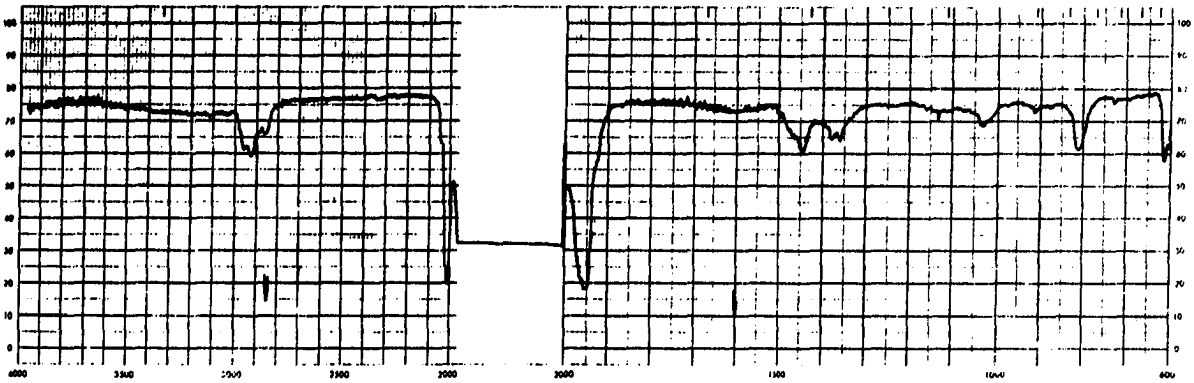
Group	Chemical Shift-δ
CH_3 (singlet)	1.91
C_5H_4 (triplet)	4.80
C_5H_4 (doublet)	5.00

Difficulty in obtaining correct C, H elemental analysis possibly due to decomposition in transit indicates that $Co(CO)_2(\pi-C_5H_4CH_3)$ is less stable than $Co(CO)_2(\pi-C_5H_5)$.

It should be noted that $Co(CO)_2(\pi-C_5H_4CH_3)$ could also be synthesized by distillation at 58°/o.1 mmHg,

IR, NMR SPECTRA OF $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$

IR



NMR

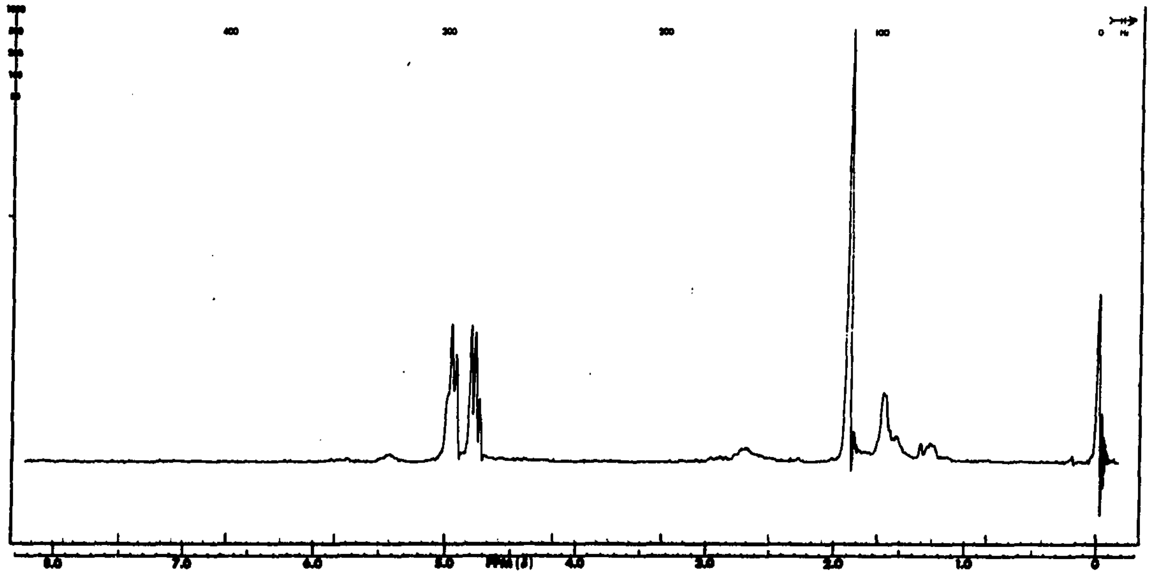


FIGURE 38

IR DATA OF $Co(CO)_2(\pi-C_5H_4CH_3)$-neat

Absorption	Intensity	Assignment
2960	m	
2928	m	
2860	w	
2045(Sh)		
2009	vs	-CO [a]
1965(Sh)		
1954	vs	-CO [a]
1445	w	
1380	w	
1360	w	
1033	w	Cp [b]
810	m	Cp [b]
615	m	
605	m	

a:Ref. 91.

b:Ref. 109.

TABLE 24

the product then being purified on the vacuum line as follows:

$$\underset{F(A)}{RT \sim 0^\circ \sim -30^\circ} \sim -196^\circ \qquad (n=3)$$

Fraction (A) contained $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$.

---

5. Reaction of $C_5H_5CH_3$ with $Mo(CO)_6$

Summary: It was found that $C_5H_5CH_3$ and $(C_5H_5CH_3)_2$ reacted with $Mo(CO)_6$ at 120° after several days according to the equations:

$$2C_5H_5CH_3 + 2Mo(CO)_6 \rightarrow [Mo(CO)_3(\pi\text{-}C_5H_4CH_3)]_2 + 6CO + H_2$$
$$(C_5H_5CH_3)_2 + 2Mo(CO)_6 \rightarrow [Mo(CO)_3(\pi\text{-}C_5H_4CH_3)]_2 + 6CO + H_2$$

$Mo(CO)_6$ (1015.0 mgm, 3.9038 mmol; 2685.4 mgm, 10.172 mmol) was placed in a reactor and $C_5H_5CH_3$ (1067.6 mgm, 13.323 mmol) or $(C_5H_5CH_3)_2$ (3951.4 mgm, 24.656 mmol) was combined with the $Mo(CO)_6$. The reactor vessel was placed in an oil bath and heated at 120°.

Gas bubbles and a light pink solution were observed after twelve hours. After three days the reactor was removed from the oil bath, allowed to cool to ambient temperature. Then the reactor was cooled to 0°, and the reaction mixture filtered in air; the residue ($Mo(CO)_6$; 1306.2 mgm, 4.9477 mmol; 48.640% recovery) was washed four times with

10 ml portions of pentane. The washings and filtrate were placed on a chromatograph column packed with alumina in hexane and eluted with a 50:50 mixture of Et_2O and pentane. The product collected as a red band was obtained after removal of excess solvent. The infrared spectrum absorptions (taken in Nujol) were identical to that observed for pure $[Mo(CO)_3(\pi-C_5H_4CH_3)]_2$ [58,88] and are listed in table 25.

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(2) SYNTHESIS OF $C_5H_4(SiH_3)(CH_3)$

Summary: It was found that the new compound, $C_5H_4(SiH_3)(CH_3)$, could be synthesized in 99% yield based on the amount of $K[C_5H_4CH_3]$ employed when dry $K[C_5H_4CH_3]$ and H_3SiBr were combined at -78° for one hour according to the equation:

$$K[C_5H_4CH_3] + H_3SiBr \rightarrow KBr + C_5H_4(SiH_3)(CH_3)$$

(a) Preparation of $K[C_5H_4CH_3]$

In the dry bag, 609.5 mgm (15.59 mmol) of potassium metal, cut up into small pieces, were placed in a reactor; and from the vacuum line, 2098.0 mgm (26.182 mmol) of methycyclopentadiene (stored at -78°; infrared spectrum and n.m.r. spectrum shown in figure 39 indicate a mixture of 1 and 2 isomers) and approximately 20 ml of diethyl

IR DATA OF $[Mo(CO)_3(\pi-C_5H_4CH_3)]_2$

	Absorption	Intensity	Assignment a
	3047	m	Cp
Nujol	2920	vs	
Nujol	2852	vs	
	2054	w	
	2011	w	
	1957	vs	-CO
	1912	vs	-CO
Nujol	1459	s	
Nujol	1375	s	
Nujol	1160	w	
	1030	w	Cp
	768	s	Cp
Nujol	717	w	
	673	s	

a:Ref. 88.

TABLE 25

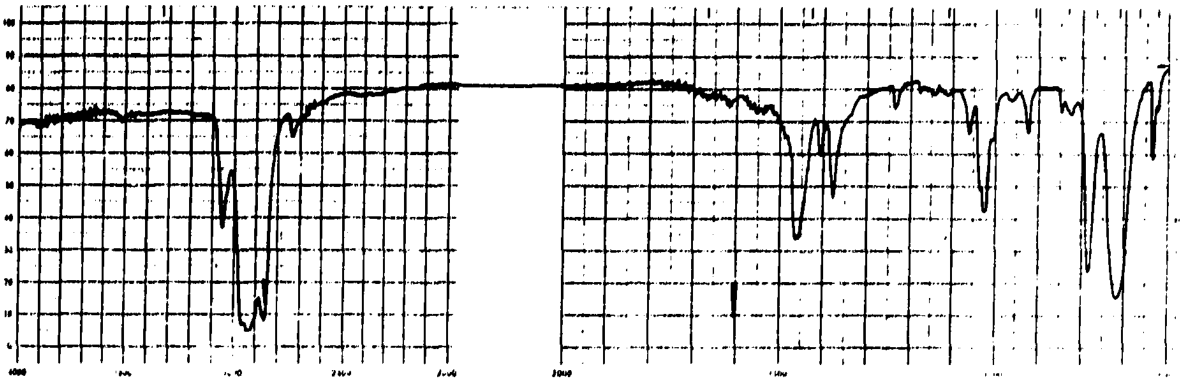
ether (degassed twice) were condensed in the reactor cooled to -196°. The reactor was warmed to -78° by means of a dry ice-acetone bath and held at this temperature during the reaction. Initially, the reaction was evidenced by the evolution of gas bubbles; and within thirty minutes, a white residue settled to the bottom of the reactor. After twelve hours, complete reaction of all the potassium occurred, since the reactor was intermittently warmed to room temperature and shaken. Then the reactor was cooled to -196°, and a non-condensible gas was pumped away; excess methylcyclopentadiene and ether were removed from the reactor held at -30° by slowly condensing in a -78° dry ice-acetone trap. The resulting white residue in the reactor was dried thoroughly by warming the reactor to room temperature and then to 60° in order to drive off any adhering volatile material which was collected in a -196° trap open to the pump. Drying was considered complete after four hours. 1741.4 mgm (14.730 mmol) of $K[C_5H_4CH_3]$ were produced. The infrared spectrum and n.m.r. spectrum (taken in diethyl ether) of $K[C_5H_4CH_3]$ are shown in figure 39 . The n.m.r. spectrum is consistent with that observed for $Na[C_5H_4CH_3]$.[118]

(b) Preparation of $C_5H_4(SiH_3)(CH_3)$

Silyl Bromide (3682.5 mgm, 33.178 mmol) was condensed in the reactor containing $K[C_5H_4CH_3]$ previously prepared in part (a). Upon warming from -196° to -78°, a yellow-

IR, NMR SPECTRA OF K[$C_5H_5CH_3$]

IR



NMR

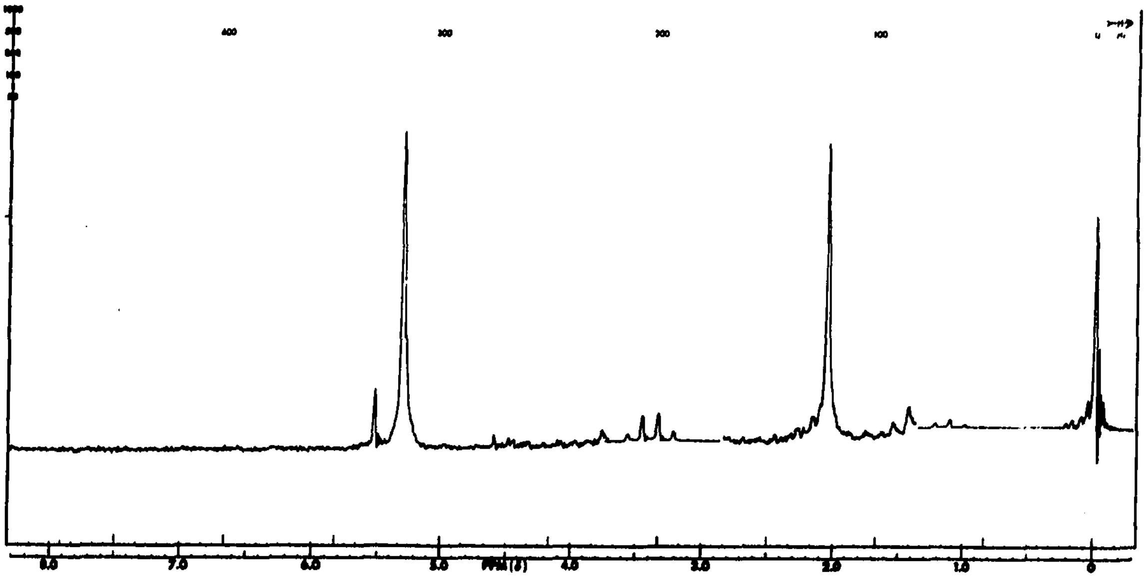


FIGURE 39

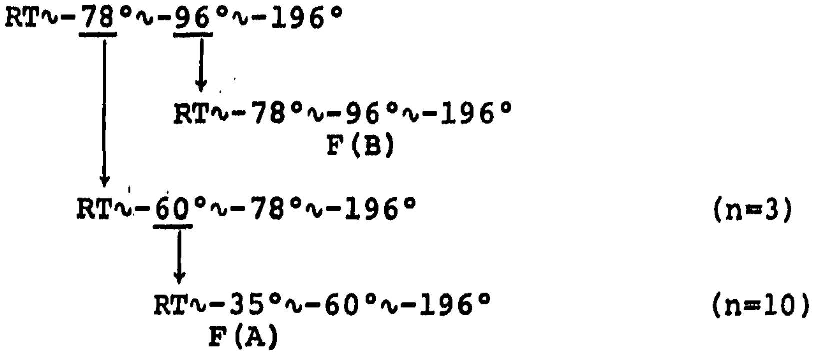
IR DATA OF K[$C_5H_4CH_3$]

	Absorption	Intensity	Assignment[b]
	3049[a]	m	Cp
Nujol	2920	vs	
Nujol	2852	vs	
	2817	m	
	2734	m	
Nujol	1459	s	
	1404	s	Cp
Nujol	1375	s	
Nujol	1160	w	
	1035(Sh)		
	1023	s	Cp
	1005(Sh)		
	822	w	Cp
	785	vs	Cp
	715	vs	Cp
	637	s	Cp
	625(Sh)		

a:identical to frequency observed in halocarbon 25-5S grease.
b:Ref. 109, 110.

TABLE 26

brown residue appeared instantly. After one hour, the reactor was again cooled to -196°, and no non-condensible gas was removed. Then the reactor was allowed to warm slowly to room temperature, and the volatile materials removed from the reactor were separated as follows:



126.5 mgm (1.139 mmol) of H_3SiBr were gained by the reactor.

The following materials were identified:

$\underline{SiH_4}$: Fraction (C) [a trace observed in the infrared spectrum].

$\underline{H_3SiBr}$: Fraction (B) [2037.8 mgm, 18.355 mmol; 55.34% recovery based on the amount of H_3SiBr initially employed; identified by infrared spectrum identical to that observed for pure H_3SiBr [98]].

$\underline{C_5H_4(SiH_3)(CH_3)}$: Fraction (A) [1606.1 mgm, 14.570 mmol; 98.99% yield based on the amount of $K[C_5H_4CH_3]$ initially employed]. $C_5H_4(SiH_3)(CH_3)$ is a colorless, air stable liquid which fumes initially in air. Its odor is similar to that of $C_5H_5SiH_3$.

(c) Identification and Characterization

1. Commercial Analysis of $C_5H_4(SiH_3)(CH_3)$: From the vacuum line, 50 mgm of sample were condensed in an analysis tube cooled to -196°; the tube was sealed by fusing a portion of the tube below the 12/30 joint connecting the tube to the vacuum line. The sample was stored in a freezer until sent for analysis. The following values were obtained:

Found: C - 65.17%; H - 9.17%; Si - 25.28%

Calculated: C - 65.38%; H - 9.14%; Si - 25.48%

2. Melting Point of $C_5H_4(SiH_3)(CH_3)$: From the vacuum line, approximately one half centimeter of sample was condensed in a 5 mm n.m.r. tube cooled to -196°. Upon warming to -146° by means of a methylcyclopentane bath, the sample formed a clear liquid in the bottom of the tube. No further determination was performed.

3. Boiling Point of $C_5H_4(SiH_3)(CH_3)$: Due to lack of a sufficient amount of $C_5H_4(SiH_3)(CH_3)$ no boiling point determination was attempted.

4. Density of $C_5H_4(SiH_3)(CH_3)$: A preweighed (also preheated in an oven) one milliliter volumetric flask was filled to the mark with a sample of $C_5H_4(SiH_3)(CH_3)$. The volumetric flask was then weighed. The density of $C_5H_4(SiH_3)(CH_3)$ was calculated to be 0.8319 gm/ml at 25.5°.

5. Index of Refraction of $C_5H_4(SiH_3)(CH_3)$: Two drops of sample were placed on the polished quartz surface

of a refractometer standardized against acetone at 25.5°. The index of refraction of $C_5H_4(SiH_3)(CH_3)$ was observed to be 1.4774 at 25.5° using the sodium D line.

6. Vapor Pressure of $C_5H_4(SiH_3)(CH_3)$: No vapor pressure determination was attempted, since vapor pressure data on $C_5H_5SiH_3$ were not consistent.

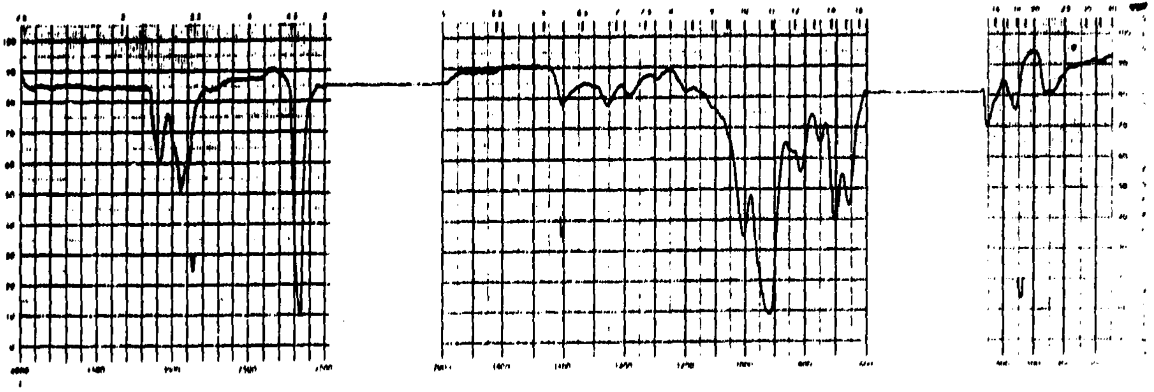
7. Infrared Spectrum of $C_5H_4(SiH_3)(CH_3)$: The infrared spectrum of $C_5H_4(SiH_3)(CH_3)$ determined in the gas phase at 1 to 2 torr is shown in figure 40, and the principle absorptions are given in table 27.

8. Nuclear Magnetic Resonance of $C_5H_4(SiH_3)(CH_3)$: From the vacuum line, a neat liquid sample of $C_5H_4(SiH_3)(CH_3)$ was condensed in a 5 mm n.m.r. tube cooled to -196°. After addition of a small amount of $Si(CH_3)_4$, the tube (still cooled to -196°) was sealed with an oxygen torch by heating a small portion of the tube below the 12/30 joint. The sample tube was stored at -196° until placed in the n.m.r. tube holder. The n.m.r. spectrum of a neat sample of $C_5H_4(SiH_3)(CH_3)$ is shown in figure 40, and the chemical shifts observed at room temperature are as follows:

Group		Chemical Shift-δ
$-CH_3$	(singlet)	2.02
$-SiH_3$	(singlet)	3.50
vinyl protons	(broad peak)	6.16

IR, NMR (RT) SPECTRA OF $C_5H_4(SiH_3)(CH_3)$

IR



NMR

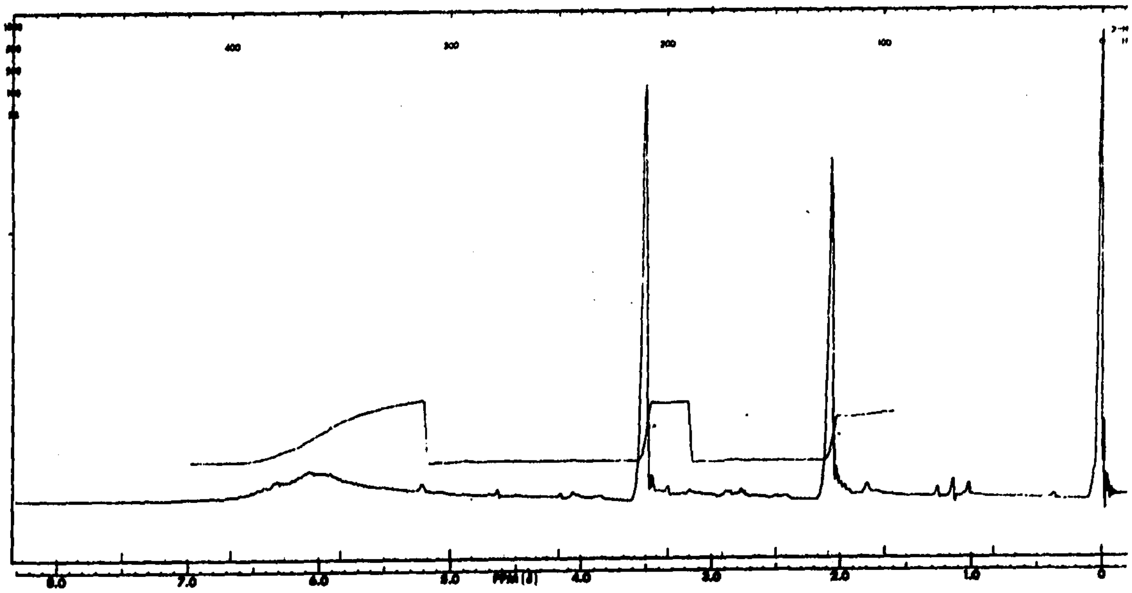


FIGURE 40

IR DATA OF $C_5H_4(SiH_3)(CH_3)$

Absorption	Intensity	Assignment
3090	s	Cp [a]
2938	s	
2882	s	
2057	vs	Si-H [b]
1605	w	
1452	w	
1380	w	
1103	w	
1001	s	Cp [a]
915	vs	SiH_3 def.vib. [b]
870	w	
810	w	
750	m	
700	s	Cp [a]
685	m	
558	w	
459(Sh)		
428	w	Si-C [c]

a:Ref. 109.

b:Ref. 98.

c:Ref. 92.

TABLE 27

A dilute sample of $C_5H_4(SiH_3)(CH_3)$ in CCl_4 was prepared, and chemical shifts at room temperature are as follows:

Group	Chemical Shift- δ
$-CH_3$	2.07
$-SiH_3$	3.50
vinyl protons (broad peak)	6.18

A temperature-dependent n.m.r. study was carried out to determine the preferred stereochemical configuration of $C_5H_4(SiH_3)(CH_3)$. A detailed analysis of the results are given in Chapter V, section B.

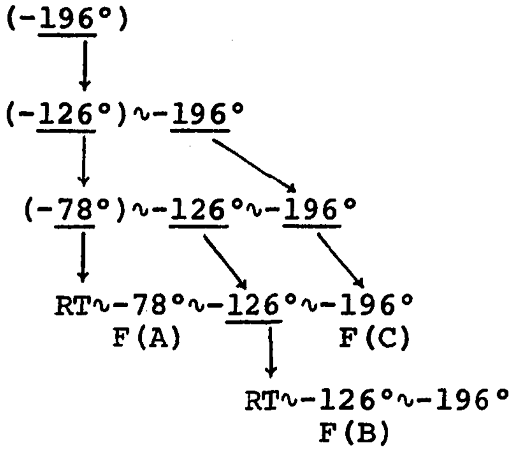
(d) Reactions of $C_5H_4(SiH_3)(CH_3)$

1. Reaction of $C_5H_4(SiH_3)(CH_3)$ with HCl at -78°

Summary: It was found that cleavage of the Si-C bond resulted when $C_5H_4(SiH_3)(CH_3)$ and HCl were combined for several days at -78° according to the equation:

$$C_5H_4(SiH_3)(CH_3) + HCl \rightarrow C_5H_5CH_3 + H_3SiCl$$

From the vacuum line, 503.3 mgm (4.566 mmol) of $C_5H_4(SiH_3)(CH_3)$ and 268.9 mgm (7.375 mmol) of HCl were condensed in a reactor cooled to -196°. Upon warming to -78°, a dark (red-brown) liquid resulted. After several days at -78°, the reactor was cooled to -196°, and a non-condensible gas was removed. Then the reactor was warmed slowly to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

HCl: Fraction (C) [14.9 mgm, 0.409 mmol; 5.54% recovery based on the amount of HCl initially employed; some HCl lost during transfer; identified by infrared spectrum identical to that observed for pure HCl [101]].

H_3SiCl: Fraction (B) [192.2 mgm, 2.888 mmol; 63.24% yield based on the amount of $C_5H_4(SiH_3)(CH_3)$ initially employed; identified by infrared spectrum identical to that observed for pure H_3SiCl [98]].

$C_5H_5CH_3$ and $C_5H_4(SiH_3)(CH_3)$: Fraction (A) [identified by infrared spectrum identical to that expected for a mixture of $C_5H_5CH_3$ and $C_5H_4(SiH_3)(CH_3)$].

$\underline{[C_5H_4(SiH_3)(CH_3)]_2}$: Colorless non-volatile liquid [378.7 mgm; identified by infrared spectrum identical to the spectrum of the liquid produced in the reaction in section (d)-1 of Exp. II-B-1.

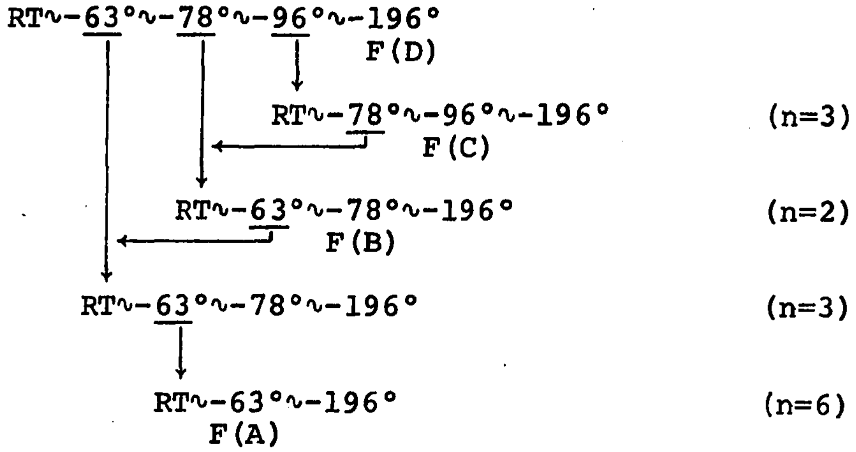
---

2. Reaction of $C_5H_4(SiH_3)(CH_3)$ with $N(CH_3)_3$

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_4(SiH_3)(CH_3)$ and $N(CH_3)_3$ were combined for several hours at room temperature according to the equation:

$$C_5H_4(SiH_3)(CH_3) + N(CH_3)_3 \rightarrow C_5H_4(CH_3)_2 + H_3Si\text{-}N(CH_3)_2$$

From the vacuum line, 291.0 mgm (2.640 mmol) of $C_5H_4(SiH_3)(CH_3)$ and 184.9 mgm (3.128 mmol) of $N(CH_3)_3$ were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for several hours, a trace amount of white residue was observed to settle to the bottom of the reactor. Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was allowed to warm to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

$\underline{SiH_4}$: Fraction (D) [a trace amount seen in the infrared spectrum].

$\underline{N(CH_3)_3}$: Fraction (C) [167.9 mgm, 2.840 mmol; 90.81% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$\underline{H_3Si\text{-}N(CH_3)_2}$: Fraction (B) [15.6 mgm, 0.207 mmol; 7.86% yield based on the amount of $C_5H_4(SiH_3)(CH_3)$ initially employed; identified by infrared spectrum identical to that observed for pure $H_3Si\text{-}N(CH_3)_2$ [103]].

$\underline{C_5H_4(SiH_3)(CH_3)}$: Fraction (A) [256.2 mgm, 2.324 mmol; 88.04% recovery based on the amount of $C_5H_4(SiH_3)(CH_3)$ initially employed; identified by infrared spectrum identical to that observed previously for pure $C_5H_4(SiH_3)(CH_3)$].

$C_5H_4(CH_3)_2$: Fraction (A) [a trace amount seen in the infrared spectrum].

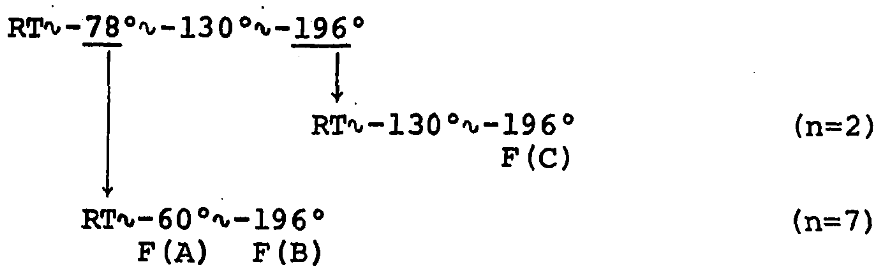
3. Reaction of $C_5H_4(SiH_3)(CH_3)$ with Potassium Metal in 1,2 dimethoxyethane (1,2DME)

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_4(SiH_3)(CH_3)$ and potassium metal were combined at room temperature using 1,2DME as the solvent according to the equation:

$$2C_5H_4(SiH_3)(CH_3) + K + \text{``3H''} \rightarrow K[C_5H_4CH_3] + C_5H_5CH_3 + 2SiH_4$$

In the dry bag, 123.4 mgm (3.156 mmol) of potassium metal, cut up into very small pieces, were placed in a reactor; and from the vacuum line, 487.6 mgm (4.424 mmol) of $C_5H_4(SiH_3)(CH_3)$ and 595.3 mgm (6.606 mmol) of 1,2DME (monoglyme; distilled over $LiAlH_4$, redistilled over potassium metal; and degassed twice) were condensed in the reactor cooled to -196°. As the reactor began to warm slowly to room temperature, a dark blue solution appeared instantly; evolution of gas bubbles could also be observed. After five minutes at ambient temperature, a dark solution resulted. After twelve hours, the reactor was cooled to -196°, and a small amount of non-condensible gas was removed.

The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



432.8 mgm were gained by the reactor.

The following materials were identified:

SiH_4: Fraction (C) [37.4 mgm, 1.16 mmol; 26.22% yield based on the amount of $C_5H_4(SiH_3)(CH_3)$ initially employed; identified by infrared spectrum identical to that observed for pure SiH_4 [102]].

$C_5H_5CH_3$ and $C_5H_4(SiH_3)(CH_3)$: Fraction (B) [46.5 mgm; identified by infrared spectrum identical to that expected for a mixture of $C_5H_5CH_3$ and $C_5H_4(SiH_3)(CH_3)$].

1,2DME: Fraction (A) [553.1 mgm, 6.137 mmol; 92.91% recovery based on the amount of 1,2DME initially employed; identified by infrared spectrum identical to that observed for pure 1,2DME [113]].

$K[C_5H_4CH_3]$ and $[C_5H_4(SiH_3)(CH_3)]_2$: White-brown solid liquid residue [556.2 mgm]. An infrared spectrum showed absorptions due to $K[C_5H_4CH_3]$ and possibly $[C_5H_4(SiH_3)(CH_3)]_2$.

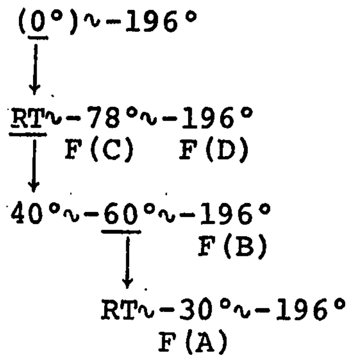
---

4. Reaction of $C_5H_4(SiH_3)(CH_3)$ with $Co_2(CO)_8$ at 0°

Summary: It was found that cleavage of the Si-C bond occurred when $C_5H_4(SiH_3)(CH_3)$ and $Co_2(CO)_8$ were combined for several hours at 0° according to the equation:

$$C_5H_4(SiH_3)(CH_3)+Co_2(CO)_8 \rightarrow Co(CO)_2(\pi\text{-}C_5H_4CH_3)+H_3SiCo(CO)_4+2CO$$

In the dry bag, 509.6 mgm (1.490 mmol) of $Co_2(CO)_8$ were placed in a reactor; and from the vacuum line, 327.3 mgm (2.969 mmol) of $C_5H_4(SiH_3)(CH_3)$ were condensed into the reactor at -196°. Then the reactor was allowed to warm slowly to -30°; since no visible reaction took place at -30°, the reactor was warmed to 0°. After twelve hours at 0°, the reactor was cooled to -196°, and a non-condensible gas was removed. The volatile materials removed from the reactor at 0° were separated as follows:



195.6 mgm were gained by the reactor.

The following materials were identified:

$\underline{SiH_4}$: Fraction (D) [a trace amount seen in the infrared spectrum].

$\underline{C_5H_4(SiH_3)(CH_3)}$: Fraction (C) [91.6 mgm, 0.831 mmol; 28.30% recovery based on the amount of $C_5H_4(SiH_3)(CH_3)$ initially employed; identified by infrared spectrum identical to that previously observed for pure $C_5H_4(SiH_3)(CH_3)$].

$\underline{H_3SiCo(CO)_4}$: Fraction (B) [80.0 mgm, 0.3959 mmol; 26.57% yield based on the amount of $Co_2(CO)_8$ initially employed; identified by infrared spectrum identical to that observed for pure $H_3SiCo(CO)_4$[114]].

$\underline{C_5H_5CH_3}$: Fraction (B) [a trace amount seen in the infrared spectrum].

$Co(CO)_2(\pi\text{-}C_5H_4CH_3)$: Fraction (A) [2.6 mgm, 0.013 mmol; 0.87% yield based on the amount of $Co_2(CO)_8$ initially employed; identified by infrared spectrum identical to that observed previously for pure $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$].

solid residue: Dark red non-volatile liquid [672.1 mgm]. An infrared spectrum showed absorptions due to $Co_2(CO)_8$ and possibly $[C_5H_5CH_3]_2$.

CHAPTER IV

EXPERIMENTAL (III)

(A) MISCELLANEOUS REACTIONS OF H_3SiBr

1. Reaction of H_3SiBr with C_5H_6 at -78°

Summary: It was found that no reaction occurred when H_3SiBr and C_5H_6 were combined for one hour at -78° according to the equation:

$$H_3SiBr + C_5H_6 \rightarrow N.R.$$

From the vacuum line, H_3SiBr (570.1 mgm, 5.135 mmol) and C_5H_6 (325.3 mgm, 4.930 mmol) were condensed in a reactor cooled to -196°. The reactor was held at -78° by means of a dry ice-acetone bath for one hour then warmed to room temperature. No visible reaction was observed. After thirty minutes, the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and a small amount of volatile material was enclosed in an infrared cell. The infrared spectrum identified this volatile material as a mixture of H_3SiBr and C_5H_6.

---

2. Reaction of H_3SiBr with $K[C_5H_5]$ in Dimethyl Ether at -78°

Summary: It was found that the new compound, $C_5H_5SiH_3$, could also be synthesized in the presence of solvent at -78° according to the equation:

$$H_3SiBr + K[C_5H_5] \rightarrow KBr + C_5H_5SiH_3$$

In the dry bag, potassium metal (200.00 mgm, 0.0511 mmol), cut up into small pieces, was placed in the bottom of the filter tube (Figure 41); and from the vacuum line, C_5H_6 (34.1 cm, 5.25 mmol) and approximately 4 ml of dimethyl ether were condensed in the tube at -196°. The tube was warmed to -78° and held at this temperature during the reaction. Evolution of gas bubbles commenced the reaction; after fifteen minutes, a light blue solution resulted; after one hour, a white solution resulted. Then H_3SiBr (33.1 cm, 4.90 mmol) was condensed in the solution still at -78°, and the reaction mixture was stirred magnetically overnight at -78°. The tube was allowed to warm to room temperature, and the volatile materials removed from the tube were separated as follows:

VACUUM LINE FILTER TUBE

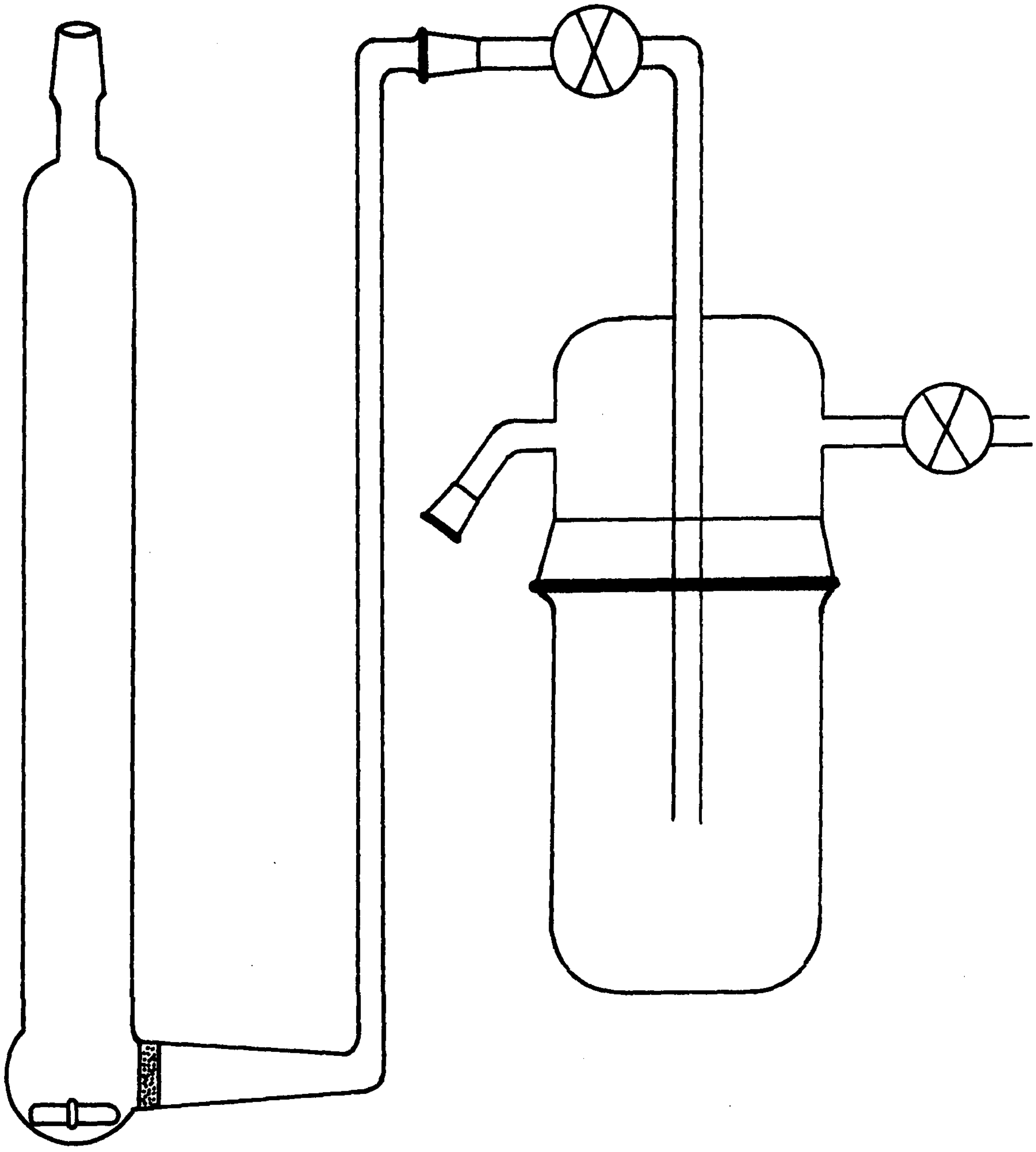
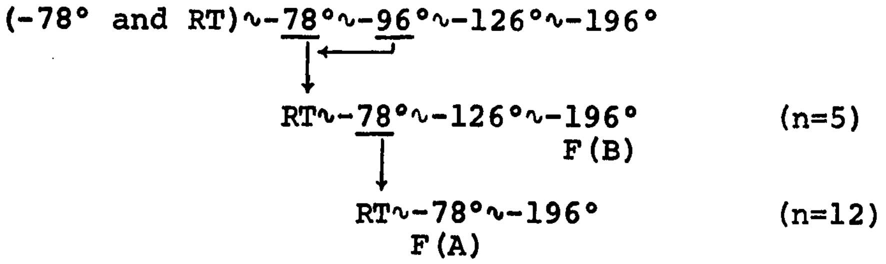


FIGURE 41



The following materials were identified:

$(CH_3)_2O$ and C_5H_6: Fraction (B) [identified by infrared spectrum expected for a mixture of $(CH_3)_2O$ and C_5H_6].

$C_5H_5SiH_3$: Fraction (A) [identified by infrared spectrum identical to that observed previously for $C_5H_5SiH_3$; confirmed by n.m.r. spectrum (taken at room temperature) which showed a strong peak at 3.50δ relative to TMS].

---

3. Reaction of H_3SiBr with $Hg[Cr(CO)_3(\pi-C_5H_5)]_2$

Summary: It was found that no reaction occurred when $Hg[Cr(CO)_3(\pi-C_5H_5)]_2$ and H_3SiBr, at an ideal gas pressure of 7.47 atm, were combined for several hours at room temperature according to the equation:

$$Hg[Cr(CO)_3(\pi-C_5H_5)]_2 + H_3SiBr \rightarrow N.R.$$

$Hg[Cr(CO)_3(\pi-C_5H_5)]_2$ (12.8 mgm, 0.212 mmol) were placed in a reactor; and from the vacuum line, H_3SiBr (76.5 mgm, 0.689 mmol) was condensed in the reactor cooled to -196°. The reactor was allowed to warm slowly to room temperature. After several hours at ambient temperature, no physical change was observed. The reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:

$$\underset{F(A)}{RT \sim -130° \sim -196°}$$

0.8 mgm were gained by the reactor.

The following materials were identified:

$\underline{H_3SiBr}$: Fraction (A) [identified by infrared spectrum identical to that observed for pure H_3SiBr [98]].

$\underline{Hg[Cr(CO)_3(\pi-C_5H_5)]_2}$: Bright yellow solid [13.6 mgm, 0.226 mmol; 106% recovery based on the amount of $Hg[Cr(CO)_3(\pi-C_5H_5)]_2$ initially employed; identified by infrared spectrum identical to that observed for pure $Hg[Cr(CO)_3(\pi-C_5H_5)]_2$ [88]].

---

4. Reaction of H_3SiBr with $H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$

Summary: In a qualitative experiment, it was found that no reaction occurred when $H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and H_3SiBr were combined for thirty minutes at 0° according to the equation:

$$H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + H_3SiBr \rightarrow N.R.$$

In the dry bag, approximately 100 mgm of $H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ were placed in the special reactor (Figure 42); and from the vacuum line, about 2 ml of H_3SiBr were condensed in the reactor at -196°. Upon warming to 0°, the hydride dissolved, resulting in an orange solution. After fifteen minutes, the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:

$$\underset{F(A)}{RT \sim -130° \sim -196°}$$

The following materials were identified:

H_3SiBr: Fraction (A) [identified by infrared spectrum identical to that observed for pure H_3SiBr [98]].

$H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$: Yellow-pink solid; sublimed at 40°.

SPECIAL REACTOR

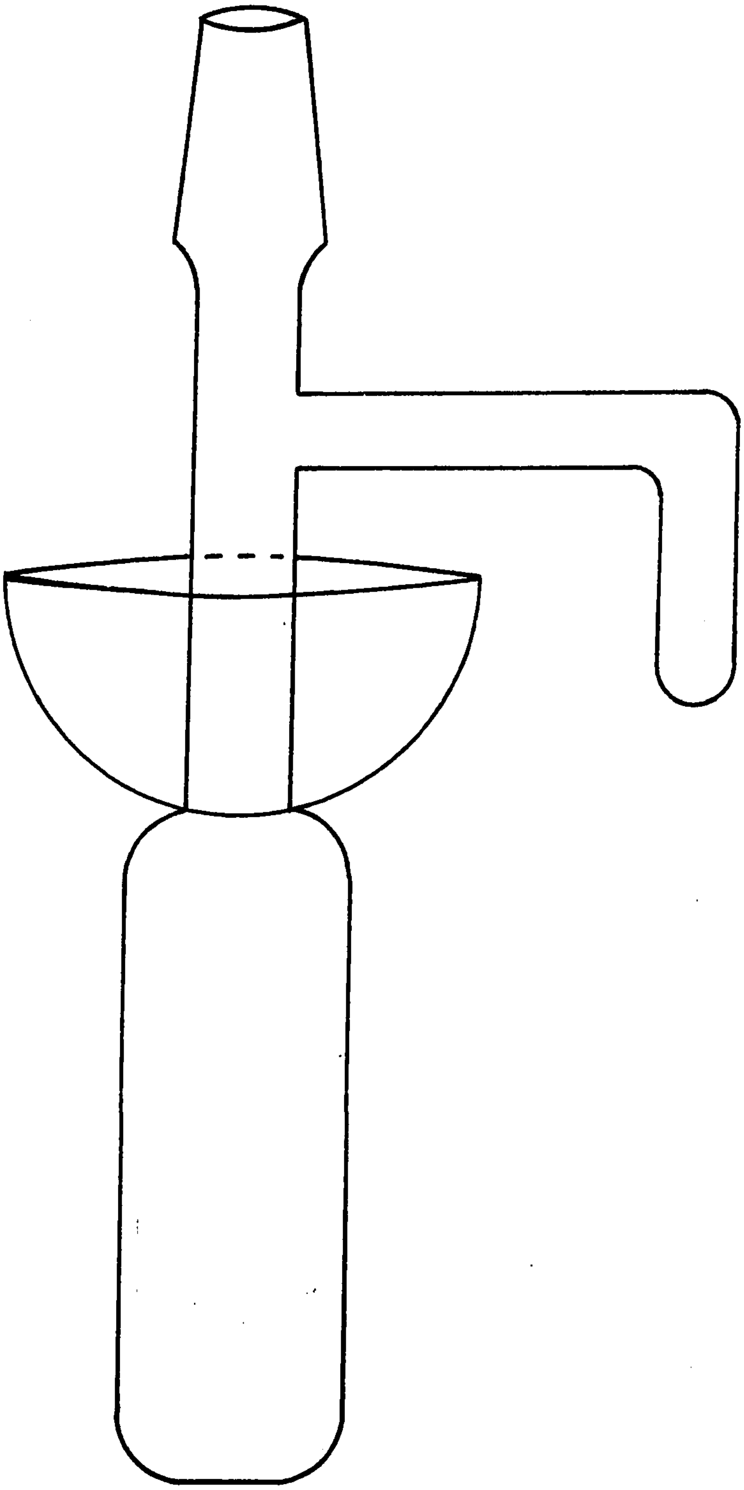


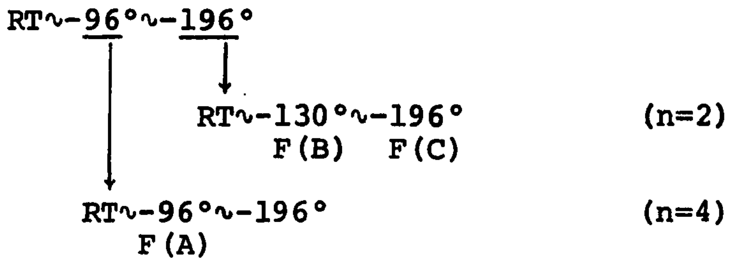
FIGURE 42

5. Reaction of H_3SiBr with C_6H_5HgCl

Summary: It was found that cleavage of the Hg-Cl bond occurred when C_6H_5HgCl and H_3SiBr, at an ideal gas pressure of 7.74 atm, were combined for several days at room temperature according to the equation:

$$2C_6H_5HgCl + 4H_3SiBr \rightarrow HgBr_2 + Hg(C_6H_5)_2 + H_2ClSi\text{-}SiH_2Br + H_3SiCl + SiH_4 + \text{"HBr"}$$

In the dry bag, 361.1 mgm (1.153 mmol) of C_6H_5HgCl were placed in a reactor; and from the vacuum line, H_3SiBr (786.7 mgm, 7.086 mmol) was condensed in the reactor cooled to -196°. The reactor was allowed to warm to room temperature; no physical change was observed after one hour. After several days at ambient temperature, the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



42.0 mgm were gained by the reactor.

The following materials were identified:

SiH_4: Fraction (C) [14.4 mgm, 0.448 mmol; 63.3% yield based on the amount of H_3SiBr initially employed; identified by infrared spectrum identical to that observed for pure SiH_4 [102]].

H_3SiCl and H_3SiBr: Fraction (B) [650.6 mgm; identified by infrared spectrum expected for a mixture of H_3SiCl and H_3SiBr [98]].

$H_2ClSiSiH_2Br$: Fraction (A) [65.8 mgm, 0.374 mmol; 52.5% yield based on the amount of H_3SiBr initially employed; mol. wgt. calc.-175.6, found-177.8: 1.02%; the infrared spectrum was similar to that expected for compounds of H_3SiSiH_2X [119,120], or H_2SiBr_2 [121,122,123,124] and $(H_3Si)_2$ [125,126]; the absorptions are given in table 28.

complex mixture: White solid [403.1 mgm] assumed to be a mixture of Hg, $HgBr_2$, and possibly $Hg(C_6H_5)_2$.

---

6. Reaction of H_3SiBr with $Hg[Co(CO)_4]_2$

Summary: It was found that cleavage of Hg-Co bond occurred when H_3SiBr and $Hg[Co(CO)_4]_2$, at an ideal gas pressure of 4.40 atm, were combined for several days at room temperature according to the equation:

$$Hg[Co(CO)_4]_2 + 4H_3SiBr \rightarrow Hg + CoBr_2 + H_3SiCo(CO)_4 + (H_2SiBr)_2 + SiH_4 + 4CO + \tfrac{1}{2}H_2$$

IR DATA OF $H_2ClSiSiH_2Br$

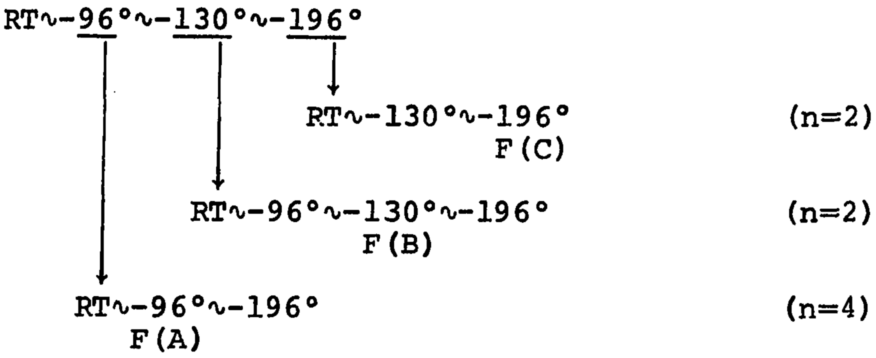
Absorption	Intensity	Assignment
2210	s	Si-H [a]
1113	w	
935	s	SiH_2 [b]
925	s	
838	vs	SiH_2 [b]
552	m	Si-Cl [a]
460	s	Si-Br [a]

a:Ref. 98.

b:Ref. 121.

TABLE 28

In the dry bag, 325.0 mgm (0.5991 mmol) of $Hg[Co(CO)_4]_2$ were placed in a reactor; and from the vacuum line, H_3SiBr (447.4 mgm, 4.030 mmol) was condensed in the reactor cooled to -196°. Upon warming to room temperature and sitting for one hour, a yellow-green coloration was observed, and the reactor became warm. After several days at ambient temperature, the reactor was cooled to -196°, and a non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



54.8 mgm were gained by the reactor.

The following materials were identified:

$\underline{H_2}$ and $\underline{CO}$: Non-condensible gas [mol. wgt. found-14.06; assumed to be a mixture of H_2 and CO].

$\underline{SiH_4}$: Fraction (C) [25.4 mgm, 0.791 mmol; 19.6% yield based on the amount of H_3SiBr initially employed; identified by infrared spectrum identical to that observed for pure SiH_4[102]].

$\underline{H_3SiBr}$: Fraction (B) [322.8 mgm, 2.908 mmol; 72.15% recovery based on the amount of H_3SiBr initially employed; identified by infrared spectrum identical to that observed for pure H_3SiBr [98]].

$\underline{H_3Si\text{-}Co(CO)_4}$ and $\underline{(H_2BrSi)_2}$: Fraction (A) [22.1 mgm; identified by infrared spectrum expected for a mixture of $H_3Si\text{-}Co(CO)_4$ and $(H_2BrSi)_2$].

$\underline{CoBr_2}$: A green solid.[127]

Hg: A silver solid.

(B) MISCELLANEOUS REACTIONS OF CHROMIUM

1. Reaction of $Cr(CO)_6$ with $HSiCl_3$ at 86°

Summary: In a qualitative experiment, it was found that no reaction occurred when $Cr(CO)_6$ and $HSiCl_3$, at an ideal gas pressure of 6.25 atm, were combined for several hours at 86°.

$Cr(CO)_6$ (333.5 mgm, 1.516 mmol) was placed in a reactor; and from the vacuum line, $HSiCl_3$ (649.0 mgm, 4.791 mmol) was condensed in the reactor cooled to -196°. The reactor was warmed to room temperature and then heated to 86°. No physical changed was observed. Then the reactor was cooled to -196°, and a small amount of

IR DATA OF $(H_2BrSi)_2$

Absorption	Intensity	Assignment
2218(Sh)		
2208	s	Si-H [a]
932	s	SiH_2 [b]
868(Sh)		
835	vs	SiH_2 [b]
542	w	
460	s	Si-Br [c]

a:Ref. 98.

b:Ref. 121

TABLE 29

non-condensible gas was removed. The volatile materials removed from the reactor at room temperature consisted of a mixture of $Cr(CO)_6$ [100] and $HSiCl_3$ [128] identified by infrared spectrum. The white solid in the reactor was identified by infrared spectrum to be $Cr(CO)_6$.

---

2. Reaction of $[Cr(CO)_3(\pi-C_5H_5)]_2$ with $HSiCl_3$ at 110°

Summary: It was found that decomposition occurred when $[Cr(CO)_3(\pi-C_5H_5)]_2$ and $HSiCl_3$, at an ideal gas pressure of 6.72 atm, were combined for several hours at 110°.

$[Cr(CO)_3(\pi-C_5H_5)]_2$ (31.4 mgm, 0.0781 mmol) was placed in a reactor; and from the vacuum line, $HSiCl_3$ (393.2 mgm, 2.903 mmol) was condensed in the reactor cooled to -196°. The reactor was warmed to room temperature and then heated at 110° for two hours. A black residue resulted which, after removal of the excess $HSiCl_3$, was dissolved in acetone, filtered and dried by means of a water aspirator. An attempt to sublime the black residue failed.

---

3. Reaction of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ with $(CH_3)_3SiCl$

Summary: In a qualitative experiment, it was found that $(CH_3)_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ could be synthesized when $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ and $(CH_3)_3SiCl$ were combined for one hour at 0° according to the equation:

$$K[Cr(CO)_3(\pi\text{-}C_5H_5)]+(CH_3)_3SiCl \rightarrow KCl+(CH_3)_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$$

In the dry bag, approximately 500 mgm of $K[Cr(CO)_3(\pi\text{-}C_5H_5)]$ were placed in the special reactor; and from the vacuum line, approximately 2 ml of $(CH_3)_3SiCl$ were condensed in the reactor cooled to -196°. Upon warming to room temperature, the reactor became warm. After several hours at ambient temperature, the reactor was cooled to -196°, and a small amount of non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:

RT∿-30°∿-60°∿-196°
F(A) F(B)

The bottom of the reactor was warmed to 50° and the cup filled with liquid nitrogen; a yellow solid was collected near the cold portion of the cup.

The following materials were identified:

$\underline{C_5H_5Si(CH_3)_3}$: Fraction (B) [identified by infrared spectrum identical to that observed previously for $C_5H_5Si(CH_3)_3$].

$\underline{(CH_3)_3SiCl}$: Fraction (A) [identified by infrared spectrum identical to that observed for pure $(CH_3)_3SiCl$ [129]].

$\underline{(CH_3)_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)}$: Green-yellow solid. An infrared spectrum (taken in Nujol) showed the following absorptions: 1952, 1927, 1903, 1897, 839, 633 cm^{-1}; $\nu(Si\text{-}CH_3) = 1248\ cm^{-1}$. It should be noted that $[Cr(CO)_3(\pi\text{-}C_5H_5)]_2$ has absorptions at [88] 1905, 1888, 813, 635 cm^{-1}, so that $(CH_3)_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ appears to rapidly decompose at room temperature forming dimeric species.

---

4. Reaction of $\underline{H\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)}$ with $\underline{PF_5}$

Summary: It was found that a complex solid mixture occurred when $H\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and PF_5, at an ideal gas pressure of 11.4 atm, were combined for several days at room temperature.

In the dry bag, 28.9 mgm (0.143 mmol) of H-Cr$(CO)_3(\pi-C_5H_5)$ were placed in a reactor; and from the vacuum line, PF_5 (131.2 mgm, 1.041 mmol) was condensed in the reactor cooled to -196°. Upon warming to room temperature, the yellow color of the hydride changed to dark blue-green instantly. After several days at ambient temperature, the reactor was cooled to -196°, and a non-condensible gas was removed. The reactor was warmed to room temperature and the volatile materials removed from the reactor were separated as follows:

$$\begin{array}{ll} \mathrm{RT}\sim-130^\circ\sim-\underline{160^\circ}\sim-196^\circ & \\ \qquad\qquad\quad\downarrow & \\ & \mathrm{RT}\sim-130^\circ\sim-160^\circ\sim-196^\circ \\ & \qquad\qquad\quad \mathrm{F(A)} \end{array}$$

2.5 mgm were lost by the reactor.

The following materials were identified:

<u>PF_5</u>: Fraction (A) [130.3 mgm, 1.034 mmol; 99.31% recovery based on the amount of PF_5 initially employed; identified by infrared spectrum identical to that observed for pure PF_5 [104]].

complex mixture: Dark blue-green solid. An infrared spectrum (Nujol mull) showed absorption due to [88] $[Cr(CO)_3(\pi-C_5H_5)]$ (1900, 1885 cm^{-1}) and possibly $[Cr(CO)_3(\pi-C_5H_5)]F$ (2100, 2022, 1805 cm^{-1}) or other flourinated species. No n.m.r. spectrum was observed.

(C) MISCELLANEOUS REACTIONS OF MOLYBDENUM

1. Reaction of $K[Mo(CO)_3(\pi-C_5H_5)]$ with $(CH_3)_3SiCl$

Summary: In a qualitative experiment, it was found that no reaction occurred when $K[Mo(CO)_3(\pi-C_5H_5)]$ and $(CH_3)_3SiCl$ were combined for several hours at room temperature according to the equation:

$$K[Mo(CO)_3(\pi-C_5H_5)] + (CH_3)_3SiCl \rightarrow N.R.$$

In the dry bag, approximately 2.0 gm of $K[Mo(CO)_3(\pi-C_5H_5)]$ were placed in the special reactor; and from the vacuum line, about 3 ml of $(CH_3)_3SiCl$ were condensed in the reactor cooled to -196°. Upon warming to room temperature and standing for one hour, a brown residue was observed. The reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were not separated. The bottom of the reactor was warmed to 60° and the cup filled with liquid nitrogen. No residue sublimed from the brown residue at 60° or 90°.

---

2. Reaction of H-Mo(CO)$_3$ (π-C_5H_5) with $(CH_3)_3SiH$

Summary: In a qualitative experiment, it was found that no reaction occurred when H-Mo(CO)$_3$ (π-C_5H_5) and $(CH_3)_3SiH$, at an ideal gas pressure of 1.2 atm, were combined for several minutes at room temperature according to the equation:

$$\text{H-Mo(CO)}_3(\pi\text{-}C_5H_5) + (CH_3)_3SiH \rightarrow \text{N.R.}$$

In the dry bag, approximately 100 mgm of H-Mo(CO)$_3$ (π-C_5H_5) were placed in the special reactor; and from the vacuum line, about 2 ml of $(CH_3)_3SiH$ were condensed in the reactor cooled to -196°. Upon warming to room temperature, the hydride dissolved resulting in a bright orange solution. After thirty minutes at ambient temperature, the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile material was removed from the reactor; the infrared spectrum was identical to that observed for pure $(CH_3)_3SiH$.[130]

(D) REACTION OF H_3CBr WITH $K[C_5H_5]$ AT -78°

1. Reaction of H_3CBr with $K[C_5H_5]$ at -78°

Summary: In a qualitative experiment, it was found that no reaction occurred when dry $K[C_5H_5]$ and H_3CBr

were combined at 78° according to the equation

$$K[C_5H_5] + H_3CBr \rightarrow N.R.$$

K$[C_5H_5]$ was prepared in a reactor as previously described in Chapter II, Section (B) and H_3CBr was condensed in the reactor at -78°. After one hour, the volatile material was removed from the reactor at room temperature. An infrared spectrum identified this material as pure H_3CBr.[131]

(E) MISCELLANEOUS REACTIONS OF TOLUENE AND PHENYLSILANE

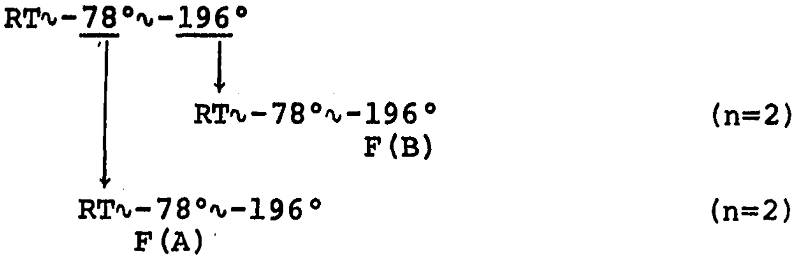
1. <u>Reaction of C_6H_5-CH_3 with HCl</u>

<u>Summary</u>: It was found that no reaction occurred when C_6H_5-CH_3 and HCl, at an ideal gas pressure of 17.7 atm, were combined for several days at room temperature according to the equation:

$$C_6H_5\text{-}CH_3 + HCl \rightarrow N.R.$$

From the vacuum line, C_6H_5-CH_3 (462.3 mgm, 5.018 mmol) and HCl (591.2 mgm, 16.21 mmol) were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for several days, no reaction was observed.

Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

HCl: Fraction (B) [589.8 mgm, 16.18 mmol; 99.76% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

C_6H_5-CH_3: Fraction (A) [472.6 mgm, 5.130 mmol; 102.2% recovery based on the amount of C_6H_5-CH_3 initially employed; identified by infrared spectrum identical to that observed for pure C_6H_5-CH_3 [113]].

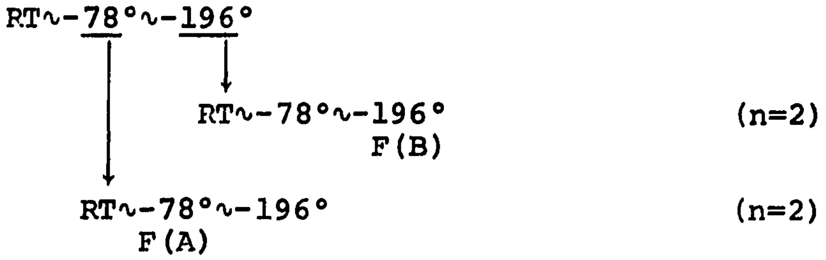
---

2. Reaction of C_6H_5-CH_3 with $N(CH_3)_3$

Summary: It was found that no reaction occurred when C_6H_5-CH_3 and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$C_6H_5\text{-}CH_3 + N(CH_3)_3 \rightarrow \text{N.R.}$$

From the vacuum line, C_6H_5-CH_3 (515.2 mgm, 5.592 mmol) and $N(CH_3)_3$ (1.163 mgm, 19.67 mmol) were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for several days, no reaction was observed. Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

$\underline{N(CH_3)_3}$: Fraction (B) [832.8 mgm, 14.09 mmol; 71.61% recovery based on the amount of $N(CH_3)_3$ initially employed; small amount of sample lost during transfer; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

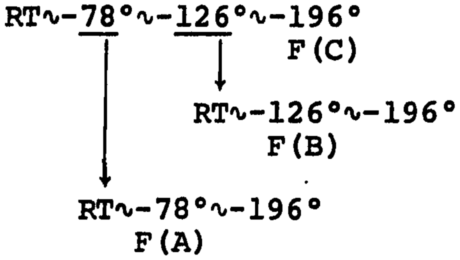
$\underline{C_6H_5\text{-}CH_3}$: Fraction (A) [515.2 mgm, 5.556 mmol; 99.34% recovery based on the amount of C_6H_5-CH_3 initially employed; identified by infrared spectrum identical to that observed for pure $C_6H_5-CH_3$ [113]].

3. Reaction of $C_6H_5-SiH_3$ with HCl

Summary: It was found that cleavage of the Si-C bond occurred when $C_6H_5-SiH_3$ and HCl, at an ideal gas pressure of 9.20 atm, were combined for several days at room temperature according to the equation:

$$C_6H_5-SiH_3 + HCl \rightarrow C_6H_6 + H_3SiCl$$

From the vacuum line, $C_6H_5-SiH_3$ (798.4 mgm, 7.378 mmol) and HCl (307.2 mgm, 8.426 mmol) were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for several days, no reaction was observed. Then the reactor was cooled to -196°, and a small amount of non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



The following materials were identified:

HCl: Fraction (C) [123.4 mgm, 3.384 mmol; 40.17% recovery based on the amount of HCl initially employed; identified by infrared spectrum identical to that observed for pure HCl [101]].

H_3SiCl: Fraction (B) [65.5 mgm, 0.984 mmol; 13.3% yield based on the amount of C_6H_5-SiH_3 initially employed; identified by infrared spectrum identical to that observed for pure H_3SiCl [98]].

C_6H_6 and C_6H_5-SiH_3: Fraction (A) [768.8 mgm; identified by infrared spectrum identical to that expected for a mixture of C_6H_6 and C_6H_5-SiH_3].

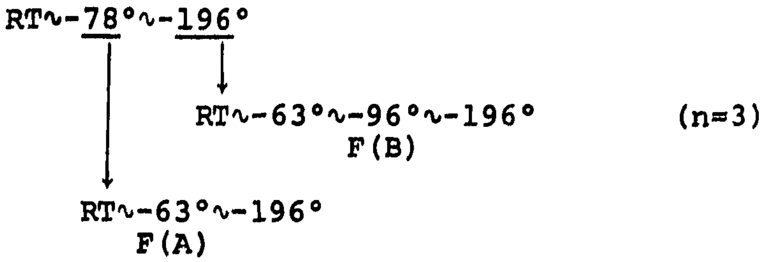
---

4. Reaction of C_6H_5-SiH_3 with $N(CH_3)_3$

Summary: It was found that no reaction occurred when C_6H_5-SiH_3 and $N(CH_3)_3$ were combined for several days at room temperature according to the equation:

$$C_6H_5\text{-}SiH_3 + N(CH_3)_3 \rightarrow \text{N.R.}$$

From the vacuum line, C_6H_5-SiH_3 (517.0 mgm, 4.777 mmol) and $N(CH_3)_3$ (385.8 mgm, 6.527 mmol) were condensed in a reactor cooled to -196°. Upon warming to room temperature and sitting for several days, a small amount of white needle crystals settled to the bottom of the reactor. Then the reactor was cooled to -196°, and no non-condensible gas was removed. The reactor was warmed to room temperature, and the volatile materials removed from the reactor were separated as follows:



2.9 mgm were gained by the reactor.

The following materials were identified:

$N(CH_3)_3$: Fraction (B) [363.0 mgm, 6.141 mmol; 94.09% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

C_6H_5-SiH_3: Fraction (A) [453.1 mgm, 4.187 mmol; 87.64% recovery based on the amount of C_6H_5-SiH_3 initially employed; small amount of material lost during transfer; identified by infrared spectrum identical to that observed previously for pure C_6H_5-SiH_3 [97]].

CHAPTER V

DISCUSSION AND CONCLUSIONS

(A)

Physical, Spectroscopic, and Chemical Properties of the New Compounds $H_3Si-M(CO)_3(\pi-C_5H_5)$; (M=Cr, Mo, W)

(a) Synthetic Results

The syntheses of the novel silyl-metal derivatives of chromium, molybdenum, and tungsten are considered significant since these compounds are the silicon analogues of the known carbon compounds $H_3C-M(CO)_3(\pi-C_5H_5)$; (M=Cr, Mo, W).[2] It was found that the σ-silyl-π-cyclopentadienyl Tricarbonyl derivatives of Group VI b elements could be synthesized in 20-40% yields based on the amount of the appropriate potassium-metal salt, $K[M(CO)_3(\pi-C_5H_5)]$, initially placed in the reactor from the reaction of H_3SiBr at an ideal gas pressure of 8-10 atm according to the reaction:

$$K[M(CO)_3(\pi-C_5H_5)] + H_3SiBr \rightarrow KBr + H_3Si-M(CO)_3(\pi-C_5H_5) \qquad (1)$$

Other products formed from reaction (1) were a mixture of CO and H_2, SiH_4 (trace amounts), $M(CO)_6$, and a brown pyrophoric residue assumed to be $[(C_5H_5)_2M]^+[M(CO)_3(\pi-C_5H_5)]^-$.[1,132] The combined results of the syntheses are summarized in Table 30. It should be noted that the yields for $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ and $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ are 10-40

SYNTHETIC RESULTS OF THE NEW COMPOUNDS, $H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)$

M	$K[M(CO)_3(\pi\text{-}C_5H_5)]$	H_3SiBr (added)	H_3SiBr (recovered)	$M(CO)_6$ (produced)	$H_3Si\text{-}M$ (sublimed)	Yield[a] (%)
Cr	926.2 mgm 3.856 mmol	648.1 mgm 5.839 mmol	235.9 mgm 2.125 mmol	33.4 mgm 0.152 mmol	341.2 mgm 1.039 mmol	38.11
Mo	2482.0 mgm 8.6644 mmol	933.1 mgm 8.406 mmol	49.4 mgm 0.445 mmol	253.2 mgm 0.951 mmol	988.8 mgm 3.501 mmol	40.96
W	1734.6 mgm 4.6605 mmol	615.4 mgm 5.544 mmol	83.8 mgm 0.755 mmol	150.5 mgm 0.4277 mmol	352.3 mgm 0.9673 mmol	20.76

a:yield based on $K[M(CO)_3(\pi\text{-}C_5H_5)]$

TABLE 30

times better than those reported[2] for the methyl-metal analogues; these higher yields being ascribed to the use of a higher boiling solvent with 1,2-dimethoxyethane (b.p. 84°) in preference to tetrahydrofuran (b.p. 65°) are due to the fact that the cleavage of the metal-carbonyl bond occurs at 75° for $Mo(CO)_6$ and 110° for $Cr(CO)_6$ and $W(CO)_6$.[1]

(b) Thermal Stability

The thermal decomposition experiment performed on $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ definitely indicates that no decomposition resulted when $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$; (m.p. 94-96°) was heated for one hour at 160°; in contrast, the compound, $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$, has been reported[2] to decompose at its melting point (124°). Consequently, it is assumed that the silyl group stabilizes $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ with respect to thermal decomposition. It is therefore concluded that $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ is more thermally stable than $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$.

It has been proposed that π-interaction or[32] $d_\pi\text{-}d_\pi$ bonding between silicon and cobalt is responsible for the greater thermal stability of $H_3SiCo(CO)_4$ over $H_3CCo(CO)_4$, since $H_3SiCo(CO)_4$ was recovered in 50% yield after being heated for fifteen minutes at 120°[114]; whereas, $H_3CCo(CO)_4$ has been reported[27] to decompose at its melting point (-23°). Analogizing from the comparison of the noticeable difference in the thermal stabilities of the silyl-cobalt and methyl-cobalt compounds, it is also possible to envisage a similar π-interaction between silicon and molybdenum to account for the greater thermal stability of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$.

The compound, $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, was observed to melt in the temperature range 129-130°, probably with some decomposition; however, the methyl-chromium analogue has been reported [2] to be quite unstable with no melting point recorded. In this research a melting point determination performed on $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ found that this compound completely decomposed at 85°. Thus, it appears that $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ is more thermally stable than $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$.

The compound, $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$, melted at 112° without noticeable decomposition; the methyl-tungsten derivatives has been reported [2] not to decompose at its melting point (145°). From a comparison of these results, it is not possible to determine whether $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ is more thermally stable than $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$. It could be concluded that the methyl-tungsten compound is, at most, as stable as the silyl-tungsten compound.

The pattern of melting points for the methyl-metal derivatives shows an increase from $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ (least stable) to $H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ (most stable), but the trend of melting points for the silyl-metal compounds follows the order of the metal hydrides ($H\text{-}M(CO)_3(\pi\text{-}C_5H_5)$)[1]

and the metal-metal derivatives of the type, R_3M'-M(CO)$_3$ (π-C_5H_5); (M=Cr, Mo, W; M'=Ge, Sn, Pb; R=CH_3, C_6H_5).[5,133,134] That is, for a given metal-metal series, the metal-molybdenum compound melts below the metal-chromium and metal-tungsten analogues. The melting point trends are summarized below and in tables 34,35 for the above-mentioned Group IV-Group VI b organometallic derivatives.

Compound	H-M	H_3C-M	H_3Si-M
Cr	57-58° (d)	85° (d)	129-130°
Mo	50-52° (d)	124° (d)	94-96°
W	66-67°	145°	110-112°

Difficulty in obtaining a correct silicon elemental analysis on H_3Si-Cr(CO)$_3$(π-C_5H_5) due to decomposition in transit is reasonable in that this compound is the least thermally stable of the silyl-metal series. All three compounds are readily sublimable in the temperature range 60-90°, sensitive to air-oxidation, discolor in a nitrogen atmosphere, but can be stored indefinitely at -20° *in vacuo*.

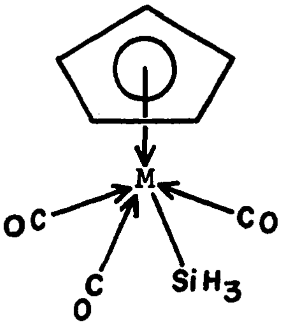
A factor which affects the relative thermal stability of an organometallic compound of the form R_3Si-M(CO)$_3$(π-C_5H_5) is the type of substituent on silicon.

For R=CH_3, the trimethylsilyl derivatives of molybdenum and tungsten have been reported [9] to sublime (with some decomposition) at 100°; in this research it was found that the trimethylsilyl-chromium compound rapidly decomposed at room temperature. When R=Cl, the trichlorosilyl-molybdenum compound appears to be as stable as the R=H and R=CH_3 substituents, since it has been reported [7] to melt without decomposition at 150°; also $(CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ has been reported [135] to undergo no thermal decomposition after being heated for one hour at 160°, and $(C_6H_5)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ has also been reported [5] to be a stable compound (m.p. 162°).

The type of substituent on silicon also affects the thermal stability of compounds of the type $R_3SiCo(CO)_4$.[136] The silyl-cobalt [114] and the trichlorosilyl-cobalt [136] compounds have been reported to show no or little decomposition at room temperature; however, the triflourosilyl-cobalt analogue has been reported [33] to undergo complete decomposition due to destabilization through back-bonding by flourine thus reducing π-interaction between silicon and cobalt. Also, it has been reported [136,137] that the trimethylsilyl- and triphenylsilyl-cobalt tetracarbonyls undergo completely different decomposition reactions. As a consequence, it may be concluded that bulky and highly electronegative substituents on silicon tend to cause destabilization, while chloro and hydride substituents offer added stabilization to the cobalt tetracarbonyl group.[136]

(c) Infrared Analysis

In this research, two carbonyl stretching frequencies were observed for the H_3C-metal compounds (Beckman IR-8); however, using cyclohexane as the solvent, three carbonyl stretching frequencies have been reported (Perkin-Elmer 621 Spectrometer).[54] It was found that three fundamental carbonyl stretching vibrations were observed for the silyl-metal derivatives (Nujol). Since this number of infrared absorption bands in the carbonyl region for the H_3Si-metal compounds agrees with the number of absorption bands observed for the H_3C-metal analogues, this agreement suggests that the silyl-metal and methyl-metal derivatives have the same symmetry and therefore similar structures. The model used for the structure is assumed to be the same as the crystal structure of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$[52] and pictures the transition metal as sandwiched between the cyclopentadienyl group above and by the silyl moiety and the three carbonyl groups below. A pictorial representation illustrating this sandwich-type arrangement is shown below:



In the case of the metal hydride (replacement of H_3Si by H), it is difficult to determine the exact[1,2] position of the hydrogen atom which is thought to be partially shared by the three carbonyls. A low temperature ^1H n.m.r. study on $H\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ [138] has shown that the hydrogen atom undergoes rapid intramolecular exchange with the carbonyls at room temperature. In this research, a temperature-dependent ^1H n.m.r. study (Figure 6) on $H\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ revealed that at room temperature a complex signal was observed for the Cp group; however, when the sample was cooled to -40° the complex signal resolved into a sharp, single peak characteristic of five equivalent ring protons. These results appear to support the idea of exchange processes occurring at room temperature with exchange decreasing as the temperature is lowered.

A summary of the observed carbonyl stretching frequencies for the hydride, methyl-, and silyl-metal compounds is given in table 31. The H-Cr stretching frequency (unpublished as 1828 cm^{-1} [92]) was observed in this research at 1711 cm^{-1} which falls within the known H-M region.[139]

Infrared analysis of the silyl-metal derivatives contains information regarding the extent of metal-carbonyl interaction and the nature of the $H_3Si\text{-}M$ linkage of Group VI b elements. Because it is observed that the

IR DATA FOR COMPOUNDS OF THE TYPE X-$M(CO)_3(\pi-C_5H_5)$ [a]

H-M	ν(-CO)cm^{-1}			ν(M-H)cm^{-1}	Solvent
Cr	2014 (2020)		1937 (1938)	1711 (1828) [b]	
Mo	2025 (2027)		1949 (1940)	n.ob. (1790) [c]	 CS_2
W	2019 (2026)		1938 (1935)	n.ob. (1845) [c]	 CS_2
H_3C-M					
Cr	2003		1941		
Mo	2017 (2018)	 (1950)	1940 (1946) [d]		 C_6H_{12}
W	2015 (2015)	 (1939)	1932 (1935) [d]		 C_6H_{12}
H_3Si-M				(Si-H)cm^{-1}	
Cr	1999	1943	1918	2102	
Mo	2005	1948	1925	2100	
W	2005	1940	1931	2100	

a:all spectra taken in Nujol except where noted

b:Ref. 92.

c:Ref. 90.

d:Ref. 54

TABLE 31

three carbonyl stretching frequencies of $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ are lower in energy than the corresponding carbonyl frequencies of the molybdenum and tungsten analogues, these lower frequencies suggest a decreased carbon-oxygen force constant which subsequently implies a larger chromium-carbon force constant. That is, for the system, $R_3Si\text{-}M\Rightarrow C{=}\underset{\cdot\cdot}{\ddot{O}}$, the observed carbonyl ($C{=}O$) stretching vibration would be at a lower frequency than for the system, $R_3Si\text{-}\ddot{M}\text{—}C\overset{\leftarrow}{\equiv}O{:}$. The smaller multiple bond character in the C-O linkage should result in an increased M-C bond order and therefore an increased Cr-C force constant.[53]

A lowering in the Si-H stretching frequency was also observed for the silyl-metal derivatives, and these observed frequencies (table 32) are among the lowest yet recorded. The general trend in the Si-H stretching frequency of the silyl halides is that the Si-H frequency decreases with decreasing electronegativity of a halide.[114] For the series of silyl-metal compounds $H_3Si\text{-}Ge(CH_3)_3$, $H_3Si\text{-}Co(CO)_4$, $H_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$, $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, the trend in ν(Si-H) (table 32) does not correlate with the electronegativities of the transition metal[140] attached to the silyl group. The trend suggests that $Cr(CO)_3(\pi\text{-}C_5H_5)^-$ is less electronegative than $Co(CO)_4^-$; from arguments given in the next section concerning the relative electronegativity of the groups attached to the SiH_3 moiety, it has been concluded that $Cr(CO)_3(\pi\text{-}C_5H_5)^-$

IR DATA FOR COMPOUNDS OF THE TYPE H_3Si-X

H_3Si-X	$\nu(Si-H)cm^{-1}$
$-F$ [a]	2206
$-Cl$ [a]	2201
$-Br$ [a]	2200
$-I$ [a]	2192
$-O-SiH_3$ [b]	2174
$-N(SiH_3)_2$ [c]	2165
$-N(CH_3)_2$ [d]	2158
$-C_5H_5$ [e]	2154
$-Ge(CH_3)_3$ [f]	2152
$-Co(CO)_4$ [h] , $-O-CH_3$ [g]	2150
$-FeH(CO)_4$ [i]	2142
$-Mn(CO)_5$ [j] , $-Fe(CO)_4SiH_3$ [i]	2136
$-Fe(CO)_2(\pi-C_5H_5)$ [k]	2103
$-Cr(CO)_3(\pi-C_5H_5)$ [e]	2102(2107-CCl_4)
$-Mo(CO)_3(\pi-C_5H_5)$ [e]	2100(2104-CCl_4)
$-W(CO)_3(\pi-C_5H_5)$ [e]	2100

a:Ref. 98.

b:Ref. 141.

c:Ref. 142

d:App. E, Table 45.

e:pp. 178, 88, 118, 150

f:Ref. 143.

g:Ref. 144.

h:Ref. 114.

i:Ref. 145.

j:Ref. 146.

k:Ref. 10

TABLE 32

is more electronegative than $Co(CO)_4^-$. This is reasonable since it is known that $HCo(CO)_4$ [147] is a stronger acid than $HCr(CO)_3(\pi-C_5H_5)$. [1] Since the lower Si-H frequency occurs for the more electronegative group $Cr(CO)_3(\pi-C_5H_5)$, it can be concluded that electronegativity arguments lead to confusing results concerning the lowering of the Si-H stretching frequency.

If attention is focused on the series H_3SiF, $(H_3Si)_2O$, $(H_3Si)_3N$ in table 32, it is seen that the lower ν(Si-H) in the case of $(H_3Si)_3N$ can be explained as $(p\rightarrow d)\pi$ interaction occurring between the lone pair electrons in the p orbital of nitrogen and the empty "d" orbitals of appropriate symmetry of silicon.[70,112,148,149] Since the Si-H frequencies of $(H_3Si)_2O$ and $(H_3Si)_3N$ do not occur as expected from electronegativity arguments between F and Cl, the actual position of ν(Si-H) in $(H_3Si)_3N$ suggests that π-interaction is responsible for the low Si-H stretching frequency. By analogy with $(H_3Si)_3N$, it may be concluded that the lowering of the Si-H frequency for the series $H_3Si-Co(CO)_4$, $H_3Si-Fe(CO)_2(\pi-C_5H_5)$, $H_3Si-Cr(CO)_3(\pi-C_5H_5)$ etc. also reflects π-interaction between the empty "d" orbitals of appropriate symmetry of silicon with the filled "d" orbitals of the transition metal. Thus, $(d\rightarrow d)\pi$ interaction may be postulated as explaining the lowering of the Si-H stretching frequency in the organometallic chemistry of silicon.

(d) ^{1}H n.m.r. Analysis

It was found that a sharp, single peak was observed for the five equivalent cyclopentadienyl ring protons, and a sharp, single peak was observed for the three equivalent silyl protons on samples of $H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)$; (M=Cr,Mo,W). ^{1}H n.m.r. spectra also observed for the methyl-metal analogues were similar in appearance noting that the chemical shift of the methyl group was upfield relative to the silyl signal. Thus, it can be concluded that the similarities in the ^{1}H n.m.r. spectra support the similarity in structure between the silyl-metal and methyl-metal derivatives. Chemical shifts for the hydride, methyl-, and silyl-metal derivatives are listed in table 33.

It has been proposed that ^{1}H n.m.r. chemical shifts of the H_3C group [90] and $\pi\text{-}C_5H_5$ group [53] should be a measure of the relative electronegativity or amount of negative charge on the metal atom; hence, some statements concerning the relative position of the H_3Si chemical shift and the $\pi\text{-}C_5H_5$ chemical shift in the series $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$, $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ can be made. Since it is seen that the chemical shift of the Cp group in $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ is upfield relative to the Cp chemical shifts of the silyl-molybdenum and silyl-tungsten compounds, this upfield shift appears to correlate with the fact that chromium is more electronegative than molybdenum and tungsten. This same trend in the chemical

^{1}H n.m.r. - δ FROM $Si(CH_3)_4$ FOR COMPOUNDS OF THE TYPE

$X\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ [a]

H-M	Cp	H_3C	H_3Si	Solvent
Cr	5.09 (4.78) [b]			C_6H_{12}
Mo	5.47 (5.30) [b]			C_6H_{12}
W	5.57 (5.34) [b]			C_6H_{12}
H_3C-M				
Cr	4.84 (4.76)	0.68 (0.68) [b]		CCl_4
Mo	5.35 (5.27)	0.38 (0.34) [b]		CCl_4
W	5.46 (5.38)	0.42 (0.40) [b]		CCl_4
H_3Si-M				
Cr	4.89		4.12	
Mo	5.35		3.85	
W	5.50		3.82	

a:all spectra taken in diethyl ether with $Si(CH_3)_4$ as internal standard.

b:Ref. 90.

TABLE 33

shift is also observed for the hydride and methyl-metal derivatives as given above and for compounds of the type $R_3M'-M(CO)_3(\pi-C_5H_5)$; ($M=Cr, Mo, W$; $M'=Si, Ge, Sn, Pb$; $R=CH_3$, C_6H_5) given in table 34 and 35.

It was found that the Cp chemical shifts of $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ and $H_3Si-W(CO)_3(\pi-C_5H_5)$ occur at the same position. This closeness in Cp chemical shifts can be explained by considering the lanthanide contraction [43] of tungsten which results when the addition of more charge to the nucleus of an atom outweighs the repulsion between valence electrons and electrons in the filled, inner shells. As a result, the size of the tungsten atom is about the same size as the molybdenum, since the increased nuclear charge on tungsten pulls the added outer valence electrons closer to the nucleus; this lanthanide contraction that occurs for tungsten explains why tungsten has not only the same atomic radius but also about the same electronegativity as molybdenum. [150] Therefore, in the two systems, $H_3Si-Mo(CO)_3(\pi-C_5H_5)$ and $H_3Si-W(CO)_3(\pi-C_5H_5)$, the five ring protons are equally perturbed by nearly identical transition metal atoms with the result that the Cp chemical shifts for the two compounds are expected to and indeed do occur at about the same position.

It was also found that the chemical shift of the H_3Si group is downfield relative to the chemical shift of the H_3C group. This position of the chemical shift of the

SPECTROSCOPIC DATA FOR COMPOUNDS OF THE TYPE $(CH_3)_3M'-M(CO)_3(\pi-C_5H_5)$

$(CH_3)_3M'-M$	M.P.	$\nu(-CO)cm^{-1}$			Solvent	$\delta(\pi-Cp)$	Solvent
Si-Cr	R.T. (d)	1952	1927	1904	Nujol		
Si-Mo	100°	1974	1955	1890	Nujol	5.20	? [a]
Si-W	100°	2027	1935	1898	Nujol	5.44	? [a]
Ge-Cr	86-88°	1982	1915	1890	C_6H_6	4.75	$CDCl_3$ [b]
Ge-Mo	84°	1997	1920	1897	C_6H_6	5.24	$CDCl_3$ [b]
	87-88°	1999	1929	1905	C_6H_6	4.58	C_6H_6 [c]
Ge-W		1996	1916	1895	C_6H_6	5.33	$CDCl_3$ [b]
	106-107°	2010	1931	1908	C_6H_{12}	5.30	C_6H_6 [c]
Sn-Cr	109°	1977	1907	1897	C_6H_6	4.75	$CDCl_3$ [b]
Sn-Mo	98-99°	1990	1915	1890	C_6H_6	5.24	$CDCl_3$ [b]
	97-98.5°	1997	1922	1895	CCl_4	5.41	$CHCl_3$ [d]
Sn-W		1986	1907	1883	C_6H_6	5.33	$CDCl_3$ [b]
	119-120°	1994	1915	1891	CCl_4	5.47	$CHCl_3$ [d]

TABLE 34

$(CH_3)_3M'-M$	M.P.	$\nu(-CO)\ cm^{-1}$	Solvent	$\delta(\pi-Cp)$	Solvent
Pb-Cr					
Pb-Mo	93-95°	1992 1921 1895	CCl_4	5.28	$CHCl_3$[d]
Pb-W					

a:Ref. 9.

b:Ref. 133.

c:Ref. 134.

d:Ref. 5.

TABLE 34 cont.

SPECTROSCOPIC DATA FOR COMPOUNDS OF THE TYPE $(C_6H_5)_3M'-M(CO)_3(\pi-C_5H_5)$ [a]

$(C_6H_5)_3M'-M$	M.P.	ν(-CO)cm^{-1}			Solvent	δ(π-Cp)	Solvent
Ge-Cr	229-230° (d)	1996	1932	1911	CCl_4	4.90	$CDCl_3$
Ge-Mo	219-222° (d)	2008	1925	1918	CCl_4	5.21	$CDCl_3$
Ge-W	240° (d)	2004	1930	1911	CCl_4	5.36	$CDCl_3$
Sn-Cr	219-221°	1987	1932	1897	CCl_4	4.84	$CDCl_3$
Sn-Mo	211-214° (d)	2004	1934	1909	CCl_4	5.55	acetone
Sn-W	227-228°	2014	1927	1902	CCl_4	5.26	$CDCl_3$
Pb-Cr	195-197° (d)	1985	1925	1902	CCl_4	5.05	THF
Pb-Mo	200° (d)	2002	1934	1910	CCl_4	5.39	$CDCl_3$
Pb-W	214-215° (d)	1999	1927	1907	CCl_4	5.43	$CDCl_3$

a:Ref. 5.

TABLE 35

silyl protons is expected since silicon is less electronegative than carbon; decreasing electronegativity gives decreasing chemical shifts.[43,85]

It is also noticed that $\delta(\pi\text{-}C_5H_5)$ for the above hydride, methyl, and silyl derivatives is insensitive to the particular type of X group attached to the transition metal. The Cp chemical shifts for $CpV(CO)_4$ and $CpCo(CO)_2$ also appear at the same position (5.00δ). Another interesting feature is that $\delta(\pi\text{-}C_5H_5)$ for the compounds $X\text{-}W(CO)_3(\pi\text{-}C_5H_5)$; ($X=H$, SiH_3) occurs at about the same position as $\delta(\pi\text{-}C_5H_5)$ for $K[C_5H_5]$-5.60δ.

In table 36, the chemical shifts of the Cp group are plotted for various types of X groups attached to $Mo(CO)_3(\pi\text{-}C_5H_5)$; it appears that for the electron-withdrawing group Cl and for groups with electron-withdrawing substituents (CF_3, $SnCl_3$, $Sn(CH_3)_2Cl$), $\delta(\pi\text{-}C_5H_5)$ is downfield relative to groups with electron-releasing substituents ($M(CH_3)_3$; M=Si, Ge, Sn, Pb; $M(Ph_3)_3$; M=Ge, Sn, Ph). If the CH_3 and $Mo(CO)_3(\pi\text{-}C_5H_5)$ groups appear to fall at the end of the region occupied by the electron-releasing groups, then this region may be regarded as a transition place from electron-releasing to electron-withdrawing. That the SiH_3 group falls in this region may lend support to the idea that SiH_3 is slightly electron-with drawing.[151] The same trend occurs for similar groups attached to $(\pi\text{-}C_5H_5)(CO)_2Fe$ (Table 37). In both

^1H n.m.r. DATA FOR COMPOUNDS OF THE TYPE (π-C_5H_5)Mo(CO)$_3$-X

	$\delta(\pi\text{-}C_5H_5)$ [a]		
	5.15	$Si(CH_3)_3$	
$(C_6H_5)_3Ge$	5.20	$Ge(CH_3)_3$, $Sn(CH_3)_3$	
$(C_6H_5)_3Pb$	5.25		
$(C_6H_5)_3Sn$		$Pb(CH_3)_3$, H	
Cl	5.30	$Mo(CO)_3(\pi\text{-}C_5H_5)$	(5.31)
CH_3		CH_3	(5.32)
	5.35	CH_3, SiH_3	(5.35)
$(CH_3)_2ClSn$			
	5.40		
	5.45	H	
	5.50		
	5.55		
CF_3	5.60		
Cl_3Sn	5.65		
	5.70	K	
	5.75		
	5.80		
	5.85		
	5.90	Cl	
X-$(CO)_3$MoCp		CpMo$(CO)_3$-X	

a:Ref. 106.

Table 36

^1H n.m.r. DATA FOR COMPOUNDS OF THE TYPE $(\pi\text{-}C_5H_5)Fe(CO)_2\text{-}X$

$\delta(\pi\text{-}C_5H_5)$ [a]	
3.50	SiH_3
.	
.	
4.30	CH_3
4.35	
4.40	
4.45	
4.50	
4.55	$Si(CH_3)_3$
4.60	
4.65	
4.70	CH_3
4.75	H, $Ge(C_6H_5)_3$ (4.74) $Sn(C_6H_5)_3$, $Pb(C_6H_5)_3$
4.80	$Fe(CO)_2(\pi\text{-}C_5H_5)$ (4.79)
4.85	
4.90	$Sn(CH_3)_3$ (4.89)
4.95	CF_3 (4.94)
5.00	I (5.01) SnI_3, Cl (5.02)
5.05	
5.10	
5.15	
5.20	$SnCl_3$

$CpFe(CO)_2\text{-}X$

a:Ref. 106.

Table 37

tables 36, 37, the $Si(CH_3)_3$ group appears near the top. Why $Sn(CH_3)_3$ falls beneath $Fe(CO)_2(\pi-C_5H_5)$ has not been satisfactorily explained. The most remarkable feature about table 37 is that the SiH_3 group appears to be more electronegative than the CH_3 group.

From table 38, it appears that the general electronegativity trend is present (F>Cl>I>Br) for X groups bonded to SiH_3. With electronegativity in mind, the presence of the Cp group makes $Cr(CO)_3(\pi-C_5H_5)$ more electronegative than $Co(CO)_4$. And if the chemical shift of the SiH_3 group appears to indicate π-interaction between silicon and the transition metal, then table 38 may suggest that $Fe(CO)_2(\pi-C_5H_5)$, $Mn(CO)_5$, $Mo(CO)_3(\pi-C_5H_5)$, and $W(CO)_3(\pi-C_5H_5)$ affect the chemical shift of the SiH_3 group thus appearing to be electron-donating groups and hence increasing the electronegativity of silicon possibly through π-interaction.

Because of the complex nature of π-bonding, which is not fully understood at present, the trend in ^1H n.m.r.[152] chemical shifts for such compounds exhibiting π-interaction is also complex. Thus, the observed chemical shifts can offer only a qualitative means for trying to explain this little understood area. Correlation between $\delta(\pi-C_5H_5)$ and ν(-CO) for some organometallic compounds of iron not bonded to silicon has been attempted.[53] And evidence for π-donor effects in the H_3C-M linkage from coupling

^1H n.m.r. DATA FOR COMPOUNDS OF THE TYPE H_3Si-X

	$\delta(H_3Si)$	
	3.45	I (3.44)[99]
(C_5H_5)	3.50	$Fe(CO)_2(\pi$-$C_5H_5)$ (3.52)[10]
	3.55	
	3.60	$Mn(CO)_5$ (3.59)[146]
	3.65	
		$Fe(SiH_3)(CO)_4$ (3.67)[145]
	3.70	
	3.75	
	3.80	$W(CO)_3(\pi$-$C_5H_5)$ (3.82)
	3.85	$Mo(CO)_3(\pi$-$C_5H_5)$ (3.85)
	4.00	$Co(CO)_4$ (4.02)[114]
	4.05	
	4.10	
		$Cr(CO)_3(\pi$-$C_5H_5)$ (4.12)
	4.15	
	4.20	Br (4.20)[99]
	4.35	$N(CH_3)_2$ (4.34)[99,151]
	4.40	
	4.45	$N(SiH_3)_2$ (4.44)[99,158]
	4.50	OCH_3 (4.49)[99]
	4.55	
		Cl (4.59)[99]
	4.60	$OSiH_3$ (4.61)[99,158]
	4.75	F (4.76)[99]
	H_3Si-X	

Table 38

constants has also been reported.[153]

In any particular system of nuclei , the nuclear magnetic resonance absorption is a function of four effects which describe the amount of shielding about the nucleus being observed.[154] The sum of the four factors are additive and give the total screening σ_A, i.e.,

$$\sigma_A(\text{total}) = \sigma_A^{\text{dia}} + \sigma_A^{\text{para}} + \sigma_B + \sigma_A^{\text{deloc}} \qquad (2)$$

where σ_A^{dia} (diamagnetic currents) arises from the rotation of the electrons of each atom about its own nucleus and lead to inductive effects whereby the electronegativity of the group attached to the nucleus being observed influences the resonance; σ_A^{para} is small when the electrons are in pure s states for hydrogen nuclei as in H_3Si and $C_5H_5^-$; σ_B accounts for the combined effect of the diamagnetic and paramagnetic atomic currents on other atoms, and σ_A^{deloc} arises from the magnetic effects of interatomic currents in which electrons move from one atom to another present in ring systems such as $C_5H_5^-$.

For the hydrogen nucleus, it is assumed that the σ_A^{dia} term predominates the contribution to σ_A (total). It should be possible therefore to obtain a qualitative understanding of π-interaction in the silicon species from table 39. With the hydrogen chemical shift for the H_3Si group controlled by the diamagnetic term, the following relationships are obtained (δ=chemical shift):

$$\delta(H_3C\text{-}H)-\delta(H_3C\text{-}X) = A; \quad \delta(H_3Si\text{-}H)-\delta(H_3Si\text{-}X) = B \qquad (3)$$

The term A contains diamagnetic effects and shielding. No π-interaction is, of course, present in these carbon species. The term B contains diamagnetic effects, shielding and π-interaction. The difference (Ω) between A and B represents the difference between methyl and silyl derivatives which might be related to the extent of $(d\rightarrow d)\pi$ bonding between the X substituent and silicon. Table 39 list Ω values of various H Si-X compounds; the Ω values for the silyl-metal derivatives are below the Ω values for compounds in which $(p\rightarrow d)\pi$ interaction is also proposed.

The concept of variable electronegativity has been developed elsewhere [155,156], and the results of similar calculations are given in table 40. Here χ is the electronegativity of silicon or carbon in which three hydrogens and an X substituent are attached to silicon or carbon. If $\chi(H_3C\text{-}X)$ is plotted against (A) (Table 40), a straight line is obtained since methyl derivatives are expected to show little deviation in bonding and no π-interaction with carbon; however, when $\chi(H_3Si\text{-}X)$ is plotted against (B) (Table 40), a curve is obtained which might possibly be related to π-interaction between silicon and the X substituent.

A, B, AND Ω VALUES FOR COMPOUNDS OF THE TYPE H_3M-X

H_3M-X	A	B	Ω
F	-4.00 [b]	-1.56 [d]	2.44
Cl	-2.68 [b]	1.39 [d]	1.29
Br	-2.32 [b]	-.97 [d]	1.35
I	-1.85 [b]	-.24 [d]	1.61
CN	-1.54 [b]	-.60 [d]	.94
$N(MH_3)$ [a]	-2.03 [b]	-1.24 [d]	.79
$S(MH_3)$	-1.91 [b]	-1.15 [d]	.76
OMH_3	-3.10 [b]	-1.41 [d]	.69
$Mn(CO)_5$	-.08 [c]	.39 [e]	.47
$Mo(CO)_3Cp$	.25	.65	.40
$Cr(CO)_3Cp$	.55	.92	.37
$W(CO)_3Cp$	.29	.62	.33
$Fe(CO)_2Cp$	.02 [c]	.32 [f]	.30

a:known π-interaction

b:Ref. 157.

c:Ref. 85.

d:Ref. 158.

e:Ref. 146.

f:Ref. 10.

TABLE 39

χ VALUES FOR COMPOUNDS OF THE TYPE H_3Si-X AND H_3C-X

X	$\chi(H_3Si-X)$	$\chi(H_3C-X)$
F	16.43	16.24
Cl	11.11	10.96
Br	9.31	9.19
I	8.78	8.66
OCH_3	8.26	9.14
$N(CH_3)_2$	7.93	7.88
O	22.19	9.14
N	15.16	7.86
S	12.43	8.13

TABLE 40

(e) Reactions of $H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ and $H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)$

Reactions of the silyl-metal and methyl-metal derivatives were studied in order to compare and contrast the similarities and differences between the organometallic chemistries of silicon and carbon. Attention was given to strengths of the Si-metal and C-metal linkages towards protonic reageants and the behavior of silicon's "d" orbitals towards complexing reageants. The study was pursued to determine how these compounds behaved in the various types of reactions: (1) bond cleavage, (2) adduct formation, (3) reaction with PF_5, and (4) reaction with H_2O.

(1) Bond cleavage with HCl: It was found the HCl cleaved the Si-metal bond (M=Cr,Mo,W) at room temperature forming the metal hydride and H_3SiCl according to the equation:

$$H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow H\text{-}M(CO)_3(\pi\text{-}C_5H_5) + H_3SiCl \quad (4)$$

Eq (4) is in agreement with the report [135] that HCl readily cleaves the Si-Fe bond in the compound $(CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ according to the equation:

$$(CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5) + HCl \rightarrow H\text{-}Fe(CO)_2(\pi\text{-}C_5H_5) + (CH_3)_3SiCl \quad (5)$$

Under similar conditions, HCl also cleaved the C-metal bond (M=Mo,W) forming the metal chloride according to the equations:

$$H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5) + HCl \rightarrow H\text{-}M(CO)_3(\pi\text{-}C_5H_5) + H_3CCl \qquad (6)$$

$$H\text{-}M(CO)_3(\pi\text{-}C_5H_5) + H_3CCl \rightarrow Cl\text{-}M(CO)_3(\pi\text{-}C_5H_5) + CH_4 \qquad (7)$$

in which the metal hydride formed in the intermediate step reacts with H_3CCl. Eq (7) is in agreement with the known method of preparing the metal chloride of molybdenum which occurs according to the equation:

$$H\text{-}M(CO)_3(\pi\text{-}C_5H_5) + CCl_4 \rightarrow Cl\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + HCCl_3 \qquad (8)$$

The explanation for these differing reactions of the Si-metal and C-metal linkages can be rationalized by considering bond strengths [159] given below:

E (kcal/mole) - bond energy

$H_3Si\text{-}H$: 76	$H_3C\text{-}Cl$: 78
$H_3Si\text{-}Cl$:87-93	$H_3C\text{-}H$: 91

Thermodynamically, it can be concluded that the formation of the Si-Cl bond is favored over the Si-H bond, and the formation of the C-H bond is favored over the C-Cl bond.

This novel method Eq (6,7) of preparing the metal chlorides of molybdenum and tungsten led to inconclusive results in the case of $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, since a polychlorinated complex solid mixture was assumed to result.

(2) Adduct Formation: It was found that trimethylamine formed adducts at room temperature with all three silyl-metal derivatives according to the equation:

$$H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)+N(CH_3)_3 \rightarrow [(CH_3)_3N,SiH_3]^+[M(CO)_3(\pi\text{-}C_5H_5)]^- \quad (9)$$

with the ratio of $H_3Si\text{-}M$ to $N(CH_3)_3$ being:

M	$H_3Si\text{-}M:N(CH_3)_3$
Cr	1.00:0.92
Mo	1.00:1.09
W	1.00:0.63

The infrared spectrum (Figure 43) of the $H_3Si\text{-}W$ adduct also confirmed that it was indeed the least complexed of the three adducts due to dissimilarity with the spectra of the chromium and molybdenum adducts (Figure 43).

Under similar conditions, it was found that the $N(CH_3)_3$ did not react with the methyl-metal derivatives. Thus, it can be concluded that the presence of silicon's empty "d" orbitals are responsible for the formation of trimethylamine adduct with the silyl-metal derivatives.

It has been reported that the formation of trimethylamine adducts with $H_3SiCo(CO)_4$ [114], $H_3SiMn(CO)_5$ [146], and $(H_3Si)_2Fe(CO)_4$ [37,145], in which two molecules of $N(CH_3)_3$ are coordinated to the silyl group occurs according to

IR SPECTRA OF $[Me_3N,SiH_3]^+[M(CO)_3Cp]^-$

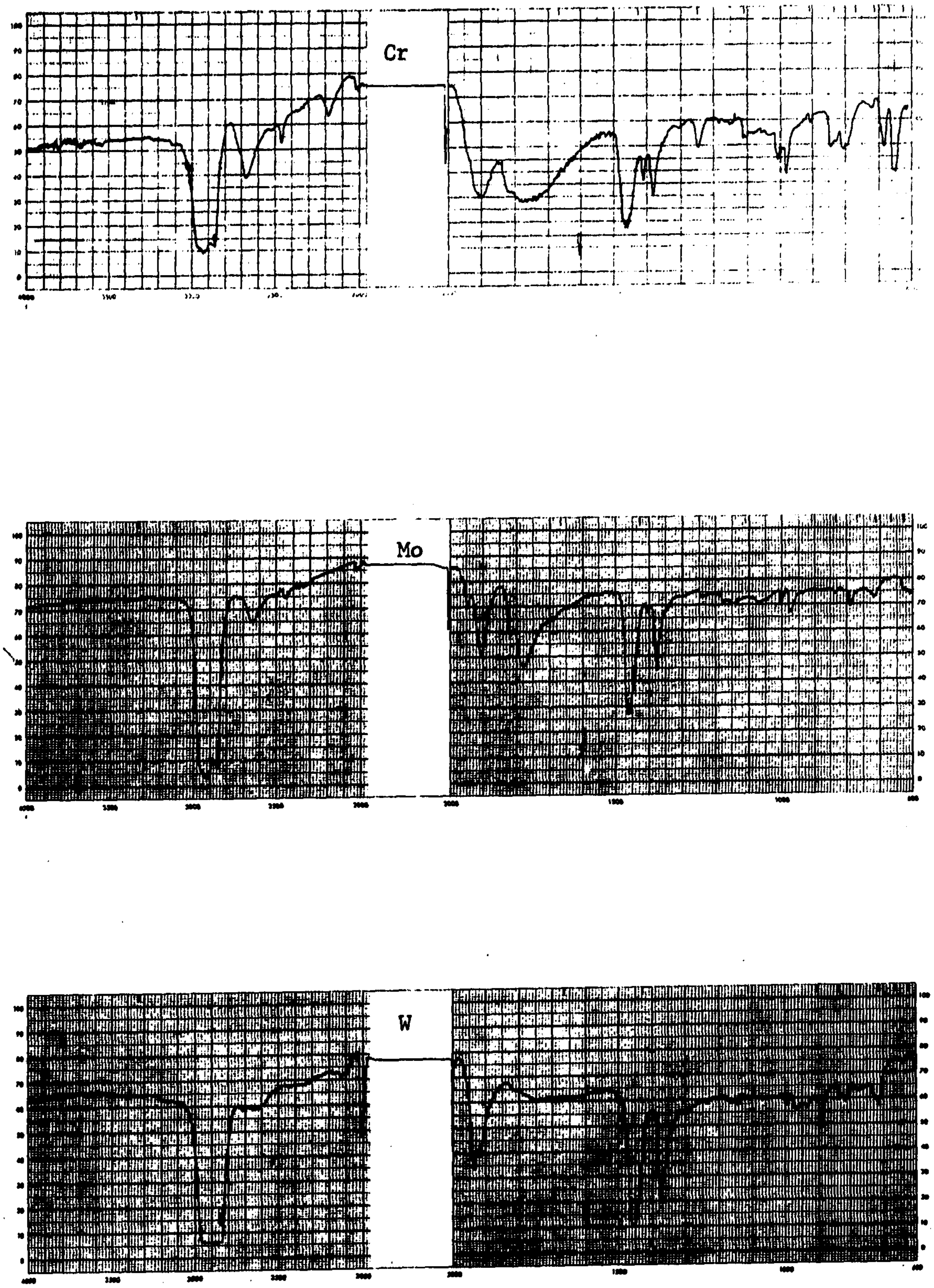


FIGURE 43

the equations:

$$H_3SiCo(CO)_4 + 2N(CH_3)_3 \rightarrow [2(CH_3)_3N,SiH_3]^+[Co(CO)_4]^- \quad (10)$$

$$H_3SiMn(CO)_5 + 2N(CH_3)_3 \rightarrow [2(CH_3)_3N,SiH_3]^+[Mn(CO)_5]^- \quad (11)$$

$$(H_3Si)_2Fe(CO)_4 + 2N(CH_3)_3 \rightarrow [(CH_3)_3N,SiH_3]_2^+[Fe(CO)_4]^- \quad (12)$$

The formation of these 1:2 trimethylamine adducts can be explained by realizing that the absence of the cyclopentadienyl ring reduces steric hindrance and consequently allows a second trimethylamine molecule to enter a position formerly occupied by the ring. Steric hindrance may also result from the type of substituent on silicon as well as on the metal. An example of this steric factor on silicon is the reported 1:1 trimethylamine adduct formed in the case of $R_3SiCo(CO)_4$ [136] and $R_3SiMn(CO)_5$ [41] where $R=CH_3$. According to the equations,

$$(CH_3)_3SiCo(CO)_4 + N(CH_3)_3 \rightarrow [(CH_3)_3N,Si(CH_3)_3]^+[Co(CO)_4]^- \quad (13)$$

$$(CH_3)_3SiMn(CO)_5 + N(CH_3)_3 \rightarrow [(CH_3)_3N,Si(CH_3)_3]^+[Mn(CO)_5]^- \quad (14)$$

only one molecule of $N(CH_3)_3$ is coordinated to the bulky $(CH_3)_3Si$ groups. To support the idea of steric hindrance on both the metal and silicon, it has been reported [114] that $(CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ does not react with $N(CH_3)_3$.

It was also found that $HN(CH_3)_2$ formed adducts with the silyl-metal derivatives at room temperature according to the equation:

$H_3Si-M(CO)_3(\pi-C_5H_5)+HN(CH_3)_2 \rightarrow [(CH_3)_2NH,SiH_3]^+[M(CO)_3(\pi-C_5H_5)]^-$ (15

with the ratio of H_3Si-M to $HN(CH_3)_2$ being:

M	$H_3Si-M:HN(CH_3)_2$
Cr	1.00:1.26
Mo	1.00:1.64
W	1.00:2.06

A silicon-metal adduct having more than one molecule of $HN(CH_3)_2$ coordinated to the $(CH_3)_3Si$ group has been reported[136] to occur according to the equation:

$$2(CH_3)_3SiCo(CO)_4 + (X+1)HN(CH_3)_2 \rightarrow [X(CH_3)_2NH,Si(CH_3)_3]^+[Co(CO)_4]^- + HCo(CO)_4 + (CH_3)_3Si-N(CH_3)_2 \quad (16)$$

Under similar conditions, it was found that $HN(CH_3)_2$ also reacted with the methyl-metal derivatives of chromium and molybdenum to form a different type of dimethylamine adduct according to the equation:

$$H_3C-M(CO)_3(\pi-C_5H_5) + HN(CH_3)_2 \rightarrow [(CH_3)_3NH]^+[M(CO)_3(\pi-C_5H_5)]^- \quad (17)$$

However, the dimethylamine adducts of silylmolybdenum and methyl-molybdenum derivatives were observed to decompose in an analogous way according to the equations:

$$[(CH_3)_2NH,SiH_3]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^- \xrightarrow{70°} H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + H_3Si\text{-}N(CH_3)_2 \quad (18)$$

$$[(CH_3)_3NH]^+[Mo(CO)_3(\pi\text{-}C_5H_5)]^- \xrightarrow{R.T.} H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + N(CH_3)_3 \quad (19)$$

These observations are in agreement with the results of Eq (16) since it can be assumed that $HCo(CO)_4$ and $(CH_3)_3Si\text{-}N(CH_3)_2$ result from the decomposition of the dimethylamine adduct, viz.,

$$[(CH_3)_2NH,Si(CH_3)_3]^+[Co(CO)_4]^- \xrightarrow{R.T.} HCo(CO)_4 + (CH_3)_3Si\text{-}N(CH_3)_2 \quad (20)$$

Eq (20) tends to support the idea that $HN(CH_3)_2$ does not cleave the Si-metal linkage in the case of molybdenum and cobalt.

The preparation of the trimethylsilyl derivatives of molybdenum and tungsten has been reported [9] to occur according to the equation:

$$H\text{-}M(CO)_3(\pi\text{-}C_5H_5) + (CH_3)_3Si\text{-}N(CH_3)_2 \xrightarrow{60°} (CH_3)_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5) + HN(CH_3)_2 \quad (21)$$

The trimethylgermyl-metal derivatives of molybdenum and tungsten have been reported [133] to form in a similar manner.

From results previously described concerning the reactions of silyl-metal derivatives with $HN(CH_3)_2$ and the results of the reaction of $(CH_3)_3SiCo(CO)_4$ with $HN(CH_3)_2$ it appears that these results are not in agreement with those obtained by Lappert and co-workers, since (1) Eq (18) favors the formation of the metal hydride at 70°, and Eq (20) favors the formation of the metal hydride at room temperature; (2) trimethylsilyl derivatives are considered to be less stable than trichlorosilyl- and silyl-metal derivatives, and the absence of Lappert's and co-worker mention of the synthesis of a trimethylsilyl-chromium derivative causes some doubt, since the thermal stability of the chromium and molybdenum derivatives are expected to be about the same [5] ; and (3) it has been reported [135] that $HN(CH_3)_2$ cleaves the Si-Fe bond in the compound, $(CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$.

Some points in favor of their syntheses of the trimethylsilyl-metal derivatives of molybdenum and tungsten are: (1) the reaction of the metal hydride with $(CH_3)_3Si\text{-}N(CH_3)_2$ was carried 10° below the decomposition of the dimethylamine-silyl complex; (2) three strong characteristic carbonyl infrared frequencies verify the structure of $(CH_3)_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ and eliminate the possible isolation of a dimethylamine adduct; (3) the Cp chemical shifts reported for the trimethylsilyl derivatives are very close to the Cp chemical shifts observed for the silyl-metal analogues; and (4) as stated before, the presence of the cyclopentadienyl ring on the metal and the presence of the bulky $(CH_3)_3Si$ group does not favor the formation of a dimethylamine adduct.

(3) Reaction with PF_5: It was found that PF_5 reacted with both the silyl-metal and methyl-metal derivatives (M=Cr, Mo, W) at room temperature according to the equations:

$$H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5)+PF_5 \rightarrow \text{complex solid mixture}+H_3SiF+PF_3 \quad (22)$$

$$H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)+PF_5 \rightarrow \text{complex solid mixture}+ \qquad PF_3 \quad (23)$$

In Eq (22) $HSiF_3$ and SiF_4 were also identified but no H_3CF or CF_4 were observed to form in Eq (23).

Polyflourination was assumed to occur in the reactions of PF_5 with $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ and $H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$, since no ^1H n.m.r. spectra were obtained on samples of the complex residues even though they were soluble in deuterated acetone giving dark green solutions.

In the case of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$, ^1H n.m.r. spectra (taken in deuterated acetone) on both samples of the complex solid residue from Eq (22) and Eq (23) showed two sharp peaks, one occurring at about the same position as the Cp chemical shift of $(\pi\text{-}C_5H_5)Mo(CO)_3Cl$. Although elemental analysis was inconclusive, the following species may have been formed:

$$2H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)\ 5PF_5 \rightarrow F\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + F_4PMo(CO)_3(\pi\text{-}C_5H_5) + 2SiF_4 + 4PF_3 + 3H_2 \tag{24}$$

$$2H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + 5PF_5 \rightarrow F\text{-}Mo(CO)_3(\pi\text{-}C_5H_5) + F_4PMo(CO)_3(\pi\text{-}C_5H_5) + 2CF_4 + 4PF_3 + 3H_2 \tag{25}$$

The other ^1H n.m.r. peak could possibly be due to the proposed metal-phosphorus species, a peak which occurred at about the same position in the spectra of $H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ and $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$.

In the case of $H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$ and $H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$, identical ^1H n.m.r. spectra (taken in deuterated acetone) obtained on samples of the complex solid residues from Eq (22) and Eq (23) indicate that Eq (24) and Eq (25) may have resulted in each case.

It has been reported [136] that PF_5 reacts with $(CH_3)_3SiCo(CO)_4$ according to the equation:

$$(CH_3)_3SiCo(CO)_4 + PF_5 \rightarrow \text{solid residue} + (CH_3)_3SiF \tag{26}$$

No examination was reported on the residue and no PF_3 was identified either. However, a likely possibility for the solid residue could have been $F\text{-}Co(CO)_4$ and/or $F_4P\text{-}Co(CO)_4$. The reaction of $CH_3H_2SiCo(CO)_4$ with PF_5 has been reported [160] to proceed quite differently as $CH_3F_2SiCo(CO)_4$ and $HCo(CO)_3(PF_3)$ were produced in good yields.

(4) Reaction with H_2O: It was found that the silyl-metal derivatives showed slight reactions with water; the products of a reaction were a small amount of non-condensible gas, SiH_4 (trace amounts), and a white gelatinous residue. Upon removal of water from the reaction vessel, a solid material probably the metal hydride, could have been formed in the following sequence:

$$H_3Si\text{-}M(CO)_3(\pi\text{-}C_5H_5) + H_2O \rightarrow H_3SiOH + H\text{-}M(CO)_3(\pi\text{-}C_5H_5) \quad (27)$$

$$2H_3SiOH \rightarrow (H_3Si)_2O + H_2O \quad (28)$$

$$(H_3Si)_2O + 3H_2O \rightarrow 2SiO_2 + 6H_2 \quad (29)$$

$$(H_3Si)_2O + 2H_2 \rightarrow H_2O + 2SiH_4 \quad (30)$$

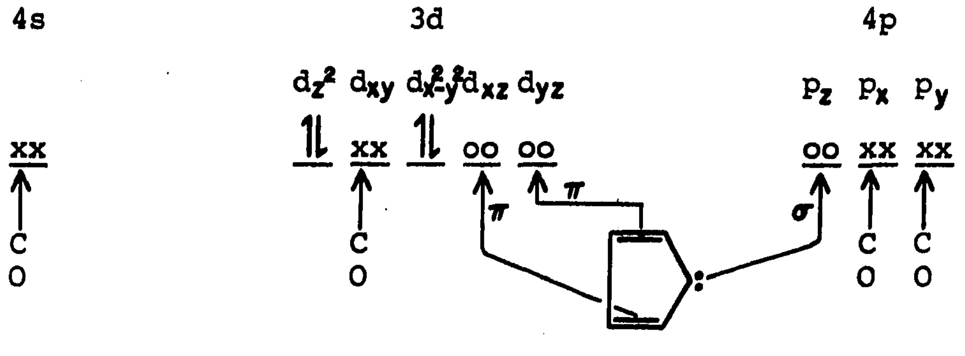
While the H_3C-metal compounds have been reported [2] to be inert to water, it appears that the H_3Si-metal derivatives undergo slight reaction with water. It has also been reported [135] that $(CH_3)_3Si\text{-}Fe(CO)_2(\pi\text{-}C_5H_5)$ does not react with water.

In summary, it can be assumed that the silyl group adds greater thermal stability to the silyl-metal derivatives relative to the methyl-metal analogues (except for W); infrared and ^1H n.m.r. spectra appear to give evidence for π-interaction between silicon and the transition metal; and the formation of trimethyl- and less stable dimethylamine adducts is a consequence of the presence of silicon's empty "d" orbitals.

(f) Nature of d_{π}-d_{π} interaction

Since σ-silyl-π-cyclopentadienyl Tricarbonyl derivatives of Group VI b are the first compounds linking $M(CO)_3(\pi\text{-}C_5H_5)$ to the H_3Si moiety, the nature of the Si-metal linkage is important due to the vacant "d" orbitals of silicon. Carbon in $H_3C\text{-}M(CO)_3(\pi\text{-}C_5H_5)$ has no available "d" orbitals; therefore the C-metal bond is assumed to be a pure sigma bond resulting from the overlap between the one empty sp^3 hybrid orbital in H_3C and a filled hybrid metal orbital. The C-metal bond ($H_3C \leftarrow M$) can therefore be postulated as a co-ordinate covalent bond from the metal to carbon (Chapter I-A). With carbon's "d" orbitals too high in energy to be involved in chemical bonding, carbon behaves differently from silicon whose "d" orbitals are low enough in energy to participate in chemical bonding.

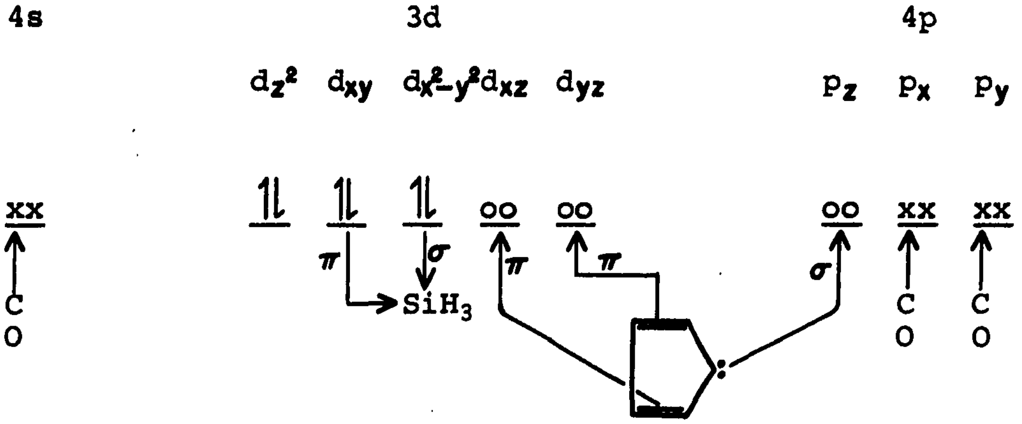
To determine the proper bonding scheme for a compound of the general type, $X\text{-}M(CO)_3(\pi\text{-}C_5H_5)$:. ($X=Cl$, H_3Si, H), appropriate orbital combinations may be generated by group theoretical operations using the local symmetries of the particular structure. As an example, for the compound $V(CO)_4(\pi\text{-}C_5H_5)$ or written $(\pi\text{-}C_5H_5)V(CO)_4$ with symmetry in mind, it has been proposed [53] that one of the dsp^3 (generated from s, p_z, $d_{x^2-y^2}$, p_x, p_y) is used in forming a forward sigma bond to the ring(the $C_5H_5^-$ group) and the other four hybrid orbitals forming co-ordinate covalent bonds with the four CO ligands. Using the specified hybrid orbitals, a square pyramidal structure is obtained, a structure which appears to be a suitable arrangement of the ligands around the central transition metal with least distortion. From group theory, it can be shown that the most likely combination of hybridized symmetry orbitals of vanadium used in the sigma bonding network under C_4 symmetry is s, p_z, $d_{x^2-y^2}$, p_x, p_y. The p_z hybrid orbital can form a sigma bond to the ring, and the remaining hybrid orbitals form bonds with the carbonyl ligands. The unhybridized "d_{xz}" and "d_{yz}" orbitals are left to form π-bonds with the ring by donation of the ring's remaining four pi electrons to these vacant "d_{xz}" and "d_{yz}" orbitals. A representation depicting the positions of the 18 electrons in $(\pi\text{-}C_5H_5)V(CO)_4$ with the $C_5H_5^-$ group assumed to be a six-electron donor is shown below:[161]



or

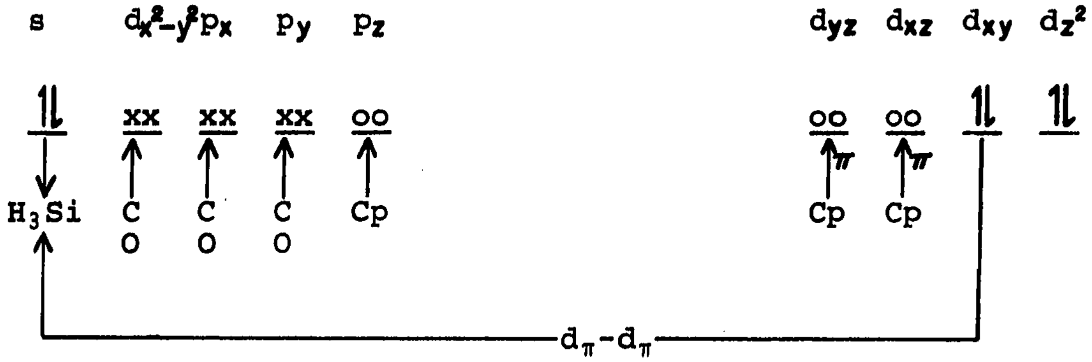
hybrid orbitals

The compound, $(\pi\text{-}C_5H_5)Cr(CO)_3SiH_3$, can be generated from $(\pi\text{-}C_5H_5)V(CO)_4$ by removing one carbonyl ligand and adding the SiH_3 group; the SiH_3 group is not in parentheses since it is not an electron-donating ligand but rather accepts a pair of electrons from chromium to form a coordinate covalent sigma bond. The representation depicting the positions of the 18 electrons in $(\pi\text{-}C_5H_5)Cr(CO)_3SiH_3$ with the $C_5H_5^-$ group assumed to be a six-electron donor is shown below:



or

hybrid orbitals



The transfer of one of chromium's non-bonding "d" electron pairs into a vacant "d" orbital of appropriate symmetry of silicon can be postulated as π-interaction or d_π-d_π bonding between silicon and chromium.

With silicon taken as the point of reference (instead of chromium), the representation depicting the position of the three electrons in silicon's partially filled and vacant "d" orbitals in $(\pi\text{-}C_5H_5)Cr(CO)_3SiH_3$ is shown below:

hybrid orbitals

Because silicon has vacant "d" orbitals, it can be theorized that a base should form a co-ordinate covalent bond with silicon. And it is indeed found that $H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$ does react with the bases $N(CH_3)_3$ and $HN(CH_3)_2$ forming adducts of the type, $[Base,SiH_3]^+[Cr(CO)_3(\pi\text{-}C_5H_5)]^-$. Similar arguments also can be made for molybdenum and tungsten.

(g) Nature of $K[M(CO)_3(\pi\text{-}C_5H_5)]$; M=Cr, Mo, W

It should be noted that the potassium-metal salts, $K[M(CO)_3(\pi\text{-}C_5H_5)]$; (M=Cr, Mo, W), are bright yellow in a solution of 1,2-dimethoxyethane blanketed by a carbon monoxide atmosphere. But in the absence of solvent, the potassium-metal salts of chromium and tungsten appear as yellow solids while the potassium-molybdenum salt appears as a light pink solid. The thermal stabilities of the potassium-metal salts range from tungsten and molybdenum as the most stable (stored *in vacuo* at room temperature) to chromium as the least stable (stored *in vacuo* at -78°).

The infrared spectra of the anions $M(CO)_3(\pi\text{-}C_5H_5)$ have been reported [162], and the carbonyl stretching frequencies are listed below:

Compound	ν(-CO)cm^{-1} [a]	
Zn[Cr(CO)$_3$(π-C$_5$H$_5$)]$_2$	1892	1775
Zn[Mo(CO)$_3$(π-C$_5$H$_5$)]$_2$	1897	1779
Zn[W(CO)$_3$(π-C$_5$H$_5$)]$_2$	1892	1774 [b]

a:all spectra taken in DMF (N,N-dimethylformamide as the ionizing solvent.)

b:fourfold molar excess of $(C_2H_5)_4NBr$ added.[163]

Although the above compounds and the Hg derivatives have been stipulated to be covalent in nature[88,164], the potassium-metal analogues are different since they are[19,92,165] ionic in nature due to the low frequency CO absorptions as in $[(C_4H_9)_4N]^+[Mo(CO)_3(\pi-C_5H_5)]^-$. The combined infrared spectra observed in the carbonyl region for K[M(CO)$_3$(π-C$_5$H$_5$)] are shown in figure 44 and the carbonyl absorptions are given below:

Compound	ν(-CO)cm^{-1} [b]		
K[Cr(CO)$_3$(π-C$_5$H$_5$)]	1900	1770	1695
K[Mo(CO)$_3$(π-C$_5$H$_5$)]	1900	1770	1700
K[W(CO)$_3$(π-C$_5$H$_5$)]	1898	1762	1696

b:all spectra taken in Nujol

IR SPECTRA OF K[M(CO)$_3$Cp]

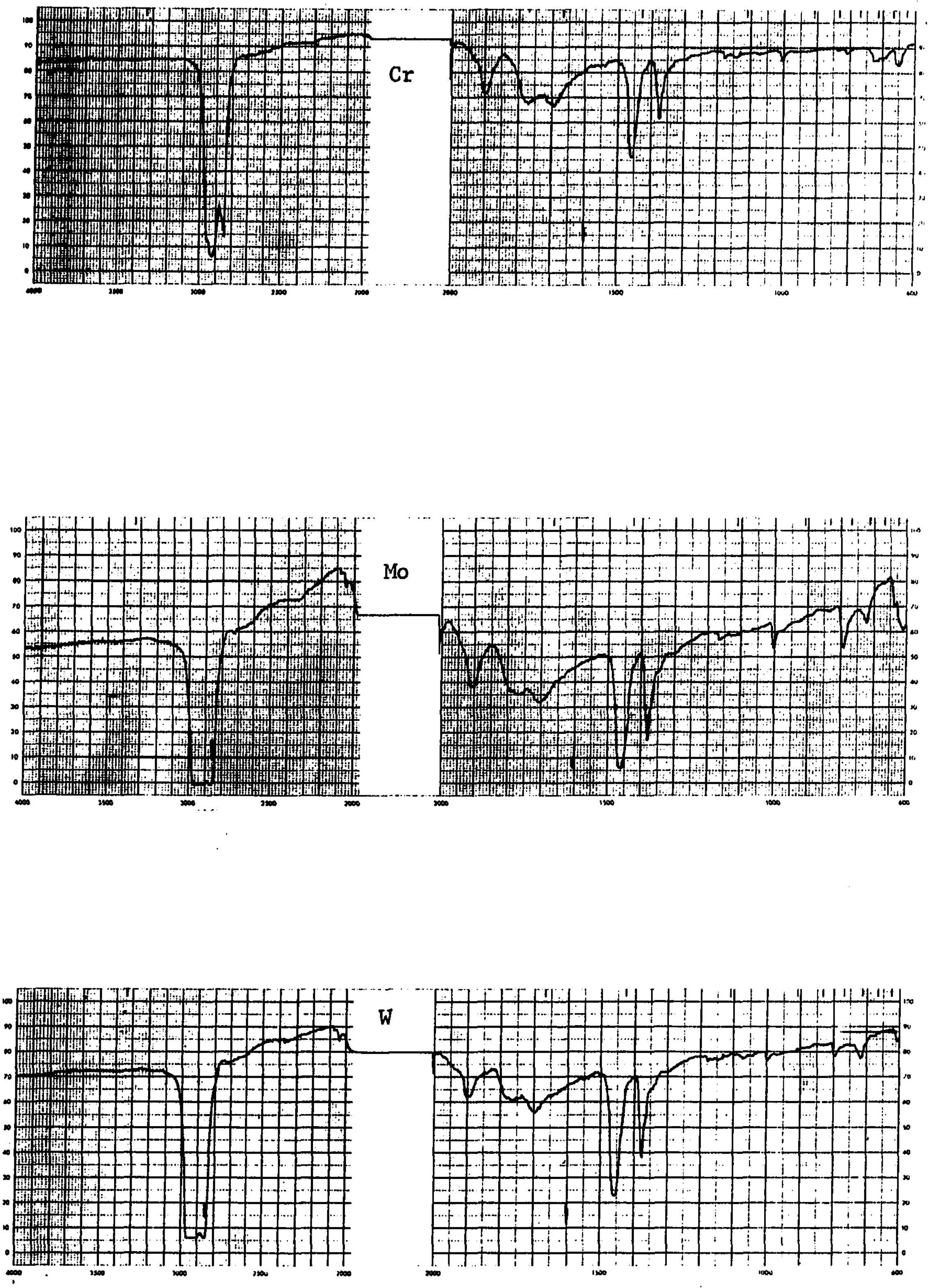
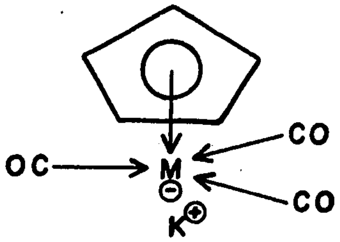


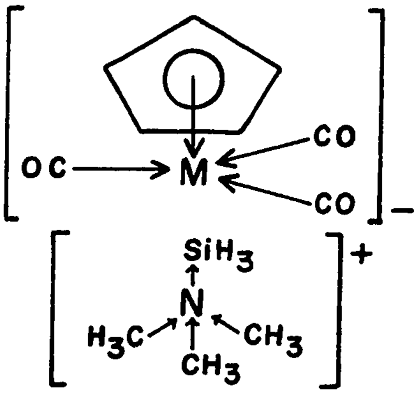
FIGURE 44

The similarities in the positions of ν(-CO) for $M(CO)_3(\pi-C_5H_5)$ (in solution) and $M(CO)_3(\pi-C_5H_5)$ (in the solid state) appear to lend support of the proposed structures of the silyl-amine adducts which have been previously formulated to be of the ionic type, $[Base,SiH_3]^+[M(CO)_3(\pi-C_5H_5)]^-$. Such structures based on the assumed structure of $K[M(CO)_3(\pi-C_5H_5)]$ can now be anticipated as shown below:

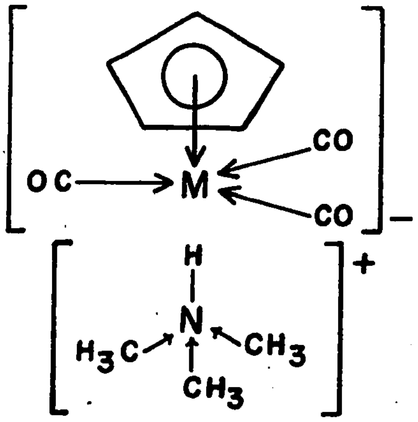
$K[M(CO)_3(\pi-C_5H_5)]$
M=Cr, Mo, W



$[(CH_3)_3N,SiH_3]^+[M(CO)_3(\pi-C_5H_5)]^-$
M=Cr, Mo, W



$[(CH_3)_3NH]^+[M(CO)_3(\pi-C_5H_5)]^-$
M=Cr, Mo



(B)

(1) Physical, Spectroscopic, and Chemical Properties of the New Compounds, $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$

(a) Physical Properties

It was found that $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$ could be synthesized from potassium metal in diethyl ether and cyclopentadiene or methylcyclopentadiene by the interaction of silyl bromide with the appropriate, dry potassium salt *in vacuo* at -78°, viz.;

$$K[C_5H_5] + H_3SiBr \rightarrow KBr + C_5H_5SiH_3 \qquad (31)$$

$$K[C_5H_4CH_3] + H_3SiBr \rightarrow KBr + C_5H_4(SiH_3)(CH_3) \qquad (32)$$

a volatile material having an above empirical formula was produced in 90% yield based on the amount of the appropriate potassium salt.

$C_5H_5SiH_3$, a white solid which melted at -94° *in vacuo* without decomposition and a clear liquid at room temperature, boiled between 59-60° and was stable to air oxidation and moisture. $C_5H_4(SiH_3)(CH_3)$ formed a glass at -140°, was a clear, stable liquid *in vacuo* at room temperature, and was less stable to air oxidation and moisture. A summary of the physical properties of cyclopentadiene, methylcyclopentadiene and the new silyl-cyclopentadiene derivatives are given below:

Compound	m.p.	b.p.	$d_{25°}$	$n^D_{25°}$
C_5H_6 [a]	-97°	41-42°	0.8021	1.4429
$C_5H_5CH_3$ (isomeric)	-98°	65-73°	0.8005	1.4486
$C_5H_5SiH_3$	-94°	59-61°	0.8211	1.4750
$C_5H_4(SiH_3)(CH_3)$	-140°	n.ob.	0.8319	1.4774

a:Ref. 127.

It should be realized that $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$ were synthesized for the first time analogous to known methods of preparation in which an alkali[63] or grignard[62] cyclopentadienide was reacted with a mono or polyhalide of silicon (Introduction Eq (29) and Eq (30)). The novel preparation of monomeric species of $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$ is remarkable since $C_5H_5CH_3$ has been obtained after thermal cracking of $(C_5H_5CH_3)_2$ (a petroleum by-product), and $C_5H_4(CH_3)_2$ can be obtained only after a laborious, multi-stepped synthetic scheme. [166,167]

(b) <u>Infrared Analysis of $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$</u>

Figure 37 (Table 22) and figure 40 (Table 27) show the infrared absorption spectra of the silylcyclopentadiene derivatives. It was found that ν(Si-H) for $C_5H_5SiH_3$ (2152 cm^{-1}) and $C_5H_4(SiH_3)(CH_3)$ (2154 cm^{-1}) were not shifted significantly from ν(Si-H) for $C_6H_5SiH_3$ (2155 cm^{-1}).[97,168] However, the lower Si-H stretching frequency in compounds having pi electrons suggest that $p_\pi \rightarrow d_\pi$ interaction may be present, since it has also been proposed that (p→d)π bonding may be operative in $H_3Si{-}O{-}CH_3$ [144] and $H_3SiN(CH_3)_3$.[148,112]

Organometallic compounds of the type C_5H_5MX (where M=metal; X=C_5H_5, halide, CO, etc.; n=1,2,...) may exist in four different bonding environments each having a characteristic local symmetry for the C_5H_5 ligand; an ionic specie such as KC_5H_5 has local D_{5h} symmetry (one νCH) [169] ; a centrally σ-bonded ligand such as $C_5H_5VCl_2$ has local C_{5v} symmetry (two νCH) [92] ; a diene-type σ-bonded grouping such as C_5H_5HgBr has local C_s symmetry (five νCH) [170] ; and a π-bonded such as $C_5H_5Mn(CO)_3$ also has local C_{5v} symmetry.[171] While it is somewhat difficult to state with assurance the type of bonding in a particular molecule, spectroscopic observations will permit a reasonable description of the nature of the bonding to be ascertained. Infrared selection rules suggest that only four strong normal vibrations of the C_5H_5 anion are expected for ionic species; absorption bands around 1100 cm^{-1} are typical of centrally σ-bonded and π-bonded systems; a metal-ring vibration (observed with CsBr optics) for light metals has also been associated with centrally and diene-type σ-bonded complexes; whereas, a greater number of bands in the far infrared region, C=C bands [172,173] , and slightly shifted bands of C_5H_6 are indicative of diene-type σ-bonded molecules.

The infrared absorptions of the C_5H_5 moiety in $C_5H_5SiH_3$ (liquid between KBr disks), 3130(w), 3102(m), 3085(m), 3000(w), 1608(w), 1462(w), 1380(w), 1287(w), 1111(w), 1086(w), 1002(Sh), 982(s), 821(m), 787(s), 693(vs), and 645(s) cm^{-1}, were similar to those observed for C_5H_6 [173] [174] (liquid between KBr disks). The only difference in the two spectra was the appearance of additional bands at 2156(Si-H), 936(SiH_3), 787 and 693 cm^{-1}. Because the region above 3000 cm^{-1} (νCH) offers a clear distinction between σ-bonded and π-bonded cyclopentadienyl systems, [175] the infrared (time scale=10^{-13}sec^{-1} [176]) spectrum of a molecule nonrigid on the n.m.r. time scale (10^{-3} sec^{-1} [175]) will be the spectrum produced by the instantaneous (slow-migration) configuration. It may therefore be concluded that the number of bands predicted by group theory (four-C_s^{σ} vs one-C_{5v}^{π}) above 3000 cm^{-1} [175], the similar absorptions observed for C_5H_6 and $C_5H_5SiH_3$, and the low frequency (ν(Si-C)=425cm^{-1}; Table 22) absorption [92] are all consistent with and justification for a σ-bond between silicon and the cyclopentadienyl ligand in the organometallic molecule $C_5H_5SiH_3$. From similar analogies $C_5H_4(SiH_3)(CH_3)$ may also be established as a diene-type σ-bonded molecule.

(c) Production of Low Temperature ^{1}H n.m.r. Studies

An A-60 Analytical NMR Spectrometer was employed to obtain low temperature spectra for the silyl derivatives of cyclopentadiene and methylcyclopentadiene. This instrument was equipped with a V-6040 NMR Variable Temperature Controller (heater and sensor units) which was calibrated between -60° and +40°, a temperature probe assembly, a manifold and heat exchanger, and a large dewar containing a copper coil. Production of low temperature was achieved by placing the sample in a cold, gaseous nitrogen stream that passed at a constant rate through the probe, across the sample and emerged at the top. Dry, gaseous nitrogen, obtained from a nitrogen cylinder, was passed through the copper coils cooled with liquid nitrogen to -196°. Temperatures of -50° could be reached under the condition where the gaseous nitrogen flow was set at 18 without ejection of the sample tube. The spinning rate, however, was increased also to keep the sample tube from slowing down.

The temperature probe was calibrated with methanol for the -60° to +40° range, since the difference between the CH and OH signals is a linear function of temperature.[177]

^1H n.m.r. spectra for $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$ were taken at the coldest temperature (-50°) first. Then, a warmer temperature was selected, and the sample was allowed 5-10 minutes to come to equilibrium or until assurance that no temperature drift in the signal for TMS was observed. Most spectra were taken at a 500 or 1000 sweep width (cps).

(d) Low Temperature ^1H n.m.r. Analysis

It has been stated that [178] "...a great mistake in the interpretation of n.m.r. spectra is to base an interpretation on a single resonance signal...This warning is warranted because there exist several distinct processes by which non-equivalent nuclei appear to be equivalent... An exchange process is a process where nuclei of the same atomic species are in different molecular environments but due to rapid positional exchange between these environments the spectrometer is capable of recording only the average resonance signal rather than the resonance signal for the nucleus in each environment. Temperature dependence of an n.m.r. spectrum indicates that such a process is present...Elimination of the presence of these processes as an explanation of a single resonance signal is necessary before a valid sterochemical conclusion can be reached..." Of the two types of exchange processes--intramolecular and intermolecular--only intramolecular exchange processes will be considered since dilution with an inert solvent which should slow down intermolecular exchange rates had no effect on the proton resonance signals observed in this research.

An example of exchange processes is shown in figure 46 in which the proton signals of the CH_3 and OH groups in H_3C-OH were observed as singlets at room temperature (hydrogen bonding phenomenon); but at -40°, the proton

NMR SPECTRA (RT, -50°) OF H_3C-OH

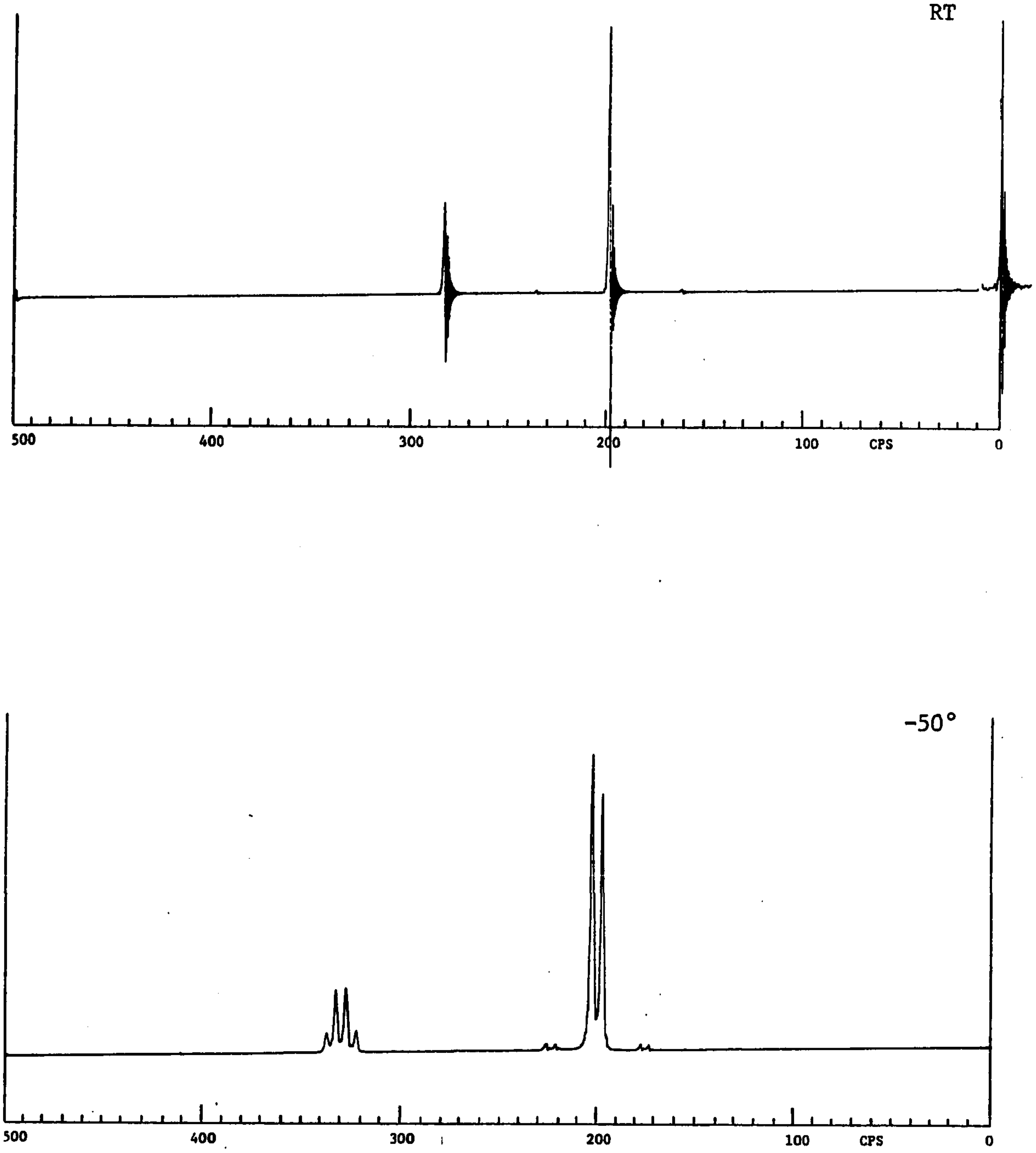


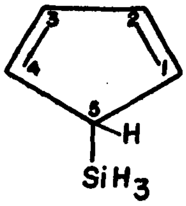
FIGURE 45

signal for the H_3C group resolved into a doublet, and the proton signal for the OH group resolved into a quartet due to the reduction of the intermolecular exchange processes.

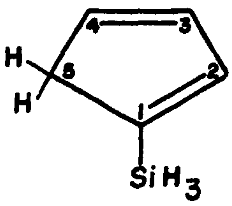
The broad proton resonances observed at room temperature for $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$, figure 36 and figure 40, are indicative of intramolecular exchange processes occurring in these organometallic cyclopentadienyl systems as fine structure was not observed upon dilution. In order to determine the stereochemistries of $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$, i.e., to determine which ring carbon the silyl group attaches itself to when silyl bromide reacts with $K[C_5H_5]$ or $K[C_5H_4CH_3]$ in the absence of solvent at -78°, it was necessary to reduce intramolecular rearrangements in these compounds by the application of low temperature in ^1H n.m.r. studies.

(1) Structure of $C_5H_5SiH_3$

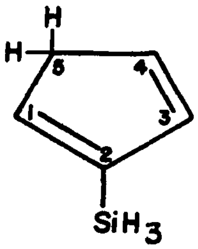
It was assumed that the n.m.r. spectrum at -50° of a neat sample of $C_5H_5SiH_3$ which had been promptly cooled to -196° after synthesis would be due to only one of the three isomeric structures (I, II, or III), and that this would represent the molecule formed by the initial attack of $H_3Si^{\oplus}$ upon $C_5H_5^-$.



I



II



III

If Structure II represented the major isomer of $C_5H_5SiH_3$ at -50°, then the expected proton signal of the silyl grouping would be either (1) a singlet due to non-interaction of the silyl group with the ring protons or (2) a complex multiplet due to the coupling caused by the two equivalent protons at the 5-position and the vinyl protons. Thus, Structure II can be disregarded since neither the signal in (1) or (2) was observed at -50° (Figure 47).

By a similar argument, if Structure III were the contributing specie at -50°, then the expected proton signal would be either (1) a singlet due to non-interaction with the ring protons, or (2) a complex multiplet due to the coupling caused by vinyl protons and possibly the two methylene protons. Structure III can also be eliminated.

If Structure I were the predominating isomer at -50°, then the expected proton signal for the silyl group would be split into a doublet by coupling with the unique proton at the 5-position carbon. Since the doublet was found experimentally at -50°, it may be concluded that the silyl group is indeed attached initially to the saturated carbon (5-position) of the ring at the moment of attack by the electrophile $H_3Si^{\oplus}$ on $K[C_5H_5]$. It should be noted that the ^{29}Si satellites were also observed as doublets: $J(^{29}Si\text{-}H)$ = 206Hz, and the unique hydrogen proton signal appeared complex due to coupling with the silyl and vinyl protons.

NMR SPECTRUM (-50°) OF $C_5H_5SiH_3$

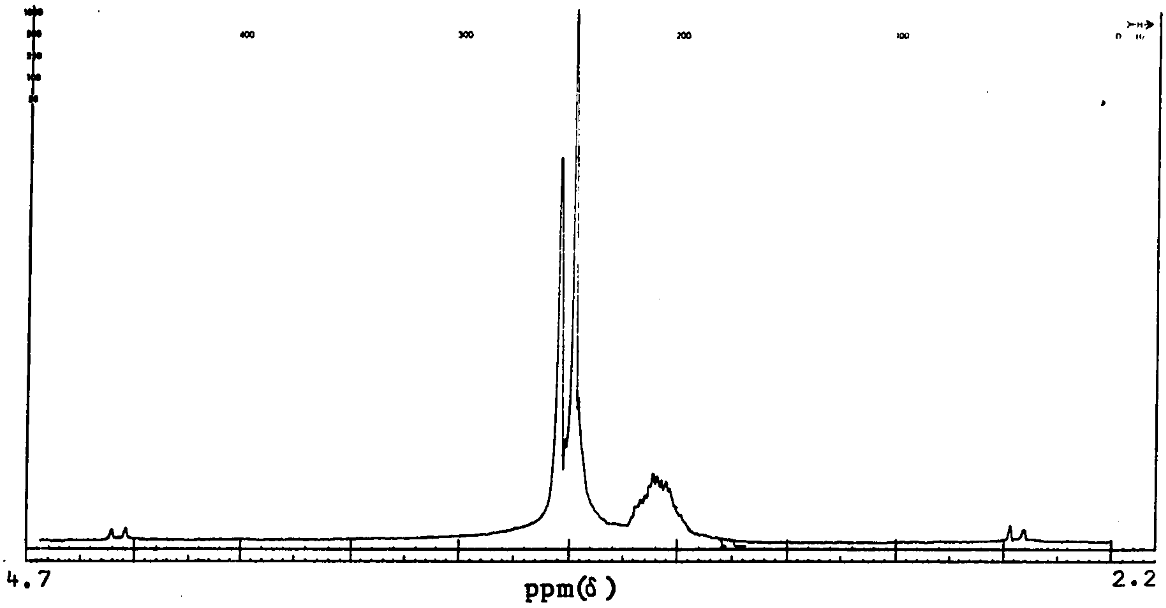


FIGURE 46

NMR SPECTRA (-50°, -30°, -20°) OF $C_5H_5SiH_3$

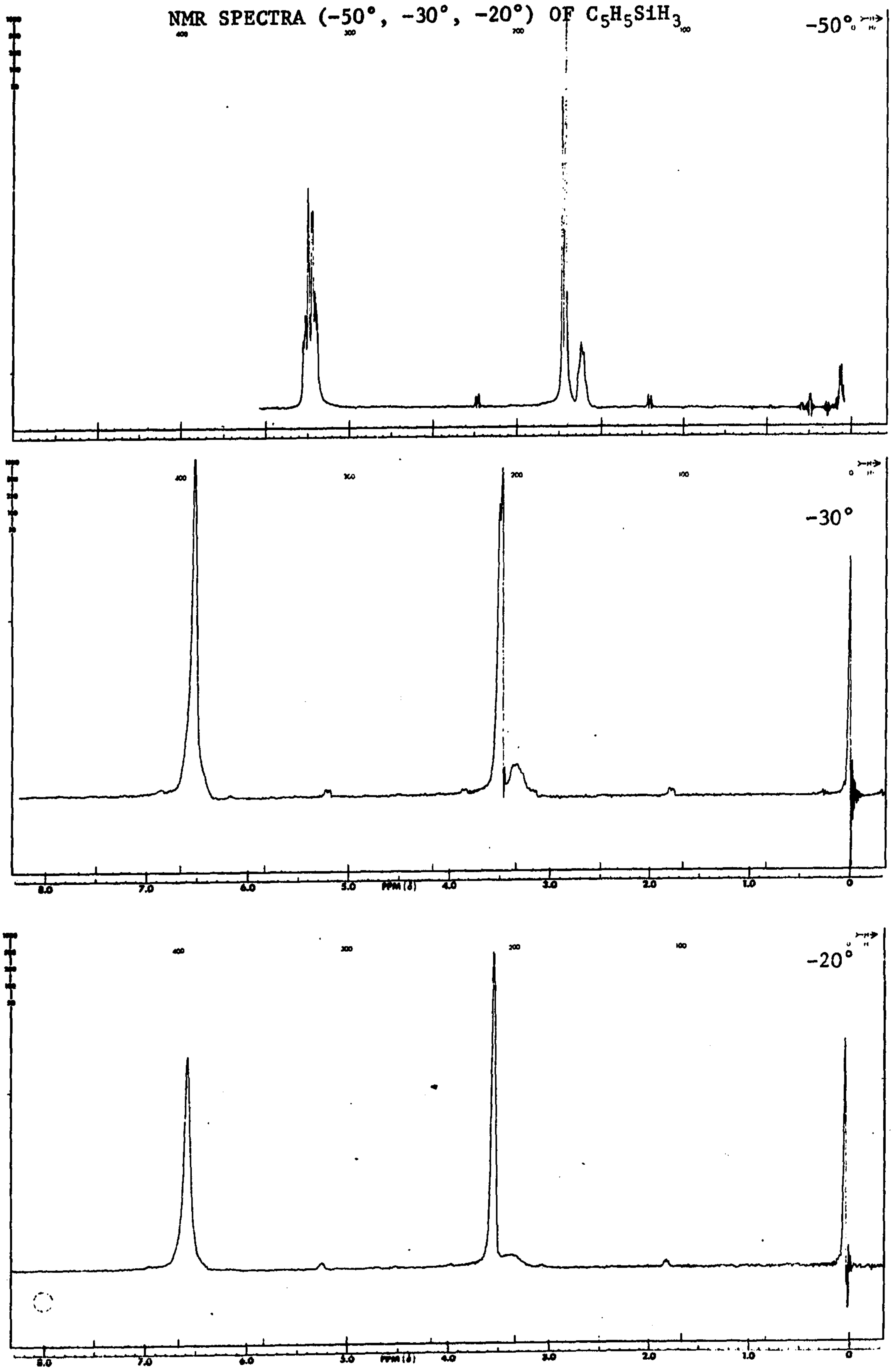
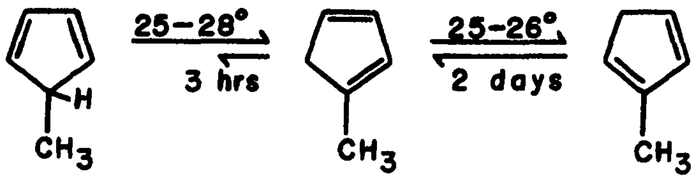


FIGURE 47

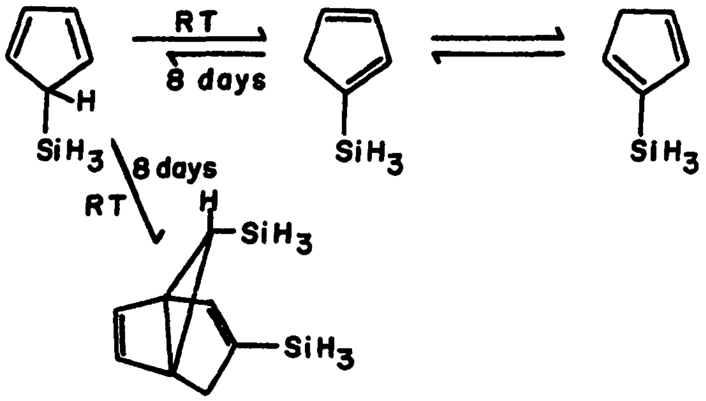
When the temperature probe was warmed from -50° to -40° to -30°, it was observed that the silyl doublet partially collapsed (Figure 48); and at -20°, total collapse (Figure 48) of the doublet and loss of structure in the vinyl region indicated that intramolecular rearrangement (loss of stationary configuration) had commenced. At this point, the sample was removed from the n.m.r. holder and allowed to warm to room temperature. After it had remained at ambient temperature for eight days, the tube was placed back in the holder, and the resulting ^1H n.m.r. spectrum taken at room temperature showed the same two peaks previously recorded at -20° plus new peaks in the silyl region appearing at 3.74δ, 3.92δ, and 4.09δ (intensity ratios--2.71:0.73:1.00). The temperature of the sample was lowered to -20° with no change in the signals, then to -30° with no change in the signals; but at -40° the original silyl peak split into a doublet. Complete loss of structure in the vinyl region was also observed.

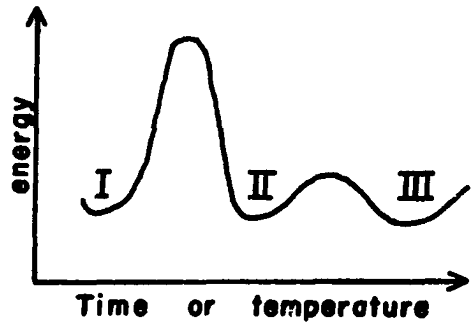
It should also be noted that (1) when a freshly prepared sample of $C_5H_5SiH_3$ was heated to 60° for several minutes then redistilled, the resulting proton signals for the silyl group appeared at 3.50δ (original peak) and 3.70δ (new peak), and (2) the proton signals from the non-volatile portion of a sample of $C_5H_5SiH_3$ held at room temperature for two weeks appeared at 3.73δ as a doublet [179,180] and 3.89δ (complex). It appears that these new peaks were due to the formation of isomers II, III, and dimeric species.

The scheme proposed for the isomerization of 5-methylcyclopentadiene, i.e., [179]

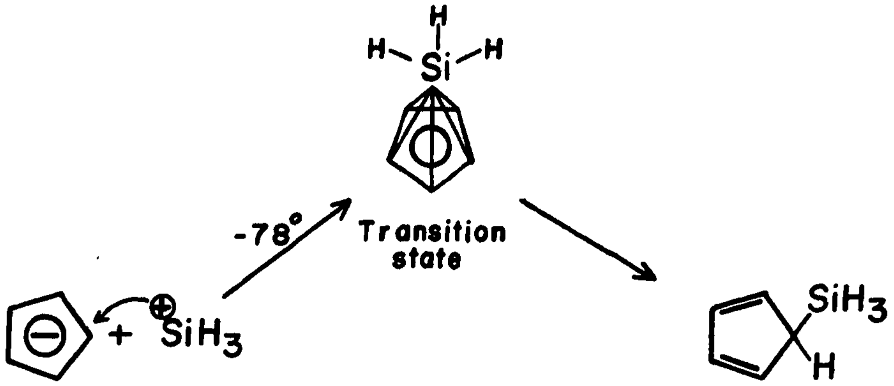


can now be proposed in an analogous manner for the isomerization of 5-silylcyclopentadiene, since experimental data indicate the presence of hindered thermodynamic equilibrium among the isomeric silylcyclopentadienes I, II, and III, e.g.,



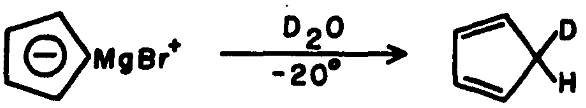


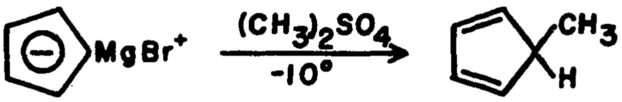
The apparently large potential barriers for the isomeric interconversions [179] ($5 \rightleftharpoons 1 \rightleftharpoons 2$) explains why the 5-isomer is still present at equilibrium. Thus, it may be concluded that when the ionic specie $H_3Si^{\oplus}$ attaches itself to the cyclopentadienyl anion,  (equivalent carbon atoms), the carbon atom under attack automatically becomes the 5-position, e.g., [181,180]



Scheme I

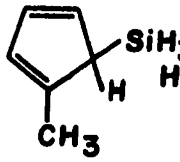
Scheme I is in complete agreement with the known deuteration [180] and methylation [179] reactions, viz.,



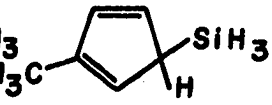


POSSIBLE STRUCTURES OF $C_5H_4(SiH_3)(CH_3)$

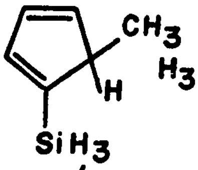
I'



II'

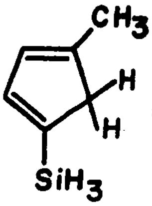


III'

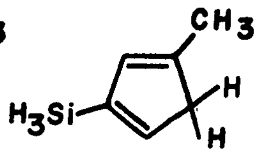


IV'

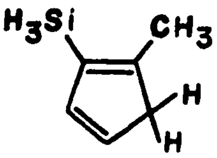
V'



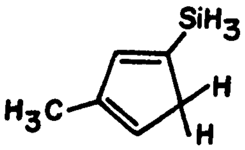
VI'



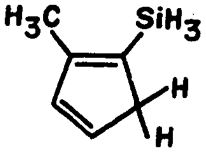
VII'



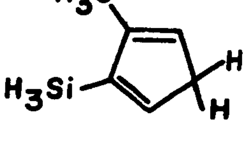
VIII'



IX'



X'



XI'

FIGURE 48

(2) Structure of $C_5H_5(SiH_3)(CH_3)$

Following reasoning similar to the case of $C_5H_5SiH_3$, Structures II′-V′ can be eliminated, since no doublets were observed for the silyl and methyl proton signals at -50°; similarly, Structures VI′-X′ can be eliminated, since no triplets were observed for the silyl or methyl proton signals at -50°; and Structure XI′ is eliminated since a four atom center interaction would be small and no singlets were observed either. However, assuming appreciable allylic interaction, the silyl and methyl proton signals would be split into doublets due to the vinyl protons. Structure XI′ may also be eliminated due to its stereochemically rigid configuration.[181]

If Structure I′ were the contributing isomer at -50°, then the expected proton signals for the silyl and methyl groups assuming splitting through a three atom (H_3Si-C-CH_3) interaction would be two quartets at -50°. Since the quartets were found experimentally (Figure 49) it may be concluded that the silyl and methyl groups were attached initially to the saturated carbon (5-position) of the ring at the moment of attack by the electrophile $H_3Si^{\oplus}$ on $K[C_5H_4CH_3]$. It should be noted that the ^{29}Si satellites were also observed as quartets: $J(^{29}Si-H) = 206Hz$.

When the temperature probe was warmed from -50° to -20°, the silyl quartet transformed into a triplet and

NMR SPECTRUM (-50°) OF $C_5H_4(SiH_3)(CH_3)$

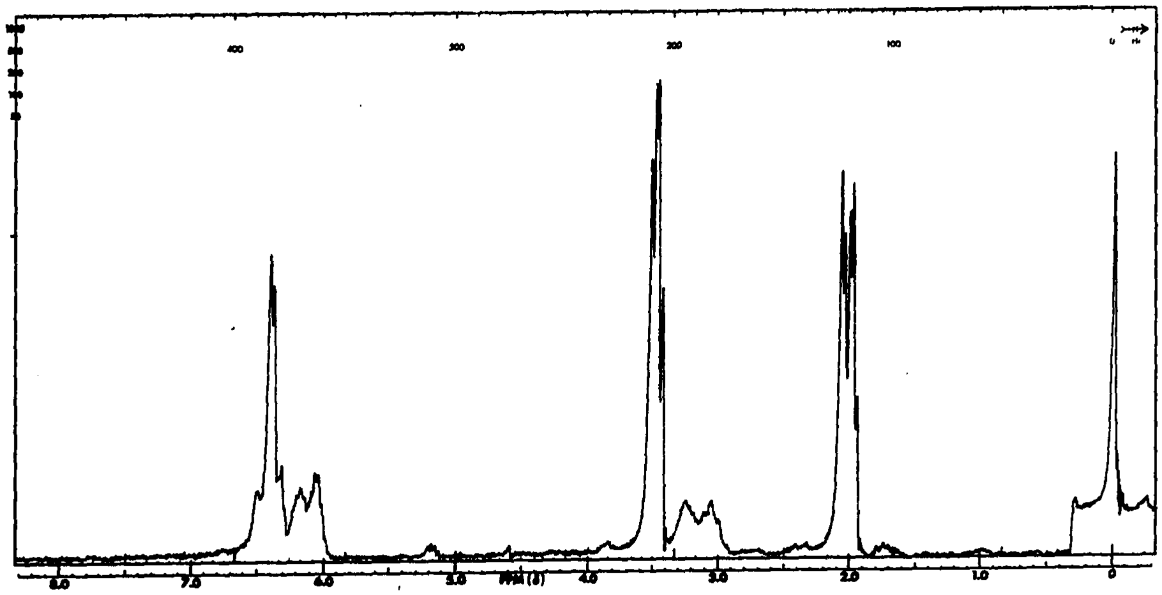


FIGURE 49

NMR SPECTRA (-50°, -20°, +10°) OF $C_5H_4(SiH_3)(CH_3)$

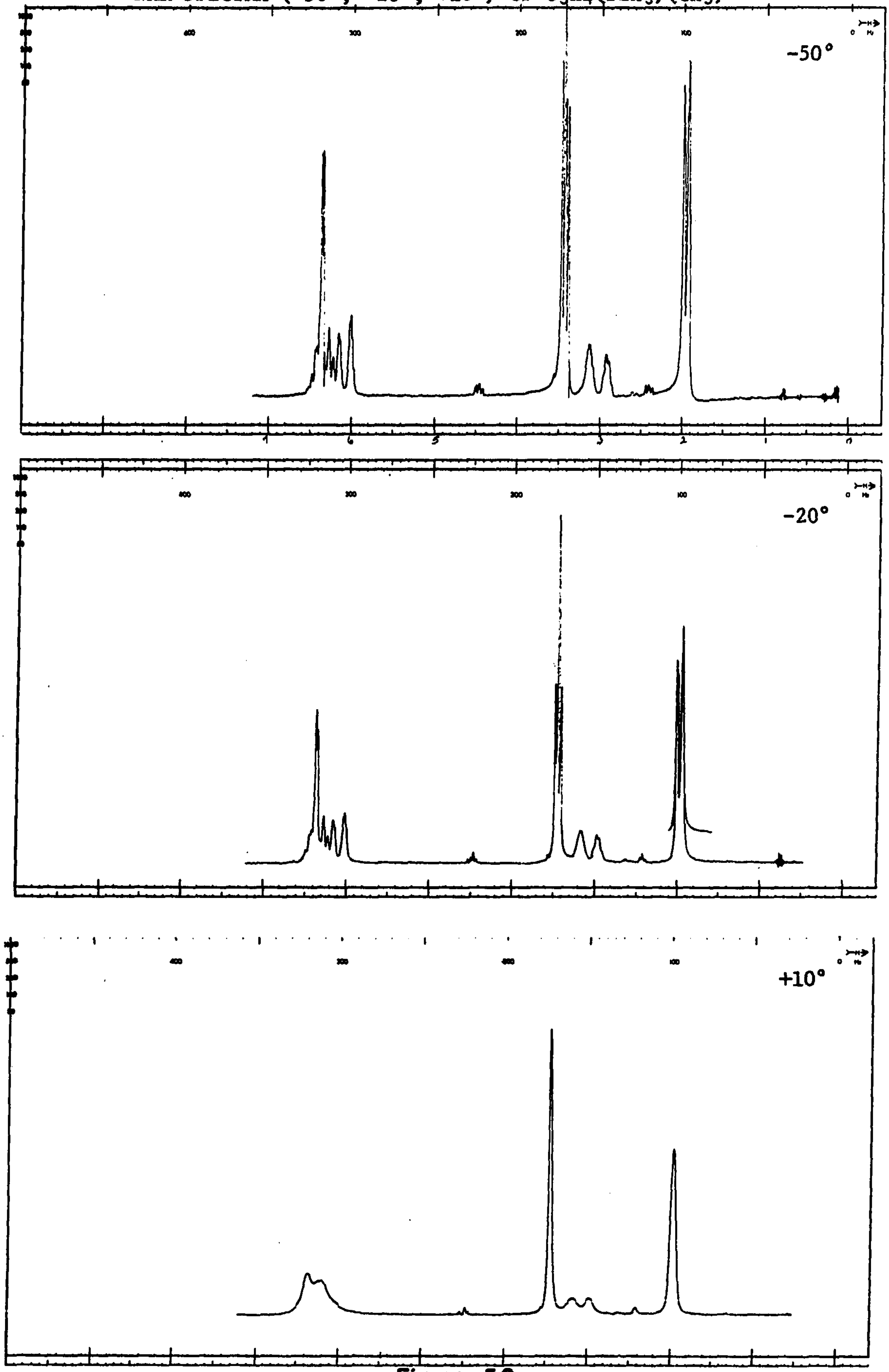
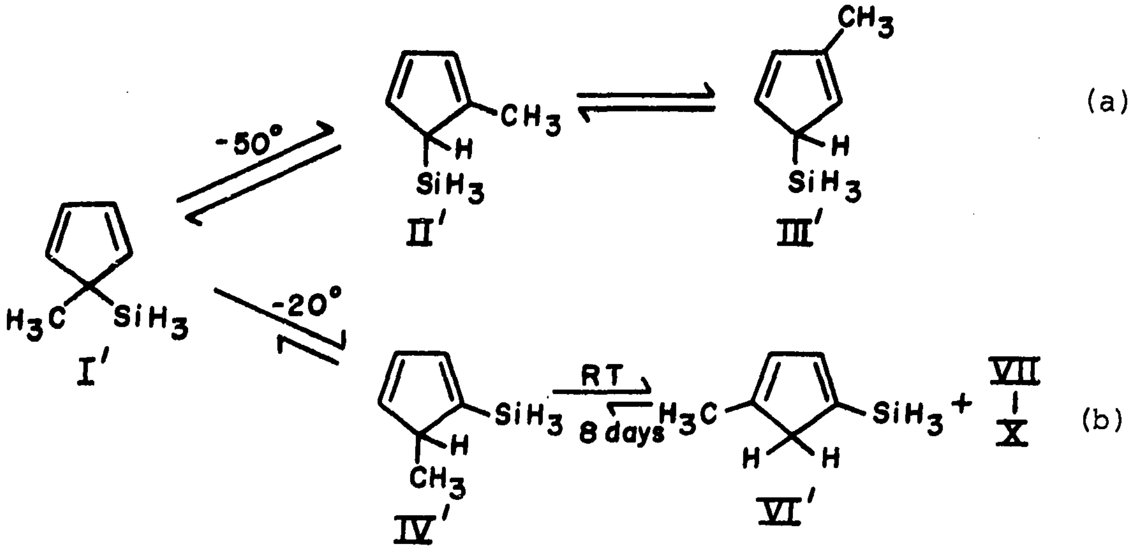


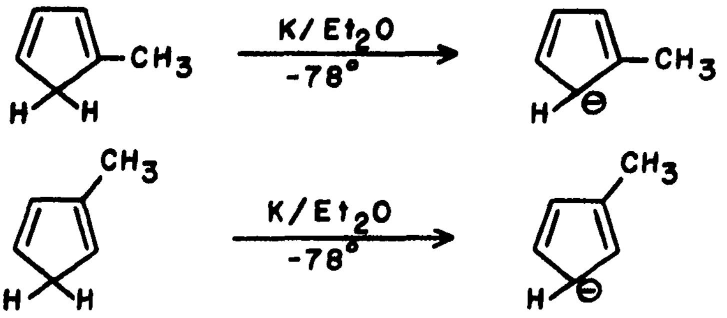
Figure 50

the methyl quartet into a doublet; Structure I′ may have undergone a rearrangement to IV′. At +10°, total collapse of the triplet and doublet along with loss of structure in the vinyl region indicate that intramolecular rearrangement had commenced. At this point the sample was removed from the n.m.r. holder and allowed to warm to room temperature. After it had remained at ambient temperature for eight days, the sample tube was placed back in the holder; the resulting spectrum taken at room temperature showed the same two peaks previously observed at +10° plus new peaks in the silyl region appearing at 3.83δ and 4.05δ (intensity ratio--0.2:1.00). The temperature was lowered to -20° with no change in the structure of the signals; at -30°, the original peaks (silyl and methyl) resolved into triplets (an apparent triplet in the methyl region was observed at -50° for $C_5H_4(CH_3)Si(CH_3)_3$ [94]); and at -40°, the original silyl and methyl signals resolved into an apparent triplet and a quartet respectively.

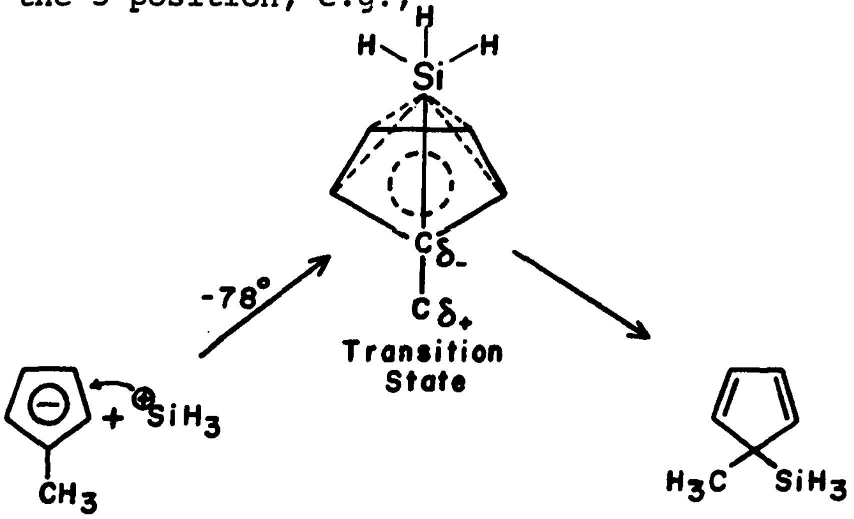
A scheme can now be proposed for the isomerization of 5-silyl, 5-methylcyclopentadiene (similar to that for $C_5H_4(CH_3)Si(CH_3)_3$ [94]) because experimental data again indicate the presence of hindered thermodynamic equilibrium among the possible isomers, e.g.;



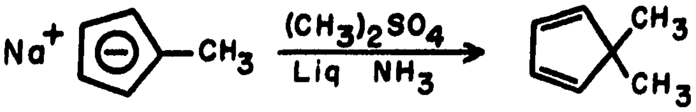
The low temperature isomerization (a) is the proposed [94] scheme for $C_5H_4(CH_3)Si(CH_3)_3$. However, at no time was the proton resonance signal for the silyl group observed as a doublet thus casting some doubt on the validity of (a). The apparently large potential barrier for the isomeric interconversions (5-,5-⇄1-,4-) explains why the 5-,5-isomer is still present at equilibrium. And the 5-,5-disubstituted alkyl cyclopentadiene has been stated to isomerize in a similar manner.[182] It may be concluded that (1) the n.m.r. spectrum of the methylcyclopentadienyl anion (Figure 39) corresponds to four equivalent cyclopentadienyl protons (5.60δ) and three equivalent methyl protons (2.00δ). Consequently, the following structures which could be drawn in the formation of the $C_5H_4CH_3$ anion from $C_5H_5CH_3$ (1,2-isomer mixture), viz.,



represent non-equivalent ring carbon atoms and therefore are not responsible for the attack at the 5-position; (2) the ring carbon atom attached to the methyl carbon atom is more negatively polarized [183] than the other ring carbon atoms; and (3) due to this polarization, the ionic specie $H_3Si^{\oplus}$ attaches itself to this more negatively polarized ring carbon atom which then automatically becomes the 5-position, e.g.,



Scheme III appears to be in agreement with the known methylation reaction, viz., [184]



A summary of the low temperature ^{1}H n.m.r. data taken at -50° for $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$ is given in table 41. Table 42 gives a summary of the chemical shifts of mono- and disubstituted cyclopentadienyl derivatives, and table 43 lists the chemical shifts of alkali metal cyclopentadienides of sodium and potassium.

(3) Fluxional (Nonrigid) Molecules

Stereochemically rigid molecules are nonfluxional in behavior showing structure in their proton resonance signals at room temperature; furan [185], pyrrole [185], and indene [186] are examples of these rigid nolecules. In the indenyl system which shows an ABX resonance pattern, the vinyl proton closest to the aromatic ring absorbs at a lower field than the vinyl proton furthest away from the aromatic ring (Table 44). The ABX pattern observed at room temperature for indene clearly establishes it as a nonfluxional molecule.[186] Similarly, $(\pi\text{-}C_5H_5)Fe(CO)_2$ (1-indenyl) shows an ABX pattern at room temperature and therefore does not exhibit fluxional behavior; it should

^{1}H n.m.r. (-50°) DATA FOR $C_5H_5SiH_3$ AND $C_5H_4(SiH_3)(CH_3)$[a]

Compound	δ(methylene protons)	δ(silyl protons)	δ(vinyl protons)	
	complex	doublet	doublet	singlet
$C_5H_5SiH_3$	3.24	3.44	6.40	6.50
	J(3.25Hz)	J(3.25Hz)	J(1.80Hz)	
		J(^{29}Si-H:206Hz)		
	(methyl protons)	(silyl protons)	(vinyl protons)	
	quartet	quartet	doublet	doublet
$C_5H_4(SiH_3)(CH_3)$	2.04	3.48	6.00	6.36
	J(2.50Hz)	J(2.50Hz)	J(1.80Hz)	J(2.00Hz)
		J(^{29}Si-H:206Hz)		

a:relative to $Si(CH_3)_4$.

TABLE 41

^{1}H n.m.r. CHEMICAL SHIFTS OF MONO- AND DISUBSTITUTED METHYL DERIVATIVES OF CYCLOPENTADIENE

Substituents	δ (room temp)	Protons	Peak Structure	J(Hz)
1-methyl[a]	1.96	methyl	doublet	1.7
	2.70	methylene	multiplet	
	6.4-6.0	vinyl	multiplet	
2-methyl[a]	1.95	methyl	multiplet	
	2.80	methylene	multiplet	
	6.31-5.90	vinyl	multiplet	1.7
5-methyl[a]	1.08	methyl	doublet	7.8
	3.03	methylene	quartet	7.8
	6.35	vinyl	broad	
5,5-dimethyl[b]	2.35	methyl	sharp	
	6.25	vinyl	sharp	

a:Ref. 117.

b:Ref. 166.

TABLE 42

^{1}H n.m.r. (Room Temperature) DATA FOR CYCLOPENTADIENIDES OF SODIUM AND POTASSIUM

Compound	$\delta(C_5H_5)$	$\delta(CH_3)$	solvent
$Na[C_5H_5]$ [a]	5.62		THF
$Na[C_5H_4CH_3]$ [b]	5.42	2.13	THF
$K[C_5H_5]$	5.60		Et_2O
$K[C_5H_4CH_3]$	5.30	2.06	Et_2O

a:Ref. 111, 118.

b:Ref. 118.

TABLE 43

VINYL CHEMICAL SHIFTS OF FLUXIONAL MOLECULES

	H(1)H(4)		H(2)H(3)
Furan[a]	7.42		6.37
Pyrrole[a]	6.68		6.22
CpFe(CO)$_2$ (1-indenyl)[b]	6.72		6.53
indene[a]	6.14		6.66
indenylSn(CH$_3$)$_3$[b]	6.58		6.80
CpFe(CO)$_2$C$_5$H$_5$[c]	6.70		6.00
C$_5$H$_5$Cu(C$_2$H$_5$)$_3$[d]	6.95		6.57
cyclopentadiene[a]	----	(6.40)	----
C$_5$H$_5$Si(CH$_3$)$_3$[e]	6.40		6.80
C$_5$H$_4$(CH$_3$)Si(CH$_3$)$_3$[f]	6.20		6.70
C$_5$H$_5$SiH$_3$	6.40		6.50
C$_5$H$_4$(SiH$_3$)(CH$_3$)	6.00		6.36

a:stereochemically rigid
b:Ref. 188, 192.
c:Ref. 187, 189.
d:Ref. 193.
e:Ref. 181, 93.
f:Ref. 94.

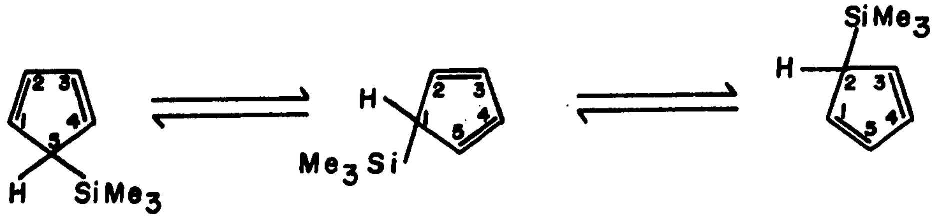
TABLE 44

be noted that in this compound the vinyl proton closest to the metal absorbs at the lower field instead of the vinyl proton closest to the aromatic ring. Based on these indenyl investigations it was purported that the unstructured resonance signal for the sigma bonded cyclopentadienyl moiety of certain organometallic compounds, was due to the nonrigid nature of the carbon-metal bond, and that ring-whizzing was ascribed to 1,2 shifts or 1,3 shifts.[187,189,192] In contrast to (π-C_5H_5,Fe(CO)$_2$ (1-indenyl), indenyltrimethyl compounds of silicon, germanium, and tin have been reported to exhibit fluxional behavior[192]; with the vinyl proton closest to the Group IV metal assumed to absorb at the higher field, it was proposed that these metals also change their σ-bonded character through 1,3 shifts.

Further development of this trend in fluxional behavior of special types of molecules is observed in the cyclopentadienyl derivatives of copper[193] and silicon.[175] In the n.m.r. spectrum of cyclopentadienyl(triethylphosphine) copper, the proton resonance (in sulfur dioxide at -70°) occurring at the lower field was assigned to the vinyl proton closest to the transition metal; whereas, in the n.m.r. spectrum of cyclopentadienyltrimethylsilane, the proton resonances (in CS_2 at 2°) occurring at the higher field were assigned to the vinyl proton closest to the Group IV metal. It may therefore be stated that fluxional molecules can show exchange-broadening (proton resonance averaging) through either 1,3 shifts for electron-rich metals or 1,2 shifts for electron-deficient metals.

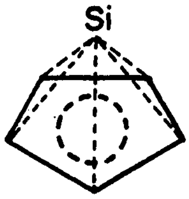
(4) Metallotropic and Prototropic Rearrangements

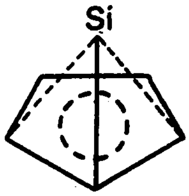
The energy of activation of metallotropic transformation occurring by Scheme IV is only 3 kcal/mole [93] :



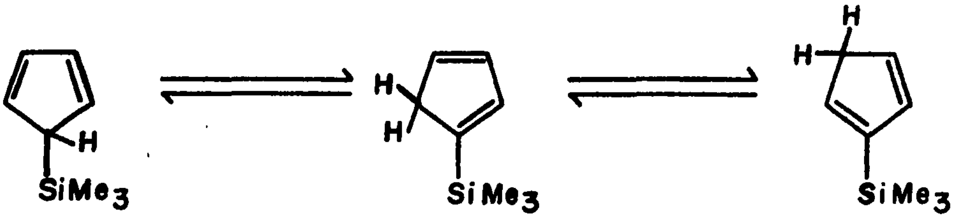
Scheme IV

From theoretical considerations [195,196] , the metal appears to form weak bonds with the pi orbitals of the ring since the vacant "d" orbitals of silicon can have electron acceptor affinity, and two transitions states have been proposed to account for either random or 1,2 shifts, i.e.,

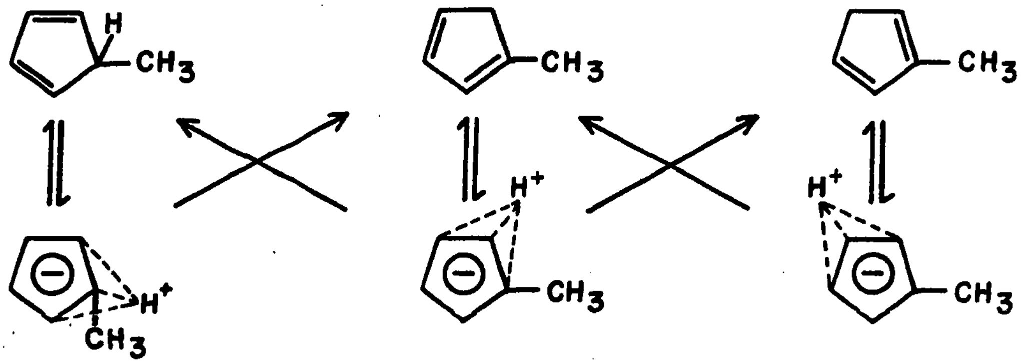




The energy of activation of prototropic transformation occurring by Scheme V [181] and Scheme VI [179] has been assumed to be greater than the energy of activation of metallotropic rearrangement since (1) the rate of migration of a proton is slower than the rate of non-metal or metal migration[181,194,197] and (2) the migration of a proton whose 2p orbitals lie very high in energy occurs through the formation of a three-center bond since the proton cannot form the above transition states and whose movement is confined to the periphery of the ring, e.g.,



Scheme V



Scheme VI

In view of the previous examples and the arguments stated therin, it may now be suggested that (1) the n.m.r. spectra of cyclopentadiene (Figure 34) and methylcyclopentadiene (Figure 37; 1,2-isomer mixture) clearly establish these compounds as rigid molecules and therefore nonfluxional in behavior since their proton resonances show structure at room temperature; (2) based on the variable temperature studies conducted on $C_5H_5Si(CH_3)_3$ [90,94,175] and $C_5H_4M'(CH_3)CH_3$; (M =Si, Ge, Sn, Pb) [94,198] , Figure 50 shows the predominant presence of isomer I´ (Figure 49) at -50° with isomers IV´ and V´ apparently present at -20° since a triplet (silyl) and a doublet (methyl) are shown distinctly. Metallotropic as well as prototropic [175] rearrangements appear to be simultaneously occurring mechanisms whereby silicon changes it σ-bonded configuration because partial collapse of the resonance signal in the vinyl region, two resonance signals in the methylene region, and a doublet (methyl protons) were all observed at -20°. After a deliberate attempt to extablish thermodynamic equilibrium between the isomers, the reappearance of triplets (-30°) and quartets (-40°) in the silyl and methyl regions and structure in the vinyl region may indicate that metallotropic and prototropic rearrangements occur at about the same rate in $C_5H_5(SiH_3)(CH_3)$; (3) from the irreversible loss of structure in the vinyl region (also observed for $C_5H_5Sn(CH_3)_3$[94,175]), it appears that the barrier of migration is small in $C_5H_5SiH_3$ and is lower than the barrier in $C_5H_4(SiH_3)(CH_3)$; and (4) the proposition that metallotropic processes occur reversibly by showing temperature-dependent n.m.r. spectra while prototropic processes occur [199,200] irreversibly by not showing temperature-dependent n.m.r.

spectra [175] satisfactorily describe the observed changes in the n.m.r. spectra of $C_5H_5SiH_3$ but not those of $C_5H_4(SiH_3)(CH_3)$.

In summary it has been concluded from infrared analysis that the Si-C bond in the silylcyclopentadienyls is indeed a sigma bond but that the presence of silicon's empty "d" orbitals appear to be responsible for the fluxional nature of $C_5H_5SiH_3$ and $C_5H_4(SiH_3)(CH_3)$[195,196] since proton migration is not rapid enough to account for the reversible-temperature n.m.r. spectra.

(e) Reactions of $C_5H_5SiH_3$ and $C_5H_5CH_3$

(1) Bond Cleavage with a Protonic Reageant--HCl

It was found that HCl cleaved the Si-C bond at -78° and at room temperature according to the equation:

$$C_5H_5SiH_3 + HCl \rightarrow C_5H_6 + H_3SiCl \qquad (33)$$

Eq (33) can be rationalized by considering the following bond energies: [159]

E(kcal/mole)		-	Bond Energy	
Si-H:	76		C-Cl:	73
Si-Cl:	91		C-H:	91

Under similar conditions, HCl reacted with $C_5H_5CH_3$ forming a complex solid mixture with no H_3CCl or other volatile product being observed.

(2) Bond Cleavage with a Base--$N(CH_3)_3$

It was found that $N(CH_3)_3$ cleaved the Si-C bond at room temperature according to the equation:

$$C_5H_5SiH_3 + N(CH_3)_3 \rightarrow C_5H_5CH_3 + H_3Si\text{-}N(CH_3)_2 \qquad (34)$$

Eq (34) can be rationalized by considering the following bond energies: [70,159]

E(kcal/mole)		-	Bond Energy	
C-Si:	78		C-N:	73
C-C:	83		Si-N:	87

$H_3Si\text{-}N(CH_3)_2$ also appears to be favored due to the possible transfer of the lone pair of electrons on nitrogen to an empty "d" orbital of silicon forming a $(p_N \rightarrow d_{Si})\pi$ bond. Under similar conditions, it was found that $C_5H_5CH_3$ did not react with $N(CH_3)_3$.

(3) Bond Cleavage with Potassium Metal

It was found that potassium metal (in an etheral solvent) cleaved the Si-C bond at -78° and at room temperature according to the equation:

$$3C_5H_5SiH_3 + 2K \rightarrow \text{"Si"} + 2K[C_5H_5] + C_5H_6 + 2SiH_4 \qquad (35)$$

It should also be noted that KOH (used as the deprotonating agent instead of potassium metal) also produced the same products with $C_5H_5SiH_3$ shown in Eq (35). Eq (35) is different from the known reactions: [77]

$$C_6H_5SiH_3 + 2Na \rightarrow NaSiH_3 + C_6H_5Na \tag{36}$$

$$C_6H_5SiH_3 + 3C_6H_5Na \rightarrow (C_6H_5)_4Si + 3NaH \tag{37}$$

where sodium metal cleaves the Si-C bond. Thus, it was concluded that the silyl analogue of $C_5H_4(CH_3)_2$ could not be synthesized from $C_5H_5SiH_3$ and potassium metal.

Under similar conditions, potassium metal (in an etheral solvent) reacted with $C_5H_5CH_3$ (a mixture of 1,2-isomers; no 5-isomer present) according to the equation:

$$C_5H_5CH_3 + K \rightarrow K[C_5H_5CH_3] + 1/2H_2 \tag{38}$$

which is analogous to a known reaction of Na. [198,175]

(4) Bond Cleavage with $Co_2(CO)_8$

It was found that $Co_2(CO)_8$ cleaved the Si-C bond at -30° to 0° according to the equation:

$$C_5H_5SiH_3 + 2Co_2(CO)_8 \rightarrow \text{"}C_5H_4(Co(CO)_4)_2\text{"} + HCo(CO)_4 + H_3SiCo(CO)_4 \tag{39}$$

The formation of $C_5H_4(Co(CO)_4)_2$ was assumed in order to account for the presence of C-H stretching frequencies and the absence of Si-H frequencies in the infrared spectrum of the non-volatile liquid residue.

Under similar conditions, $Co_2(CO)_8$ reacted with $C_5H_5CH_3$ according to the equation:

$$2C_5H_5CH_3 + Co_2(CO)_8 \xrightarrow{u.v.} 2Co(CO)_2(\pi\text{-}C_5H_4CH_3) + 4CO + H_2 \quad (40)$$

(5) Reaction with $Mo(CO)_6$

It was found that $Mo(CO)_6$ reacted with $C_5H_5SiH_3$ at 127° according to the equation:

$$2C_5H_5SiH_3 + 2Mo(CO)_6 \rightarrow [Mo(CO)_3(\pi\text{-}C_5H_4SiH_3)]_2 + 6CO + H_2 \quad (41)$$

Due to very small yields of $[Mo(CO)_3(\pi\text{-}C_5H_4SiH_3)]_2$, identification was based on the infrared spectrum.

Under similar conditions, $Mo(CO)_6$ reacted with $C_5H_5CH_3$ according to the equation:

$$2C_5H_5CH_3 + Mo(CO)_6 \rightarrow [Mo(CO)_3(\pi\text{-}C_5H_4CH_3)]_2 + 6CO + H_2 \quad (42)$$

$[Mo(CO)_3(\pi\text{-}C_5H_4CH_3)]_2$ has been prepared elsewhere by a different method.[58]

(f) Reactions of $C_5H_4(SiH_3)(CH_3)$

(1) Bond Cleavage with HCl

It was found that HCl cleaved the Si-C bond at room temperature according to the equation:

$$C_5H_4(SiH_3)(CH_3) + HCl \rightarrow C_5H_4(CH_3)_2 + H_3SiCl \quad (43)$$

$C_5H_4(CH_3)_2$ was observed in the infrared spectrum due to the inseparable mixture $C_5H_4(CH_3)_2$ and $C_5H_4(SiH_3)(CH_3)$.

(2) Bond Cleavage with $N(CH_3)_3$

It was found that $N(CH_3)_3$ cleaved the Si-C bond according to the equation:

$$C_5H_4(SiH_3)(CH_3) + N(CH_3)_3 \rightarrow C_5H_4(CH_3)_2 + H_3Si\text{-}N(CH_3)_2 \qquad (44)$$

(3) Bond Cleavage with Potassium Metal

It was found that potassium metal (in an etheral solvent) cleaved the Si-C bond at room temperature according to the equation:

$$3C_5H_4(SiH_3)(CH_3) + 2K \rightarrow \text{"Si"} + 2K[C_5H_4CH_3] + C_5H_5CH_3 + 2SiH_4 \qquad (45)$$

(4) Bond Cleavage with $Co_2(CO)_8$

It was found that $Co_2(CO)_8$ cleaved the Si-C bond at 0° according to the equation:

$$C_5H_4(SiH_3)(CH_3) + Co_2(CO)_8 \rightarrow Co(CO)_2(\pi\text{-}C_5H_4CH_3) + H_3Si\text{-}Co(CO)_4 + 2CO \qquad (46)$$

Eq (46) is similar to Eq (40) except that $Co(CO)_2(\pi\text{-}C_5H_4CH_3)$ was formed in place of $HCo(CO)_4$.

(C)

Miscellaneous Reactions

(1) Reactions of H_3SiBr

It was found (Exp. III, A-2) that $C_5H_5SiH_3$ could also be synthesized in the presence of a solvent ($(CH_3)_2O$); however, purification of $C_5H_5SiH_3$ (separation of $C_5H_5SiH_3$ from $(CH_3)_2O$) was a long process involving many distillation steps. Thus, the preferred method for synthesizing $C_5H_5SiH_3$ is in the absence of solvent. Under similar conditions, it was found (Exp. III, C-1) that H_3CBr did not react with dry $K[C_5H_5]$ in the absence of solvent at -78°.

It was found (Exp. III, A-3, 4) that H_3SiBr did not react with $Hg[Cr(CO)_3(\pi\text{-}C_5H_5)]_2$ or $H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$ at room temperature, since the Hg-Cr is extremely strong and HCl has been shown to cleave the $H_3Si\text{-}Mo$ bond.

However, it was found (Exp. III, A-5,6) that H_3SiBr cleaved the Hg-Cl and Hg-Co bonds at room temperature. In the case of $C_6H_5Hg\text{-}Cl$, the new compound, $H_2ClSi\text{-}SiH_2Br$ was produced in 52% yield; whereas, in the case of $Hg[Co(CO)_4]_2$, the novel synthesis of $H_3SiCo(CO)_4$ and the new compound, $(H_2BrSi)_2$, produced these compounds as an inseparable mixture. It has been reported[146,156] that for the following reactions,

$$2H_3SiCo(CO)_4 + HgI_2 \rightleftharpoons Hg[Co(CO)_4]_2 + 2H_3SiI \qquad (47)$$

$$2F_3SiCo(CO)_4 + HgBr_2 \rightleftharpoons Hg[Co(CO)_4]_2 + 2F_3SiBr \qquad (48)$$

the equilibrium lies completely to the right; however, in this research the following equilibria were also observed:

$$2H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5) + HgBr_2 \rightleftharpoons Hg[Cr(CO)_2(\pi\text{-}C_5H_5)]_2 + 2H_3SiBr \qquad (48)$$

$$H_3Si\text{-}Co(CO)_4 + HgBr_2 \leftrightharpoons Hg[Co(CO)_4]_2 + 2H_3SiBr \qquad (49)$$

APPENDIX

(A)

REAGEANTS AND SOLVENTS

Ammomium Hydroxide (NH_4OH)-Baker-was used as obtained.

Bis(Cobalt tetracarbonyl)Mercury ($Hg[Co(CO)_4]_2$)-prepared in Chem 366. The infrared spectrum was identical to the published spectrum. [201]

Bromobenzene (C_6H_5Br)-Fischer-was used as obtained.

Calcium Hydride (CaH_2)-Ventron-was used as obtained.

Calcium Sulfate (Anhydrous) or Drierite ($CaSO_4$)-Fischer-was used as obtained.

Carbon Monoxide (CO)-Matheson-was used as obtained.

Chromic Chloride Hexahydrate ($CrCl_3 \cdot 6H_2O$)-Baker-was used as obtained.

Chromium Hexacarbonyl ($Cr(CO)_6$)-Strem-was used as obtained. The infrared spectrum (in the gas phase and in CCl_4) was identical to the published spectrum. [98]

Cobalt Octacarbonyl ($Co_2(CO)_8$)-Strem-was used as obtained. The infrared spectrum (in Nujol) was identical to the published spectrum. [115]

Cyclopentadiene (C_5H_6; mol. wgt. calc.-66.1, found-65.9: 0.30%)-was used after thermal cracking (heating [86] between 170-200°) of dicyclopentadiene. The distillate collected at 43° in a receiver was cooled to 0° by an ice-water slush and then stored in a take-off tube at -78°. The infrared spectrum was identical to the published spectrum.[108]

Deuterated Acetone ($D_3CC(O)CD_3$)-was used after transferring to a take-off tube and degassing twice.

Dicyclopentadiene ($(C_5H_6)_2$)-Aldrich-was used as obtained.

Diethyl Ether (Anhydrous) ($CH_3CH_2OCH_2CH_3$=Et_2O)-Mallinckrodt-was used as obtained. The infrared spectrum was identical to the published spectrum.[101]

Diglyme (diethylene glycol dimethyl ether=$CH_3OCH_2CH_2OCH_2CH_2OCH_3$)-Ansul-was used after distilling over CaH_2, then vacuum distilling over $LiAlH_4$.

Dimethylamine ($HN(CH_3)_2$; mol. wgt. calc.-45.08, found-45.59: 1.13%)-Matheson-was used after distillation:

RT	-78°	-96°	-196°
		F(A)	F(B)

Fraction (A) was retained; fraction (B) was discarded. The infrared spectrum was identical to the published spectrum.[101]

Dimethyl Ether (H_3COCH_3=Me_2O)-Matheson-was used as obtained. The infrared spectrum was identical to the published spectrum.[101]

Hydrogen Bromide (Anhydrous) (HBr)-Matheson-was used as obtained. The infrared spectrum was identical to the published spectrum.[101]

Hydrogen Chloride (HCl; mol. wgt. calc.-36.46, found-36.63: 0.47%)-Matheson-was used as obtained. The infrared spectrum was identical to the published spectrum.[101]

Iron Pentacarbonyl ($Fe(CO)_5$)-Strem-was used as obtained.

Lithium Aluminum Hydride ($LiAlH_4$)-Ventron-was used as obtained.

Magnesium Metal Turnings (Mg)-Baker-were used as obtained.

Mercury-A. H. Thomas-triply distilled, was used as obtained.

Methylcyclopentadiene ($C_5H_5CH_3$; mol. wgt. calc.-80.13, found-79.48: 0.80%)-was used after thermal cracking[171] (heating between 170-200°) of methylcyclopentadiene dimer. The distillate collected at 75° in a receiver was cooled to 0° by an ice-water slush and then stored in a take-off tube at -78°. The infrared spectrum and n.m.r. spectrum were identical to the published spectra.[108,117]

Methylcyclopentadiene Dimer ($(C_5H_5CH_3)_2$)-Strem and Enjay-was used as obtained.

Methyl Iodide (H_3CI; mol. wgt. calc.-141.94, found-142.65: 0.50%)-Columbia-was used after distillation *in vacuo*. The infrared spectrum and n.m.r. spectrum (relative to cyclohexane) were identical to the published spectra.[113]

Molybdenum Hexacarbonyl ($Mo(CO)_6$)-Climax-was used as obtained. The infrared spectrum was identical to the published spectrum.[98]

Monoglyme or 1,2-dimethoxyethane ($CH_3OCH_2CH_2OCH_3$=1,2DME)-Aldrich-was used after distilling under a nitrogen atmosphere over $LiAlH_4$, and then saturating the distillate with deoxygenized nitrogen.

Nickel Chloride Hexhydrate ($NiCl_2 \cdot 6H_2O$)-Mallinckrodt-was used as obtained.

Nitrogen-Norman Supply-liquid and gaseous deoxygenized nitrogen were used as obtained from the tank.

Nujol-Plough-was used as obtained.

Phenyltrichlorosilane ($C_6H_5SiCl_3$)-Union Carbide-was used as obtained. The infrared spectrum was identical to the published spectrum.[97]

Phosphorous Pentaflouride (PF_5; mol. wgt. calc.-125.97, found-126.48:0.40%)-Matheson-was used after distillation:

RT -130° -196°
F(A) F(B)

Fraction (A) was discarded; fraction (B) was retained. The infrared spectrum was identical to the published spectrum.[105]

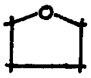
Potassium Metal (K)-Mallinckrodt-was used as obtained.

Sodium Hydroxide (NaOH)-Mallinckrodt-was used as obtained.

Sodium Metal (Na)-Mallinckrodt-was used as obtained.

Sulfur Hexaflouride (SF_6; mol. wgt. calc.-146.07)-Matheson-used as the standard to calculate molecular weight bulbs.

Sulfuric Acid (H_2SO_4)-Baker-was used as obtained.

Tetrahydrofuran (C_4H_8O=  =THF)-Mallinckrodt-was used after drying over CaH_2, distilling under a nitrogen atmosphere over $LiAlH_4$, and then saturating the distillate with deoxygenized nitrogen.

Thionyl Chloride ($SOCl_2$)-Fischer-was used after distillation under a nitrogen atmosphere.

Trichlorosilane ($HSiCl_3$)-Union Carbide-was used after distillation

RT∿-96°∿-196°
F(A) F(B)

Fraction (A) was retained; fraction (B) was discarded.

Trimethylamine ($N(CH_3)_3$; mol. wgt. calc.-59.11, found-59.67: 0.95%)-Matheson-was used after distillation

RT∿-78°∿-96°∿-196°
F(A) F(B)

Fraction (A) was retained; fraction (B) was discarded. The infrared spectrum was identical to the published spectrum.[101]

Trimethylchlorosilane ($(CH_3)_3SiCl$; mol. wgt. calc.-108.64, found-108.73: 0.01%)-Columbia-was used after distillation

RT∿-78°∿-96°∿-196°
F(A) F(B) F(C)

Fractions (A) and (B) were retained; fraction (C) was discarded. The infrared spectrum was identical to the published spectrum.[130]

Trimethylsilane ($(CH_3)_3SiH$)-Pierce Chemical Co.-was used after distillation

RT∿-96°∿-196°
F(A) F(B)

Fraction (A) was retained; fraction (B) was discarded. The infrared spectrum was identical to the published spectrum.[129]

Tungsten Hexacarbonyl ($W(CO)_6$)-Climax-was used as obtained.

(B)

SOME APPARATUS AND EQUIPMENT USED IN THIS RESEARCH

Flow Meter

Glass Pressure (Borosilicate) Reactor - fitted with a Porter-Fischer stopcock - of approximate capacity 23 ml.

Heating Coil

Heating Mantle - 250 ml, 500 and 1000 ml sizes

Magnetic Stirrer

Magnetic Stirring Bar - 1/2" and 1" sizes

Oil Bath - mineral

Polyethylene Glove Bag - Instruments for Research and Industry, 108 Franklin Ave., Chaltenham, Pennsylvania, 19012, 17 x 17 and 27 x 27 sizes.

Standard (Borosilicate) Take-off Tubes - fitted with ₮ 12/30 male joint and ₮ 24/40 stopcocks.

Standard Bench - top microware

Steam-heated Oven

Torch - oxygen and methane

Vacuum Pump

Vacuum Oven - maximum temperature 200°

Variac

(C)

COMMERCIAL ANALYSES DATA

Cr	mg sample	mgSiO_2	%Si	
	10.090	1.244	5.62	
	8.840	1.490	7.86	
	8.141	1.832	10.50	(calc.-12.09)

	mg sample	mgH_2O	%H	
	2.703	1.020	4.22	
	9.886	3.080	3.49	(calc.-3.47)

	mg sample	mgCO	%C	
	2.704	3.660	36.94	
	9.886	14.710	40.60	(calc.-41.37)

Mo	mg sample	mgSiO_2	%Si	
	3.450	0.758	10.25	(calc.-10.17)

	mg sample	mgH_2O	%H	
	2.318	0.670	3.23	(calc.-2.91)

	mg sample	mgCO	%C	
	2.318	2.890	34.02	(calc.-34.79)

W	mg sample	mgSiO_2	%Si	
	4.013	0.685	7.97	(calc.-7.71)
	4.815	0.745	7.22	

	mg sample	mgH_2O	%H	
	3.900	0.780	2.28	(calc.-2.15)

	mg sample	mgCO	%C	
	3.900	3.800	26.59	(calc.-26.39)

Compound	Calculated %	Found %
$C_5H_5SiH_3$	C - 62.42	C - 62.70
	H - 8.38	H - 8.62
	Si - 29.19	Si - 28.81
$C_5H_4(SiH_3)(CH_3)$	C - 65.38	C - 65.17
	H - 9.14	H - 9.17
	Si - 25.48	Si - 25.28

$Co(CO)_2(\pi-C_5H_4CH_3)$

mg sample	mgH_2O	%H
6.610	3.270	5.42 (calc.-3.64)
6.738	3.350	5.56
6.177	3.580	6.49

mg sample	mgCO	%C
6.610	14.510	58.67 (calc.-49.51)
6.738	14.550	58.93
6.177	15.050	66.49

$[W(CO)_3(\pi-C_5H_5)]Cl$

mg sample	mgH_2O	%H
2.876	0.260	1.01
7.102	0.800	1.26 (calc.-1.51)

mg sample	mgCO	%C
2.876	2.670	25.35
7.100	6.590	25.32 (calc.-23.57)

mg sample	$meqAgNO_3$ (.01N)	%Cl
4.281	1.170	9.70 (calc.-9.94)

$C_5H_5SiH_3$

mg sample	mgSiO_2	%Si
10.270	6.340	28.81 (calc.-29.19)
mg sample	mgH_2O	%H
4.608	0.550	8.62 (calc.-8.38)
mg sample	mgCO	%C
4.608	10.590	62.70 (calc.-62.42)

$C_5H_4(SiH_3)(CH_3)$

mg sample	mgSiO_2	%Si
6.705	3.632	25.28 (calc.-25.48)
mg sample	mgH_2O	%H
2.613	2.140	9.17 (calc.-9.14)
mg sample	mgCO	%C
2.613	6.240	65.17 (calc.-65.38)

SUMMARY OF ANALYSIS

Compound	Calculated %	Found %
$H_3Si-Cr(CO)_3(\pi-C_5H_5)$	C - 41.37 H - 3.47 Si - 12.09	C - 40.60 H - 3.49 Si - 10.50
$H_3Si-Mo(CO)_3(\pi-C_5H_5)$	C - 34.79 H - 2.91 Si - 10.17	C - 34.02 H - 3.23 Si - 10.25
$H_3Si-W(CO)_3(\pi-C_5H_5)$	C - 26.39 H - 2.15 Si - 7.71	C - 26.59 H - 2.28 Si - 7.97

		(Found %)		
non-volatile liquids from:	H	C	Si	F
(Exp. II, B(1), d-1) $C_5H_5SiH_3$ + HCl →	8.31	67.99	1.07	
(Exp. II, B(2), d-1) $C_5H_4(SiH_3)(CH_3)$ + HCl →	8.74	68.53	3.33	
solid residues from:				
(Exp. II, A(2), d-5) H_3Si-Mo + PF_5 →	1.98	22.86		21.38
(Exp. II, A(3), d-4) H_3Si-W + PF_5 →	2.38	25.55		9.10

(D)

Standardization of Grignard Reageant

(1) Standardization of NaOH--potassium biphthalate (KHP) was dissolved in 20 ml of distilled water and titrated with NaOH using phenolphthalein as the indicator at the end point. Duplicate determinations were performed.

flask + KHP	77.1812	flask + KHP	91.1155
flask	76.6690	flask	90.5075
wt. of KHP	0.5122g	wt. of KHP	0.6080g
final buret	7.22ml	final buret	8.85ml
initial buret	5.90ml	initial buret	7.30ml
NaOH added	1.32ml	NaOH added	1.55ml

$$N_B = \frac{\text{(wt. of KHP)/(mol. wgt. of KHP)}}{\text{Vol of NaOH added}}$$

$$N_B^1 = \frac{(0.5122/204.23)\text{eq}}{1.32 \times 10\ 1} = 1.90\text{N}$$

$$N_B^2 = \frac{(0.6080/204.23)\text{eq}}{1.55 \times 10\ 1} = 1.92\text{N}$$

$\text{avg.}N_{NaOH} = 1.91\text{N}$

(2) Standardization of HCl--33.2 ml of concentrated HCl(12N) were placed in a 500 ml volumetric flask and diluted to the mark with distilled water. After thorough mixing, duplicate determinations were performed on this solution using 12 ml aliquot and titrating with NaOH using phenolphthalein as the indicator at the end point.

#1		#2	
final buret -	12.83ml	final buret -	24.00ml
initial buret -	0.00ml	initial buret -	11.20ml
NaOH added -	12.83ml	NaOH added -	12.80ml

$$N_A = N_B(V_B/V_A)$$

$$N_A^1 = (1.91N)(12.83/12.0) = 2.04N$$

$$N_A^2 = (1.91N)(12.80/12.0) = 2.04N$$

$$\text{avg.}N_A = 2.04N$$

(3) Hydrolysis (Standardization) of Grignard Reageant--C_6H_5MgBr (Duplicate determinations were performed on the C_6H_5MgBr solution).

A 5 ml aliquot of the C_6H_5MgBr solution was pipetted into 20 ml of distilled H_2O; slight hissing occurred in this transfer. Excess HCl was added to the reaction mixture which was back-titrated with NaOH using methyl orange as the indicator at the end point. Hydrolysis occurred according to the equation:

$$C_6H_5MgBr + H_2O \rightarrow C_6H_6 + Mg(OH)Br$$
$$Mg(OH)Br \rightarrow Mg^{+2} + Br^- + OH^-$$

Addition of Excess HCl

#1	#2
final buret - 9.00ml	final buret - 16.00ml
initial buret - 2.00ml	initial buret - 9.00ml
HCl added - 7.00ml	HCl added - 7.00ml

Back-Titration with NaOH

#1	#2
final buret - 2.20ml	final buret - 4.15ml
initial buret - 1.00ml	initial buret - 3.00ml
NaOH added - 1.20ml	NaOH added - 1.15ml

(4) Calculation of Strength of the Grignard Reageant

(1)-Total milliequivalents of HCl added =

$N_A V_A$ = (2.04N)(7.00ml) = 14.28 meq

(2)-Total milliequivalents of NaOH added =

$N_B V_B$ = (1.91N)(1.2ml) = 2.29 meq

(3) = (1)-(2) = total milliequivalent of OH present from hydrolysis reaction = 14.28 - 2.29 = 11.99 meq

(1)-Total milliequivalents of HCl added =

$N_A V_A$ = (2.04N)(7.00ml) = 14.28 meq

(2)-Total milliequivalents of NaOH added =

$N_B V_B$ = (1.91N)(1.15ml) = 2.19 meq

(3) = (1)-(2) = total milliequivalent of OH present from hydrolysis reaction = 14.28 - 2.20 = 12.08 meq

$$N^1_{C_6H_5MgBr} = \frac{11.99\text{ meq}}{5.0\text{ml}} = 2.40\text{N}$$

$$N^2_{C_6H_5MgBr} = \frac{12.08\text{ meq}}{5.0\text{ml}} = 2.42\text{N}$$

$$\text{avg.}N_{C_6H_5MgBr} = 2.41\text{N}$$

(E) IR DATA OF $H_3SiN(CH_3)_2$

Absorption	Intensity	Assignment [a]
2965	m	$-N(CH_3)_2$
2830	m	$-N(CH_3)_2$
2760	m	$-N(CH_3)_2$
2158	vs	Si-H
1450	s	$-N(CH_3)_2$
1238	w	$-N(CH_3)_2$
1155	m	$-N(CH_3)_2$
1045	m	$-N(CH_3)_2$
930	vs	SiH_3 def.vib.
730	m	$-N(CH_3)_2$

a:Ref. 101, 142.

TABLE 45

(F) IR DATA OF NUJOL, $N(CH_3)_3$, AND $HN(CH_3)_2$

NUJOL [202]

2920	vs
2852	vs
1459	s
1375	s
1160	w
717	w

$N(CH_3)_3$ [101]		$HN(CH_3)_2$ [101]	
2938	vs	2960	vs
2850	vs	2895	vs
1446	vs	1455	s
1268	s	1228	w
1173	s	1155	s
1090	w	1035	s
1042	vs	720	vs
824	s		

TABLE 46

(G)

REACTION OF HBr WITH $N(CH_3)_3$

Summary: It was found that $[(CH_3)_3^+NH]Br^-$ could be synthesized in 98.8% yield based on the amount of HBr initially employed by the interaction of $N(CH_3)_3$ with HBr, at an ideal gas pressure of 1.63 atm, for several minutes at room temperature according to the equation:

$$HBr + N(CH_3)_3 \rightarrow [(CH_3)_3^+NH]Br^-$$

From the vacuum line, 126.2 mgm (1.559 mmol) of HBr were condensed in a reactor cooled to -196° followed by 156.0 mgm (2.639 mmol) of $N(CH_3)_3$. Upon warming to room temperature, a white solid material formed immediately. After sitting for thirty minutes at ambient temperature the reactor was cooled to -196°, and no non-condensible gas was observed. The volatile materials removed from the reactor at room temperature were separated as follows:

RT∿-96°∿-196° (n=2)

215.7 mgm were gained by the reactor.

The following materials were identified:

$N(CH_3)_3$: Fraction (A) [64.2 mgm, 1.09 mmol; 41.2% recovery based on the amount of $N(CH_3)_3$ initially employed; identified by infrared spectrum identical to that observed for pure $N(CH_3)_3$ [101]].

$\underline{[(CH_3)_3^+NH]Br^-}$: [215.7 mgm, 1.540 mmol; 98.8% yield based on the amount of HBr initially employed; identified by infrared spectrum similar to that expected for $[(CH_3)_3^+NH]Br^-$ or $[(C_2H_5)_3^+NH]Cl^-$ [205,203]]. The infrared absorptions are given in table 46.

IR DATA FOR $[(CH_3)_3NH]^+Br^-$

	Absorption	Intensity	Assignment[b]
	3033	m	CH_3
	3020	m	CH_3 asymm.str.
	2965[a]	m	CH_3 asymm.str.
Nujol	2933		
Nujol	2860		
	2598	vs	N-H str.
	2510	m	N-H str.
	2479	s	
	2405	w	
Nujol	1475		
	1426	m	CH_3 symm.def.
	1400	m	CH_3 symm.def.
Nujol	1365		
	1256	s	CH_3 rk.
	1240(Sh)		
	1178	w	
	1054	w	
	983	vs	skeletal
	810	w	
Nujol	715	w	

a:observed in Kel F grease.

b:Ref. 203, 204, 205.

TABLE 47

(H) EQUATION OF STATE OF $C_5H_5CH_3$ (isomeric)

$$\log P(\text{mm}) = -1462/T + 7.0984$$

Pob(mm)	log Pob	$1/T \times 10^{-3} (°K)^{-1}$	log Pcalc	Pcalc(mm)
0.50	-0.301	4.38	-0.305	0.49
0.91	-0.041	4.18	-0.013	0.97
1.76	0.245	4.03	0.207	1.61
2.17	0.336	3.94	0.338	2.18
2.60	0.415	3.89	0.411	2.58
3.39	0.530	3.84	0.484	3.05
5.64	0.751	3.66	0.747	5.59
6.45	0.810	3.61	0.821	6.62

TABLE 48

(I) MOLECULAR WEIGHTS OF COMPOUNDS USED OR SYNTHESIZED IN THIS RESEARCH

Compound	Mol. Wgt.
$Cr(CO)_6$	220.1
$Mo(CO)_6$	264.0
$W(CO)_6$	351.9
$[Cr(CO)_3(\pi\text{-}C_5H_5)]_2$	402.2
$[Mo(CO)_3(\pi\text{-}C_5H_5)]_2$	490.1
$[W(CO)_3(\pi\text{-}C_5H_5)]_2$	666.2
$K[Cr(CO)_3(\pi\text{-}C_5H_5)]$	240.2
$K[Mo(CO)_3(\pi\text{-}C_5H_5)]$	284.2
$K[W(CO)_3(\pi\text{-}C_5H_5)]$	372.2
$H\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$	202.1
$H\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$	246.1
$H\text{-}W(CO)_3(\pi\text{-}C_5H_5)$	334.1
$H_3C\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$	216.1
$H_3C\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$	260.1
$H_3C\text{-}W(CO)_3(\pi\text{-}C_5H_5)$	348.1
$H_3Si\text{-}Cr(CO)_3(\pi\text{-}C_5H_5)$	232.2
$H_3Si\text{-}Mo(CO)_3(\pi\text{-}C_5H_5)$	276.2
$H_3Si\text{-}W(CO)_3(\pi\text{-}C_5H_5)$	346.2

TABLE 49

Compound	Mol. Wgt.
$[Mo(CO)_3(\pi\text{-}C_5H_4CH_3)]_2$	518.2
$[Mo(CO)_3(\pi\text{-}C_5H_4SiH_3)]_2$	550.4
$Na[C_5H_5]$	88.08
$K[C_5H_5]$	104.24
C_5H_6	66.10
$C_5H_5CH_3$	80.13
$C_5H_5SiH_3$	96.21
$C_5H_4(SiH_3)(CH_3)$	110.2
$Co_2(CO)_8$	341.9
$Co(CO)_2(\pi\text{-}C_5H_5)$	180.1
$Co(CO)_2(\pi\text{-}C_5H_4CH_3)$	194.1
H_3SiBr	111.0
$C_6H_5SiH_3$	108.2
$Fe(CO)_5$	195.9
$[Fe(CO)_2(\pi\text{-}C_5H_5)]_2$	355.9
$Ni(\pi\text{-}C_5H_5)_2$	189.9

TABLE 49 cont.

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