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To Lexie and Marla

THE UNIVERSITY OF ALBERTA

SILICON DERIVATIVES OF TRANSITION METALS

BY

© WALTER JETZ

A THESIS

SUBMITTED TO THE FACULTY OF GRADUATE STUDIES

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of

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DEPARTMENT OF CHEMISTRY

EDMONTON, ALBERTA

SPRING, 1970

THE UNIVERSITY OF ALBERTA

FACULTY OF GRADUATE STUDIES

The undersigned hereby certify that they have read, and recommend to the Faculty of Graduate Studies for acceptance, a thesis entitled

"SILICON DERIVATIVES OF TRANSITION METALS"

submitted by WALTER JETZ, in partial fulfilment of the requirements for the degree of Doctor of Philosophy.

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April 20, 1970
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Date

ABSTRACT

The reactions of silanes with transition metal carbonyls have been investigated under various conditions. Several types of silyl derivatives of transition metal carbonyls were prepared. The thermal reactions of $[M(CO)_n]_2$ or $[\pi C_5H_5M(CO)_n]_2$ and $R_{3-n}Cl_nSiH$ gave $R_{3-n}Cl_nSiM(CO)_n$ or $R_{3-n}Cl_nSiM(CO)\pi C_5H_5$ (R = H, CH_3, C_6H_5; M = transition metal). Conformational effects were observed in the infrared spectra of some unsymmetrically substituted silyl derivatives. The thermal reaction of Cl_3SiH with $[\pi C_5H_5Fe(CO)_2]_2$ gave $Cl_3SiFe(CO)_2\pi C_5H_5$, $[\pi C_5H_5Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)\pi C_5H_5]^-$, $[\pi C_5H_5Fe(CO)_3]^+FeCl_4^-$ and $(Cl_3Si)_2HFe(CO)\pi C_5H_5$.

The latter of these $(Cl_3Si)_2HFe(CO)\pi C_5H_5$ was also prepared from $Cl_3SiFe(CO)_2\pi C_5H_5$ and Cl_3SiH under ultraviolet irradiation. This photochemical reaction, which was found to be general, yielded numerous silyl transition metal hydrides. Thus, $Fe(CO)_5$ and Cl_3SiH yielded $Cl_3SiHFe(CO)_4$ with evolution of carbon monoxide. Under more vigorous conditions disubstituted silyl derivatives were obtained (e.g. $(Cl_3Si)_2Fe(CO)_4$).

The behavior of these hydrides as acids has been studied. With amine bases the ammonium salts were formed. Using $(C_2H_5)_3N$ with $Cl_3SiHMn(CO)_2\pi C_5H_5$ in hexane $[(C_2H_5)_3NH]^+$ $[Cl_3SiMn(CO)_2\pi C_5H_5]^-$ was precipitated quantitatively. These anions were employed to displace halide ions from tin

resulting in silyl-tin transition metal derivatives. A reaction of $[(C_2H_5)_3NH]^+[\ Cl_3SiMn(CO)_2\pi C_5H_4CH_3]^-$ and $SnCl_4$ gave $Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$ and $Cl_2Sn[Mn(CO)_2(SiCl_3)\pi C_5H_4CH_3]_2$.

In many instances mass spectrometry, nmr and infrared proved indispensable tools in the determination of molecular composition and assignment of structure.

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CHAPTER I

A Review of Main Group IV* Derivatives of Transition Metal Carbonyls

This brief review is limited to the study of compounds with group IV-transition metal bonds which are a subgroup in main group-transition metal bonding. Over the past decade the interest in this field has grown immensely. Thus the present state of knowledge makes it undesireable to cover the whole field in a brief review. Coverage has therefore been restricted to compounds with bonds between transition metal carbonyls and silicon, germanium, tin and lead. Carbon forms a variety of ligands as will be evident in the following sections and could be treated as a separate topic. Its relation to the present investigation is of indirect interest and therefore it will not be elaborated upon. For lead, the most metallic of the group IV elements, fewer complexes are known than for germanium and tin. Recent research employing silane ligands is rapidly advancing to fill the gaps in our knowledge.

Most work in this field has been done with the carbonyls of manganese and iron. The volume of work tapers off sharply beyond the chromium and cobalt groups. Generally, the carbonyls of the vanadium and nickel groups and their derivatives have low thermal stabilities. A substantial

---

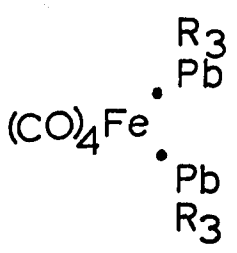
* Group IV shall hereafter refer to main group IV elements.

number of phosphine and cyclopentadienyl stabilized compounds of these elements are, however, known: $(Ph_3P)_2Pt(GePh_3)_2$ [25], $\pi C_3H_5Pd(PPh_3)SnCl_3$ [154], $(Ph_3P)_2Pt(Cl)SnCl_3$ [31], $(Ph_3P)_2Pt(SiCl_3)_2$ [40], $(Ph_3P)_2Pt(Cl)GePh_3$ [84], $Cp_2Ti(Cl)GePh_3$ [59], $Cp_2Zr(Cl)SiPh_3$ [32].

Of the elements of the first transition metal series, chromium, manganese, iron, and cobalt are most abundant. In the second and third transition metal series, molybdenum and tungsten are also readily available. Technetium is not readily available. The investigation of rhenium, ruthenium, osmium, rhodium and iridium has undoubtedly lagged because of their rarity and high price.

Historical Development

The earliest studies involving the synthesis of group IV-transition metal bonds were undertaken by Hein *et al.* In 1942 these workers reported $(R_3Pb)_2Fe(CO)_4$ and $[R_2PbFe(CO)_4]_2$ (R = Ph or cyclohexyl) [94] which were obtained in aqueous or methanol reactions of $Ca[HFe(CO)_4]_2$ and Ph_3PbOH. Although the stoichiometries of these compounds were correctly assigned at that time, their structures and bonding remained obscure. In 1947, Hein and Heuser suggested structures for these compounds which were shown by the representations below [95]:



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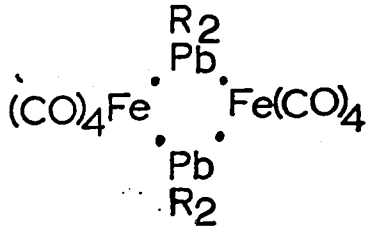
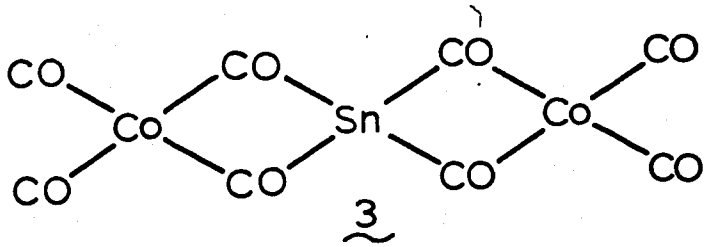


2

The concept of covalent bonding in these complexes at that time was still a matter of uncertainty. In 1942 Heiber and Teller reported $Sn[Co(CO)_4]_2$ [102], synthesized in a high pressure carbon monoxide reaction of a mixture of finely powdered cobalt metal, cobalt halide and tin metal. These authors suggested a structure involving bridging and terminal carbon monoxides, 3.



3

Spectroscopically, this structure can be readily disproved and is no longer accepted. Hieber and Breu investigated the subject of tin-cobalt complexes further and in 1956 reported compounds which included $Bu_3SnCo(CO)_4$, $Bu_2Sn[Co(CO)_3]_2$ and $Me_2Sn[Co(CO)_4]_2$ [108,110]. In 1957 Hein *et al.* reported $Ph_3PbCo(CO)_4$ [97]. These compounds were obtained from reactions of $Na^+[Co(CO)_4]^-$ and the corresponding organotin or lead halides. Employing a similar

synthetic method, Piper *et al.* prepared $Me_3SiFe(CO)_2Cp$ [187]. In 1960 King and Stone obtained $[Bu_2SnFe(CO)_4]_2$ [130] in reactions between $Fe(CO)_5$ and $Bu_2Sn(CH=CH_2)_2$ or $K_2^+[Fe(CO)_4]^=$ and Bu_2SnCl_2.

A systematic approach for the synthesis of complete series of complexes, involving either a complete group of transition metals bonded to the same group IV ligand or consecutive group IV elements bonded to the same transition metal was not evident prior to 1960. From 1962 - 1964, group IV-transition metal bonding experienced the beginning of a period of rapid growth. The scope of the field was recognized by several workers and considerable attention was given to the synthesis of group IV-transition metal derivatives and related compounds. The reports in 1962 by Gorsich, who synthesized and studied various manganese-pentacarbonyl derivatives of tin and lead such as $Ph_3SnMn(CO)_5$, $Ph_3PbMn(CO)_5$, $Me_2Sn[Mn(CO)_5]_2$ and $Me_2Pb[Mn(CO)_5]_2$ [85], in 1963 by Seyferth *et al.* of $Ph_3GeMn(CO)_5$ [194], and in 1964 by Nesmeyanov *et al.* who expanded the series to the rhenium analogs such as $Ph_3PbRe(CO)_5$, $Ph_2Sn[Re(CO)_5]_2$ and $PhSn[Re(CO)_5]_3$ [159], clearly demonstrated the potential of the field. The ease with which transition metal carbonyl anions can displace halides from germanium, tin and lead played a large role in the rapid development of this field. The extensive series, $Ph_3MM'(CO)_3Cp$, where M = Ge, Sn or Pb; M' = Cr, Mo

or W [160], from the work of Nesmeyanov *et al.* are examples of products from anion reactions.

The growth of this field to date may in part be attributed to the ready availability of starting materials such as $Fe(CO)_5$, $Fe_2(CO)_9$, $Mn_2(CO)_{10}$, $Re_2(CO)_{10}$, $Cr(CO)_6$, $Mo(CO)_6$, $W(CO)_6$, $[CpFe(CO)_2]_2$ or $[CpMo(CO)_3]_2$. Table I*. lists a representative number of group IV-transition metal carbonyl derivatives and their appropriate references. Compounds with mixed substituents on the group IV ligand or substituted transition metal carbonyls such as $-Mn(CO)_4^-$ PPh_3 are not included in the list, but often can be found in references to related complexes. A more detailed list can be found in several reviews [193,156].

---

*In this Table, and throughout this work, the following abbreviations will be employed: Me = CH_3, Et = C_2H_5, Bu = n-C_4H_9, Ph = C_6H_5, Cp = π bonded cyclopentadienyl group, acac = acetylacetonate, THF = tetrahydrofuran.

TABLE I

Group IV-Transition Metal Carbonyl Compounds

M_T[a]	M_{IV}[a]	Compound	Ref.
Cr	Si	$Cl_3SiCr(CO)_3Cp$	‡
		$Cl_3SiHCr(CO)_2C_6H_6$	‡
Cr	Ge	$Ph_3GeCr(CO)_3Cp$	160,178
		$[Ph_4As][Cl_3GeCr(CO)_5]$	191
		$[Ph_3P)_2N]_2[I_2GeCr_2(CO)_{10}]$	192
Cr	Sn	$Ph_3SnCr(CO)_3Cp$	160,178,198
		$[Ph_4As][Cl_3SnCr(CO)_5]$	191
		$[(Ph_3P)_2N]_2[I_2SnCr_2(CO)_{10}]$	192
Cr	Pb	$Ph_3PbCr(CO)_3Cp$	160,178
Mo	Si	$Cl_3SiMo(CO)_3Cp$	‡
		$Me_3SiMo(CO)_3Cp$	‡
		$[CpMo(CO)_4][CpMo(CO)_2(SiCl_3)_2]$	‡
Mo	Ge	$Cl_3GeMo(CO)_3Cp$	169
		$Me_3GeMo(CO)_3Cp$	34
		$Et_3GeMo(CO)_3Cp$	34,83
		$Ph_3GeMo(CO)_3Cp$	160,178
		$Cl_3GeMoCl(CO)_3bipy$	140
		$[Ph_4As][Cl_3GeMo(CO)_5]$	191
		$[Ph_4As]_2[(Cl_3Ge)_2Mo(CO)_4]$	191
Mo	Sn	$Cl_3SnMo(CO)_3Cp$	21,22,24,33
		$Me_3SnMo(CO)_3Cp$	33,177
		$Ph_3SnMo(CO)_3Cp$	2,33,152,160,178
		$Cl_2Sn[Mo(CO)_3Cp]_2$	22,24,160

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Mo	Sn	$Me_2Sn[Mo(CO)_3Cp]_2$	178
		$Ph_2Sn[Mo(CO)_3Cp]_2$	160,198
		$ClSn[Mo(CO)_3Cp]_3$	166
		$Cl_3SnMoCl(CO)_3bipy$	71,140
		$I_3SnMoI(CO)_3bipy$	140
		$[Ph_4As][Cl_3SnMo(CO)_5]$	191
Mo	Pb	$Ph_3PbMo(CO)_3Cp$	158,160,178,198
W	Si	$Me_3SiW(CO)_3Cp$	32
W	Ge	$Cl_3GeW(CO)_3Cp$	169
		$Et_3GeW(CO)_3Cp$	34,83
		$Ph_3GeW(CO)_3Cp$	160,178
		$Cl_3GeWCl(CO)_3bipy$	140
		$[Ph_4As][Cl_3GeW(CO)_5]$	191
		$[(Ph_3P)_2N]_2[I_2GeW_2(CO)_{10}]$	192
W	Sn	$Cl_3SnW(CO)_3Cp$	21,24
		$Me_3SnW(CO)_3Cp$	31,33,178
		$Ph_3SnW(CO)_3Cp$	158,160,178
		$Cl_2Sn[W(CO)_3Cp]_2$	158
		$Ph_2Sn[W(CO)_3Cp]_2$	158,198
		$ClSn[W(CO)_3Cp]_3$	166
		$Cl_3SnWCl(CO)_3bipy$	71,140
		$I_3SnWI(CO)_3bipy$	140
		$[Ph_4As][Cl_3SnW(CO)_5]$	191
		$[(Ph_3P)N]_2[I_2SnW_2(CO)_{10}]$	192

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
W	Pb	$Ph_3PbW(CO)_3Cp$	158,160,178,198
Mn	Si	$H_3SiMn(CO)_5$	7,8,10
		$Cl_3SiMn(CO)_5$	‡
		$Me_3SiMn(CO)_5$	‡
		$Ph_3SiMn(CO)_5$	‡
		$[Ph_2SiMn(CO)_4]_2$	‡
		$Cl_3SiHMn(CO)_2Cp$	‡
Mn	Ge	$Cl_3GeMn(CO)_5$	162,171
		$Br_3GeMn(CO)_5$	171
		$Me_3GeMn(CO)_5$	42
		$Ph_3GeMn(CO)_5$	119,129,163,194,198
		$H_2Ge[Mn(CO)_5]_2$	55
		$Cl_2Ge[Mn(CO)_5]_2$	171
		$Ph_2Ge[Mn(CO)_5]_2$	163
		$[Ph_2GeMn(CO)_4]_2$	163
		$ClGe[Mn(CO)_5]_3$	171
Mn	Sn	$Cl_3SnMn(CO)_5$	33,63,85,119
		$Br_3SnMn(CO)_5$	63,85,119
		$Me_3SnMn(CO)_5$	33,63
		$Ph_3SnMn(CO)_5$	63,85,119,164
		$(C_6F_5)_3SnMn(CO)_5$	205
		$Cl_2Sn[Mn(CO)_5]_2$	85,113
		$Me_2Sn[Mn(CO)_5]_2$	85

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Mn	Sn	$Ph_2Sn[Mn(CO)_5]_2$	85
		$(C_6F_5)_2Sn[Mn(CO)_5]_2$	205
		$[Ph_2SnMn(CO)_5]_2$	205
		$ClSn[Mn(CO)_5]_3$	166,204
		$ISn[Mn(CO)_5]_3$	204
		$MeSn[Mn(CO)_5]_3$	204
		$PhSn[Mn(CO)_5]_3$	204
Mn	Pb	$Me_3PbMn(CO)_5$	85
		$Ph_3PbMn(CO)_5$	63,85,119
		$Me_2Pb[Mn(CO)_5]_2$	85
		$Et_2Pb[Mn(CO)_5]_2$	85
Re	Si	$Cl_3SiRe(CO)_5$	‡
		$Ph_3SiRe(CO)_5$	‡
Re	Ge	$Br_3GeRe(CO)_5$	164
		$Ph_3GeRe(CO)_5$	84,119,198
		$Ph_2Ge[Re(CO)_5]_2$	164
Re	Sn	$Cl_3SnRe(CO)_5$	63,119,159
		$Br_3SnRe(CO)_5$	119,159
		$Me_3SnRe(CO)_5$	63,119
		$Ph_3SnRe(CO)_5$	63,119,159
		$Cl_2Sn[Re(CO)_5]_2$	204
		$Br_2Sn[Re(CO)_5]_2$	159
		$Me_2Sn[Re(CO)_5]_2$	204

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Re	Sn	$Ph_2Sn[Re(CO)_5]_2$	119,159,204
		$ClSn[Re(CO)_5]_3$	159,204
		$BrSn[Re(CO)_5]_3$	159
		$MeSn[Re(CO)_5]_3$	204
		$Sn_2[Re(CO)_5]_6$	159
Re	Pb	$Ph_3PbRe(CO)_5$	63,119,159
Fe	Si	$H_3SiHFe(CO)_4$	9,11
		$(H_3Si)_2Fe(CO)_4$	9,11
		$Cl_3SiHFe(CO)_4$	‡
		$(Cl_3Si)_2Fe(CO)_4$	‡
		$Ph_3SiHFe(CO)_4$	‡
		$[Et_4N][Cl_3SiFe(CO)_4]$	‡
		$[Me_4N][Ph_3SiFe(CO)_4]$	‡
		$[Cl_2SiFe(CO)_4]_2$	‡
		$Cl_3SiFe(CO)_2Cp$	‡
		$(Cl_3Si)_2HFe(CO)Cp$	‡
		$Me_3SiFe(CO)_2Cp$	150,187
Fe	Ge	$I_3GeFeI(CO)_4$	142
		$(Cl_3Ge)_2Fe(CO)_4$	142
		$(I_3Ge)_2Fe(CO)_4$	142
		$Ph_2GeFe_2(CO)_8$	26
		$(Me_2Ge)_3Fe_2(CO)_6$	26,65

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Fe	Ge	$[Cl_2GeFe(CO)_4]_2$	142
		$[Me_2GeFe(CO)_4]_2$	65
		$Ge[Fe(CO)_4]_4$	65
		$[Ph_4As][Cl_3GeFe(CO)_4]$	191
		$Cl_3GeFe(CO)_2Cp$	167
		$Et_3GeFe(CO)_2Cp$	83
		$Ph_3GeFe(CO)_2Cp$	194
		$Cl_2Ge[Fe(CO)_2Cp]_2$	79
		$Me_2Ge[Fe(CO)_2Cp]_2$	79
		$I_2Ge[Fe(CO)_2Cp]_2$	79
		$H_2Ge[Fe(CO)_2Cp]_2$	79
Fe	Sn	$(Cl_3Sn)_2Fe(CO)_4$	142
		$Cl_3SnFeCl(CO)_4$	142
		$(Me_3Sn)_2Fe(CO)_4$	57,65,126
		$[Et_3Sn]_2Fe(CO)_4$	126
		$(Ph_3Sn)_2Fe(CO)_4$	57,58,97,98
		$[Me_2SnFe(CO)_4]_2$	65,125,126
		$[Bu_2SnFe(CO)_4]_2$	55,57,99,117, 126,130
		$[Ph_2SnFe(CO)_4]_2$	65,98
		$Sn[Fe(CO)_4]_4$	55,57,65
		$Sn_2[Fe(CO)_4]_5$	112
		$Me_4Sn_3[Fe(CO)_4]_4$	57,65,80,125, 200

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Fe	Sn	$Bu_4Sn_3[Fe(CO)_4]_4$	55
		$[Ph_4As][Cl_3SnFe(CO)_4]$	191
		$Cl_3SnFe(CO)_2Cp$	21,22,73,100
		$Br_3SnFe(CO)_2Cp$	2,73
		$I_3SnFe(CO)_2Cp$	73
		$Me_3SnFe(CO)_2Cp$	33,177
		$Ph_3SnFe(CO)_2Cp$	33,85,100,147
		$Cl_2Sn[Fe(CO)_2Cp]_2$	21,22,24,73, 100,147
		$I_2Sn[Fe(CO)_2Cp]_2$	79,180
		$Me_2Sn[Fe(CO)_2Cp]_2$	79
		$Sn[Fe(CO)_2Cp]_4$	165
Fe	Pb	$(Et_3Pb)_2Fe(CO)_4$	126
		$(Ph_3Pb)_2Fe(CO)_4$	94,95,98
		$[Me_2PbFe(CO)_4]_2$	65,95
		$[Ph_2PbFe(CO)_4]_2$	94,96,97,98
		$Pb[Fe(CO)_4]_4$	65
		$Me_3Pb_3[Fe(CO)_4]_4$	65
Ru	Si	$Cl_3SiRu(CO)_2Cp$	20
		$[Cl_3SiRu(CO)_4]_2$	56
		$[Me_3SiRu(CO)_4]_2$	56
Ru	Ge	$I_2Ge[Ru(CO)_2Cp]_2$	20
Ru	Sn	$(Me_2Sn)_2Ru(CO)_4$	58
		$(Ph_3Sn)_2Ru(CO)_4$	58

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Ru	Sn	$[Ph_4As]_2[(Cl_3Sn)_2Ru(CO)_2Cl_2]$	135
		$Me_{10}Sn_4Ru_2(CO)_6$	56
		$Cl_3SnRu(CO)_2Cp$	20
		$Me_2Sn[Ru(CO)_2Cp]_2$	20
		$Cl_2Sn[Ru(CO)_2Cp]_2$	20
Co	Si	$H_3SiCo(CO)_4$	6,7,8,90
		$F_3SiCo(CO)_4$	90
		$Cl_3SiCo(CO)_4$	37,64,90,190
		$Me_3SiCo(CO)_4$	12,150
		$Ph_3SiCo(CO)_4$	37,64,127
		$Cl_3SiHCo(CO)Cp$	‡
		$(Cl_3Si)_2Co(CO)Cp$	‡
		$CH_2CHSiCo_3(CO)_9$	128
		$[SiCo_3(CO)_9]_2$	128
Co	Ge	$Cl_3GeCo(CO)_4$	64,183
		$I_3GeCo(CO)_4$	64,185
		$Ph_3GeCo(CO)_4$	64,183
		$Cl_2Ge[Co(CO)_4]_2$	168,183
		$I_2Ge[Co(CO)_4]_2$	180
		$Me_2Ge[Co(CO)_4]_2$	183
		$Cl_3GeCoCl(CO)Cp$	141
		$I_3GeCoI(CO)Cp$	141
		$(Cl_3Ge)_2Co(CO)Cp$	141
		$(Br_3Ge)_2Co(CO)Cp$	141

TABLE I (continued)

M_T [a]	M_{IV} [a]	Compound	Ref.
Co	Sn	$Cl_3SnCo(CO)_4$	64,185
		$I_3SnCo(CO)_4$	64,185
		$Me_3SnCo(CO)_4$	17,18,28,33,64,183
		$Ph_3SnCo(CO)_4$	17,18,28,64,98,183
		$Cl_2Sn[Co(CO)_4]_2$	2,22,23,24,180
		$I_2Sn[Co(CO)_4]_2$	2,23,180
		$Me_2Sn[Co(CO)_4]_2$	108,183
		$Ph_2Sn[Co(CO)_4]_2$	23,98,183
		$Bu_2Sn[Co(CO)_4]_2$	108
		$acac_2Sn[Co(CO)_4]_2$	185
		$acac_2SnCo_2(CO)_7$	182,184
		$ClSn[Co(CO)_4]_3$	166,181
		$FSn[Co(CO)_4]_3$	185
		$MeSn[Co(CO)_4]_3$	179,181
		$PhSn[Co(CO)_4]_3$	181
		$CH_3CO_2Sn[Co(CO)_4]_3$	185
		$Sn[Co(CO)_4]_4$	185
		$BuSnCo_3(CO)_9$	116
		$Cl_3SnCoCl(CO)Cp$	141
		$I_3SnCoI(CO)Cp$	141
		$(Cl_3Sn)_2Co(CO)Cp$	141
		$(I_3Sn)_2Co(CO)Cp$	141
Co	Pb	$CH_3CO_2PbCo(CO)_4$	145

TABLE I (continued)

M_T[a]	M_{IV}[a]	Compound	Ref.
Co	Pb	$Et_3PbCo(CO)_4$	64,127
		$Ph_3PbCo(CO)_4$	64,92,97
		$Ph_2Pb[Co(CO)_4]_2$	98
Rh	Si	$Cl_3SiHRh(CO)Cl(PPh_3)_2$	93
Rh	Sn	$Me_3SnRh(CO)_2(PPh_3)_2$	46,47
		$[Et_4N]_2[Cl_3SnRh(CO)Cl_2]$	137
		$[Et_4N]_2[(Cl_3Sn)_2Rh(CO)Cl]$	137,218
		$[Et_4N]_2[(Cl_3Sn)_3Rh(CO)]$	137
Ir	Si	$Cl_3SiHIrCl(CO)(PPh_3)_2$	36
		$Me_3SiHIrCl(CO)(PPh_3)_2$	36,92
Ir	Sn	$Cl_3SnIrCl_2(CO)(PPh_3)_2$	202
		$Cl_3SnIrH_2(CO)(PPh_3)_2$	202
		$[Me_4N][Cl_3SnIr(CO)Cl_3]$	202
		$Me_3SnIr(CO)_3PPh_3$	46,47
		$Me_2Sn[Ir(CO)_3PPh_3]_2$	46,47
Ni	Si	$Cl_3SiNi(CO)Cp$	ǂ
		$[Me_4N][Ph_3SiNi(CO)_3]$	143
Ni	Ge	$Et_3GeNi(CO)Cp$	83
N	Sn	$Cl_2Sn[Ni(CO)Cp]_2$	180

a M_T = Transition metal, M_{IV} = Group IV element

ǂ Compound prepared for the first time in this work.

Summary of Transition Metal Carbonyl Complexes

Most transition metal elements form carbonyl complexes. These are the main source in group IV-transition metal bonding and specifically the present study. Table II lists some of the most useful binary transition metal carbonyls from the synthetic standpoint.

TABLE II

Binary Transition Metal Carbonyls

$Cr(CO)_6$	$Mn_2(CO)_{10}$	$Fe(CO)_5$	$Fe_3(CO)_{12}$	$Co_2(CO)_8$	$Ni(CO)_4$
$Mo(CO)_6$	$Te_2(CO)_{10}$	$Ru(CO)_5$	$Ru_3(CO)_{12}$		
$W(CO)_6$	$Re_2(CO)_{10}$	$Os(CO)_5$	$Os_3(CO)_{12}$		

A variety of modifications of these complexes can be accomplished by replacing one or more carbon monoxides with other ligands donating an equal number of electrons to the transition metal atom, according to the Effective Atomic Number rule, which is briefly described in a later section. If the cyclopentadienyl radical, a five electron donor ligand when π bonded, is employed, another interesting and relatively air stable series of mixed π cyclopentadienyl-carbonyl complexes is obtained.

TABLE III

Cyclopentadienyl Transition Metal Carbonyls

$CpV(CO)_4$	$[CpCr(CO)_3]_2$	$CpMn(CO)_3$	$[CpFe(CO)_2]_2$	$CpCo(CO)_2$
$CpNb(CO)_4$	$[CpMo(CO)_3]_2$	$CpTe(CO)_3$	$[CpRu(CO)_2]_2$	$CpRh(CO)_2$
$CpTa(CO)_4$	$[CpW(CO)_3]_2$	$CpRe(CO)_3$	$[CpOs(CO)_2]_2$	$CpIr(CO)_2$

Several reviews summarize the synthetic methods and properties of the complexes [44,124,132,212]. Other elaborate mixed carbonyl series can be synthesized in which amines, phosphines or arsines replace one or more carbon monoxides. The change of ligands is often employed to modify physical or chemical properties, in order to make experimental work more feasible or allow spectroscopic studies. Iron pentacarbonyl is a yellow toxic liquid with a relatively high vapour pressure. The triphenylphosphine derivative, $Ph_3PFe(CO)_4$, is a nonvolatile crystalline solid which is insensitive to air and thermally more stable than $Fe(CO)_5$. Similarly, $Mn_2(CO)_8(PPh_3)_2$ [176] and $Co_2(CO)_6(PPh_3)_2$ [109] are more resistant to oxidation than the parent carbonyl analogs. The series $M(CO)_6$, where M = Cr, Mo or W, is very stable thermally and quite unreactive in numerous reactions. However, if one or more carbon monoxides are replaced by other ligands, then the new species are generally more susceptible to oxidation and also more reactive to other reagents. For example $\pi C_6H_6Cr(CO)_3$ and Cl_3SiH yield

$Cl_3SiHCr(CO)_2\pi C_6H_6$ [121], while $bipyMo(CO)_4$ and Cl_4Sn yield $bipyMo(CO)_3Cl(SnCl_3)$ [140]. The parent carbonyls, $Cr(CO)_6$ or $Mo(CO)_6$ are unreactive in these reactions.

Synthetic Methods

The development of group IV-transition metal bonding paralleled the discovery and recognition of several general synthetic methods. These can be divided into the following classes: displacement by metal carbonyl anions, insertion of Ge(II) or Sn(II) halides, elimination of a neutral molecule, oxidative elimination and oxidative addition reactions.

1. Displacement by Metal Carbonyl Anions

By far the most versatile and widely studied synthetic method for the preparation of group IV-transition metal bonds involved the reaction of alkali salts, generally the sodium salts, of transition metal carbonyls and group IV halides or organohalides. This method has been employed successfully for germanium, tin and lead derivatives and in some cases silyl derivatives of transition metal carbonyls.

The metal carbonyl anions can be generated in several ways:

$$Mn_2(CO)_{10} \xrightarrow{Na/Hg\ THF} Na^+[Mn(CO)_5]^- \quad (43) \qquad [I.1]$$

$$Fe_3(CO)_{12} \xrightarrow{Na/Hg\ THF} Na_2^+[Fe(CO)_4]^= \quad (131) \qquad [I.2]$$

$$Mo(CO)_6 \xrightarrow{Na^+\ C_5H_5^-} Na^+[Mo(CO)_3Cp]^- \quad (78,186) \qquad [I.3]$$

$$Co_2(CO)_8 \xrightarrow{MeOH} [Co(MeOH)_6]^{2+}[Co(CO)_4]_2^- \quad (107) \quad [I.4]$$

A more detailed summary of these can be found in a review by Wender and Pino [212].

Employing the appropriate ratio of metal carbonyl anion with the group IV halide, this method enables the replacement of one to four halide ions. In successive reaction steps, compounds containing chains of three, four or even five different metal atoms can be synthesized. Examples of these reactions are illustrated below:

$$Ph_3SnCl + Mn(CO)_5^- \rightarrow Ph_3SnMn(CO)_5 + Cl^- \quad (85) \quad [I.5]$$

$$Me_3SiCl + Fe(CO)_2Cp^- \rightarrow Me_3SiFe(CO)_2Cp + Cl^- \quad (187) \quad [I.6]$$

$$Ph_3GeBr + W(CO)_3Cp^- \rightarrow Ph_3GeW(CO)_3Cp + Br^- \quad (178) \quad [I.7]$$

$$H_3SiI + Co(CO)_4^- \rightarrow H_3SiCo(CO)_4 + I^- \quad (6,7,8) \quad [I.8]$$

$$Ph_3PbCl + Cr(CO)_3Cp^- \rightarrow Ph_3PbCr(CO)_3Cp + Cl^- \quad (178) \quad [I.9]$$

$$Me_2SnCl_2 + Mn(CO)_5^- \rightarrow Me_2ClSnMn(CO)_5 + Cl^- \quad (177) \quad [I.10]$$

$$Ph_2PbCl_2 + 2Co(CO)_4^- \rightarrow Ph_2Pb[Co(CO)_4]_2 + 2Cl^- \quad (98) \quad [I.11]$$

$$MeSnCl_3 + 3Co(CO)_4^- \rightarrow MeSn[Co(CO)_4]_3 + 3Cl^- \quad (179,181) \quad [I.12]$$

$$SnCl_4 + 4Fe(CO)_2Cp^- \rightarrow Sn[Fe(CO)_2Cp]_4 + 4Cl^- \quad (165) \quad [I.13]$$

$$Me_2SnCl_2 + 2Re(CO)_5^- \rightarrow Me_2Sn[Re(CO)_5]_2 + 2Cl^- \quad (119) \quad [I.14]$$

$$2Ph_2SnCl_2 + 2Fe(CO)_4^{=} \rightarrow [Ph_2SnFe(CO)_4]_2 + 4Cl^- \quad (98) \quad [I.15]$$

$$(OC)_5MnSnMe_2Cl + Mo(CO)_3Cp^- \rightarrow (OC)_5MnSnMe_2Mo(CO)_3Cp + Cl^- \quad (177) \quad [I.16]$$

$$[Cp(OC)_2Fe]_2SnCl_2 + 2Mo(CO)_3Cp^- \rightarrow [Cp(OC)_2Fe]_2Sn[Mo(CO)_3Cp]_2 \quad (69) \quad [I.17]$$

$$[Cp(OC)_2Fe]_2SnCl_2 + Re(CO)_5^- \rightarrow [Cp(OC)_2Fe]_2SnClRe(CO)_5 + Cl^- \quad (165) \quad [I.18]$$

2. Insertion of Germanium(II) and Tin(II) Halides

The first insertion reaction involved mercury and $CpFe(CO)_2Co(CO)_4$ in the synthesis of $CpFe(CO)_2HgCo(CO)_4$ [69]. Similarly the halides of germanium(II) and tin(II) are known to insert into the metal-metal bonds of dimeric transition metal carbonyls or transition metal halides. Conditions for these reactions vary from room temperature to 200°C and a solvent may or may not be employed:

$$[CpNi(CO)]_2 + SnCl_2 \rightarrow Cl_2Sn[Ni(CO)Cp]_2 \quad (180) \quad [I.19]$$

$$[CpFe(CO)_2]_2 + SnBr_2 \rightarrow Br_2Sn[Fe(CO)_2Cp]_2 \quad (180) \quad [I.20]$$

$$ClFe(CO)_2Cp + SnCl_2 \rightarrow Cl_3SnFe(CO)_2Cp \quad (21) \quad [I.21]$$

$$IFe(CO)_2Cp + SnCl_2 \rightarrow ICl_2SnFe(CO)_2Cp \quad (151) \quad [I.22]$$

$$[CpFe(CO)_2]_2 + GeCl_2 \rightarrow Cl_2Ge[Fe(CO)_2Cp]_2 \quad (167) \quad [I.23]$$

$$Mn_2(CO)_{10} + SnCl_2 \rightarrow Cl_2Sn[Mn(CO)_5]_2 \quad (113) \quad [I.24]$$

$$Co_2(CO)_8 + SnI_2 \rightarrow I_2Sn[Co(CO)_4]_2 \quad (180) \quad [I.25]$$

$$[Cr_2(CO)_{10}]^{-2} + SnI_2 \rightarrow \{I_2Sn[Cr(CO)_5]_2\}^{-2} \quad (190) \quad [I.26]$$

$$[W_2(CO)_{10}]^{-2} + GeI_2 \rightarrow \{I_2Ge[W(CO)_5]_2\}^{-2} \quad (192) \quad [I.27]$$

In the reactions with transition metal carbonyl halides, Cl_3GeH is believed to be a source of $GeCl_2$ and hydrogen chloride, and therefore, these reactions are included in the section by some authors:

$$ClMn(CO)_5 + Cl_3GeH \rightarrow Cl_3GeMn(CO)_5 \quad (169) \quad [I.28]$$

$$ClFe(CO)_2Cp + Cl_3GeH \rightarrow Cl_3GeFe(CO)_2Cp \quad (167) \quad [I.29]$$

3. Elimination of a Neutral Molecule

A variety of molecular fragments are preferentially eliminated in the formation of group IV-transition metal bonds:

$Co_2(CO)_8 + 2Cl_3SiH \rightarrow H_2 + 2Cl_3SiCo(CO)_4$ (37) [I.30]

$Mn_2(CO)_{10} + 2Cl_3SiH \rightarrow H_2 + 2Ph_3SiMn(CO)_5$ (119) [I.31]

$Fe_3(CO)_{12} + 6Cl_3SiH \rightarrow 3H_2 + 3(Cl_3Si)_2Fe(CO)_4$ (120) [I.32]

$2Ru_3(CO)_{12} + 6Me_3SiH \rightarrow 3H_2 + 3[Me_3SiRu(CO)_4]_2$ (56) [I.33]

$2HMn(CO)_5 + GeH_4 \rightarrow H_2 + H_2Ge[Mn(CO)_5]_2$ (155) [I.34]

$Fe_3(CO)_{12} + Ph_2GeH_2 \rightarrow xH_2 + Ph_2GeFe_2(CO)_8$ (26) [I.35]

$HW(CO)_3Cp + Me_3SnNMe_2 \rightarrow HNMe_2 + Me_3SnW(CO)_3Cp$ (31) [I.36]

$HMo(CO)_3Cp + Me_3SiNMe_3 \rightarrow HNMe_2 + Me_3SiMo(CO)_3Cp$ (32) [I.37]

$ClHgFe(CO)_2Cp + SnCl_2 \rightarrow Hg + Cl_3SnFe(CO)_2Cp$ (22) [I.38]

$Hg[Fe(CO)_2Cp]_2 + SnCl_2 \rightarrow Hg + Cl_2Sn[Fe(CO)_2Cp]_2$ (24) [I.39]

$ClMn(CO)_5 + Cl_3GeH \rightarrow HCl + Cl_3GeMn(CO)_5$ (169) [I.40]

$ClFe(CO)_2Cp + Cl_3GeH \rightarrow HCl + Cl_3GeFe(CO)_2Cp$ (167) [I.41]

The last two reactions have been classified under insertion reactions. As these classifications are somewhat arbitrary, one cannot, with justification, exclude them from this section.

4. Oxidative Elimination and Oxidative Addition Reactions.

Essentially both types of reactions are similar, in that the coordination number and oxidation state of the transition metal are increased. With molecules which obey the "Effective Atomic Number" (E.A.N.), a two electron donor

ligand (i.e. CO, PPh_3, NC_5H_5 etc.) is eliminated prior to the addition of the new ligands. Electronically unsaturated molecules (generally limited to the second and third transition metal series) may add one electron donor ligands in order to satisfy the E.A.N. rule. Examples of both types are given below:

$$bipyW(CO)_4 + SnCl_4 \rightarrow Cl_3SnW(CO)_3Clbipy + CO \quad (140)\ [I.42]$$

$$bipyW(CO)_4 + 2SnCl_4 \rightarrow (Cl_3Sn)_2W(CO)_3bipy + CO \quad (140)\ [I.43]$$

$$Fe(CO)_5 + Cl_3SiH \rightarrow Cl_3SiHFe(CO)_4 + CO \quad (120)\ [I.44]$$

$$Fe(CO)_5 + 2Cl_3SiH \rightarrow (Cl_3Si)_2Fe(CO)_4 + CO \quad (121)\ [I.45]$$

$$Cl_3SiFe(CO)_2Cp + Cl_3SiH \rightarrow (Cl_3Si)_2HFe(CO)Cp + CO \quad (121)\ [I.46]$$

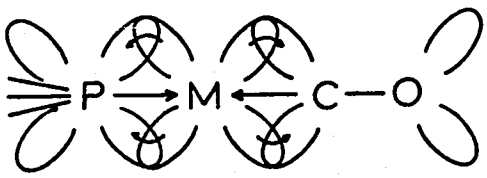
$$(Ph_3P)_2Rh(CO)Cl + Cl_3SiH \rightarrow Cl_3SiHRh(CO)Cl(PPh_3)_2 \quad (93)\ [I.47]$$

$$(Ph_3P)_2Ir(CO)Cl + Cl_3SiH \rightarrow Cl_3SiHIr(CO)Cl(PPh_3)_2 \quad (36)\ [I.48]$$

General Discussion

The transition metals in most carbonyl complexes are stabilized in a low oxidation state by ligands such as carbon monoxide, tertiary phosphines, tertiary arsines and a variety of cyclic olefins. In addition to the σ bond, these ligands have empty orbitals which are capable of π type overlap with the transition metal d orbitals. If the symmetry of the orbitals is favourable, a π type of interaction may occur between the filled d orbitals of the transition metal and the vacant p orbitals of carbon monoxide and cyclopentadiene or the vacant d orbitals of phosphines and arsines. Excess

electrons donated to the electropositive transition metal by the ligands are partly drained back onto the ligand by the π system, such that the complex may attain a favourable electronic configuration. This synergic process is shown below:



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The ability of the antibonding π orbital of carbon monoxide to accept electrons, makes the carbon monoxide stretching vibration in the infrared spectrum very sensitive to the electron density on the molecule. For example, the carbonyl stretching values of the isoelectronic series, $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^=$ are 2037 cm^{-1}, 1883 cm^{-1} and 1788 cm^{-1} respectively.[3] Electronegative ligands, having a tendency to withdraw electrons, also shift carbon monoxide stretching frequencies to higher values. A more detailed discussion is given by Cotton and Wilkinson [53].

Almost all transition metal carbonyls obey the Effective Atomic Number (E.A.N.) rule occasionally referred to as the "inert gas rule" [1]. This rule requires that the number of valence electrons of the transition metal atom plus the number of lone pair electrons donated by the ligands equals the electronic configuration of the succeeding inert gas, which implies that the d orbitals of the

transition metal are completely filled. With this arrangement several properties are predictable; the compounds must be diamagnetic as there are no unpaired electrons, and the stoichiometries of these compounds must be such as to allow the transition metal to attain a filled d shell.

To test whether or not a molecule obeys the E.A.N. rule, the electrons in the valence shell are added. If the transition metal atom is arbitrarily assigned an oxidation state of zero, then the required number of electrons donated by the ligands are obtained by subtracting from the atomic number of the succeeding inert gas the atomic number of the transition metal.

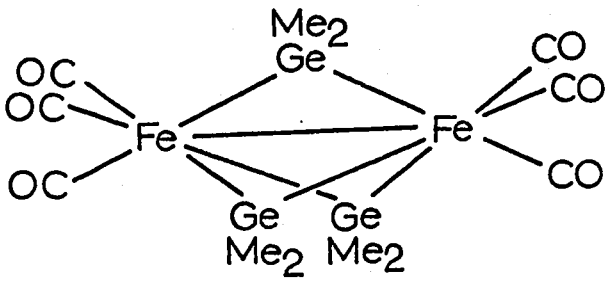
The most common ligands; carbon monoxide, tertiary phosphines and arsines, each donate two electrons. Terminal halogens and group IV ligands, each contribute one electron. Conjugated olefins such as benzene or cycloheptatriene donate two electrons per double bond, while a π bonded cyclopentadiene supplies five electrons. A bridging halogen supplies three electrons to a system of two transition metals, whereas a bridging group IV ligand donates one electron to each transition metal atom.

For example, applying the E.A.N. rule to $Ph_3SnMo(CO)_3Cp$ [160,178], the molybdenum atom requires 12 electrons from the ligands. If five are supplied by the π bonded cyclopentadiene, two from each carbon monoxide and one from triphenyl-

tin, then a total of 12 electrons are donated by the ligands.

For $(Me_2Ge)_3Fe_2(CO)_6$,[26] each iron atom requires ten electrons from the ligand to attain the inert gas electronic configuration. If the carbon monoxides donate six electrons and the bridging germanes supply three electrons to each iron atom, then it gains nine of the ten required electrons. For the molecule to obey the E.A.N. rule a metal-metal bond between the iron atoms is postulated which is also consistent with its diamagnetic property. A short internuclear distance of 2.74 Å between the iron atoms is evidence for a metal-metal bond [26].

The structures for both $(Me_2Ge)_3Fe_2(CO)_6$[26], 5 and $Fe_2(CO)_9$[189], 6, have been determined by X-ray crystallography:



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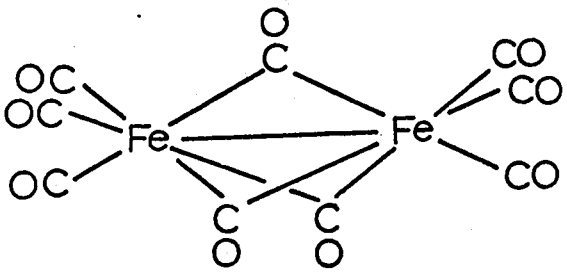

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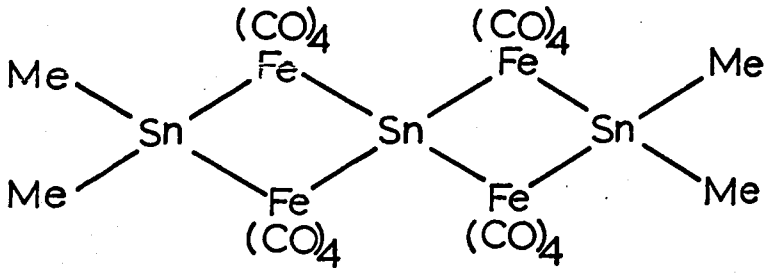
Note the iron-iron distance in $Fe_2(CO)_9$ is 2.46 Å, considerably shorter than in $(Me_2Ge)_3Fe_2(CO)_6$, which is 2.76 Å. Both values are, however, within known bonding distances.[149] The difference appears to be related to the difference in the iron-germanium and iron-carbon distances of the bridging system, which are 2.40 Å and 1.77 Å respectively.

Other related molecules, for which the structures have been determined by X-ray crystallography, are $Me_4Sn_3Fe_4(CO)_{16}$ [200] and $SnFe_4(CO)_{16}$ [149]:



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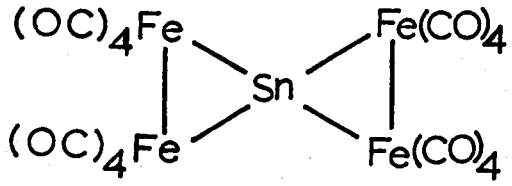

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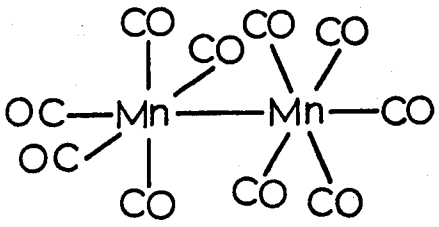
If electrons are summed in $Me_4Sn_3Fe_4(CO)_{16}$, 7, no metal-metal bond between iron atoms is required. This is consistent with the observed X-ray data. The shortest iron-iron distance in this molecule is 4.18 Å, which is too large for any significant bonding. On the other hand, $SnFe_4(CO)_{16}$, 8, requires bonding between two pairs of iron atoms. The two types of iron-iron distances are 2.87 Å and 4.69 Å, which are clearly bonding and non-bonding.

Metal-metal bonds as are encountered in $Fe_2(CO)_9$ [189] or $Co_2(CO)_8$ [199] are a common occurrence and are presently generally accepted. It must be remembered, however, that prior to the pioneering work in X-ray crystallography in 1957 by Rundle and Dahl who determined the structure of $Mn_2(CO)_{10}$ [60] and Wilson and Shoemaker who solved the structure of $[CpMo(CO)_3]_2$ [214], it was not clear whether the short metal-metal distance and the diamagnetic character of the molecules were due to metal-metal bonds or electron pairing through the bridging ligands.



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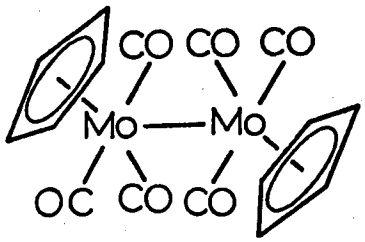

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Both, $Mn_2(CO)_{10}$ and $[CpMo(CO)_3]_2$ possess no bridging ligands and the two symmetric halves are held together only by metal-metal bonds.

CHAPTER II

The Synthesis of Manganesepentacarbonyl Derivatives of Silicon, Germanium, Tin and Lead

Introduction

Some of the first bimetallic compounds containing covalent bonds between manganese and the group IV metals were reported in 1962 by Gorsich, who prepared a series of manganesepentacarbonyl derivatives in which the tin or lead ligand was directly bonded to manganese. The general formula of these complexes is $R_{4-n}M[Mn(CO)_5]_n$, where R = Me, Et, Ph, or halogen; M = Sn or Pb; n = 1 or 2 [85]. The series was extended by Seyferth *et al.* to include $Ph_3GeMn(CO)_5$ [194]. This early work utilizes one of the most versatile preparative methods for the synthesis of transition metal-group IV bonds, which have been described in Chapter I:

$$Ph_{4-n}SnCl_n + nN\overset{+}{a}[Mn(CO)_5]^- \rightarrow R_{4-n}Sn[Mn(CO)_5]_n + nNaCl \quad [II.1]$$

With organosilyl chlorides a large change in chemical behavior is observed and the versatile reaction method for the preparation of derivatives of germanium, tin and lead rarely yields the anticipated silyl derivatives. Aylett and Campbell obtained $H_3SiMn(CO)_5$ from H_3SiI and $NaMn(CO)_5$, [7,8] one of the rare instances in which a

silicon-transition metal bond has been prepared by the anion method. The related complex, $Ph_3SiMn(CO)_5$ does not form by this reaction route but as shown in the present work, is obtained from a thermal reaction between Ph_3SiH and $Mn_2(CO)_{10}$.

Treatment of phenylgermanium or phenyltin manganese-pentacarbonyls with hydrogen chloride, chlorine or bromine in carbon tetrachloride yields the halogen analogs. The less soluble halides generally precipitate from solution:[163]

$$Ph_3GeMn(CO)_5 + 3Br_2 \rightarrow Br_3GeMn(CO)_5 + BrC_6H_5 \qquad [II.2]$$

The mixed organohalides such as $Ph_2ClSnMn(CO)_5$ or $PhCl_2SnMn(CO)_5$ can be prepared by refluxing mixtures of the proper stoichiometries of the pure organo and pure halogeno derivatives. Redistribution on the group IV metal occurs in the following manner [85]:

$$2Ph_3SnMn(CO)_5 + Cl_3SnMn(CO)_5 \rightarrow 3Ph_2ClSnMn(CO)_5 \qquad [II.3]$$

Although in some later studies mixed organohalogen tin or germanium derivatives have been prepared directly from the group IV organohalides and the appropriate stoichiometric quantity of manganesepentacarbonyl anion [85,119,163], this method is not often employed for the preparation of such compounds. The redistribution method or partial replacement of phenyl groups at critically controlled

conditions of temperature, solvent type and the quantity of halogen reagent is favored [85,163].

The number and complexity of molecules with metal-metal bonds increased rapidly and it appeared at that stage that any reasonable molecular system could be assembled by a proper sequence of reaction steps. Numerous interesting results have been reported. For example, Nesmeyanov *et al.* synthesized $ClGe[Mn(CO)_5]_3$ [171] in a reaction of $Cl_3GeMn(CO)_5$ and two moles of $NaMn(CO)_5$, and $(CO)_5MnSnCl[Fe(CO)_2Cp]_2$ [165] from $Cl_2Sn[Fe(CO)_2Cp]_2$ and $NaMn(CO)_5$. The reaction of $ClPh_2SnRe(CO)_5$ and $NaMn(CO)_5$ yields $(CO)_5MnSnPh_2Re(CO)_5$ [161] and similarly $ClPh_2SnMn(CO)_5$ and C_6F_5Li yields $C_6F_5Ph_2SnMn(CO)_5$ [205].

In reactions such as these, unexpected results are occasionally encountered. For example two moles of $Br_2PhGeMn(CO)_5$ and four moles of $NaMn(CO)_5$ yields $\{PhGe[Mn(CO)_5]_2\}_2$ [171]. The reaction of $ClSn[Mn(CO)_5]_3$ and $NaMn(CO)_5$ yields $Sn_2[Mn(CO)_5]_6$ [166], while $[Ph_2SnMn(CO)_5]_2$ [205] is obtained from $ClPh_2SnMn(CO)_5$ and C_6F_5Li.

Most compounds studied in this chapter have been synthesized and reported by other workers [85,194]. However, prior to this work little or no systematic approach to study these compounds seemed evident. A study of the trend in chemical and physical properties of the series of complexes in which the group IV ligand is consecutively changed from silicon to lead appeared valuable. The series,

$Ph_3MMn(CO)_5$ (M = Si, Ge, Sn, Pb) appeared complete [85,194] but one of the members, $Ph_3SiMn(CO)_5$ was described as extremely unstable in air.[85] The authentic complex $Ph_3SiMn(CO)_5$, however, was synthesized in the present work by an alternative route and shows a remarkable stability in air at room temperature [119]. The nature of the extremely unstable silicon complex remains unexplained.

The manganesepentacarbonyl derivatives are highly symmetric and therefore of interest for force constant studies [39] which have been undertaken by R. S. Gay in this laboratory. The accurate and detailed infrared data of the carbonyl stretching region, which are required for the studies, were in most cases not available. The study of this section was undertaken to obtain consistent infrared spectra of high quality and to compare the chemical and physical properties of the complexes within this series.

RESULTS AND DISCUSSION

1. Synthesis

The simplest and most direct route for the preparation of $Ph_3MMn(CO)_5$ (M = Ge, Sn, Pb) involves reaction of the sodium salt of manganesepentacarbonyl with the corresponding triphenyl-group IV halide. The reduction of $Mn_2(CO)_{10}$ by sodium amalgam yields the anion, $Mn(CO)_5^-$ [43].

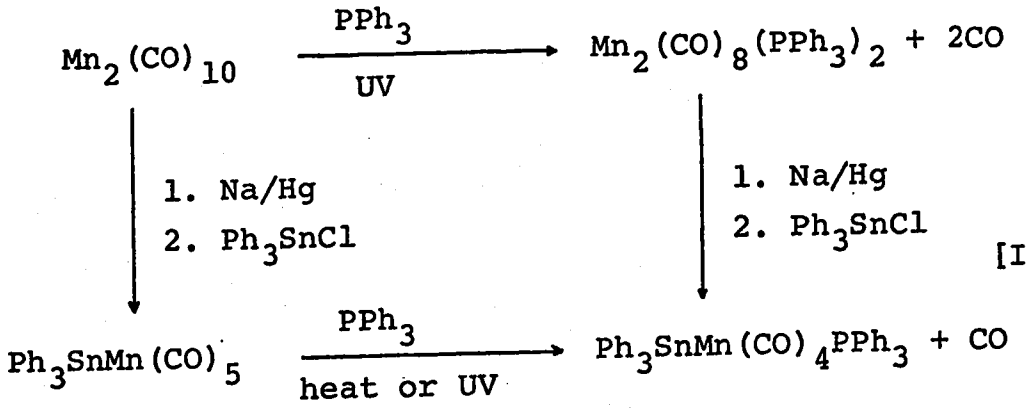
$$Mn_2(CO)_{10} \xrightarrow[THF]{1\%\ Na/Hg} 2Na^+[Mn(CO)_5]^- \qquad [II.4]$$

The desired triphenyl-group IV halide is introduced slowly under a nitrogen atmosphere. In these reactions equimolar quantities of anion and group IV halides are employed [85]:

$$Ph_3SnCl + [Mn(CO)_5]^- \rightarrow Ph_3SnMn(CO)_5 + Cl^- \qquad [II.5]$$

In the formation of the metal-metal bond, a halide ion is eliminated and the reaction mixture generally results in a solution of unattractive appearance. This can be filtered and the product precipitated with the addition of water to the filtrate. It is, however, more convenient to draw off the THF at reduced pressure, extract the residue with hot hexane and cool the filtrate in a refrigerator. The latter procedure generally results in a pure, coarse, crystalline product from the first crystallization.

The substitution of one carbon monoxide with triphenylphosphine on $Ph_3SnMn(CO)_5$ yields *trans* $Ph_3SnMn(CO)_4PPh_3$ [85]. For the preparation of this complex, two convenient synthetic routes can be followed. These are represented in the following scheme:



[II.6]

Either route poses no experimental problems and results in the same geometric isomer. Irradiation of $Mn_2(CO)_{10}$ in the presence of excess PPh_3 in hexane solution yields approximately 70% $Mn_2(CO)_8(PPh_3)_2$ based on the initial amount $Mn_2(CO)_{10}$ used. The phosphine adduct has a large molecular weight and precipitates. At this stage the orange microcrystalline material is sufficiently pure for further use. Reduction of $Mn_2(CO)_8(PPh_3)_2$ by sodium analgam in THF yields the salt, $Na^+[Mn(CO)_4PPh_3]^-$. The subsequent reaction step is analogous to that with $Na^+[Mn(CO)_5]^-$. The final product $Ph_3SnMn(CO)_4PPh_3$, is sparingly soluble in hexane. For the recrystallization, mixtures of dichloromethane-hexane were employed.

The alternative route, reaction of triphenylphosphine with $Ph_3SnMn(CO)_5$, is perhaps somewhat more direct and more convenient. Substitution of carbon monoxide can be effected either thermally or by ultraviolet irradiation as has been pointed out by Gorsich [85] and was found in the present work. The reaction with the least side products and probably that of highest yield involves heating a mixture of $Ph_3SnMn(CO)_5$ in excess triphenylphosphine in a Carius tube at 180°C. Yields of $Ph_3SnMn(CO)_4PPh_3$ are almost quantitative based on $Ph_3SnMn(CO)_5$.

In principle, the reaction of equimolar quantities of $Na^+[Mn(CO)_5]^-$ and $SnCl_4$ or $SnBr_4$ should yield $X_3SnMn(CO)_5$ (X = Cl, Br). This route, however, is rarely employed. The cleavage of phenyl groups by chlorine or bromine results in the chloro or bromo analogs in high yields. For example, a carbon tetrachloride solution of $Ph_3SnMn(CO)_5$ in the presence of chlorine or bromine precipitates the trichloro or tribromo analogs virtually quantitatively in a pure state [85]:

$$Ph_3SnMn(CO)_5 + 3X_2 \rightarrow X_3SnMn(CO)_5 + 3XPh \qquad [II.7]$$

These halogen derivatives are far more moisture sensitive than the phenyl analogs and decompose below their melting point. For infrared spectroscopic purposes, saturated hexane solutions yield carbonyl bands of intermediate intensity.

Prior to this work, the existence and stability of a covalent silicon-manganese bond was a matter of uncertainty. The reaction of $Na^{+}[Mn(CO)_5]^{-}$ and Ph_3SiCl produces a scarlet crystalline material which decomposes rapidly to $Mn_2(CO)_{10}$, Ph_6Si_2 and Ph_3SiOH [85]. With this evidence at hand it was assumed by Gorsich that the scarlet material was $Ph_3SiMn(CO)_5$. It is further interesting to note, that the reaction of SiH_4 and $HMn(CO)_5$ produces a colored material from which no compound containing silicon-manganese bonds could be isolated [155].

Silicon-transition metal bonding was relatively unexplored prior to 1966, when the only well established silyl transition metal carbonyl derivatives, $Me_3SiFe(CO)_2Cp$ [187] and $R_3SiCo(CO)_4$ (R = Cl, organic group) [37] appeared to demonstrate their stability. Although the former was prepared by utilizing the anion method, the latter was synthesized from R_3SiH and $Co_2(CO)_8$. Chalk and Harrod suggest the following reaction steps [37]:

$$2R_3SiH + Co_2(CO)_8 \rightarrow HCo(CO)_4 + R_3SiCo(CO)_4 \qquad [II.8]$$

$$R_3SiH + HCo(CO)_4 \rightarrow H_2 + R_3SiCo(CO)_4 \qquad [II.8a]$$

$$\text{or} \quad 2HCo(CO)_4 \rightarrow H_2 + Co_2(CO)_8 \qquad [II.8b]$$

It appeared that of the group IV elements, silicon should not be chemically unique and that silicon manganese complexes should have properties similar to those of the manganese analogs of germanium, tin and lead. The present study showed that the synthetic method used for

the silyl-cobalt complexes could be generalized, and employed Ph_3SiH and $M_2(CO)_{10}$, where M = Mn or Re, at elevated temperatures to prepare $Ph_3SiM(CO)_5$:

$$2Ph_3SiH + M_2(CO)_{10} \rightarrow 2Ph_3SiM(CO)_5 + H_2 \qquad [II.9]$$

These reactions are carried out in thick-walled Pyrex tubes at approximately 150°C. A solvent may be employed but it is not essential since both reactants are in the liquid state at the reaction temperature. At this temperature, the hydrides $HM(CO)_5$ which may be intermediates would not be expected to survive in these reactions and have not been isolated. The infrared spectra and physical properties are very similar to those of the germanium and tin analogs. They possess exceptional stability in air at room temperature. A more detailed study of silicon-transition metal bonding follows in the next chapter.

2. Infrared Spectra

The infrared data of most early publications, prior to 1963, for carbonyl stretching bands are unsuited for accurate force constant calculations. This can be attributed to two main reasons. Firstly, the use of chloroform and other similar polar solvents for the infrared medium, which were very popular because of their excellent solvent properties, increased the band widths to an extent which made high resolution impossible. Band widths of 10 to 20 wave-

numbers are quite common in chloroform. Under such conditions, weaker bands less than 10 wave numbers from some major band will not be properly resolved and may at best appear as shoulders. More recently, it had been recognized that hydrocarbons such as cyclohexane, hexane, heptane or any similar paraffins give far superior infrared spectra in the carbonyl region, providing the compound is sufficiently soluble [15,188]. In these solvents band widths for the carbonyl stretching vibrations are reduced to a fraction of those observed in chloroform. The extinction coefficients for carbonyl stretching modes are extremely large and therefore very dilute solutions, of the order of 10^{-3} to 10^{-4} molar give excellent spectra. The low solubility is partly compensated by the large extinction coefficients.

Secondly, the resolution of grating instruments, which are more commonly used today, is far superior to the prism spectrometers that were more popular a decade ago. In general the advanced technology of infrared spectrometers has assisted in the tabulation of extremely accurate infrared data on carbonyl stretching frequencies.

The symmetry of $Ph_3MMn(CO)_5$ is taken as C_{4V} in the force constant determination. This also applies to the rheniumpentacarbonyl series. In these approximate calculations*, the Ph_3M ligand, which has a threefold axis

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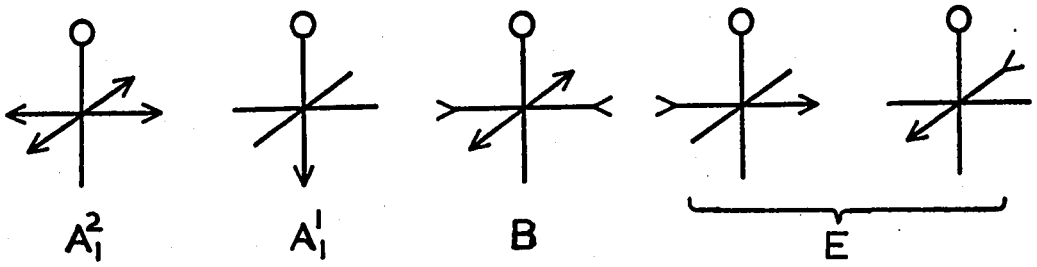
* Calculations were carried out by R.S. Gay, using the method of Cotton and Kraihanzel [51].

about the M-Mn bond, is treated as a point group since it does not appear to affect the pattern of the carbon monoxide stretching frequencies of the $Mn(CO)_5$ entity. Applying group theory, it is possible to predict the number of infrared and Raman active carbonyl vibrations [51]. Symmetry coordinates are shown schematically below:



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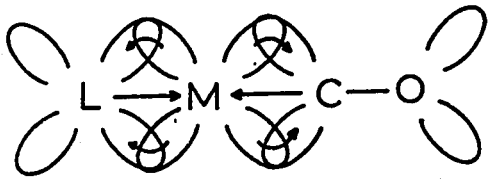
For C_{4v} symmetry, three infrared active carbonyl stretching bands are expected, two A, and a doubly degenerate E mode. These are also Raman active, while the B mode is only Raman active [51]. The E mode is the most intense band in the spectrum. Of the two A_1 modes, the A_1^2 is of highest energy, corresponding to the symmetric stretch of the four carbon monoxides in the equatorial plane. The A_1^1 mode may appear above or below the E mode or may be accidentally degenerate with it. Examples of all three possibilities may be observed in Fig. 13-16 and 20-23, the infrared spectra for $Me_{3-n}Cl_nSiM(CO)_5$ (M = Mn,Re). In Fig. 14,15, 21,22 it may be noted that the Raman active B mode is observable in the infrared, and is most intense for the

less symmetric molecules in which there are mixed substituents on the silicon atom; e.g. $Me_2ClSiMn(CO)_5$, $MeCl_2SiMn(CO)_5$, etc. The reduced symmetry, however, is not sufficient to cause splitting of the E mode as has been observed in the spectra of some fluorocarbon analogs [213]. The trimethyl and trichlorosilyl derivatives approach closest to cylindrical symmetry, which may partly account for the extremely weak B mode.

In the force constant calculations by the Cotton-Kraihanzel (CK) method [51], the use of the three infrared active bands allows the prediction of the value for the B mode. This internal consistency was thought to provide a check on the proper assignment of the modes.

As has been pointed out by Graham [86], there are important implications in the relative magnitudes of the force constants, k_1 and k_2 the force constants of the carbon monoxides *trans* and *cis* to the ligand L respectively. In the CK method, it is assumed that carbon monoxide is one of the best acceptors of π electrons; consequently k_1 is always greater than k_2. The force constant is in part a reflection of the electron population in the π antibonding orbital of carbon monoxide. The carbonyls in the equatorial plane share only one set of d orbitals with L. Since both, L and the *trans* carbon monoxide undergo π bonding with the same two transition metal d orbitals (dxz and dyz using the L-M-CO axis as the z axis) the ability of L to accept or release π electrons

is believed to influence the value for k_1 more than k_2. The competition between L and the *trans* carbon monoxide for π electrons is shown in the diagram below:



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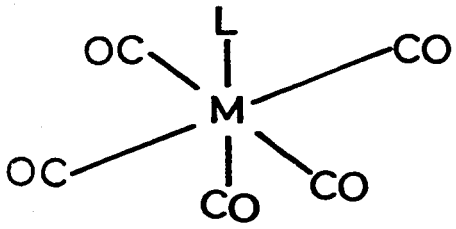

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The values for k_2 also vary with different ligands, L. Shifts of band frequencies in the infrared spectra are observed in the same direction as for the axial carbon monoxide. Highly electronegative substituents on the group IV metal shift all carbon monoxide stretching frequencies to higher values, note Fig. 13-16. For example, the CK force constants, k_1 and k_2 for $Ph_3SnMn(CO)_5$ and $Cl_3SnMn(CO)_5$ are 16.34, 16.64 and 16.91, 17.31 mdyne/Å respectively [119].

More recently, force constant calculations for $LMn(CO)_5$ have been refined by using ^{13}CO-enriched compounds. By this approach, the assumption made in the CK method, that $k_1 > k_2$ is not required and for $Ph_3MMn(CO)_5$ (M = Sn, Ge) it was found that $k_1 < k_2$ [81]. However, for several other ligands, there is reasonable agreement between the values obtained by the latter method and the CK values.

Although the reasoning behind the relationship of relative force constants and π bonding ability of ligands remains qualitatively unaltered, the assumptions made by the CK method and therefore the conclusions based on the CK values have limited justification.

3. Bonding and Structure

A question that arises is to what extent is a ligand affected by the π-acceptor ability of the group *trans* to it. Although the concept of multiple metal-metal bonding is relatively new and not universally accepted, evidence for multiple bonding is obtained from the comparison of the X-ray data for the structures of $Ph_3SnMn(CO)_5$ and $Ph_3SnMn(CO)_4PPh_3$. Triphenylphosphine in the latter molecule is in the *trans* position to the triphenyltin ligand. It is well known that with increasing bond order, the interatomic distances determining the bond are reduced. For example, the carbon-carbon bond distances in simple hydrocarbons for single, double and triple bonds are 1.54 Å, 1.34 Å and 1.20 Å respectively. The predicted tin-manganese bond distance would be 2.85 Å using half of the manganese-manganese bond distance, 1.46 Å in $Mn_2(CO)_{10}$ [60] plus half the tin-tin distance, 1.39 Å in the cyclic hexamer of diphenyl tin [175]. The tin-manganese bond distance in $Ph_3SnMn(CO)_5$ is 2.67 Å [210], a considerable short-

ening over the expected value. In $Ph_3SnMn(CO)_4PPh_3$, however, the tin manganese bond distance is even more reduced, 2.62 Å [29]. The weaker π bonding ability of the triphenylphosphine, compared to that of carbon monoxide, is believed to enhance the π bonding between the tin and manganese atoms, resulting in the reduced bond distance.

It would be interesting to note the difference in bond lengths if $Ph_3SnMn(CO)_4PPh_3$ were capable of existing in the *cis* configuration. It appears that the *cis* configuration is electronically more favored, but bulky substituents prefer the sterically less hindered *trans* arrangement. It has been vividly demonstrated that the size of substituents play an important role in determining the stereospecific arrangement in octahedral molecules [142]. For example, in species such as $(X_3M)FeX(CO)_4$ (X = Cl, Br, I; M = Ge, Sn) only the *cis* isomer was observed. For $(Cl_3M)_2Fe(CO)_4$ (M = Ge, Sn), both the *cis* and *trans* isomers have been isolated. In solution the *trans* isomer rapidly converts to the *cis* isomer. For $(X_3M)_2Fe(CO)_4$ (X = Br, I; M = Ge, Sn), however, only the *trans* isomers were detected. According to this evidence, *cis* $Ph_3SnMn(CO)_4PPh_3$ would not be expected to be stable and is not known to exist.

A classic example of multiple metal-metal bonding is displayed by $Re_2Cl_8^{-2}$ which has the shortest known rhenium-rhenium bond distance, 2.24 Å [52]. The chlorines on the adjacent rhenium atoms are eclipsed, a sterically un-

favorable arrangement, in order to be capable of attaining proper orbital overlap for a quadruple bond. This symmetric arrangement allows to rationalize a σ, two π and one δ bond [54].

EXPERIMENTAL

All anion reactions were carried out under a static atmosphere of nitrogen, and during the workup extreme care was taken to minimize exposure of compounds to air in solution or crystalline state. A detailed discussion on the handling of air sensitive compounds is given by Shriver [195].

Melting points were determined on a Kofler Hot Stage, an instrument that allows observation of minute changes on microcrystalline material. The heating rate of the sample ranged from 3° to 5°C per minute. The values thus obtained were not corrected.

For the measurement of precise infrared band positions in the carbonyl stretching region, a Perkin Elmer Model 337 grating spectrometer equipped with an expanded scale readout accessory (Part No. 220-0058) and a Hewlett Packard Model 7127A recorder was employed. Sodium chloride or potassium bromide cells having a 0.5 mm path length were used. At three inches per minute chart speed in the region between 2200 cm^{-1} to 1700 cm^{-1}, 100 cm^{-1} was recorded over 13 cm of chart paper. Each expanded spectrum was calibrated above the region of interest by introducing a gas cell containing carbon monoxide into the sample beam at the appropriate time during a continuous scan. The

bands were then measured by interpolation using CO band No. 31 as a reference point [118]. The linearity of the wavenumber scale in this interval was established by using gaseous deuterium chloride. The deviation in duplicate spectra did not exceed one cm^{-1}; thus, the quoted values are well within the limits of $\pm$ 1 cm^{-1}. The solvents for infrared purposes were either spectral grade cyclohexane or methylene chloride in case of low solubility in cyclohexane. Generally, cyclohexane solutions containing 10^{-4} to 10^{-3} molar carbonyl compounds result in spectra in which the transmittance of the major bands is 20 - 60 %. As a rough guide 1.0 to 1.5 mg/ml may be used for most complexes with molecular weights between 300 to 500.

Reagent grade THF was freed from moisture and peroxides by distillation from $LiAlH_4$, and was used immediately after purification. All other solvents employed were reagent grade without further purification.

Sodium amalgam was prepared in aliquots of 75 to 100 gm by introducing small quantities of sodium metal to vigorously stirred mercury under a nitrogen atmosphere until the total weight of sodium amounted to approximately 1.0%.

For reactions in sealed tubes, Carius tubes of approximately 60 - 70 ml volume, fitted with 14/20 standard taper joints were employed. The reaction mixture in these

was sealed under vacuum with the sample at liquid nitrogen temperature.

Chemicals were either commercially available or prepared by standard synthetic procedures as noted below. In cases where the purity was in doubt, purification by recrystallization or sublimation was performed.

Triphenylgermanium bromide, Ph_3GeBr. This was prepared using the method described by Johnson and Harris [123]. One recrystallization from a mixture of dichloromethane-hexane elevated the melting point of this material from 121-133°C to 135-138°C.

Triphenyltin chloride, Ph_3SnCl This compound was purchased from M & T Chemicals Inc. It was used without purification.

Triphenyllead chloride, Ph_3PbCl. This compound was prepared using the method described by Gilman and Robinson [82]. Tetraphenyllead (20 gm, 0.04 mol) was dissolved in refluxing chloroform. Dry hydrogen chloride was passed through the solution for 20 minutes with vigorous stirring. During this process the solution became slightly turbid. The stirring reaction mixture was refluxed for an additional 20 minutes. The reaction mixture was then allowed to cool to room temperature and filtered. A white needle-like crystalline material slowly precipitated from solution in the refrigerator. One additional recrystallization from chloroform

resulted in a melting point of 206 - 208°C.

Triphenylphosphine, Ph_3P and Triphenylsilane, Ph_3SiH. These were purchased from M & T Chemical Inc., or Peninsular Chemresearch Inc. and used without further purification.

Dimanganesedecacarbonyl, $Mn_2(CO)_{10}$. For the preparation of this complex, the method described by King [132] was followed. The product thus available was purified by slow sublimation onto a watercooled jacket at a pressure of less than 0.01 mm of mercury.

Dirheniumdecacarbonyl, $Re_2(CO)_{10}$. This synthetic method is described in reference 132. Dirhenium heptoxide, Re_2O_7, (50 gms, 0.02 moles), available from Alfa Inorganics Inc., was placed in a 500 ml rocking autoclave. Approximately 50 ml of small glass beads were added, to assist agitation. After flushing once with 500 psi of carbon monoxide, the autoclave was pressurized to 3100 psi of carbon monoxide. The temperature was slowly raised to 240°C. With continuous slow rocking this temperature was maintained for 20 hrs. After cooling the equipment to room temperature, the combined mixture of black appearance was placed in a large sublimer. At 40 - 50°C and a pressure less than 0.01 mm mercury, $Re_2(CO)_{10}$ was deposited on the water cooled probe. After an additional sublimation, pure white crystalline material was obtained. The yield of $Re_2(CO)_{10}$ was 45.7 gm, approximately 62%.

Triphenylgermaniummanganesepentacarbonyl, $Ph_3GeMn(CO)_5$. A solution of 5.7 gm Ph_3GeBr (15.0 mmol) in 20 ml dry THF was slowly added to a THF solution containing $Na^+[Mn(CO)_5]^-$ (15.4 mmol), prepared from 3.0 gm $Mn_2(CO)_{10}$ in 45 ml dry THF over excess sodium amalgam. After addition was complete, the mixture was magnetically stirred at room temperature for an additional 30 minutes. The solvent was removed at reduced pressure and the dirty gray residue was extracted with several 40-ml aliquots of hot hexane. The combined extracts were filtered hot and then slowly cooled in the refrigerator. A coarse white crystalline material precipitated from solution. The solvent was decanted and the crystalline product dried at reduced pressure. The melting point of $Ph_3GeMn(CO)_5$ was sharp at 162 - 164°C (lit. mp 162 - 164°C) [194] after an additional recrystallization from hexane.

Triphenyltinmanganesepentacarbonyl, $Ph_3SnMn(CO)_5$

A solution of 5.8 gm Ph_3SnCl (15.4 mmol) in 20 ml dry THF was slowly added to a vigorously stirred solution of $Na^+[Mn(CO)_5]^-$ (15.4 mmol) prepared from 3.0 gm $Mn_2(CO)_{10}$ in 45 ml dry THF over excess sodium amalgam. After addition was complete, stirring at room temperature was prolonged for an additional 30 minutes. The solvent was stripped off at reduced pressure, resulting in a dirty gray oily residue. This was extracted with several 40-ml aliquots of hot hexane. The combined hot solution was filtered and then slowly

cooled in the refrigerator. A coarse white crystalline material precipitated from the solution. The hexane was poured off and the product dried at reduced pressure. Recrystallization from hot hexane resulted in a product, $Ph_3SnMn(CO)_5$ melting sharply at 150 - 151°C (lit. mp 150-152°C) [85].

Triphenylleadmanganesepentacarbonyl, $Ph_3PbMn(CO)_5$.

A solution of 7.1 gm Ph_3PbCl (15.4 mmol) in 20 ml THF was slowly added to a vigorously stirring solution of $Na^+[Mn(CO)_5]^-$ (15.4 mmol) prepared from 3.0 gm of $Mn_2(CO)_{10}$. After the mixture was stirred for an additional 30 minutes, the THF was removed at reduced pressure leaving a dirty brown residue. This was extracted with several small aliquots of hot hexane. The combined solution was filtered hot and slowly cooled in the refrigerator. Pale yellow, coarse plate-like crystals precipitated. The solvent was decanted and the product dried in vacuum. The melting point of $Ph_3PbMn(CO)_5$ was 141 - 144°C (lit. mp 146-148°C) [85]. Exposure to light for a prolonged period of time darkens this complex; however, a sample stored in the dark under nitrogen showed no visible change in three years.

Trichlorotinmanganesepentacarbonyl, $Cl_3SnMn(CO)_5$.

Dry chlorine gas was passed through a solution of 1.5 gm $Ph_3SnMn(CO)_5$ (2.8 mmol) in 40 ml dichloromethane at room temperature for 20 minutes. The solution turned slowly from colorless to pale yellow. Excess chlorine and

dichloromethane were removed at a reduced pressure yielding a yellow crystalline solid. This was recrystallized from hot carbon tetrachloride. Slow cooling of the hot filtrate in a refrigerator precipitated pale yellow needles of $Cl_3SnMn(CO)_5$ (0.69 gms, 60%), which decomposed above 174°C (lit. dec. 168°C)[85].

Tribromotinmanganesepentacarbonyl, $Br_3SnMn(CO)_5$.

A solution of 1.5 gm $Ph_3SnMn(CO)_5$ (2.8 mmol) in 40 ml of carbon tetrachloride was brought to reflux. Bromine was slowly added until the brown color persisted. The mixture was then refluxed with stirring for an additional 25 minutes. This was then filtered hot and the excess bromine and carbon tetrachloride stripped off at reduced pressure, resulting in a yellow crystalline solid. Recrystallization from hot carbon tetrachloride yielded a yellow crystalline solid, $Br_3SnMn(CO)_5$ (0.92 gms, 74% yield), melting at 148 - 150°C (lit. mp 145 - 147°C)[85].

Triphenyltintriphenylphosphinemanganesetetracarbonyl, $Ph_3SnMn(CO)_4PPh_3$.

Method A.

A solution of 200 ml cyclohexane containing 4.0 gm $Mn_2(CO)_{10}$ (8.2 mmol) and 9.0 gm PPh_3 (3.4 mmol) was exposed to ultraviolet irradiation for 14 hours using a 450 watt Hanovia lamp in a water cooled quartz jacket. An orange microcrystalline product precipitated. This was filtered

off and dried resulting in 3.60 $Mn_2(CO)_8(PPh_3)_2$. The filtrate was exposed to ultraviolet light for an additional 22 hours yielding an additional 3.40 gm of $Mn_2(CO)_8(PPh_3)_2$. The combined product, $Mn_2(CO)_8(PPh_3)_2$ (7.0 gm) corresponds to 80% yield based on the amount $Mn_2(CO)_{10}$ used. One gm of the orange microcrystalline product was recrystallized twice from dichloromethane-hexane mixtures. The coarse, reddish-orange, crystalline material had a melting point of 127 - 130°C (lit. mp 189 - 190°C) [176]. In dichloromethane the infrared spectrum in the carbonyl region shows one strong band at 1952 cm^{-1} plus a medium shoulder at 1980 cm^{-1}.

Anal. Calc. for $C_{44}H_{30}Mn_2O_8P_2$: C, 61.5; H, 3.5; P, 7.2. Found: C, 61.5; H, 3.7; P, 6.2.

The sodium salt, $Na^+[Mn(CO)_4PPh_3]^-$ was prepared from 2.0 gm $Mn_2(CO)_8(PPh_3)_2$ (2.3 mmol) in vigorously stirring dry THF over sodium amalgam. After 20 minutes, the amalgam was removed and the solution cleared of any adhering amalgam by washing with several aliquots of pure mercury. A solution of 1.1 gm Ph_3SnCl (2.3 mmol) in 25 ml dry THF was slowly added. After addition was complete, the reaction mixture was stirred for an additional 30 minutes at room temperature. The THF was removed at reduced pressure and the residue extracted with dichloromethane. Pentane was slowly added to the clear filtrate until the solution became slightly turbid. Slow cooling of this mixture in the refrigerator resulted in the formation of

white needle-like crystalline material. An additional recrystallization from the same solvent pair resulted in a crystalline product $Ph_3SnMn(CO)_4PPh_3$, melting at 226 - 228°C.

Method B.

A mixture of 1.5 gm $Ph_3SnMn(CO)_5$ (2.8 mmol) and 0.79 PPh_3 (3.0 mmol) was sealed under vacuum in a 60 - 70 ml thick walled Pyrex tube without solvent. The tube was heated at 160°C for five hours. After the tube cooled slowly to room temperature, it was further cooled to liquid nitrogen temperature and cracked open to release the carbon monoxide formed. The crystalline residue was extracted with dichloromethane and filtered. Hexane was slowly added until the mixture became slightly turbid. A white crystalline product precipitated slowly at refrigerator temperature. The product, $Ph_3SnMn(CO)_4PPh_3$ was identical in all respects to that obtained by method A.

Triphenylsilylmanganesepentacarbonyl, $Ph_3SiMn(CO)_5$

Method A.

A solution of 2.61 gm Ph_3SiH (10 mmol) and 1.96 gm $Mn_2(CO)_{10}$ (5.0 mmol) was refluxed in methylcyclohexane for 140 hours. The progress of the reaction was followed by infrared spectroscopy, which gave evidence of a new band near 2100 cm^{-1} after 24 hours. To a 35 ml aliquot of methylcyclohexane solution was added 15 gm Florisil (100-200

mesh) and the solvent was removed at reduced pressure on a rotary evaporator. The adsorbed sample was then placed on a 2.2 x 17 cm Florisil column made up with hexane. Elution with hexane yielded first a yellow band $Mn_2(CO)_{10}$ by infrared) followed slowly by a colorless oil, Ph_3SiH. Continued elution with hexane-benzene (1:1) yielded $Ph_3SiMn(CO)_5$ which was recrystallized from hexane. The overall yield based on $Mn_2(CO)_{10}$ was approximately 8%.

Method B

A mixture of 1.5 gm Ph_3SiH (5.8 mmol) and 1.0 gm $Mn_2(CO)_{10}$ (2.6 mmol) was heated in a sealed evacuated tube at 160 - 165°C, during which two layers were present and gas evolution was noted at the interphase. After 35 hours the tube was cooled to room temperature, then to liquid nitrogen temperature and opened to release the gas pressure produced in the reaction. From the mixture, the unreacted $Mn_2(CO)_{10}$ was sublimed off under vacuum at room temperature. The residue was recrystallized from hexane, affording 0.41 gm $Ph_3SiMn(CO)_5$ (35% yield).

Triphenylrheniumpentacarbonyl, $Ph_3SiRe(CO)_5$

A mixture of 1.79 gm Ph_3SiH (6.9 mmol) and 1.50 gm $Re_2(CO)_{10}$ (2.3 mmol) was sealed under vacuum in a 60 - 70 ml Carius tube at liquid nitrogen temperature. The tube was heated at 160 - 165°C for 24 hours. After cooling to room temperature, the tube was further cooled to liquid

nitrogen temperature and opened to release the gas pressure. The solid product was adsorbed onto 20 gms of Florisil with dichloromethane. The dry adsorbed material was placed on top of a Florisil column (16 x 2.2 cm) made up with hexane. Elution with hexane resulted first in $Re_2(CO)_{10}$ (by infrared) then Ph_3SiH. Continued elution with benzene-hexane mixtures (1:1) yielded a Ph_3SiH - $Ph_3SiRe(CO)_5$ mixture. This was recrystallized twice from hot hexane, which on cooling resulted in pure $Ph_3SiRe(CO)_5$ melting at 157 - 158°C.

TABLE IV

Analytical Data, Melting Points and Color of Group IV Derivatives

Compound	mp°C	Color	Calculated % C	Calculated % H	Found % C	Found % H
$Ph_3SiMn(CO)_5$	160-163	white	60.80	3.33	60.99	3.46
$Ph_3GeMn(CO)_5$	162-164	white	55.37	3.03	55.44	3.18
$Ph_3SnMn(CO)_5$	150-152	white	50.69	2.77	50.47	2.79
$Ph_3PbMn(CO)_5$	142-144	yellow	-	-	-	-
$Ph_3SiRe(CO)_5$	157-158	white	47.17	2.58	47.70	2.60
$Cl_3SnMn(CO)_5$	d < 174	p.yellow	-	-	-	-
$Br_3SnMn(CO)_5$	146-148	yellow	10.85	0.00	11.14	0.00
$Ph_3SnMn(CO)_4PPh_3$	210-213	white	61.65	3.88	61.68	3.79

TABLE V

Carbonyl Stretching Frequencies [a] and Assignments

Compound	A_1^2	B	A_1^1	E
$Ph_3SiMn(CO)_5$	2098	2030	2003	2003
$Ph_3GeMn(CO)_5$	2097	2032	2002	2006
$Ph_3SnMn(CO)_5$	2093	2027	2002	2002
$Ph_3PbMn(CO)_5$	2091	2029	2003	2003
$Ph_3SiRe(CO)_5$	2118	2044	2003	2012
$Cl_3SnMn(CO)_5$	2126	--	2039	2046
$Br_3SnMn(CO)_5$	2122	2060	2037	2043
$Ph_3SnMn(CO)_4PPh_3$	--	--	--	1952

[a] In cyclohexane, cm^{-1}

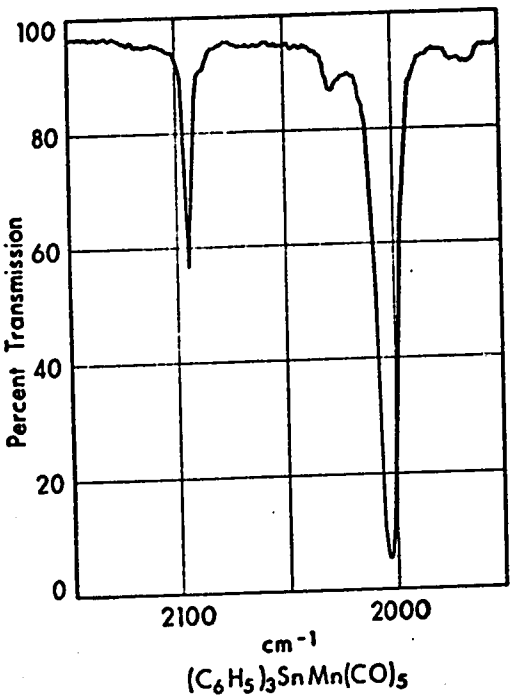


Figure 1

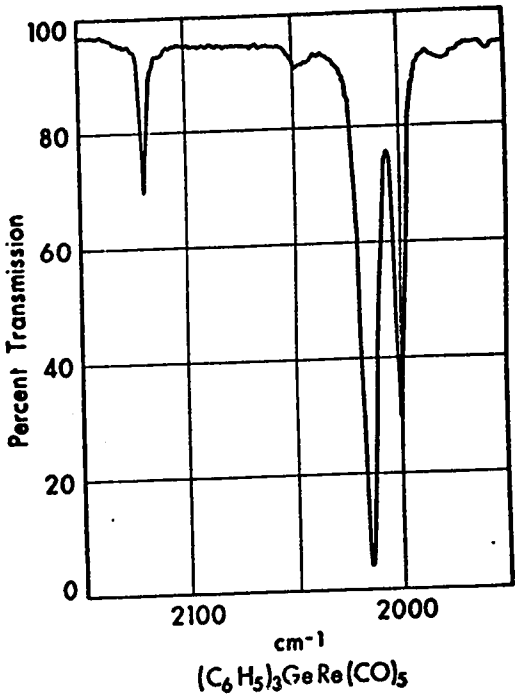


Figure 2

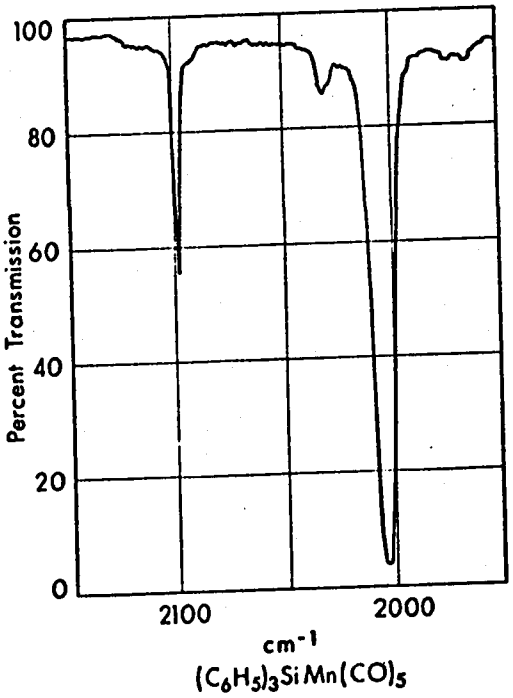


Figure 3

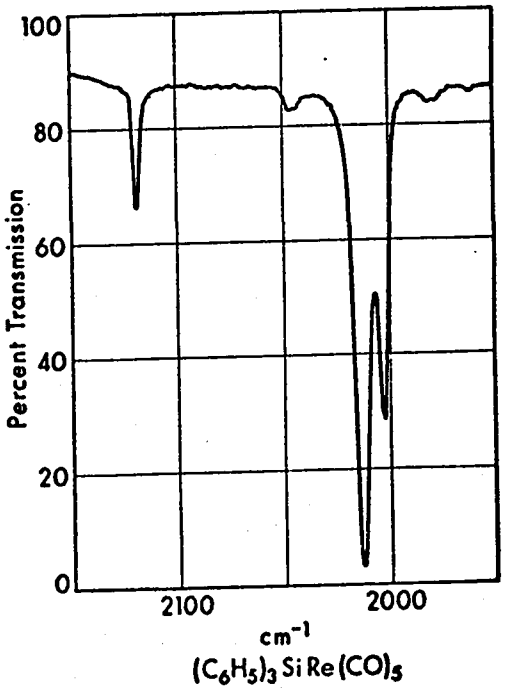


Figure 4

CHAPTER III

Thermal Reactions of Silanes with Transition Metal Carbonyls

Introduction

The first silyl-transition metal carbonyl complex with a covalent metal-metal bond, $Me_3SiFe(CO)_2Cp$, reported in 1956 by Piper *et al.*, was prepared in an anion reaction employing Me_3SiCl and $Na^+[Fe(CO)_2Cp]^-$ [187]. This complex remained the only known compound of this type until 1965 when Chalk and Harrod obtained $R_3SiCo(CO)_4$, (R = Cl, Ph, EtO, etc.) from the reaction of R_3SiH with $Co_2(CO)_8$ [37]. The present investigation, employing the latter approach, resulted in numerous silyl-transition metal complexes and proved this synthetic route a general method for the preparation of silyl-transition metal bonds.

More recently several studies of silyl-transition metal bonding have been reported. From a structural standpoint, $CH_2 = CHSiCo_3(CO)_9$ and $[SiCo_3(CO)_9]_2$ reported by Kettle [128] appear exceedingly interesting, although there is now some reason to doubt their existence [87,138]. Aylett and Campbell synthesized several of the parent silyl derivatives such as $H_3SiCo(CO)_4$ [6], $H_3SiMn(CO)_5$ [7] and $(H_3Si)_2Fe(CO)_4$ [9] by employing the carbonylate anions and H_3SiI. The formation of $Me_3SiM(CO)_3Cp$ (M = Mo,W) in reactions between Me_3SiNMe_2 and $HM(CO)_3Cp$ has been reported by Lappert *et al.*[32] The reaction of $Fe(CO)_5$ or $Ni(CO)_4$ with

Ph_3SiLi results in the corresponding anions, $Ph_3SiFe(CO)_4^-$ and $Ph_3SiNi(CO)_3^-$ [143]. It was found after the initial results of the present work had been communicated [120] that Cl_3SiH and $Ru_3(CO)_{12}$ react to form $[Cl_3SiRu(CO)_4]_2$ [56].

RESULTS AND DISCUSSION

1. Syntheses and Chemical Properties.

The thermal reactions of silanes with dinuclear transition metal carbonyls yield silyl derivatives of transition metal carbonyl complexes. The formation of the silicon transition metal bond requires the breaking of transition metal-metal and silicon-hydrogen bonds. This process can be represented in the following general terms:

$$M\text{-}M + HSi \xrightarrow{\Delta} H\text{-}M + Si\text{-}M \qquad [III.1]$$

The transition metal hydride thus formed may further react in two possible ways as is suggested by equations III.2 and III.3:

$$2H\text{-}M \longrightarrow H_2 + M\text{-}M \qquad [III.2]$$

$$H\text{-}M + HSi \longrightarrow H_2 + Si\text{-}M \qquad [III.3]$$

Reaction III.2 would regenerate starting material, which in turn would react with more silane and according to equation III.3 the hydride would react directly with silane and form product. There is evidence that both processes may be occurring simultaneously. For example, $HMn(CO)_5$ is not stable thermally. It dimerizes above room temperature to $Mn_2(CO)_{10}$ with the elimination of hydrogen [111]. MacDiarmid *et al.* found that the formation of $Me_3SiMn(CO)_5$ required temperatures

between 130 - 140°C, when $Mn_2(CO)_{10}$ and Me_3SiH were employed, whereas with $HMn(CO)_5$ and Me_3SiH the reaction proceeds at 25°C [150].

Of the dinuclear transition metal carbonyls, only $Co_2(CO)_8$ is known to react with silanes at room temperature* [37]. Other carbonyls require temperatures between 70 - 180°C to proceed at a reasonable rate. Since most silanes employed boil below the reaction temperature, closed reaction vessels which are capable of withstanding considerable pressure must be employed. For example, the boiling points of Cl_3SiH and Me_3SiH are 33°C and 7°C respectively. Thick walled Pyrex tubes, known as Carius tubes, are most convenient. These can be sealed with the reactants under vacuum. With trichlorosilane, reactions at temperatures up to 200°C have been carried out successfully in these tubes.

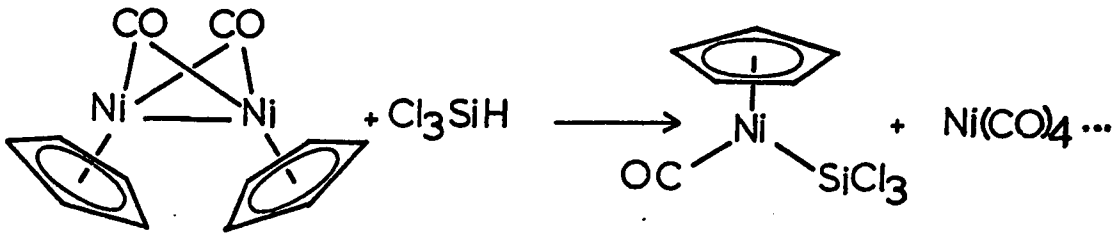
The yields of the products in these reactions vary from 5 - 100% based on the carbonyl starting material. Silane is used in excess and generally serves also as the reaction solvent. Carbon monoxide, which is always formed in the partial decomposition in most reactions appears to help stabilize the carbonyl products and starting materials at the reaction temperature. Reactions with carbonyls such as $Re_2(CO)_{10}$,

---

* The reaction of $[CpNi(CO)]_2$ and Cl_3SiH which was carried out at 45 - 50°C in a sealed tube probably proceeds at room temperature at a moderate rate.

$Mn_2(CO)_{10}$ or $Fe(CO)_5$ are almost quantitative, while those with $[CpNi(CO)]_2$ and $[CpMo(CO)_3]_2$ form considerable quantities of $Ni(CO)_4$ and $Mo(CO)_6$. For example, the reactions of Cl_3SiH and $Re_2(CO)_{10}$ is rapid and almost quantitative at 160°C to yield $Cl_3SiRe(CO)_5$, whereas the synthesis of $Cl_3SiNi(CO)Cp$ in the reaction of Cl_3SiH and $[CpNi(CO)]_2$ is accompanied by extensive decomposition.

$$Re_2(CO)_{10} \xrightarrow{Cl_3SiH} Cl_3SiRe(CO)_5 + H_2 \qquad [III.4]$$



14 15

[III.5]

The relative rates at which these reactions proceed appear to depend to a great extent on the total electronegativity of the substituents on the silyl starting material. If $Mn_2(CO)_{10}$ is reacted under similar conditions with a series of silanes such as $Me_{3-n}Cl_nSiH$, the reaction rate increases by a factor of approximately ten when n is increased by one. For example, the reaction of Cl_3SiH and $Mn_2(CO)_{10}$ yields quantitatively $Cl_3SiMn(CO)_5$ at 130°C in approximately 4 - 5 hours, while the reaction of Me_3SiH and $Mn_2(CO)_{10}$ at 160°C showed considerable quantities of unreacted $Mn_2(CO)_{10}$ after 20 hours.

$$Mn_2(CO)_{10} \xrightarrow{Me_{3-n}Cl_nSiH} Me_{3-n}Cl_nSiMn(CO)_5 + H_2 \quad [III.6]$$

The influence on the reaction rates of phenyl or hydrogen is approximately the same as that of methyl groups. A similar trend is observed with different transition metal carbonyls. For example, the relative ease with which Cl_3SiH appears to react with the dinuclear carbonyls is shown below:

$$[CpCr(CO)_3]_2 < Mn_2(CO)_{10} < [CpFe(CO)_2]_2 < Co_2(CO)_8 \leqslant [CpNi(CO)]_2$$

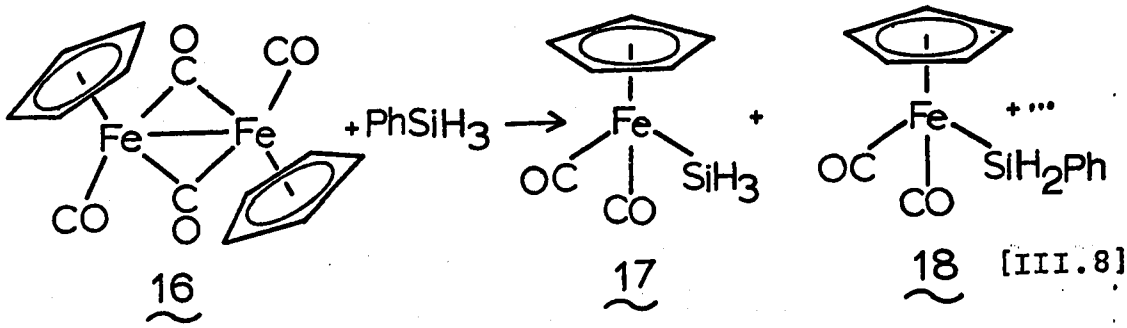
The products of reactions between silanes and dinuclear transition metal carbonyls are not always predictable. In some cases more than one silyl transition metal derivative is isolated; in such cases, by the proper choice of reaction conditions the course of the reaction can sometimes be controlled to yield mainly the desired component. For example, the reaction of Ph_2SiH_2 and $Mn_2(CO)_{10}$ between 140 - 150°C yields only $Ph_2HSiMn(CO)_5$. Above 150°C for a prolonged period of time the reaction yields $[Ph_2SiMn(CO)_4]_2$, as well as $Ph_2HSiMn(CO)_5$ and a substantial quantity of decomposed material.

$$Mn_2(CO)_{10} \xrightarrow[140\text{-}150°C]{Ph_2SiH_2} Ph_2HSiMn(CO)_5 + H_2 \quad [III.7]$$

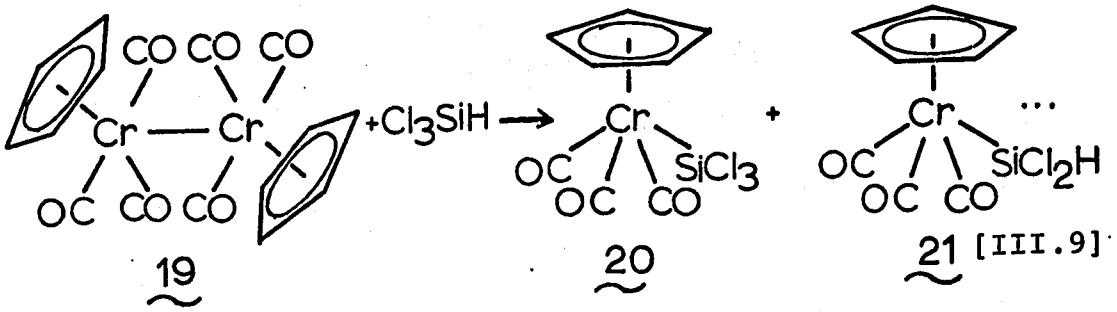
$$Mn_2(CO)_{10} \xrightarrow[\text{above } 150°C]{Ph_2SiH_2} Ph_2HSiMn(CO)_5 + [Ph_2SiMn(CO)_4]_2 + \ldots \quad \text{[III.7a]}$$

The formation of $[Ph_2SiMn(CO)_4]_2$ appears to resemble the formation $[ClMn(CO)_4]_2$ from $ClMn(CO)_5$ [38]. In both processes carbon monoxide is lost upon heating in the formation of the dimers. The reaction of Ph_2SiH_2 and $[CpFe(CO)_2]_2$ on the other hand, at similar conditions yields only $Ph_2HSiFe(CO)_2Cp$, showing no signs of other silyl derivatives or decomposition.

The reaction of $PhSiH_3$ and $[CpFe(CO)_2]_2$ at 130 - 140°C yields approximately equimolar quantities of $Ph\ H_2SiFe(CO)_2Cp$ and $H_3SiFe(CO)_2Cp$ and similarly, the reaction of Cl_3SiH and $[CpCr(CO)_3]_2$ at 120 - 130°C yields $Cl_3SiCr(CO)_3Cp$ and $HCl_2SiCr(CO)_3Cp$.



16 17 18 [III.8]



19 20 21 [III.9]

Both reactions are extremely slow below 100°C, and at the elevated temperatures formation of the two products in each of the reactions appears to take place at approximately the same rate. Considerable decomposition is also observed.

The breaking of bonds other than silicon-hydrogen on the silyl starting materials is relatively uncommon in these reactions, suggesting that other more complex processes are occurring than is indicated by the general reactions, equations III 1-3.

Silicon-transition metal bonds can also be synthesized in which, formally, one carbon monoxide molecule is replaced by two silyl groups, shown by the general equation below:

$$(OC)_nM + 2\ H\text{-}Si \xrightarrow{\Delta} (OC)_{n-1}M\begin{matrix}Si\\Si\end{matrix} + CO + H_2 \qquad [III.10]$$

Examples of these are $(Cl_3Si)_2Fe(CO)_4$ and $(Cl_3Si)_2Co(CO)Cp$, which are formed in reactions of Cl_3SiH and $Fe(CO)_5$ or $CpCo(CO)_2$ respectively. These reactions proceed at relatively high temperature and the possibility exists that the carbonyl starting material forms first some type of polynuclear species (e.g. $Fe_3(CO)_{12}$) which then reacts with the silane to form the observed product.

The reaction of Cl_3SiH and $CpCo(CO)_2$, yielding $(Cl_3Si)_2Co(CO)Cp$ also forms a substantial quantity of $Cl_3SiCo(CO)_4$, as well as unidentified black residues. Replacement of the cyclopentadienyl ring by carbon monoxide

from decomposition is also observed in the reaction of Cl_3SiH and $[CpMo(CO)_3]_2$, which yields $Mo(CO)_6$ in addition to $Cl_3SiMo(CO)_3Cp$. Dicobalt octacarbonyl, if formed in the reaction, would react with Cl_3SiH to form $Cl_3SiCo(CO)_4$ [37].

A temperature dependence of the products is also observed in the reactions of Cl_3SiH and $Fe_3(CO)_{12}$ or $Fe(CO)_5$. If $Fe_3(CO)_{12}$ and Cl_3SiH are employed, the reaction proceeds at 70 - 80°C forming $(Cl_3Si)_2Fe(CO)_4$ in near quantitative yield. At the same temperature $Fe(CO)_5$ and Cl_3SiH show no appreciable reaction, but between 140 - 150°C $(Cl_3Si)_2Fe(CO)_4$ forms rapidly in high yield. If the same reaction mixtures are heated above 160°C, the major product is $[Cl_2SiFe(CO)_4]_2$. In all these reactions, minute quantities of a compound, later recognized as $Cl_3SiHFe(CO)_4$, were observed in the infrared spectra of the crude products. This hydride, a liquid at room temperature, was not isolated from these reactions because of its extreme sensitivity to air. (cf. Chapter V; the ultraviolet irradiation of $Fe(CO)_5$ and Cl_3SiH yields $Cl_3SiHFe(CO)_4$).

It appears that in these reactions, the hydride $Cl_3SiHFe(CO)_4$ is an intermediate which subsequently reacts to form the other observed products. To account for these, several reasonable reaction paths can be suggested for the above processes:

$$Fe(CO)_5 + Cl_3SiH \rightarrow Cl_3SiHFe(CO)_4 + CO \qquad [III.11]$$

$$2Cl_3SiHFe(CO)_4 \rightarrow H_2 + [Cl_3SiFe(CO)_4]_2 \qquad [III.12]$$

$$Cl_3SiHFe(CO)_4 + Cl_3SiH \rightarrow H_2 + (Cl_3Si)_2Fe(CO)_4 \qquad [III.13]$$

$$[Cl_3SiFe(CO)_4]_2 + Cl_3SiH \rightarrow Cl_3SiHFe(CO)_4 + (Cl_3Si)_2Fe(CO)_4 \qquad [III.14]$$

$$[Cl_3SiFe(CO)_4]_2 \rightarrow (Cl_3Si)_2Fe(CO)_4 + "Fe(CO)_4"$$
$$"Fe(CO)_4" + Cl_3SiH \rightarrow Cl_3SiHFe(CO)_4 \qquad [III.15]$$

$$2(Cl_3Si)_2Fe(CO)_4 \rightarrow 2Cl_4Si + [Cl_2SiFe(CO)_4]_2 \qquad [III.16]$$

The product in equation III.12 has been synthesized from $Cl_3SiHFe(CO)_4$ in the presence of tetrafluoroethylene, as described in Chapter V. When $[Cl_3SiFe(CO)_4]_2$ is heated in a sealed tube above 100°C, the products shown in equation III.17 are formed.

$$[Cl_3SiFe(CO)_4]_2 \xrightarrow{\Delta} [Cl_2SiFe(CO)_4]_2 + Cl_4Si + Fe(CO)_5 \qquad [III.17]$$

Equation III.14 is analogous to the suggested pathway for the reaction of $Co_2(CO)_8$ and Cl_3SiH [37]. The net change in equations III.14 and III.15 is identical. To understand the complexity of these reactions more data is required than is presently at hand. The reaction of Cl_3SiH and $[CpFe(CO)_2]_2$ is also exceedingly complex, and forms the subject of Chapter IV.

The successful isolation of a certain product in these

reactions is greatly dependent upon the thermal stability of the complex in the reaction mixture at the reaction temperature. If the breakdown of a species or further reaction steps are faster than its formation, then yields of this specific component will be extremely low. For example, if $Cl_3SiHFe(CO)_4$ is an intermediate in the reaction of $Fe_3(CO)_{12}$ and Cl_3SiH, then above 70°C it would rapidly react to form $(Cl_3Si)_2Fe(CO)_4$.

The physical and chemical properties of the silyl transition metal carbonyls allow the use of usual experimental techniques in the isolation of the complexes from their reaction mixtures. Two of the most conveniently employed techniques for the purification of these compounds are crystallization from hexane and sublimation under high vacuum.

Handling of these complexes in their pure crystalline state in air for periods up to one hour results in no noticeable decomposition in most cases, but in the crude state or in solution, decomposition takes place very rapidly, especially if the sample is exposed to light. For a series of complexes such as $Me_{3-n}Cl_nSiMn(CO)_5$, the solubility in hexane increases as is shown below:

$$Cl_3SiMn(CO)_5 < MeCl_2SiMn(CO)_5 < Me_2ClSiMn(CO)_5 < Me_3SiMn(CO)_5$$

For example, in hexane, $Cl_3SiMn(CO)_5$ crystallizes quite

rapidly at approximately 0°C, while a hexane solution of $Me_3SiMn(CO)_5$, cooled to -78°C, slowly crystallizes $Me_3SiMn(CO)_5$. Melting points of these compounds follow the reverse order, i.e., $Cl_3SiMn(CO)_5$ is the highest melting.

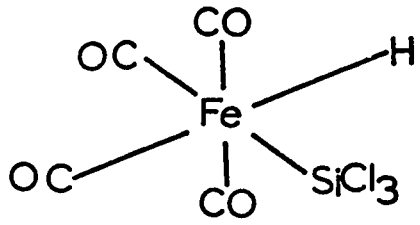
For sublimation, the triphenyl- and diphenylsilyl-derivatives such as $Ph_3SiMn(CO)_5$ and $Ph_2HSiMn(CO)_5$, show exceedingly low vapour pressures, making this isolation technique inconvenient, but the methylchloro-series such as $Me_{3-n}Cl_nSiRe(CO)_5$ and $Me_{3-n}Cl_nSiFe(CO)_2Cp$ show vapour pressure trends which are similar to the solubility order shown above. For example $Cl_3SiMn(CO)_5$ sublimes above 60°C at a pressure less than 0.01 mm mercury and is efficiently deposited onto a water-cooled probe. The trimethyl analog, $Me_3SiMn(CO)_5$ sublimes rapidly at room temperature under vacuum. To prevent the product from passing into the cold trap, the probe should be cooled to -78°C.

To safeguard against the toxicity of these complexes, which is unknown but probably high, the experiments were carried out in the fume hood. Iron pentacarbonyl is an extreme example of a volatile highly toxic material; its handling in the fume hood is absolutely essential. Some of the methylsilyl derivatives also display unpleasant odors (e.g. $Me_3SiMn(CO)_5$, $(MeCl_2Si)_2Fe(CO)_4$).

2. Infrared Spectra

Application of group theory to carbonyl complexes of regular molecular symmetry allows the prediction of the maximum possible infrared and Raman active carbon monoxide vibrations [51]. In molecules with unsymmetric substituents, the reduced symmetry occasionally allows observation in the infrared of vibrations, which would be only Raman-active in the fully symmetric molecule. The monosubstituted octahedral system is described in Chapter II. For $LM(CO)_5$, which has a C_{4v} symmetry, three infrared-active modes are predicted and observed.

The disubstituted octahedral complexes may exist in either the *cis* or *trans* configuration. For *trans*-$L_2M(CO)_4$, which has a D_{4h} symmetry, only one infrared active mode is predicted, while *cis*-$L_2M(CO)_4$ has a C_{2v} symmetry for which four infrared active modes are predicted[51]. Note in Chapter II for $Ph_3SnMn(CO)_4PPh_3$, only one carbon monoxide vibration was observed, consistent with a C_{4v} symmetry in which the Ph_3Sn and Ph_3P groups are in a *trans* arrangement. On the other hand, $Cl_3SiHFe(CO)_4$, $(Cl_3Si)_2Fe(CO)_4$, $[Cl_2SiFe(CO)_4]_2$ and $[Ph_2SiMn(CO)_4]_2$, each show four relatively strong carbon monoxide stretching vibrations, consistent with the *cis* arrangement:



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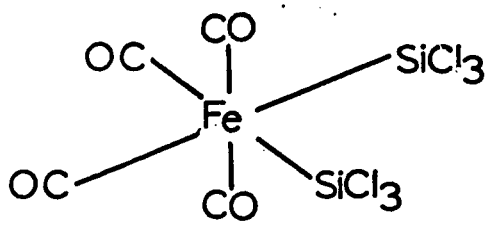

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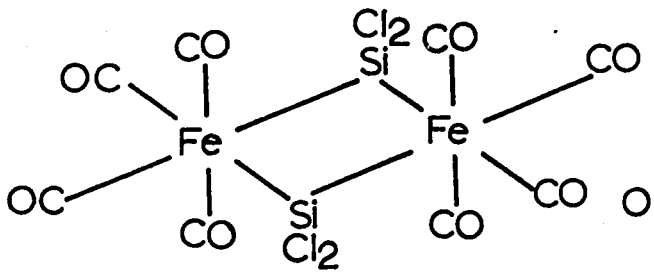

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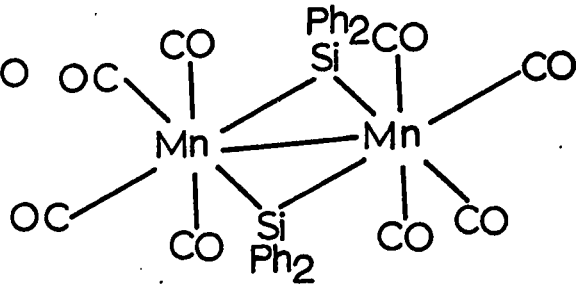

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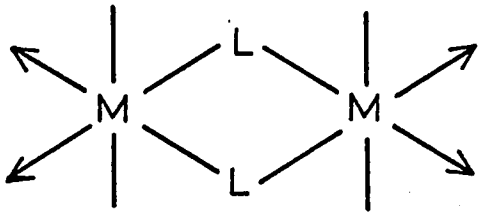
The infrared spectra of these complexes are shown in Figures 91, 42 and 45, 44. For $[Cl_2SiFe(CO)_4]_2$ and $[Ph_2SiMn(CO)_4]_2$ the infrared spectra yield essentially the same number of carbon monoxide stretching bands as would be predicted for the symmetric halves of the molecules. If the four membered silyl-transition metal ring is planar, then the molecules are highly symmetric and only four carbon monoxide stretching bands are predicted. Coupling between certain carbon monoxide vibrations on adjacent metals can result in zero

dipole moments:

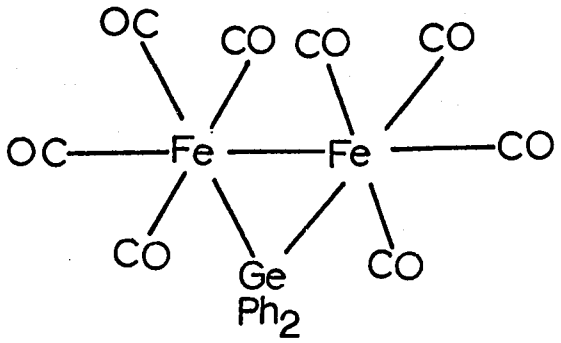


26

IR inactive mode

This type of structure is borne out for $[Ph_2SiMn(CO)_4]_2$ by the preliminary X-ray crystallographic results [62] which yield a planar silyl-manganese ring system with a manganese-manganese distance of 2.874 Å.

For $Ph_2GeFe_2(CO)_8$ [27], a monobridging analog, the symmetry is greatly reduced; consequently a greater number of carbonyl stretching modes are infrared active. This molecule shows seven carbon monoxide stretching bands in the infrared spectrum.



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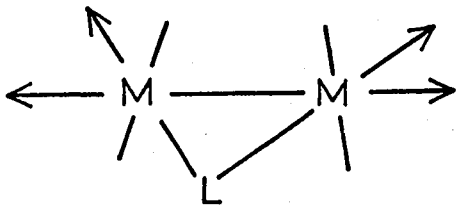
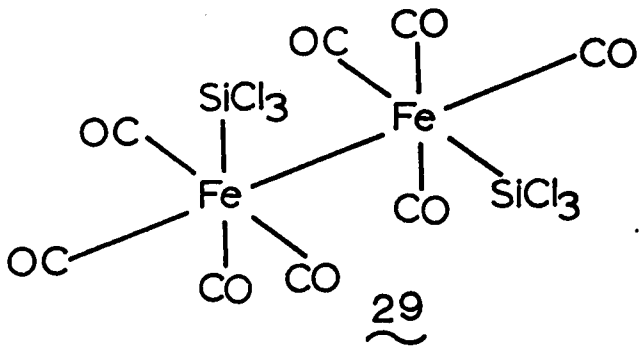


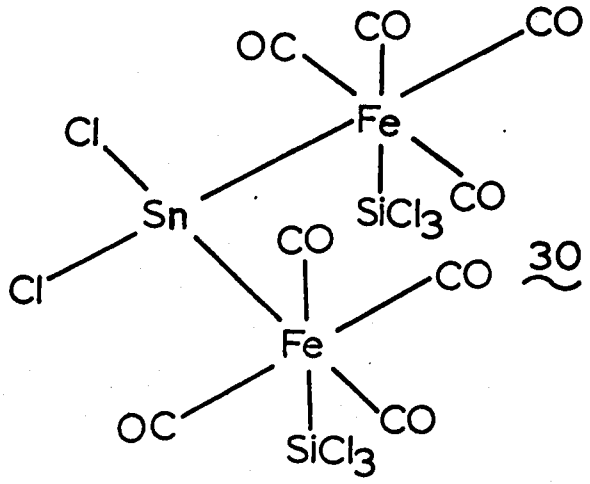
28

IR active mode

Prediction of the number of infrared active carbon monoxide stretching bands is difficult for molecules which do not have rigidly defined structures:



29



30

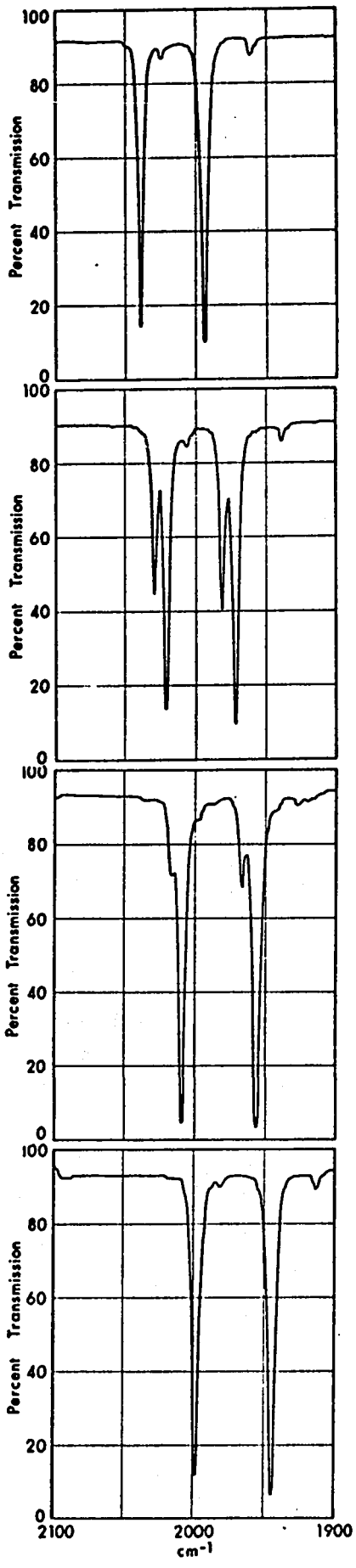
The infrared spectra of these molecules are shown in Figures 70 and 97-98. Rotation about the iron-iron bond in $[Cl_3SiFe(CO)_4]_2$ or rotation about the iron-tin

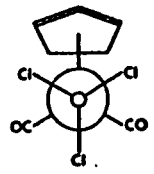
bonds in $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ provides for numerous conformations. One can predict the number of bands for various reasonable conformations and combinations of *cis* and *trans* geometry and compare these with the number observed.

3. Conformational Effects

Molecules in which rotation about a specific bond can bring about structurally different isomers may display conformational effects in their infrared spectra, as well as in other physical phenomena. The infrared spectra of the symmetric molecules, $Cl_3SiFe(CO)_2Cp$ and $Me_3SiFe(CO)_2Cp$, shown in Fig. 24 and 27 do yield the number of predicted carbonyl stretching bands. Figures 25 and 26 are the infrared spectra of the unsymmetric analogs, $MeCl_2SiFe(CO)_2Cp$ and $Me_2ClSiFe(CO)_2Cp$. Both of these complexes contain two carbonyl ligands, but show four relatively strong carbonyl stretching bands. This unexpected feature, in which the number of carbon monoxide stretching vibrations exceed the number of carbon monoxide ligands in a molecule, strongly suggests the presence of conformational isomers in solution. Rotation about the iron-silicon bond is believed to cause these effects. The Newman projections of the possible isomers causing the observed infrared spectra are depicted in Figures 5 - 8.

With reference to the Newman representation of

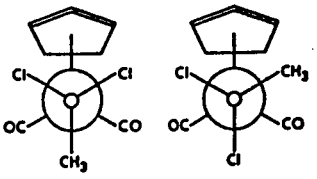




I

Figure 5

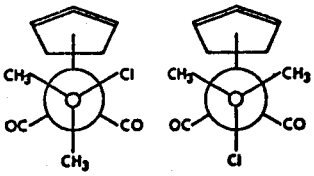
$Cl_3SiFe(CO)_2C_5H_5$



I II

Figure 6

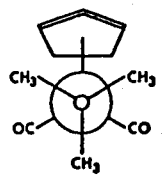
$CH_3Cl_2SiFe(CO)_2C_5H_5$



I II

Figure 7

$(CH_3)_2ClSiFe(CO)_2C_5H_5$



I

Figure 8

$(CH_3)_3SiFe(CO)_2C_5H_5$

$MeCl_2SiFe(CO)_2Cp$ which is shown in Fig. 6, on the statistical basis alone, conformer II would have twice the probability of conformer I. The intensity of the individual carbon monoxide vibration is related to the dipole moment change of the vibration and the concentration of the particular isomer. At equilibrium the relative concentration of the isomers will depend on the relative energy of the individual conformations. The relative intensities, therefore, cannot be readily assigned to any particular conformation. Similar effects have subsequently been observed by Herber and Goscinny in their study of $Cl_2Sn[Fe(CO)_2Cp]_2$ and $Cl_2Ge[Fe(CO)_2Cp]_2$, by a combination of Mössbauer and infrared spectroscopy [100]. These molecules can be pictured as structural analogs of $MeCl_2SiFe(CO)_2Cp$ in which the methyl group in Fig. 6 is replaced by $Fe(CO)_2Cp$.

If rotation about the iron-silicon bond in $MeCl_2SiFe(CO)_2Cp$ were sufficiently slow, then the conformational effect should also be observed in the nmr spectrum by the appearance of two resonance signals for the methyl protons. For example, dimethylformamide shows absorptions due to the methyl groups as a doublet at room temperature. These are of equal intensity 0.25 ppm apart. Above 150°C they merge together into a singlet, as rotation about the carbon-nitrogen bond becomes too rapid for nmr to resolve the two conformations [115]. In the

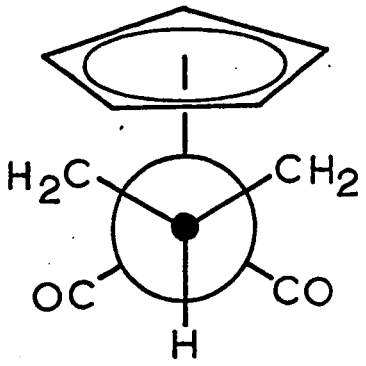
temperature range from 33°C to -70°C, $MeCl_2SiFe(CO)_2Cp$ in carbon disulfide shows only one type of methyl proton resonance. Below -70°C, however, the complex gels from solution. Rotation about the iron-silicon bond in this temperature range appears to be too rapid to resolve the conformations on the nmr time scale, which is approximately a factor of 10^8 to 10^{10} slower than that of infrared spectroscopy.

Recently, Nesmeyanov *et al.* obtained $MeCl_2GeFe(CO)_2Cp$ [172] from an insertion reaction of $GeCl_2$ and $MeFe(CO)_2Cp$ in dioxane. This product shows the presently anticipated four carbonyl stretching bands in the infrared spectrum at 2036 cm^{-1}, 2025 cm^{-1}, 1991 cm^{-1} and 1979 cm^{-1}. It is interesting to note, that when the infrared sample was cooled to -40°C, these authors found that the bands at 2036 cm^{-1} and 1991 cm^{-1} disappeared from the infrared spectrum. This latter observation has important implications related to our findings in the nmr spectrum of $MeCl_2SiFe(CO)_2Cp$. The likely explanation is that the population of the higher energy state is depleted by the Boltzmann principle, before the rate of interconversion of conformers is slowed sufficiently to permit the observation of the two conformations on the nmr time scale. There may exist a relatively large energy difference between the two conformations and a relatively small potential barrier from the higher energy state to the lower

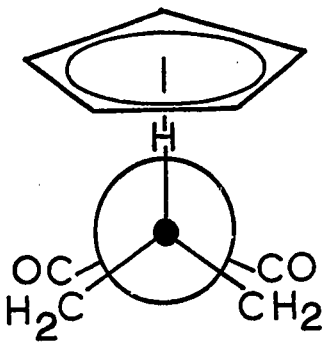
energy state. Population of the less stable conformer decreases therefore as the temperature is lowered. The signal for the methyl protons observed at room temperature in the nmr of $MeCl_2SiFe(CO)_2Cp$ is most probably an average of the methyl proton resonance in the two chemical enviroments, which are observed for the two conformations in the infrared spectrum. When the nmr sample is gradually cooled, only the isomer of lower energy remains, and at best one might observe a small shift, the signal being due to one isomeric form instead of an average of both conformations.

A similar doubling of bands was earlier observed by King in the carbonyl region of the infrared spectrum for π-$C_3H_5Mo(CO)_2Cp$ [134]. The occurrence of four bands rather than the expected two carbon monoxide vibrations was originally attributed to *cis-trans* isomerism involving a bidentate π allyl group at the base of a square pyramid. However, this molecule may assume tautomeric isomers similar to those observed for $MeCl_2SiFe(CO)_2Cp$ if the barrier to rotation about the iron-π allyl axis can be overcome. This similarity can be shown in the Newman projection, Fig. 6, if the chlorines are replaced by the methylene groups, the methyl by hydrogen, silicon by carbon and iron by molybdenum. The *cis-trans* isomerism in π-$C_3H_5Mo(CO)_2Cp$ has been rejected by Davison and Rode

on the basis of an nmr study [68]. These authors propose configurational isomers in which the π allyl group may rotate in some fashion such that the *syn* and *anti* protons remain unchanged. The net change appears to be the same as 180° rotation of the π allyl group about the iron-π allyl axis:



31



32

More complex conformational effects are observed in the infrared spectra of molecules, which allow the unsymmetric ligand to assume a greater number of orientations. For the symmetric silyl complex, $Cl_3SiMo(CO)_3Cp$, three infrared active carbonyl stretching bands are predicted and observed, while the mixed methylchloro analog, $MeCl_2SiMo(CO)_3Cp$, shows four resolved carbon monoxide stretching bands. These are shown in Figures 40 and 41. Similarly, four bands are predicted and observed for $(Cl_3Si)_2Fe(CO)_4$, while the mixed methylchloro derivative, $(MeCl_2Si)_2Fe(CO)_4$ shows six distinct strong stretching

vibrations .plus a medium shoulder on one of the strong bands, shown in Figures 42 and 43.

The infrared spectrum of the carbon monoxide stretching vibrations for $(MeO)_3SiFe(CO)_2Cp$* is shown in Figure 9. In this molecule rotation about the iron-silicon bond

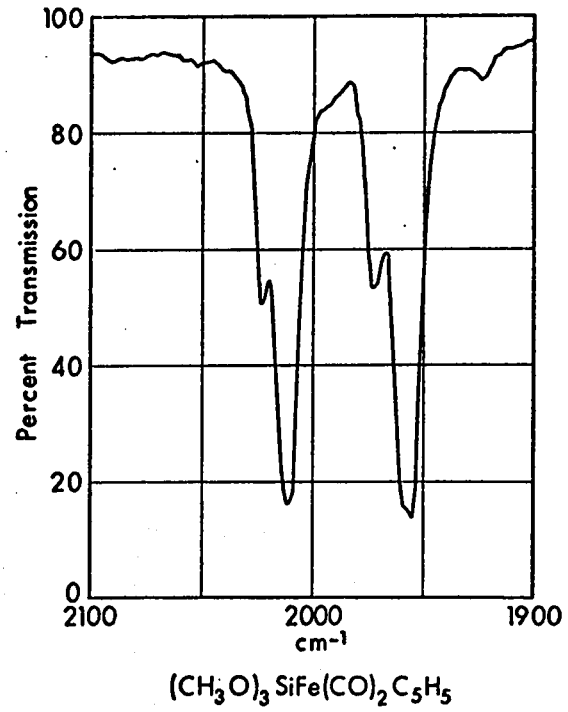


Figure 9

alone would not produce drastically different conformations. However, when this rotation is coupled with the rotation about the silicon-oxygen bond, it provides for an exceedingly complex system of conformations, since the Si-O-Me bond angle is approximately 105°. These rotations are depicted in 33.

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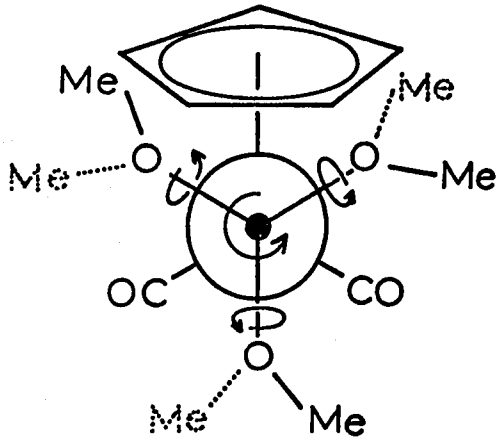
* The preparation of $(MeO)_3SiFe(CO)_2Cp$ is described in Chapter IV.



33

The infrared spectra of the reaction mixture involving $Cl_3SiFe(CO)_2Cp$ and isopropyl alcohol, Me_2HCOH,* show analogous conformational effects. The latter two cases show very broad carbonyl bands. The silyl ligand, $Si(OCHMe_2)_3$, can assume numerous orientations, caused by rotation about the silicon-oxygen and oxygen-carbon bonds. The infrared spectrum of $(Me_2HCO)_3SiFe(CO)_2Cp$ is shown in Figure 65e (cf. Chapter IV).

Recently, conformational effects in the infrared spectra of other compounds have been discovered. For example, $MeCl_2SnFe(CO)_2Cp$ [114] and $\pi Ph_3C_3Co(CO)_3PPhMe_2$, 34, [174], each shows four relatively strong terminal carbonyl stretching bands.

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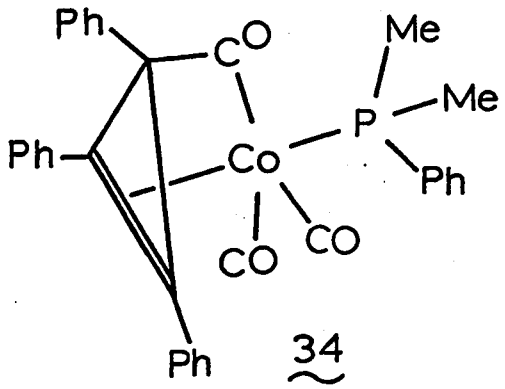
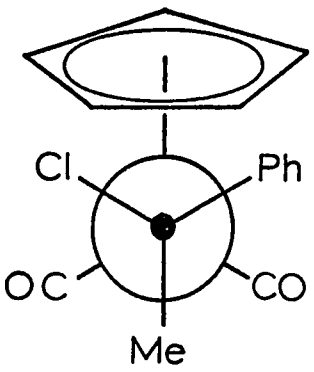
* The reaction is described in Chapter IV.



34

In all molecules discussed up to this point, which show conformational effects in the infrared spectra, the silyl ligands contain only two types of substituents (i.e. $X_2YSiFe(CO)_2Cp$). For example, $MeCl_2SiFe(CO)_2Cp$ shows two sets of two carbonyl stretching bands. For a molecule of the type $XYZSiFe(CO)_2Cp$, three different conformations are possible and three sets of two bands might be observed in the infrared spectrum. The reaction of PhMeClSiH and $[CpFe(CO)_2]_2$ yields $PhMeClSiFe(CO)_2Cp$, a totally unsymmetric molecule. The Newman projections of the three possible conformations brought about by the rotation about the iron-silicon bond are shown in 35, 36 and 37.



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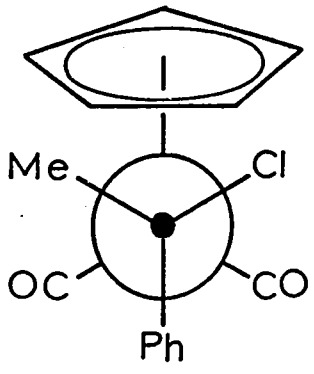
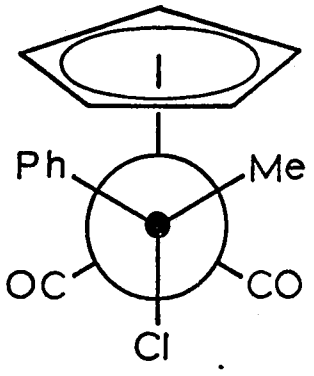


36



37

The infrared spectum in the carbon monoxide stretching region for this molecule is shown in Fig. 33, which shows four poorly resolved bands. From the comparison of the carbonyl stretching values for $PhCl_2SiFe(CO)_2Cp$ and $MeCl_2SiFe(CO)_2Cp$, Table X, it is evident that the influence of a methyl or phenyl group on the carbon monoxide stretching vibration is very similar. On this basis conformations 35 and 36 would be expected to show very similar values for carbon monoxide stretching vibrations. Recently, $MeClHSiFe(CO)_2Cp$ has been synthesized in a reaction of $Na^+[Fe(CO)_2Cp]^-$ and $MeCl_2SiH$ [48]. This molecule does show the anticipated three sets of two carbonyl stretching bands Figure 10:

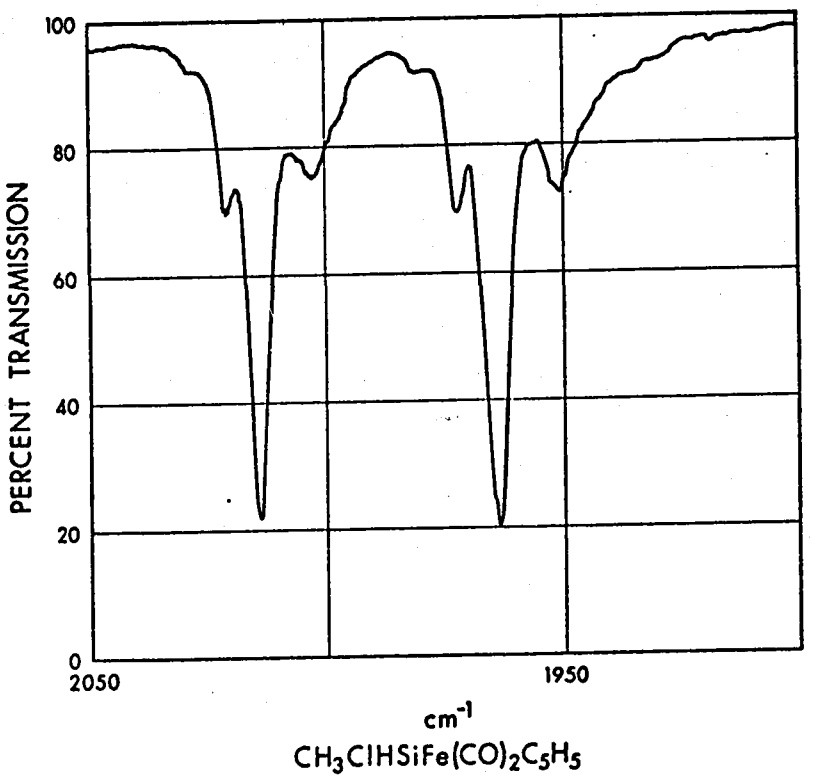
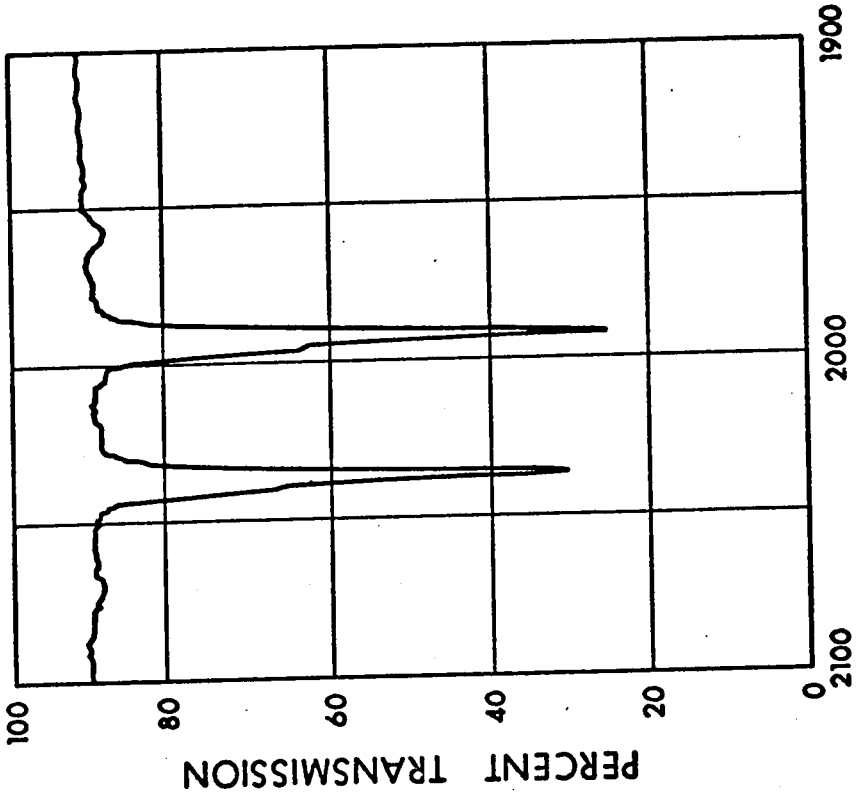


Figure 10

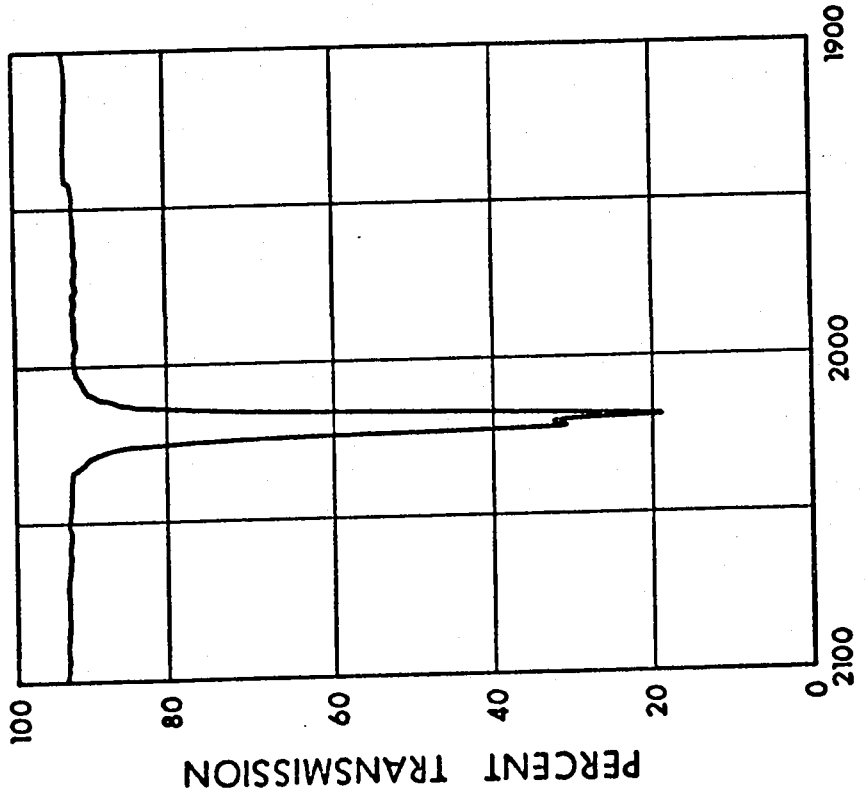
The high frequency bands in the infrared spectra of $Cl_3SiFe(CO)_2Cp$, $H_3SiFe(CO)_2Cp$, $Ph_3SiFe(CO)_2Cp$ and $Me_3SiFe(CO)_2Cp$ are at 2039 cm^{-1}, 2010 cm^{-1}, 2005 cm^{-1} and 1998 cm^{-1} respectively, note Table X. The trend in values for the low frequency band is very similar. The difference in values for $Me_3SiFe(CO)_2Cp$ and $Ph_3SiFe(CO)_2Cp$ is seven wave numbers, while the difference in values for $Me_3SiFe(CO)_2Cp$ and $H_3SiFe(CO)_2Cp$ is twelve wave numbers. It would appear that a minimum difference in the electronegativity of the substituents on the silyl group must exist before the different conformations of the molecule are resolved in the infrared spectrum. It is interesting to note that the difference in the values of the high frequency band for $Ph_3SiFe(CO)_2Cp$ and $H_3SiFe(CO)_2Cp$ is only five wave numbers; consequently the conformations of the unsymmetric molecules for the $Ph_{3-n}H_nSiFe(CO)_2Cp$ series are not resolved in the infrared spectra, Fig. 28-31.

Unsymmetrically substituted cyclopentadienyl groups also may cause conformational effects in the infrared spectra. For example, the infrared spectra of $Cl_3SiFe(CO)_2\pi C_5H_4CH_3$ and $(Cl_3Si)_2HFe(CO)\pi C_5H_4CH_3$, Fig. 11 and 12, show four and two carbonyl stretching bands respectively. Similar tautomeric isomers, as for the unsymmetric silyl derivatives, may be postulated when the cyclopentadiene is rotated about the iron cyclopentadiene axis.



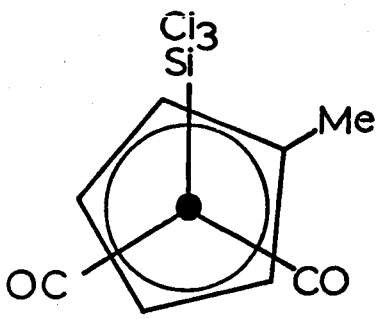
$Cl_3SiFe(CO)_2C_5H_4CH_3$

Figure 12



$(Cl_3Si)_2HFe(CO)C_5H_4CH_3$

Figure 11



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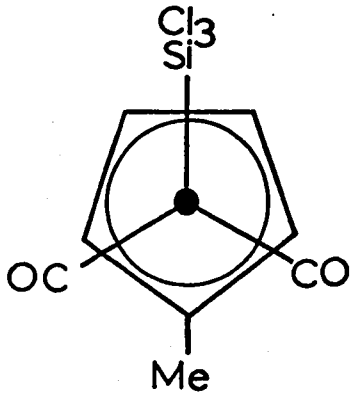
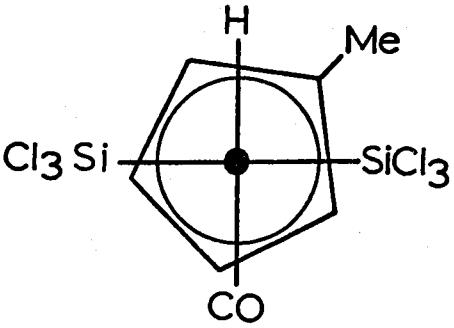


39

$Cl_3SiFe(CO)_2\pi C_5H_4CH_3$



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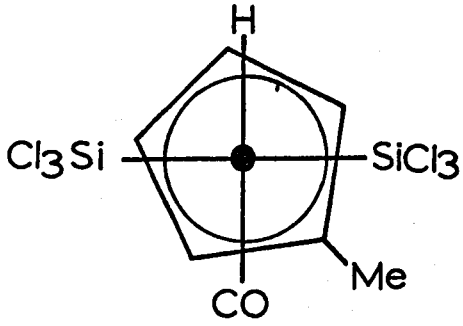


41

$(Cl_3Si)_2HFe(CO)\pi C_5H_4CH_3$

Complexes which show conformational effects in the infrared spectra have a tendency to show varying melting points. These appear to drop and broaden with time after crystallization in the cold. Immediately after a crystalline sample has been isolated and freed of the solvent, its melting point is generally sharp and relatively high. However, if the melting point is determined the following day on a sample stored under nitrogen at room temperature,

its melting point may be several degrees lower and may be spread over a range of 10 - 20°C. The melting point of $MeCl_2SiFe(CO)_2Cp$ demonstrates an extreme example of this physical change. When the melting point of this complex is taken within 30 minutes after crystallization at -15° its value is 99 - 102°C. If the sample is stored under nitrogen at room temperature for several hours, melting occurs over the whole range from 45° - 100°C. This complex is thermally very stable. A sample stored in a sealed ampule, at room temperature for one year, showed no noticeable decomposition.

It appears that crystallization of $MeCl_2SiFe(CO)_2Cp$ from a solution at reduced temperature takes place with the complex in a preferred conformation. As the temperature is raised, thermal randomization occurs slowly, in which the methyl group may assume any of the orientations effected by rotation around the iron-silicon bond. The melting points then correspond to isomeric mixtures.

In one instance, as noted earlier, an inseparable mixture of $Cl_3SiCr(CO)_3Cp$ and $HCl_2SiCr(CO)_3Cp$ was obtained. The infrared spectrum of the mixture showed six bands of which three were sharp, and were assigned to the trichlorosilyl derivative; the three broader bands, each appearing as expected 7 - 14 cm^{-1} to lower frequency than the corresponding sharp band, could logically be assigned to the

dichlorosilyl derviative.

The frequencies of carbon monoxide stretching vibrations are generally influenced by the electron density on the molecule, which is partly transmitted into the carbon monoxide antibonding orbitals. The isoelectronic series, $Ni(CO)_4$, $Co(CO)_4^-$ and $Fe(CO)_4^=$, which shows bands at 2037 cm^{-1}, 1883 cm^{-1} and 1788 cm^{-1} respectively [3], demonstrate examples of these shifts. Electronegative substituents on the ligands or electronegative ligands do show similar effects. An electronegative ligand has the tendency to withdraw electrons from the molecular systems which shifts the vibration frequencies of the carbon monoxides to higher values. Several series of analogs in which the change of substituents on the silyl group show a gradual shift in carbonyl stretching values are shown in Tables IX, X and XI. Correlation of the values for the $X_3SiFe(CO)_2Cp$ (X = Cl, H, Ph, Me) yields a relative order of electronegativities of the substituents on the silicon atom.

$$Cl > H > Ph > Me$$

EXPERIMENTAL

General procedures described in Chapter II are also applicable in the present section.

Unless otherwise stated, the reactions were carried out in Carius tubes with an approximate volume of 60 - 70 ml. These were constructed of thick walled 17 mm inside diameter Pyrex tubing, which had a 14/20 standard taper joint attached at one end by a 15 cm length of thick-walled 5 mm inside diameter tubing. Prior to the addition of reagents, the Carius tube was flushed out with nitrogen. The solid crystalline starting materials were weighed and placed directly into these tubes. Nonvolatile liquids such as Ph_2SiH_2, $PhSiH_3$, and $Fe(CO)_5$ were syringed into the tube. The Carius tube was then attached to a vacuum system and evacuated with the sample at liquid nitrogen temperature. Volatile reagents such as Cl_3SiH and Me_3SiH were distilled into a measuring finger and then the required liquid volume was transferred by distillation into the Carius tube at reduced pressure. In most reactions, no solvents were employed; however if solvents were used, these were distilled into the Carius tube. When all materials had been placed into the Carius tube, it was sealed off under vacuum along the narrow tubing. The seal was carefully annealed with a soft flame, a required procedure if the tube is to withstand maximum pressure. After the reaction mixture had been exposed to the reaction

conditions, it was slowly cooled to room temperature, then liquid nitrogen temperature, and cracked open along the narrow tubing to release the gases formed in the reaction. Volatile silanes, that had been used in excess, were removed at reduced pressure into a cold trap and stored for further use. The products remaining in the tube, if exceedingly volatile, were sublimed directly onto a cold finger or into a Schlenk tube. The less volatile products were extracted with hexane or dichloromethane, depending on the solubility of the complex. The major methods for purification of the complexes were crystallization and sublimation. The relative sharpness of melting points and constant infrared spectra, after repeated crystallization or sublimation, were taken as indications of purity. This was confirmed by elemental analysis of carbon and hydrogen, or carbon, hydrogen and chlorine. Agreement between the calculated and found values within $\pm$ 0.3% were taken as acceptable values. Analysis in which the values were somewhat outside the range of $\pm$ .3% but was in agreement with the stoichiometries determined by mass spectroscopy, were also accepted as in agreement with the anticipated compounds, providing other data supported the assignment.

Analyses were generally performed by Mrs. Darlene Mahlow and Mrs. Andrea Dunn in the Microanalytical Laboratory of this department. Samples which required

the analysis of other elements were sent to A. Bernhardt, Microanalytisches Laboratorium, Mühlheim, Germany; F. Pascher, Mikroanalytisches Laboratorium, Bonn, Germany, or Schwarzkopf, Microanalytical Laboratory, Woodside 77, N. Y. In cases where duplicate analyses have been performed for carbon, hydrogen and chlorine in this department and elsewhere, the results determined in this department were generally in better agreement with the theoretical values of the compound. This may in part be due to the use of fresh samples stored in a sealed ampule in a refrigerator, as well as, special interest allotted to handling of samples of low robustness. It is essential that the number of observed carbonyl stretching bands in the infrared spectrum does not exceed the number of predicted bands, unless they can be accounted for in terms of isomers.

For nmr, 50 - 100 mg of the crystalline complexes were placed directly into an nmr tube attached to a standard-taper ground glass joint. These were attached to a vacuum system. The required amount of solvent and tetramethylsilane (TMS), as the internal standard, were distilled into the nmr tube under vacuum. The sample was then frozen in liquid nitrogen and the tube sealed off. Volatile, air-sensitive solid complexes were sublimed directly into the nmr tube. Samples prepared in this manner were stored in liquid nitrogen until used. The nmr spectra were recorded on

Varian Nuclear Magnetic Resonance Spectrometers, Models A-60, 56-60A or HA100.

The analytical data, color, melting points, infrared data and nuclear magnetic resonance data are given in Tables VI-XI at the end of the chapter. The melting points are uncorrected.

Chemicals

The silanes, Cl_3SiH, $MeCl_2SiH$, Me_2ClSiH, Me_3SiH, Ph_2SiH_2, $PhSiH_3$, PhMeClSiH, $Me(EtO)_2SiH$, $PhCl_2SiH$ etc. have been purchased from the following suppliers: Alfa Inorganics, Inc., Beverly Mass.; Pierce Chemicals Company, Rockford, Illinois; Columbia Organic Chemicals, Co., Inc., Columbia, S.C; Peninsular Chemresearch Inc., Gainesville, Fla.

Of the solvents employed, n-pentane, n-hexane and n-heptane were Phillips pure grade. Fisher reagent grade dichloromethane was distilled from calcium hydride and used within several days.

Handling of all toxic materials and those possessing vile odors such as tetracarbonyl nickel, pentacarbonyl iron, and bicyclopentadiene was carried out in the fume hood.

π-Cyclopentadienylcarbonylnickel Dimer, $[CpNi(CO)]_2$:

The synthetic method described by King [132] was followed. Tetracarbonyl nickel (60 ml., 79 gm. 0.465 mol) was added to a 200 ml benzene solution, containing 31.2 gm

Cp_2Ni (0.165 mol). As the mixture was heated under gentle reflux for five hours, the green color of Cp_2Ni turned the characteristic blood-red of $[CpNi(CO)]_2$. After the reaction was complete, the reaction mixture was allowed to cool to room temperature. The excess $Ni(CO)_4$ and benzene were removed at reduced pressure into a -78°C trap. Nitrogen was admitted to the flask and the dark residue was extracted with 400 - 500 ml of anhydrous diethyl ether in four aliquots. The combined extract was passed through a 2 cm x 15 cm alumina column to affect removal of $Cp_3Ni_3(CO)_2$. The column was washed with diethyl ether until all red $[CpNi(CO)]_2$ was removed. From the combined red solution, diethyl ether was removed at reduced pressure leaving a dark red product, $[CpNi(CO)]_2$.

π-Cyclopentadienyldicarbonyliron Dimer, $[CpFe(CO)_2]_2$:

Portions of this starting material were purchased from Strem Chemicals Inc., Danvers, Mass., and portions were synthesized using the route described by King [132]. A mixture of 500 ml dicyclopentadiene (3.8 mol) and 100 ml pentacarbonyl iron (146 gm., 0.74 mol) was heated under a gentle reflux at atmospheric pressure. The carbon monoxide formed in the reaction was allowed to escape through a bubbler in the fume hood. The temperature was maintained between 135°C to 145°C. When most of the refluxing of

$Fe(CO)_5$ subsided, the reaction mixture was allowed to cool to room temperature. A brown-violet, crystalline material separated from solution. This was filtered and washed with several small portions of pentane, yielding a coarse violet-brown, crystalline material which was used in this state of purity in further experiments.

π-Cyclopentadienyltricarbonylchromium, Dimer $[CpCr(CO)_3]_2$:

The synthetic method described by King and Stone [131] was employed. A 500 ml three-neck flask under nitrogen was charged with 50 ml diethylene glycol ("diglyme," Ansul Ether 141, dried by distillation from $LiAlH_4$ at reduced pressure) and 1.4 gm sodium metal (0.06 mole). This was heated slowly until the sodium metal showed signs of melting. At this point, the mixture was vigorously shaken for several minutes, which resulted in dispersion of the sodium metal into sodium sand. With the reaction vessel cooled to room temperature an excess of freshly cracked cyclopentadiene (prepared by the method described in this reference) was added slowly. After all sodium sand was consumed 8.8 gm of $Cr(CO)_6$ (0.04 mol) was added and the mixture refluxed until very little $Cr(CO)_6$ was sublimed into the bottom of the condenser. During this reaction $Cr(CO)_6$ was scraped back into the reaction mixture at regular intervals. The resulting yellow solution of $Na^+[Cr(CO)_3Cp]^-$ was allowed to

cool to room temperature. The reaction mixture was then treated with 7.2 gm of allyl bromide (0.06 mol), which is an exothermic reaction step. The solution turned from yellow to dark green. To this 10 ml methanol and then 200 ml water was added, which precipitated $[CpCr(CO)_3]_2$ and other water insoluble materials. The residue was filtered and dried. This was placed under nitrogen into a sublimer and heated at 110 - 120°C at a pressure less than 0.01 mm mercury. A dark, blue-green material deposited on the water cooled probe. The product, $[CpCr(CO)_3]_2$, was used in this state of purity.

π-Cyclopentadienylmolybdenumtricarbonyl Dimer, $[CpMo(CO)_3]_2$; π-Cyclopentadienylcobaltdicarbonyl, $\pi CpCo(CO)_2$; π-Methylcyclopentadienylirondicarbonyl Dimer, $[\pi MeC_5H_4Fe(CO)_2]_2$;.... were purchased from Strem Chemical Inc., Danvers, Mass.

Trichlorosilylmanganesepentacarbonyl, $Cl_3SiMn(CO)_5$:

A sample of 3.0 gm $Mn_2(CO)_{10}$ (7.7 mmol) in 5 - 6 ml Cl_3SiH (excess) was heated at 130 - 140°C until the color of the reaction mixture turned from intense orange to pale yellow. After the excess Cl_3SiH had been removed, the crude crystalline product was transferred into a sublimer under a nitrogen atmosphere. Careful exclusion of air is necessary at this stage. At room temperature and less than 0.01 mm mercury pressure, trace amounts of unreacted $Mn_2(CO)_{10}$

were sublimed onto a water-cooled probe. The temperature was then raised to 65°C and sublimation was continued onto a clean probe. A white crystalline material, $Cl_3SiMn(CO)_5$, was deposited. Its yield was 5.07 gm, (15.4 mmol) quantitative based on $Mn_2(CO)_{10}$ used. A fraction of this product was recrystallized from hot hexane. The coarse, white, crystals which were deposited at refrigerator temperature had a melting point of 130 - 131°C.

Methyldichlorosilylmanganesepentacarbonyl, $MeCl_2SiMn(CO)_5$:

A mixture of 2.10 gm $Mn_2(CO)_{10}$ (5.4 mmol) and 3 - 4 ml $MeCl_2SiH$ (excess) was reacted at 135 - 140°C until the color of the reaction mixture turned from orange to pale yellow. As the Carius tube was cooled coarse white crystals precipitated. After the excess $MeCl_2SiH$ was removed, the crude crystalline material was transferred under nitrogen into a sublimer. At room temperature trace amounts of unreacted $Mn_2(CO)_{10}$ and small quantities of $MeCl_2SiMn(CO)_5$ were deposited onto a water-cooled probe at less than 0.01 mm mercury pressure. Sublimation was then continued at 35 - 40°C onto a clean sublimer probe, affording 2.5 gm of $MeCl_2SiMn(CO)_5$ (8.1 mmol, 75% based on $Mn_2(CO)_{10}$ used). This was recrystallized from hexane, yielding a white, coarse, crystalline product at refrigerator temperature. Its melting point was 93 - 94°C.

Dimethylchlorosilylmanganesepentacarbonyl, $Me_2ClSiMn(CO)_5$:

A sample of 2.05 gm $Mn_2(CO)_{10}$ (5.25 mmol) in 7.0 ml Me_2ClSiH (excess) was heated with agitation* at 140°C until the reaction mixture turned from orange to pale yellow. The excess Me_2ClSiH was removed at reduced pressure, yielding a pale yellow, oily residue. This was dissolved in hexane and filtered under nitrogen. The clear filtrate was slowly cooled to -78°C, affording 2.32 gm of pale yellow, crystalline material, $Me_2ClSiMn(CO)_5$ (8.05 mmol, 77%, based on $Mn_2(CO)_{10}$ used). After an additional recrystallization its melting point was 45 - 47°C. The infrared spectrum indicated the presence of small amounts of $Mn_2(CO)_{10}$ at this stage. The product was then sublimed from a Schlenk tube at room temperature onto a -78°C probe at less than 0.01 mm mercury (sublimation distance 10 - 15 cm). The sublimate was recrystallized twice from pentane at -78°C. The melting point of the pure product thus obtained was 50 - 51°C.

Trimethylsilylmanganesepentacarbonyl, $Me_3SiMn(CO)_5$:

A solution of 2.06 gm $Mn_2(CO)_{10}$ in 3 - 4 ml Me_3SiH (excess) was heated at 150 - 160°C for 15 hours. Some gray and black deposits formed on the wall of the Carius tube,

* Mechanical agitation in a heated oil bath is described in the experimental section of Chapter IV.

indicating partial decomposition. The excess Me_3SiH was removed at reduced pressure, leaving a dark oily residue. This was sublimed directly from the Carius tube at room temperature onto a probe cooled with liquid nitrogen. The white, crystalline deposit, $Me_3SiMn(CO)_5$, was washed from the probe with pentane into a Schlenk tube, resulting in a clear colorless solution. This was cooled to -78°C slowly, affording white, transparent crystals. The melting point of these, $Me_3SiMn(CO)_5$, is 40 - 41°C. From the dark residue left behind in the Carius tube, 1.1 gm of unreacted $Mn_2(CO)_{10}$ was isolated (identified by infrared).

Phenylmethylchlorosilylmanganesepentacarbonyl, $PhMeClSiMn(CO)_5$:

A mixture of 1.5 gm $Mn_2(CO)_{10}$ (3.85 mmol) and 1.6 - 1.8 ml PhMeClSiH (slight excess) was heated at 140 - 150°C until the orange reaction mixture turned pale yellow. The viscous oily reaction product, in the Carius tube, slowly crystallized in the refrigerator over a period of two weeks. The removal of excess PhMeClSiH at reduced pressure proved extremely slow and was discontinued after several hours. The reaction mixture was dissolved in pentane and filtered under nitrogen, resulting in a clear colorless solution. Cooling this to -78°C precipitated a microcrystalline material. A repeated crystallization, by cooling to -20°C, then slowly to -78°C, yielded a white, coarse, crystalline product, $PhMeClSiMn(CO)_5$,

mp 44 - 45°C.

Phenyldichlorosilylmanganesepentacarbonyl, $PhCl_2SiMn(CO)_5$:

A sample of 2.0 gm $Mn_2(CO)_{10}$ (5.12 mmol) in 4.0 ml $PhCl_2SiH$ (excess) was heated at 130 - 140°C for six hours. During this process two liquid layers formed with the intense orange $Mn_2(CO)_{10}$ at the bottom and gas evolved at the interphase. The reaction mixture was allowed to cool when the appearance of the solution was a uniform pale yellow. The excess $PhCl_2SiH$ was removed at reduced pressure, which proved extremely slow. The residue was extracted with 30-35 ml hexane, filtered, and the clear filtrate was allowed to cool slowly in the refrigerator. A white crystalline material precipitated. An additional recrystallization from 20 ml hexane afforded white, transparent crystals, mp 62 - 64°C.

Diphenylsilylmanganesepentacarbonyl, $Ph_2HSiMn(CO)_5$:

A mixture of 2.25 gm $Mn_2(CO)_{10}$ (5.78 mmol) and 5.0 ml Ph_2SiH_2 (excess) was heated at 150° for eight hours. Dark deposits on the wall of the Carius tube indicated partial decomposition. The reaction products were extracted with hexane and filtered. The clear, pale yellow filtrate was cooled to -78°C, yielding a pale yellow, crystalline material. Two additional recrystallizations from pentane at -78°C resulted in a white, crystalline product,

$Ph_2HSiMn(CO)_5$, which had a melting point at 42 - 44°C.

Bis-μ-diphenylsilyl-bis(manganesetetracarbonyl), $[Ph_2SiMn(CO)_4]_2$:

The hexane insoluble residue from the foregoing reaction was dissolved in a minimum amount of dichloromethane and filtered, resulting in a clear, intensely yellow solution. Hexane was slowly added to the top surface of the dichloromethane filtrate, in such a way that two solvent layers of different density remained. As the two solvent layers diffused into each other, yellow crystals slowly deposited on the wall of the Schlenk tube. These were washed with pentane and dried at reduced pressure. The product, $[Ph_2SiMn(CO)_4]_2$, decomposes slowly above 215°C.

Trichlorosilylrheniumpentacarbonyl, $Cl_3SiRe(CO)_5$:

A mixture of 1.0 gm $Re_2(CO)_{10}$ (1.53 mmol) and 1.0 ml Cl_3SiH (excess) was heated at 160°C for eight hours during which time the colorless solution attained a slightly yellow appearance. Cooling the Carius tube to room temperature crystallized a white product from the reaction mixture. After excess Cl_3SiH was removed at reduced pressure, the crude crystalline product, $Cl_3SiRe(CO)_5$, (1.41 gm, 3.06 mmol, quantitative based on $Re_2(CO)_{10}$ used) was dissolved in hot hexane, filtered and the clear solution was allowed to cool slowly in the refrigerator. Coarse, white crystals formed, which had a melting point of 169.0-

169.5°C. The solubility of $Cl_3SiRe(CO)_5$ was approximately 450 mg per 100 ml in warm hexane. Sublimation can be effected at 45 - 50°C and a pressure less than 0.01 mm mercury.

Methyldichlorosilylrheniumpentacarbonyl, $MeCl_2SiRe(CO)_5$:

A solution of 1.0 gm $Re_2(CO)_{10}$ (1.53 mmol) in 1.0 ml $MeCl_2SiH$ (excess) was heated at 160°C for five hours during which the colorless transparent solution turned very pale yellow. This reaction temperature was apparently too drastic for the formation of only $MeCl_2SiRe(CO)_5$, as indicated by a complex infrared spectrum of the crude reaction product. Unidentified products of side reactions were formed in very low yields. The crude crystalline reaction product was washed with 30 ml of cold hexane. The remaining crystalline material was dissolved in warm hexane, filtered and the clear solution was cooled in the refrigerator, affording 0.6 gm $MeCl_2SiRe(CO)_5$. Its melting point after an additional recrystallization from pentane was 118 - 120°C.

Dimethylchlorosilylrheniumpentacarbonyl, $Me_2ClSiRe(CO)_5$:

A sample of 1.06 gm $Re_2(CO)_{10}$ (1.62 mmol) in 5.8 - 6.0 ml Me_2ClSiH was heated at 150°C for 55 hours, during which time no change in color was apparent. The infrared spectrum of the crude reaction product indicated the presence of trace amounts of unreacted $Re_2(CO)_{10}$. After

removal of the excess Me_2ClSiH, the crude product was sublimed at room temperature onto a -78°C probe at less than 0.01 mm mercury pressure, resulting in the deposit of a white powdery material. This was washed into 30 ml pentane giving a clear, colorless solution. Stepwise cooling to -78° afforded huge, white crystals of the product, $Me_2ClSiRe(CO)_5$, mp 85 - 88°C. This final product appeared to contain trace amounts of $MeCl_2SiRe(CO)_5$, indicated by the presence of a very weak band in the infrared spectrum at the position of the most intense carbonyl band of this compound. Repeated recrystallizations and sublimations did not improve the purity of this complex appreciably.

Trimethylsilylrheniumpentacarbonyl, $Me_3SiRe(CO)_5$:

A mixture of 1.06 gm $Re_2(CO)_{10}$ (1.62 mmol), 3.8 ml Me_3SiH (excess) and 3.0 ml hexane were heated at 160°C for 92 hours. After excess Me_3SiH and hexane were removed at reduced pressure, the residue was extracted with 40 ml hexane, filtered and then the filtrate was slowly cooled to -78°C, yielding a white, crystalline solid. This was sublimed from a Schlenk tube at room temperature onto a -78°C probe at less than 0.01 mm mercury pressure. The sublimate was washed into a Schlenk tube using 40 ml pentane. At -78°C a white product crystallized from the colorless solu-

tion. The melting point of $Me_3SiRe(CO)_5$ is 54 - 55°C.

Trichlorosilyl-π-cyclopentadienylirondicarbonyl, $Cl_3SiFe(CO)_2Cp$:

The reaction of $[CpFe(CO)_2]_2$ and Cl_3SiH, the characterization of the products and their properties are described in Chapter IV.

Methyldichlorosilyl-π-cyclopentadienylirondicarbonyl, $MeCl_2SiFe(CO)_2Cp$:

A sample of 1.5 gm $[CpFe(CO)_2]_2$ (4.23 mmol) in 1.0 ml $MeCl_2SiH$ (excess) was heated at 130°C until the color of the reaction mixture changed from brown to cream-yellow. After the excess $MeCl_2SiH$ was removed, the residue was extracted with pentane and filtered. The filtrate, a clear, yellow solution was slowly cooled, yielding 0.96 gm of yellow crystals, $MeCl_2SiFe(CO)_2Cp$ (3.3 mmol, 39% based on $[CpFe(CO)_2]_2$ employed). The melting point shortly after crystallization was 98 - 101°C. The infrared spectrum showed four relatively strong carbonyl stretching bands, Fig. 25. A repeated melting point several hours after isolation of this material was between 45 - 100°C. Repeated crystallization and sublimation did not alter the infrared spectrum, and the melting point was again between 99 - 102°C, if taken within 30 minutes after isolation of the crystalline material from a cold source.

The molecular weight was determined osmometrically to be 294; the calculated value for $MeCl_2SiFe(CO)_2Cp$ is 291. The mass determination of the molecular ion on a MS9 mass spectrometer was 289.9028; the calculated value for $C_8H_8O_2{}^{56}Fe^{28}Si^{35}Cl_2$ is 289.9026.

Dimethylchlorosilyl-π-cyclopentadienylirondicarbonyl, $Me_2ClSiFe(CO)_2Cp$:

A mixture of 2.0 gm $[CpFe(CO)_2]_2$ (5.65 mmol) and 6.0 ml Me_2ClSiH (excess) was heated at 140°C until the reddish-brown color of $[CpFe(CO)_2]_2$ changed to yellow. Some decomposition was indicated by the presence of insoluble gray material in the reaction mixture. After the excess Me_2ClSiH had been removed, the residue was extracted with hexane, filtered, and the clear yellow filtrate was then cooled to -78°C affording a pale yellow, sticky, crystalline material melting at 82 - 85°C. After some time had elapsed with the crystals at room temperature under nitrogen, the melting point tended to be lower and broad.

Trimethylsilyl-π-cyclopentadienylirondicarbonyl, $Me_3SiFe(CO)_2Cp$:

A solution of 2.0 gm $[CpFe(CO)_2]_2$ (5.65 mmol) in 3.0 ml Me_3SiH (excess) and 3.0 ml hexane was heated at 160°C for 30 hours. The reaction mixture turned from reddish-brown to light brown with some gray deposits. After the volatile

components, excess Me_3SiH and hexane were drawn off at reduced pressure, the residue was sublimed at room temperature onto a -78°C probe at less than 0.01 mm mercury pressure. The resulting pale-yellow, crystalline material was washed into 40 ml pentane. The clear, pale-yellow solution was cooled to -78°C, yielding a yellow, crystalline material. After two additional recrystallizations from pentane at -78°C, the pale-yellow, sticky product $Me_3SiFe(CO)_2Cp$ had a melting point of 55 - 58°C.

Phenyldichlorosilyl-π-cyclopentadienylirondicarbonyl, $PhCl_2SiFe(CO)_2Cp$:

A sample of 2.0 gm $[CpFe(CO)_2]_2$ (5.65 mmol) in 3.0 ml $PhCl_2SiH$ (excess) was heated at 130°C for six hours during which time the reddish-brown mixture turned pale-yellow. An attempt to draw off the excess $PhCl_2SiH$ at reduced pressure failed, because of the low vapour pressure of $PhCl_2SiH$. The reaction mixture was extracted with pentane and filtered. The clear, pale-yellow filtrate was allowed to cool slowly in the refrigerator, which resulted in the formation of a yellow, crystalline product, $PhCl_2SiFe(CO)_2Cp$. After an additional recrystallization at similar conditions its melting point was 81 - 83°C.

Phenylmethylchlorosilyl-π-cyclopentadienylirondicarbonyl, $PhMeClSiFe(CO)_2Cp$:

A mixture of 3.03 gm $[CpFe(CO)_2]_2$ (8.55 mmol) and 5.0 ml PhMeClSiH (excess) was heated at 140°C until the reddish-brown mixture turned pale-yellow. The combined oily material was extracted with hexane, filtered, and the clear filtrate was slowly cooled to -78°C, resulting in a product contaminated with unreacted $[CpFe(CO)_2]_2$. This mixture was sublimed at 50°C onto a water cooled probe at less than 0.01 mm mercury pressure. The sublimate was recrystallized twice in minimum amounts of pentane. The resulting yellow, crystalline product $PhMeClSiFe(CO)_2Cp$ had a melting point of 80 - 81°C.

Triphenylsilyl-π-cyclopentadienylirondicarbonyl, $Ph_3SiFe(CO)_2Cp$:

A mixture of 4.5 gm $[CpFe(CO)_2]_2$ (12.7 mmol), 7.9 gm Ph_3SiH (30.2 mmol) and 5 ml benzene was heated at 140°C for five days. The reddish-brown color of the reaction mixture showed no appreciable change. This was extracted with hot hexane and filtered. Cooling slowly in the refrigerator deposited yellow and reddish-brown crystals (apparently $Ph_3SiFe(CO)_2Cp$ and $[CpFe(CO)_2]_2$ respectively). This was dissolved in a minimum volume of 1:1 mixture of benzene-hexane and passed through a 2 cm x 5 cm column of Florisil

made up in 1:1 benzene-hexane solution. The yellow product passed rapidly through the column while the reddish-brown layer remained in the top 2 cm of Florisil. The solvent was removed from the benzene-hexane eluent, leaving a yellow crystalline material. This was recrystallized from a minimum volume of hot hexane. The product, $Ph_3SiFe(CO)_2Cp$, which crystallized at refrigerator temperature, had a melting point of 158 - 160°C.

Diphenylsilyl-π-cyclopentadienylirondicarbonyl, $Ph_2HSiFe(CO)_2Cp$:

A solution of 2.03 gm $[CpFe(CO)_2]_2$ (5.7 mmol) in 3.0 ml Ph_2SiH_2 (excess) and 5.0 ml benzene was heated at 140°C for 20 hours. The color of the reaction mixture turned from reddish-brown to yellow and the infrared spectrum showed no bands due to bridging carbon monoxides. The crude material was extracted with hexane and filtered. The clear yellow filtrate was slowly cooled in the refrigerator, affording a yellow crystalline product, $Ph_2HSiFe(CO)_2Cp$. After an additional recrystallization its melting point was 94 - 96°C.

Silyl-π-cyclopentadienylirondicarbonyl, $H_3SiFe(CO)_2Cp$:

A mixture of 3.25 gm $[CpFe(CO)_2]_2$ (9.18 mmol) and 10 ml $PhSiH_3$ (excess) was heated at 135°C for 72 hours, during which the reddish-brown mixture turned light-brown. The excess

$PhSiH_3$ was removed at reduced pressure. The semisolid crystalline residue was placed into a sublimer. Over a period of approximately ten days, a pale-yellow product was deposited in the cold trap at -78°C. No noticeable quantities of any materials were observed on the water-cooled probe at these conditions. This light yellow material was recrystallized from pentane at -78°C, yielding a coarse yellow crystalline product with a melting point of 77 - 78°C.

Phenylsilyl-π-cyclopentadienylirondicarbonyl, $PhH_2SiFe(CO)_2Cp$:

The oily residue from the above reaction was dissolved in pentane and filtered. The clear yellow solution was slowly cooled to -78°C, affording a yellow crystalline product, $PhH_2SiFe(CO)_2Cp$. After an additional recrystallization at similar conditions, its melting point was 45 - 47°C.

Methyldiethoxysilyl-π-cyclopentadienylirondicarbonyl, $Me(EtO)_2SiFe(CO)_2Cp$:

This reaction was carried out in a 100 ml thick-walled Pyrex pressure vessel, cappable bottle with crown top to accept a perforated bottle cap, over a self-sealing rubber liner (Labglass Inc., LG-3921 and LG-3922). A needle penetrating the seal allowed a constant check on the internal pressure by a gauge attached to the needle.

The reaction vessel was charged with 5.0 gm $[CpFe(CO)_2]_2$

(14.1 mmol) and 15 ml of $Me(EtO)_2SiH$ (excess), sealed and heated at reflux (pressure maintained below 50 psi) for 15 hours. Some gas was allowed to escape at regular intervals as the pressure slowly built up above 50 psi. The combined mixture was distilled at reduced pressure through a 2-inch fractionating column containing glass helices. At room temperature, most of $Me(EtO)_2SiH$ distilled. The fraction distilling at 40°C was collected, diluted with pentane, and slowly cooled at -78°C. A pale-yellow crystalline material formed. After an additional recrystallization at similar conditions, the solvent was removed. The product, $Me(EtO)_2SiFe(CO)_2Cp$, was a liquid at room temperature.

Bis-trichlorosilylirontetracarbonyl, $(Cl_3Si)_2Fe(CO)_4$:

Method A.

A mixture of 1.0 gm $Fe_3(CO)_{12}$ (2.0 mmol) and 1.6 ml Cl_3SiH (excess) was heated at 75°C until all $Fe_3(CO)_{12}$ was consumed, as indicated by the change in color of the reaction mixture from dark green to yellow. After excess Cl_3SiH was removed, the crude sample was sublimed at room temperature onto a water-cooled probe at less than 0.01 mm mercury pressure. The pale-green crystalline material thus obtained was recrystallized from hot hexane to afford a white crystalline product, $(Cl_3Si)_2Fe(CO)_4$, melting point 96 - 97°C.

Method B

A solution of 5.0 ml $Fe(CO)_5$ (37 mmol) and 5.0 ml Cl_3SiH (excess) was heated at 140°C for 20 hours. The appearance of the reaction mixture seemed unchanged, however slow cooling in the refrigerator precipitated a white crystalline material. After the excess Cl_3SiH was removed, the isolation and purification of Method A was followed. The infrared spectrum of the crude reaction product indicated the presence of small quantities of $[Cl_2SiFe(CO)_4]_2$.

Bis-μ-dichlorosilyl-bis-(irontetracarbonyl), $[Cl_2SiFe(CO)_4]_2$:

Method A

A solution of 2.0 ml $Fe(CO)_5$ (14.9 mmol) and 1.7 - 1.8 ml Cl_3SiH (17.5 mmol) was heated at 170°C for 15 hours. A cream-colored powdery material precipitated from solution. After the excess Cl_3SiH was removed, the crude material was sublimed at room temperature and less than 0.01 mm mercury. At these conditions small quantities of $(Cl_3Si)_2Fe(CO)_4$ were deposited onto the water-cooled probe. With all $(Cl_3Si)_2Fe(CO)_4$ removed, sublimation was continued at 60°C, yielding a faintly yellow crystalline material. This was dissolved in a small quantity of dichloromethane and filtered. Hexane was slowly added to the clear filtrate until the solution became turbid. This was allowed to cool in the refrigerator, resulting in the precipitation of a

faintly yellow crystalline product, $[Cl_2SiFe(CO)_4]_2$, which decomposes above 200°C.

Method B

A mixture of 1.0 gm $Fe_3(CO)_{12}$ (2.0 mmol) and 1.0 ml Cl_3SiH (10 mmol) was heated at 160°C for 24 hours. As the reaction mixture was allowed to cool to room temperature large crystals formed in the reaction mixture. One of the large crystals was isolated. Its infrared spectrum in the carbonyl stretching region was identical to that of $[Cl_2SiFe(CO)_4]_2$. The complex decomposes above 200°C. For the isolation and purification of the bulk of the crude material the same procedure as in Method A was employed.

Bis-(methyldichlorosilyl)irontetracarbonyl, $(MeCl_2Si)_2Fe(CO)_4$:

A sample of 4.0 gm $Fe_3(CO)_{12}$ (7.9 mmol) in 6.0 ml $MeCl_2SiH$ (excess) was heated at 85°C until the reaction mixture turned from green to yellow-brown. After the excess $MeCl_2SiH$ was removed, the viscous oily material was washed with pentane into a sublimer. The solvent was removed at reduced pressure and the residue sublimed at 50°C onto a -78°C probe at less than 0.01 mm mercury pressure. Sublimation was repeated twice at 40°C. The resulting sticky, semisolid crystals had a melting point of 105 - 107°C.

Trichlorosilyl-π-cyclopentadienylchromiumtricarbonyl, $Cl_3SiCr(CO)_3Cp$ and Dichlorosilyl-π-cyclopentadienylchromium-tricarbonyl, $Cl_2HCr(CO)_3Cp$:

A mixture of 1.21 gm $(CpCr(CO)_3]_2$ (3.0 mmol) and 10 ml Cl_3SiH was heated at 120°C for three days, during which time dark green material precipitated. After the excess Cl_3SiH was removed the residue was extracted with several aliquots of hot hexane. The combined colorless, clear filtrate was cooled to -78°C, resulting in a white, fine, crystalline product. This was slowly sublimed at room temperature onto a water cooled probe at less than 0.01 mm mercury pressure. The faintly green crystalline deposit had a melting point of 120 - 132°C. Its infrared spectrum in the carbonyl stretching region showed six bands of medium to strong intensity. Three of these were relatively sharp while the remaining three were somewhat broader. The sharp bands at 2028 cm^{-1}, 1972 cm^{-1} and 1952 cm^{-1} were assigned to $Cl_3SiCr(CO)_3Cp$, while the broader bands at 2021 cm^{-1}, 1962 cm^{-1} and 1938 cm^{-1} were assigned to $Cl_2HSiCr(CO)_3Cp$. The mass spectrum of this mixture, given in Table XXV, Chapter VI, show the parent ions and breakdown framentation for both $Cl_3SiCr(CO)_3Cp$ and $Cl_2HSiCr(CO)_3Cp$. Attempts at separation were unsuccessful, since these complexes tend to decompose rapidly in solution.

Trichlorosilyl-π-cyclopentadienylmolybdenumtricarbonyl, $Cl_3SiMo(CO)_3Cp$:

The reaction of $[CpMo(CO)_3]_2$ and Cl_3SiH is described in Chapter IV.

Methyldichlorosilyl-π-cyclopentadienylmolybdenumtricarbonyl, $MeCl_2SiMo(CO)_3Cp$:

A sample of 2.0 gm $[CpMo(CO)_3]_2$ (4.1 mmol) in 2.0 ml $MeCl_2SiH$ (excess) was heated at 125°C until the reddish-brown material turned into an oily brown substance. After removal of the excess $MeCl_2SiH$, the residue was washed with pentane into a sublimer. The solvent was evaporated and the residue was sublimed at 50°C onto a water-cooled probe at less than 0.01 mm mercury pressure. The cream-colored crystalline sublimate of $MeCl_2SiMo(CO)_3Cp$ (2.0 gm, 5.6 mmol, 68% based on $[CpMo(CO)_3]_2$ employed) had a melting point at 99 - 101°C.

Trichlorosilyl-π-cyclopentadienylnickelcarbonyl, $Cl_3SiNi(CO)Cp$:

A mixture of 1.5 gm $[CpNi(CO)]_2$ (4.9 mmol) and 2.0 ml Cl_3SiH (excess) was warmed in a water bath at 40 - 50°C for three hours, during which the dark red mixture became very viscous. After the excess Cl_3SiH was removed, the unattractive oily residue was washed with pentane into a sublimer. The solvent was slowly pumped off at low vacuum and the

oily residue was sublimed at room temperature onto a water-cooled probe at less than 0.01 mm mercury pressure. The coarse, red, crystalline product, $Cl_3SiNi(CO)Cp$, after an additional sublimation, had a melting point of 38 - 40°C.

Bis-trichlorosilyl-π-cyclopentadienylcobaltcarbonyl, $(Cl_3Si)_2Co(CO)Cp$:

A solution of 2.0 ml $CpCo(CO)_2$ (15.5 mmol) and 7.0 ml Cl_3SiH (excess) was heated at 110°C for five hours, during which the reaction mixture turned from a dark brown liquid to a black semisolid. After the excess Cl_3SiH was removed, some additional liquid of low volatility and pale-yellow crystals were trapped at -78°C. The residue was sublimed at 110°C onto a water-cooled probe at less than 0.01 mm mercury pressure. The microcrystalline sublimate was washed with two small aliquots of pentane and resublimed at similar conditions. The cream-colored, fine, crystalline product, $(Cl_3Si)_2Co(CO)Cp$, decomposed above 210°C.

Trichlorosilylcobalttetracarbonyl, $Cl_3SiCo(CO)_4$:

The pale yellow, crystalline material that was trapped out at -78°C in the above reaction was recrystallized twice from pentane at -78°C, affording an air-sensitive crystalline product, $Cl_3SiCo(CO)_4$. Its infrared spectrum shows three relatively strong carbonyl stretching bands at 2117, 2062 and 2037 cm^{-1}. (Reported values in ref. 64 for $Cl_3SiCo(CO)_4$ are 2117, 2062 and 2037 cm^{-1}).

TABLE VI

Analytical Data, Colors and Melting Points of Silylmanganese and Silylrhenium Derivatives

Compound	M.P.°C	Color	Calculated %			Found %		
			C	H	Cl	C	H	Cl
$Cl_3SiMn(CO)_5$	130-131	white	18.23	0.00	32.28	18.83	0.00	31.79
$MeCl_2SiMn(CO)_5$	93-94	white	23.32	0.98	22.94	23.15	0.99	22.90
$Me_2ClSiMn(CO)_5$	50-51	white	29.13	2.10	12.28	29.18	2.05	12.93
$Me_3SiMn(CO)_5$	40-41	white	35.83	3.38	-	35.39	3.34	-
$Cl_3SiRe(CO)_5$	169-170	white	13.04	0.00	23.09	12.92	0.00	23.06
$MeCl_2SiRe(CO)_5$	119-120	white	16.37	0.69	16.10	16.66	0.94	16.50
$Me_2ClSiRe(CO)_5$	85-88	white	20.03	1.44	8.44	19.63	1.51	8.72
$Me_3SiRe(CO)_5$	54-55	white	24.06	2.27	-	24.04	2.40	-
$PhCl_2SiMn(CO)_5$	62-64	white	35.60	1.36	19.11	35.42	1.49	19.04
$PhMeClSiMn(CO)_5$	44-45	white	41.10	2.30	10.11	41.22	2.38	10.32
$Ph_2HSiMn(CO)_5$	42-44	white	53.97	2.93	-	53.80	3.35	-

TABLE VIII

Analytical Data, Colors and Melting Points of Silyliron Derivatives

Compound	M.P.°C	Color	Calculated %			Found %		
			C	H	Cl	C	H	Cl
$Cl_3SiFe(CO)_2Cp$	128-130	yellow	27.00	1.62	34.15	27.10	2.21	31.90
$MeCl_2SiFe(CO)_2Cp$	99-102	yellow	33.02	2.77	24.37	33.03	2.94	25.78
$Me_2ClSiFe(CO)_2Cp$	82-85	yellow	39.95	4.10	13.10	40.05	4.10	13.14
$Me_3SiFe(CO)_2Cp$	55-58	yellow	48.01	5.64	-	47.25	5.48	-
$H_3SiFe(CO)_2Cp$	77-78	yellow	40.41	3.87	-	40.39	3.71	-
$PhH_2SiFe(CO)_2Cp$	45-47	yellow	54.79	4.53	-	55.79	4.60	-
$Ph_2HSiFe(CO)_2Cp$	94-96	yellow	63.34	4.48	-	63.44	4.71	-
$Ph_3SiFe(CO)_2Cp$	158-160	yellow	68.81	4.62	-	70.00	4.31	-
$PhCl_2SiFe(CO)_2Cp$	81-83	yellow	44.22	2.85	20.08	44.37	3.01	17.68
$PhMeClSiFe(CO)_2Cp$	80-81	yellow	50.55	3.94	10.66	50.54	3.97	9.80
$Me(EtO)_2(CO)_2Cp$	Liq. R.T.	yellow	46.46	5.85	-	46.34	5.83	-

TABLE VIII

Analytical Data, Colors and Melting Points of Silyl Transition Metal Derivatives

Compound	M.P.°C	Color	Calculated %			Found %		
			C	H	Cl	C	H	Cl
$[Ph_2SiMn(CO)_4]_2$	d<215	yellow	55.10	2.89	-	55.27	3.06	-
$[Cl_2SiFe(CO)_4]_2$	d<200	pale yellow	18.00	0.00	26.57	17.61	0.29	24.09
$(Cl_3Si)_2Fe(CO)_4$	96-97	white	11.00	0.00	48.70	11.13	0.31	48.24
$(MeCl_2Si)Fe(CO)_4$	105-107	white	18.20	1.53	35.82	18.24	1.60	35.67
$Cl_3SiMo(CO)_3Cp$	149-151	cream	25.32	1.33	28.02	25.52	1.32	28.40
$MeCl_2SiMo(CO)_3Cp$	99-101	cream	30.10	2.25	19.75	30.15	2.72	19.61
$Me_3SiMo(CO)_3Cp$	d<68	white	41.51	4.43	-	41.53	5.56	-
$Cl_3SiCr(CO)_3Cp$ [a]		white	-	-	-	-	-	-
$HCl_2SiCr(CO)_3Cp$ [a]		white	-	-	-	-	-	-
$Cl_3SiNi(CO)Cp$	38-40	red	25.17	1.76	37.15	25.07	1.74	36.29
$(Cl_3Si)_2Co(CO)Cp$	d<210	cream	17.12	1.20	50.53	17.42	1.54	49.87
$Cl_3SiCo(CO)_4$		pale yellow	15.73	0.00	-	14.22	0.37	-

a. Isolated as inseparable mixture, characterized mass spectrometrically.

TABLE IX

Infrared Carbonyl Streching Frequency Data and Proton Nmr Data of Silylmanganese and Silylrhenium Derivatives

Compound	Infrared Data [a] ν(CO) cm^{-1} A_1^2	B	A_1^1	E	^{13}C	Nmr Data Solvent	τ(Me)
$Cl_3SiMn(CO)_5$	2123m	2056vw	2035vs	2035vs	2001w		
$MeCl_2SiMn(CO)_5$	2114m	2051w	2026vs	2016vs	1991w	CD_2Cl_2	8.77
$Me_2ClSiMn(CO)_5$	2105m	2036w	2015s	2006vs	1969w	CD_2Cl	9.10
$Me_3SiMn(CO)_5$	2094m	2012vw	2001s	1992vs	1959w	CD_2Cl_2	9.50
$Cl_3SiRe(CO)_5$	2140m		2030s	2038vs	2005w	-	-
$MeCl_2SiRe(CO)_5$	2131m	2061n	2018s	2027vs	1997w	CD_2Cl	8.88
$Me_2ClSiRe(CO)_5$	2123m	2049m	2010s	2015vs	1976w	CD_2Cl_2	9.09
$Me_3SiRe(CO)_5$	2112m		2001vs	2001vs	1969w	CD_2Cl_2	9.50
$PhCl_2SiMn(CO)_5$	2114m	2051w	2025vs	2022vs	1988	-	-
$PhMeClSiMn(CO)_5$ [b]	2105m	2039m	2005s	2014vs	1980w	CCl_4	8.85
$Ph_2HSiMn(CO)_5$ [c]	2104m	2029w	1998ssh	2006vs	1965w	CCl_4	-

a. In cyclohexane or hexane

b. τ(Ph) = 2.2 - 2.9

c. τ(Ph) = 2.2 - 2.8, τ(H) = 4.60, ν(Si-H) = 2089 cm^{-1}, broad.

TABLE X

Infrared Carbonyl Stretching Frequency Data and Proton Nmr Data for Silyliron Derivatives

Compound	Infrared Data [a] ν(CO) cm^{-1}						Nmr Data Solvent	τ(Cp)	τ(Me)	τ(Ph)
$Cl_3SiFe(CO)_2Cp$		2039s	2025w		1995s	1962w	CH_3CN	4.87	---	
$MeCl_2SiFe(CO)_2Cp$	2131m	2022s	2008w	1983m	1973s	1941w	CD_2Cl_2	5.05	8.87	
$Me_2ClSiFe(CO)_2Cp$	2017m	2010vs	1998w	1968m	1957vs	1928w	CD_2Cl_2	5.19	9.21	
$Me_3SiFe(CO)_2Cp$		1998s	1982w		1944s	1913w	CD_2Cl_2	5.33	9.64	
							Solvent	τ(Cp)	τ(H)	τ(Ph)
$H_3SiFe(CO)_2Cp$		2010s			1962s		CD_2Cl_2	5.15	6.25	----
$PhH_2SiFe(CO)_2Cp$		2007s			1958s		CD_2Cl_2	5.27	5.15	2.1-2.9
$Ph_2HSiFe(CO)_2Cp$		2006s			1955s		$CDCl_3$	4.31	5.32	2.1-2.9
$Ph_3SiFe(CO)_2Cp$		2005s			1954s		----	---	---	----
$PhCl_2SiFe(CO)_2Cp$	2029vs	2025s		1981vs	1977s					
$PhMeClSiFe(CO)_2Cp$ [b]	2015msh	2011s		1968m	1959s		CCl_4	5.44	---	2.3-3.0
$Me(EtO)_2SiFe(CO)_2Cp$ [c]	2008s	2002s		1955s	1946s		$CDCl_3$	5.17		

a. In cyclohexane or hexane

b. $\tau(CH_3) = 9.03$

c. $\tau(CH_3Si) = 9.44$, $\tau(CH_3\text{-}C) = 8.73$, $\tau(C\text{-}CH_2\text{-}O) = 6.15$

TABLE XI

Infrared Carbonyl Stretching Frequency Data[a] for Silyl Transition Metal Derivatives

Compound	ν(CO) cm^{-1}						
$[Ph_2SiMn(CO)_4]_2$	2047m	2005s	1976m	1968s	1928vw		
$[Cl_2SiFe(CO)_4]_2$	2094s	2053sh	2048ssh	2046vs	2037w		
$(Cl_3Si)_2Fe(CO)_4$	2125m	2078m	2071vs	2061s			
$(MeCl_2Si)_2Fe(CO)_4$[b]	2109s	2061m	2057s	2047m	2040msh	2034vs	2029m
$Cl_3SiMo(CO)_3Cp$[c]	2047s	1976m		1959vs	1926s		
$MeCl_2SiMo(CO)_3Cp$[d]	2027s	1965m	1960s	1936vs	1904w		
$Me_3SiMo(CO)_3Cp$	1999s	1926m		1899vs	1869w		
$Cl_3SiCr(CO)_3Cp$[e]	2028s	1972m		1952vs			
$HCl_2SiCr(CO)_3Cp$[e]	2021s	1962m		1938vs			
$Cl_3SiNi(CO)Cp$	1962						
$(Cl_3Si)_2Co(CO)Cp$	2056vs	2008w					
$Cl_3SiCo(CO)_4$	2117m	2062m	2037s				

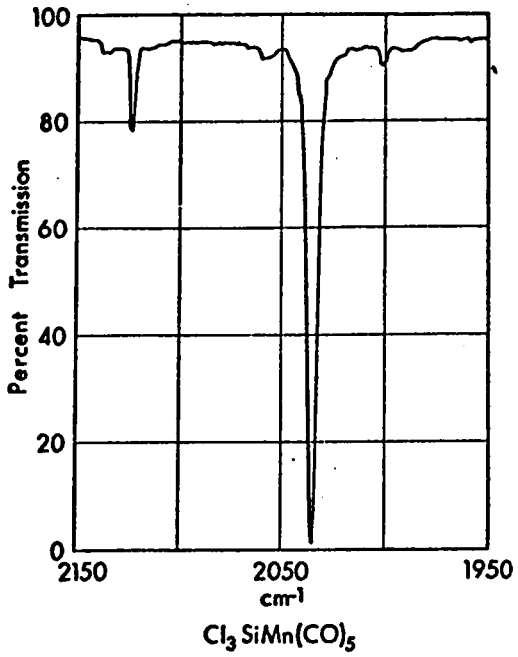
a In cyclohexane or hexane

b In CD_2Cl_2 τ(Me) = 8.65

c In CD_2Cl_2 τ(Cp) = 4.42

d In CD_2Cp τ(Me) = 5.83, τ(Cp) = 9.26

e Mixture of $Cl_3SiCr(CO)_3Cp$ and $HCl_2SiCr(CO)_3Cp$



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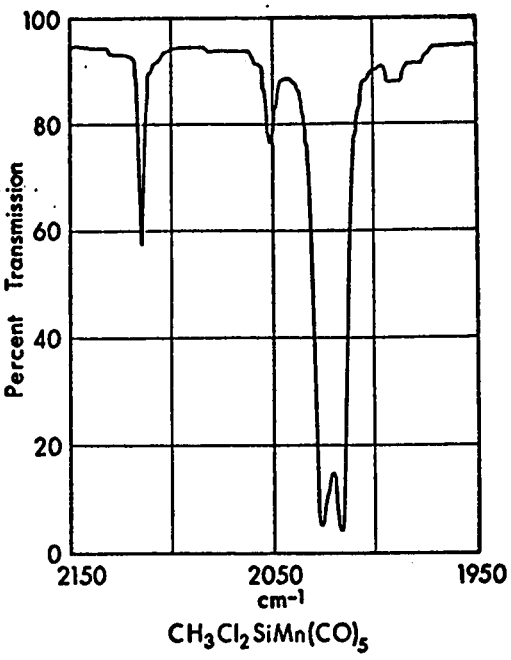

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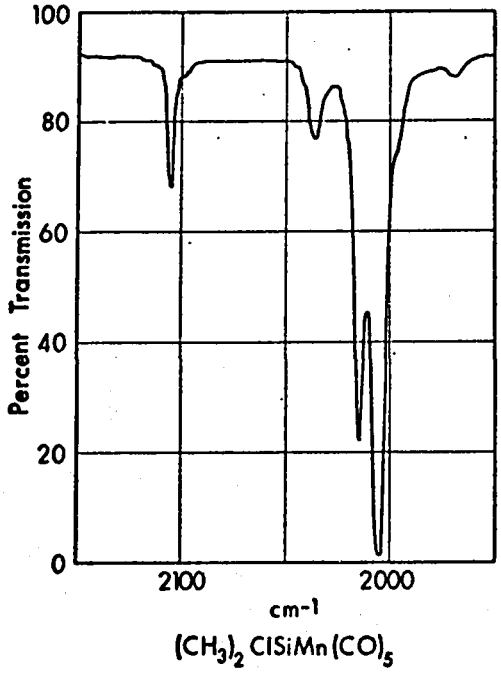

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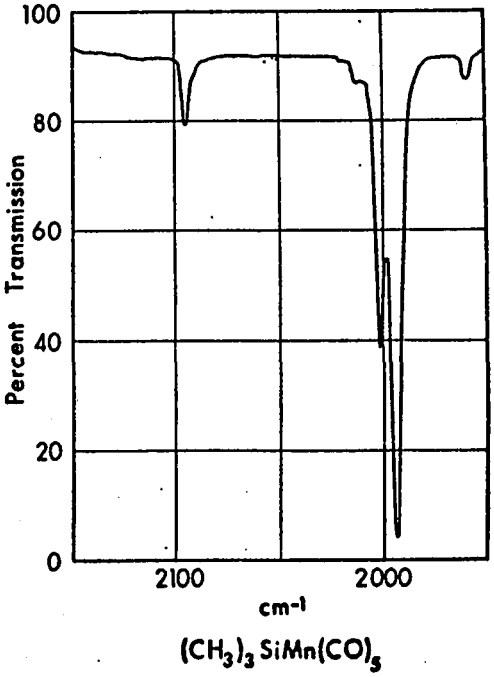

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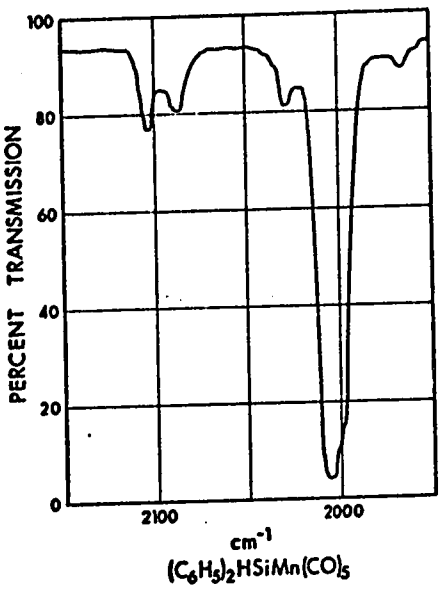

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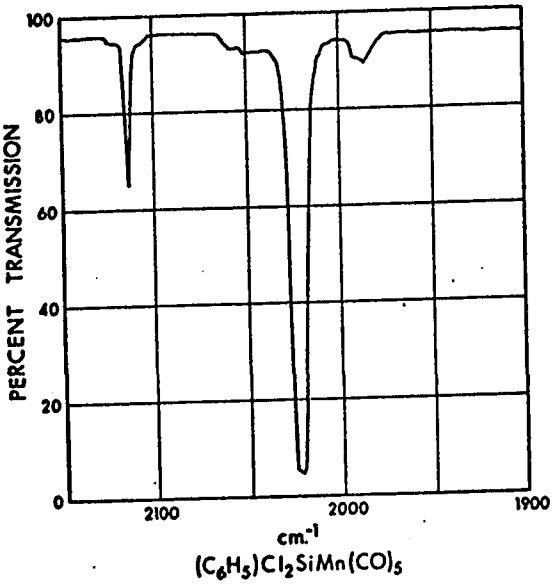

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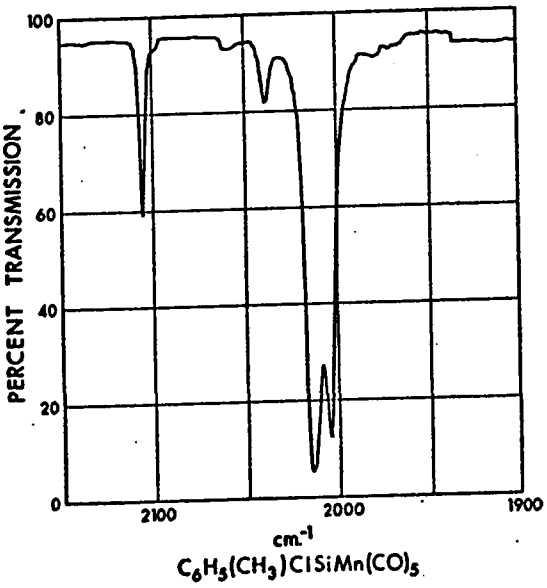

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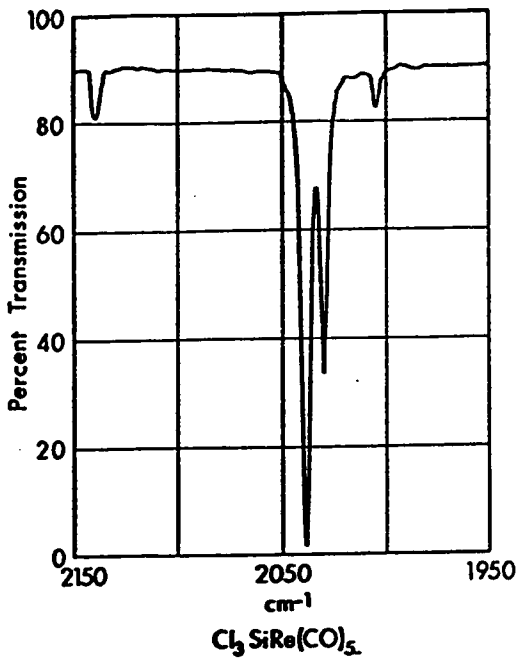

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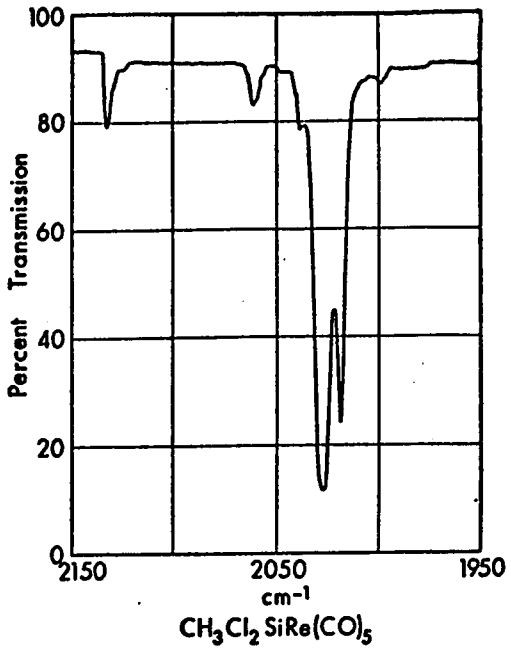

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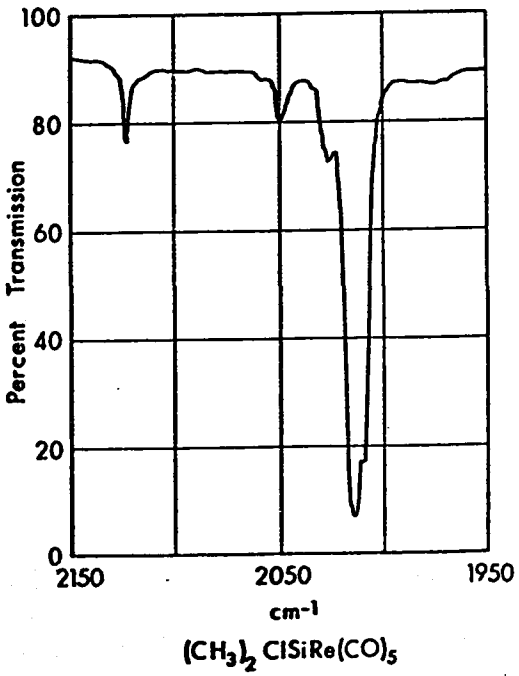

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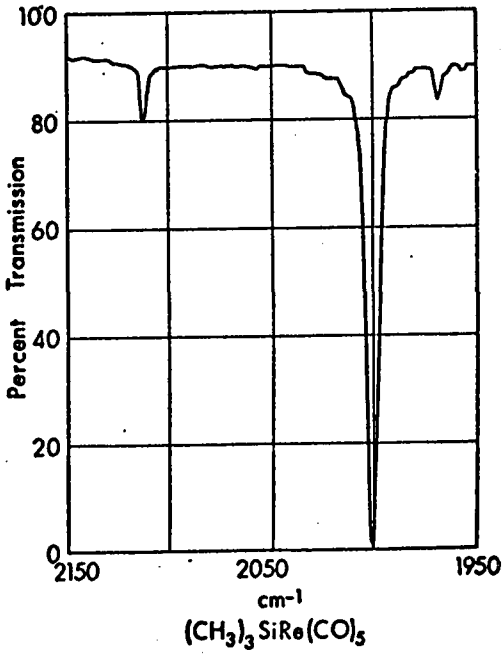

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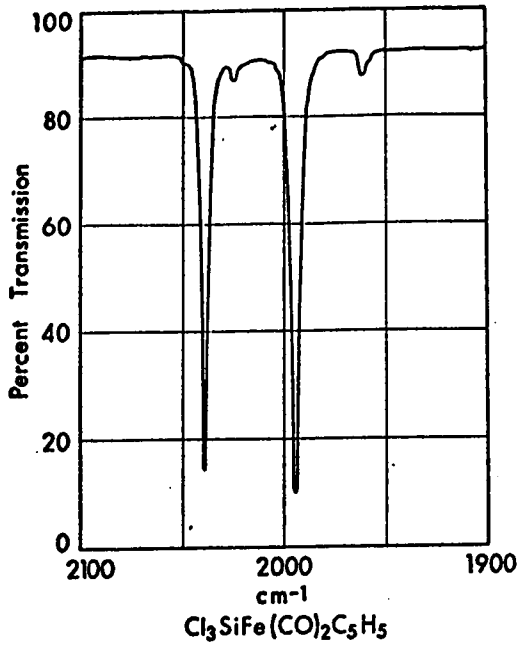

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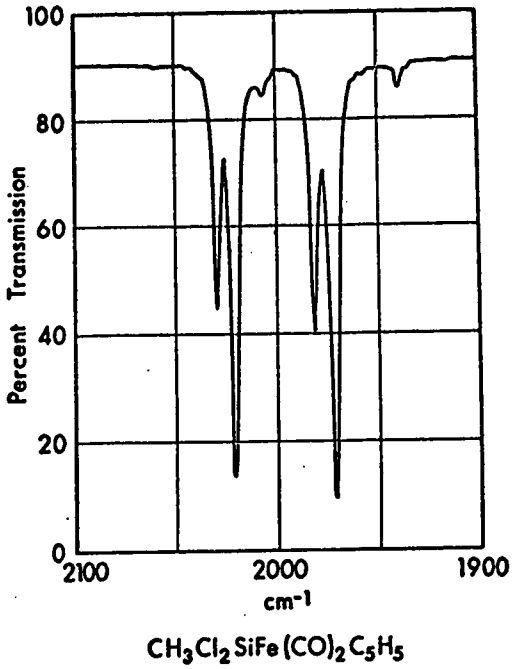

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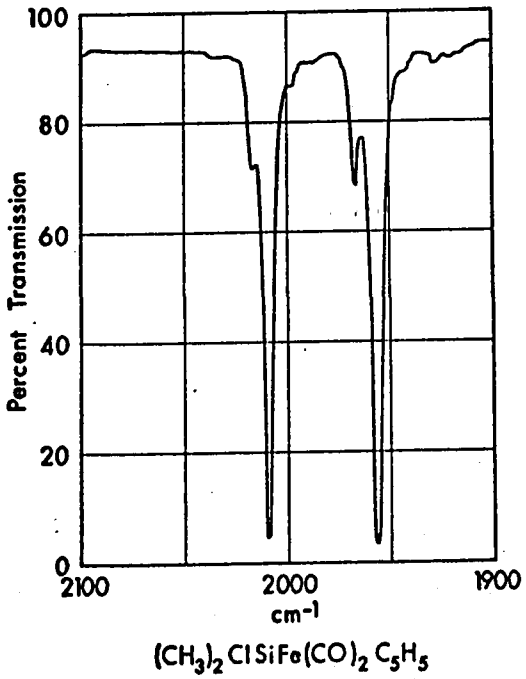

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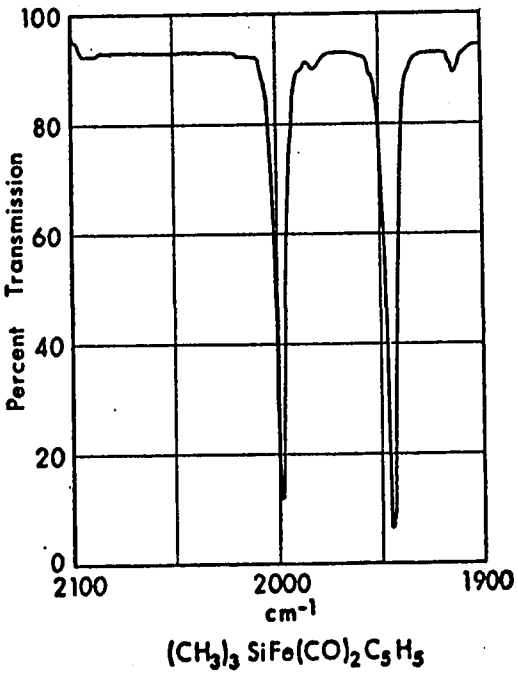

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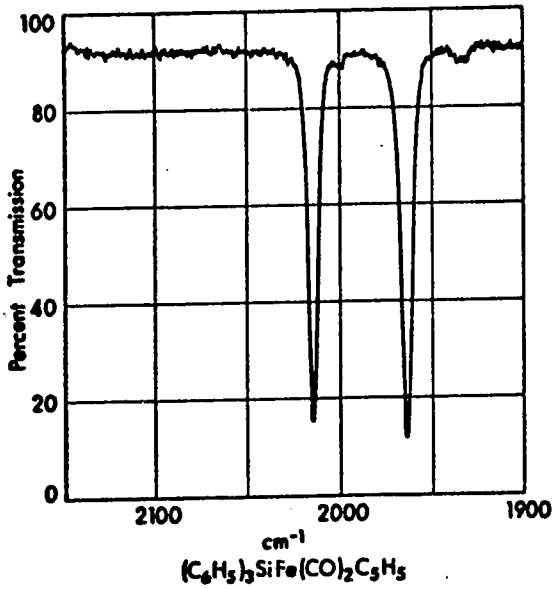

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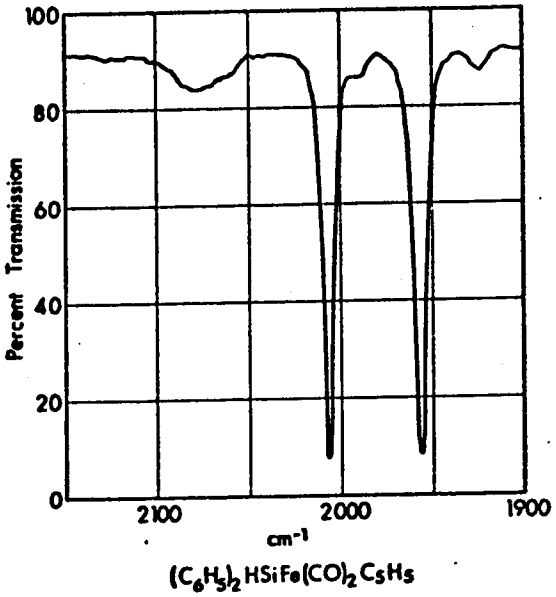

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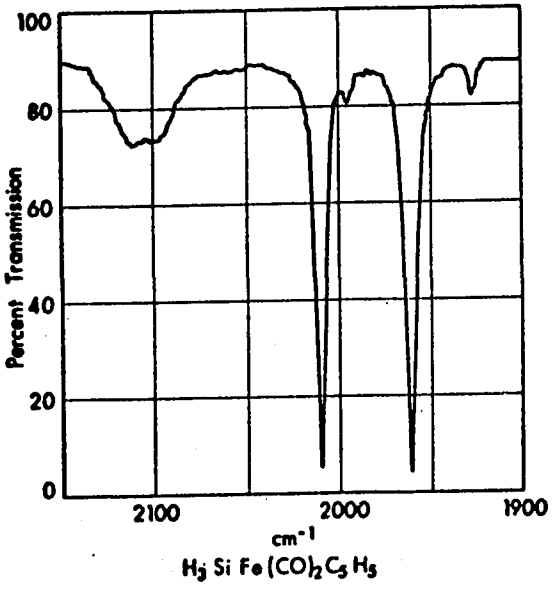

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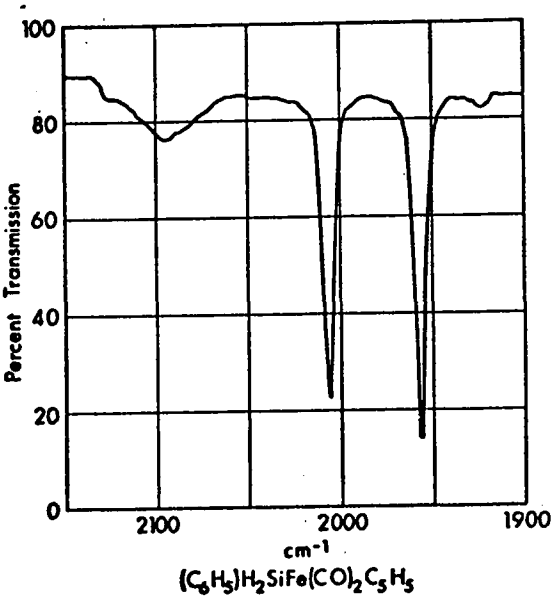

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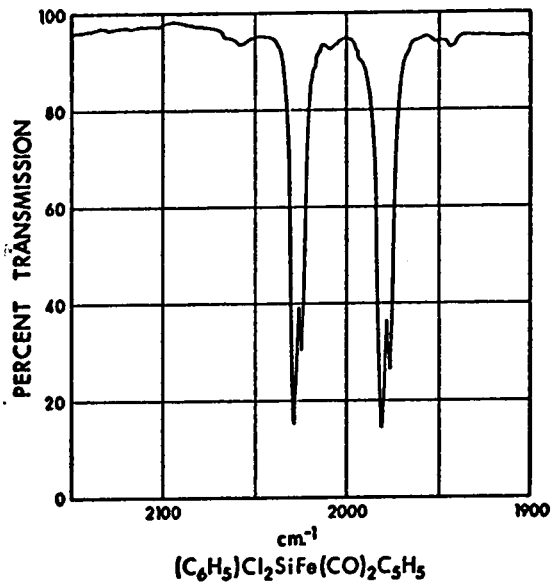

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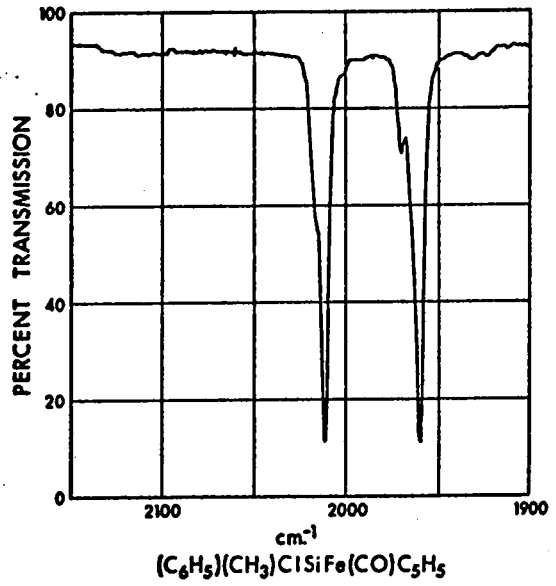

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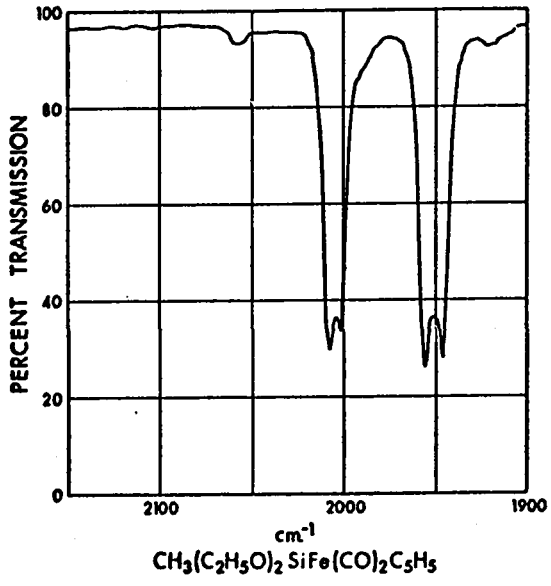

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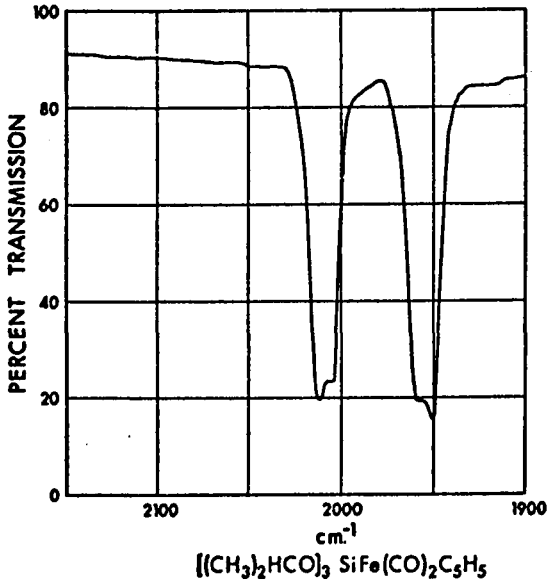

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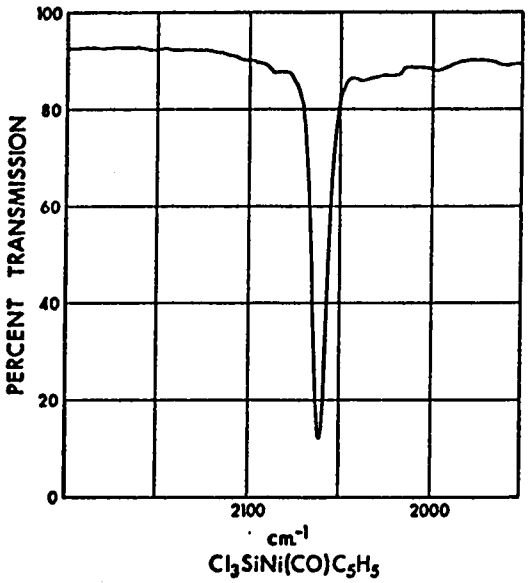


Figure 36

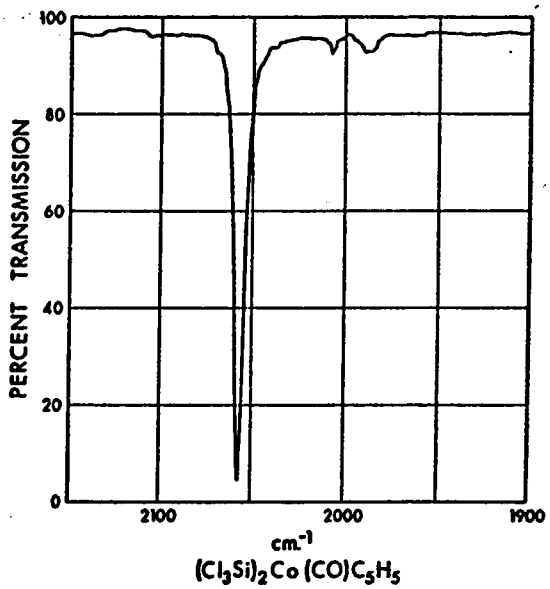


Figure 37

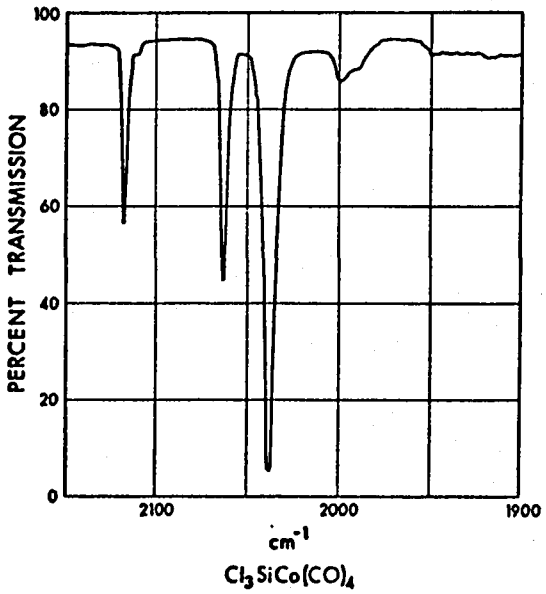


Figure 38

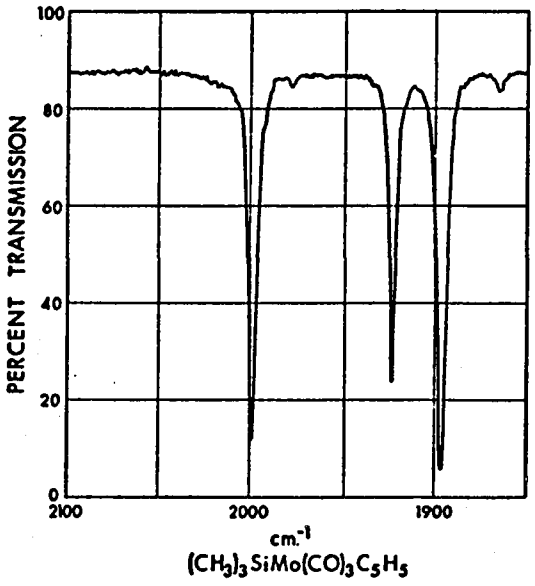
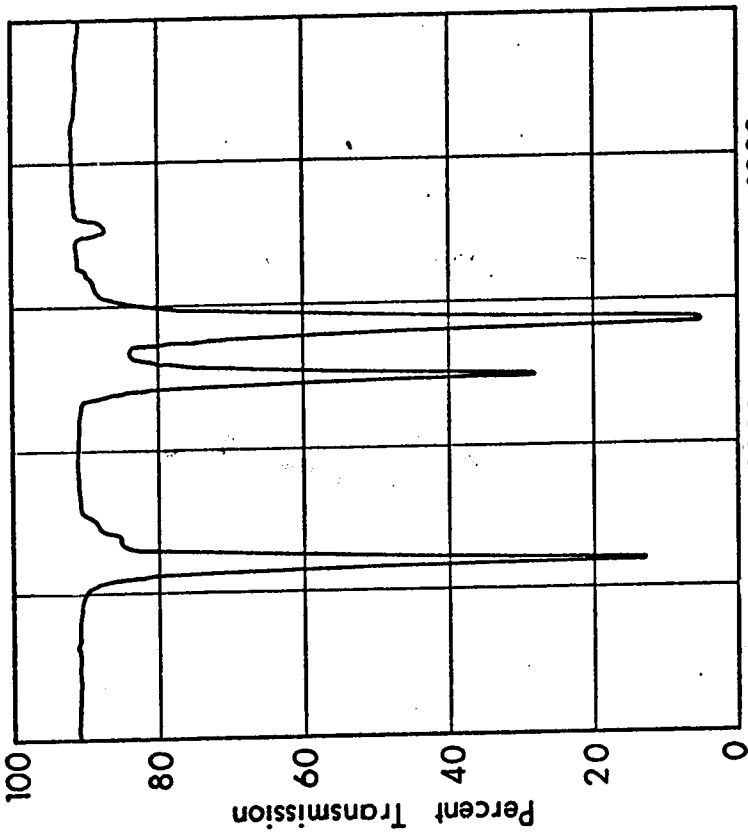
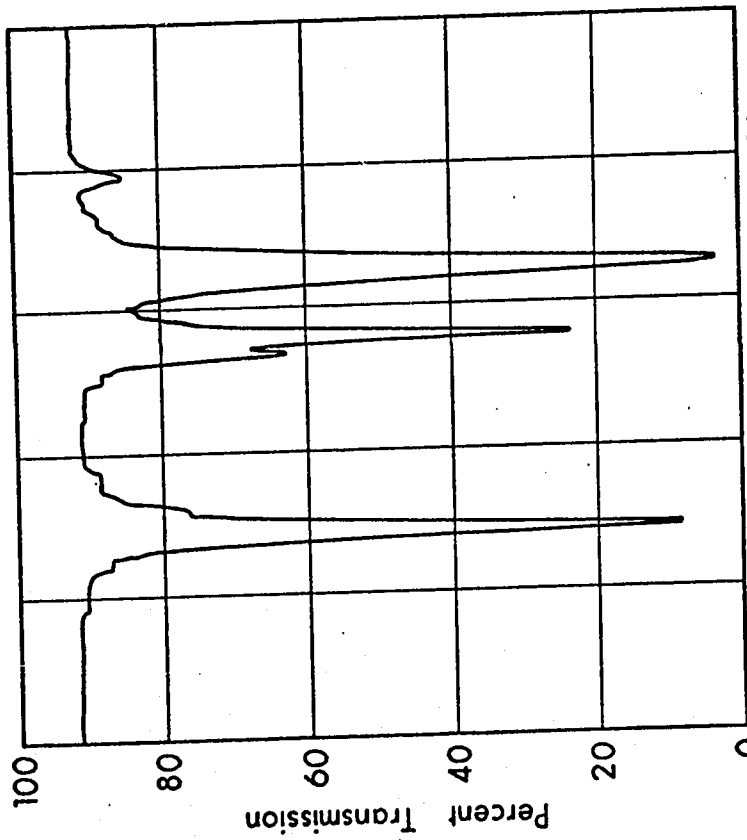


Figure 39



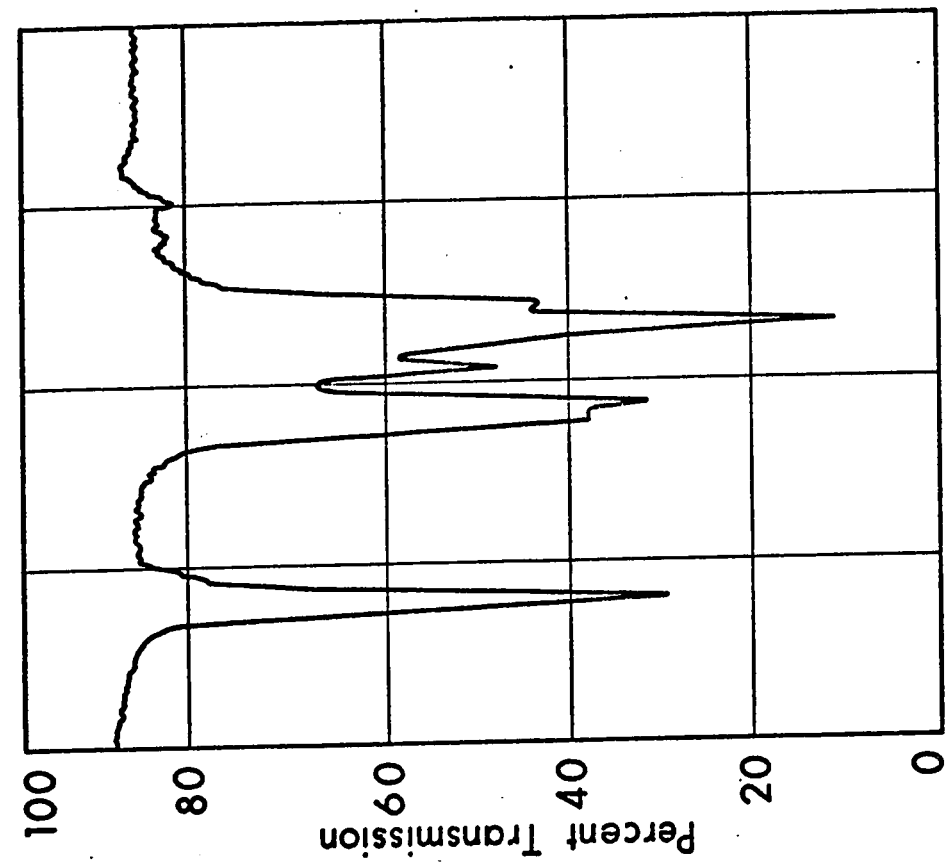
$Cl_3SiMo(CO)_3C_5H_5$

Figure 41



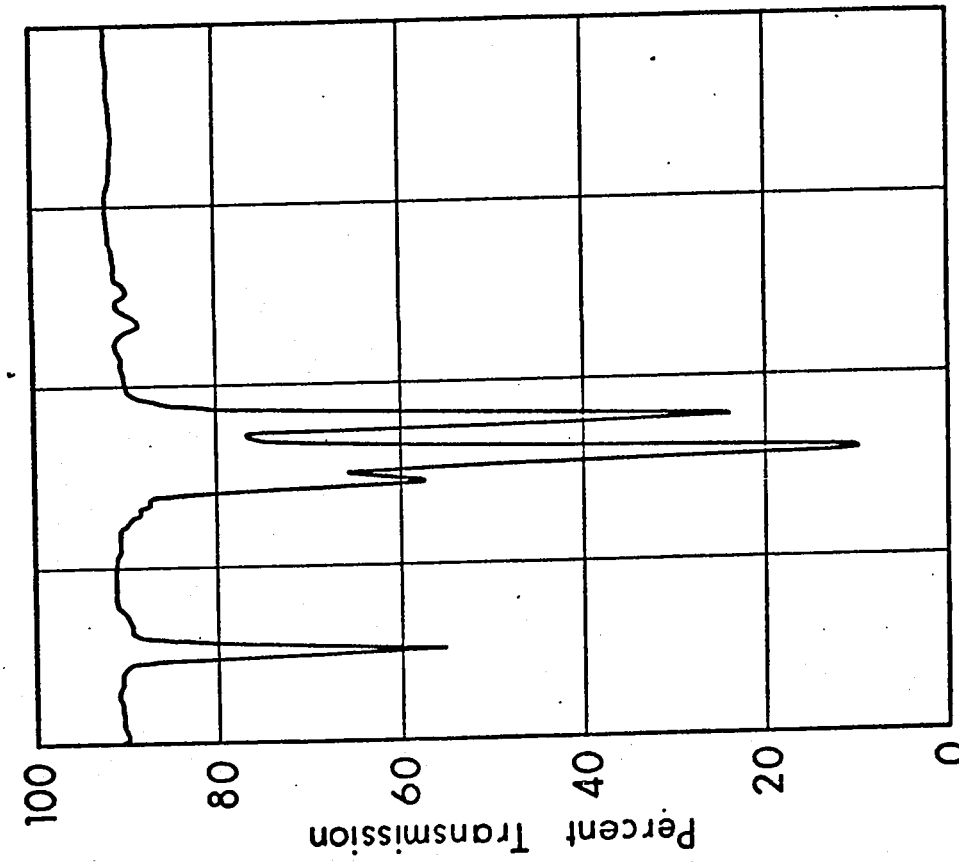
$CH_3Cl_2SiMo(CO)_3C_5H_5$

Figure 40



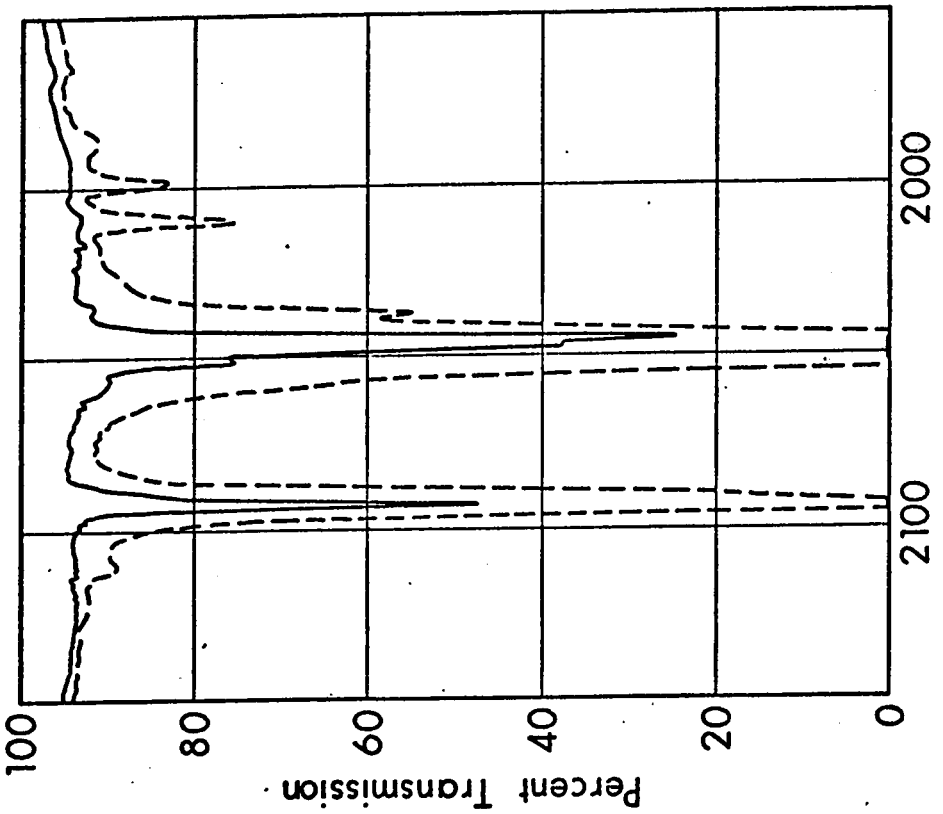
$(CH_3Cl_2Si)_2Fe(CO)_4$

Figure 43



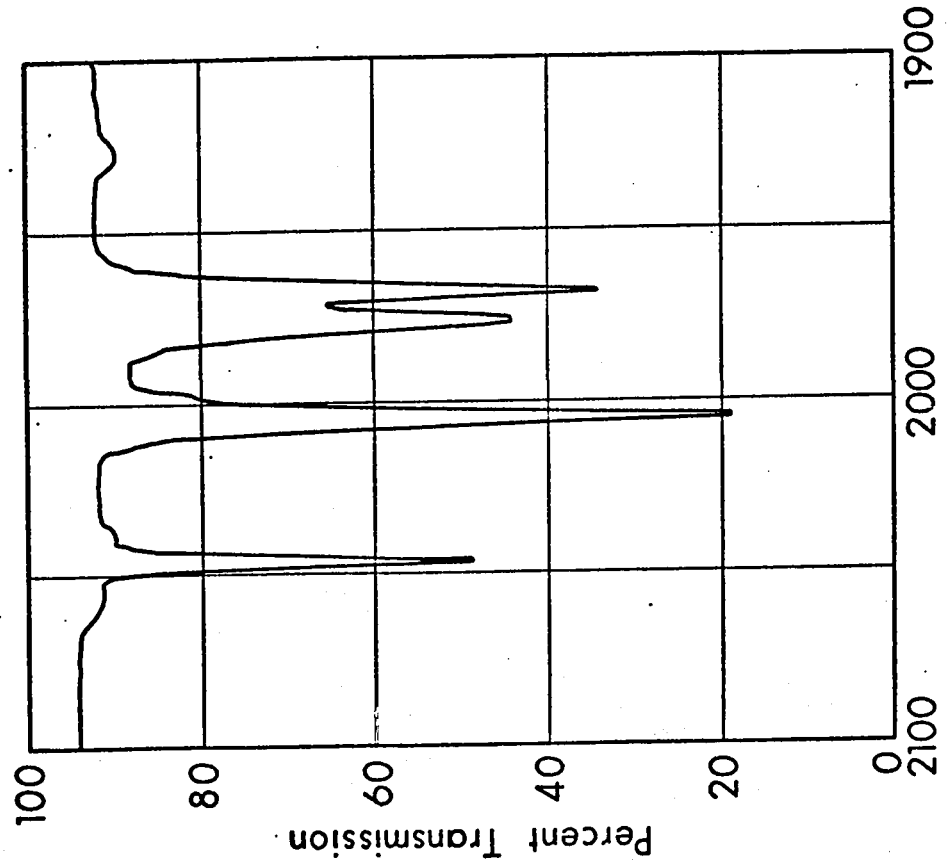
$(Cl_3Si)_2Fe(CO)_4$

Figure 42



$[Cl_2SiFe(CO)_4]_2$

Figure 45



$[(C_6H_5)_2SiMn(CO)_4]_2$

Figure 44

CHAPTER IV

The Thermal Reaction of Trichlorosilane and π-Cyclopentadienylirondicarbonyl Dimer; Properties of Products and Preparations of Derivatives.

Introduction

There are innumerable cases in chemistry where the same reactants yield different products at different reaction conditions, and it is of interest to mention several recent examples in the metal carbonyl field. Products such as $R_2GeFe_2(CO)_8$, $[R_2GeFe(CO)_4]_2$ $(R_2Ge)_2Fe_2(CO)_7$ and $(R_2Ge)_3Fe_2(CO)_6$; (R = Me or Ph) are obtained from reactions of R_2GeH_2 and $Fe_2(CO)_9$ or $Fe_3(CO)_{12}$ [27]. The successive loss of carbon monoxides, which are replaced by germanium-iron bonds, appears to occur in steps at different rates.

The reaction of $Fe(CO)_5$ and Bu_3SnCl yields several products, depending on the reaction conditions [55]. Fast reflux for 70 hours yields $Sn[Fe(CO)_4]_4$ as the final product. At milder conditions, $[Bu_2SnFe(CO)_4]_2$, as well as $Bu_4Sn_3Fe_4(CO)_{16}$ are isolated.

In the reaction of $Na^+[Co(CO)_4]^-$ and $(Acac)_2SnCl_2$ it was discovered that the rate of addition of the carbonyl anion determined the final product [182,184]. Fast addition of $Na^+[Co(CO)_4]^-$ to $Acac_2SnCl_2$ yields $(Acac)_2SnCo_2(CO)_7$ whereas slow addition of $Na^+[Co(CO)_4]^-$ yields $(Acac)_2SnCo_2(CO)_8$.

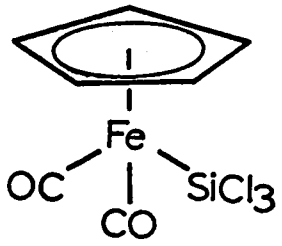
From the reaction of Cl_3SiH and $[CpFe(CO)_2]_2$ several

products may be isolated over a range of reaction conditions. These are studied in the present Chapter. Most of the thermal reactions of $Me_{3-n}Cl_nSiH$ with dinuclear carbonyl complexes described in Chapter III yield only one product, which generally is the analog of the final and most stable product from the reaction of Cl_3SiH and $[CpFe(CO)_2]_2$. These reactions may also perhaps proceed by a complex array of reaction paths through numerous intermediates, but their formation would be slower than their subsequent conversion to the final product.

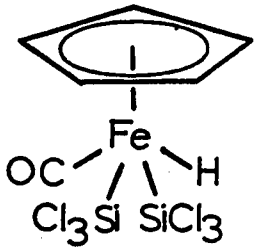
The order in which the results are presented in the following section is aimed at familiarizing the reader first with the diverse nature of the products and their characterization. Speculative suggestions about the mode of reaction and reasonable explanations for observed spectroscopic results are put forward throughout the text.

RESULTS AND DISCUSSION

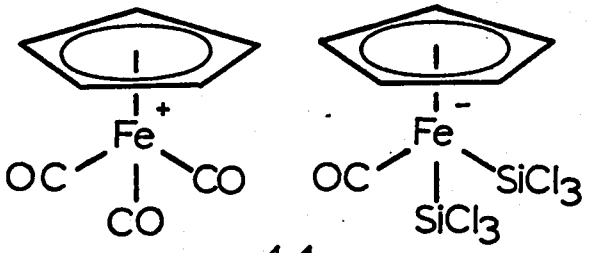
Over a range of reaction conditions π-cyclopentadienylirondicarbonyl dimer and trichlorosilane yield several silyl-iron carbonyl derivatives. The products thus far isolated are shown below:



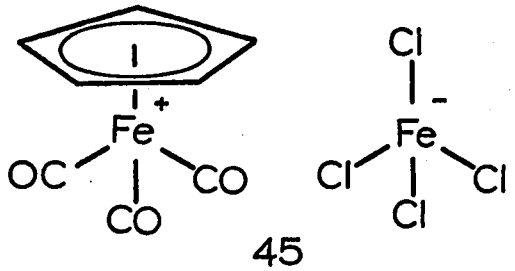
42



43



44



45

In these molecules the ligands surrounding the iron atoms are arranged in a distorted tetrahedral fashion (neglecting for the moment the hydrogen ligand in 43) in which the

cyclopentadienyl ring occupies one of the apexes.

1. Properties and Characterization

Complexes 42 - 45 display a wide range of physical and chemical properties. Compound 42, $Cl_3SiFe(CO)_2Cp$ is covalent, thermally very stable and does not undergo any further reaction with Cl_3SiH at temperatures up to 180°C. Compound 43, $(Cl_3Si)_2HFe(CO)Cp$ is covalent in nonpolar solvents such as pentane, hexane or heptane but in donor organic solvents, such as acetonitrile or acetone, this hydride undergoes partial or complete ionic dissociation as a strong acid. Compound 44, $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$ is ionic and sparingly soluble in dichloromethane; however, in acetonitrile or acetone the compound is very soluble and nearly totally dissociated. Compound 45, $[CpFe(CO)_3]^+FeCl_4^-$ is ionic and insoluble in dichloromethane. It dissolves in acetone but decomposes rapidly in solution. The survival of these products in the reaction mixture may in part be due to these properties.

With Ph_4AsCl in a polar medium the hydrogen on the iron atom in $(Cl_3Si)_2HFe(CO)Cp$, may be replaced by the bulky cation, Ph_4As^+, yielding $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$.

$$(Cl_3Si)_2HFe(CO)Cp + Ph_4AsCl \rightarrow Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^- + HCl \qquad [IV.1]$$

If the reaction is carried out in acetone, then the product may immediately be extracted with dichloromethane after removal of the acetone at reduced pressure. The reaction of $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$, 44, with Ph_4AsCl in acetone yields $ClFe(CO)_2Cp$ and $Ph_4\overset{+}{As}[(Cl_3Si)_2Fe(CO)Cp]^-$. This reaction is relatively slow and requires approximately

$$[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^- + Ph_4AsCl \rightarrow Ph_4\overset{+}{As}[(Cl_3Si)_2Fe(CO)Cp]^- + ClFe(CO)Cp + CO \quad [IV.2]$$

one hour at room temperature for the evolution of carbon monoxide to cease. Since both reactants in equation IV.1 are dissociated, then the formation of $Ph_4\overset{+}{As}[(Cl_3Si)_2Fe(CO)Cp]^-$ is a metathetical ionic reaction, and hydrogen chloride is eliminated with the reaction solvent. In the formation of $ClFe(CO)_2Cp$, however, carbon monoxide must be eliminated prior to the formation of the iron-chlorine bond:

$$[CpFe(CO)_3]^+Cl^- \rightarrow ClFe(CO)_2Cp + CO \quad [IV.3]$$

If the red colored $ClFe(CO)_2Cp$ is stirred in the presence of $NaBPh_4$ under carbon monoxide pressure, the reverse process takes place [67]. If the yellow $[CpFe(CO)_3]^+BPh_4^-$ is stirred at room temperature in the presence of Ph_4AsCl, the solution turns slowly red with evolution of carbon monoxide:

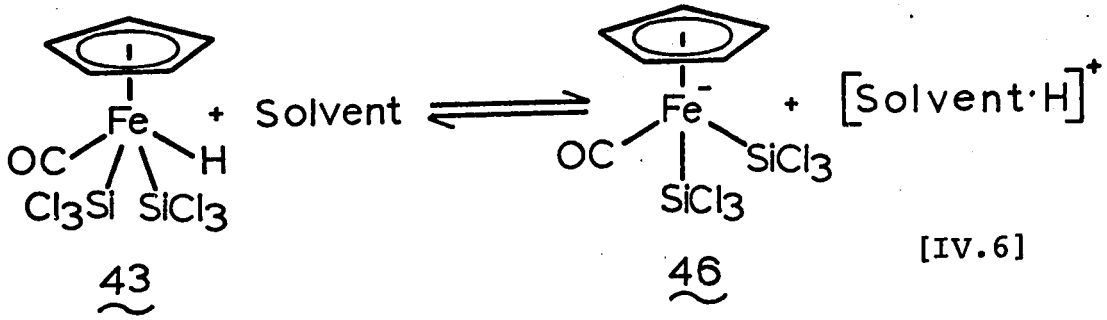
$$ClFe(CO)_2Cp + NaBPh_4 \xrightarrow{\text{CO pressure}} [CpFe(CO)_3]^+BPh_4^- \quad [IV.4]$$

$$[CpFe(CO)_3]^+BPh_4^- + Ph_4AsCl \rightarrow ClFe(CO)_2Cp + Ph_4AsBPh_4 + CO \qquad [IV.5]$$

2. Infrared Spectra

Of particular interest are the carbon monoxide stretching frequencies relative to the charge on the species. A high electron density on the molecule will partly be transmitted into the carbon monoxide antibonding orbitals and shift the carbon monoxide vibrations to lower frequencies. This is clearly demonstrated by the isoelectronic series; $Ni(CO)_4$, $[Co(CO)_4]^-$ and $[Fe(CO)_4]^=$, which has been pointed out in Chapters I and II. For comparison of relative frequencies of the carbonyl stretching vibrations, the infrared spectra of $(Cl_3Si)_2HFe(CO)Cp$, 43, in the undissociated and dissociated form, $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$, $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$, 44, and $[CpFe(CO)_3]^+FeCl_4^-$, 45, are shown on the same scale in Fig. 46 - 50.

The spectra of $(Cl_3Si)_2HFe(CO)Cp$, in the undissociated form in hexane and dissociated form in acetone are shown in Fig. 46 and 47 respectively.



43 46 [IV.6]

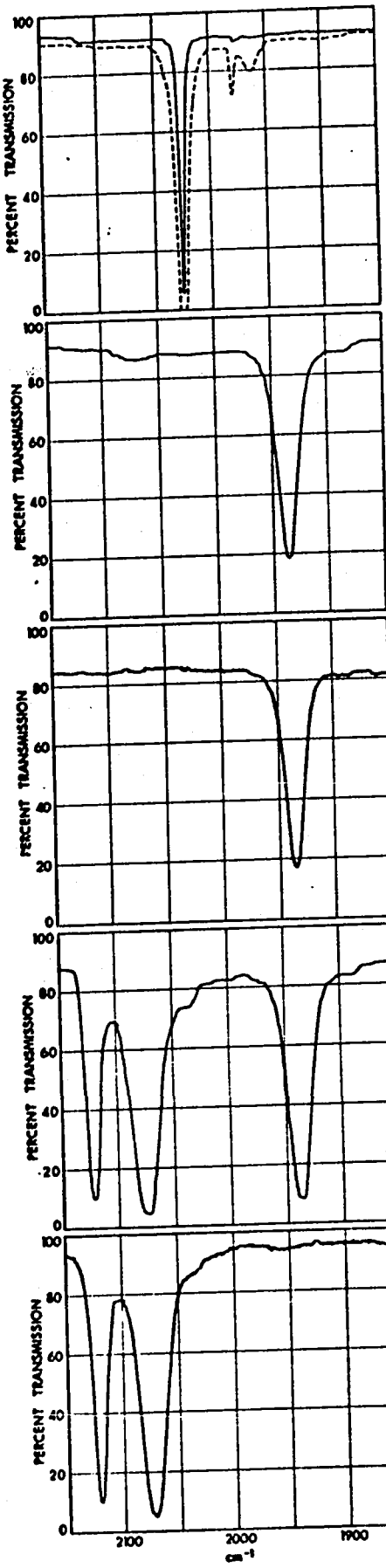


Figure 46
$(Cl_3Si)_2HFe(CO)Cp$
in Hexane

Figure 47
$(Cl_3Si)_2HFe(CO)Cp$
in Acetone

Figure 48
$[Ph_4As]^+[(Cl_3Si)_2Fe(CO)Cp]^-$
in Acetone

Figure 49
$[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$
in Acetone

Figure 50
$[CpFe(CO)_3]^+[FeCl_4]^-$
in Acetone

The electrons which no longer are involved in the iron-hydrogen bond upon dissociation, cause a shift of the carbon monoxide stretching frequency from 2025 cm^{-1} to 1936 cm^{-1}, a net shift of 89 wavenumbers. The weak broad band at 1960 cm^{-1} in Fig. 46 was assigned to the iron-hydrogen stretching vibration, while the adjacent sharp band at 1976 cm^{-1} is the ^{13}C-O vibration. The spectrum of $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$, in Fig. 48 is identical to Fig. 47. The change in cation appears to have no significant influence on the carbon monoxide vibration.

For similar reasons, a net positive charge on a species shifts the carbon monoxide vibration to a higher value. For example, if $[CpFe(CO)_3]^+$ is compared to $CpMn(CO)_3$, which shows the carbon monoxide vibration at 2028 cm^{-1} and 1946 cm^{-1}, an average shift of approximately 110 cm^{-1} to a higher value is observed. The infrared spectra in Fig. 48, 49 and 50 demonstrate carbon monoxide vibrations due to common anions and cations. The anion $[(Cl_3Si)_2Fe(CO)Cp]^-$ is observed at low frequency in Fig. 48 and 49, while the cation $[CpFe(CO)_3]^+$ is observed at high frequency in Fig. 49 and 50.

The infrared spectra of the ionic compounds in the crystalline state are considerably more complex than those in solution. The band patterns and positions of the carbon monoxide vibrations are to a large extent determined by the

particle size and their environment. This technique for the preparation of infrared samples may suffer any number of shortcomings described by Szymanski [201]. The mull spectra of $[CpFe(CO)_3]^+[Cl_3Si)_2Fe(CO)Cp]^-$, 44, and $[CpFe(CO)_3]^+FeCl_4^-$, 45, are shown in Figures 53 and 54. The high frequency portion of each spectra, which is due to the same cation, suggests that the carbon monoxide stretching vibrations are greatly influenced by the anion.

3. Nuclear Magnetic Resonance Spectra

The relative chemical shifts of the cyclopentadienyl protons on anions, cations and neutral molecules employing $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$, 44, $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$, $(Cl_3Si)_2HFe(CO)Cp$, 43 and $Cl_3SiFe(CO)_2Cp$, 42, in acetonitrile are shown in the nmr spectra, Fig. 55-58. Parallel to the observed carbonyl stretching frequencies, the shielding of the cyclopentadienyl protons by a high electron density on the species shifts the proton resonance to higher field. Thus the cyclopentadienyl proton resonance of anions is observed at high field, while that for cations is observed at low field. The τ values for $[CpFe(CO)_3]^+$, $Cl_3SiFe(CO)_2Cp$ and $[(Cl_3Si)_2Fe(CO)Cp]^-$ in acetonitrile are 4.25, 4.87 and 5.37 respectively.

For $[CpFe(CO)_3]^+FeCl_4^-$, 45, which contains a paramagnetic anion, no resonance signal was observed; however, a saturated acetone solution of $[CpFe(CO)_3]^+BPh_4^-$, which

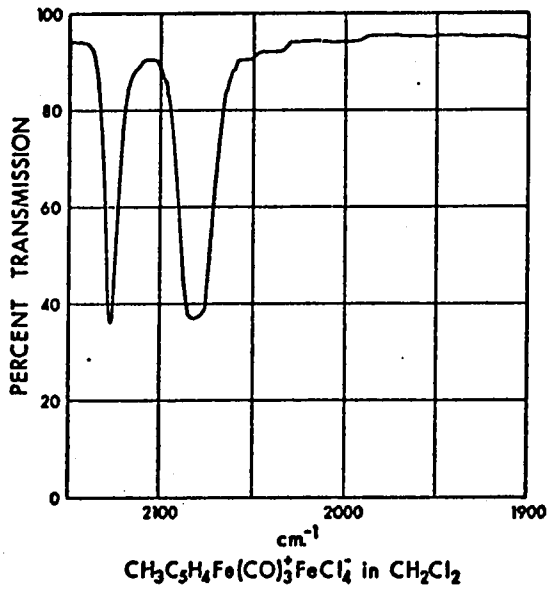


Figure 51

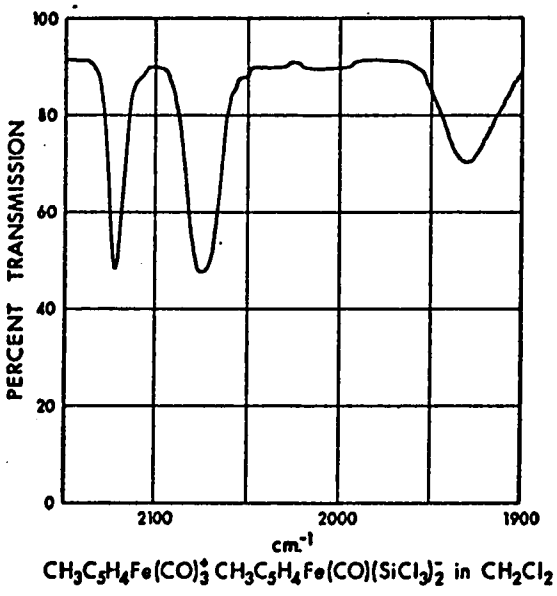


Figure 52

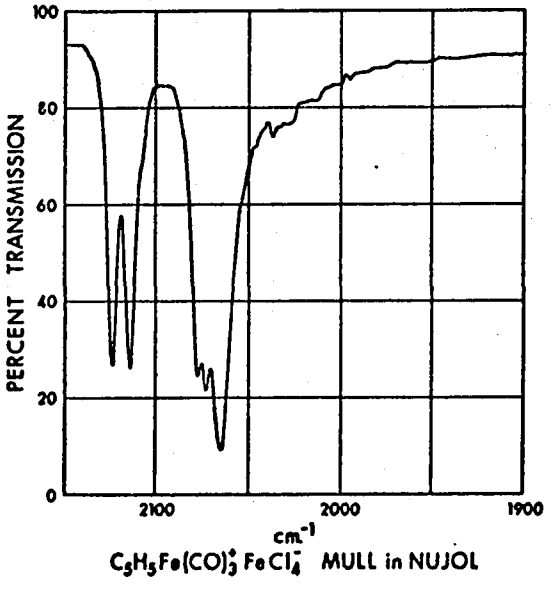


Figure 53

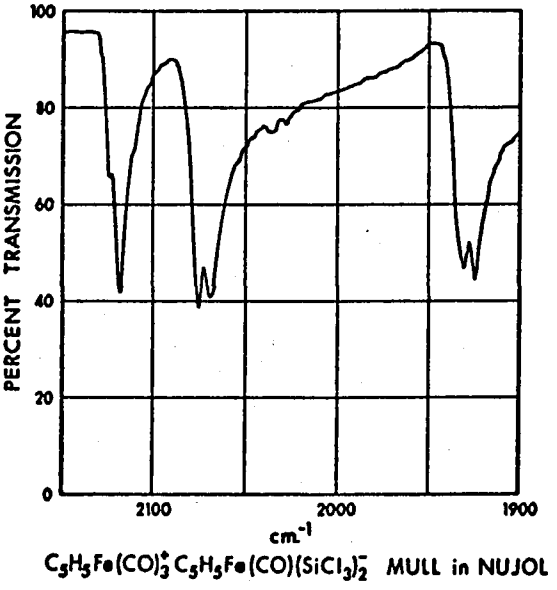


Figure 54

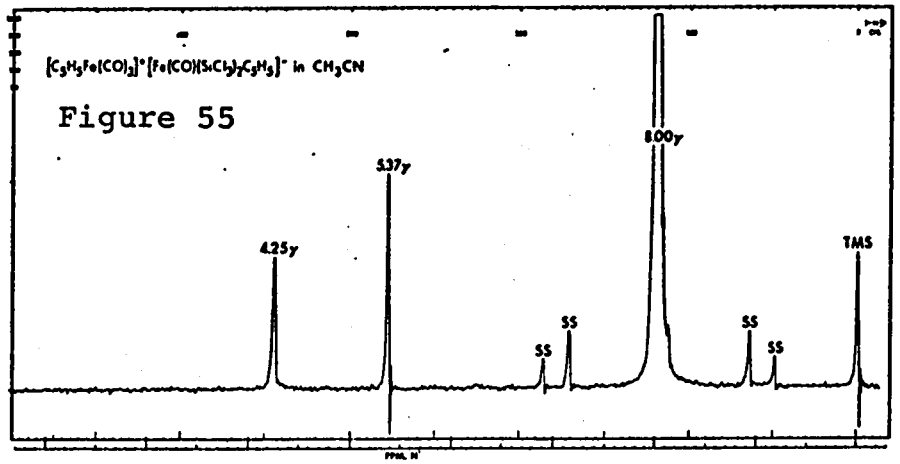


Figure 55

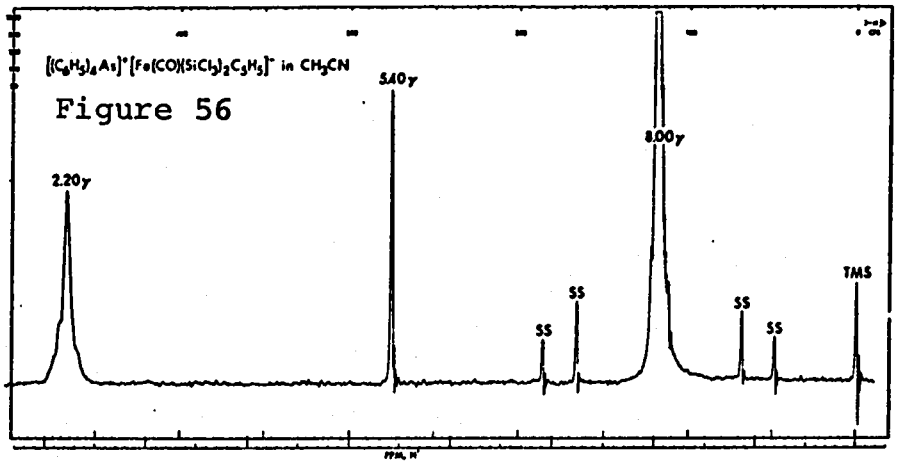


Figure 56

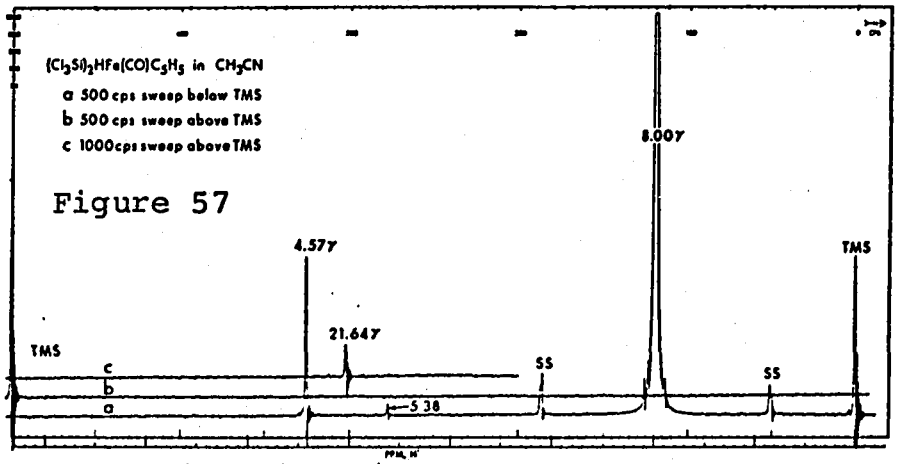


Figure 57

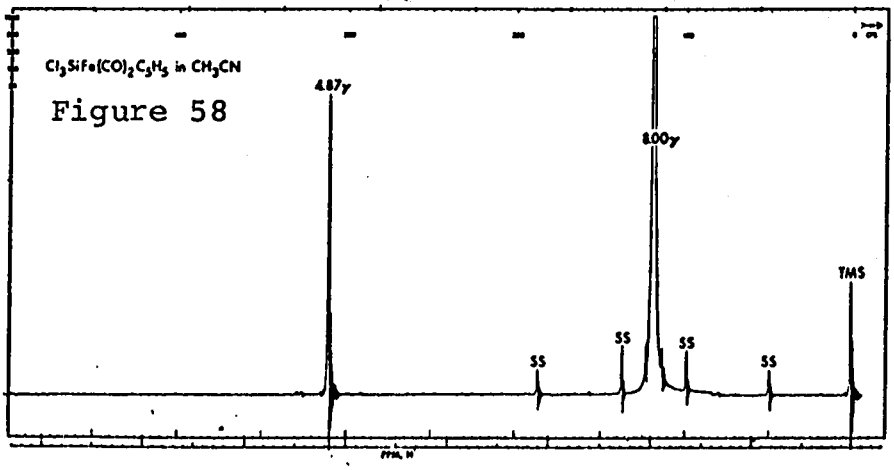
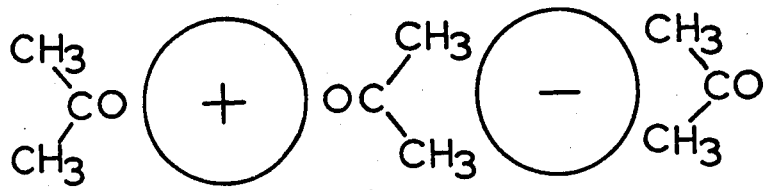


Figure 58

has the same cation, shows the cyclopentadienyl protons at 3.87τ (note Table XVI). In acetone $[CpFe(CO)_3]^+$ $[(Cl_3Si)_2Fe(CO)Cp]^-$, 44, shows the cyclopentadienyl proton resonance at 3.85τ and 5.40τ. While the change in solvent appears to have no significant effect on the anion, the proton resonance on the cation is shifted 0.40τ units to lower fields, when acetonitrile was replaced by acetone as the nmr solvent. The manner in which the ions are solvated by acetonitrile or acetone may perhaps explain this shift. In both of these polar solvents the anion would be in close proximity to methyl groups, while the cation would be surrounded either by the nitrogens of acetonitrile or the oxygens of acetone:



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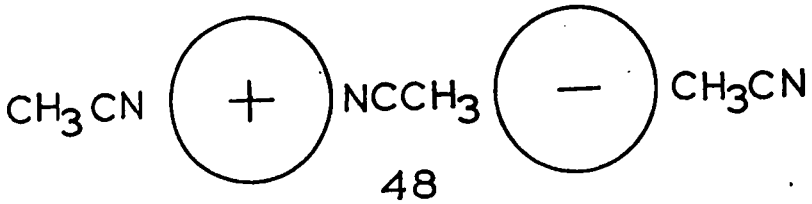


48

The degree of dissociation of $(Cl_3Si)_2HFe(CO)Cp$ is largely dependent on the solvent. In acetonitrile, CH_3CN, dissociation occurs only to a small extent:

$$(Cl_3Si)_2HFe(CO)Cp \rightleftharpoons H^+ + [(Cl_3Si)Fe(CO)Cp]^- \qquad [IV.7]$$

This can be observed in the nmr spectrum for $(Cl_3Si)_2HFe(CO)Cp$ in acetonitrile, Fig. 57, by the appearance of a weak signal at 5.38τ, corresponding to the cyclopentadienyl protons on the anion. These features are shown in more detail in Fig. 59 which also shows an accurate integration of the relative intensities. For an nmr sample containing approximately 100 mg of hydride in 0.4 ml acetonitrile, an integration ratio of 154:9.5 for the undissociated and dissociated cyclopentadienyl protons was found. Assuming the system is at equilibrium, an equilibrium constant, K, in acetonitrile can be calculated:

$$K_a = \frac{[H^+][(Cl_3Si)_2Fe(CO)Cp^-]}{[(Cl_3Si)_2HFe(CO)Cp]} = \frac{[0.038]^2}{[0.56]} = 2.6 \times 10^{-3}$$

$$pK_a = 2.6$$

According to this value, $(Cl_3Si)_2HFe(CO)Cp$ is one of the strongest known acids in acetonitrile.*

---

* I. M. Kolthoff, S. Bruckenstein and M. K. Chantooni, Jr., J. Am. Chem. Soc., 83, 3927 (1961), report pK_a values for $HClO_4$ and HBr, the strongest known acids in acetonitrile of <2 and 5.5 respectively.

In acetone, $(Cl_3Si)_2HFe(CO)Cp$ is completely dissociated. The cyclopentadienyl proton resonance is approximately at 5.3 - 5.4τ and no high field proton in the τ21-22 region can be detected.

The effects of adding a base to $(Cl_3Si)_2HFe(CO)Cp$, in acetonitrile are shown in Fig. 59-61. Successive additions of 0.01 ml of pyridine to the nmr sample, containing approximately 100-120 mg of hydride, caused an inversion of the intensity ratio for the proton resonance absorption on the undissociated and dissociated complex. The weak signal 890 cps below TMS appears to be the resonance signal for the proton on the nitrogen of the pyridine, (i.e. $^{+}HNC_5H_5$).

The nmr spectrum of the high field proton, which is bonded directly to iron, shows additional fine structure at high amplitude on an expanded scale, Fig. 62. The main resonance absorption is at 21.64τ. The protons coupled to ^{29}Si are observed at $J(H\text{-}Fe\text{-}^{29}Si)$ = 20.0 cps. The integrated intensity of these signals relative to the main absorption is approximately 10%. The natural abundance of the ^{29}Si isotope, which has a spin of $\pm$ 1/2, is 4.7%. Since there are two silicon atoms in the molecule, the statistical probability for the presence of one ^{29}Si isotope in the molecule is 9.4%.

A weaker set of satellites is observed at J = 14.5 cps. These are believed to be due to the protons coupled

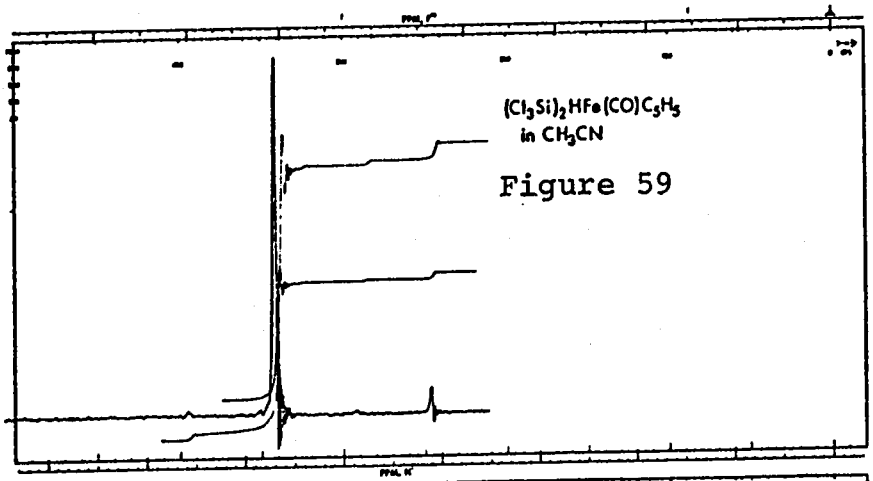


Figure 59

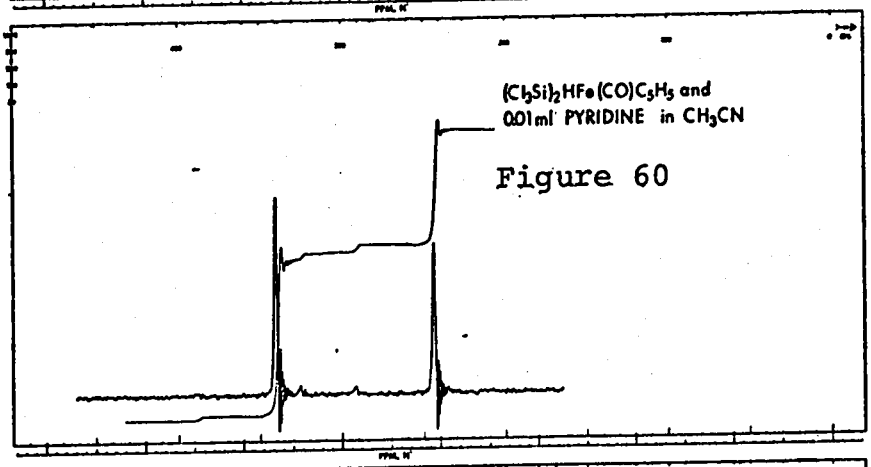


Figure 60

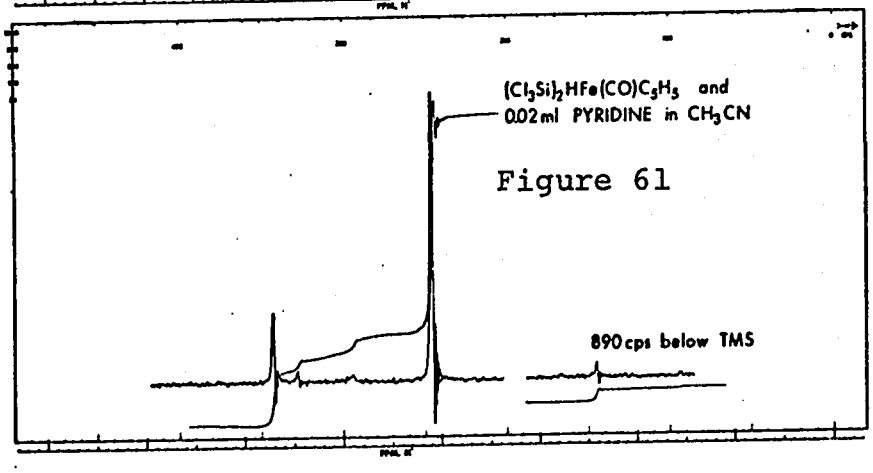


Figure 61

to ^{57}Fe, which has a spin of $\pm$ 1/2 and a natural isotope abundance of 2.2%. There are no known reports of proton resonance coupling to ^{57}Fe, and this tentative assignment is made on the basis of approximate intensity ratio. The possibility that the weak bands at J = 14.5 cps are due to coupling of the high field proton to ^{13}C of the cyclopentadienyl ring has not been ruled out with certainty.

The sharpness of the nmr signals suggests that compounds 42-44 are diamagnetic. For the proposed structures at the beginning of this chapter, the complexes do obey the E.A.N. rule (e.g. each iron atom obtains a total of 10 electrons from the ligands). In $[CpFe(CO)_3]^+FeCl_4^-$, 45, the anion is paramagnetic. The $FeCl_4^-$ ion is a tetrahedral d^5 system with five unpaired electrons. Because of the extreme insolubility of $[CpFe(CO)_3]^+FeCl_4^-$ in most solvents, a sufficiently pure sample for analysis was not obtained.

The reaction of $[\pi CH_3C_5H_4Fe(CO)_2]_2$ and Cl_3SiH yields the methylcyclopentadienyl analogs of compounds 42 - 45. These are far more soluble than their cyclopentadienyl counterparts. For example, $Cl_3SiFe(CO)_2\pi C_5H_4CH_3$ and $(Cl_3Si)_2HFe(CO)\pi\text{-}C_5H_4CH_3$ are extremely soluble in hexane, $[\pi CH_3C_5H_4Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)\pi C_5H_4CH_3]^-$ is very soluble in dichloromethane, and $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$ is moderatly soluble in dichloromethane. A sufficiently pure sample of this complex for analysis was obtained. The magnetic susceptibility was also measured.

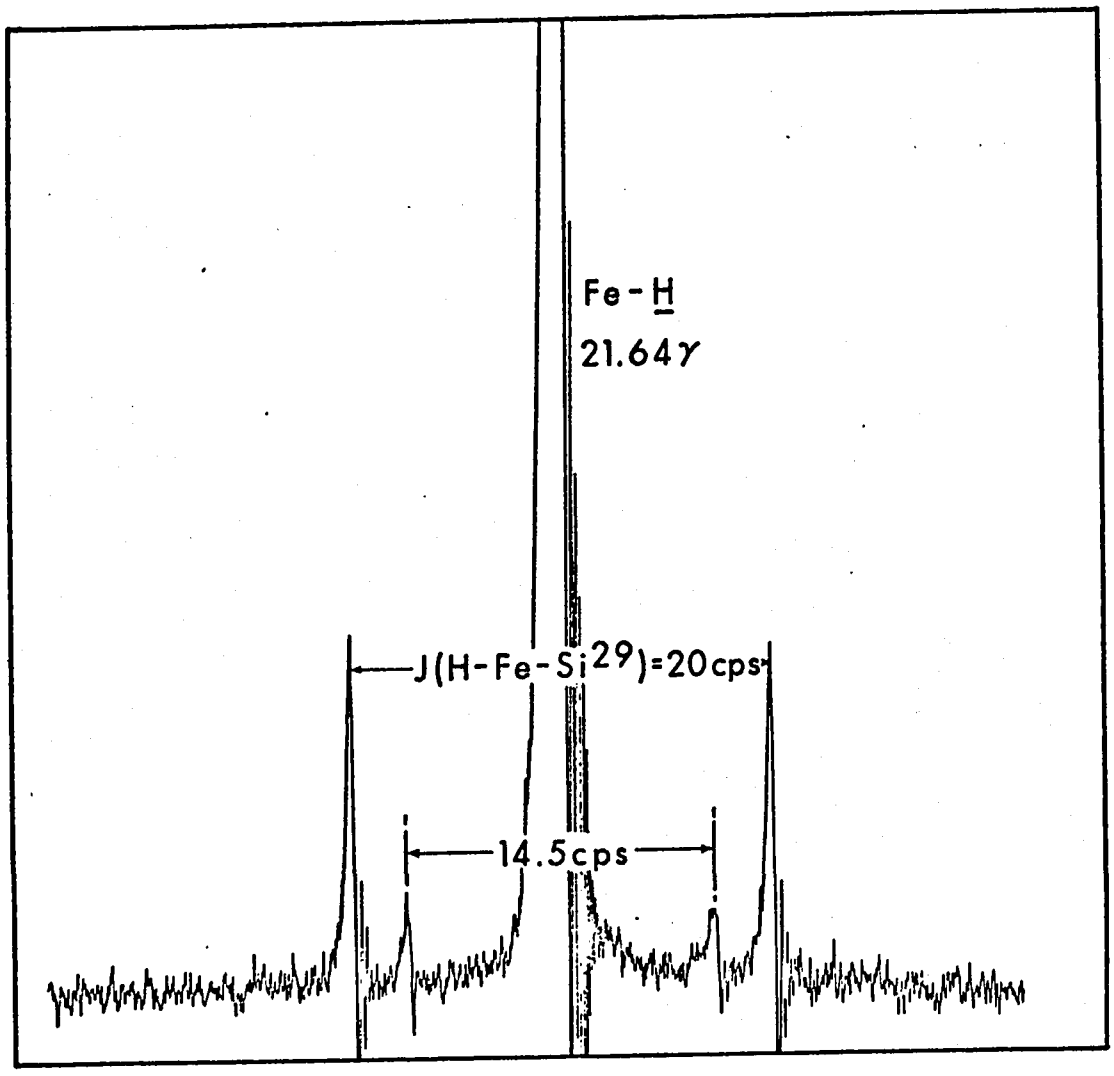


Figure 62

4. Magnetic Susceptibility of $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$

The iron atom in the anion of $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$ is in the plus (III) oxidation state and a tetrahedral environment. In this state, the magnetic moment, μ, of iron is always very close to the spin only value of 5.9 B.M. (Bohr Magnetons) due to the five unpaired electrons [52].

The gram susceptibility of a sample, Xgm(s), can be determined by measuring the increase in weight, $\Delta f(std)$, in an inhomogeneous magnetic field of an accurately weighed standard, m(std), and the increase in weight, $\Delta f(s)$, of the accurately weighed sample, m(s). For example, using $HgCo(SCN)_4$ as a standard (three unpaired electrons), Xgm(std) = 16.27 cgs units. The experimental values can be related to the number of unpaired electrons, n, in the complex [53]:

$$Xgm(s) = \frac{\Delta f(s)}{\Delta f(std)} \cdot \frac{m(std)}{m(s)} \cdot Xgm(std)$$

The uncorrected molar magnetic susceptibility is:

$$X_M^{unc.} = Xgm \cdot Mol.\ Wt.$$

The magnetic moment μ is:

$$\mu = 2.83\sqrt{X_M^{corr}(T-\theta)}$$

The diamagnetic contributions X_M^D, are relatively small and can be omitted in an approximation:

$$\chi_M^{corr.} = \chi_M^{unc.} - \chi_M^{D} \approx \chi_M^{unc.} = \chi_M$$

Making further approximations, by employing the absolute temperature, T, instead of (T-θ), (θ is known as the Weiss constant), the magnetic moment, μ, is:

$$\mu = 2.83\sqrt{\chi_M T} = \sqrt{n(n+2)}$$

The molecular weight, Mol. Wt., is then:

$$\text{Mol. Wt.} = \frac{n(n+2)}{8.25 \times 10^{-2}}$$ see Experimental section:

With five unpaired electrons, n = 5, a molecular weight of 425 was calculated. The molecular weight of $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$, is 417. The calculated value is less than 2% high, so that the susceptibility measurement confirms the initial formulation.

5. Conductivity Measurements

The degree of ionization of complexes in polar solvents may be established from conductance measurements. The equivalent conductance of potassium chloride, which is a uni-uni-valent salt of a 10^{-3} molar aqueous solution, is approximately 147 cm^2 $equiv^{-1}$ ohm^{-1} [66].

Conductivity measurements in acetone at two different concentrations were performed on a number of ionic and nonionic compounds studied in this chapter. The values are given in Table XII. The nonionic complexes $ClFe(CO)_2Cp$ and $Cl_3SiFe(CO)_2Cp$, show the anticipated low values for Λ_m

TABLE XII

Conductivity Measurements,[a,b,c]

Compound	MW	mg/25 ml	Molarity x 10^{-3}	Resistance x 10^{5}	Λ
$Cl_3SiFe(CO)_2\pi Cp$ [d]	311	9.8	1.26	0.720	3.1
		21.1	2.72	0.410	2.5
$(Cl_3Si)HFe(CO)\pi Cp$	419	10.6	1.01	0.0185	150
		23.6	2.25	0.0090	138
$(Cl_3Si)Fe_2(CO)_4\pi Cp_2$	623	16.4	1.05	0.0193	139
		36.6	2.35	0.0094	127
$Ph_4AsFe(CO)(SiCl_3)_2\pi Cp$	801	21.1	1.05	0.0225	119
		59.2	2.96	0.0080	118
$CpFe(CO)_3BPh_4$	524	14.0	1.07	0.0210	125
		29.7	2.27	0.0108	114
$ClFe(CO)\pi Cp$ [d]	212	6.2	1.17	2.0	1.2
		20.7	3.91	1.2	0.6

a. $\Lambda = \frac{1000\ \bar{L}}{C} = \frac{1000\ K}{CR}$ $cm^2\ mol^{-1}\ ohm^{-1}$

b. Resistance of the solvent was 0.12×10^6 ohm at beginning of experiment and 0.12×10^6 ohm at end of experiment.

c. Cell constant was 0.28 cm^{-1}.

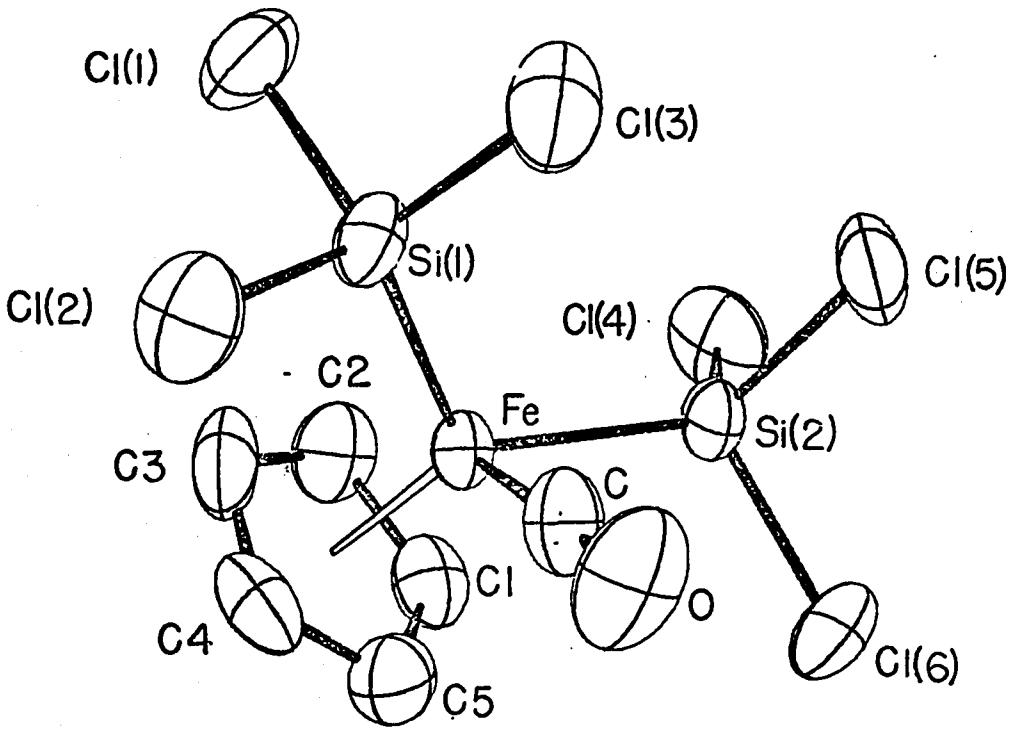
d. Values were rapidly changing within the first 10 seconds after dilution of the compound.

The conductance values, Λ , for the ionic complexes, all are between 110 - 150 cm^2 $equiv^{-1}$ ohm^{-1}. The magnitude of these values and the increase in equivalent conductance at lower concentration are in good agreement with reported values for completely dissociated uni-uni-valent salts [76].

6. Structures

Recently Ibers *et al.* have determined the structure of $(Cl_3Si)_2HFe(CO)Cp$, 43, using a sample supplied by this laboratory. The X-ray crystallographic structure and the interatomic data are given in Figure 63 and Table XIII [153]. The hydrogen bonded to the iron atom is not shown, since it was not detected by X-ray crystallography; nevertheless, there is little doubt as to where it is likely to be situated. The angles between CCp-Fe-Si(1), CCp-Fe-Si(2) and Si(1)-Fe-Si(2), note Table XIII, are all greater than 109°, leaving sufficient room for the hydrogen in the region defined by these three angles. In an alternative manner [153], the position of the hydrogen may be reviewed as *trans* to the carbon monoxide at the base of a square pyramid, in which the cyclopentadienyl ring forms the apex.

The structure of $Cl_3SnFe(CO)_2Cp$, which would be expected to be similar to that of $Cl_3SiFe(CO)_2Cp$, 42, also shows the distorted tetrahedral arrangement of the ligands, as indicated by the X-ray crystallographic determination [30]. Replacement of carbon monoxide by a silyl group or a silyl



$C_5H_5Fe(H)CO(SiCl_3)_2$

L. Manojlovic-Muir, K.W. Muir, and J.A. Ibers(1969)

Fe-Si = 2.252 Å

Figure 63

TABLE XIII

Selected Intramolecular Distances and Angles [153]

Distance	Å	Angle	Deg.
Fe-Si(1)	2.252(3)	CCp-Fe-Si(1)	119.4
Fe-Si(2)	2.252(3)	CCp-Fe-Si(2)	118.1
Fe-C	1.758(9)	CCp-Fe-C	125.8
Fe-CCp[a]	1.718	Si(1)-Fe-Si(2)	115.3(1)
Fe-C(1)	2.099(8)	Si(1)-Fe-C	85.1(3)
Fe-C(2)	2.084(7)	Si(2)-Fe-C	84.4(3)
Fe-C(3)	2.089(8)	Fe-C-O	177.0(10)
Fe-C(4)	2.086(10)	Fe-Si(1)-Cl(1)	116.7(1)
Fe-C(5)	2.106(11)	Fe-Si(1)-Cl(2)	112.2(2)
$Fe-C_{ring}$(av.)[b]	2.093(4)	Fe-Si(1)-Cl(3)	115.8(1)
Si(1)-Cl(1)	2.049(4)	Fe-Si(2)-Cl(4)	115.3(1)
Si(1)-Cl(2)	2.060(4)	Fe-Si(2)-Cl(5)	115.8(1)
Si(1)-Cl(3)	2.043(4)	Fe-Si(2)-Cl(6)	112.2(1)
Si(2)-Cl(4)	2.049(4)	Fe-Si-Cl (av.)	114.7(8)
Si(2)-Cl(5)	2.048(4)	Cl(1)-Si(1)-Cl(2)	103.5(2)
Si(2)-Cl(6)	2.061(4)	Cl(1)-Si(1)-Cl(3)	104.3(2)
Si-Cl (av.)	2.052(3)	Cl(2)-Si(1)-Cl(3)	102.7(2)
C-O	1.132(10)	Cl(4)-Si(2)-Cl(5)	104.6(2)
C(1)-C(2)	1.395(14)	Cl(4)-Si(2)-Cl(6)	103.9(2)
C(2)-C(3)	1.404(13)	Cl(5)-Si(2)-Cl(6)	103.7(2)
C(3)-C(4)	1.396(17)	Cl-Si-Cl (av.)	103.8(3)
C(4)-C(5)	1.443(15)	C(5)-C(1)-C(2)	109.9(9)
C(5)-C(1)	1.383(13)	C(1)-C(2)-C(3)	107.8(10)
C-c (av.)	1.404(10)	C(2)-C(3)-C(4)	108.0(10)
		C(3)-C(4)-C(5)	107.9(9)
		C(4)-C(5)-C(1)	106.3(10)
		C-C-C (av.)	108.0(6)

a. CCp is the centroid of the cyclopentadienyl ring.

b. Standard deviations of averaged quantities are estimated from the range of the individual measurements.

group by carbon monoxide on $Cl_3SiFe(CO)_2Cp$ would yield the anion or cation of $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$, 44 respectively.

7. Temperature Dependence of Products.

This reaction appears very complex and the limited available data allow only speculative suggestions about possible reaction paths. In a simplified representation, the reaction can be written in the following general terms:

Starting materials ⟶ [Intermediates] ⟶ Products [IV.8]

The terms "Intermediates and Products" are employed loosely in this text, since compounds 43 - 45, which may be isolated as products are apparently intermediates in the formation of 42.

The yields of the individual components are very sensitive to reaction conditions. For example, in a reaction at 130°C for 30 minutes, all of $[CpFe(CO)_2]_2$ is consumed, as indicated by the color change from brown to yellow. The products from this reaction contain mainly 44, a considerable amount of 43 and a small quantity of 42. If a similar reaction mixture is heated at the same temperature for a prolonged period of time, then the products of the reaction yield mainly 42, trace amounts of 43 and some 44. In a very narrow range of reaction conditions, (e.g. at 120-130°C for 15 minutes), the products contain considerable amounts

of unreacted $[CpFe(CO)_2]_2$, but a fourth component, $[CpFe(CO)_3]^+FeCl_4^-$, 45, may be isolated in appreciable quantities. There is evidence of the presence of other products which have not been characterized. For example, when the excess unreacted Cl_3SiH is distilled from the reaction mixture at reduced pressure and stored in a closed container at room temperature, the solution becomes slowly brown and eventually precipitates some flaky insoluble material, which may be the result of decomposed $HFe(CO)_2Cp$. Above 170°C the solid products, after removal of Cl_3SiH, contain some oily substance which does not show carbonyl bands in the infrared spectrum. This substance could be some form of higher silanes or silyl-cyclopentadienyl compounds.

Employing samples of 2.0 gm $[CpFe(CO)_2]_2$ (5.65 mmol) and 7.7 - 8.0 ml Cl_3SiH (excess), this reaction has been carried out at temperatures between 110 - 180°C at constant reaction times of 30 minutes. Yields of individual components have been determined by infrared spectroscopy. The values are tabulated in Table XIV and are plotted in Figure 64. Column seven in Table XIV, representing the percentage of accountable products by combining 42, 43 and 44, relative to the total weight of crude product after removal of excess unreacted Cl_3SiH, column three, does not add up to 100%. Insoluble residues remaining, after extraction with dichloromethane and the oily substance at the higher temperatures,

TABLE XIV

Temperature Dependence of Products.[a]

Exp. No.	Reaction Temperature °C	Total Weight of Reaction Products gm	Yield mmol 42	Yield mmol 43	Yield mmol 44	Total weight[b] % of 42, 43 and 44
1	110	2.22	>0.05	0.10	>0.50	---
2		2.24	>0.05	0.14	>0.50	---
3	120	2.82	0.11	0.73	1.66	47
4		2.80	0.13	0.87	1.47	45
5	130	3.61	0.23	1.48	3.49	77
6		3.60	0.26	1.51	3.46	77
7	140	3.72	0.60	2.01	3.04	77
8		3.75	0.63	1.87	2.94	73
9	150	3.73	1.25	2.03	2.48	74
10		3.70	1.20	1.85	2.35	67
11	160	3.69	1.84	1.76	2.00	69
12		3.70	1.81	1.73	2.02	69
13	170	3.53	3.81	1.05	0.61	56
14		3.54	3.50	0.92	0.69	52
15	180	3.37	5.16	0.44	0.07	54
16		3.31	4.73	0.43	0.05	49

a. Each reaction was carried out with 2.00 gm $\pm$ 0.01 $[CpFe(CO)_2]_2$ (5.65 mmol) and 7.7 ml $\pm$ 0.1 Cl_3SiH in a 60 - 70 ml Carius tube.

b. Based on the total weight of the reaction products.

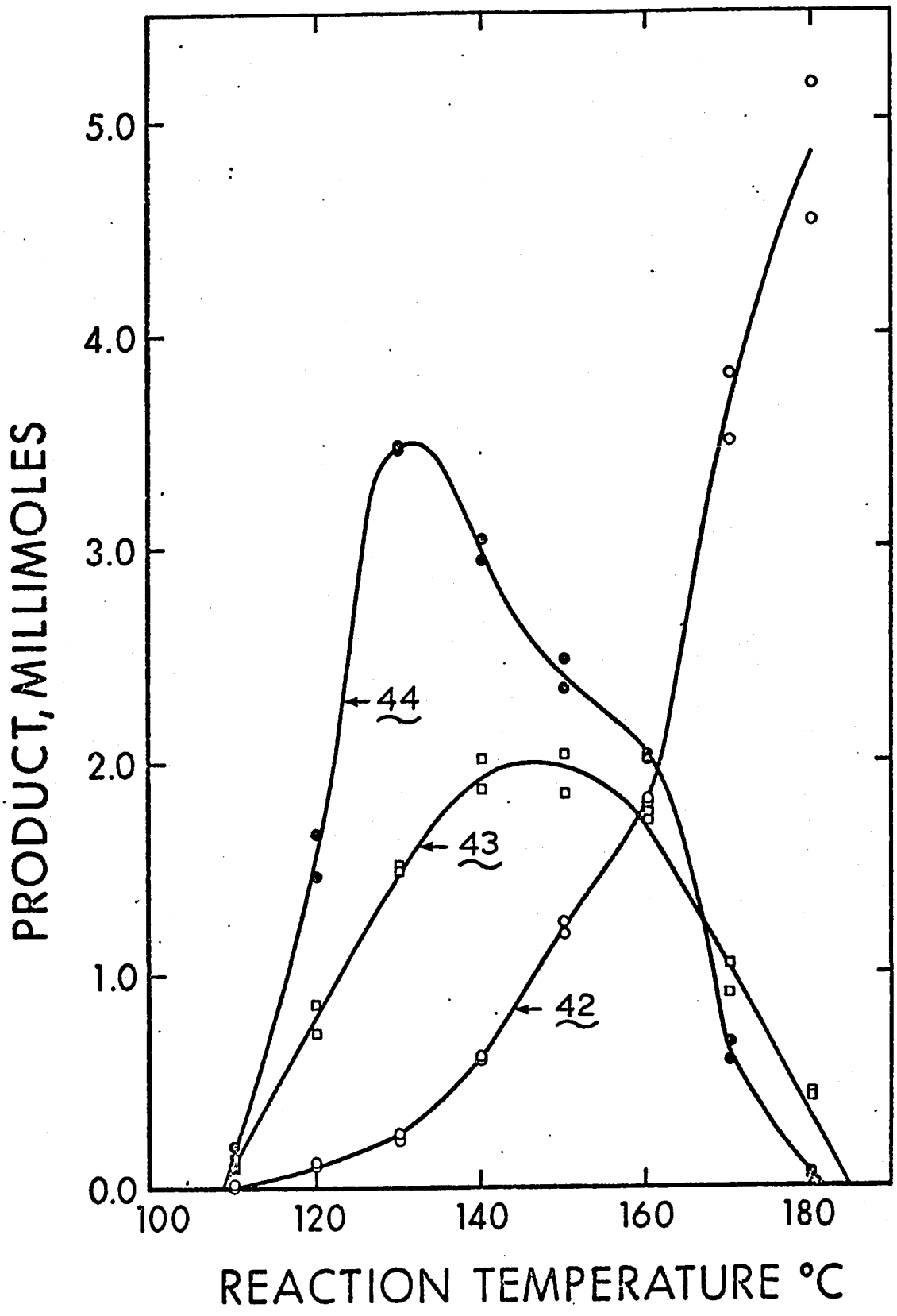

PRODUCT, MILLIMOLES
5.0
4.0
3.0
2.0
1.0
0.0
100
120
140
160
180
REACTION TEMPERATURE °C
44
43
42

Figure 64

appear to account for most of this discrepancy.

Drawing attention to Figure 64, it is most important to keep in mind that it does not represent a normal kinetic study and that the conclusions that can be drawn from it are very much more limited. The main purpose of this study, in which equal amounts of starting materials were reacted for a constant period of time at different temperatures, was to determine the temperature range for the optimum yields of the individual components at reasonable reaction times. There are, however, several points of interest in Figure 64. Firstly, the use of 5.65 mmoles $[CpFe(CO)_2]_2$ yields a combined molar quantity of 5.2 - 5.6 mmoles of compounds 42, 43 and 44 at all temperatures above 130°C. Below 130°C a considerable amount of unreacted $[CpFe(CO)_2]_2$ is present. Secondly, there appears no simple additive relationship between any two components. Thirdly, irregularities in all three curves appear to coincide in the same temperature range. Although no concrete conclusions about possible reaction mechanisms can be drawn from these data, it does tend to suggest that the three components interconvert in some complex pattern and finally result in compound 42. A number of reasonable intermediate steps for this reaction may be suggested.

$$[CpFe(CO)_2]_2 \xrightarrow{Cl_3SiH} [CpFe(CO)_3]^+[Cl_3SiHFe(CO)Cp]^- \qquad [IV.9]$$

$$[CpFe(CO)_3]^+[Cl_3SiHFe(CO)Cp]^- \xrightarrow{Cl_3SiH} [CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^- + H_2 \quad [IV.10]$$

$$[CpFe(CO)_3]^+[Cl_3SiHFe(CO)Cp]^- \xrightarrow{Cl_3SiH} HFe(CO)_2Cp + (Cl_3Si)_2HFe(CO)Cp + CO \quad [IV.11]$$

$$[CpFe(CO)_3]^+[Cl_3SiHFe(CO)Cp]^- \xrightarrow{Cl_3SiH} Cl_3SiFe(CO)_2Cp + Cl_3SiH_2Fe(CO)Cp + CO \quad [IV.12]$$

$$Cl_3SiH_2Fe(CO)Cp \xrightarrow{Cl_3SiH} (Cl_3Si)_2HFe(CO)Cp + H_2 \quad [IV.13]$$

$$[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^- \xrightarrow{Cl_3SiH} Cl_3SiFe(CO)_2Cp + (Cl_3Si)_2HFe(CO)Cp + CO \quad [IV.14]$$

$$[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^- \longrightarrow 2Cl_3SiFe(CO)_2Cp \quad [IV.15]$$

$$[CpFe(CO)_3]^+FeCl_4^- + (Cl_3Si)_2HFe(CO)Cp \longrightarrow [CpFe(CO)_3]^+](Cl_3Si)_2Fe(CO)_2Cp]^- + HCl\cdot FeCl_3 \quad [IV.16]$$

Equations IV.9 and IV.10 are analogous to the intermediate steps suggested for the reaction of $Fe(CO)_5$ and Cl_3SiH, note Chapter III. The independent more rapid growth in yield of 43, compared to the yield of 42 between 110-150°C, as well as the suggested evidence for $HFe(CO)_2Cp$ could be explained by equation IV.11. The dihydride, $Cl_3SiH_2Fe(CO)Cp$ in equations IV.12 and IV.13, if capable of existing, would be expected to be of extremely low stability (e.g. $Cl_3SiHCo(CO)Cp$ is much less thermally and air stable than $(Cl_3Si)_2Co(CO)Cp$, a generally observed trend with other related complexes). Although equation IV.14 and IV.15

appear likely, according to the data in Figure 64, (note the complete disappearance of 44 in the reaction mixture at higher temperature), a sample of 44 in Cl_3SiH at temperatures up to 180°C resulted in no noticeable quantity of 42 or 43. In a polar environment all compounds in equation IV.16 would be partly dissociated and therefore no significant net reaction would be expected. Although this investigation suggests several correlations among the products, the complexity of the reaction leaves much more room for speculation.

When a reaction of $[CpFe(CO)_2]_2$ and excess Cl_3SiH is allowed to proceed to completion, then only $Cl_3SiFe(CO)_2Cp$, 42, is obtained in 50% yield, based on $[CpFe(CO)_2]_2$. The intermediate, $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$ 44, apparently provides only the anion or cation for the formation of $Cl_3SiFe(CO)_2Cp$, 42. The counter ion may form some other intermediate, which eventually results in the decomposition residues.

At a later stage of this work it was discovered that under ultraviolet irradiation, $Cl_3SiFe(CO)_2Cp$, 42, may be converted to $(Cl_3Si)_2HFe(CO)Cp$, 43, in the presence of Cl_3SiH.

$$Cl_3SiFe(CO)_2Cp + Cl_3SiH \rightarrow (Cl_3Si)_2HFe(CO)Cp + CO \quad [IV.17]$$

The ability of ultraviolet irradiation to replace one

carbon monoxide with Cl_3SiH proved to be a general reaction and forms in part the subject of Chapter V.

With other silanes such as $MeCl_2SiH$, Me_2ClSiH and Me_3SiH, $[CpFe(CO)_2]_2$ does not yield methylsilyl analogs of 43 and 44. These reactions become progressively slower with the increase in the number of methyl group on the silane starting material. If these reactions do proceed by a similar mechanism, then the reaction of the intermediates in subsequent steps is more rapid than their formation, and only the end products are obtained (e.g. $MeCl_2SiFe(CO)_2Cp$, $Me_2ClSiFe(CO)_2Cp$ and $Me_3SiFe(CO)_2Cp$).

8. Analysis by Infrared

The concentration of a compound in solution may be correlated to the band height of a carbon monoxide stretching vibration in the infrared spectrum, by employing the Lambert-Beer Law as expressed by the mathematical equation below:

$$A = abc$$

A is the absorbancy or optical density, a is the absorbancy index or coefficient of extinction, b is the pathlength and c is the concentration. The extinction coefficient, a, is constant for a given vibration in the compound and b is constant for a given set of infrared cells. The absorbancy, A, is then directly proportional to the concentration, c.

If the band heights of selected infrared vibrations are measured in the infrared spectra which are obtained by using known weights of pure samples of the compound, an empirical working curve can be constructed which then can be employed to calculate the concentration of the same compound in the reaction mixture from the infrared spectrum of a known weight of crude material dissolved in the same solvent.

In the analysis of compounds 42 - 44 by infrared spectroscopy, several features made the use of this method feasible. The reaction mixture, after removal of the excess unreacted Cl_3SiH, is a powdery yellow material which is moderately air stable for short periods of time. This conveniently allows weighing of samples of desired quantity and handling of the samples in ordinary volumetric glass ware. With oily, air sensitive materials this procedure could not readily be employed. Compounds 42 and 43 are hexane soluble and the carbonyl stretching frequencies are well separated. Compound 44 is completely insoluble in hexane and therefore does not interfere in the analysis. After the measurements on compounds 42 and 43 in hexane have been performed, the insoluble fraction may be washed with pentane and the same procedure repeated on compound 44 in dry acetone. Because of the numerous measurements which were required in determining the values in Table XIV or

Figure 64 a substantial degree of uncertainty must be assumed. For example $[CpFe(CO)_2]_2$ for each reaction was weighed and each reaction was timed. The weight of a sample was obtained from the difference of two weighings. Samples were diluted in volumetric ware and the resultant infrared band heights were measured. A similar procedure was followed for both the calibration of the standards and the consequent analysis of the samples. It becomes evident that the accumulation of small errors from individual operations adds to a substantial overall uncertainty of the plotted values in Figure 64. The magnitude of the error would probably vary with each component and concentration range. An estimated error of $\pm$ 5% appears a reasonable approximation. It seems probable however, that the deviation in the results of duplicate runs is a result of the heterogeneous character of the reaction, which is entirely unsuitable for the usual kind of kinetic study.

9. Reaction of $Cl_3SiFe(CO)_2Cp$ with Protic Reagents

Chlorosilanes are extremely susceptible to moisture and hydrolyze rapidly in the presence of water. The reactivity of the silicon-chlorine bond with other protic reagents was investigated. A hexane solution containing $Cl_3SiFe(CO)_2Cp$, $\underset{\sim}{42}$, appeared insensitive to methanethiol, MeSH. The infrared spectrum of the reaction mixture which had been stirred at room temperature for several hours showed only unreacted $Cl_3SiFe(CO)_2Cp$. The addition of

methanol, MeOH, to a hexane solution containing $Cl_3SiFe(CO)_2Cp$, caused rapid evolution of hydrogen chloride. The reaction is extremely fast, yielding $(MeO)_3SiFe(CO)_2Cp$ with no apparent decomposition. This product, $(MeO)_3SiFe(CO)_2Cp$, shows a complex carbonyl infrared spectrum, Fig. 9 which is discussed in terms of conformational isomerism, Chapter III.

A mixture of t-butyl alcohol, Me_3COH, and $Cl_3SiFe(CO)_2Cp$, in hexane at room temperature for ten hours, showed no noticeable change in the infrared spectrum. Heating this reaction mixture in steps to 100°C resulted only in partial decomposition. The reaction of isopropylalcohol, Me_2HCOH, and $Cl_3SiFe(CO)_2Cp$, does proceed but it is extremely slow. The successive substitution of chlorines can be observed by the gradual change of the carbonyl stretching pattern in the infrared spectrum. At 55°C the reaction goes to completion in approximately 100 hours. The infrared spectra of this reaction mixture taken at intervals of 20 - 25 hours are shown in Fig. 65, a-e. The successive replacement of chlorines becomes slower as the silicon atom becomes surrounded by bulky substituents. For example, the first chlorine appears completely replaced in 20 - 24 hours while the replacement of the third chlorine requires 70 - 75 hours:

$$Cl_3SiFe(CO)_2Cp + Me_2HOH \xrightarrow{20\text{-}25\ hr.} (Me_2HCO)Cl_2SiFe(CO)_2Cp + HCl \qquad [IV.18]$$

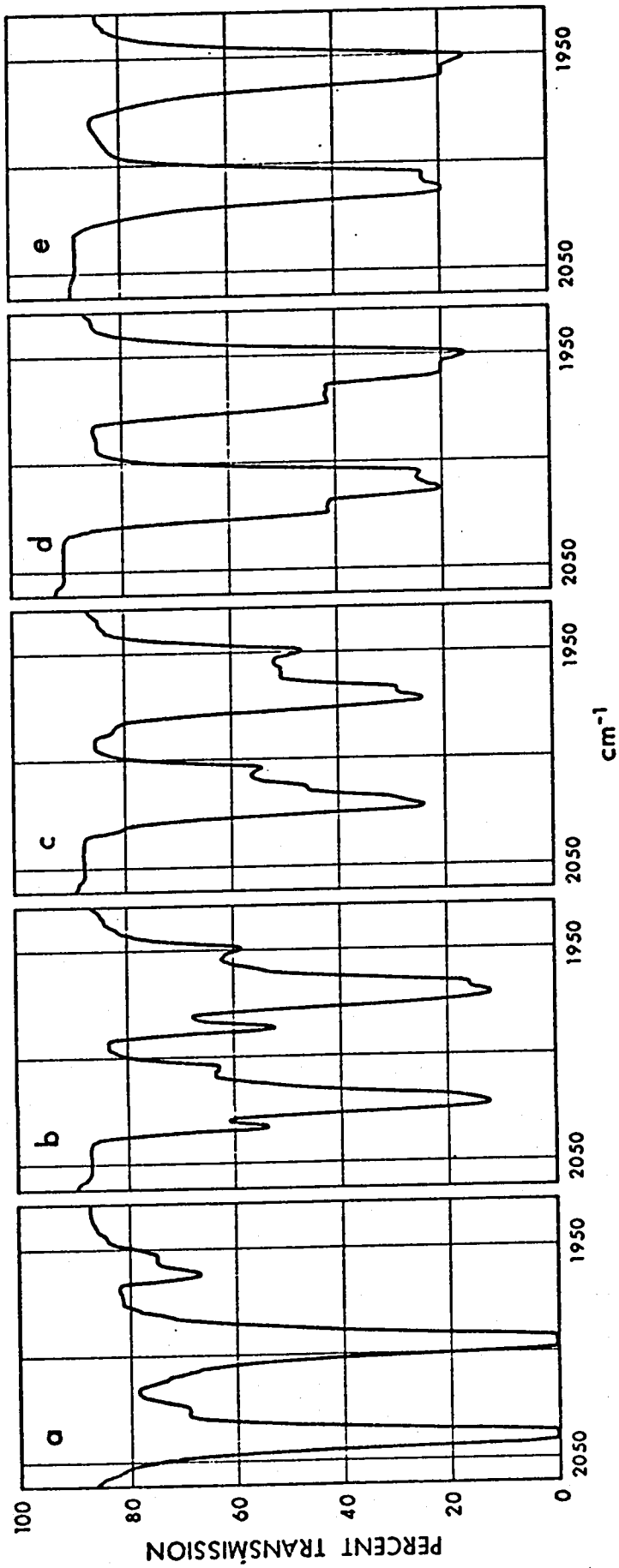


Figure 65

Reaction mixture of $Cl_3SiFe(CO)_2Cp$ and Me_2HCOH in hexane at 55°C; scan of reaction mixture, a after five minutes, b after 20 - 25 hours, c after 45 - 50 hours, d after 70 - 75 hours, and e after 100 hours.

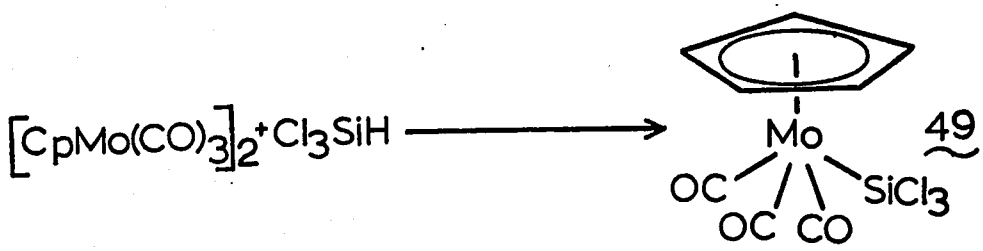
$$(Me_2HCO)Cl_2SiFe(CO)_2Cp + Me_2HCOH \xrightarrow{40\text{-}45\ hr.} (Me_2HCO)_2ClSiFe(CO)_2Cp + HCl \qquad [IV.19]$$

$$(Me_2HCO)_2ClSiFe(CO)_2Cp + Me_2HCOH \xrightarrow{70\text{-}75\ hr.} (Me_2HCO)_3SiFe(CO)_2Cp + HCl \qquad [IV.20]$$

The intermediates, $(Me_2HCO)Cl_2SiFe(CO)_2Cp$ and $(Me_2HCO)_2ClSiFe(CO)_2Cp$, have not been isolated and the relative rates of replacement of chlorines have been estimated from the change with time observed in the infrared spectra.

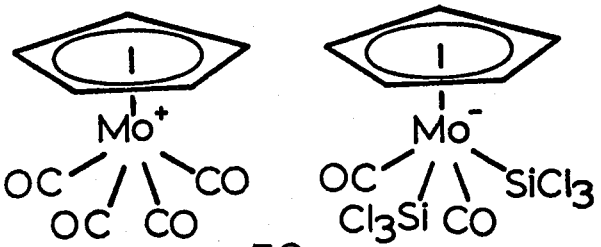
10. The reaction of $[CpMo(CO)_3]_2$ and Cl_3SiH

The reaction of $[CpMo(CO)_3]_2$ and Cl_3SiH appears to proceed by a similar complex mechanism as the reaction of $[CpFe(CO)_2]_2$ and Cl_3SiH. In the same temperature range the reaction proceeds at a much slower rate and is accompanied by extensive decomposition. The products so far isolated are shown in equation IV.21.



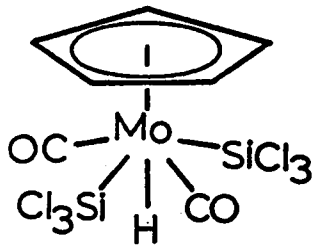
49

[IV.21]



50

Attempts to isolate the molybdenum analog of $(Cl_3Si)_2HFe(CO)Cp$, 43, have not been successful and it is questionable whether the steric requirements of such a molecule would permit its existence.

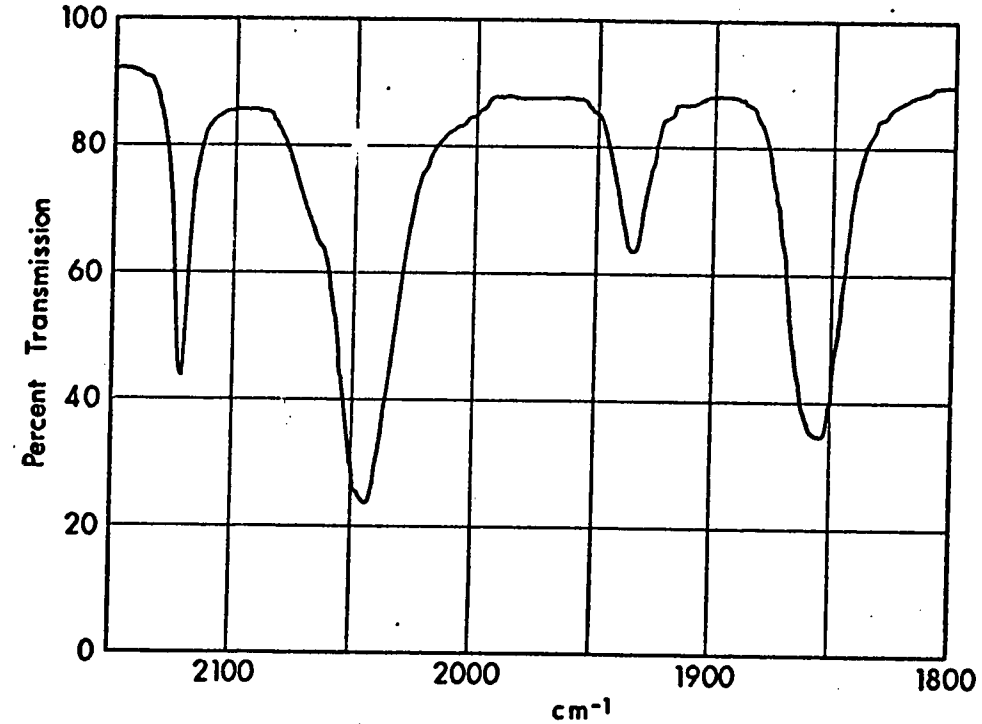


51

The infrared spectra of $[CpMo(CO)_4]^+[(Cl_3Si)_2Mo(CO)_2Cp]^-$ in solution and solid state are shown in Figures 66 and 67. Analogous as to the infrared spectra of the iron analog, the bands above 2000 cm^{-1}, are the carbon monoxide vibrations of the cation, while those below 2000 cm^{-1} correspond to the carbon monoxide vibrations of the anion. The intensity pattern of the carbon monoxide vibrations of the anion suggests a *trans* arrangement of the silyl groups [14,152] in a structure which can be viewed as a square pyramid with the cyclopentadiene at the apex.

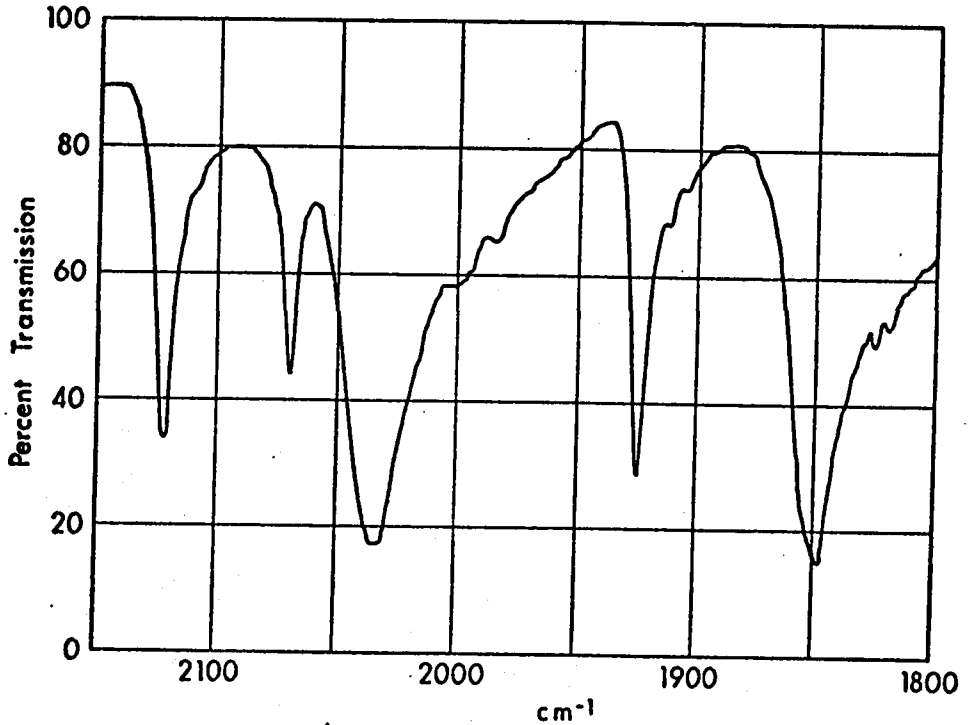
The nmr spectra of $Cl_3SiMo(CO)_3Cp$ and $[CpMo(CO)_4]^+[(Cl_3Si)_2Mo(CO)_2Cp]^-$ are shown in Figures 68 and 69. These demonstrate the chemical shifts of the cyclopentadienyl protons as influenced by the electron density on the cation, anion and neutral species.

Finer details of the reaction processes and the chemical properties of the products will form the subject of a future investigation.



$C_5H_5Mo(CO)_4^+$ $C_5H_5Mo(CO)_2(SiCl_3)_2^-$ in ACETONE

Figure 66



$C_5H_5Mo(CO)_4^+$ $C_5H_5Mo(CO)_2(SiCl_3)_2^-$ MULL in NUJOL

Figure 67

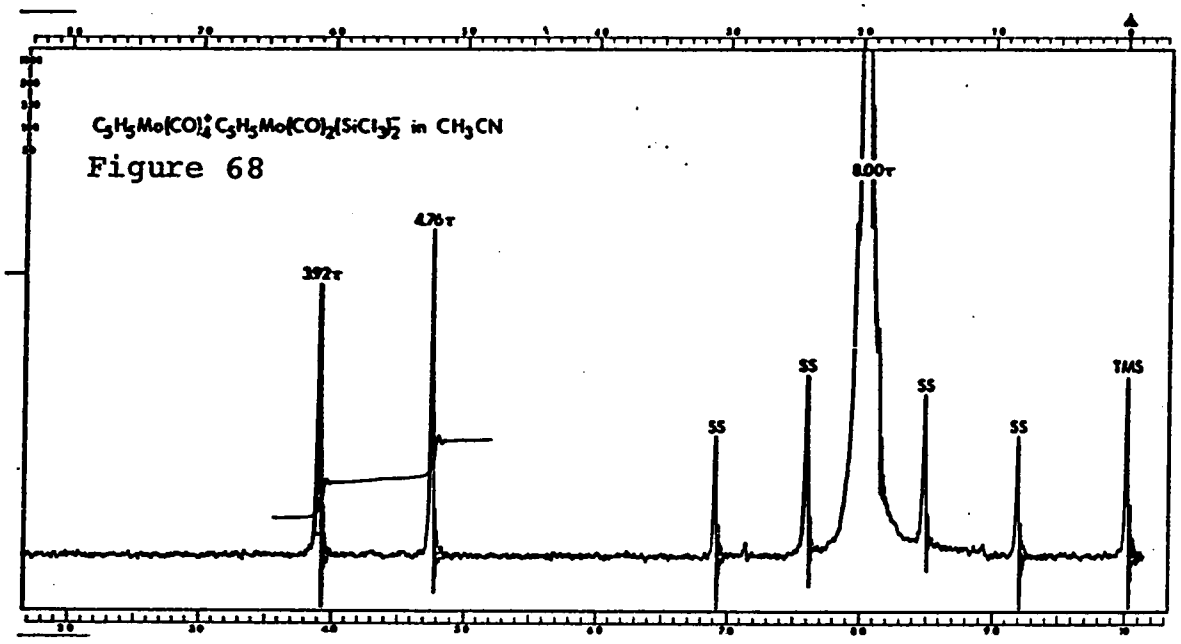


Figure 68

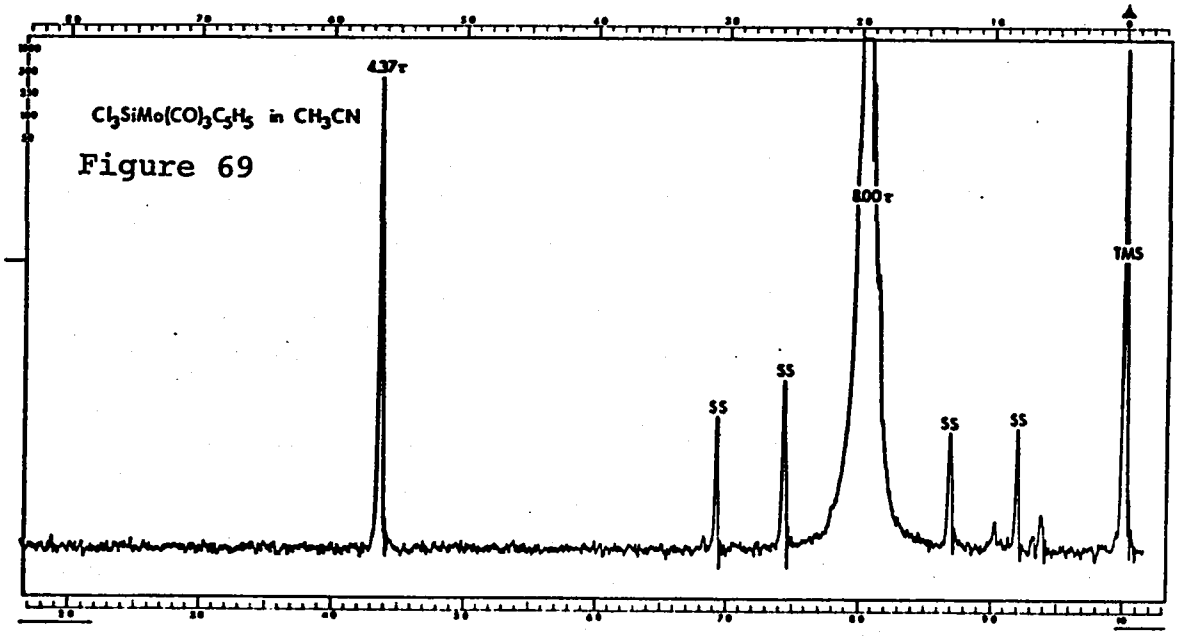


Figure 69

EXPERIMENTAL

Starting materials and general synthetic techniques are the same as described in Chapters II and III. All reactions involving trichlorosilane at elevated temperature were carried out in Carius tubes. The reactants were sealed in these under vacuum at liquid nitrogen temperature. Exposure of all compounds to air, either in solution or the crystalline state, was kept to a minimum at all phases of the experiments. Nitrogen was employed as the inert atmosphere.

Solvents.

Reagent grade pentane, hexane and heptane were used without further purification. Fisher reagent grade dichloromethane was distilled from calcium hydride and used within several days. Reagent grade acetone was distilled from potassium permanganate onto anhydrous potassium carbonate, from which it was in turn distilled and stored under nitrogen.

Trichlorosilyl-π-cyclopentadienylirondicarbonyl, $Cl_3SiFe(CO)_2Cp$ (Compound 42):

A sample of 2.0 gm $[CpFe(CO)_2]_2$ (5.65 mmol) in 7.0 ml Cl_3SiH (excess) was heated at 140°C for 30 minutes during which the reddish-brown color of the reaction mixture changed to yellow. The Carius tube was allowed to cool

to liquid nitrogen temperature. The tube was opened along the constricted section to release the gases formed in the reaction. The excess Cl_3SiH was removed at reduced pressure and the residue transferred into a Schlenk tube. This was extracted with several aliquots of warm pentane. The infrared spectrum of this solution showed three relatively strong carbonyl stretching bands. The pentane was evaporated at reduced pressure, resulting in a yellow crystalline material. This was sublimed at room temperature onto a water-cooled probe at less than 0.01 mm mercury pressure. This sublimation was extremely slow and was carried out over several days. After no further deposit of yellow crystalline product was observed at room temperature, the combined sublimate was dissolved in a minimum of hot hexane, filtered and the filtrate allowed to cool slowly in the refrigerator. A coarse, yellow, crystalline product, $Cl_3SiFe(CO)_2Cp$, formed, which had a melting point of 128 - 130°C. For yield refer to graph in Fig. 64 at specified reaction conditions.

Bis-trichlorosilyl-π-cyclopentadienylironcarbonylhydride, $(Cl_3Si)_2HFe(CO)Cp$ (Compound 43):

Sublimation of the residue from the pentane extraction from the above reaction was continued at 60°C onto a water cooled probe at less than 0.01 mm mercury pressure. Slowly a white microcrystalline material deposited on the probe.

This was dissolved in a minimum amount of hot hexane and the solution filtered. Cooling of the clear colorless filtrate in the refrigerator yielded a coarse, needle-like, pale yellow, crystalline material, $(Cl_3Si)_2HFe(CO)Cp$, at 131 - 132°C. For yields, refer to graph in Fig. 64 at specified reaction conditions.

π-Cyclopentadienylirontricarbonyl-Bis-trichlorosilyl-π-cyclopentadienylironcarbonylate, $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$ (Compound 44):

Dichloromethane was added to the pentane-insoluble residue from the above reaction, resulting in a yellow solution. The infrared spectrum of this showed three relatively strong broad carbonyl streching bands. The dichloromethane solution with the partly dissolved crude product was heated under a slight pressure and filtered hot, yielding an intensely yellow clear solution. This was allowed to cool slowly in the refrigerator, and precipitated a yellow needle-like crystalline product, $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$. This ionic complex is sparingly soluble in cold dichloromethane. It decomposed above 225°C.

π-Cyclopentadienylirontricarbonyl Tetraphenylborate, $[CpFe(CO)_3]^+BPh_4^-$:

The synthetic method described by Wilkinson *et al.*[67] was employed in the preparation of this complex. In the fume hood, a 50 ml cappable vessel, described in Chapter III

page 107, was charged with 1.38 gm $ClFe(CO)_2Cp$ (6.50 mmol), 2.35 gm $NaBPh_4$ (6.86 mmol) and 10 ml dry acetone. With a Teflon coated magnetic bar inside, the reaction vessel was sealed and attached to a carbon monoxide source *via* a needle piercing a rubber seal provided in the cap. The air in the reaction vessel was swept out with carbon monoxide. Under a carbon monoxide pressure of 40 psig the solution was stirred magnetically at room temperature until the red color of the reaction mixture changed to yellow. During this process a yellow microcrystalline solid precipitated. This was recrystallized from large volumes of dry acetone, affording a yellow crystalline product, $[CpFe(CO)_3]^+BPh_4^-$, which decomposed slowly above 180°C.

The Reaction of Compound 43 and Ph_4AsCl

Tetraphenylarsonium-Bis-trichlorosilyl-π-cyclopentadienyl-ironcarbonylate, $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$:

Ten ml of dry acetone was added to a mixture of 0.70 gm $(Cl_3Si)_2HFe(CO)Cp$ (1.67 mmol) and 0.70 gm Ph_4AsCl (1.67 mmol). This was stirred at room temperature until all the materials dissolved. During this process the solution turned from colorless to yellow. Immediately after all materials dissolved, the acetone was removed at reduced pressure, leaving an oily crystalline material which upon washing with hexane crystallized completely. This residue was dissolved in 10 ml of dichloromethane and filtered.

Hexane (20 ml) was carefully added to the top of the clear yellow filtrate, resulting in two clear layers of different density. This was carefully set aside in the refrigerator. As the two layers slowly diffused into one another, large yellow crystals formed on the wall of the vessel. After crystallization appeared complete, the product was washed with hexane, yielding 1.20 gm $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$ (1.50 mmol, 90% yield). Its melting point was 142 - 145°C.

The Reaction of Compound 44 and Ph_4AsCl to form $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$ and $ClFe(CO)_2Cp$:

A 50 ml three-neck flask was charged with 0.845 gm Ph_4AsCl (2.02 mmol) and 15 ml dry acetone. The reaction was attached to a gas burette and 1.20 gms of $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$ (1.93 mmol), dissolved in 10 ml dry acetone, was slowly added from an addition funnel into the stirring reaction mixture. The solution turned slowly from yellow to orange, and finally to red, with a slow evolution of carbon monoxide. Over a period of one hour, 50.5 ml of gas was evolved at room temperature and 690 - 700 mm mercury pressure. This corresponds to approximately 42 ml at STP (1.88 - 1.90 mmol). The infrared spectrum of the evolved gas was identical to that of carbon monoxide. The acetone was removed at reduced pressure leaving an oily red material. Addition of a small quantity of pentane crystallized the oily

material. The pentane was evaporated and the red, crystalline residue was sublimed at 45°C onto a water-cooled probe at less than 0.01 mm mercury pressure. Red, crystalline $ClFe(CO)_2Cp$ sublimed (0.327 gm, 1.54 mmol, 80% based on compound 44 employed). Its melting point was 49 - 50°C.

The residue, a light cream powdery material, was washed with several small aliquots of pentane. It was then dissolved in 20 ml dichloromethane and filtered, resulting in a clear yellow solution. Hexane (30 ml) was carefully added to the top of the yellow filtrate and the resulting two layer system set aside in the refrigerator. The product deposited on the wall of the vessel, and was identical to that obtained from the reaction of $(Cl_3Si)_2HFe(CO)Cp$ and Ph_4AsCl. Its yield was 1.36 gms (1.70 mmol, 88% based on compound 44).

Yields of 42, 43 and 44; Dependence on Temperature:

A sample of 40 gm of coarse, crystalline $[CpFe(CO)_2]_2$ was finely ground to a powdery material of uniform appearance. Employing this material, 16 Carius tubes of approximate volume of 60 - 70 ml were charged each with 2.00 gm $\pm$ 0.01 $[CpFe(CO)_2]_2$ (5.65 mmol) and 7.7 ml $\pm$ 0.1 Cl_3SiH. These were sealed under vacuum with the sample at liquid nitrogen temperature. Carius tubes were immersed in a 2.5 gallon oil bath (Dow Corning 710 Fluid) thermostated at 110°C. The tubes were attached to a reciprocating,

mechanical, shaking device and allowed to react for 30 minutes timed with a stop watch. This procedure was repeated at 120°C, 130°C, 140°C, 150°C, 160°C, 170°C and 180°C. Two Carius tubes were reacted at each temperature. After each tube was removed from the oil bath, it was allowed to cool slowly to room temperature and then was placed into liquid nitrogen. Consecutively, each was opened to release the gases formed in the reaction. The excess Cl_3SiH was removed at reduced pressure and stored for further use. The crude, powdery product from each reaction was accurately weighed as recorded in Table XIV. The samples were labelled and stored separately under nitrogen.

Analysis by Infrared Spectroscopy:

The instrument was calibrated and the settings were maintained unchanged throughout the complete experiment. At the end of the experiment, the instrument was checked for deviations from the initial settings.

Accurately weighed (to within $\pm$ 0.1 mg) pure samples of $Cl_3SiFe(CO)_2Cp$, 42, and $(Cl_3Si)_2HFe(CO)Cp$, 43, ranging from 0.1 to 1.5 mg per ml at narrowly spaced intervals, were combined and dissolved in 25 ml hexane using volumetric flasks. The infrared spectra of these solutions in the carbonyl region were recorded at 1.5 inches per minute chart speed on the external recorder. The band heights from the base line were measured for compounds 42 and 43. These were plotted against the corresponding concentrations,

resulting in smooth curves. These curves were then employed as calibration standards for solutions of unknown concentrations of compounds 42 and 43. A similar procedure was followed for $[CpFe(CO)_3]^+[(Cl_3Si)_2Fe(CO)Cp]^-$, 44, in acetone, for which a smooth curve was obtained at concentrations ranging from 1.0 to 6.0 mg per ml.

From each reaction an accurately weighed sample of crude powdery product, (25 - 50 mg) was dissolved in 25 ml hexane employing volumetric flasks. The infrared spectrum of each solution was recorded and the peak heights from the base line were measured. The corresponding interpolated concentrations of compounds 42 and 43 were read from the calibration chart. Using these values, the total number of mmoles of compounds 42 and 43 were calculated and recorded in Table XIV.

The hexane-insoluble residue containing compound 44 was washed with 2 - 3 aliquots of pentane. After this residue was dried by evaporation under a nitrogen stream, 10 ml of dry acetone was pipetted into the flask and the carbonyl infrared spectrum recorded. The concentration of compound 44 was obtained from the calibration chart. Using these values the total number of mmoles of compound 44 in the reaction was calculated and recorded in Table XIV. The values in columns 4, 5 and 6 were plotted against the reaction temperature, Fig. 64, showing a curve for each product in the reaction mixture.

The Reaction of $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]_2$ and Cl_3SiH:

A mixture of 2.44 gm $[\pi\text{-}CH_3C_5H_4Fe(CO)_2]$ (6.38 mmol) and 12 ml Cl_3SiH (excess) was heated at 115°C for 10 hours in a Carius tube. After the excess Cl_3SiH was drawn off, the reaction mixture was extracted with two 40 ml aliquots of hexane, leaving a bright yellow, powdery residue. The hexane was evaporated at reduced pressure resulting in an oily, brown material. This was washed into a sublimer with pentane. After removal of the pentane, the oily residue was sublimed onto a water-cooled probe at room temperature at less than 0.01 mm mercury pressure. A yellow liquid slowly deposited on the probe. The infrared spectrum of this shows two major bands at 2036 cm^{-1} and 1991 cm^{-1} with shoulders of medium intensity on each band at 2040 cm^{-1}, 1996 cm^{-1} respectively, Fig.12 . After no additional liquid $Cl_3SiFe(CO)_2\pi C_5H_4CH_3$ deposited, sublimation was continued at 60°C onto a clean probe. Slowly a white, crystalline material deposited. This was recrystallized from a small quantity of hexane at refrigerator temperature yielding a needle-like, white, crystalline product, $(Cl_3Si)_2HFe(CO)\pi C_5H_4CH_3$. Its melting point is 121 - 122°C.

The hexane-insoluble, yellow residue was extracted with 40 ml of dichloromethane and filtered, yielding an intensely yellow solution. Hexane was slowly added to the top of the dichloromethane filtrate. Coarse needle-like

crystals rapidly formed at the interface, as the two liquids layers were gently disturbed. The product, $[\pi CH_3C_5H_4Fe(CO)_3]^+[Cl_3Si)_2Fe(CO)\pi C_5H_4CH_3]^-$, decomposes slowly above 105°C.

The undissolved residue from the dichloromethane extraction was extracted with more dichloromethane. After the first two extractions, the dichloromethane was only faintly yellow. The infrared spectrum of succeeding extractions showed no bands due to $[(Cl_3Si)_2Fe(CO)\pi C_5H_4CH_3]^-$ in the carbonyl region, while those due to $[\pi CH_3C_5H_4Fe(CO)_3]^+$ were of medium intensity. The undissolved yellow residue thus remaining, $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$, was analyzed for carbon, hydrogen and chlorine and the magnetic susceptibility was measured.

Magnetic Susceptibility of $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$:

The measurements were performed at 23.3°C.* An accurate weight of a standard, $HgCo(SCN)_4$, 19.36 mg was weighed in the magnetic field. The increase in weight,

* Measurements were carried out by E. D. Day in this department on a Magnetic forces and sample weights balance using a Cahn Gram Electrobalance. Field was provided by a Varian Model V-4004 four-inch electromagnet system (V-2300A Power Supply, V-2301 Current Regulator) with tapered pole caps to provide a constant field times field gradient.

$\Delta f(HgCo(SCN)_4)$ = 0.3755 mg. Similarly an accurate weight of $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$, 5.068 mg was weighed in the magnetic field, $\Delta f([\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-)$ = 0.2100 mg. Employing the relationship:

$$Xgm = \frac{\Delta f(s)}{\Delta f(std} \cdot \frac{m(std)}{m(S)} \cdot Xgm(std)$$

$$Xgm(HgCo(SCN)_4) = 16.27 \text{ cgs units at } 23.3°C$$

$$Xgm([\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-) = \frac{0.2100}{0.3755} \cdot \frac{19.396}{5.068} \cdot 16.27 \text{ cgs}$$

$$= 34.82 \text{ cgs units}$$

Using this value in the following approximate relationship:

$$\text{Mol.Wt.} = \frac{\mu^2}{(2.83)^2 TXgm} = \frac{n(n+2)}{(2.83)^2 TXgm} = \frac{n(n+2)}{8.25 \times 10^{-2}}$$

Values for n, the number of unpaired electrons of 1, 2, 3, 4 and 5 yield corresponding molecular weights of 36.4, 97.0, 182, 291 and 425. The molecular weight of $[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$ is 417. The measurement is in excellent agreement with a five unpaired electron system.

Conductance Measurements

A Phillips Model PR 9500 conductivity bridge was employed in conjunction with a cell containing a set of one cm^2 platinum plates one cm apart. Measurements were performed under nitrogen. The cell constant, K, was determined using a 0.0200 N KCl aqueous solution for which $\bar{L}$ in the equation: $\Lambda = \frac{1000\bar{L}}{C} = \frac{1000K}{CR}$ is 0.002768 cm^{-1}

ohm^{-1} at 25°C. The resistance, R, of the solution was found 1.0×10^2 ohm, ($K = \bar{L}R = 0.002768$ ohm^{-1} cm^{-1} 1.0×10^2 ohm = 0.2768 cm^{-1} ≈ 28 cm^{-1}). Measurements were performed at two different concentations, c. The experimental values are listed in Table XII.

Reaction of $Cl_3SiFe(CO)_2Cp$, 42, with MeOH, $(MeO)_3SiFe(CO)_2Cp$:

To a magnetically stirred hexane solution containing 1.68 gm $Cl_3SiFe(CO)_2Cp$ (5.40 mmol) was slowly added 2.0 ml of MeOH (excess). During this process, hydrogen chloride was given off, evidenced by the characteristic pungent odor. After one hour at room temperature, the reaction mixture was filtered and cooled to -78°C, resulting in the formation of a pale yellow, crystalline material. After an additional recrystallization from 20 ml hexane, cooled in the refrigerator, the product $(MeO)_3SiFe(CO)_2Cp$, a coarse, sticky, crystalline material had a melting point of 49 - 50°C.

Reaction of $Cl_3SiFe(CO)_2Cp$, 42, with Me_2HCOH. $(Me_2HCO)_3SiFe(CO)_2Cp$:

A mixture of 1.50 gm $Cl_3SiFe(CO)_2Cp$ (4.82 mmol) and 3.0 ml Me_2HCOH (excess) in 30 ml hexane was magnetically stirred at 55°C for 140 - 150 hours. The progress of the reaction was followed by infrared at 20 - 25 hour

intervals. These are shown in Fig. 65. The successive substitution of chlorine is evidenced by the appearance of a new set of multiplets. When the reaction appeared complete, it was filtered and cooled to -78°C. Crystallization was not observed. The solvent was drawn off at reduced pressure, leaving a light brown, oily material, $(Me_2HCO)_3SiFe(CO)_2Cp$.

Trichlorosilyl-π-cyclopentadienylmolybdenumtricarbonyl, $Cl_3SiMo(CO)_3Cp$:

A sample of 2.43 gm $[CpMo(CO)_3]_2$ (4.95 mmol) in 7.0 ml Cl_3SiH (excess) was heated in a Carius tube at 130°C for 10 hours, during which the reaction mixture turned from reddish-brown to dark gray. After removal of excess Cl_3SiH, the residue was extracted with several aliquots of hot hexane and filtered. The combined colorless filtrate was cooled to -78°C, precipitating a white, microcrystalline material. This was sublimed at 65°C onto a water-cooled probe at less than 0.01 mm mercury pressure. The cream colored deposit was dissolved in hot hexane, filtered and allowed to cool slowly in the refrigerator, yielding a coarse, cream colored, crystalline material, $Cl_3SiMo(CO)_3Cp$, which melted at 149 - 150°C.

π-Cyclopentadienylmolybdenumtetracarbonyl-Bis-trichlorosilyl π-Cyclpentadienylmolybdenumdicarbonylate, $[CpMo(CO)_4]^+[(Cl_3Si)_2Mo(CO)_2Cp]^-$:

To the hexane insoluble residue from the above reaction dichloromethane was added, resulting in a yellow solution, which showed four relatively strong carbonyl stretching bands. The solution was heated under a slight pressure and filtered hot, resulting in an intensely yellow filtrate. Needle shaped crystals formed as the solution slowly cooled in the refrigerator. This product, $[CpMo(CO)_4]^+$ $[(Cl_3Si)_2Mo(CO)_2Cp]^-$ is sparingly soluble in cold dichloromethane.

TABLE XV

Analytical Data, Colors and Melting Points

Compound	M.P.°C	Color	Calculated %			Found %		
			C	H	Cl	C	H	Cl
$Cl_3SiFe(CO)_2Cp$ 42[a]	128-130	yellow	27.00	1.62	34.15	27.06	1.89	34.49
$(Cl_3Si)_2HFe(CO)Cp$ 43	130-131	p.yellow	17.21	1.44	50.78	17.27	1.78	50.28
$(Cl_3Si)_2Fe_2(CO)_4Cp_2$ 44[c]	d>220 [b]	yellow	27.00	1.62	34.15	27.03	1.73	34.17
$Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]$[d]	142-145	yellow	44.97	3.14	26.55	44.99	3.19	26.70
$(MeO)_3SiFe(CO)_2Cp$	49-50	yellow	40.29	4.73	0.00	40.02	4.72	0.18
$(Me_2HCO)_3SiFe(CO)_2Cp$	below RT	yellow	50.26	6.86	0.00	49.66	7.38	0.15
$ClFe(CO)_2Cp$	88-92	red	39.58	2.37	16.69	38.94	2.33	16.28
$ClFe(CO)_2\pi C_5H_4CH_3$	49-51	red	42.43	3.12	15.65	42.47	3.11	15.97
$Cl_3SiFe(CO)_2\pi C_5H_4CH_3$	below RT	yellow	-	-	-	-	-	-
$(Cl_3Si)_2HFe(CO)\pi C_5H_4CH_3$	121-122	white	19.42	1.86	49.14	19.49	1.99	48.57
$(Cl_3Si)_2Fe_2(CO)_4(\pi C_5H_4CH_3)_2$	d>105	yellow	29.53	2.17	32.68	29.59	2.17	32.61
$[\pi C_5H_4CH_3Fe(CO)_3]^+FeCl_4^-$		yellow	24.94	1.70	34.03	26.42	2.03	34.05
$Cl_3SiMo(CO)_3Cp$[a]	149-151	white	25.32	1.33	28.02	25.52	1.32	28.40
$(Cl_3Si)_2Mo_2(CO)_6Cp_2$		yellow	25.32	1.33	28.02	25.26	1.31	28.47

a. Described in Chapter III.

b. Sealed Capillary

c. Calc. Fe = 17.93, Si = 9.02; found Fe = 17.49, Si = 8.27.

d. Calc. O = 2.00, Si = 7.01, Fe = 6.97, As = 9.35; found O = 2.11, Si = 9.62, Fe = 6.86, As = 6.25.

TABLE XVI

Infrared Data of Carbonyl Stretching Vibrations [a]

Compound	ν(CO) cm^{-1}					
$Cl_3SiFe(CO)_2Cp$, 42 [b]	2039s	1995vs				
$(Cl_3Si)_2HFe(CO)Cp$, 43 [c]	2025 [d]	1936 [e]				
$[CpFe(CO)_3]^+](Cl_3Si)_2Fe(CO)Cp]^-$, 44 [b]	2121s	2074vs	1936s			
$[CpFe(CO)_3]^+FeCl_4^-$, 45	2121s	2074vs				
$[CpFe(CO)_3]^+BPh_4^-$ [g]	2121s	2074vs				
$Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$ [h]	1936					
$(MeO)_3SiFe(CO)_2Cp$ [i]	2023msh	2014ssh	2010s	1971m	1961ssh	1955s
$(Me_2HCO)_3SiFe(CO)_2Cp$	2011vs	2005s	1958s	1950vs		
$ClFe(CO)_2Cp$ [j]	2055s	2050sh	2013vs			
$ClFe(CO)_2\pi C_5H_4CH_3$	2051s	2047sh	2008vs			
$Cl_3SiFe(CO)_2\pi C_5H_4CH_3$	2040msh	2034s	1996msh	1992vs		
$(Cl_3Si)_2HFe(CO)\pi C_5H_4CH_3$	2023ssh	2019s				
$[\pi C_5H_4CH_3Fe(CO)_3]^+[(Cl_3Si)_2Fe(CO)\pi C_5H_4CH_3]^-$ [k]	2118s	2070vs	1934s			
$[\pi CH_3C_5H_4Fe(CO)_3]^+FeCl_4^-$ [k]	2118s	2070vs				
$Cl_3SiMo(CO)_3Cp$	2041s	1976m	1959vs			
$[CpMo(CO)_4]^+[(Cl_3Si)_2Mo(CO)_2Cp]^-$	2021s	2067msh	2045vs	1935m	1857s	

a. Ionic complexes in acetone, covalent compounds in hexane
b. τ(Cp) = 4.87 in acetonitrile
c. τ(Cp) = 4.57 and 5.38 in acetonitrile, τ(Cp) = 5.3 - 5.4 in acetone
d. In hexane
e. In acetone
f. τ(Cp) = 4.25 and 5.37 in acetonitrile, τ(Cp) = 3.85 and 5.40 in acetone
g. τ(Cp) = 3.87, τ(Ph) = 2.3 - 3.2 in acetone
h. τ(Cp) = 5.40, τ(Ph) = 2.2 center of multiplet in acetonitrile
i. τ(Cp) = 5.00, τ(Me) = 6.37 in acetonitrile
j. τ(Cp) = 4.99 in acetonitrile
k. In dichloromethane.

CHAPTER V

Photochemical Preparations of Silyl Transition Metal Hydrides; Properties and Preparation of Derivatives.

Introduction

A wide range of transition metal hydrides are known and the scope of their study is rapidly expanding with the development of instrumentation. Hydride complexes such as $HCo(CO)_4$, $HReCp_2$ and $HPtCl(PPh_3)_2$, are of particular interest since they can be studied by a number of spectroscopic methods. The first transition metal hydrides, $HCo(CO)_4$ [45], [101] and $H_2Fe(CO)_4$ [45,103] were characterized between 1930 - 1940; however, $HReCp_2$ was the first hydride for which in 1955 a metal proton signal was observed in the nmr spectrum at very high field [19,49,137]. The study of this molecule represents a turning point in transition metal hydride chemistry and presently high field nmr signals are known to be characteristic for protons bonded to transition metals.

The number and variety of transition metal hydrides complexes has since expanded immensely. Some examples follow.

$$NaW(CO)_3Cp + CH_3COOH \rightarrow HW(CO)_3Cp + \ldots \quad (186) \quad [V.1]$$

$$(Ph_3P)_2Fe(CO)_3 + H^+ \rightarrow [(Ph_3P)]_2Fe(CO)_3H^+ + \ldots \quad (54) \quad [V.2]$$

$$PtCl(SiMePh_2)(PMe_2Ph)_2 + HCl \rightarrow HPtCl(PMe_2Ph)_2 + \ldots \quad (39) \quad [V.3]$$

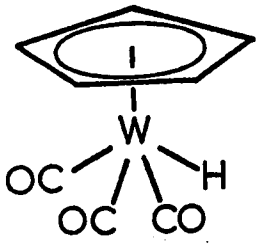
$$Na_2Fe(CO)_4 + H_3SiI \rightarrow H_3SiHFe(CO)_4 + \ldots \quad (9,11) \quad [V.4]$$

$HRhCl(SiMe_3)(PPh_3)_2 + H_2O\cdot diglyme \quad H_2RhCl(PPh_3)_2 + \ldots$ (93) [V.5]

$Cr(CO)_6 + Et_4NBH_4 \rightarrow Et_4N^+[HCr_2(CO)_{10}]^- + \ldots$ (4) [V.6]

$Fe_3(CO)_{12} + OH^-/CH_3COOH \rightarrow [HFe_3(CO)_{11}]^- + \ldots$ (35,61) [V.7]

The hydrogen in transition metal hydrides may be either terminal or bridging. Examples of terminal hydrides are provided by the first five equations, e.g:



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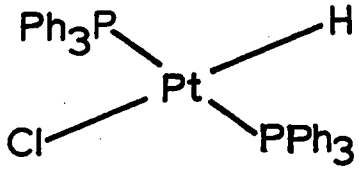
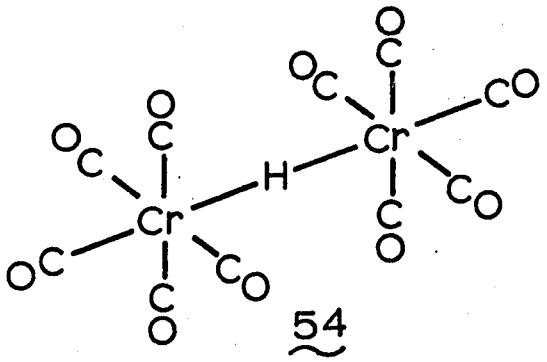


53

For the bridging hydrides, as in the last two equations, the metal-hydrogen-metal bond is linear in $[HCr_2(CO)_{10}]^-$, while it is bent in $[HFe_3(CO)_{11}]^-$:



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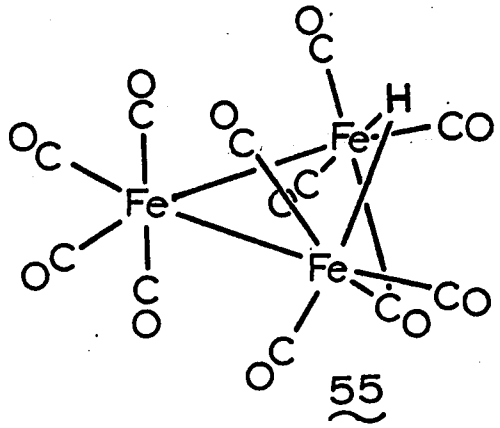


55

The E.A.N. rule is not obeyed in all cases. For example, $HPtCl(PMe_2Ph)_2$ and $H_2RhCl(PPh_3)_2$ attain only six

and seven of the eight and nine required electrons. Electronically unsaturated molecules of this type have a tendency to add an HX unit (HX = H_2, CH_3I, HCl, $HSiCl_3$, etc) to attain the inert gas electronic configuration. For example, $Rh(CO)Cl(PPh_3)_2$ and $Ir(CO)Cl(PPh_3)_2$ add Cl_3SiH to form $Cl_3SiHRh(CO)Cl(PPh_3)_2$ [93] and $Cl_3SiHIr(CO)Cl(PPh_3)_2$ respectively [36]. These reactions are often referred to as oxidative addition reactions [70]. Electronically unsaturated carbonyl complexes of the first transition metal series are very unstable and have a high tendency to attain the krypton electronic configuration. Thus the cobalt analog, $Co(CO)Cl(PPh_3)_2$ is not known as a stable compound.

It has been well established that carbon monoxide can be eliminated photochemically and replaced by other ligands [197]. For example, the irradiation of a hexane solution of $Mn_2(CO)_{10}$ and PPh_3 precipitates $Mn_2(CO)_8(PPh_3)_2$ [176]. The irradiation of $Fe(CO)_5$ yields $Fe_2(CO)_9$ [196]. In both cases a carbon monoxide molecule is apparently lost first, forming the reactive intermediates; "$Mn_2(CO)_9$" [209] and "$Fe(CO)_4$" respectively. These then rapidly react with PPh_3, or in the second case $Fe(CO)_5$, to form the observed products. Reactions of this type can be represented in the following manner:

$$M(CO)_n \xrightarrow{h\nu} [M(CO)_{n-1}]^{\ddagger} + CO \xrightarrow{L} M(CO)_{n-1}L \qquad [V.8]$$

The reactive intermediate, $[M(CO)_{n-1}]^{\ddagger}$, although of

short lifetime may be considered analogous to the "unsaturated" rhodium and iridium d^8 complexes mentioned above. It appeared as the present work developed, that addition of Si-H bonds to these unsaturated intermediates would be worthy of investigation; indeed, irradiation of $Fe(CO)_5$ in the presence of Cl_3SiH was found to yield $Cl_3SiHFe(CO)_4$ presumably via an $Fe(CO)_4^{\ddagger}$ intermediate. This reaction proved to be rather general and by this method a variety of novel silyl transition metal hydrides have been synthesized, as will be described in this Chapter.

The hydrogen atoms on most complex, transition metal hydrides are acidic. For example, $HCo(CO)_4$ is essentially completely dissociated in aqueous solution [104,105] and with bases such as ammonia, the ammonium salt $H_4N^+[Co(CO)_4]^-$ forms [10]. Most of the other simple carbonyl hydrides such as $HMn(CO)_5$ [111] or $HMo(CO)_3Cp$ [77,186] are extremely weak acids (i.e. Ka for $HMn(CO)_5 = 0.8 \times 10^{-8}$ in aqueous solution) and do not form salts with weak bases [111]. The disilyl hydride, $(Cl_3Si)_2HFe(CO)Cp$ described in Chapter IV, is also a very strong acid (estimated Ka = 2.6×10^{-3} in acetonitrile). With the tetraphenylarsonium cation, the salt, $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$, has been prepared. The monosilyl hydrides such as $Cl_3SiHFe(CO)_4$ or $Cl_3SiHMn(CO)_2Cp$ are also acidic and form salts with Et_3N or Et_4NCl. Closely related to this is the work by Aylett and Campbell on some silyl-amine reactions. These authors found

that the silyl carbonyls, $H_3SiCo(CO)_4$ [6,8,10] and $H_3SiMn(CO)_5$ [6,7,10], form 1:2 adducts with Me_3N. These adducts are formulated as $[H_3Si(NMe_3)_2^+][Co(CO)_4]^-$ and $[H_3Si(NMe_3)_2]^+[Mn(CO)_5]^-$. The disubstituted silyl complex, $(H_3Si)_2Fe(CO)_4$ [9,11], also forms only a 1:2 adduct, $(H_3Si)_2Fe(CO)_4 \cdot 2NMe_3$, raising in our view some question about the nature of this adduct. It is interesting to note that for the related dihydride, $H_2Fe(CO)_4$, $Ka_1 = 3.6 \times 10^{-5}$ and $Ka_2 = 1.1 \times 10^{-14}$ [16,19,41,137], making the carbonylate monohydride an extremely weak acid. A reasonable explanation for the nature of the ionic silyl transition metal salts is suggested in this Chapter.

RESULTS AND DISCUSSION

1. Syntheses and Properties

The ultraviolet irradiation of carbonyl transition metal complexes, in the presence of a silane, leads to the formation of silyl-transition metal hydrides with the loss of carbon monoxide. In these reactions, a carbon monoxide ligand is apparently ejected by a sufficiently energetic photon, producing the unsaturated intermediate, V.9. In subsequent reaction steps, it may recombine with carbon monoxide to form starting material, V.10, or add a silane and yield the observed product, V.11:

$$M(CO)_n \xrightarrow{h\nu} M(CO)_{n-1}^{\ddagger} + CO \qquad [V.9]$$

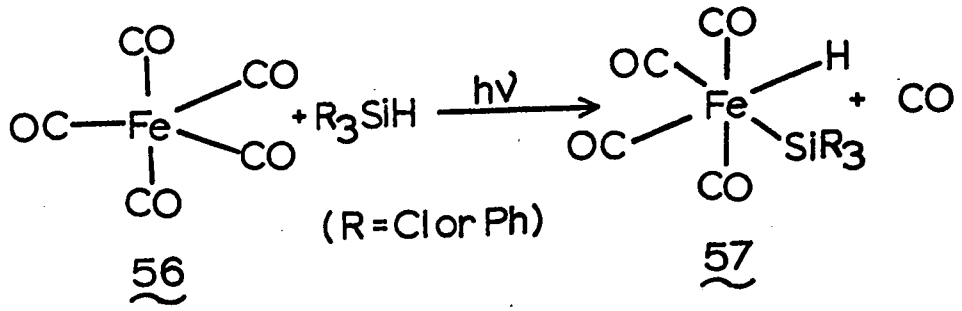
$$M(CO)_{n-1}^{\ddagger} + CO \longrightarrow M(CO)_n \qquad [V.10]$$

$$M(CO)_{n-1}^{\ddagger} + Si\text{-}H \longrightarrow SiHM(CO)_{n-1} \qquad [V.11]$$

At atmospheric pressure, carbon monoxide is sparingly soluble in hexane and escapes from solution. The concentration of silane is always much greater than that of carbon monoxide and therefore the formation of product, V.11, from $M(CO)_{n-1}^{\ddagger}$ is favoured as the main reaction.

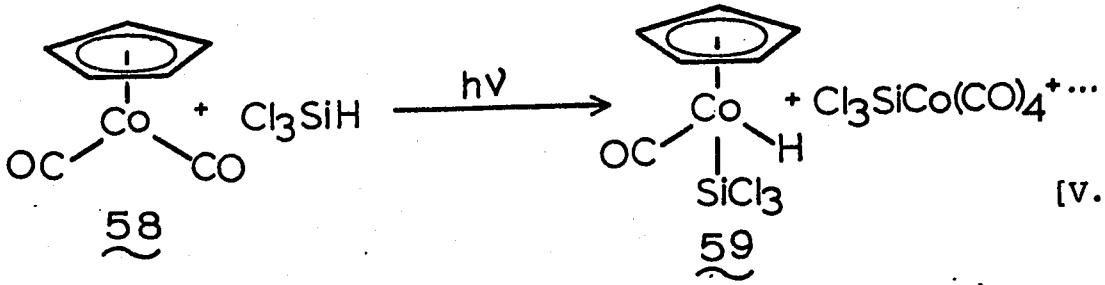
The relative rates at which these reactions proceed with a variety of silanes are qualitatively consistent with a unimolecular dissociative process, V.9. In contrast to the thermal reactions described in Chapters III and IV, the relative rates at which silyl-transition metal deriva-

tives form in ultraviolet reactions with silanes, appear independent of the electronegativity of the substituents on the silyl starting material. For example, $Fe(CO)_5$ reacts at approximately the same rate at room temperature with Cl_3SiH as with Ph_3SiH to form $Cl_3SiHFe(CO)_4$ or $Ph_3SiHFe(CO)_4$ respectively:



56 57 [V.12]

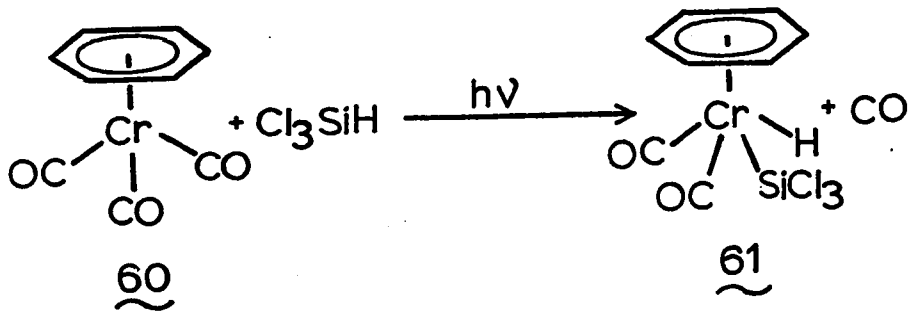
The relative reaction rates do, however, vary with different transition metal carbonyl starting materials. The reaction of Cl_3SiH and $CpCo(CO)_2$, under ultraviolet irradiation, does not yield $Cl_3SiHCo(CO)Cp$ until the reaction mixture is allowed to warm to 45 - 50°C. (These observations refer to the use of the same ultraviolet source in all reactions, i.e. 100 watt utility lamp, c.f. experimental section). This anomalous reaction, requiring an elevated temperature to proceed, is thus far not understood.



58 59 [V.13]

The silyl transition metal hydrides display a wide range of physical and chemical properties. The low melting $Cl_3SiHCo(CO)Cp$ is very air sensitive in its impure state and in solution. The pure, crystalline material may, however, be handled in dry air for brief periods of time without substantial decomposition. In the formation of $Cl_3SiHCo(CO)Cp$ a substantial amount of $Cl_3SiCo(CO)_4$ is also formed. The necessity to increase the reaction temperature appears to reduce the yield of the hydride drastically, resulting in a reaction mixture of extremely unpromising appearance.

The product $Cl_3SiHCr(CO)_2C_6H_6$, from the ultraviolet reaction of $C_6H_6Cr(CO)_3$ and Cl_3SiH, is insoluble in hexane. It precipitates in yellow, microcrystalline form



60 61 [V.14]

from the reaction mixture and shows very little decomposition*. A near quantitative conversion of $C_6H_6Cr(CO)_3$

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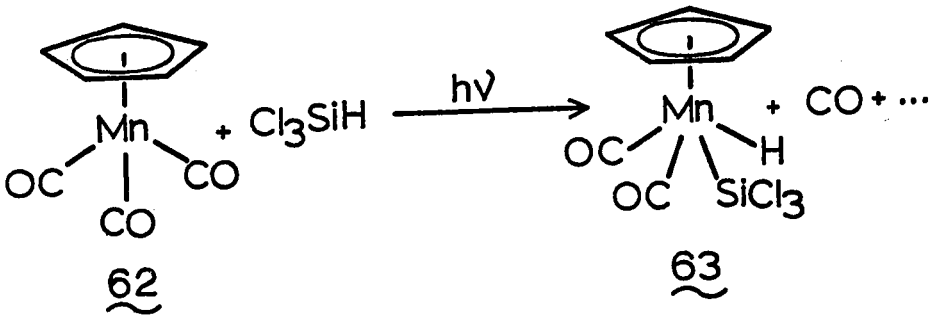
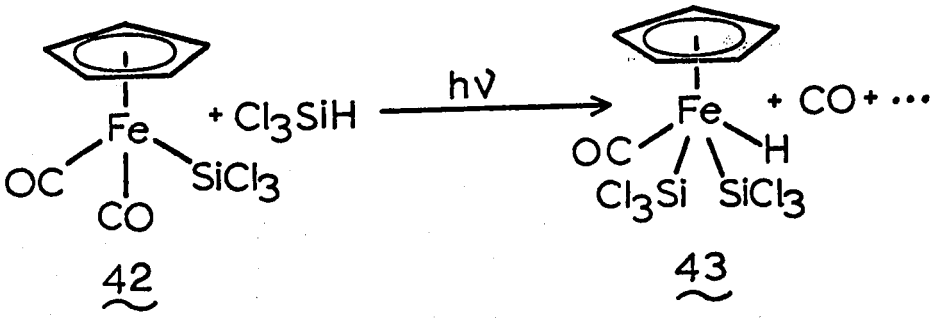
* When the reaction was repeated by W. J. Jacobs in this laboratory, employing the 450 watt Hanovia lamp instead of the 100 watt ultraviolet source, $(Cl_3Si)_2Cr(CO)_2C_6H_6$, was obtained, which resembles $(Cl_3Si)_2Co(CO)Cp$ (cf. Chapter III) in stability, solubility and melting point.

may be obtained in oxygen-free hexane or heptane, under prolonged irradiation, in the presence of excess Cl_3SiH. In the crystalline state the hydride is moderately air stable, but in dichloromethane at room temperature decomposition occurs rapidly in the presence of trace amounts of air.

The complexes, $Cl_3SiHMn(CO)_2Cp$, 63, and $(Cl_3Si)_2HFe(CO)Cp$, 43, obtained at room temperature from ultraviolet reactions of Cl_3SiH with $CpMn(CO)_3$ or $Cl_3SiFe(CO)_2Cp$, are very similar in appearance and stability. Their formation is accompanied by a considerable amount of decomposition. Both crystallize from hexane as pale yellow needles which are moderately air stable.



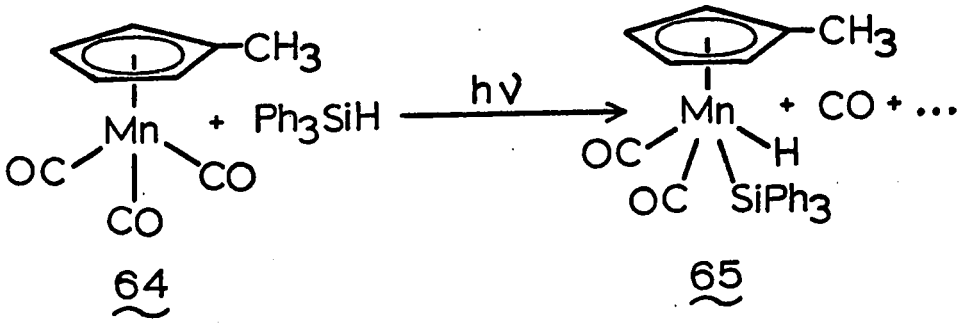
62 63 [V.15]



42 43 [V.16]

The disilyl hydride, $(Cl_3Si)_2HFe(CO)Cp$, 43, was originally prepared in a thermal reaction; (cf. Chapter IV). The

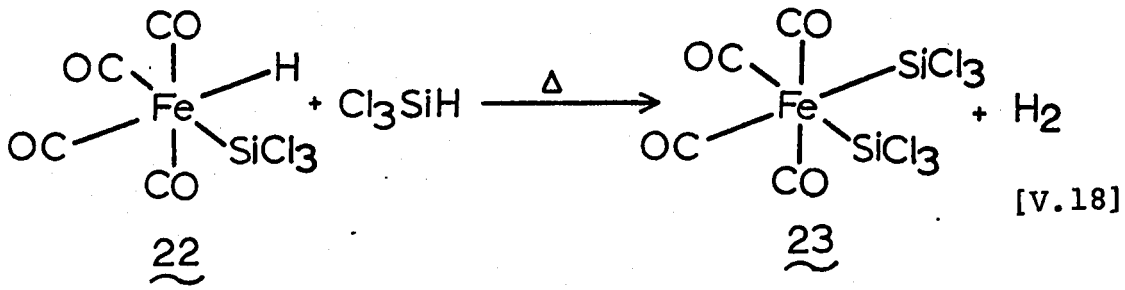
reaction of $\pi CH_3C_5H_4Mn(CO)_3$ and Ph_3SiH yields crystalline $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$:



64 65 [V.17]

The trichlorosilyl analog, $Cl_3SiHMn(CO)_2\pi C_5H_4CH_3$, is a liquid at room temperature.

The hydride $Cl_3SiHFe(CO)_4$, is an extremely air-sensitive liquid at room temperature, but in its formation from $Fe(CO)_5$ and Cl_3SiH, very little decomposition is observed under prolonged ultraviolet irradiation. For high yields of $Cl_3SiHFe(CO)_4$, cooling of the irradiated reaction mixture is essential. Above room temperature a substantial amount of $(Cl_3Si)_2Fe(CO)_4$ is formed as a side product:



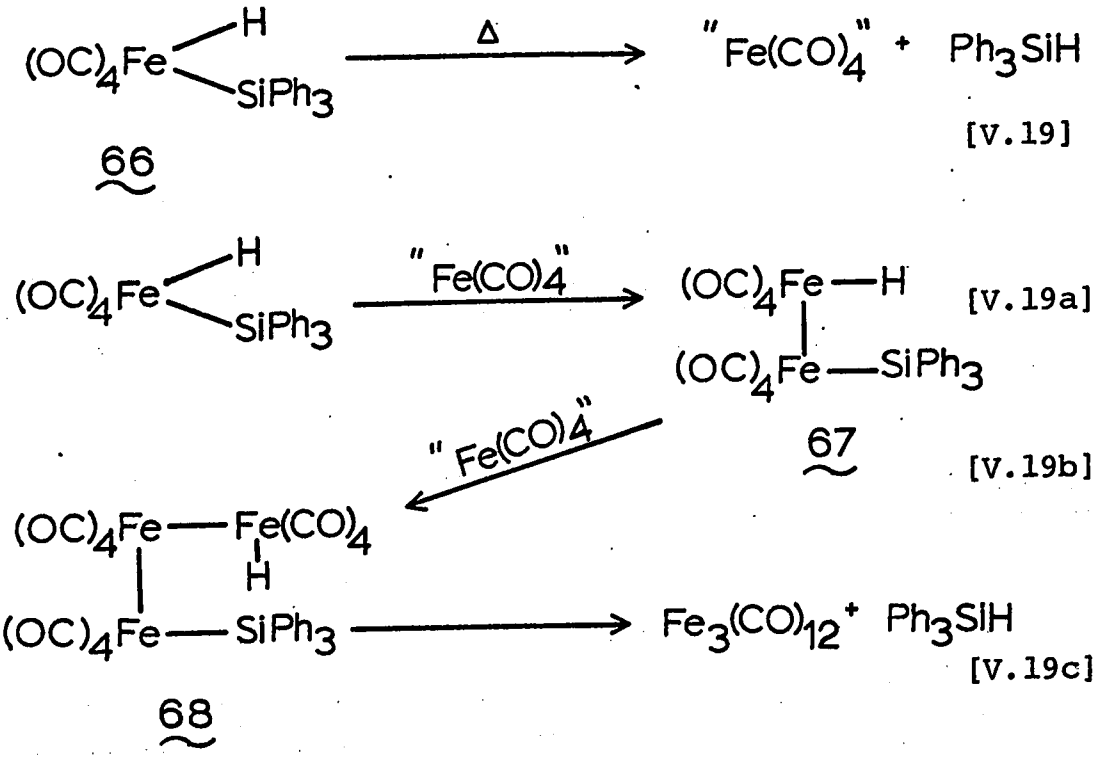
22 23 [V.18]

At -78°C, $Cl_3SiHFe(CO)_4$ crystallizes from hexane as a white, coarse, crystalline material. Sublimation into a cold trap at -78°C yields white transparent needles. The triphenyl-

silyl analog, $Ph_3SiHFe(CO)_4$, is a white crystalline product at room temperature and in its pure state may be handled in air for brief periods without appreciable oxidation

When $Ph_3SiHFe(CO)_4$ is heated in hexane above room temperature the solution turns rapidly dark green, forming Ph_3SiH, $Fe(CO)_5$ and $Fe_3(CO)_{12}$. The products were identified by infrared. The bands at 2023 cm^{-1} and 2000 cm^{-1} were assigned to carbonyl stretching bands of $Fe(CO)_5$ and at 2129 cm^{-1} (broad) to the silicon-hydrogen stretching vibration of Ph_3SiH. From the solution a dark, crystalline product, $Fe_3(CO)_{12}$ was isolated. Its infrared spectrum showed bands at 2046 cm^{-1}, 2023 cm^{-1} and a very weak broad band at 1840 cm^{-1}.

It is suggested that under slight heating in solution, $Ph_3SiHFe(CO)_4$ dissociates into Ph_3SiH and "$Fe(CO)_4$". An electronically unsaturated species like "$Fe(CO)_4$" would decompose or react rapidly with some other species in solution. In the absence of replacement ligands such as triphenylphosphine or carbon monoxide, successive insertion of "$Fe(CO)_4$" into the iron-hydrogen or iron-silicon bonds of $Ph_3SiHFe(CO)_4$ with the final eliminations of Ph_3SiH is one possible explanation for the formation of $Fe_3(CO)_{12}$:



66 [V.19]

67 [V.19a] [V.19b]

68 [V.19c]

Numerous other processes may be occurring simultaneously. This reaction shows considerable decomposition and the encounter of carbon monoxide with "$Fe(CO)_4$" would most probably result in $Fe(CO)_5$. Heating of $Cl_3SiHFe(CO)_4$ in solution yields no detectable amounts of $Fe_3(CO)_{12}$, but mainly $(Cl_3Si)_2Fe(CO)_4$ and some gray insoluble residues.

Triphenylphosphine readily replaces Ph_3SiH from $Ph_3SiHFe(CO)_4$ and $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$ to yield $Ph_3PFe(CO)_4$ and $Ph_3PMn(CO)_2\pi C_5H_4CH_3$ respectively. Recent kinetic studies* of reactions of $R_3SiHMn(CO)_2Cp$ with

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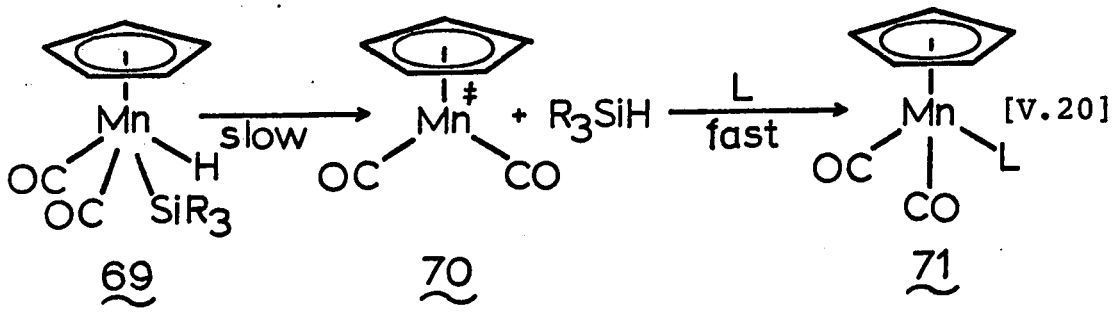
* Kinetic studies carried out by A. J. Hart-Davis in this laboratory.

triphenylphosphine and other ligands have proven to be first order in carbonyl starting material and independent of replacement ligand, L, when R is a phenyl group, which would be consistent with the suggested mechanism below:



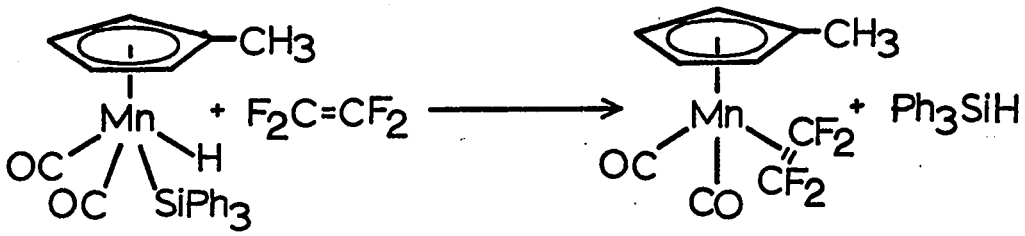
69 70 71 [V.20]

The reaction rate varies with different R groups on the starting material, (e.g. rate for $Ph_3SiHMn(CO)_2Cp$ >> $Cl_3SiHMn(CO)_2Cp$). The rate-determining step may be the formation of the reactive intermediate, which then rapidly accepts a ligand, L. These kinetic results support the suggested electronically, unsaturated intermediate when silane is replaced by other ligands. The above mechanism is similar to the mechanism suggested for the formation of the hydride, which would be the reverse process.

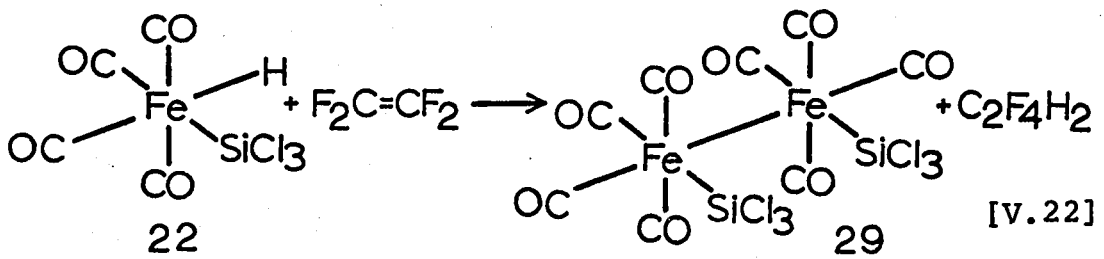
It is interesting to note in the study by Chalk and Harrod that the bonding of silyl groups in the iridium complexes is mainly determined by the electronegativity of the substituents on the silyl moiety. The reaction of $(EtO)_3SiH$ and $Ir(CO)Cl(PPh_3)_2$ yields $(EtO)_3SiHIr(CO)Cl(PPh_3)_2$ [36]. When this product is slightly heated at reduced pressure the reaction is reversed and $(EtO)_3SiH$ and

$Ir(CO)Cl(PPh_3)_2$ may be recovered. With the trichlorosilyl analog, $Cl_3SiHIr(CO)Cl(PPh_3)_2$ [36], synthesized in a similar manner, a temperature of 200°C was required to effect the reverse process, while Ph_3SiH forms no adduct with $Ir(CO)Cl(PPh_3)_2$.

It is generally observed that a triphenylsilyl group is more easily displaced than a trichlorosilyl group in these derivatives. For example, tetrafluoroethylene displaces Ph_3SiH on $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$ at room temperature, to yield $(C_2F_4)Mn(CO)_2\pi C_5H_4CH_3$,* while on $Cl_3SiHFe(CO)_4$ it only abstracts the hydrogen, forming $[Cl_3SiFe(CO)_4]_2$ and HF_2CCF_2H:



65 72 [V.21]



22 29 [V.22]

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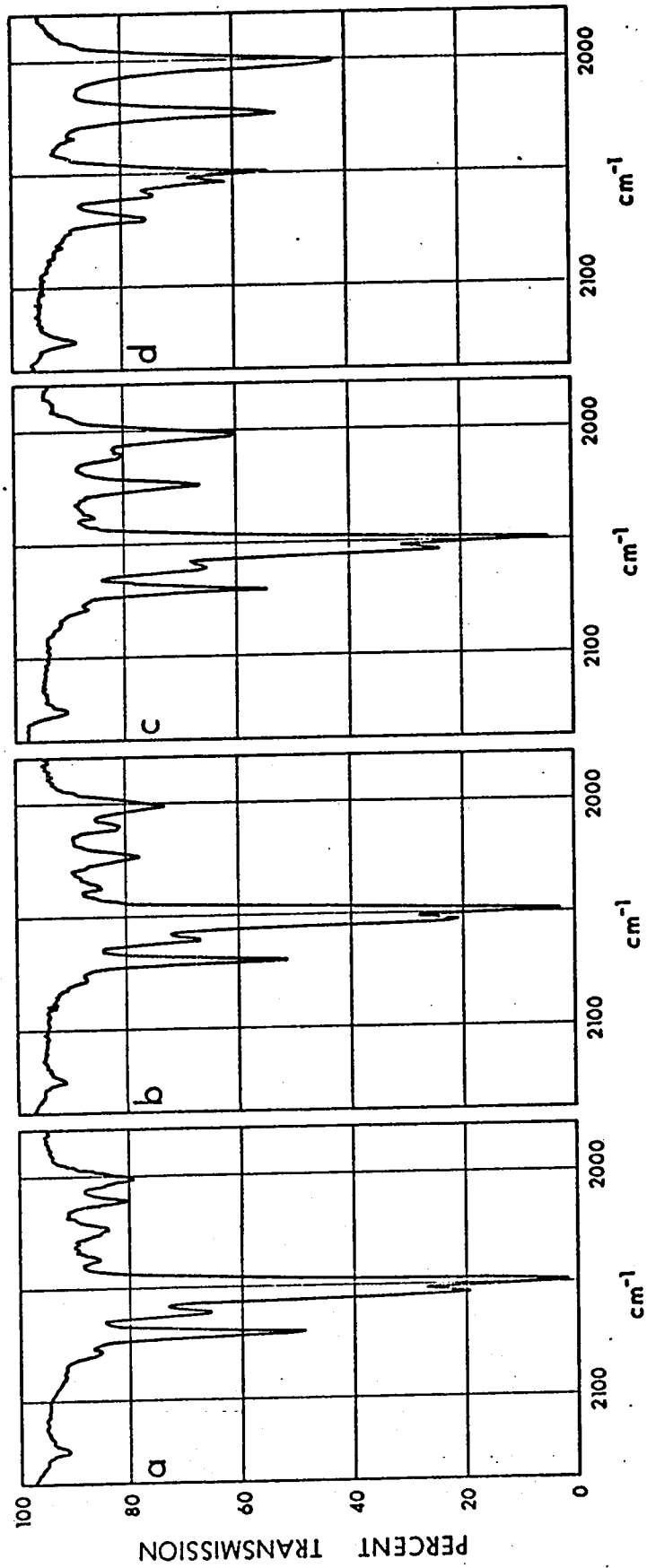
* Reaction carried out by W. J. Jacobs in this laboratory to compare the reactivity of $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$ to that of $Cl_3SiHFe(CO)_4$.



$[Cl_3SiFe(CO)_4]_2$ in HEXANE

Figure 70

a. Immediate scan after complex was dissolved
b. Immediate rescan, dissolved for approximately 3 minutes
c. Scanned after 30 minutes
d. Scanned after 90 minutes

The formation and chemical properties of $[Cl_3SiFe(CO)_4]_2$ are rather peculiar. It precipitates in a bright yellow, coarse, crystalline form in near quantitative yield from a mixture of $Cl_3SiHFe(CO)_4$ and excess tetrafluoroethylene in a small amount of pentane or hexane, when the mixture is allowed to warm up from -78°C to room temperature and gently shaken. Removal of the solvent and other volatile materials leaves the dimeric complex in a pure, crystalline state which is moderately air stable. In solution this compound breaks down very rapidly to $Fe(CO)_5$ and other unidentified residues. The infrared spectra of the carbonyl stretching vibrations for $[Cl_3SiFe(CO)_4]_2$ in hexane are shown in Fig. 70. Spectrum (a) is an immediate scan after the sample was dissolved and spectrum (b) is an immediate rescan (i.e. approximately 3 minutes later). Spectra (c) and (d) are rescans at 30 and 90 minutes respectively. Approximately 10% of the original complex remained in solution after 90 minutes.

When $[Cl_3SiFe(CO)_4]_2$ is heated in the solid state under vacuum, it slowly melts above 120°C to a semisolid of moist appearance and then resolidifies to a pale yellow powder, which was shown by infrared to consist mainly of $[Cl_2SiFe(CO)_4]_2$. As the reaction cooled to room temperature, small quantities of liquid (shown by mass spectro-

metry to be a mixture of Cl_4Si and $Fe(CO)_5$) deposited on the wall of the reaction vessel.

$$[Cl_3SiFe(CO)_4]_2 \xrightarrow{\Delta} [Cl_2SiFe(CO)_4]_2 + Cl_4Si + Fe(CO)_5 \qquad [V.23]$$

In carbon tetrachloride transition metal carbonyl hydrides such as $HFe(CO)_2Cp$ or $HMo(CO)_3Cp$ are known to exchange hydrogen with chlorine of the solvent to yield $ClFe(CO)_2Cp$ or $ClMo(CO)_3Cp$ and chloroform [186]. A similar reaction appears to take place when $Cl_3SiHMn(CO)_2Cp$ is dissolved in carbon tetrachloride. The nmr spectrum of $Cl_3SiHMn(CO)_2Cp$ in carbon tetrachloride, immediately after preparation of the nmr sample, does show the cyclopentadienyl and manganese protons at 5.1 τ and 19.8 τ respectively, but the signals are very broad, showing signs of deterioration. After several hours at room temperature the sample decomposed completely in the sealed nmr tube, forming a black residue. The solvent from the decomposed sample was carefully distilled into a clean nmr tube in a vacuum system. The nmr spectrum of this showed only one signal at 2.80 τ corresponding to chloroform. The anticipated counter product, $Cl_3SiMnCl(CO)_2Cp$, which would resemble $Cl_3SnCoCl(CO)Cp$ [141] was not isolated.

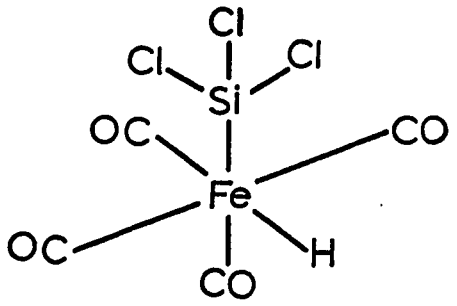
2. Structures

The hydrogen in transition metal hydrides does occupy a definite coordination site and is not associated

loosely to balance the electronic charge only. For transition metal-hydrogen stretching vibrations to be observed in the infrared spectrum, a covalent bond must exist between these nuclei. The transition metal-hydrogen stretching vibrations are of relatively weak intensity compared to the carbonyl stretching bands, but for some compounds they can be observed in concentrated solutions. The broad, weak band at 1960 cm^{-1} in Fig. 46, was assigned to the iron-hydrogen stretching vibration of $(Cl_3Si)_2HFe(CO)Cp$. In carbon tetrachloride, the manganese-hydrogen stretching vibration of $Cl_3SiHMn(CO)_3Cp$ is observed at 1887 cm^{-1} and the carbonyl stretching bands at 2026 cm^{-1} and 1975 cm^{-1}. The infrared spectrum of the deuterium analog, $Cl_3SiDMn(CO)_2Cp$, which was prepared from $CpMn(CO)_3$ and Cl_3SiD, confirms this assignment. At a similar concentration in carbon tetrachloride, the band at 1887 cm^{-1} is lacking; however, a new band at 1360 cm^{-1}, the manganese-deuterium stretching vibration, is observed. The carbonyl stretching bands are at 2026 cm^{-1} and 1973 cm^{-1}. Coupling between the manganese-hydrogen and carbon monoxide stretching bands is very small. A change of approximately two wavenumbers only is observed in the low frequency carbonyl band. More extensive coupling between the osmium-hydrogen and carbon monoxide stretching vibrations in $H_2Os(CO)_4$, causes shifts in the low frequency carbonyl bands of 10 - 20 cm^{-1} to higher frequency, relative to

those of $D_2Os(CO)_4$ [146].

The increased internuclear distance of 3.40 Å between the rhenium atoms in $HRe_2Mn(CO)_{14}$ [41] compared to the rhenium-rhenium distance of 3.02 Å in $Re_2(CO)_{10}$ [60], also suggests a definite position of the hydrogen, although it was not located by X-ray crystallography. In the nmr spectrum, Fig. 62, equal coupling of the iron-proton in $(Cl_3Si)_2HFe(CO)Cp$ to ^{29}Si in both silyl positions indicates the location of the hydrogen equidistant to both silyl groups which are chemically equivalent. The relatively small size of the hydrogen as a ligand may allow substantial distortions of the adjacent ligand from the regular structure. For example, in $Cl_3SiHFe(CO)_4$, 73, it could be

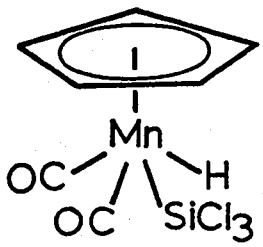


73

expected that the H-Fe-CO bond angle in the equatorial plane be less than 90°, while the corresponding CO-Fe-CO bond angle be greater than 90°. With sufficiently bulky ligands replacing the hydrogen, alternative isomeric arrangements which are structurally more favoured may be anticipated (cf. Chapter II for discussion of $(CO)_4Fe(SnX_3)_2$ (X = Cl, Br, I)).

It has been suggested, on the basis of infrared

results , that molecules such as $CpMo(CO)_2LI$ (L - tertiary phosphine or phosphite) may exist in the *cis* or *trans* form in which the carbon monoxides, iodine and the ligand, L, form the base of a distorted square pyramid with cyclopentadiene at the apex [14,72]. These molecules show two intense carbonyl stretching absorptions in the infrared spectrum. For the *cis* isomer, the band at higher frequency is more intense, while the band at lower frequency is more intense for the *trans* isomer. The infrared spectra of the silyl transition metal hydrides $Cl_3SiHMn(CO)_2Cp$, $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$, and $Cl_3SiHCr(CO)_2C_6H_6$, which show a more intense high frequency band in each case, are consistent with the *cis* structural arrangement:



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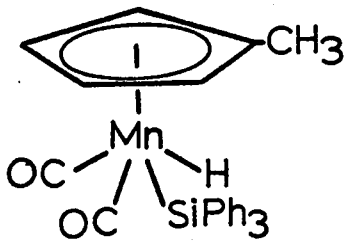

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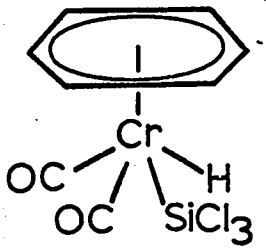


61

In Figures 71, 72 and 73 are shown the infrared spectra of these molecules. When the hydrogen is replaced by bulky ligands such as Cl_3Sn , $PhCl_2Sn$ or Ph_2ClSn , then the intensity pattern of the carbon monoxide stretching vibration in the infrared spectra are inverted, suggesting the *trans* arrangement. The infrared spectra of $Cl_3Sn(Cl_3Si)Mn(CO)_2Cp$, $Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$,

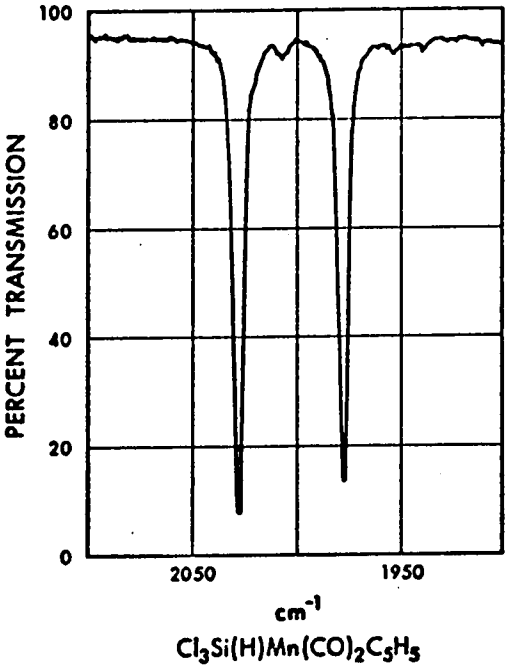


Figure 71

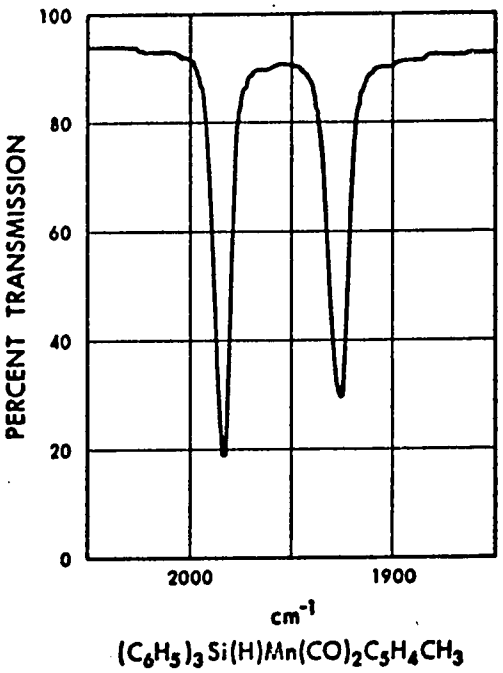


Figure 72

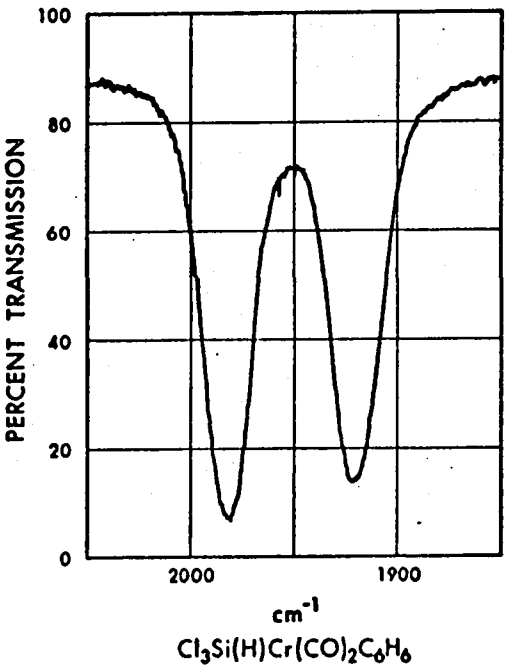


Figure 73

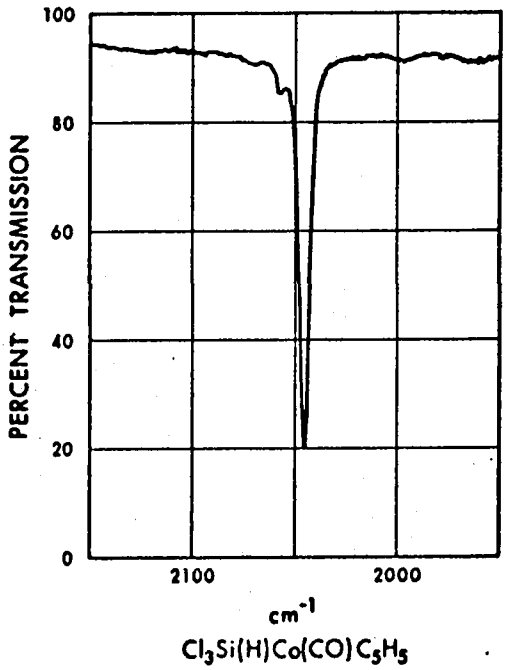
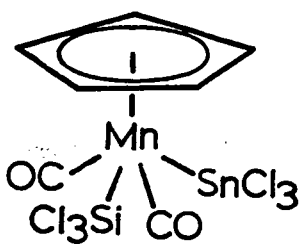


Figure 74

$PhCl_2Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$ and $Ph_2ClSn(Cl_3Si)Mn(CO)_2$ $\pi C_5H_4CH_3$ are shown in Figures 75 - 78 which are consistent with the suggested *trans* arrangement.*



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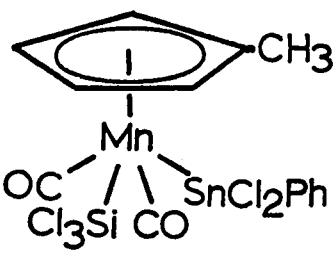

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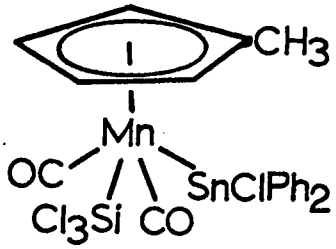

76

3. Acidic Properties of Hydrides.

Complexes in which the hydrogen is bonded directly to the transition metals are generally referred to as hydrides, implying that the hydrogen is of hydridic nature. Most complex hydrides are, as noted above, acids and in aqueous media dissociate to yield the carbonylate ion. For $HCo(CO)_4$ and $HMn(CO)_5$, Ka values are approximately 1.0 and 0.8×10^{-7} respectively [104,105,111]. An exception to these is Cp_2ReH, which acts as a Lewis base. Its base strength is similar to that of ammonia [88], and with boron trifluoride it forms an adduct, Cp_2ReHBF_3 [122].

Chlorosilyl derivatives are extremely sensitive to moisture, and in aqueous media hydrolyze very rapidly. In polar organic solvents, the silyl-transition metal hydrides

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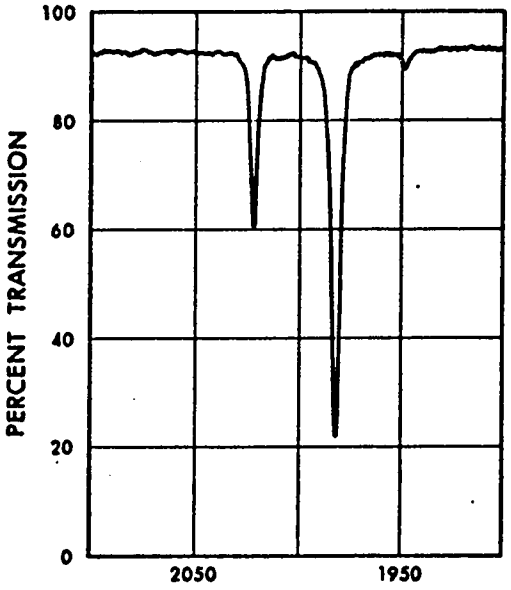
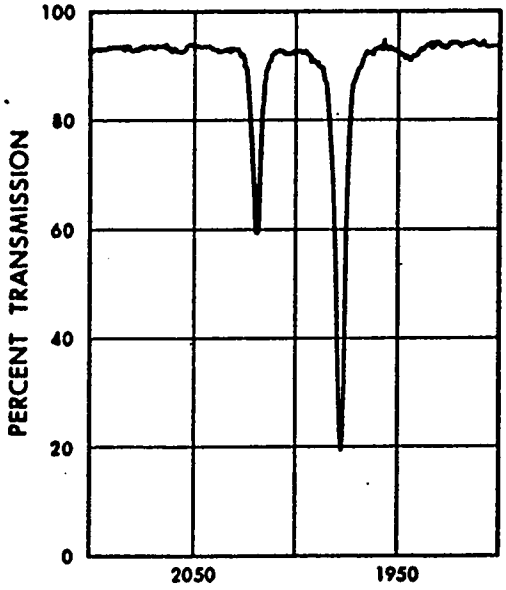
*The infrared spectrum of $(Cl_3Si)_2Cr(CO)_2C_6H_6$, prepared by W. J. Jacobs in this laboratory is also consistent with the *trans* arrangement.



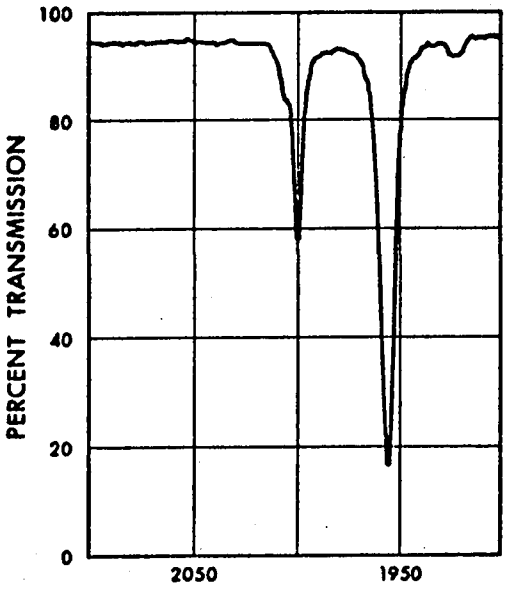
$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_5$

Figure 75



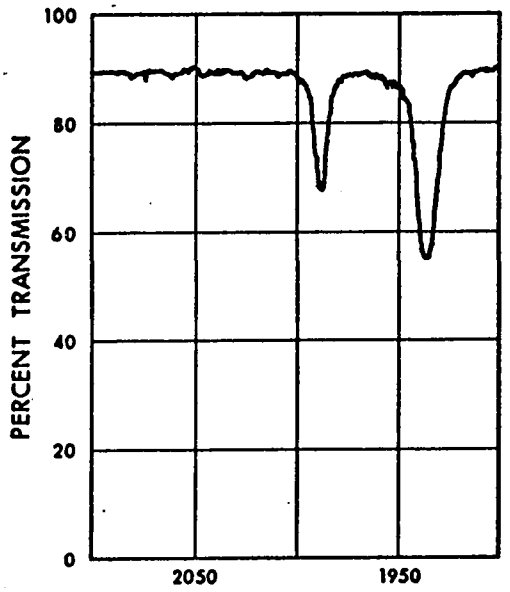
$Cl_3Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$

Figure 76



$C_6H_5Cl_2Sn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$

Figure 77



$(C_6H_5)_2ClSn(Cl_3Si)Mn(CO)_2C_5H_4CH_3$

Figure 78

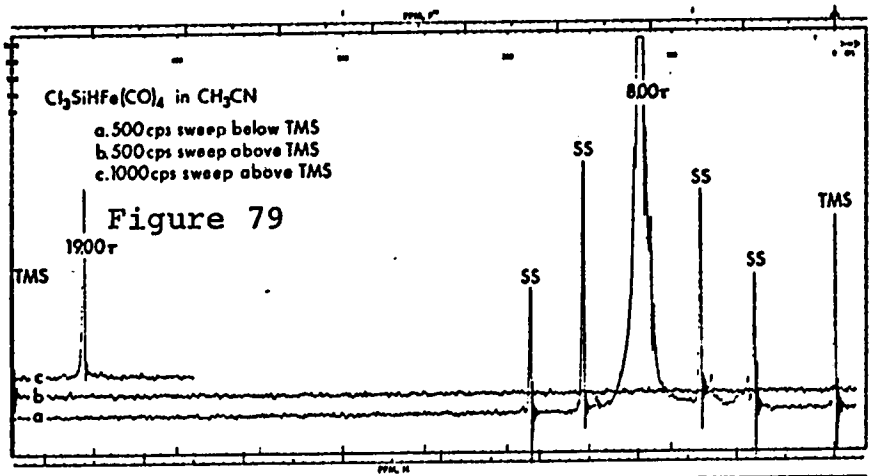


Figure 79

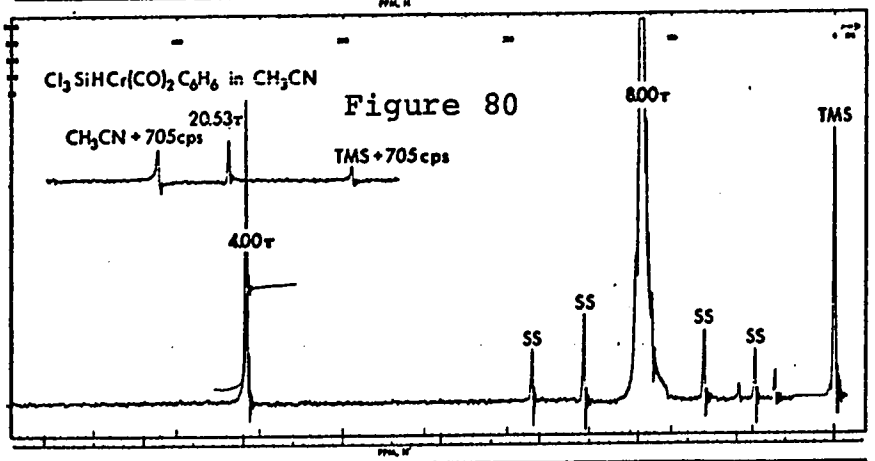


Figure 80

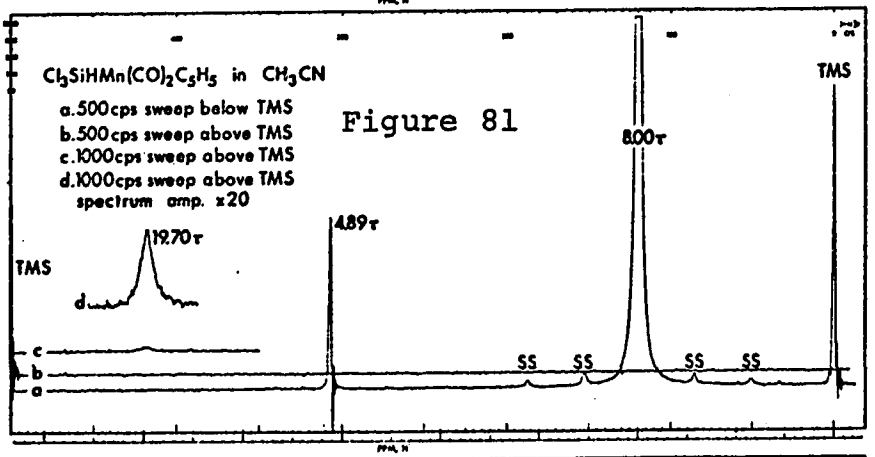


Figure 81

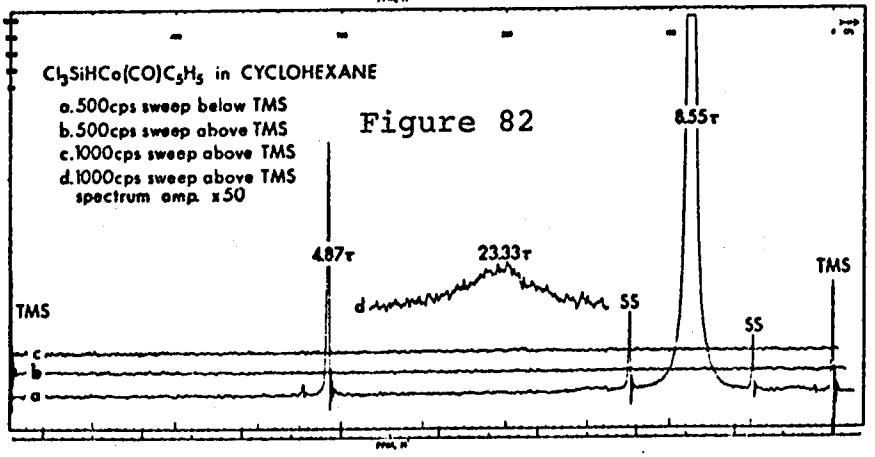


Figure 82

are acidic. For example, $(Cl_3Si)_2HFe(CO)Cp$ in acetonitrile has a Ka value of approximately 2.6×10^{-3}, and the cyclopentadienyl protons of the dissociated and undissociated species can be observed in the nmr spectrum. In acetone it is completely dissociated. The tetraphenylarsonium salt, $Ph_4As^+[(Cl_3Si)_2Fe(CO)Cp]^-$ can be prepared (cf. Chapter IV).

The monosubstituted chlorosilyl hydrides are much weaker acids and show no signs of dissociation in acetonitrile when stable in that solvent. The nmr spectra of $Cl_3SiHFe(CO)_4$, $Cl_3SiHCr(CO)_2C_6H_6$, $Cl_3SiHMn(CO)_2Cp$ and $Cl_3SiHCo(CO)Cp$ are shown in Figures 79-82. Cyclohexane was employed as solvent for $Cl_3SiHCo(CO)Cp$, which immediately decomposes in acetonitrile. All spectra show sharp signals in the low field region. The absorptions of protons bonded to manganese and cobalt are very broad signals at high field. This broadening is presumed to be due to the quadrupole moment of these transition metals. The natural abundance of the isotopes (^{55}Mn, spin 5/2; ^{59}Co, spin 7/2), is 100%. Chromium and iron do not have isotopes of significant abundance with a quadrupole moment, and the protons bonded to these transition metals show sharp signals in the nmr spectra.

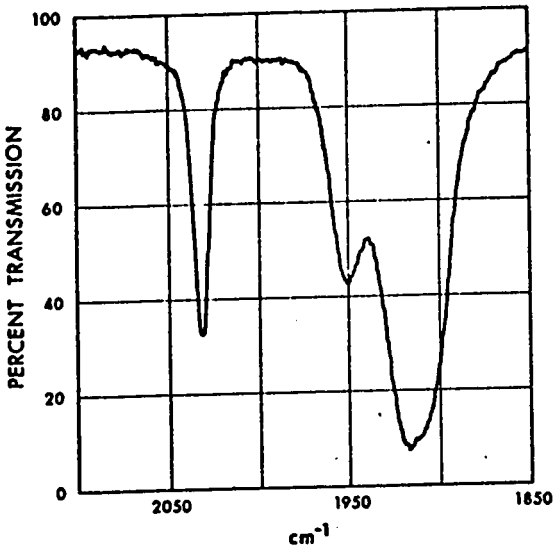
Although these hydrides show no signs of dissociation in acetonitrile, they are sufficiently acidic to form adducts with tertiary amines. The addition of triethyl-

amine to a hexane solution of $Cl_3SiHFe(CO)_4$ immediately precipitates a white microcrystalline product, which is apparently $Et_3NH^+[Cl_3SiFe(CO)_4]^-$. This salt is extremely air sensitive and therefore was not analyzed directly. The tetraethylammonium analog, $Et_4N^+[Cl_3SiFe(CO)_4]^-$, can be prepared by passing nitrogen through a dichloromethane solution containing $Cl_3SiHFe(CO)_4$ and Et_4NCl. This salt is far more air stable, and in its pure crystalline state can be handled in air for brief periods of time without apparent decomposition. The infrared spectra of $Et_4N^+[Cl_3SiFe(CO)_4]^-$, $Et_4N^+[Ph_3SiFe(CO)_4]^-$, $Et_3NH^+[Ph_3SiFe(CO)_4]^-$ and $Me_4N^+[Cl_3SiFe(CO)_4]^-$, are shown in Figures 83 - 86. The major carbonyl stretching bands of all these iron tetracarbonyl salts are very similar.

The basic chemical difference between the triethyl and tetraethylammonium salts appears to depend on the ability of the former to dissociate reversibly:

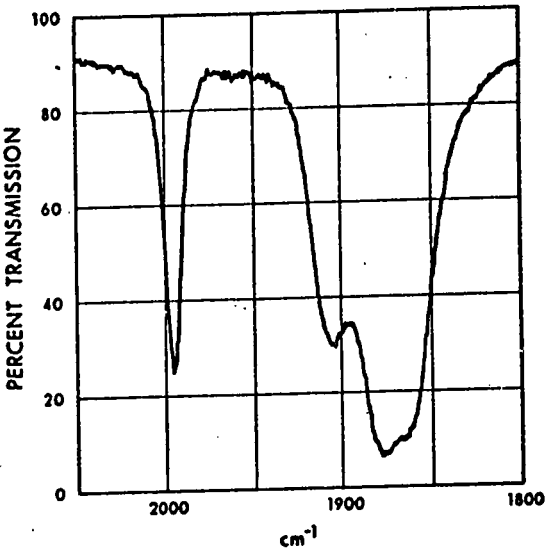
$$Et_3NH^+[Cl_3SiFe(CO)_4]^- \rightleftarrows Et_3N + Cl_3SiHFe(CO)_4 \qquad [V.24]$$

The extreme suceptibility of $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ to air can then be explained by the formation of $Cl_3SiHFe(CO)_4$, which is extremely air sensitive. A similar dissociative process cannot take place with $Et_4N^+[Cl_3SiFe(CO)_4]^-$ and the salt is more air stable. The infrared spectrum of $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ in dichloromethane, Fig. 88, shows further evidence in support of this type of reversible



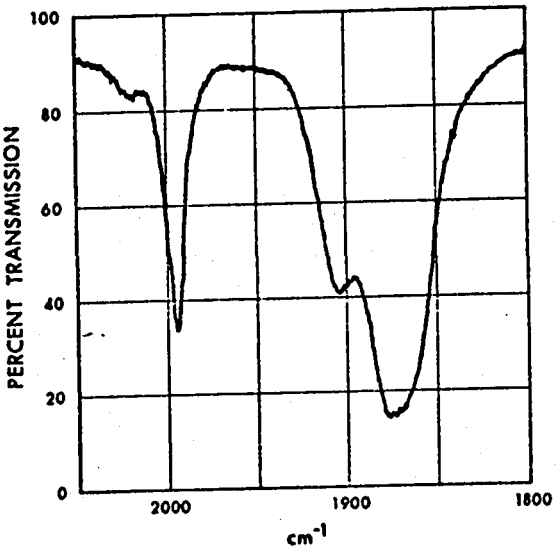
$(C_2H_5)_4N^+Cl_3SiFe(CO)_4^-$ in CH_2Cl_2

Figure 83



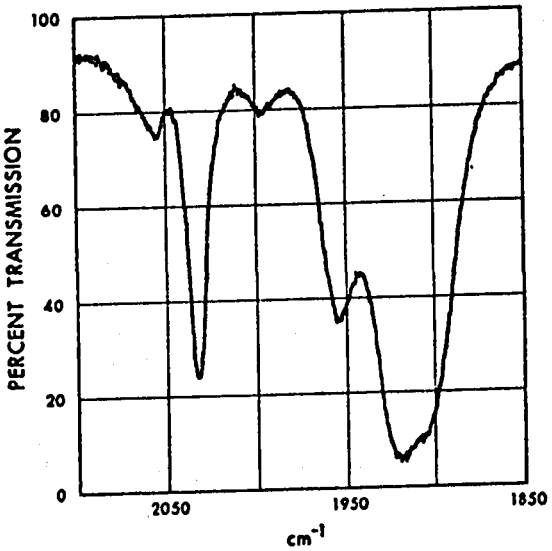
$(C_2H_5)_4N^+(C_6H_5)_3SiFe(CO)_4^-$ in CH_2Cl_2

Figure 84



$(C_2H_5)_3NH^+(C_6H_5)_3SiFe(CO)_4^-$ in CH_2Cl_2

Figure 85



$(CH_3)_4N^+Cl_3SiFe(CO)_4^-$ in CH_2Cl_2

Figure 86

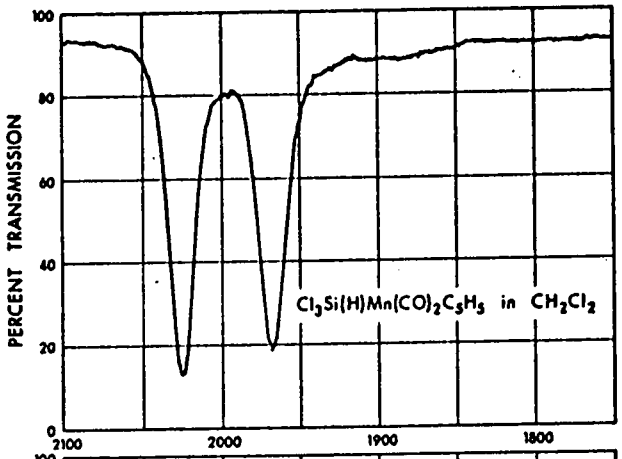


Figure 87

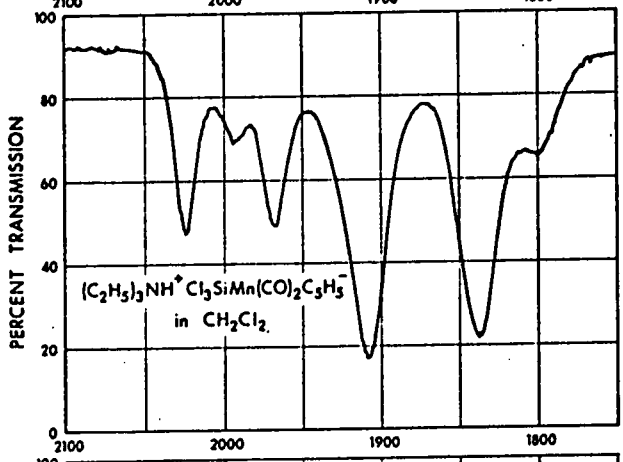


Figure 88

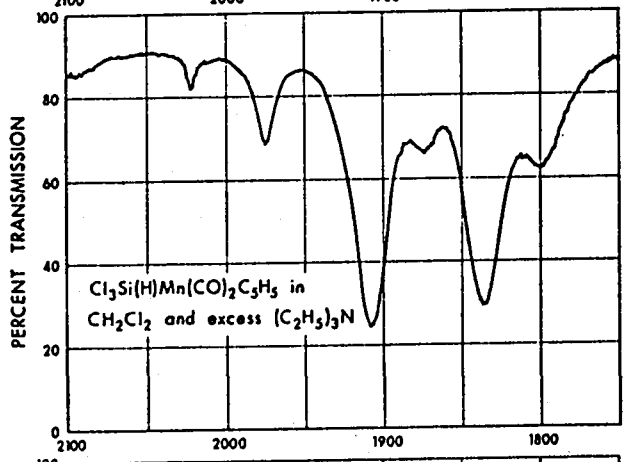


Figure 89

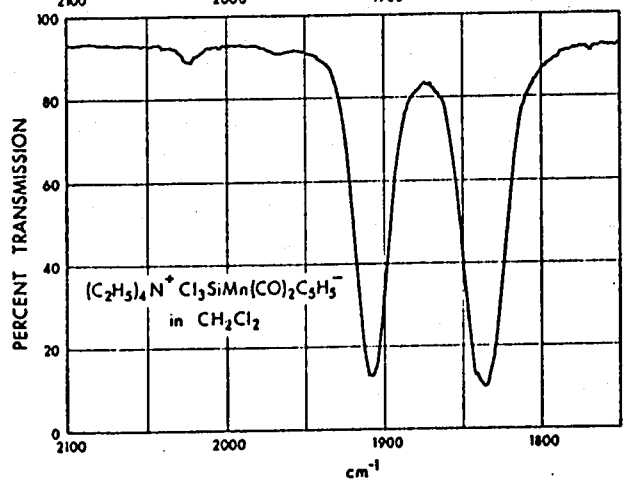


Figure 90

equilibrium for the triethylammonium salts.

The infrared spectra of $Cl_3SiHMn(CO)_2Cp$ and $Et_4N^+[Cl_3SiMn(CO)_2Cp]^-$ in dichloromethane, Fig. 87 and 90, show the predicted two carbonyl stretching bands for each complex. In dichloromethane, $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$, Fig. 88 shows bands due to both $Cl_3SiHMn(CO)_2Cp$ and $[Cl_3SiMn(CO)_2Cp]^-$:

$$Et_3NH^+[Cl_3SiMn(CO)_2Cp]^- \rightleftarrows Et_3N + Cl_3SiHMn(CO)_2Cp \qquad [V.25]$$

The effects of excess Et_3N are shown in Fig. 89, the equilibrium is shifted to the left. The presence of additional bands in Fig. 88 and 89, than those which can be assigned to $Cl_3SiHMn(CO)_2Cp$ and $[Cl_3SiMn(CO)_2Cp]^-$ suggests that a more complex system of equilibria is present than is indicated by the above equation. The stability of $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ in air is comparable to that of $Cl_3SiHMn(CO)_2Cp$, allowing a satisfactory characterization by elemental analysis.

The tendency of these complexes to dissociate is also reflected in their observed melting points. For example, $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ melts between 28-31°C, while $Et_4N^+[Cl_3SiMn(CO)_2Cp]^-$ only slowly decomposes above 190°C. Similar differences are observed with other triethyl and tetraethylammonium salts.

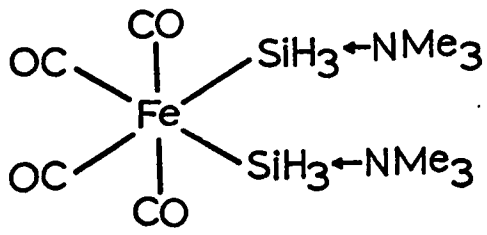
The triphenylsilyl-transition metal hydrides show lower acidities than the trichlorosilyl analogs. When

triethylamine was added to a hexane solution of $Ph_3SiHFe(CO)_4$, a quantitative precipitation of the salt was observed, but when triethylamine was added to a hexane solution of $Ph_3SiHMn(CO)_2Cp$ no apparent change occurred. The infrared spectrum of $Ph_3SiHMn(CO)_2Cp$ and triethylamine in dichloromethane showed only unreacted hydride. If the equilibria observed in the infrared spectra of the triethylammonium salts in dichloromethane are correllated to acidities, a relative order of acidities can be estimated for these hydrides in dichloromethane:

$$Cl_3SiFe(CO)_4 > Ph_3SiHFe(CO)_4 > Cl_3SiHMn(CO)_2Cp > Ph_3SiHMn(CO)_2Cp$$

The silyl transition metal carbonyl derivatives, $H_3SiCo(CO)_4$, $H_3SiMn(CO)_5$ and $(H_3Si)_2Fe(CO)_4$ reported by Aylett *et al.* behave as Lewis acids [6,7,9]. With trimethylamine these form 1:2 adducts which are postulated to be ionic complexes such as $[H_3Si(NMe_3)_2]^+[Co(CO)_4]^-$ [6] and $[H_3Si(NMe_3)_2]^+[Mn(CO)_5]^-$ [7]. Surprisingly, $(H_3Si)_2Fe(CO)_4$ also forms only a 1:2 adduct with excess trimethylamine, $(H_3Si)_2Fe(CO)_4.2NMe_3$ [9,11]. Its infrared spectrum in the solid shows carbon monoxide stretching bands at 2078m, 2042m, 1991s, 1917s, 1868vs, 1842ssh cm^{-1}. The hydride $H_3SiHFe(CO)_4$ [9] also forms an adduct, but of uncertain composition relative to trimethylamine, $H_3SiHFe(CO)_4.nNMe_3$ [11], which shows carbon monoxide stretching bands at 2055sh, 2050m, 2044, 1990m, 1919m and 1863vs cm^{-1}.

The former of these amine adducts, $(H_3Si)_2Fe(CO)_4.2NMe_3$ was postulated by Aylett as "partly ionic" with one amine coordinated to each silyl group, 77, [9,11]; $H_3SiHFe(CO)_4.nNMe_3$



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was formulated as an ionic complex, $[H_3Si.nNMe_3]^+[HFe(CO)_4]^-$ [11]. The precise nature of these complexes remains somewhat of an uncertainty, according to the data in the publications of Aylett and his coworkers [9,11].

Comparison of the data of these authors to our infrared results for the triethyl and tetraethylammonium salts of $Cl_3SiHFe(CO)_4$, $Ph_3SiHFe(CO)_4$, and $Cl_3SiHMn(CO)_2Cp$, does shed some light on these anomalies. The infrared data for the related irontetracarbonyl derivatives and irontetracarbonylate salts are shown in Table XVII. Note the relative values for carbonyl stretching vibrations of $[Ph_3SiFe(CO)_4]^-$ and the low frequency region of the trimethyl amine adducts, $(H_3Si)_2Fe(CO)_4.2NMe_3$ and $H_3SiFeH(CO)_4.nNMe_3$ [11]. The trimethylamine adducts described by Aylett *et al.* [9,11] probably more closely resemble ionic complexes such as $[H_3Si(NMe_3)_2]^+[H_3SiFe(CO)_4]^-$ and $Me_3NH^+[H_3SiFe(CO)_4]^-$, which are capable of reversible dissociation:

TABLE XVII

Infrared Data of Irontetracarbonyl Derivatives

Compound	cm^{-1}					
$(H_3Si)_2Fe(CO)_4$ [a,b,c]	2092s	2040vs	2036sh	2021vs		
$H_3SiFeH(CO)_4$ [a,b,c]	2107m	2050s	2044vs	2036vs		
$(H_3Si)_2Fe(CO)_4.2NMe_3$ [b,d]	2078m	2042m	1991s	1917s	1868vs	1842sh
$H_3SiFeH(CO)_4.nNMe_3$ [c,d]	2055sh	2050m	2044m	1990m	1919m	1863vs
$Et_4N^+[HFe(CO)_4]^-$ [e]				2015w	1937sh	1897vs
$Na_2^+[Fe(CO)_4]^=$ [b,f]						1786
$Cl_3SiHFe(CO)_4$	2124m	2069m	2058s	2053s		
$Ph_3SiHFe(CO)_4$	2097m	2036m	2026s	2018s		
$Et_4N^+[Cl_3SiFe(CO)_4]^-$			2031s	1950m	1916vs	1904sh
$Et_4N^+[Ph_3SiFe(CO)_4]^-$			1995s	1907m	1879vs	1865sh

a. Gas phase, 0.5-2.5 mm pressure,

b. B. J. Aylett, J. M. Campbell and A. Walton, J. Chem. Soc. (A) 2110 (1969); ref.11

c. Spectra complex, with broad band and shoulders in addition to the quoted values.

d. In Nujol.

e. J. P. Thomas, Diss. Abs. 26, 1942 (1965).

f. In aqueous solution.

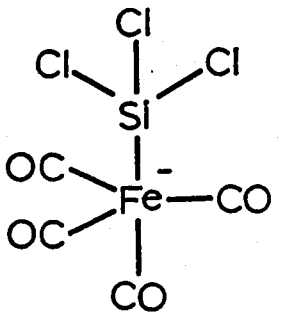
$$[H_3Si(NMe_3)_2]^+[H_3SiFe(CO)_4]^- \rightleftarrows 2Me_3N + (H_3Si)_2Fe(CO)_4 \qquad [V.26]$$

$$Me_3NH^+[H_3SiFe(CO)_4]^- \rightleftarrows Me_3N + H_3SiFeH(CO)_4 \qquad [V.27]$$

The shifts in band frequencies of 5 - 10 cm^{-1} of $[H_3SiFe(CO)_4]^-$, relative to $[Ph_3SiFe(CO)_4]^-$, is also observed in other molecules which are related in a similar manner. For example, $H_3SiFe(CO)_2Cp$ and $Ph_3SiFe(CO)_2Cp$ show carbon monoxide vibrations at 2010, 1962 cm^{-1} and 2005, 1954 cm^{-1} respectively (cf. Chapter III). The main contribution in the carbonyl infrared spectrum for these complexes is due to the silylirontetracarbonylate, $[H_3SiFe(CO)_4]^-$. Additional bands observed by Aylett in the spectrum of $Me_3NH^+[H_3SiFe(CO)_4]^-$ at 2044 cm^{-1} and 2050 cm^{-1} correspond with the reported values for $H_3SiFeH(CO)_4$ [11], not unexpected in view of the dissociation which is proposed here. The infrared spectrum of $(H_3Si)_2Fe(CO)_4$ shows numerous shoulders in addition to the main broad carbonyl stretching bands, given in Table XVII, which does not allow unambiguous recognition of $(H_3Si)_2Fe(CO)_4$ by infrared, when it is present in small quantities in some other compound. The infrared spectra of $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$, Fig. 88 and 89 show also bands that cannot be attributed to $Cl_3SiHMn(CO)_2Cp$ or $[Cl_3SiMn(CO)_2Cp]^-$. Other more complex equilibria than are suggested by the above equations, either in the original synthesis of these ionic complexes,

or in solution when the complex is dissolved, may perhaps form species which have their own distinct infrared spectra. For example, the infrared spectrum in dichloromethane of the precipitate from the reaction of $Cl_3SiHFe(CO)_4$ and Me_3N in hexane, shows all the bands anticipated for $[Cl_3SiFe(CO)_4]^-$, but also several other bands which could not be assigned to any known species. Recrystallization of this material from a dichloromethane-hexane mixture, or the addition of excess trimethylamine, resulted in products having very complex infrared spectra.

Ideally, the anion $[Cl_3SiFe(CO)_4]^-$ should be isostructural with $Cl_3SiCo(CO)_4$, which has a trigonal bipyramidal structure.



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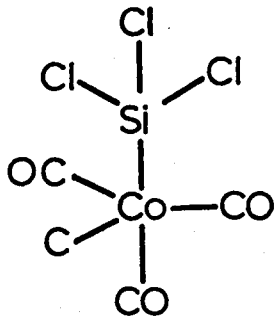

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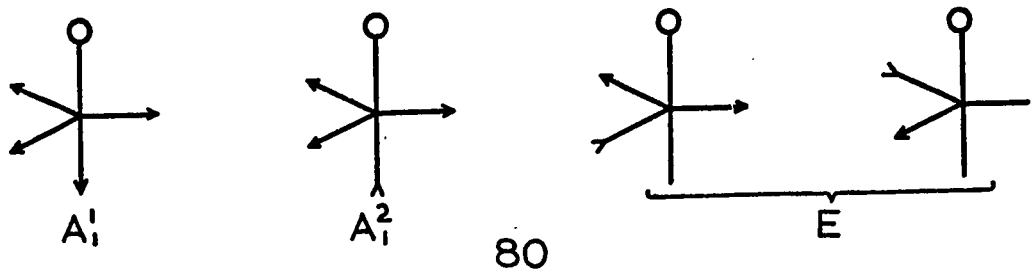
For C_{3v} symmetry,[50] these complexes should show three infrared active carbon monoxide vibrations. The carbon monoxide stretching modes for an $XM(CO)_4$ system, shown below, are highly coupled. The symmetric stretch of all



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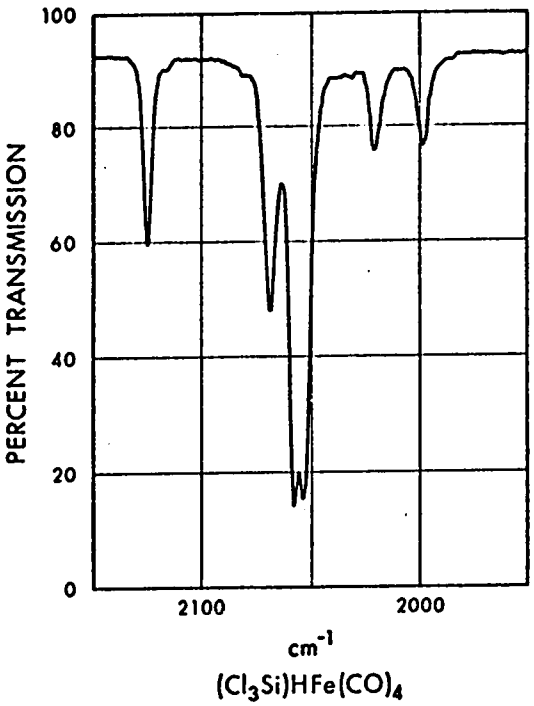
carbon monoxides, A_1^1 mode, is of highest energy, while the E modes are of lowest energy. The infrared spectrum for $Cl_3SiCo(CO)_4$ is shown in Fig 38. The intense, low frequency band in the infrared spectrum for $[Cl_3SiFe(CO)_4]^-$, Fig. 83 and 86, shows signs of splitting, suggesting that a pure C_{3v} symmetry surrounding the iron atom is not present in the molecule. The infrared spectra of $Et_4N^+[Ph_3SiFe(CO)_4]^-$ and $Et_3NH^+[Ph_3SiFe(CO)_4]^-$, Fig. 84 and 85, are very similar to those of the chlorosilyl analog.

A study by Edgell *et al.* of $Na^+[Co(CO)_4]^-$, in THF-water mixtures, indicates that *ion pairing* of the cobalt tetracarbonylate ion lowers it symmetry, as indicated by the splitting of the carbonyl band in the infrared spectrum [72]. An undisturbed tetrahedral symmetry of $[Co(CO)_4]^-$ would show only one carbon monoxide vibration. In pure THF, three carbon monoxide frequencies are observed. These merge into one, smooth, symmetric band when water is added to the solution. In conjunction with conductivity measurements over a concentration range, Edgell *et al.* proposed [72], that water hydrates the sodium ions such that they become too bulky for effective ion pairing.

The apparent splitting of the E mode in the infrared spectra of the $[R_3SiFe(CO)_4]^-$ anions, Fig. 83 - 86 may

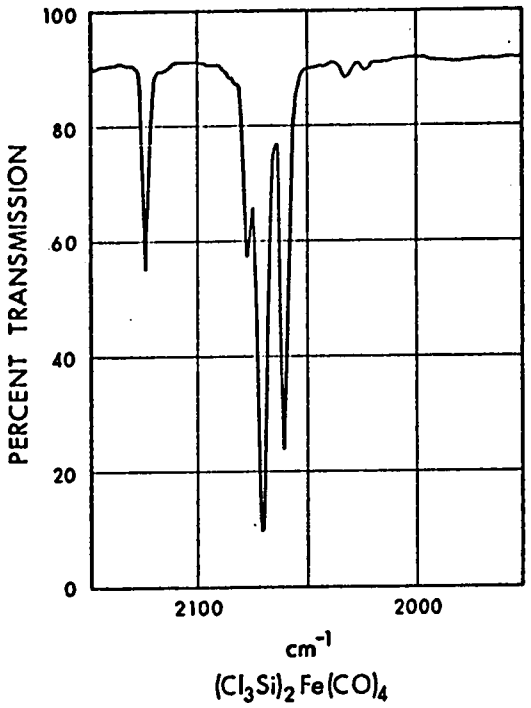
perhaps also be due to ion pairing. The infrared spectra of the related octahedral complexes, $Cl_3SiHFe(CO)_4$, $(Cl_3Si)_2Fe(CO)_4$ and $Ph_3SiHFe(CO)_4$ in hexane and dichloromethane are shown in Fig. 91-94. The weak, low frequency bands at 2023 cm^{-1} and 2000 cm^{-1} in Fig. 91 and 93 are due to trace amounts of $Fe(CO)_5$, which forms in the decomposition of these hydrides. Fig. 93 and 94 demonstrate the contrast in resolution of the same complex in hexane or dichloromethane as solvent. The triethyl and tetraethylammonium salts are insoluble in hexane and in dichloromethane, Fig. 83 - 86, extensive band broadening is observed. Comparison of the infrared spectra for $[Cl_3SiFe(CO)_4]^-$ and $[Ph_3SiFe(CO)_4]^-$ to the spectra for $Cl_3SiHFe(CO)_4$, $Ph_3SiHFe(CO)_4$ and $(Cl_3Si)_2Fe(CO)_4$ does suggest considerable similarity.

In ion pairing, two extreme possibilities may be envisaged which could explain the observed anomalies in the infrared spectra. Firstly, the approach of the cation in ion pairing could cause a distortion of the ligands on the anion from a trigonal bipyramidal structure to an octahedral arrangement, 81; and secondly, the basic trigonal bipyramidal structure of the anion remains unchanged, but the close proximity of the cation removes the degeneracy of the E modes, 82.



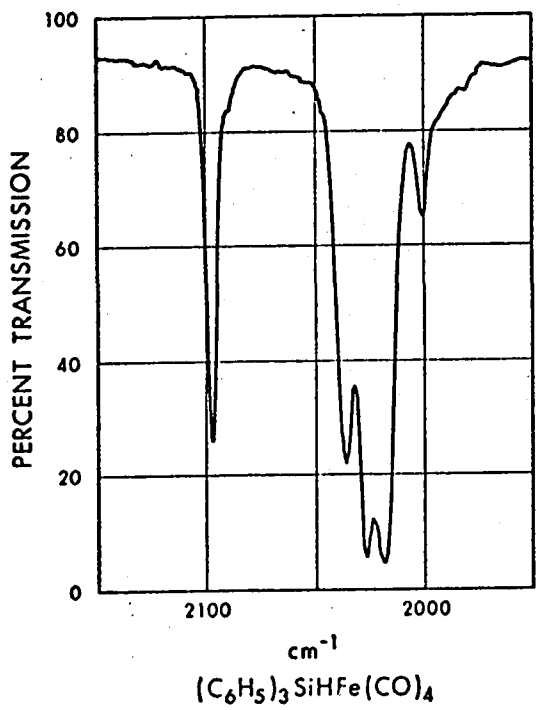
$(Cl_3Si)HFe(CO)_4$

Figure 91



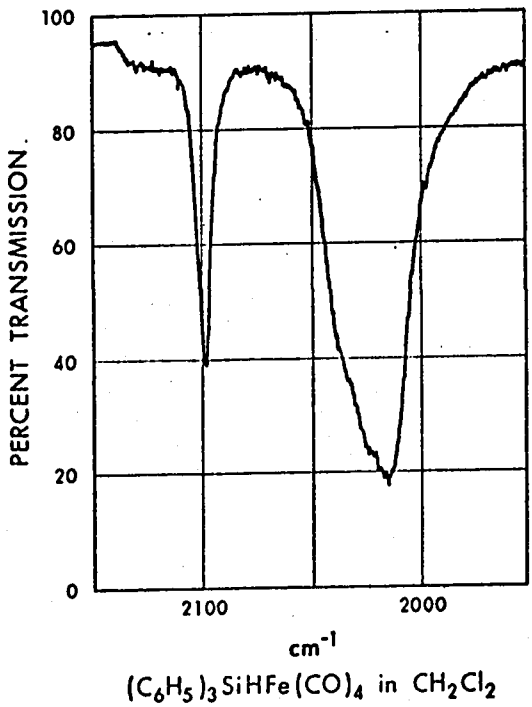
$(Cl_3Si)_2Fe(CO)_4$

Figure 92



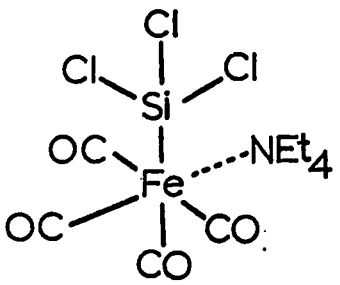
$(C_6H_5)_3SiHFe(CO)_4$

Figure 93



$(C_6H_5)_3SiHFe(CO)_4$ in CH_2Cl_2

Figure 94



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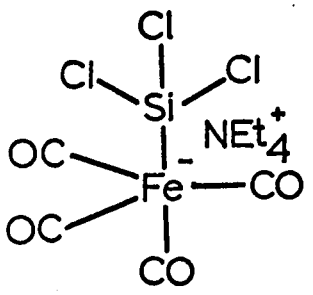

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Either of these two structural arrangements would be consistent with the observed infrared spectra.

Although small distortions of the ligands caused by the crystal packing may be expected in the solid state, it seems unlikely that a cation will occupy a distinctive coordination position. For example, the basic structure of the anion in $Et_4N^+[HFe_3(CO)_{11}]^-$, in the crystalline state, is essentially the same as that of $Fe_3(CO)_{12}$ [61]. The structure of $Et_4N^+[Cl_3SiFe(CO)_4]^-$ as suggested by 81 seems unlikely to be achieved, but represents a limiting distortion.

The cobalt tetracarbonyl derivatives of the unsymmetric group IV ligands, such as $MeH_2SiCo(CO)_4$ [13,91], $PhCl_2GeCo(CO)_4$ [183], and $Ph_2ClSnCo(CO)_4$ [185], show splitting of the E mode in the carbonyl stretching region. Close proximity of the cation in any of the three positions between the equatorial carbonyls, 82, could cause a similar lowering of the symmetry, as is observed for the above unsymmetric cobalt tetracarbonyl derivatives. The detailed nature of these complexes in solution, however, is not known.

4. Reactions of Anions

The chemistry of the silyl carbonylate salts is virtually unexplored, but initial investigations in this work indicate that they form a new source of carbonyl anions which may be employed in syntheses of metal-metal bonds between group IV elements and transition metals. These anions displace chlorides on sufficiently strong Lewis acids such as $SnCl_4$, but the hydrides do not react with $SnCl_4$:

$$Cl_3SiHMn(CO)_2Cp + SnCl_4 \xrightarrow{X} HCl + Cl_3Sn(Cl_3Si)Mn(CO)_2Cp \qquad [V.28]$$

The chemical behavior of these salts resembles that of the trimethylamine adduct reported by Aylett *et al.* For example, $H_3SiMn(CO)_5$ is inert to hydrogen chloride, but the adduct, $[H_3Si(NMe_3)_2]^+[Mn(CO)_5]$, reacts rapidly with hydrogen chloride, forming H_3SiCl, $HMn(CO)_5$ and Me_3NHCl [10].

The reactions of the silyl carbonylates with tin halides are very similar to those described in Chapter II: (e.g. $Ph_3SnCl + Na^+[Mn(CO)_5]^- \rightarrow Ph_3SnMn(CO)_5 + NaCl$).

$$Et_4N^+[Cl_3SiFe(CO)_4]^- + SnCl_4 \rightarrow Et_4NCl + Cl_3Sn(Cl_3Si)Fe(CO)_4 \qquad [V.29]$$

$$Et_3NH^+[Cl_3SiFe(CO)_4]^- + Cl_3Sn(Cl_3Si)Fe(CO)_4 \rightarrow Et_3N.HCl + Cl_2Sn[Fe(CO)_4SiCl_3]_2 \qquad [V.30]$$

$$Et_3NH^+[Cl_3SiMn(CO)_2Cp]^- + Ph_2SnCl_2 \rightarrow Et_3N.HCl + Ph_2ClSn(Cl_3Si)Mn(CO)_2Cp \quad [V.31]$$

$$Et_3NH^+[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]^- + Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3 \rightarrow Et_3N.HCl + Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2 \quad [V.32]$$

These reactions are carried out in dichloromethane.* For monosubstitution on the tin atom it is essential that the anion in solution is added slowly to a solution containing excess $SnCl_4$. The disubstituted tin derivatives such as $Cl_2Sn[Cl_3SiMn(CO)_2Cp]_2$ may be obtained by adding two moles of the ammonium salt to one mole of $SnCl_4$; however, it is more convenient and the side reactions are more easily controlled, when equimolar quantities of $Cl_3Sn(Cl_3Si)Mn(CO)_2Cp$ and $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ are reacted. The reaction of equimolar $Cl_3Sn(Cl_3Si)Fe(CO)_4$ and $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ in dichloromethane precipitated $Cl_3Sn[Fe(CO)_4SiCl_3]_2$**, an orange yellow, crystalline

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* Dichloromethane slowly reacts with amines to form ammonium salts of undetermined composition. These reactions, however, are much slower than the above anion reactions and do not interfere significantly.

**Preliminary results of the crystal structure determination for $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ yield the following data: orthorhombic unit cell, P2,2,2 space group, Cell dimensions; a = 11.82 Å, b = 10.41 Å, and c = 9.86 Å, density = 2.15 gm/cc, two asymmetric units/unit cell. Personal communication K. A. Simpson and M. J. Bennett of this department.

material, when the reaction mixture is allowed to warm up slowly from -78°C to room temperature. If this reaction mixture is allowed to remain at room temperature then $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ slowly redissolves with evolution of carbon monoxide, resulting in a dark red, transparent solution. After removal of the solvent, a red, viscous oil remains which does not readily crystallize. Eventually some crystalline material forms after several weeks in a dichloromethane-hexane mixture. This appears to be some ionic complex such as $Et_3NH^+[Fe_2(CO)_7Si_2SnCl_9]^-$, however, this material has not been fully characterized.

Recrystallization of $Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2$ from a benzene-hexane solution yields a coarse, orange crystalline product which contains one benzene molecule per three complex molecules, $Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2 \cdot 1/3C_6H_6$. The composition of this crystalline material remained unchanged when it was exposed to high vacuum for several hours. The benzene protons are observed in the nmr spectrum at 2.68 τ in deuterated dichloromethane.

Silyl transition metal tin derivatives which have thus far been synthesized, employing the new silyl transition metal anions are listed in Table XX. In reactions of $Et_3NH^+[Cl_3SiMn(CO)_2\pi C_5H_5CH_3]^-$ with the $Cl_{3-n}SnPh_n$ series, the reaction becomes progressively slower with the increase in n. When n=2, the reaction is exceedingly slow and the

yield of the product is very low. For n=3 no product (i.e., $Ph_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$) has so far been isolated.

It is interesting to note in these reactions that the silicon-chlorine bond is relatively inert compared to the tin-chlorine bond. This apparently is related to the difference in ionic character of these bonds. The silicon-chlorine bond has a greater degree of covalent character than the tin-chlorine bond, and although chlorosilanes are occasionally used in anion reactions for the preparation of silicon transition metal bonds, this synthetic method is not as commonly employed for the silicon derivatives as for the germanium and tin analogs.

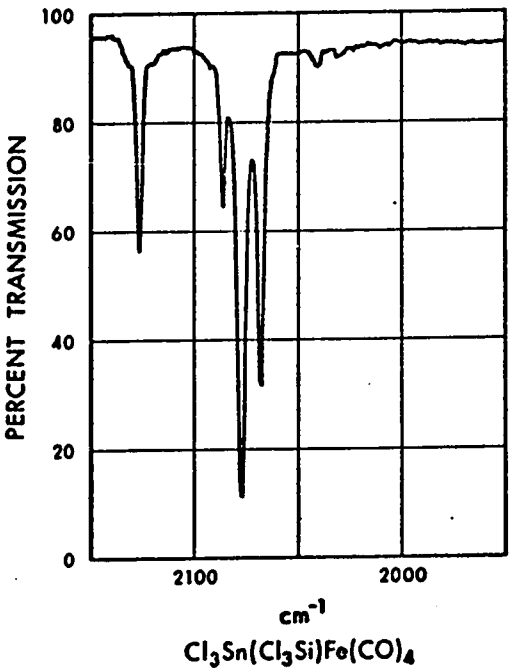


Figure 95

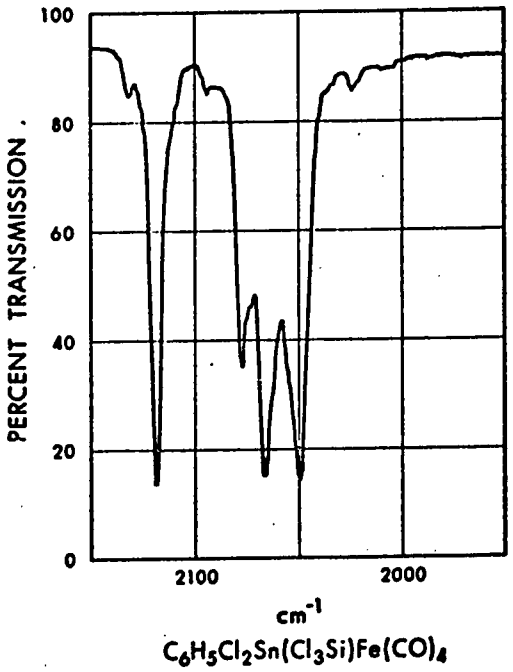


Figure 96

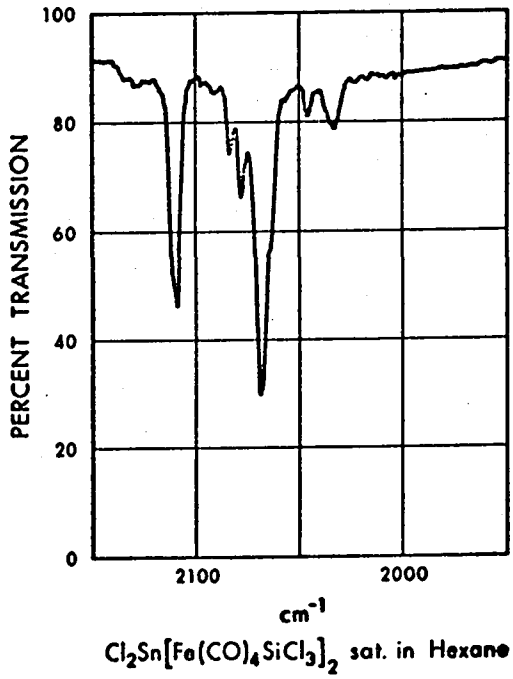


Figure 97

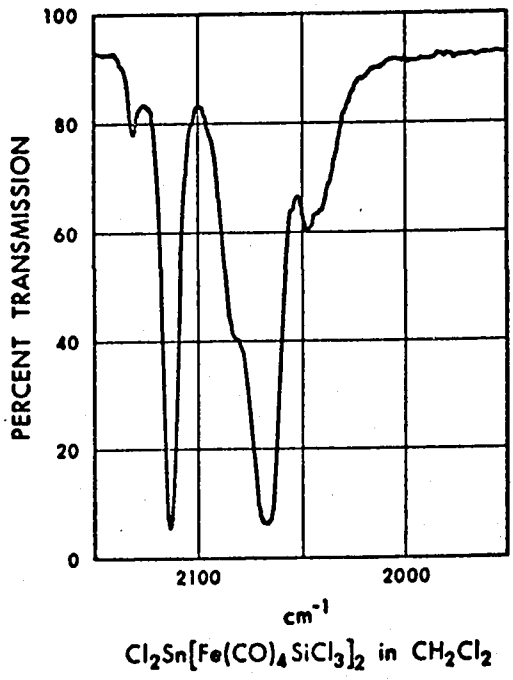


Figure 98

EXPERIMENTAL

Starting materials and general techniques described in Chapters II, III and IV are applicable in this section.

In the preparation of silyl transition metal hydrides, all reactions were carried out in the fume hood, with the reaction mixture at atmospheric pressure. The reaction mixture was open to an oil-filled bubbler which allowed the carbon monoxide formed in the reaction to escape. Large scale reactions, 200-250 ml, were carried out in a Pyrex vessel equipped with a water-cooled, quartz finger, joined by a 60/50 standard taper ground glass joint. A 450 watt ultraviolet light source (Hanovia High Pressure Mercury, 679A) attached to a power supply, was placed inside the quartz finger. Reactions on a smaller scale, 40 - 60 ml, were carried out in a quartz vessel equipped with a water cooled finger and a reflux condenser. This system was irradiated externally with a 100 watt ultraviolet light source (Hanovia Utility Lamp, 616A).

Nitrogen was passed through the reaction vessel, prior to the addition of the starting materials and the solvent. An inert atmosphere was maintained by the carbon monoxide formed in the reaction. In the isolation and purification procedure, utmost precautions were taken to maintain an inert atmosphere.

Starting Materials

πCyclopentadienylcobaltdicarbonyl, $CpCo(CO)_2$;

πBenzenechromiumtricarbonyl, $\pi C_6H_6Cr(CO)_3$; and πCyclopentadienylmanganesetricarbonyl, $CpMn(CO)_3$ were purchased from Strem Chemicals Inc., 150 Andover St., Danvers, Mass.

πMethylcyclopentadienylmanganesetricarbonyl, $\pi CH_3C_5H_4Mn(CO)_3$ was obtained from the Ethyl Corporation, 100 Park Avenue, New York 17, N.Y.

Tetrafluoroethylene, $CF_2=CF_2$, was purchased from Peninsular Chemresearch Inc., Gainsville, Florida, 14318.

Deuterated trichlorosilane and dichloromethane, Cl_3SiD and CD_2Cl_2 were purchased from Merck, Sharp and Dohme of Canada Limited, Montreal.

Trichlorosilylirontetracarbonylhydride, $Cl_3SiHFe(CO)_4$:

The large scale ultraviolet reaction - vessel was charged with 15 ml $Fe(CO)_5$ (22 gm, 0.11 mol), 20 ml Cl_3SiH (27 gm, 0.20 mol) and 180 ml heptane. With the 450 watt, water-cooled, ultraviolet source the reaction mixture was irradiated for 24 hours. During this process carbon monoxide evolved quite rapidly, initially, but very slowly at the end. The reaction mixture was decanted under nitrogen into a 500 ml round bottom flask equipped with a stopcock. At reduced pressure, the volume of the reaction mixture was reduced to 120 - 150 ml, eliminating almost all unreacted Cl_3SiH. The remaining solution was filtered under

nitrogen pressure through a 10 - 20 μ glass sinter. The yellow, clear filtrate was cooled to -78°C, which resulted in the crystallization of a white product. The cold solvent was decanted and the vessel refilled with 100 ml pentane. The clear solution was again cooled to -78°C, which crystallized a white material. This recrystallization process in pentane was repeated 3 - 4 times. The cold solution was decanted and the remaining pentane was removed at reduced pressure, leaving a viscous, pale yellow, oily product, $Cl_3SiHFe(CO)_4$, at room temperature. An infrared spectrum of this material showed the presence of trace amounts of $Fe(CO)_5$. The product (26.0 gm, 0.086 mol, 78% based on $Fe(CO)_5$ employed) at this stage was sufficiently pure for further reactions. For higher purity, slow sublimation into a -78°C trap under high vacuum yielded white, needle shaped crystals. The compound was extremely air sensitive and was not analyzed directly. Moderately air stable derivatives of this hydride have been synthesized and characterized.

Trichlorosilyl-π-cyclopentadienylmanganesedicarbonylhydride, $Cl_3SiHMn(CO)_2Cp$:

A mixture of 1.01 gm $CpMn(CO)_3$ (4.95 mmol), 70 ml Cl_3SiH (excess) in 50 ml hexane was irradiated with a 100 watt ultraviolet source for nine hours. A water-cooled finger inside the reaction mixture maintained the reaction

temperature below 30°C. The progress of the reaction was followed by infrared, which showed a new band at 2028 cm^{-1} in the carbonyl stretching region, increasing in intensity with time. After nine hours reaction time the carbonyl stretching bands of the hydride and starting material were of equal intensity. Considerable decomposition was also noted. The volume of the reaction mixture was reduced to 20 ml under vacuum. The remaining solution was filtered hot and the clear yellow filtrate cooled to -78°C, which precipitated a yellow, microcrystalline material. This was isolated and sublimed at room temperature onto a water-cooled probe at less than 0.01 mm mercury pressure, depositing unreacted $CpMn(CO)_3$. After sublimation of $CpMn(CO)_3$ had ceased, the temperature was elevated to 60°C and sublimation continued, depositing pale yellow, crystalline $Cl_3SiHMn(CO)_2Cp$ (0.324 gm, 1.05 mmol, 21% based on $CpMn(CO)_3$ employed). This was recrystallized from a minimum amount of hot hexane, resulting in needle-shaped, pale yellow crystals, which had a melting point of 82 - 83°C.

Trichlorosilyl-π-cyclopentadienylmanganesetricarbonyl-deuteride, $Cl_3SiDMn(CO)_2Cp$:

A similar procedure as for the synthesis of $Cl_3SiHMn(CO)_2Cp$ was followed, employing Cl_3SiD.

Bis-trichlorosilyl-π-cyclopentadienylironcarbonylhydride, $(Cl_3Si)_2HFe(CO)Cp$:

This hydride was originally prepared as one of the components in the thermal reaction between $[CpFe(CO)_2]$ and Cl_3SiH (cf. Chapter IV).

A sample of 0.65 gm $Cl_3SiFe(CO)_2Cp$ (2.09 mmol) in a solution of 6.0 ml Cl_3SiH (excess) and 45 ml hexane was irradiated with the 100 watt ultraviolet source for four hours. A water cooled finger inside the reaction mixture maintained the reaction temperature below 30°C. Dark deposits on the wall of the reaction vessel indicated substantial decomposition. The infrared spectrum of the final reaction mixture showed that approximately 90% of the starting material was consumed. At reduced pressure, the volume of the reaction mixture was reduced to 30 ml, eliminating most of the unreacted Cl_3SiH. The remaining solution was filtered warm and the clear, yellow filtrate was cooled to -78°C, precipitating a yellow microcrystalline material. This was isolated and sublimed at room temperature onto a water cooled probe at less than 0.01 mm mercury pressure, depositing the unreacted yellow $Cl_3SiFe(CO)_2Cp$. After sublimation of $Cl_3SiFe(CO)_2Cp$ had ceased, the temperature was raised to 65°C and sublimation of a pale yellow, microcrystals continued. The yield, 0.32 gm of $(Cl_3Si)_2HFe(CO)Cp$ (0.76 mmol) was 37% based on

$Cl_3SiFe(CO)_2Cp$ employed. This complex was recrystallized from hexane.

Trichlorosilyl-π-cyclopentadienylcobaltcarbonylhydride, $Cl_3SiHCo(CO)Cp$:

A mixture of 2.0 ml $CpCo(CO)_2$ (2.8 gm, 15.5 mmol) and 7.0 ml Cl_3SiH (excess) in 50 ml hexane was irradiated with the 100 watt ultraviolet source for four hours at a temperature below 30°C. The infrared spectrum of the reaction mixture showed only unreacted $CpCo(CO)_2$. Cooling of the reaction mixture was discontinued and the irradiation was resumed for an addional three hours, during which the temperature of the reaction mixture rose to 40 - 50°C. At this stage all of the $CpCo(CO)_2$ was consumed. The infrared spectrum showed bands at 2117, 2062, 2045 and 2037 cm^{-1}. (Reported values for $Cl_3SiCo(CO)_4$ are at 2117, 2063 and 2037 cm^{-1} [64]). The reaction mixture was filtered under nitrogen and the clear, yellow filtrate was cooled to -78°C, which crystallized a yellow material of crude, oily appearance. The cold solution was decanted. The yellow, oily material was sublimed at room temperature onto a water-cooled probe at a pressure less than 0.01 mm mercury. A coarse, yellow, crystalline product, $Cl_3SiHCo(CO)Cp$, was deposited. After the complex was resublimed twice, its melting point was 31 - 33°C. In the impure state the hydride was extremely air sensitive.

Trichlorosilyl-π-benzenechromiumdicarbonylhydride, $Cl_3SiHCr(CO)_2\pi C_6H_6$:

A sample of 1.04 gm $\pi C_6H_6Cr(CO)_3$ (4.85 mmol) in 10 ml Cl_3SiH (excess) and 40 ml hexane was irradiated with a 100 watt ultraviolet source for 28 hours. A water-cooled finger in the reaction mixture maintained the reaction temperature below 30°C. The infrared spectrum of the reaction mixture showed no new band, but the concentration of $\pi C_6H_6Cr(CO)_3$ was greatly diminished. The yellow, crystalline material which precipitated showed no noticeable decomposition. The solvent and excess Cl_3SiH were decanted and the yellow precipitate was sublimed at 65°C onto a water-cooled probe at less than 0.01 mm mercury pressure. A yellow, crystalline material, unreacted $\pi C_6H_6Cr(CO)_3$, deposited. The residue of lower volatility was dissolved in a minimum amount of dichloromethane and filtered under nitrogen. Hexane was slowly added to the clear, yellow filtrate until the solution became turbid. This was slowly cooled to -78°C, precipitating a fine yellow crystalline product. After an additional recrystallization in a similar manner, the product, $Cl_3SiHCr(CO)_2C_6H_6$ had a melting point of 114.0 - 114.5°C.

Triphenylsilylirontetracarbonylhydride, $Ph_3SiHFe(CO)_4$:

A mixture of 15 ml $Fe(CO)_5$ (22 gm, 0.11 mol) and 25.5 gm Ph_3SiH (0.098 mol) in 180 ml heptane was irradiated with a 450 watt ultraviolet source for 22 hours. Initially the

carbon monoxide evolution was rapid, (i.e. one bubble per sec) but at the end of the reaction time it had virtually stopped. A small amount of decomposition was observed. The reaction mixture was filtered under nitrogen and the clear, pale-yellow solution was slowly cooled in the refrigerator. A massive amount of white coarse crystalline material formed. A small portion of this was recrystallized from pentane, resulting in a white crystalline product $Ph_3SiHFe(CO)_4$, having a melting point of 85 - 87°C. When this hydridewas heated in solution, it decomposed rapidly and the solution turned dark green.

Triphenylsilyl-π-methylcyclopentadienylmanganesedicarbonyl-hydride, $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$:

A mixture of 20 ml $\pi CH_3C_5H_4Mn(CO)_3$ (0.128 mol) and 21 gm Ph_3SiH (0.081 mol) in 180 ml heptane was irradiated with the 450 watt ultraviolet source for ten hours. The progress of the reaction was followed by the carbon monoxide evolution, which had virtually stopped at the end of the reaction. The reaction mixture was filtered under nitrogen and the clear, yellow filtrate was allowed to cool slowly in the refrigerator. A massive quantity of pale, yellow crystals precipitated. A small fraction of this was recrystallized from hexane, forming coarse, pale, yellow crystals, $Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$ having a melting point of 95 - 96°C.

Bis(trichlorosilylirontetracarbonyl), $[Cl_3SiFe(CO)_4]_2$:

A sample of 2 - 3 gm $Cl_3SiHFe(CO)_4$ was slowly sublimed under high vacuum into a 60 - 70 ml Carius tube equipped with a Teflon valve. Similarly, 5.0 ml pentane was distilled into a Carius tube. The tube was then attached to a vacuum system equipped with a manometer, and tetrafluoroethylene (1.2 liter at STP) was introduced at liquid nitrogen temperature. The reaction mixture was then warmed slowly to room temperature. Gentle agitation of the tube immediately precipitated a coarse, bright yellow, needle-like crystalline material. (During this process the Carius tube was kept behind a protective shield. Tetrafluoroethylene under pressure is potentially dangerous, since it may polymerize violently). The excess tetrafluoroethylene and pentane were removed at reduced pressure. The remaining product, $[Cl_3SiFe(CO)_4]_2$ decomposed above 90°C. The mass spectrum of the unreacted tetrafluoroethylene showed ions such as $C_4F_8^+$, $C_4F_7^+$, $C_3F_6H^+$, $C_2F_4H_2^+$ and $C_2F_4H^+$ which are not present in the sample prior to the reaction. The infrared spectrum was complicated by the rapid decomposition of the complex in solution.

Bis-μ-dichlorosilyl-bis-irontetracarbonyl, $[Cl_2SiFe(CO)_4]_2$:

This complex was originally prepared in a thermal reaction between $Fe(CO)_5$ and Cl_3SiH above 160°C (cf. Chapter

III). A sample of 0.20 gm $[Cl_3SiFe(CO)_4]_2$ (0.33 mmol) was placed in a 25 ml Carius tube equipped with a Teflon valve. The tube was evacuated and then slowly heated. At 120 - 130°C, the compound melted to an orange-brown semisolid, which resolidified at this temperature, in approximately ten minutes, to a powdery yellow solid, $[Cl_2SiFe(CO)_2]_2$, which was identified by infrared; this reaction proceeded in high yield. The mass spectrum of the gaseous reaction products contained the ions $SiCl_4^+$ and $Fe(CO)_5^+$ as well as their fragments.

Tetraethylammonium Trichlorosilylirontetracarbonylate, $Et_4N^+[Cl_3SiFe(CO)_4]^-$:

Nitrogen was bubbled for one hour through a solution of 16.3 gm $Cl_3SiHFe(CO)_4$ (54.0 mmol) and 8.57 gm Et_4NCl (52.0 mmol) in 70 ml of dichloromethane. After the reaction appeared complete, the solvent was removed at reduced pressure resulting in a cream colored, crystalline material. This crude product was washed with several aliquots of hexane, yielding 21.1 gm of $Et_4N^+[Cl_3SiFe(CO)_4]^-$ (48.5 mmol, 93% based on Et_4NCl employed). This was dissolved in a minimum amount of dichloromethane, filtered, and the clear, colorless filtrate was placed into the refrigerator. After several hours coarse, plate-like, white crystals formed, which decomposed gradually above 260°C.

Triethylammonium Trichlorosilylirontetracarbonylate, $Et_3NH^+[Cl_3SiFe(CO)_4]^-$:

The solution containing the hydride, $Cl_3SiHFe(CO)_4$, from a reaction of 20 ml $Fe(CO)_5$ (0.148 mol) and 30 ml Cl_3SiH (excess) in 180 ml heptane, irradiated for 14 hours with a 450 watt ultraviolet source, was reduced in volume to 120 - 140 ml at reduced pressure. This was filtered under nitrogen pressure, resulting in a clear, yellow solution. With the clear filtrate cooled to approximately -50°C, triethylamine was slowly added, while the reaction mixture was magnetically stirred. A dense white microcrystalline material precipitated immediately. When the addition of triethylamine precipitated no additional product, the solution was decanted and the crystalline material was washed with several aliquots of pentane containing small amounts of triethylamine. The resulting product, 30.9 gm $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ (0.077 mol, 52% based on $Fe(CO)_5$ employed) was extremely air sensitive and has on some occasions turned into a semisolid at room temperature. This salt has not been analyzed; however, employing this material more air stable derivatives have been synthesized and analyzed.

Tetramethylammonium Trichlorosilylirontetracarbonylate, $Me_4N^+[Cl_3SiFe(CO)_4]^-$

Nitrogen was bubbled for 90 minutes through a solution

containing 24 gm $Cl_3SiHFe(CO)_4$ (0.079 mol) and 8.8 gm Me_4NCl (0.080 mol) in 70 ml dichloromethane. The Me_4NCl had been dried under high vacuum for several days. After the reaction appeared complete, the solvent was removed at reduced pressure, leaving a white, crystalline material. This was washed with several aliquots of pentane and then dissolved in a minimum amount of dichloromethane and filtered. The colorless, clear filtrate was placed in the refrigerator. After several hours white, plate-like crystalline $Me_4N^+[Cl_3SiFe(CO)_4]^-$ formed; this compound was quite air sensitive.

Tetraethylammonium Trichlorosilyl-π-cyclopentadienylmanganesedicarbonylate, $Et_4N^+[Cl_3SiMn(CO)_2Cp]^-$:

A mixture of 0.50 gm $Cl_3SiHMn(CO)_2Cp$ (1.6 mmol) and 0.26 gm Et_4NCl (1.5 mmol) was stirred magnetically at room temperature in dichloromethane. The reaction mixture slowly gave off hydrogen chloride, which was allowed to escape through a bubbler. Nitrogen was passed through the solution to sweep out the hydrogen chloride. The reaction mixture was then filtered. Hexane was carefully added to the top of the clear, yellow filtrate, forming two layers of different density. As the hexane slowly diffused into the dichloromethane, large yellow crystals formed on the wall of the vessel. The product, $Et_4N^+[Cl_3SiMn(CO)_2Cp]^-$, slowly darkened above 190°C and

melted at 280°C.

Triethylammonium Trichlorosilyl-π-cyclopentadienylmanganesedicarbonylate, $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$:

Triethylamine was added dropwise to a hexane solution containing 0.69 gm $Cl_3SiHMn(CO)_2Cp$ (2.2 mmol). The solution became cloudy immediately and a yellow material oiled out, finally solidifying to a pale, yellow powder. This was dissolved in 15 ml dichloromethane and filtered. Hexane was added slowly and the product $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ oiled out of solution. After vigorous shaking, the oily material crystallized to a pale, yellow solid, melting at 28-31°C. The infrared spectrum in the carbonyl stretching region showed bands at 2026, 1969, 1907 and 1839 cm^{-1} in dichloromethane. In dichloromethane $Cl_3SiHMn(CO)_2Cp$, showed bands at 2026 cm^{-1} and 1969 cm^{-1}.

Trichlorotintrichlorosilyl-π-cyclopentadienylmanganesedicarbonyl, $Cl_3Sn(Cl_3Si)Mn(CO)_2Cp$:

To a stirring dichloromethane solution containing 0.25 ml $SnCl_4$ (0.55 gm, 2.1 mmol), 0.35 gm $Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ in 10 ml dichloromethane was added dropwise. The reaction mixture was allowed to remain at room temperature for 30 minutes after the addition was complete and then the solvent was removed at reduced pressure. The resulting pale, yellow solid was dissolved in hexane, filtered, and the clear

solution was placed in the refrigerator. Coarse, pale, yellow crystals slowly formed. The product, $Cl_3Sn(Cl_3Si)Mn(CO)_2Cp$, melted at 161 - 163°C.

Trichlorotintrichlorosilyl-π-methylcyclopentadienylmanganesedicarbonyl, $Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$:

A solution of 10 ml $\pi CH_3C_5H_4Mn(CO)_3$ (0.061 mol) and 10 ml Cl_3SiH (excess) in 180 ml hexane was irradiated with a 450 watt ultraviolet source for 12 hours. Extensive decomposition was observed. The reaction mixture was filtered and the clear, yellow solution cooled to -78°C, precipitating a dense, cream colored material. The cold solvent was decanted and the remaining hexane and unreacted Cl_3SiH were removed at reduced pressure. The oily material was dissolved in pentane, yielding a clear, yellow solution. Excess Et_3N was slowly added until no additional material precipitated from solution (This precipitate, $Et_3NH^+[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]^-$, was not analyzed but was used directly in the succeeding step in the preparation of derivatives.) This oily product was washed with several aliquots of pentane containing small quantities of Et_3N. It was dissolved in 15 ml dichloromethane and slowly added to a dichloromethane solution containing 1.5 ml Cl_4Sn (excess). After addition was complete, the reaction mixture was stirred at room temperature for an additional 30 minutes. The dichloromethane was

removed at reduced pressure, leaving a yellow residue. This was extracted with hot hexane and filtered. A considerable quantity of yellow material remained undissolved. The clear, yellow filtrate was cooled slowly in the refrigerator. Large, yellow crystals separated from solution. The product, $Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$, melted at 115 - 117°C.

Dichloro-bis(trichlorosilyl-π-methylcyclopentadienylmanganesedicarbonyl), $Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2$:

The hexane insoluble residue from the above reaction was dissolved in 15 ml benzene and filtered, yielding a clear, orange-yellow solution. To this, hexane was slowly added until the mixture became cloudy. This was set aside in the refrigerator. At 1 - 2 hours intervals small aliquots of additional hexane were added. Fine orange-yellow crystals precipitated from solution. The product, $Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2$, decomposed slowly above 180°C. Note the analytical values in Table XX. This complex precipitated with one benzene molecule per three complex molecules, $Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2\ 1/3\ C_6H_6$. The nmr spectrum of this compound in deuterated dichloromethane showed the benzene proton absorption at 2.68 τ. A sample which was placed under high vacuum for a prolonged period of time showed no change in composition.

Phenyldichlorotintrichlorosilyl-π-methylcyclopentadienyl-manganesedicarbonyl, $PhCl_2Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$:

A stirred dichloromethane solution containing 2.05 gm $Et_3NH^+[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]^-$ (4.8 mmol) was cooled to -78°C. To this 3.0 ml $PhSnCl_3$ (excess) was added and the mixture was warmed slowly to room temperature. After one hour at room temperature the solvent was removed at reduced pressure, leaving an oily residue. The residue was washed with 20 ml of cold hexane to remove most of the excess $PhSnCl_3$. The remaining residue was then extracted with several aliquots of hot hexane and filtered. The combined filtrate was slowly cooled in the refrigerator yielding a pale yellow, crystalline product, $Ph\ Cl_2Sn(SiCl_3)Mn(CO)_2\pi C_5H_4CH_3$. Its melting point, after an additional recrystallization from hexane, was 111 - 112°C.

Diphenylchlorotintrichlorosilyl-π-methylcyclopentadienyl-manganesedicarbonyl, $Ph_2ClSn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$:

A solution of 2.30 gm $Et_3NH^+[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]^-$ (5.40 mmol) in 50 ml dichloromethane was cooled to -78°C. To this stirring mixture 1.78 gm Ph_2SnCl_2 (5.2 mmol) was added. The reaction mixture was allowed to warm to room temperature and stirring was continued over night. The solvent was removed at reduced pressure, leaving a light-brown, oily material. This was extracted with a minimum amount of hot hexane and filtered. At refrigerator

temperature a very pale, yellow, microcrystalline product, $Ph_2ClSn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$, precipitated. This compound was sparingly soluble in hexane at room temperature. The product darkened rapidly between 135 - 140°C and melted above 145°C.

Trichlorotintrichlorosilylirontetracarbonyl, $Cl_3Sn(Cl_3Si)Fe(CO)_4$:

A magnetically stirred solution containing 14.0 ml Cl_4Sn (0.12 mol) in 100 ml dichloromethane was cooled to -78°C. Slowly 30.9 gm $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ (0.077 mol) dissolved in 40 ml dichloromethane was added. After addition was complete the reaction mixture was maintained at -78°C for an additional five minutes, and then warmed slowly to room temperature. At room temperature the reaction mixture was stirred for 20 minutes. The solvent was removed at reduced pressure, resulting in a cream colored powdery product. Under nitrogen this was extracted with five 60 ml aliquots of dry, oxygen-free benzene. The combined, colorless, clear filtrate was cooled until it solidified. At reduced pressure the benzene was slowly removed, leaving a white microcrystalline product, 26.0 gm $Cl_3Sn(Cl_3Si)Fe(CO)_4$ (0.050 mol, 65% based on $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ employed). A small fraction of this was dissolved in warm hexane, from which coarse, white crystals precipitated in the refrigerator. The melting

point of $Cl_3Sn(Cl_3Si)Fe(CO)_4$ in a sealed capillary was 114-115°C. Approximately 24.0 gms of benzene insoluble material was recovered.

Dichlorotin-bis(trichlorosilylirontetracarbonyl), $Cl_2Sn[Fe(CO)_4SiCl_3]_2$:

A magnetically stirred solution containing 29.3 gm $Cl_3Sn(Cl_3Si)Fe(CO)_4$ (0.055 mol) in 100 ml dichloromethane was cooled to -78°C. Slowly, 22.5 gm $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ (0.056 mol) in 30 ml dichloromethane was added. All crystalline material dissolved slowly forming an intensely orange-red solution. After addition was complete the reaction mixture was allowed to warm to room temperature. As the temperature gradually increased a dense, orange-yellow, crystalline material precipitated. At room temperature, evolution of gas became pronounced. The dichloromethane was quickly decanted and the crystalline material was washed with two 30 ml aliquots of cool dichloromethane. A small portion of the product was dissolved in a minimum amount of warm dichloromethane and filtered. Coarse, orange crystals formed slowly at refrigerator temperature. The product, $Cl_2Sn[Fe(CO)_4SiCl_3]_2$, rapidly changed color to a darker orange at 165 - 167°C and darkened above 250°C.

When this product is not immediately isolated after its formation and is allowed to remain in the reaction mixture at room temperature, it redissolves with evolution of

carbon monoxide. The resulting reaction mixture is a deep, red, transparent solution.

A mixture of 0.88 gm $Cl_2Sn[Fe(CO)_4SiCl_3]_2$ (1.1 mmol) and 0.18 gm Et_4NCl (1.1 mmol) in 20 ml dichloromethane was stirred at room temperature until evolution of gas ceased. The solution changed slowly from yellow to red and a total of 29.4 ml gas at room temperature and 695 mm mercury pressure (at STP 24.5 ml, 1.1 mmol) was collected. The solvent was removed at reduced pressure leaving a red, oily material. This was washed with several aliquots of pentane. The transparent, red, oily residue was dissolved in 40 ml dichloromethane. Hexane was added to the top of the dark, red solution, resulting in two liquid layers. Over a period of approximately 3 - 4 weeks the hexane diffused into the dichloromethane and some red crystals, surrounded by an oily material, formed. These were isolated and dried. When this crystalline material was heated it slowly turned yellow. At 145°C some melting activity was observed and above 160°C it decomposed. Its infrared spectrum showed bands at 2096 cm^{-1} medium, 2045 very strong, 2030 strong and 1938 weak.

Anal. Calc. for $C_{15}H_{20}Cl_9Fe_2NO_7SnSi_2$: C, 19.3; H, 2.2; Cl, 34.2; N, 1.5. Found: C, 19.9 - 20.2; H, 3.4 - 3.5; Cl, 35.6 - 36.3; N, 2.0 - 2.5.

Phenyldichlorotintrichlorosilylirontetracarbonyl, $PhCl_2Sn(Cl_3Si)Fe(CO)_4$:

A solution of 42.7 gm $Et_3NH^+[Cl_3SiFe(CO)_4]^-$ (1.06 mol) in 50 ml dichloromethane was slowly added to a magnetically stirred solution of 50 ml dichloromethane containing 36.2 gm $PhSnCl_3$ (0.120 mol) at -78°C. After addition was complete the reaction mixture was allowed to warm to room temperature. The solvent was removed at reduced pressure, leaving a yellow, oily material. This was extracted with hexane and filtered. The clear, yellow filtrate was cooled to -78°C separating a cream, microcrystalline material. The product $PhCl_2Sn(Cl_3Si)Fe(CO)_4$ melted below room temperature to a yellow oil.

TABLE XVIII

Analytical Data, Color and Melting Points of Silyl Transition Metal Hydrides [a]

			Calculated %			Found %		
Compound	M.P.°C	Color	C	H	Cl	C	H	Cl
$Cl_3SiHCr(CO)_2C_6H_6$	114-115	yellow	29.88	2.20	33.07	29.87	2.22	30.09
$Cl_3SiHMn(CO)_2Cp$	83-83	p.yellow	26.99	1.94	34.14	26.55	1.81	34.81
$Cl_3SiDMn(CO)_2Cp$	82-83	p.yellow	26.90	2.25	-	27.56	2.06	-
$(Cl_3Si)_2HFe(CO)Cp$	130-131	p.yellow	17.21	1.44	50.78	17.27	1.78	50.28
$Cl_3SiHCo(CO)Cp$	31-33	yellow	25.07	2.10	36.99	26.67	2.03	37.06
$Ph_3SiHFe(CO)_4$	85-87	white	61.69	3.77	-	61.69	3.75	-
$Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$	95-96	p.yellow	69.32	5.14	-	69.66	5.15	-

a. The air sensitive hydrides $Cl_3SiHFe(CO)_4$ and $Cl_3SiHMn(CO)_2\pi C_5H_4CH_3$ were not analyzed for carbon, hydrogen and chlorine, but were used as starting materials for the preparation of derivatives.

TABLE XIX

Infrared Carbonyl Stretching Data and Proton Nmr Data for Silyl Transition Metal Hydrides

Compound	Infrared Data [a] ν(CO) cm^{-1}				Nmr Data [h] τ(M-H)	τ(Cp-H)
$Cl_3SiHFe(CO)_4$ [b]	2124m	2069m	2058s	2053s	19.00	
$Cl_3SiHCr(CO)_2C_6H_6$ [c]	1982vs	1922s			20.53	4.00
$Cl_3SiHMn(CO)_2Cp$ [e]	2028vs	1972s	(2026vs	1975s) [d]	19.70 [i]	4.89
$Cl_3SiDMn(CO)_2Cp$ [d,f]	2026vs	1973s			-	-
$(Cl_3Si)_2HFe(CO)Cp$ [g]	2025				21.64	4.57
$Cl_3SiHCo(CO)Cp$	2045				23.33 [j,k]	4.87
$Ph_3SiHFe(CO)_4$ [b]	2097m	2036m	2026s	2018s	-	-
$Ph_3SiHMn(CO)_2\pi C_5H_4CH_3$	1983vs	1926s			21.50 [i]	5.70 [i]

a. In hexane
b. Shows additional bands due to $Fe(CO)_5$
c. In dichloromethane.
d. In carbon tetrachloride
e. The ν(Mn-H) = 1889 cm^{-1}, in carbon tetrachloride at 1887 cm^{-1}
f. The ν(Mn-D) in carbon tetrachloride at 1360 cm^{-1}
g. The ν(Fe-H) = 1960 cm^{-1}
h. In acetonitrile
i. Broad
j. In cyclohexane
k. Very broad.

TABLE XX

Analytical Data, Colors and Melting Points of Hydride Derivatives

Compound	M.P.°C	Color	Calculated %			Found %		
			C	H	Cl	C	H	Cl
$[Cl_3SiFe(CO)_4]$	d>90	yellow	15.89	0.00	35.18	15.87	0.00	34.99
$Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ [a]	28-31	p.yellow	37.75	5.12	25.71	37.84	5.59	26.32
$Et_4N^+[Cl_3SiMn(CO)_2Cp]^-$ [b]	d>190	yellow	40.88	5.72	24.13	40.78	6.31	24.36
$Et_4N^+[Cl_3SiFe(CO)_4]^-$ [c]	d>260	white	33.32	4.66	24.59	32.45	4.62	24.95
$Me_4N^+[Cl_3SiFe(CO)_4]^-$ [d]	-	white	25.47	3.42	28.19	18.87	3.76	25.63
$Cl_3Sn(Cl_3Si)Mn(CO)_2Cp$	161-163	p.yellow	15.70	0.94	39.72	15.67	1.06	38.90
$Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$	115-117	yellow	17.48	1.28	38.71	17.56	1.31	38.74
$Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2$ [e]	d>180	yellow	25.00	1.86	32.80	24.89	1.90	32.93
$PhCl_2Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$	111-112	white	28.41	2.18	29.94	27.84	2.07	30.46
$Ph_2ClSn(Cl_2Si)Mn(CO)_2\pi C_5H_4CH_3$	d>145	white	37.96	2.71	22.41	38.36	2.93	22.43
$Cl_3Sn(Cl_3Si)Fe(CO)_4$	114-115	white	9.11	0.00	40.33	9.13	0.00	40.73
$Cl_2Sn[Cl_3SiFe(CO)_4]_2$	d>160	orange	9.10	0.00	35.71	12.04	0.15	35.73
$PhCl_2Sn(Cl_3Si)Fe(CO)_4$	<25	white	21.11	0.88	31.15	22.05	1.26	28.79

a. Nitrogen, calc. 3.39%; found 3.95%.

b. Nitrogen, calc. 3.18%; found 3.26%

c. Nitrogen, calc. 1.50%; found 1.98%

d. Extremely hygroscopic

e. Solvent in crystalline material, analysis for $Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2 \cdot 1/3C_6H_6$

TABLE XXI

Infrared Data for Carbonyl Stretching Vibrations [a]

Compound	cm^{-1}							
$[Cl_3SiFe(CO)_4]_2$ [b]	2114w	2079w	2070m	2061m	2053s	2049vs	2037w	2011w
$Et_4N^+[Cl_3SiFe(CO)_4]^-$	2031s	1950m	1916vs	1904ssh				
$Me_4N^+[Cl_3SiFe(CO)_4]^-$	2032s	1953m	1919vs	1902ssh				
$Et_3NH^+[Ph_3SiFe(CO)_4]^-$	1994s	1904m	1876vs	1864ssh				
$Et_4N^+[Ph_3SiFe(CO)_4]^-$	1995s	1907m	1879vs	1865ssh				
$Et_3NH^+[Cl_3SiMn(CO)_2Cp]^-$ [c]	2026m	1969m	1907s	1839s				
$Et_4N^+[Cl_3SiMn(CO)_2Cp]^-$			1910s	1839s				
$Cl_3Sn(Cl_3Si)Mn(CO)_2Cp$	2022m	1981s						
$Cl_3Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$	2018m	1978s						
$Cl_2Sn[Cl_3SiMn(CO)_2\pi C_5H_4CH_3]_2$	2010m	1988s	1966ssh	1961vs	1939m			
$PhCl_2Sn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$	2000m	1957s						
$Ph_2ClSn(Cl_3Si)Mn(CO)_2\pi C_5H_4CH_3$	1990m	1939s						
$Cl_3Sn(Cl_3Si)Fe(CO)_4$	2127m	2086m	2077vs	2067s				
$Cl_2Sn[Cl_3SiFe(CO)_4]_2$	2111ssh	2108s	2082w	2077m	2068vs	2063msh	2045w	2032w
$PhCl_2Sn(Cl_3Si)Fe(CO)_4$	2118s	2078m	2066s	2049s				

a. Infrared medium, hexane used for non-ionic compounds; dichloromethane used for ionic complexes.

b. Spectrum changes rapidly in solution, new bands growing at 2024 and 2000 cm^{-1}

c. Additional bands at 1993 cm^{-1} and 1800 cm^{-1}

CHAPTER VI

Mass Spectrometry

Introduction

Some of the first compounds to be studied by mass spectrometry were the volatile organometallics in the determination of the occurrence of isotopes, as well as, isotopic abundances [5]. These can be determined by mass spectrometry with a high degree of accuracy. However, only recently have high resolution spectrometers, capable of handling masses of 1000 and more, become commercially available.

Mass spectrometry has since been used for the determination of molecular weights of compounds, elemental composition analysis, thermochemical data including ionization potentials, heats of formation and bond dissociation energy, etc. [207]. The heat of formation of $MeF_2SiCo(CO)_4$ and the silicon cobalt bond dissociation have been calculated from the appearance potentials of the observed ions [193].

Several authors have demonstrated that carbonyls lose carbon monoxide in a stepwise fashion. For example, the mass spectra of the mononuclear complexes, $M(CO)_x$, show ions such as $M(CO)_n^+$ (n = 0-6, M = Cr, Mo, W [217]; n = 0-5, M = Fe [215]; n = 0-4, M = Ni [215]). Similar fragmentation occurs with the polynuclear carbonyl complexes, such as

$M_x(CO)_y$. For $M_2(CO)_{10}$, fragmentation corresponding to $M_2(CO)_n^+$ are observed (n = 0-10, M = Mn, Re [147,216]). For $M_3(CO)_{12}$ fragments such as $M_3(CO)_n^+$ are observed (n = 0-12, M = Fe, Ru [133,147]) and $Co_4(CO)_{12}$ shows $Co_4(CO)n^+$ for n = 0-12 [133]. It has been suggested that the presence of $Fe(CO)_5^+$ in the mass spectrum of $Fe_3(CO)_{12}$ favours bridging carbonyls in the molecule [147].

Most transition metals have distinctive isotope abundances, which allow rapid identification of molecular fragments, when the isotope pattern of the particular combination of atoms is known. Using the natural abundances of isotopes, patterns for any fragment can be calculated [207].

The usefulness of mass spectrometry in synthetic inorganic chemistry can hardly be overemphasized in elucidating molecular composition, as well as structural information.

RESULTS AND DISCUSSION

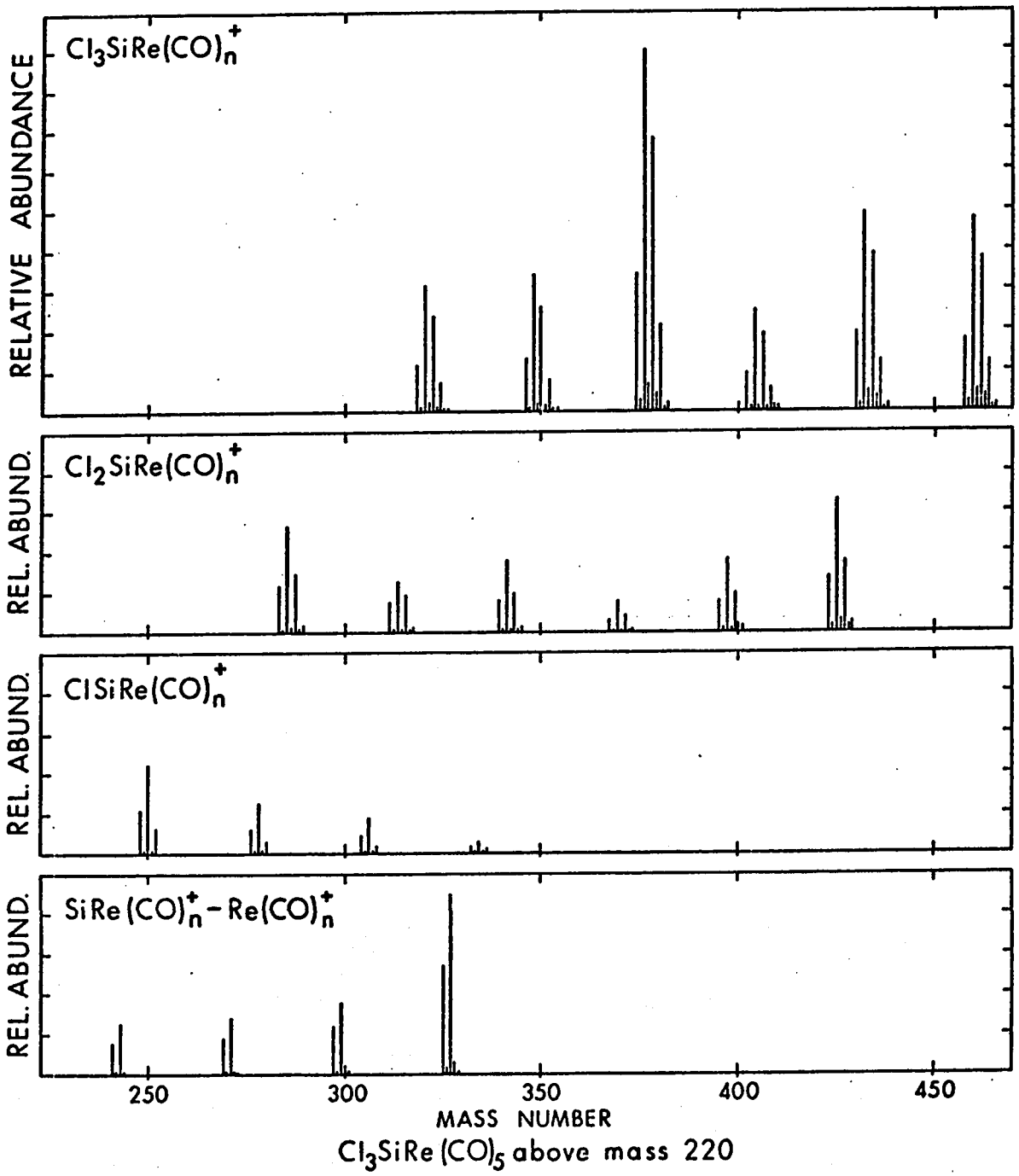
With reference to the present work, the main purposes of mass spectrometry are to identify molecules and to gain structural information. This is accomplished by correlating the observed mass numbers in the mass spectrum to the elements that are present in the compound. The presence in the mass spectrum of fragments which contain bonded atoms or groups suggests (but does not prove) that the same atoms or group are bonded in the molecule. For example, in the mass spectrum of $Ph_3SiMn(CO)_5$ the fragment Ph_3Si^+ are very intense, but weak peaks corresponding to to masses such as $PhMn(CO)_n^+$ are also observed. This molecule shows $Ph_3SiMn(CO)_n^+$ (n=0-5) as well as smaller fragments. The most abundant ion of these is Ph_3SiMn^+, while those for n=1 and 3 are relatively weak. The exact mass of the parent ion was measured, m/e = 454.0066. The calculated value for $Ph_3SiMn(CO)_5$ is 454.0069. This relatively simple case demonstrates the type of information that can be gained from a mass spectrum.

The requirement of exceedingly small samples for mass spectra is an added advantage in studies of reactions which yield minute quantities of product. Impurities or mixtures of compounds may be identified simultaneously, if the masses of the ions do not overlap extensively. The mass spectrum of the products from the thermal reaction of $[CpCr(CO)_3]_2$ and Cl_3SiH demonstrate an example in which more than one compound may be identified in one spectrum. The infrared

spectrum of the white, crystalline product shows six carbonyl stretching bands which appear as three sets of doublets of equal intensity. The expected product, $Cl_3SiCr(CO)_3Cp$, should show three carbonyl stretching vibrations in the infrared spectrum. The mass spectrum of this product immediately sheds light on this problem (cf. Table XXV). The isotope pattern of the parent ions and their framentation are in agreement with results that would be expected for a mixture of $Cl_3SiCr(CO)_3Cp$ and $HCl_2SiCr(CO)_3Cp$. Due to the similarity in physical properties and relatively low stability of these compounds, separation is not readily accomplished.

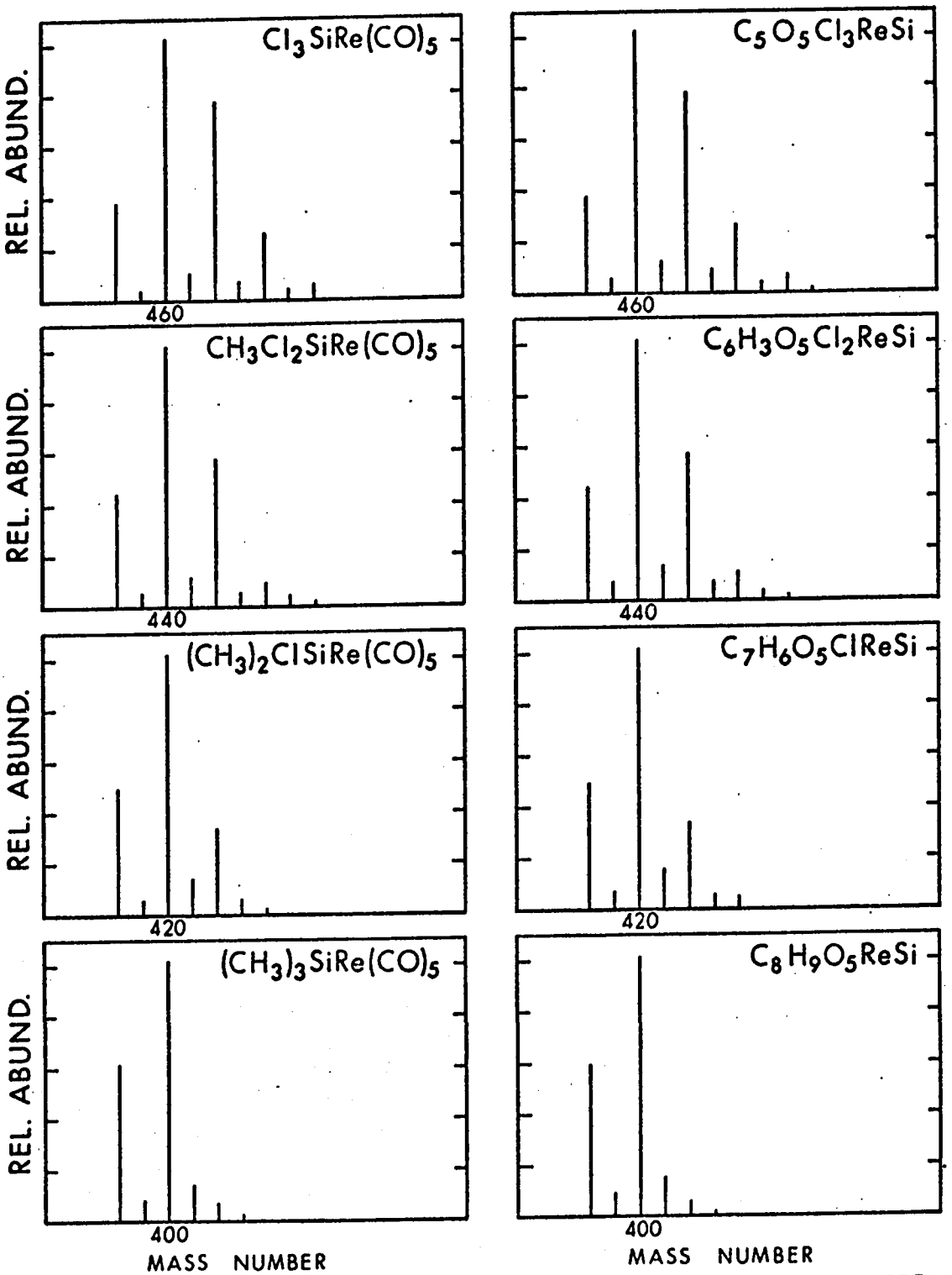
Ideally, it is hoped that a mass spectrum will show the molecular ion as a set of peaks of highest nominal mass; and further, that the various fragments formed in the breakdown of the molecule do not overlap, so that any isolated pattern is due to one specific species. The mass spectrum of $Cl_3SiRe(CO)_5$, shows some of these features. Several series of fragmentation patterns, each series characterized by the loss of 0, 1, 2 or 3 chlorines from the parent molecule, have been separated from the overall spectrum for convenience in Fig. 99. Each of these series is made up of a succession of fragments formed by consecutive loss of a carbonyl group (28 mass units).

The abundance of ions becomes progressively less with the consecutive loss of chlorines. The bottom series



$Cl_3SiRe(CO)_5$ above mass 220

Figure 99



$(CH_3)_{3-n}Cl_nSiRe(CO)_5$

Figure 100

assigned to $SiRe(CO)_n^+$ and $Re(CO)_n^+$ does not show ions for $SiRe(CO)_5^+$. The isotope pattern and masses of the $Re(CO)_n^+$ series is very similar to the $SiRe(CO)_n^+$ series, since the natural abundance of ^{28}Si is 92.2%. It is most probable that the $Re(CO)_n^+$ series causes the major contribution to the observed ions in the bottom series, Fig. 99.

The predicted and observed isotope patterns for the $Cl_{3-n}(CH_3)_nSiRe(CO)_5$ (n = 0-3) are shown in Fig. 100. The isotope pattern for any combination of atoms which make up a fragment can be computed,* or estimated for simple systems.

For fragments in which extensive overlapping occurs, the predicted isotope patterns are not applicable. For molecules in which hydrogen atoms are lost readily, over-

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* The predicted isotope patterns and weighted mean peak masses were computed with the program ISOCOM6. This program was written by E. H. Brooks and R. S. Gay and is based on the algorithm described by Carrick and Glockling (A. Carrick and F. Glockling, J. Chem. Soc. (A) 40 (1967)). Mass and abundance data for all naturally occurring isotopes are read from a magnetic tape file. Sources for the isotope masses are: (L. A. Konig, J. H. E. Mattauch and A. H. Wapstra, Nuclear Physics 31, 18 (1962)) and the abundances have been taken from abundance tables ("Introduction to Mass Spectrometry and Its Applications" by Robert W. Kiser, Prentice Hall Inc., Englewood Cliff. N.J. 1965.

lapping of fragments makes the observed isotope patterns misleading. For example, several values in Tables XXIX and XXX for relative ion abundances in the mass spectra for $Cl_3SiHCr(CO)_2C_6H_6$, $(Cl_3Si)_2HFe(CO)Cp$ and $Cl_3SiHMn(CO)_2Cp$ have been estimated, because fragments due to the loss of hydrogen atoms are of comparable abundance to those due to the loss of carbon monoxide.

Most of the fragmentation, observed in the mass spectra of molecules encountered in this study, involves the loss of carbon monoxide, chlorine and methyl groups. These also can cause considerable overlapping for molecules, which yield fragments with wide isotopic spread. For example, the difference in mass between two methyl groups and one carbon monoxide is only two mass units, and the difference between one chlorine plus one methyl group and two carbon monoxide molecules is six mass units. Therefore in the breakdown of molecules such as $MeCl_2SiMo(CO)_3Cp$ or $(MeCl_2Si)_2Fe(CO)_4$, considerable overlapping of fragments is observed. Molybdenum has seven relatively abundant isotopes while chlorine has two. Combinations of several chlorines or molybdenum and chlorines show dominant isotope spreads up to 20 mass units wide for simple molecules. With the aid of computed isotope patterns, fragments that are only partly overlapping can be resolved by calculating the abundance of each isotope component, using peaks which do not overlap. Addition of all resolved components making

up a certain pattern should then yield the observed isotope pattern in the mass spectrum.

In the mass spectrom of $Cl_2Sn[Fe(CO)_4SiCl_3]_2$, for example, the parent ion is observed at m/e = 794. The fragmentation shows an exceedingly complex spectrum. Overlapping of fragments becomes progressively more extensive at intermediate masses. The resolved fragmentation and isotope patterns, above mass 100 for $Cl_2Sn[Fe(CO)_4SiCl_3]_2$, is shown in Fig. 101. Consecutive loss of chlorines is shown by the separation of the spectrum into three horizontal series and consecutive loss of carbon monoxides is shown by the repeated isotope patterns of varying intensity. This representation is not intended to be an accurately resolved analysis of the observed mass spectrum, but to demonstrate the complexity of a mass spectrum for molecules of this type when all fragmentation series are superimposed on one scale.

In this Figure it is also evident that the abundance of ions diminishes gradually with the consecutive loss of chlorine. The fragmentation series due to $Cl_mSnFe_2(CO)_nSiCl_3^+$ and $Cl_mSnFe(CO)_n^+$ are relatively weak and have been excluded. Nevertheless the bare (i.e. carbon-monoxide free) ions such as $Cl_2SnFe_2SiCl_3^+$, $ClSnFe_2^+$ or $SnFe_2^+$ are generally very abundant in mass spectra and probably contribute considerably to other

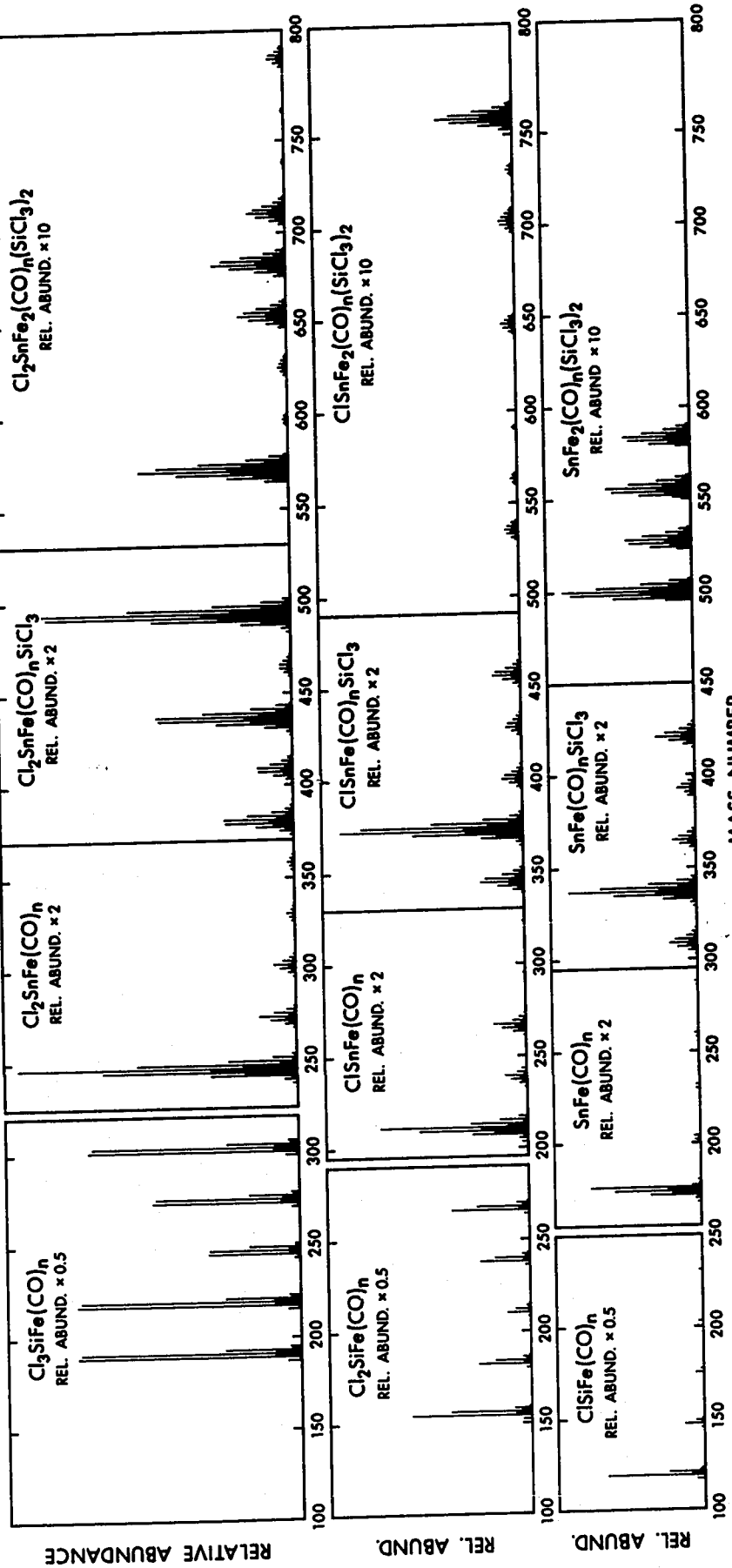
RELATIVE ABUNDANCE
REL. ABUND.
REL. ABUND.
MASS NUMBER
$Cl_3SiFe(CO)_n$
REL. ABUND. ×0.5
$Cl_2SnFe(CO)_n$
REL. ABUND. ×2
$Cl_2SnFe_2(CO)_n(SiCl_3)_2$
REL. ABUND. ×10
$Cl_2SiFe(CO)_n$
REL. ABUND. ×0.5
$ClSnFe(CO)_n$
REL. ABUND. ×2
$Cl_2SnFe(CO)_nSiCl_3$
REL. ABUND. ×2
$ClSnFe_2(CO)_n(SiCl_3)_2$
REL. ABUND. ×10
$ClSiFe(CO)_n$
REL. ABUND. ×0.5
$SnFe(CO)_n$
REL. ABUND. ×2
$SnFe(CO)_nSiCl_3$
REL. ABUND. ×2
$SnFe_2(CO)_n(SiCl_3)_2$
REL. ABUND ×10
100
150
200
250
300
350
400
450
500
550
600
650
700
750
800

Figure 101

closely adjacent fragments.

The parent ions for many compounds are extremely weak or do not appear in the mass spectra. For example, the highest observed masses for $RSn[Co(CO)_4]_3$ correspond to $RSnCo_3(CO)_{11}^+$ [179,181]. In the mass spectra of the silyl transition metal hydrides, $(Cl_3Si)_2HFe(CO)Cp$ shows no parent ion, while for $Cl_3SiHCr(CO)_2C_6H_6$ and $Cl_3SiHMn(CO)_2Cp$, the parent ion is very weak. The dominant fragments of highest masses correspond to the loss of one chlorine from the molecular ions.

The exact mass of a species can only be measured if the abundance of ions corresponding to that species is sufficiently large. For molecules which do not yield sufficiently intense parent ions, a more intense peak of lower mass can be measured if the composition of the fragment is in doubt. For example, the fragment of highest mass for $(Cl_3Si)_2HFe(CO)Cp$ was measured m/e - 382.7717. The calculated value for the mass of $^{35}Cl_4{}^{37}ClSi_2HFe(CO)Cp$ is 382.7719.

Compounds of low volatility may yield adequate mass spectra at elevated probe temperature. This occasionally causes reactions to occur which produce new compounds. The mass spectrum for $Cl_3SiHCr(CO)_2C_6H_6$ at probe temperatures up to 90°C shows virtually no ions above the parent ion. However, at 120°C, ions of masses corresponding to $(C_6H_6)_2Cr_2(CO)Si_2Cl_4^+$, $C_6H_6Cr_2(CO)_4Si_2Cl_3^+$

etc. may be recognized. Dimerization of $Cl_3SiHCr(CO)_2C_6H_6$ with the loss of hydrogen chloride could account for the observed spectrum. Similarly for $Ph_3SiHFe(CO)_4$, up to 100°C probe temperature no adequate mass spectrum is obtained. At 105°C the observed mass spectrum corresponds to $Ph_2SiFe_2(CO)_8$, Table XXXII. For the ionic complex, $[CpFe(CO)_3]^+[CpFe(CO)(SiCl_3)_2]^-$ virtually no ions appear until the complex is heated to 200°C on the probe. At this temperature numerous fragments of medium intensity, containing cyclopentadiene, iron and trichlorosilyl units, can be recognized in a continuous spectrum of weak peaks at every mass up to approximately 1000, suggesting the formation of high molecular weight species in the pyrolysis of this compound.

Lewis *et al.* [147] report that the mass spectrum of $Re_2(CO)_{10}$ shows the presence of ions such as $Re_2(CO)_nC^+$, but lacks ions such as $Re_2(CO)_nO^+$, which provides evidence that the bonding of carbon monoxide to transition metals occurs via the carbon atom. The complexes, $[Cl_2SiFe(CO)_4]_2$ and $[Ph_2SiMn(CO)_4]_2$ have similar structural arrangements of the ligands about the basic four membered ring of alternate silicon and transition metal atoms. However, to satisfy the E.A.N. rule a manganese-manganese bond is required in $[Ph_2SiMn(CO)_4]_2$. Both molecules yield parent ions in the mass spectrum, as well as fragments due to the loss of eight consecutive carbon monoxide

molecules. If in the fragmentation process no new bonds were formed, then $[Ph_2SiMn(CO)_4]_2$ should show a fragment due to Mn_2^+, while the mass spectrum for $[Cl_2SiFe(CO)_4]_2$ should not yield Fe_2^+. However, a peak at m/e = 111.8696 corresponding to Fe_2^+ (calculated mass for Fe_2 = 111.8698) allows no concrete conclusions about the mode of its formation, since the spectra are obtained at elevated temperatures. The ligands are thought to be lost in a stepwise manner. The formation of an iron-iron bond, after the first silyl bridge is lost, may be a possible explanation for the formation of the iron-iron bond. The mass spectrum of $[Ph_2SiMn(CO)_4]_2$ also shows a peak due to Mn_2^+ at m/e - 109.8759 (calculated mass for Mn_2 = 109.8762).

The partial mass spectra of a representative number of compounds are given in Tables XXII - XXXII. Small fragments and masses which cannot be assigned unambiguously have not been included. The main object was the characterization of these compounds. The detailed mass spectral studies of these complexes would form an enormous field and could be treated as a separate topic.

EXPERIMENTAL

Mass spectra were obtained with an AET MS9 double focusing mass spectrometer operating at 70 ev ionizing energy and an accelerating voltage of 8000 volts. Samples were introduced directly into the source on the end of a probe near the ionizing electron beam. The choice of temperature was determined on the basis of thermal stability and volatility of the compounds. The nominal masses, m/e, were determined by counting from the low masses which are known. Spectra which showed larger gaps at higher masses made the procedure of counting difficult occasionally, and the exact mass of the parent ion was used for comparison.

TABLE XXII

Mass Spectrum of $Ph_3SiMn(CO)_5$

Ion	n	m/e	Rel. Abund. [a]
$Ph_3SiMn(CO)_n^+$ [b]	5	454	0.26
	4	426	0.09
	3	398	-
	2	370	0.21
	1	342	-
	0	314	1.90
Ph_3Si^+		259	100.00

a. Most intense peak is assigned 100.00

b. Measured m/e for $Ph_3SiMn(CO)_5$ = 454.0066; calculated 454.0069

TABLE XXIII

Mass Spectrum of $Me_3SiRe(CO)_5$

Ion	n	m/e[a]	Rel. Abund.[b]
$Me_3SiRe(CO)_n^+$	5	400	91
	4	372	2.1
	3	344	8.5
	2	316	34
	1	288	2.4
	0	260	2.2
$Me_2SiRe(CO)_n^+$	5	385	42
	4	357	100
	3	329	57
	2	301	28
	1	273	13
	0	245	14
$MeSiRe(CO)_n^+$	5	370	2.0
	4	342	6.4
	3	314	51
	2	286	21
	1	258	16
	0	230	2.1
$Re(CO)_n^+$	5	327	1.8
	4	299	20
	3	271	17
	2	243	24
	1	215	4.3
	0	187	2.0

a. m/e values for ^{187}Re-containing fragments

b. Most intense peak assigned 100.

TABLE XXIV

Mass Spectra of $[Ph_2SiMn(CO)_4]_2$ and $[Cl_2SiFe(CO)_4]$[a]

Ion	n	m/e	Rel. Abund.[b]
$Ph_4Si_2Mn_2(CO)_n^+$[c]	8	698	15.4
	7	670	0.1
	6	642	4.6
	5	614	1.0
	4	586	66.7
	3	558	15.3
	2	530	3.1
	1	502	8.2
	0	474	20.0
$Ph_4Si_2Mn^+$		419	100.0
$Cl_4Si_2Fe_2(CO)_n^+$[d]	8	534	7.7
	7	506	42.3
	6	478	46.0
	5	450	73.4
	4	422	100.0
	3	394	80.8
	2	366	23.0
	1	338	24.5
	0	310	30.7

a. m/e values for $^{35}Cl_3{}^{37}Cl$ containing fragments

b. Most intense peak in spectrum is assigned 100.0

c. Measured mass at m/e 697.9465; calculated value of $[Ph_2SiMn(CO)_4]_2$ is 697.9459.

d. Measured mass at m/e = 533.6554; calculated value for $^{35}Cl_3{}^{37}ClSi_2Fe_2(CO)_8$ is 533.6554.

TABLE XXV

Mass Spectrum of a Mixture of $Cl_3SiCr(CO)_3Cp$ and $HCl_2SiCr(CO)_3Cp$

Ion	n	m/e[a]	Rel. Abund.[b]
$Cl_3SiCr(CO)_nCp^+$ [c]	3	334	0.58
	2	306	0.15
	1	278	1.11
	0	250	3.61
$Cl_2SiCr(CO)_nCp^+$	3	299	0.50
	2	271	0.11
	1	243	0.15
	0	215	0.69
$SiCr(CO)_nCp^+$	3	229	0.01
	2	201	2.42
	1	173	6.43
	0	145	6.47
$CrCp^+$		117	28.50
Cr^+		52	100.00
$HCl_2SiCr(CO)_nCp^+$	3	300	3.65
	2	272	1.15
	1	244	5.62
	0	216	29.20
$HClSiCr(CO)_nCp^+$	3	265	1.24
	2	237	0.39
	1	209	0.35
	0	181	0.62
$CpCrCl^+$		152	6.54
Cl_3Si^+		133	1.00
Cl_2Si^+		98	1.42
$ClSi^+$		63	16.80

a. m/e values for ^{52}Cr containing fragments.

b. The most abundant peak in spectrum is assigned 100.00

c. m/e values for $^{35}Cl_3$ containing fragments.

TABLE XXVI

Mass Spectra of $Cl_3SiMo(CO)_3Cp$ and $MeCl_2SiMo(CO)_3Cp$

Ion	n	m/e[a]	Rel. Abund.[b]
$Cl_3SiMo(CO)_nCp^+$ [c]	3	380	22.4
	2	352	37.1
	1	324	58.4
	0	296	100.0
$Cl_2SiMo(CO)_nCp^+$	3	245	15.9
	2	317	5.3
	1	289	2.5
	0	261	9.4
$MeCl_2SiMo(CO)_nCp^+$	3	360	16.3
	2	332	30.0
	1	304	35.2
	0	276	100.0
$MeClSiMo(CO)_nCp^+$	3	325	4.2
	2	297	2.1
	1	269	1.6
	0	241	3.2

a. m/e values for ^{98}Mo containing fragments

b. The most abundant peak in spectrum is assigned 100.0

c. m/e values for $^{35}Cl_3$ containing fragments.

TABLE XXVII

Mass Spectra of $(Cl_3Si)_2Fe(CO)_4$ and $(MeCl_2Si)_2FeCO)_4$

Ion	n	m/e	Rel. Abund. [a]
$Cl_6Si_2Fe(CO)_n^+$ [b]	4	436	1.8
	3	408	2.5
	2	380	12.5
	1	352	64.0
	0	324	21.0
$Cl_5Si_2Fe(CO)_n^+$ [c]	4	401	9.7
	3	373	4.0
	2	345	3.1
	1	317	0.2
	0	289	4.3
$Cl_3SiFe(CO)_n^+$ [d]	4	301	0.1
	3	273	5.7
	2	245	3.2
	1	217	3.8
	0	189	19.3
$Cl_2SiFe(CO)^+$		182	3.3
Cl_2SiFe^+		154	61.8
Cl_3Si^+		133	8.2
Cl_2Si^+		98	6.9
$ClSi^+$		63	100.0
$Fe(CO)_n^+$	4	168	6.7
	3	140	8.2
	2	112	11.9
	1	84	12.7
	0	56	40.8

(continued....)

TABLE XXVII (continued)

Ion	n	m/e	Rel. Abund.[a]
$Me_2Cl_4Si_2Fe(CO)_n^+$ [e]	4	396	0.8
	3	368	3.2
	2	340	31.2
	1	312	100.0
	0	284	74.4
$MeCl_4Si_2Fe(CO)_n^+$ [e]	4	381	3.2
	3	353	4.8
	2	325	4.0
	1	297	2.4
	0	169	2.5
$Me_2Cl_3Si_2Fe(CO)_n^+$ [d]	4	361	13.6
	3	333	4.8
	2	305	4.0
	1	277	4.2
	0	249	3.3
$MeCl_2Si^+$		113	29.6
Cl_2Si^+		98	30.4
$ClSi^+$		63	96.0
$Fe(CO)_n^+$	4	168	4.1
	3	140	10.4
	2	112	14.4
	1	84	28.9
	0	56	74.3

a. The most intense peak in the spectrum is assigned 100.0
b. m/e values for $^{35}Cl_5{}^{37}Cl$ containing fragments
c. m/e values for $^{35}Cl_4{}^{37}Cl$ containing fragments
d. m/e values for $^{35}Cl_3$ containing fragments

TABLE XXVIII

Mass Spectra of $Cl_3SiFe(CO)_2Cp$ and $MeCl_2SiFe(CO)_2Cp$

Ion	n	m/e [a]	Rel. Abund. [b]
$Cl_3SiFe(CO)_nCp^+$ [c]	2	310	5.4
	1	282	12.7
	0	254	48.1
$Cl_2SiFeICO)_nCp^+$	2	275	3.5
	1	247	0.9
	0	219	0.6
Cl_3SiFe^+		189	0.6
$ClFeCp^+$		156	100.0
$SiFeCp^+$		149	1.8
Cl_3Si^+		133	0.9
$FeCp^+$		121	10.8
$SiCp^+$		93	21.2
$SiFe^+$		84	1.3
Cp^+		65	9.7
Fe^+		56	27.0
$MeCl_2SiFe(CO)_nCp^+$ [d]	2	290	6.9
	1	262	28.2
	0	234	100.0
$Cl_2SiFe(CO)_nCp^+$	2	275	2.1
	1	247	1.5
	0	219	1.0

(continued...)

TABLE XXVIII (continued)

Ion	n	m/e [a]	Rel. Abund. [b]
$MeClSiFe(CO)_nCp^+$	2	255	6.5
	1	227	1.7
	0	199	2.9
$ClFeCp^+$		156	9.1
$SiFeCp^+$		149	2.3
$CpSiMeCl^+$		143	2.1
$FeCp^+$		121	22.9
$CpSiCl^+$		115	1.7
$CpSiMe^+$		108	47.9
$CpSi^+$		93	84.4
$SiCl^+$		63	6.9
Fe^+		56	21.4

a. m/e values for ^{35}Cl containing fragments

b. The most intense peak in the mass spectrum is assigned 100.0

c. Measured mass at m/e = 311.8449; calculated value for $^{37}Cl^{35}Cl_2SiFe(CO)_2Cp$ 311.8444.

d. Measured mass at m/e = 289.9028; calculated value for $Me^{35}Cl_2SiFe(CO)_2Cp$ 289.9026.

TABLE XXIX

Mass Spectrum of $(Cl_3Si)_2HFe(CO)Cp$ [a]

Ion	m/e	Rel. Abund. [b]
$Cl_5Si_2HFe(CO)Cp^+$ [c,d]	383	2.3
$Cl_5Si_2HFeCp^+$ [d]	355	0.1
$Cl_5Si_2FeCp^+$ [d]	354	0.2
$Cl_3SiFe(CO)Cp^+$	282	22.1
$Cl_3SiFeCp^+$	254	96.1
$Cl_2SiFe(CO)Cp^+$	247	4.7
$Cl_2SiFeCp^+$	219	1.1
Cl_3SiFe^+	189	0.9
$ClFeCp^+$	156	100.0
Cl_2SiFe^+	154	6.6
Cl_3Si^+	133	4.4
$FeCp^+$	121	27.3

a. The parent ion $Cl_6Si_2HFe(CO)Cp$ is not observed.

b. The most intense peak in the spectrum is assigned 100.0

c. Measured mass at m/e = 382.7717; calculated value for $^{35}Cl_4{}^{37}ClSiHFe(CO)Cp$ 382.7719.

d. m/e values for $^{35}Cl_4{}^{37}Cl$ containing fragments.

TABLE XXX

Mass Spectra of $Cl_3SiHCr(CO)_2C_6H_6$ and $Cl_3SiHMn(CO)_2Cp$

Ion	m/e [a]	Rel. Abund. [b]
$Cl_3SiHCr(CO)_2C_6H_6^+$	320	0.3
$Cl_3SiCr(CO)_2C_6H_6^+$	319	0.1
$Cl_2SiHCr(CO)_2C_6H_6^+$	285	21.0
$Cl_2SiCr(CO)_2C_6H_6^+$	284	1.0
$Cl_3SiHCrC_6H_6^+$	264	3.4
$Cl_2SiHCr(CO)C_6H_6^+$	257	0.4
$Cl_2SiCr(CO)C_6H_6^+$	256	0.5
$Cl_2SiHCrC_6H_6^+$	229	7.8
$Cl_2SiCrC_6H_6^+$	228	1.4
$HCr(CO)_2C_6H_6^+$	187	3.7
$Cr(CO)_2C_6H_6^+$	186	51.0
Cl_3SiCr^+	185	1.6
$ClCrC_6H_6^+$	165	28.0
$Cr(CO)C_6H_6^+$	158	100.0
Cl_2SiCr^+	150	1.6
Cl_3Si^+	133	11.6
$HCrC_6H_6^+$	131	2.0
$CrC_6H_6^+$	130	67.0
$ClSiCr^+$	115	1.5

(continued...)

TABLE XXX (continued)

Ion	m/e [a]	Rel. Abund. [b]
$Cl_3SiHMn(CO)_2Cp^+$	310	trace
$Cl_3SiHMn(CO)_2Cp^+$	282	1.8
$Cl_3SiMn(CO)Cp^+$	281	0.2
$Cl_2SiHMn(CO)Cp^+$	275	11.6
$Cl_2SiMn(CO)Cp^+$	274	0.6
$Cl_3SiHMnCp^+$	254	25.6
$Cl_3SiMnCp^+$	253	3.1
$Cl_2SiHMnCp^+$	219	6.2
$Cl_2SiMnCp^+$	218	1.2
$Mn(CO)_2Cp^+$	176	15.6
$HClMnCp^+$	156	1.9
$ClMnCp^+$	155	19.9
$HMn(CO)Cp^+$	149	0.4
$Mn(CO)Cp^+$	148	100.0
Cl_3Si^+	133	15.7
$HMnCp^+$	121	0.8
$MnCp^+$	120	45.3

a. m/e values for ^{52}Cr-containing fragment

b. The most intense peak in the spectrum is assigned 100.0.

TABLE XXXI

Mass Spectrum of $[Cl_3SiFe(CO)_4]_2$

Ion	n	m/e	Rel. Abund.[a]
$Cl_6Si_2Fe_2(CO)_n^+$ [b]	8	604	1.1
	7	576	0.2
	6	548	0.2
	5	520	1.2
	4	492	1.0
	3	464	5.1
	2	436	2.8
	1	408	2.0
	0	380	3.1
$Cl_5Si_2Fe_2(CO)_n^+$ [c]	8	569	0.5
	7	541	0.1
	6	513	0.5
	5	485	0.1
	4	457	0.1
	3	429	0.3
	2	401	0.2
	1	373	0.2
	0	345	0.3
$Cl_4Si_2Fe_2(CO)_n^+$ [d]	8	534	-
	7	506	0.1
	6	478	0.1
	5	450	0.1
	4	422	0.4
	3	394	0.6
	2	366	1.4
	1	338	30.4
	0	310	1.5

(continued...)

TABLE XXXI (continued)

Ion	n	m/e	Rel. Abund.[a]
$Cl_3SiFe(CO)_n^+$	4	301	15.8
	3	273	24.3
	2	245	14.6
	1	217	31.2
	0	189	37.7
Cl_3Si^+		133	6.9
$Fe(CO)_n^+$	4	168	20.5
	3	140	24.8
	2	112	32.8
	1	84	70.5
	0	56	100.0

a. The most intense peak in the spectrum is assigned 100.0
b. M/e values for $^{35}Cl_5{}^{37}Cl$ containing fragments
c. m/e values for $^{35}Cl_4{}^{37}Cl$ containing fragments
d. m/e values for $^{35}Cl_3{}^{37}Cl$ containing fragments

TABLE XXXII

Mass Spectrum of $Ph_3SiHFe(CO)_4$ at 105°C [a]

Ion	n	K	m/e	Rel. Abund.[b]
$Ph_3SiFe_2(CO)_n^+$	8		518	0.6
	7		490	1.3
	6		462	1.6
	5		434	0.8
	4		406	1.6
	3		378	1.2
$-Ph_2SiFe(CO)_k^+$	2	4	350	3.5
	1	3	322	2.1
	0	2	294	2.4
		1	266	0.1
		0	238	0.3
$Ph_3SiFeICO)_2^+$			371	0.1
$Ph_3SiHFe(CO)^+$			344	0.1
Ph_3SiHFe^+			316	0.5
Ph_3SiH^+			260	45.5
Ph_3Si^+			259	10.2
Ph_2SiH^+			183	26.2
Ph_2Si^+			182	100.0
$Fe(CO)_n^+$	4		168	1.1
	3		140	0.4
	2		112	1.0
	1		84	3.1
	0		56	2.7

a. No ions were obtained below 100°C

b. The most intense peak in the spectrum is assigned 100.0

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