SYNTHESIS AND CHEMISTRY OF
METALLOMETALLOCENES

By

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SYNTHESIS AND CHEMISTRY OF
METALLOMETALLOCENES

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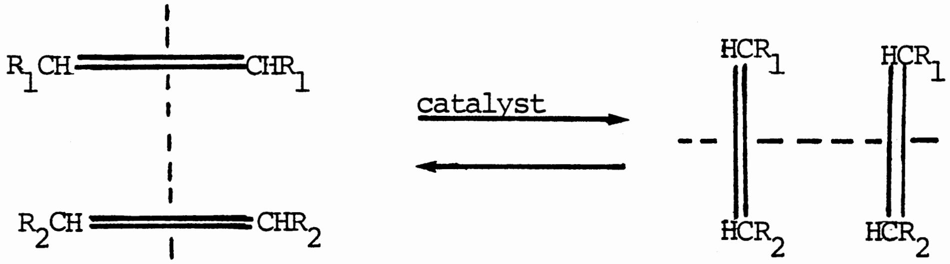
CHAPTER I

INTRODUCTION

The olefin methathesis reaction is one of the most interesting catalytic reactions that has been discovered[1]. This reaction has been called at various times olefin disproportionation and olefin dismutation. The term olefin metathesis, as coined by Calderon[2], will be used.

Olefin metathesis, the reaction shown in Equation 1, is the breaking of carbon-carbon double bonds of two olefins and the reformation of these bonds with the fragments scrambled.

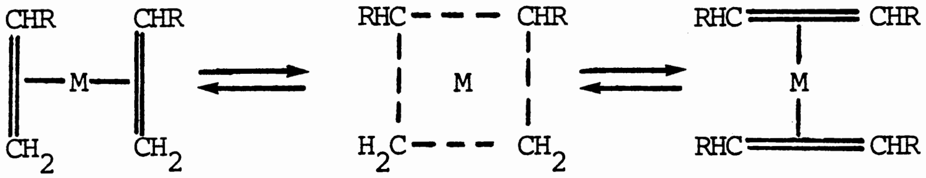


(1)

The first non-catalytic reaction of this type was the conversion of propylene to ethylene and butene at 725°C[3]. More importantly, olefin metathesis can be easily promoted by heterogeneous and homogeneous catalysts at much lower temperatures. Illustrative examples are the conversion of propylene into ethylene and 2-butene using activated molybdenum hexacarbonyl supported on alumina at 163°C[4], and olefin metathesis using WCl_6-EtOH-$EtAlCl_2$ (the first homogeneous catalyst to be discovered) at 20°C[5].

Because of the wide interest in this type of reaction not only from a commercial but also from a theoretical view, the mechanisms have been studied in detail. However, Haines and Leigh[6] point out that "no single mechanism has been suggested to explain all olefin metathesis reactions . . ." They also point out that experimental evidence apparently calls for the synchronous making and breaking of double bonds. If this assumption is correct, then this reaction is formally a concerted [2+2]-cycloaddition, thermally forbidden according to the Woodward-Hoffman rules[7]. This implies that excessively high activation energies are required for normal thermal activation as evidenced by the high temperature (725°C) used for the non-catalytic conversion of propylene. However, through the use of transition metal catalysts this thermal barrier is lowered and these reactions have been commercially practical. Of the many proposed mechanisms, two are of particular historical interest.

One mechanism proposed by Bradshaw[8] involves a "quasi-cyclobutane" transition state (Equation 2) which is a symmetrical intermediate, i.e., four equivalent carbons are involved in the bonding. Because of this equivalency, the transition state may "unzip" either to give starting or scrambled materials. Although Pettit and co-workers[9] have provided convincing evidence against such a "quasi-cyclobutane" species, extrapolation of such a notion to the mechanism of alkyne metathesis is attractive (see ahead).

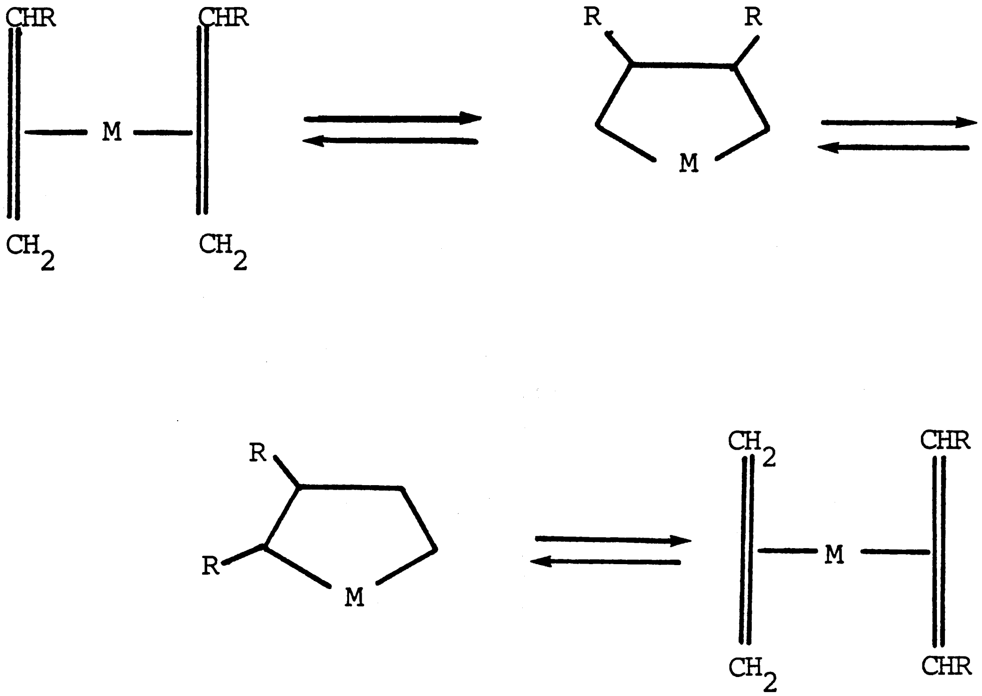


(2)

Katz[10] and Eaton et al.[11] demonstrated that certain rhodium catalyzed systems involved a metal-carbon σ-bonded intermediate instead of a direct metal-catalyzed electro-cyclic rearrangement. Based upon this work, Grubbs and Brunch[12] reported a possible carbon-metal σ-bonded species as an intermediate in a tungsten-catalyzed olefin metathesis reaction. Based upon the intermediate suggested by Katz and Eaton et al., Grubbs proposed the mechanism shown in Equation 3.

Currently, the most favored mechanism, suggested first by Casey[13], for olefin metathesis incorporates features of the Grubbs mechanism and that suggested by Pettit[9] involves a metal-carbenoid intermediate.

The metathesis reaction is not limited to alkenes; alkynes undergo a similar reaction. Banks and co-workers[14] have proposed a mechanism similar to the "quasi-cyclobutane" one suggested by Bradshaw. They have proposed a four membered intermediate formed by two acetylenes, i.e., a cyclobutadienoid species.



(3)

Transition metal carbonyl complexes act as catalysts for the cyclotrimerization of acetylenes to benzene derivatives. Meriwether[15] has proposed that metallocyclopentadiene complexes are intermediates in the cyclotrimerization of disubstituted acetylenes. Illustrative examples of metallocyclopentadiene complexes are shown in Figure 1. These complexes were formed by coupling two diphenylacetylene molecules[16,17].

Greco and co-workers[18] studied acetylene complexes of tungsten and molybdenum, and proposed a decomposition scheme which included a metallocyclic intermediate to explain the formation of both cyclotrimerization and metathesis products.

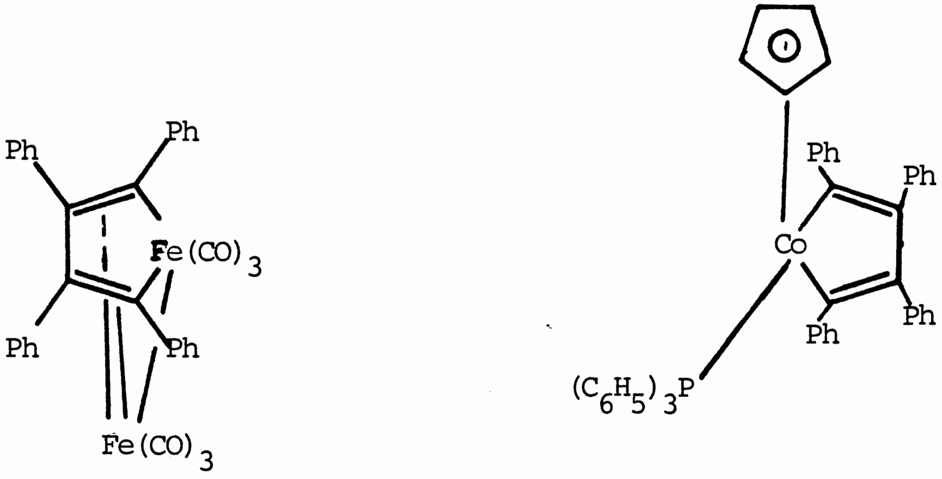
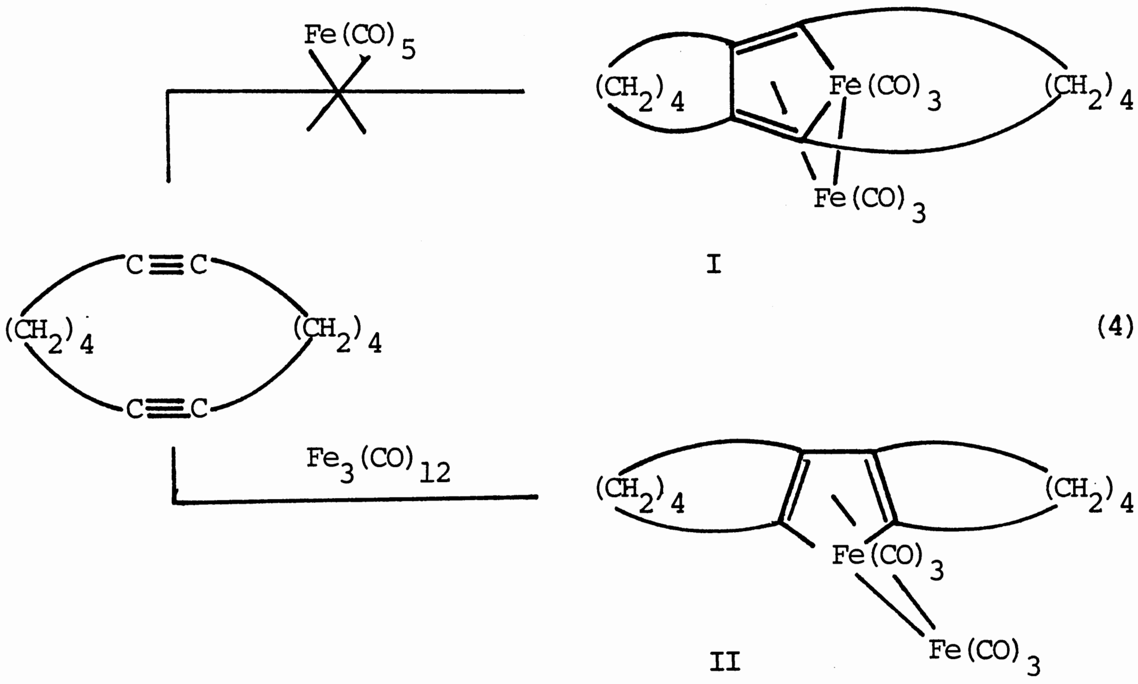


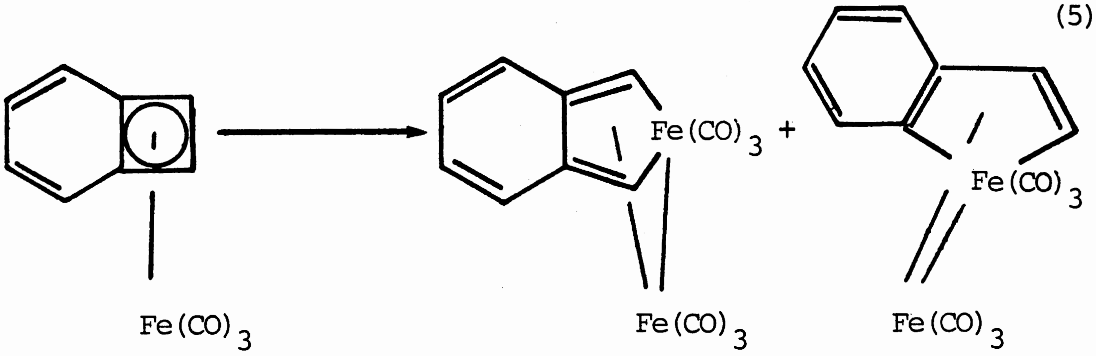
Figure 1. Examples of Metallocyclopentadiene Complexes.

Bau[19] examined the product of the reaction shown in Equation 4 and established that it was ferrole II and not, as previously reported[20], the expected species, ferrole I.



(4)

Pettit and co-workers[21], based upon their work with cyclobutadiene systems, proposed and then investigated the explanation, that instead of postulating isomerization of I into II, the product was most easily rationatized by considering the reaction of $Fe(CO)_5$ with a transient (cyclobutadiene) iron tricarbonyl complex. They reported that the products of the reaction of (benzocyclobutadiene)tricarbonyliron complex with $Fe_3(CO)_{12}$ were not interconverted (Equation 5). The suggestion was made that cyclobutadiene metal complexes might well be involved in the mechanism of alkyne methathesis.

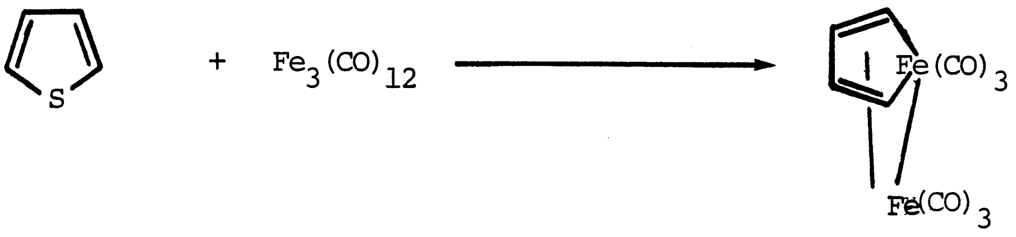


(5)

It is the interest in the mechanisms of the metathasis, as well as the oligomerization, of alkenes and alkynes that has lead to the synthesis and study of the chemistry of metallocyclic complexes.

Several methods are used to synthesize these metallocyclic complexes. Two specific methods which have been little studied involve the displacement reaction of a heterocyclopentadiene, viz. thiophene, and the insertion of metal carbonyl species into cyclobutadiene-metal complexes. A summary of the understanding of these two methods follows.

In 1959 Hubel and Weiss[22] reported that the reaction of iron dodecacarbonyl with acetylene at atmospheric pressure yielded orange crystals with the empirical formula $(C_2H_2)_2Fe_2(CO)_6$. A year later, Kaesz and co-workers[23] reported the novel reaction of thiophene with triiron dodecacarbonyl in which there is removal of the sulfur atom from the thiophene ring with subsequent replacement by an iron atom of an iron tricarbonyl group. The compound obtained had the same properties as that of the orange crystals produced by Hubel and was assigned the structure III (Equation 6).

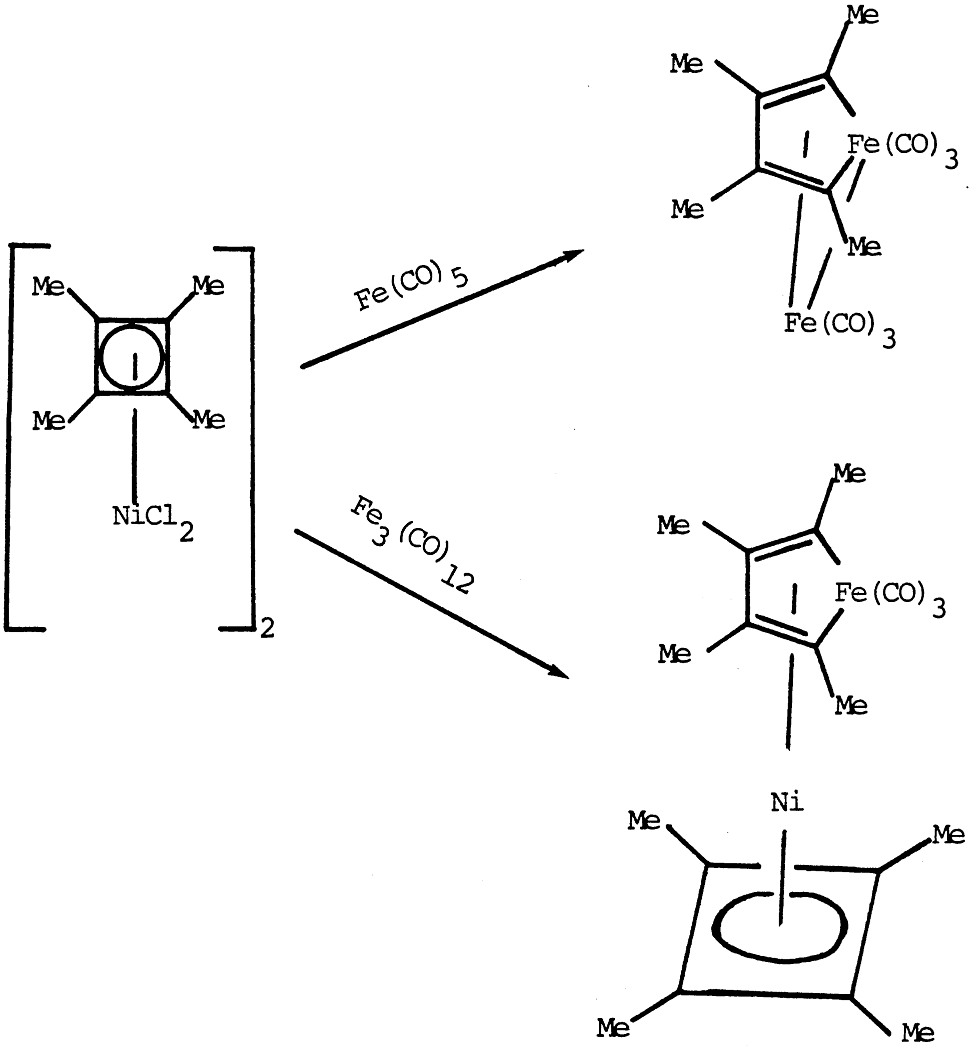


III

(6)

Recently, the proposed structure was confirmed by an X-ray crystallographic study and a modified method for producing the parent ferrole (III) in better yield from thiophene and $Fe_3(CO)_{12}$ in n-heptane was developed by Weiss[24].

In 1967 Bruce and co-workers[25] reported that the reaction of triiron dodecarbonyl with (tetramethylcyclobutadiene)nickel chloride dimer yielded, in addition to (tetramethylcyclobutadiene) tricarbonyliron, a small amount of a complex with the empirical formula $(CH_3)_8C_8NiFe(CO)_3$. Determination of the structure by X-ray crystallographic analysis[26], in 1970, showed it to be complex IV (Equation 7).



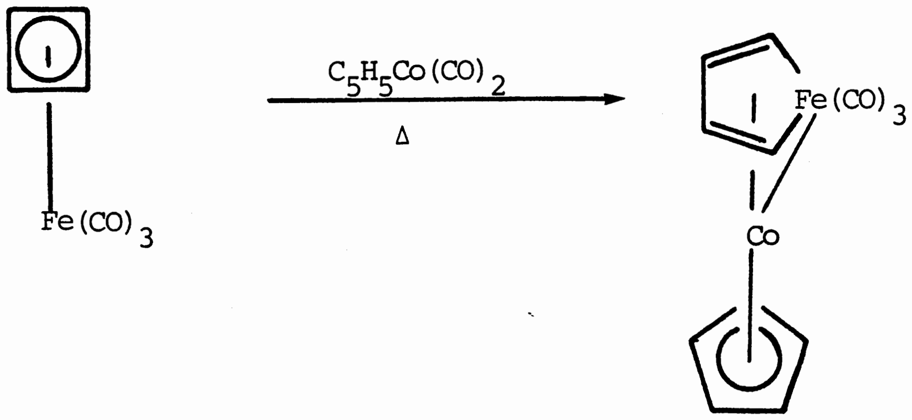
(7)

IV

The reaction depicted in Equation 7 represented the first example of insertion of a metal carbonyl species into a cyclobutadiene-metal complex. The formation of complex IV was of special significance since prior to the work in our laboratory it represented the only known mixed binuclear metallocyclic complex.

Photochemically induced insertion was reported by Rosenblum and co-workers[27] as a secondary reaction in the photochemical preparation of cyclobutadiene(cyclopentadienyl)cobalt using (cyclopentadienyl) dicarbonylcobalt. The only other reports of insertion outside of our laboratory involve thermal[28] or photochemical[29] insertion of $Fe(CO)_3$ into (benzocyclobutadiene)tricarbonyliron to give the ferroles shown in Equation 5.

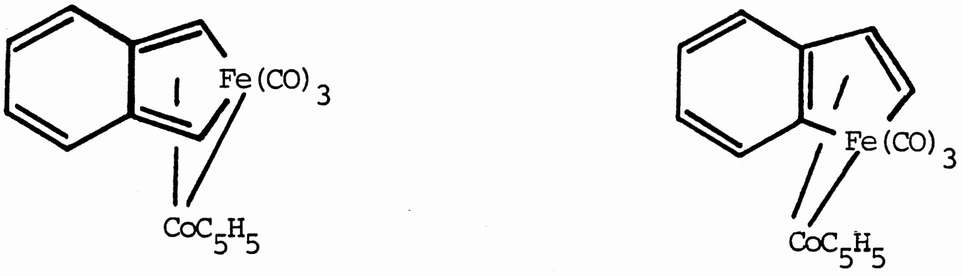
In our laboratory McKennis[30] has observed the facile insertion of a transition metal moiety into the cyclobutadiene nucleus of the very stable, aromatic molecule $C_4H_4Fe(CO)_3$ to yield the new metallocycle II complex V. Interestingly, the reaction of $C_4H_4Fe(CO)_3$ with $C_5H_5Co(CO)_2$ affords complex V in fair yield, (Equation 8), whereas reaction with $Fe_3(CO)_{12}$, even under the most vigorous conditions, fails to give any of the analogous insertion product, viz. ferrole (III). Recently, Yamazaki and co-workers[31] have informed us of their independent preparation and identification by X-ray crystallographic analysis of di-and tetrasubstituted derivatives of complex V by the reaction of di-and tetrasubstituted-η^5-cyclopentadienyltri-phenylphosphine(cobaltocyclopentadiene) and nonacarbonyldiiron.



(8)

V

The preparation and the chemistry of the benzo derivatives of complex V, sym- and unsym-benzoferracobaltocene (VI and VII respectively), have been examined in our laboratory by Radnia[32] (Figure 2).

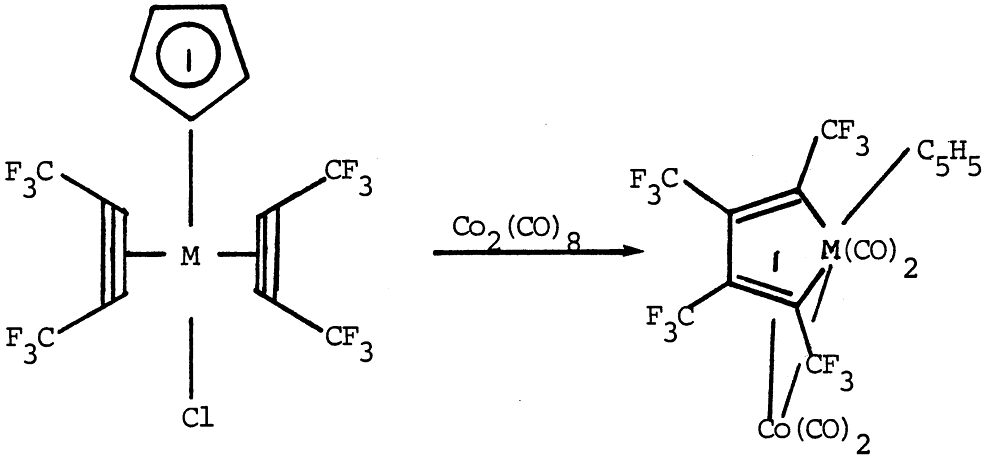


VI

VII

Figure 2. Sym- and unsym-benzoferracobaltocece (VI and VII).

Recently, Davidson[33] has reported the preparation of another type of mixed metallocyclopentadiene complex from the reaction of $Co_2(CO)_8$ with bis-hexafluorobut-2-yne complexes (Equation 9).



(9)

The interest in these metallocycles has been great not only from a mechanistic, but also from a theoretical viewpoint. Hoffmann and Thorn[34] consider the delocalized (aromatic) system as having carbon-carbon bonds of nearly equal bond length while a localized system has alternating short-long-short carbon-carbon bonds. They report that systems with the metallocyclopentadienyls structure have bond lengths consistent with localized double bonds but certain binuclear metallocycles show delocalized bonding with nearly equal C-C bond lengths.

CHAPTER II

STATEMENT OF THE PROBLEM

The metallocyclic species have been proposed as possible intermediates in the catalytic metathesis of alkynes. Because the discovery of these complexes has occurred only in recent years, the chemical properties of these binuclear metallocyclic complexes have not been adequately investigated. Most attention has been directed toward preparation of these complexes and the investigation of physical structure. Of special interest is the mixed binuclear metallometallocenes which have only very recently been discovered and only a few such complexes exist.

The rhodium analog of ferracobaltocene was to be prepared via insertion of a rhodium moiety into (cyclobutadiene)tricarbonyliron. The expected ferrarhodocene was to be studied to provide more information about the physical and chemical nature of this new type of complex.

At the start of this work, the structure of binuclear complexes were known for the nickel/iron complex and the sym- and unsym-benzoferracobaltocenes. The structure for the parent complex, ferracobaltocene, has not been determined. The relative positioning of the metals in the expected ferrorhodocene would be determined by x-ray crystallographic analysis to provide information about the parent complexes and information which is of theoretical interest.

Alternate methods of preparation were to be evaluated relative to their synthetic usefulness. Additionally, the physical and chemical nature of the prepared metallometallocenes and derivatives were to be investigated through measurement of physical properties by characterization of the products of acetylation and benzylation, and from mass spectra fragmentation patterns.

CHAPTER III

RESULTS AND DISCUSSION

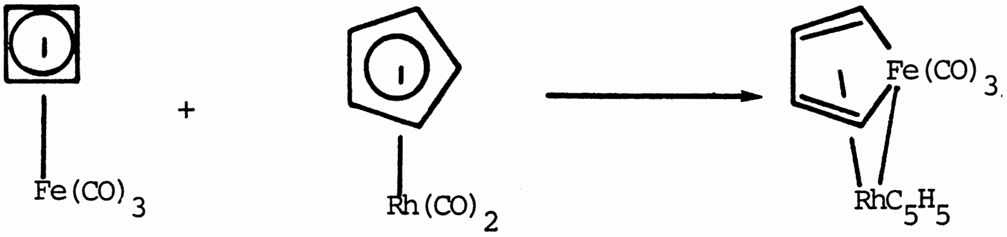
Synthesis and Chemistry of Metallometallocenes

Synthesis and Structure of Ferrarhodocene (VIII)

In the Introduction several cases of insertion of metal carbonyl moieties into cyclobutadiene-metal complexes were discussed. Several of these metallocyclic complexes have been prepared by McKennis[30] and Radnia[32] (viz. V, VI, and VII) to evaluate their physical and chemical properties. In continuation of this study, the rhodium analogs were prepared. The relative positioning of the metals and the fluxional behavior of the rhodium complex VIII were studied. Additionally, some aspects of the chemistry of the complexes prepared by McKennis and Radnia were examined.

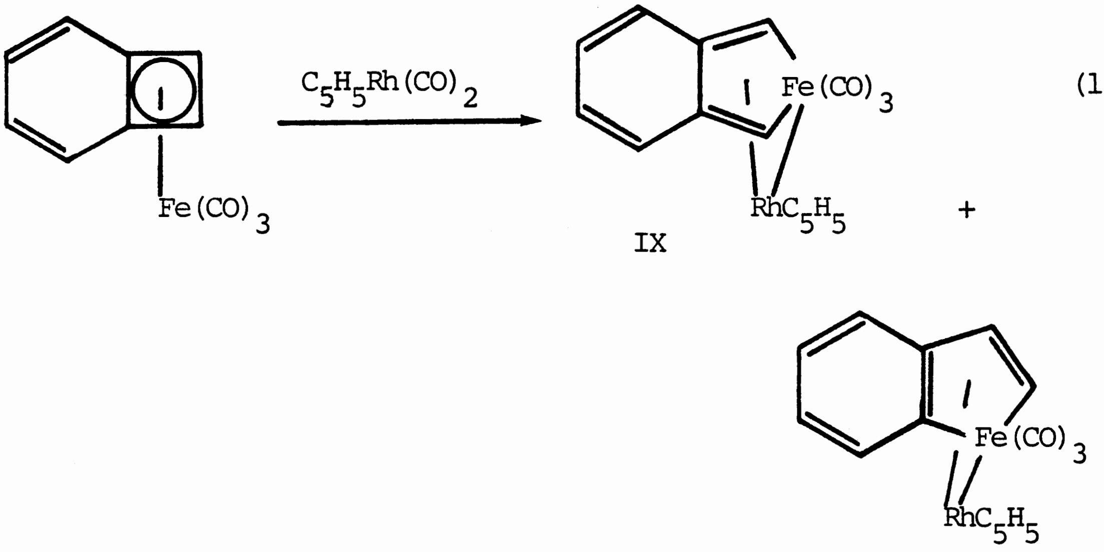
[Tricarbonyl(ferracyclopentadiene)]-η^5-cyclopentadienylrhodium (VIII) was prepared from the insertion reaction of (cyclobutadiene) tricarbonyliron with (cyclopentadienyl)dicarbonylrhodium (Equation 10).

Sym- and *unsym*-[tricarbonyl(benzoferracyclopentadiene)]-η^5-cyclopentadienylrhodium (IX and X) were prepared from the reaction of (benzocyclobutadiene)tricarbonyliron with (cyclopentadienyl) dicarbonylrhodium (Equation 11).



VIII

(10)



IX

X

(11)

The structure of complex VIII was determined by X-ray crystallographic analysis of a crystal obtained from a mixture of acetone and water. The X-ray data is tabulated in Tables I-IV. The structure is that of a "sandwich", or metallocene compound in which the rhodium is "sandwiched" between two parallel rings; one a cyclepentadienyl and the other a ferracyclopentadiene ring. The rhodium atom is 2.18Å (average) from each carbon of the cyclopentadienyl ring and 2.14Å (average) from the ferracyclopentadiene carbons.

TABLE I

CRYSTAL DATA*

Formula	$C_{16}H_{11}O_3RhFe$
Mol. Wt.	$\lambda = 359.8953$
	$a = 14.453(11)$
	$b = 12.060(5)$
	$c = 14.016(6)$
	$\alpha = \beta = \gamma = 90°$, orthorhombic
	2491 independent observations
	$R = 5.7$
	$P2_1/m$
	$Z = 8$, $d_{cal} = 1.950\ g\ cm^{-3}$

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*Error in parentheses are deviations in the last significant figure.

TABLE II

POSITIONAL PARAMETERS FOR $RhFeC_{12}O_3H_9$

	x(θ(x))	y(θ(y))	z(θ(z))
Fe	0.1006(1)	0.1330(1)	0.2144(1)
Rh	0.2461(1)	0.1539(0)	0.1122(0)
C1	0.2468(12)	0.1074(9)	-0.0382(6)
C2	0.3356(10)	0.1424(13)	-0.0148(8)
C3	0.3298(10)	0.2544(12)	0.0142(7)
C4	0.2366(11)	0.2865(8)	0.0082(6)
C5	0.1851(8)	0.1970(10)	-0.0239(6)
C6	0.1945(8)	0.0217(7)	0.1991(6)
C7	0.2844(8)	0.0499(9)	0.2287(7)
C8	0.2934(8)	0.1589(9)	0.2578(7)
C9	0.2089(8)	0.2176(7)	0.2487(6)
C10	0.0220(9)	0.0483(10)	0.1490(8)
C11	0.0407(8)	0.2590(10)	0.1924(8)
C12	0.0651(8)	0.1036(8)	0.3298(7)
O10	-0.0261(7)	-0.0086(10)	0.1079(7)
O11	0.0062(7)	0.3443(8)	0.1803(8)
O12	0.0429(6)	0.0865(7)	0.4078(5)
H1	0.2295	0.4686	0.4389
H2	0.3932	0.4060	0.4803
H3	0.3841	0.3032	0.0340
H4	0.2121	0.3635	0.0272
H5	0.1168	0.3082	0.4632
H6	0.1803	-0.0539	0.1711
H7	0.3377	-0.0062	0.2305
H8	0.3552	0.1936	0.2794
H9	0.2054	0.3006	0.2602

TABLE III

BOND ANGLES (°) AND DISTANCES (Å) FOR $RhFeC_{12}O_3H_9$

Fe-C6	1.922(10)	Fe-C6-C7	116.8(7)
Fe-C9	1.930(10)	Fe-C9-C8	117.2(7)
Fe-C10	1.781(12)	C6-C7-C8	113.8(10)
Fe-C11	1.776(12)	C7-C8-C9	111.6(10)
Fe-C12	1.727(10)	C1-C2-C3	107.7(12)
Fe-Rh	2.557(2)	C2-C3-C4	107.6(12)
C6-C7	1.41(2)	C3-C4-C5	108.6(10)
C7-C8	1.38(2)	C4-C5-C1	107.6(12)
C8-C9	1.42(2)	C5-C1-C2	108.4(11)
C10-010	1.14(2)	Fe-C10-010	177.7(12)
C11-011	1.16(2)	Fe-C11-011	175.9(12)
C12-012	1.16(1)	Fe-C12-012	177.8(10)
Rh-C1	2.182(9)	Rh-Fe-C10	107.0(4)
Rh-C2	2.205(12)	Rh-Fe-C11	102.7(4)
Rh-C3	2.195(13)	Rh-Fe-C12	141.9(4)
Rh-C4	2.168(10)	Rh-Fe-C6	54.9(3)
Rh-C5	2.166(10)	Rh-Fe-C9	54.6(3)
Rh-C6	2.140(9)	C6-Fe-C11	157.4(5)
Rh-C7	2.132(10)	C9-Fe-C10	161.6(5)
Rh-C8	2.153(10)	C6-Fe-C9	79.9(4)
Rh-C9	2.131(9)	C6-Fe-C10	89.6(5)
		C9-Fe-C11	89.2(5)
		C9-Fe-C12	96.8(4)
		C6-Fe-C12	99.8(4)

TABLE IV

THERMAL PARAMETERS FOR $RhFeC_{12}O_3H_9$

	U11	U22	U33	U12	U13	U23
Fe	40(1)	40(1)	40(1)	-3(1)	0(1)	0(0)
Rh	42(1)	40(0)	32(0)	-1(0)	0(0)	1(0)
C1	95(12)	61(6)	37(4)	-14(7)	7(6)	6(4)
C2	48(10)	114(11)	50(6)	-16(9)	14(6)	3(7)
C3	83(12)	85(8)	44(5)	-35(8)	7(6)	4(6)
C4	93(12)	51(5)	41(4)	-3(6)	-1(6)	10(4)
C5	61(10)	78(7)	31(4)	6(6)	-7(5)	-9(4)
C6	58(9)	35(4)	46(5)	-4(4)	5(5)	2(3)
C7	44(9)	65(6)	44(5)	14(6)	-4(5)	11(4)
C8	51(8)	77(7)	43(5)	-11(6)	-17(5)	2(5)
C9	58(8)	46(4)	32(3)	-4(5)	-2(4)	-2(4)
C10	52(10)	85(8)	52(6)	-23(7)	3(6)	-18(6)
C11	39(8)	65(7)	78(7)	-2(6)	-4(6)	-1(6)
C12	43(8)	46(4)	52(5)	-8(5)	4(5)	1(4)
O10	90(9)	152(10)	84(6)	59(7)	-2(6)	39(7)
O11	92(8)	77(6)	149(9)	34(6)	-20(7)	17(6)
O12	91(7)	86(6)	56(4)	-24(5)	19(4)	2(4)

Anisotropic thermal parameters in the form:

$$\exp[-2\pi^2(U_{11}h^2a^{*2} + U_{22}k^2b^{*2} + U_{33}l^2c^{*2} + 2U_{12}hka^*b^* + 2U_{13}hla^*c^* + 2U_{23}klb^*c^*)] \times 10^3$$

Errors in parentheses are deviations in the last significant figure.

The rhodium-iron distance is 2.56Å. The positioning of the rhodium relative to the other atoms can be seen in Figures 3 and 4. The perpendicular distance from the rhodium to the plane of each ring has been calculated as 1.73Å for the rhodium-cyclopentadienyl distance and 1.83Å for rhodium-ferracyclopentadienyl.

Another feature that makes this a "sandwich" complex is the essentially flat or planar structure of each ring. In the ferrocyclopentadienyl ring the position of the iron has been calculated to be only 7.3° (or 0.19Å) above the plane formed by the four carbons. This compares to the calculated values of 8.8° (or 0.23Å) for ferrole[24].

The cyclic systems of the metallocenes have been shown to be "aromatic like" not only in their chemistry but in physical structure. For the purpose of this work a delocalized (aromatic) system will be taken to have nearly equal C-C bond lengths. A normal sp^3-sp^3 carbon-carbon single bond length is 153Å, and that of a double bond is 1.33Å. In benzene however, the carbon-carbon bond lengths are 1.40Å. In complex <u>VIII</u> the X-ray data indicates that the carbon-carbon bond lengths are equal within experimental error (C_6-C_7 = 142 (±0.02)Å, C_8-C_7 = 1.38 (±0.02)Å, C_8-C_9 = 1.42 (±0.02)Å) and are between the normal carbon-carbon single and double bonds. However, to show that there is delocalization, one must show that the carbon-iron bond (1.926Å) is shorter than a carbon-iron single bond of an appropriate model. Although the existence of a suitable model is debatable, it has been suggested that the length of a carbon-iron single bond is 2.03Å[35].

In view of the relatively short carbon-iron bond, which suggests

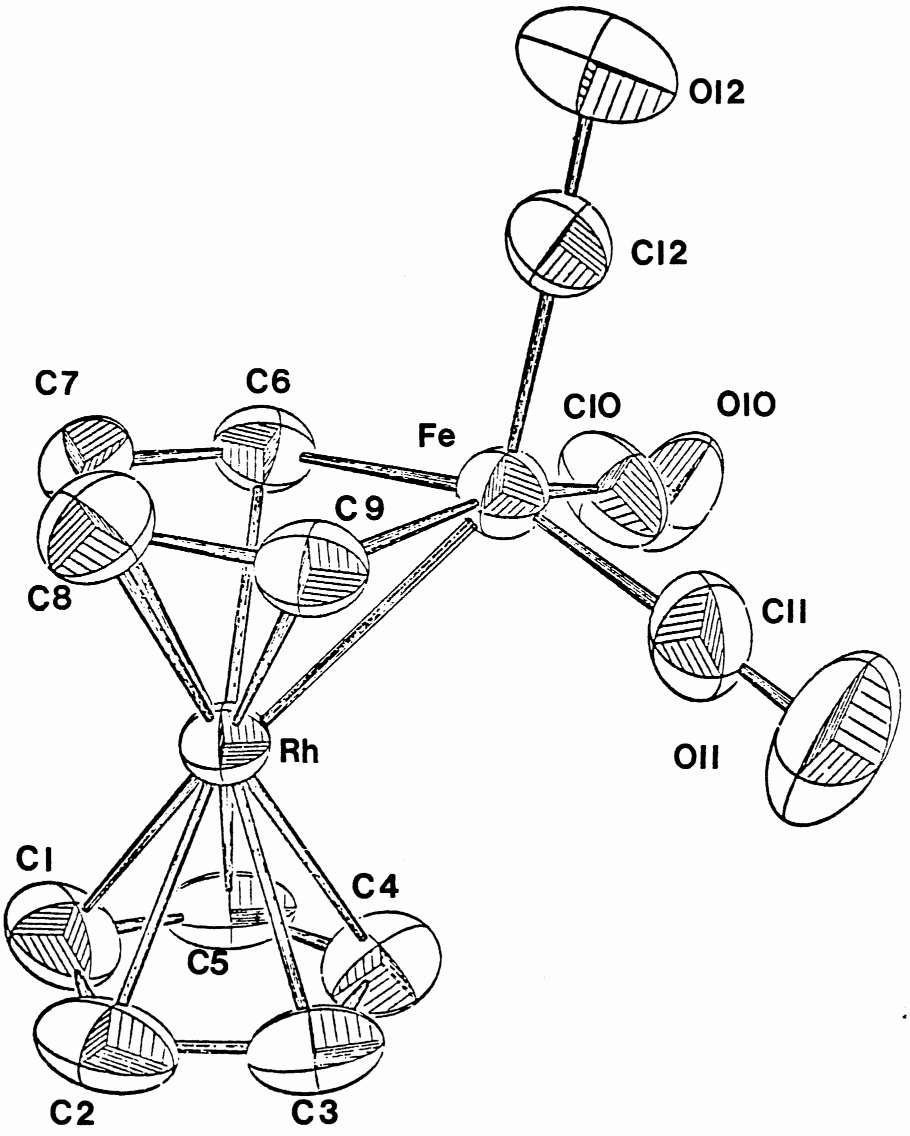


Figure 3. Molecular Geometry of $C_{12}H_9O_3FeRh$.

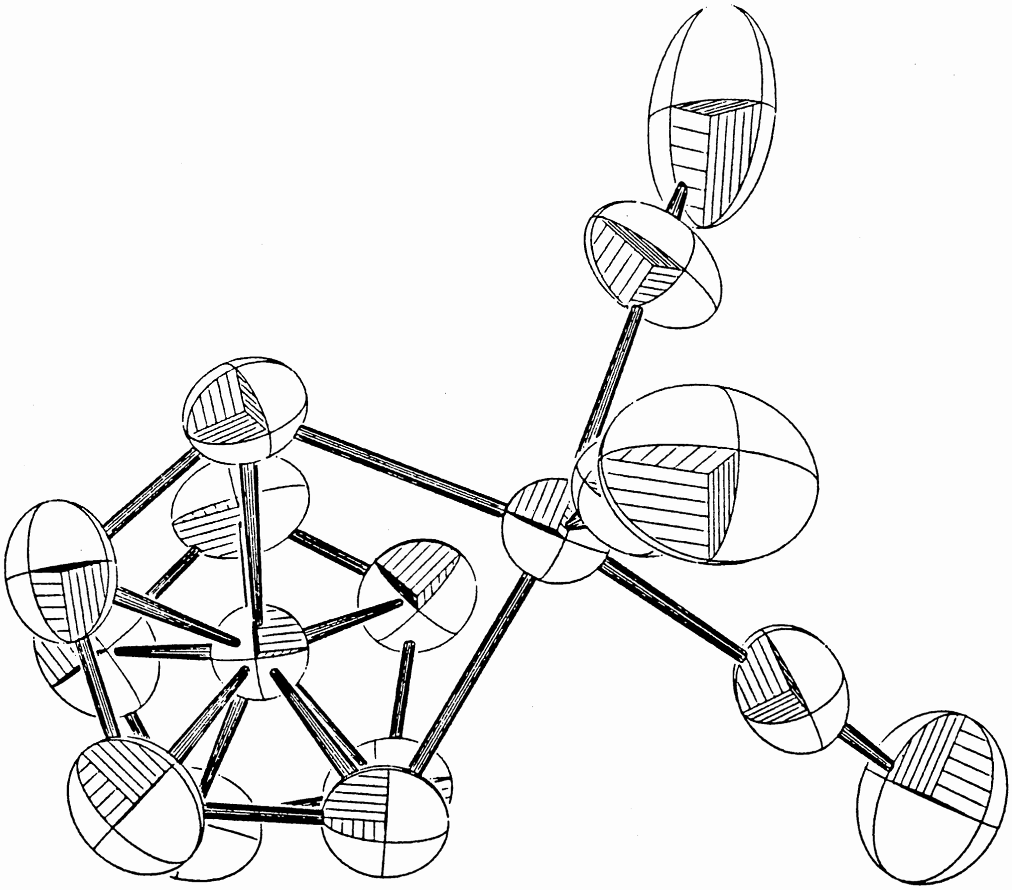


Figure 4. Perspective Along the Axis Perpendicular to the Metallocycle Ring Passing Through Rhodium.

multiple bond character, the similar carbon-carbon bond lengths, and chemistry typical of aromatic compounds (see ahead), this new binuclear metallocycle probably should best be considered as an aromatic species, a metallometallocene. Due to the similarity of its ^{1}H-NMR and ^{13}C spectra and its chemistry with that of ferrarhodocene, complex <u>VIII</u>, the cobalt analog complex <u>V</u>, also will be considered a metallometallocene even though its structure has not been definitively determined by X-ray crystallography.

Study of the ^{1}H-NMR Spectra of Metallometallocenes

In assigning protons to the ^{1}H-NMR spectra of ferrole (<u>III</u>) Dettlaf and Weiss[24] assigned the farthest upfield resonance signals (centered at 6.2δ) to the protons adjacent to the metal (X,X') and the signals at 6.8δ to the protons away from the metal (A,A'). They assigned these signals to an AA'XX' system with coupling constants: $J_{AX} = J_{A'X'} = 5.3$, $J_{AX'} = J_{A'X} = 2.3$, $J_{AA'} = 2.4$, and $J_{XX'} = 0Hz$. (Figure 5).

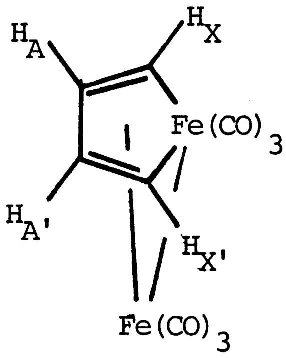


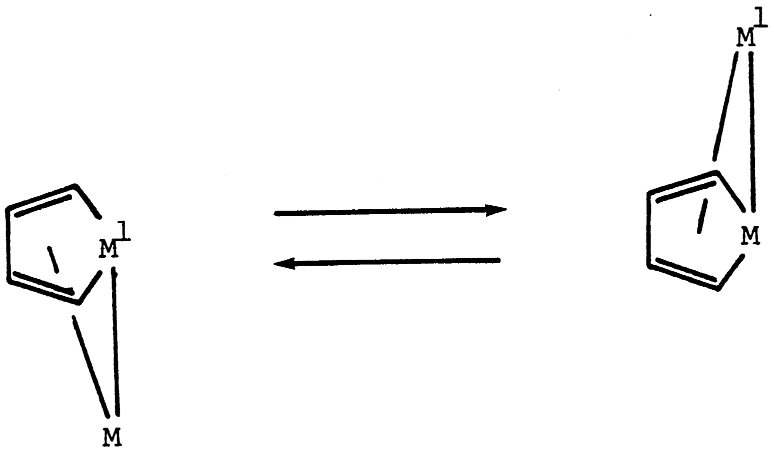
Figure 5. Nomenclature for Assignment of Ferrole.

Rosenblum[27] made a similar assignment for the cobaltole system. The interpretation was that the metal of the metallocyclic ring shields the protons attached to the carbon adjacent to the metal. However, this is not consistent with the ^{1}H-NMR spectra of the metallocyclic compounds prepared in our laboratory. The complexes sym-benzoferrole, sym-benzoferracobaltocene (VI), and 3-benzoyl-ferracobaltocene, all exhibit singlets integrating for 2 protons at δ8.19, 7.72, and 7.3 respectively. These are the farthest downfield protons. Also, the assignment of the most downfield signals to the protons next to the metal is consistent with the spectrum of the 2-acetylferracobaltocene (XIII) which has a triplet at 5.70δ integrating for one proton, a doublet of doublets at 5.84δ integrating for one proton, and a doublet of doublets at 7.38δ also representing one proton.

A computer program, Nicholle NMRCAL, that simulates ^{1}H-NMR spectrum from δ and J values was used to further investigate the assignments and coupling constants. This program was run on the computer associated with the Varian XL-100 NMR spectrometer. The simulated spectrum for ferrole was the same if the assignments made by Weiss were reversed (i.e., X = X' = 6.8δ and A = A' = 6.2δ), using the original coupling constants in each case. The theory of NMR spectra is consistent with this observation[36]. In other words, as far as the simulation of spectra is concerned, the assignment of Weiss could have been error. The simulation of spectra for ferracobaltocene was also a good "fit" regardless of the assignment. But the spectrum of ferrarhodocene, complex VIII, is a AA'XX' system which is complicated by rhodium-proton coupling. The best simulated spectral "fit" to the sample spectrum assigned the most downfield signal to the proton nearest the metal and the upfield signal to the protons away from the metal: $\delta_{X'} = \delta_X = 7.1$, $\delta_{A'} = \delta_A = 6.2$, $J_{X'A} = J_{XA} = 4.5$, $J_{X'A} = J_{XA'} = 2.2$, $J_{X'X} = 0$, $J_{A'A} = 2.1$, $J_{A'Rh} = J_{ARh} = 1.2$, and $J_{XRh} = J_{X'Rh} = 0$Hz. Several notable features are found; one, the through metal coupling is zero as shown with ferrole and ferrocobaltocene; secondly, the rhodium appears to be coupled with only the protons away (H_A & $H_{A'}$) from the metal. Figures 6, 7, 8, and 9 show the simulation spectra compared to the original spectra.

Fluxional Behavior

The fluxional behavior of several metallocene systems have been investigated. A mechanism has been proposed which involves the "flipping" of the organic moiety from one metal atom to the other, or ring tautomerism (see Equation 13) that occurs in a number of metallocyclopentadiene complexes in which each metal atom has the same number of CO or C_5H_5 ligands of Equation 12[37].



(12)

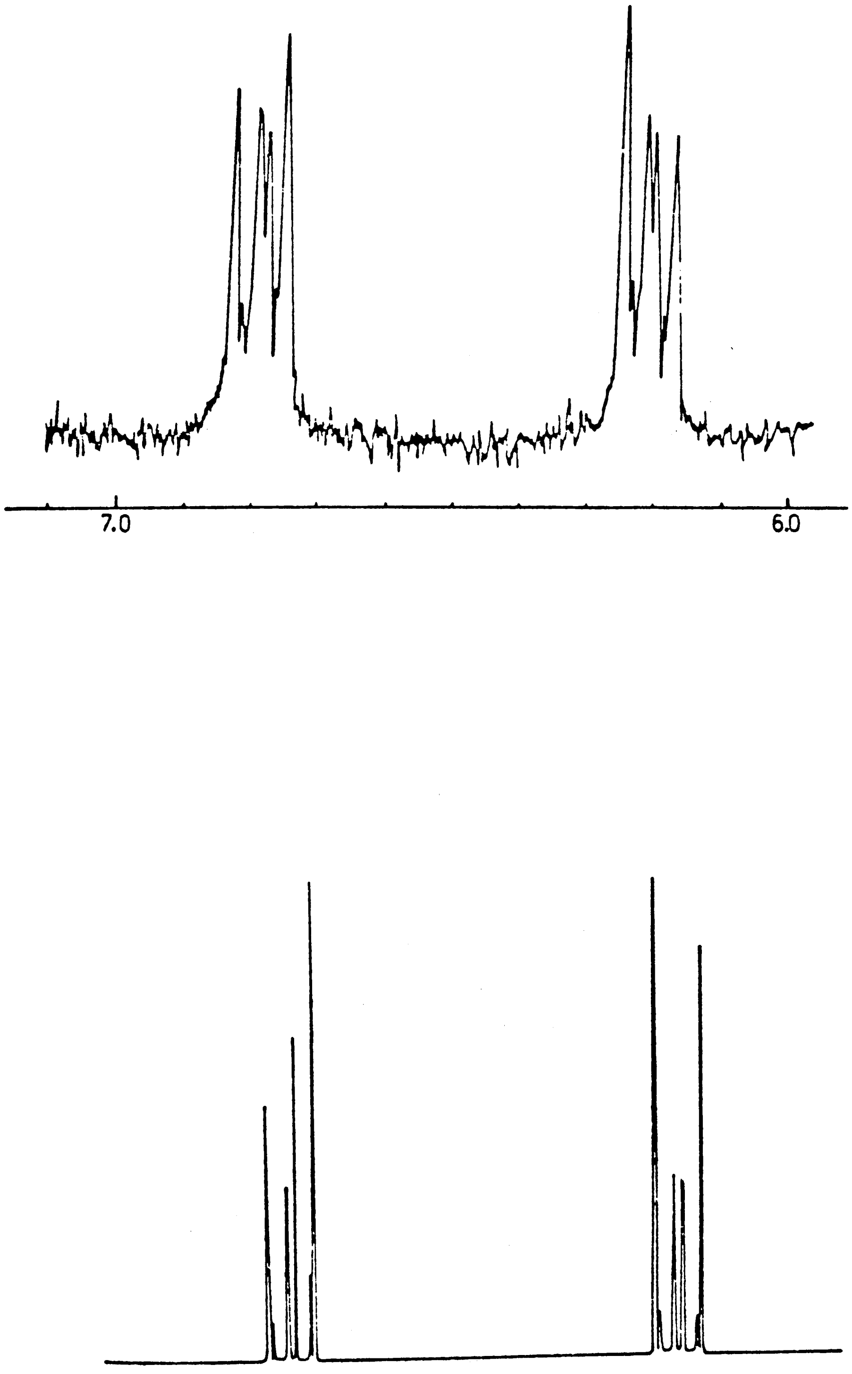


Figure 6. Top, ^{1}H-NMR Spectra of Ferrole by Weiss. Bottom, Simulated ^{1}H-NMR by Weiss.

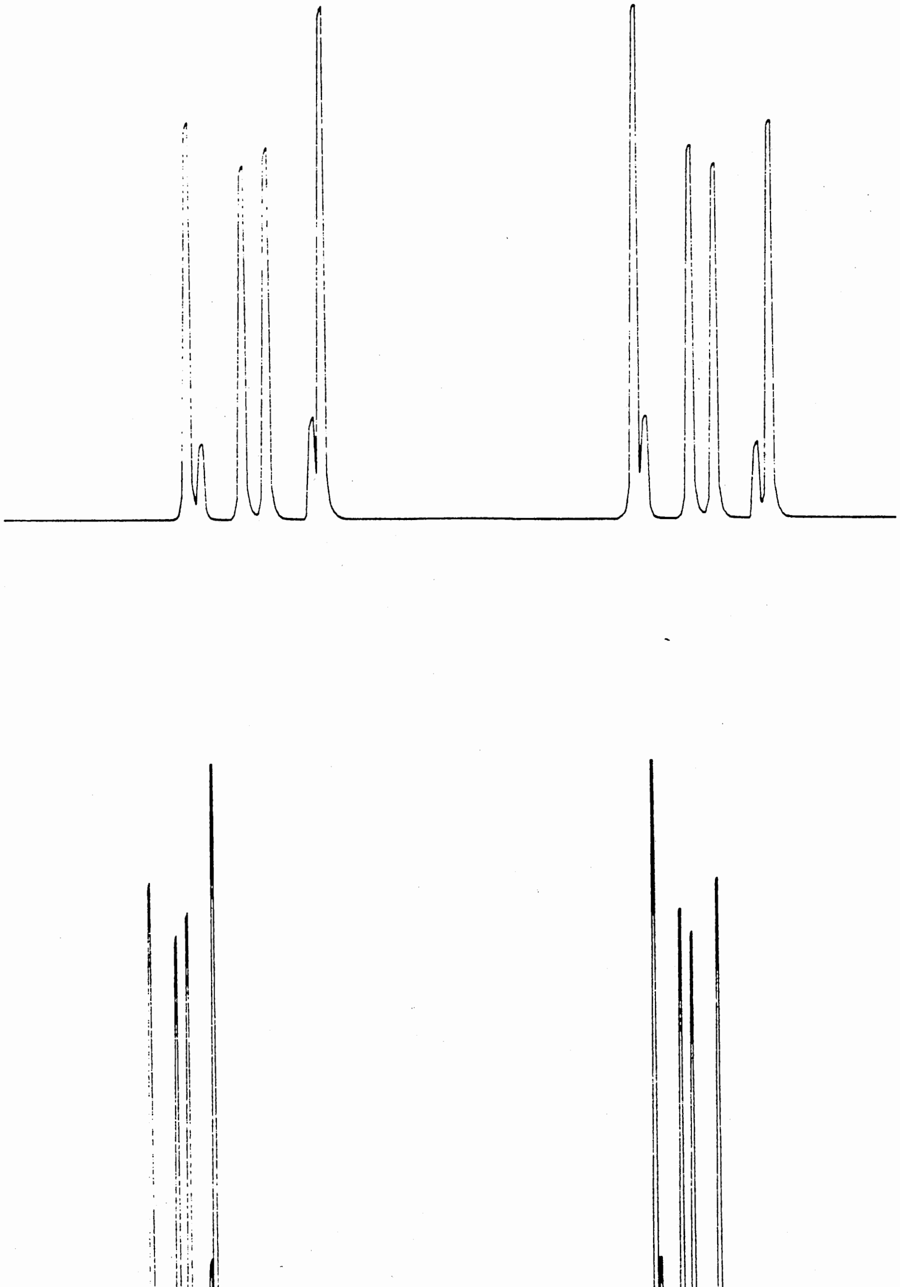
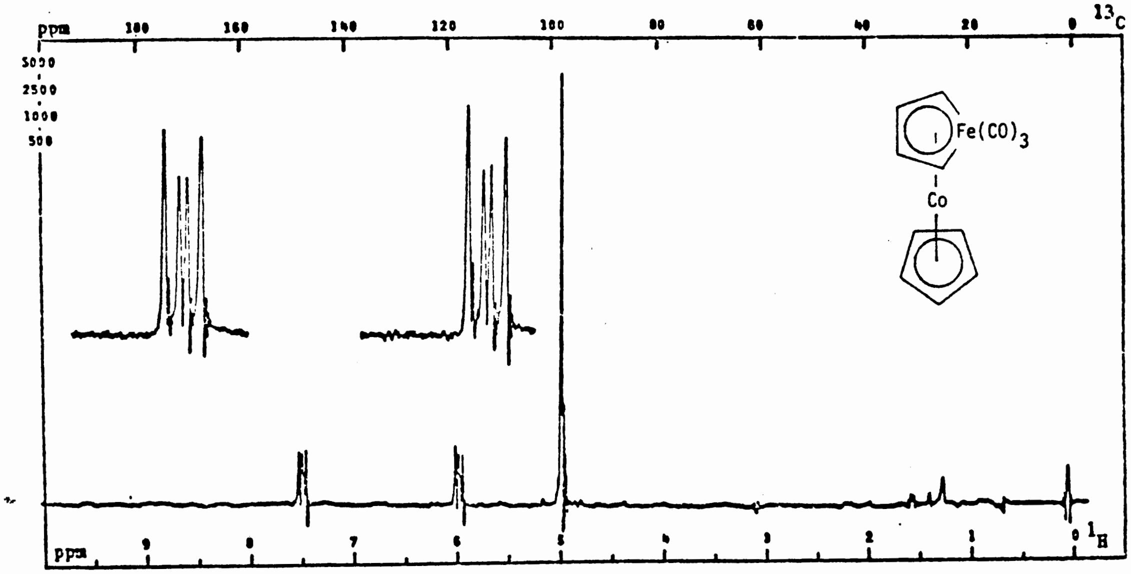


Figure 7. Simulated ^{1}H-NMR Spectra. Top, Using Assignments of Weiss. Bottom, Using Reversed Assignments.



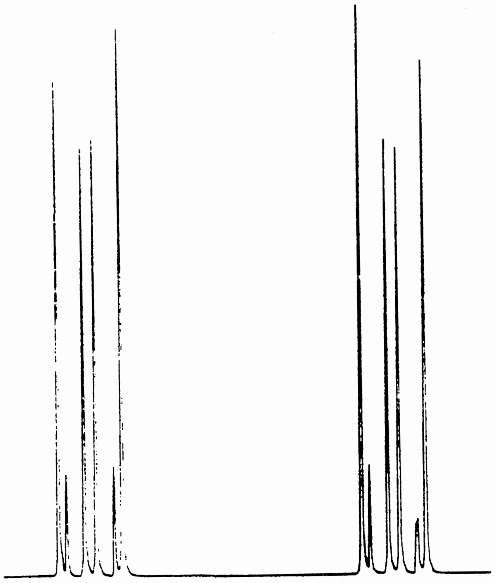


Figure 8. Top, ^{1}H-NMR Spectra of Ferracobaltocene. Bottom, Simulated Spectra.

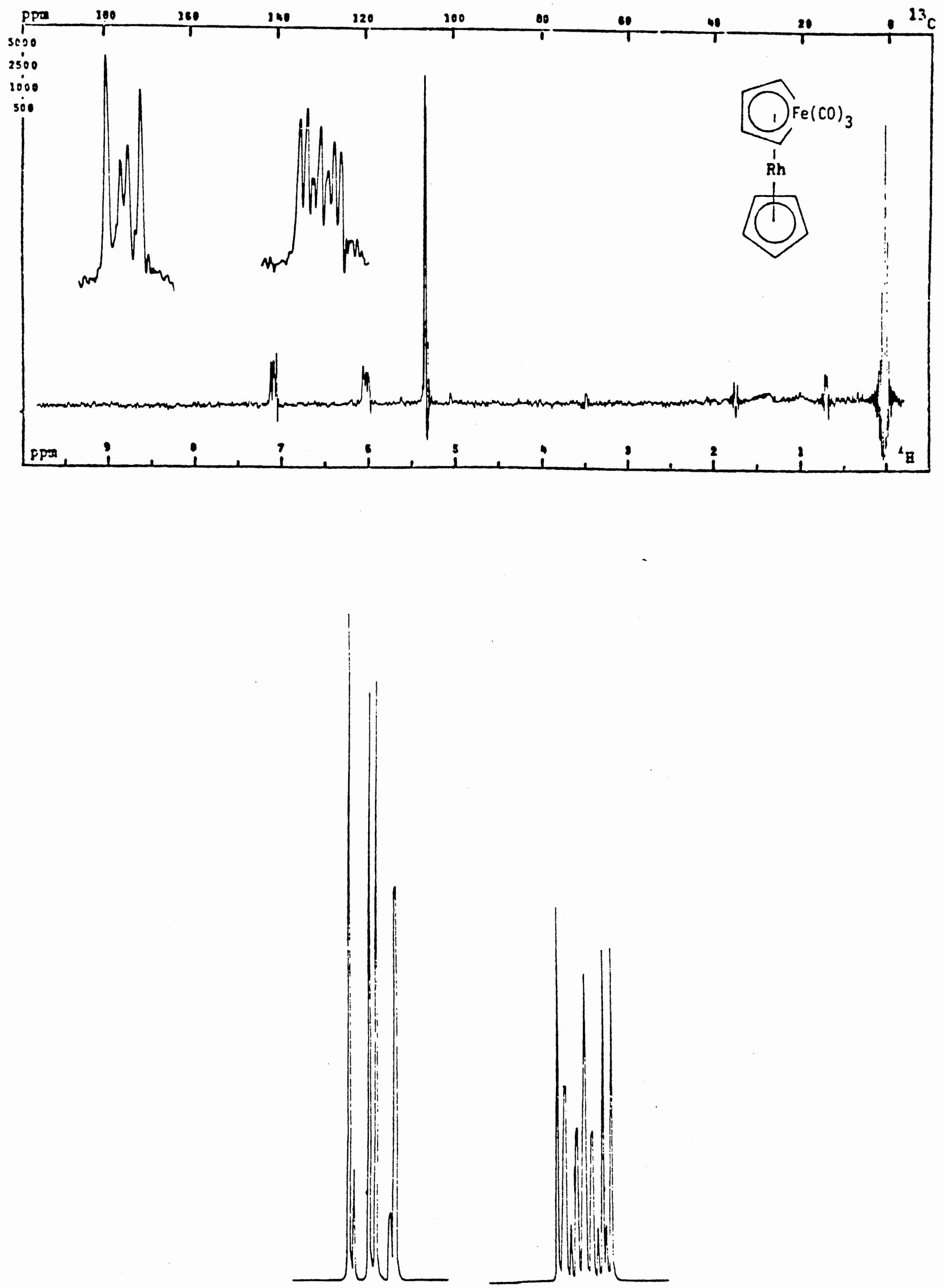
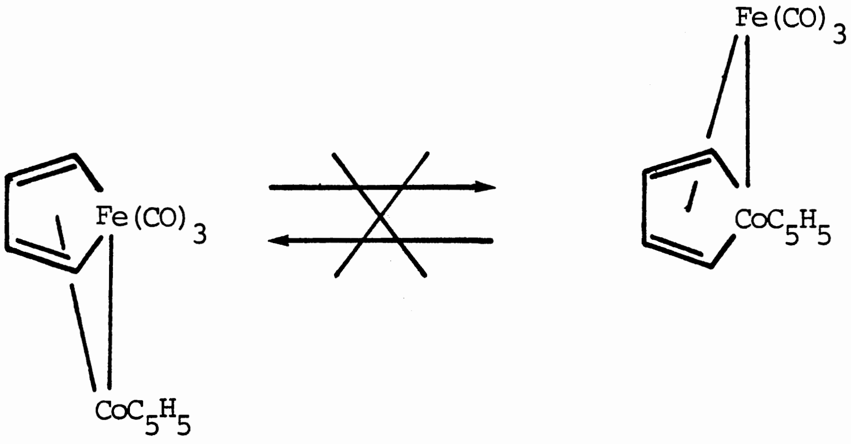


Figure 9. Top, ^{1}H-NMR Spectra of Ferrarhodocene. Bottom, Simulated Spectra.

Examination by McKennis and Radnia of the variable temperature ^{1}H-NMR spectra of sym-benzoferracobaltocene (VI) and ferracobaltocene (V) did not reveal any evidence for fluxional behavior. The ^{1}H-NMR of ferrarhodocene (VIII), in acetone-d_6 from room temperature down to -70°C and in decane from room temperature to +155°C contain no line broading that would indicate fluxional behavior (Equation 13).



(13)

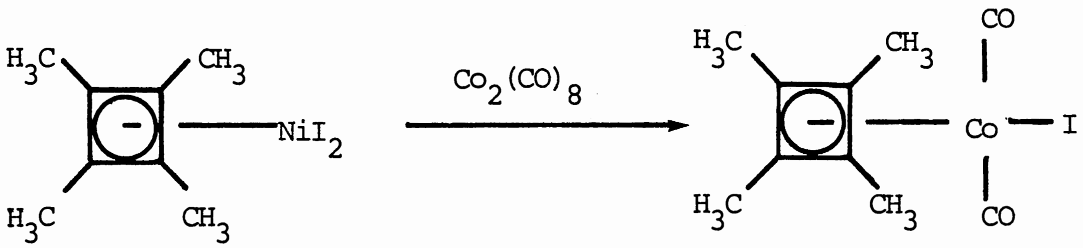
From molecular models of the 2-acetylferracobaltocene (XIII) two conformation might be preferred as shown in Figure 10. One might be able to "see" this preference by ^{1}H-NMR spectroscopy by looking at the methyl resonance signal. If there are preferred orientations, then one would expect at least two signals. Examination of the ^{1}H-NMR spectrum of complex XIII in methylene chloride at room temperature down to -80°C did not show splitting. There are two possible explanations for the ^{1}H-NMR data, either the acetyl moiety is free to rotate and no preferred orientation at low temperature exists or that at room temperature the acetyl moiety is already in a preferred orientation. The latter possibility could be explored by trying to exceed the rotation barrier thermally. This aspect was not investigated.

Figure 10. Possible conformations of 2-acetylferracobaltocene.

Synthesis of Metallometallocenes

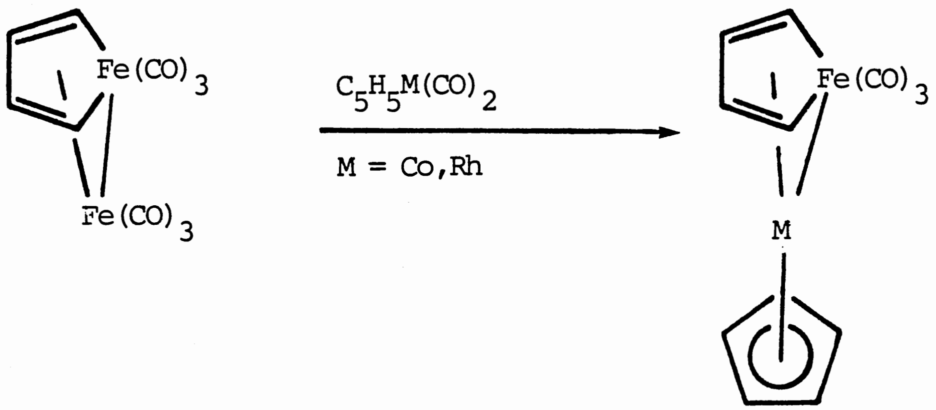
The use of these metallometallocenes in synthetic work is inhibited by the low yields of the insertion reaction and the high cost of starting materials. Yields of some of the complexes are: ferrole, 18%; ferracobaltocene (V), 15-30%; ferrarhodocene (VIII), 2.4%; *unsym*-benzoferracobaltocene (VII), 5.2%; *sym*-benzoferracobaltocene (VI), 26.8%. Costs of the starting materials are usually in excess of $40-$50 per gram.

To increase the utility of these complexes, alternate preparatory methods were evaluated. One of the synthetic methods for the preparation of Π-cyclobutadiene metal complexes is the use of ligand exchange reactions. An illustrative example is the exchange of diiodo(tetramethcyclobutadienyl)nickel with the octacarbonyldicobalt[38] as shown in Equation 14.



(14)

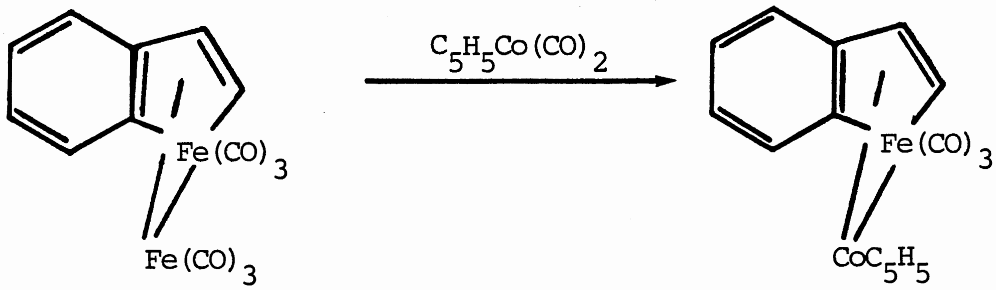
In view of the preceding, the ligand exchange reaction of ferrole and (cyclopentadienyl)dicarbonylcobalt was investigated (Equation 15). Yields impressively proved to be very good, but were dependent upon the reaction condition. In dilute solutions (usually 1g of reactants in 15-20 ml of solvent) yields averaged 32% based upon the starting amount of ferrole, but averaged 62% if based upon amount of ferrole recovered (i.e., the amount consumed). In concentrated solutions, i.e., with 2 g of reactants in 1-2 ml of solvent, yields were much higher, averaging 88%. The reaction of ferrole with (cyclopentadienyl)dicarbonylrhodium, in concentrated solution, proceeded in a yield of 9% if based upon starting ferrole and 78% based on recovered ferrole.



(15)

Although this is not as dramatic an increase in yield as with ferracobaltocene, a good *overall* yield can nonetheless be realized through recycling the large amount of unreacted starting materials.

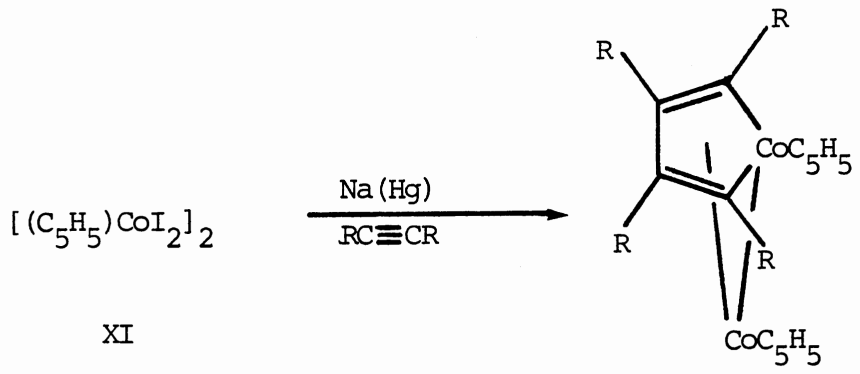
Preparation of *unsym*-benzoferracobaltocene (*VII*) using the insertion reaction of (benzocyclobutadiene)tricarbonyliron and (cyclopentadienyl)dicarbonylcobalt results in low yield, and difficulty is encountered in its separation from its isomer[32]. On the other hand, *unsym*-benzoferrole is easy to produce and can then be converted to the *unsym*-benzoferrocobaltocene (*VII*) by ligand exchange in a relatively good yield of 35% (Equation 16).



(16)

Therefore, a relatively high-yield, low-cost synthetic path to these metallometallocenes and their substituted analogs would be to first prepare the appropriate ferrole (low yield but also low cost), then to convert it to the desired metallometallocene, and then to introduce additional functionality if desired (to be discussed later).

The reduction of diiodo(cyclopentadienyl)cobalt dimer (XI) in the presence of acetylenes produces a binuclear metallocycle[39] (Equation 17).

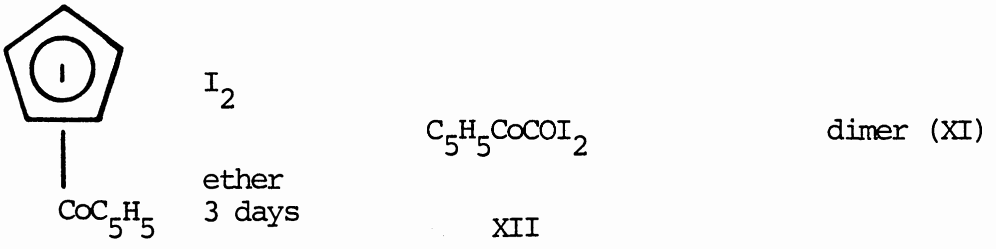


XI

(17)

The dimer is prepared[40,41] from diiodo(cyclopentadienyl)carbonylcobalt (Equation 18).

Using this information, the following reactions were investigated with the hope of improving the preparation of ferracobaltocene (Equation 19).

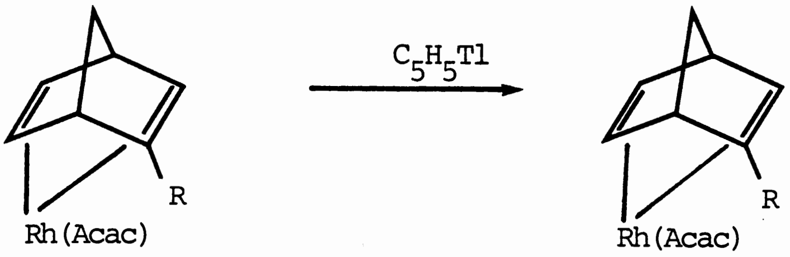


(18)

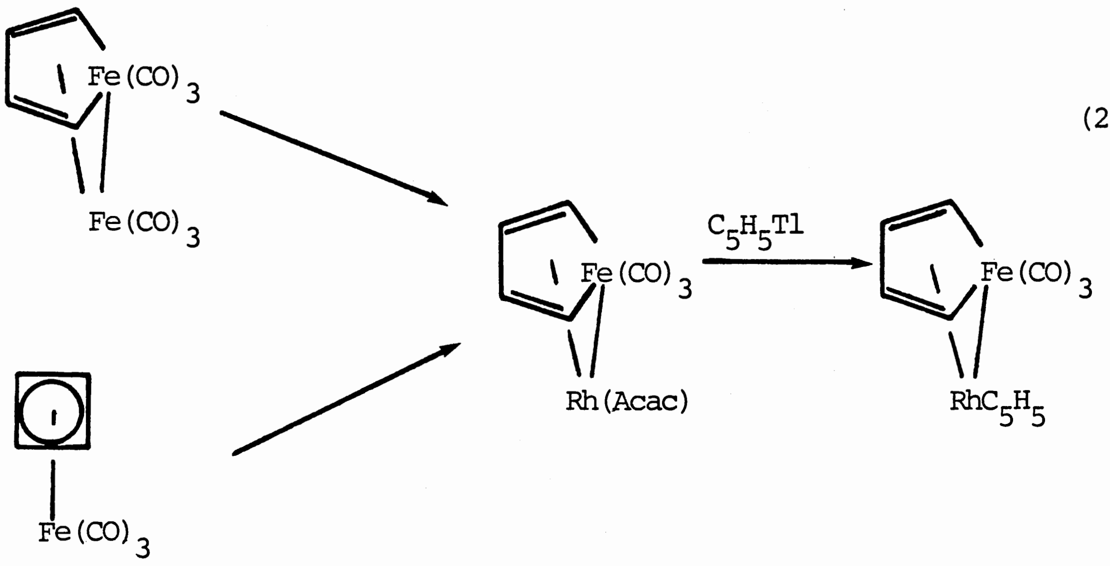
$$\begin{aligned}
&\text{ferrole} + \text{XII or XI} \xrightarrow{?} \text{complex V}\\
&\text{ferrole} + \text{XII or XI} \xrightarrow{Zn} \text{complex V}\\
&C_4H_4Fe(CO)_2 + \text{XII} \xrightarrow{?} \text{complex V}\\
&C_4H_4FE(CO)_2 + \text{XII} \xrightarrow{ZN} \text{complex V}
\end{aligned} \qquad (19)$$

Only one reaction yielded ferracobaltocene. The reaction of ferrole and diiodo(cyclopentadienyl)carbonylcobalt (XII) with zinc added to facilitate the removal of I_2 from the cobalt by α-elimination yielded a small amount of ferrocobaltocene (V) (3mg, 5%).

On the basis of the transformation developed by Chizkevskii and Koridze[42] shown in Equation 20, the reactions of (pentane-2, 4-dionate)dicarbonylrhodium with ferrole or (cyclobutadienyl)tricarbonyliron were investigated as possible synthetic routes to ferrarhodocene or intermediate binuclear RH(Acac) species (Equation 21). Unfortunately, the sequence proved unrewarding.



(20)



(21)

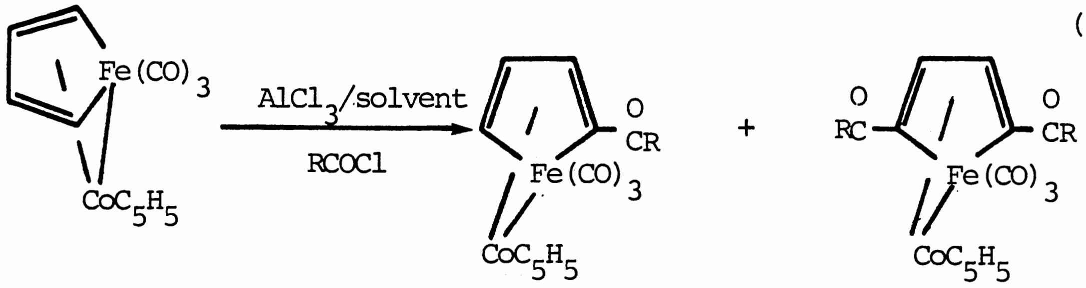
Reactions of Metallometallocenes

A. Acylation Studies. Aromatic compounds are readily acylated by a Friedel-Crafts reaction. The combination of reagents used most commonly for aromatic acylation consists of the aromatic hydrocarbon, an acyl component (e.g., AlX_3) and a Lewis acid catalyst (e.g., AlX_3). Although the mechanism beyond the initial stage still remains to be elucidated, the acylating agent is considered to be either an oxonium complex RC(X)---$\overset{+}{O}$---$\overset{-}{Al}X_3$ or an ion-pair $[RCO]^{\oplus}$ $[AlX_4]^{\oplus}$.

The isomeric acyl species 2- and 3-acetyl- and 2- and 3-benzoylferracobaltocene have been prepared[32,43] by the insertion reaction of (cyclopentadienyl)dicarbonylcobalt with acetyl- and (benzoylcyclobutadiene)tricarbonyliron, respectively. The latter species can be conveniently prepared by the appropriate Friedel-Crafts acylation of (cyclobutadiene)tricarbonyliron. The yields of the insertion process for the acetyl-and benzoylcyclobutadiene complexes were 35% and 58%, respectively. No attempts were made to maximize the yields by variation of the reaction conditions. In both insertion reactions the 2- and 3-acylferracobaltocene derivatives were obtained in a ratio of _ca_. 1:3. If indeed the metallometallocenes are best regarded as aromatic or pseudo-aromatic systems, it was anticipated that they should undergo facile Friedel-Crafts acylation, quite possibly with exclusive acylation of the cyclopentadienyl (C_5H_5) ring, presumably the most electronically rich site in the molecules. As a consequence, the direct acetylation and benzoylation of complexes _III_, _V_, and _VIII_ were studied with respect to the isolation and characterization of products, optimization of yields, and gross mechanistic features of the acylation. The reactions used either acetyl chloride or benzoyl chloride as the acyl component and aluminum chloride as the catalyst.

The acetylation of ferracobaltocene interestingly produced two substituted products; a mono acetyl derivative in which the group was exclusively in the 2 position, _viz_. complex XIII, $R=CH_3$, and a 2,5 diacylated compound, complex _XIV_, $R=CH_3$. There was no indication of any other substituted products. The yields, but not the site of acylation, were dependent upon the solvent used (Equation 22).

(22)



V XIII XIV

The commonly used solvents in the Friedel-Crafts ketone synthesis are carbon disulfide and nitrobenzene. In carbon disulfide the reaction is heterogeneous throughout the reaction owing to the insolubility of aluminum chloride and the oxonium complex. Nitrobenzene on the other hand, being a polar solvent solvates the aluminum chloride and the acyl chloride- aluminum chloride complex and usually the aluminum chloride complex of the resulting ketone. Methylene chloride is a solvent intermediate in polarity which does not dissolve aluminum chloride, but is a good solvent for the acylating complex and a fair solvent for the resulting complex. The yields of acylation in various solvents are presented in Table V. The yields in Table V indicate that for a given solvent the ratio of the mono to di acetyl product is 3 or 4 to 1.

The addition of a base to facilitate the removal of the proton bound to the carbon being acylated was examined. 2,6-Di-tert-butyl pyridine was added to the acetylation reaction in methylene chloride of both ferrole (to be discussed later) and ferracobaltocene (V). This addition appeared to inhibit the acylation.

TABLE V

YIELDS OF 2-ACETYL- AND 2,5-DIACETYLFERRACOBALTOCENE, XIII AND XIV RESPECTIVELY VS SOLVENT, AT ROOM TEMPERATURE

Complex XIII

Solvent	Typical[a]	High[a]	Typical[b]	High[b]
CS_2	17	17.3	29	40.6
CH_2Cl_2	43	49.6	55	63.2
Nitrobenzene	--[d]	--[d]	--[d]	--[d]
CH_2Cl_2 + TBP[c]	24	30.1	34	44
Complex XIV				
CS_2	6.0	25.6	18	40.6
CH_2Cl_2	11.5	14.3	18	18
Nitrobenzene	--[d]	--[d]	--[d]	--[d]
CH_2Cl_2 + TBP[c]	11.5	12.7	18	18

[a] Based upon starting amount of complex V.

[b] Based upon recovered (i.e., amount consumed) complex V.

[c] 2.6-Di-tert-butyl pyridine (0.6 mmol).

[d] No acetyl product found.

The acetylation of ferrole provided several interesting results. In practice the relative ratio of the reactants: moles of substrate: moles of catalyst: moles of acylating agent is 1:1:1.1. When this ratio was used for the acetylation of ferrole (III) in carbon disulfide only, the 2-acetyl (complex XV) product, which was very unstable in solution, was obtained in a yield similar to that obtained for the 2-acetylferracobaltocene (XIII). However, when the ratio 1:7:7.1 was used not only the 2-acetyl (complex XV) compound but also two other compounds, were produced. One of the two compounds probably was the di-acetylated product as suggested by mass spectroscopy. Due to time limitations, the difficulties in separation and purification, and the unstable nature of these complexes, limited effort was directed toward their identification. The use of methylene chloride and 2,6-di-tert-butylpyridine gave similar results as obtained in the other case, i.e., a better yield with the chloride as solvent, but a lower yield with the addition of the pyridine.

Benzoylation of complexes III, V, and VIII yielded products only in the case of complex V. The 2-benzoyl complex (XVII) was produced along with a small amount of a purple unknown.

The ^{1}H-NMR spectra of the substituted complexes are shown in Figures 11, 12, 13, 14, and 15.

A tenable mechanism for the acetylation process must account for the following: only the two and five positions are substituted and the ratio of the mono-to the di-acetyl product is only 3 or 4 to 1. Furthermore, the question arises: after mono acylation which supposedly deactivates the ring, why is there additional acylation?

From the ^{1}H-NMR and ^{13}C-NMR spectra, shown in Table VI, the carbon atoms (and their associated protons) adjacent to the metal should be electronically deficient compared to the other two carbon atoms (and their associated protons), since the former signals are farther downfield.

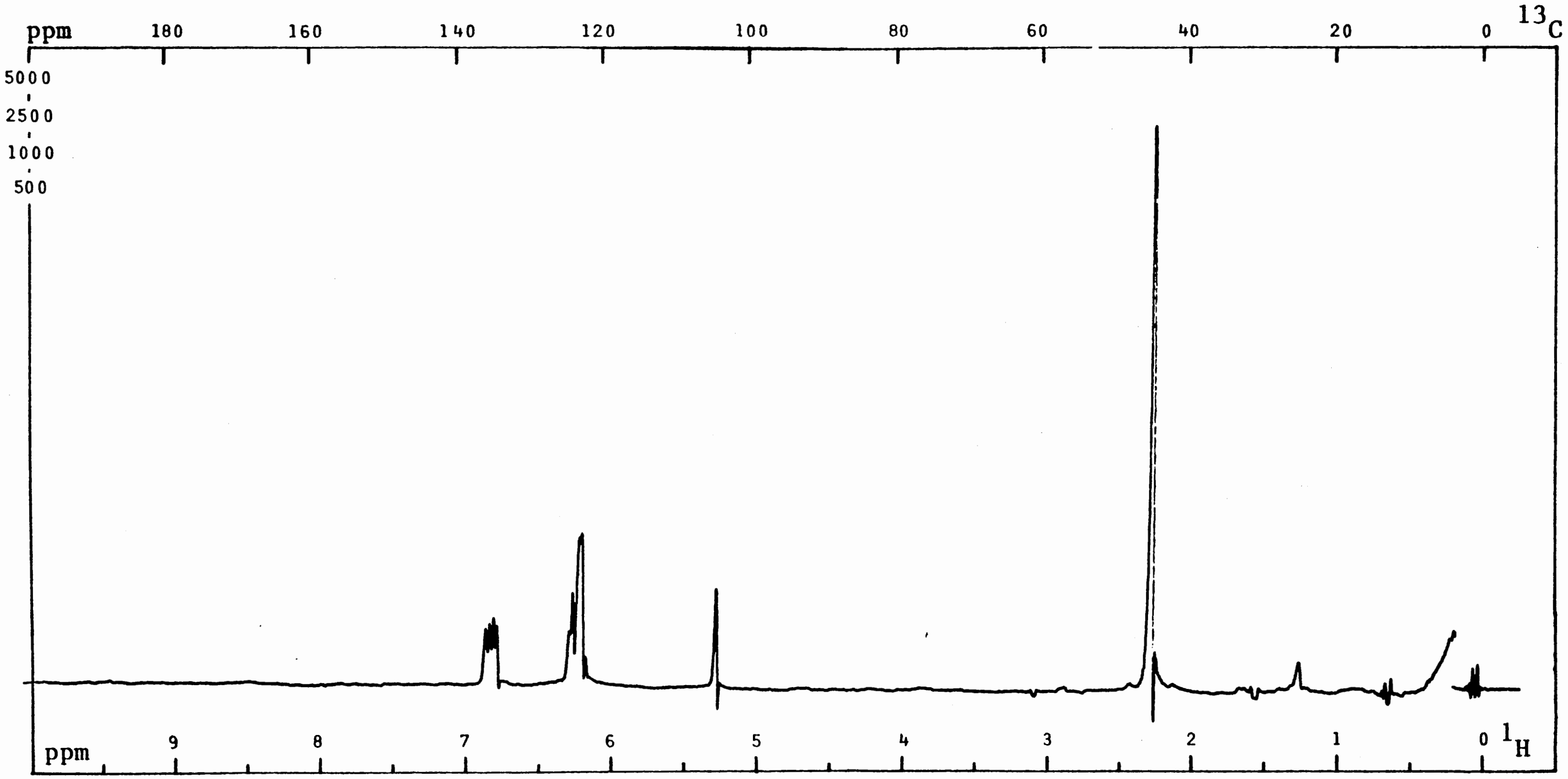


Figure 11. ^{1}H-NMR Spectrum (CS_2) of 2-Acetylferrole.

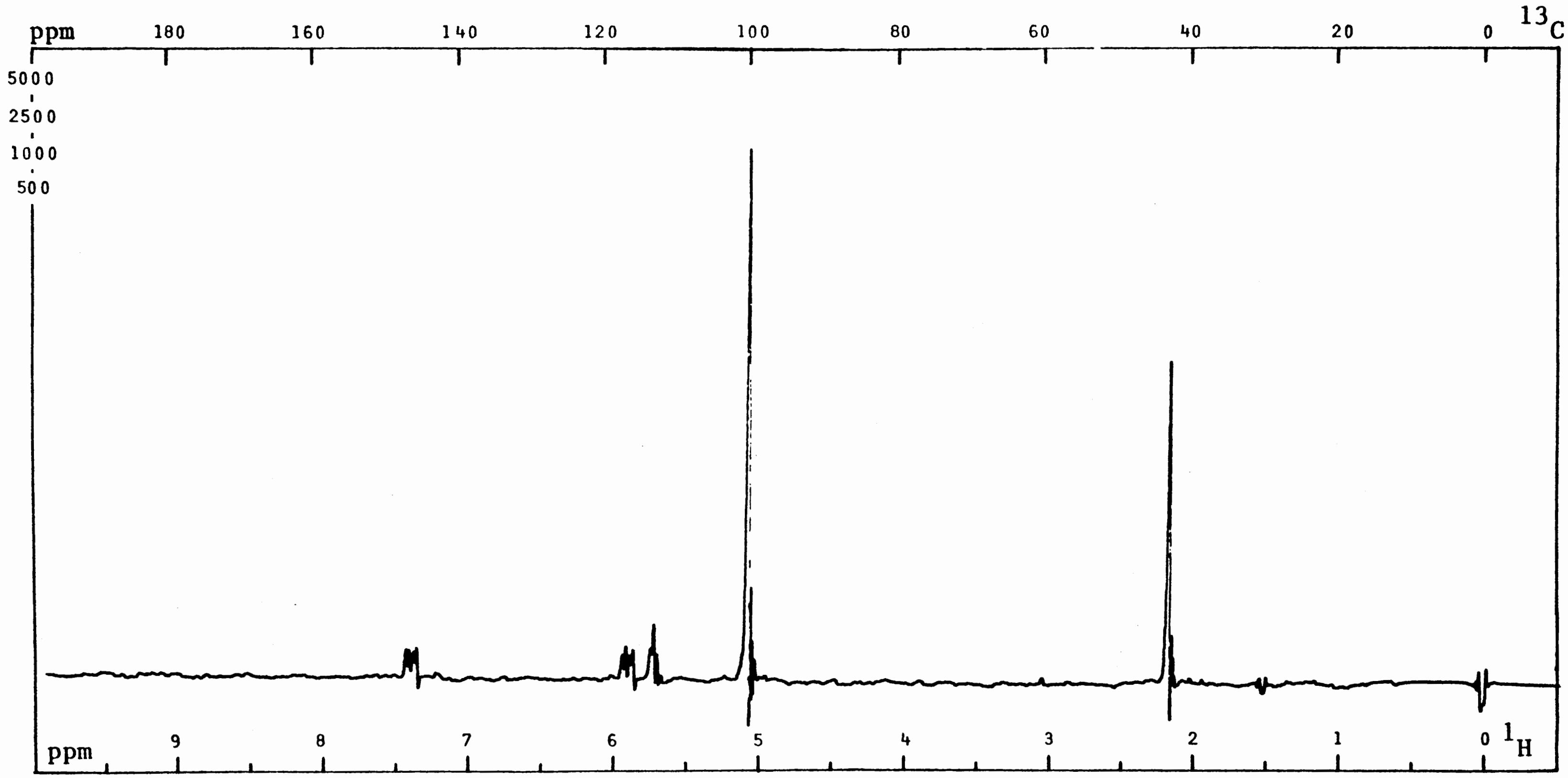


Figure 12. ^{1}H-NMR Spectrum (CS_2) of 2-Acetylferracobaltocene.

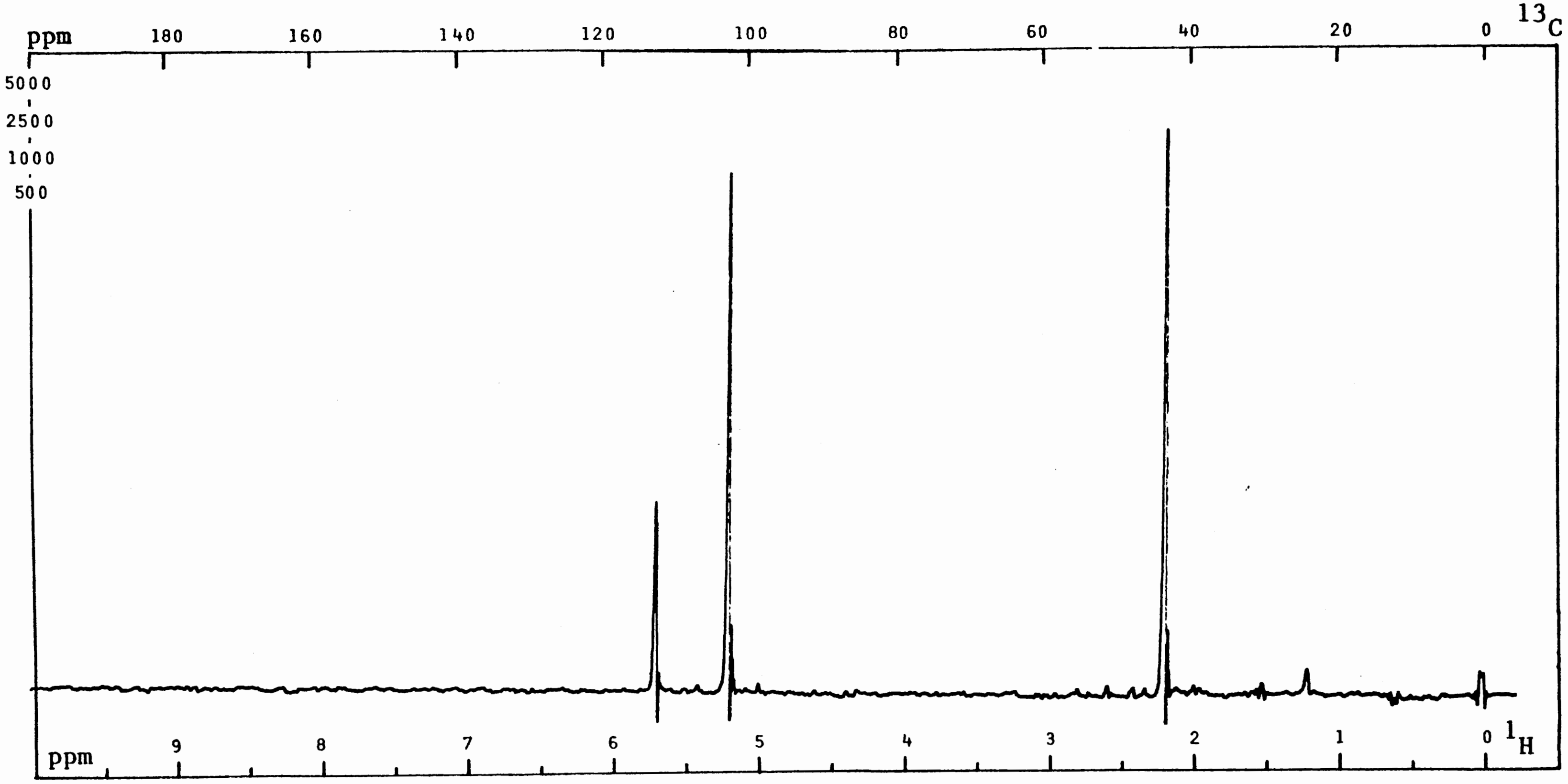


Figure 13. ^{1}H-NMR (CS_2) Spectrum of 2,5-Diacetylferracobaltocene.

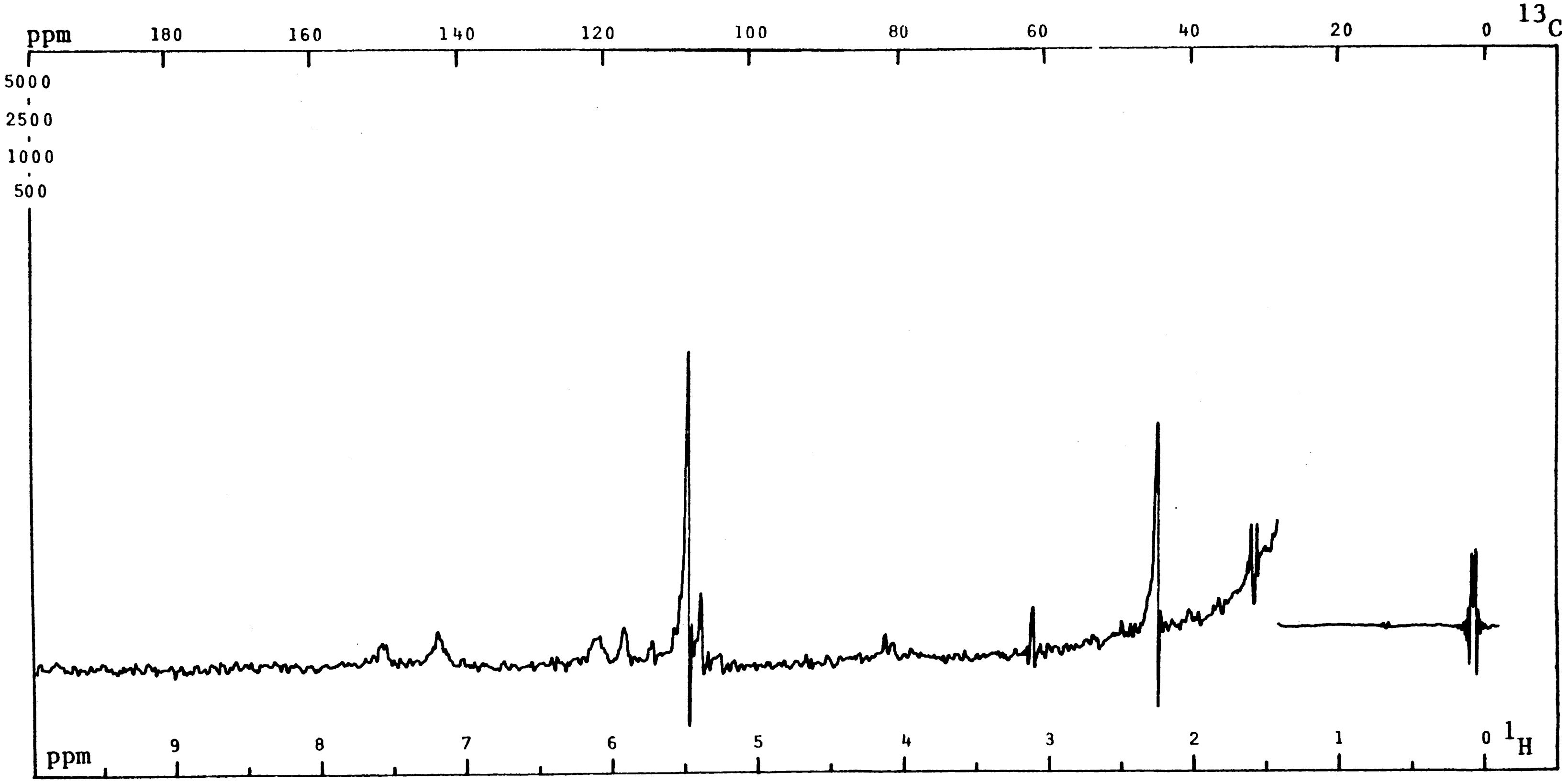


Figure 14. ^{1}H-NMR (CS_2) Spectrum of 2-Acetylferrarhodocene.

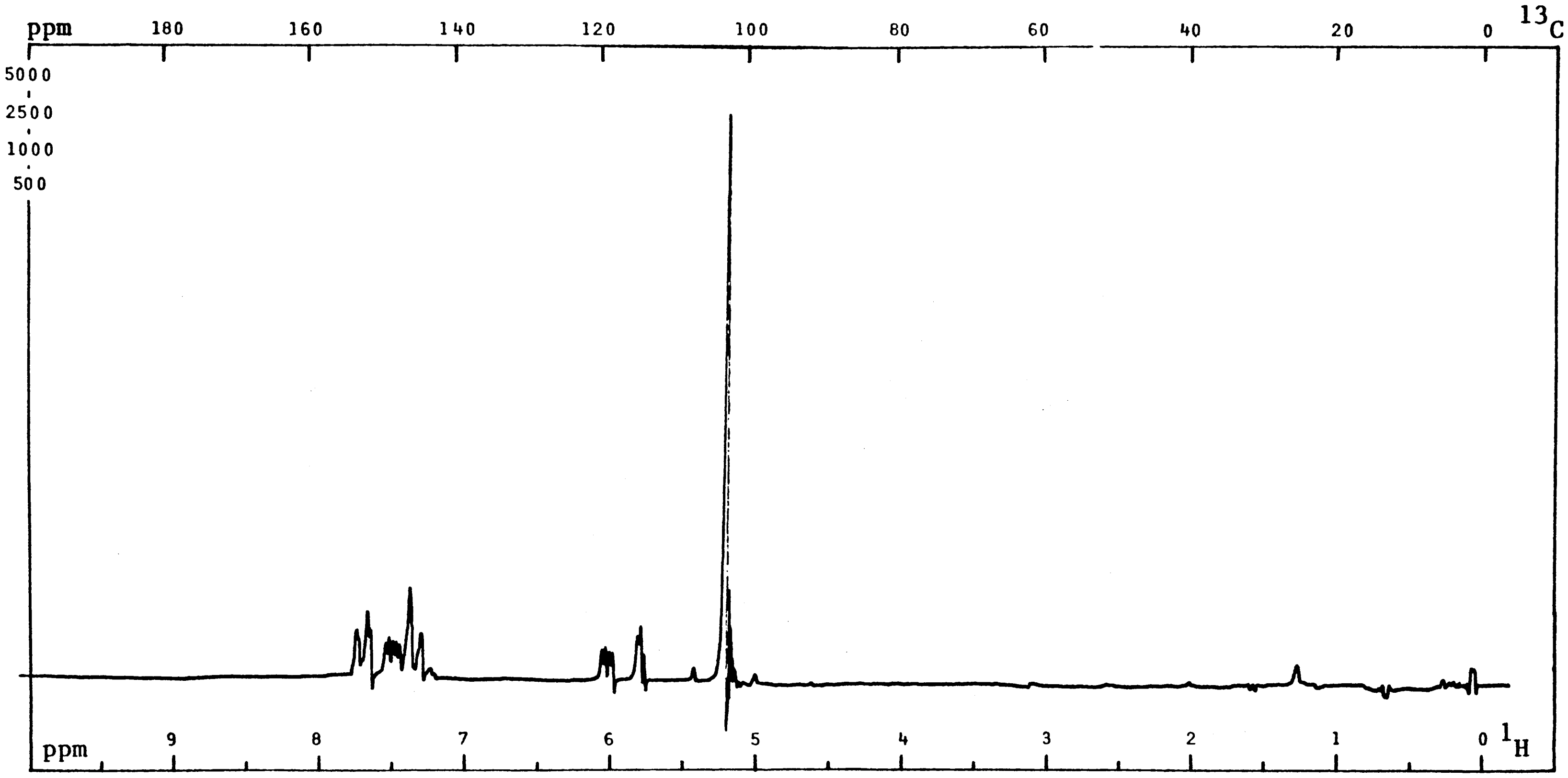


Figure 15. ^{1}H-NMR (CS_2) Spectrum of 2-Benzoylferracobaltocene.

TABLE VI

^{1}H-NMR SPECTRUM (CS_2) DATA

Complex	H_1	H_2	H_3	H_4	CP
VIII	7.12("dd")	6.02(m)	6.02(m)	7.12("dd")	5.30(s)
V	7.39("dd")	5.88("dd")	5.88("dd")	7.39("dd")	4.88(s)
III	6.75("dd")	6.15("dd")	6.15("dd")	6.75("dd")	

Complex	C_1	C_2	C_3	C_4	CP
VIII	148.9	98.7	98.7	148.9	82.9
V	157.0	101.4	101.4	157.0	81.1
III	156.4	112.1	112.1	156.4	

However, these are in fact the carbon atoms that are acylated. Speculation as to the reasons for this must involve a consideration of the bonding involved in the metallometallocene and the conclusions of protonation experiments.

If ferracobaltocene (V) is initially envisioned in terms of a diene complex as shown below, the iron with eight electrons is two electrons short of the inert gas structure. The pair of nonbonding electrons of cobalt can form a coordinate covalent bond with iron with the subsequent development of a partial positive charge. This partial charge is balanced by substantial forward coordination from the Π system resulting in polarization shown in Figure 16.

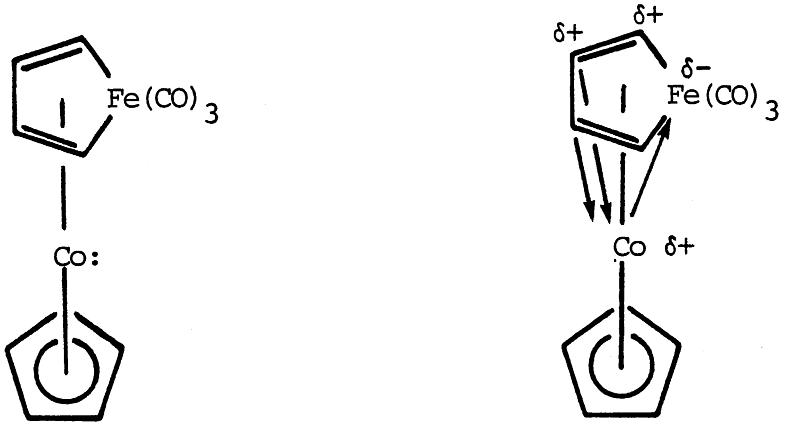


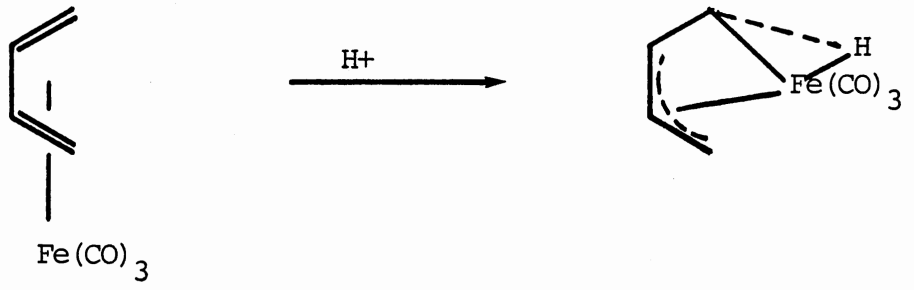
Figure 16. Bonding Involved in Metallometallocene.

The result is a dynamic symbiotic system of back donation creating partial positive charge which is simultaneously balanced by forward coordination.

B. Protonation Studies. Brookhart[44], in a study to elucidate the reaction of polyolefin transition metal complexes with simple electrophiles, suggested that when the electrophile is a proton, in the protonated species, a metal hydride may be bridging between the iron and a carbon in the protonated species. An illustrative example is shown in Equation 23.

The ^{1}H-NMR spectrum of protonated ferracobaltocene in trifluroacetic acid is shown in Figure 17. The metal hydride signal is 16.8 ppm upfield from TMS. This is one of the highest metal hydride signals reported. The spectrum of the species was independent of the associated counter-anion, or the acid used; identical spectra were obtained with CD_3CO_2H, HCl in CS_2, H_2SO_4 in SO_2 or $HBF_4 \cdot Et_2O$ in glacial acetic acid. Protonation of ferrarhodocene in TFA/$DCCl_3$ yielded a protonated species similar to that obtained for the cobaltocene as evidenced by the similarity of the ^1H-NMR spectra, compare Figures 17 and 18.

(23)



The absence of any appreciable ^{103}Rh coupling in absorption for the metal hydride indicates that the iron atom and not the rhodium atom has been protonated. The magnitude ^{103}Rh-H coupling is normally in the range 15-30 Hz. The ^{13}C-NMR spectra of these complexes in TFA/$DCCl_3$ or HCl/SO_2 unfortunately were not well resolved, but nonetheless did not reveal a unique carbon atom.

The preceding data coupled with spin decoupling and deuteration studies suggest the proton assignment and structure proposed in Equation 24.

Based upon the preceding acylation and protonation studies, it is proposed that the electrophilic attack proceeds first with the acylation or protonation of the iron in a fast step to give the

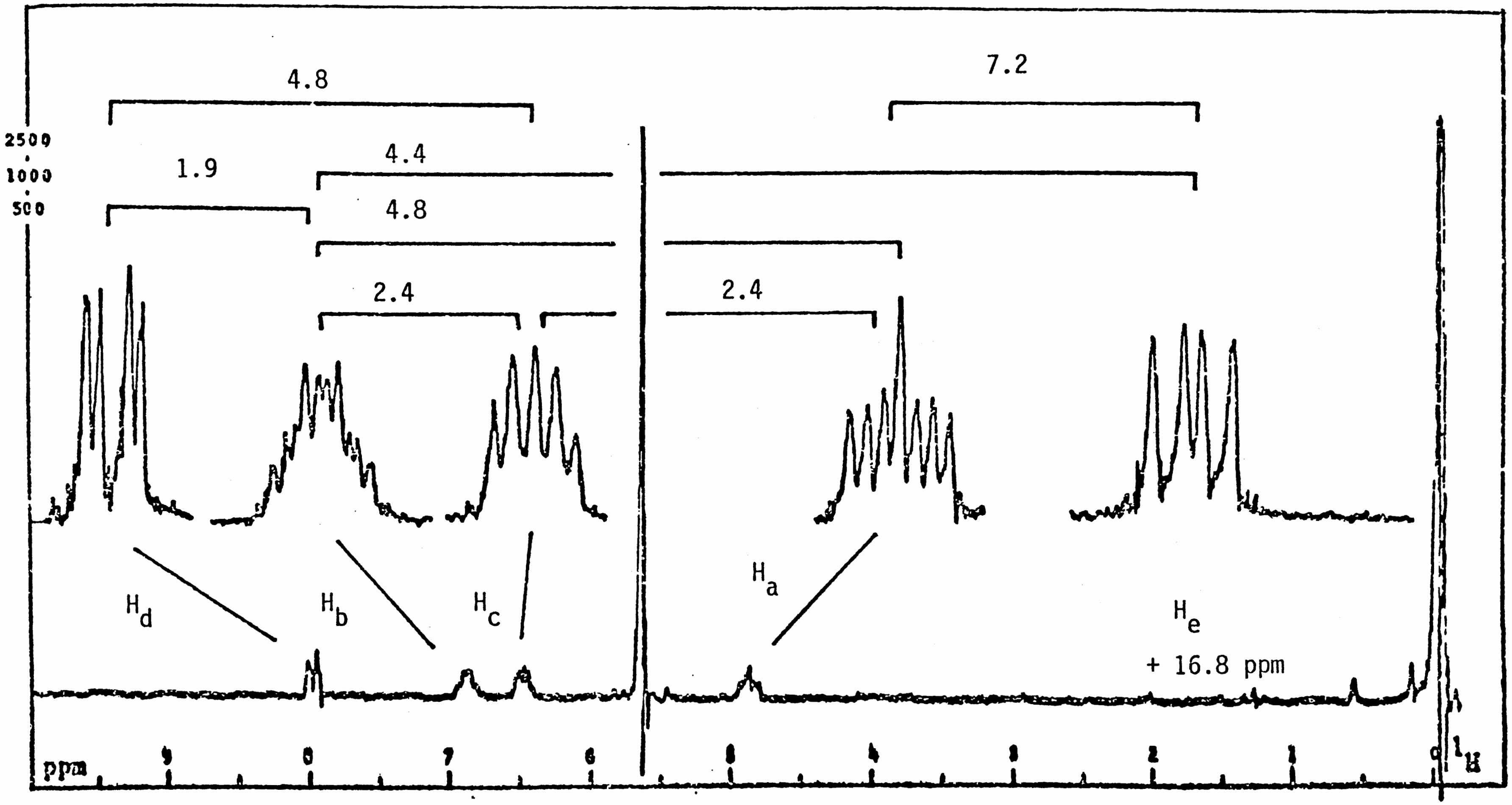


Figure 17. ^{1}H-NMR Spectrum of Ferracobaltocene in TFA.

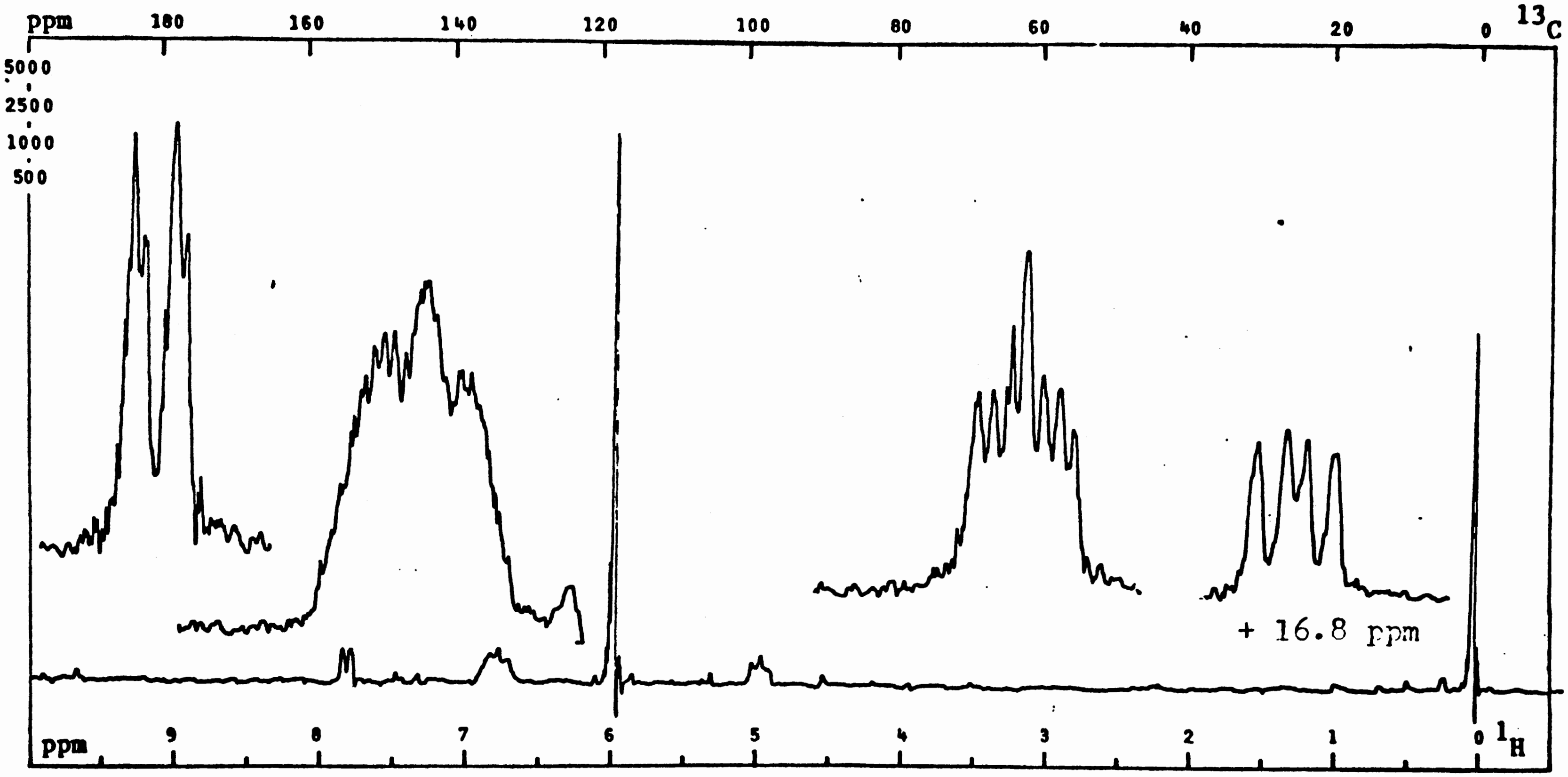
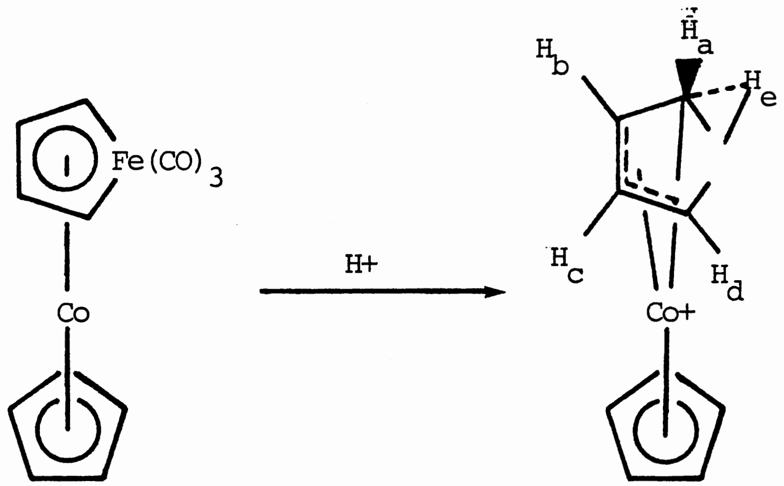


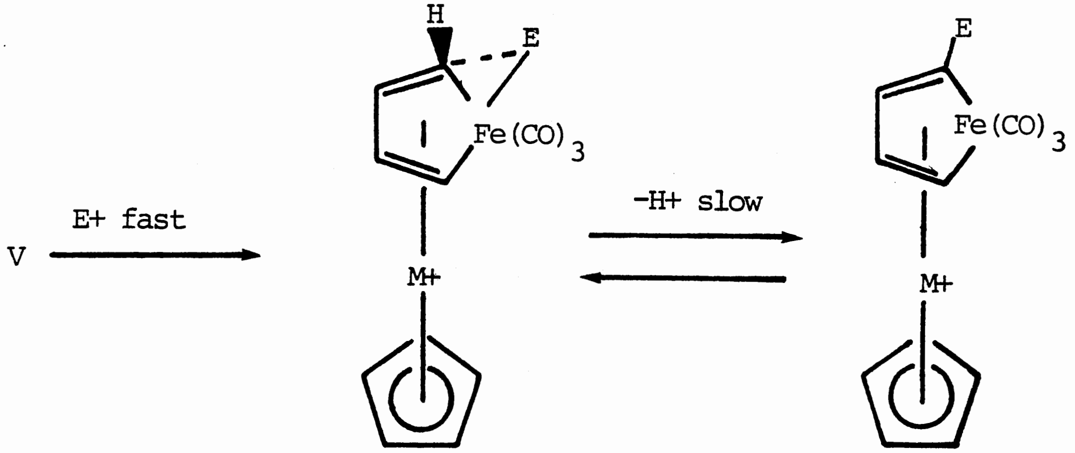
Figure 18. ^{1}H-NMR of Ferrarhodocene in TFA and $DCCl_3$.

bridging species, followed by a slow migration of the electrophile to the carbon, with simultaneous loss of a proton, Equation 25. The possibility of migration of the electrophile to the carbon before loss of the proton cannot be ruled out.



(24)

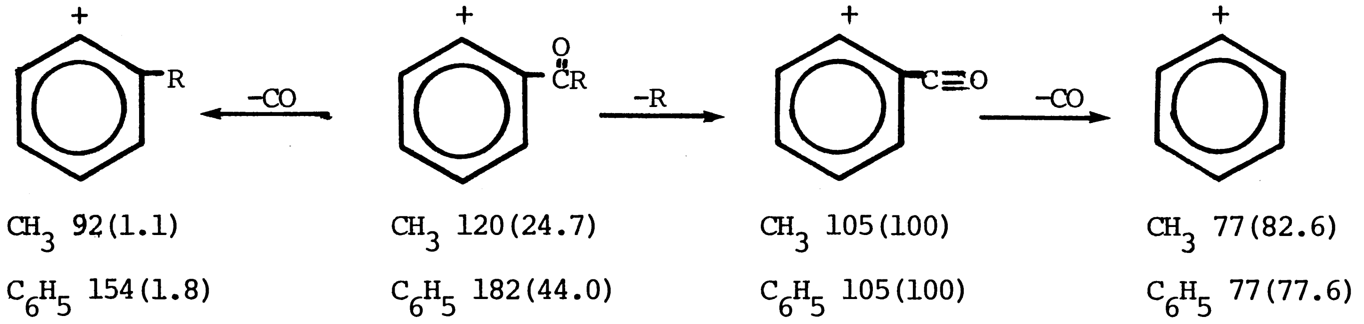
(25)



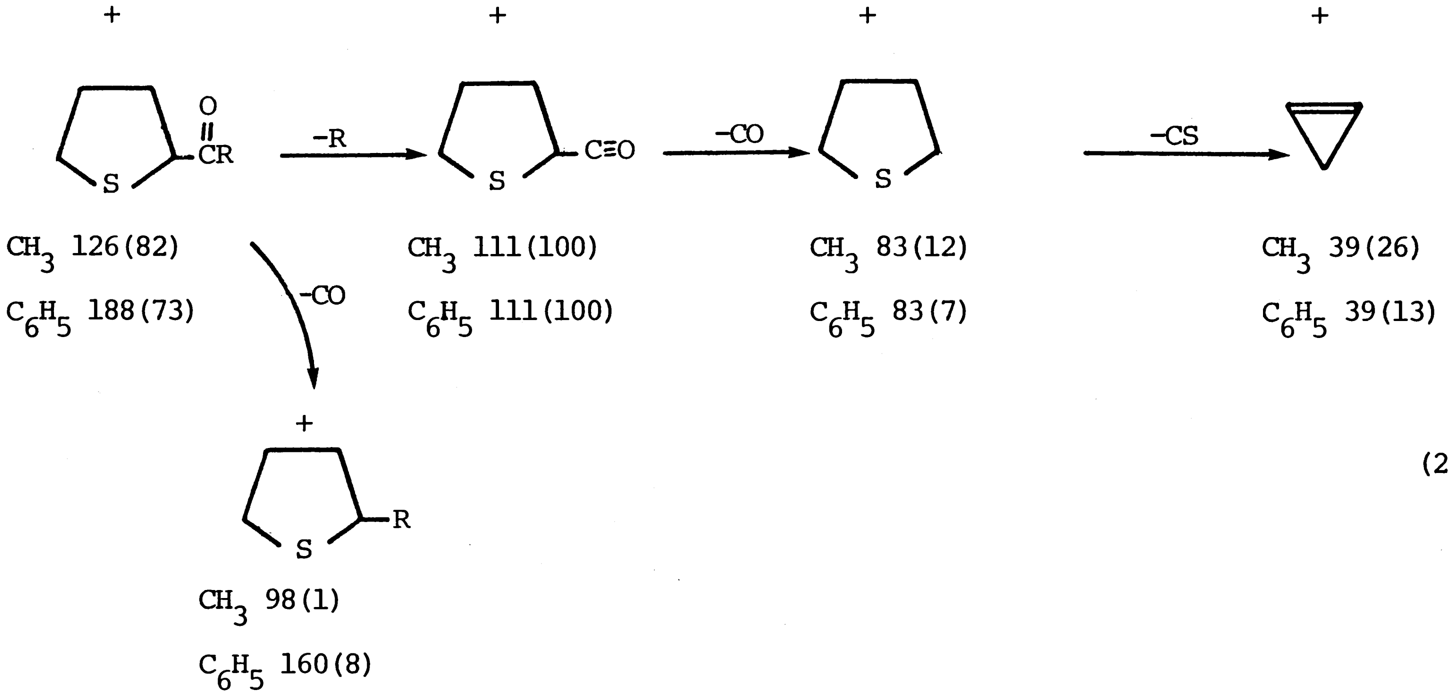
Mass Spectral Fragmentation of Substituted Metallometallocenes

Analysis of the mass spectral fragmentation data for the substituted metallometalocene complexes provides an interesting comparison within the group and with model compounds.

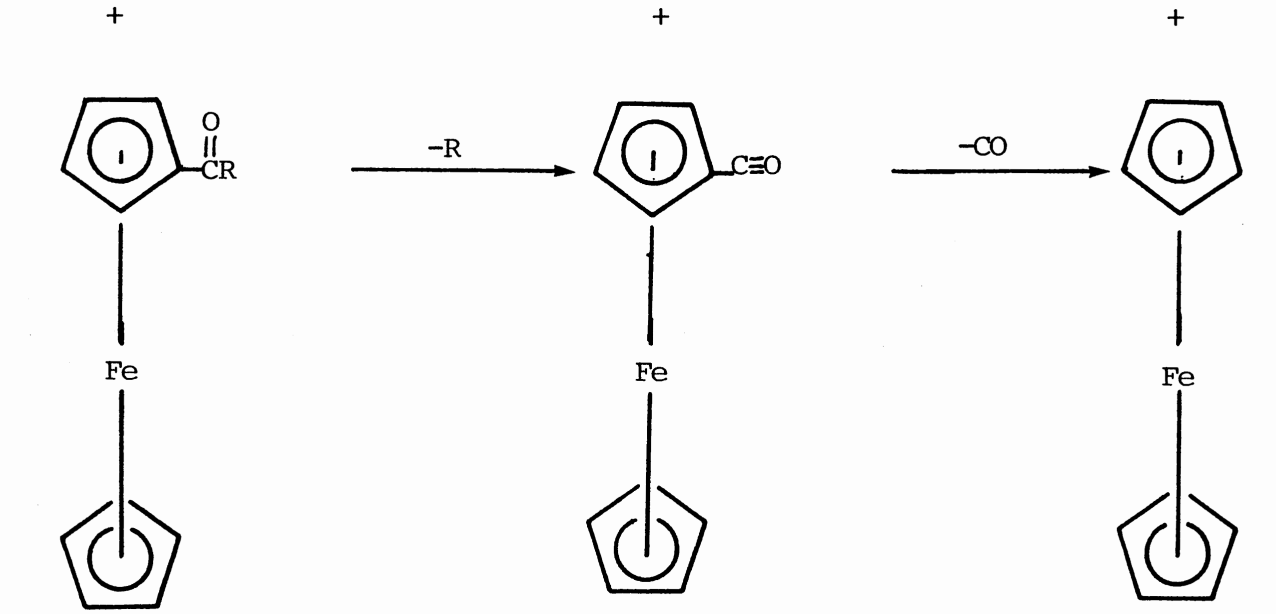
The major fragmentation paths for acetophenone, benzophenone[45], 2-acylthiophene[46], and acetyl or benzoyl substituted ferrocene[47] are shown in Equations 26, 27, and 28. The most notable feature is the loss of the methyl or phenyl group first followed by the loss of CO. There is little indication of loss of CO first. The benzoyl substituted ferrocene seems quite stable showing little or no significant fragmentation pattern. The major fragmentation path of acetyl and benzoyl(cyclobutadiene)tricarbonyliron, (Equation 29), contains the typical loss of the 3 CO ligands, which is then followed by the loss of acetylene (C_2H_2), and by the sequential loss of CO and methyl or phenyl. There is no evidence of the loss of the methyl or phenyl group first. A notable feature is the lack of a peak corresponding to the loss of the third CO ligand when $R=C_6H_5$. A comparison of the fragmentation pattern for 2-acetylferrole, 2-acetylferracobaltocene, and 2-acetylferrarhodocene, (Equation 30) with the model complexes reveals that the complexes have mass spectra very similar to that of (2-acetylcyclobutadiene)tricarbonyliron but with an important difference. The cyclobutadiene ring exclusively looses C_2H_2 to give the substituted acetylenic complex and does not lose HC_2COR to give the parent acetylene complex. The 2-acetyl binuclear complexes on the other hand, lose both C_2H_2 and HC_2COCH_3


+
R
−CO
+
O
CR
−R
+
C≡O
−CO
+
CH_3 92(1.1)
C_6H_5 154(1.8)
CH_3 120(24.7)
C_6H_5 182(44.0)
CH_3 105(100)
C_6H_5 105(100)
CH_3 77(82.6)
C_6H_5 77(77.6)

(26)


+
O
CR
S
CH3 126(82)
C6H5 188(73)
-R
+
C≡O
S
CH3 111(100)
C6H5 111(100)
-CO
+
S
CH3 83(12)
C6H5 83(7)
-CS
+
CH3 39(26)
C6H5 39(13)
-CO
+
R
S
CH3 98(1)
C6H5 160(8)

(27)



(28)

CH_3 228(100)

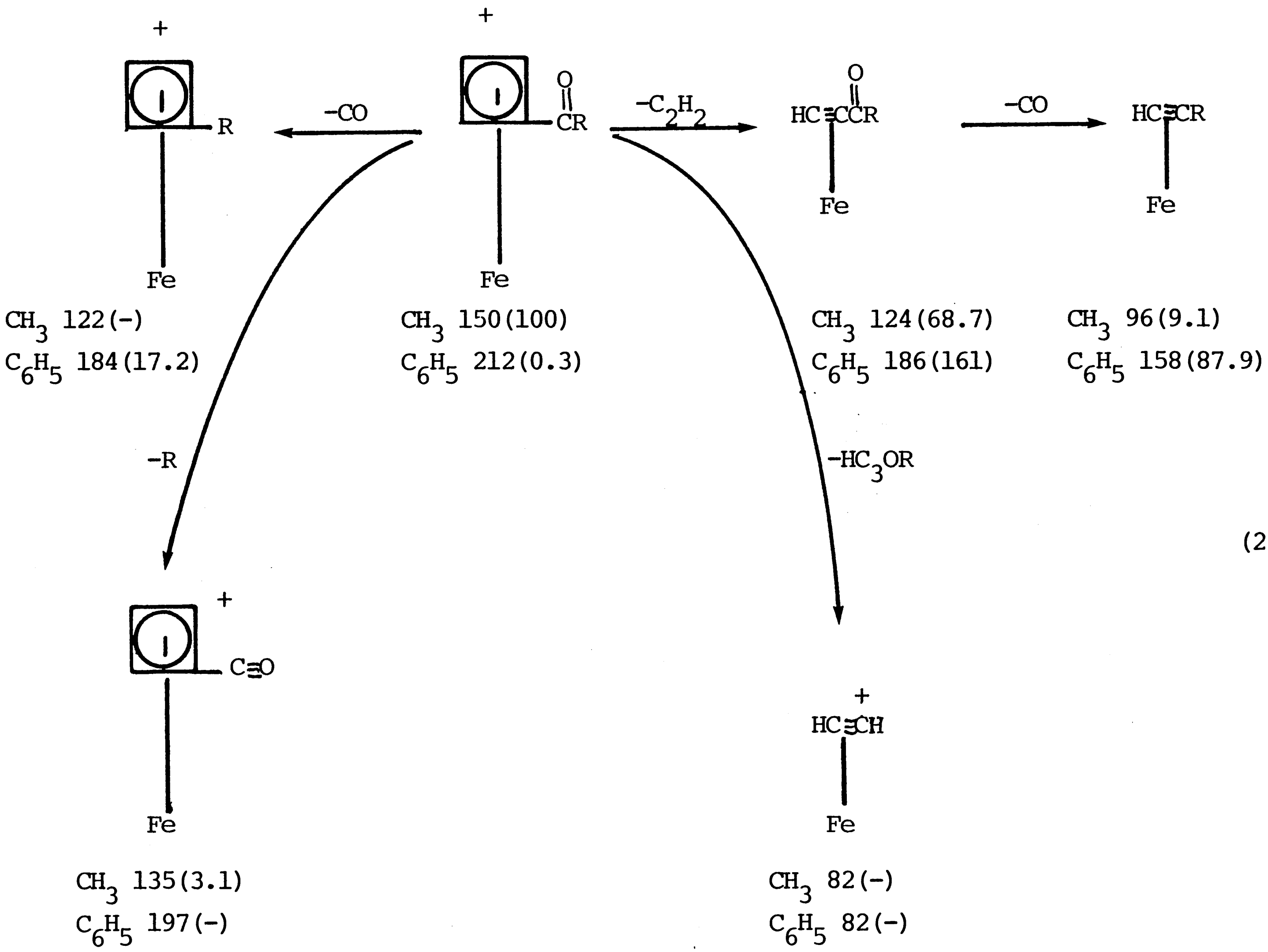
C_6H_5 290(100)

CH_3 213(13)

C_6H_5 213(1.5)

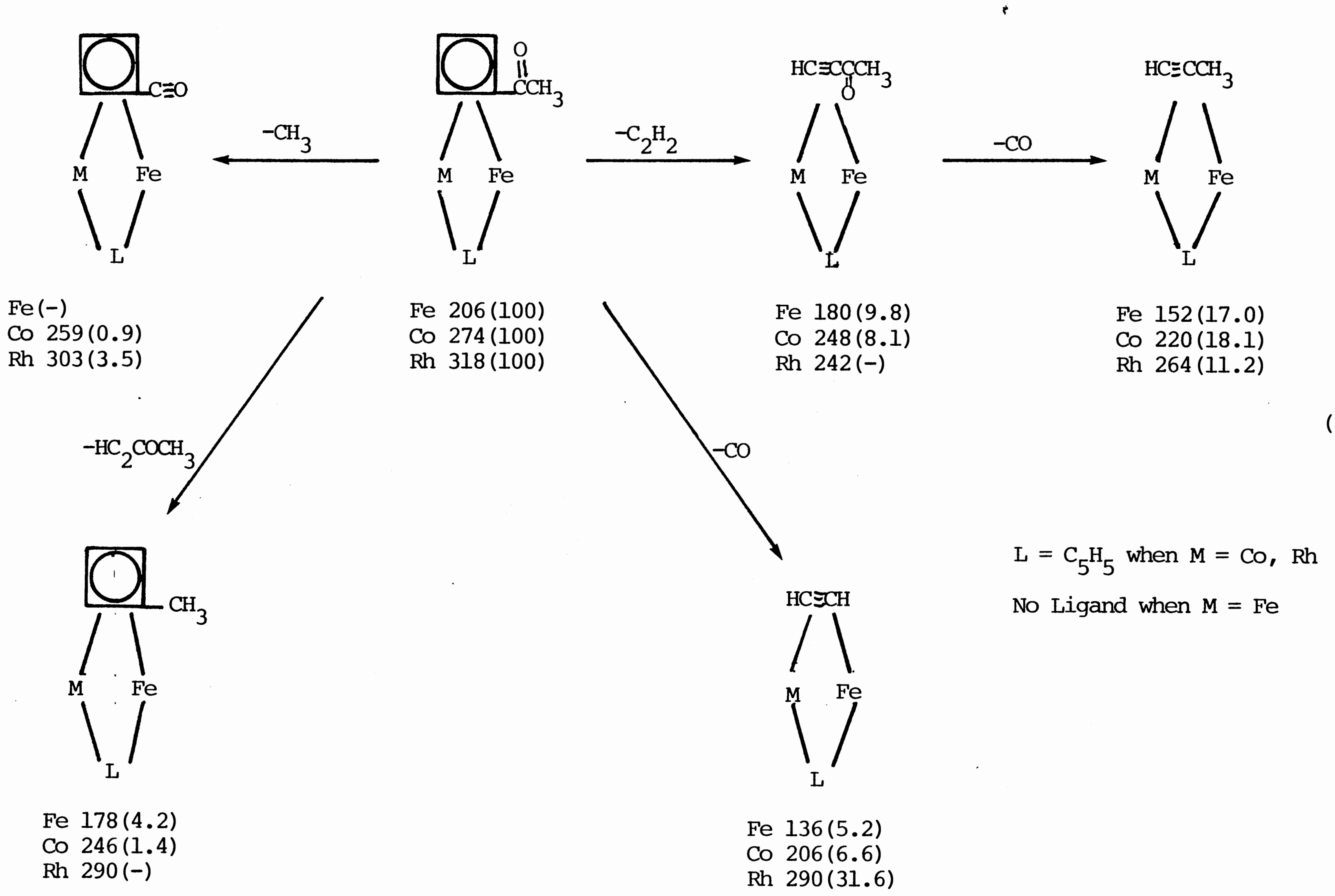
CH_3 185(63)

C_6H_5 185(4)



+
O
CR
Fe
-CO
-C$_2$H$_2$
HC≡CCR
O
-CO
HC≡CR
Fe
R
Fe
CH$_3$ 122(-)
C$_6$H$_5$ 184(17.2)
CH$_3$ 150(100)
C$_6$H$_5$ 212(0.3)
CH$_3$ 124(68.7)
C$_6$H$_5$ 186(161)
CH$_3$ 96(9.1)
C$_6$H$_5$ 158(87.9)
-R
-HC$_3$OR
C≡O
Fe
CH$_3$ 135(3.1)
C$_6$H$_5$ 197(-)
HC≡CH
Fe
CH$_3$ 82(-)
C$_6$H$_5$ 82(-)

(29)



(30)

L = C_5H_5 when M = Co, Rh

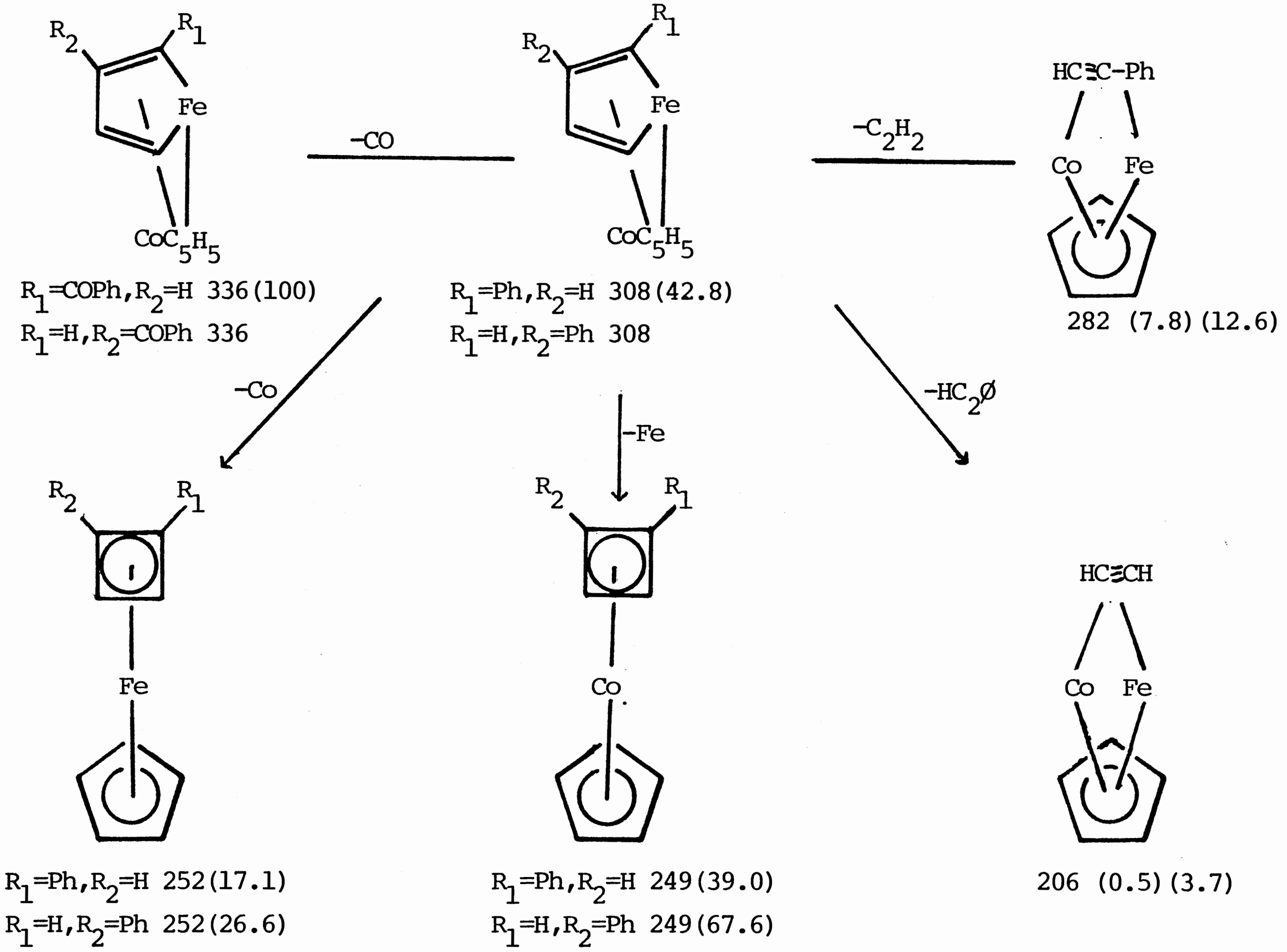
No Ligand when M = Fe

to roughly the same extent. However, the same comparison for the analogous 2-benzoyl complexes (Equation 31) results in the conclusion that 2-benzoylferracobaltocene is not like its analogs nor the model compounds. This complex loses the carbonyl first (after loss of the 3 CO ligands), then the loss of either metal in preference to the loss of C_2H_2. This complex also shows no tendency to lose $HC_2C_6H_5$. Similar observations were found from the analysis of the mass spectrum of the 3-benzoylferracobaltocene[32] (Equation 31).

The reduction of 2-acetyl- and 2-benzoylferracoboltocene with sodium borohydride yielded the corresponding secondary alcohols <u>XVIII</u> and <u>XIX</u>. A comparison was made of the mass spectra of these alcohols (Equation 32) with the main fragmentation pathways of a secondary metallocenecarbonol (Equation 33). The significant differences are: (a) complexes <u>XVIII</u> and <u>XIX</u> have a greater tendency to lose H_2O; (b) they do not readily lose the cyclopentadienyl fragment; and (c) the model complexes show a migration of an OH moiety to the metal while the complexes <u>XVIII</u> and <u>XIX</u> do not.

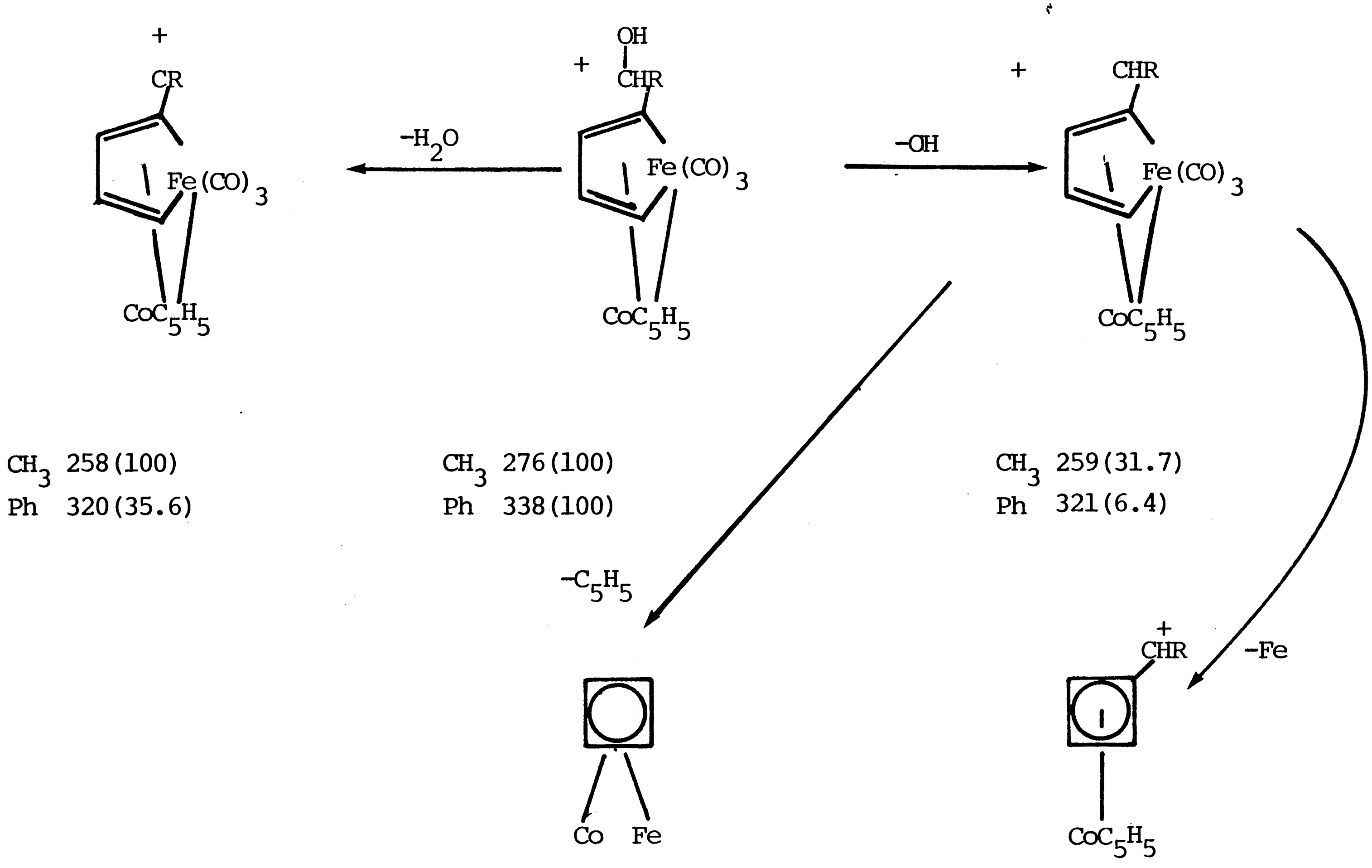
The major fragmentation pathway for complex <u>VIII</u> is shown in Equation 34. After the sequential loss of the 3 CO ligands, which is typical for carbonyl complexes, there is loss of C_2H_2.

Curiously, the mass spectral fragmentation for the diacetyferracobaltocene possesses no favored pathways.



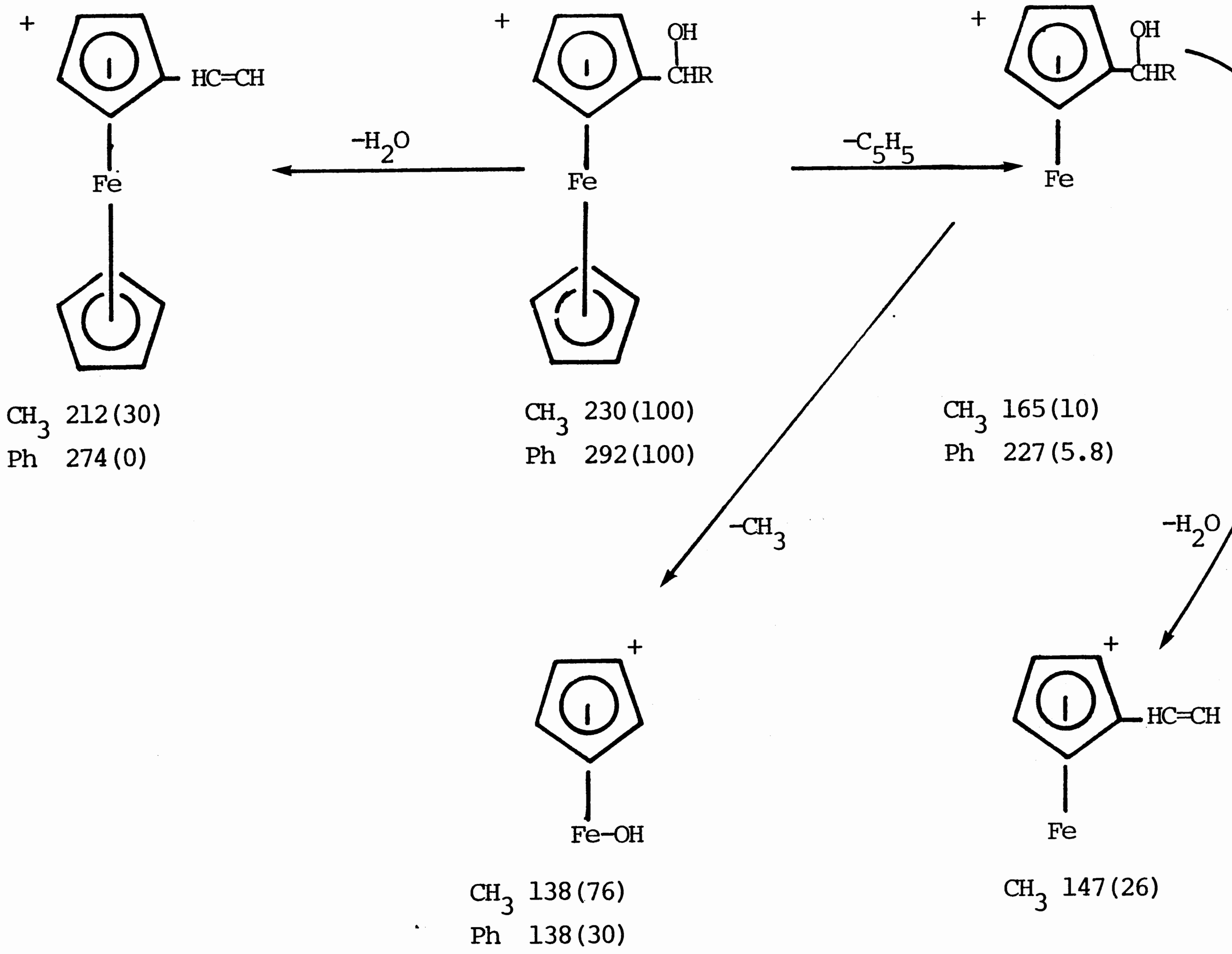
R1
R2
Fe
CoC5H5
R1=COPh,R2=H 336(100)
R1=H,R2=COPh 336
−CO
R1=Ph,R2=H 308(42.8)
R1=H,R2=Ph 308
−C2H2
HC≡C−Ph
Co
Fe
282 (7.8)(12.6)
−Co
−Fe
−HC2Ø
R1=Ph,R2=H 252(17.1)
R1=H,R2=Ph 252(26.6)
R1=Ph,R2=H 249(39.0)
R1=H,R2=Ph 249(67.6)
HC≡CH
206 (0.5)(3.7)

(31)

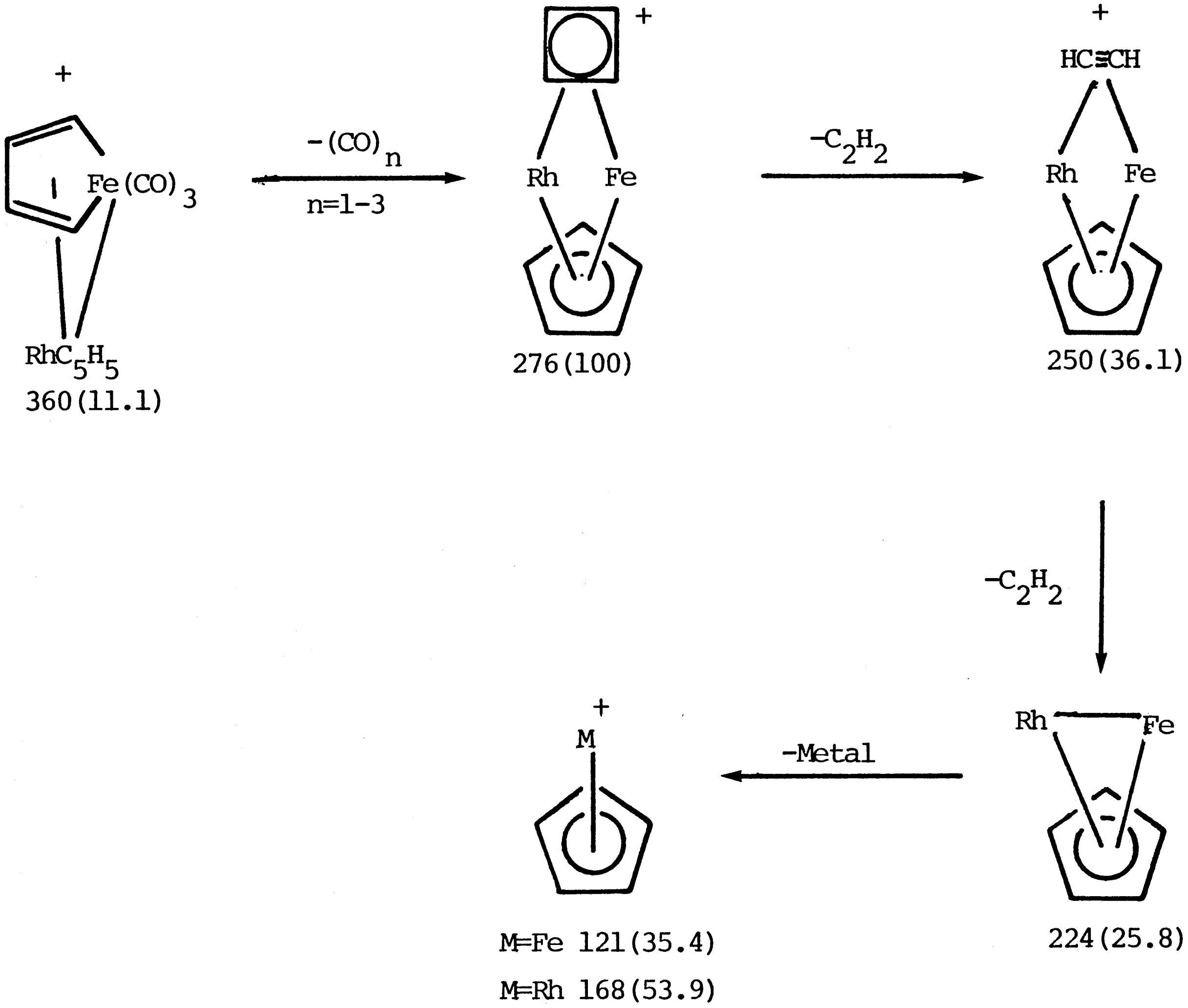


+
CR
Fe(CO)3
CoC5H5
−H2O
OH
+
CHR
Fe(CO)3
CoC5H5
−OH
+
CHR
Fe(CO)3
CoC5H5
CH3 258(100)
Ph 320(35.6)
CH3 276(100)
Ph 338(100)
CH3 259(31.7)
Ph 321(6.4)
−C5H5
+
CHR
−Fe
Co
Fe
CoC5H5

(32)


+
HC=CH
Fe
CH3 212(30)
Ph 274(0)
-H2O
+
OH
CHR
Fe
CH3 230(100)
Ph 292(100)
-C5H5
+
OH
CHR
Fe
CH3 165(10)
Ph 227(5.8)
-CH3
-H2O
+
Fe-OH
CH3 138(76)
Ph 138(30)
+
HC=CH
Fe
CH3 147(26)

(33)



+
Fe(CO)$_3$
RhC$_5$H$_5$
360(11.1)
-(CO)$_n$
n=1-3
+
Rh
Fe
276(100)
-C$_2$H$_2$
+
HC≡CH
Rh
Fe
250(36.1)
-C$_2$H$_2$
Rh
Fe
224(25.8)
-Metal
+
M
M=Fe 121(35.4)
M=Rh 168(53.9)

(34)

CHAPTER IV

EXPERIMENTAL

Preparation and Reactions

Experimental Conditions and Instrumentation

Solvents were reagent grade and were degassed by purging with dried nitrogen for fifteen minutes. Nitrogen was dried by passage through a drying tube containing anhydrous calcium sulfate and molecular sieves.

Proton NMR and ^{13}C-NMR spectra were recorded on a Perkin-Elmer 60 MHz R24B or a varian XL-100 high resolution NMR spectrometer with tetramethylsilane (TMS) used as an internal standard. Infrared spectra were obtained at ambient temperature using a Perkin-Elmer 681 infrared spectrophotometer. High resolution mass spectra were obtained on a CEC·21-100B Double Focusing Mass Spectrometer.

Yields are reported as: % based upon starting amount of limiting reagent/% based upon recovered amount of limiting reagent. If only one percentage is reported, it is based upon starting material unless otherwise noted.

Cyclopentadiene

Dicyclopentadiene (50 ml) was placed in a 100 ml round bottom flask equipped with a fractional distillation column. Cyclopentadiene

(30 ml) was obtained by distillation of the dimer; the first 5 ml of the distillate was discarded and the next 30 ml was collected in a receiver kept in an ice bath. The vapor temperature was kept around 42°C and not allowed to exceed 45°c. The collected distillate was distilled again, with 20 ml collected. The product was stored in an ice bath until needed.

Cyclopentadienylthallium

Cyclopentadienylthallium was either purchased from Strem Chemical Inc. or prepared by modification of either of two published procedures. In one procedure, a modification of the method of Blanto[48], 50.0 g (0.10 mol) of thallous sulfate was added to a solution of 20 g (0.35 mol) of potassium hydroxide in 40 ml water. The resulting mixture was warmed slightly to solublize undissolved thallous sulfate and was then filtered to remove a yellow solid contaminate. After the filtrate was cooled to room temperature, 10 g (0.15 mol) of twice-distilled cyclopentadiene was added. The bright yellow precipitate which formed was collected by filtration, washed with cold methanol, and air dried. The yield of (cyclopentadiene)thallium was 33 g (81%). Because this material was bright yellow and should have been pale yellow, attempts were made to purify it by sublimation (80°C/0.01 mm). The material collected was still bright yellow, the residue a dark brown. Recrystallization from methanol or acetone appeared to cause decomposition. Using another procedure, 10.0 g (0.16 mol) of twice-distilled cyclopentadiene dissolved in 150 ml of hexane was treated with 20 g (0.08 mol) of thallous ethoxide (Aldrich Chemical). Cyclopentadienylthallium, as a pale precipitate

(18.4 g, 85%), was formed. The precipitate was collected by filtration, washed with cold methanol and air dried. This material was sublimed at 80°C/0.01 mm immediately before use.

Dichlorotetracarbonyldirhodium (Rhodium Carbonyl Chloride)

Dichlorotetracarbonyldirhodium (rhodium carbonyl chloride) was either purchased from Strem Chemicals Inc. or prepared by a modification of the method of McCleverty and Wilkinson[49]. An apparatus similar to that described was charged with 15.0 g (0.057 mol) of rhodium (*III*) chloride trihydrate. Carbon monoxide was passed slowly through the system while the sample was heated in an oil bath maintained at 100°C. During the reaction, the orange dichlorotetracarbonyldirhodium sublimed about halfway up the reaction tube. After five hours the apparatus was cooled to room temperature, and the orange-red crystals were collected by scraping the vessel, with the last traces of the desired compound washed out with dry benzene. This procedure yielded 11.3 g (96%). Both the purchased and prepared materials were purified by sublimation (60°C/0.01 mm).

Dicarbonyl-Π-(Cyclopentadienyl)dicarbonylrhodium

A modification of the method of Dickson and Tailly[50] was followed. Freshly sublimed dicarbonylchlororhodium dimer (0.55 g, 2.8 mmol) and (1.5 g, 5.6 mmol) freshly sublimed cyclopentadienylthallium in 40 ml hexane were heated at reflux under nitrogen for 66 hours. The reaction mixture was filtered under nitrogen while hot. As the solution cooled, a dark brown precipitate was formed in the dark red solution. This material was removed by filtration and subsequent examination of its IR spectrum (CS_2) revealed no carbonyl peaks. Removal of solvent from the red solution yielded a red solid. The material sought is a red oil. The red solid was extracted with pentane. Removal of pentane in vacuo yielded a small amount of red oil. Due to the formation of the brown precipitate and the very low yield the preparation was again attempted with several modifications. In the previous attempt, the cyclopentadienylthallium used was the bright yellow material prepared using the method of Neswayner and Blanto[48]. This time, cyclopentadienylthallium prepared from thallous ethoxide was used. Additionally, only 35 ml of hexane and a reflux time of 16 hours was used. The sample was cooled before filtration under nitrogen. No precipitate formed. Removal of solvent yielded 0.15 g (78%) of the orange-red oil, (cyclopentadienyl)-dicarbonylrhodium. The ^{1}H-NMR spectrum exhibited a sharp single cyclopentadienyl resonance at δ5.35 in hexane [lit. δ5.46 ($CDCl_3$)][50].

[Tricarbonyl(ferracyclopentadiene)]-η^5-cyclopentadienylrhodium, (Ferrarhodocene) (VIII)

Method A. A solution of freshly prepared (cyclopentadienyl) dicarbonylrhodium (0.55 g, 2.4 mmol) and (cyclobutadiene)tricarbonyliron (0.40 g, 2.1 mmol) in 25 ml of n-octane was heated under nitrogen at reflux for 24 hr. The black solution was filtered through Celite, and the insoluble material and Celite were washed with Skelly B and ether. The light solvents were removed under reduced pressure leaving a dark yellow solution. Resolution into components was accomplished by column chromatography using deactivated alumina.

The unchanged starting materials were removed as a light yellow band by Skelly B. A second yellow band was removed by Skelly B. Removal of solvent under reduced pressure from this second fraction yielded 19 mg (2.4%) of complex VIII, a yellow solid, mp 69.5-71.5°C; IR (Skelly B) 2035(vs), 1965(vs) cm^{-1}; ^{1}H-NMR (CS_2) δ 5.30(5,s,C_5H_5), 6.2(2,m,H_2+H_3, J_{H2-H1} = 4.5, J_{H3-H1} = 2.2, J_{H2-H3} = 2.1, J_{H2-H4} = 2.2, J_{H2-H5} = 1.2, J_{H3-H4} = 4.5, J_{H3-H5} = 1.2 Hz), 7.1(2,H_1=H_4, "dd",J_{H1-H2} = 4.5, J_{H1-H3} = 2.2, J_{H1-H4} = 0, J_{H1-H5} = 0, J_{H4-H2} = 2.2, J_{H3-H4} = 4.5, J_{H4-H5} = 0 Hz); ^{13}C-NMR (CS_2) 82.9(J_{C-H} = 5.8 Hz, C_5H_5), 98.7($J_{C2(3)-H}$ = 162, $J_{C2(3)-Rh}$ = 5.8 Hz), 211.9(CO): high resolution mass spectrum, m/e 359.8953 (calculated 359.8944); mass spectrum (relative intensity)(assignment), m/e 360(11.1)(M^+), 332 (20.5)(M^+-CO), 304(27.4)(M^+-2CO), 276(100)(M^+-3CO), 250(36.5)(M^+-3CO,-C_2H_2), 224(25.8)(M^+-3CO,-2C_2H_2), 220(1.8)(M^+-3CO,-Fe), 184(10.5) (M^+-3CO,-C_2H_5), 168(53.5)(M^+-3CO,-2C_2H_5,Fe), 159(7.8)(M^+-3CO,-2C_2H_2, -C_5H_5), 142(5.2)(M^+-3CO,-3C_2H_5,-Fe).

Method B. Ferrole (III), (0.807 g, 2.4 mmol) and (cyclopentadienyl)dicarbonylrhodium (0.545 g, 2.43 mmol) in 2 ml of degassed n-octane were stirred under N_2 at 136°C for eight hours. The resulting dark black mixture was filtered through Celite. The reaction flask and the Celite cake both were washed with pentane and ether. The light solvents of the combined filtrates were removed under low pressure leaving a dark yellow solution. Resolution into components was accomplished by column chromotography using deactivated alumina. Unchanged starting material (0.86 g) was removed as a bright yellow band by Skelly B. The composition of this band was calculated, using ^{1}H-NMR data, to be 0.15 g of cyclopentadienyldicarbonyl rhodium and 0.72 g of ferrole. A second yellow band was removed by Skelly B. Removal of solvent under reduced pressure yielded 67.5 mg (8.8%/77.5%) of complex VIII. The melting point and ^{1}H-NMR and ^{13}C spectra are identical to those obtained for complex VII in Method A.

Sym- and Unsym-Tricarbonyl[(ferrabenzocyclopentadiene)]-η^5-cyclopentadienylrhodium (sym- and unsym-benzoferrarhodocene) (IX and X)

A solution of 0.12 g (0.5 mmol) of (benzocyclobutadiene)tricarbonyliron and 0.10 g (0.05 mmol) of (cyclopentadienyl)dicarbonylrhodium in n-octane contained in a 3-neck flask equipped with gas inlet, outlet adapters and a reflux condenser, was heated at reflux for 15 hours. Resolution into components was accomplished by column chromotography using a 1 X 30 cm column of deactivated alumina. Unchanged starting material was removed by elution with Skelly B. A yellow band was removed by benzene.

This yellow band was tentatively identified by high resolution mass spectroscopy as a mixture of sym- and unsym-benzoferrarhodocene (IX and X), high resolution mass spectrum, m/e 409.9103 (calculated 409.9096); mass spectrum (relative intensity)(assignment), m/e 410(13.2)(M^+), 382(16.9)(M^+-CO), 354(21.1)(M^+-2CO), 326(100)(M^+-3CO), 300(10.6)(M^+-3CO,-C_2H_2), 244(10.9)(M^+-3CO,-C_2H_2,-Fe,-C_6H_4), 121 (1.4)(M^+-3CO,-Rh,-C_8H_6). Neither separation of the isomers using column chromatography nor recrystillation from pentane at -78°C was successful.

Dicarbonyl(pentane-2,4-dionato)rhodium

The method of Varshavskii and Cherkasova[51] was used. To 20 ml of dimethylformaniline in a 50-ml Erlenmeyer flask was added 4 ml of acetylacetone and 1.0 g rhodium chloride trihydrate. When the flask was covered with a watch glass and the solution was boiled for 30 minutes, the dark red solution turned an orange-yellow. After being cooled to room temperature, the solution was diluted with twice its volume of water to give a large amount of a crimson precipitate, which was removed by filtration. The precipitate was washed with ethanol and ether. Recrystillization from hexane gave red-green long needles, melting point 151-153°C, lit.[51] mp 153-155°C; IR (petroleum ether) 2083s, 2064w, 2015s, 1987w, (in CS_2) 1376m, 1278m, 1198w, 1110w, 935w, 782m cm^{-1}, these are in good agreement with the literature values [51] (petroleum ether) 2083, 2066, 2015, 1987, and (CS_2) 1374, 1276, 1193, 1126, 933, and 782cm^{-1}.

Attempted Reaction of Dicarbonyl(pentane2,4-dionato)rhodium, ("$Rh(CO)_2Acac$") with Ferrole (III)

A solution of 0.059 g (0.18 mmol) ferrole (III), and 0.089 g (0.35 mmol) or $Rh(CO)_2Acac$ in 20 ml of n-octane was heated at reflux for five hours. ^1H-NMR and IR spectra indicated that no discernible reaction had taken place.

A solution of 0.059 g (0.18 mmol) of ferrole (III), and 0.043 g (0.17 mmol) of $Rh(CO)_2Acac$ in 20 ml of benzene was heated at reflux for five hours. The ^{1}H-NMR and IR spectra of the crude reaction material were essentially identical to those of the initial materials.

A third reaction was run using similar amounts of reactants but using ethyl cyclohexane at reflux (135°C). At the end of the five-hour reaction period, the ^{1}H-NMR spectrum of the crude reaction solution contained only resonance signals for ferrole. Column chromatography on deactivated alumina yielded only unchanged ferrole.

Attempted Reaction of Dicarbonyl(pentane-2,4-dionato)rhodium "Rh(CO)$_2$Acac" with (Cyclobutadiene)tricarbonyliron

To a solution of 0.10 g (2.35 mmol) of Rh(CO)$_2$Acac in 7 ml of toluene was added 0.07 g (0.36 mmol) of (cyclobutadiene)tricarbonyliron. The resulting solution was heated at reflux (120°C for eight hours. The ^{1}H-NMR and IR spectra of the reaction mixture indicated that no reaction had taken place. Column chromatography on deactivated alumina yielded only unchanged (cyclobutadiene)tricarbonyliron.

Acylation of Tricarbonyl(ferracyclopentadiene)-η^5-cyclopentadienylrhodium [Ferrarhodocene (Complex VIII)]

In a 3-neck flask, equipped with gas inlet and outlet adapters and a rubber septum, containing 3 ml of carbon disulfide, was added 0.019 g (1.4 mmol) of aluminum chloride. This mixture was kept under nitrogen and cooled in an ice bath. After fifteen minutes 0.012 g (1.4 mmol) of acetyl chloride in 2 ml of carbon disulfide was added dropwise from a syringe over a 30 minute period. The resulting suspension of the acylium complex was kept under nitrogen and stirred at 0°C for fifteen minutes. Then 0.043 (1.2 mmol) of ferrarhodocene, (VIII), in 3 ml of carbon disulfide was added dropwise by syringe over a fifteen minute period. The resulting mixture was allowed to come to room temperature and was then stirred for an additional four hours. At the end of the reaction time, the dark yellow mixture was poured into a 250 ml-separatory funnel containing about one hundred grams of crushed ice and 20 ml of methylene chloride. The reaction flask was washed with about twenty grams of ice and 20 ml of methylene chloride. These washings were added to the separatory funnel. After the contents were shaken, the organic layer was removed and saved. The aqueous layer was extracted three times with 40 ml portions of methylene chloride. The combined organic extracts were washed three times with 100 ml of water and dried over anhydrous magnesium sulfate. After removal of solvent under reduced pressure, the residue was chromotographed over deactivated alumina. The sample was introduced onto a 1 X 30 cm column using Skelly B. Elution with Skelly B yielded one band leaving one yellow band at the top of the column. This second band was removed by methylene chloride.

After removal of solvent under reduced pressure, the first band (Skelly B) yielded 0.0350 g of complex VIII, i.e., unchanged starting material, as confirmed by spectral examination.

The second band yielded 0.005 g (11%/59%) of a yellow solid, 2-acetylferrarhodocene, (XVI): mp 85-87°C; IR (CS_2) 2035(vs), 1970(vs), 1960(vs), 1678(w) cm^{-1}; ^1H-NMR (CS_2) δ 2.2(3,s,CH_3), 5.42(5,s,C_5H_5), 5.85(2,m,H_2&H_3), 7.5(1,m,H_4); high resolution mass spectrum, m/e 401.9111 (calculated 401.9052); mass spectrum (relative intensity) (assignments), m/e 402 (8.8)(M^+), 374(8.2)(M^+-CO), 346(39.4)(M^+-2CO), 318(100)(M^+-3CO), 264(11.2)(M^+-3CO,-C_2H_2-CO), 262(5.3)(M^+-3CO,-Fe), 234(8.8)(M^+-3CO,-Fe,-CO), 259(31.2)(M^+-3CO,-HC_2COCH_3).

[Tricarbonyl(ferracyclopentadiene)]-η^5-cyclopentadienylcobalt [Ferrarcobaltocene, (V)]

Method A. A solution of 1.0 g (3.0 mmol) of ferrole (III), and 0.625 g (3.5 mmol) of (cyclopentadienyl)dicarbonylcobalt in 10 ml of n-octane was stirred under nitrogen at 136°C for 12 hours. The solution, initially pale red and then darkening to dark red purple, was filtered through Celite with both reaction flask and Celite washed with pentane and ether. The light solvents were removed from the combined filtrates and washings under reduced pressure. The components were separated by column chromatography. The first band, a bright yellow, and the second band, a dark red, are both removed by Skelly B with poor resolution; therefore a 2 X 40 cm column is necessary to achieve good separation. After removal of solvent under reduced pressure, the first band (yellow) yielded 0.486 g of a dark brown oil which consisted solely of unchanged ferrole (III) based on its ^{1}H-NMR spectrum. The second band (red) yielded 0.240 g (32%/62%) of ferracobaltocene (V), a red solid, mp 50-52°C; IR (Skelly B) 2035(vs), 1965(vs) cm^{-1}; ^{1}H-NMR (CS_2) δ 4.88(5,s,C_5H_5), 5.88(2,"dd",H_2=H_3, J_{H2-H1} = 5.2, J_{H3-H1} = 2.4, J_{H2-H3} = 2.1, J_{H2-H4} = 2.4, J_{H3-H4} = 5.2 Hz), 7.39(2,"dd",H_1=H_4, J_{H1-H2} = 5.2,

J_{H1-H3} = 2.4, J_{H1-H4} = 0, J_{H4-H2} = 2.4, J_{H4-H3} = 5.2 Hz); ^{13}C-NMR (CS_2) δ 81.1 (J_{C-H} = 180 Hz, C_5H_5), 101.4($J_{C2(3)-H}$ = 167 Hz), 157 ($J_{C1(4)-H}$ = 156 Hz), 206 (CO); high resolution mass spectrum, m/e 315.9185 (calculated 315.9232); mass spectrum (relative intensity) (assignment), m/e 316(19.2)(M^+), 288(18.0)(M^+-CO), 260(26.8)(M^+-2CO), 232(100)(M^+-3CO), 206(31.2)(M^+-3CO,-C_2H_5), 180(31.4)(M^+-3CO,-2C_5H_5), 176(2.5)(M^+-3CO,-Fe), 140(16.0)(M^+-3CO,-C_2H_5), 124(35.9)(M^+-3CO, -2C_2H_5,-Fe), 115(15.1)(M^+-3CO,-3C_2H_5,-Fe).

Method B. Ferrole (III) (0.50 g, 151 mmol) and 1.4 g (7.8 mmol) of (cyclopentadienyl)dicarbonylcobalt in 2 ml of n-octane were stirred under nitrogen at 136°C for eight hours. Use of the work-up and separation scheme from Method A resulted in 0.42 g (88%, based upon starting amount of ferrole) of ferrocobaltocene (V). The melting point and ^1H-NMR spectrum agree with those for complex V made in Method A.

Diiodo(cyclopentadienyl)carbonylcobalt

A modification of the method of King[40] was used. A mixture of 1.0 g (5.6 mmol) of (cyclopentadienyl)dicarbonylcobalt and 1.5 g (5.9 mmol) of iodine in approximately fifteen milliliters of anhydrous diethyl ether was stirred under nitrogen for three days. Gas evolution and the formation of a black precipitate occurred immediately. At the end of the reaction period, the black crystalline precipitate was collected by filtration, washed with diethyl ether and pentane, and dried to give 1.90 g (87%) of diiodo(cyclopentadienyl)carbonylcobalt, IR (CH_2Cl_2) 2040, Lit[40] (KBr) 2045.

Diiodocyclopentadienylcobalt

A modification of the method of Roe and Maitlis[41] was employed. Diiodo(cyclopentadienyl)carbonylcobalt (1.0 g) was stirred under reflux in hexane (50 ml) for one hour. The solution was filtered, and the collected grey-black solid was washed with dichloromethane. The weight of the desired compound after being dried under vacuum was 0.74 g (84%). Since this complex is soluble only in coordinating solvents in which it decomposes, and only elemental analysis is given in the referenced literature: the assumption was made that the correct material was made.

Reaction of Diiodo(cyclopentadienyl)carbonylcobalt with Ferrole (III)

Method A. Diiodo(cyclopentadienyl)carbonylcobalt 0.075 g (0.19 mmol) with 0.061 g (0.19 mmol) of ferrole (III), were added to 10 ml of degassed n-octane contained in a 3-neck flask at room temperature. The resulting mixture was heated at 125°C under nitrogen for nine hours. The course of the reaction was followed by IR spectroscopy, monitoring the absorption peaks at 2078, 2039, 2003, 1989, and 1930 cm^{-1}. For the spectral examination, 0.1 ml of the reaction mixture was diluted with 2 ml of n-octane. The IR spectra did not change over the entire reaction time. When the mixture was not stirred, the liquid phase was light yellow green containing a finely divided black precipitate.

At the end of the reaction time, the solution was filtered through a fine glass disk funnel containing Celite. The reaction flask and Celite pad were washed with methylene chloride. Surprisingly, methylene chloride dissolved the black precipitate. The methylene chloride was removed under reduced pressure leaving a bright yellow solution (octane) and an unidentified black precipitate. This solution was removed by pipet. The precipitate was washed with pentane, the pentane being added to the octane solution. The pentane was removed under reduced pressure. Column chromatography on deactivated alumina yielded 0.02 g of unchanged ferrole (III), identified by its ^{1}H-NMR spectrum. The nature of the black precipitate was not pursued due to time limitation.

Method B. Diiodo(cyclopentadienyl)carbonylcobalt (0.075 g, 0.19 mmol), ferrole (III), (0.061 g, 0.19 mmol), and 0.024 g (0.37 mmol) of zinc dust were added to 10 ml of degassed n-octane contained in a 3-neck flask. The resulting mixture was heated at 125°C for nine hours. The course of the reaction was followed by IR spectroscopy as in Method A. There were no spectral changes during the reaction time. When the reaction mixture was not stirred, a finely divided black precipitate settled to the bottom of the flask and the solution was a light green. When the temperature reached approximately 115°C, the finely divided black precipitate changed to a very coarse black precipitate. After being cooled, the mixture was filtered through Celite. Washing with methylene chloride did not dissolve the precipitate as in Method A. Column chromatography using Skelly B and deactivated alumina yielded one yellow band (0.0344 g) of unchanged ferrole (III), identified by its ^{1}H-NMR spectrum, and a very small amount (2.7 mg) of complex V, also identified by its ^{1}H-NMR spectrum.

Attempted Reaction of Diiodo(cyclopentadienyl) carbonylcobalt with (Cyclobutadiene)tricarbonyliron

Method A. (Cyclobutadiene)tricarbonyliron (0.08 g, 0.42 mmol) and diiodo(cyclopentadienyl)carbonylcobalt (0.168 g, 0.42 mmol) were added to 10 ml of degassed n-octane contained in a 3-neck flask. The resulting mixture under nitrogen was heated at 125°C for five hours. The reaction was followed by IR spectroscopy using samples of 0.1 ml of the reaction mixture diluted with 4 ml of octane. The IR spectra did not change throughout the reaction time. Column chromatography using deactivated alumina and Skelly B yielded only a very small amount of unchanged (cyclobutadiene)tricarbonyliron.

Method B. Used the same amounts and procedure as in Method A but added 0.05 g (0.83 mmol) of zinc dust as one of the starting materials. Column chromatography yielded only unchanged (cyclobutadiene)tricarbonyliron.

Attempted Reaction of Diiodo(Cyclopentadienyl) cobalt with Ferrole

Diiodo(cyclopentadienyl)cobalt (0.10 g, 0.13 mmol) and 0.04 g (0.13 mmol) of ferrole were added to 10 ml of tetrahydrofuran (THF). The resulting solution was heated under nitrogen at reflux for four hours. After removal of THF under reduced pressure, column chromatography yielded only unchanged ferrole.

Reaction of Diiodo(Cyclopentadienyl)cobalt with (Cyclobutadiene)tricarbonyliron

Diiodo(cyclopentadienyl)cobalt (0.1 g, 0.13 mmol) and 0.025 g (0.13 mmol) of (cyclobutadiene)tricarbonyliron were added to 10 ml of THF. The resulting solution was heated under nitrogen at reflux for four hours. After removal of THF under reduced pressure, column chromatography yielded no material eluted by Skelly B, but a very faint unidentified yellow material was removed by methanol. The amount of material collected was too small to permit characterization.

Reaction of Unsym-benzoferrole with (Cyclopentadienyl)dicarbonylcobalt

A solution of 0.079 g (0.2 mmol) of unsym-benzoferrole and 0.054 g (0.3 mmol) of (cyclopentadienyl)dicarbonylcobalt in 10 ml n-octane, contained in a 3-neck 25 ml flask equipped with gas inlet/outlet adapters and a reflux condenser, was heated at reflux under nitrogen for 12 hours. Removal of solvent under reduced pressure yielded 0.103 g of crude product. Resolution into components effected by column chromatography using deactivated alumina and Skelly B as eluant. From the chromatography 0.074 g of unchanged benzoferrole, identified by its ^{1}H-NMR spectrum, and 0.0259 g (34.5%) of a red oil, identified as unsym-[Tricarbonyl(ferrabenzocyclopentadiene)]-η^5-cyclopentadienylcobalt, complex VII on the basis of its NMR spectrum[32]: ^{1}H-NMR (CS_2) δ 4.56(1,s), 6.69(1,d), 6.80-7.16(2,m), 7.23(1,d), 7.70(1,d), and 8.1(1,d).

Acylation of [Tricarbonyl(ferracyclopentadiene)] -η^5-cyclopentadienylcobalt

In CS_2. To 5 ml of degassed carbon disulfide contained in a 3-neck 25 ml flask, equipped with gas inlet/outlet adapters and a rubber septum, was added 0.21 g (1.58 mmol) of aluminum trichloride. This mixture was kept under nitrogen and cooled in an ice bath. With vigorous stirring 0.14 g (1.7 mmol, 1.1 eq) of acetyl chloride in 2 ml of carbon disulfide was added dropwise over a fifteen minute period. The resulting cloudy mixture was stirred for fifteen additional minutes at 0°C. Ferracobaltocene (V) (0.5 g, 1.58 mol) in 2 ml of carbon disulfide was then added dropwise using the same equipment and time period used for the addition of the acetyl chloride. The resulting dark red mixture was allowed to come to room temperature and was stirred for an additional four hours. During the reaction period a dark red tar-like material which had formed on the walls of the reaction flask interferred with proper stirring. At the end of the reaction period, the mixture was poured into a 250 ml separatory funnel containing about one hundred grams of crushed ice and 20 ml of methylene chloride (CH_2Cl_2). The reaction flask was washed with ice (ca. 20 g) and 20 ml of CH_2Cl_2, and the washings were added to the separatory funnel. After the contents of the funnel were shaken, the organic layer was removed and saved. The aqueous layer was extracted three times with 40 ml portions of CH_2Cl_2. The combined organic extracts were extracted three times with 100 ml portions of water and dried over anhydrous magnesium sulfate. After removal of the solvent under reduced pressure, the residue was chromatographed over deactivated alumina. The sample was introduced onto the 1 X 30 cm column using Skelly B and just enough CH_2Cl_2 to bring about dissolution. Elution with Skelly B yielded one dark red band and left another dark red band on the top of the column. Separation of this latter band into two dark red bands was achieved by successive additions of benzene and methylene chloride.

Removal of solvent from the first band (Skelly B) yielded 0.25 g of ferracobaltocene (V), unreacted starting material as revealed by ^{1}H-NMR spectral examination.

Removal of solvent from the second band (benzene) yielded 0.05 g (9%/19%) of 2-acetylferracobaltocene (XIII), as a red solid, mp 82-84°C; IR (CS_2) 2035(vs), 1970(vs,shoulder), 1960(vs), 1673(w) cm^{-1}; ^{1}H-NMR (CS_2) δ 2.16(3,w,CH_3), 5.04(5,s,C_5H_5), 5.70(1,"t",H_3), 5.84(1,"dd",H_2), 7.38(1,"dd",H_4; ^{13}C-NMR (CS_2) δ 29.8(CH_3), 82.4 (C_5H_5), 96.9(C_2), 159.2(C_4), 173.2(C_1), 207(C=O); high resolution mass spectrum, m/e 357.9541 (calculated 357.9334); mass spectrum (relative intensity)(assignment), m/e 358(6.6)(M^+), 330(18.0)(M^+-CO), 302(29.4)(M^+-2CO), 274(100)(M^+-3CO), 248(8.1)(M^+-3CO,-C_2H_2), 220 (18.1)(M^+-3CO,-C_2H_2-CO), 218(11.2)(M^+-3CO,-Fe), 190(5.9)(M^+-3CO), 206(6.6)(M^+-3CO,-HC_2COCH_3), 205(41.6)(M^+-3CO,-HC_2OCH_3,-H).

Removal of solvent from the third band (methylene chloride) yielded 0.04 g (6%/11%) of diacetyferracobaltocene (XIV), a red solid, mp 114.5-116°C; IR (CS_2) 2040(vs), 1980(vs), 1965(vs), 1675(w); ^{1}H-NMR (CS_2) δ 2.18(6,s,CH_3), 5.18(5,s,C_5H_5), 5.68(2,s,H_2H_3); ^{13}C-NMR (CS_2) δ 28.3(CH_3), 83.4(C_5H_5), 996.6($C_{2(3)}$), 173.3($C_{1(4)}$), 207.8 and

211.9(CO); high resolution mass spectrum, m/e 399.9507 (calculated 399.9444); mass spectrum (relative intensity)(assignment), m/e 400(4.4)(M^+), 372(7.8)(M^+-CO), 344(0.3)(M^+-2CO), 316(100)(M^+-3CO), 248(4.3)(M^+-3CO,-HC_2COCH_3),247(5.6)(M^+-3CO,=HC_2COCH_3,-H), 260(6.5)(M^+-3CO,-Fe), 232(3.5)(M^+-4CO,-Fe); 204(2.3)(M^+-5CO,-Fe).

In CH_2Cl_2. To 2.5 ml of degassed methylene chloride was added 0.42 g (3.2 mmol) of aluminum trichloride. This mixture was kept under nitrogen and cooled to 0°C. With vigorous stirring 0.25 g (3.2 mmol) of acetyl chloride in 1 ml of methylene chloride was added dropwise over a three minute period. The resulting clear solution was stirred for an additional fifteen minutes at 0°C. Then 0.2 g (0.63 mmol) of ferracobaltocene (V) in 1 ml of solvent was added dropwise over a ten minute period. This dark red mixture was allowed to come to room temperature and to react for a total of three hours.

At the end of the reaction period, the mixture was poured into a 250 ml separatory funnel containing crushed ice (ca. 100 g) and 20 ml of CH_2Cl_2. The reaction flask was washed with ice (ca. 20 g) and 20 ml of methylene chloride, and the washings were added to the separatory funnel. After the contents were shaken, the organic layer was removed and saved. The aqueous layer was extracted with three 40 ml portions of methylene chloride. The combined organic extracts were extracted with three 100 ml portions of water and dried over anhydrous magnesium sulfate. After removal of solvent under reduced pressure, resolution into components was achieved by column chromatography using deactivated alumina. The sample was introduced onto the 1 X 30 cm column using Skelly B and just enough CH_2Cl_2 to bring about dissolution. Elution with Skelly B yielded one dark red band while leaving another dark red band on the top of the column. Resolution of this band into two dark red bands was effected by successive additions of benzene and methylene chloride.

Removal of solvent from the first band (Skelly B) yielded 0.04 g of ferracobaltocene (V); unchanged starting material as identified by its ^{1}H-NMR spectrum.

Removal of solvent from the second band (benzene) yielded 0.11 g (50%/63%) of 2-acetylferracobaltocene (XIII). The melting point and the ^{1}H-NMR and IR spectra agree with those obtained for the corresponding complex produced using CS_2 as solvent.

Removal of solvent from the third band (methylene chloride) yielded 0.04 g of 2,5-diacetylferracobaltocene (XIV). The melting point and the ^{1}H-NMR and IR spectra agree with those obtained for the corresponding complex produced using CS_2 as solvent.

In CH_2Cl_2 with 2,6-Di-tert-butyl Pyridine Added. The same procedure and work-up as in the previous method using methylene chloride as solvent was followed, with the rapid addition of 0.12 g (0.60 mmol) of 2,6-di-tert-butyl pyridine just after the addition of the ferracobaltocene (V), but before the mixture was allowed to come to room temperature. Resolution into components was achieved by column chromatography yielding 0.06 g of unchanged ferrocobaltocene (V), 0.07 g of the 2-acetylferrocobaltocene (XIII), (30%/44%), and 0.0259 g of the 2,5-diacetylferrocobaltocene (XIV), (10%/45%). The melting points and the ^{1}H-NMR and IR spectra agree with those for the corresponding complexes produced using CS_2 as solvent.

In Nitrobenzene. To 10 ml of nitrobenzene at 0°C was added 0.05 g (0.4 mmol) of aluminum trichloride. To this mixture was added dropwise 0.032 g (0.41 mmol) of acetyl chloride in 10 ml of nitrobenzene. The resulting mixture was stirred at 0°C for 30 minutes. At the end of this time, 0.11 g (0.4 mmol) of ferracobaltocene (V) in 10 ml was added dropwise. The resulting red mixture was allowed to come to room temperature and then allowed to react for four more hours. The work-up was identical to that used in acetylation reaction in carbon disulfide. The nitrobenzene was removed by vacuum distillation. Column chromatography yielded only the unchanged starting complex V.

Benzoylation of [Tricarbonyl(ferracyclopentadiene)]-η^5-cyclopentadienylcobalt

In CS_2. To 5 ml of degassed carbon disulfide contained in a 3-neck 25 ml flask, equipped with gas inlet/outlet adapters and a rubber septum, was added 0.21 g (1.58 mmol) of aluminum trichloride. This mixture was kept under nitrogen and cooled in an ice bath. With vigorous stirring a solution of 0.25 g (1.58 mmol) of benzoyl chloride in 2 ml of carbon disulfide was added dropwise over a fifteen minute period. The resulting cloudy mixture was stirred for fifteen additional minutes at 0°C. To this mixture a solution of 0.5 g (1.58 mmol) of ferracobaltocene (V) in 2 ml of CS_2 was added dropwise using the same equipment and time period used for the addition of the benzoyl chloride solution. The resulting dark red mixture was allowed to come to room temperature and was stirred for an additional four hours. At the end of the reaction period, the mixture was poured into a 250 ml separatory funnel containing about one hundred grams of crushed ice and 20 ml of CH_2Cl_2. The reaction flask was washed with ice (ca. 20 g) and 20 ml of CH_2Cl_2, and the washings were added to the separatory funnel. After the contents of the funnel were shaken, the organic layer was removed and saved. The aqueous layer was extracted with three 40 ml portions of CH_2Cl_2. The combined organic extracts were extracted with three 100 ml portions of water and dried over anhydrous magnesium sulfate. After removal of solvent under reduced pressure, resolution into components was effected by column chromatography using deactivated alumina. The sample was introduced onto the 1 X 30 cm column using Skelly B. Skelly B eluted one dark red band and left another dark red band at the top of the column. The latter band was eluted with benzene, leaving a light purple material which was eluted with methylene chloride.

Removal of solvent from the first band (Skelly B) yielded 0.19 g of ferracobaltocene (V); (unchanged starting material identified by its ^{1}H-NMR spectrum).

Removal of solvent from the second band (benzene) yielded 0.08 (11%/31%) of a red solid, 2-benzoylferracobaltocene (XVII); mp 130-131°C; IR (CS_2) 2035(vs), 1972(vs), 1960(vs), 1645(w)cm^{-1}; ^{1}H-NMR (CS_2) δ 514(5,s,C_5H_5), 5.75(1,"t",H_3), 5.95(1,dd,H_2), 7.24 and 7.67 (5,m,ArH), 7.45(1,dd,H_4); high resolution mass spectrum, m/e 419.9404 (419.9495 calculated); mass spectrum (relative intensity) (assignment), m/e 420(16.7)(M^+), 392(13.6)(M^+-CO), 364(31.4)(M^+-2CO), 336(100) (M^+-3CO), 308(42.8)(M^+-3CO,-CO), 282(7.8)(M^+-4CO,-C_2H_2), 252(17.1)

(M^+-4CO,-Fe), 249(39.0)(M^+-5CO), 128(2.7)(M^+-4CO,-Fe,COC_5H_5).

Removal of solvent from the third band (methylene chloride) yielded 0.9 mg of a brown-purple oil; IR (CS_2): 2070(m), 2060(m), 2040(m), 2005(m,shoulder), 2000(s), 1990(m,shoulder), 1795(s), 1773 (s)cm^{-1}; ^{1}H-NMR ($CDCl_3$) δ; 7.2-7.7(m), 7.9-8.2(m).

[Tricarbonyl(2-α-hydroxymethyl ferracyclopentadiene)]-η^5-cyclopentadienylcobalt (XVIII)

2-Acelytferracobaltocene (XIII), (50 mg, 0.14 mmol) was dissolved in 10 ml of degassed methanol contained in a 3-neck 25 ml flask. The resulting solution was kept under nitrogen and cooled in an ice bath. After 0.3 g (8 mmol) of sodium borohydride (98%, crushed pellets) was added, the solution was stirred for fifteen minutes at 0°C and then for three hours at room temperature. The resulting dark red solution was added to 50 g of ice in a 250 ml separatory funnel. The reaction flask was washed with methylene chloride and ice to remove deposits, and then the washings were added to the separatory funnel. After the removal of the organic layer, the aqueous layer was extracted with three 40 ml portions of methylene chloride. The combined organic washings were washed three times with 40 ml portions of water. The organic layer was then dried over anhydrous magnesium sulfate. The removal of solvent by reduced pressure yielded 49 mg (97%) of the desired complex XVIII as a red oil; IR (CS_2) 2016(vs), 1965(vs) cm^{-1}; ^{1}H-NMR (CS_2) δ 1.23(3,d,CH_3), 1.75(1,s,OH), 4.35 (1,q,$CHCH_3$), 4.92(5,s,C_5H_5), 5.6(1,t,H_3), 5.8(1,"dd",H_2), 7.3(1,"dd", H_4); ^{1}H-NMR (CS_2 + D_2O) δ 1.23(3,d,CH_3), 4.35(1,q,$CHCH_3$), 4.92 (5,s,C_5H_5), 5.6(1,t,H_3), 5.8(1,"dd",H_2), 7.3(1,"dd",H_4); high resolution mass spectrum, m/e 359.9495 (359.9534 calculated); mass spectrum (relative intensity)(assignment), m/e 360(2.5)(M^+), 332 (54.7)(M^+-CO), 304(36.3)(M^+-2CO), 276(100)(M^+-3CO), 258(167)(M^+-3CO, -H_2O), 232(30.9)(M^+-3CO,-H_2O,-C_2H_2), 259(31.7)(M^+-3CO,-OH), 203 (170.5)(M^+-3CO,-OH,-Fe), 150(38.8)($C_2H_2CoCp^+$), 141(7.9)($C_2H_2CoFe^+$), 124(218.7)($MCpCo^+$), 115(27.3)($CoFe^+$), 78(23.0)($C_6H_6{}^+$).

[Tricarbonyl(2-α-hydroxybenzoylferracyclopentadiene)]-η^5-cyclopentadienylcobalt (XIX)

2-Benzoylferracobaltocene (XVII), (38 mg, 0.09 mmol), was dissolved in 10 ml of degassed methanol contained in a 3-neck 25 ml flask. The resulting solution was kept under nitrogen and cooled to 0°C. After 0.3 g (8 mmol) of sodium borohydride (98%, crushed pellets) was added, the solution was stirred for fifteen minutes at 0°C and then for three hours at room temperature. The resulting dark red solution was added to 50 g of ice in a 250 ml separatory funnel. The reaction flask was washed with methylene chloride and ice to remove deposits and then the washings were added to the separatory funnel. After the removal of the organic layer, the aqueous layer was extracted with three 40 ml portions of methylene chloride. The combined organic washings were washed three times with 40 ml portions of water. The organic layer was then dried over anhydrous magnesium sulfate. The removal of solvent by reduced pressure yielded 35 mg (94%) of the desired complex XIX as a red oil: IR (CS_2) 2030(vs), 1960(vs) cm^{-1}; ^1H-NMR (CS_2) δ 1.16(1,s,OH), 4.96(5,s,C_5H_5), 5.3(1,s,CHC_6H_5), 5.64(1,"t",H_3), 5.81(1,dd,H_2), 7.04-7.4(7,m,H_4 and ArH); high resolution mass spectrum, m/e 421.9818 (421.9651 calculated); mass spectrum (relative intensity)(assignment), m/e 422(4.9)(M^+), 394(9.1)(M^+-CO), 366(10.0)(M^+-2CO), 338(100)(M^+-3CO), 320(35.6)(M^+-3CO,-H_2O)(M^+-3CO,-H_2O,-C_2H_2), 321(M^+-3CO,-OH), 265(251.6)(M^+-3CO,-OH,-Fe), 150(16.2)($C_2H_2CoCp^{+}$), 141(1.2)($C_2H_2CoFe^+$), 124 (101.5)($CpCo^+$), 115(9.3)($CoFe^+$), 78(12.5)($C_6H_6^+$).

Formylation of Ferracobaltocene (V)

To a mixture of 0.12 ml (9.48 mmol) of phosphorus oxychloride and 0.08 ml (0.48 mmol) of N-methylformanilide was added 0.1 g (0.32 mmol) ferracobaltocene (V). The resulting mixture was stirred at room temperature under nitrogen for 24 hours. The red reaction mixture was mixed with 25 g of ice. The resulting solution was extracted three times with 25 ml of ether. The combined organic layers were washed twice with 25 ml of 5% hydrochloric acid in water. The acidic washes were extracted twice with 25 ml of ether. The combined ether layers were dried with anhydrous magnesium sulfate. Removal of solvent under reduced pressure yielded approximately 0.1 g of a dark brown solid: ^{1}H-NMR (acetone d_6) δ; 2.0(s), 3.1(s), 7.2(s), 8.35(s). The ^{1}H-NMR spectrum was inconclusive in determining if formylation had occurred.

Triiron dodecacarbonyl

The method of McFarlane and Wilkinson[52] was used without change.

Ferrole (III)

A modification of the method of Dettlaf and Weiss[24] was employed.

To a 3-neck 500 ml flask equipped with gas inlet/outlet adapters and a Soxhlet extractor, was added 10 ml (120 mmol) of thiophene and 400 ml of n-heptane. The Soxhlet thimble was charged with 24 g (48 mmol) of triiron dodecacarbonyl. The contents of the flask were heated to reflux and maintained at reflux until the $Fe_3(CO)_{12}$ was dissolved (three days). At the end of the reaction time, the solution was filtered through Celite followed by washing of both the flask and Celite with pentane and ether. Removal of solvent yielded a yellow precipitate. Column chromatography on alumina using Skelly B yielded 2.0 g (13%) of a bright yellow solid. The ^1H-NMR spectrum in CS_2 gave resonance lines at δ 6.2 and δ 6.85 (lit.[24] δ 6.2 and δ 6.8).

Attempted Reaction of $Fe_3(CO)_{12}$ and 2,4-Diphenylthiophene

The identical method for the preparation of ferrole was used, but with the substitution of 2,4-diphenylthiophene (15 g, 64 mmol) for thiophene. After work-up, ^1H-NMR spectral and column chromatography analysis indicated that the expected diphenylferrole was not made.

Acylation of [Tricarbonyl(ferracyclopentadiene)]-η^5-cyclopentadienyliron (III)

Method A. To 10 ml of degassed carbon disulfide contained in a 3-neck 25 ml flask, equipped with gas inlet/outlet adapters and a rubber septum, was added 0.2 g (1.5 mmol) of aluminum trichloride. This mixture was kept under nitrogen and cooled in an ice bath. Acetyl chloride (0.13 g, 1.65 mmol) in 5 ml of carbon disulfide was added dropwise over a fifteen minute period with the use of a syringe. The resulting mixture was stirred an additional fifteen minutes. Ferrole (III) (0.5 g, 1.5 mmol) in 5 ml of carbon disulfide was added dropwise over a fifteen minute period. The resulting dark brown, cloudy mixture was allowed to come to room temperature and was stirred for an additional two hours.

At the end of the reaction period, the mixture was poured into a 250 ml separatory funnel containing about one hundred grams of crushed ice and 20 ml methylene chloride. The reaction flask was washed with ice (ca. 20 g) and 20 ml of methylene chloride; the washings were added to the separatory funnel. After the contents of the flask were shaken, the organic layer was removed and saved. The aqueous layer was extracted three times with 40 ml portions of methylene chloride. The combined organic extracts were extracted three times with 100 ml portions of water and dried over anhydrous magnesium sulfate. After removal of solvent under reduced pressure, the residue was chromatographed over deactivated alumina. The sample was introduced onto the 1 X 30 cm column using Skelly B. Elution with Skelly B yielded one light yellow band and left another darker yellow band on the top of the column. Removal of this band was accomplished using methylene chloride.

Removal of solvent from the first band (Skelly B) yielded 0.28 g of ferrole (III); unchanged starting material as revealed by its ^{1}H-NMR spectrum.

Removal of solvent from the second band (methylene chloride) yielded 0.06 g (11%/19%) of 2-acetylferrole (XV), a yellow solid, which is unstable in solution, mp 70-72°C; IR (CS_2) 2155(vs), 2080(vs), 2040(vs), 2010(vs), 1995(vs), 1680(w) cm^{-1}; ^{1}H-NMR (CS^2) δ 2.22(3,s, CH_3), 6.16(2,m,H_2 & H_3), 5.76(1,dd,H_4); high resolution mass spectrum, m/e 373.8895 (calculated 373.8812); mass spectrum, (relative intensity) (assignment), m/e 374(6.7)(M^+), 346(20.0)(M^+-CO), 318(29.2)(M^+-2CO), 290(27.2)(M^+-3CO), 262(27.9)(M^+-4CO), 234(83.2)(M^+-5CO), 206(100) (M^+-6CO), 180(9.8)(M^+-6CO,-C_2H_2), 152(17.0)(M^+-7CO,-C_2H_2), 150(8.6) (M^+-6CO,-HC_2COCH_3), 137(42.0)(M^+-6CO,-HC_2COCH_3,-H).

Method B. The same procedure and work-up was used as in Method A with the following changes: the initial amount of carbon disulfide was reduced to 3 ml; 0.84 g (7.1 mmol) of acetyl chloride, 1.40 g (7.0 mmol) aluminum trichloride and 0.5 g (1.5 mmol) of ferrole (III) were used. The amount of diluent used for the addition of acetyl chloride and ferrole (III) was reduced to 2 ml. Resolution into components was accomplished by column chromatography over deactivated alumina giving the following results: one band was eluted by Skelly B, one band by benzene and two bands by methylene chloride.

Removal of solvent from the first band (Skelly B) yielded 0.19 g of unchanged ferrole (III) the second band (benzene) yielded 0.02 g (4%/11%) of 2-acetylferrole (XV). The melting point and the ^{1}H-NMR and IR spectra agree with those obtained in Method A. The third band (first band brought down by methylene chloride) yielded 0.03 g of a yellow compound. The ^{1}H-NMR and IR spectra did not conclusively reveal the structures of this compound. The ^{1}H-NMR spectra contains many unassignable resonance lines. The IR (CS_2) spectrum contains absorptions at 2063(s), 2000(broad), 1765(s), and 1680(s) cm^{-1}.

The second band eluted by methylene chloride yielded 0.01 g of a yellow compound. Its ^1H-NMR spectrum also contains many resonance lines. The IR (CS_2) spectrum contains absorptions at 2070(s), 2005(s), and 1680(s) cm^{-1}. Although the high resolution mass spectrum contains many peaks that appear to be superfluous, there is a hint as to the structure of one of these unknowns. The following fragmentation pattern indicates that the second compound is possibly a diacetylferrole. Note that those peaks corresponding to M^+ minus 6 CO's are missing due either to high sample inlet temperature or the use of the wrong scan. Mass spectrum, (relative intensity) (assignment) m/e; 192(5.3)(M^+,-Fe,-6CO), 166(14.3)(M^+,-Fe,-6CO,-C_2H_2), 138(17.3)(M^+,-Fe,-7CO,-C_2H_2), 110(7.6)(M^+,-Fe,-8CO,-C_2H_2), 124(1.2) (M^+,-Fe,-6CO,-HC_2COCH_3).

In CH_2Cl_2. To 2.5 ml of degassed methylene chloride was added 0.40 g (3.0 mmol) of aluminum trichloride. The white suspension was kept under nitrogen and cooled to 0°C. Acetyl chloride (0.24 g, 3.1 mmol) in 1 ml of methylene chloride was added dropwise over a three minute period. The resulting clear solution was stirred for an additional fifteen minutes at 0°C. Ferrole (III) (0.2 g, 0.6 mmol) in 1 ml of solvent was then added dropwise over a ten minute period. The dark brown mixture was allowed to come to room temperature and to react for a total of three hours. At the end of the reaction period, the mixture was poured into a 250 ml separatory funnel containing crushed ice (ca. 100 g) and 20 ml of methylene chloride. The reaction flask was washed with ice (ca. 20 g) and 20 ml of methylene chloride, and the washings were added to the separatory funnel. After the contents were shaken, the organic layer was removed and saved. The aqueous layer was extracted three times with 40 ml portions of methylene chloride. The combined organic layer was extracted three times with 100 ml of water and dried over anhydrous magnesium sulfate. After removal of solvent under reduced pressure, resolution into components was achieved by column chromatography using deactivated alumina. The sample was introduced onto the 1 X 30 cm column using Skelly B and just enough methylene chloride to bring about dissolution. Elution with Skelly B yielded one yellow band while leaving another yellow band on the top of the alumina which was removed by benzene.

Removal of solvent from the first band (Skelly B) yielded 0.04 g of unchanged ferrole (III), as identified by its ^{1}H-NMR spectrum.

Removal of solvent from the second band (benzene) yielded 0.02 g (11%/13%) of the 2-acetylferrole (XV). The melting point and ^{1}H-NMR spectrum agree with those obtained for the corresponding complex produced using CS_2 as solvent.

In CH_2Cl_2 with 2,6-Di-tert-butyl Pyridine Added. The same procedure and work-up as in the previous method using methylene chloride as solvent was followed, but with the rapid addition of 0.12 g (0.60 mmol) of 2,6-di-tert-butyl pyridine just after the addition of the ferrole (III), but before the mixture was allowed to come to room temperature. Resolution into components was achieved by column chromatography and yielded 0.05 g of unreacted ferrole (III), as identified by its ^{1}H-NMR spectrum, and 0.04 g (19%/25%) of the 2-acetylferrole (XV). The melting points and ^{1}H-NMR spectrum agree with the corresponding complex produced using CS_2 as solvent.

Benzoylation of [Tricarbonyl(ferracyclopentadiene)]-η^5-cyclopentadienyliron

In CS_2. To 5 ml of degassed carbon disulfide in a 3-neck 25 ml flask, equipped with gas inlet/outlet adapters and a rubber septum, was added 0.21 g (1.58 mmol) of aluminum trichloride. This mixture was kept under nitrogen and cooled to 0°C. With vigorous stirring 0.25 g (1.58 mmol) of benzoyl chloride in 2 ml of carbon disulfide was added dropwise over a fifteen minute period. The resulting cloudy mixture was stirred for fifteen additional minutes at 0°C. To this mixture 0.5 g (1.58 mmol) of ferrole (III) in 2 ml of carbon disulfide was added dropwise. The resulting dark red mixture was allowed to come to room temperature and was stirred for an additional four hours. At the end of the reaction period, the mixture was poured into a 250 ml separatory funnel containing ice (*ca.* 20 g) and 20 ml of methylene chloride. The reaction flask was washed with about twenty grams of ice and 20 ml of methylene chloride, and the washings were added to the separatory funnel. After the contents of the flask were shaken, the organic layer was removed and saved. The aqueous layer was extracted with three portions of 40 ml of methylene chloride. The combined organic extracts were extracted three times with 100 ml portions of water and dried over anhydrous magnesium sulfate. After removal of solvent under reduced pressure, separation of components was achieved by column chromatography using deactivated alumina. The sample was introduced onto the 1 X 30 cm column using Skelly B. One dark yellow band was removed by Skelly B. Removal of solvent yielded only starting ferrole (III).

U. V. data

Weight of sample in g/liter; λ max in nm (absorbance; molar absorptivity).

Ferrole, (III). 0.0204; 196 (2.388; 38,830), 300 (0.2768; 4,500), 404 (0.1592; 2,590).

Ferracobaltocene, (V). 0.0212; 202 (2.634; 45,460), 248 (1,338; 17,260), 338 (0.303; 5,230), 367 (0.394; 6,800), 507 (0.114; 1,970).

Ferrarhodocene, (VIII). 0.0192; 194 (1.816; 34,040), 208 (1,848; 34,640), 293 (0.3710; 6,970), 335 (0.289; 5,420), 434 (0.114; 2,140).

Sym-benzoferrole. 0.0720 g, 197 (2,603; 13,800), 250 (0.687; 3,640), 350 (0.217; 1,150).

Unsym-benzoferrole. 0.0110, 197 (1,477; 51,070), 240 (0.619; 21,400), 330 (0.109; 3,769), 407 (0.099; 3,423), 480 (0.039; 1,350).

BIBLIOGRAPHY

1. Trotman-Dickenson, A. F., Comprehensive Inorganic Chemistry, Vol. 4, Pergamon Press, Oxford, England, 1973, 857.

2. Caldeon, N., paper presented at the XXIIIrd IUPAC Meeting, Boston, Mass., August 1971, paper 559.

3. Schneider, V. and Frohlich, P. K., Ind. and Eng. Chem., 23, 1405 (1931).

4. Banks, R. L. and Bailey, G. C., Ind. and Eng. Chem. (Product Res. and Development) 3, 170 (1964).

5. Calderon, N., Chen, H. Y., Scott, K. W., Tetrahedron Lett., 3327, (1967).

6. Haines, R. J. and Leigh, G. J., J. Chem. Soc. Rev., 4, 155 (1975).

7. Woodward, R. B. and Hoffmann, R., The Conservation of Orbital Symmetry, Verlag Chemie Academic Press, Weinheim, Germany, 1970.

8. Bradshaw, C. P. C., Howman, A. J., Turner, L., J. Catalysis, 7, 269 (1967).

9. Lewands, G. S. and Pettit, R., Tetrahedron Lett., 789, (1971).

10. Katz, T. and Cerefice, S., J. Am. Chem. Soc., 91, 6520 (1969).

11. Eaton, P. E., Cassar, L., Halpern, J., J. Am. Chem. Soc., 92, 3515 (1970).

12. Grubbs, R. H. and Brunch, T. K., J. Am. Chem. Soc., 94, 2538 (1972).

13. Casey, C. B. and Burkhardt, T. J., J. Am. Chem. Soc., 96, 7808 (1974).

14. Pennella, F., Banks, R. L., Bailey, G. C., J. C. S. Chem. Commun., 1548 (1968).

15. Meriwether, L. S., Leot, M. F., Colthup, E. C., Kennerly, G. W., J. Org. Chem., 27, 3930 (1962).

16. Hubel, W. and Braye, E. H., J. Inorg. Nucl. Chem., 10, 250 (1959).

17. Yamazaki, H. and Hagihara, N., J. Organometal. Chem., 7, 22 (1967).

18. Greco, A., Pirinoli, F., Dallasta, F., J. Organometal. Chem., 60, 115 (1973).

19. Chin, H. B. and Bau, R., J. Am. Chem. Soc., 95, 5068 (1973).

20. King, R. B. and Haiduc, I., J. Am. Chem. Soc., 94, 4044 (1972).

21. Davis, R. E., Barnett, B. L., Amiet, R. G., Merk, W., McKennis, J. S., Pettit, R., J. Am. Chem. Soc., 96, 7108 (1974).

22. Hubel, W. and Weiss, E., Chem. and Ind., 703 (1959).

23. Kaesz, H. D., King, R. B., Manuel, T. A., Nichols, L. D., Stone, F. G. A., J. Am. Chem. Soc., 82, 4749 (1960).

24. Dettlaf, G. and Weiss, E., J. Organometal. Chem., 108, 213 (1976).

25. Bruce, R., Moseley, K., Maitlis, P. M., Can. J. Chem., 45, 2011 (1967).

26. Epstein, E. F. and Dahl, L. F., J. Am. Chem. Soc., 92, 502 (1970).

27. Rosenblum, M. and North, B., J. Am. Chem. Soc., 90, 1060 (1968), and Rosenblum, M., North, B., Wells, D., Giering, W. P., J. Am. Chem. Soc., 94, 1239 (1972).

28. Davis, B. L., Barnett, B. L., Amiet, R. G., Merk, W., McKennis, J. S., Pettit, R., J. Am. Chem. Soc., 96, 7108 (1974).

29. Victor, R. and Ben-Shoshan, R., J. C. S. Chem. Commun., 93 (1974).

30. McKennis, J. S., XXIVth Pentasectional American Chemical Society Meeting, Tulsa, Oklahoma, Spring, 1978.

31. Yamazaki, R., private communication.

32. Radnia, P., Doctor of Philosophy Thesis, Oklahoma State University, July, 1981.

33. Davidson, J. L., J. C. S. Chem. Commun., 749 (1980).

34. Hoffmann, R. and Thorn, D. L., Inorg. Chem., 17, 126 (1978).

35. Mills, O. S. and Redhouse, A. D., J. Chem. Soc., A, 1282 (1968).

36. Diehl, P., Fluck, E., Kosfeld, R., NMR Vol. 5, Springer-Verlag, New York, New York, 1971, 110.

37. Bennett, M. A., Johnson, R. N., Turney, T. W., Inorg. Chem., 15, 107 (1976).

38. Maitlis, P. M. and Games, M. L., Chem. Ind., 1624 (1963).

39. Lee, W. and Brintzinger, H. H., J. Organometal. Chem., 209, 401 (1981).

40. King, R. B., Inorg. Chem., 5, 82 (1966).

41. Roe, D. M. and Maitlis, P. M., J. Chem. Soc., A, 3173 (1971).

42. Chizhevsky, A. A., Koridze, V. I., Bakhmutov, V. I., Kolobova, N. E., J. Organometal. Chem., 206, 361 (1981).

43. McKennis, J. S., unpublished results.

44. Brookhart, M., Whitesides, T. H., Crockett, J. M., Inorg. Chem., 15, 1550 (1976).

45. Stenhager, E., Abrahamsson, S., McLafferty, F. W., Atlas of Mass Spectral Data, Vol. I, Interscience Publisher, New York, New York, 1969.

46. Bowie, J. H., Cooks, R. G., Lawesson, S. O., Nolde, C., J. Chem. Soc., B, 616 (1967).

47. Mandelbaum, A. and Cais, M., Tetrahedon Lett., 3847 (1964), and Egger, H., Monat. Chem., 97, 602 (1966).

48. Nesmayaner, P. and Blunto, F., Organic Chem., Vol. I, 575.

49. McCleverty, J. A. and Wilkinson, G., Inorg. Syn., VIII, 211.

50. Dickson, R. S. and Tailly, G. R., Aust. J. Chem, 23, 1531 (1970).

51. Varshavskii, Y. S. and Cherkasova, T. G., Zh. Neorg. Khem., 12, 899 (1967).

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