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### THE UNIVERSITY OF OKLAHOMA

#### GRADUATE COLLEGE

# SYNTHESIS AND HIGH PRESSURE REACTIONS OF ARYLSILANES CHROMIUMTRICARBONYL COMPLEXES AND THEIR DERIVATIVES

#### A DISSERTATION

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### SUBMITTED TO THE GRADUATE FACULTY

in partial fulfillment of the requirements for the

degree of

DOCTOR OF PHILOSOPHY

By HUBERT WAYNE BECK Norman, Oklahoma

SYNTHESIS AND HIGH PRESSURE REACTIONS OF ARYLSILANES CHROMIUMTRICARBONYL COMPLEXES AND THEIR DERIVATIVES

APPROVED BY

**DISSERTATION COMMITTEE** 

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#### CHAPTER I

#### INTRODUCTION

## A. <u>Objective</u>

The use of high pressure to study the physical properties of materials is not new, for during the nineteenth century the range of pressures available in the laboratory was extended to a few thousand atmospheres, but studies were mainly centered on the physical properties of substances. Even today it is probably fair to state that at least 99 percent of all chemical reaction systems which have been investigated have been studied at atmospheric pressure or less. Of those which have been studied at high pressures, there are relatively few in which the pressure has exceeded 500 atmospheres. Therefore, a whole new area of high pressure chemistry remains to be explored since many chemical reactions which either do not occur at atmospheric pressure, proceed extremely slowly, or give very small yields, proceed rapidly and give good yields when conducted at elevated pressures.

The primary objective of this research was to conduct selected inorganic and organometallic reactions at high pressures and temperature

ranging from 0° to 600°. Much of the research was originally exploratory in nature but was expected to show the advantages of high pressure techniques on reactions with a gas because the increase in pressure was capable of producing a shift in the chemical equilibrium in a desired direction and increasing the rate at which equilibrium was obtained for previously unreported reactions. An examination of the similarities and differences between the proposed products was expected to further enhance the understanding of the factors involved in their chemistry. The systems will be described with respect to chemical reactions as well as a description of the conditions required for reaction. The necessary reaction conditions can most easily be expressed with a graph (Figure 1) which describes areas of reaction and nonreaction. Reactions do not simply take place as an on/off process; however, if for a uniform time the temperature/pressure conditions to obtain a uniform (i.e., 10%) amount of reaction are compared, a meaningful representation of the pressure relationship can normally be obtained.

#### B. <u>High Pressures</u>

1. General Considerations: High pressure chemistry is a recently emerging research field and a large collection of scientific data is being assembled by a relatively small group of workers. Much of the chemical work has been conducted at pressures not significantly greater than one atmosphere but these studies have also shown that the use of high pressure techniques can be of considerable benefit to many problems in the study of chemical reactions, equilibria, synthetic chemistry and theoretical chemistry. High pressure can greatly alter the chemical





reactivity. Forcing the molecules of gases or liquids closer together strongly accelerates reactions; produces large shifts in equilibria; changes the balance between competing processes; modifies the structure of complex products; and makes possible the synthesis of completely new substances, unobtainable at normal pressures.

It has been shown that the rate of bimolecular processes in aqueous solution can be increased or decreased by application of external pressure, and the logarithm of the velocity constant, at constant temperature varied linearly with pressure up to approximately 500 atmospheres. Other general effects of pressure are the enhancement of the catalytic effect of weak acids and bases, acceleration of ionic and radical polymerization, and overcoming of steric hindrances to chemical reactions.<sup>1-4</sup>

One important reason for the lack of more high pressure data is the additional experimental problems which are encountered. Greater efforts are usually needed to gain meaningful measurements on compressed samples. Commercial equipment is now more readily available for the lower range of pressure but much of it is still fairly expensive.

The following discussion is limited to pressures below 10,000 atmospheres since that is the region utilized in this research and since mass-action effects are rapidly diminished in magnitude per unit increase in pressure above the 2 kbar region. In this region gases approach the density of liquids and become less compressible. Several reviews and articles are available which offer more details.<sup>1-7</sup>

To specify the state of a pure liquid or gas, the mass of the substance and then any two of three additional variables, pressure P,

volume V, and the temperature T must be specified. Pressure is a thermodynamic intensity factor whose common units are listed in Table 1. On a macroscopic level pressure is a stress that is uniform in all directions and can be defined as force (F) per unit area (A).<sup>8</sup>

$$P = F/A \tag{1}$$

According to the Kinetic Theory of Gases this concept is expressed as the force over the entire surface of a vessel resulting from the rate of exchange of momentum of molecules with this surface. The basis for elastic collisions is the mutual repulsion of the electron clouds of two impinging, non-bonding molecules in close proximity. In the more condensed states, i.e., liquids, solids or highly compressed gases, pressure is provided by mutual repulsion of like charges per unit area and the individual molecules may or may not have significant momentum.

The modern terminology on pressure varies depending on what type of phenomenon is being studied and in what type of laboratory it is being used. In these discussions the term vacuum will be used when referring to pressures below 1 atm; low pressure will designate the region between 1 and 50 atm; moderate pressure will be used for pressures from 50 to 250 atm; and high pressure will define the region from 250 to  $10^4$  atm.

2. High Pressure Equipment: The uses of pressure in the laboratory is greatly affected by the apparatus and method used to generate it. The types of equipment can be placed into four general groups: shock, Bridgman anvil, multiple anvil, and piston-cylinder devices.

# TABLE I

۰.

# Standard Pressure Units

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Much of the work on solid samples was done by Bridgman<sup>9-11</sup> using a pair of cylindrical pistons which were forced together by a hydraulic press. Such devices are commonly referred to as Bridgman anvils.

The piston-cylinder method, which was used in this research, was one of the earliest type of high pressure devices. The simplest method for fluids, gas or liquid, consists of completely filling and sealing a vessel or "bomb" below the desired final temperature, and then heating it. If the final temperature is above the critical point of one of the components, a large internal pressure (about 2 kbar maximum) can be generated. The pressure can be adjusted by control of the temperature and starting mass. The true piston-cylinder apparatus consists of a cylinder sealed at one end with a movable piston at the other. The fluid is placed in the cylinder and reduced in volume by driving the piston into the container. Intensification of the pressure is obtained by driving a large piston with the primary pressure. The large piston is connected to a smaller piston in a secondary cylinder. The upper pressure limit is determined by the ratio of internal to external radii of all cylinders containing the pressure and the strength of material used in construction.

One frequently used design of pump for the piston-cylinder uses hydraulic oil to drive the large piston and the smaller piston reduces compressed gases. While the cylinder can be "heat treated" or supported by additional supporting layers, the piston cannot be supported at the cylinder. Hamann<sup>3</sup> and Comings<sup>12</sup> have detailed the mathematical formulation for maximum pressure of a thick cylindrical vessel. They can be

written in the form of an equation

$$P_{max} = \sigma_{u} \frac{(K^{2}-1)}{AK^{2}+(2-A)}$$
(2)

where K = the outside to inside diameters

- A = a constant which depends on initial assumptions of stress distribution
- $\sigma_{i}$  = ultimate tensile strength

3. The Effect of Pressure Upon Simple Types of Equilibrium:

a. Gas Reactions: Any discussion on chemical equilibrium under pressure should certainly begin with a mixture of ideal gases. The perfect gas, or the ideal gas, is an invented substance, defined by certain properties which are <u>not</u> possessed by any actual substance but which are supposed to be approached by every actual gas as its pressure is indefinitely diminished. The properties of such gases conform to the ideal equation of state

$$PV = nRT$$
(3)

This equation can be applied to real gases as a good approximation only at low pressures or at sufficiently high temperatures.

The thermodynamic potential, or difference in free energy of a perfect gas between two pressures, at constant temperature is given for one mole by the equation

$$G_2 = G_1 + RT \ln(P_2/P_1)$$
 (4)

For the discussion of chemical equilibrium in a mixture of ideal gases,

chemical potential is usually employed. If we choose the mole as the capacity factor and deal with the system at constant temperature and pressure, then the molar free energy is clearly the chemical potential,  $\mu$ ,

$$\mu_{i} = \left(\frac{\partial G}{\partial n_{i}}\right)_{P,T,n_{i}(j\neq i)}$$
(5)

A condition for phase equilibrium is that the chemical potential of any one component of the reaction mixture be equal in each phase. For a mixture this is expressed by:

$$\Sigma \mu_1 dn_1 = 0 \tag{6}$$

The chemical potential of each of the components can be described by:

$$\mu_{i} = \mu_{i}^{\circ} = RTlnP_{i}$$
 (7)

where  $\mu_i^{\circ}$  is the potential at a partial pressure of one atm and  $P_i$  is the partial pressure of the component.

Following standard methods, <sup>13</sup> it can be shown

$$\Delta G^{\circ} = -RTlnK_{p}$$
 (8)

where

$$Kp = \frac{P_{C}^{q} P_{D}^{r}}{P_{A}^{k} P_{B}^{m}}$$
(9)

for the chemical reaction: kA + mB qC + rD (10)

By combining equation 7 with

 $P_i = PN_i$ (11)

we obtain

$$Kp = P^{\Delta n} \left( \frac{N_C^q \quad N_D^r}{N_A^1 \quad N_B^m} \right)_{equil} = P^{\Delta n} K_N$$
(12)

where  $\Delta n$  is the change in the number of moles in the course of the reaction. Since

$$\left(\frac{\partial \ln Kp}{\partial P}\right)_{\rm T} = 0 \tag{13}$$

and

$$\Delta n = \frac{P \Delta V}{RT}$$
(14)

for ideal gases, when the logarithm of equation 12 is differentiated with respect to pressure at constant temperature, one obtains:

$$\left(\frac{\partial \ln K_{\rm N}}{\partial P}\right)_{\rm T} = -\frac{\Delta V}{R T}$$
(15)

Above 1000 atmospheres the "ideal gas" approximation bears little relation to the real behavior of non-polar gases like N<sub>2</sub> and is even a worse approximation for polar gas molecules. In systems of real gases at high pressures a value of Kp is no longer an equilibrium constant, it is pressure dependent.<sup>4,13</sup> Instead of the "ideal gas" relation, the equation of state can be expressed by the "co-volume" equation.<sup>1</sup>

$$\mathbf{p}(\mathbf{V}-\boldsymbol{\alpha}) = \mathbf{R}\mathbf{T} \tag{16}$$

or a virial equation 13

$$PV = RT + BP + CP^2 + DP^3 + \dots$$
 (17)

If a new term fugacity, f, is defined as a measure of escaping tendency as given by Lewis and Randall,<sup>13</sup> it can be shown that

$$\left(\frac{\partial \ln f}{\partial P}\right)_{\rm T} = \frac{\rm V}{\rm RT} \tag{18}$$

and

$$\ln \frac{f_2}{P_2} = \int_0^{P_2} (\frac{V}{RT} - \frac{1}{P}) dP$$
 (19)

If a suitable equation of state is known for the gas, it may be substituted in equation 19. The free energy can then be estimated from

$$G-G^{\circ} = RTlnf$$
 (20)

Such calculations on real non-polar gases, generally show that at high pressures the free energy and fugacity are larger than the ideal values.

Based on the data for  $N_2$  and CO at 150°, it appears that the useful extent to which an equilibrium can be displaced by the application of a pressure of 4000 atmospheres is indicated by a change in the Gibbs function of 10 kcal/mol for each mole of gas which disappears.<sup>1</sup>

There are other equations which approximate the data on real gases at moderate pressures but do not provide a sufficiently satisfactory solution at high pressures. With rare exceptions, these questions are useful only over a limited range of pressures, which becomes more narrow for mixtures of gases whose critical temperatures are very different.<sup>4</sup> b. Equilibria in Liquid Phases: The problems and methods for handling the deviations of real liquid solutions from ideal behavior are similar to those of gases except activities are substituted for concentrations in the thermodynamic equations. Thus, these analogous equations can be written:<sup>4</sup>

$$\left(\frac{\partial \ln a_{i}}{\partial P}\right)_{T} = \frac{v_{i}}{RT}$$
 (21)

$$\left(\frac{\partial \ln K}{\partial P}\right)_{\rm T} = -\frac{\Delta V}{RT}$$
(22)

where  $\Delta V$  is the volume change during reaction, calculated from the partial molar volumes,  $\overline{v_i}$ .

It has already been stated that at high pressures the compressibility of liquids is considerable. For example, if the change in volume is -25 cm<sup>3</sup>/mol, the pressure is 4000 atmospheres, and temperature is 100°, then the ratio of the molal equilibrium constant,  $K_N$ , to its value at one atmosphere is 26.3.

c. Chemical Equilibrium in Gas-Liquid Systems: The calculation of equilibrium concentrations in gas-liquid systems are based on the considerations discussed in the previous sections. In the gaseous phase the relationships between the fugacity and mole fraction must be considered in regard to its relation to the liquid phase. Gonikberg<sup>4</sup> showed that the solubility of a liquid in a gas is a complex function of pressure and all calculations in which an ideal mixture of gases is assumed invalid at high pressures. The calculation of equilibrium must take into account the solubility of the gas in the liquid. This solutility, of course, lowers the concentration and the activity of the liquid. Unfortunately, there are almost no experimental data on the chemical equilibrium in this type of system at high pressure. Consideration must also be given to reactions in the critical region in which the system will become one phase.

d. Chemical Equilibria in Gas-Solid Systems: It is often assumed that changes in the amount of substances in the solid phase, taking place during reactions in heterogeneous systems consisting of solid and gaseous phases do not affect the equilibrium in the gaseous phase. This is true only for systems at moderate pressure when the activity of solids is close to unity.<sup>1,8</sup> At high pressures, the increase in activity of solids, the adsorption and solubility of gases in solid phases (or solids in gaseous phase), should be taken into account. But again, experimental data on these problems are scanty and not extremely precise.<sup>1-4</sup>

4. Dependence of the Reaction Rate on Pressure:

a. <u>Homogeneous Gas Reactions</u>: Besides its influence on the position of a chemical equilibrium, pressure is also important in affecting rates of chemical reaction. For the simplest types of reaction, the general model is the bimolecular reaction.

According to the kinetic theory of gases, the formula for the number of collisions per second between like molecules in one cc of gas A and B is: $^{2,4,8}$ 

$$Z_{o} = \pi N_{A} N_{B} (r_{A} + r_{B})^{2} \sqrt{\frac{8RT}{\pi \mu}}$$
(23)

where N is the number of molecules, r is the radius, and  $\mu$  is the reduced molecular weight.

It can also be shown that the rate constant (k) is given by:

$$k = \frac{L}{10^{3}N_{A}N_{B}} Z_{o} \exp(-E/RT)$$
 (24)

where L is the Avogadro number.

Equation 24 is only valid for low pressures and appropriate corrections become inadequate at high pressures. At present there appears to be few equations of state for real gases and gaseous mixtures which adequately describe their compressibility when the gas density approaches that of liquids.<sup>4</sup> Thus the application of collision equations to high pressure reaction has limits.

The thermodynamic framework provided by the transition state theory is usually applied to chemical reactions under pressure to discuss rate constants which are given by:

$$k_2 = (t)(kT/h)K_C^{*}$$
 (24)

where t is the probability of decay to products of the activated complex, k is the Boltzman constant, h is the Planck constant, and  $K_{C}^{*}$  is the equilibrium constant between reactants and activated complex.

In a mixture of ideal gases, there is no dependence on pressure for the bimolecular rate constant. The same is true for monomolecular reactions. But for real gases it is necessary to rewrite equation 25 as: 25 as:  $k_2 = t \frac{kT}{h} K_N^* v$  (26)

where v is the molar volume of the mixture at equilibrium and since

$$\kappa_{f} = \kappa_{r} \kappa_{N} p^{\Delta n}$$
 (27)

a new expression can be written by taking logarithms and differentiating

with respect to pressure:

$$\left(\frac{\partial \ln k_2}{\partial P}\right)_{\rm T} = \left(\frac{\partial \ln Pv}{\partial P}\right)_{\rm T} - \left(\frac{\partial \ln K_{\rm Y}}{\partial P}\right)_{\rm T}$$
 (28)

At this point, the pressure dependence of  $K_{\gamma}^{*}$  is often neglected, but this leads to increasing errors with increasing pressure.

b. Reaction Rates in Solutions:<sup>2,4</sup> The pressure derivative of the rate constant for reactions in solution is expressed in terms of the activation volume,  $\Delta V^*$ :

$$\left(\frac{\partial \ln k}{\partial P}\right)_{\rm T} = -\frac{\Delta {\rm v}^{\star}}{{\rm RT}}$$
 (29)

where this volume is the difference of partial molal volumes between the reactants and activated complex. Equation 29 is valid only if the rate constant is expressed in pressure-independent concentration units (mole fraction or molality). There is no exact expression known for the behavior of  $\Delta V^*$  with pressure, so equation 29 is usually applied to a graphical method to obtain the value of  $\Delta V^*$  at 1 atmosphere.

It is often assumed that the activation volume can be broken into two terms:

$$\Delta \mathbf{v}^* = \Delta \mathbf{v}_r^* + \Delta \mathbf{v}_s^* \tag{30}$$

the difference in volume due to the reactants and complex  $(\Delta V_r^*)$  and the change in the volume of the solvent  $(\Delta V_s^*)$ . More recently Asano and LeNoble<sup>14</sup> discussed their data by dividing the activation volume into three terms: the van der Waals volume change  $(\Delta V_w^*)$ , the void volume change  $(\Delta V_w^*)$  and the expansion volume change  $(\Delta V_E^*)$ . Unexpectedly the results indicated that  $\Delta V_{u}^{*}$  was a minor factor.

#### C. Cleavage Reactions of Silicon-Carbon Bonds

During the last 50 years, research in the field of organosilicon chemistry has undergone intense development, especially in connection with the expansion of commercial silicone products. These products have wide application primarily because of their resistance toward thermal oxidation decomposition. Their resistance toward chemical reagents is also lower. Silicon is markedly less electronegative than carbon on Pauling's scale (1.8 to 2.5). For this reason the silicon-carbon bond has a 12% ionic character and undergoes relatively facile heterolytic fission by ionic reagents with an attack of either the electrophilic atom on carbon or of a nucleophilic atom on silicon or both.

Acid cleavage of the phenyl-silicon linkage, leading to the replacement of silicon with hydrogen, follows typical aromatic electrophilic substitution reaction pathways. Since it is also one of the simplest reactions of this kind it has been studied in great detail. Eaborn and co-workers have performed extensive investigations on this reaction.<sup>15-17</sup> The compound in the studies were of the general type  $PhSiR_3$ , which made it possible to conduct the process with cleavage of only the most labile bond, Ph-Si, and to use the reaction as a model for studies of the laws governing electrophilic aromatic substitution.

The essential feature of these reactions is acid-catalyzed bond cleavage involving the attack of a solvated proton on the substrate molecule. The overall mechanism can be written as follows if anhydrous HCl is used,



Also the possibility exists that a nucleophilic coordination occurs simultaneously leading to the formation of a closed transition state.



Some of the previously reported work with HCl may provide a background for this research. The reaction of p-methoxyphenyltrimethyl-silane in aqueous methanol and aqueous dioxan was studied with both HClO<sub>4</sub> and HCl.<sup>18</sup> Perchloric acid accelerated the reaction much more strongly than hydrochloric, making less probable the formation of a four-centered transition state when water is present.

Benkeser and his group<sup>19</sup> devoted a paper to cleavage of the Si-C bond in substituted derivatives of phenylsilanes using hydrogen chloride in aqueous acetic acid. Again, water was present. The same authors<sup>20</sup> also estimated the effect of alkyl radicals on the rate of cleavage of the silicon atom, and found it to decrease in the series

PhSiMe<sub>3</sub> > PhSiEt<sub>3</sub> > PhSi(i-Pr)<sub>3</sub>. Study of the isotope effect of the solvent,<sup>16</sup> conducted in dioxan-25% water-HCl system at 50°C confirmed that proton transfer to the substrate takes place in the rate-determining step of the process.

Significant retardation of the silicon-aryl bond cleavage was found by electron-withdrawing substituents<sup>21</sup> attached to the silicon atom and may even prevent the reaction from occurring at all. Consequently arylchlorosilanes are resistant to cleavage by acid.<sup>22,23,39,40</sup> Conversely, this type of substitution facilitates nucleophilic attack on the silicon by imparting to it a greater positive charge.<sup>24,25</sup>

The splitting reaction brought about by the action of metal salts, AlCl<sub>3</sub>, PCl<sub>3</sub>, SbCl<sub>5</sub>, FeCl<sub>3</sub>, and PCl<sub>5</sub> with HCl resulted in the formation of chlorosilane and benzene, for example:

$$PhSiC1_{3} + HC1 \qquad C_{6}H_{6} + SiC1_{4}$$
(33)

A more recent investigation<sup>26</sup> of the reaction indicated that no cleavage occurred under moderate conditions of less than 80° if carefully purified reagents were used. At higher temperatures, rapid cleavage did take place when water was present, and the actual cleavage reagent was postulated as  $HAlCl_4$ . A complex reaction between PhSiCl<sub>3</sub> and AlCl<sub>3</sub> at 250° produced benzene and polymeric products, though the exact nature of the reaction was not determined.<sup>27</sup>

The above experiments show that HCl has been used to cleave the Ph-Si bond but in almost every case water was present to promote ionization of the weakly dissociated acid. When water was not present, a Lewis acid such as AlCl<sub>3</sub> was usually employed to increase the ionization of HCl. As noted above, other acids have been employed successfully.

D. Arene Chromium Tricarbonyl Complexes.

The chemical reactivity of arenes has been found to be greatly

altered by complexation in arene chromium tricarbonyl complexes. The complexes are much less prone to electrophilic attack than the free arene (a point to be questioned later). Chlorobenzene chromium tricarbonyl undergoes rapid nucleophilic substitution at the para position with NaOCH, to yield the anisole complex,<sup>29</sup> and benzene chromium tricarbonyl reacts in both acid-<sup>30,31</sup> and base-<sup>32,33</sup> catalyzed deuterium exchange under conditions where the free arenes do not react. Other studies have shown that both benzoic<sup>29,34,35</sup> acid and phenol<sup>36</sup> are weaker acids than their respective complex, and that aniline is a stronger base than aniline chromium tricarbonyl. 34 These data are consistent with, but do not necessarily imply an electron withdrawing character for the Cr(CO), group. For example, Kussanov et al., <sup>33</sup> have shown that under conditions analogous to those in which  $BF_3 \cdot D_2 O$  catalyzes deuterium exchange in  $C_6^{H_6}Cr(CO)_3$ ,  $BF_3 \cdot H_20$  will protonate the chromium atom. White and Farone 37,38 have stated that arene chromium tricarbonyls have strong Lewis acid properties and promote ionic type reactions by coordination of the chromium atom. Other workers have reported the isolation of [ArCr(CO)<sub>3</sub>Cl]SbCl<sub>6</sub><sup>41</sup> where Ar was hexamethylbenzene and the chlorine was coordinated to the metal atom. The compound was the product of the reaction of ArCr(CO), with SbC1, in dichloromethane at room temperature. Furthermore, the reaction of HgCl, with the same arene chromium complex gave a product of the formula ArCr(CO)<sub>3</sub>·2HgCl<sub>2</sub>.<sup>42</sup> The authors suggested that this 1:2 adduct was either (1) a non-electrolyte with both mercury atoms coordinated to the transition metal, (2) an anionic species such as [ArCr(CO), HgCl][HgCl,], which has been observed for some iron-mercury amine derivatives, or (3) a compound containing the mercuric chloride coordinated to the oxygen of

the carbonyl group. The authors felt the best formulation was the anionic species where the Hg atom coordinated to the metal atom with electron donation from the chromium to the mercuric chloride. These experiments offer an alternative explanation for difference in reaction of the complexes.

The solvolysis of benzyl chloride chromium tricarbonyl<sup>43</sup> and the hydrolysis of benzyl alcohol chromium tricarbonyl<sup>41</sup> have both been found to occur at a rate  $10^5$  times faster than the free arenes. It was generally accepted that metal ligand bonding could be divided into two parts, the forward coordination from ligand to metal and the back-donation from filled metal d orbitals to vacant antibonding orbitals of the ligand, thus, these workers concluded that the data was consistent with a net donation of density from the Cr(CO)<sub>3</sub> group, a +R effect.

More conclusive evidence for the electron-withdrawing nature of the Cr(CO)<sub>3</sub> molety can be found in the semiempirical molecular orbital calculations of both Caroll and McGlynn<sup>44</sup> and of Brown and Rawlinson,<sup>45</sup> which have shown a net positive charge on the arene ring.

Studies of the nmr spectra of arene chromium tricarbonyl complexes have been interpreted in terms of an electron withdrawing character for the  $Cr(CO)_3$  group.<sup>46-55</sup> Khandkawoa and Gubin<sup>46-49</sup> concluded that there is no significant change in the  $\pi$ -electron density of benzene upon its coordination to the  $Cr(CO)_3$  group; moreover, the  $\pi$ -electron cloud polarizability even increases somewhat. The changes in reactivity were attributed to a varying ring  $\sigma$ -framework effectively charged upon coordination.

Other studies of the transmission of substituent effects in complexed arenes by Reeves et al.,<sup>36,54</sup> and by Brown and coworkers<sup>45,53,55</sup> have shown no significant reduction in the transmission of  $\pi$ -substituent effects in arenes upon complexation with Cr(CO)<sub>3</sub>.

Arene chromium tricarbonyl complexes do show differences in product distribution as compared to that found in free arenes. For example the acetylation of toluene chromium tricarbonyl<sup>56</sup> proceeds apparently with more difficulty than toluene and yields a different isomer distribution. The authors suggested that the high proportion of meta isomer may be associated with steric hindrance to the departing proton by the superimposed carbonyl groups at the ortho- and para-positions. Brown and Hughes<sup>57</sup> more recently attempted kinetic studies of the acetylation of benzene chromium tricarbonyl. It was shown that the Lewis acid, AlCl<sub>3</sub>, reacts directly at the chromium atom to give  $Cr^{II}(Al_2Cl_6)(CS_2)_2$ ; consequently no theoretical conclusions on relative reactivities of free arene and  $\pi$ -bonded arenes can be drawn from the system. They suggested that electrophilic substitution at the metal atom may occur on Fiedel Crafts reactions of all metal-organic systems.

#### E. Chromium

Chromium is a d-block transition metal of group VIB having the following configuration in its outermost electron shell:  $3d^{5}4s^{1}$ . It is a refractory metal of high melting and boiling points which is reported to be stable to attack by most chemicals at low temperatures but reacts with many substances at high temperatures  $^{58}$  (>1000°). Industrial chromium is most important for its use in steels where it improves the mechanical properties and increases the corrosion resis-

tance.<sup>59</sup> Steels containing more than 10% chromium are designated "stainless" because of their resistance to corrosion and oxidation.

During electrodeposition, chromium absorbs considerable quantities of H<sub>2</sub>, forming two unstable hydrides.<sup>58</sup> It reacts with several of the common <u>aqueous</u> acids with evolution of H<sub>2</sub>. If pure Cr is used, it dissolves in <u>aqueous</u> HCl with formation of  $Cr^{+2}$  ions in the absence of 0<sub>2</sub>,<sup>60</sup> but reacts with anhydrous HCl only at temperatures above 600° where the products are CrCl<sub>2</sub> and H<sub>2</sub>.<sup>61,62</sup>

A common property of d-group transition elements is their capacity for forming complexes with many neutral compounds that stabilize low oxidation states of the metal. Low oxidation states imply high electron density on the metal which can be delocalized into the vacant orbitals of the ligands.

#### F. Chromium Hexacarbonyl

Chromium hexacarbonyl,  $Cr(CO)_6$ , was first prepared in low yields in 1927 by the reaction of  $CrCl_3$  with phenylmagnesium bromide and CO in ether, followed by hydrolysis of the product.<sup>63</sup> Other methods of preparation include the pressure reaction of CO with a chromium halide in a solution such as benzene or ether, or the reduction of Cr(III) acetate with Mg in anhydrous pyridine under pressure.<sup>63</sup>

Hieber and Romberg<sup>64</sup> reported that  $Cr(CO)_6$  is very stable toward air oxidation. It is not affected by concentrated HCl or anhydrous HCl and is only slowly attacked by  $H_2SO_4$ .<sup>58</sup> Chlorine oxidizes it to  $CrCl_3$  with evolution of CO and phosgene. An additional example of the exceptional resistance of  $Cr(CO)_6$  to chemical attack (at least in comparison to  $Mo(CO)_6$  and  $W(CO)_6$ ) was reported by Werner.<sup>65</sup> Cr(CO)\_6 is unaffected by SO<sub>3</sub> even at 160° whereas  $Mo(CO)_6$  and  $W(CO)_6$  react at -10°.

Upon thermal decomposition,  $Cr(CO)_6$  generally forms an adherent coating of chromium metal and CO. However,  $Cr(CO)_6$  pyrolyzed at 500° gives chromium oxide,  $Cr_2O_3$ .<sup>66</sup> The decomposition at one atmosphere and 210° was reported to be complete after three minutes; at 195° the decomposition was complete in 11 minutes.<sup>67</sup>

G. Anhydrous Chromium(II) Chloride

Chromium(II) chloride can be prepared by the reduction of  $CrCl_3$  in a stream of H<sub>2</sub> containing HCl at 500°, reaction of Cr with HCl at 1200°, or reaction of dry HCl with an anhydrous Cr(II) compound.<sup>61</sup> It has also been prepared by reducing  $CrCl_3$  with stiochiometric amounts of Cr.  $CrCl_2$  is very hydroscopic, is rapidly oxidized and dissolves in H<sub>2</sub>O to give sky-blue solutions.<sup>58</sup> Because of this sensitivity of Cr(II) to oxidation, all manipulations should be conducted in an all glass system or a glove box.  $CrCl_2$  has also been produced from the reaction of  $CrCl_3$  with excess chromium in a closed container.<sup>68</sup>

H. Anhydrous Chromium(III) Chloride

Chromium(III) chloride is a violet solid with a melting point of 1152° and is generally prepared by halogenation of the metal or by reacting SOC1<sub>2</sub> with the hydrated chloride. 58

I. Historical Summary

The earlier work of Nicholls and Whiting<sup>29</sup> with arene chromium

tricarbonyl complexes developed the groundwork for numerous studies on the effect of coordination with the Cr(CO), group; however, few reports have described the chemistry of arylsilane metal complexes. There appear to be no reports of their reactions at high pressures. The substances  $PhSiMe_3Cr(CO)_3$ , <sup>69</sup> p-(Me\_3Si)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>Cr(CO)<sub>3</sub>, <sup>70</sup> and p-Me<sub>3</sub>  $SiC_{6}H_{4}RCr(CO)_{3}^{71}$  where R = NMe<sub>2</sub> or Me have been reported as well as some novel compounds of the general formula (PhRSiCH2XCH2)Cr(CO)3 (R = Ph when  $X = CH_2$  and R = Me when  $X = SiMe_2$ ) which contain silicon in a small ring.<sup>72</sup> Recently a Russian patent<sup>73</sup> alluded to compounds of the type reported in this research. The free phenylchlorosilanes have been reported inert toward anhydrous HC1 at temperatures up to 200°.<sup>21,23,39,40</sup> The reaction of Cr metal with anhydrous HCl has been reported to yield  $CrCl_2$  and  $H_2$ , <sup>61,62</sup> but only at temperatures in excess of 600°. Other workers have reported data on the reduction of CrCl<sub>3</sub> to CrCl<sub>2</sub> as

$$2CrC1_2 + H_2 = 2CrC1_2 + 2HC1$$
 (34)

Finally Cr(CO) has been reported unreactive to anhydrous HC1.58

#### CHAPTER II

#### EXPERIMENTAL

#### A. Vacuum Systems and Techniques

It is a standard procedure to handle volatile material that is air sensitive or poisonous in a vacuum system, but the technique is also extremely useful for manipulating small amounts of material since the system is essentially closed and loss of material is difficult. The basic principles of vacuum systems have been described  $^{75-78}$  and only the details most applicable to this research are described in the following sections.

1. <u>Vacuum System</u>: All work at reduced pressures was done in a vacuum system constructed of borosilicate (Pyrex 7740) glass, Teflon quick-opening stopcocks (Fischer and Porter Co., Warminster, Pa.; #9285C40) and precision ground high vacuum glass stopcocks (Eck and Krebs; Long Island, N. Y.; #P5010). The various parts of the vacuum system and the apparatus connected to it were joined in several ways. Removable conical joints with standard taper (S) 12/30 were used and lubricated with Apiezon M grease as were any ground glass stopcocks. The system was evacuated using a Model 1405 "Welch Duo-Seal" forepump in series with a liquid nitrogen trap. Prior to the mainpulation of any material, the entire system was evacuated to its maximum capacity,
usually  $10^{-3}$  to  $10^{-4}$  mm Hg. (The system with fresh, degassed grease and pump oil could be evacuated to 5 x  $10^{-5}$  mm Hg).

2. <u>Pressure Measurements</u>: Pressures of less than one atmosphere were measured using a mercury manometer. The pressure was determined by measuring the level of the two columns with a meter stick calibrated in millimeters and readable to  $\pm$  0.3 mm. For very low pressures, more accurate measurements were made using a McLeod gauge.

3. <u>Temperature Measurements</u>: The temperature of the gases in the calibrated portion of the vacuum line was measured with a thermometer suspended directly next to the vacuum system. The temperature was read to  $\pm$  0.3° after thermal equilibration. Temperatures above room temperature were measured with a mercury thermometer or with a chromel-alumel thermocouple. A Leeds and Northup potentiometer (Model 8690) with a reference junction at 0° was used with the thermocouple.

Low temperature measurements were made using a pentane in glass thermometer (accurate to  $\pm 2^{\circ}$ ) or the chromel-alumel thermocouple.

4. <u>Production of Low Temperature-Slush Baths</u>: 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 solvents with appropriate melting points<sup>79,80</sup> (Table II). The addition of heat to the bath causes the solid to melt but will not raise the temperature.

Temperatures near the sublimation point of  $CO_2$  (-78°) were obtained as either acetone or isopropanol mixtures of "dry ice" and the solvent.

Freezing		Freezing	
Point °C	Compound	Point °C	Compound
+ 6.5	cyclohexane	-57.5	chloral
+ 5.7	nitrobenzene	-60.0	<b>amyln</b> aphthalene
+ 5.5	benzene	-63.5	chloroform
+ 2.0	eucalyptol	-70.0	1:1 mixture CC1, & CHC1,
0.0	H <sub>2</sub> O	-78.0	carbon dioxide/acetone mixture
- 6.0	acetonyl	-83.6	ethyl acetate
- 6.6	aniline	-89.5	isopropyl alcohol
- 9.0	methyl salicilate	-95.0	toluene
-11.0	diethyleneglycol	-96.7	methylene chloride
-12.0	t-amyl alcohol	-97.8	methano1
-15.3	benzyl alcohol	-111.6	carbon disulfide
-18.0	octyl alcohol	-112.4	n-butyl bromide
-20.0	butyl benzoate	-117.9	iso-propyl chloride
-22.9	carbon tetrachloride	-117.2	iso-amyl alcohol
-25.0	diethyl sulfate	-119.0	ethyl bromide
-30.6	bromobenzene	-120.0	ethanol
-33.0	chlorotolune	-122.8	n-propyl chloride
-33.0	dipsopyl ketone	-123.1	n-butyl chloride
-35.6	ethylene dichloride	-126.3	methylcyclohexane
-37.3	anisole	-127.0	n-propyl alcohol
-42.0	diethyl ketone	-129.0	allyl alcohol
-43.8	tetrachloroethane	-130.0	n-pentane
-45.0	cyclohexanone	-131.2	i-butyl bromide
-45.2	chlorobenzene	-136.4	ally1 chloride
-48.0	n-hexanol	-138.7	ethyl chloride
-50.0	ethyl malonate	-145.0	1:1 pentane & isopentane
-55.0	diacetone alcohol	-160.5	iso-pentane

## Table II. Slush Bath Temperatures

# 5. <u>Vacuum Separation of Volatile Materials</u>: Mixtures of volatile materials were separated by fractional condensation or vaporization, using traps maintained at low temperatures. The following notation will be used to facilitate descriptions of the various separations:

RT 
$$\sim -96^{\circ} \sim -196^{\circ}$$
 (n times)  
(A)  
(RT)  $\sim -134^{\circ} \sim -196^{\circ}$  (n times)  
(B) (C)

This diagram means that a mixture was allowed to warm to room temperature (RT) from -196° without applying any external heat and <u>without pumping</u>. As soon as all of the material had transferred, the stopcocks on the traps were closed. In special circumstances distillations were performed with pumping and this is specifically stated. The symbol "n" signifies that the material was distilled from a trap at one temperature to a trap at another temperature. In the above example, the material was passed through traps held at -96° and then condensed in a trap held at -196°. A vertical arrow indicates that a new distillation scheme was employed. A capital letter below the temperature signifies a fraction which was later identified. If no capital letter is present under a certain trap, this signifies that either the fraction in that trap was not identified or there was no material in the trap.

The "n times" signifies the following operations upon the trap:

$$\begin{array}{cccc} \text{RT} & \sim -96^{\circ} & \sim -196^{\circ} & (n=1) \\ & & \\ & \text{RT} & \sim -96^{\circ} & \sim -196^{\circ} & (n=2) \\ & & \\ & & \\ & & \text{RT} & \sim -96^{\circ} & \sim -196^{\circ} & (n=3) \\ & & & (A) & (B) \end{array}$$

The process ends when n is reached, that is when no more material is observed in the -196° trap. The process is then continued until no additional material is found in the -96° trap, for example:

RT 
$$\sim -96^{\circ} \sim -196^{\circ}$$
  
(A)  $\stackrel{+}{\text{RT}} \sim -96^{\circ} \sim -196^{\circ}$   
(A)  $\stackrel{+}{\text{RT}} \sim -96^{\circ} \sim -196^{\circ}$   
(A) (B)

Fractions with the same capital letter are combined.

6. <u>Molecular Weight Measurements</u>: The molecular weight (MW) of volatile compounds was determined using the method of Dumas. In such determinations the gas was assumed to follow the ideal gas equation since the pressure did not exceed 0.5 atmospheres. Knowledge of 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 an ideal gas,

$$PV = nRT = \frac{g}{MW} RT$$
 (35)

therefore,

$$MW = gRT/PV$$
(36)

where P = Pressure in atmospheres

V = Volume in liters R = Gas constant 0.08205  $\frac{1-atm}{K}$  mole g = Weight of sample in grams T = Temperature, °K

MW = Molecular weight.

Molecular weights of a two component mixture ("mixed molecular weight") were determined by use of the equation:

$$MW = f_1(MW)_1 + f_2(MW)_2$$
(37)

 $f_1, f_2$  = Mole fraction of component 1 and 2 MW<sub>1</sub>, MW<sub>2</sub> = Molecular weight of 1 and 2 MW = Molecular weight of mixture

A mathematical error analysis showed that the measurement of pressure without the aid of a cathetometer contributes most to the observed error. This error however is within the 1% criteria of purity.<sup>81</sup>

Care was taken not to carry out molecular weight determinations at the saturation vapor pressure at room temperature of materials. In such circumstances the molecular weight could be considerably in error due to absorption on the glass surfaces of the molecular weight bulb.

7. <u>Melting Point Measurements</u>: Melting points of compounds were obtained using sealed melting point capillaries (under Argon) and a heated aluminum block. All values reported are uncorrected.

8. <u>Commercial Analyses</u>: Commercial analysis was obtained from Galbraith Laboratories, Inc., Knoxville, Tennessee. Arc-emission spectra were obtained from the Department of Geology, University of Oklahoma. 9. <u>Criteria of Purity</u>: The purity of materials used in this research was checked by at least two of 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. Vapor pressure at a known temperature to within 1% of
 the calculated (or literature) value or to within approximately ± 2.0
 mm Hg, whichever was the least.

c. Infrared spectrum to agree with a published spectrum or to a spectrum previously determined in this laboratory on a pure sample.

d. Commercial analyses on new compounds to agree within1-2% of the theoretical percentages.

e. Mass spectral fragmentation pattern. The mass spectra of mixed or pure compounds were frequently recorded in order to determine whether the fragmentation pattern was consistent with the properties of the mixture or pure compound expected on the basis of other measurements. When studying a pure compound, the identification of the parent molecular ion was considered to be of considerable importance but not absolutely required. The high sensitivity of the mass spectrometer was extensively employed for qualitative and gross quantitative interpretations of compounds.

f. Nuclear magnetic resonance spectrum to agreement with the expected ratio of the area under the resonance signals, the position of chemical shifts, and the nature of the fine structure observed in the signals. In addition, the absence of extraneous signals was used as an indication of a compound.

g. Melting or boiling point within  $\pm$  0.5° of the literature value, and a range not exceeding 1.5".

h. X-ray diffraction pattern matching published spectra with no extraneous peaks.

### B. Pressure Apparatus and Techniques

1. <u>High Pressure System</u>: The method employed to generate the high pressures involved both a thermal and a hydraulic intensifier technique. The general features of this system were first described by Moscony and MacDiarmid.<sup>82,83</sup> Since several modifications have been made on the system a detailed description will follow.

There are seven basic segments to the high pressure system: gas supply, gas pressure booster, hydraulic pump, temperature and pressure control unit, microreactor, appropriate values and connecting tubing, and finally the reaction container (gold tube).

a. Gas supply. The gas supply used was compressed nitrogen from a standard gas cylinder whose tank pressure was maintained between 2,000 and 2,700 psi. Other gases could be employed as the pressuring media; and, when the pressuring gas was also one of the reactants, the microreactor was used as the reaction container.

b. Gas booster. The gas was connected to the gas pressure booster (High Pressure Equipment Company, Erie, Pennsylvania) which consisted of a 60,000 psi booster cylinder with a thirty to one ratio of areas, a stroke length of six inches, and a 4.7 cubic inch volume displacement per stoke (Figure 2).

c. Hydraulic pump. The piston of the booster was actuated by an oil hydraulic ram system capable of supplying oil with a pressure





с С





35

Figure 4. Microreactor.

up to 3,000 psi. The maximum oil pressure was controlled by an adjustable relief valve (Waterman Hydraulics, Chicago, Illinois, model 1503-3-3000). The oil was driven by a hydraulic pump (Baldor Electric Company, Fort Smith, Arkansas, type 35C11-157) until the preset oil pressure was reached, then the relief valve bypassed the piston and returned the flow of oil to the reservoir.

d. Control unit. Next, the nitrogen gas was transmitted to the high pressure-high temperature hydrothermal research unit (Tem-Press Research, State College, Pennsylvania, Model HB-1B-4). This unit provided connections for four microreactors and included a furnace, an automatic temperature controller, and a high pressure Bourdon gauge for each position (Figure 3). The temperatures attained at the reactors were not the same as those shown on the controllers since there was a temperature gradient between the controlling thermocouple and the microreactor. In order to more accurately measure the temperature of reaction, a Chromel-alumel thermocouple was inserted into a thermocouple well in the wall of the microreactor and the temperature calculated from readings taken with a millivolt potentiometer (Leeds and Northrup Company, Philadelphia, Pennsylvania). By using measurements from a microreactor with several wells, temperatures monitored in the thermocouple wells were estimated to be within 2°C at lower temperatures and 5°C at temperatures above 400°C.

e. Microreactor. The microreactors (Tem-Press Research) were constructed from (250 mm o.d. x 7.5 mm i.d.) René 41 alloy and the assembly is shown in Figure 4. A two-way, straight, high pressure valve was added to the microreactor to prevent the loss of all pressure when the assembly was removed from the system.

For reactions conducted in the pressure range between 50 and 5,000 psi, the microreactor was fitted with a three way valve with two connections on the pressure side. One of these connections was used for the microreactor, and the second one was attached to a Bourdon gauge, which was calibrated for this lower pressure range.

The nipples, reducer, coupling glands, collars, and valves were constructed of Type 316 stainless steel. This assembly is tightened by means of a vise and wrench. The seals of the microreactor are hardened, hollow coned connecting tubing (nipples) which were pressed into conical metal seatings.

f. Connections. Capillary pressure tubing (1.6 mm o.d. x 0.16 mm i.d., 316 stainless steel) was used to connect the intensifier to the distribution manifold. This tubing was flexible and yet provides little volume. Appropriate "tee" joints, "cross" joints, and valves were mounted as required.

All parts of the high pressure system beyond the gas booster were rated for at least 60,000 psi and 300° for extended periods of time.

g. Reaction container. The final segment of the high pressure system was the reaction container. This unit consisted of encapsulating the reactants in a noble, malleable metal, in this case short lengths of 3.0 mm o.d. x 2.9 mm i.d. gold tubing. These ampules were placed in the microreactor where the pressure of the nitrogen gas was transferred to the reactants by pressing the maleable gold wall. The assumption was made that the gold tube was crushed until the pressure inside the tube was approximately equal to the pressure of the nitrogen gas.



Figure 5. Gold Tube Ready for Sealing.

gas. A discussion of the typical procedure for one experiment will further demonstrate the utility of this procedure.

A S 12/30 male ground glass joint was cut in half to produce a S 12/15 male joint. To the small end of the joint was joined a 10 mm segment of 3.0 mm i.d. glass tubing keeping the weight of the joint at a minimum. (A cap could be made using a similar procedure and a S 12/30 female joint.)

One end of a 40-cm length of gold tube was inserted into the small end of the connecting adaptor made above. The glass and gold were heated in a Meeker burner. "Black wax" (Apiezon W) was applied to the region where the gold entered the glass and the glass reheated to work the wax between the gold and glass. When the glass and wax cooled to room temperature a tight vacuum seal was formed.

The opposite end of the gold tube was flattened with smooth faced pliers. The flattened end was then sealed by melting the gold with a  $CH_4/O_2$  torch.

The gold tube was connected to vacuum system and evacuated to  $10^{-4}$  mm Hg and closed to the pump. One hour later the closed system was opened to a manometer, and if no pressure was detected, the seals were assumed to be leak free. This length of gold was sufficient for several experiments; the tube simply became shorter after each run. If the final seal, described below, was near enough to the black wax to cause it to flow, a moistened length of asbestos tape was wrapped around the seal to dissipate most of the heat. The gold tube is shown in Figure 5.

The gold tube and its male joint were weighed after which all manipulations were made by holding the tube with a clean, soft cotton

towel. Any solid reactant was deposited in the bottom of the gold tube by using a funnel whose stem (2.5 mm o.d., 400 mm length) was small enough to fit inside the gold tube. This procedure prevented the deposition of solid along the length of the gold tube. Such deposits caused errors in weighings since not all of the solid was in the final length of the ampule. Furthermore, if there was foreign material at the point of closure and sealing, a pressure tight seal could not be made and such gold ampules usually gave erroneous results. This sample addition was made in a dry bag under an inert atmosphere when using air sensitive materials. The cap was then used while weighing.

The gold tube was reconnected to the vacuum system and slowly evacuated. If the solid had a vapor pressure at 22° of greater than  $10^{-4}$  mm Hg the end of the tube was cooled below the 1 mm vapor pressure temperature but above -17°. This procedure allowed all gases and any water (1 mm v.p. = -17°<sup>84</sup>) to be removed from the reaction system without transferring any solid to the vacuum system. A high rate of evacuation also caused "bumping" of the solid and a consequent redistribution of the powder along the gold tube and into the vacuum system.

A portion of the previously purified volatile gas was expanded into a calibrated portion of the vacuum system which included the mercury manometer. After the gas and vacuum system attained thermal equilibrium, the amount of gas was determined by an ideal gas law calculation using the known folume (V) of the calibrated vacuum line (which included a correction for the volume of the manometer), the temperature (T) (measured with a thermometer calibrated to 0.1° and

hanging on the vacuum line), and the pressure (P) (measured to  $\pm$  0.3 mm Hg). This amount of gas was condensed into the lower end of the gold tube at -196°.

The amount of volatile gas added was also determined at a later stage by a weighing procedure, if the gold tube did not rupture at room temperature. The two methods produced values that agreed to within 0.5%.

The gold tube was flattened with the pliers at a point approximately 8 cm from the bottom of the gold tube, with care taken to ensure that the edges of the tube were touching. The liquid nitrogen level was moved as close as possible to the seal and a seal made with a  $H_2/O_2$  torch using one of the following procedures.

If all of the reactants had 1 mm vapor pressure temperatures that were significantly higher than -196°, the flattened portion of gold tube was heated with a larger and cooler flame to dull red and until the metal just barely melted. Then a smaller but hotter flame was used to cut the gold tube at a point above the seal. The ampule was dropped into a dewar of liquid nitrogen for temporary storage. During these manipulations the bottom of the gold tube was held with a large pair of tweezers which were also convenient for extraction of the gold ampules from dewars.

If any of the reactants had a 1 mm vapor pressure close to -196° the above procedure could allow some material to escape because of the low heat capacity of the liquid nitrogen and gold tube. When such conditions existed, a rapid cut, made with a small, hot flame, produced the best results.

If several gold ampules were stored in the same dewar, a thin wire was wrapped around the ampule and identification made on a tab attached to the other end. Such a wire also served as a convenient handle when transfers were conducted.

The bottom portion of the microreactor was held near its top by a heavy vice and the bottom was cooled to -196°, ensuring that the hollow cavity was completely filled with liquid nitrogen. The gold tube was removed from its dewar and inserted into the microreactor and the liquid level again increased to the top of the microreactor. If the liquid nitrogen level in the microreactor was maintained, less nitrogen gas from the gas cylinder was required to reach a specified pressure.

The cap nut was then tightened with a 16-in wrench. The required torque was not measured but gained through experience. The complete microreactor was attached to the high temperature-high pressure hydrothermal research unit. The bottom of the microreactor was maintained at -196° through the employment of a dewar and moveable "jack" resting on the furnace unit. The microreactor was pressured to the final specified pressure before removing the dewar, and then heated to the desired temperature while maintaining the pressure by slowly bleeding the excess pressure.

The microreactor was held at these conditions for 18 hours to ensure attainment of equilibrium before rapid cooling in ice water and then liquid nitrogen. During the cooling period the pressure was maintained at the reaction pressure again through a "bleed" valve. Only after the microreactor had reached a temperature of  $-196^{\circ}$  was the

pressure slowly released.

While at -196° the microreactor was remounted in the vice, the cap nut removed, and the frozen gold ampule extracted by inverting the microreactor. Again temporary storage was provided by a dewar of liquid nitrogen.

A gold tube opening device (Figure 6), was constructed from a large, solid glass, vacuum stopcock, a \$ 12/30 male, a \$ 19/22 male, and a \$ 19/22 female ground glass joint. Glass beads were used in the bottom of the opener to adjust the final position of the gold ampule which must extend into the bore of the stopcock. The cap, which allowed direct and rapid insertion of the gold ampule into the device, was held secure by heavy rubber bands.

The gold tube was dropped into the cutting device and the cap secured. The bottom of the device containing the glass beads was cooled to -196°. (The stopcock was not allowed to cool because the grease would freeze and caused leaks.) The entire system was evacuated through three -196° traps. If no leaks were detected the opener was warmed to room temperature and  $H_20$ ,  $CO_2$  and any other condensable material previously on the gold surface were removed. (The  $H_20$  condensed on the ampules during transfer operations in the open air.) Again a check was made for leaks. If the ampule did not leak at 22°/  $10^{-4}$  mm Hg it was removed from the cutter and weighed. This value employed in conjunction with the weight of solid reactants and the weight of the gold yielded a value for amount of volatile reactant used. If the tube was weighed, it was returned to the vacuum system and evacuated. The opening device was recooled to -196° and the





contents of the traps removed. The gold tube we the stopcock through the gold ampule, pinching : dewar was removed from the opener and all volat: in the first -196°. A check was made for any m produced by the reaction. If it was present in it was identified and then removed.

The material remaining in the -196° tr identified using the standard high vacuum techn other sections.

If the gold tube leaked (prior to cutt could be evacuated and the  $H_2^0$  removed, all vol collected in the first -196° trap and attempts the mixture. This procedure was not desirable, all indications of the presence of non-condense ampule were lost; the  $H_2^0$  or  $0_2$  could react wit and separation could be difficult.

2. Low Pressure Glass Systems:

a. Glass Pressure Reactor with Val container has been shown to withstand internal mospheres<sup>85</sup> and such a device is illustrated in wall cylindrical vessel, the maximum pressure is related to the ultimate tensile strength  $\sigma$ . to internal diameter K by the following equati

 $P = \sigma(K-1)$ 

The tensile strength of pyrex glass may be tak





contents of the traps removed. The gold tube was opened by turning the stopcock through the gold ampule, pinching it into two parts. The dewar was removed from the opener and all volatile material collected in the first -196°. A check was made for any noncondensable material produced by the reaction. If it was present in significant amounts, it was identified and then removed.

The material remaining in the -196° trap was separated and identified using the standard high vacuum techniques described in other sections.

If the gold tube leaked (prior to cutting) before the system could be evacuated and the  $H_2^0$  removed, all volatile material was collected in the first -196° trap and attempts were made to separate the mixture. This procedure was not desirable, though useful, since all indications of the presence of non-condensable material from the ampule were lost; the  $H_2^0$  or  $0_2$  could react with reactants or products; and separation could be difficult.

2. Low Pressure Glass Systems:

a. Glass Pressure Reactor with Valve. A cylindrical glass container has been shown to withstand internal pressures up to 50 atmospheres<sup>85</sup> and such a device is illustrated in Figure 7. For a thin wall cylindrical vessel, the maximum pressure (P) which can be contained is related to the ultimate tensile strength  $\sigma$  and the ratio of external to internal diameter K by the following equation:

$$\mathbf{P} = \sigma(\mathbf{K} - 1) \tag{38}$$

The tensile strength of pyrex glass may be taken as 120 atmospheres



Figure 7. Glass Pressure Reactor

for temperatures up to 200°.<sup>86</sup> It is prudent to allow a large safety factor when designing an experiment to account for unique stresses in each glass vessel.

This type of glass reactor was constructed from a 4 mm needle valve (Fischer and Porter Company, Warminster, Pennsylvania; cat. no. 795-609-0004). The autogenous pressure generated inside the glass vessel was estimated by using the ideal gas equation and the specified temperature, the volume of the container, and the known quantity of gas. It was found that cooling or heating the Teflon key to temperatures significantly different than room temperature caused gas leaks at the valve; therefore, only the bottom of the glass reactor could be manipulated with respect to temperature.

b. Glass Pressure Ampule. When a final temperature above 150° was desired, a glass pressure reactor without a Teflon valve was used (Figure 8). The procedure involved the use of a pyrex glass ampule constructed of heavy walled, borosilicate glass (35 mm o.d., 25 mm i.d., 250 mm long) with a 300 mm length of capillary tubing (10 mm o.d., 2.5 mm i.d.) attached to one end. The ampule had the same pressure rating as described in section B.2.a., if the final seal is properly annealled. The following discussion illustrates the use of this glass ampule.

Solid reagents were added to the reactor as a fine powder before joining the reactor to the vacuum system by the use of a Cajon ultratorr metal adapting system (Cajon Company; Cleveland, Ohio; cat. no. 6UT-6) (Figure 8). The volatile gas was condensed into the glass reactor at -196 and then the reactor sealed with a  $CH_4/O_2$  torch maintaining the maximum length of glass capullary tubing, but without overheating



Figure 8. Glass Pressure Ampule and Adapter.

the metal adaptor.

The entire glass ampule was placed in a vertical tube furnace. This type of glass ampule has contained 25 atmospheres at 300° for extended periods.

After cooling to 22° and then -196°, the glass ampule was opened by inserting the scored, capillary end into one end of a thick walled rubber vacuum hose. A male 3 12/30 male ground glass joint was inserted into the opposite end and both ends sealed with "black wax" (Apiezon W). After evacuating the entire system, the stem of the ampule was snapped at the scored mark; and any non-volatile gases were measured, identified, and removed.

All material which volatilized at  $22^{\circ}/10^{-4}$  mm Hg was separated by standard vacuum condensation techniques and any remaining solid was removed under an inert atmosphere in a glove bag.

### C. Ambient Pressure Apparatus and Techniques

1. <u>Strohmeier Apparatus</u>: All of the chromium tricarbonyl complexes were prepared under conditions similar to the original method of Nicholls and Whitting<sup>29</sup> using excess arylsilane as the only solvent. A Strohmeier apparatus<sup>87</sup> (Figure 9) was modified so that the reaction flask could be attached to the reflux apparatus with a ground glass male joint. This modification facilitated the transfer of reagents between the vacuum and reflux systems. It was found that warming the side arm to approximately 175° with a flexible heating tape (Briscoe Manufacturing Company, Columbus, Ohio; cat. no. BIH-4-1/2) increased the flow of hot arylsilane over the  $Cr(CO)_6$  which



Figure 9. Modified Strohmeier Apparatus.

had sublimed into the middle condensor. A Strohmeier apparatus of the general dimension described in the original paper was found suitable to handle approximately seven grams of  $Cr(CO)_6$  without clogging. A mercury bubbler was attached to the apparatus at the top condensor and a positive pressure ( $\sim$  30 mm Hg) of argon was maintained throughout the system during the entire time of reaction.

2. <u>General Synthesis of Chromium Tricarbonyl Complexes</u>: In a nitrogen filled glove bag, the appropriate liquid arylsilane was placed in a 50-ml round bottom flask with  $Cr(CO)_6$ . The container was closed with a ground glass stopcock attached to two ground glass joints before transfer from the dry bag to the vacuum system. The mixture was degassed by successive freezings to -196° and pumping at  $10^{-4}$  mm Hg. The flask was filled to atmospheric pressure with argon and transported to the Strohmeier apparatus which had a stream of argon flowing through it for at least five minutes.

A significant decrease in yields was observed when nitrogen was substituted for argon as the inert atmosphere. All initial attempts to synthesize these complexes using diglyme and other ether solvents were unsuccessful since any water or oxygen greatly reduced the yield of desired compounds. Mixture of viscous oils and green chromium salts were found and no adequate purification technique was found to purify these mixtures.

Attempts to purify these complexes by chromatographic techniques on alumina, florisil, or silica resulted in the apparent reaction of the silicon-halide bonds with the absorbant or no separation. All experiments were conducted in a dry-box under an argon atmosphere

and with degassed and purified solvents. The absorbants were heated under a vacuum for 7 days and pretreated with Me<sub>2</sub>SiCl<sub>2</sub>.

The reaction mixture was heated to reflux with a heating mantle and stirred with a Teflon coated magnetic stirring bar. Heating was continued until the  $Cr(CO)_6$  was completely consumed (approximately 16 hours or until excessive decomposition occurred. The resultant yellowbrown solution was cooled to room temperature under argon and the excess ligand was removed under vacuum at 50°/10<sup>-4</sup> mm Hg.

The remaining yellow solid was sublimed at least three times at  $70^{\circ}/10^{-4}$  mm Hg using liquid nitrogen in the cold finger of a vacuum sublimer. The sublimate consisted of a bright yellow solid which turned green in air. The compounds were placed under argon in screw cap glass vials, which had been taped and then sealed with black wax. The vials were stored at  $-10^{\circ}$  in the absence of light.

#### D. Spectroscopic Equipment and Techniques

1. <u>Infrared Absorption Spectra</u>: Infrared absorption spectra were obtained for volatile materials by confining a gaseous sample in a cell (10 cm path length) fitted with KBr (5 mm thick) windows which were sealed on with Glyptal resin. Infrared spectra of solid materials were taken with the solid dispersed in a mull (Nujol mineral oil or Kel-F #10 fluorocarbon oil), a KBr pellet, or as a solution in cyclohexane and CS<sub>2</sub>. When the oils were used, the samples were examined as a smear between KBr plates. Samples of air sensitive compounds were prepared under argon in a dry bag.

Absorption spectra were obtained in the 4,000 to 300  $\rm cm^{-1}$ 

region using a Beckman Model IR-10 double beam, grating spectrophotometer. In addition a Beckman Model IR-12 double beam grating spectrometer was used in the 2,200 to 1,700 cm<sup>-1</sup> range to obtain more accurate measurements of the carbonyl stretching frequencies of the complexes. The calibration of the IR-10 was checked after each spectrum with a polystyrene film.<sup>88</sup> For the high resolution spectra the IR-12 was calibrated with carbon monoxide gas<sup>89</sup> at 180 mm Hg in a 100-mm gas cell. Absorption maxima were located with a reproducibility of 1 cm<sup>-1</sup>.

2. <u>Nuclear Magnetic Resonance Spectra</u>: Proton magnetic resonance spectra were recorded on a Varian Associates T-60 spectrometer which was operated at a fixed frequency of 60 MHz. Spectra were obtained at 37° on spinning samples contained in sealed (5 mm o.d.) borosilicate (Pyrex) glass tubes.

Proton shifts in both the free arenes and complexes were measured on solutions of about 5% by weight in CC1<sub>4</sub> and cyclohexane. Cyclohexane was used as the internal reference, if not already present as the solvent, and all chemical shifts were adjusted to TMS by adding 1.42 ppm. Peak areas were measured using an electronic integrator.

3. <u>Mass Spectra</u>: Mass spectral fragmentation patterns were obtained using a Hitachi-Perkin Elmer RMU-7E Mass Spectrometer. The instrument was operated at an ionization potential of 70 electron volts, an ionization current of 50 microamperes, an ion source temperature of 100°, an accelerating potential of 3,600 volts, and a pressure of between  $10^{-6}$  and 5 x  $10^{-5}$  mm Hg as measured by the unit's vacuum gauge.

The solid samples were introduced into the ion source chamber by means of a direct sample-injection probe. The relative ion in-

tensities were estimated by measurement of the peak heights on the recorder chart paper. Intensities were reported relative to an arbitrary value of 100 assigned to the most abundant ion peak and as a percent of total ion current. The relative abundance of all isotope clusters was in agreement with the calculated pattern<sup>90</sup> except where noted. Perfluorokerosine was used as an internal standard to obtain m/e values for all compounds.<sup>91</sup>

4. <u>Powder X-ray Diffraction Spectra</u>: Power X-ray spectra<sup>92</sup> were obtained using a Norelco water cooled X-ray Diffraction unit, type 12046, with a copper target (CuKα 1.542A) and a nickel filter (0.00075 inch). The unit was operated at 40 kilovolts accelerating potential and 20 milliamps accelerating current. Samples were run as powders in a Debye-Scherrer camera (5.73 cm i.d.) or as a coating on a lithium borate glass slide with a diffractometer. When the camera was employed the powder was packed into a thin walled tube which was rotated. If the slide method was used, the sample was filtered through a 200 mesh wire screen on to a thin film of petroleum jelly.

E. Reagents

The reagents used in the course of this research were: <u>Antimony Trifluoride</u> - (SbF<sub>3</sub>, Ozark-Mahoning, lot PR 7-1-63) was heated at 150°/10<sup>-4</sup> mm Hg for 24 hours before use.

Argon - (Ar, Linde, High Purity) was used as obtained.

<u>Benzene</u> -  $(C_6H_6)$ , Fischer Scientific, reagent grade) was agitated with concentrated  $H_2SO_4$ , washed with  $H_2O$ , and then distilled three times. The benzene was stored over a column of Linde molecular sieves. Infrared<sup>93</sup> and mass<sup>94</sup> spectrum were identical to literature reports.

- <u>Benzene Chromium Tricarbonyl</u>  $((C_{6}H_{6})Cr(CO)_{3})$  was prepared by the general method described in section C.2 using excess benzene as the only solvent.  $Cr(CO)_{6}$  (10.2087 g, 0.0464 mol) and 100.0 ml of benzene (87.8 g, 1.124 mol) were reacted for 16 hours. The excess benzene was removed at  $22^{\circ}/10^{-4}$  mm Hg leaving a yellow solid which was sublimed three times yielding  $C_{6}H_{6}Cr(CO)_{3}$  (8.6644 g, 0.0405 mol). The infrared  $^{29,95,96}$  and mass  $^{97,98}$  spectra corresponded to literature reports as did the melting point.  $^{89}$
- <u>Carbon tetrachloride</u> (CCl<sub>4</sub>, Merck, reagent grade) was refluxed over  $P_A O_{10}$  followed by distillation.

Chlorodimethylphenylsilane - (PhSiMe<sub>2</sub>Cl, Pierce Chemical, lot 3092-10)

was fractionally distilled under an N<sub>2</sub> atmosphere before use; the infrared spectrum was identical to literature reports.<sup>99,100</sup> Chlorotrimethylsilane - (Me<sub>3</sub>SiCl, Peninsular Chemresearch) was

fractionally condensed as follows:

RT  $\sim -164^{\circ} \sim -196^{\circ}$  (3 times)  $\downarrow^{*}$ RT  $\sim -45^{\circ} \sim -196^{\circ}$  (3 times) A

Fraction A was retained as Me<sub>3</sub>SiCl, infrared<sup>101-103</sup> and mass<sup>104</sup> spectra were identical with literature reports. <u>Cyclohexane</u> - (C<sub>6</sub>H<sub>12</sub>, Mallinckrodt, Spectral grade, lot 72927) was dried over MgSO<sub>4</sub> before use.

Chromium Hexacarbonyl - (Cr(CO)<sub>6</sub>, Strem Chemical, lot 1343F) was

sublimed at 50°/10<sup>-4</sup> mm Hg before use. Infrared<sup>105,106</sup> and mass<sup>107,108</sup> spectra were identical to literature reports. <u>Dichlorodimethylsilane</u> - (Me<sub>2</sub>SiCl<sub>2</sub>, Peninsula Chemresearch) was

. fractionally condensed:

RT  $\sim -64^{\circ} \sim -196^{\circ}$  (3 times)  $\downarrow^{\downarrow}$ RT  $\sim -45^{\circ} \sim -196^{\circ}$  (3 times) A

Fraction A was retained as Me<sub>2</sub>SiCl<sub>2</sub>, infrared<sup>109-111</sup> and mass<sup>104,112</sup> spectra were identical to literature reports. <u>Dichloromethylphenylsilane</u> - (PhSiMeCl<sub>2</sub>, Dow Corning, lot 012871) was fractionally distilled under N<sub>2</sub> before use; infrared<sup>99,103</sup> and mass<sup>104</sup> spectra were identical to literature reports.

<u>Diethylether</u> - (Et<sub>2</sub>0, Mallinckrodt, reagent grade) was fractionally

distilled before use from a solution with LiAlH<sub>4</sub>.

<u>Diglyme</u> - (Dimethyl ether of diethylene glycol, Ansul Chemical) was refluxed over CaH<sub>2</sub> and then distilled.

Dimethylphenylsilane - (PhSiMe, H, Peninsula Chemresearch, lot 3456)

was fractionally distilled prior to use; the infrared spectrum 110,111 was identical to literature reports.

Gold - (H2, Au, Matthey Bishop) was heated under vacuum before use.

<u>Hydrogen</u> - (H<sub>2</sub>, Big Three Industries) was passed through a -196° trap before use.

<u>Hydrogen Chloride</u> - (HCl,, Matheson Gas Products, technical grade) was purified by vacuum condensation:

> RT  $\sim -160^{\circ} \sim -196^{\circ}$  (2 times)  $\downarrow^{\downarrow}$ RT  $\sim -130^{\circ} \sim -196^{\circ}$  (2 times) (A)

Fraction A was retained as HC1, the infrared<sup>93</sup> and mass<sup>113</sup> spectra were identical to literature reports.

- Lithium Aluminum Hydride (Alfa Inorganics, lot M1346) was refluxed for 24 hours with diethylether under a nitrogen atmosphere. The solution was filtered and the filtrate used as source of LiAlH,.
- <u>Mercury</u> (Hg, Bethlehem Apparatus Co., triple distilled) was used as obtained.

Methyltrichlorosilane - (MeSiCl<sub>2</sub>, Eastman, lot 7022) was distilled:

RT  $\sim -96^{\circ} \sim -196^{\circ}$  (3 times)  $\downarrow^{\downarrow}$ RT  $\sim -134^{\circ} \sim -196^{\circ}$  (2 times) (A)

Fraction A was retained as MeSiCl<sub>3</sub>. The infrared<sup>102,109</sup> and mass<sup>104,114</sup> spectra were identical to those published.

- <u>Nitrogen</u> (N<sub>2</sub> gas, Big Three Industries) was used as obtained when employed as the intensifying medium in the high pressure apparatus. <u>Liquid nitrogen</u> - (Linde, High Purity Dry) was used as obtained. Nitrogen gas for the dry bag and dry box was "bleed" gas from the liquid nitrogen cylinder.
- <u>Oxygen</u> (0<sub>2</sub>, Big Three Industries) was passed through a -96° trap at one atmosphere before use.

<u>Phenylsilane</u> - (PhSiH<sub>3</sub>) was prepared according to the procedure of Ward<sup>115</sup> using PhSiCl<sub>3</sub> (44.5 g, 0.210 mol) and LiAlH<sub>4</sub> (37.5 g, 0.99 mol). The mixture was fractionally distilled at reduced pressure and the fraction which distilled at 26-29°/ 18 mm Hg was saved. This clear liquid was purified by vacuum distillation as follows:

RT  $\sim -63.5^{\circ} \sim -196^{\circ}$  (5 times)

Fraction A was saved as PhSiH<sub>3</sub> (19.3 g, 0.178 mol, 84.8% yield) and had an infrared spectrum<sup>116</sup> and boiling point expected for PhSiH<sub>3</sub>, (Lit.<sup>117</sup> b.p. 29°/18.5 mm Hg).

Silicon Tetrafluoride - (SiF<sub>4</sub>, Matheson) was used as obtained; mol. wt. calcd. 104.1, found 104.2; infrared<sup>118,119</sup> and mass spectra<sup>120,121</sup> were identical to that given in the literature.

<u>Silver Tetrafluoroborate</u> - (AgBF<sub>4</sub>, Ozark-Mahoning, lot DW-2-134) was used as obtained.

Tetrachlorosilane - (SiCl, Union Carbide, lot 150080371) was

fractionally condensed before use:

RT  $\sim -130^{\circ} \sim -196^{\circ}$  (2 times)  $\downarrow^{\circ}$ RT  $\sim -112^{\circ} \sim -196^{\circ}$  (2 times) (A)

Fraction A was retained as SiCl<sub>4</sub>, infrared<sup>101,109</sup> and mass<sup>104</sup> spectra were identical to literature reports.

- <u>Toluene Chromium Tricarbonyl</u> (PhCH<sub>3</sub>Cr(CO)<sub>3</sub>, Strem Chemical, lot 355) was sublimed at  $70^{\circ}/10^{-4}$  mm Hg before use.
- Trichlorophenylsilane (PhSiCl<sub>3</sub>, Matheson, Coleman and Bell) was fractionally distilled under N<sub>2</sub> before use; infrared<sup>99,103,116,122</sup> and mass<sup>104</sup> spectra were identical to literature reports.
- <u>Trimethylphenylsilane</u> (PhSiMe<sub>3</sub>, Marshallton Research Laboratory, lot 29611) was fractionally distilled prior to use; the infrared spectrum<sup>123-125</sup> was identical to literature reports.

Zinc difluoride - (ZnF2, Ozark-Mahoning, lot R-6-67C) was heated at

150°/10<sup>-4</sup> mm Hg for 24 hours before use.

#### F. Experiments Conducted During This Research

#### 1. Syntheses of Complexes

a. Synthesis of  $PhSiCl_3Cr(CO)_3$ . The general procedure described in section C.2. was used to react phenyltrichlorosilane (29720 mg, 188.0 mmol) and  $Cr(CO)_6$  (6080 mg, 27.63 mmol). The resultant yellow solid was vacuum sublimed four times and consisted of  $PhSiCl_3Cr(CO)_3$  (6796 mg, 19.55 mmol; 70.8% yield based on initial  $Cr(CO)_6$ ; m.p. 107-109°; found: C, 31.27; H, 1.72; Cl, 30.38%;  $C_9H_5Cl_3CrO_3Si$  calcd.: C, 31.10; H, 1.45; Cl, 30.69%; IR v(C)) 1999 and 1939 cm<sup>-1</sup>).

b. Synthesis of  $PhSiMeCl_2Cr(CO)_3$ . The same procedure was used to react phenylmethyldichlorosilane (35594 mg, 186.2 mmol) and  $Cr(CO)_6$  5691 mg, 25.86 mmol) to form yellow  $PhSiCl_2MeCr(CO)_3$ (6390 mg, 19.53 mmol; 75.5% yield based on initial  $Cr(CO)_6$ ; m.p. 78-80°; found: C, 36.88; H, 2.60; Cl, 21.42%;  $C_{10}H_8Cl_2CrO_3Si$  calcd.: C, 36.71; H, 2.46; Cl, 21.67%; IR:  $\nu(CO)$  1993, 1933, and 1925 cm<sup>-1</sup>).

c. Synthesis of  $PhSiMe_2ClCr(CO)_3$ . The previous procedure was utilized to react phenyldimethylchlorosilane (275504 mg, 220.0 mmol) and  $Cr(CO)_6$  (8489 mg, 38.57 mmol) to form yellow  $PhSiClMe_2Cr(CO)_3$ (9392 mg, 30.62 mmol; 79.4% yield based on initial  $Cr(CO)_6$ ; m.p. 74-75°; found: C, 42.87; H, 3.50; Cl, 11.70%;  $C_{11}H_{11}ClCrO_3Si$  calcd.: C, 43.07; H, 3.61; Cl, 11.56%; IR:  $\nu(CO)$  1986, 1927, 1919 cm<sup>-1</sup>).

d. Synthesis of  $PhSiMe_3Cr(CO)_3$ . Following the previous procedure,  $PhSiMe_3$  (20163 mg, 134.2 mmol) and  $Cr(CO)_6$  (4153 mg, 18.87 mmol) were used to form yellow  $PhSiMe_3Cr(CO)_3$  (4921 mg, 17.19 mmol;
91.1% yield based on initial  $Cr(CO)_6$ ; m.p. 72-73°, lit.<sup>69</sup> 72-73°; IR: v(CO) 1982 and 1915 cm<sup>-1</sup>).

2. Reactions of the Complexes

a. Reactions of the Complexes with HCl at Autogenous Pressures.
 Summary: The reactions of the chromium tricarbonyl complexes
 with HCl at low pressure were found to cleave the silicon group from
 the aromatic ring yielding the appropriate chlorosilane and benzene
 chromium tricarbonyl.

i. Reaction of  $PhSiMe_3Cr(CO)_3$  with HC1. In a nitrogen filled glove bag  $PhSiMe_3Cr(CO)_3$  (175.4 mg, 0.6126 mmol) was placed in a 25-ml glass pressure reactor. The vessel was evacuated and an excess of HC1 (232.2 mg, 6.368 mmol) was condensed into the reactor. The stopcock was closed and the mixture was allowed to warm and stand at room temperature (22°) for 16 hours. The vessel was opened and the material which volatilized at  $22^{\circ}/10^{-4}$  mm Hg was transferred into the vacuum system. This material was separated by vacuum distillation as follows:

RT 
$$\sim -78^{\circ} \sim -196^{\circ}$$
 (3 times)  
(B)  
RT  $\sim -45^{\circ} \sim -196^{\circ}$  (3 times)  
(C) (A)

A yellow-green solid residue, part of which remained in the reactor, was removed and vacuum sublimed at  $70^{\circ}/10^{-4}$  mm Hg to produce a yellow sublimate (D) and a green residue (E). The following materials were identified from the final reaction mixture:

<u>Me<sub>3</sub>SiCl</u>: Fraction A (66.6 mg, 0.613 mmol; 100% yield based on initial complex; identified by infrared spectrum; 101-103 confirmed by mass spectrum 104). <u>HCl</u>: Fraction B (206.0 mg, 5.650 mmol; identified by infrared spectrum 93,126

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confirmed by mass spectrum<sup>113</sup>).

<u>C<sub>6</sub>H<sub>6</sub></u>: Fraction C (2.7 mg, 0.035 mmol; 5.6% yield based on initial complex; identified by infrared spectrum<sup>93</sup>).

<u> $C_{6}H_{6}Cr(C0)_{3}$ </u>: Fraction D (121.1 mg, 0.5655 mmol; 92.3% recovery based on initial complex; identified by infrared spectrum; <sup>29,95,96</sup> confirmed by mass spectrum; <sup>97,98</sup> and m.p.<sup>89</sup>).

<u>Cr<sub>2</sub>O<sub>3</sub></u>: Fraction E (2.8 mg, 0.018 mmol; 6.0% yield based on initial complex, identified by x-ray diffraction<sup>135</sup>).

ii. Reaction of PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub> with HCl. Using a procedure similar to that of the preceeding section, PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub> (193.1 mg, 0.6295 mmol) was reacted with HCl (266.2 mg, 7.302 mmol) at 22° for 24 hours. The volatile materials were vacuum distilled as previously outlined. The non-volatile green solid remaining in the reactor was vacuum sublimed to produce a yellow sublimate (D) and a green residue (E). The following material was identified as being in the final reaction mixture:

<u>Me\_SiCl\_2</u>: Fraction A (78.6 mg, 0.609 mmol; 96.8% yield based on initial complex; identified by infrared spectrum; 109-111 confirmed by mass spectrum 104-112).

<u>HC1</u>: Fraction B (244.0 mg, 6.693 mmol; identified by infrared spectrum<sup>93,126</sup>).

<u>C<sub>6</sub>H<sub>6</sub></u>: Fraction C (13.7 mg, 0.176 mmol; 28.0% yield based on initial complex; identified by infrared spectrum<sup>93</sup>).

 $\underline{C_{6}H_{6}Cr(CO)}_{3}$ : Fraction D (106.3 mg, 0.4963 mmol; 78.8% yield based on initial complex; identified by infrared spectrum; <sup>29,95,96</sup> confirmed by mass spectrum<sup>97,98</sup>).

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<u>Cr</u> $_{2^{-3}}$ : Fraction E (12.5 mg, 0.082 mmol; 26.0% yield based on initial complex; identified by x-ray diffraction<sup>135</sup>).

111. Reaction of  $PhSiMeCl_2Cr(CO)_3$  with HCl at 22°. Using a procedure similar to that of section F.2.a.i.,  $PhSiMeCl_2Cr(CO)_3$ (227.4 mg, 0.6942 mmol) was reacted with HCl (751.0 mg, 20.59 mmol) for 18 hours. All volatile material was vacuum separated as follows:

RT 
$$\sim -96^{\circ} \sim -196^{\circ}$$
 (2 times)  
 $\downarrow$  (A)  
RT  $\sim 15^{\circ} \sim -196^{\circ}$  (3 times)  
(B) (C)

The yellow solid remaining in the reactor was vacuum sublimed at  $70^{\circ}/10^{-4}$  mm Hg to a yellow sublimate (D) and a green residue (E). The following materials from the final reaction mixture were identified: <u>HC1</u>: Fraction A (737.9 mg, 20.24 mmol; 2.7% yield based on initial complex; identified by infrared spectrum; <sup>105,106</sup> confirmed by mass spectrum<sup>107,108</sup>).

 $\underline{Cr(CO)}_{6}$ : Fraction B (4.1 mg, 0.019 mmol; 2.7% yield based on initial complex; identified by infrared spectrum; 105,106 confirmed by mass spectrum 107,108).

<u>PhSiMeCl</u>: Fraction C (13.6 mg, 0.0712 mmol; 10.2% yield based on initial complex; identified by mass spectrum<sup>203</sup>).

PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub>: Fraction D, starting material (197.6 mg, 0.604 mmol; 87.0% recovery; identified by infrared spectrum;<sup>127</sup> confirmed by mass spectrum<sup>128</sup>).

<u>Cr<sub>2</sub>O<sub>3</sub></u>: Fraction E (2.4 mg; 0.016 mmol; 4.6% yield based on initial complex; identified by x-ray diffraction<sup>135</sup>).

iv. Reaction of  $PhSiMeCl_2Cr(CO)_3$  with HCl at 100°. Using the general procedure described in section F.2.a.i.,  $PhSiMeCl_2Cr(CO)_3$ (492.0 mg, 1.311 mmol) was reacted at 100° with HCl (310.1 mg, 8.505 mmol) for 15 hours. The volatile material was vacuum distilled as follows:

The non-volatile material from the reactor was vacuum sublimed to give a yellow sublimate (E) and pale green residue (F). The following materials from the final reaction mixture were identified: <u>HC1</u>: Fraction A (301.3 mg, 8.241 mmol; identified by infrared spectrum<sup>93,126</sup>).

<u>C\_H</u>: Fraction B (21.2 mg, 0.271 mmol; 20.7% yield based on initial complex; identified by infrared spectrum<sup>93</sup>).

<u>Cr(CO)</u><sub>6</sub>: Fraction C (trace amount; identified by infrared spectrum<sup>105,106</sup>). <u>MeSiCl</u><sub>3</sub>: Fraction D (38.1 mg, 0.254 mmol; 19.4% yield based on the initial complex; identified by infrared spectrum;<sup>78</sup> confirmed by mass spectrum<sup>104,114</sup>).

<u>PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub></u>: Fraction E, starting material (333.7 mg, 1.020 mmol; 77.8% recovery; identified by infrared spectrum;<sup>127</sup> confirmed by mass spectrum<sup>128</sup>).

<u>Cr</u> $_{2}$ <sup>O</sup> $_{3}$ : Fraction F (12.3 mg, 0.081 mmol; 12.2% yield based on initial complex).

v. Reaction of PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> with HCl at 150°. Using a procedure similar to that in section F.2.a.i., PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> (139.0 mg, 0.3999 mmol) was reacted with HCl (301.1 mg, 8.258 mmol) at 150° for 24 hours. All volatile material was vacuum distilled as follows:

RT 
$$\sim -78^{\circ} \sim -196^{\circ}$$
 (2 times)  
 $\downarrow$  (A)  
RT  $\sim 22^{\circ} \sim -196^{\circ}$  (2 times)  
(B) (C)

The yellow-green solid remaining in the reactor was vacuum sublimed at  $70^{\circ}/10^{-4}$  mm Hg to give a yellow solid (D) and a green residue (E). The following materials from the final reaction mixture were identified:

<u>HC1</u>: Fraction A (294.8 mg, 8.085 mmol; 97.9% recovery; identified by infrared spectrum<sup>93,126</sup>).

 $\underline{Cr(CO)}_6$ : Fraction B (traces, identified by infrared spectrum<sup>105,106</sup>). <u>PhSiCl\_3</u>: Fraction C (9.0 mg, 0.045 mmol; 11.2% yield based on initial complex; identified by mass spectrum<sup>104</sup>).

<u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub></u>: Fraction D (117.7 mg, 0.3386 mmol; 84.7% recovery; identified by mass spectrum<sup>129</sup>).

<u>Cr<sub>2</sub>0<sub>3</sub></u>: Fraction E (3.4 mg, 0.022 mmol; 11.0% yield based on initial complex; identified by x-ray diffraction<sup>135</sup>).

Similar reactions conducted at 0° and 100° gave no indications of reaction.

b. High Pressure Reactions of Arylsilane Complexes with HC1.

<u>Summary</u>: At high pressures HC1 was found to cleave the carbon-silicon bond of arylsilane chromium tricarbonyl complexes as shown:

$$(OC)_{3}CrPh-SiR_{3} + HC1 \rightarrow C_{6}H_{6}Cr(CO)_{3} + R_{3}SiC1$$
(39)

1. Reaction at  $150^{\circ}/4082$  atm. Using the general procedure described in section B.l.g.,  $PhSiCl_3Cr(CO)_3$  (43.0 mg, 0.123 mmol) was reacted in a gold tube with anhydrous HCl (93.8 mg, 2.57 mmol) at  $150^{\circ}/4082$  atm for 16 hours. When opened a small amount of noncondensable gas (A) was observed. All other volatile  $(22^{\circ}/10^{-4}$  mm Hg) material was vacuum distilled as follows:

RT 
$$\sim -78^{\circ} \sim -196^{\circ}$$
 (2 times)  
 $\downarrow$  (B)  
RT  $\sim -45^{\circ} \sim -196^{\circ}$  (2 times)  
 $\downarrow$  (C)  
RT  $\sim 0^{\circ} \sim -196^{\circ}$  (2 times)  
(D) (E)

The gold tube retained a red solid (F) which turned green in air. When heated to  $50^{\circ}/10^{-4}$  mm Hg a clear liquid (G) was condensed from the tube. All material was removed in a dry bag under an inert atmosphere.

The following materials from the final reaction mixture were identified:

<u>CO, H</u><sub>2</sub>: Fraction A (noncondensable gas; CO identified by infrared spectrum;<sup>93,126</sup> Co, H<sub>2</sub> confirmed by mass spectrum<sup>130</sup>). <u>HC1</u>: Fraction B (761.0 mg, 2.087 mmol; identified by infrared spectrum<sup>93,126</sup>). SiCl<sub>4</sub>: Fraction C (6.1 mg, 0.036 mmol; 29.1% yield based on initial complex; identified by infrared spectrum; <sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>).

<u>C\_6H\_6</u>: Fraction E (3.0 mg, 0.038 mmol; 31.1% yield based on initial complex; identified by infrared spectrum; <sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>Cr(CO)\_6</u>: Fraction D (18.2 mg, identified by infrared spectrum<sup>105,106</sup>). <u>CrCl\_3, CrCl\_2</u>: Fraction F ( $\sim$  17.1 mg red solid; qualitative test for Cr and Cl positive; identified by powder x-ray spectrum<sup>133-135</sup>). <u>PhSiCl\_3</u>: Fraction G (17.2 mg, 0.0813 mmol; 66.1% yield based on initial complex; identified by mass spectrum<sup>204</sup>).

2. Reaction at  $120^{\circ}/4082$  atm.

<u>Reactants</u>: PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> (43.3 mg, 0.125 mmol); HCl (64.2 mg, 1.76 mmol). <u>Final Reaction Mixture</u>: <u>SiCl</u><sub>4</sub> (5.3 mg, 0.031 mmol; 24.8% yield based on initial complex; identified by infrared spectrum; <sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>). <u>HCl</u> (61.6 mg, 1.69 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>C<sub>6</sub>H<sub>6</sub> (2.6 mg, 0.033 mmol; 26.6% yield based on initial</u> complex; identified by infrared spectrum, <sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> starting material (31.3 mg, 0.090 mmol; 72.0% yield based</u> on initial complex; identified by mass spectrum<sup>129</sup>).

3. Reaction at 100°/4082 atm.

<u>Reactants</u>: PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> (47.5 mg, 0.137 mmol); HCl (60.8 mg, 1.67 mmol). <u>Final Reaction Mixture</u>: <u>SiCl</u><sub>4</sub> (2.9 mg, 0.017 mmol; 12.5% yield based on initial complex; identified by infrared spectrum; <sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>). <u>HCl</u> (59.1 mg, 1.62 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>Cr(CO)</u><sub>6</sub> (1.4 mg, 0.0064 mmol; 4.7% yield based on initial complex; identified by infrared spectrum<sup>105,106</sup>). <u>C<sub>6</sub>H<sub>6</sub></u> (1.3 mg, 0.017 mmol; 12.1% yield based on initial complex; identified by infrared spectrum; <sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub></u>, <u>C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub></u> (identified by mass spectrum<sup>29,95,96,129</sup>). <u>CrCl<sub>3</sub></u>, <u>CrCl<sub>2</sub></u> (identified by powder x-ray spectrum<sup>133-135</sup>).

# 4. Reaction at 50°/4082 atm.

<u>Reactants</u>: <u>PhSiCl\_3Cr(CO)\_3</u> (89.3 mg, 0.257 mmol). <u>HCl</u> (127.6 mg, 3.50 mmol). <u>Final Reaction Mixture</u>: <u>CO, H<sub>2</sub></u> (noncondensable gas; identified by infrared<sup>93,126</sup> and mass spectrum<sup>130,136</sup>). <u>HCl</u> (125.7 mg, 3.45 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>Cr(CO)\_6</u> (1.0 mg, 0.004 mmol; 3.5% yield based on initial complex; identified by infrared spectrum<sup>105,106</sup>). <u>PhSiCl\_3Cr(CO)\_3</u>, starting material (83.2 mg, 0.239 mmol; 93% recovery.)

## 5. Reaction at 125°/1020 atm.

<u>Reactants</u>: <u>PhSiCl<sub>3</sub>Cr(CO)</u> (48.9 mg, 0.141 mmol). <u>HC1</u> (77.7 mg, 2.13 mmol). <u>Final Reaction Mixture</u>: <u>CrCl<sub>3</sub></u>, <u>CrCl<sub>2</sub></u> ( $\sim$  20.1 mg, violet solid; identified by powder x-ray spectrum<sup>133-135</sup>). <u>C<sub>6</sub>H<sub>6</sub></u> (1.7 mg, 0.022 mmol; 15.6% yield based on initial complex; identified by infrared spectrum;<sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>HC1</u> (64.9 mg, 1.78 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>SiCl<sub>4</sub></u> (3.0 mg, 0.0178 mmol; 12.6% based on initial complex; identified by infrared spectrum;<sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>). <u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> (38.2 mg, 0.110 mmol; identified by mass spectrum<sup>129</sup>).</u>

### 6. Reaction at 100°/1020 atm.

<u>Reactants</u>: <u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub></u> (71.4 mg, 0.205 mmol). <u>HCl</u> (269.6 mg, 7.394 mmol). <u>Final Reaction Mixture</u>: <u>SiCl<sub>4</sub></u> (1.1 mg, 0.006 mmol; 2.9% yield based on initial complex; identified by infrared spectrum; <sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>). <u>Cr(CO)<sub>6</sub></u> (5.8 mg, 0.026 mmol; 25.3% yield based on

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on initial complex; identified by infrared spectrum<sup>105,106</sup>). <u>HC1</u> (268.4 mg, 7.361 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub></u>, <u>C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub></u> ( $\sim$  65.9 mg; mixture of yellow solids; identified by mass spectrum<sup>29,95,96,129</sup>). <u>CO, H<sub>2</sub></u> (noncondensable gas; identified by infrared<sup>93,126</sup> and mass spectra<sup>130,136</sup>).

ii. Reaction of PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> with HCl at High Pressures.

<u>Summary</u>: Using the general procedure described in section B.l.g., PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> and HCl were found to react at high pressure to cleave the silicon-carbon bond and to form mixtures of CrCl<sub>3</sub> and CrCl<sub>3</sub>.

1. Reaction at 100°/4082 atm.

<u>Reactants: PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub></u> (316.0 mg, 0.966 mmol; <u>HCl</u> (127.6 mg, 3.50 mmol).

Final Reaction Mixture: MeSiCl<sub>3</sub> (147.0 mg, 0.983 mmol; 101.9% yield based on initial complex; identified by infrared spectrum;<sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>).  $\underline{C}_{6}\underline{H}_{6}$  (77.0 mg, 0.986 mmol; 102.0% yield based on initial complex; identified by infrared spectrum;<sup>93</sup> confirmed by mass spectrum<sup>94</sup>).  $\underline{Cr(CO)}_{6}$  (940 mg, 0.427 mmol; 88.4% yield based on initial complex; identified by infrared spectrum;<sup>105,106</sup> confirmed by mass spectrum<sup>107,108</sup>). <u>HC1</u> (69.3 mg, 1.90 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>CO, H<sub>2</sub></u> (noncondensable gas; molecular weight of 22.7 identified by mass spectrum<sup>130,137</sup>). <u>CrC1<sub>3</sub></u>, <u>CrC1<sub>2</sub></u> ( $\sim$  500 mg; identified by powder x-ray spectrum<sup>133-135</sup>).

# 2. Reaction at 55°/4082 atm.

<u>Reactants: PhSiMeCl<sub>2</sub>Cr(CO)</u> (49.5 mg, 0.151 mmol); <u>HCl</u> (150.6 mg, 4.13 mmol).

Final Reaction Mixture: CO, H<sub>2</sub> (noncondensable gas; identified by infrared<sup>93,120</sup> and mass spectra<sup>130,136</sup>); MeSiCl<sub>3</sub> (17.0 mg, 0.114 mmol; 75.1% yield based on initial complex; identified by infrared spectrum;<sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>). HCl (146.2 mg, 4.01 mmol; identified by infrared spectrum<sup>93,126</sup>). Cr(CO)<sub>6</sub> (4.2 mg, 0.0189 mmol; 25.0% yield based on initial complex; identified by infrared spectrum;<sup>105,106</sup> confirmed by mass spectrum<sup>107,108</sup>). C<sub>6</sub>H<sub>6</sub> (9.4 mg, 0.121 mmol; 80% yield based on initial complex. PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> (9.6 mg; 0.029 mmol; identified by mass spectrum.)

#### 3. Reaction at $22^{\circ}/4082$ atm.

<u>Reactants</u>: <u>PhSiMeCl<sub>2</sub>Cr(CO)</u> (41.9 mg, 0.128 mmol); <u>HCl</u> (149.8 mg, 4.11 mmol).

Final Reaction Mixture: PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> (39.9 mg, 0.122 mmol; 95.3% recovery; identified by mass spectrum<sup>128</sup>); <u>HCl</u> (150.2 mg, 4.12 mmol; identified by infrared spectrum; <sup>93,126</sup> <u>MeSiCl<sub>3</sub></u> (trace; identified by infrared spectrum; <sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>).

#### 4. Reaction at 100°/1020 atm.

<u>Reactants</u>: <u>PhSiMeCl\_Cr(CO)</u> (46.0 mg, 0.141 mmol); <u>HCl</u> (279.6 mg, 7.67 mmol).

<u>Final Reaction Mixture</u>: <u>MeSiCl</u><sub>3</sub> (7.0 mg, 0.047 mmol; 33.3% yield based on initial complex; identified by infrared spectrum; <sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>). <u>HCl</u> (277.1 mg, 7.60 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>Cr(CO)</u><sub>6</sub> (2.0 mg, 0.0091 mmol; 1.3% yield based on initial complex; identified by infrared spectrum<sup>105,106</sup>). <u>PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub>, C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> (mixture identified by mass spectrum<sup>29,95,96,128</sup>).</u>

#### 5. Reaction at 55°/1020 atm.

<u>Reactants</u>: <u>PhSiMeCl<sub>2</sub>Cr(CO)</u> (50.1 mg, 0.153 mmol); <u>HCl</u> (172.0 mg, 4.72 mmol).

Final Reaction Mixture: PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> (48.9 mg, 0.149 mmol; 97.4% recovery; identified by mass spectrum<sup>128</sup>). HCl (176.2 mg, 4.83 mmol; 102.3% recovery; identified by infrared spectrum<sup>93,126</sup>). Cr(CO)<sub>6</sub> (trace amounts; identified by infrared spectrum<sup>105,106</sup>).

6. Reaction at 22°/1020 atm. No apparent reaction was detected between PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> and HCl at 22°/1020 atm.

c. Reaction of  $C_{6}H_{6}Cr(CO)_{3}$  and HCl at 250°/4082 atm: <u>Summary</u>: Benzene chromium tricarbonyl reacts with HCl at 250°/4082 atm to yield CO,  $C_{6}H_{6}$ ,  $C_{6}H_{12}$ ,  $C_{6}H_{5}CH_{3}$ ,  $C_{6}H_{11}CH_{3}$  and  $CrCl_{3}$ .

Using the general procedure described in section B.l.g.,  $C_6H_6Cr(CO)_3$  (123.0 mg, 0.574 mmol) and HCl (228.3 mg, 6.26 mmol) were allowed to react at 250°/4082 atm for 16 hours. A noncondensable gas (A) was observed when the tube was opened. The volatile materials were separated:

> RT  $\sim -96^{\circ} \sim -196^{\circ}$  (3 times) (B) (C)

A violet solid (D) was recovered from the gold tube. The following materials from the final reaction mixture were identified: <u>CO</u>: Fraction A (small amounts; identified by infrared spectrum;<sup>93,126</sup> confirmed by mass spectrum<sup>130</sup>). <u>C<sub>6</sub>H<sub>6</sub>, C<sub>6</sub>H<sub>12</sub>, C<sub>6</sub>H<sub>5</sub>CH<sub>3</sub>, C<sub>6</sub>H<sub>11</sub>CH<sub>3</sub></u>: Fraction B (mixture of mainly benzene

and cyclohexene with traces of toluene and methylcyclohexane. Infrared<sup>93</sup> and mass<sup>94,138-140</sup> spectra were identical to those expected for the mixture).

<u>HC1</u>: Fraction C (161.9 mg, 4.44 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>CrC1<sub>3</sub></u>: Fraction D (89.2 mg, 0.563 mmol; violet solid identified by x-ray diffraction.

d. Reaction of  $C_{6}H_{6}Cr(CO)_{3}$  and  $H_{2}$  at 22°/5 atm: <u>Summary</u>: No apparent reaction occurred between  $C_{6}H_{6}Cr(CO)_{3}$  and  $H_{2}$  at 22° and 5 atmospheres.

Using the general procedure described in section F.2.a.i.,  $C_6H_6Cr(CO)_3$  (239.3 mg, 1.117 mmol) and H<sub>2</sub> (15.1 mg, 7.51 mmol) were allowed to react at 22° and autogenous pressure for 12 hours. Materials found in the final reaction mixture were:  $C_6H_6Cr(CO)_3$ : Starting material (231.5 mg, 1.081 mmol; 96.8% recovery; identified by infrared spectrum;<sup>29,95,96</sup> confirmed by mass spectrum<sup>97,98</sup>).  $H_2$ : (13.7 mg, 6.79 mmol; noncondensable gas; identified by mass spectrum<sup>136</sup>).

e. Reaction of  $C_{6}H_{6}Cr(CO)_{3}$  with MeSiCl<sub>3</sub> at 100°/4082 atm: <u>Summary</u>: There was no apparent reaction of MeSiCl<sub>3</sub> with  $C_{6}H_{6}Cr(CO)_{3}$  at 100°/4082 atm.

The general procedure described in section B.1.g. was used to react MeSiCl<sub>3</sub> (127.3 mg, 0.8516 mmol) and  $C_{6}H_{6}Cr(CO)_{3}$  (104.5 mg, 0.4880 mmol) at 100°/4082 atm for 16 hours. Materials which were volatile at 22°/10<sup>-4</sup> mm Hg were vacuum separated as follows:

A yellow solid (D) was recovered from the gold tube. The following materials were identified as being in the final reaction mixture: <u>MeSiCl\_3</u>: Fraction A (120.7 mg, 0.8074 mmol; 94.7% recovery; identified by infrared spectrum; 102,109 confirmed by mass spectrum 104,114). <u>C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub></u>: Fraction D (91.7 mg, 0.428 mmol; 87.7% recovery; identified by mass spectrum<sup>29,95,96</sup>).

f. Thermal Decomposition of Complexes:

i. Low Pressure.

<u>Summary</u>: The arylsilane chromium tricarbonyl complexes were found to undergo a small amount of decomposition (< 6%) at 100° according to the following equation:

$$2\operatorname{ArCr}(\operatorname{CO})_{2} \rightarrow \operatorname{Cr}(\operatorname{CO})_{4} + 2\operatorname{Ar} + \operatorname{Cr}^{\circ}$$
(40)

1. Thermal Decomposition of  $PhSiCl_3Cr(CO)_3$  at 100°. Under an argon atmosphere,  $PhSiCl_3Cr(CO)_3$  (48.0 mg, 0.138 mmol) was placed in a 30-ml glass pressure ampule. The ampule was evacuated to  $10^{-4}$  mm Hg and sealed. The glass ampule was heated to, and then held at 100° for 16 hours before cooling to -196°. When the vessel was opened, a manometer reading indicated only a very small amount of noncondensable gas (A) was present. A material (B) which was volatile at  $22^{\circ}/10^{-4}$  mm Hg was removed. A yellow solid (C) was recovered from the ampule under argon.

The following compounds were identified as being in the final

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reaction mixture:

<u>CO</u>: Fraction A (noncondensable gas; identified by mass spectrum<sup>130</sup>). <u>PhSiCl<sub>3</sub>, Cr(CO)<sub>6</sub></u>: Fraction B (2.8 mg; 5.8% decomposition; identified by mass spectrum<sup>99,103,105,106,116,122</sup>).

<u>PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub></u>: Fraction C (44.3 mg, 0.127 mmol; 92.4% recovery; identified by mass spectrum<sup>129</sup>).

2. Thermal Decomposition of  $PhSiMe_3Cr(CO)_3$  at 100°. Using the procedure from section F.2.f.i.1.  $PhSiMe_3Cr(CO)_3$  (248.0 mg, 0.8661 mmol) decomposed at 150° to give:

<u>PhSiMe</u><sub>3</sub>: (4.4 mg, 0.042 mmol; 4.9% yield based on initial complex; identified by infrared spectrum;<sup>123,124</sup> confirmed by mass spectrum). <u>Cr(CO)</u><sub>6</sub>: (4.2 mg, 0.019 mmol; 2.2% yield based on initial complex; identified by infrared spectrum;<sup>105,106</sup> confirmed by mass spectrum<sup>107,108</sup>). <u>PhSiMe<sub>3</sub>Cr(CO)<sub>3</sub>: (230.9 mg, 0.8063 mmol; 93.1 recovered; identified</u> by mass spectrum<sup>142</sup>).

3. Thermal Decomposition of  $PhSiMeCl_2Cr(CO)_3$  at 100°. Using the procedure from section F.2.f.i.1.,  $PhSiMeCl_2Cr(CO)_3$ (386.6 mg, 1.182 mmol) decomposed at 100° to give: <u>PhSiMeCl\_2</u>: (12.4 mg, 0.065 mmol; 5.5% yield; identified by infrared spectrum; <sup>99,103,105,106,116,122</sup> confirmed by mass spectrum<sup>104</sup>). <u>Cr(CO)\_3</u>: (6.6 mg, 0.030 mmol; 2.5% yield, identified by infrared spectrum<sup>105,106</sup>). <u>PhSiMeCl\_2Cr(CO)\_3</u>: (358.5 mg, 1.096 mmol; 92.7% recovery; identified by mass spectrum<sup>147</sup>).

4. Thermal Decomposition of PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub> at
100°. Using the procedure found in section F.2.f.i.l., PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub>
(354.7 mg, 1.156 mmol) decomposed at 100° to give:

<u>PhSiMe<sub>2</sub>C1</u>: (6.3 mg, 0.0370 mmol; 3.2% yield; identified by infrared spectrum; <sup>99,100</sup> confirmed by mass spectrum<sup>104</sup>).

 $\underline{Cr(CO)}_6$ : (3.5 mg, 0.0162 mmol; 1.4% yield; identified by infrared spectrum; 105,106 confirmed by mass spectrum 107,108).

PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub>: (338.6 mg, 1.104 mmol; 95.5 recovery; identified by mass spectrum<sup>128</sup>).

ii. High Pressure Decomposition of Chromium Tricarbonyl Complexes:

<u>Summary</u>: The chromium tricarbonyl complexes of aromatic compounds were found to undergo a small amount (< 3%) of decomposition at 22°/4082 atm as summarized in the following equation:

$$2\operatorname{ArCr}(\operatorname{CO})_{3} \rightarrow 2\operatorname{Ar} + \operatorname{Cr}(\operatorname{CO})_{6} + \operatorname{Cr}^{\circ}$$
(41)

1. High Pressure Decomposition of  $PhSiMe_3Cr(CO)_3$ : Using the general procedure described in section B.l.g.,  $PhSiMe_3Cr(CO)_3$ (99.8 mg, 0.348 mmol) was heated to 22°/4082 atm in a gold ampule. After the tube was opened, the volatile material (22°/10<sup>-4</sup> mm Hg) was vacuum distilled as follows:

RT 
$$\sim +6^{\circ} \sim -196^{\circ}$$
 (2 times)  
(A) (B)

A yellow solid (C) was recovered from the gold ampule by sublimation leaving a dark solid residue. The following compounds were identified as present in the final mixture:

 $\underline{Cr(CO)}_6$ : Fraction A (trace amount; identified by infrared spectrum). <u>PhSiMe</u><sub>3</sub>: Fraction B (0.6 mg, 0.004 mmol; 1% yield based on initial complex; identified by mass spectrum<sup>141</sup>).

<u>PhSiMe<sub>3</sub>Cr(CO)<sub>3</sub></u>: Fraction C (95.3 mg, 0.333 mmol; 95.7% recovery; identified by mass spectrum<sup>142</sup>).

2. High Pressure Decomposition of  $PhSiMeCl_2Cr(CO)_3$ : When the general procedure described in section F.2.f.ii.l., was applied to  $PhSiMeCl_2Cr(CO)_3$  (200.0 mg, 0.611 mmol) at 22°/4082 atm, the following materials were identified in the final reaction mixture.

PhSiMeCl\_Cr(CO)\_3: (192.5 mg, 0.588 mmol; 96.3% recovery; identified by mass spectrum<sup>128</sup>).

 $\underline{Cr(CO)}_6$ : ( $\sim$  0.8 mg, 0.004 mmol; 1.2% yield based on initial complex; identified by infrared spectrum<sup>105,106</sup>).

<u>PhSiMeC1</u><sub>2</sub>: (1.2 mg, 0.0063 mmol; 1.0% yield based on initial complex; identified by mass spectrum<sup>203</sup>).

3. High Pressure Decomposition of  $C_6H_6Cr(CO)_3$ : When the general procedure described in section B.l.g. was applied to  $C_6H_6Cr(CO)_3$  (69.2 mg, 0.323 mmol) at 200°/4082 atm, the following materials were identified from the final reaction mixture.

<u>C\_H\_6</u>: (23.9 mg, 0.306 mmol; 94.7% yield based on initial complex; identified by infrared spectrum; <sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>Cr(CO)\_6</u>: (26.8 mg, 0.122 mmol; 75.3% yield based on initial complex; identified by infrared spectrum; <sup>105,106</sup> confirmed by mass spectrum<sup>107,108</sup>). <u>Black solid</u>: (Power x-ray diffraction showed no crystalline materials except Cr°; <sup>135</sup> positive qualitative test for chromium).

4. High Pressure Decomposition of  $PhCH_3Cr(CO)_3$ : When the general procedure described in section B.l.g. was applied to  $PhCH_3Cr(CO)_3$  (125.9 mg, 0.552 mmol) at 22°/4082 atm, no apparent reaction was detected.

g. Reaction of Arylsilane Chromiumtricarbonyl Complexes with H<sub>2</sub>O:

<u>Summary</u>: The arylsilane chromium tricarbonyl complexes reacted with degassed  $H_2^0$  at 25° to yield substances containing Si-O-Si linkages and Cr(CO)<sub>3</sub> groups complexed with some of the phenyl groups as shown in the following equation:

$$PhSiMe_{x y}Cr(CO)_{3} + H_{2}O \rightarrow (PhSiMe_{x y/2})_{m}Cr(CO)_{3} + yHC1$$
(42)

i. Reaction of  $PhSiCl_3Cr(CO)_3$  with  $H_2O$ . Under a nitrogen atmosphere  $PhSiCl_3Cr(CO)_3$  (60.2 mg, 0.173 mmol) was placed in a glass pressure reactor. The reactor was evacuated to  $10^{-4}$  mm Hg and degassed  $H_2O$  (1000.0 mg, 55.5 mmol) was condensed into the vessel at -196°. The reactor was permitted to warm to, and held at, room temperature for 16 hours. After cooling to -196°, the reactor gave no indications of the presence of a noncondensable gas. The material which volatized at  $22^{\circ}/10^{-4}$ mm Hg was separated in the vacuum system as follows:

RT 
$$\sim -78^{\circ} \sim -196^{\circ}$$
 (2 times)  
(A) (B)

The yellow nonvolatile residue (C) was removed from the reactor in a dry bag. The following substances from the final reaction mixture were identified:

<u>H<sub>2</sub>O</u>: Fraction A (994.3 mg, 55.18 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>HC1</u>: Fraction B (14.1 mg, 0.387 mmol; 74.5% yield based on initial complex; identified by infrared spectrum<sup>93,126</sup>).

 $(PhSiO_{3/2})_{x}Cr(CO)_{3}$ : Fraction C (identified by mass spectrum as a complex mixture of silicone polymers with  $Cr(CO)_{3}$  groups present; the infrared contained a broad band at 1040 cm<sup>-1</sup> (v-SiOSi),<sup>122,143</sup> and two broad bands at 1950 and 1890 cm<sup>-1</sup> (v-CO of  $Cr(CO)_{3}$  group);<sup>122</sup> but there was no apparent band due to the Si-Cl bond).

ii. Reaction of  $PhSiMeCl_2Cr(CO)_3$  with  $H_2O$ : When the

above procedure was applied to  $PhSiMeCl_2Cr(CO)_3$  (193.6 mg, 0.592 mmol) and H<sub>2</sub>O (995.8 mg, 55.26 mmol), the substances in the final mixture were:

<u>HC1</u>: (29.9 mg, 0.819 mmol, 69.2% yield based on initial complex; identified by infrared spectrum<sup>93,126</sup>).

<u>(PhSiMeO)  $Cr(CO)_3$ </u>: (identified by mass spectrum<sup>122</sup> as a complex mixture of silicone polymers with Cr(CO)<sub>3</sub> groups present; the infrared spectrum contained bands at 1030 ( $\nu$  Si-O),<sup>122,143</sup> 1265 ( $\delta$  SiCH<sub>3</sub>),<sup>122</sup> 1975 ( $\nu$  C-O) and 1900 cm<sup>-1</sup> ( $\nu$  CO)).

111. Reaction of  $PhSiMe_2ClCr(CO)_3$  with  $H_2O$ : Using the procedure described in section F.2.g.i.,  $PhSiMe_2ClCr(CO)_3$  (508.0 mg, 1.66 mmol) and degassed  $H_2O$  (1113.0 mg, 61.76 mmol) was reacted for 20 hours. The following materials were identified as being in the final reaction mixture.

<u>HC1</u>: (60.9 mg, 1.67 mmol; 100.6% yield based on the initial complex; identified by infrared spectrum 93,126).

<u>H\_20</u>: (1088.9 mg, 60.43 mmol; identified by infrared spectrum  $^{93,126}$ ). <u>PhSiMe\_0HCr(CO)\_3, (PhSiMe\_2)\_0Cr(CO)\_3</u>: (identified by mass spectrum to contain chromium tricarbonyl complexes of the silanol and siloxane  $^{122}$ ).

iv. Reaction of  $PhSiMe_3Cr(CO)_3$  with  $H_2O$ : PhSiMe\_3Cr(CO)\_3 was not observed to react with degassed  $H_2O$  at 22°.

h. Reaction of Arylsilane Complexes with  $0_2$ : <u>Summary</u>: The major reaction at 0° between an arylsilane chromium tricarbonyl complex and  $0_2$  was incomplete oxidation to HCl,  $H_20$ ,  $C0_2$ ,  $Cr_20_3$  and silicon dioxide.

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1. Reaction of PhSiCl<sub>2</sub>Cr(CO)<sub>2</sub> with O<sub>2</sub>:

In a nitrogen atmosphere  $PhSiCl_3Cr(CO)_3$  (85.0 mg, 0.245 mmol) was placed in a glass pressure reactor. The reactor was evacuated to  $10^{-4}$  mm Hg and O<sub>2</sub> (~ 1 ml) was condensed into the vessel at -196°/ 1 atm. The reactor was allowed to warm towards room temperature. At approximately 0° an extremely violent and exothermic reaction occurred, resulting in the rupture of the glass vessel during most of the attempts). The vessel was cooled to -196° and opened to a manometer. The noncondensable, O<sub>2</sub>, was removed. The remaining volatile material  $(22^{\circ}/10^{-4} mm Hg)$  was vacuum distilled as follows:

RT 
$$\sim -145^{\circ} \sim -196^{\circ}$$
 (5 times)  
 $\downarrow$  (A)  
RT  $\sim -45^{\circ} \sim -196^{\circ}$  (3 times)  
(B) (C)

A dark-green solid (D) was recovered from the reactor.

The following materials were identified as being in the final reaction mixture:

<u>HC1</u>: Fraction A (25.3 mg, 0.697 mmol; 94.8% yield based on C1 in initial complex; identified by infrared spectrum  $^{93,126}$ ). <u>H<sub>2</sub>0</u>: Fraction B (5.0 mg, 0.28 mmol; identified by infrared spectrum  $^{93,126}$ ). <u>CO<sub>2</sub></u>: Fraction C (897.0 mg, 2.038 mmol; 92.6% yield based on C in initial complex; identified by infrared spectrum;  $^{93,126}$  confirmed by mass spectrum  $^{137}$ ).

<u>Cr<sub>2</sub>O<sub>3</sub>, (SiO<sub>2</sub>)</u>: Fraction D (46.2 mg; identified by powder x-ray diffraction to contain  $Cr_2O_3^{135}$  and by arc-emission spectroscopy to contain silicon, assumed to be (SiO<sub>2</sub>)<sub>n</sub>). ii. Reaction of PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> with 0<sub>2</sub>:

Using the general procedure described in section F.2.h.i.,  $PhSiMeCl_2Cr(CO)_3$  (80.5 mg, 0.246 mmol) was reacted with excess  $O_2$  at room temperature. The following materials from the final mixture were identified:

HC1: (16.0 mg, 0.440 mmo1; 89.4% yield based on Cl in initial complex; identified by infrared spectrum<sup>93,126</sup>

<u>CO</u><sub>2</sub>: (30.8 mg, 0.701 mmol; 28.5% yield based on C in initial complex; identified by infrared spectrum;  $^{93,126}$  confirmed by mass spectrum  $^{137}$ ). <u>Cr(CO)</u><sub>6</sub>: (traces identified from infrared spectrum  $^{105,106}$ ). <u>C<sub>6</sub>H<sub>6</sub></u>: (4.1 mg, 0.052 mmol; 21.1% yield based on initial complex; identified by infrared spectrum  $^{93}$ ).

<u>Solid residue</u>: ( $\sim$  56.7 mg; shown by powder X-ray diffraction to contain  $Cr_2O_3^{135}$  and by arc emission spectroscopy to contain chromium and silicon in large amounts; infrared spectrum showed presence of Si-O-Si bonds<sup>122</sup>).

iii. Reaction of  $PhSiMe_2ClCr(CO)_3$  with  $0_2$ : When the general procedure described in section F.2.h.i. was used with  $PhSiMe_2ClCr(CO)_3$  (105.6 mg, 0.344 mmol) and excess  $0_2$  the following materials were found in the final reaction mixture: <u>HC1</u>: (11.6 mg, 0.318 mmol; 92.4% yield based on initial complex; identified by infrared spectrum<sup>93,126</sup>).

<u>CO</u><sub>2</sub>: (134.2 mg, 3.049 mmol; 80.6% yield based on initial complex; identified by infrared spectrum; <sup>93,126</sup> confirmed by mass spectrum<sup>137</sup>). <u>H<sub>2</sub>O</u>: (10.1 mg, 0.555 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>Cr(CO)</u><sub>6</sub>: (trace amounts detected in infrared spectrum<sup>105,106</sup>). <u>Dark solid</u>: (shown by powder X-ray diffraction to contain  $Cr_{2}O_{3}$ ).<sup>135</sup> iv. Reaction of  $PhSiMe_3Cr(CO)_3$  with  $O_2$ : Using the procedure described in section F.2.h.i.,  $PhSiMe_3Cr(CO)_3$  (189.1 mg, mmol) was reacted with excess  $O_2$  at room temperature. The following substances were identified as being in the final reaction mixture: <u>H\_20</u>: (74.9 mg, 4.16 mmol; 45.0% yield based on H in initial complex; identified by infrared spectrum<sup>93,126</sup>).

<u>CO</u><sub>2</sub>: (322.6 mg, 7.33 mmol; 92.5% yield based on C in initial complex; identified by infrared spectrum;  $^{93,126}$  confirmed by mass spectrum  $^{137}$ ). <u>PhSiMe</u><sub>3</sub>: (traces detected in infrared  $^{123,124}$  and mass spectra  $^{107,108}$ ). <u>Cr(CO)</u><sub>6</sub>: (traces detected in infrared  $^{105,106}$  and mass spectra <u>Cr<sub>2</sub>O<sub>3</sub>, (SiO<sub>2</sub>)</u><sub>n</sub>: (identified by powder X-ray diffraction to contain Cr<sub>2</sub>O<sub>3</sub><sup>135</sup> and by arc-emission spectroscopy to contain silicon, assumed to be (SiO<sub>2</sub>)<sub>n</sub>).

v. Reaction of PhCH Cr(CO) with Oxygen:

When the general procedure described in section F.2.h.i. was applied to  $PhCH_3Cr(CO)_3$  and  $O_2$ , no apparent reaction occurred at room temperature. During the reaction of  $PhCH_3Cr(CO)_3$  with  $O_2$  at 22°/4082 atm, the gold tube was melted by the exothermic reaction and all the material escaped.

vi. Reaction of  $C_6H_6Cr(CO)_3$  with Oxygen:

When the general procedure described in section F.2.h.i., was applied to  $C_6^{H_6}Cr(CO)_3$  and oxygen, no apparent reaction occurred at 22° after 24 hours.

3. Reactions of the Free Ligands:

a. Reaction of the Ligands with HCl at Autogenous Pressures: Summary: At low pressure and room temperature HCl was found to cleave the silicon-carbon bond of PhSiMe<sub>3</sub> and PhSiMe<sub>2</sub>Cl. Elevated temperatures were required to cleave the bond in PhSiMeCl<sub>2</sub> and no cleavage was observed in PhSiCl<sub>3</sub> at temperatures below 220°.

i. Reaction of  $PhSiMe_3$  with HCl at 25°:

In a nitrogen filled glove bag  $PhSiMe_3$  (468.5 mg, 3.117 mmol) was placed in a 25-ml glass pressure reactor. The vessel was attached to the vacuum system and degassed by successive freezings of the sample to -196° with appropriate pumping. Anhydrous HCl (558.4 mg, 15.31 mmol) was condensed into the reactor. The mixture was then allowed to warm and stand at room temperature (22°) for 16 hours. The vessel was then opened and the volatile material (22°/10<sup>-4</sup> mm Hg) transferred into the vacuum system. This mixture was separated by vacuum techniques as follows:

RT 
$$\sim -78^{\circ} \sim -196$$
 (3 times)  
 $\downarrow$  (A)  
RT  $\sim -45^{\circ} \sim -196$  (3 times)  
(B) (C)

The following compounds from the final reaction mixture were identified: <u>HC1</u>: Fraction A (443.7 mg, 12.17 mmol; identified by infrared spectrum<sup>93,126</sup>).

<u>C\_H</u>: Fraction B (216.9 mg, 2.777 mmol; 89.1% yield based on initial arylsilane; identified by infrared spectrum: <sup>93</sup> confirmed by mass spectrum<sup>94</sup>).

<u>Me\_SiCl</u>: Fraction C (337.9 mg, 3.110 mmol; 99.8% yield based on initial arylsilane; identified by infrared spectrum; <sup>101-103,109</sup> confirmed by mass spectrum<sup>104</sup>).

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ii. Reaction of PhSiMe<sub>2</sub>Cl with HCl at 22°: Using the general procedure described in section F.3.a.i., PhSiMe<sub>2</sub>Cl (783.9 mg, 4.592 mmol) was reacted at 22° with HCl (341.6 mg, 9.369 mmol) for 24 hours. After reaction the volatile material was vacuum distilled as follows leaving a liquid residue, D:

RT 
$$\sim -78^{\circ} \sim -196^{\circ}$$
 (3 times)  
 $\downarrow$  (A)  
RT  $\sim -45^{\circ} \sim -196^{\circ}$  (3 times)  
(B) (C)

The following materials from the final reaction mixture were identified: <u>HC1</u>: Fraction A (221 mg, 6.07 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>C<sub>6</sub>H<sub>6</sub></u>: Fraction B (246.1 mg, 3.150 mmol; 68.6% yield based on initial arylsilane; identified by infrared spectrum:<sup>93</sup> confirmed by mass spectrum<sup>94</sup>).

<u>Me<sub>2</sub>SiCl<sub>2</sub></u>: Fraction C (411.0 mg, 3.184 mmol; 69.3% yield based on initial arylsilane; identified by infrared spectrum; 109-111 confirmed by mass spectrum 104,112).

PhSiMe\_C1: Fraction D (425.4 mg, 1.387 mmol; 30.2% recovery; identified by mass spectrum<sup>99,116,122</sup>).

iii. Reaction of PhSiMeCl<sub>2</sub> with HCl:

1. Reaction at 200°: Using the general procedure described in section F.3.a.i., a mixture of  $PhSiMeCl_2$  (237.5 mg, 1.243 mmol) and HCl (148.8 mg, 4.081 mmol) were placed in the glass pressure ampule and heated to 200° for 16 hours. Material which was volatile at 22°/10<sup>-4</sup> mm Hg was vacuum distilled as follows:

 The following compounds from the final reaction mixture were identified: <u>HC1</u>: Fraction A (132.0 mg, 3.620 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>C<sub>6</sub>H<sub>6</sub></u>: Fraction B (32.2 mg, 0.425 mmol; 34.2% yield based on initial arylsilane, identified by infrared spectrum;<sup>93</sup> confirmed by mass spectrum<sup>94</sup>).

<u>SiMeCl</u><sub>3</sub>: Fraction C (61.9 mg, 0.413 mmol; 33.2% yield based on initial arylsilane; identified by infrared spectrum;<sup>102,109</sup> confirmed by mass spectrum<sup>104</sup>).

<u>PhSiMeCl</u><sub>2</sub>: Fraction D (155.6 mg, 0.814 mmol; 65.5% recovery; identified by infrared spectrum; <sup>99,103</sup> confirmed by mass spectrum<sup>104</sup>).

2. Reactions at 100°: Using the procedure described in sections F.2.a.i. and F.e.a.iii., PhSiMeCl<sub>2</sub> and HCl were reacted at 100° for 15 hours.

<u>Reactants</u>: <u>PhSiMeCl</u><sub>2</sub> (783.9 mg, 4.101 mmol); <u>HCl</u> (378.0 mg, 10.36 mmol).

<u>Final Reaction Mixture</u>: <u>PhSiMeCl</u> (779.4 mg, 4.078 mmol; 99.4% recovery; identified by infrared spectrum; <sup>99,103</sup> confirmed by mass spectrum<sup>104</sup>). <u>HCl</u>: (361.8 mg, 9.922 mmol; 95.8% recovery; identified by infrared spectrum<sup>93,126</sup>).

iv. Reaction of PhSiCl<sub>3</sub> with HCl at Autogeneous Pressures:
 1. Reaction at 220°: Using the general procedure
 described in section F.2.a.i. and F.3.a.i., PhSiCl<sub>3</sub> and HCl were re acted at 220° for 16 hours.

<u>Reactants</u>: <u>PhSiCl</u><sub>3</sub> (132.1 mg, 0.624 mmol); <u>HCl</u> (112.0 mg, 3.072 mmol).
<u>Final Reaction Mixture</u>: <u>PhSiCl</u><sub>3</sub> (129.7 mg, 0.613 mmol; 98.2% recovery;
identified by infrared spectrum;
99,103,116,122
confirmed by mass spectrum<sup>104</sup>;

<u>HC1</u>: (111.4 mg, 3.05 mmo1; 99.3% recovery; identified by infrared spectrum <sup>93,126</sup>).

2. Reactions conducted at 100° and 22° did not yield any cleavage products.

b. Reactions of Arenes at High Pressure:

i. Reaction of PhSiCl<sub>3</sub> with HCl at High Pressures: <u>Summary</u>: The reactions of PhSiCl<sub>3</sub> with HCl at high pressures were found to obey the general equation:

$$PhSiCl_{3} + HCl \rightarrow C_{2}H_{2} + SiCl_{4}$$
(43)

1. Reaction at 220°/4082 atm: Using the general procedure described in section B.1.g.,  $PhSiCl_3$  (132.1 mg, 0.6244 mmol) was reacted with HC1 (44.8 mg, 1.23 mmol) in a glass ampule at 220°/4082 atom for 24 hours. After cooling, the material which was volatile at 0°/10<sup>-4</sup> mm Hg was vacuum distilled as follows:

RT 
$$\sim -96^{\circ} \sim -196^{\circ}$$
 (2 times)  
 $\downarrow$  (A)  
RT  $\sim -45^{\circ} \sim -196^{\circ}$  (4 times)  
(B) (C)

A clear liquid (D) was left in the reaction vessel. The following compounds from the final reaction mixture were identified: <u>HC1</u>: Fraction A (40.5 mg, 1.11 mmol; identified by infrared spectrum<sup>93,126</sup>). <u> $C_{6}H_{6}$ </u>: Fraction B (10.7 mg, 0.137 mmol; 22.0% yield based on the initial arylsilane; identified by infrared spectrum;<sup>93</sup> confirmed by mass spectrum<sup>94</sup>).

SiCl<sub>4</sub>: Fraction C (18.5 mg, 0.109 mmol; 17.6% yield based on initial

arylsilane; identified by infrared spectrum; <sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>).

PhSiCl<sub>3</sub>: Fraction D (96.2 mg, 0.455 mmol; 72.9% recovery; identified by mass spectrum<sup>104</sup>).

#### 2. Reaction at 150°/4082 atm:

<u>Reactants:</u> PhSiCl<sub>3</sub> (66.2 mg, 0.313 mmol); <u>HCl</u> (88.6 mg, 2.43 mmol).
<u>Final Reaction Mixture:</u> PhSiCl<sub>3</sub> (55.1 mg, 0.260 mmol, 83.2% recovery;
identified by infrared spectrum<sup>93,126</sup>). <u>SiCl<sub>4</sub></u> (9.6 mg, 0.056 mmol;
17.9% yield based on initial arylsilane; identified by infrared spectrum;
<sup>126,131,132</sup> confirmed by mass spectrum<sup>104</sup>). <u>HCl</u> (86.6 mg, 2.37 mmol;
13.1% yield based on initial arylsilane; identified by mass spectrum<sup>94</sup>).

### 3. Reaction at 120°/4082 atm:

<u>Reactants</u>: <u>PhSiCl</u><sub>3</sub> (142.1 mg, 0.672 mmol); <u>HCl</u> (88.6 mg, 2.43 mmol). <u>Final Reaction Mixture</u>: <u>PhSiCl</u><sub>3</sub> (142.9 mg, 0.675 mmol; 100.4% recovery; identified by mass spectrum<sup>104</sup>). <u>HCl</u> (87.9 mg, 2.41 mmol; 99.2% recovery; identified by infrared spectrum<sup>93,126</sup>).

#### 4. Reaction at 200°/1020 atm:

<u>Reactants</u>: <u>PhSiCl</u><sub>3</sub> (141.3 mg, 0.668 mmol); <u>HCl</u> (155.0 mg, 4.25 mmol).
<u>Final Reaction Mixture</u>: <u>PhSiCl</u><sub>3</sub> (129.9 mg, 0.614 mmol; 91.9% recovery;
identified by infrared spectrum; <sup>99,103,116,122</sup> confirmed by mass spectrum <sup>104</sup>).
<u>HCl</u> (154.6 mg, 4.24 mmol; 99.8% recovery; identified by infrared spectrum <sup>93,126</sup>).

### 5. Reaction at 150°/1020 atm:

<u>Reactants:</u> <u>PhSiCl</u><sub>3</sub> (264.6 mg, 1.251 mmol); <u>HCl</u> (160.8 mg, 4.411 mmol). <u>Final Reaction Mixture</u>: <u>PhSiCl</u><sub>3</sub> (250.0 mg, 1.182 mmol; 94.5% recovery; identified by infrared spectrum;<sup>99,103,116,122</sup> confirmed by mass spectrum<sup>104</sup>). 11. Reaction of PhSiMeCl<sub>2</sub> with HCl at High Pressures: <u>Summary</u>: The reaction between PhSiMeCl<sub>2</sub> and HCl at high pressures was found to obey the general equation:

$$PhSiMeCl_{2} + HC1 \rightarrow C_{6}H_{6} + MeSiCl_{3}$$
(44)

1. Reaction at  $100^{\circ}/4082$  atm: Using the general procedure described in section B.l.g., PhSiMeCl<sub>2</sub> (59.4 mg, 0.311 mmol) was reacted with HCl (104.6 mg, 2.87 mmol) in a glass pressure reactor at  $100^{\circ}/4082$  atm for 14 hours. All material which was volatile at  $0^{\circ}/10^{-4}$  mm Hg was vacuum distilled as follows:

RT 
$$\sim -96^{\circ} \sim -196^{\circ}$$
 (3 times)  
 $\downarrow$  (A)  
RT  $\sim -45 -196^{\circ}$  (4 times)  
(B) (C)

A clear liquid (D) was retained in the glass reactor. The following compounds from the final reaction mixture were identified: <u>HC1</u>: Fraction A (96.6 mg, 2.65 mmol; identified by infrared spectrum<sup>93,126</sup>). <u> $C_{6}H_{6}$ </u>: Fraction B (18.0 mg, 0.23 mmol; 74.0% yield based on initial arylsilane; identified by infrared spectrum;<sup>93</sup> confirmed by mass spectrum<sup>94</sup>).

<u>MeSiCl</u><sub>3</sub>: Fraction C (26.0 mg, 0.177 mmol; 56.9% yield based on initial arylsilane; identified by infrared spectrum;<sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>).

<u>PhSiMeCl</u>: Fraction D (13.7 mg, 9.0978 mmol; 31.4% recovery; identified by mass spectrum<sup>104</sup>).

#### 2. Reaction at 50°/4082 atm:

<u>Reactants</u>: <u>PhSiMeCl</u> (59.1 mg, 0.309 mmol); <u>HCl</u> (36.5 mg, 1.00 mmol). <u>Final Reaction Mixture</u>: <u>MeSiCl</u> (22.2 mg, 0.148 mmol; 47.9% yield based on initial arylsilane; identified by infrared spectrum; <sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>). <u>C</u><sub>6</sub>H<sub>6</sub> (12.7 mg, 0.162 mmol; 52.4% yield based on initial arylsilane; identified by infrared spectrum; <sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>PhSiMeCl</u> (27.4 mg, 0.143 mmol; 46.3% recovery; identified by mass spectrum<sup>104</sup>). <u>HCl</u> (31.1 mg, 0.853 mmol; identified by infrared spectrum<sup>93,126</sup>).

3. Reaction at 22°/4082 atm:

<u>Reactants</u>: <u>PhSiMeCl</u> (59.4 mg, 0.311 mmol); <u>HCl</u> (58.7 mg, 1.61 mmol). <u>Final Reaction Mixture</u>: <u>MeSiCl</u> (2.9 mg, 0.019 mmol; 6.1% yield based on initial arylsilane; identified by infrared spectrum; <sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>). <u>C<sub>6</sub>H<sub>6</sub></u> (1.0 mg, 0.013 mmol; 4.2% yield based on initial arylsilane; identified by infrared spectrum; <sup>93</sup> confirmed by mass spectrum<sup>94</sup>). <u>HCl</u> (56.5 mg, 1.55 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>PhSiMeCl</u> (50.7 mg, 0.265 mmol; 85.2% recovery; identified by mass spectrum<sup>104</sup>).

## 4. Reaction at 50°/1020 atm:

<u>Reactants</u>: <u>PhSiMeCl</u><sub>2</sub> (59.4 mg, 0.311 mmol); <u>HCl</u> (40.8 mg, 1.12 mmol). <u>Final Reaction Mixture</u>: <u>PhSiMeCl</u><sub>2</sub> (56.2 mg, 0.294 mmol; 94.5% recovery; identified by mass spectrum<sup>104</sup>). <u>HCl</u> (40.4 mg, 1.11 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>MeSiCl</u><sub>3</sub> (1.3 mg, 0.0087 mmol; 2.8% yield based on initial arylsilane; identified by infrared spectrum;<sup>102,109</sup> confirmed by mass spectrum<sup>104,114</sup>). <u>C<sub>6</sub>H<sub>6</sub></u> (traces, detected in mass spectrum<sup>94</sup>). iii. Reaction of  $C_6H_6$  and HCl at 22°/4082 atm: No apparent reaction occurred between  $C_6H_6$  and HCl at 22°/4082 atm when reacted for 24 hours.

c. Reaction of the free Lignads with  $0_2$ :

i. Reaction of PhSiCl<sub>3</sub> with Oxygen: When the general procedure described in section F.2.h.i. was applied to PhSiCl<sub>3</sub> (1331 mg, 6.292 mmol) with excess oxygen at 22°, no apparent reaction occurred.

ii. Reaction of PhSiMeCl<sub>2</sub> with Oxygen: When the general procedure described in section F.2.h.i. was applied to PhSiMeCl<sub>2</sub> (1023 mg, 5.352 mmol) with excess oxygen at 22°, no apparent reaction was detected.

iii. Reaction of PhSiMe<sub>2</sub>Cl with Oxygen: When the general procedure described in section F.2.h.i. was applied to PhSiMe<sub>2</sub>Cl (985.8 mg, 5.774 mmol) with excess oxygen at 22°, no apparent reaction was detected.

iv. Reaction of PhSiMe<sub>3</sub> with Oxygen: When the general procedure described in section F.2.h.i. was applied to PhSiMe<sub>3</sub> (712.2 mg, 4.74 mmol) and excess oxygen at 22°, no apparent reaction was detected.

4. <u>High Pressure Reactions of Cr(CO)</u>, with HC1:

a. The Reaction of Cr(CO)<sub>6</sub> and HCl at High Pressures and Temperature Above 300°:

<u>Summary</u>: It was found that at 4000 atmospheres and temperatures in excess of 300° Cr(CO)<sub>6</sub> and HCl reacted in quantitative yields after 18 hours. The reaction is summarized by the following equations:

$$2Cr(CO)_{2} + 6HC1 \rightarrow 2CrCl_{2} + 3H_{2} + 12CO$$
 (45)

$$2CO \rightarrow CO_{2} + C \tag{46}$$

Equations 45 and 46 can be summed to yield the total equation:  $2Cr(CO)_6 + 6HC1 \rightarrow 2CrCl_3 + 3H_2 + 6CO_2 + 6C$  (47)

1. Chromium Hexacarbonyl and Hydrogen Chloride at 500°/4082 atm: Chromium hexacarbonyl (30.3 mg, 0.138 mmol) was placed in the gold tube and HCl (98.6 mg, 2.70 mmol) was condensed into the tube. The tube was sealed and held at 500°/4082 atm for 18 hours. When the tube was opened, a noncondensable gas (A) was observed. The remaining volatile material was distilled as follows:

> RT  $\sim -145^{\circ} \sim -196^{\circ}$  (5 times) B C

A clean separation could not be achieved and a mixed molecular weight measurement was used to obtain yields. A nonvoltaile, black solid (D) was removed from the gold ampule in a dry bag, and then water extracted in the presence of SnCl<sub>2</sub> to yield a black solid. The following materials were identified in the final reaction mixture.

<u>H</u><sub>2</sub>: Fraction A (small amounts; identified by mass spectrum<sup>136</sup>). <u>CO<sub>2</sub>, HC1</u>: Fraction B and C (2.675 mmol gas; infrared spectrum identical to that expected for a mixture of CO<sub>2</sub> and HC1;<sup>93,126</sup> confirmed by mass spectrum<sup>113,137</sup>). <u>CO<sub>2</sub></u> (19.2 mg, 0.437 mmol; 105.8% yield based on initial Cr(CO)<sub>6</sub>); <u>HC1</u> (81.6 mg, 2.24 mmol).

<u>CrCl<sub>3</sub>, C</u>: Fraction D (25.8 mg, powder x-ray spectrum identical to  $CrCl_3$ ;<sup>134,135</sup> the black solid was assumed to be powdered carbon. By difference  $CrCl_3$  was 21.2 mg, 0.134 mmol, 97.1% yield based on initial  $Cr(CO)_6$ ; C, 4.6 mg, 0.383 mmol, 92.5% yield based on  $Cr(CO)_6$ ). 11. Chromium Hexacarbonyl and HCl at  $350^{\circ}/4082$  atm: A procedure identical with part a above was conducted with Cr(CO)<sub>6</sub> (67.9 mg, 0.309 mmol) and HCl (170.9 mg, 4.687 mmol) at  $350^{\circ}/4000$  atm. The following materials were identified in the final reaction mixture: <u>H<sub>2</sub>, CO</u>: Fraction A (small amounts; identified by mass spectrum<sup>130,136</sup>). <u>CO<sub>2</sub>, HCl</u>: Fractions B and C (4.273 mmol gas; infrared spectrum identical to that expected for a mixture of CO<sub>2</sub> and HCl;<sup>93,126</sup> confirmed by mass spectrum;<sup>113,136</sup> CO<sub>2</sub> (022.7 mg, 0.515 mmol; 55.6% yield) based on Cr(CO)<sub>6</sub> employed; HCl (137.0 mg, 3.758 mmol).

<u>CrCl<sub>3</sub>, C</u>: Fraction D (54.9 mg, powder x-ray spectrum identical to  $CrCl_3$ ;<sup>135</sup> CrCl<sub>3</sub>, 49.0 mg, 0.309 mmol; 100.2% yield based on  $Cr(CO)_6$  employed, C, 5.9 mg, 0.49 mmol; 52.9% yield based on  $Cr(CO)_6$ .

b. The Reaction of Chromium Hexacarbonyl and Hydrogen Chloride at High Pressure and Temperatures at 300° and Below: <u>Summary</u>: It was found that  $Cr(CO)_6$  and HCl reacted at temperatures between 125° and 300° and high pressures according to one or both of the following equations:

$$2Cr(CO)_6 + 6HC1 \rightarrow 2CrCl_3 + 3H_2 + 12CO$$
 (48)

$$Cr(CO)_{6} + 2HC1 \rightarrow CrCl_{2} + H_{2} + 6CO$$
 (49)

i. Reaction of Cr(CO)<sub>6</sub> and HCl at 300°/4082 atm: Chromium hexacarbonyl (61.5 mg, 0.280 mmol) and hydrogen chloride 188.4 mg, 5.166 mmol) were reacted at 300°/4000 atm for 16 hours. When the gold ampule was opened a nonvolatile gas (A) was observed, identified and discarded. The volatile material was fractionally separated by the following procedure:

$$\begin{array}{ccc} \mathrm{RT} \sim 0^{\circ} \sim -196^{\circ} & (2 \text{ times}) \\ \mathrm{B} & \mathrm{C} \end{array}$$

A solid (D) was removed from the gold ampule under an inert atmosphere. The following materials were identified in the final reaction mixture:  $\underline{H}_{2}$ . CO: Fraction A (1.98 mmoles mixed molecular weight 26.2, mole fraction  $\underline{H}_{2}$  = 0.298, 1.2 mg, 0.59 mmol; mole fraction CO = 0.702, 38.9 mg, 1.39 mmol; mixture identified by mass spectrum<sup>113,136</sup>).  $\underline{Cr(CO)}_{6}$ : Fraction B (no  $Cr(CO)_{6}$  was found in this experiment but at milder conditions  $Cr(CO)_{6}$  was found in this fraction).  $\underline{HC1}$ : Fraction C (160.1 mg, 4.391 mmol; identified by infrared spectrum;<sup>93,126</sup> confirmed by mass spectrum<sup>113</sup>).

<u>CrCl<sub>3</sub>, CrCl<sub>2</sub></u>: Fraction D (42.0 mg; powder x-ray identical to that expected for a mixture of CrCl<sub>3</sub> and CrCl<sub>2</sub>;  $^{133-135}$  CrCl<sub>3</sub> (34.2 mg, 0.2158 mmol; 77.2% yield based on Cr(CO)<sub>6</sub> employed); yields are based on initial Cr(CO)<sub>6</sub> and final weight of solid. CrCl<sub>2</sub>, 7.8 mg, 0.063 mmol; 17.3% yield based on initial Cr(CO)<sub>6</sub>.

ii. Reaction of  $Cr(CO)_6$  and HCl at  $300^\circ/2041$  atm: <u>Reactants</u>:  $Cr(CO)_6$  (118.8 mg, 0.5398 mmol); HCl (262.4 mg, 7.196 mmol). <u>Final Reaction Mixture</u>: HCl (215.9 mg, 5.921 mmol);  $CrCl_3$  (34.5 mg, 0.218 mmol; 40.4% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$  (38.3 mg, 0.312 mmol; 57.8% yield based on initial  $Cr(CO)_6$ . Traces of H<sub>2</sub> and CO were observed.

iii. Reaction of  $Cr(CO)_6$  and HCl at  $300^\circ/612$  atm: <u>Reactants</u>:  $Cr(CO)_6$  (73.6 mg, 0.3467 mmol); HCl (117.3 mg, 4.864 mmol). <u>Final Reaction Mixture</u>: HCl (149.9 mg, 4.110 mmol);  $CrCl_3$  (9.5 mg, 0.0599 mmol; 17.3% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$ ;  $CrCl_2$  (35.2 mg, 0.287 mmol; 82.7% yield based on initial  $Cr(CO)_6$ ). Traces of H<sub>2</sub> and CO. iv. Reaction of  $Cr(CO)_6$  and HCl at  $300^\circ/340$  atm: <u>Reactants</u>:  $Cr(CO)_6$  (57.6 mg, 0.262 mmol); HCl (41.1 mg, 1.13 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (6.0 mg, 0.027 mmol); HCl (22.2 mg, 0.610 mmol);  $CrCl_3$  (7.7 mg, 0.049 mmol; 19% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$  (22.8 mg, 0.186 mmol; 71.0% yield based on initial  $Cr(CO)_6$ ); H<sub>2</sub> and CO in small amounts.

v. Reaction of  $Cr(CO)_6$  and HCl at 250°/4082 atm: <u>Reactants</u>:  $Cr(CO)_6$  (286.6 mg, 1.300 mmol); HCl (285.1 mg, 7.819 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (198.1 mg, 0.9001 mmol); HCl (249.2 mg, 6.834 mmol);  $CrCl_3$  )29.4 mg, 0.186 mmol; 14.3% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$  (26.4 mg, 0.214 mmol; 16.5% yield based on initial  $Cr(CO)_6$ ); H<sub>2</sub> and CO in small amounts.

vi. Reaction of  $Cr(CO)_6$  and HC1 at 250°/1020 atm: <u>Reactants</u>:  $Cr(CO)_6$  (105.1 mg, 0.4776 mmol); HC1 (124.2 mg, 3.408 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (57.3 mg, 0.260 mmol); HC1 (108.7 mg, 2.982 mmol);  $CrCl_3$  (0.4 mg, 0.002 mmol; 0.5% yield based on initial  $Cr(CO)_6$ ;  $CrCl_2$  (26.4 mg, 0.215 mmol; 45.0% yield based on initial  $Cr(CO)_6$ ); small amounts of H<sub>2</sub> and CO with mixed molecular weight of 27.0.

vii. Reaction of  $Cr(CO)_6$  and HCl at 250°/408 atm: <u>Reactants</u>:  $Cr(CO)_6$  (104.7 mg, 0.4757 mmol); HCl (96.1 mg, 2.63 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (58.0 mg, 0.264 mmol); HCl (78.7 mg, 2.16 mmol);  $CrCl_3$  (3.1 mg, 0.020 mmol; 4.1% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$  (23.7 mg, 0.193 mmol; 40.5% yield based on initial  $Cr(CO)_6$ ); small amounts of H<sub>2</sub> and CO.

viii. Reaction of Cr(CO)<sub>6</sub> and HCl at 200°/4082 atm: <u>Reactants</u>: Cr(CO)<sub>6</sub> (80.7 mg, 0.367 mmol); HCl (246.8 mg, 6.769 mmol).

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Final Reaction Mixture:  $Cr(CO)_6$  (72.6 mg, 0.330 mmol); HCl (242.8 mg, 6.658 mmol);  $CrCl_3$  (5.8 mg, 0.037 mmol; 10% yield based on initial  $Cr(CO)_6$ ); small amounts of H<sub>2</sub> and CO.

ix. Reaction of  $Cr(CO)_6$  and HCl at 200°/4082 atm: <u>Reactants</u>:  $Cr(CO)_6$  (49.5 mg, 0.225 mmol); HCl (184.0 mg, 5.048 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (44.3 mg, 0.201 mmol); HCl (178.4 mg, 4.892 mmol);  $CrCl_3$  (6.0 mg, 0.038 mmol; 17% yield based on initial  $Cr(CO)_6$ ); small amounts of H<sub>2</sub> and CO.

x. Reaction of  $Cr(CO)_6$  and HCl at 200°/612 atm: <u>Reactants</u>:  $Cr(CO)_6$  (91.4 mg, 0.415 mmol); HCl (204.0 mg, 5.596 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (78.0 mg, 0.354 mmol); HCl (198.0 mg, 5.430 mmol);  $CrCl_3$  (7.0 mg, 0.044 mmol; 11% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$  (2.0 mg, 0.016 mmol; 3.9% yield based on initial  $Cr(CO)_6$ ); small amounts of H<sub>2</sub> and CO.

xi. Reaction of  $Cr(CO)_6$  and HCl at 200°/340 atm: <u>Reactants</u>:  $Cr(CO)_6$  (66.6 mg, 0.303 mmol); HCl (65.1 mg, 1.79 mmol). <u>Final Reaction Mixture</u>: (5.9 mg, 0.037 mmol; 12% yield based on initial  $Cr(CO)_6$ );  $CrCl_2$  (1.6 mg, 0.013 mmol; 4.2% yield based on initial  $Cr(CO)_6$ ); small amounts of H<sub>2</sub> and CO.

xii. Reaction of  $Cr(CO)_6$  and HCl at  $150^{\circ}/4082$  atm: <u>Reactants</u>:  $Cr(CO)_6$  (68.4 mg, 0.311 mmol); HCl (37.9 mg, 1.04 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (68.2 mg, 0.310 mmol); HCl (38.0 mg, 1.04 mmol); CrCl<sub>3</sub> (trace amounts); H<sub>2</sub> and CO (trace amounts).

xiii. Reaction of  $Cr(CO)_6$  and HCl at 125°/4082 atm: <u>Reactants</u>:  $Cr(CO)_6$  (81.5 mg, 0.370 mmol); HCl (223.1 mg, 6.118 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_6$  (81.0 mg, 0.368 mmol); HCl (223.1 mg, 6.119 mmol). 5. The Low Pressure Reactions of Cr(CO), with HC1:

<u>Summary</u>: The reactions of  $Cr(CO)_6$  with HCl at autogenous pressures are reported in this section. It was found that  $Cr(CO)_6$  and HCl reacted at temperatures above 125° and at low pressures between 1 and 50 atm according to the following equation:

$$Cr(CO)_6 + 2HC1 \rightarrow CrC1_2 + H_2 + 6CO$$
 (50)

a. The Reaction of  $Cr(CO)_6$  and HCl at  $300^\circ/10$  atm: In this low pressure reaction  $Cr(CO)_6$  (0.0576 g, 0.2617 mmol) was placed in the glass pressure reactor then HCl (0.2221 g, 6.092 mmol) was condensed into a glass reactor and sealed with a torch. The ampule was held at  $300^\circ/10$  atm for 18 hours. The ampule was opened at -196° and a check made for noncondensable material (A). All material which volatilized at 22° was fractionally distilled by the following method:

 $\begin{array}{ccc} \text{RT} & \sim & 0^{\circ} & \sim & -196^{\circ} \\ & & & \text{B} & & \text{C} \end{array} \tag{2 times}$ 

A white and pink solid (D) was removed from the glass ampule in a N<sub>2</sub> atmosphere. The following materials were identified in the final reaction mixture:

<u>H<sub>2</sub>, CO</u>: Fraction A (mixed molecular weight of 24.4. CO was identified by infrared spectrum;  $^{93,126}$  confirmed by mass spectrum;  $^{130}$  H<sub>2</sub> identified by mass spectrum).  $^{136}$ 

<u>Cr(CO)</u><sub>6</sub>: Fraction B (3.0 mg, 0.014 mmol; identified by infrared spectrum; <sup>105,106</sup> confirmed by mass spectrum<sup>107,108</sup>).

<u>HC1</u>: Fraction C (203.4 mg, 5.578 mmol; identified by infrared spectrum; <sup>93,126</sup> confirmed by mass spectrum<sup>113</sup>).

<u>CrCl<sub>3</sub>, CrCl<sub>2</sub></u>: Fraction D (pink solid gives powder x-ray spectrum expected for CrCl<sub>3</sub> and CrCl<sub>2</sub>);<sup>133-135</sup> CrCl<sub>3</sub> (2.7 mg, 0.017 mmol; 6.5% yield based on initial Cr(CO)<sub>6</sub>); CrCl<sub>2</sub> (28.4 mg, 0.231 mmol; 88.3% yield based on initial Cr(CO)<sub>6</sub>).

b. Reaction of  $Cr(CO)_{6}$  and HCl at 200°/10 atm: <u>Reactants</u>:  $Cr(CO)_{6}$  (217.7 mg, 0.9893 mmol); HCl (266.9 mg, 7.320 mmol). <u>Final Reaction Mixture</u>:  $Cr(CO)_{6}$  (46.2 mg, 0.210 mmol); HCl (212.6 mg, 5.831 mmol);  $CrCl_{2}$  (93.6 mg, 0.762 mmol; 77.0% yield based on initial  $Cr(CO)_{6}$ ).

c. Reaction of Cr(CO)<sub>6</sub> and HCl at 150°/10 atm: See section B.2.1. and F.5.a. for general procedure.

<u>Reactants</u>: Cr(CO)<sub>6</sub> (170.7 mg, 0.7757 mmol); HCl (262.4 mg, 7.198 mmol). <u>Final Reaction Mixture</u>: Cr(CO)<sub>6</sub> (172.1 mg, 0.7820 mmol); HCl (263.1 mg, 7.215 mmol); CrCl<sub>2</sub> (trace).

6. Fluorination Attempts:

a. Reaction of  $PhSiMe_2ClCr(CO)_3 + AgBF_4$ : Solid AgBF\_4 (3.5877 g, 0.018429 mol) was mixed with  $PhSiMe_2ClCr(CO)_3$  (258.5 mg, 0.8427 mmol) in a glass pressure reactor under a niyrogen atmosphere. The reaction in the solid phase started shortly after mixing with the production of a gas. After 4 hours at room temperature all volatile material was collected in the vacuum line at -196°. A noncondensable gas (A) was detected, analyzed, and discarded. The remaining material was fractionally distilled as follows:

RT 
$$\sim -120^{\circ} \sim -196^{\circ}$$
 (3 times)  
 $\downarrow$  (B)  
RT  $\sim -78^{\circ} \sim -196^{\circ}$  (3 times)  
(C) (D)
The following compounds were identified in the final reaction mixture:

<u>CO</u>: Fraction A (noncondensable gas, molecular weight 29.1; infrared spectrum identical to that of CO with traces of  $BF_3$  present.<sup>126</sup> <u>BF\_3, SiF\_4, Me\_2SiF\_2, MeSiF\_3</u>: Fraction B (179.6 mg, infrared agreed with that expected for the mixture;<sup>118,119,126,144,145</sup> mass spectrum confirmed the mixture<sup>121</sup>).

<u>MeSiF<sub>3</sub>, Me<sub>2</sub>SiF<sub>2</sub></u>: Fraction D (39.6 mg, identified by infrared spectrum; <sup>144,145</sup> confirmed by mass spectrum<sup>121</sup>).

b. Reaction of  $PhSiMe_2C1$  with  $AgBR_4$ : Solid  $AgBF_4$  (5.2676 g, 0.027059 mol) was mixed with  $PhSiMe_2C1$  (1108.8 mg, 6.495 mmol) in a glass pressure reactor under a nitrogen atmosphere. An immediate exothermic reaction occurred. The mixture was held at 22° for 14 hours. The material which was volatile at 22°/10<sup>-4</sup> mm Hg was vacuum distilled as follows:

RT 
$$\sim -120^{\circ} \sim -196^{\circ}$$
 (3 times)  
 $\downarrow$  (A)  
RT  $\sim -78^{\circ} \sim -196^{\circ}$  (3 times)  
(B) (C)

Further attempts to purify the gases were unsuccessful. The following material was identified from the final reaction mixture:  $\underline{\text{SiF}_4, \text{Me}_2\text{SiF}_2, \text{MeSiF}_3, \text{BF}_3}$ : Fraction A (0.1796 g, identified by infrared spectrum; <sup>118</sup>, 119, 126, 144, 145</sup> confirmed by mass spectrum<sup>121</sup>).  $\underline{\text{MeSiF}_3, \text{Me}_2\text{SiF}_2}$ : Fraction C (0.2675 g, identified by infrared spectrum; <sup>118</sup>, 119, 126, 144, 145</sup> confirmed by mass spectrum<sup>121</sup>).

c. Reaction of  $PhSiMe_2ClCr(CO)_3$  with  $SbF_3$ : In a glass pressure reactor was placed  $PhSiMe_2ClCr(CO)_3$  (316.5 mg, 1.032 mmol) with SbF<sub>3</sub> (5.000 g, 0.0280 mol) using 25 ml of degassed diethylether as a solvent. The reactor was held at 30° for 12 hours when the ether solution was removed by filtration under a nitrogen atmosphere. The ether solution was fractionated by vacuum techniques as follows:

RT 
$$\sim -63^{\circ} \sim -196^{\circ}$$
 (3 times)  
(A)

The following materials were identified from the final reaction mixture: <u>PhSiMe\_F</u>: Fraction A (0.1373 g, 0.8903 mmol; 86.3% yield based on initial PhSiMe\_ClCr(CO)<sub>3</sub>; identified by infrared spectrum;<sup>146</sup> confirmed by mass spectrum.<sup>147</sup>

7. <u>Reaction of PhCH<sub>3</sub>Cr(CO)<sub>3</sub> with PhCCl<sub>3</sub></u>: Tolune chromium tricarbonyl (1.429 g, 15.51 mmol) was reacted with trichlorotoluene (13.470 g, 68.91 mmol) in the Strohmeier apparatus described in section C.2., using excess trichlorotoluene as the only solvent. The mixture was heated to 100° for 4 hours, when all solvent was removed at 30°/ $10^{-4}$  Hg leaving a dark solid. This solid was washed with five 10 ml portions of diethylether through a glass filter under a nitrogen atmosphere. The ether was stripped from the mixture leaving viscous, orange oil. The infrared spectrum was consistent with that expected for a mixture of PhCH<sub>3</sub>Cr(CO)<sub>3</sub>, <sup>96</sup> PhCCl<sub>2</sub>CCl<sub>2</sub>CCl<sub>2</sub>C<sub>6</sub>H<sub>5</sub><sup>148</sup> and other products, including polymeric compounds. Mass spectra agreed with this suggestion.

8. Reaction of  $Cr(CO)_6$  and PhCCl<sub>3</sub>: Chromium hexacarbonyl (5.254 g, 0.02387 mol) was mixed with PhCCl<sub>3</sub> (47.321 g, 0.2421 mol) in the Strohmeier apparatus. Shortly after applying heat, an extremely exothermic reaction occurred starting with a sudden change in color

to blue and then immediately to a dark brown viscous oil. Infrared and mass spectral data suggested the presence of  $PhCC1_2CC1_2Ph$  and a mixture of polymeric compounds with some of the phenyl groups  $\pi$ -bonded to  $Cr(CO)_3$  groups.

9. <u>Reaction of PhCF<sub>3</sub> and Cr(CO)<sub>6</sub></u>: Chromium hexacarbonyl (5.0755 g, 0.02306 mol) was refluxed with PhCF<sub>3</sub> (17.829 g, 0.12202 mol) in the Strohmeier apparatus using 50 ml of diglyme as the solvent. After 16 hours, the excess diglyme was removed at  $50^{\circ}/10^{-4}$  mm Hg producing a yellow oil mixed with a black solid. The oil was extracted with 50 ml diethylether leaving a dark green pyrophoric solid which gave a positive test for the presence of chromium. The ether was stripped (22°/200 mm Hg) from the yellow oil (B). Further attempts to purify the yellow oil were unsuccessful. The infrared and mass spectra corresponded to those expected for PhCF<sub>3</sub>Cr(CO)<sub>3</sub> mixed with traces of diglyme, PhCF<sub>3</sub> and other products, possibly including PhCF<sub>2</sub>CF<sub>2</sub>Ph and (PhCF<sub>2</sub>)<sub>x</sub>.

10. Reaction of PhSiH<sub>3</sub> and Cr(CO)<sub>6</sub>: Chromium hexacarbonyl 5.213 g, 0.02369 mol) was refluxed with PhSiH<sub>3</sub> (3.790 g, 0.05031 mol) in the Strohmeier apparatus using 90 ml of diglyme as the solvent. After 8 hours the excess solvent was removed at  $50^{\circ}/10^{-4}$  mm Hg and the resulting oily solid extracted with diethylether leaving a brown solid which was very soluble in acetone. The ether solution was stripped producing a yellow, oily solid. Further attempts at purification of either solid were unsuccessful. Mass spectra of both solids showed a complicated pattern suggesting a mixture of polymeric materials. The infrared spectra of both solids had two bands in the 2000 to 1850 cm<sup>-1</sup> region characteristic of the Cr(CO)<sub>3</sub> group, and the spectrum of the yellow

ether soluble solid showed a band at 2180 cm<sup>-1</sup>, indicative of Si-H bonds.  $^{122}$ 

11. Reaction of PhSiMe<sub>2</sub>H with Cr(CO)<sub>6</sub>: Chromium hexacarbonyl (4.9686 g, 0.022578 mol) was refluxed with PhSiMe<sub>2</sub>H (8.891 g, 0.06524 mol) in 30 ml of diglyme using the Strohmeier apparatus. After 10 hours, the excess solvent was removed at  $50^{\circ}/10^{-4}$  mm Hg and the resulting mixture was extracted with diethylether. After removing the ether a yellow oily solid resulted. Further attempts to purify this product were unsuccessful, but results suggested the presence of at least one major and two minor solid yellow products. The mass spectrum showed the fragmentation pattern and parent peak expected for PhSiMe<sub>2</sub>HCr(CO)<sub>3</sub>. The infrared spectrum contained band at 2175  $\nu$  (Si-H)<sup>122</sup>, 1980 and 1917 cm<sup>-1</sup> ( $\nu$  (CO) of Cr(CO)<sub>3</sub> group).<sup>95,96</sup>

The reaction was repeated using excess PhSiMe<sub>2</sub><sup>H</sup> as the only solvent. A resulting oily yellow solid gave data identical to that previously obtained.

12. Synthesis of PhSi(OEt)<sub>3</sub>: Chromium hexacarbonyl (3.9846 g, 0.018107 mol) was mixed in the Strohmeier apparatus with PhSi(OEt)<sub>3</sub> (10.923 g, 0.0454 mol) using 50 ml of diglyme as solvent. The solution was refluxed for 6 hours before performing a water-ether extraction with 50 ml portions of each liquid. The ether layer was saved and stripped at  $22^{\circ}/\sqrt{200}$  mm Hg leaving a yellow oil. Further attempts to purify this product were unsuccessful. Infrared and mass spectra confirmed the presence of PhSi(OEt)<sub>3</sub>Cr(CO)<sub>3</sub>.

#### 13. Reactions of Chromium with HC1:

<u>Summary</u>: Powdered chromium metal and anhydrous HCl reacted at high pressure to yield CrCl<sub>3</sub>, CrCl<sub>2</sub> and hydrogen.

a. Reaction of Cr with HCl at  $600^{\circ}/4082$  atm: Powdered chromium metal (37.1 mg, 0.714 mmol) was placed in the bottom of a gold tube using a long stem funnel made from 3 mm o.d. glass tubing and a disposable pipet. The gold tube was <u>slowly</u> evacuated to  $10^{-3}$  mm Hg and then heated to 300° with pumping for 15 minutes. After cooling, HCl (216.7 mg, 5.944 mmol) was condensed into the tube with liquid nitrogen. The gold tube was sealed and held at  $600^{\circ}/4082$  atm for 18 hours. When the tube was opened, a noncondensable gas (A) was observed. The quantity of gas was too small to obtain accurate data on its molecular weight or the amount of gas present. The remaining volatile material was vacuum distilled as follows:

> RT  $\sim -130^{\circ} \sim -196^{\circ}$  (2 times) (B)

A nonvolatile solid in the solid tube was extracted with ten 5-ml portions of distilled water leaving a nonsoluble metallic solid (C) and a water soluble product (D). The solid would also react with  $CCl_4$ , forming  $CHCl_3$ . This reaction indicates the presence of a metal hydride.<sup>197</sup>

The following materials were identified in the final reaction mixture:

<u>H</u><sub>2</sub>: Fraction A (small amounts; identified by mass spectrum<sup>136</sup>). <u>HC1</u>: Fraction B (200.1 mg, 5.488 mmol; identified by infrared spectrum<sup>93,126</sup>). <u>Cr</u>: Fraction C (23.6 mg, 0.454 mmol; 63.6% recovery; identified by powder x-ray diffraction<sup>135</sup>).

<u>Water soluble product</u>: Fraction D (31.5 mg; shown by powder x-ray diffraction to contain CrCl<sub>3</sub>.

b. Reaction of Cr and HCl at 500°/4082 atm:
<u>Reactants</u>: HCl (166.9 mg, 4.577 mmol), Cr (45.0 mg, 0.865 mmol).
<u>Final Reaction Mixture</u>: HCl (148.0 mg, 4.059 mmol), Cr (30.4 mg, 0.585 mmol; 67.6% recovery). Water soluble product (33.5 mg; violet solid shown by powder x-ray diffraction to contain CrCl<sub>2</sub><sup>134,135</sup>).

c. Reaction of Cr and HCl at 300°/4082 atm:
<u>Reactants</u>: HCl (58.8 mg, 1.614 mmol), Cr (43.0 mg, 0.827 mmol).
<u>Final Reaction Mixture</u>: HCl (48.5 mg, 1.330 mmol), Cr (30.5 mg,
0.587 mmol: 70.9% recovery). Water soluble product (26.0 mg, violet solid shown by powder x-ray diffraction to contain CrCl<sub>3</sub> and CrCl<sub>2</sub><sup>133-135</sup>).

d. Reaction of Cr and HCl at 120°/4082 atm:
<u>Reactants</u>: HCl (202.8 mg, 5.563 mmol), Cr (39.2 mg, 0.754 mmol).
<u>Final Reaction Mixture</u>: HCl (164.7 mg, 4.517 mmol), Cr (32.8 mg, 0.631 mmol; 83.7% recovery). Water soluble products (15.6 mg, violet solid shown by powder x-ray diffraction to contain CrCl<sub>3</sub><sup>134,135</sup> as the only crystalline compound.)

e. Reaction of Cr and HCl at 75°/4082 atm: <u>Reactants</u>: HCl (208.5 mg, 5.718 mmol), Cr (44.7 mg, 0.860 mmol). <u>Final Reaction Mixture</u>: HCl (201.5 mg, 5.527 mmol), Cr (39.7 mg, 0.764 mmol; 88.8% recovery). Water soluble product (11.7 mg).

f. Reaction of Cr and HCl at 24°/4082 atm: Reactants: HCl (229.6 mg, 6.296 mmol), Cr (82.4 mg, 1.585 mmol). Final Reaction Mixture: HCl (198.5 mg, 5.445 mmol), Cr (73.3 mg, 1.410 mmol; 89.0% recovery). Water soluble product (12.0 mg, identified by powder x-ray diffraction to contain  $CrCl_3^{134,135}$ ).

g. Reaction of Cr and HCl at 300°/340 atm:
<u>Reactants</u>: HCl (176.8 mg, 4.848 mmol), Cr (16.9 mg, 0.325 mmol).
<u>Final Reaction Mixture</u>: HCl (116.5 mg, 3.195 mmol), Cr (12.8 mg,
0.246 mmol; 75.7% recovery). Water soluble product (11.7 mg, pink
solid shown by powder x-ray diffraction to contain CrCl<sub>3</sub> and CrCl<sub>2</sub><sup>133-135</sup>).

h. Reaction of Cr and HCl at 200°/340 atm:
<u>Reactants</u>: HCl (250.3 mg, 6.865 mmol), Cr (117.4 mg, 2.258 mmol).
<u>Final Reaction Mixture</u>: HCl (230.9 mg, 6.334 mmol), Cr (105.1 mg,
2.021 mmol; 89.5% recovery). Water soluble product (19.8 mg, pink
solid shown by powder x-ray diffraction to contain CrCl<sub>3</sub> and CrCl<sub>2</sub><sup>133-135</sup>).

i. Reaction of Cr and HCl at 100°/340 atm:
<u>Reactants</u>: HCl (241.6 mg, 6.625 mmol), Cr (98.7 mg, 1.898 mmol).
<u>Final Reaction Mixture</u>: HCl (236.3 mg, 6.482 mmol), Cr (88.0 mg,
1.692 mmol; 89.2% recovery). Water soluble product (15.1 mg, white solid shown by powder x-ray diffraction to contain CrCl, <sup>133,135</sup>).

j. Reaction of Cr and HCl at 22°/340 atm: <u>Reactants</u>: HCl (181.3 mg, 4.972 mmol), Cr (120.3 mg, 2.314 mmol). <u>Final Reaction Mixture</u>: HCl (179.6 mg, 4.926 mmol), Cr (109.9 mg, 2.114 mmol; 91.4% recovery). Water soluble product (8.2 mg).

k. Reaction of Cr and HCl at 400°/10 atm:
<u>Reactants</u>: HCl (462.0 mg, 12.672 mmol), Cr (350.6 mg, 6.743 mmol).
<u>Final Reaction Mixture</u>: HCl (461.0 mg, 12.643 mmol), Cr (349.9 mg, 6.729 mmol; 99.8% recovery). Water soluble product (~1.2 mg, trace).

1. Reaction of Cr and HCl at 300°/10 atm:

<u>Reactants</u>: HCl (959.6 mg, 26.32 mmol), Cr (306.7 mg; 5.898 mmol). <u>Final Reaction Mixture</u>: HCl (957.8 mg, 26.27 mmol), Cr (304.1 mg, 5.849 mmol; 99.2% recovery). Water soluble product (1.6 mg).

m. Reaction of Cr and HCl at  $100^{\circ}/10$  atm: There was no apparent reaction between chromium and hydrogen chloride under these conditions.

### CHAPTER III

### DISCUSSION

### A. Arylsilane Chromium Tricarbonyl Complexes

### 1. Preparation of the $\pi$ -complexes:

All of the  $\pi$ -complexes were synthesized by a method similar to that of Nicholls and Whiting<sup>29</sup> (Table III). Initially nitrogen was used

$$Ar + Cr(CO)_{6} + ArCr(CO)_{3} + 3CO$$
 (51)

as an inert atmosphere, but the substitution of argon was found to produce higher yields and fewer undesirable side-reactions. The  $\pi$ -complexes of PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub>, PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> and PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub> were prepared for the first time from Cr(CO)<sub>6</sub> and the corresponding arylsilane. The compound, PhSiMe<sub>3</sub>Cr(CO)<sub>3</sub>, was prepared in greater yields than previously reported.<sup>69</sup> When argon was used as the inert atmosphere, no additional solvents were employed in the experiments which yielded the best results. The mixtures were held at their respective reflux temperatures until all of the Cr(CO)<sub>6</sub> was consumed or excessive decomposition occurred. In a normal reaction, when a temperature in excess of 100° was attained, the solution turned a pale yellow and then darkened to a brown color. The general reaction is typified by the equation for PhSiCl<sub>2</sub>.

$$PhSiCl_{3} + Cr(CO)_{6} \rightarrow PhSiCl_{3}Cr(CO)_{3} + 3CO$$
(52)

The reaction was conducted in a semi-closed system to exclude

### TABLE III

### Synthesis of Chromium Tricarbonyl Complexes

Product	Yield	M.p.	Calculated			Found		
			С	н	C1	С	H	Cl
PhSiCl <sub>3</sub> Cr(CO) <sub>3</sub>	70.8%	107-109°	31.10	1.45	30.69	31.27	1.72	30.38
PhSiMeC1 <sub>2</sub> Cr(CO) <sub>3</sub>	75.5%	78-80°	36.71	2.46	21.67	36.88	2.60	21.42
PhSiMe2ClCr(CO)3	79.4%	74-75°	43.07	3.61	11.56	42.87	3.50	11.70
$PhSiMe_3Cr(CO)_3^a$	91.1%	72-73°	-	-	-	-	-	-

a. Previously reported.<sup>69</sup>

oxygen and water but a mercury bubbler facilitated the removal of gaseous carbon monoxide, driving the reaction toward completion.

A second method was used to prepare PhSi(OEt)<sub>3</sub>Cr(CO)<sub>3</sub>, PhSiMe<sub>2</sub> HCr(CO)<sub>3</sub>, PhSiH<sub>3</sub>Cr(CO)<sub>3</sub> and PhCF<sub>3</sub>Cr(CO)<sub>3</sub> from Cr(CO)<sub>6</sub> and the proper aromatic compound. In these latter reactions, diglyme was employed as the solvent. In each case, a yellow solid was isolated by stripping off the solvent at  $50^{\circ}/10^{-4}$  mm Hg. The mass spectra and infrared spectra confirmed the presence of the desired  $\pi$ -complex but other impurities were also present. Recrystallization, sublimation and chromatography techniques failed to produce a product with a narrow melting point. The primary impurity appeared to be diglyme or a complex with diglyme as a ligand since diglyme was always observed in the infrared and mass spectra. This conclusion is also supported by the formation of diglyme complex when C<sub>6</sub>H<sub>6</sub>Mo(CO)<sub>3</sub> is heated in diglyme.<sup>149</sup>

$$C_6H_6Mo(CO)_3 + CH_3OCH_2CH_2OCH_2CH_2OCH_3 \rightarrow (dig)_3Mo(CO)_3$$
 (53)

A similar intermediate to II can be proposed with chromium as the central atom. This is one advantage of using diglyme as the solvent since the intermediate would not be predicted to be highly stable.

The important point of the preparation is the new procedures which eliminated most of the side reaction by using the modified Strohmeier apparatus,<sup>89</sup> to increase yields and prepare novel compounds.

#### 2. Thermal Decomposition:

The arene chromium tricarbonyls are generally thermally stable at temperatures below 250°.<sup>28</sup>  $C_{6}H_{6}Cr(CO)_{3}$  did not decompose in a mass spectrometer until a temperature of 300° was attained.<sup>150</sup> It is generally maintained that substituents which are electron-withdrawing decrease the extent of back-donation from the metal to the carbonyl ligand by decreasing the electron density on the metal.<sup>28</sup> Recently, it was reported that the effect on the aromatic ring of coordination with the  $Cr(CO)_{3}$ group was a considerable change of effective positive charge on the  $\sigma$ -orbitals and that no essential change of the  $\pi$ -electronic charge of the arene takes place.<sup>46-49</sup> Since the  $\pi$ -complexes prepared in this research generally had side-chains with large group electronegativities, and, as stated above, the  $Cr(CO)_{3}$  group withdraws electron density from the  $\sigma$ -orbitals, the question of thermal stability was of great interest.

All the arylsilane  $\pi$ -complexes were found to decompose only slightly at 180° when heated in vacuo for 6 hours, as summarized in Table IV. The volatile products of decomposition were Cr(CO)<sub>6</sub>, CO and the free arene. The general equation for decomposition can be written as:

$$2ArCr(CO)_{3} \xrightarrow{\text{heat}} 2Ar + Cr(CO)_{6} + Cr$$
(54)

Above 150° there was some additional decomposition of  $Cr(CO)_6$  to produce CO and more Cr.

This data was not totally unexpected since all the complexes were prepared at temperatures in excess of  $170^{\circ}$ . PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> was synthesized at temperatures above 200° with little decomposition as demonstrated by the large yield. The data does show that there are

TABLE	IV
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Complex	Temperature	Pressure, Atm	% Decomposition
PhSiCl <sub>3</sub> Cr(CO) <sub>3</sub>	100° 22° 22°	< 1 < 1 4082	5.8 0 1.0
PhSiMeC12 <sup>Cr(CO)</sup> 3	100° 22° 22°	< 1 < 1 4082	5.5 0 3.0
PhSiMe2ClCr(CO)3	100°	< 1	3.2
PhSiMe <sub>3</sub> Cr(CO) <sub>3</sub>	100°	< 1	4.9
PhHCr (CO) 3	200°	4082	95
PhCH <sub>3</sub> Cr (CO) <sub>3</sub>	22°	4082	0

Decomposition of Chromium Tricarbonyl Complexes\*

\* All reactions were held at stated reaction conditions for 6 hours.

no gross differences in the thermal stability due to changes in the group electronegativity of the side chain.

The stability of the complexes at 4082 atmospheres was also investigated and the results are also summarized in Table IV. The decomposition products at 22°/4082 atm were the same compounds observed at 200° and low pressures. It was observed that an increase in pressure to 4082 atmospheres caused a small amount of decomposition to occur at a temperature where no previous decomposition was detected. Thus the actual reactant in any reaction of the complexes under pressure with HCl to yield a chromium chloride could be Cr,  $Cr(CO)_6$  or some intermediate rather than the  $\pi$ -complex. It will be shown later that the reactant is not  $Cr(CO)_6$  since this compound does not react below 125° but the complex does. The possibility that chromium metal is the reactant has not been ruled out since 200 mesh chromium metal will react under conditions similar to those required for reaction of the complexes.

3. Mass Spectra of the Chromium Carbonyl Complexes:

A large number of compounds containing silicon have been studied mass spectrometrically. They have been popular subjects because they are relatively easy to prepare and have convenient volatilities. Although mass spectrometry has been used to characterize in depth inorganic compounds of silicon most of the detailed investigations have concerned organometallic derivatives. The mass spectra of metal carbonyl compounds are usually characterized by sequential loss of carbon monoxide from the parent molecular ion and only processes with very low energy requirements can compete with this decarbonylation.<sup>151</sup>

<u>Summary</u>. The mass spectra confirmed the analyses of the complexes by showing the parent ion and a fragmentation pattern expected

for the compound. The mass spectra of the chromium carbonyl complexes were characterized by sequential loss of carbon monoxide; and in several, the simultaneous loss of more than one CO group was observed. In general, any fragment which included the CO ligand had a low relative abundance. In the regions of common ions, the spectra of the complex and its free arylsilane showed significantly altered intensities. The occurrence of ion-molecule reactions in the mass spectrometer was also noted. The spectra were reproducible if the sample inlet pressures were identical, but this proved to be a demanding requirement; however, even at different inlet pressures, the gross features were reproducible.

The mass spectra of  $PhSiCl_3Cr(CO)_3$ ,  $PhSiMeCl_2Cr(CO)_3$ ,  $PhSiMe_2$ ClCr(CO)<sub>3</sub> and  $PhSiMe_3Cr(CO)_3$  are reported in Appendicies A, B, C, and D, respectively. The spectra of the free ligand were also recorded for comparative purposes so any unique trait of the instrument would be relatively constant. These ligand spectra are reported in Appendicies E, F, G, and H, respectively.

The observed spectra of these complexes were similar to those reported for other metal carbonyl complexes 97,98,150,152-155 and were characterized by successive losses of CO groups to give peaks for  $[ArCr(CO)_n]^+$  fragments where n = 2,3,1 or 0 and Ar = an arylsilane. The pattern for n = 2 was either extremely weak or absent for it was detected only at higher inlet pressures in the spectra of Ar = PhSiCl<sub>3</sub>. Also, at higher inlet pressures, lower intensity peaks were detected and assigned to ions of the type  $[(Ar minus R)Cr(CO)_n]^+$  where n = 3,2,1,0; R = Me or Cl. In general, the peaks containing the CO ligand of the type  $ArCr(CO)_n^+$  or  $Cr(CO)_n^+$  were only observed in low relative abundances.

A representation of the fragmentation pattern for  $PhSiCl_3Cr(CO)_3$  is shown in Figure 10.

For each compound, the fragment assigned to  $Cr^+$  ion was the most intense, except where  $Ar = PhSiMe_2Cl$  when the  $ArCr^+$  peak dominated, and the  $Cr^+$  peak was the second most intense  $(Cr^+/ArCr^+ = 0.85)$ . In the spectra of both the ligands and complexes, the fragmentation pattern resulting from the successive removal of groups from the silicon atom was observed, although the relative intensities of the corresponding ions were significantly altered upon complex formation. The  $Ar^+$  peak was much weaker in the spectrum of the complex as compared to the corresponding silane. Also, there was a series of peaks of low intensities which had a m/e ratio and isotopic cluster pattern expected for a  $CrR^+$ fragment (R = Cl or Me). The fragment was assumed to be the result of a rearrangement of the type: <sup>156</sup>

$$[CrC_{6}H_{5}SiR_{3}]^{+} \rightarrow CrR^{+} + C_{6}H_{5}SiR_{2}$$
 (58)

Earlier workers reported that metal carbonyl complexes undergo ion-molecule reactions in the mass spectrometer to give peaks at m/e ratios greater than the parent ion.<sup>153,154</sup> At high sample inlet pressures  $(5 \times 10^{-5} \text{ mm Hg})$ , a series of low intensity peaks (T  $\leq$  1.0) at m/e ratios corresponding to ions of the type  $[\operatorname{ArCr}_2(\operatorname{CO})_n]^+$  (n = 2,3) were observed. However, no ions of the type  $[\operatorname{Ar}_2\operatorname{Cr}(\operatorname{CO})_n]^+$  of  $[\operatorname{Ar}_2\operatorname{Cr}]^+$  were observed even where the ratio of intensities of  $[\operatorname{ArCr}_2(\operatorname{CO})_3]^+$  to parent ion was 0.6 as reported for the case Ar = PhSiCl<sub>3</sub>.

In the spectra of  $PhSiCl_3Cr(CO)_3$  there were peaks at m/e ratios corresponding to  $[PhSiCl_2Cr_2(CO)_2]^+$  and  $[PhSiCl_3Cr_2(CO)_n]^+$  (n = 1,0). For Ar = PhSiMe\_2Cl, ions of the type  $[PhSiMe_2Cr(CO)]^+$  and  $ArCr_2^+$  were



Figure 10. Fragmentation Pattern for PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub>.

observed. All these extremely weak peaks were at m/e ratios less than the parent ion and close to interfering patterns of more prominent fragments. Thus, the isotopic pattern could not be reasonably confirmed and assignment is not certain.

There has been conflicting reports about the presence of a peak at an m/e ratio of 40  $(C_{3}H_{4}^{+})$  in the spectra of previous arene chromium tricarbonyls.<sup>97,98,152</sup> The low pressure spectra of these phenylsilane complexes had a m/e 40 peak of approximately equal intensity to that of the m/e 39 peak. When higher pressures were employed, the m/e 40 peak was not observed, nor was it found in the spectra of the uncomplexed arylsilanes. Perhaps this fragment experiences a reaction in the mass spectrometer at higher pressures.

Using the data presented in Appendixies A through D, two interesting trends were derived. First, as more chlorine groups replace methyl groups on the silicon atom, the relative amount of fragmentation increased, reducing the abundance of the parent ion.

Pahl<sup>158,159</sup> defined a parent-ion stability as

$$W_{p} = 1 - W_{z}, \qquad (55)$$

$$W_{z} = \Sigma I_{f} / (I_{p} + \Sigma I_{f}).$$
 (56)

 $W_z$  is the parent-ion decomposition probability,  $I_p$  is the intensity of the undecomposed parent ions (including isotopic ions), and  $\Sigma I_f$  is the total intensity of all of the other (singly charged) ions in the mass spectrum. Equations 55 and 56 can be combined to obtain

$$W_{p} = I_{p} / (I_{p} + \Sigma I_{f}).$$
 (57)

where

This is the same procedure as summing the fraction of total ion intensity of peaks resulting from the isotopic cluster pattern and comparing that sum to the total ion intensity for the complex. The relative stabilities of the parent ions were found to be in the order:  $PhSiMe_3Cr(CO)_3^+ >$  $PhSiMe_2ClCr(CO)_3^+ > PhSiCl_3Cr(CO)_3^+ > PhSiMeCl_2Cr(CO)_3^+$  at low inlet pressures, as shown in Table V. At higher inlet pressure the same basic order was found, except the last two compounds were interchanged.

Second, the fragmentation patterns for the successive removal of groups from the silicon, while maintaining the complexation of the phenyl ring with the Cr(CO), grouping, was found to result in the preferential cleavage of chlorine groups as compared to the methyl In the spectra of the complexes, the same trend was noted for groups. fragments which did not contain the  $Cr(CO)_n$  group. This was exactly the reverse of the behavior noted previously for uncomplexed PhSiMeC1, 104,151 and for both PhSiMeCl, and PhSiMe,Cl (Appendix F and G) as measured in this laboratory. These spectra taken during this research showed more detail but generally corresponded to the previously reported results for the uncomplexed arylsilane. Also Beynon states that in compounds of the type R<sub>2</sub>SiCl<sub>2</sub> cleavage of an R-Si bond is twice as probable as cleavage of a Si-Cl bond.<sup>151</sup> In RSiCl<sub>3</sub> compounds, cleavage of Si-Cl bonds is somewhat enhanced, whereas in R3SiCl compounds, breakage of R-Si bonds predominates.

The above stability order and the relative amounts of bond cleavage would be expected on the basis of electronegativity arguments. The  $Cr(CO)_3$  group has a strong electron-withdrawing effect on the  $\sigma$ orbitals of the aromatic ring.<sup>50,160</sup> Since chlorine is more electro-

# TABLE V

# Parent Ion Stability

# Stability, Wp

Compound	Low Inlet Pressures	High Inlet Pressures
PhSiMe3 <sup>Cr(CO)</sup> 3	0.0425	0.0533
PhSiMe <sub>2</sub> ClCr(CO) <sub>3</sub>	0.034	0.0389
PhSiMeC12Cr(CO)3	0.0035	0.0158
PhSiCl <sub>3</sub> Cr(CO) <sub>3</sub>	0.00122	0.0208

•...•

negative than a methyl group, loss of a chlorine atom would tend to better stabilize the ion's positive charge and the partial positive charge from the effect of the  $Cr(CO)_3$  group. Since the fragments without the  $Cr(CO)_n$  group present were assumed formed by successive losses of CO groups and then the Cr atom, their comparative stabilities would logically be controlled by the relative abundance of the various larger parent species.

The reason for the relative position of  $PhSiCl_3Cr(CO)_3$  in the trend shown in Table V, is not fully understood but might be partially explained on the basis of increasing  $\pi$ -bonding between silicon and chlorine. It has been argued<sup>161</sup> that (p→d)  $\pi$ -backbonding between chlorine and silicon occurs and the effect is to increase the negative charge density in the d-orbitals of silicon. Consequently, the capacity of silicon to accept electron density from the ring is decreased, and, thus, the negative charge density in the ring is increased. The magnitude of this transfer of electron density for an extra chlorine may compensate for the larger electronegativity of chlorine over a methyl group.

It might be proposed that the order of bond dissociation energies be assigned on the basis of the relative intensities of the ions, but the previous discussion suggest that erroneous conclusions would result. Bond dissociation energies in the initial neutral molecule and in the corresponding positively charged ion seemed to be significantly different. The mean dissociation energy of a Si-Cl bond is approximately 116 kcal/mole while that of a Si-Me bond is significantly lower at about 85 kcal/mole.<sup>24</sup> Also the relative abundance of the ionized species may be kinetically controlled instead of thermodynamically controlled. The thermal decomposition data indicated that the mass spectra of the  $\pi$ -complexes were relatively unaffected by thermal decomposition effects in the mass spectrometer during the runs.

4. Infrared Spectra of the Chromium Complexes:

Previous infrared work on  $\pi$ -arene complexes of chromium tricarbonyl was conducted by Fritz and Manchot<sup>162,163</sup> in the 3000 to 300 cm<sup>-1</sup> region. Their data were reassigned<sup>164</sup> and confirmed<sup>53</sup> by later workers. Humphrey discussed the shifts in the internal frequencies of some arenes due to  $\pi$ -complex formation.<sup>165</sup> A number of other workers have reported on the vibrational spectra of this type of complex.<sup>95,96,166,167</sup> The work of Buttery and co-workers showed that the spectra of these complexes in the solid phase are strongly influenced by intermolecular coupling, and, consequently, an investigation of their spectra in solution is necessary to obtain valid information concerning individual molecules.<sup>167</sup> Additionally, a great deal of work on the vibrational spectra of  $\pi$ -arene complexes has assumed that the concept of "local symmetry" is a valid approximation; although Davidson and Riley<sup>96</sup> have questioned the general use of this concept.

The infrared spectra of these complexes are reported in Table VI and shown in Figures 11-14, but because of the work of Buttery and co-workers,  $^{167}$  solution spectra in both CS<sub>2</sub> and cyclohexane were obtained. Only the v(COO) modes were observed and measured in very dilute cyclohexane solutions. The bands were assigned by comparing the observed spectra with the reported spectra of similar complexes and uncoordinated ligands.  $^{53,95,96,99,100,116,123,162-167}$ 

Although Davidson and Riley<sup>96</sup> reported splitting of the E mode

	IR Absorption Frequencies ( $cm^{-1}$ ) of $\pi$ -complexes <sup>a</sup>								
PhSiMe 3	Cr(CO) <sub>3</sub>	PhSiMe2	C1Cr(CO) <sub>3</sub>	PhSiMeC	1 <sub>2</sub> Cr(CO) <sub>3</sub>	PhSiC13	Cr(CO) <sub>3</sub>	Assignment	
cs <sub>2</sub>	KBr	cs <sub>2</sub>	KBr	cs <sub>2</sub>	KBr	cs <sub>2</sub>	KBr		
3077vw	de			3080vw	*	3001vw		ν (CH) ring	
2959m	2958w	2961vw		2970vw	2970vw	2957vw	2965vw	ν (CH) ring	
2900vw		2910vw		2927 <del>v</del> w				ν (CH) methyl	
1979vs	1955vs	1985vs	1963vs	1990vs	1975vs	1997vs	1975vs	ν (C-O)	
1907vs	1865vs	1916vs	1973vs	1920vs	1880vs	1935vs	1893vs	ν (C-O)	
1401vw	1392vw	1402vw		1400w	1399w	1400vw	مية قفا الله علي	δ (Si-C) methyl	
1365vs		1362vw		1364vw		1367vw			
1289w	1286w	1290w		1287m		1290w	يون الآن من عن	δ (C-H) ring	
1268vw	1265vw	د کے برد خت	خت ساجر ہے					δ (Si-C-H) methyl	
1256s	1245m	1260m	1254w	1265m				δ (Si-C-H) methyl	
1163vw	1147vw	1161vw	یک متد علم ہیں	1160w	ain ait 27 Ca	1163vw		δ (CH)	
1107s	1100m	1112m	يقط نحله ججم وهو	1114s		1117s	1080m	δ (H-C-Si) ring	
1019vw	<del>تہ ہے جر کن</del>	1015vw		1014w		1015vw	1025m	δ (CH) ring	
991w	<b></b>	990vw	~	990w	میں ملے اور	991vw	وی وی دی ک	$\nu$ (C-C) ring	

PhSiMe 3	Cr (CO) <sub>3</sub>	PhSiMe 2	C1Cr(CO) <sub>3</sub>	PhSiMeC	C1 <sub>2</sub> Cr(CO) <sub>3</sub>	PhSiC13	Cr(CO) <sub>3</sub>	Assignment
cs <sub>2</sub>	KBr	cs <sub>2</sub>	KBr	cs <sub>2</sub>	KBr	cs <sub>2</sub>	KBr	
843s	837s	840m	839w				فلت الحاجير بي	ν <b>(Si-C)</b>
810vw	809vw	814s	809w			802vw	795w	δ (CH) ring
خفه همه وهور		795m		793s	780m	<u> </u>	785w	δ (CH) ring
754m	747vw			753m				δ (CH) ring
693w	787vw	695vw		694 <del>w</del>		717m	715vw	
652s	653m	652s	652s	648s	652m	645s	641vw	δ (Cr-C-O)
620s	621m	619s	618s	615s	615m	612s	607vw	δ (C-C) or δ (Cr-C-O)
				559s		594m	585w	ν (SiCl)
535m	525w	532m	526w	534m	530w			δ (CrCO) or ν (Cr-C)
		492w		503s	<b></b>	518m	515vw	ν (Si-Cl)
471w		472w		467 <del>w</del>	470 <del>v</del> w	465w	460vw	ν (Cr-C) or δ (CrCO)
	420vw	الناب سير عليه التاري		<b></b>	425vw		430vw	δ (C-C) ring

TABLE VI (continued)

a. s - strong, m - medium, w - weak, v - very

b. Possible assignments were made in conjunction with references.



Figure 11. Infrared Spectrum of PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub>.



Figure 12. Infrared Spectrum of PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub>.



Figure 13. Infrared Spectrum of PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub>.



Figure 14. Infrared Spectrum of PhSiMe<sub>3</sub>Cr(CO)<sub>3</sub>.

of the C-O stretching frequency in all of the studied complexes with a side chain when in dilute cyclohexane, splitting of the E mode was observed in these new complexes only in the cases of  $PhSiMeCl_2Cr(CO)_3$ and  $PhSiMe_2ClCr(CO)_3$ . In more concentrated  $CS_2$  solutions, just two bands were found for each compound, in agreement with an effective local symmetry of  $C_{3v}$  for the  $Cr(CO)_3$  group. These correspond to the vibrations of symmetry  $A_1$  and E. Since the lower frequency band was split as reported above, it was assigned to the E mode.

The trends in C-O stretching frequencies correlated well with the expected ease of electron donation from the aromatic ligand (as measured by group electronegativity of the side-chain) and v(CO) for either the A<sub>1</sub> or the E mode (Figures 15 and 16). Thus, as the group electronegativity increased the stretching band shifted to a higher frequency.

5. NMR of the Chromium Complexes:

Summary. In the nmr spectra of arylsilanes and their chromium tricarbonyl complexes, the aromatic protons of the arylsilane exhibited complex multiplets, while the aromatic protons of the complexes, except for  $PhSiMe_3Cr(CO)_3$ , were resolved into two intricate clusters. The integration of these clusters indicated that there were 3 protons in the downfield multiplet and 2 protons in the upfield one. The results of the complexes also displayed a relative spectral shift among the aromatic protons as compared to that of the corresponding free arylsilane. Typically, a large, upfield shift of 2.1-2.5 ppm (relative to the corresponding arylsilane) for the aromatic protons was observed upon complex formation.



Figure 15. A Mode of v(CO) for PhRCr(CO)<sub>3</sub> vs. Electronegativity of the R Group.



Figure 16. E Mode of v(CO) for PhRCr(CO)<sub>3</sub> vs. Electronegativity of the R Group.

Table VII summarizes the spectra of both the chromium tricarbonyl complexes and, for comparison, their corresponding free arylsilane. The spectra of the complexes are shown in Figures 17, 18, 19 and 20. The low-field resonance pattern can be readily assigned to the ring protons by analogy with other chromium tricarbonyl derivatives, <sup>51,52,168,169</sup> and by the integration of the area under the curve. The high-field singlet was assigned to the methyl protons by a similar method.

The results given in Table VII show three main characteristics that differentiate the chemical shifts of the arylsilane chromium tricarbonyls from those of the 1 e arylsilane. First the effect of the silicon substituent on the aromatic protons differs in the two spectra. The spectra of the chromium complexes were not easily interpreted since the aromatic protons appears to form a complicated AA'BB'C spectrum.<sup>170</sup> But previous workers<sup>171</sup> have interpreted the spectra of isopropylbenzene chromium tricarbonyl as due to the temperature dependence of a conformation equilibrium about the ring-metal bond. The exchange was described as a two component equilibrium between conformers (III) and (IV).



(59)

(III)

(IV)

	-							
Group	coup PhSiMe <sup>b</sup> 3		PhSiMe <sub>2</sub> Cl		PhSiMe	<sup>C1</sup> 2	PhSiCl <sub>3</sub>	
	Complex	Neat	Complex	Neat	Complex	Neat	Complex	Neat
сн <sub>з</sub>	0.30	0.28	0.70	0.60	1.06	0.93	بربية النف الذي برباة	
с <sub>6</sub> н <sub>5</sub>	4.95	7.11	4.97	7.20	4.97	7.20 <sup>.</sup>	4.66	7.33
	5.05	7.13	5.07	7.24	5.07	7.23	4.76	7.36
	5.16	7.20	5.17	7.27	5.17	7.27	4.86	7.43
	5.26	7.24		7.30		7.32		7.46
	5.35	7.30	5.37	7.35	5.46	7.35	5.27	7.49
	5.42	7.35	5.46	7.45	5.55	7.57	5.41	7.53
		7.39	5.59	7.50	5.63	7.62	5.52	7.66
		7.43		7.57		7.68		7.73
		7.46		7.62		7.72		7.78
		7.51						7.82

Chemical Shifts ( $\delta$ -ppm) of  $\pi$ -Complexes<sup>a</sup>

Solutions <u>ca</u>. 0.1 M CCl<sub>4</sub>. a.

b. <u>cf</u>. data from reference 69.

TABLE VII



Figure 17. NMR of PhSiMe<sub>3</sub>Cr(CO)<sub>3</sub>.



Figure 18. NMR of PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub>.



Figure 19. NMR of PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub>.




Electronic effects of an electron releasing group favored (III) but steric interactions favored (IV). For an electron withdrawing group the  $\pi$ -electron density is greatest at the meta-positions and conformer (IV) would be favored by both effects; thus, the ortho- and para-protons would be deshielded by the Cr-CO bond relative to the meta-protons.

The spectra of the arylsilane chromium tricarbonyl complexes are consistent with a conformer of type (IV) where the ortho- and paraprotons were shifted down-field relative to the meta-proton.

Second, there was a large upfield shift of the aromatic protons resonance in the complex relative to the free ligand. It is assumed that an appropriate blend of the following three effects would explain these shifts.<sup>50,169</sup> First, the protons could be shielded by the metal atom. Second, a modification of the ring current could return the position of the protons to that for a normal alkene proton. And finally, the strong electron withdrawing effect of the  $Cr(CO)_3$  group could cause a shift to lower fields.

The third and last major feature of the spectra of the complexes was that they showed a solvent effect. McFarlane and  $\operatorname{Grim}^{51}$  have reported the chemical shifts of benzene chromium tricarbonyl in CDCl<sub>3</sub> differ substantially from those obtained in benzene solution. In this research a shift range of 0.05 to 0.30 ppm was found between the spectra of the CCl<sub>4</sub> and cyclohexane solutions with the resonance in CCl<sub>4</sub> shifted downfield except for PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> in which case they were shifted slightly upfield. The solutions of the free arylsilane showed a similar downfield shift, however, the magnitude was somewhat smaller. Since, in a given solvent, the effect is greater for the chromium carbonyl complexes

and the association shift is stronger the more acidic the proton,<sup>170</sup> then the C-H bond of the ring for the complexes should be more polarized than in the free arylsilane.

6. Reactions of the Chromium Complexes:

a. Reactions with  $0_2$ . The literature contains few reports of the reaction of arylchlorosilanes with molecular oxygen at low temperatures. The ignition limits of mixtures of oxygen with MeSiCl<sub>3</sub>, Me<sub>2</sub>SiCl<sub>2</sub>, and Me<sub>3</sub>SlCl were studied by Galis, Liebhafsky and Getz<sup>172</sup> who found that the mixture could be ignited by a spark if the critical  $0_2$  content was larger than 10% by volume.

The tetraalkysilanes are quite stable to oxygen at their normal boiling point, since they can be distilled in air without oxidation. In air, trimethylphenylsilane was partially oxidized at 400° to a combination of siloxanes, formic acid, formaldehyde, biphenyl, phenol, carbon monoxide, carbon dioxide and hydrogen.<sup>124</sup> Depending on the experimental conditions, the proportion of organosilane oxidized varied from 1 to 48%. Separate experiments showed that the glass reactor used did not catalyze the oxidation.

In this study the reactions of pure oxygen with both the free and complexed arylchlorosilanes were conducted at 0° and initial low pressure. The chromium tricarbonyl complexes usually underwent a violent, exothermic reaction. The products included  $CO_2$ ,  $H_2O$ ,  $Cr_2O_3$ , very small amounts of unreacted ligand, traces of benzene, and, when the ligand contained chlorine, major amounts of HC1. The reactions were not reproducible with respect to yields.

None of the corresponding neat ligands underwent reactions at conditions below 22°/5 atm. This could imply that the Si-Me, Si-Cl and

Si-Ph linkages are more resistant to oxidation than the same linkages in the complex. It could be argued that the  $Cr(CO)_3$  group withdraws electron density from the ring, thus increasing the electronegativity of the ring carbon. (The group electronegativity for the  $(CO)_3 CrC_6 H_5$ substituent has been determined to be 8.95 as compared to 7.67 for the corresponding  $C_6 H_5$  substituent.<sup>48</sup>) This increased electronegativity could increase the polar nature of other bonds to silicon.

It is also possible that the complexes reacted more readily because the oxygen initially attacked the Cr(CO)<sub>3</sub> group and, thus, the free ligands would not be expected to react in the same manner.

It should be noted that conclusions derived from a direct comparison of these reactions may be erroneous since the complexes, while initially igniting at a lower temperature and pressure due to the exothermic nature of the confined reaction.

Since none of the starting complex, its derivatives, or oxidized derivatives of the free arylsilane were found in the final reaction mixture and the free arylsilanes did not react under similar initial conditions, it is tempting to suggest that attack at the  $Cr(CO)_3$  group accounts for the differences in reaction but under the same conditions PhCH<sub>3</sub>Cr(CO)<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> did not react. PhCH<sub>3</sub>Cr(CO)<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> did not react. PhCH<sub>3</sub>Cr(CO)<sub>3</sub> and C<sub>6</sub>H<sub>6</sub>Cr(CO)<sub>3</sub> did, however, react at the same temperature and 4000 atm; unfortunately, the gold tube was melted by the exothermic reaction and the composition of the products was not able to be determined.

b. Randomization of Phenylchlorosilanes. Randomization reactions of phenylchlorosilanes have been reported when these compounds were heated in sealed containers.<sup>173</sup> Only moderate temperatures ( $\sim$  150°)

were required when a catalyst (usually A1Cl<sub>3</sub>) was present. Since chromium salts and carbonyl derivatives are known catalysts for other reactions, each of the compounds reported in this research was checked for such rearrangements. None was observed at conditions up to 200°/ 4000 atm.

c. Reactions of the Complexes with H<sub>2</sub>O.

Summary. The presence of the  $Cr(CO)_3$  groups in the arylchlorosilanes did not grossly alter the reaction of the silicon-chlorine bond with water. In no examined case was the presence of a silicon-chlorine bond detected in the final products. Thus, reaction to at least the silanol stage was totally effected in all cases. Further reaction and condensation to the siloxane occurred for each compound except PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub>, where only partial condensation was observed.

The phenylmethylchlorosilanes are very important industrially because they are intermediates in the manufacture of a variety of phenyl- or methyl-containing silicone liquids, rubbers, and solids which are silicone polymers.<sup>58</sup> These polymers usually result from the cleavage of the silicon-chloride bond by hydrolysis which leads to the initial formation of the corresponding silanol. These silanols usually condense to form the siloxane and water. The general reactions are given by equations 60 and 61. The reactions of triorganochlorosilanes can be stopped at the silanol stage with the least difficulty.<sup>174</sup>

$$R_{3}SiC1 + H_{2}O \rightarrow R_{3}SiOH + HC1$$
 (60)

$$2R_{3}SIOH \rightarrow R_{3}SIOSIR_{3} + H_{2}O$$
 (61)

The mechanism proposed for the hydrolysis involves the initial nucleophilic attack on silicon by the oxygen atom, but the complete reaction mechanism is uncertain. The proposed scheme is

$$2H_20 + R_3SiC1 \rightarrow HO-Si-C1 \rightarrow R_3SiOH + H_30^+ + C1^-$$
 (62)  
H-O-H R  
H

The driving force behind these reactions is the increased stability of the Si-O bond over that of the Si-Cl bond. The reactions are further promoted by the removal of the liberated HCl.

Steric factors of the organic grouping are known to have a considerable effect on the reaction rate. The presence of bulky organic groups attached to the silicon generally suppresses the silanol condensation.

The reactions of  $H_2^0$  with the chromium tricarbonyl complexes of the arylchlorosilanes were conducted to determine if the presence of the more bulky  $Cr(CO)_3$  group suppressed the silanol condensation. It was also of interest to see if the electron withdrawing nature of the  $Cr(CO)_3$  group would grossly affect the rate of reaction by making the silicon atom more positive resulting in a more stable transition state.

The complexes were reacted with excess  $H_2^0$  at 22°, a temperature where the arylchlorosilanes are known to yield complete convertions to

siloxanes.<sup>25</sup> The complexes reacted to yield products which contained no evidence for Si-Cl or Si-OH bonds (except in the case of  $PhSiMe_2ClCr(CO)_3$ ); however, the amount of HCl recovered was not 100% of the expected amount, but there was a small amount of a chromium compound containing chlorine. The mass spectra suggested that part of the phenyl rings were not bonded to a Cr(CO)<sub>3</sub> group in the final polymers, thus, a chromium chloride could nicely account for both the missing Cr and Cl. Only in the case of PhSiMe<sub>2</sub>ClCr(CO)<sub>3</sub>, when approximately half of the final mixture was the complexed silanol, did the presence of Cr(CO)<sub>3</sub> group appear to hinder the condensation to the siloxane. The uncomplexed silanol or siloxane were not observed in any of the cases examined.

The electron-withdrawing effect of the  $Cr(CO)_3$  did not increase the polar nature of the silicon-carbon bond enough to cause cleavage at that location. Thus,  $PhSiMe_3Cr(CO)_3$  could be shaken with large quantities of an ether/water mixture and recovered unchanged.

d. Reactions with HCl. <u>Summary</u>: In this study several parameters were varied to describe the nature of the interaction between anhydrous hydrogen chloride and the chromium tricarbonyl complexes or the free arylsilane. These changes included the physical conditions of temperature and pressure as well as modification of the arylsilane by changing the groups attached to the silicon and the coordination of the  $Cr(CO)_3$  group to the aromatic ring. The reactions with HCl clearly demonstrated the influence of pressure on the cleavage of the siliconphenyl linkage as the major reaction. Table VIII summarizes the experimental results. Several trends are apparent. First, for both the complexes and free arylsilanes, cleavage of the silicon-phenyl bond

## TABLE VIII

Substance	Тетр	Percent Reaction at Listed Pressure		
•	<u>°C</u>	$10 \text{ atm}^{b}$	<u>1026 atm</u>	<u>4080 atm</u>
PhSiMe 3	22°	99%		<b>800 800 800 800</b>
PhSiMe3Cr(CO)3	22°	100%	جلب بلك خلق حلو	
PhSiMe2Cl	22°	69%	يتين وتلك الله جيل	مند ين من سن
PhSiMe2ClCr(CO)3	22°	97%	فحو والأندخان مري	والله البلة الله عنك
PhSiMeC12	22° 50° 100° 200°	0% 0% 0% 33%	 	6% 48% 57%
PhSiMeCl <sub>2</sub> Cr(CO) <sub>3</sub>	22° 50° 100°	0% 0% 19%	0% 33%	2% 75% 100%
PhSiCl <sub>3</sub>	120° 150° 220°	 0%	0% 0%	0% 18% 17%
PhSiCl <sub>3</sub> Cr(CO) <sub>3</sub>	50° 100° 120° 150°	  0%	0% 2% 12.6%	0% 12.5% 25% 29%

High Pressure Silicon-Phenyl Cleavage Reactions with HCl<sup>a</sup>

a. Yield based on recovered chlorosilane at equilibrium after 16 hours.b. Autogenous pressure calculated using the ideal gas equation, <u>ca</u>.

10 atm.

became more difficult as chlorine replaced methyl groups. Second, when the  $Cr(CO)_3$  group was coordinated to the phenylsilane the conditions for cleavage were somewhat milder. Third, an increase in pressure lowered the minimum temperature required for a measurable amount of reaction.

The reaction of HCl with  $PhSiR_3Cr(CO)_3$  results in the formation of a series of products including benzene,  $R_3SiCl$ , chromium chlorides and chromium hydride. In this section the reaction to form benzene (and its complex with  $Cr(CO)_3$ ) and  $R_3SiCl$  is discussed. The reactions which lead to the formation of nonvolatile chromium products are discussed in sections IIIB and IIIC.

The heterolytic fission of the silicon-phenyl linkage by hydrogen halides has been long considered to be an electrophilic substitution reaction involving a  $\sigma$ -complex.<sup>15-17</sup> However, no evidence exists which clearly eliminates the possibility of a four-center transition state (I). Additionally, as noted in the review in Chapter I, almost all of the previously reported reactions were conducted in the presence of water. When care was taken to remove all traces of H<sub>2</sub>O, the reactivity was, usually, either greatly reduced or eliminated. The  $\sigma$ -complex mechanism, however, is consistent with the observation that the addition of electronegative groups to the silicon hinders the cleavage reaction. This is reasonable since the silicon removes electron density from the carbon and ring through both its  $\sigma$ - and  $\pi$ -orbitals, making the linked carbon more positive and hindering attack by the positive ion, H<sup>+</sup>. It should be noted that the probability of reaction via some type of four-center mechanism would be increased by the attachment of electronegative atoms to the silicon. This substitution would cause the silicon-carbon bond to become more polar, increasing the likelihood of coordination of the silicon with the negative end of the HCl molecule.

There have been several recent communications to support this concept of interaction between the silicon atom and its attached ring. After an nmr study of substituted phenyltrimethylsilanes, Vignollet and Maire<sup>176</sup> concluded that the principle effect of the SiMe $_3$  group on the ring was inductive, but that a small donation of electrond did occur to form a (p-d)  $\pi$ -bond. Bock and Alt<sup>177</sup> conducted charge-transfer studies on silyl- and alkylbenzenes and stated that the substituent effects on the benzene molecular orbitals can be rationalized in terms of inductive polarization (+  $I_{SiR_3}$  > +  $I_{CR_3}$ ) as well as strong electron back-donation  $C\pi \rightarrow Si$  from the benzene  $\pi$  system into the empty silicon atomic orbitals of  $\pi$  symmetry. Other recent nmr experiments<sup>161</sup> suggest that (p-d)  $\pi$ -bonding is significant in PhSiCl<sub>3</sub>. This type of bonding occurs between silicon and chlorine and contributes substantially to the electronic properties of the SiCl, group by shifting charge density to the central silicon atom from the chlorine and consequently decreasing the capacity of silicon to accept electron density from the phenyl ring relative to that expected for a hypothetical SiCl, group in which no chlorine silicon  $\pi$ -bonding occurs. However, the  $\pi$ -acceptor capacity of silicon for the ring electron density increases on substitution of a chlorine atom for an alkyl group in SiR, compounds.

Isomer distribution and relative rate constants for bromination of compounds of the type  $PhSiMe_{3-n}Cl$  were explained in terms of a contribution by both inductive and (p-d)  $\pi$ -character of the silicon-phenyl

bond.178

The reaction of PhSiCl<sub>3</sub> with HCl is thermodynamically possible at 25°/1 atm, (See Appendix I), however, no reaction was observed up to 220°/5 atm. Although the exact magnitude of the effect of pressures up to 4,000 atmospheres on this reaction is not known, in general, a reaction involving the disappearance of gas molecules can be assisted by pressure to the extent of approximately 5 kcal per mole of gas that disappears during reaction at room temperature but this value increases in proportion to the increase in absolute temperature.<sup>1</sup>

The reason the reaction of PhSiCl<sub>3</sub> with HCl did not occur at 25° and low pressure is believed associated with a kinetic rather than a thermodynamic problem. Besides its influence on the position of chemical equilibrium, pressure is also important in affecting rates of chemical reactions. The effect of the pressure may simply be to increase the solubility of the arylsilane or complex in HCl or to increase the activity of the reactants. (Highly compressed gases, like liquids, have considerable solvating properties; for example, quartz will dissolve in supercritical steam.<sup>1</sup>) These reactions were carried out above the critical temperature (51.4°) of HCl, which has a density of 0.9 g/cc at 400°/2000 atm.<sup>179</sup> Also, the melting point of benzene at 4000 atmospheres is approximately 100°<sup>180</sup> and the melting points of substituted benzenes should be even higher.

The effect of the pressure may be to increase the rate constant of reaction since no cleavage was observed below 1000 atmosphere and at the lowest reaction temperature at 4000 atmospheres. Up to pressures of about 1000 atmosphere, the more important effects of pressure on

rates of reactions is the increase in activities of reactants. At higher pressures, significant changes in the rate constant occur.<sup>1,3</sup>

The increase in rate constant with pressure is directly proportional to the decrease in volume of the system and is approximated by the relationship

$$\frac{(\partial \ln k)}{(\partial P)_{T}} = -\frac{\Delta V}{RT}^{*}$$
(63)

where  $\Delta V^*$  is the partial molar volume difference between the starting materials and the transition state in the transition state theory.<sup>2</sup> Thus, intermolecular repulsion is overcome so that particular groups are brought into more intimate contact. It is also necessary to consider the interaction of a solvent with the activated species. (This solvent could be one of the reactants in excess quantities.) The volume of activation term can be split into two terms,  $\Delta V_r^*$  and  $\Delta V_s^*$ , where  $\Delta V_r^*$  is the volume change of the reacting molecules when they form the transition state, while  $\Delta V_s^*$  is the accompanying change in volume of the surrounding liquid, arising principally from changes in the electrostriction.<sup>3</sup>

The pressure increase will favor either of the proposed mechanisms. The formation of a four-centered transition state would result in a decreased volume for the system, thus favoring reaction. Four-centered rearrangements have been shown to be pressure accelerated.<sup>181</sup> The  $\sigma$ -complex mechanism would also be pressure enhanced since the dense polar fluid, HCl, could tend to stabilize the transition state by coordination to the developing ionic species thus making the magnitude of  $\Delta V_s^*$  term larger. Since high pressure is known to increase ionization, it is also possible that the rate could be accelerated by the increased formation of ionized HC1, viz.,

$$3HC1 \rightarrow H_2C1^+ + HC1_2^-$$
(64)

It has already been reported that HCl has a density comparable to common liquids at 400°/2000 atm. Since the maximum conditions of reaction in this research were at twice this pressure and one-half this temperature (200°/4000 atm), the density of HCl would be expected to increase even more. In alcohols, the proportion of hydrogen-bonded "polymers" increases with rising pressure, and  $\Delta V_s^*$  is about 4 cm<sup>3</sup>/mol for formation of the hydrogen bond.<sup>182</sup> Increasing pressure also greatly increases the ionization of fluid water; and, when compressed to the density of molten sodium hydroxide, water has about the same electrical properties as sodium hydroxide.<sup>183,184</sup> Thus pressure could produce an increase in the ionization of HCl similar to that found with H<sub>o</sub>O.

The influence of the  $Cr(CO)_3$  group is to increase the amount of reaction at the same conditions or lower the conditions required for a detectable amount of reaction. This is a thermodynamic effect rather than kinetic. However, a kinetic effect is also expected. The arylsilicon bond in substituted phenyltrimethylsilane is much more readily cleaved by base in aqueous methanol when complexed with  $Cr(CO)_3$  than in the free arylsilane. The rate enhancement by the  $Cr(CO)_3$  group was at least 500-fold.<sup>185</sup> Since all experiments in this research were to attain equilibrium because each reaction was conducted for 16 hours, and no additional reaction was noted after 8 hours, kinetic measurements were not made. The only kinetic effect observed was the possible rate increase when high pressure was applied.

Support for an ionic type mechanism is found in the work of White and Fasona.<sup>37,38</sup> They reported that  $\operatorname{ArCr(CO)}_3$  type compounds reacted with free halide ions and suggested that these complexes could serve as effective catalysts in certain electrophilic substitution reactions by promoting ionic-type reactions. If the mechanism of these reactions involve the interaction of the chromium atom with the anion or negative end of the ionic species, such interactions would partially support both the formation of the chromium chlorides and the rate acceleration under pressure by increasing the concentration of  $\operatorname{H}_2\operatorname{Cl}^+$ .

As previously stated, substitution of strongly electron-withdrawing substituents on the silicon atom is known to increase the difficulty of rupturing the aryl-silicon bond. Using the group electronegativity values for the  $C_{6}H_5$ - and  $Cr(CO)_3C_6H_5$ -moieties calculated by Guvin and Khandarova<sup>47,48</sup> and the values for SiCl<sub>3</sub>, SiMeCl<sub>2</sub>, SiMe<sub>2</sub>Cl and SiMe<sub>3</sub>calculated according to Huheey's group electronegativity method, <sup>186-190</sup> certain relationships can be correlated (Appendix J). For the <u>uncomplexed</u> arene systems both SiMe<sub>3</sub> and SiMe<sub>2</sub>Cl were predicted to be electron donating to the ring, but the other two groups should be electron withdrawing. These conclusions are consistent with both previous work and the results of this study. For example, at low pressure both PhSiMe<sub>3</sub> and PhSiMe<sub>2</sub>Cl reacted at or near 22° with HCl, to give cleavage, but the other arylsilanes did not react except at elevated conditions.

When the  $Cr(CO)_3$  group is bonded to the phenyl ring, all of the silicon groupings are predicted to be electron donating. Again, in agreement with this prediction, the ease of reaction was found to be in the expected order with PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub> being the least reactive; and the conditions for reaction in comparison to the uncomplexed arene were reduced. Cleavage was observed in PhSiMeCl<sub>2</sub>Cr(CO)<sub>3</sub> at 100° and low pressures, but at the same conditions no reaction of the pure ligand was detected. No cleavage reaction with HCl was observed for PhSiCl<sub>3</sub> or its  $\pi$ -complex at 150° and low pressure. Since the  $\pi$ -complex decomposed above 150° and the reaction was more complex than just the cleavage reaction, a direct comparison at 220° could not be made for PhSiCl<sub>3</sub>Cr(CO)<sub>3</sub>.

The ability of the  $Cr(CO)_3$  moiety to stabilize a positive charge which develops on the ring or a side-chain of the ligand during reaction has been discussed. <sup>41,191</sup> It was proposed that the bond between the phenyl ring and the chromium atom functioned in much the same manner as the Cr-CO bond with a forward coordination and a back donation. Anderson and Brown<sup>192</sup> have suggested a method for measuring this effect. They proposed that the  $v(CO) E/A_1$  intensity ratio could be related to the importance of the  $\pi$ -acceptor character of arenes in ArCr(CO)<sub>3</sub> systems.

Following their suggestion the measured intensity ratio from high resolution spectra of the complexes of  $PhSiCl_3$ ,  $PhSiMeCl_2$ ,  $PhSiMe_2Cl$ , and  $PhSiMe_3$  were found to be 1.16, 1.30, 1.61 and 1.62 respectively. Thus  $PhSiCl_3$  with the most electronegative side group was predicted to be the best  $\pi$ -acceptor. This suggests that the more

electron density which is withdrawn from the ring by a side-group, the greater is the ability of the phenyl ring to accept additional density from the  $Cr(CO)_3$  group. The same trend is observed in the v(CO) frequencies and is well correlated with group electronegativities, i.e., as the group electronegativity of the side chain increased, the stretching of the C-O bond shifted to higher frequencies (Figures 11 and 12). This shift is frequently explained in terms of decreased  $(d \rightarrow p)$   $\pi$ -bonding between chromium and the CO group. Thus, it would seem that as backbonding between chromium and CO groups decreased, backbonding from chromium to the arylsilane increased.

e. The Reaction of Benzyl Halides with Arene Chromium Tricarbonyls. When PhCCl<sub>3</sub> was reacted with either  $Cr(CO)_6$  or PhCH<sub>3</sub>Cr(CO)<sub>3</sub> the main product was a polybenzoyl type polymer, however, (PhCCl<sub>2</sub>)<sub>2</sub> was also a reaction product. Although Bamford and coworkers have shown that Mo(CO)<sub>6</sub> reacts with organic halides via a free-radical mechanism,<sup>193</sup> Tarona and White<sup>38</sup> use the polymerization of benzyl chloride, catalyzed by ArMo(CO)<sub>3</sub> compounds, as evidence that carbonium ions and not radicals were involved. In a later paper<sup>37</sup> they used the fact that ArCr(CO)<sub>3</sub> compounds are catalysts in Friedel-Crafts reactions to further support the carbonium ion theory. They suggested ArCr(CO)<sub>3</sub> had strong affinity for halide ions since this type of compound reacts with R<sub>4</sub>NX. As noted in Chapter I, other workers<sup>92,57,194</sup> have found that ArCr(CO)<sub>3</sub> can be oxidized by halogen containing compounds.

This oxidation seems reasonable since these complexes are closely related to the bis-arene chromium complexes and their electrochemical oxidation

$$(C_{6}H_{6})_{2}Cr^{\circ} \rightarrow (C_{6}H_{6})_{2}Cr^{+1} + e^{-}$$
 (65)

has been shown by polarographic techniques<sup>28</sup> to be a reversible, one step process.

However, the fact that (PhCCl<sub>2</sub>)<sub>2</sub> was found in the final reaction mixture, suggests that a radical mechanism could still be involved. One such radical mechanism could involve the reversible oxidationreduction transition as follows:

$$\operatorname{ArCr}(\operatorname{CO})_{2} + \operatorname{RX} \rightarrow [\operatorname{ArCr}(\operatorname{CO})_{2}]X + \operatorname{R}$$
 (66)

$$\mathbf{R} \cdot + \mathbf{R} \to \mathbf{R} - \mathbf{R} \tag{67}$$

There appears to be no evidence to exclude the possibility of a carbene formed by  $\alpha$ -elimination of another chlorine atom. The carbene could then insert in the C-Cl bond of PhCC1<sub>3</sub> to produce the observed dimer. The problem is compounded by the data on the reaction of PhCF<sub>3</sub> with Cr(CO)<sub>6</sub>. Using conditions similar to those in the reaction of PhCCl<sub>3</sub>, PhCF<sub>3</sub> was found to give PhCF<sub>3</sub>Cr(CO)<sub>3</sub> as the major product. Traces of a polymeric material were observed but the yields were very low. White and Farome<sup>37</sup> reported that ArCr(CO)<sub>3</sub> promoted 100% polymerization of benzyl fluoride to polybenzyl.

Thus the exact mechanism of the reaction of  $ArCr(CO)_3$  or  $Cr(CO)_6$  with alkyl halides does not appear to be firmly established.

## B. Reaction of Cr(CO)<sub>6</sub> with HC1

After the reactions of the arene chromium tricarbonyl complexes with anhydrous HCl at high pressure, a non-volatile violet solid which turned green in air was observed in the final reaction mixture. Examination of the solid by powder x-ray diffraction procedures showed it to be a mixture of anhydrous  $\text{CrCl}_3$  and  $\text{CrCl}_2$ .<sup>133-135</sup> This data suggested a more detailed study of the high pressure reaction of HCl with chromium in the zero oxidation state.

Chromium hexacarbonyl is a compound which meets the zero oxidation state requirement. The hexacarbonyl was also chosen because of its general similarities to the chromium tricarbonyl complexes and its possible presence in the reaction mixture. In section F.2.f., Cr(CO)<sub>6</sub> was shown to be one of the decomposition products of the arene chromium tricarbonyl complexes.

Thermodynamic calculations (see Appendix K) indicate that the reaction of  $Cr(CO)_6$  with anhydrous HCl at 25° is feasible and  $CrCl_3$  rather than CrCl, as the thermodynamically expected product.

$$2Cr(CO)_{2} + 6HC1 \rightarrow 2CrC1_{2} + 3H_{2} + 12CO$$
 (68)

$$Cr(CO)_6 + 2HC1 \rightarrow CrC1_2 + H_2 + 6CO$$
 (69)

At 300° both reactions have large negative values for  $\Delta G$ , but do not occur at low pressures. In fact, several authors<sup>58,195</sup> state that  $Cr(CO)_6$  does not react with HC1. If the thermodynamic calculations are correct, then the problem seems to be kinetic.

The reaction of  $Cr(CO)_6$  with HCl may be sterically hindered by the six carbon monoxide molecules which are arranged around the central metal atom in such a way as to effectively block the attack of the acid on the chromium. It has previously been shown that the value of  $\Delta V^*$  is more negative in sterically hindered reactions than in analogous reactions which are not sterically hindered.<sup>155-157,174</sup> This means that an increase in rate may be the result of an increase in pressure.

But an increase in pressure would be expected to adversely affect the equilibrium of either reaction 68 or 69 since carbon monoxide, a gas, is a product in both. Thus it is possible to find a maximum in the amount of reaction in a set time.

An increase in pressure did produce a reaction, and the percent yields of  $\operatorname{CrCl}_3$ ,  $\operatorname{CrCl}_2$  and total reaction for the reaction of  $\operatorname{Cr}(\operatorname{CO})_6$ with HCl are shown in Table IX. Several interesting trends can be observed from the graphs in Figures 21 through 27. These graphs are not intended to be used for exact calculations but are intended to merely demonstrate the general trends.

If temperature and yields are plotted at constant pressure as in Figures 21 and 22, the reactions are observed to occur only at temperatures above approximately 125°, irregardless of the pressure. The decomposition temperature of  $Cr(CO)_6$  at one atmosphere is reported to be  $130^\circ$ ,  $^{64,195}$  and, therefore, it appears that decomposition of  $Cr(CO)_6$  is necessary for reaction and suggests that either the metal or  $Cr(CO)_X$ , X = 1-5, may be the actual reactant. As stated in Chapter I, the decomposition of  $Cr(CO)_6$  at 200°/1 atm is complete in less than 15 minutes but in this research, yields of chromium chloride near 100% are observed only at 20 atmospheres pressure. At 4000 atm the yields increase with temperature until complete reaction is obtained above approximately 300°.

At low pressure CrCl, is the major product and its yield is

## TABLE IX

Reaction of 1	HC1 W	lith Cr	<sup>(CO)</sup> 6
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Temperature	Pressure	Reactants	(mmol)	Yi	elds <sup>a</sup> %	······
(°C)	(Atms)	Cr(CO) <sub>6</sub>	HC1	CrCl <sub>3</sub> <sup>b</sup>	CrCl <sub>2</sub> <sup>b</sup>	Total <sup>C</sup>
500	4082	0.138	2.70	100	0	100
350	4082	0.309	4.69	100	0	100
300	4082	0.280	5.17	77	23	100
300	2041	0.540	7.20	40	58	100
300	612	0.347	4.86	17	83	100
300	340	0.262	1.13	19	81	90
300	20	0.262	6.09	6	88	95
250	4082	1.300	7.82	14	16	31
250	1050	0.478	3.41	<1	45	45
250	408	0.476	2.63	4	. 40	50
200	4082	0.367	6.77	16	0	11
200	612	0.415	5.60	11	4	15
200	340	0.303	1.79	12	4	17
200	20	0.989	7.32	0	79	79
150	4082	0.311	1.04	<1	0	<1
150	20	0.776	7.20	0	<1	<1
125	4082	0.370	6.12	0	0	0

a. Yields were determined after 16 hours.

b. % yield based on initial Cr(CO)<sub>6</sub>.

c. % reaction based on Cr(CO)<sub>6</sub> recovered.















Figure 24. Reaction of HC1 with Cr(CO)<sub>6</sub> at 250°C.



Figure 25. Reaction of  $Cr(CO)_6$  with HCl at 300°C.









increased by an increase in temperature (see Figure 21). The yield of  $CrCl_3$  also appears to increase as the temperature is increased and if the yield of  $CrCl_2$  approaches 100% then the yield of  $CrCl_3$  must decrease to zero. (The reaction of HCl with Cr° at 650°/1 atm yields only  $CrCl_2$ .)

However, thermodynamic calculations at one atmosphere support the other possibility; the yield of CrCl<sub>3</sub> should increase with temperature and the yield of CrCl<sub>2</sub> first increase and then decrease with an increase in temperature.

Only above approximately 650°K is

$$2CrCl_3 + H_2 = 2CrCl_2 + 2HCl$$
 (70)

equation 70, as written, the favored reaction (Figure 27). A plot of  $\Delta G$  versus temperature for equations 68 and 69 shows that  $\operatorname{CrCl}_2$  should become the more stable product above 600° (Figure 26). The tensile strength of the glass ampules above 300°, however, prevented confirmation of this behavior of the system.

At 4000 atmospheres  $CrCl_3$  is the major product and becomes the only detectible chloride at 350°. As the temperature is increased the yield of  $CrCl_2$  first increases, goes through a maximum and then decreases as suggested in the previous discussion.

The dramatic change that an increase in pressure produces in the course of a reaction can be seen in Figures 23, 24 and 25, which are plots of yields versus pressure at constant temperature.

At 200° an increase in pressure decreases the amount of total reaction and the yield of  $CrCl_2$  but increases the yield of  $CrCl_3$ . The graph at 250° (Figure 24) shows the same trend but the magnitude of

change per unit increase in pressure is smaller. At 300° an increase in pressure does not seem to alter the total yield but does increase the yield of CrCl<sub>3</sub> and decreases the yield of CrCl<sub>2</sub>.

Thus, it appears that the reaction to produce Cr(II) species is favored at low pressures and high temperatures while the Cr(III) state is favored at high pressures and low temperatures.

In this reaction the fact that the reaction occurs at <u>low</u> <u>pressure</u> if the temperature is above 125° suggests that a prior dissociation of HCl is not required as suggested for arene chromium tricarbonyl complexes because at these conditions there is no liquid or dense fluid phase.

At high pressures and temperatures in excess of  $300^{\circ}$ , traces of  $CO_2$  were observed in the reaction of  $Cr(CO)_6$  with HC1. The amount of  $CO_2$  increased until at 500°, it represented 100% yield according to reaction 71. The production of  $CO_2$  can be accounted for by the following equilibrium:

$$C + CO_2$$
 2CO (71)

At 810° and 46.6 atmospheres, when pure CO was allowed to attain equilibrium, it represented only 30.5% by volume of the final mixture.<sup>196</sup> It was also reported that the concentration of CO decreased as the pressure was increased to 46 atmospheres.

C. Reaction of Chromium Metal with HCl

Since both chromium hexacarbonyl and arene chromium tricarbonyls are known to decompose to the metal and carbon monoxide at high temperatures, 58-63 a series of reactions of 120 mesh powder chromium

with anhydrous hydrogen chloride were conducted. In section F.s.4., chromium metal was shown to be one of the decomposition products of arene chromium tricarbonyl complexes and thus small amounts may be present during reactions of these compounds at elevated temperatures. In the previous section, it was shown that  $Cr^{\circ}$  could be the actual reacting species in the reaction of  $Cr(CO)_{6}$  and HC1.

Calculations also indicate that the reaction of chromium with anhydrous hydrogen chloride at 25° is thermodynamically possible (Appendix L).

Again CrCl<sub>3</sub> would be the more thermodynamically stable product as compared to CrCl<sub>2</sub> when considering the following equations:

$$2Cr^{\circ} + 6HC1 \rightarrow 2CrC1_3 + 3H_2$$
(72)

or

$$\operatorname{Cr}^{\circ} + 2\operatorname{HC1} \rightarrow \operatorname{CrC1}_{2} + \operatorname{H}_{2}$$
 (73)

These comparative stabilities reverse at temperatures above approximately 300° (as shown in Figure 27) but both reactions still possess negative values for the  $\Delta G$  of reaction.

The reactions conducted during this study (Table X, Figure 28) show that there is little or no reaction of chromium with anhydrous HCl at pressures below 10 atmospheres and temperatures less than 400°. Previous experiments by other workers<sup>61,62</sup> have shown that chromium does react with wet HCl or hydrochloric acid at 25° and 1 atmosphere. Reactions performed at pressures in excess of 10 atmospheres did produce reactions which consumed up to 36% of the initial metal. In each case a microscopic examination of the product

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TABLE	X	

Reaction	of	Chromium	with	HC1
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Temperature	Pressure	Reactan	ts (mmol)	% Reaction*
°C	(Atms)	Cr°	HC1	
600°	4082	0.714	5.944	36.4
500°	4082	0.865	4.577	32.4
300°	4082	0.827	1.614	29.1
120°	4082	0.754	5.563	16.3
75	4082	0.860	5.718	11.2
24	4080	1.585	6.296	11.0
300°	340	0.325	4.848	. 24.5
200° 340		2.258	6.865	10.5
100°	340	1.898	6.625	10.8
22°	340	2.314	4.972	8.6
400°	10	6.743	12.672	0.2
300°	10	5.898	26.32	0.8
100°	10	2.462	7.613	0
25°	10	1.975	6.221	0

\* Based on recovered chromium after 16 hours.



Figure 28. Reaction of Cr with HC1 at 4082 Atmospheres.

mixture revealed that the reaction was confined to the outer layers of the metal and thus the lack of diffusion of HCl through the reaction products to the inter metal area was proposed as one reason for the limited yields. The graph of the amount of reaction versus temperature (Figure 28) showed a nearly linear relationship between 100% and 600°.

The relative amounts of  $CrCl_3$  and  $CrCl_2$ , calculated from the amount of chromium and chlorine consumed, seemed to closely follow the results found in the analogous reaction of  $Cr(CO)_6$ . The determination of the exact amounts of  $CrCl_3$  and  $CrCl_2$  by direct individual measurements was prevented by the inability to separate these two products from the unreacted metal without changing them.

The procedure used to measure the amount of unreacted chromium was to dissolve the two chlorides in distilled water. The water was removed and the metal dried under vacuum before weighing.  $CrCl_2$  is known to be water soluble while  $CrCl_3$  is soluble if in the presence of trace amounts of  $Cr^{+2}$  ions.

The major effect of pressure is seen to affect the kinetics of the reaction. Only partial or indirect answers to questions about the primary interaction can be given because the reactions are very slow at low pressure. Additionally, they may be more complex than imagined at first glance. And the true reactants or reactive intermediates have not been directly observed. Since chromium does react with HCl which is partially ionized in  $H_2O$  and pressure is known to increase the amount of ionization, the effect of pressure may speed the reaction by increasing the activity of an ionic reactant.

Another interesting feature of this series of reactions was an extremely reactive product observed in some of the reactions conducted at 4000 atmospheres and temperatures above 500°. This product was not always reproducable but seemed to be present in the final mixture most often if the microreactor was rapidly cooled to ambient conditions. The product was identified as a chromium hydride since it was tentatively unstable and no trace was observed after about 30 minutes. The product would react with distilled and degassed  $H_2O$ under a nitrogen atmosphere to produce a gas that bubbled out of the water. The amount of gas produced was too small to be identified but was assumed to be  $H_2$ . When 0.1 ml of spectrograde CCl<sub>4</sub> was added to the final reaction mixture, a peak could be observed in a nmr spectrum which corresponded to HCCl<sub>3</sub>. Such a reaction with CCl<sub>4</sub> is typical of metal hydrides.

There was a color change to a dark gray or black in samples which gave the above reaction. And, finally, in several samples the calculated ratio of chromium consumed to chlorine consumed was only slightly greater than one. Such would be the situation when a water soluble product which contained chromium but no chlorine was formed. The formation of a chromium hydride would, indeed, be consistent with all the above observations.

	Appendix A.	Mass Spectrum of	$3^{\text{PhSiCI}}3^{\text{Cr}(00)}3$
m/e	I	Т	Assignment
400	1.49	.40	$\operatorname{ArCr}_{2}(\operatorname{CO})_{3}^{+}$
398	1.00	.27	11
370	0.74	.20	$\operatorname{ArCr}_2(\operatorname{CO})_2^+$
346	2.35	.64	$PhSiCl_3Cr(CO)_3^+$
342	0.44	.12	ArCr <sub>2</sub> CO <sup>+</sup>
335	0.07	.02	$PhSiCl_2Cr_2(CO)_2$
318	0.13	.04	PhSiCl <sub>3</sub> Cr(CO) <sub>2</sub>
314	0.34	.09	ArCr <sub>2</sub> +
311	0.97	.26	PhSiCl <sub>2</sub> Cr(CO) <sub>3</sub> <sup>+</sup>
290	0.45	.12	PhSiCl <sub>3</sub> Cr(CO) <sup>+</sup>
266	1.56	.42	PhSiCl <sub>3</sub> Cr <sup>+</sup>
265	2.27	.62	11
264	12.96	3.51	11.
263	3.04	.82	n
262	10.05	2.72	<sup>-</sup> 11
255	.17	.05	$PhSiCl_2Cr(CO)^+$
227	• 33	.09	PhSiCl <sub>2</sub> Cr <sup>+</sup>
210	.45	.12	PhSiC13+
177	2.07	.56	PhSiCl <sub>2</sub> +
175	3.23	.87	11

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	Appendix A	(contin	ued)	
	m/e	Ĩ	T	Assignment
	140	· <b>.</b> 77	.21	PhS1C1 <sup>+</sup>
	133	1.06	.29	sici <sub>3</sub> +
	115	.69	.19	CrSiCl <sup>+</sup> or Cr(CO)Cl <sup>+</sup>
	106	1.38	.37	C6H5Si <sup>+</sup>
	105	3.71	1.01	C6 <sup>H5</sup> Si <sup>+</sup>
	103	2.40	.65	C <sub>6</sub> <sup>H</sup> 3 <sup>Si⁺</sup>
	101	1.12	.30	C <sub>6</sub> HSi <sup>+</sup>
	89	3.59	.97	CrC1 <sup>+</sup>
	88	1.96	•53	, <b>n</b>
	87	8.38	2.27	11
	80	6.58	1.78	Cr(CO) <sup>+</sup> , C <sub>4</sub> H <sub>4</sub> Si <sup>+</sup> , CrSi <sup>°</sup>
	79	4.04	1.09	C₄ <sup>H</sup> ₃Si <sup>+</sup>
	78	1.62	•44	C <sub>6</sub> H <sub>6</sub> <sup>+</sup>
	77	13.16	3.56	C <sub>6</sub> H <sub>5</sub> +
	76	1.38	.37	C <sub>6</sub> H <sub>4</sub> <sup>+</sup>
•	65	12.92	3.50	sic1 <sup>+</sup>
	64	2.11	.57	"
	63	35.23	9.54	n
	54	9.90	2.68	Cr <sup>+</sup>
	53	41.62	11.27	11
	52	100.00	27.08	11
	51	9.64	2.61	C <sub>4</sub> H <sub>3</sub> <sup>+</sup>
	50	17.89	4.85	Cr <sup>+</sup>
	39	1.58	.43	C <sub>3</sub> H <sub>3</sub> <sup>+</sup>

.
Appendix A	(continu	ed)	
m/e	I	T	Assignment
36	2.76	.75	HC1 <sup>+</sup>

a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless they provide significant fragmentation information.

	Appendix	B. Mass	Spectrum of PhSiMeCl <sub>2</sub> Cr(CO) <sub>3</sub>
m/e	I	T	Assignment
328	2.14	.44	PhSiMeCl <sub>2</sub> Cr(CO) <sub>3</sub> +
326	3.18	.65	11
311	.16	.03	$PhSiCl_2Cr(CO)_3^+$
291	1.11	.23	PhSiMeClCr(CO)3+
283	.30	.06	$PhSiCl_2Cr(CO)_2^+$
270	.78	.16	PhSiMeCl <sub>2</sub> CrCO <sup>+</sup>
246	3.66	.75	PhSiC12MeCr <sup>+</sup>
245	4.64	.95	11
244	19.22	3.94	11 .
243	7.19	1.47	11
242	29.95	6.14	tt
240	1.73	<b>.3</b> 5	11
235	.26	.05	PhSiMeC1CrC0 <sup>+</sup>
207	.64	.13	PhSiMeClCr <sup>+</sup>
200	2.92	,60	PhSiMeCr(CO) <sup>+</sup>
190	58	.12	PhSiMeCl <sup>+</sup>
177	1.31	.27	PhSiCl2+
175	2.21	.45	11
157	5.10	1.05	PhSiMeC1 <sup>+</sup>
156	1.90	. 39	11

Appendix B	(contin	uea)
m/e	I	Т
155	12.03	2.47
122	1.70	.35
121	2.86	.59
120	6.20	1.27
119	5.73	1.17
117	1.56	.32
115	1.25	.26
113	.80	.16
106	2.49	.51
105	20.47	4.20
103	4.38	.00
93	5.41	1.11
92	1.21	.25
91	13.75	2.82
90	1.04	.21
89	1.61	.33
87	4.30	.88
81.	1.03	.21
80	5.78	1.19
79	7.42	1.52
78	3.39	.69
77	6.83	1.40
67	3.03	.62
66	1.40	.29

Assignment PhSiMeC1<sup>+</sup>  ${\tt PhSiMeCl_2Cr}^{+2}$ = °7<sup>H</sup>8<sup>Si⁺</sup> C7H7Si<sup>+</sup> CrC<sub>5</sub>H<sub>5</sub>+ SiMeCl<sup>+</sup><sub>2</sub> + CrSiCl<sup>+</sup> SiMeC12+ C6H5Si<sup>+</sup> \*\* C6H3Si<sup>+</sup>  $c_{5}H_{5}si^{+}$ c<sub>5<sup>H</sup>4</sub>si<sup>+</sup>  $c_{5}H_{3}Si^{+}, c_{7}H_{7}^{+}, CrC_{3}H_{3}^{+}$ CrC<sub>3</sub><sup>H</sup>2 CrC1<sup>+</sup> CrC1<sup>+</sup> C4H5Si  $crco^+$ ,  $c_4H_4Si^+$ 

SiMeC1<sup>+</sup>  $C_6H_5^+$ CrMe<sup>+</sup> or  $C_3H_3Si^+$  $C_3H_2Si^+$ 

Appendix 1	B (continu	ied)	
m/e	I	T	Assignment
65	7.50	1.54	<b>51</b> C1 <sup>+</sup>
64	1.57	• 32	**
63	17.30	3.55	sic1 <sup>+</sup>
55	1.04	.21	C2H3Si <sup>+</sup>
54	8.16	1.67	Cr <sup>+</sup>
53	36.46	7.47	"
52	100.00	20.50	", C <sub>4</sub> H <sub>4</sub> +
51	6.33	1.30	с <sub>4</sub> н <sub>3</sub> +
50	13.94	2.86	Cr <sup>+</sup>
43	8.19	1.68	SiMe+
40	2.49	.51	с <sub>3</sub> н <sub>4</sub> +
· 39	2.67	.55	с <sub>3</sub> н <sub>3</sub> +
38	8.12	1.66	нс1+
36	27.24	5.58	HC1 <sup>+</sup>

a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless they provide significant fragmentation information.

	Appendix	C. Mass	Spectrum of	$PhSiMe_2ClCr(CO)_3^-$
m/e	I	T		Assignment
358	.43	.07		$\operatorname{ArCr}_{2}(\operatorname{CO})_{3}^{+}$
330	•22	.04		$\operatorname{ArCr}_{2}(\operatorname{CO})_{2}^{+}$
308	1.67	.28		PhSiMe <sub>2</sub> ClCr(CO) <sub>3</sub> <sup>+</sup>
307	6.56	1.21		11
306	12.90	2.20		п.
291	.38	.06		PhSiMeClCr(CO) <sub>3</sub> +
287	.81	.14		PhSiMeClCr <sub>2</sub> (CO) <sup>+</sup>
274	.22	• 04		$PhSiMe_2ClCr_2^+$
<b>27</b> 2	2.58	•44		$PhSiMe_2Cr(CO)_3^+$
271	8,55	1.46		11
267	.48	.08		PhSiMe2CrC0+
250	1.88	. 32		PhSiMe2ClCrC0+
226	2.69	.46		PhSiMe <sub>2</sub> ClCr <sup>+</sup>
225	7.96	1.36		11
224	31.72	5.41		11
223	22.10	3.77		. 11
222	100.00	17.04		u
221	2.42	.41		
220	4.46	.76		
215	.65	.11		PhSiMe2CrC0 <sup>+</sup>

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Appendix C (continued)

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m/e	I	T	Assignment
207	.59	.10	PhSiMeC1Cr <sup>+</sup>
187	.65	.11	PhSiMe <sub>2</sub> Cr <sup>+</sup>
185	.86	.15	PhSiCrC0 <sup>+</sup>
170	.97	.16	PhSiMe2C1+
157	4.09	.70	PhSiMeC1 <sup>+</sup>
155	10.65	1.81	PhSiMeC1+ .
137	3.44	. 59	PhSiMe2+
136	12.90	2.20	11
135	83.01	14.15	11
125	.97	.16	PhSiMe <sub>2</sub> C1CrC0 <sup>+2</sup>
120	1.34	.23	PhSiMe <sup>+</sup>
119	4.62	.79	C7H7SI <sup>+</sup>
117	1.94	• 33	C <sub>7</sub> H <sub>5</sub> Si <sup>+</sup> , CrC <sub>5</sub> H <sub>5</sub>
115	1.94	• 33	<b>Cr</b> SiCl <sup>+</sup> or CrClCO <sup>+</sup>
112	1.13	.19	PhSiMe <sub>2</sub> ClCr <sup>+2</sup>
111	2.10	• 36	11
107	5.86	1.00	C <sub>6</sub> H <sub>7</sub> Si <sup>+</sup>
106	1.40	•24	c <sub>6</sub> <sup>H</sup> 6 <sup>S1<sup>+</sup></sup>
105	10.27	1.75	c <sub>6</sub> H₅si <sup>+</sup>
103	2.04	• 35	с <sub>6</sub> н <sub>3</sub> si <sup>+</sup>
93	3.55	.60	SiMe <sub>2</sub> Cl <sup>+</sup> plus C <sub>5</sub> H <sub>5</sub> Si <sup>+</sup>
91	6.40	1.09	c <sub>5</sub> H <sub>3</sub> Si, c <sub>7</sub> H <sub>7</sub> <sup>+</sup>
89	2.31	2.39	" plus CrCl <sup>+</sup>
87	2.81	.48	CrC1 <sup>+</sup>

Appendix C (continued)

m/e	I	T	Assignment
83	3.33	.57	C₄H <sub>7</sub> S1 <sup>+</sup>
81	2.10	.36	C₄H₅SI <sup>+</sup>
80	3.44	.59	<b>CrCO<sup>+</sup></b> plus C <sub>4</sub> H <sub>4</sub> Si <sup>+</sup>
79	2.37	.40	C4H3SI <sup>+</sup>
78	1.77	.30	с <sub>6</sub> н <sub>6</sub> +
77	3.76	.64	с <sub>6</sub> н <sub>5</sub> .
69	1.72	.29	C <sub>3</sub> H <sub>5</sub> Si <sup>+</sup>
67	2.04	. 35	C <sub>3</sub> H <sub>3</sub> Si <sup>+</sup>
<b>6</b> 6	1.18	.20	c <sub>3<sup>H</sup>2</sub> si <sup>+</sup>
65	2.85	.49	SiC1 <sup>+</sup> plus C <sub>5</sub> H <sub>5</sub> <sup>+</sup>
63	6.77	1.15	SiC1 <sup>+</sup>
· 59	1.94	.33	C2H7Si <sup>+</sup>
58	1.88	.32	°2 <sup>H</sup> 6Si <sup>+</sup>
57	2.15	.37	°2 <sup>H</sup> 5Si <sup>+</sup>
55	1.94	.33	°2 <sup>H</sup> 3Si <sup>+</sup>
54	3.57	.61	Cr <sup>+</sup>
53	12.97	2.21	n
52	84.62	14.42	83
51	2.04	.35	C4H3 <sup>+</sup>
50	6.38	1.09	Cr <sup>+</sup>
44	1.74	• 30	CH4Si <sup>+</sup>
43	4.84	.82	CH <sub>3</sub> Si <sup>+</sup>

 a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless they provide significant fragmentation information.

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	Appendi	x D. Mass	Spectrum of PhSiMe <sub>3</sub> Cr(CO) <sub>3</sub>
m/e	I	T	Assignment
338	.24	.07	ArCr <sub>2</sub> (CO) <sub>3</sub> <sup>+</sup>
310	.26	.07	ArCr <sub>2</sub> (CO) <sub>2</sub> <sup>+</sup>
288	1.53	.42	$PhSiMe_3Cr(CO)_3^+$
287	4.06	1.10	
286	12.66	3.45	"
284	.97	.26	n
271	.88	•24	$PhSiMe_2Cr(CO)_3^+$
243	.37	.10	$PhSiMe_2Cr(CO)_2^+$
231	2.07	.57	PhSiMe <sub>3</sub> CrCO <sup>+</sup>
230	4.47	1.22	11
215	.89	•24	PhSiMe2CrC0 <sup>+</sup>
204	7.41	2.02	PhSiMe3Cr <sup>+</sup>
203	21.49	5.85	"
202	78.58	21.39	N
201	2.03	.55	· • •
200	4.03	1.13	11
187	1.73	.47	PhSiMe2Cr <sup>+</sup>
137	1.23	.33	PhSiMe2
136	1.84	.50	11
135	22.35	6.08	n

Appendix I	) (continue	d) ·
m/e	I	Т
129	1.12	.30
123	.95	.26
121	1.01	.27
119	1.47	.50
115	1.08	.29
107	2.27	.62
105	4.10	1.11
101	1.12	.30
95	1.36	.37
94	2.05	•56
93	2.10	.57
91	1.49	.41
81	1.04	.28
80	2.16	.59
77	1.36	. 37
<b>73</b> ·	1.43	. 39
67	1.49	.41
66	1.01	.27
59	1.34	.36
57	1.30	.35
55	1.14	.31
54	3.13	.85
53	12.76	3.47

Assignment  $C_8H_5Si^+$   $C_7H_{11}Si^+$   $C_7H_9Si^+$   $C_7H_7Si^+$   $C_6H_7Si^+$  $C_6H_5Si^+$ 

CrSiMe<sup>+</sup> or Cr(CO)Me<sup>+</sup>

 $C_{5}H_{5}Si^{+}$   $C_{5}H_{5}Si^{+}$ ,  $C_{7}H_{7}^{+}$   $C_{4}H_{5}Si^{+}$   $crco^{+}$ ,  $C_{4}H_{4}Si^{+}$   $C_{6}H_{5}^{+}$   $Me_{3}Si^{+}$   $C_{3}H_{3}Si^{+}$   $C_{3}H_{2}Si^{+}$   $C_{2}H_{7}Si^{+}$   $C_{2}H_{5}Si^{+}$ ,  $C_{4}H_{4}^{+}$  $cr^{+}$  Appendix D (continued)

m/e	I	Т	Assignment
52	100.00	27.21	Cr <sup>+</sup>
50	5.85	1.59	11
45	2.01	.55	CH5Si <sup>+</sup>
43	6.11	1.66	CH3S1+

 a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless they provide significant fragmentation information.

	Арре	endix E.	Mass Spectrum of $PhSiCl_3^a$
m/e	I	T	Assignment
<b>21</b> 4	1.34	0.19	PhSiCl <sub>3</sub> +
212	4.75	0.66	11
<b>2</b> 11	0.96	0.13	tt
210	4.56	0.63	11
179	1.20	0.17	PhSiCl2+
178	1.20	0.17	17
177	7.29	1.01	11
176	2.16	0.30	11
175	13.86	1.92	11
174	1.10	0.15	C <sub>6</sub> H <sub>4</sub> SiC1 <sub>2</sub> <sup>+</sup>
137	10.31	1.43	sic1 <sub>3</sub> <sup>+</sup>
136	2.88	0.40	11
135	31.41	4.35	11
134	2.01	0.28	τι
133	33.19	4.59	11
127	1.20	0.17	c2SiH2C1+
125	3.12	0.43	c2SiHC12, c2SiH2C1 <sup>+</sup>
123	3.60	0.50	C2SIHC12+
115	1.34	0.19	c <sub>6</sub> <sup>H</sup> ₅c1 <sup>+</sup>
114	2.78	0.38	11

ADDENGIY C (CONCINGED)	ADD	endix	E (	(continued)
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m/e	I	Т	Assignment
113	2.01	0.28	C6H5C1+
112	3.84	0.53	11
103	1.44	0.20	Sicl <sub>2</sub> <sup>+</sup>
102	1.53	0.21	11
101	3.17	0.44	11
100	10.02	1.39	"
99	1.92	0.27	17
98	12.95	1.79	11
79	1.97	0.27	$c_{6}^{H}_{50}^{+}c_{4}^{SiH}_{3}^{+}$
78	2.21	0.31	с <sub>6</sub> н <sub>5</sub> +
<b>7</b> 7	41.97	5.81	с <sub>6</sub> н <sub>5</sub> +
76	13.14	1.82	с <sub>6</sub> н4+
75	10.79	1.49	c <sub>6</sub> H <sub>3</sub> +
74	12.85	1.78	C <sub>6</sub> H <sub>2</sub> +
73	3.88	0.54	с <sub>6</sub> н+
66	2.35	0.33	C6H6 C3SIH2
65	33.57	4.65	C <sub>6</sub> H <sub>5</sub> <sup>+</sup> , sic1 <sup>+</sup>
64	3.84	0.53	C5H4+
63	66.19	9.16	$c_{5}H_{3}^{+}$ sic1 <sup>+</sup>
62	2.93	0.40	с <sub>5</sub> н <sub>2</sub> +
<b>53</b> .	11.99	1.66	с <sub>4</sub> н <sub>5</sub> +
52	6.95	0.96	C4H4 CH3C1+
51	100.00	13.84	C <sub>4</sub> H <sub>3</sub>
50	73.09	10.11	с <sub>4</sub> н <sub>2</sub> <sup>+</sup> сн <sub>3</sub> с1 <sup>+</sup>

Appendix E	(continue	ed)	
m/e	I	T	Assignment
49	4.56	0.63	с <sub>4</sub> н <sup>+</sup>
39	15.44	2.14	с <sub>3</sub> н <sub>3</sub> +
38	10.07	1.39	HC1 <sup>+</sup>
37	24.46	3.38	c1 <sup>+</sup>
36	21.73	3.01	HCL
35	72.23	10.00	c1 <sup>+</sup>

a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless small peaks provide significant information.

Assignment	T	I	m/e
PhSiMeC12+	0.81	4.00	194
**	0.52	2.56	193
"	3.97	19.66	192
**	0.80	3.97	191
U	5.34	26.46	<b>19</b> 0
PhSiC12+	0.27	1.33	180
11	2.61	12.95	179
11	1.63	8.10	178
11	15.62	77.44	177
11	2.82	14.00	176
11	20.17	100.00	175
PhSiMeC1+	0.31	1.54	157

155

149

140

139

125

123

115

114

Mass Spectrum of PhSiMeCl<sub>2</sub><sup>a</sup> Appendix F.

+ 2 PhSiMeC1+ 0.31 1.54 11 4.92 0.99 1.44 0.29 Unassigned PhSiC1<sup>+</sup> 0.94 0.19 C6H4SIC1<sup>+</sup> 1.86 0.37 11 1.44 0.29 1.33 0.27 11 SiMeC12+ 1.26 6.26 PhC1+ 1.54 0.31 181

Appendix F (continued)

m/e	I	T	Assignment
113	7.95	1.60	S1MeCl2 <sup>+</sup>
112	1.33	0.27	PhC1 <sup>+</sup>
105	1.87	0.38	PhS1 <sup>+</sup>
103	1.33	0.27	c <sub>6</sub> H <sub>3</sub> si <sup>+</sup>
95	1.03	0.21	PhSiMeCl <sub>2</sub> <sup>+</sup> , C <sub>5</sub> H <sub>7</sub> Si <sup>+</sup>
94	1.74	0.35	C5H6S1 <sup>+</sup>
92	1.69	0.34	c <sub>5</sub> <sup>H</sup> ₄si <sup>+</sup>
91	21.64	4.36	C <sub>7</sub> H <sub>7</sub> <sup>+</sup> , C <sub>5</sub> H <sub>3</sub> Si <sup>+</sup>
89	1.85	0.37	PhSiC12+2
88 1/2	2.10	0.42	II
87 1/2	3.28	0.66	11
79	1.49	0.30	C4H4Si <sup>+</sup>
78	5.28	1.07	CH3SIC1+
77	20.92	4.22	с <sub>6</sub> н <sub>5</sub> +
<b>76</b> -	4.29	0.86	с <sub>6</sub> н <sub>4</sub> +
75	1.54	0.31	° <sub>6</sub> <sup>H</sup> 5 <sup>+</sup>
74	1.69	0.34	с <sub>6</sub> н <sub>2</sub> +
66	1.13	0.23	с <sub>5</sub> н <sub>6</sub> +
65	11.56	2.33	sic1 <sup>+</sup>
64	1.54	0.31	с <sub>5</sub> н <sub>4</sub> +
63	26.05	5.25	sic1 <sup>+</sup>
53	3.74	0.76	C <sub>4</sub> H <sub>5</sub> <sup>+</sup>
52	2.36	0.48	C4H4 <sup>+</sup> , CH3C1 <sup>+</sup>
51	18.00	3.63	C <sub>4</sub> H <sub>3</sub> <sup>+</sup>

Appendix	F (continue	d)	
m/e	I	T	Assignment
50	7.95	1.63	сн <sub>3</sub> с1 <sup>+</sup>
41	1.18	0.24	C3H5+
40	2.53	0.51	с <sub>з</sub> н <sub>4</sub> +
39	4.51	0.91	с <sub>з</sub> н <sub>з</sub>
38	5.59	1.13	HC1 <sup>+</sup>
36	13.79	2.78	HC1 <sup>+</sup>
35	1.13	0.23	cı+

 a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless small peaks provide significant information.

			-
m/e	I	T	Assignment
172	4.05	0.70	$PhSiMe_2C1^+$
171	1.77	0.30	**
170	12.42	2.13	11
159	1.09	0.19	PhSiMeC1 <sup>+</sup>
158	4.89	0.84	11
157	49.69	8.53	11
156	12.84	2.20	11
155	100.00	17.17	11
154	1.40	0.24	11
140	0.94	0.16	PhSiC1 <sup>+</sup>
139	6.96	1.20	C6H4SIC1+
136	1.46	0.25	PhSiMe2+
135	10.29	1.77	*1
129	1.04	0.18	$c_2^{H_5}sicl_2^+$
127	0.73	0.12	91
120	1.77	0.30	PhSiMe <sup>+</sup>
119	5.72	0.98	C7 <sup>H</sup> 7 <sup>Si⁺</sup>
117	1.51	0.26	C7 <sup>H</sup> 5 <sup>Si⁺</sup>
108	1.14	0.20	C6H8SI <sup>+</sup>
107	1.92	0.33	C <sub>6</sub> H <sub>7</sub> Si <sup>+</sup>

Appendix G. Mass Spectrum of PhSiMe<sub>2</sub>C1

Appendix G (continued)

m/e	I	T	Assignment
106	1.46	0.25	C6H6SI
105	13.72	2.36	°6 <sup>H</sup> 5Si <sup>+</sup>
104	1.14	0.20	C6 <sup>H4S1+</sup>
103	7.38	1.27	C6 <sup>H3</sup> S1 <sup>+</sup>
95	10.91	1.87	SiMe <sub>2</sub> C1 <sup>+</sup> ,C <sub>5</sub> H <sub>7</sub> Si <sup>+</sup>
94	3.12	0.54	SiMe2 <sup>C1<sup>+</sup>,C5<sup>H</sup>6<sup>S1<sup>+</sup></sup></sup>
93	29.31	5.03	SiMe2C1,C5 <sup>H5Si<sup>+</sup></sup>
92	4.05	0.70	C5H4Si <sup>+</sup>
91	47.51	8.15	C2SIH4CI
89	3.27	0.56	C5 <sup>H2</sup> Si <sup>+</sup>
84	4.16	0.71	C4SIH8+
81	2.08	0.36	C4SiH5+
80	1.66	0.29	C <sub>4</sub> SiH <sub>4</sub> <sup>+</sup> ,SiMeC1 <sup>+</sup>
79	10.55	1.81	PhSiMeC1 <sup>+2</sup>
78 1/2	2.29	0.39	PhSiMeC1 <sup>+2</sup>
78	46.78	8.03	PhSiMeC1 <sup>+2</sup> ,SiMeC1 <sup>+</sup>
77 1/2	10.24	1.76	PhSiMeC1 <sup>+2</sup>
77	13.10	2.25	C6 <sup>H5</sup> +
76	2.13	0.37	C <sub>6</sub> H <sub>4</sub> <sup>+</sup>
75	1.56	0.27	C6H3+
74	3.27	0.56	C6 <sup>H2</sup> +
73	3.74	0.64	C6H <sup>+</sup>
67	4.00	0.69	с <sub>3</sub> siн <sub>3</sub> +
66	2.39	0.41	C <sub>5</sub> H <sub>6</sub> <sup>+</sup>

Appendix G	(continued	1)	
m/e	I	T	Assignment
65	24.95	4.28	sici <sup>+</sup> ,c <sub>5</sub> H <sub>5</sub>
<b>64</b>	3.33	0.57	C <sub>5</sub> H <sub>4</sub> +
63	54.05	9.28	sic1 <sup>+</sup> ,c <sub>5</sub> H <sub>3</sub> <sup>+</sup>
53	5:93	1.02	c <sub>4</sub> H <sub>5</sub> +
52	2.44	0.42	сн <sub>3</sub> с1 <sup>+</sup> ,с <sub>4</sub> н <sub>4</sub> <sup>+</sup>
51	5.30	0.91	C4H3+
50	2.29	0.39	сн <sub>3</sub> с1 <sup>+</sup>
43	2.49	0.43	SiCH3+
39	1.40	0.24	C <sub>3</sub> H <sub>3</sub>

a. I is the % intensity of the largest peak. T is the % intensity
of the total ion current. Only peaks with I greater than 1.00 are
reported unless small peaks provide significant information.

	App	endix H.	Mass Spectrum of PhSiMe 3
m/e	I	Т	Assignment
<b>15</b> 1	2.37	1.04	PhSiMe3+
150	15.41	6.79	"
137	4.36	1.92	PhSiMe2+
136	9.77	4.31	**
135	100.00	44.08	. 11
121	1.78	0.78	PhSiMeH <sup>+</sup>
119	3.11	1.37	PhSiCH2+
107	3.13	1.38	C <sub>6</sub> H <sub>7</sub> Si <sup>+</sup>
106	1.18	0.52	C6H6Si <sup>+</sup>
105	7.46	3.29	C6H5Si <sup>+</sup>
95	1.07	0.47	C <sub>5</sub> H <sub>7</sub> Si <sup>+</sup>
93	2.79	1.23	C5H5SI <sup>+</sup>
91	3.16	1.39	C5H3SI
83	1.45	0.64	C <sub>7</sub> H <sub>7</sub> Si <sup>+</sup>
81	1.25	0.55	C4H5SI
79	2.16	0.95	C₄H₃Si <sup>+</sup>
77	2.09	0.92	C <sub>6</sub> H <sub>5</sub> +
74	1.53	0.67	SiMe3
73	3.66	1.61	SiMe3+
69	1.23	0.54	C <sub>3</sub> H <sub>5</sub> Si <sup>+</sup>

Appendix H	(continue	ed)	
m/e	I	T	Assignment
67 1/2	2.89	1.23	PhSiMe2+2
<b>67</b>	2.19	0.97	c <sub>3</sub> H₃si <sup>+</sup>
66	1.20	0.53	c <sub>5</sub> H <sub>6</sub> <sup>+</sup> ,c <sub>3</sub> H <sub>2</sub> Si <sup>+</sup>
<b>65</b> .	1.50	0.66	с <sub>5</sub> н <sub>5</sub> +
59	1.53	0.67	C <sub>2</sub> H <sub>7</sub> Si <sup>+</sup>
58	1.00	0.44	SiMe2+
57	1.49	0.66	°2 <sup>H</sup> 5 <sup>Si⁺</sup>
55	2.63	1.16	°2 <sup>H</sup> 3 <sup>Si⁺</sup>
53	5.86	2.58	C4H5+
51	2.57	1.13	C4H3+
45	3.91	1.72	Sich5+
44	1.50	0.66	SiCH4+
43	9.29	4.09	SiMe <sup>+</sup>
39	1.38	0.61	с <sub>3</sub> н3+

 a. I is the % intensity of the largest peak. T is the % intensity of the total ion current. Only peaks with I greater than 1.00 are reported unless small peaks provide significant information.

Appendix I. The Calculation of  ${\rm \Delta G}$  for Reaction of PhSiCl\_3 with HCl

The reaction of phenyltrichlorosilane at 202° can be written as follows:

$$PhSiCl_{3(g)} + HCl_{(g)} \rightarrow C_{6}^{H} + SiCl_{4(g)}$$
 (74)

Values for  $\Delta H_{298}$  and  $S_{298}$  were

	<sup>ΔH</sup> 298 kcal/mol	S <sub>298</sub> cal/mol°
PhSiC1 199,202	-109.9 <sup>a</sup>	100.58
HC1 <sup>198</sup>	-22.05	44.64
C6 <sup>H6</sup> 198	19.82	64.34
SiC14 <sup>198</sup>	-151.8	79.00

The values of HCl, SiCl<sub>4</sub>,  $C_{6}^{H}_{6}$  and PhSiCl<sub>3</sub> at 500°K/latm were found by adding the correction terms:

	H <sub>T</sub> -H <sub>298</sub> cal/mol	ST-S298 cal/mol°
PhSiC1 199,202	10666	23.28
HC1 <sup>200</sup>	1410	3.61
C6H6 <sup>201</sup>	5360	13.41
sic1 <sub>4</sub> <sup>200</sup>	4655	11.88

Using  $\Delta G = \Delta H - T\Delta S$ , the free energy at 500°K/latm was calculated

$$\Delta G_{500} = -1.46 - 500 (-3.48) 10^{-3}$$
(75)

$$\Delta G_{500} = +0.3 \text{ kcal/mol}$$
 (76)

Using  $\Delta G = \Delta H - T\Delta S$ , the free energy at 298°K/latm was calculated for the gaseous state

$$\Delta G_{298} = 0 + 6.1 \tag{77}$$

$$\Delta G_{298} = 6.1 \text{ kcal/mol}$$
 (78)

If the calculations are made for

$$PhSiCl_{3(\ell)} + HCl_{(g)} + C_{6}^{H}_{6(\ell)} + SiCl_{4(\ell)}$$
 (79)

at 298°K/latm using:

	$\Delta H_{298}$ kcal/mol	S298 cal/mol°
PhSiC13	-109.9	75.22
HC1	-22.05	44.64
с <sub>6</sub> н <sub>6</sub>	11.72	41.30
SiCl <sub>4</sub>	-158.9	60.34

$$\Delta G_{298} = -15.23 - (298)(-18.22) \ 10^{-3} \tag{80}$$

$$\Delta G_{298} = -9.8 \text{ kcal/mol.}$$
(81)

Appendix J. The Calculation of Group Electronegativities

The electronegativities of the silyl groups were calculated by assuming variable electronegativity of the central silicon atom in the group and equalization of electronegativity in all bonds as suggested by Huheey.<sup>166-170</sup> The equation used to find the electronegativity for a

> X -W Y Z

group was

$$X_{m} = \frac{a_{W}^{b} x^{b} y^{b} z + a_{X}^{b} w^{b} y^{b} z + a_{Y}^{b} w^{b} x^{b} z + a_{Z}^{b} w^{b} x^{b} y + b_{W}^{b} x^{b} y^{b} z^{\delta} w^{XYZ}}{b_{X}^{b} y^{b} w + b_{X}^{b} z^{b} w + b_{X}^{b} y^{b} z + b_{Y}^{b} z^{b} w}$$
(82)

where  $a = \frac{I-A}{2}$  (83)

$$\mathbf{b} = \mathbf{I} + \mathbf{A} \tag{84}$$

and I is the ionization potential, A is the electron affinity, and  $\delta$ is the partial charge resulting from electron gain or loss. Sometimes a is termed the inherent electronegativity and b termed the charge coefficient. Values for a and b were obtained from Huheey's papers and electronegativities are in Mulliken units. The values used were

		176
	a	Ъ
S1	7.30	9.04
C1	9.38	11.30
Me	7.37	3.24
Ph	8.03	1.21

The following values were obtained from equation 82:

$$\chi_{\text{SiMe}_3} = 7.36 + 0.96 \delta_{\text{SiMe}_3}$$
 (85)

$$\chi_{\text{SiMe}_2\text{Cl}} = 7.58 + 1.22 \delta_{\text{SiMe}_2\text{Cl}}$$
 (86)

$$\chi_{\text{SiMeCl}_2} = 7.95 + 3.35 \, \delta_{\text{SiMeCl}_2}$$
 (87)

$$x_{\text{SiCl}_3} = 8.77 + 2.66 \, \delta_{\text{SiCl}_3}$$
 (88)

Equations 85, 86, 87, and 38 were each used in turn with equation

$$\chi_{\rm m} = 8.95 - 0.89 \, \delta_{\rm Cr(CO)} {}_{3}{}^{\rm C}_{6}{}^{\rm H}_{5}$$
 (89)

which is the group electronegativity for the  $Cr(CO)_{3}C_{6}H_{5}$ -group obtained from the work of Gubin and Khandkarova.<sup>84</sup> The formulas used for two bonding groups were

$$a_1 + b_1 \delta_1 = a_2 + b_2 \delta_2$$
 (90)

and

$$\delta_1 + \delta_2 = 0 \tag{91}$$

When bonded to a  $Cr(CO)_{3}C_{6}H_{5}$  group, the silyl groups have the following electronegativities.

$$\chi_{SiMe_3} = 8.19$$
 (92)

$$\chi_{SiMe_2C1} = 8.37$$
 (93)

$$\chi_{SiMeCl_2} = 8.74$$
 (94)

$$x_{\text{SiCl}_3} = 8.91$$
 (95)

When bonded to a  $C_6^{H_5}$  group the electronegativities are:

$$\chi_{SiMe_3} = 7.66$$
 (96)

$$\chi_{SiMe_2C1} = 7.80$$
 (97)

$$\chi_{\text{SiMeCl}_2} = 8.01 \tag{98}$$

$$\chi_{\text{SiCl}_3} = 8.26$$
 (99)

Appendix K. The Calculation of  $\Delta G$  for Reaction of Cr(CO)<sub>6</sub> with HCl

When  $Cr(CO)_6$  reacts with anhydrous HCl, two different equations can be written depending on which chloride is formed. The reaction to produce  $CrCl_3$  will be considered first. (Initial data listed on next page.)

$$Cr(CO)_6 + 3HC1 \rightarrow CrCl_3 + 3/2 H_2 + 6CO$$
 (100)

Using

$$\Delta G = \Delta H - T \Delta S$$
 (101)

$$\Delta G_{298} = 30.7 - (298)(143.6) 10^{-3}$$
(102)

$$\Delta G_{298} = -12.1 \text{ kcal/mol}$$
(103)

also

$$\Delta G_{500} = 32.8 - (500)(168.2) 10^{-3}$$
(104)

$$\Delta G_{500} = -51.3 \text{ kcal/mol}$$
(105)

On the other hand, to produce  $CrCl_2$ .

$$Cr(CO)_6 + 2HC1 \rightarrow CrCl_2 + H_2 + 6CO$$
 (106)

$$\Delta G_{298} = 48.6 - (298)(170.0) \ 10^{-3} \tag{107}$$

$$\Delta G_{208} = -2.0 \text{ kcal/mole} \tag{108}$$

and

$$\Delta G_{500} \approx 50.5 - (500)(196.4) 10^{-3}$$
(109)

(110)

 $\Delta G_{500} = -47.7 \text{ kcal/mol}$ 

	<sup>ΔH</sup> 298	<sup>ΔH</sup> 500	<sup>S</sup> 298	<sup>\$</sup> 500
Cr(CO) <sub>6</sub>	-257.6	-245.4	83.18	86.58
HC1	-22.1	-20.6	31.21	34.81
<sup>H</sup> 2	0	1.4	31.21	34.81
CO	-26.4	-24.4	47.30	52.35
CrC1 <sub>3</sub>	-134.6	-130.1	30.0	33.11
CrC12	-94.6	-91.1	27.4	30.51

Values taken from ref. 198, 200, and Handbook of Chemistry and Physics.

Appendix L. The Calculation of  $\Delta G$  for Reaction of Cr° with HCl

When Cr° reacts with anhydrous HCl, two different equations can be written depending on which chloride is found. The reaction which yields chromium in the +3 oxidation state will be considered first.

The reaction of Cr° with HCl can be written:

$$Cr^{\circ} + 3HC1 \rightarrow CrC1_3 + 3/2 H_2$$
 (111)

The value of  $\Delta G_{298}$  for the above reaction is -49.69 kcal/mol.<sup>198</sup> Using

$$\Delta G = \Delta H - T \Delta S \tag{112}$$

and values for  $\Delta H$  and  $\Delta S$  obtained from reference 200. The following values of  $\Delta G$  for equation calculated for the listed temperatures.

Temperature °K	∆G kcal/mol	∆H kcal/mol	ΔS (e.u.)
298°	-49.69	-68.42	-62.7
500°	-33.19	-67.27	-68.2
600°	-24.59	-66.64	-70.09
800°	-6.72	-65.30	-73.22

Appendix L (continued)

Similar calculations can be performed for the equation:

$$Cr^{\circ} + 2HC1 \rightarrow CrC1_{2} + H_{2}$$
(113)

obtaining the listed values:

Cemperature °K	ΔG kcal/mol	ΔH kcal/mol	ΔS (e.u.)
298°	-39.61	-50.44	-36.31
500°	-29.61	-49.58	-39.93
600°	-23.87	-48.60	-43.31
800°	-13.47	-48.12	-43.31

The reactions of Cr° with HCl in this report were conducted with an excess of HCl to promote the maximum amount of reaction under pressure and thus the following reaction was of interest:

$$CrCl_{2} + HCl \rightarrow CrCl_{2} + 1/2 H_{2}$$
 (114)

Repeating the previous method the following values were obtained:

Temperature °K	∆G kcal/mol	ΔH kcal/mol	<b>∆S (e.u.)</b>
298°	-10.08	-17.98	-26.42
500°	-3.59	-17.70	-28.22
600°	+0.78	-17.54	-28.87
700°	+3.24	-17.36	-29.42
800°	+6.75	-17.18	-29.92

## BIBLIOGRAPHY

- 1. R. S. Bradley and D. C. Munro, <u>High Pressure Chemistry</u>, Pergamon Press, New York, N. Y., 1965.
- 2. S. W. Benson, <u>The Foundations of Chemical Kinetics</u>, McGraw-Hill, New York, N. Y., 1960, pp. 510-517.
- 3. S. D. Hamann, in <u>High Pressure Physics and Chemistry</u>, R. S. Bradley, ed., Academic Press, New York, N. Y. 1963.
- 4. M. G. Gonikberg, <u>Chemical Equilibria and Reaction Rates at High</u> <u>Pressures</u>, Israel Program for Scientific Translation, Jerusalem, 1963.
- 5. C. C. Bradley, <u>High Pressure Methods in Solid State Research</u>, Plenum Press, New York, N. Y., 1969.
- 6. P. W. Bridgman, <u>The Physics of High Pressure</u>, G. Bell, London, 1952.
- 7. C. A. Eckert, "High Pressure Kinetics in Solution," in <u>Ann. Rev.</u> <u>Phys. Chem.</u>, <u>23</u>, 239 (1972).
- 8. W. J. Moore, <u>Physical Chemistry</u>, Prentice-Hall, Englewood Cliffs, N. J., 1962.
- 9. P. W. Bridgman, Phys. Rev., <u>48</u>, 825 (1935).
- 10. P. W. Bridgman, J. Appl. Phys., <u>12</u>, 461 (1941).
- 11. P. W. Bridgman, Proc. Roy. Soc. (London) A, 203, 1 (1950).
- 12. E. W. Comings, <u>High Pressure Technology</u>, McGraw-Hill, New York, N. Y., 1956.
- 13. G. N. Lewis and M. Randall, <u>Thermodynamics</u>, revised by K. S. Pitzer and L. Brewer, McGraw-Hill, New York, N. Y., 1961.
- 14. T. Asano and W. J. LeNoble, Rev. Phys. Chem. Japan, <u>43</u>, 82 (1973).

- 16. R. W. Bott, C. Eaborn, and P. M. Greasley, J. Chem. Soc., 4804 (1964).
- 17. C. Eaborn, J. Chem. Soc., 4858 (1956).
- 18. C. Eaborn, J. Chem. Soc., 3148 (1953).
- 19. R. A. Benkeser and H. R. Krysiak, J. Amer. Chem. Soc., <u>75</u>, 4528 (1953).
- 20. R. A. Benkesu and F. Clark, J. Amer. Chem. Soc., 82, 4881 (1960).
- G. V. Motsarev and A. Ya Yakuborich. Zh. Obshch. Khim., <u>35</u>, 1056 (1965); Chem. Abstr., <u>63</u>, 11604 (1965).
- 22. C. H. Van Dyke, "Synthesis and Properties of the Silicon-Halogen and Silicon-Halogenoid Bond," in <u>Organometallic Compounds of</u> <u>the Group IV Elements</u>, A. G. MacDiarmid, Ed., Marcel Dekker, Inc., 1972.
- 23. A. Ya Yakubovich and G. V. Motsarev, Zh. Obshch. Khim., <u>23</u>, 412 (1953); Chem. Abstr., <u>48</u>, 3286 (1954).
- E. A. V. Ebsworth, "Physical Basis of the Chemistry of the Group IV Elements," in <u>The Bond to Carbon</u>, A. G. MacDiarmid, ed., Marcel Dekker, New York, N. Y., 1968, pp. 1-105.
- 25. R. J. H. Voorhoeve, <u>Organohalosilanes, Precursors to Silicones</u>, Elsevier Publishing Company, New York, N. Y., 1967.
- 26. J. D. Austin, C. Eaborn and J. D. Smith, J. Chem. Soc., 4744 (1963).
- 27. E. G. Rochow and W. F. Gilliam, J. Amer. Chem. Soc., <u>67</u>, 1772 (1945).
- H. Zeiss, P. J. Wheatley and H. J. S. Winkler, <u>Benzenoid-Metal</u> <u>Complexes</u>, Ronald Press Company, New York, N. Y., 1966.
- 29. B. Nicholls and M. C. Whitting, J. Chem. Soc., 551 (1959).
- 30. D. N. Kursanov, J. N. Setkina, N. K. Baranetskaya, V. I. Zdanovich and K. N. Anisimov., Proc. Acad. Sci. USSR, <u>190</u>, 127 (1970).
- 31. C. P. Lillya and R. A. Sahatjian, Inorg. Chem., <u>11</u>, 889 (1972).
- 32. M. Ashraf, Can. J. Chem., 50, 118 (1972).

- 33. D. N. Kursanov, V. N. Setkina and B. G. Bribov, J. Organometal. Chem., <u>37</u>, C35 (1972).
- 34. E. O. Fischer, H. Essler, W. Frohlich, J. P. Mortensen and W. Semmlinger, Chem. Ber., <u>91</u>, 2763 (1958).
- 35. M. Ashraf and W. R. Jackson, J. Chem. Soc., Perkin Trans. 2, 103 (1972).
- 36. A. Wu, E. R. Biehl, and P. C. Reeves, J. Chem. Soc., Perkin Trans. 2, 449 (1972).
- 37. T. F. White and M. F. Farona, J. Organometal. Chem., <u>37</u>, 119 (1972)
- 38. M. F. Farona and J. F. White, J. Amer. Chem. Soc., <u>93</u>, 2826 (1971).
- 39. G. Fritz and D. Kummer, Z. Anorg. Allg. Chem., 308, 105 (1961).
- 40. A. Ya. Yakubovich and G. V. Motsarev, Zh. Obshch. Khim., <u>25</u>, 1748 (1955); Chem. Abstr., <u>50</u>, 5550 (1956).
- 41. T. D. Holmes, D. A. K. Jones and R. Pettit, J. Organometal. Chem., <u>4</u>, 324 (1965).
- 42. K. Edgar, B. F. G. Johnson, J. Lewis, and S. B. Wild, J. Chem. Soc. A, 2851 (1968).
- 43. W. S. Trahanovsky and D. K. Wells, J. Am. Chem. Soc., <u>91</u>, 5870 (1969).
- 44. D. G. Carroll and S. P. McGlynn, Inorg. Chem., 7, 1285 (1968).
- 45. D. A. Brown and R. M. Rawlinson, J. Chem. Soc. A, 1530 (1969).
- 46. S. P. Gubin, V. S. Khandkarova and A. Z. Kreindlin, J. Organometal. Chem., <u>64</u>, 229 (1974).
- J. S. Khandkarova and S. P. Gubin, J. Organometal. Chem., <u>22</u>, 149 (1970).
- 48. S. P. Gubin and V. S. Khandkarova, J. Organometal. Chem., <u>22</u>, 449 (1970).
- 49. V. S. Khandkarova, S. P. Gubin and B. A. Kvasov, J. Organometal. Chem., <u>23</u>, 509 (1970).
- 50. R. V. Emanuel and E. W. Randall, J. Chem. Soc., A, 3002 (1969).
- 51. W. McFarlane and S. O. Grim, J. Organometal. Chem., <u>5</u>, 147 (1966).

52. J. T. Price and T. S. Sorensen, Can. J. Chem., 46, 515 (1968).

- 53. D. A. Brown and D. G. Carroll, J. Chem. Soc., 2822 (1965).
- 54. A. Wu, E. R. Biehl and P. C. Reeves, J. Organometal. Chem., <u>33</u>, 53 (1971).
- 55. D. A. Brown and H. Sloan, J. Chem. Soc., 3849 (1962).
- 56. G. E. Herberish and E. O. Fischer, Chem. Ber., <u>95</u>, 2803 (1962).
- 57. D. A. Brown and F. J. Hughes, Inorg. Chim. Acta, <u>1</u>, 448 (1967).
- 58. F. A. Cotton and G. Wilkinson, <u>Advanced Inorganic Chemistry</u>, 3rd ed., Interscience, New York, N. Y., 1972.
- M. C. Udy, "Physical Properties of Chromium, Its Alloys and Metallurgical Use," in <u>Chromium</u>, Vol. 2, Reinhold, New York, 1956.
- 60. H. Lux, L. Eberle and D. Darre, Chem. Ber., <u>97</u>, 503 (1964).
- 61. F. Hein and S. Herzog, in <u>Handbook of Preparative Inorganic</u> Chemistry, 2, Academic Press, New York, 1965.
- 62. J. Koppel, Z. Anorg. Allgem. Chem., <u>45</u>, 359 (1905).
- 63. F. Calderazzo, R. Ercoli and G. Natta, "Metal Carbonyls: Preparation, Structure, and Properties," in <u>Organic Syntheses via Metal</u> Carbonyls, Interscience, New York, 1968.
- 64. W. Hieber and E. Romberg, Z. Anorg. Allgem. Chem., <u>221</u>, 321 (1935).
- 65. R. P. M. Werner, Chem. Ber., <u>94</u>, 1207 (1961).
- 66. H. Lux and G. Illmanm, Chem. Ber., <u>92</u>, 2364 (1959).
- 67. L. D. Segal, O. D. Krichevskaya, Ν. Λ. Belvzerskii, Ν. Ε. Kolobova, and K. N. Anisimov, Russ. J. Inorg. Chem., <u>12</u>, 592 (1967).
- J. D. Corbelt, R. J. Clark and T. F. Mundy, Jr., Inorg. Nucl. Chem., <u>25</u>, 128 (1963).
- 69. D. Seyferth and D. L. Alleston, Inorg. Chem., 2, 417 (1963).
- 70. T. F. Tula and D. Seyferth, Inorg. Chem., 7, 1245 (1968).
- 71. H. P. Fritz and C. G. Kreiter, J. Organometal. Chem., <u>7</u>, 427 (1967).

- 72. N. S. Nametkin, V. M. Vdovin, V. A. Poletaev, E. Sh. Finkel'shtein and A. Yu Koshevnik, Dokl. Akad. Nauk SSSR, <u>208</u>, 868 (1973); Chem. Abstr., <u>78</u>, 159793 (1973).
- 73. G. I. Magomedov, V. G. Syrkin, A. S. Frenkel, A. V. Medvedeva and A. N. Artemov, USSR Pat. 379,579; Chem. Abstr., <u>79</u>, 78956 (1973).
- 74. T. Rigg and D. B. Innes, Can. J. Chem. Eng., <u>46</u>, 450 (1969).
- 75. W. L. Jolly, <u>Synthetic Inorganic Chemistry</u>, Prentice-Hall, Englewood Cliffs, New Jersey, 1970.
- 76. R. E. Dodd and P. E. Robinson, <u>Experimental Inorganic Chemistry</u>, Elsevier Publishing Co., New York, N. Y., 1957.
- 77. S. Dushman, <u>Scientific Foundations of Vacuum Techniques</u>, John Wiley and Sons, Inc., New York, N. Y., 1949.
- 78. R. T. Sanderson, <u>Vacuum Manipulations of Volatile Compounds</u>, John Wiley and Sons, Inc., New York, N. Y., 1948.
- 79. J. C. Bryan, Chemist Analyst, 29, 71 (1940).
- 80. R. E. Rondeau, J. Chem. Eng. Data., <u>11</u>, 124 (1966).
- 81. A. P. Hagen, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania, 1968.
- 82. J. J. Moscony, Ph.D. Dissertation, University of Pennsylvania, Philadelphia, Pennsylvania, 1965.
- J. J. Moscony, R. I. Harker and A. G. MacDiarmid, Rev. Sci. Instr., <u>38</u>, 138 (1967).
- 84. D. R. Stull, Ind. Eng. Chem., 39, 517 (1947), ibid. 1684.
- 85. R. P. Rhodes, J. Chem. Educ., <u>40</u>, 423 (1963).
- 86. G. P. Helliwell, J. Chem. Educ., <u>41</u>, 575 (1964).
- 87. W. Strohmeier, Chem. Ber., 94, 2490 (1961).
- 88. A. D. Cross, <u>Introduction to Practical Infrared Spectroscopy</u>, 2nd ed., Butterworths, London, 1964, p. 42.
- 89. B. Nicholls and M. C. Whiting, J. Chem. Soc., 469 (1960).
- 90. R. J. Robinson, C. G. Warner, and R. S. Gohlke, J. Chem. Ed., 47, 467 (1970).

- 91. F. W. McLafferty, Anal. Chem., 28, 306 (1956).
- 92. B. D. Cullity, <u>Elements of X-Ray Diffraction</u>, Addison-Wesley Publishing Co., Reading, Mass. 19591.
- 93. R. H. Pierson, A. N. Fletcher and E. S. Gantz, Anal. Chem., <u>28</u>, 1218 (1956).
- 94. Am. Petro. Inst. Res. Proj. 44, Serials 175, 250, 304, 417, 1591 and 1612.
- 95. R. D. Fischer, Chem. Ber., <u>93</u>, 165 (1960).
- 96. G. Davidson and E. M. Riley, Spectrochim. Acta, A <u>27</u>, 1649 (1971).
- 97. S. Pignataro and F. P. Lossing, J. Organometal. Chem., <u>10</u>, 531 (1967).
- 98. J. Muller and P. Goser, Chem. Ber., <u>102</u>, 3314 (1969).
- 99. M. E. Grenoble and P. J. Launer, App. Spec., 14, 85 (1960).
- 100. V. H. Kriegsmann and G. Engelhardt, Z. Anor. Allg. Chem., <u>310</u>, 320 (1961).
- 101. G. D. Grant and A. L. Smith, Anal. Chem., 30, 1016 (1958).
- 102. M. C. Tobin, J. Amer. Chem. Soc., <u>75</u>, 1788 (1953).
- 103. A. L. Smith and J. A. McHard, Anal. Chem., <u>31</u>, 1174 (1959).
- 104. N. N. Sokolov, K. A. Andrianov and S. M. Akimova, Z. Obs. Khim., <u>25</u>, 678 (1955).
- 105. V. Caglioti, G. Sartori and C. Furlani, J. Inorg. Nucl. Chem., <u>13</u>, 22 (1960).
- 106. S. L. Shufler, H. W. Sternberg and R. A. Friedel, J. Amer. Chem. Soc., <u>78</u>, 2687 (1956).
- 107. D. R. Bidinosti and N. S. McIntyre, Can. J. Chem., <u>45</u>, 641 (1967).
- 108. R. E. Winters and R. W. Kiser, Inorg. Chem., 4, 157 (1965).
- 109. A. L. Smith, J. Chem. Phys., 21, 1997 (1953).
- 110. A. L. Smith and N. C. Angelotti, Spectrochim. Acta, <u>14</u>, 412 (1959).
- 111. H. W. Thompson, Spectrochim. Acta, 16, 238 (1960).
- 112. Cat. Mass Spec. Data, Thermo. Res. Cntr. Data Proj., Serial 28.
- 113. Am. Petro. Inst. Res. Proj. 44, Serial 93.
- 114. Cat. Mass Spec. Data, Thermo. Res. Cntr. Data Proj., Serial 29.
- 115. L. G. L. Ward, Inorg. Syn., <u>11</u>, 161 (1968).
- 116. V. H. Kriegsmann and K. H. Schowtka, Z. Physik Chem., <u>209</u>, 261 (1958).
- 117. A. E. Finholt, A. C. Bond Jr., K. E. Wilzbach and H. I. Schlesinger, J. Am. Chem. Soc., 69, 2692 (1947).
- 118. E. A. Jones, J. S. Kirby-Smith, P. J. H. Woltz and A. H. Nielsen, J. Chem. Phys., <u>19</u>, 242 (1951).
- 119. J. W. Linnett and D. F. Heath, J. Chem. Phys., 19, 801 (1951).
- 120. V. H. Dibeler and F. L. Mohler, J. Res. Nat. Bur. of Standards, 40, 25 (1948).
- 121. E. Schnell and E. G. Rochow, J. Amer. Chem. Soc., 78, 4178 (1956).
- 122. A. L. Smith, Spectrochim. Acta, 16, 87 (1960).
- 123. H. Gilman, R. K. Ingham, and A. G. Smith, J. Org. Chem., <u>18</u>, 1743 (1953).
- 124. J. Benes, V. Chvalovsky and V. Bazant, Collect. Czech. Chem. Commun., <u>26</u>, 1617 (1961).
- 125. J. Knizek, V. Chvalovsky and M. Horak, Collect. Czech. Chem. Commun., <u>29</u>, 2935 (1964).
- 126. K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, John Wiley and Sons, New York, N. Y., 1963.
- 127. Figure 14 and Table VI, This Dissertation.
- 128. Appendix B, This Dissertation.
- 129. Appendix A, This Dissertation.
- 130. Am. Petro. Inst. Res. Proj. 44, Serial 156.
- 131. R. R. Haun and W. D. Harkins, J. Amer. Chem. Soc., 54, 3917 (1932).
- 132. D. A. Long, T. V. Spencer, D. N. Waters and L. A. Woodward, Proc. Roy. Soc. (London), <u>A240</u>, 499 (1957).

133. L. L. Handy and N. W. Gregory, J. Chem. Phys., <u>19</u>, 1314 (1951).

- 134. L. L. Handy and N. W. Gregory, J. Amer. Chem. Soc., <u>74</u>, 891 (1952).
- 135. Powder Diffraction File. Joint Committee on Powder Diffraction Standards, published American Society for Testing and Materials, 1972.
- 136. Am. Petro. Inst. Res. Proj. 44, Serials 452, 1579 and 1593.
- 137. Am. Petro. Inst. Res. Proj. 44, Serials 157, 1582 and 1596.
- 138. Am. Petro. Inst. Res. Proj. 44, Serials 118, 216, 1585, 1589 and 1605.
- 139. Am. Petro. Inst. Proj. 44, Serial 217.
- 140. Am. Petro. Inst. Res. Proj. 44, Serials 176, 251, 305 and 418.
- 141. Appendix H, This Dissertation.
- 142. Appendix D, This Dissertation.
- 143. R. E. Richards and H. W. Thompson, J. Chem. Soc., 124 (1949).
- 144. R. L. Collins and J. R. Nielsen, J. Chem. Phys., 23, 351 (1955).
- 145. H. Kriegsmann, Z. Elektrochem., <u>62</u>, 1088 (1957).
- 146. Figure 15 and Table VI, This Dissertation.
- 147. Appendix C, This Dissertation.
- 148. C. Liebermann and T. Homeyer, Ber., <u>12</u>, 1971 (1879).
- 149. R. P. M. Werner and T. H. Coffield, in <u>Advances in the Chemistry</u> of the Coordination Compounds, S. Kirschner ed., Macmillan Co., New York, N. Y., 1961, p. 535.
- 150. S. Pignataro and F. P. Lossing, J. Organometal. Chem., <u>11</u>, 571 (1968).
- 151. T. H. Beynon, <u>Mass Spectrometry and its Application to Organic</u> Chemistry, Elsevier Publishing Co., New York, N. Y., 1960.
- 152. J. Muller and K. Fenderl, Chem. Ber., <u>103</u>, 3128 (1970).
- 153. J. Muller and K. Fenderl, Chem. Ber., <u>104</u>, 2199 (1971).
- 154. T. R. Gilbert, W. P. Leach and J. R. Miller, J. Organometal. Chem., <u>56</u>, 295 (1973).

- 155. R. B. King, Appl. Spectrosc., 23, 536 (1969).
- 156. N. Maoz, A. Mendelbaum and M. Cais, Tetrahedron Lett., 2087 (1965).
- 157. Figure 13 and Table VI. This Dissertation.
- 158. M. Pahl, Z. Naturforsch., 9b, 188 (1954).
- 159. M. Pahl, Z. Naturforsch., 9b, 418 (1954).
- 160. G. M. Bodner and L. J. Todd, Inorg. Chem., <u>13</u>, 360 (1974).
- 161. G. M. Whitesides, J. G. Selgestad, S. P. Thomas, D. W. Andrews, B. A. Morrison, E. T. Panek and J. San Filippo, Jr., J. Organometal. Chem., <u>22</u>, 365 (1970).
- 162. H. P. Fritz and J. Manchot, Spectrochim. Acta, <u>18</u>, 171 (1962).
- 163. H. P. Fritz and J. Manchot, Z. Naturforsch., <u>17b</u>, 710 (1962).
- 164. D. M. Adams, J. Chem. Soc., 1771 (1964).
- 165. R. E. Humphrey, Spectrochim. Acta, <u>17</u>, 93 (1961).
- 166. G. Davidson and E. M. Riley, J. Organometal. Chem., <u>19</u>, 101 (1969).
- 167. H. T. Buttery, G. Keeling, S. F. A. Kettle, I. Paul and P. J. Stamper, Disc. Faraday Soc., <u>47</u>, 48 (1969).
- 168. K. Schlogl, H. Falk and G. Haller, Monatsh. Chem., <u>98</u>, 82 (1967).
- 169. A. Mangini and F. Taddei, Inorg. Chem. Acta, 2, 8 (1968).
- 170. T. A. Pople, W. G. Schneider and Bernstein, <u>High Resolution</u> <u>Nuclear Magnetic Resonance</u>, McGraw-Hill, New York, N. Y., 1959.
- 171. W. R. Jacoson, W. B. Jennings, S. C. Rennison and R. Spratt, J. Chem. Soc., 1214 (1969).
- 172. E. W. Balis, H. A. Liebhafsky and D. H. Getz, Ind. Eng. Chem., <u>41</u>, 1459 (1949).
- 173. R. O. Sauer, U. S. Pat. 2,730,540 (1956); Chem. Abstr., <u>50</u>, 12108 (1956).
- 174. L. H. Sommer, E. W. Pietrusza and F. C. Whitmore, J. Amer. Chem. Soc., <u>68</u>, 2282 (1946).
- 175. L. Schafer, G. M. Begun, S. J. Cyvin, Spectrochim. Acta, A, <u>28</u>, 803 (1972).

176.	Y. Vignollet and J. C. Maire, J. Organomet. Chem., <u>17</u> , P43 (1969).
177.	H. Bock and H. Alt, J. Amer. Chem. Soc., <u>92</u> , 1569 (1970).
178.	J. Vcelak and V. Chvalovsky, Collect. Czech. Chem. Commun., <u>38</u> , 1055 (1973).
179.	W. D. Harder and E. U. Franck, Ber. Bunsenges. physik. Chem., <u>76</u> , 1106 (1972).
180.	J. Akella and G. C. Kennedy, J. Chem. Phys., <u>55</u> , 793 (1971).
181.	C. Walling and M. Naiman, J. Amer. Chem. Soc., <u>84</u> , 2628 (1962).
182.	A. H. Ewald, Discuss. Faraday Soc., <u>22</u> , 138 (1956).
183.	A. Bodansky and W. Kauzman, J. Phys. Chem., <u>66</u> , 177 (1962).
184.	H. G. David and H. G. Drickamer, Trans. Faraday Soc., <u>55</u> , 72 (1959).
185.	P. J. Dossor, C. Eaborn and D. R. M. Walton, J. Organometal. Chem., <u>71</u> , 207 (1974).
186.	J. E. Huheey, J. Phys. Chem., <u>68</u> , 3073 (1964).
187.	J. E. Huheey, J. Phys. Chem., <u>69</u> , 3284 (1965).
186.	J. E. Huheey, J. Phys. Chem., 70, 2086 (1966).
189.	J. E. Huheey, J. Chem. Phys., <u>45</u> , 405 (1966).
190.	J. E. Huheey, J. Org. Chem., <u>31</u> , 2365 (1966).
191.	A. Ceccon and S. Sartori, J. Organometal. Chem., 50, 161 (1973).
192.	W. P. Anderson and T. L. Brown, J. Organometal. Chem., <u>32</u> , 343 (1971).
193.	C. H. Bamford, G. C. Eastmond and F. J. T. Fildes, Chem. Commun., <u>144</u> , 146 (1970).
194.	M. H. B. Stiddard and R. E. Townsend, J. Chem. Soc. A, 2355 (1969).
195.	E. W. Abel and F. G. A. Stone, Quart. Reviews, <u>24</u> , 498 (1970).
196.	K. Jellinek and A. Diethelm, Z. Anorg. Chem., <u>124</u> , 203 (1922).
197.	K. M. MacKay, <u>Hydrogen Compounds of the Metallic Elements</u> , E.&F.N. Spon Ltd., London, 1966, p. 13.

- 198. M. Kh. Karapet'yants and M. L. Karapet'yants, <u>Thermodynamic Con-</u> stants of <u>Inorganic and Organic Compounds</u>, Ann Arbor - Humphrey Science Publishers, Ann Arbor, Mich., 1970.
- 199. J. Van Dalen and P. J. Van Den Berg, J. Organometal. Chem., <u>24</u>, 277 (1970).
- 200. Bulletin 584, U.S. Bureau of Mines, 1960.
- 201. D. R. Stull, E. F. Westrum, Jr. and G. C. Sinke. <u>The Chemical</u> <u>Thermodynamics of Organic Compounds</u>, John Wiley and Sons, New York, N. Y., 1969.
- 202. R. M. Golosova, S. F. Arkhipeva, A. M. Mosin and M. Kh. Karapet'yants, Russ. J. Phys. Chem., <u>41</u>, 781 (1967).
- 203. Appendix F, This Dissertation.
- 204. Appendix E, This Dissertation.