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SOME ASPECTS OF SILICON–TRANSITION-METAL CHEMISTRY

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I. Introduction

Compounds with silicon–transition-metal bonds fall into two distinct classes, which until recently showed no points of connection. The first class comprises the metal silicides: typical binary examples are FeSi,

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$CoSi_2$, and V_3Si, and some have been known for more than 100 years (*59*). Other more complex types containing three or more components, such as Mn_5Si_3C, are also known. They all form three-dimensional giant lattices, often of an unusual and complicated kind, and can best be considered as intermediate in nature between alloy systems and macromolecular covalent compounds. The study of silicides has considerably intensified in the past decade, since it has been found that some show promise as electronic materials, while at the same time they are strong and highly resistant to chemical attack. A number of books and general reviews may be noted (*18, 257, 318, 340, 360, 423*).

The second class consists of molecular compounds containing one or more silicon–transition-metal bonds. The first example, $Me_3SiFe(CO)_2$-(η^5-C_5H_5), was prepared in 1956 (*359*), but nearly 10 years then elapsed before other compounds were described (*26, 94*). These heralded many more, and now examples are known in which silicon is bonded to almost every transition metal (Fig. 1). Curiously, no Si–Ag compounds have been described; there are also no reports of derivatives of lanthanides or actinides. Most work has involved Fe, Co, Pt, Mn, Re, Mo, Ru, and Ni, in roughly decreasing order of frequency. Almost all well-characterized molecular silicon–transition-metal compounds known at present are diamagnetic; some possible exceptions are noted in Section II,F. The most recent comprehensive reviews of the area were published in 1973 (*134*) and 1974 (*235*), covering the literature until 1971 and 1972, respectively; these contain details of earlier reviews. Other surveys of certain aspects have also appeared, two of them very recently (*24, 25, 201*).

In this article the intention is to place the main emphasis on studies of molecular silicon–transition-metal compounds, in particular those from the author's laboratory and those that have been reported since the comprehensive reviews noted above. As, however, it is now known that these molecular compounds can act as convenient precursors for certain transition-metal silicides, aspects of the properties of silicides will also be outlined, and relationships between the two classes of compounds examined. Compounds with bonds between transition metals

Sc	**Ti**	**V**	**Cr**	**Mn**	**Fe**	**Co**	**Ni**	**Cu**	**Zn**
Y	**Zr**	*Nb*	**Mo**	Tc	**Ru**	**Rh**	**Pd**	Ag	**Cd**
La	**Hf**	*Ta*	**W**	**Re**	**Os**	**Ir**	**Pt**	**Au**	**Hg**
Ac									

FIG. 1. Transition metals known to form molecular compounds with bonds to silicon are shown in bold-face type; dubious examples are in italics. No derivative of any lanthanide or actinide element is known.

and other group IV elements, namely C, Ge, Sn, and Pb, will be referred to only in so far as they provide illuminating parallels or contrasts with the corresponding silicon derivatives.

II. Preparative Routes to Molecular Compounds

The most important synthetic routes continue to be (1) the elimination of an alkali halide between the salt of a transition-metal anion and a silicon halide, and (2) oxidative addition and addition–elimination reactions. The present position regarding the scope and limitations of these and other routes is outlined in this section.

A. REACTION OF A TRANSITION-METAL ANION WITH A SILICON HALIDE

Table I shows recent applications of this method together with some earlier results of particular interest.

1. The Anion

Considering first the transition-metal-containing anion (*174*), it is clear that the most used are $M(CO)_3(Cp)^-$ (M = Cr, Mo, W; Cp = η^5-C_5H_5), $Mn(CO)_5^-$, $Re(CO)_5^-$, $Fe(CO)_2(Cp)^-$ and $Co(CO)_4^-$; in the case of doubly charged species, $Fe(CO)_4^{2-}$ has been employed with limited success, but no use has been made of anions of higher charge such as $Co(CO)_3^{3-}$ (*175, 176*). Neither have successful applications of binuclear or polynuclear anions yet been reported, although a low yield of a compound thought to be $SiH_3Fe(CO)_4Fe(CO)_4SiH_3$ resulted from the reaction of $[Fe_2(CO)_8]^{2-}$ and H_3SiI in ether (*80*). Reactions involving anions in which one or more carbonyl groups are replaced by tertiary phosphines have also proved unrewarding except in the case of $[Co(CO)_3(PPh_3)]^-$ (*138*). Although steric factors are clearly significant (see below), there seems no reason why systems of this kind should not be more generally applicable, given a sensible choice of silicon halide and solvent.

The relative electronegativities of some of these groups appear to increase in the order (*147, 174*)

$$Fe(CO)_4 < Fe(CO)_2(Cp) < Re(CO)_5 < Mn(CO)_5 < Co(CO)_4$$

while the nucleophilicities of the derived anions correspondingly decrease in the same order: It is interesting that a recent kinetic study of

TABLE I

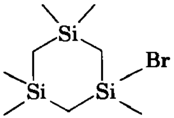
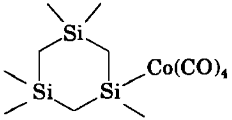
REACTIONS OF ANIONS WITH SILICON HALIDES

Entry	Anion[a]	Silicon halide	Solvent[b]	Success[c]	Remarks	Ref.
1	$V(CO)_6^-$	H_3SiI	Ether, isopentane	✓	—	(*8*)
2		$MePh_2SiCl$	THF	×	—	(*273*)
3	$Cr(CO)_3(Cp)^-$	R_3SiCl	Ether	×	Similarly Mo, W	(*357*)
4		H_3SiBr	None	✓	Similarly Mo, W	(*214*)
5		R_3SiX	Nonpolar solvents	✓	PR_4^+ cation	(*302*)
6	$Cr_2(CO)_{10}^{2-}$	R_2SiX_2	THF	×	Succeeded with Ge, Sn	(*315*)
7	$Mo(CO)_3(Cp)^-$	Me_3SiBr	Cyclohexane	✓	[d]	(*306*)
		$MeHSiCl_2$	Cyclohexane	✓	Forms ClMeHSi–Mo deriv.[d]	(*306*)
		$RSiCl_3 (R = H, Me)$	Cyclohexane	✓	Forms Cl_2RSi–Mo deriv.[d]	(*306*)
		$SiX_4 (X = Cl, Br)$	Cyclohexane	✓	Forms X_3Si–Mo deriv.[d]; similarly Cr, W	(*306*)
8	$Mo(CO)_3(Cp)^-$	R_3SiCl	Cyclohexane or methylcyclohexane	✓	Similarly W; compounds labile in polar solvents	(*310*)
9	$Mo(CO)_3(cp)^-$	$R_2(CH_2{=}CH)SiCl$	Not stated	✓	Similarly W	(*308*)
10		R_5Si_2X	Cyclohexane	✓	Similarly W[d]	(*300*)
		$XSiR_2SiR_2X$	Cyclohexane	✓	Forms $XSiR_2SiR_2$–Mo deriv.; similarly W[d]	(*300*)
11	$Mo(CO)_3(C_7H_7)^-$	Ph_3SiCl	THF	×	Succeeded with Ge, Sn	(*255*)
12	$Mo(CO)_2(PPh_3)(Cp)^-$	Ph_3SiCl	THF	×	—	(*138*)
13	$Mn(CO)_5^-$	H_3SiI	Ether, isopentane	✓	Similarly Re	(*7, 28, 29*)
14		H_2SiI_2	Ether, isopentane	✓	Only disubstd. deriv. found; similarly Re	(*32*)
15		H_2SiCl_2	*n*-Hexane	✓	Mono- and disubstd. derivs. found	(*2*)
16		Me_3SiBr	Pentane	✓	—	(*194*)
17		Me_3SiBr	Cyclohexane	✓	[d]	(*306*)
18		Me_3SiCl	None	✓	—	(*62a*)
19		$Me_{2n+1}Si_nX$ $(n = 1, 2)$	None	✓	—	(*335*)

20		Me_3SiCl	THF	×	PPh_3 also present	(*146*)
21		$\overline{CH_2CH_2CH_2Si}(R)Cl$	*n*-Hexane	✓	Low yield, much Si–O–Si	(*136*)
22		R_3SiCl	Ether, CH_2Cl_2	×	$Ph_3PNPPh_3^+$ cation, succeeded with Ge, Sn	(*151*)
23	$Mn(CO)_5^-$	Ph_3SiCl	THF	×	Similarly Re	(*138*)
	$Mn(CO)_4(PPh_3)^-$	Ph_3SiCl	THF	×	—	(*138*)
24	$Mn(CO)_3L_2^-$	R_3SiX	THF	×	Similarly Ge, but Sn successful	(*350*)
25	$Fe(CO)_4^{2-}$	H_3SiI	Me_2O, isopentane	✓	Some $SiH_3FeH(CO)_4$ also produced	(*38, 39*)
26		Me_3SiI	THF	×	Si–O–C derivative formed	(*54, 331*)
27		$ClMe_2Si(CH_2)_3Cl$	Ether	✓	Cyclic $\overline{CH_2(CH_2)_2SiMe_2Fe}(CO)_4$ (I) produced	(*132*)
28	$Fe(CO)_2(Cp)^-$	Me_3SiCl	THF	✓	—	(*359*)
29		R_3Si^*Cl	THF	✓	Optically active MePhNpSi deriv. (Np = 1-naphthyl)	(*92*)
30		H_2SiI_2	Benzene, isopentane	✓	Only disubstd. deriv. found	(*32*)
31		$R_2(CH_2{=}CH)SiCl$	Not stated THF	✓	—	(*123, 308*)
32		$ClRHSiFe(CO)_2(Cp)$	Methylcyclohexane	✓	$HRSi[Fe(CO)_2(Cp)]_2$ produced	(*309*)
33		$\overline{CH_2(CH_2)_3Si}(R)Cl$	THF	✓	—	(*136*)
34	$Fe(CO)_2(Cp)^-$	$[ClMe_2SiCH_2—]_2$	THF	✓	$[—CH_2SiMe_2Fe(CO)_2(Cp)]_2$ produced	(*271, 272*)
		Me_2HSiCl	THF	✓	—	(*271, 272*)
		$Me_3Si(SiMe_2)_nCl$ $(n = 1–3)$	THF	✓	—	(*271, 272*)
		$Cl(SiMe_2)_nCl$ $(n = 2, 3)$	THF	✓	Disubstd. deriv. formed.	(*271, 272*)
35		$Me_{2n+1}Si_nCl$ $(n = 1–4)$	THF	✓	$n = 3(i\text{-})$; $n = 4(t\text{-})$isomer	(*335*)
		$(ClMe_2Si)_4Si$	THF	✓	$Si[SiMe_2Fe(CO)_2(Cp)]_4$ produced	(*335*)
36		$XSiMe_2SiMe_2X$	Cyclohexane	✓	$XMe_2SiSiMe_2Fe(CO)_2(Cp)$ formed[d]	(*300*)
37		$RSiCl_3$ (R = H, Me)	Cyclohexane	✓	Cl_2RSi–Fe deriv. formed[d]	(*306*)
		Me_3SiBr	Cyclohexane	✓	[d]	(*306*)
		$RMeSiCl_2$ (R = H, Me)	Cyclohexane	✓	ClRMeSi–Fe deriv. formed[d]	(*306*)

(*table continues*)

TABLE I (Continued)

Entry	Anion[a]	Silicon halide	Solvent[b]	Success[c]	Remarks	Ref.
38	$Co(CO)_4^-$	H_3SiI	Ether, Me_2O	√	—	(26, 29)
39		H_2SiI_2	Ether	√	Disubstd. deriv. only	(29)
40	$Co(CO)_4^-$	H_2SiCl_2	Ether	√	Mono- and disubstd. derivs.	(2)
		$HSiCl_3$	Ether	√	Monosubstd. deriv. only	(2)
		Me_2HSiCl	Ether	√	—	(2)
41		Ph_3SiCl	THF	×	$(Ph_3Si)_2O$ produced	(138)
42		Me_3SiCl	Ether	√	—	(336)
		Me_2SiCl_2	Ether	×	No isolable Si–Co product	(336)
		$RSiCl_3$ (R = Me, Cl)	Ether	×	$Cl_2RSiOCCo_3(CO)_9$ formed	(336)
		Me_nSiCl_{4-n} (n = 0–3)	THF	×	$Cl_{3-n}Me_nSiO(CH_2)_4(CO)Co(CO)_4$ formed	(336)
43		SiI_4	n-Hexane	√	$(OC)_4CoSiCo_3(CO)_9$ produced	(396)
44			Methylcyclohexane	√	 formed, also di- and trisubstd. analogs[e]	(186)
45	$Co(CO)_3(PPh_3)^-$	Ph_3SiCl	THF	√	*trans*-$Ph_3SiCo(CO)_3(PPh_3)$ formed	(138)
46	$Co_3(CO)_{10}^-$	R_3SiCl (R = Me, Ph)	Ether	×	$Me_3SiOCCo_3(CO)_9$ produced	(312)
47	$Co[P(OR)_3]_4^-$	R_3SiCl	Not stated	×	—	(325)
48	$Ir(CO)_4^-$	H_3SiI	Ether	√	—	(37)
49	$M(PF_3)_4^-$ (M = Rh, Ir)	R_3SiCl	Ether	×	Ge analog similar, but Sn analog successful	(51)

[a] Cp = η^5-C_5H_5.

[b] THF = tetrahydrofuran

[c] Refers to formation (√) or nonformation (×) of silicon–metal derivative.

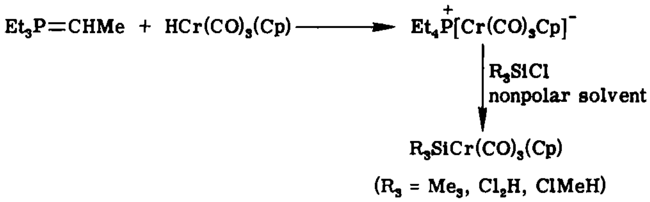
[d] Products decompose in THF, yielding Si–O–Si derivatives.

[e] Similar derivatives prepared from $M(CO)_3(Cp)^-$ (M = Cr, Mo, W), $Fe(CO)_2(Cp)^-$, and $Mn(CO)_5^-$.

the reaction of benzyl chloride with some of these anions showed that the rates fell in the order (*322*)

$$Fe(CO)_4^{2-} > Mn(CO)_5^- > Co(CO)_4^-$$

and it was concluded that nucleophilic attack by $Co(CO)_4^-$ in this system was unimportant; the extent of ion pairing and the ease of removal of Cl^- were, however, highly significant. Nearly all studies involving silicon halides have used Na^+ or, less commonly, K^+ as the counterion, and there are no systematic studies of the effects of ion pairing. Two reactions involving large cations have been reported: the first (*302*) was successful,



$$\begin{tikzcd} Et_3P{=}CHMe + HCr(CO)_3(Cp) \arrow[r] & Et_4\overset{+}{P}[Cr(CO)_3Cp]^- \arrow[d, "R_3SiCl", "\text{nonpolar solvent}"'] \\ & R_3SiCr(CO)_3(Cp) \end{tikzcd} \qquad (1)$$

$(R_3 = Me_3,\ Cl_2H,\ ClMeH)$

but the second (*151*) was not.

$$(PNP)^+Mn(CO)_5^- + R_3SiCl \xrightarrow[\text{or } CH_2Cl_2]{\text{ether}} [PNP]^+[Mn(CO)_4Cl_2]^- + \cdots \qquad (2)$$

In the latter case, where $(PNP)^+ = (Ph_3P{=}N{=}PPh_3)^+$, it was shown in a separate experiment that $Me_3SiMn(CO)_5$ quickly reacts with $(PNP)^+Cl^-$ to give $(PNP)^+[Mn(CO)_4Cl_2]^-$ as a major product, so that any silicon–metal compound formed initially would be rapidly destroyed.

There have been no successful syntheses using carbonylate anions with halide or pseudohalide substituents. Indeed, it is known that cyanide-containing anions react with organosilicon halides to give isonitrile derivatives (*50*), e.g.,

$$Na[(\eta^3\text{-}C_3H_5)Mn(CO)_3CN] + R_3SiX \rightarrow (\eta^3\text{-}C_3H_5)Mn(CO)_3(CNSiR_3) \qquad (3)$$

2. *The Silicon Halide*

Several effects are related to the nature of the silicon halide. Hydrido halides usually react readily with a range of anions, while organosilicon halides may not; for instance, H_2SiCl_2 reacts with $Co(CO)_4^-$ in ether giving good yields of silicon–cobalt derivatives (*2*), while Me_2SiCl_2 does not (*336*). This is probably related in the main to the electron-accepting properties of hydridosilicon halides, since the compounds SiH_3X behave as Lewis acids of modest strength (*22*), but their analogs R_3SiX are much weaker.

Bulky groups can be tolerated when only one metal group is to be attached to each silicon atom, as for example in the following successful reaction (*92*):

$$\text{MePh(1-naphthyl)SiCl} + \text{Fe(CO)}_2\text{(Cp)}^- \xrightarrow{\text{THF}} \text{MePh(1-naphthyl)SiFe(CO)}_2\text{(Cp)} \quad (4)$$

When attempts are made to attach two or more such groups, however, steric effects may become critical. Reactions of anions with di-, tri-, and tetrahalides usually result in monosubstituted products, e.g. (*2, 306*),

$$\text{RSiCl}_3 + \text{Mo(CO)}_3\text{(Cp)}^- \xrightarrow{\text{cyclohexane}} \text{RCl}_2\text{SiMo(CO)}_3\text{(Cp)} \qquad (\text{R} = \text{H,Me}) \quad (5)$$

$$\text{HSiCl}_3 + \text{Co(CO)}_4^- \xrightarrow{\text{ether}} \text{HCl}_2\text{SiCo(CO)}_4 \quad (6)$$

Disubstituted products result only when dihydridosilicon halides are used or in the special case of reactions with $Fe(CO)_2(Cp)^-$ (*2, 29, 32, 309*), e.g.,

$$\text{H}_2\text{SiI}_2 + \text{M(CO)}_5^- \xrightarrow{\text{ether}} \text{H}_2\text{Si[M(CO)}_5]_2 \qquad (\text{M} = \text{Mn,Re}) \quad (7)$$

$$\text{MeHSiCl}_2 + \text{Fe(CO)}_2\text{(Cp)}^- \xrightarrow{\text{methylcyclohexane}} \text{HMeSi[Fe(CO)(Cp)]}_2 \quad (8)$$

The sole reported example of a product with more than two metal atoms attached to silicon is the cluster derivative $(OC)_9Co_3SiCo(CO)_4$, made from SiI_4 and $Co(CO)_4^-$ in *n*-hexane (*396*); here the steric effects are reduced as a result of Co–Co bond formation (see Section V,B).

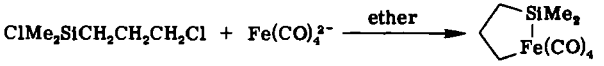
The nature of the halogen attached to silicon also affects the reaction; where comparisons can be made, iodides react more rapidly and completely than chlorides, e.g. (*2, 29, 32*),

$$\text{H}_2\text{SiI}_2 + \text{M(CO)}_n^- \rightarrow \text{H}_2\text{Si[M(CO)}_n]_2 \quad (9)$$

$$\text{H}_2\text{SiCl}_2 + \text{M(CO)}_n^- \rightarrow \text{H}_2\text{ClSi[M(CO)}_n] + \text{H}_2\text{Si[M(CO)}_n]_2 \quad (10)$$

where $M(CO)_n^-$ is $Co(CO)_4^-$ or $Mn(CO)_5^-$. In the first case, only disubstituted products could be isolated. This parallels previous observations made on analogous germanium compounds (*109*): Ph_2GeBr_2 gave disubstituted products with a range of metal anions, whereas Ph_2GeCl_2 did not. All this is consistent with the idea noted earlier that the role of the leaving halide ion is important. Furthermore, there are a number of examples of cases in which organogermanium and organotin halides react successfully with transition-metal anions, but organosilicon halides do not (e.g., *138, 151, 255, 263, 315*). This may well be related to greater ionic character of Ge–X and Sn–X bonds as compared with Si–X, and a consequently enhanced tendency for halogen to leave as X^-.

Silicon compounds with both silicon–halogen and carbon–halogen bonds can react using both these functions; an interesting example is the synthesis of the ferrasilacyclopentane (I) (*132*):



(I) (11)

3. *The Solvent*

In a few cases (Table I, entries 4, 18, and 19), successful syntheses have been carried out by direct reaction between a solid metal carbonylate and liquid silicon halide; usually, however, a solvent is employed.

Because transition-metal anions can be prepared conveniently in tetrahydrofuran solution, this cyclic ether was often used in earlier attempts to prepare silicon–metal compounds. It is now generally realized, however, that tetrahydrofuran can frustrate these attempts in two ways. First, it promotes electrophilic attack by the silicon compound on oxygen atoms of coordinated carbonyl groups; this leads to the formation of products with Si–O bonds (*54, 138, 262, 300, 306, 310, 336, 337*), e.g.,

$$\mathrm{Ph_3SiCl + Mn(CO)_5^- \xrightarrow{THF} (Ph_3Si)_2O + Mn_3(CO)_{14}^- + \cdots} \tag{12}$$

$$\mathrm{Me_3SiI + Fe(CO)_4^{2-} \xrightarrow{THF} (Me_3SiOC)_4Fe_2(CO)_6 + \cdots} \tag{13}$$

$$\mathrm{Ph_3SiCl + Co(CO)_4^- \xrightarrow{THF} (Ph_3Si)_2O + CoCl_2 + \cdots} \tag{14}$$

In fact, preparations involving tetrahydrofuran are successful only when using the highly nucleophilic species $Fe(CO)_2(Cp)^-$ and, in a solitary example, $Co(CO)_3(PPh_3)^-$ (*138*) [which is more nucleophilic than $Co(CO)_4^-$; note however that $Mn(CO)_4(PPh_3)^-$ did not yield Si–Mn products (*138*)]:

$$\mathrm{Me_3SiCl + Fe(CO)_2(Cp)^- \xrightarrow{THF} Me_3SiFe(CO)_2(Cp)} \tag{15}$$

$$\mathrm{Ph_3SiCl + Co(CO)_3(PPh_3)^- \xrightarrow{THF}} \textit{trans}\text{-}\mathrm{Ph_3SiCo(CO)_3(PPh_3)} \tag{16}$$

$$\mathrm{Ph_3SiCl + Mn(CO)_4(PPh_3)^- \xrightarrow{THF} (Ph_3Si)_2O + ClMn(CO)_3(PPh_3)_2 + [Mn(CO)_4(PPh_3)]_2 + \cdots} \tag{17}$$

The role of tetrahydrofuran in facilitating silicon transfer from metal to oxygen is further discussed in Section III,F,2.

The second harmful effect of tetrahydrofuran is that it may undergo ring opening and insert into the silicon–transition-metal bond, again with the formation of a siloxy derivative (*252, 336, 337*); e.g.*

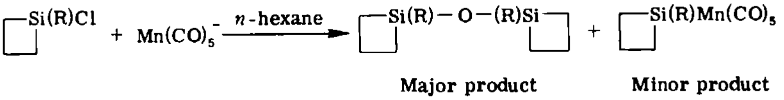
$$Me_nCl_{3-n}SiCl + Co(CO)_4^- \xrightarrow{THF} Me_nCl_{3-n}SiO(CH_2)_4COCo(CO)_4 \qquad (18)$$

This possibility had been recognized in the case of simple silyl compounds many years ago (*20*):

$$H_3SiI + \overline{CH_2(CH_2)_3O} \rightarrow H_3SiO(CH_2)_4I \rightarrow \text{decomposition products} \qquad (19)$$

Consequently, in the early work with hydridosilicon derivatives, diethyl ether was normally used; in the case of very volatile products, dimethyl ether offered some practical advantages. It was tacitly assumed that a polar solvent was essential in order to dissolve, at least partly, the transition-metal carbonyl derivative. More recently, however, it has become clear that alkanes, although nonpolar, provide a very suitable reaction medium, and can be used in cases where ethers, for example, are inimical to the products (*8, 32, 306, 310*). The hydrocarbon, besides acting as a diluent for the silicon halide, seems to assist the separation of alkali halide from the surface of the reacting transition-metal carbonyl salt.

Even with alkanes as the reaction medium, extensive formation of siloxanes can sometimes occur, as in the reaction between a silacyclobutane derivative and $Mn(CO)_5^-$ (*136*):



(20)

4. *Conclusions*

In summary, this procedure will be most effective with an anion of high nucleophilicity, an iodosilane of low steric requirements, and a nonpolar solvent. Reactions usually begin at low temperatures, although long shaking at room temperature may be needed for completion. The method can be capricious, and occasionally a familiar system may yield no product at all, with no obvious explanation. Nevertheless, it has considerable extra potential, particularly for the synthesis of silicon derivatives of polynuclear metal carbonyls.

* Additional CO insertion to give an acyl derivative has also occurred in this case.

B. REACTION OF A THALLIUM METAL CARBONYLATE WITH A SILICON HALIDE

This variant of the normal route using alkali metal salts (Section II,A) depends on the fact that metallic thallium reacts smoothly with some metal carbonyls to give $TlM(CO)_n$ species. These Tl(I) compounds are slightly soluble in hydrocarbons and react readily with iodosilanes (*8, 121*):

$$Tl + V(CO)_6 \xrightarrow{\text{benzene}} TlV(CO)_6 \xrightarrow[\text{isopentane}]{H_3SiI} H_3SiV(CO)_6 \tag{21}$$

$$2Tl + Co_2(CO)_8 \rightarrow TlCo(CO)_4 \xrightarrow[\text{isopentane}]{H_3SiI} H_3SiCo(CO)_4 \tag{22}$$

The method is limited by the tendency of some Tl(I) metal carbonylates to disproportionate, even at low temperatures, e.g. (*79*),

$$3TlMn(CO)_5 \xrightarrow{-40°C} Tl[Mn(CO)_5]_3 + 2Tl \tag{23}$$

C. REACTION OF A SILYL ALKALI-METAL COMPOUND WITH A METAL HALIDE

Table II lists preparations or attempted preparations using this route.

The method is of limited applicability, since although silyl alkali metal compounds R_3SiM are known when R_3Si is $H_{2n+1}Si_n$ (n = 1–5), $Me_{2n+1}Si_n$ (n = 1, 3, 4), and $Me_nPh_{3-n}Si$ (n = 0–2), and several dilithium derivatives $Li(SiPh_2)_nLi$ (n = 4–6) have also been described, all are rather difficult to prepare and handle (*24*). It will be seen that only some of them have yet been used to prepare silicon–transition-metal compounds.

The interesting group of anionic derivatives $R_3SiM(CO)_5^-$ (M = Cr, Mo, W) have been prepared in the following way (*254*):

$$R_3SiLi + Et_4N^+[ClM(CO)_5]^- \xrightarrow{THF} Et_4N^+[R_3SiM(CO)_5]^- \tag{24}$$

D. REACTIONS WITH MERCURY SILYL COMPOUNDS

Some applications of the use of substituted disilyl mercury compounds, $Hg(SiX_3)_2$ (X = Me,Cl), are shown in Table III; there is an early review article (*421*). In most cases, the mercury compound reacts with a metal–halogen bond to give a silicon halide and mercury as byproduct, e.g. (entry 1),

$$Mo(CO)_3(Cp)Cl + Hg(SiMe_3)_2 \rightarrow Me_3SiMo(CO)_3(Cp) + Me_3SiCl + Hg \tag{25}$$

TABLE II

Reactions of Silyl Alkali Metal Compounds with Metal Halides

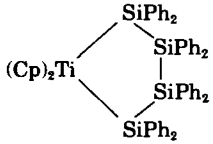
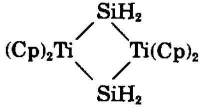
Entry	Silyl alkali metal derivative/solvent	Metal halide	Product	Ref.
1	$Si_4Ph_8Li_2$/THF	$(Cp)_2TiCl_2$		*(239)*
2	H_3SiK/glyme	$(Cp)_2TiCl_2$		*(232)*
3	Ph_3SiLi/THF	$(Cp)_2MCl_2$(M = Zr, Hf)	$Ph_3SiM(Cl)(Cp)_2$	*(273)*
4	Ph_3SiLi/THF	$(Cp)_2VCl_2$	No Si–V deriv. isolated	*(273)*
5	R_3SiLi/THF ($R_3 = Ph_3, MePh_2$)	$ClM(CO)_5^-$(M = Cr, Mo, W)	$R_3SiM(CO)_5^-$; similarly, Ge, Sn	*(254)*
6	*i*-Me_7Si_3Li/THF	$BrMn(CO)_5$	*i*-$Me_7Si_3Mn(CO)_5$	*(335)*
	t-Me_9Si_4Li/THF	$BrMn(CO)_5$	*t*-$Me_9Si_4Mn(CO)_5$	*(335)*
	t-Me_9Si_4Li/THF	$BrMn(CO)_4(PPh_3)$	*t*-$Me_9Si_4Mn(CO)_4(PPh_3)$	*(335)*
7	H_3SiK	$BrFe(CO)_2(Cp)$	$H_3SiFe(CO)_2(Cp)$	*(9)*
8	R_3SiLi	$Cl_2Pt(PMe_2Ph)_2$	$(R_3Si)_2Pt(PMe_2Ph)_2$	*(97, 98)*
9	$PhMe_2SiLi$	CuX (X = I, CN)	$\left.\begin{array}{l}PhMe_2SiCu \cdot LiX\\(PhMe_2Si)_2CuLi \cdot LiCN\end{array}\right\}$ not isolated	*(6, 185)*
10	Ph_3SiLi	$ClAu(PPh_3)$	$Ph_3SiAu(PPh_3)$	*(43)*

TABLE III

REACTIONS WITH MERCURY DISILYL DERIVATIVES

Entry	Mercurial	Metal compound	Silicon–metal product	Ref.
1	$Hg(SiMe_3)_2$	$Mo(CO)_3(Cp)Cl$	$Me_3SiMo(CO)_3(Cp)$; similarly W	(*306*)
2	$Hg(SiCl_3)_2$	$Mn_2(CO)_{10}$	$Cl_3SiMn(CO)_5$	(*64*)
3	$Hg(SiMe_3)_2$	$Fe(CO)_5$[a]	*cis*-$(Me_3Si)_2Fe(CO)_4$	(*262*)
4	$Hg(SiMe_3)_2$	$Hg[Co(CO)_4]_2$	$Me_3SiCo(CO)_4$	(*293*)
5	$Hg(SiMe_3)_2$	$(Et_3P)_2Ir(CO)Cl$	$(Me_3Si)_2Ir(CO)(HgSiMe_3)(PEt_3)_2$	(*241*)
6	$Hg(SiMe_3)_2$	*cis*-$(Et_3P)_2PtCl_2$	*trans*-$(Me_3Si)PtCl(PEt_3)_2$	(*196*)
7	$Hg(SiMe_3)_2$	*cis*-(diphos)$PtCl_2$[b]	*cis*-$(Me_3Si)PtCl$(diphos) + *cis*-$(Me_3Si)_2Pt$(diphos)	(*112, 113*)

[a] UV irradiation needed; $Fe_2(CO)_9$ and $Fe(CO)_4Br_2$ are also effective.

[b] diphos = $Ph_2PCH_2CH_2PPh_2$.

When using the monodentate phosphine derivative shown in entry 6, only one Pt–Cl bond is broken; this is attributed to the high trans influence of the Me_3Si group in the monosubstituted and isomerized product. With a bidentate phosphine (entry 7), however, a change in stereochemistry is prevented and both mono- and disubstituted products are formed.

In the case of reaction with the Ir(I) compound in entry 5, the presumed initial product, $(Et_3P)_2Ir(CO)(SiMe_3)$, undergoes oxidative addition with further $Hg(SiMe_3)_2$ to give the Ir(III) final product shown.

The first of the two reactions using metal(0) starting materials (entry 2) is brought about by heating,

$$Hg(SiCl_3)_2 + Mn_2(CO)_{10} \rightarrow 2Cl_3SiMn(CO)_5 + Hg \tag{26}$$

while the second (entry 3) is promoted by "intense Alberta sunlight." Finally, the novel reaction between two mercury derivatives (entry 4) should be noted; the yield is quantitative.

$$Hg[Co(CO)_4]_2 + Hg(SiMe_3)_2 \xrightarrow{\text{cyclopentane}} 2Me_3SiCo(CO)_4 + 2Hg \tag{27}$$

E. REACTIONS OF TRANSITION-METAL CARBONYLS WITH Si–H COMPOUNDS GIVING H_2

Although some of these reactions could equally well be classified as oxidative addition or oxidative addition–elimination reactions, it is convenient to list them separately. There was an initial report by Chalk and Harrod (*94*) of the reaction

$$Co_2(CO)_8 + 2R_3SiH \rightarrow 2R_3SiCo(CO)_4 + H_2 \tag{28}$$

and later work that established that metal carbonyl hydrides may act as intermediates, e.g. (*41, 42, 95*),

$$Co_2(CO)_8 + R_3SiH \rightarrow HCo(CO)_4 + R_3SiCo(CO)_4 \tag{29}$$

$$HCo(CO)_4 + R_3SiH \rightarrow H_2 + R_3SiCo(CO)_4 \tag{30}$$

Following these, this method has been widely used; Table IV lists more recent applications. Only those reactions that evolve dihydrogen are included here. Oxidative addition reactions leading to metal hydride derivatives are included in Table V, while processes involving elimination of dihydrogen between hydridosilanes and metal hydride derivatives containing no carbonyl groups are deferred until Section II,G,1.

Reactions involving $Co_2(CO)_8$ proceed very readily at or below room temperature, but carbonyl derivatives of the other metals listed must be heated, sometimes quite vigorously. Thus, long heating at 150°C in a sealed tube was needed to effect the reactions shown in entries 4 and 6, and quantities of siloxanes were obtained, no doubt as the result of attack on silicon by oxygen of coordinated carbonyl groups (*335*) (cf. Section III,F,2). Ultraviolet irradiation of some of these systems can lead to different products with metal–hydrogen bonds: for example, entry 35 may be compared with entry 27 of Table V. Reactivity tends to decrease on going down a transition-metal group; thus the reactions shown in entries 1 and 7 require temperatures of 50 and 150°C respectively. Curiously, in the latter case the diphenylphosphino group appears not to become coordinated to the metal.

Dihydridosilanes and hydridodisilanes often give rise to cluster compounds (e.g., entries 9, 11, 13, 16, 19, 20, 28). It is believed that these can arise as a result of extrusion of SiR_2 groups from the precursors, e.g.,

$$RSiMe_2SiMe_2H \xrightarrow{\Delta} RSiMe_2H + :SiMe_2 \tag{31}$$

The silylene species may be coordinated to a metal center rather than being free (see Section V,C). When two Si–H groups are separated by $—(CH_2)_2—$ links, either a cyclic (entry 8) or a linear (entry 26) compound may result: the latter is somewhat unstable thermally. Correspondingly, cyclic (entry 10) or linear (entry 27) species are formed from the dihydrido derivatives $(HSiMe_2)_2X$ ($X = O,CH_2$); the linear compound with two $Co(CO)_4$ groups is again thermally unstable.

In a similar way, two or more $Co(CO)_4$ groups attached to the *same*

TABLE X

Cleavage Reactions of Silicon–Metal Compounds

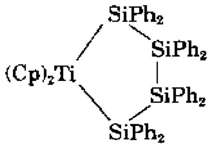
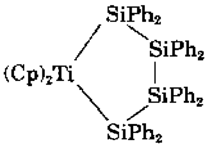
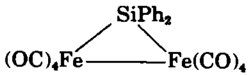
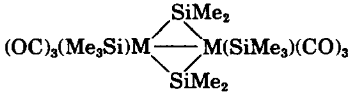
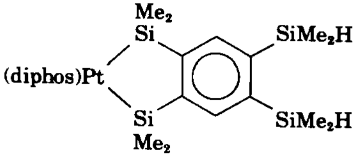
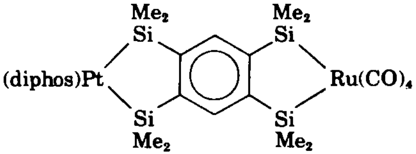
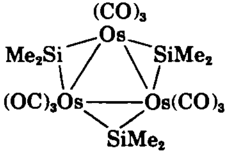
Entry	Silicon–metal compound/reagent	Success	Products	Ref.
Cleavage by dihydrogen				
1	*cis*-$(Me_3Si)_2Pt(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
2	*cis*-$(Me_3Si)PtH(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
3	*cis*-$(Me_3Si(PtCl(diphos)^a/H_2$	✓	Si–H + M–H	*(111)*
Cleavage by halogen compounds				
4	 $/CHCl_3/h\nu$	✓	$(Cp)_2TiCl_2$, Si_5Ph_{10}, C_2Cl_4	*(239)*
5	$(Ph_3Si)ZrCl(Cp)_2/HX$	✓	$Ph_3SiH + (Cp)_2ZrClX$	*(273)*
	$(Ph_3Si)ZrCl(Cp)_2/CDCl_3$	✓	? + $(Cp)_2ZrCl_2$	*(273)*
6	$H_3SiCr(CO)_3(Cp)/HCl$ (also Mo, W analogs)	✓	Si–Cl + H–M	*(214)*
7	$R_3SiCr(CO)_5^-/HCl$ (also Mo, W analogs)	✓	Si–H + Cl–M	*(254)*
7a	$(CH_2{=}CH)Me_2SiW(CO)_3(Cp)/HX$ (X = F, Br)	✓	Si–X + H–W	*(308)*
8	$F_3SiMn(CO)_5/HBr$ (also Re analog)	×	[b]	*(373)*
9	$Me_3SiMn(CO)_5/I_2$	✓	Si–I + I–Mn	*(102)*
	(also Ge, Sn, Pb analogs)		Kinetic study: Si < Ge ≪ Sn < Pb	
10	$Ph_3SiMn(CO)_5/X_2$ (X = Cl, Br)	✓	Si–X + X–Mn	*(101)*
11	$Ph_3SiMn(CO)_5/I_2$	×	—	*(101)*
12	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/Cl_2$	✓	R_3Si^*H + Cl–Mn	*(117, 118)*
13	$XRR'SiMnH(CO)_2(Cp')^c/HCl$	✓	Si–H + Cl–Mn	*(119)*
14	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe	*(330)*
15	$Me_3SiFe(CO)_2(Cp)/Cl_2$	✓	Si–Cl + Cl–Fe	*(67)*
16	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe[e]	*(67)*
17	$Me_3SiFe(CO)_2(Cp)/ICl$	✓	Si–Cl + I–Fe	*(67)*
18	$Me_3SiFe(CO)_2(Cp)/CF_3I$	✓	Si–F + I–Fe	*(67)*

TABLE X

CLEAVAGE REACTIONS OF SILICON–METAL COMPOUNDS

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
Cleavage by dihydrogen				
1	*cis*-$(Me_3Si)_2Pt(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
2	*cis*-$(Me_3Si)PtH(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
3	*cis*-$(Me_3Si(PtCl(diphos)^a/H_2$	✓	Si–H + M–H	*(111)*
Cleavage by halogen compounds				
4	 $/CHCl_3/h\nu$	✓	$(Cp)_2TiCl_2$, Si_5Ph_{10}, C_2Cl_4	*(239)*
5	$(Ph_3Si)ZrCl(Cp)_2/HX$	✓	Ph_3SiH + $(Cp)_2ZrClX$	*(273)*
	$(Ph_3Si)ZrCl(Cp)_2/CDCl_3$	✓	? + $(Cp)_2ZrCl_2$	*(273)*
6	$H_3SiCr(CO)_3(Cp)/HCl$ (also Mo, W analogs)	✓	Si–Cl + H–M	*(214)*
7	$R_3SiCr(CO)_5^-/HCl$ (also Mo, W analogs)	✓	Si–H + Cl–M	*(254)*
7a	$(CH_2{=}CH)Me_2SiW(CO)_3(Cp)/HX$ (X = F, Br)	✓	Si–X + H–W	*(308)*
8	$F_3SiMn(CO)_5/HBr$ (also Re analog)	×	^{b}	*(373)*
9	$Me_3SiMn(CO)_5/I_2$ (also Ge, Sn, Pb analogs)	✓	Si–I + I–Mn Kinetic study: Si < Ge ≪ Sn < Pb	*(102)*
10	$Ph_3SiMn(CO)_5/X_2$ (X = Cl, Br)	✓	Si–X + X–Mn	*(101)*
11	$Ph_3SiMn(CO)_5/I_2$	×	—	*(101)*
12	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/Cl_2$	✓	R_3Si^*H + Cl–Mn	*(117, 118)*
13	$XRR'SiMnH(CO)_2(Cp')^c/HCl$	✓	Si–H + Cl–Mn	*(119)*
14	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe	*(330)*
15	$Me_3SiFe(CO)_2(Cp)/Cl_2$	✓	Si–Cl + Cl–Fe	*(67)*
16	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe^e	*(67)*
17	$Me_3SiFe(CO)_2(Cp)/ICl$	✓	Si–Cl + I–Fe	*(67)*
18	$Me_3SiFe(CO)_2(Cp)/CF_3I$	✓	Si–F + I–Fe	*(67)*

13	$Fe_3(CO)_{12}$	H_2SiPh_2	Δ		(*77*)
14	$[Fe(CO)_2(Cp)]_2$	$HSiCl_3$	Δ	$Cl_3SiFe(CO)_2(Cp)$ $(Cl_3Si)_2FeH(CO)(Cp)$[d] $(Cp)Fe(CO)_3{}^+(Cl_3Si)_2Fe(CO)(Cp)^-$	(*260*)
15		$HSiPh_nCl_{3-n}$ ($n = 1, 2$)	Δ	$Ph_nCl_{3-n}SiFe(CO)_2(Cp)$	(*107*)
16	$M_3(CO)_{12}$(M = Ru, Os)	HSi_2Me_5	Δ or $h\nu$		(*76*)
17	$Ru_3(CO)_{12}$				(*182*)
18	$Os_3(CO)_{12}$	$HSiMe_3$	Δ	$Me_3SiOsH(CO)_4$ $[Me_3SiOs(CO)_4]_2$ $(Me_3Si)_2Os(CO)_4$	(*243*)
19	$H_2Os(CO)_4$	HSi_2Me_5	Δ		(*76*)
20	$[Me_3SiRu(CO)_4]_2$	$HMe_2SiSiMe_2H$		$(OC)_3Ru(\mu\text{-}SiMe_2)_3Ru(CO)_3$	(*76*)
21	$Co_2(CO)_8$	$HSiR_3$		$R_3SiCo(CO)_4$	(*323*)
22		H_2SiR_2		$HR_2SiCo(CO)_4$ $R_2SiCo_2(CO)_7$ $R_2[(OC)_4Co]SiOCCo_3(CO)_9$	(*181*)

(*table continues*)

TABLE IV (Continued)

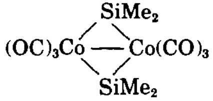
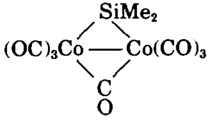
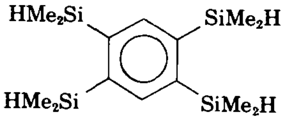
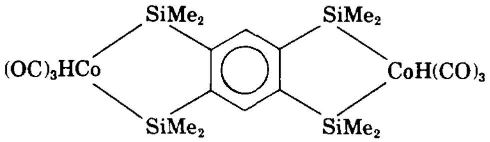
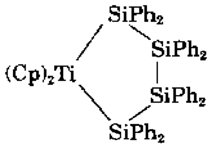
Entry	Metal carbonyl derivative	Silicon hydride	Treatment[a]	Product	Ref.
23	$Co_2(CO)_8$	H_2SiCl_2		$HCl_2SiCo(CO)_4$ $Cl_2Si[Co(CO)_4]_2$	(*2*)
		$H_2ClSiMn(CO)_5$		$HClSi[Mn(CO)_5][Co(CO)_4]$ $ClSi[Mn(CO)_5][Co_2(CO)_7]$	(*2*)
24		$HSiR_3$		$R_3SiCo(CO)_4$	(*73*)
25	$Co_2(CO)_8$	$HSi(C_6F_5)_3$	Δ	$(C_6F_5)_3SiCo(CO)_4$ [e]	(*398*)
26		$[HMe_2SiCH_2]_2$		$[(OC)_4CoSiMe_2CH_2—]_2$	(*418*)
27		$(HMe_2Si)_2X$ (X = O, CH_2)		$[(OC)_4CoSiMe_2]_2X$	(*208*)
28		$HMe_2SiSiMe_2H$		  $HMe_2SiSiMe_2Co(CO)_4$ [f]	(*268*)
29	$Co_2(CO)_8$				(*182*)

TABLE X

CLEAVAGE REACTIONS OF SILICON–METAL COMPOUNDS

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
Cleavage by dihydrogen				
1	*cis*-$(Me_3Si)_2Pt(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
2	*cis*-$(Me_3Si)PtH(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
3	*cis*-$(Me_3Si(PtCl(diphos)^a/H_2$	✓	Si–H + M–H	*(111)*
Cleavage by halogen compounds				
4	 $/CHCl_3/h\nu$	✓	$(Cp)_2TiCl_2$, Si_5Ph_{10}, C_2Cl_4	*(239)*
5	$(Ph_3Si)ZrCl(Cp)_2/HX$	✓	$Ph_3SiH + (Cp)_2ZrClX$	*(273)*
	$(Ph_3Si)ZrCl(Cp)_2/CDCl_3$	✓	? + $(Cp)_2ZrCl_2$	*(273)*
6	$H_3SiCr(CO)_3(Cp)/HCl$ (also Mo, W analogs)	✓	Si–Cl + H–M	*(214)*
7	$R_3SiCr(CO)_5^-/HCl$ (also Mo, W analogs)	✓	Si–H + Cl–M	*(254)*
7a	$(CH_2{=}CH)Me_2SiW(CO)_3(Cp)/HX$ (X = F, Br)	✓	Si–X + H–W	*(308)*
8	$F_3SiMn(CO)_5/HBr$ (also Re analog)	×	^{b}	*(373)*
9	$Me_3SiMn(CO)_5/I_2$ (also Ge, Sn, Pb analogs)	✓	Si–I + I–Mn Kinetic study: Si < Ge ≪ Sn < Pb	*(102)*
10	$Ph_3SiMn(CO)_5/X_2$ (X = Cl, Br)	✓	Si–X + X–Mn	*(101)*
11	$Ph_3SiMn(CO)_5/I_2$	×	—	*(101)*
12	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/Cl_2$	✓	R_3Si^*H + Cl–Mn	*(117, 118)*
13	$XRR'SiMnH(CO)_2(Cp')^c/HCl$	✓	Si–H + Cl–Mn	*(119)*
14	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe	*(330)*
15	$Me_3SiFe(CO)_2(Cp)/Cl_2$	✓	Si–Cl + Cl–Fe	*(67)*
16	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe^e	*(67)*
17	$Me_3SiFe(CO)_2(Cp)/ICl$	✓	Si–Cl + I–Fe	*(67)*
18	$Me_3SiFe(CO)_2(Cp)/CF_3I$	✓	Si–F + I–Fe	*(67)*

silicon atom often undergo condensation to yield clusters, e.g. (entry 22),

$$\begin{tikzcd}
H_2SiPh_2 \arrow[r, "Co_2(CO)_8"] & HPh_2SiCo(CO)_4 \arrow[r, "Co_2(CO)_8"] & Ph_2Si[Co_2(CO)_7] \ \mathbf{(II)} \arrow[d, "Co_2(CO)_8"] \\
 & & {[(OC)_4Co]Ph_2SiOCCo_3(CO)_9} \ \mathbf{(III)}
\end{tikzcd} \qquad (32)$$

It can be seen that first a Co_2 cluster (**II**) is produced, then a Co_3 unit (**III**) (accompanied by migration of silicon from metal to oxygen). This topic is taken up further in Section V,B. Other examples of the formation of $Co_2(CO)_7$ groups are shown in entries 23, 28, and 30.

A different type of sequential process is illustrated in entry 18: $Os_3(CO)_{12}$ behaves as a source of "$Os(CO)_4$" groups, and initial insertion is followed by loss of dihydrogen and metal–metal bond formation. This Os–Os bond is then attacked by further Me_3SiH (*243*).

$$\begin{tikzcd}
HSiMe_3 + \text{"}Os(CO)_4\text{"} \arrow[r] & Me_3SiOs(H)(CO)_4 \arrow[d, "-H_2"] \\
 & {[Me_3SiOs(CO)_4]_2} \arrow[d, "HSiMe_3"] \\
 & Me_3SiOsH(CO)_4 + (Me_3Si)_2Os(CO)_4 \ \text{etc.}
\end{tikzcd} \qquad (33)$$

Analogously, $Fe_3(CO)_{12}$, $Fe_2(CO)_9$, and irradiated $Fe(CO)_5$ can act as sources of "$Fe(CO)_4$" in similar reactions.

Steric factors are important in reactions of this type. The substituted cobalt carbonyl hydrides $HCo(CO)_{4-n}(PPh_3)_n$ react with increasing difficulty as n increases (entries 32–34). Another general effect is that a hydridosilane $HSiX_3$ will react more readily (and the product be more robust) as X becomes more electronegative (*227, 230*). This seems to be valid for all oxidative addition processes.

The metal carbonyl analogs $M_2(PF_3)_8$ and $HM(PF_3)_4$ (M = Rh,Ir) follow the same reaction pattern, but somewhat less readily; this is no doubt a result of steric factors, e.g. (entry 36),

$$Ir_2(PF_3)_8 + 2HSiR_3 \xrightarrow{\Delta} 2R_3SiIr(PF_3)_4 + H_2 \tag{34}$$

F. OXIDATIVE ADDITION AND OXIDATIVE ADDITION–ELIMINATION REACTIONS

This category is taken to comprise those reactions in which the formal oxidation state of the metal increases by 2.* Most of the entries in Table V involve the cleavage of Si–H or Si–Si bonds, e.g. (entries 8 and 49),

$$[Re(I)](CO)_3(Cp) + HSiPh_3 \xrightarrow{h\nu} Ph_3Si[Re(III)]H(CO)_2(Cp) + CO \tag{35}$$

$$[Pt(0)(PPh_3)_4 + Si_2Cl_6 \rightarrow (Cl_3Si)_2[Pt(II)](PPh_3)_2 + 2PPh_3 \tag{36}$$

while the most common metal oxidation states in the starting materials are Mn(I), Fe(0), Co(I), Rh(I), Ir(I), and especially Pt(0). It is not always easy, however, to decide the final metal oxidation state (e.g., entries 9 and 47). The particular case of reactions between metal carbonyl derivatives and Si–H compounds with elimination of dihydrogen has already been dealt with in Section II,E; it may be noted that such reactions commonly involve an increase in metal oxidation state of less than 2.

In both the examples given above, there is concomitant loss of one or more neutral ligands. Elimination of CO is the rule in reactions of mononuclear metal carbonyls (e.g., entry 12) and cyclopentadienyl metal carbonyls (e.g., entry 4), but not those of polynuclear carbonyls (e.g., entry 16) or carbonyl halides (e.g., entry 33). Elimination of tertiary phosphines often occurs, especially when more than two molecules are present in the initial complex; however, this is not always the case (see entry 24). Clearly, steric requirements and the dictates of the 18-electron rule determine the composition of the product, and normally act in concert; when they conflict, as in the case of $R_3SiRuH_3(PR_3)_n$ (n = 2 or 3; entry 22), variable stoichiometry may result. Chelating diphosphines, with somewhat reduced steric requirements, are usually retained (e.g., entry 19), while complexed olefins are invariably lost; the bulky ligand P(cyclohexyl)$_3$ is associated with unusual products (entries 47 and 48). Particular mention may be made of the 17-electron species $Cl_3SiVH(Cp)_2$ and $(Cl_3Si)_2V(Cp)_2$ shown

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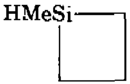
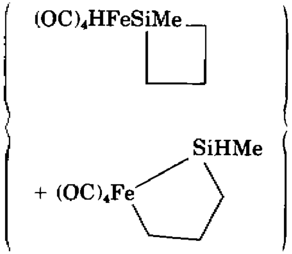
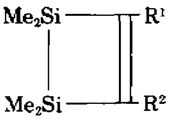
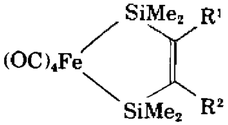
* Two reactions are included (entries 3 and 17) that involve metal–metal bonded dimers as precursors and are difficult to rationalize in this way.

TABLE V

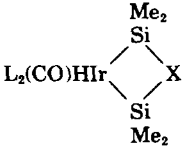
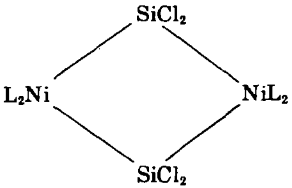
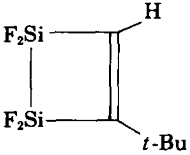
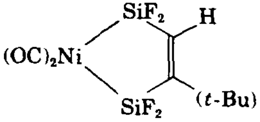
OXIDATIVE ADDITION (–ELIMINATION) REACTIONS

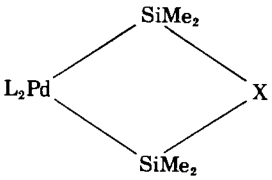
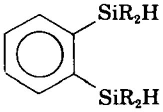
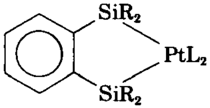
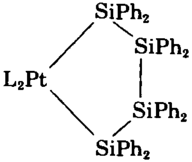
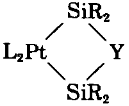
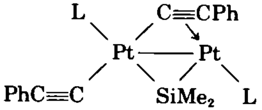
Entry	Metal derivative	Silicon compound	Treat-ment	Silicon–metal product		Ref.
1	$(Cp)_2Ti(CO)_2$	$HSiCl_3$	Δ	$Cl_3SiTi(CO)H(Cp)_2$ [a]		(*88*)
2	$(Cp)_2V$	$HSiCl_3$	Δ	$Cl_3SiVH(Cp)_2$ [b] $(Cl_3Si)_2V(Cp)_2$ [b]		(*88*)
3	$[Mo(CO)_3(Cp)]_2$	Si_2Cl_6		$Cl_3SiMo(CO)_3(Cp)$		(*197*)
4	$(Cp)Mn(CO)_3$	$HSiR_3$	hν	$R_3SiMnH(CO)_2(Cp)$		(*225*)
5	$(Cp)Mn(CO)_3$	$R_3SiSiR_2R^1$		$(R_3Si)(R_2R^1Si)Mn(CO)_2(Cp)$ [c]		(*400*)
6	$(Me\text{-}Cp)Mn(CO)_3$	HSi^*R_3 $[Si^*R_3 = MePh(1\text{-naphthyl})Si]$	hν	$R_3SiMnH(CO)_2(Me\text{-}Cp)$		(*117, 118*)
7	$(Me\text{-}Cp)Mn(CO_3)$	$HSiR^1R^2X$	hν	$XR^1R^2SiMnH(CO)_2(Me\text{-}Cp)$		(*119*)
8	$(Cp)Re(CO)_3$	$HSiPh_3$	hν	$Ph_3SiReH(CO)_2(Cp)$		(*249*)
9	$Re_2(CO)_{10}$	$HSiCl_3$	hν	? $Cl_3SiRe(CO)_4$—H—$Re(CO)_5$ [d]		(*248, 251*)
10	$Fe(CO)_5$	$HSiR_3$	hν	*cis*-$R_3SiFeH(CO)_4$		(*259*)
11		Si_2Cl_6		$[Cl_2SiFe(CO)_4]_2$		(*197*)
12		$HSiR^1R^2X$	hν	$XR^1R^2SiFeH(CO)_4$		(*395*)
13		$HSiMe_2(NEt_2)$	hν	$(Et_2N)Me_2SiFeH(CO)_4$ [e]		(*394*)
14	$Fe_2(CO)_9$				(in 2:1 ratio)	(*133*)
15	$Fe_2(CO)_9$					(*386*)

16	$Fe_3(CO)_{12}$	$HSiCl_3$	$h\nu$	*cis*-$Cl_3SiFeH(CO)_4$ *cis*-$(Cl_3Si)_2Fe(CO)_4$ (Similarly Ru, Os)	*(361)*
17	$[(Cp)Fe(CO)_2]_2$	$HSiCl_3$	$h\nu$	$(Cl_3Si)_2FeH(CO)(Cp)$	*(259)*
18	$Fe(II)H_2(PMePh_2)_4$	$HSiR_3$		$R_3SiFe(IV)H_3(PMePh_2)_3$	*(228)*
19	$(diphos)_2Fe(C_2H_4)^f$	$HSiR_3$		$R_3SiFeH(diphos)_2$ $(R_3Si)_2Fe(diphos)_2$	*(291, 355)*
20	$RuCl_2L_3$ (L = PPh_3)	$HSiR_3$		$R_3SiRuHL_2$ (R = Cl, OEt) $(R_3Si)_2RuL_2$ (R = Cl)	*(411)* *(411)*
21	RuH_2L_4 (L = PPh_3)	$HSiR_3$		$R_3SiRuH_3L_3$	*(284, 285)*
	$RuHClL_3$ (L = PPh_3) $RuCl_2L_3$ (L = PPh_3)	$HSiR_3$		$R_3SiRuHL_n$ (n = 2, 3)	*(284, 285)*
22	RuH_2L_4 (L = PR_3) $RuHClL_3$ (L = PR_3) $RuCl_2L_3$ (L = PR_3)	$HSiR_3$		$R_3SiRuH_3L_n$ (n = 2, 3) (not when R = Me, Et)	*(226)*
23	$Co(CO)_2(Cp)$	$HSiCl_3$	$h\nu/\Delta$	$Cl_3SiCoH(CO)(Cp)$	*(259)*
24	$CoH(X_2)L_3$ (L = PPh_3, X = H, N)	$HSiR_3$		$R_3SiCoH_2L_3$	*(15, 17)*
25	$(diphos)_2CoH^f$	$HSiCl_3$		$[(diphos)_2CoH_2]^+SiCl_3^-$	*(291)*
26	$(diphos)_2CoH^f$	$HSiCl_3$, Ph_3SiCl, $SiCl_4$		None; $(diphos)_2CoCl$ and $[(diphos)_2Co(H)Cl]^+Cl^-$ produced	*(16)*
27	$Rh(CO)_2(Cp)$	$HSiR_3$	$h\nu$	$R_3SiRhH(CO)(Cp)$	*(346)*
28	$RhClL_3$ (L = PPh_3, etc.)	$HSiR_3$		$R_3SiRhH(Cl)L_2$	*(230, 344)*
29	$Rh(C_8H_{12})(Cp)$	$HSiCl_3$		$(Cl_3Si)_2Rh(C_8H_{14})(Cp)$	*(195)*
	$[Rh(C_8H_{12})Cl]_2$	$HSiCl_3$		$(Cl_3Si)_2Rh(C_8H_{12})Cl$	*(195)*
	$RhClL_3$ (L = PPh_3)	$HMeSi(OSiMe_3)_2$		$Me(Me_3SiO)_2SiRhH(Cl)L_2$	*(195)*
30	$IrH(CO)L_3$ (L = PPh_3)	$HSiR_3$		$R_3SiIrH_2(CO)L_2$	*(179, 221, 223)*
31		$DSiR_3$		$R_3SiIrHD(CO)L_2$	*(180)*

(table continues)

TABLE V (Continued)

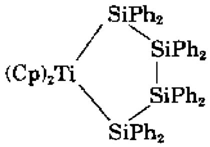
Entry	Metal derivative	Silicon compound	Treatment	Silicon–metal product	Ref.
32	$IrH(CO)L_3$	$(HMe_2Si)_2X$ ($X = O, CH_2$)			(*139, 207*)
33	$IrCl(CO)L_2$ ($L = PPh_3$)	$HSiR_3$		$R_3SiIrH(Cl)(CO)L_2$ [g]	(*70, 229*)
34	$IrX(CO)L_2$ ($L = PEt_3, PPh_3$)	H_3SiY ($Y = H, Cl, Br, I, Me, SiH_3$)		$YH_2SiIrH(X)(CO)L_2$ (exchange between X and Y possible)	(*165, 166*)
35	$IrCl(CO)L_2$ ($L = PPh_3$)	Si_2Cl_6		$(Cl_3Si)_2IrCl(CO)L_2$	(*197*)
36	$IrCl(CO)L_2$ ($L = PEt_3$)	$Hg(SiMe_3)_2$		$(Me_3Si)_2Ir(HgSiMe_3)(CO)L_2$	(*241*)
37	$[Ir(diphos)_2]^+BPh_4^-$ [f]	$HSiR_3$		$[R_3SiIrH(diphos)_2]^+BPh_4^-$	(*222*)
38	NiL_4 ($L = PPh_3$)	$HSiPh_3$		? $(Ph_3Si)_2NiL_2$ [h]	(*291*)
		$HSiCl_3$			(*291*)
39	$Ni(CO)_4$				(*100, 297*)

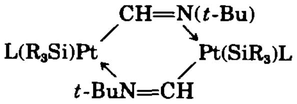
40	$L_2Pd(C_2H_4)$ ($L = PPh_3$)	$(HSiMe_2)_2X$ ($X = O, CH_2$)	 (Similarly Pt)	(*154*)
41	$L_2Pt(C_2H_4)$ ($L = PPh_3$)	$HSiR_3$ ($R = Ph, Et, OEt$, etc.; $R_3 = MeCl_2$)	$R_3SiPtHL_2$	(*161, 430*)
42		HSi^*R_3 [Si^*R_3 = MePh(1-naphthyl)Si]	$R_3Si^*PtHL_2$ (with retention)	(*163*)
43				(*182*)
44		$H(SiPh_2)_4H$		(*294*)
45		$(HR_2Si)_2Y$ ($Y = O$, o-C_6H_4, $—CH_2C_6H_4$-o)		(*158*)
46		$HSiR_3$ ($R_3 = Me_nCl_{3-n}$, $n = 0-2$)	$(R_3Si)_2PtL_2$	(*161, 430*)
47	$L_2Pt(C_2H_4)$ [L = P(cyclohexyl)$_3$]	$Me_2Si(C{\equiv}CPh)_2$		(*105*)

(*table continues*)

TABLE X

CLEAVAGE REACTIONS OF SILICON–METAL COMPOUNDS

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
Cleavage by dihydrogen				
1	*cis*-$(Me_3Si)_2Pt(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
2	*cis*-$(Me_3Si)PtH(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
3	*cis*-$(Me_3Si(PtCl(diphos)^a/H_2$	✓	Si–H + M–H	*(111)*
Cleavage by halogen compounds				
4	 $/CHCl_3/h\nu$	✓	$(Cp)_2TiCl_2$, Si_5Ph_{10}, C_2Cl_4	*(239)*
5	$(Ph_3Si)ZrCl(Cp)_2/HX$	✓	$Ph_3SiH + (Cp)_2ZrClX$	*(273)*
	$(Ph_3Si)ZrCl(Cp)_2/CDCl_3$	✓	? + $(Cp)_2ZrCl_2$	*(273)*
6	$H_3SiCr(CO)_3(Cp)/HCl$ (also Mo, W analogs)	✓	Si–Cl + H–M	*(214)*
7	$R_3SiCr(CO)_5^-/HCl$ (also Mo, W analogs)	✓	Si–H + Cl–M	*(254)*
7a	$(CH_2{=}CH)Me_2SiW(CO)_3(Cp)/HX$ (X = F, Br)	✓	Si–X + H–W	*(308)*
8	$F_3SiMn(CO)_5/HBr$ (also Re analog)	×	[b]	*(373)*
9	$Me_3SiMn(CO)_5/I_2$ (also Ge, Sn, Pb analogs)	✓	Si–I + I–Mn Kinetic study: Si < Ge ⋘ Sn < Pb	*(102)*
10	$Ph_3SiMn(CO)_5/X_2$ (X = Cl, Br)	✓	Si–X + X–Mn	*(101)*
11	$Ph_3SiMn(CO)_5/I_2$	×	—	*(101)*
12	$R_3Si^{*}MnH(CO)_2(Cp')^{c,d}/Cl_2$	✓	$R_3Si^{*}H$ + Cl–Mn	*(117, 118)*
13	$XRR'SiMnH(CO)_2(Cp')^c/HCl$	✓	Si–H + Cl–Mn	*(119)*
14	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe	*(330)*
15	$Me_3SiFe(CO)_2(Cp)/Cl_2$	✓	Si–Cl + Cl–Fe	*(67)*
16	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe[e]	*(67)*
17	$Me_3SiFe(CO)_2(Cp)/ICl$	✓	Si–Cl + I–Fe	*(67)*
18	$Me_3SiFe(CO)_2(Cp)/CF_3I$	✓	Si–F + I–Fe	*(67)*

54	Pt_3L_6 (L = t-BuNC)	$HSiR_3$		(*104*)
55	L_2PtI_2 (L = PEt_3)	H_3SiI	$IH_2SiPtI_2(H)L_2$	(*56, 58*)
56	L_2PtI_2 (L = PEt_3)	$H_3SiC{\equiv}CX$ (X = H, CF_3)	$XC{\equiv}CSiH_2PtI_2(H)L_2$ [c]	(*10*)

[a] Impure.

[b] Expected to be paramagnetic.

[c] Not isolated.

[d] Possible Re–H–Re bridge.

[e] Rearranges to $Et_2HN{\rightarrow}Me_2SiFe(CO)_4$ (see Section V,C).

[f] diphos = $Ph_2PCH_2CH_2PPh_2$.

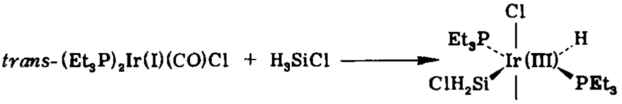
[g] With extra $HSiR_3$, loses R_3SiCl by reductive elimination, then adds more $HSiR_3$ to give $R_3SiIrH_2(CO)L_2$.

[h] Composition uncertain: as shown, this compound is expected to be paramagnetic.

[i] Uncertain compound.

as products in entry 2. These are expected to be paramagnetic, since dimerization is highly unlikely; together with the less-certain examples in entry 38, they represent the first examples of such behavior in molecular silicon–transition-metal compounds.

Attempted oxidative addition reactions involving cleavage of silicon–halogen bonds have proved unsuccessful (see entries 26 and 52), and when Si–H and Si–halogen bonds are present in the same molecule, it is the former that cleaves, even in the case of iodine (entries 34 and 55). For example,



(IV) (37)

When disilane, Si_2H_6, is used in this reaction, the Si–H linkage is broken in preference to the Si–Si bond (*165*). Silicon–carbon bonds are not usually susceptible to cleavage, although Si–alkynyl bonds provide an exception (entry 47). If both Si–H and Si–alkynyl bonds are present, however, it is the former that cleaves (entry 56). The special case of metal insertion into Si–C bonds of strained heterocycles is dealt with separately in Section II,G,2, while an isolated but interesting example of Si–Hg bond cleavage appears in entry 36.

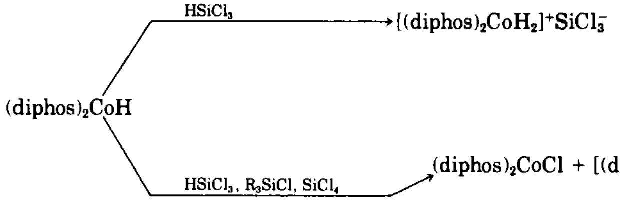
There is abundant evidence that, in any particular system, the stability of adducts formed by oxidative addition using a series of silanes $HSiX_3$ increases as X becomes more electronegative; a typical order is

$$\mathrm{HSi(aryl)_3} \leqslant \mathrm{HSi(alkyl)_3} < \mathrm{HSi(OR)_3} < \mathrm{HSiCl_3} < \mathrm{HSiF_3}$$

Thus, adducts of triarylsilanes frequently dissociate readily (i.e., undergo reductive elimination) or may exist only in solution in the presence of an excess of triarylsilane. Sometimes the only effect of the added silane may be to reduce metal ligands, e.g. (*411*),

$$\mathrm{(Ph_3P)_3RuCl_2 + Et_3SiH \rightarrow (Ph_3P)_3RuHCl + Et_3SiCl} \qquad (38)$$

while in other cases, this reduction is followed by addition of further $HSiX_3$ to the hydrido complex so formed. For this particular system, there have been conflicting reports of the products from reactions between various Ru(II) species and silanes (entries 20–22). In the most recent study (*226*), it is persuasively argued that the normal product is the Ru(IV) species $R_3SiRuH_3(PR_3)_n$ (n = 2,3), in which the metal is six- or seven-coordinate. Another controversial reaction was that between a cobalt(I) hydride and trichlorosilane (entries 25 and 26). It was first supposed that the product was a novel salt of the anion $SiCl_3^-$ [Eq. (39a)], but it was later shown that not only $HSiCl_3$ but also chlorosilanes with no Si–H bonds underwent the same reaction, giving Co(I)–Cl compounds [Eq. (39b)].

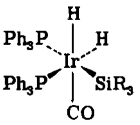


$$(diphos)_2CoH \xrightarrow{HSiCl_3} [(diphos)_2CoH_2]^+SiCl_3^- \quad (39a)$$

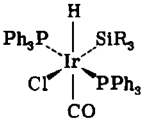
$$(diphos)_2CoH \xrightarrow{HSiCl_3,\ R_3SiCl,\ SiCl_4} (diphos)_2CoCl + [(diphos)_2CoHCl]^+Cl^- \quad (39b)$$

The high formal oxidation states of metals in some of these adducts is noteworthy, e.g., Fe(IV) (entries 17 and 18), Ru(IV) (entries 21 and 22), and Pt(IV) (entries 55 and 56). Such adducts are important because they provide definite examples of species often postulated as intermediates in oxidative addition–reductive elimination processes (compare Section II,G,1) and in homogeneous catalysis (*134, 220a, 410a*). In the case of germanium, a tris(germyl) adduct of Pt(IV) has been described (*57*), but no more than two silyl groups per metal atom are known to result from oxidative addition.

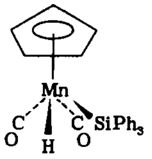
In a few cases, the stereochemistry of adducts has been elucidated from their vibrational and NMR spectra. The arrangement in compound (IV) has already been displayed, the product of the reaction in entry 30 is known to be (V) (*223*) [and this is confirmed by an X-ray study of the $GeMe_3$ analog (*202*)], while the product in entry 33 is (VI) (*229*). The adduct $Ph_3SiMnH(CO)_2(Cp)$ (entry 4) adopts a piano-stool arrangement with cis carbonyl groups (VII) (*225*), while the rhenium analog (entry 8) has both cis and trans isomers (*404*); reaction of $HSiR_3$ with $L_2Pt(olefin)$ complexes leads to formation of cis derivatives (entries 41–46).



(V)



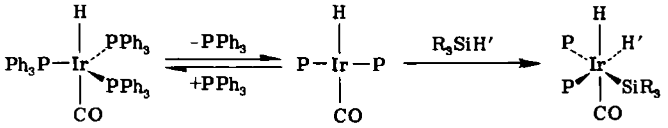
(VI)



(VII)

Some details of the crystal structure of adducts referred to in entries 8, 10, 17, 28, 47, 48, and 54 will be found in Section IV,A (*404, 403, 313,* *327, 105, 205, 104* respectively), while various cluster compounds formed by reactions analogous to oxidative addition processes are discussed in Section V,B.

Besides these determinations of static structures, further studies of the kinetics of oxidative addition to Ir(I) complexes have been made. Beginning with $Ir(CO)H(PPh_3)_3$ (**VIII**), the first step is seen as dissociation to the four-coordinate planar intermediate (**IX**). This then deforms and undergoes concerted cis addition to yield the adduct (**V**) (*179, 224*). In a comparison of group IV hydrides, Ph_3MH, the rates increased in the order $Si<Ge<Sn$; this was attributed not so much to variations in M–H bond energy but to the effects of differing polarizability and solvation of M–Ir products on the activation energy for addition.



(VIII) (IX) (V) (40)

This picture of the addition process receives support from a study of the same reaction using Ph_3SiD. The same product (V, $H' = D$) is formed initially, although H–D exchange rapidly scrambles the hydrogen positions (*180*).

G. Other Methods

1. *Elimination of Small Molecules*

Table VI lists various ways in which the elimination of small molecules has been used to produce silicon–transition-metal bonds; most can be pictured as proceeding via consecutive processes of oxidative addition and reductive elimination. Dihydrogen may result from reaction between compounds with M–H and Si–H bonds (entries 1–10).

$$L_nMH + HSiR_3 \rightarrow R_3SiML_n + H_2 \qquad (41)$$

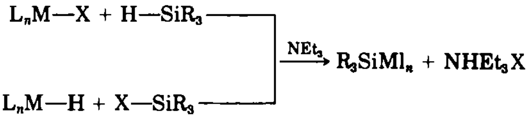
This is a good route to compounds that are functionally substituted at silicon (entries 6–10).

Alkanes can also be formed by the interaction of M–alkyl and Si–H species.

$$L_nMR + HSiR'_3 \rightarrow R'_3SiML_n + RH \qquad (42)$$

This method was unsuccessful when R was the bulky CH_2SiMe_3 group (entry 11). A six-coordinate M(IV) adduct is probable intermediate in entries 12–15, and elimination of groups other than R + H from this adduct provides a reasonable explanation for the volatile products observed in entry 12 and the formation of *cis*-$R_3SiPt(H)L_2$ in entry 15.

Elimination of hydrogen halide occurs both from M–H and Si–halogen (entry 18) and from M–halogen and Si–H systems (entries 17 and 19); a Lewis base must normally be added to drive the reaction from left to right (entries 17 and 18).



$$\left.\begin{array}{l} L_nM{-}X + H{-}SiR_3 \\ \\ L_nM{-}H + X{-}SiR_3 \end{array}\right] \xrightarrow{NEt_3} R_3SiMl_n + NHEt_3X \qquad (43)$$

By contrast, elimination of an amine to yield Si–M bonds has been achieved only between M–H and Si–N compounds (entries 20 and 21).

Elimination of alkenes has been already dealt with in Section II,F (oxidative addition–elimination), while other reactions involving elimination of dihydrogen may be found in that section and in Section II,E; this latter section includes many cases in which metal hydride species are believed to act as intermediates.

2. *Addition to* Si–C *Bonds of Strained Heterocycles*

These reactions, shown in Table VII, are chiefly a special type of oxidative addition process. Most important are those involving insertion of "$Fe(CO)_4$"; this is thought to occur via electrophilic Si–C cleavage in an essentially concerted process. Experiments with substituted silacyclobutanes have shown that the process is both regio- and stereospecific (*135*). Other metals seem reluctant to undergo this reaction: the manganese analog in entry 23 is thermally very unstable.

While silacyclopentanes and sitacyclohexanes do not appear to react in this way, it seems likely that the very strained three-membered ring in silacyclopropanes will.

3. *Formation of Adducts with* M→Si *Bonds*

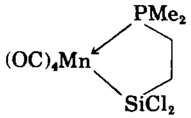
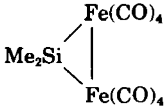
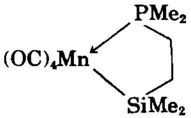
In principle, electron donation could take place from filled orbitals of a transition metal into empty silicon 3d orbitals to give adducts. Fluorosilanes in particular are known to act as Lewis acids (*23*). The somewhat confused experimental situation is summarized in Table VIII.

Initial experiments (entry 29) suggested that a 1:1 complex was

TABLE VI

ELIMINATION OF SMALL MOLECULES

Entry	Metal compound	Silicon compound	Silicon–metal product	Ref.
(a) Elimination of H_2				
1	$(Cp)_2WH_2$	$HSiCl_3$	$Cl_3SiWH(Cp)_2$	(*88*)
2	$FeH_2(diphos)_2$ ^{a}	$HSiX_3$	$X_3SiFeH(diphos)_2$ $(X_3Si)_2Fe(diphos)_2$	(*291, 355*)
3	$FeHCl(diphos)_2$ ^{a}	$HSiX_3$	$X_3SiFeCl(diphos)_2$	(*291*)
4	CoH_3L_3 (L = PPh_3)	$HSiX_3$	$X_3SiCoH_2L_3$	(*15, 17*)
5	$RhHL_3$ (L = PPh_3)	$HSiCl_3$	$(Cl_3Si)_2RhL_2$	(*195*)
6	$PtH(X)L_2$ (L = PEt_3)	$H_{4-n}SiX'_n$ (X, X′ = Cl, Br, I; n = 0–3)	*trans*-$X'_nH_{3-n}SiPtXL_2$	(*58*)
7	$PtH(X)L_2$ (L = PEt_3)	$H_3SiC{\equiv}CX$ (X = H, CF_3)	*trans*-$(XC{\equiv}CSiH_2)Pt(X)L_2$	(*10*)
8	$PtH(X)L_2$ (L = PR_3)	$(H_3Si)_2Y$ (Y = O, NH, S, Se, Te)	*trans*-$(SiH_3YSiH_2)Pt(X)L_2$ + $Y[H_2SiPt(X)L_2]_2$	(*167, 168*)
9	$PtH(X)L_2$ (L = PR_3)	$(H_3Si)_3Z$ (Z = N, P)	*trans*-$[(SiH_3)_2ZSiH_2]Pt(X)L_2$	(*168*)
10	PtH_2L_2 [L = P(cyclohexyl)$_3$]	H_3SiX (X = H, Cl, SiH_3)	*trans*-$(XSiH_2)Pt(H)L_2$	(*169*)
(b) Elimination of alkane				
11	$(Cp)_2V(CH_2SiR_3)$	$HSiEt_3$	Unsuccessful (successful with Ge,Sn)	(*372*)
12	$(bipy)NiEt_2$ ^{b}	$HSiX_3$	$(X_3Si)_2Ni(bipy)$ ^{c}	(*274, 276*)
13	NiMe(Cp)L (L = PPh_3)	$HSiCl_3$	$Cl_3SiNi(Cp)L$	(*276*)
14	$PtMe_2L_2$ [L_2 = $(Ph_2P)_2CH_2$]	$HSiMe_3$	$Me_3SiPt(Me)L_2$	(*200*)
15	*cis*-$PtMe_2L_2$ (L = PMe_2Ph)	$HSiR_3$	*cis*-$R_3SiPtHL_2$ *cis*-$(R_3Si)_2PtL_2$	(*162*)
		H_2SiPh_2	*cis*-$(HPh_2Si)_2PtL_2$	(*162*)

(c) Elimination of hydrogen halide				
16	$(Cp)_2TiCl_2$	$HSiCl_3$	Unsuccessful	(*88*)
17	$Mo(CO)_2(C_7H_7)Cl$	$HSiCl_3$[d]	$Cl_3SiMo(CO)_2(C_7H_7)$	(*255*)
18	$HMn(CO)_5$	$Cl_3SiCH_2CH_2PMe_2$[d]		(*211*)
18a	$Fe_2(CO)_9$	$HSiMe_2Cl$[d]		(*68*)
19	$Ni(Cp)_2 + NiCl_2L_2$ $(L = PPh_3)$	$HSiCl_3$	$Cl_3SiNi(Cp)L$	(*199, 203*)
(d) Elimination of amine				
20	$HMo(CO)_3(Cp)$	Me_2NSiMe_3	$Me_3SiMo(CO)_3(Cp)$ (similarly W)	(*86*)
21	$HMn(CO)_5$	$Me_2NSiMe_2CH_2CH_2PMe_2$		(*211*)

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[a] diphos = $Ph_2PCH_2CH_2PPh_2$.

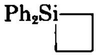
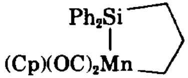
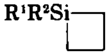
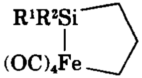
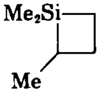
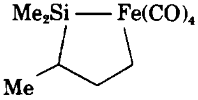
[b] bipy = 2,2′-bipyridyl.

[c] Evolves C_2H_6, also H_2, $EtSiCl_3$.

[d] NEt_3 added.

TABLE VII

ADDITION TO STRAINED HETEROCYCLIC RINGS

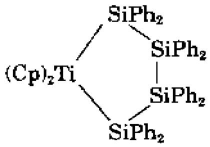
Entry	Metal compound	Silicon compound	Treatment	Silicon–metal product	Ref.
22	$TiCl_4$	$(Me_2SiCH_2)_2$	Δ	None (TiCSi formed)	*(329)*
23	$Mn(CO)_3(Cp)$		$h\nu$	 [a]	*(400)*
24	$Fe_2(CO)_9$[b]				*(131, 132, 135)*
25	$Fe_2(CO)_9$				*(135)*

[a] Decomposes at −78°C.

[b] $Fe(CO)_5$ or $Fe_3(CO)_{12}$ with irradiation can also be used.

TABLE X

CLEAVAGE REACTIONS OF SILICON–METAL COMPOUNDS

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
Cleavage by dihydrogen				
1	*cis*-$(Me_3Si)_2Pt(diphos)^a/H_2$	✓	Si–H + M–H	(*112, 113*)
2	*cis*-$(Me_3Si)PtH(diphos)^a/H_2$	✓	Si–H + M–H	(*112, 113*)
3	*cis*-$(Me_3Si(PtCl(diphos)^a/H_2$	✓	Si–H + M–H	(*111*)
Cleavage by halogen compounds				
4	 $/CHCl_3/h\nu$	✓	$(Cp)_2TiCl_2$, Si_5Ph_{10}, C_2Cl_4	(*239*)
5	$(Ph_3Si)ZrCl(Cp)_2/HX$	✓	$Ph_3SiH + (Cp)_2ZrClX$	(*273*)
	$(Ph_3Si)ZrCl(Cp)_2/CDCl_3$	✓	? + $(Cp)_2ZrCl_2$	(*273*)
6	$H_3SiCr(CO)_3(Cp)/HCl$ (also Mo, W analogs)	✓	Si–Cl + H–M	(*214*)
7	$R_3SiCr(CO)_5^-/HCl$ (also Mo, W analogs)	✓	Si–H + Cl–M	(*254*)
7a	$(CH_2{=}CH)Me_2SiW(CO)_3(Cp)/HX$ (X = F, Br)	✓	Si–X + H–W	(*308*)
8	$F_3SiMn(CO)_5/HBr$ (also Re analog)	×	^{b}	(*373*)
9	$Me_3SiMn(CO)_5/I_2$	✓	Si–I + I–Mn	(*102*)
	(also Ge, Sn, Pb analogs)		Kinetic study: Si < Ge ≪ Sn < Pb	
10	$Ph_3SiMn(CO)_5/X_2$ (X = Cl, Br)	✓	Si–X + X–Mn	(*101*)
11	$Ph_3SiMn(CO)_5/I_2$	×	—	(*101*)
12	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/Cl_2$	✓	R_3Si^*H + Cl–Mn	(*117, 118*)
13	$XRR'SiMnH(CO)_2(Cp')^c/HCl$	✓	Si–H + Cl–Mn	(*119*)
14	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe	(*330*)
15	$Me_3SiFe(CO)_2(Cp)/Cl_2$	✓	Si–Cl + Cl–Fe	(*67*)
16	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe^e	(*67*)
17	$Me_3SiFe(CO)_2(Cp)/ICl$	✓	Si–Cl + I–Fe	(*67*)
18	$Me_3SiFe(CO)_2(Cp)/CF_3I$	✓	Si–F + I–Fe	(*67*)

formed between the donor fragment $(Ph_3P)_2Pt$ and SiF_4; this complex in turn formed an adduct with 1 mol ammonia. However, later work (entries 27 and 30) indicated that the product in this system and that from $Ir(CO)H(PPh_3)_2$ and SiF_4 were ionic derivatives containing the SiF_5^- anion [1 : 1 adducts between SiF_5^- and ammonia are already known (*108a*)]. Evidently, reaction in glass vessels had led to production of hydrogen fluoride.

The interesting ligand molecule $SiF_3CH_2CH_2PMe_2$, which undergoes extensive self-association (*209*), attaches itself to iron or palladium centers via the phosphorus atom (entries 26 and 28). Further interaction then occurs between the metal atom and the SiF_3 group; this is weak in the former case but stronger in the latter, which has been described as an example of a three-center two-electron bond system. Electron donation is postulated from the filled Pd $4d_{z^2}$ orbital into 3d orbitals of both silicon atoms (*212*).

4. *Rearrangements, Anion Attack, and Miscellaneous Reactions*

a. Rearrangements. Table IXA shows three examples of rearrangements leading to silicon–metal bonds:

$$\text{Si—C—M} \rightarrow \text{C—Si—M} \qquad \text{(entries 31 and 32)} \qquad (44)$$

$$\text{Si—Si—C—M} \rightarrow \text{Si—C—Si—M} \qquad \text{(entry 33)} \qquad (45)$$

While it is tempting to ascribe these processes to an increase in bond energy on going from C–M to Si–M systems, entries 34 and 35 show

TABLE IXA

REARRANGEMENTS

Entry	Reaction	Ref.
31	$Me_2HSiCH_2Fe(CO)_2(Cp) \xrightarrow{\Delta} Me_3SiFe(CO)_2(Cp)$	(*352*)
32	$Me_2HSiCH_2Fe(CO)_2(Cp) \xrightarrow[PPh_3]{h\nu} Me_3SiFe(CO)(PPh_3)(Cp)$	(*352*)
33	$Me_3SiSiMe_2CH_2Fe(CO)_2(Cp) \xrightarrow{h\nu} Me_3SiCH_2SiMe_2Fe(CO)_2(Cp)$	(*353*)
34	$(ClCH_2)Cl_{2-x}Me_xSiFe(CO)_2(Cp) \xrightarrow{\Delta} Cl_{3-x}Me_xSiCH_2Fe(CO)_2(Cp)$ $(x = 1,2)$	(*427, 428*)
35	$(ClCH_2)Cl_2SiFe(CO)_2(Cp) \xrightarrow{AlCl_3} Cl_3SiCH_2Fe(CO)_2(Cp)$	(*427, 428*)
35a	$(BrCH_2)Me_2SiFe(CO)_2(Cp) \xrightarrow{0°C} BrMe_2SiCH_2Fe(CO)_2(Cp)$	(*427, 428*)

TABLE IXB

ANIONIC ATTACK

Entry	Metal compound	Silylanion/solvent	Silicon–metal compound	Ref.
36	$Fe(CO)_5$	Ph_3SiLi/THF	$Li[Ph_3SiFe(CO)_4]$	*(288)*
37	$Ni(CO)_4$	Ph_3SiLi/THF	$Li[Ph_3SiNi(CO)_3]$[a]	*(288)*
38	$Ni(COD)_2$[b]	Ph_3SiK/THF	$K_3[(Ph_3Si)_3Ni](THF)_3$	*(417)*
39	$Ni(COD)_2$[b]	Ph_3SiNa/glyme	$Na_2[(Ph_3Si)_2Ni](glyme)_4$	*(417)*

[a] NMe_4^+ salt also isolated.

[b] Cyclo-octa-1,5-diene.

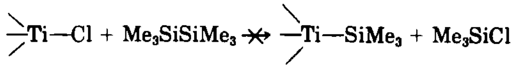
that under certain circumstances the rearrangement

$$\text{Cl—C—Si—M} \rightarrow \text{Cl—Si—C—M} \qquad (46)$$

can occur, no doubt assisted by the high Si–Cl bond energy (see also entry 35a).

b. Silyl anion attack. To the extent that alkali metal organosilyl derivatives R_3SiM are ionic in nature *(24)*, they can be regarded as sources of R_3Si^- anions, isoelectronic with tertiary phosphines. As Table IXB shows, they do indeed react with transition-metal(0) compounds to yield anionic complexes with silicon–metal bonds. As yet, little is known of the chemical behavior of these interesting species.

c. Miscellaneous reactions. Attempted reaction of the type:



$$\gt\!\text{Ti—Cl} + \text{Me}_3\text{SiSiMe}_3 \nrightarrow \gt\!\text{Ti—SiMe}_3 + \text{Me}_3\text{SiCl} \qquad (47)$$

was unsuccessful (Table IXC, entry 40), but reaction of a hydridodisilane with $Fe_2(CO)_9$ led to extrusion of Me_2Si, which then coordinated to the metal; the remaining silane added oxidatively to the metal center, giving the compound $Me_2Si{\rightarrow}FeH(CO)_3SiMe_2R$ as product (entry 45). Another attempt to produce a silylene–metal species gave a product for which the dimeric structure (**XII**) was proposed (entry 41). Metal-stabilized silylene derivatives are discussed further in Section V,C.

Formal insertion of $Fe(CO)_x$ into the Si–Si bond of a vinyldisilane leads to the interesting silicon-substituted allyl derivative (**XIV**)*

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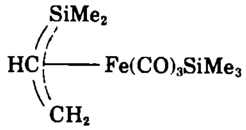
* This reaction has now been reinterpreted in terms of an η^2-substituted vinyl $Fe(CO)_4$ product (see Appendix).

TABLE IXC

MISCELLANEOUS

Entry	Reaction	Ref.
40	$(Cp)_2TiCl_2 + Me_3SiSiMe_3 \rightarrow$ No Si–Ti products	*(273)*
41	$W(CO)_6 + SiI_4 \xrightarrow{h\nu} [(OC)_5WSiI]_2(\mu\text{-}I)_2$[a] (XII)	*(392)*
42	$Mn_2(CO)_{10} + Me_3Si(Cp) \rightarrow$ $(\eta^5\text{-}Me_3SiC_5H_4)Mn(CO)_3 + Me_3SiMn(CO)_5$[b] $+ Mn(CO)_3(Cp)$[b]	*(1)*
43	*fac*-$[Ph_3SiC(O)]Re(CO)_3(diphos)$[c](XIII) $\xrightarrow{\Delta}$ *mer*-$Ph_3SiRe(CO)_3(diphos) + CO$[d]	*(14)*
44	$Fe_2(CO)_9 + CH_2{=}CHSi_2Me_5 \rightarrow$  [e] (XIV)	*(382, 385)*
45	$Fe_2(CO)_9 + HSiMe_2SiMe_2R \rightarrow Me_2Si{\rightarrow}FeH(CO)_3(SiMe_2R)$ (R = H,Me)	*(384)*

[a] Dissociates in THF solution, giving $I_2SiW(CO)_5 \cdot THF$; see also Section V,C.

[b] Minor products.

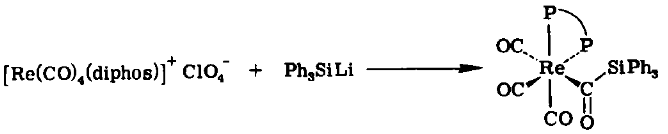
[c] diphos = $Ph_2PCH_2CH_2PPh_2$.

[d] Irreversible process.

[e] See footnote, p. 37, and Appendix.

shown in entry 44; although air-sensitive, it is stable thermally up to 80°C. Cleavage of a Si–(η^1-C_5H_5) bond and addition across a metal–metal bond is the minor reaction pathway in entry 42.

The great reluctance of silicon–metal compounds to undergo carbonyl insertion reactions, familiar in analogous C–metal chemistry, is discussed in Section III,B. Entry 43 shows the reverse process: a sila-acyl derivative (**XIII**), prepared by the reaction *(14)* of Eq. (48),



(XIII) (48)

decomposes irreversibly above about 182°C to yield a silicon–rhenium compound.

III. Reactivity of Molecular Silicon–Transition-Metal Compounds

A. GENERAL

A pattern of reactivity for typical molecular silicon–transition-metal compounds can be summarized in terms of Fig. 2.
Here we see the following modes of behavior:

(1) Cleavage of the silicon–metal bond. This includes as important subdivisions: insertion reactions, exchange of one silicon-containing group for another, and exchange of one metal-containing group for another (mode 1′).

(2) Ligand exchange at silicon, while the Si–M bond remains intact.

(3) Formation of adducts by attack of Lewis bases at silicon.

(4) Ligand exchange at the metal, while the Si–M bonds remains intact. Two important types of ligand, hydrogen (mode 4b) and carbonyl (mode 4a) are differentiated from the rest (mode 4c).

(5) Reactions involving the carbonyl group, in which oxygen acts as a nucleophile and/or carbon acts as an electrophile.

(6) Disproportionation reactions, either at a silicon or a metal center, the former being more common.

Examples of all these processes are considered next.

B. CLEAVAGE OF THE SILICON–TRANSITION-METAL BOND

Cleavage reactions, classified according to the nature of the attacking group, are collected together in Table X. Besides these, adduct formation (mode 3) and reductive elimination reactions also involve cleavage of Si–M bonds, but it is convenient to treat these separately in

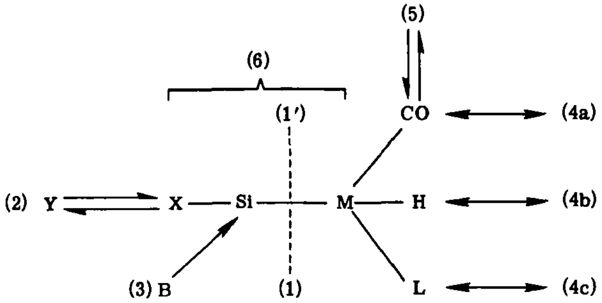
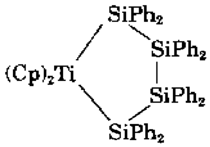
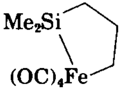
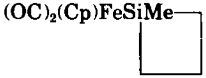
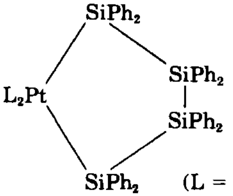


FIG. 2. Idealized reaction modes for molecular silicon–transition-metal compounds (see text).

TABLE X

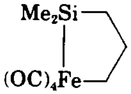
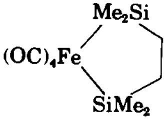
CLEAVAGE REACTIONS OF SILICON–METAL COMPOUNDS

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
Cleavage by dihydrogen				
1	*cis*-$(Me_3Si)_2Pt(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
2	*cis*-$(Me_3Si)PtH(diphos)^a/H_2$	✓	Si–H + M–H	*(112, 113)*
3	*cis*-$(Me_3Si(PtCl(diphos)^a/H_2$	✓	Si–H + M–H	*(111)*
Cleavage by halogen compounds				
4	 $/CHCl_3/h\nu$	✓	$(Cp)_2TiCl_2$, Si_5Ph_{10}, C_2Cl_4	*(239)*
5	$(Ph_3Si)ZrCl(Cp)_2/HX$	✓	$Ph_3SiH + (Cp)_2ZrClX$	*(273)*
	$(Ph_3Si)ZrCl(Cp)_2/CDCl_3$	✓	? + $(Cp)_2ZrCl_2$	*(273)*
6	$H_3SiCr(CO)_3(Cp)/HCl$ (also Mo, W analogs)	✓	Si–Cl + H–M	*(214)*
7	$R_3SiCr(CO)_5^-/HCl$ (also Mo, W analogs)	✓	Si–H + Cl–M	*(254)*
7a	$(CH_2{=}CH)Me_2SiW(CO)_3(Cp)/HX$ (X = F, Br)	✓	Si–X + H–W	*(308)*
8	$F_3SiMn(CO)_5/HBr$ (also Re analog)	×	^{b}	*(373)*
9	$Me_3SiMn(CO)_5/I_2$ (also Ge, Sn, Pb analogs)	✓	Si–I + I–Mn Kinetic study: Si < Ge ⋘ Sn < Pb	*(102)*
10	$Ph_3SiMn(CO)_5/X_2$ (X = Cl, Br)	✓	Si–X + X–Mn	*(101)*
11	$Ph_3SiMn(CO)_5/I_2$	×	—	*(101)*
12	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/Cl_2$	✓	R_3Si^*H + Cl–Mn	*(117, 118)*
13	$XRR'SiMnH(CO)_2(Cp')^c/HCl$	✓	Si–H + Cl–Mn	*(119)*
14	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe	*(330)*
15	$Me_3SiFe(CO)_2(Cp)/Cl_2$	✓	Si–Cl + Cl–Fe	*(67)*
16	$Me_3SiFe(CO)_2(Cp)/HCl$	✓	Si–Cl + H–Fe^e	*(67)*
17	$Me_3SiFe(CO)_2(Cp)/ICl$	✓	Si–Cl + I–Fe	*(67)*
18	$Me_3SiFe(CO)_2(Cp)/CF_3I$	✓	Si–F + I–Fe	*(67)*

19	$R_3Si^*Fe(CO)_2(Cp)^d/Cl_2$	√	Si–Cl + Cl–Fe	(*91, 92*)
20	$R_3Si^*Fe(CO)_2(Cp)^d/HCl$	×	—	(*91, 92*)
21	$R_3Si^*Fe(CO)_2(Cp)^d/KHF_2$	×	—	(*91, 92*)
22	$(CH_2{=}CH)Me_2SiFe(CO)_2(Cp)/HX$ (X = F, Cl, Br, I, CF_3COO, etc.)	√	Si–H + X–Fe	(*308*)
23	$(CH_2{=}CH)Ph_2SiFe(CO)_2(Cp)/HCl$	×	—	(*123*)
24	$(CH_2{=}CH)Ph_2SiFe(CO)_2(Cp)/Cl_2$	√	Si–Cl + Cl–Fe	(*123*)
25	$(CH_2{=}CH)Ph_2SiFe(CO)_2(Cp)/KHF_2$	×	—	(*123*)
26	 /HCl	√	n-$PrMe_2SiCl + FeCl_2$ [f]	(*132*)
27	 /HCl	√	n-$PrMeClSiFe(CO)_2(Cp)$ (70%) Si–Cl + H–Fe (20%)	(*136*)
28	 $/Cl_2, Br_2$	√	Si–X + X–Fe	(*136*)
29	$Me_xCl_{3-x}SiCo(CO)_4/HX$ (x = 0–2)	√[g]	Si–X + H–Co	(*215*)
30	$R_3Si^*Co(CO)_4/X_2$ (X = Cl, Br)	√	Si–X + X–Co	(*115*)
31	$R_3Si^*PtCl(PPhMe_2)_2{}^d/X_2$ (X = Br, I)	√	Si–Cl + X–Pt	(*163, 164*)
32	 $/Br_2$ $(L = PPh_3)$	√	$Si_4Ph_8Br_2 + L_2PtBr_2$	(*294*)
Cleavage by oxygen and sulfur compounds				
33	$H_3SiCr(CO)_3(Cp)/H_2O$	√	SiH_4 [h]	(*214*)
34	$F_3SiMn(CO)_5/CO$ (also Re analog)	×	[b]	(*373*)

(*table continues*)

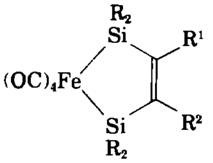
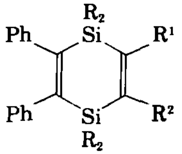
TABLE X (Continued)

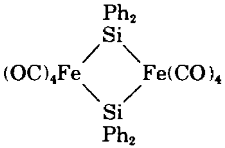
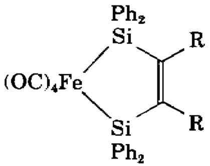
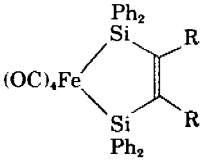
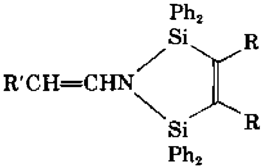
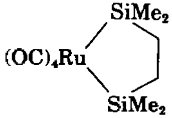
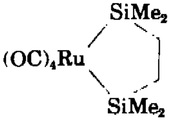
Entry	Silicon–metal compound/reagent	Suc-cess	Products	Ref.
35	$F_3SiMn(CO)_5/SO_2$	×	[b]	*(373)*
36	$Me_3SiMn(CO)_5/MeOH$	√	Si–O + H–Mn	*(193)*
37	$Me_3SiMn(CO)_5/PhCHO$	√	Si–O + $Mn_2(CO)_{10}$	*(264)*
38	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/H_2O$	√	Si*–O + ?	*(117, 118)*
39	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/MeOH$	√	Si*–O + ?	*(117, 118)*
40	$XRR'SiMnH(CO)_2(Cp')^c/H_2O$	√	Si–O + ?	*(119)*
41	$XRR'SiMnH(CO)_2(Cp')^c/MeOH$	√	Si–O + ?	*(119)*
42	$Ph_2Si[ReH(CO)_4]_2/$"H_2SiO_3"[i]	√	? + $H_2Re(CO)_8$	*(53)*
43	$Ph_3SiRe(CO)_3(diphos)^a/CO$	×	cf. Section II,G,4,c	*(14)*
44	$Me_3SiFe(CO)_2(Cp)/SO_2$	×	Insertion does occur with Ge, Sn analogs	*(65)*
45	$R_3Si^*Fe(CO)_2(Cp)^d/H_2O$	√	Si–O + ?	*(91, 92)*
46	$R_3Si^*Fe(CO)_2(Cp)^d/MeOH$	×	—	*(91, 92)*
47	$R_3Si^*Fe(CO)_2(Cp)^d/MeO^-$	×	—	*(91, 92)*
48	$(CH_2{=}CH)Ph_2SiFe(CO)_2(Cp)/H_2O$	×	—	*(123)*
49	$(CH_2{=}CH)Ph_2SiFe(CO)_2(Cp)/EtO^-$	×	—	*(123)*
50	 $/H_2O$	√	n-$PrMe_2SiOH$ + ?	*(132)*
51	$(Me_3Si)_2Fe(CO)_4/PhCHO$	√	Si–O + ?	*(264)*
52	 $/PhCHO$	√	Si–O + ?[j]	*(264)*
53	$Cl_xMe_{3-x}SiCo(CO)_4/H_2O$ (x = 1, 2)	√	Si–O + ?	*(215)*
54	$Cl_xMe_{3-x}SiCo(CO)_4/CO$ (x = 0–2)	×	Even at 90°C/4000 atm	*(215)*
55	$R_3Si^*Co(CO)_4{}^d/H_2O$	√	Si*–O + ?	*(115)*
56	$R_3Si^*PtCl(PPhMe_2)_2{}^d/PhSH$	√	Si*–H + S–Pt	*(163, 164)*
57	$R_3Si^*PtH(PPh_3)_2{}^d/PhSH$	√	Si*–H + S–Pt	*(163, 164)*
58	$R_3Si^*PtH(PPh_3)_2{}^d/PhCOCl$	√	Si*–H + Pt(Cl)OCPh	*(163, 164)*

Cleavage by nitrogen and phosphorus compounds				
59	$H_3SiMo(CO)_3(Cp)/NHMe_2/70^\circ C^k$	✓	$H_3SiNMe_2 + H{-}Mo$	(*214*)
60	$H_3SiM(CO)_3(Cp)/PF_5$ (M = Cr, Mo, W)	✓	$HSiF_3$, PF_3, PF_3O, etc.	(*214*)
61	$Me_5Si_2W(CO)_3(Cp)/Me_3P{=}CH_2$ (also Cr, Mo analogs)	✓	$Me_3P{=}CH(Si_2Me_5)^{l,m} + Me_4P^+W(CO)_3(Cp)^-$	(*305*)
62	$Ph_3SiMn(CO)_5/P(OR)_3/80^\circ C$	✓	$(Ph_3SiO)_3PO + RCOMn(CO)_3[P(OR)_3]_2$	(*376*)
63	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/PR_3$	✓	$R_3Si^*H + Mn{-}PR_3$	(*117, 118*)
64	$R_3Si^*Fe(CO)_2(Cp)/P(OPh)_3/h\nu$	✓	$R_3Si^*H + Fe{-}(o\text{-}C_6H_4O){-}P$ (see text)	(*93*)
65	$X_3SiFe(CO)_2(Cp)/Me_3P{=}CH_2$	✓	$Me_3P{=}CH(SiX_3)^{m,n} + Me_4P^+Fe(CO)_2(Cp)^-$	(*301, 303*)
66	$Me_2Si{\to}FeH(CO)_3(SiMe_2R)/PPh_3$	✓	$Fe(CO)_3(PPh_3)_2 + ?$	(*384*)
66a	$(Cl_3Si)_2Fe(CO)_4/PPh_3$	✓	$Si_2Cl_6 + Fe(CO)_n(PPh_3)_{5-n}$ ($n = 3, 4$)	(*355*)
67	$Et_3SiCo(CO)_4/PPh_3$	✓	$Si_2Et_6 + [Co(CO)_3PPh_3]_2$	(*227*)
Cleavage by silicon, germanium, and tin compounds				
68	$Me_3SiMo(CO)_3(Cp)/(Me_3M)OSiMe_3$ (Similarly W; M = Ge, Sn)	✓	$Me_3MMo(CO)_3(Cp) + (Me_3Si)_2O$	(*306, 310*)
69	$F_3SiFe(CO)_2(Cp)/Me_3P{=}C(SiMe_3)_2$	✓	$Me_3SiFe(CO)_2(Cp) + Me_3P{=}C(SiF_3)(SiMe_3)$	(*303*)
70	$R_3SiRuH_3L_3/HSiR'_3$ (L = PR_3)	✓	$R'_3SiRuH_3L_3 + HSiR_3$	(*226*)
71	$R_3SiCo(CO)_4/HSiR'_3$	✓	$R'_3SiCo(CO)_4 + HSiR_3$	(*95*)
72	$Me_3SiCo(CO)_4/HMMe_3$ (M = Ge, Sn)	✓	$Me_3MCo(CO)_4 + HSiMe_3$	(*73*)
73	$Me_3SiCo(CO)_4/Me_3GeBr$	✓	$Me_3GeCo(CO)_4 + Me_3SiBr$	(*73*)
74	$Me_3SiIrH_2(CO)(PPh_3)_2/HMMe_3$ (M = Ge, Sn)	✓	$Me_3MIrH_2(CO)(PPh_3)_2 + HSiMe_3$	(*198*)
75	$Cl_3SiNi(Cp)(PPh_3)/HGeCl_3$	✓	$Cl_3GeNi(Cp)(PPh_3) + HSiCl_3$	(*199*)
76	$R_3Si^*PtCl(PPhMe_2)_2{}^d/HSiEt_3$	✓	$Pt{-}H + HSi^*R_3$	(*112, 164*)
77	*trans*-$ClH_2SiPtCl(PEt_3)_2/H_3GeCl$	✓	*trans*-$ClH_2GePtCl(PEt_3)_2 + H_3SiCl$	(*58*)
78	$Me_3SiPtX(diphos)^q/HMMe_3$ (M = Ge, Sn)	✓	$Me_3MPtX(diphos) + HSiMe_3$	(*112, 113*)
Cleavage by hydridic reducing agents				
79	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/LiAlH_4$	✓	$HSi^*R_3 + H{-}Mn$	(*117, 118*)
80	$R_3Si^*Fe(CO)_2(Cp)^d/LiAlH_4$	✓	$HSi^*R_3 + ?$	(*91, 92*)
81	$R_3Si^*Fe(CO)_2(Cp)^d/NaBH_4$	×	—	(*91, 92*)
82	$(CH_2{=}CH)Ph_2SiFe(CO)_2(Cp)/NaBH_4$	×	—	(*123*)
83	$R_3Si^*Co(CO)_4{}^d/LiAlH_4$	✓	$HSi^*R_3 + ?$	(*114, 115*)
84	$Ph_3SiCo(CO)_4/LiAlH_4$	✓	$HSiPh_3 + ?$	(*114, 115*)

(*table continues*)

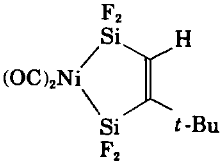
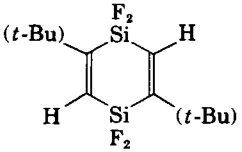
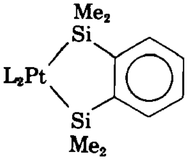
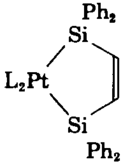
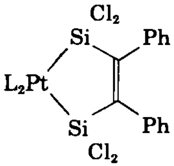
TABLE X (continued)

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
85	$R_3Si^*PtCl(PPhMe_2)_2{}^d/LiAlH_4$	√	$HSi^*R_3 + Pt + \cdots$	(*163, 164*)
86	$R_3Si^*PtH(PPh_3)_2{}^d/LiAlH_4$	√	$HSi^*R_3 + Pt + \cdots$	(*163, 164*)
Cleavage by organometallic compounds				
87	$R_3Si^*MnH(CO)_2(Cp')^{c,d}/LiMe$	√	$HSi^*R_3 + \cdots{}^o$	(*117, 118*)
88	$R_3Si^*Co(CO)_4{}^d/LiR$ (excess) (similarly Ph_3Si derivative)	√	R_3Si^*Li + ?	(*114, 115, 120*)
89	$Ph_3SiCo(CO)_4/RMgBr$	√	"$Ph_3SiMgBr$" + ?	
Cleavage by mercury compounds				
90	$R_3SiFe(CO)_2(Cp)/HgBr_2$ (also Ge, Sn analogs)	√	$R_3SiBr + \cdots$ Kinetic study: Si < Ge ≪ Sn	(*102, 103*)
91	$Me_nCl_{3-n}SiCo(CO)_4/HgX_2$ (n = 1, 2)	√	$Me_nCl_{3-n}SiX + \cdots$	(*215*)
92	$R_3Si^*Co(CO)_4{}^d/Hg(CH_3COO)_2$	√	$R_3Si^*(CH_3COO) + \cdots$	(*115*)
Cleavage by alkenes, alkynes, and nitriles				
93	$Me_3SiMn(CO)_5/C_2F_4{}^{v}/h\nu$ (also Ge, Sn analogs)	√	$Me_3SiCF_2CF_2Mn(CO)_5$	(*106*)
94	$Me_3SiMn(CO)_5/CHF{=}CF_2{}^{v}/h\nu$	√	*cis*-$CHF{=}CFMn(CO)_5 + Me_3SiF$	(*106*)
95	$F_3SiMn(CO)_5/C_2F_4$	×	No clear evidence for insertion (cf. Ref. *397*)	(*373*)
96	$Me_3SiFe(CO)_2(Cp)/CF_3C{\equiv}CR/h\nu$ (also Ge, Sn analogs) ($R = H, CF_3$)	√	$Me_3SiC(R){=}C(CF_3)Fe(CO)_2(Cp)$	(*66*)
97	$Me_3SiFe(CO)_2(Cp)/CF_2CF_2CF{=}CF/h\nu$	×	—	(*66*)
98	*cis*-$Cl_3SiFeH(CO)_4/C_2F_4$	×	$Cl_3SiFe(CO)_4Fe(CO)_4SiCl_3$ + ?	(*259*)
99	 /PhC≡CPh	√	 + ?	(*386*)

100	 $/RC\equiv CR$	√	 + · · · [q]	(*124*)
101	 $/R'CH_2CN/h\nu$	√	 + · · ·	(*124*)
102	$[Me_3SiRu(CO)_4]_2/C_7H_8$	√	$(Me_3Si)Ru_2(CO)_5(C_7H_6SiMe_3)$[r]	(*74, 75*)
103	$(Me_3Si)_2Ru(CO)_4/C_7H_8$	√	$Me_3SiRu(CO)_2(C_7H_8SiMe_3)$	(*75, 245*)
104	$(Me_3Si)_2Ru(CO)_4/C_8H_{10}$	√	$Me_3SiRu(CO)_2$(tetrahydropentalenyl)[s]	(*412*)
105	$(Me_3Si)_2Ru(CO)_4/C_8H_{14}$	√	[s]	(*412*)
106	$(Me_3Si)_2Ru(CO)_4/C_{12}H_{18}$	√	$Me_3SiRu(CO)_2$(tetrahydropentalenyl)[s]	(*281*)
107	$[Me_3SiRu(CO)_4]_2/C_8H_{12}$	√	$Me_3SiRu(CO)_2$(tetrahydropentalenyl)[s]	(*281*)
108	$[Me_3SiRu(CO)_4]_2/C_8H_{10-n}(SiMe_3)_n$ (n = 2, 3)	√	$Ru_3(CO)_8[C_8H_{6-m}(SiMe_3)_m]$[t,u] ($m$ = 2, 3)	(*244, 247, 279*)
109	 $/C_8H_8$	√	$Ru_2(CO)_5(Me_2SiCH_2CH_2SiMe_2C_8H_8)$	(*170, 171*)
110	 $/C_7H_8$	√	$Ru(CO)_2(Me_2SiCH_2CH_2SiMe_2C_7H_8)$ (see text)	(*170, 171*)
111	$(Me_3Si)_2Ru(CO)_4/C_5H_6$	√	$Me_3SiRu(CO)_2$(Cp)	(*409*)
112	$(Me_3Si)_2Ru(CO)_4/C_7H_{10}$	√	$Me_3SiRu(CO)_2(C_7H_9)$	(*409*)
113	$[Me_3SiRu(CO)_4]_2/C_8H_8$	√	$Ru_3(CO)_8(C_8H_8)$[r]	(*246, 279*)

(*table continues*)

TABLE X (Continued)

Entry	Silicon–metal compound/reagent	Success	Products	Ref.
114	$(Me_3Si)_2Ru(CO)_4/C_8H_8$	√	$Me_3SiRu(CO)_2(C_8H_8SiMe_3)$ $+ (Me_3Si)_2Ru_2(CO)_4(C_8H_6)$[t]	(*217*)
115	$(X_3Si)_2Ni(bipy)$[v]$/PhC{\equiv}CPh$ ($X_3 = Cl_3, MeCl_2$)	√	(bipy)$Ni[Ph(SiX_3)C{=}CPh(SiX_3)]$(**XVII**)	(*275, 277*)
116	 /*t*-BuC≡CH	√	 [w]	(*100, 297*)
117	$Ph_2MeSiPtHL_2/PhC{\equiv}CR$ ($L = PPh_3$; R = H, Ph)	√	$Ph_2MeSiH + L_2Pt(PhC{\equiv}CR)$	(*161*)
118	$R_3Si^*PtHL_2$[d]$/PhC{\equiv}CH$ ($L = PPh_3$)	√	$R_3Si^*H + L_2Pt(PhC{\equiv}CH)$	(*163, 164*)
119	 /PhC≡CH ($L = PPh_3$)	√	$L_2Pt(PhC{\equiv}CH)$ + ?	(*158*)
120	*cis*-$(HPh_2Si)_2PtL_2/C_2H_2/\Delta$ ($L = PPhMe_2$)	×	 (cf. entry 115)	(*159*)
121	$(Cl_3Si)_2PtL_2/PPh_3/PhC{\equiv}CPh$ ($L = PPh_3$)	×	 $+ Ph_3PCl_2$	(*390*)

122	$(Cl_3Si)_2Pt(PPh_3)_2/PhC{\equiv}CPh/PPh_3$	×	No reaction; cf. entries 120 and 121	(*197*)
123	$PhMe_2SiCu \cdot LiCN/$ (i) $n\text{-}BuC{\equiv}CH$ (ii) NH_4Cl	✓	$n\text{-}BuCH{=}CH(SiMe_2Ph)$ (major) + $n\text{-}BuC(SiMe_2Ph){=}CH_2$ (minor)	(*185*)
124	$(PhMe_2Si)_2CuLi \cdot LiCN/$ (i) $(n\text{-}Bu)C{\equiv}CH$; (ii) NH_4Cl	✓	Only $n\text{-}BuCH{=}CH(SiMe_2Ph)$	(*185*) [see also Ref. (*6*)]
Miscellaneous				
125	$(Me_3Si)_2Ru(CO)_4/Me_3SiRu(CO)_2(C_8H_8SiMe_3)$	✓	$Me_3SiRu_2(CO)_5(C_8H_8SiMe_3)$[x]	(*170, 280*)

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[a] diphos = $Ph_2PCH_2CH_2PPh_2$.

[b] Other $F_3Si{-}M$ derivatives behave similarly, where M = $Fe(CO)_2(Cp)$, $Mo(CO)_3(Cp)$, $W(CO)_3(Cp)$, and $Mn(CO)_4(PPh_3)$.

[c] Cp′ = $\eta^5\text{-}CH_3C_5H_4$.

[d] R_3Si^* = MePh(1-naphthyl)Si.

[e] Also $[Fe(CO)_2(Cp)]_2$.

[f] And other products.

[g] Only at high pressure and 90°C.

[h] Probably arises from disproportionation of $(SiH_3)_2O$, etc.

[i] Silicic acid.

[j] Also PhCH=CHPh, etc.

[k] Adduct formed at 25°C.

[l] $Fe(CO)_2(Cp)$ derivative reacts similarly.

[m] Via adduct as intermediate (see text).

[n] $Mo(CO)_3(Cp)$, $W(CO)_3(Cp)$, and $Co(CO)_4$ derivatives react similarly.

[o] Compare (*119*) and abstraction of H^+ from analogous species.

[p] Similar insertion or (insertion − Me_3SiF) products from cyclo-C_3F_6, $CF_3C{\equiv}CH$, $CF_3C{\equiv}CCF_3$, and $\overline{CF_2CF_2CF{=}CF}$.

[q] Also forms $Fe_2(CO)_6(R_2C_2)_2$ and $Fe_2(CO)_6(R_2C_2)_2SiPh_2$.

[r] Also (as major product) $(Me_3Si)_2Ru_2(CO)_5(C_7H_7)$.

[s] Major products are silicon-free compounds.

[t] Pentalene complex.

[u] Via $Me_3SiRu(CO)_2$(tetrahydropentalenyl) intermediates.

[v] bipy = 2,2′-bipyridyl.

[w] Also 2,4-di-*t*-butyl isomer.

[x] Also open-chain $Me_3SiRu_2(CO)_4(C_8H_8SiMe_3)$ and $Ru_3(CO)_8$-pentalene complexes. Note that $(Me_3Si)_2Ru(CO)_4$ acts as source of "$Ru(CO)_3$."

Sections III,D and III,G,2, respectively. Cleavages initiated thermally or photolytically will also be considered later, in Section V,A.

1. *Cleavage by Dihydrogen*

Silicon–platinum compounds still afford the only examples of this behavior (entries 1–3). While the reaction is believed to proceed via the formation of a Pt(IV) dihydrido intermediate (*134*, *235*), this species has not yet been isolated.

2. *Cleavage by Halogen Compounds*

Hydrogen halides usually cleave the silicon–metal bond in simple compounds containing Si–V, Si–Cr, Si–Fe, and Si–Co bonds; cleavage becomes more difficult with heavier transition-metal homologs. Compounds with Si–Mn (*30*) and especially Si–Re (*7*, *32*, *121*) bonds are generally much more resistant, although the special case of $R_3SiMn(H)(CO)_2(\eta^5\text{-}CH_3C_5H_4)$ should be noted (entry 13); this and related derivatives often react readily by a kind of reductive elimination process (compare entries 12, 63, and 87), associated with the close Si· · ·H approach in the molecule (Section IV,A).

The direction of attack is normally that expected for interaction between $H^{\delta+}$–$X^{\delta-}$ and a bond of polarity $Si^{\delta+}$–$M^{\delta-}$, and silicon becomes attached to the most electronegative partner. Exceptions may be noted in the case of (1) a compound with a high formal metal oxidation state (entry 5), (2) anionic derivatives (entry 7), (3) the manganese hydrido compound referred to above (entry 13), and (4) in certain vinyl–silicon compounds (entry 22, but not entry 7a), where formal reversal of polarity ("Umpolung") occurs in the Si–M bond. The lack of reactivity shown in entries 20 and 23 is probably due chiefly to steric factors. It is interesting that the silacyclobutane derivative in entry 27 reacts predominantly by ring opening, although some Si–Fe bond cleavage occurs while the ring remains intact.

Halogens themselves almost invariably bring about cleavage, often at low temperatures. An exception, involving $Ph_3SiMn(CO)_5$ and I_2, is shown in entry 11, although the trimethyl analog (entry 9) reacts readily. The interhalogen compound ICl reacts so that the most electronegative halogen atom becomes attached to silicon (entry 17), and the halogen analog CF_3I undergoes loss of CF_2 to achieve the same result (entry 18):

$$Me_3SiFe(CO)_2(Cp) + CF_3I \rightarrow Me_3SiF + IFe(CO)_2(Cp) \qquad (49)$$

Halogenated hydrocarbons often bring about substitution at silicon (see Section III,C), but in the case shown in entry 4, Si–Ti (but not Si–Si) bonds are cleaved, and rearrangement to a cyclic Si_5 derivative occurs. A radical process is postulated, similar to that observed in Ti–Ge (*422*) and H–Mn–CO (*72*) systems. Silicon–zirconium bonds are cleaved in an analogous way (entry 5).

3. *Cleavage by Oxygen and Sulfur Compounds*

Water and alcohols (or alkoxide ions) usually cause cleavage, although some exceptions amongst sterically hindered iron compounds in entries 46–49 should be noted. The direction of attack is such that Si–O compounds seem always to result, even in the case of $R_3SiMnH(CO)_2(Cp)$ derivatives (cf. Section III,B,2).

Insertion reactions with carbon monoxide or sulfur dioxide are well known for compounds with carbon–transition-metal bonds, e.g.,

$$RM(CO)_n \xrightarrow{CO} RCOM(CO)_n \tag{50}$$

$$RM(CO)_n \xrightarrow{SO_2} ROS(O)M(CO)_n \tag{51}$$

They have still not been achieved, however, for silicon–metal systems (entries 34, 35, 43, 44, 54) even in reactions at high pressure (entry 54). Moreover, one example is known of the reverse process, in which CO is extruded from a sila-acyl metal derivative (cf. Section II,G,4,c) (entry 43):

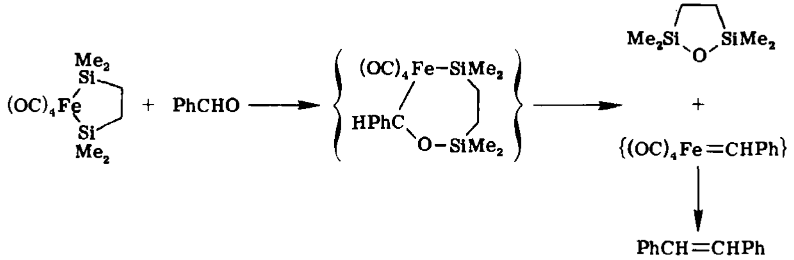
$$\underset{\textbf{(XIII)}}{fac\text{-}(Ph_3SiCO)Re(CO)_3(diphos)} \xrightarrow{>180°C} \underset{\textbf{(XV)}}{mer\text{-}Ph_3SiRe(CO)_3(diphos)} + CO \tag{52}$$

These observations are often ascribed to the greater element-to-metal bond strength on passing from carbon to silicon. But other factors must be involved, since insertion *does* occur in some related Ge–metal and Sn–metal systems (e.g., entry 44) (*24*), and it is known that Sn–metal bonds are generally stronger than the corresponding Si–metal bonds (see Section IV,D).

The reaction of benzaldehyde with various silicon–metal compounds has been studied with interesting results (entries 37, 51, 52). Apparently, insertion with Si–O bond formation is the first step, followed by loss of a metal-containing fragment. The following stages are proposed (*264*):

$$\begin{tikzcd}
\mathrm{Me_3SiMn(CO)_5 + PhCHO} \arrow[r, "5^\circ\mathrm{C}", "\mathrm{slow}"'] & \mathrm{(Me_3SiO)CHPhMn(CO)_5} \arrow[d, "80^\circ\mathrm{C}"] \\
& \mathrm{[Me_3SiOCHPh]_2 + Mn_2(CO)_{10}}
\end{tikzcd} \qquad (53)$$

$$\begin{tikzcd}
\mathrm{(Me_3Si)_2Fe(CO)_4 + PhCHO} \arrow[r, "5^\circ\mathrm{C}"] & \mathrm{Me_3SiFe(CO)_4CHPh(OSiMe_3)} \arrow[d, "25^\circ\mathrm{C}"] \\
& \mathrm{[Me_3SiOCHPh]_2} + ?
\end{tikzcd} \qquad (54)$$



(55)

The relationship between these processes and those believed to occur in metal-catalyzed hydrosilation of aldehydes and ketones (e.g., *231, 343*) has been emphasized.

Reactions of PhSH with Si–Pt compounds (entries 56 and 57) give the products expected on the basis of soft acid–soft base Pt–S interaction; it is surprising, however, that the reaction in entry 58 yields a product with Si–H rather than Si–O or Si–Cl bonds.

4. *Cleavage by Nitrogen and Phosphorus Compounds*

While tertiary amines often form quite stable adducts with N→Si bonds (see Section III,D), ammonia and primary or secondary amines normally cleave silicon–metal bonds; intermediate adducts are either not observed or found only at low temperatures (*134, 235*). Typical behavior is shown by (*28, 30, 31*)

$$\begin{tikzcd}
& \mathrm{[H_3Si\cdot 2NMe_3]^+Mn(CO)_5^-} \\
\mathrm{H_3SiMn(CO)_5} \arrow[ur, "\mathrm{NMe_3}"] \arrow[dr, "\mathrm{NH_3}"'] & \\
& \mathrm{(SiH_3)_2NH + HMn(CO)_5}
\end{tikzcd} \qquad (56)$$

In the case of entry 59, however, an adduct between $H_3SiMo(CO)_3(Cp)$ and dimethylamine can be isolated at room temperature, although it decomposes in the expected way on warming.

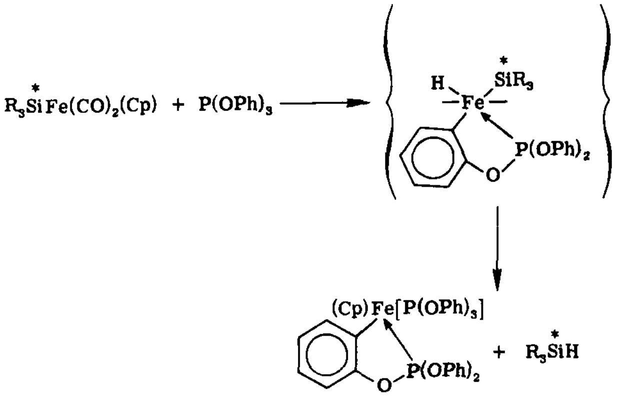
The fine balance between Si–M bond formation, cleavage, and adduct formation is well illustrated by the following system (*34*).

$$\underset{A}{F_3SiNMe_2 + HCo(CO)_4} \rightleftarrows \underset{B}{F_3SiCo(CO)_4 + HNMe_2} \rightleftarrows \underset{C}{\text{adduct}} \qquad (57)$$

When the components A are mixed, there is rapid formation of adduct C in equilibrium with the other compounds. On fractionation *in vacuo* at low temperatures, the most volatile component, dimethylamine, is readily removed, giving good yields of $F_3SiCo(CO)_4$.

The normal reaction of tertiary phosphines is to replace metal-coordinated carbonyl groups (Section III,E,1) or, less commonly, to form adducts with P→Si bonds (Section III,D). In special cases, however, cleavage of the Si–metal bond may occur directly (entries 63, 66, 66a, and 67); the manganese derivative is discussed further in Section IV,E, while the silylene–iron compound is considered again in Section V,C.

Phosphites often cause cleavage of Si–M bonds (e.g., entries 62 and 64), but not invariably (see Section III,E,1) (*93*). The reaction shown in entry 64 is an interesting example of *ortho*-hydrogen abstraction; it is suggested, by analogy with similar processes involving $R_3SiMnH(CO)_2(Cp)$ derivatives, that initial production of an Fe–H bonded intermediate is followed by reductive elimination of a hydridosilane.



(58)

The stereochemical implications of this and related reactions are considered in Section IV,E.

Phosphine methylenes, $R_3P{=}CH_2$, are strong Lewis bases and bring about cleavage of Si–M bonds with intermediate formation of an adduct (entries 61 and 65). This is a useful way of synthesizing *C*-silyl derivatives.

$$\begin{tikzcd} \mathrm{FMe_2SiFe(CO)_2(Cp)} + \mathrm{Me_3P{=}CH_2} \arrow[r] & {[\mathrm{Me_3PCH_2SiMe_2F}]^+[\mathrm{Fe(CO)_2(Cp)}]^-} \arrow[d, "\mathrm{Me_3P{=}CH_2}"] \\ & \mathrm{Me_3P{=}CH(SiMe_2F)} + \mathrm{Me_4P^+[Fe(CO)_2(Cp)]^-} \end{tikzcd} \tag{59}$$

5. *Cleavage by Main Group IV Compounds*

It has been known for some time (*134, 235*) that R_3Si groups in silicon–metal compounds can be replaced by R_3Ge or R_3Sn groups, the strength of attachment to metal being $Si < Ge < Sn$. This order is consistent with what is known of bond strengths (see Section IV,D). Some further examples of this special kind of cleavage reaction are shown in entries 72–75, 77, and 78. Replacements of one silyl group by another are also known (entries 70 and 71), e.g. (*226*),

$$\mathrm{R_3SiRuH_3L_3} + \mathrm{HSiR'_3} \rightarrow \mathrm{R'_3SiRuH_3L_3} + \mathrm{HSiR_3} \tag{60}$$

where $L = PR_3$, $R_3 = (OEt)_3$ or Cl_2Me, and $R' = F$. This reaction probably proceeds via successive reductive elimination and oxidative addition: the general rule is that the silyl group with the most electronegative substituents becomes attached to the metal. The displacement in entry 76, on the other hand, is probably a result of steric congestion in the initial Si–Pt compound.

Not only hydrido derivatives can enter into this reaction: entries 68 and 69 show that siloxy compounds and *C*-silyl-substituted phosphine methylenes also undergo exchange (*303, 306, 310*). In the latter case, the silyl group with the most electronegative substituents moves to carbon. Respective examples are

$$\mathrm{Me_3SiM(CO)_3(Cp)} + \mathrm{Me_3M'OSiMe_3} \xrightarrow{\Delta} \mathrm{Me_3M'M(CO)_3(Cp)} + \mathrm{(Me_3Si)_2O} \tag{61}$$

where M = Mo or W, and M′ = Ge or Sn, and

$$\mathrm{F_3SiFe(CO)_2(Cp)} + \mathrm{Me_3P{=}C(SiMe_3)_2} \xrightarrow[30\ \mathrm{h}]{60^\circ\mathrm{C}} \mathrm{Me_3SiFe(CO)_2(Cp)} + \mathrm{Me_3P{=}C(SiF_3)(SiMe_3)} \tag{62}$$

6. *Cleavage by Hydridic Reducing Agents*

Entries 79, 80, and 83–86 show that the potent reducing agent $LiAlH_4$ cleaves a variety of silicon–metal bonds, giving a hydridosilane. Nucleophilic attack by H^- is indicated; a discussion of the associated stereochemistry is deferred until Section IV,E. When the silicon–platinum compounds shown in entries 85 and 86 are reduced, metallic platinum is formed, but the metal-containing products in other cases have not generally been identified. Equation (63) provides an example of a compound with a robust Si–Fe bond that resists reductive cleavage (*237*) (cf. Section III,C,3).

$$Cl_3SiFe(CO)_2(Cp) \xrightarrow{LiAlH_4} H_3SiFe(CO)_2(Cp) \qquad (63)$$

Sodium borohydride seems less ready to cleave silicon–metal bonds (entries 81 and 82), and could be effective in selective reductions of the type shown above; no other hydridic reducing agents seem to have been investigated in this context.

7. *Cleavage by Organometallic and Mercury Compounds*

As shown in entry 87, methyllithium promotes the reductive elimination of R_3Si^*H from $R_3Si^*MnH(CO)_2(\eta^5\text{-}CH_3C_5H_4)$ (cf. entries 11 and 63). Stoicheiometric amounts of organolithium compounds and $R_3SiCo(CO)_4$ derivatives give products in which attack on coordinated carbonyl groups has occurred (*120*) (see Section III,F,1), but addition of further LiR leads to cleavage and formation of silicon–alkali-metal compounds (*114, 115*). Grignard reagents also induce cleavage.

Breaking of silicon–transition-metal bonds by mercury compounds is one aspect of the well-known "conversion series" in organosilicon chemistry (*22, 24, 154*). It was established at an early stage that equilibrium in the system

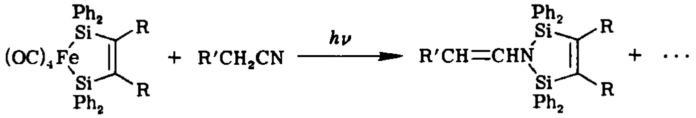
$$2H_3SiI + Hg[Co(CO)_4]_2 \rightleftarrows 2H_3SiCo(CO)_4 + HgI_2 \qquad (64)$$

lies well to the left (*26, 29*). Since most other metal carbonyl and metal carbonyl cyclopentadienyl groups are even less electronegative than $Co(CO)_4$ (see Section II,A,1), and to the extent that the conversion series is based on electronegativity values, it appears that all silicon–transition-metal bonds are likely to be cleaved by mercury halides, even the iodide. The more recent examples shown in entries 90–92 support this idea.

8. Cleavage by Alkenes, Alkynes, and Nitriles

The first six entries in this section of Table X (entries 93–98) relate to attempted insertion reactions of fluoroalkenes or fluoroalkynes into Si–Mn or Si–Fe bonds. Even in the successful cases, yields are generally low, and in some instances (e.g., entry 94) Me_3SiF is lost from the insertion product to leave a fluoroalkenyl manganese carbonyl. In the case of the iron hydrido compound in entry 98, there is formal loss of hydrogen to give the binuclear derivative $[Cl_3SiFe(CO)_4]_2$.

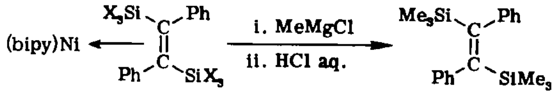
With alkynes, the ferradisilacyclopentene and diferradisilacyclobutane derivatives in entries 99 and 100 suffer cleavage of all or some of their Si–Fe bonds to yield cyclic and other products; the former compound also reacts with nitriles, forming a novel heterocycle (**XVI**).



(**XVI**) (65)

An analogous cleavage of a nickeladisilacyclopentene with alkyne is shown in entry 116. It has been pointed out (*297*) that these reactions show certain similarities to metal-catalyzed cyclotrimerization of alkynes or to cycloaddition of alkynes and substituted disilanes, postulated to involve Si–metal intermediates.

The nickel complex $(X_3Si)_2Ni(bipy)$ (X_3 = Cl_3 or $MeCl_2$) reacts with diphenylacetylene to form a violet solid, believed to be the trans isomer (**XVII**) (entry 115).

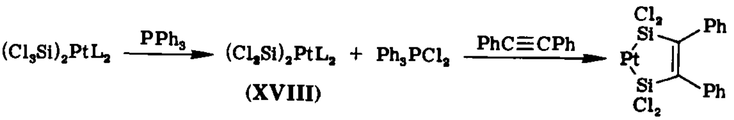


(**XVII**) (66)

Alkylation then yields the trans alkene shown; other alkynes can give rise to cis products. It seems likely that the metal–alkene complex (**XVII**) is similar to intermediates believed to occur in various catalytic processes involving nickel–bipyridyl complexes.

Analogous complexes have not been observed in the case of platinum: instead, a disilylplatinum complex (entry 120) adds ethyne with loss of hydrogen (but no Si–Pt bond cleavage) to give a platinadisilacyclopentene. A similar product (**XIX**) was claimed from the reactions of entry

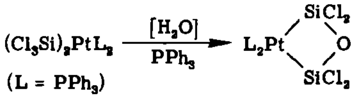
121, in which a disilylene complex (**XVIII**) was thought to act as an intermediate (L = PPh_3):



(XVIII)

(XIX) (67)

However, a reexamination of the first stage showed that PPh_3 did not abstract chlorine from $(Cl_3Si)_2PtL_2$, but rather that adventious moisture produced a cyclodisiloxane (**XX**) with properties similar to those reported for complex (**XVIII**); no addition of alkyne could be effected (entry 122).

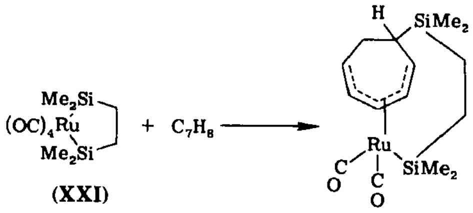


(XX) (68)

Addition of phenylacetylene to the platinum hydrido complexes $R_3Si^*PtH(PPh_3)_2$ (entries 117 and 118) leads to reductive elimination of HSi^*R_3 and formation of a Pt(0)–alkyne complex. A similar Pt(0) product is observed from the cyclic precursor in entry 119.

Representatives of the little-known class of silicon–copper compounds are formed *in situ* from organosilyllithium compounds and Cu(I) halides or pseudohalides; they can then undergo cleavage at the Si–Cu bond with alkynes (entries 123 and 124). The reaction, particularly with $(R_3Si)_2CuLi$, is regiospecific, and a route to useful vinyl derivatives.

The remaining entries in Table X summarize the extensive work carried out by Stone and his co-workers at Bristol on cleavage reactions of Si–Ru compounds by cyclic alkenes. Several themes may be discerned: one is the migration of $SiMe_3$ groups from ruthenium to the carbocyclic system. Thus, cycloheptatriene gives rise either to a compound in which a trimethylsilylcycloheptatrienyl ring bridges two ruthenium atoms (entry 102) or to one in which a trimethylsilylcycloheptadiene ring is attached to a single ruthenium atom (entry 103). Also, cyclooctatetraene can form a derivative with a $C_8H_8SiMe_3$ ring linked to ruthenium (entry 114): these migrations are believed to be intramolecular. Analogous reactions take place with the cyclic precursor (**XXI**) (entries 109 and 110).



(XXI)

(69)

Another general theme is that of dehydrogenation. The simplest examples are those of entries 111 and 112, in which cyclopentadienyl and cycloheptadienyl complexes are produced from C_5H_6 and C_7H_{10} respectively. With larger rings as starting materials, however, transannular dehydrogenative ring closure can occur to produce (presumably) $HSiMe_3$ and derivatives of pentalene (C_8H_6) or tetrahydropentalene (C_8H_{10}); in the former case, some ring substitution by Me_3Si groups is possible (entry 108). The bicyclic ring systems may be attached to one (entries 104, 106, 107), two (entry 114), or two out of a cluster of three ruthenium atoms (entries 108, 113) [see also (*280*) and entry 125]. The structures of some of these interesting compounds are discussed further in Section IV,A.

9. *Metal-Exchange Processes*

Both cleavage and re-formation of silicon–metal bonds occur in the transmetallation reactions shown in Table XI; some analogous reactions of Ge–metal and Sn–metal derivatives are shown for comparison (entries 4 and 5).

While silyl metal carbonyl derivatives are unreactive towards neutral metal carbonyls (*7*), metal carbonyl anions give rise to various displacement processes (entries 1–3). The order of displacing ability seems generally similar to that noted earlier for nucleophilicities (Section II,A,1):

$$Fe(CO)_2(Cp)^- \sim Re(CO)_5^- > Mn(CO)_5^- > Co(CO)_4^-$$

$$Mn(CO)_5^- > MH_3Fe(CO)_4^- \qquad (M = Si,Ge)$$

$$Fe(CO)_2(Cp)^- > W(CO)_3(Cp)^-$$

Processes of this kind have some synthetic utility, since they permit exchange of silicon-containing groups from the readily prepared Si–Co compounds to other metal centres. The partial exchange of groups on silanediyl derivatives also provides a route to mixed-metal systems:

$$H_2Si(ML_n)_2 + M'L_m^- \rightarrow H_2Si(ML_n)(M'L_m) + ML_n^- \qquad (70)$$

TABLE XI

METAL EXCHANGE PROCESSES

Entry	Reaction	Ref.
1	$H_3SiCo(CO)_4 + Mn(CO)_5^- \rightarrow H_3SiMn(CO)_5 + Co(CO)_4^-$	(*7*)
	$H_3SiMn(CO)_5 + Co(CO)_4^- \rightarrow$ no reaction	(*7*)
2	$(H_3Si)_2Fe(CO)_4 + Mn(CO)_5^- \rightarrow H_3SiMn(CO)_5 + SiH_2Fe(CO)_4^-$	(*429*)
3	$ClMe_2SiSiMe_2W(CO)_3(Cp) + 2Fe(CO)_2(Cp)^- \rightarrow [(Cp)(CO)_2FeSiMe_2]_2 + Cl^- + W(CO)_3(Cp)^-$	(*305*)
4	$R_3GeCo(CO)_4 + Mn(CO)_5^- \rightarrow R_3GeMn(CO)_5 + Co(CO)_4^-$ $(R_3 = Me_nH_{3-n}; n = 0-2)$	(*189*)
	$2H_3GeCo(CO)_4 + Fe(CO)_4^{2-} \rightarrow (H_3Ge)_2Fe(CO)_4 + 2Co(CO)_4^-$	(*189*)
	$(H_3Ge)_2Fe(CO)_4 + Mn(CO)_5^- \rightarrow H_3GeFe(CO)_4^- + H_3GeMn(CO)_5$	(*189*)
5	$Ph_3SnCo(CO)_4 + ML_n^- \rightarrow Ph_3SnMl_n + Co(CO)_4^-$ $[ML_n^- = Mn(CO)_5^-, Re(CO)_5^-, Fe(CO)_2(Cp)^-]$	(*333*)
	$Ph_3SnMn(CO)_5 + Fe(CO)_2(Cp)^- \rightarrow Ph_3SnFe(CO)_2(Cp) + Mn(CO)_5^-$	(*333*)
	$Ph_3SnRe(CO)_5 + Fe(CO)_2(Cp)^- \rightarrow$ no reaction	(*333*)

C. LIGAND EXCHANGE AT SILICON

This process, shown as mode 2 in Fig. 2, involves the production and reaction of functionally substituted silyl and silanediyl species. Since this occurs while the silicon–metal bond remains intact, it is not surprising that most of the entries in Table XII relate to compounds with robust Si–Mn and Si–Fe bonds; other examples involve bonds to Cr, Mo, W, Re, Pt, and even Co. The types of exchange reaction observed will be dealt with in turn.

1. *Hydrogen–Halogen Exchange* (*Entries* 1, 2, 5–9, 12, 14, 18, 19, 24, 28, 36, 37)

This is typically effected by (1) complex fluorides, such as $AgBF_4$, Ph_3CBF_4, $AgPF_6$, or $AgSbF_6$, or (2) halogenated hydrocarbons such as CCl_4, $CHCl_3$, or CBr_4. In most cases the reactions proceed at a convenient rate at room temperature, but irradiation may be needed when reagents in category (2) are used: radical processes are probably then involved. In these cases it has been noted that reaction becomes easier as the value of the Si–H infrared stretching frequency decreases (*307*). Two typical reactions are shown below (entries 1 and 6).

$$HMe_2SiCr(CO)_3(Cp) + AgBF_4 \rightarrow FMe_2SiCr(CO)_3(Cp) + Ag + BF_3 + \tfrac{1}{2}H_2 \qquad (71)$$

$$H_3SiMn(CO)_5 + n\,CDCl_3 \xrightarrow{h\nu} H_{3-n}Cl_nSiMn(CO)_5 + n\,CHDCl_2 \qquad (n = 1\text{–}3) \qquad (72)$$

Reaction (72) proceeds sequentially to form mono-, di-, and trisubstituted products, and can conveniently be followed by ^1H-NMR spectroscopy (Fig. 3).

Other reagents useful in special cases are PCl_5 (entry 14) and heated HCl (entry 5); in the latter case, hydrogen is evolved.

$$H_3SiMn(CO)_5 + n\,HCl \xrightarrow{75°C} H_{3-n}Cl_nSiMn(CO)_5 + n\,H_2 \qquad (n = 1\text{–}3) \qquad (73)$$

2. *Halogen–Halogen Exchange* (*Entries* 1, 3, 10, 20, 23, 27–29, 38, 40)

Chlorine or bromine attached to silicon can readily be exchanged for fluorine by such reagents as $AgBF_4$, $HF+BF_3$, or $AgPF_6$, as in entry 10:

$$ClR_2SiMn(CO)_5 + AgBF_4 \rightarrow FR_2SiMn(CO)_5 + AgCl + BF_3 \qquad (74)$$

This particular reaction was first carried out in the hope that it would lead via Cl^- abstraction to a cationic species (**XXII**), as shown in reaction (75); this may be regarded as either a substituted silicenium

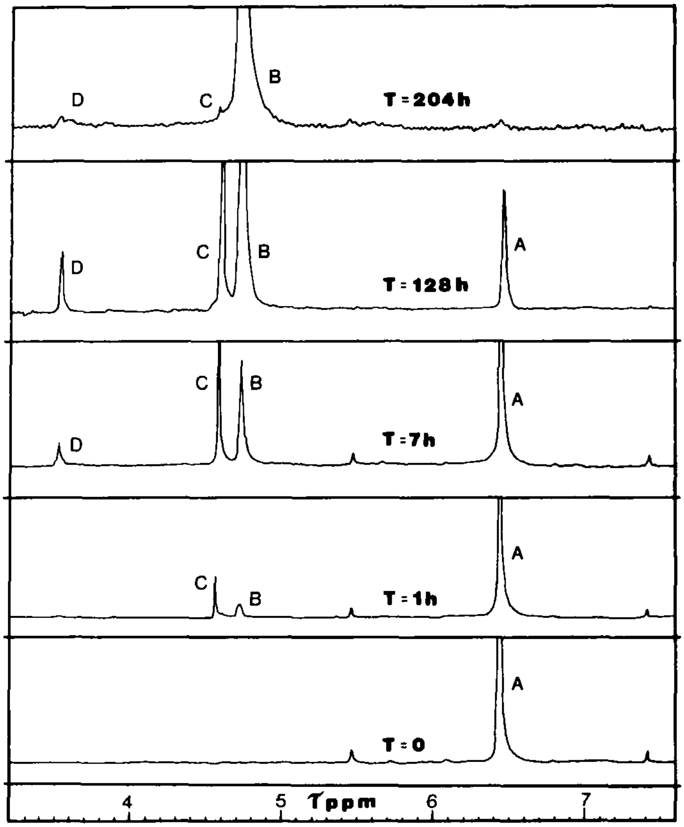


FIG. 3. NMR (^{1}H) spectra of ligand exchange between $H_3SiMn(CO)_5$ and $CDCl_3$. Key: A, $H_3SiMn(CO)_5$; B, $CHDCl_2$; C, $ClH_2SiMn(CO)_5$; D, $Cl_2HSiMn(CO)_5$.

ion (SiR_3^+) or as a metal-stabilized silylene fragment ($M^+ \leftarrow SiR_2$), analogous to known metal–carbene complexes.

$$ClR_2SiMn(CO)_5 + AgBF_4 \nrightarrow \underset{\text{(XXII)}}{[R_2SiMn(CO)_5]^+BF_4^-} + AgCl \qquad (75)$$

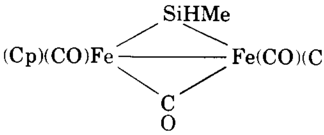
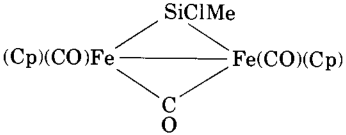
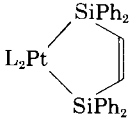
However, no evidence for the compound (**XXII**) was obtained, even as a transient intermediate. Evidently the cation is a stronger Lewis acid (for F^-) than BF_3, and the reaction proceeds as shown in Eq. (74).

It seems likely that iodine attached to silicon might be replaced by chlorine with the aid of reagents such as AgCl or $PbCl_2$, but no such reactions have been reported. The replacement of chlorine by azide, cyanate, or thiocyanate groups does proceed readily, however (entry 35).

TABLE XII

LIGAND EXCHANGE AT SILICON

Entry	Reactants	Products	Ref.
1	$X_3SiCr(CO)_3(Cp)/AgBF_4$ (also AgF, $BF_3 \cdot OEt_2$) ($X_3 = Cl_xMe_{3-x}$ (x = 1–3), HMe_2, HCl_2)	$X'_3SiCr(CO)_3(Cp)^a$ [$X'_3 = F_xMe_{3-x}$, FMe_2, F_3 (via HF_2)]	*(304)*
2	$HR_2SiCr(CO)_3(Cp)/CX_4$ (X = Cl, Br)	$XR_2SiCr(CO)_3(Cp)^a$	*(307)*
3	$(CH_2{=}CH)X_2SiMo(CO)_3(Cp)/AgBF_4$ or (HF + BF_3)	$F_3SiMo(CO)_3(Cp)^b$	*(308)*
4	$(CH_2{=}CH)X_2SiMo(CO)_3(Cp)/HBr$	$(BrCH_2CH_2)X_2SiMo(CO)_3(Cp)^b$	*(308)*
5	$H_3SiMn(CO)_5/HCl/75°C$	$H_{3-n}Cl_nSiMn(CO)_5$ (n = 1–3)	*(28, 30, 83)*
6	$H_3SiMn(CO)_5/CDCl_3/25°C$	$H_{3-n}Cl_nSiMn(CO)_5$ (n = 1–3)	*(28, 30, 83)*
7	$H_2Si[Mn(CO)_5]_2/Ph_3CBF_4/CH_2Cl_2$	$F_2Si[Mn(CO)_5]_2\ ^c$	*(32)*
8	$H_2Si[Mn(CO)_5]_2/CDCl_3/h\nu$	$Cl_2Si[Mn(CO)_5]_2\ ^c$	*(32)*
9	$H_2Si[Mn(CO)_5]_2/CBr_4/h\nu$	$Br_2Si[Mn(CO)_5]_2$	*(32)*
10	$XR_2SiMn(CO)_5/AgBF_4$ (X = Cl, Br)	$FR_2SiMn(CO)_5$	*(314)*
11	$Cl_{3-n}Ph_nSiMn(CO)_5/LiC_6F_5$/ether ($n$ = 0–2)	$(C_6F_5)_{3-n}Ph_nSiMn(CO)_5$	*(107)*
12	$HX_2SiMn(CO)_5/CX'_4$ ($X_2 = Me_2$, MeCl, Cl_2; X′ = Cl, Br)	$X'X_2SiMn(CO)_5$	*(307)*
13	$ClR_2SiMnH(CO)_2(Cp')^d/LiAlH_4$	$HR_2SiMnH(CO)_2(Cp')$	*(119)*
14	$HR_2SiMnH(CO)_2(Cp')^d/PCl_5$	$ClR_2SiMnH(CO)_2(Cp')$	*(119)*
15	$(MeO)R_2SiMnH(CO)_2(Cp')^d/BF_3$	$FR_2SiMnH(CO)_2(Cp')$	*(119)*
16	$[ClR_2SiMn(CO)_2(Cp')]^-M^{+\ d}/LiR'$	$[R'R_2SiMn(CO)_2(Cp')]^-M^+$	*(119)*
17	$[ClR_2SiMn(CO)_2(Cp')]^-M^{+\ d}/LiAlH_4$	$[HR_2SiMn(CO)_2(Cp')]^-M^+$	*(119)*
18	$HMe_2SiFe(CO)_2(Cp)/CCl_4/25°C$	$ClMe_2SiFe(CO)_2(Cp)$	*(272)*
19	$H_2Si[Fe(CO)_2(Cp)]_2/CDCl_3$	$Cl_2Si[Fe(CO)_2(Cp)]_2$	*(32)*
20	$XMe_2SiSiMe_2Fe(CO)_2(Cp)/AgBF_4$ (X = Cl, Br)	$FMe_2SiSiMe_2Fe(CO)_2(Cp)^e$	*(305)*
21	$Cl_3SiFe(CO)_2(Cp)/ROH$ or ROH/RO^-	$(RO)_{3-n}Cl_nSiFe(CO)_2(Cp)$ (n = 0–2)	*(236)*
22	$(RO)_3SiFe(CO)_2(Cp)/HPF_6$	$(RO)_{3-n}F_nSiFe(CO)_2(Cp)$ (n = 1–3)	*(316, 317)*
23	$Cl_3SiFe(CO)_2(Cp)/AgBF_4\ ^f$	$F_3SiFe(CO)_2(Cp)$	*(316, 317)*
24	$HX_2SiFe(CO)_2(Cp)/CX'_4$ ($X_2 = Me_2$, MeCl, Cl_2; X′ = Cl, Br)	$X'X_2SiFe(CO)_2(Cp)$	*(307)*
25	$Cl_3SiFe(CO)_2(Cp)/LiC_6F_5$	$(C_6F_5)_3SiFe(CO)_2(Cp)$	*(107)*

26	$Cl_3SiFe(CO)_2(Cp)/NHR^1R^2$	$(R^1R^2N)_nCl_{3-n}SiFe(CO)_2(Cp)$ [$R^1 = R^2 = Me$, $n = 2$; Et, $n = 1$; i-Pr, $n = 0$. $R^1 = H$; $R^2 = n$-Bu or i-Bu, $n = 3$; s-Bu, $n = 2$; t-Bu, $n = 1$.]	(*238*)
27	$Cl_nMe_{3-n}SiFe(CO)_2(Cp)/AgBF_4$	$F_nMe_{3-n}SiFe(CO)_2(Cp)$	(*304*)
28	$HCl_2SiFe(CO)_2(Cp)/AgBF_4$	$F_3SiFe(CO)_2(Cp)$[g,h]	(*304*)
29	$(CH_2{=}CH)Cl_2SiFe(CO)_2(Cp)/AgBF_4$ or $(HF + BF_3)$	$F_3SiFe(CO)_2(Cp)$[i]	(*308*)
30	$(CH_2{=}CH)Cl_2SiFe(CO)_2(Cp)/HBr$	$(BrCH_2CH_2)Cl_2SiFe(CO)_2(Cp)$	(*308*)
31	$(MeO)_3SiFe(CO)_2(Cp)/HBr$	$Br_2(MeO)SiFe(CO)_2(Cp)$	(*237*)
32	$(RHN)_3SiFe(CO)_2(Cp)/HCl$ or HBr	$X_3SiFe(CO)_2(Cp)$ (X = Cl, Br)	(*237*)
33	$(RHN)_3SiFe(CO)_2(Cp)/MeI$	$I(RHN)_2SiFe(CO)_2(Cp)$	(*237*)
34	$Cl_3SiFe(CO)_2(Cp)/LiAlH_4$	$H_3SiFe(CO)_2(Cp)$	(*237*)
35	$Cl_3SiFe(CO)_2(Cp)/M^+X^-$ ($X^- = N_3^-$, OCN^-, SCN^-)	$X_3SiFe(CO)_2(Cp)$	(*237*)
36	/CCl_4		(*309*)
37	$HRSi[Fe(CO)_2(Cp)]_2/CCl_4$	$ClRSi[Fe(CO)_2(Cp)]_2$	(*309*)
38	$ClRSi[Fe(CO)_2(Cp)]_2/AgBF_4$	$FRSi[Fe(CO)_2(Cp)]_2$	(*309*)
39	$PhMe_2SiFe(CO)_2(Cp)/Cr(CO)_6/\Delta$	$[(OC)_3Cr\text{-}\eta^6\text{-}C_6H_5]Me_2SiFe(CO)_2(Cp)$[j]	(*311*)
40	$Cl_3SiCo(CO)_4/AgBF_4$, $AgPF_6$	$F_3SiCo(CO)_4$	(*316*)
41	$(HPh_2Si)_2PtL_2/C_2H_2/60°C$ ($L = PPhMe_2$)		(*159*)
42	*trans*-$ClH_2SiPtClL_2/NHMe_2$ ($L = PEt_3$)	*trans*-$(Me_2N)H_2SiPtClL_2$	(*58*)

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[a] Also Mo, W analogs.

[b] Also W analogs.

[c] Also Re analogs.

[d] $R_2 = Ph(1\text{-naphthyl})$; $Cp' = \eta^5\text{-}CH_3C_5H_4$.

[e] Similarly with $M(CO)_3(Cp)$ derivatives (M = Cr, Mo, W).

[f] Also works with $AgSbF_6$, $AgPF_6$.

[g] H/F exchange also with AgF, $BF_3 \cdot OEt_2$.

[h] Via $HF_2SiFe(CO)_2(Cp)$ intermediate.

[i] Via $(CH_2{=}CH)F_2SiFe(CO)_2(Cp)$ intermediate.

[j] A similar cobalt derivative is prepared from $[(OC)_3Cr\text{-}\eta^6\text{-}C_6H_5]Me_2SiH$ and $Co_2(CO)_8$.

3. *Other Exchange Reactions*

a. Alkenyl–halogen exchange (Entries 3 *and* 29). The fluorinating agents $AgBF_4$ and $HF+BF_3$ can displace alkenyl groups from silicon attached to fluorine and a transition-metal group.

b. Halogen–alkyl (aryl) exchange (Entries 11, 16, *and* 25). Here, organolithium reagents are used to replace chlorine attached to silicon by fluoroaryl or other organo groups. Attempts to extend the reaction in entry 25 to the compounds $Cl_{3-n}Ph_nSiFe(CO)_2(Cp)$ (n = 1,2) led to cleavage of the Si–Fe bond.

c. Halogen–hydrogen exchange (Entries 13, 17, *and* 34). In certain cases where strong Si–metal bonds are present, $LiAlH_4$ can be used successfully to convert Cl–Si–M into H–Si–M units. This exchange is the reverse of that discussed in Section III,C,1.

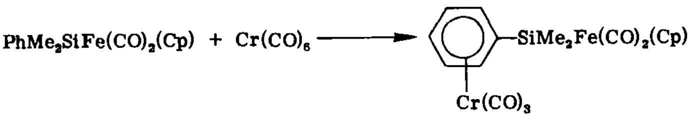
d. Alkoxy–halogen exchange (Entries 15, 22, *and* 31). This can be brought about by BF_3, HPF_6, or HBr, and may be incomplete, as in the last example.

e. Halogen–alkoxy exchange (Entry 21). When alcohols are used, exchange of chlorine is only partial, but addition of alkoxide anions leads to complete replacement.

f. Amino–halogen exchange (Entries 32 *and* 33). Hydrogen halides and even methyl iodide will cleave Si–N bonds in metal–Si–N systems to give metal–Si–halogen species.

g. Halogen–amino exchange (Entries 26 *and* 42). Steric effects are very noticeable in the former entry; this is a general characteristic of Si–N bond formation from Si–Cl compounds and amines (*21*). As with the reverse process in (f) above, the reaction is driven toward completion by the formation of amine salts.

A few other miscellaneous reactions may be noted. Vinylsilicon–metal compounds in entries 4 and 30 undergo addition of HBr in an anti-Markownikoff sense to give 2-bromoethyl derivatives; in some other related systems, HBr induces cleavage (see Section III,B,2). Also, the phenyl group in a phenyl–silicon–metal compound can undergo hexahapto interaction with a $Cr(CO)_3$ group (entry 39).



(76)

Finally, the effect of the reaction in entry 41 is to replace hydrogen at silicon by an alkenyl group.

In several other cases, compounds have been synthesized that contain potentially reactive groups attached to silicon, although their functionality has not yet been exploited. These include the methylchlorosilyl cobalt derivatives $Cl_nMe_{3-n}SiCo(CO)_4$ ($n = 1,2$) (*215*) and platinum complexes such as *trans*-$(Et_3P)_2Pt(X)SiH_2P(SiH_3)_2$ (*168*) (cf. Table VI, entries 8–10).

D. Adducts with Lewis Bases at Silicon

There are many instances of the formation of simple adducts between silicon–transition-metal compounds and Lewis bases (Table XIII), corresponding to mode 3 in Fig. 2. Compounds with SiH_3 groups react particularly readily, in the same way that iodosilane has long been known to form adducts such as $H_3SiI \cdot nNMe_3$ ($n = 1,2$) (*36, 40, 84*).

Other possibilities include compounds with Me_3Si, Me_5Si_2, and F_3Si groups, although in the last case the reaction may be complicated by simultaneous disproportionation leading to formation of $SiF_4 \cdot 2B$, where B is a Lewis base (entry 31). The Cl_3Si derivative in entry 26 does not form adducts with nitrogen or phosphorus bases, although phosphines cause slow elimination of CO (cf. Section III,E,1).

$$Cl_3SiCo(CO)_4 + PMe_3 \xrightarrow{\text{slow}} Cl_3SiCo(CO)_3(PMe_3) + CO \qquad (77)$$

Rhenium derivatives (entries 10–12) are much less ready to form adducts than their manganese analogs (entries 6, 7, 9). Thus, the adducts in entry 10 dissociate completely at room temperature.

$$H_3SiRe(CO)_5 \cdot 2NMe_3 \underset{-23^\circ C}{\overset{25^\circ C}{\rightleftharpoons}} H_3SiRe(CO)_5 + 2NMe_3 \qquad (78)$$

The diiron compound in entry 21 is also unreactive.

Tertiary amines and phosphines have received the most attention, but the use of the strong base $Me_3P{=}CH_2$ should be noted, e.g. (entry 19),

$$R_3SiFe(CO)_2(Cp) + Me_3P{=}CH_2 \rightarrow (Me_3PCH_2SiR_3)[Fe(CO)_2(Cp)] \qquad (79)$$

The methyl(trimethylsilyl)phosphines $PMe_n(SiMe_3)_{3-n}$ decrease in base strength as n decreases, until finally $P(SiMe_3)_3$ does not react at all (entries 28, 29).

TABLE XIII

ADDUCTS OF SILICON–TRANSITION-METAL COMPOUNDS WITH LEWIS BASES

Entry	Silicon compound	Lewis base, B[a]	Combining ratio	Ref.
1	$H_3SiV(CO)_6$	NMe_3, py	1:2	(*8, 121*)
2	$H_3SiCr(CO)_3(Cp)$[b]	NMe_3	1:1	(*214*)
3	$H_3SiCr(CO)_3(Cp)$[b]	$NHMe_2$	1:1.3	(*214*)
4	$R_3SiMo(CO)_3(Cp)$ ($R_3 = F_3$[c]; MeF_2[d])	$Me_3P{=}CH_2$	1:1	(*303*)
5	$Me_5Si_2Mo(CO)_3(Cp)$[c]	$Me_3P{=}CH_2$	1:1	(*305*)
6	$H_3SiMn(CO)_5$	NMe_3, py	1:2	(*27, 31*)
7	$H_3SiMn(CO)_5$	bipy	1:1	(*31*)
8	$Me_3SiMn(CO)_5$	NMe_3	1:1	(*62a*)
9	$H_2Si[Mn(CO)_5]_2$	py	1:4	(*32*)
10	$H_3SiRe(CO)_5$	NMe_3, py	1:2 (at −23°C)	(*7*)
11	$H_3SiRe(CO)_5$	bipy	[e]	(*7*)
12	$H_2Si[Re(CO)_5]_2$	py	[e]	(*32*)
13	$(H_3Si)_2Fe(CO)_4$	NMe_3, py	1:2	(*38, 39, 80*)
14	$(H_3Si)_2Fe(CO)_4$	bipy	1:1	(*38, 39, 80*)
15	$H_3SiFeH(CO)_4$	NMe_3, py	1:2	(*80*)
16	$H_3SiFeH(CO)_4$	bipy	1:1	(*80*)
17	$R_3SiFeH(CO)_4$ (R = Cl, Ph)	NEt_3	$NHEt_3^+[R_3SiFe(CO)_4]^-$ [f]	(*261*)
18	$(Cl_3Si)_2Fe(CO)_4$	NMe_3, MeCN	$(Cl_3Si \cdot nB)^+[Cl_3SiFe(CO)_4]^-$ (see text)	(*261*)

19	$R_3SiFe(CO)_2(Cp)$ $[R_3 = Me_xF_{3-x}\ (x = 0\text{–}2);\ H_3;\ (CH_2{=}CH)F_2]$	$Me_3P{=}CH_2$	1:1	(*303*)
20	$Me_5Si_2Fe(CO)_2(Cp)$	$Me_3P{=}CH_2$	1:1	(*305*)
21	$H_2Si[Fe(CO)_2(Cp)]_2$	py	[e]	(*32*)
22	$H_3SiCo(CO)_4$	NMe_3, py	1:2	(*27, 31*)
23	$H_3SiCo(CO)_4$	bipy	1:1	(*31*)
24	$Me_3SiCo(CO)_4$	NMe_3, PMe_3, PEt_3	1:1	(*44, 298*)
25	$Et_3SiCo(CO)_4$	PEt_3	1:1	(*44, 298*)
26	$Cl_3SiCo(CO)_4$	NMe_3, PMe_3	[g]	(*44, 298*)
27	$Me_3SiCo(CO)_4$	$NHMe_2$	1:1[h]	(*233*)
28	$Me_3SiCo(CO)_4$	$PMe_x(SiMe_3)_{3-x}\ (x = 1\text{–}3)$	1:1	(*298, 387*)
29	$Me_3SiCo(CO)_4$	$P(SiMe_3)_3$	[e]	(*298, 387*)
30	$H_3SiCo(CO)_4$	PMe_3	1:1	(*298, 387*)
31	$F_3SiCo(CO)_4$	NMe_3, py	1:2 (approx)[i]	(*34*)
32	*trans*-$H_2XSiPtCl(PEt_3)_2$	NMe_3	1:1	(*58*)

[a] py = pyridine; bipy = 2,2′-bipyridyl.

[b] Mo and W similar.

[c] W similar.

[d] Cr similar.

[e] No interaction.

[f] A similar adduct, $NHEt_3^+[Cl_3SiMn(CO)_2(Cp)]^-$, is formed from $Cl_3SiMnH(CO)_2(Cp)$ and NEt_3.

[g] No adduct formed; slow CO substitution may occur.

[h] The same adduct, $Me_3SiNHMe_2^+Co(CO)_4^-$, is also formed from Me_3SiNMe_2 and $HCo(CO)_4$; an excess of $NHMe_2$ leads to Si–Co bond cleavage.

[i] Some $SiF_4 \cdot 2B$ and $F_2Si[Co(CO)_4]_2$ are also formed.

Infrared spectral studies of a number of these systems have shown that adduct formation is accompanied by a fall in the carbonyl stretching frequency to a value close to that associated with the corresponding metal carbonylate anion (Table XIV). Thus bands assigned to the carbonyl stretching frequencies ν(CO) in $H_3SiCo(CO)_4$ occur between 2105 and 2025 cm^{-1}; in the adduct $H_3SiCo(CO)_4 \cdot 2NMe_3$ there is only one broad strong band at 1882 cm^{-1}, close to those observed with $Co(CO)_4^-$ at 1883 and 1861 cm^{-1}. The adduct is therefore formulated as $[H_3Si \cdot 2NMe_3]^+[Co(CO)_4]^-$. Indeed, it is believed that in all the cases shown in Table XIII except entry 17, the Lewis base molecules are

TABLE XIV

CARBONYL STRETCHING FREQUENCIES, ν(CO), OF ADDUCTS

Entry	Compound	ν(CO), cm^{-1} [a]	Ref.
1	$H_3SiMn(CO)_5$(g)	2107, 2023, 2020	*(31)*
2	$Mn(CO)_5^-$ (soln)[b]	1898, 1864	*(31)*
3	$H_3SiMn(CO)_5 \cdot 2NMe_3$(s)	1860	*(27, 31)*
4	$H_3SiMn(CO)_5 \cdot 2py$(s)	1860	*(27, 31)*
5	$H_3SiMn(CO)_5 \cdot bipy$(s)	1850	*(31)*
6	$H_2Si[Mn(CO)_5]_2$(soln)[c]	2086, 2012, 1990	*(32)*
7	$H_2Si[Mn(CO)_5]_2 \cdot 4py$(soln)[d]	1900, 1865	*(32)*
8	$H_3SiRe(CO)_5$(g)	2110, 2028, 2018	*(7)*
9	$Re(CO)_5^-$(soln)[b]	1850	*(7)*
10	$H_3SiRe(CO)_5 \cdot 2NMe_3$(s)[e]	1990, 1970, 1900	*(7)*
11	$H_3SiRe(CO)_5 \cdot 2py$(s)[e]	1990, 1890	*(7)*
12	$(H_3Si)_2Fe(CO)_4$(g)	2092, 2040, 2021	*(39)*
13	$Fe(CO)_4^{2-}$(soln)[b]	1786	*(39)*
14	$FeH(CO)_4^-$(soln)[b]	1897	*(39)*
15	$(H_3Si)_2Fe(CO)_4 \cdot 2NMe_3$(s)	1917, 1868	*(39)*
16	$(H_3Si)_2Fe(CO)_4 \cdot 2py$(s)	1900, 1880	*(80)*
17	$(H_3Si)_2Fe(CO)_4 \cdot bipy$(s)	1875	*(80)*
18	$H_3SiFeH(CO)_4$(g)	2107, 2050, 2044, 2036	*(39)*
19	$H_3SiFeH(CO)_4 \cdot 2NMe_3$(s)	1920, 1863	*(80)*
20	$H_3SiFeH(CO)_4 \cdot 2py$(s)	1895, 1880	*(80)*
21	$H_3SiFeH(CO)_4 \cdot bipy$(s)	1890	*(80)*
22	$H_3SiCo(CO)_4$(g)	2105, 2050, 2025	*(31)*
23	$Co(CO)_4^-$(soln)[b]	1883, 1861	*(31)*
24	$H_3SiCo(CO)_4 \cdot 2NMe_3$(s)	1870	*(27, 31)*
25	$H_3SiCo(CO)_4 \cdot 2py$(s)	1882	*(27, 31)*
26	$H_3SiCo(CO)_4 \cdot bipy$(s)	1870	*(31)*

[a] Only chief bands given.

[b] Sodium salt in tetrahydrofuran.

[c] In cyclohexane.

[d] In pyridine.

[e] Cooled below −40°C.

attached to silicon, with consequent charge separation, i.e.,

$$R_3SiML_m + nB \rightarrow (R_3Si \cdot nB)^+ML_m^- \qquad (n = 1,2) \qquad (80)$$

In the case of silanediyl derivatives, both metal fragments can be lost as anions, e.g. (entry 9),

$$H_2Si[Mn(CO)_5]_2 + 4NC_5H_5 \rightarrow (H_2Si \cdot 4NC_5H_5)^{2+}[Mn(CO)_5]_2^- \qquad (81)$$

The reluctance of derivatives of $Re(CO)_5$ and $Fe(CO)_2(Cp)$ in entries 10–12 and 21 to form adducts can now be readily understood, since these are known to be poor leaving groups as anions. This is, of course, related to their high nucleophilicity, already referred to in Section II,A,1.

This picture of adduct formation is confirmed by an X-ray diffraction study of the adduct $Me_3SiCo(CO)_4 \cdot PMe_2(SiMe_3)$ (*387*). This consists of clearly separated $[Me_2P(SiMe_3)_2]^+$ cations and tetrahedral $Co(CO)_4^-$ anions. Further support comes from ^{1}H-NMR measurements, outlined in Table XV, although these are restricted because of the low solubility of the adducts in most nonreacting solvents. It can be seen that on adduct formation (entries 2 → 3 and 4 → 5) there is a marked decrease in chemical shift and increase in ^{29}Si–H coupling constant. The first effect is related to the deshielding associated with formation of singly or doubly charged cations. It may also be noted that the small change in the value of τ on passing from entry 6 to 7 is consistent with the known

TABLE XV

SPECTROSCOPIC DATA FOR ADDUCTS OF Si–Mn AND Si–Re COMPOUNDS

Entry	Compound	τ(Si–H)	J(^{29}Si–H) (Hz)	ν_{as}(Si–H) (cm^{-1})	Ref.
1	SiH_4	6.80[a]	202[a]	2180[b]	(*22*)
2	$H_3SiMn(CO)_5$	6.41[a]	196[a]	2156[b]	(*30*)
3	$(H_3Si \cdot 2py)^+Mn(CO)_5^-$	4.95[c]	274[c]	2205[d]	(*7, 83*)
4	$H_2Si[Mn(CO)_5]_2$	5.96[e]	173[e]	2060[f]	(*32, 121*)
5	$(H_2Si \cdot 4py)^{2+}[Mn(CO)_5]_2^-$	3.65[c]	336[c]	2230[c]	(*32, 121*)
6	$H_3SiRe(CO)_5$	6.70[a]	186[a]	2144[b]	(*7*)
7	$H_3SiRe(CO)_5 \cdot 2NMe_3$	6.48[g]	—	—	(*7*)

[a] TMS solution.

[b] Gas phase.

[c] Pyridine-d_5 solution.

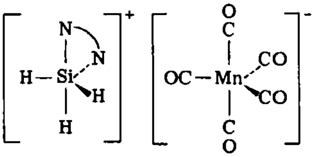
[d] Nujol mull.

[e] Benzene-d_6 solution.

[f] Cyclohexane solution.

[g] Trimethylamine solution at 0°C, adduct largely dissociated.

weakness of the rhenium adduct. Regarding the second effect, the size of the ^{29}Si–H coupling constant is related to the amount of s character in the Si–H bond (*149*), and the observed values show that there is a dramatic increase in s character in passing from entry 1 to 3 to 5. This is consistent with the trend expected for the geometries shown in Fig. 4, although this treatment is undoubtedly oversimplified. Adducts of 2,2′-bipyridyl, for example, will probably favor a structure in which axial–equatorial bridging occurs, e.g. (**XXIII**).



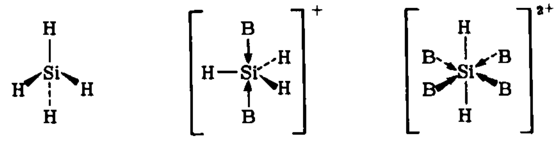
(XXIII)

Values of the Si–H asymmetric stretching frequency ν_{as}(Si–H) also increase on passing from entry 1 to 3 to 5, again consistent with the formation of cations having charges of +1 and +2, and consequent increased ionic character in the Si–H bonds.

The adducts shown in entries 13–16 of Table XIII deserve further attention because there has been some doubt as to their true composition. In the original work (*39*), the trimethylamine adducts were formulated as: $(H_3Si \cdot NMe_3)_2^{2+}Fe(CO)_4^-$ and $(H_3Si \cdot n NMe_3)^+FeH(CO)_4^-$ (where the value of n was not known); values of ν(CO) in these complexes were more appropriate for a singly charged than a doubly charged anion. Soon afterwards, Graham and his co-workers (*261*) showed that some related species underwent proton abstraction on reaction with Lewis bases (Table XIII, entry 17).

$$R_3SiFeH(CO)_4 + NEt_3 \rightarrow NHEt_3^+[R_3SiFe(CO)_4]^- \quad (R = Cl,Ph) \qquad (82)$$

They therefore suggested that $H_3SiFeH(CO)_4$ was likely to react in the same way. However, further examination of a number of related sys-



Hybridization in Si–H bonds	sp^3	sp^2	sp
s Character in Si–H bonds	25%	33%	50%

FIG. 4. Hybridization and bond type in SiH_4, $(SiH_3 \cdot 2B)^+$, and $(SiH_2 \cdot 4B)^{2+}$.

tems (*80*) has shown that (1) the stoichiometry of corresponding adducts of $(H_3Si)_2Fe(CO)_4$ and $H_3SiFeH(CO)_4$ is similar, (2) the values of $\nu(CO)$ all correspond to those expected for singly charged anions (see Table XIV), and (3) the catalytic effect of amine salts on the cleavage of Si–Fe bonds by HCl invalidates the original evidence for symmetrical addition of amine molecules to silyl groups in $(H_3Si)_2Fe(CO)_4$ (*39*). All the evidence is therefore consistent with the formulations shown as (**XXIV**) and (**XXV**).

$$(H_3Si \cdot 2B)^+[H_3SiFe(CO)_4]^- \qquad (H_3Si \cdot 2B)^+[HFe(CO)_4]^-$$

(**XXIV**) (**XXV**)

Similar anionic species $H_3MFe(CO)_4^-$ (M = Si, Ge) have resulted from exchange reactions (cf. Section III,B,9), while the rather weak unsymmetrical interaction of bases with $(Cl_3Si)_2Fe(CO)_4$ gives rise to a related anion (Table XIII, entry 18).

$$(Cl_3Si)_2Fe(CO)_4 + nB \rightarrow (Cl_3Si \cdot nB)^+[Cl_3SiFe(CO)_4]^- \qquad (B = NMe_3, MeCN) \tag{83}$$

In hydrido species, $R_3SiFeH(CO)_4$, the silicon atom is the most electrophilic site when R is H, but the Fe hydrogen atom takes over that role when more electronegative groups are attached to silicon (R = Cl, Ph).

The chemical reactivity of the adducts can be either greater or less than that of the parent silicon–transition-metal compound. For example, $H_3SiMn(CO)_5$ is unreactive towards anhydrous HCl at room temperature, but its adducts ($B = NC_5H_5, NMe_3$) react readily at low temperatures (*30*).

$$H_3SiMn(CO)_5 \cdot 2B + 3HCl \xrightarrow[\text{rapid}]{-80^\circ C} H_3SiCl + HMn(CO)_5 + 2BH^+Cl^- \tag{84}$$

The rhenium analog behaves similarly, being cleaved quickly by protic reagents in the presence of pyridine, although inert in its absence (*7*).

On the other hand, some very reactive silyl–metal compounds can be stabilized if they form strong adducts. The silyl iron derivative $H_3SiFeH(CO)_4$ reacts very rapidly with oxygen, giving a bright flash and producing CO, CO_2, volatile siloxanes, and an off-white or brown powder (*39*). The pyridine adduct $H_3SiFeH(CO)_4 \cdot 2(py)$ gives the same products, but in this case reaction is very slow (*80*). Moreover, $H_3SiCo(CO)_4$ decomposes slowly *in vacuo* at room temperature, while $H_3SiCo(CO)_4 \cdot 2NMe_3$ is unchanged after a year, and reacts only slowly with air (*31*). Attempts were made to stabilize the extremely labile vanadium derivative $H_3SiV(CO)_6$ in the same way by complexing, but without success; the adducts are probably not sufficiently stable towards dissociation (*8*, *121*).

E. SUBSTITUTION OF LIGANDS AT THE TRANSITION METAL

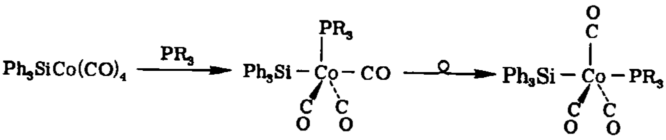
This process, represented as mode 4 in Fig. 2, is exemplified by the reactions in Table XVI. It may be further subdivided according to the nature of the ligands.

1. *Substitution of* CO *Groups*

The most studied reaction involves the replacement of carbonyl groups by tertiary phosphines. This proceeds most readily in the case of cobalt derivatives, manganese compounds must usually be heated, and iron compounds require irradiation (except in the case of entry 13).

The stereochemistry of the final product is normally such that the tertiary phosphine is trans to the silyl group, both in five-coordinate (entries 20–25) or six-coordinate (entries 1 and 5) situations. An obvious exception is the cyclic compound in entry 2, which has no option but to take a cis arrangement. In the case of the six-coordinate complexes $(Cl_3Si)_2Fe(CO)_3(PPh_3)$ and $Cl_3SiRuH(CO)_3(PPh_3)$ (entries 13 and 15), the three carbonyl groups adopt a mer arrangement and again the phosphine is trans to a silyl group.

It had been suggested some years ago (*150*) on the basis of kinetics measurements that substitution of $Ph_3GeMn(CO)_5$ by phosphines led initially to the cis isomer; with bulky phosphines, this then rearranged to the trans species. A similar effect has now been demonstrated for $Ph_3SiCo(CO)_4$ (*227*) (entry 24) by infrared methods: an equatorially substituted compound (**XXVI**) is apparently first formed, and this slowly rearranges to the axially substituted product (**XXVII**).



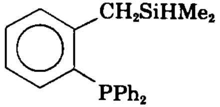
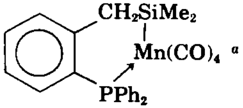
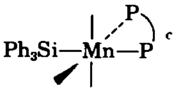
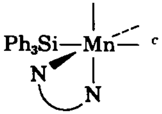
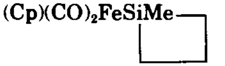
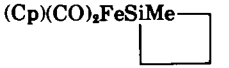
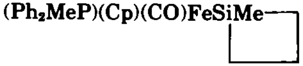
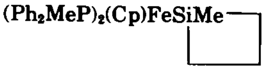
(XXVI) (XXVII)

(85)

This is consistent with variable-temperature ^{13}C-NMR studies on a range of derivatives $R_3ECo(CO)_4$ (E = C, Si, Ge, Sn, Pb; R = F, Cl, Me, Bu, Bz, Ph). These studies showed that the rate of intramolecular rearrangement, leading to exchange of axial and equatorial carbonyl groups, is strongly dependent on steric factors (*296*). Thus isomers with one or two bulky substituents should be quite long-lived.

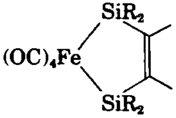
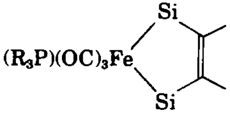
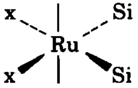
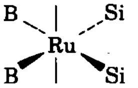
TABLE XVI

SUBSTITUTION OF TRANSITION-METAL LIGANDS

Entry	Reactants	Products	Ref.
A. Carbonyl substitution			
1	$Ph_3SiMn(CO)_5/PPh_3$/decalin/130°C	*trans*-$Ph_3SiMn(CO)_4(PPh_3)$	(*376, 377*)
2	 $/Mn_2(CO)_{10}$/50°C		(*13*)
3	$Ph_3SiMn(CO)_5$/diphos^b	 like (**XV**)	(*377*)
4	$Ph_3SiMn(CO)_5$/bipy^d		(*377*)
5	$F_3SiMn(CO)_5/PPh_3$	*trans*-$F_3SiMn(CO)_4(PPh_3)^e$	(*373*)
6	$Me_3SiFe(CO)_2(Cp)/PR_3/h\nu$	$Me_3SiFe(CO)(Cp)(PR_3)$	(*270*)
7	$Ph_3SiFe(CO)_2(Cp)/PPh_3/h\nu$	$Ph_3SiFe(CO)(Cp)(PPh_3)$	(*123*)
8	$R_3Si^*Fe(CO)_2(Cp)^f/PPh_3/h\nu$	$R_3Si^*Fe(CO)(Cp)(PPh_3)$	(*91, 92*)
9	$R_3Si^*Fe(CO)_2(Cp)^f/P(OEt_3)/h\nu$	$R_3Si^*Fe(CO)(Cp)[P(OEt)_3]$	(*93*)
10	$(Me_5Si_2)CH_2Fe(CO)_2(Cp)/PPh_3/h\nu$	$Me_3SiCH_2SiMe_2Fe(CO)(Cp)(PPh_3)$	(*353*)
11	 $(Cp)(CO)_2FeSiMe$ $/PPh_3/h\nu$	 $(Ph_3P)(Cp)(CO)FeSiMe$	(*136*)
12	 $(Cp)(CO)_2FeSiMe$ $/PMePh_2/h\nu$	 $(Ph_2MeP)(Cp)(CO)FeSiMe$ +  $(Ph_2MeP)_2(Cp)FeSiMe$	(*136*)

(*table continues*)

TABLE XVI (Continued)

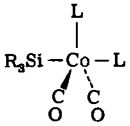
Entry	Reactants	Products	Ref.
13	$(Cl_3Si)_2Fe(CO)_4/PPh_3$/heat (similarly, Ru,[g] Os)	*mer*-$(Cl_3Si)_2Fe(CO)_3(PPh_3)$	(*361*)
14	 $/PR_3/h\nu$		(*124*)
15	$Me_3SiFe(CO)_2(Cp)/RNC/h\nu$ (R = cyclohexyl)	$Me_3SiFe(CO)(Cp)(CNR) + Me_3SiFe(Cp)(CNR)_2$	(*96*)
16	*cis*-$(Cl_3Si)_2Ru(CO)_4/^{13}CO$/25°C	 x = exchange site	(*365*)
17	*trans*-$(Cl_3Si)_2Ru(CO)_4/^{13}CO/h\nu$	cis Isomer as above	(*365*)
18	*cis*-$Cl_3SiRuH(CO)_4/PPh_3$	*mer*-$Cl_3SiRuH(CO)_3(PPh_3)$	(*361*)
19	*cis*-$(Cl_3Si)_2Ru(CO)_4$/diphos,[b] bipy,[d] cyclic polyenes[h]	 [i]	(*364*)
20	$H_3SiCo(CO)_4/PPh_3$[j]	*trans*-$H_3SiCo(CO)_3(PPh_3)$	(*29*)
21	$Cl_3SiCo(CO)_4/PR_3$ (R = Me, Et, F)	*trans*-$Cl_3SiCo(CO)_3(PR_3)$	(*44*)
22	$Me_3SiCo(CO)_4/PPh_3/h\nu$	*trans*-$Me_3SiCo(CO)_3(PPh_3)$	(*44*)
23	$Cl_3SiCo(CO)_4/P(n\text{-}Bu_3)$	*trans*-$Cl_3SiCo(CO)_3[P(n\text{-}Bu)_3]$ (compare Ge, Sn analogs—see text)	(*341*)

24	$Ph_3SiCo(CO)_4/PR_3$	*cis*-$Ph_3SiCo(CO)_3(PR_3)$ → trans isomer	(*227*)
25	$Ph_3SiCo(CO)_4/PMePh_2$	$Ph_3SiCo(CO)_3(PMePh_2)$ + $Ph_3SiCo(CO)_2(PMePh_2)_2$	(*227*)
B. Hydrogen substitution or reaction			
26	$Cl_3SiWH(Cp)_2/CCl_4$	$CHCl_3$ + ?	(*88*)
27	$Cl_3SiMnH(CO)_2(Cp)/CCl_4$	(?)$Cl_3SiMnCl(CO)_2(Cp)$ + $CHCl_3$	(*259*)
28	$Cl_3SiFeH(CO)_4$/isoprene	$Cl_3SiFe(CO)_3[\eta^3\text{-}(CH_2CHCMe_2)]^k$	(*122*)
29	$R_3SiRuH_3(PR_3)_3/D_2$	$R_3SiRuH_{3-x}D_x(PR_3)_3$	(*226*)
30	$R_3SiRuH_3(PR_3)_n/CCl_4$, $CDCl_3$, or I_2 (n = 2, 3)	$R_3SiRuH_2X(PR_3)_n$ (X = Cl or I)	(*226*)
31	$F_3SiCoH_2(PPh_3)_3/CO$	$F_3SiCo(CO)_2(PPh_3)_2$(+ H_2 + PPh_3)	(*17*)
C. Substitution of other ligands			
32	$[Me_3SiRu(CO)_4]_2/X_2$ (X = Br,I)	*trans*-$Me_3SiRuX(CO)_4$	(*19*)
33	*trans*-$Me_3SiRuX(CO)_4/PPh_3/LiAlH_4$	$Me_3SiRuH(CO)_3(PPh_3)$	(*19*)
34	*trans*-$Me_3SiRuX(CO)/M(CO)_5^-$ (M = Mn,Re)	$Me_3SiRu(CO)_4[M(CO)_5]$	(*19*)

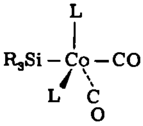
---

[a] Re analogue does not eliminate CO (cf. Table IV, entry 7).
[b] diphos = $Ph_2PCH_2CH_2PPh_2$.
[c] Inferred structure from infrared data.
[d] bipy = 2,2′-bipyridyl.
[e] Re similar.
[f] R_3Si^* = PhMe(1-naphthyl)Si.
[g] Reacts at room temperature.
[h] See also Ref. (*279*).
[i] Bridged derivatives also possibly formed.
[j] Slow reaction.
[k] Via substituted σ-allyl derivative.

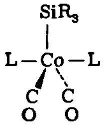
In the case of disubstituted cobalt derivatives, it is believed that representatives of the three isomers (**XXVIII**)–(**XXX**) can be prepared by reaction (86) (entry 25), reaction (87) (entry 31), and reaction 88 (Table IV, entry 33).



(XXVIII)



(XXIX)



(XXX)

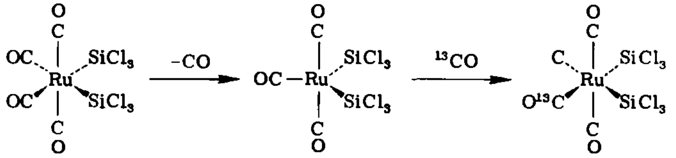
$$\mathrm{Ph_3SiCo(CO)_4 + 2PMePh_2 \rightarrow \underset{\textbf{(XXVIII)}}{Ph_3SiCo(CO)_2(PMePh_2)_2} + 2CO} \qquad (86)$$

$$\mathrm{F_3SiCoH_2(PPh_3)_3 + 2CO \rightarrow \underset{\textbf{(XXIX)}}{F_3SiCo(CO)_2(PPh_3)_2} + H_2 + PPh_3} \qquad (87)$$

$$\mathrm{HCo(CO)_2(PPh_3)_2 + HSiF_3 \rightarrow \underset{\textbf{(XXX)}}{F_3SiCo(CO)_2(PPh_3)_2} + H_2} \qquad (88)$$

These compounds seem stable with respect to isomerization, in accord with the ideas discussed in the previous paragraph.

The cis isomer of $(Cl_3Si)_2Ru(CO)_4$ undergoes easy exchange of the two CO groups trans to silicon (but not the other two) at room temperature (entry 16); the process is thought to be intramolecular, with a five-coordinate intermediate (**XXXI**) in which the nonexchanging carbonyl groups occupy axial positions of the trigonal bipyramid.



(XXXI) (89)

The trans isomer will exchange only under photochemical excitation, and then gives rise to the same products as the cis compound (entry 17). Certain bidentate ligands also react with *cis*-$(Cl_3Si)_2Ru(CO)_4$ to give chelate derivatives of the same stereochemistry (entry 19). Apart from this work, there are few reports about the effect of bidentate ligands in general, although it is interesting that nitrogen and phosphorus donors seem to give different types of derivatives with $Ph_3SiMn(CO)_5$ (entries 3 and 4).

Five other points may be noted. (1) Triethyl phosphite reacts in the same way as a tertiary phosphine in entry 9, although phosphites often behave differently (see Section III,B,4). (2) The monosubstituted iron derivatives in entries 6–12 and 15 have a chiral center at iron. This point is taken up further in Section IV,E. (3) In no case has carbonyl insertion been observed as a concomitant to carbonyl substitution (compare Section III,B,3), even though this process is common for corresponding organo derivatives, as in

$$\mathrm{RMn(CO)_5 + PPh_3 \rightarrow RCOMn(CO)_4(PPh_3)} \tag{90}$$

Indeed, almost the reverse process of C–M bond breaking and Si–M bond formation may be seen in entry 10. (4) Germanium and tin analogs of $Cl_3SiCo(CO)_4$ react with tri-*n*-butylphosphine to give ionic products (*341*), as in

$$\mathrm{Cl_3MCo(CO)_4 + 2P(}n\mathrm{\text{-}Bu)_3 \rightarrow \{Co(CO)_3[P(}n\mathrm{\text{-}Bu)_3]_2\}^+MCl_3^-} \tag{91}$$

where M = Ge or Sn, but there is no indication that the silicon compound can behave in this way (entry 23) (cf. Section II,F). Nor is there any indication that radical chain processes occur with the silicon compound, although there is evidence for them in the reaction between $Cl_3SnCo(CO)_4$ and group V donors (*3*). (5) Isocyanide substitution appears similar to that of tertiary phosphines, but has been little studied (entry 15).

2. *Substitution or Reaction of Hydrogen Ligands*

When the silicon–transition-metal bond is reasonably strong, hydrogen attached to the metal may be replaced (mode 4b in Fig. 2) by halogens (entries 26, 27, and 30) or deuterium (entry 29). In the case of the ruthenium example, halogenation can be followed by reductive elimination of R_3SiH (*226*).

$$\mathrm{R_3SiRuH_2Cl(PR_3)_n \rightarrow R_3SiH + RuHCl(PR_3)_3} \qquad (n = 2, 3) \tag{92}$$

In entry 28 is an example of Fe–H addition to conjugated dienes, while the Si–Fe bond remains intact. With isoprene, the initial product from 1,4-addition is a σ-allyl compound, which then rearranges with loss of CO to a π-allyl derivative. This opens a useful route to other functionally substituted derivatives.

$$\begin{tikzcd}
\mathrm{Cl_3SiFeH(CO)_4 + CH_2{=}C(Me)CH{=}CH_2} \arrow[r] & \mathrm{Cl_3SiFe(CO)_4(CH_2CH{=}CMe_2)} \arrow[d, "-\mathrm{CO}"] \\
 & \mathrm{Cl_3SiFe(CO)_3(\eta^3\text{-}CH_2CHCMe_2)}
\end{tikzcd} \tag{93}$$

Reductive elimination of dihydrogen occurs in entry 31, together with loss of PPh_3, to give the usual five-coordination found for Co(I) derivatives.

3. *Substitution or Addition of Other Ligands*

As yet, there are few examples of this process (mode 4c in Fig. 2), although it offers considerable potential when strong Si–M bonds are present. After the metal–metal bond in $[Me_3SiRu(CO)_4—]_2$ has been replaced by a metal–halogen bond (entry 32), the resulting *trans*-$Me_3SiRuX(CO)_4$ can undergo either reduction (entry 33) or substitution by metal carbonylate groups (entry 34). Under this heading may also be mentioned an example of oxidative addition at the metal center while the metal–silicon bond remains intact (*56, 58*).

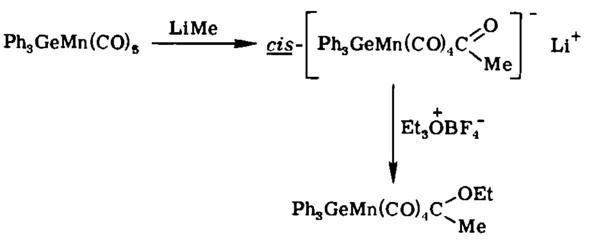
$$\underset{[4]}{\textit{trans}\text{-}IH_2SiPt(II)I(PEt_3)_2} \xrightarrow{HI} \underset{[6]}{IH_2SiPt(IV)HI_2(PEt_3)_2} \qquad (93a)$$

F. Reactions at the Metal Carbonyl Group

These reactions correspond to mode 5 in Fig. 2, and fall into two categories. The first involves the formation of carbene precursors, while the second concerns the migration of silicon from metal to oxygen.

1. *Reactions with Organolithium Derivatives*

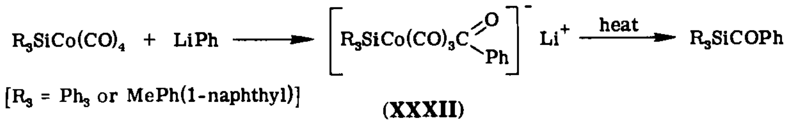
The reaction of transition-metal carbonyls with organolithium compounds to give metal carbene complexes is now well known; it can also take place when the metal is linked to a group IV atom, as in the following series of reactions (*426*).



$$Ph_3GeMn(CO)_5 \xrightarrow{LiMe} \textit{cis}\text{-}\left[Ph_3GeMn(CO)_4C\begin{smallmatrix}\nearrow O\\ \searrow Me\end{smallmatrix}\right]^- Li^+ \xrightarrow{Et_3\overset{+}{O}BF_4^-} Ph_3GeMn(CO)_4C\begin{smallmatrix}\nearrow OEt\\ \searrow Me\end{smallmatrix} \qquad (94)$$

Analogous germanium–molybdenum, germanium–tungsten (*145*), germanium–cobalt (*89*), tin–cobalt, and lead–cobalt (*144*) carbene derivatives are known.

In the case of silicon, addition of phenyllithium occurs quite analogously, and the resulting ionic derivative (**XXXII**) has been isolated as a salt of the $[(Ph_3P)_2N]^+$ cation. On heating, the lithium salt decomposes to give a benzoylsilane (*120*) (cf. Section III,B,7).

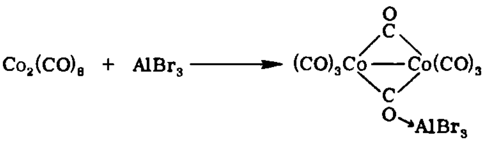


(**XXXII**) (95)

There is no evidence as yet for silyl-substituted carbyne derivatives, analogous to the tin–chromium compound $Ph_3SnCr(CO)_4(\equiv CNEt_2)$ (*184*).

2. *Migration of Silicon from Metal to Oxygen*

It was recognized at an early stage in the development of silicon–transition-metal chemistry that silicon–oxygen compounds often appeared, either as by-products from preparations or as decomposition products on heating or even on storage. At first, adventitious hydrolysis or oxidation was blamed, but it soon became clear that attack on silicon by oxygen of coordinated carbonyl groups was responsible. Since metal carbonyls are known to form adducts with Lewis acids such as compound (**XXXIII**) (*286*),



(**XXXIII**) (96)

while silicon compounds often function as Lewis acids (*23, 24*), this seems very reasonable.

Reference has already been made in Section II,A,3 to the harmful effects of polar solvents, in particular tetrahydrofuran, in the preparation of silicon–transition-metal compounds from a silicon halide and a transition-metal anion (*61, 137, 138, 300, 305, 306, 310, 331, 337*). Frequently, silicon–oxygen rather than silicon–metal compounds result, e.g. (*138, 306, 336*),

$$Mo(CO)_2(Cp)(PPh_3)^- + Ph_3SiCl \xrightarrow[\text{(Ref. }\mathit{138}\text{)}]{\text{THF}} (Ph_3Si)_2O + HMo(CO)_3(Cp)(PPh_3) + \cdots \quad (97)$$

$$W(CO)_3(Cp)^- + Me_3SiBr \xrightarrow[\text{(Ref. }\mathit{306}\text{)}]{\text{THF}} (Me_3Si)_2O + [W(CO)_3(Cp)]_2 + \cdots \quad (98)$$

$$Co(CO)_4^- + MeSiCl_3 \xrightarrow[\text{(Ref. }\mathit{336}\text{)}]{\text{ether}} MeCl_2SiOCCo_3(CO)_9 + \cdots \quad (99)$$

Disiloxanes may be a major product even when the reaction is carried out in nonpolar solvents (*136*) (see Table I, entry 21).

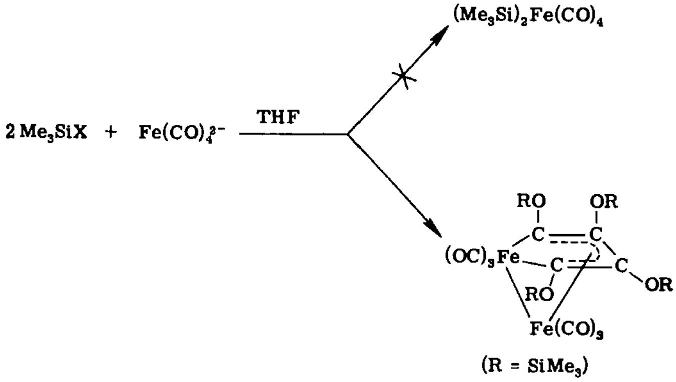
In all such cases, the reaction is seen as an electrophilic attack by the silicon compound on an oxygen atom of a coordinated carbonyl group, leading initially to a Si–O–C–M linkage (*336*). This process will be facilitated by a polar solvent of high dielectric constant, since under these conditions the metal carbonylate group will become more like a free anion (i.e., less ion pairing will occur) and consequently the oxygen atom will carry a greater effective negative charge.

A related effect is that silicon–transition-metal compounds, once formed, undergo Si–M bond cleavage when dissolved in polar solvents (*252, 262, 300, 305, 306, 310*). The products are often complex, but have been shown to include a cluster compound in one case involving cobalt (*252*).

$$Me_3SiCo(CO)_4 \xrightarrow{THF} Me_3SiOCCo_3(CO)_9 + Me_3SiOCH{=}CHCH_2CH_3 + \cdots \qquad (100)$$

The first product of this reaction, which should be compared with Eq. (18) in Section II,A,3, is a derivative of the well-known $—CCo_3(CO)_9$ cluster, with a tetrahedral CCo_3 grouping; the product in Eq. (99) is similar. The second product in Eq. (100) is clearly derived from attachment of tetrahydrofuran to a trimethylsilyl group, followed by rearrangement.

Also, *cis*-$(Me_3Si)_2Fe(CO)_4$ dissolves in tetrahydrofuran to give a red solution that contains Si–O derivatives (*262*). These seem to be different, however, from the product of the reaction between Me_3SiI and $Fe(CO)_4^{2-}$ in the same solvent (*331*) [referred to in Eq. (13) and Table I, entry 22], which is known to be a tetrasiloxy derivative of a ferracyclopentadiene (*54*).



(101)

It seems likely that tetrahydrofuran, acting as a Lewis base toward silicon centers, promotes charge separation and incipient formation of carbonylate anions, just as described in Section III,D. The oxygen atoms in coordinated carbonyl groups are thereby made more nucleophilic, leading to formation of Si–O–C–M links, as discussed above. Consistent with this, $Cl_3SiCo(CO)_4$ is unchanged after a solution of it in tetrahydrofuran has been refluxed; it is also known to be unreactive towards Lewis bases such as NMe_3 (Table XIII, entry 26) and $Co(CO)_4^-$ (*336*).

On heating, a number of silicon–transition-metal compounds give a disiloxane as one of the volatile products [*29,* Eq. (102); *41; 42; 95,* Eq. (103); *215; 306,* Eq. (104)]. For example,

$$H_3SiCo(CO)_4 \xrightarrow{\Delta} H_2 + CO + SiH_4 + (SiH_3)_2O + HCo(CO)_4 + SiH_2[Co(CO)_4]_2 + \cdots \tag{102}$$

$$Et_3SiCo(CO)_4 \xrightarrow{\Delta} (Et_3Si)_2O + \cdots \tag{103}$$

$$Me_3SiMo(CO)_3(Cp) \xrightarrow{\Delta} (Me_3Si)_2O + \cdots \tag{104}$$

An extreme example of this behavior is afforded by $H_3SiV(CO)_6$, which decomposes almost quantitatively at room temperature according to Eq. (105). (*8, 121*).

$$2H_3SiV(CO)_6 \xrightarrow{25^\circ C} (SiH_3)_2O + V(CO)_6 + [V(CO)_5C]_n \tag{105}$$

After removal of volatile products, a yellow vanadium carbonyl carbide remains. In all these cases, it seems likely that there is initial electron donation from oxygen to silicon, followed by Si–M bond cleavage. As supporting evidence, two products from the controlled heating of $Me_3SiCo(CO)_4$ are reasonable intermediates in such a process (*252*).

$$Me_3SiCo(CO)_4 \xrightarrow[50\ h]{105^\circ C} Me_3SiOCCo_3(CO)_9 + (Me_3SiOC)_4Co_2(CO)_4 + \cdots \tag{106}$$

This migration of silicon from metal to oxygen will be discussed further in connexion with silicide formation in Section V,A.

G. Disproportionation, Reductive Elimination, and Other Reactions

1. *Disproportionation about Silicon or Metal*

The disproportionation equilibrium (107) is common among silicon compounds, especially hydrides and fluorides (*22, 24*); the right-hand side is generally favored (R = H, halogen, etc.).

$$2R_3SiX \rightleftarrows R_2SiX_2 + R_4Si \tag{107}$$

Relevant examples include

$$2R_3SiCo(CO)_4 \rightarrow R_4Si + R_2Si[Co(CO)_4]_2 \tag{108}$$

[R = H (Ref. *29*); R = F (Ref. *34*)] and

$$2H_3SiMn(CO)_5 \rightarrow SiH_4 + H_2Si[Mn(CO)_5]_2 \tag{109}$$

(Ref. *30*). Also, $Cl_3SiCo(CO)_4$ yields $SiCl_4$ on heating at 150°C, although the nature of the other products is not known (*42*). These reactions are strongly base-catalyzed (cf. Ref. *35* and Table XIII, entry 31); examples are also known with other group IV elements, e.g. (*341*),

$$Cl_3SnCo(CO)_4 \xrightarrow{THF} SnCl_4 + Cl_2Sn[Co(CO)_4]_2 \tag{110}$$

Disproportionation about the transition metal is much less common: one example involves a silyl iron hydride (*259*).

$$cis\text{-}Cl_3SiFeH(CO)_4 \xrightarrow{\Delta} (Cl_3Si)_2Fe(CO)_4 + \cdots \tag{111}$$

2. *Reductive Elimination of Silicon Hydrides*

It is useful to gather together under this heading a number of reactions of compounds in which an R_3Si group and a hydrogen atom are attached to the same transition-metal center:

$$R_3Si\text{-}M(H)L_m \rightarrow R_3SiH + ML_n \tag{112}$$

These may be described either as a type of Si–M cleavage reaction or as a migration of hydrogen from metal to silicon. Clearly they represent the reverse process to the well-known oxidative addition reaction discussed in Section II,F.

Compounds of the class $R_3SiMnH(CO)_2(Cp)$ have been mentioned already in this connection (*117–119, 225, 259*) (Table X, entries 12, 13, 63, and 87). Reactions with tertiary phosphines, chlorine, methyllithium, or an excess of HCl all lead to elimination of R_3SiH ("de-insertion"), as in

$$R_3SiMnH(CO)_2(Cp) \xrightarrow{PPh_3} R_3SiH + Mn(CO)_2(Cp)(PPh_3) \tag{113}$$

In a related reaction between $R_3SiFe(CO)_2(Cp)$ and $P(OPh)_3$, migration of *ortho*-hydrogen from a phenyl group first provides an iron–hydrogen bond, and this is followed by reductive elimination of R_3SiH (*93*) [Section III,B,4, Eq. (58)].

The *cis*-hydrido compound $Ph_3SiFeH(CO)_4$ eliminates triphenylsilane when either heated alone (*259*) or treated with triphenylphosphine (*355*).

$$\begin{tikzcd}
 & HSiPh_3 + Fe(CO)_5 + Fe_3(CO)_{12} + \cdots \qquad (114) \\
Ph_3SiFeH(CO)_4 \arrow[ur, "\Delta"] \arrow[dr, "PPh_3"'] & \\
 & HSiPh_3 + Fe(CO)_n(PPh_3)_{5-n} \quad (n = 3, 4) \qquad (115)
\end{tikzcd}$$

Silylhydrido derivatives of ruthenium (*226*) and cobalt (*17*) undergo reactions rather similar to that shown in Eq. (115).

$$\begin{tikzcd}
 & HSiR_3 + RuH_2(CO)(PR_3)_3 \qquad (116) \\
\begin{matrix} R_3SiRuH_3(PR_3)_n \\ (n = 2, 3) \end{matrix} \arrow[ur, "CO"] \arrow[dr, "CCl_4"'] & \\
 & R_3SiRuH_2Cl(PR_3)_n \arrow[d] \\
 & R_3SiH + RuHCl(PR_3)_3 \qquad (117)
\end{tikzcd}$$

$$R_3SiCoH_2(PR'_3)_3 \xrightarrow{CO} HSiR_3 + CoH(CO)(PR'_3)_3 \qquad (118)$$

These eliminations generally proceed more readily as R in R_3Si becomes larger and less electronegative.

Finally, reactions (119) and (120) make an interesting comparison with reactions (115) and (118).

$$(Cl_3Si)_2Fe(CO)_4 \xrightarrow[\text{Ref. } 355]{PPh_3} Si_2Cl_6 + Fe(CO)_n(PPh_3)_{5-n} \quad (n = 3, 4) \qquad (119)$$

$$Et_3SiCo(CO)_4 \xrightarrow[\text{Ref. } 227]{PPh_3} Si_2Me_6 + [Co(CO)_3(PPh_3)]_2 \qquad (120)$$

3. *Miscellaneous Reactions*

The preparation of the interesting silaallyl species (**XIV**)* has already been described (Section II,G,4,c). On photolysis, it gives trimethyl-

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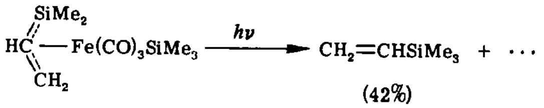
* See footnote, p. 37, and Appendix.

vinylsilane as one product; the mechanism is as yet not certain, but it is interesting that a very similar yield of the same product, $CH_2{=}CHSiMe_3$, is obtained by irradiation of $CH_2{=}CHSi_2Me_5$ and $Fe(CO)_5$, and it may well be that the same intermediate is involved (*385*).



$$HC(SiMe_2)(CH_2)—Fe(CO)_3SiMe_3 \xrightarrow{h\nu} \underset{(42\%)}{CH_2{=}CHSiMe_3} + \cdots \qquad (121)$$

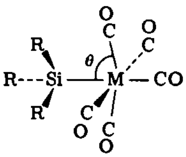
(XIV)

IV. Information from Physical Methods

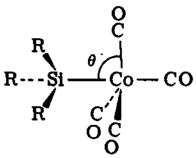
A. Electron and X-Ray Diffraction Studies

Table XVII lists compounds studied by these techniques and the silicon–metal bond lengths obtained.

The volatile compounds in the first four entries were suitable for gas-phase electron diffraction studies. Their octahedral (entries 1–3) and trigonal bipyramidal (entry 4) geometries are shown in formulas (**XXXIV**) and (**XXXV**). In each case, it was found that the carbonyl groups cis to the silyl group were tilted towards it, such that values of θ ($Si\hat{M}C_{cis}$) were (**XXXIV**, M = Mn, R = H), 85½°; (**XXXIV**, M = Mn, R = F), 87°; (**XXXIV**, M = Re, R = H), 85°; and (**XXXV**, R = H), 82°. Such distortions are frequently seen in the structures of solid metal-carbonyl derivatives, but it is important to establish that they also occur in molecules in the gas phase, uncomplicated by intermolecular interactions and crystal packing effects. It has been suggested that these distortions arise as a result of (1) unequal competition between a silyl group and the carbonyl group trans to it for π-bonding interactions with the transition-metal atom, and/or (2) some bonding interaction between silicon and the carbonyl groups cis to it in the molecule (i.e., equatorial CO) (*63, 374, 380*). No clear preference between these proposals can be established at present.



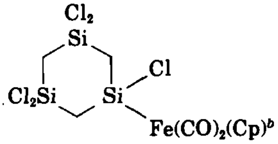
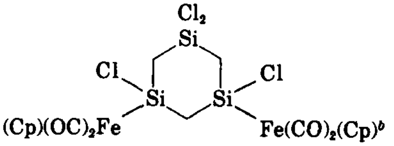
(**XXXIV**; M = Mn or Re)



(**XXXV**)

TABLE XVII

STRUCTURAL DETERMINATIONS OF SILICON–METAL COMPOUNDS

Entry	Compound	*d*(Si–M) (pm)[a]	Ref.
A. Electron diffraction determinations			
1	$H_3SiMn(CO)_5$ (**XXXIV**)	241	(*369*)
2	$F_3SiMn(CO)_5$ (**XXXIV**)	236	(*371*)
3	$H_3SiRe(CO)_5$ (**XXXIV**)	256	(*370*)
4	$H_3SiCo(CO)_4$ (**XXXV**)	238	(*28, 374*)
B. X-Ray diffraction determinations			
5	$[H_2SiTi(Cp)_2]_2{}^b$ (**XXXVII**)	216	(*232*)
6	$Ph_3SiZrCl(Cp)_2{}^b$ (**XXXVI**)	281	(*326*)
7	$(Et_2Si)_2W_2(CO)_8H_2$ (**XLII**)	259; 270	(*52*)
8	$Cl_2PhSiMnH(CO)_2(Cp)^b$ (**XLIII**)	231	(*403*)
9	$[Ph_2SiMn(CO)_4]_2$ (**LXI**)	240	(*402*)
10	$Ph_3SiMnH(CO)_2(Cp)^b$ (**XLIII**)	242	(*248, 251*)
11	*trans*-$Me_3SiMn(CO)_4(PPh_3)$ (**XXXIV**; axial CO replaced)	245	(*125*)
12	$Me_3SiMn(CO)_5$ (**XXXIV**)	250	(*216*)
13	$(Me_3Si)_3SiMn(CO)_5$ (**XXXIV**)	256	(*338*)
14	$Ph_3SiReH(CO)_2(Cp)^b$ (**XLIII**)	249	(*404*)
15	$Cl_2PhSiRe_2(CO)_9H$	251	(*404*)
16	$(Et_2Si)_2Re_2(CO)_6H_4$ (**XLI**)	253	(*127*)
17	$(Ph_2Si)_2Re_2(CO)_8$ (**XXXIX**)	254	(*53, 127*)
18	$(Ph_2Si)Re_2(CO)_8H_2$ (**XXXVIII**)	254	(*173*)
19	$(Et_2Si)_2Re_2(CO)_7H_2$ (**XL**)	255	(*128*)
20	$Me_3SiRe(CO)_5$ (**XXXIV**)	260	(*126*)
21	$(Me_3Si)_3SiRe(CO)_5$ (**XXXIV**)	267	(*126*)
22	$Cl_3SiFe(CO)_4^-NEt_4^+$ (analogous to **XXXV**)	222	(*256*)
23	$(MeF_2Si)_2FeH(CO)(Cp)^b$ (**XLIV**)	225	(*405*)
24	$(Cl_3Si)_2FeH(CO)(Cp)^b$ (**XLIV**)	225	(*313*)
25		226	(*240*)
26		228	(*240*)
27		231	(*399*)

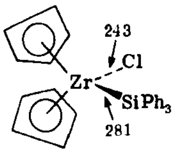
(*table continues*)

TABLE XVII (*Continued*)

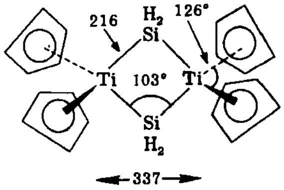
Entry	Compound	d(Si–M) (pm)[a]	Ref.
28	*trans*-$(Cl_3Si)_2Fe(CO)_4$ **(XLV)**	233	(*419*)
29	$(Me_2PhSi)_2FeH(CO)(Cp)$[b] **(XLIV)**	234	(*403*), [cited in Ref. (*419*)]
30	$Me_2PhSiFe(Cp)(PMe_2Ph)_2$[b]	234	(*419*)
31	*cis*-$Ph_3SiFeH(CO)_4$, analogous to **(XLVI)**	242	(*403*), [cited in Ref. (*128*)]
32	*cis*-$(Me_3Si)_2Fe(CO)_4$ **(XLVI)**	246	(*419*)
33	$(Me_3Si)_2(\mu\text{-}SiMe_2)_2Ru_2(CO)_6$ **(XLVII)**	239, 249, 251	(*130*)
34	$Me_3SiRu(CO)_2[C_7H_7(C_6F_5)(SiMe_3)]$ **(XLVIII)**	243	(*245*)
35	$Me_3SiRu_2(CO)_4(C_8H_8SiMe_3)$ **(IL)**	244	(*170, 204*)
36	$(C_8H_8SiMe_2CH_2CH_2)Me_2SiRu_2(CO)_5$ **(L)**	246	(*170, 204*)
37	$Me_3SiRu_2(CO)_5(C_7H_6SiMe_3)$ **(LI)**	246	(*74, 242*)
38	$(OC)_4CoSiCo_3(CO)_9$ **(LII)**	222, 229	(*396*)
39	$F_3SiCo(CO)_4$ **(XXXV)**	223	(*177*)
40	$Cl_3SiCo(CO)_4$ **(XXXV)**	225	(*375*)
41	$Me_2P(SiMe_3)_2^+Co(CO)_4^-$ **(LIII)**	see text	(*387*)
42	$Cl_3SiRhH(Cl)(PPh_3)_2 \cdot xSiHCl_3$ ($x \approx 0.4$) **(LIV)**	220	(*327*)
43	$\overline{SiMe_2OMe_2SiIr}H(CO)(PPh_3)_2$ **(LXII)**	241	(*140, 207*)
44	$(\mu\text{-}SiMe_2)Pt_2[P(cyclohexyl)_3]_2(C{\equiv}CPh)_2$ **(LIX)**	226; 244	(*105*)
45	$N(C_2H_4O)_3SiPtCl(PMe_2Ph)_2$ **(LVI)**	229	(*160*)
46	*trans*-$Ph_2MeSiPtCl(PMe_2Ph)_2$ **(LV)**	229	(*321*), [cited in Ref. (*134*)]
47	$[Ph_2MeSiPt(t\text{-}BuNC)(\mu\text{-}t\text{-}BuN{=}CH)]_2$ **(LX)**	231	(*104*)
48	(*S*)-(+)-*trans*-$R_3Si^*PtCl(PMe_2Ph)_2$[c] **(LV)**	232	(*156*)
49	$\{Et_3SiPt[P(cyclohexyl)_3](\mu\text{-}H)\}_2$ **(LVIII)**	233	(*205*)
50	*trans*-$H_3SiPtH[P(cyclohexyl)_3]_2$ **(LV)**	238	(*169*)

[a] To nearest pm; precision normally such that s.d. ≤ 0.5 pm.
[b] Cp = $(\eta^5\text{-}C_5H_5)$.
[c] R_3Si^* = MePh(1-naphthyl).

Regarding silicon–metal bond lengths, it can be seen by comparison of entries 1–4, 12, 13, 20, 21, and 39 that d(Si–M) decreases as R changes in **(XXXIV)** and **(XXXV)** in the order R = Me_3Si > Me > H > F. This implies that both steric and electronic factors are significant; the longest bonds are observed when bulky ligands of low electronegativity are attached to silicon. Whether, as has been proposed (*126, 338*), the long bond lengths in entries 13 and 21 correspond to an essentially single covalent bond, all others being more or less contracted by d_π–d_π interaction (or some other effect), remains an open question. The difficulties of estimating such "covalent single-bond lengths" are emphasised in Ref. (*134*) and in many of the papers cited in Table XVII. Moreover, now that experimental bond data are available for a wider range of compounds, it is clear that there are wide variations in the length of any given bond, amounting to about 25 pm in the case of Si–Mn and Si–Fe compounds. It still remains true, however, that by far the longest silicon–metal bond recorded is that in the zirconium derivative of entry 6 (**XXXVI**), a compound in which the metal has a formal d^0 configuration and in which, consequently, no d_π–d_π interaction is expected.



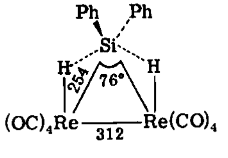
(XXXVI)*



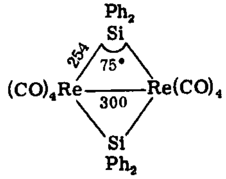
(XXXVII)

Strangely, the shortest Si–M distance reported (entry 5) is also in a formally d^0 situation. The compound (**XXXVII**) is prepared by the reaction of $KSiH_3$ and $(\eta^5\text{-}C_5H_5)_2TiCl_2$ in glyme: the reason for its anomalously short Si–Ti bond is not clear.

There has been much interest in the possibility of Si· · ·H· · ·M bridging, first suggested in connection with the compound $(Ph_2Si)Re_2(CO)_8H_2$ (entry 18) (*173, 250*). Although the hydrogen atoms were not located, infrared spectral evidence supported a structure (**XXXVIII**), with some H· · ·Si interaction. However, a series of related compounds (**XXXIX**)–(**XLI**) (entries 16, 17, and 19) have now been studied, and since their structural parameters are very similar to each other and to those of compound (**XXXVIII**), it seems most reasonable to suppose that only terminal Re–H bonds are present. In particu-



(XXXVIII)



(XXXIX)

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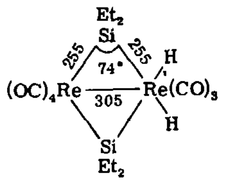
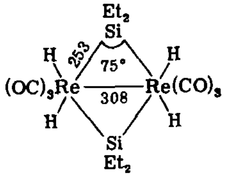
* All distances in this and following structures in picometers.

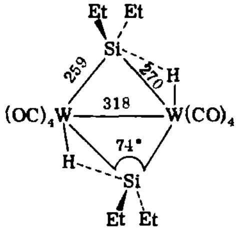
lar, the fact that all Si–Re distances in the unsymmetrical compound (**XL**) are the same argues strongly against any hydrogen bridging. A Raman study of compound (**XXXVIII**) and its deuterated version was interpreted by the authors (*12*) in terms of a bridged structure, but the data are equally consistent with terminal Re–H (Re–D) bonds. It appears that M—H· · ·Si interaction will be significant only when steric constraints force the hydrogen atom close to silicon. This seems to occur in the tungsten derivative (**XLII**, entry 7), in which the Si–W distances are markedly different; the W_2Si_2 ring and four of the carbonyl groups lie approximately in a plane.



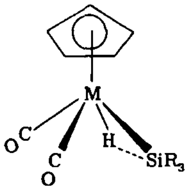
(**XL**)



(**XLI**)



(**XLII**)



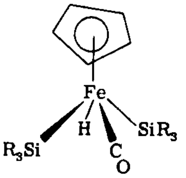
(**XLIII**)

Similarly, the two cis-dicarbonyl manganese compounds (**XLIII**, M = Mn, R_3 = $PhCl_2$ or Cl_3, entries 8 and 10) are sterically constricted, and location of the positions of the hydrogen atoms has given definite evidence for bridging. The Mn–H distances are 149 and 155 pm respectively, while the Si· · ·H distances are 179 and 176 pm, only about 20% greater than the normal length for a Si–H bond (148 pm). Significant Si· · ·H interaction is consistent with the known tendency of these compounds to lose R_3SiH in reductive elimination processes (see Section III,G,2). On the other hand, the analogous rhenium derivative (**XLIII**; M = Re, R = Ph) (entry 14) is less hindered because of the greater size of the rhenium atom; the Si· · ·H distance is correspondingly longer, with no significant interaction. A similar situation obtains in the cis-octahedral compound $Ph_3SiFeH(CO)_4$ (entry 31): the hydrogen atom is 164 pm from iron but 273 pm from silicon—much too far for effective interaction. The compound $Cl_2PhSiRe_2(CO)_9H$ (entry

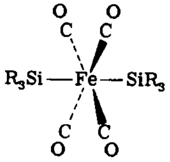
15), made by irradiating a mixture of $HSiPhCl_2$ and $Re_2(CO)_{10}$ (*248, 251*), appears to involve a Re· · ·H· · ·Re bridge, but no details of the structure apart from the Si–Re bond length have yet been published.

There is only one example as yet of the effect of substituting carbonyl by tertiary phosphine: *trans*-$Me_3SiMn(CO)_4(PPh_3)$ (entry 11) adopts a structure like that of formula (**XXXIV**), except that the axial carbonyl group is replaced. The Si–Mn bond length decreases somewhat, but the main change concerns the tilting of equatorial carbonyl groups towards silicon. This is now irregular, with values for θ of about 87° for two cis carbonyls and about 81° for the remaining two. The authors attribute this to a minimizing of steric effects. There is also only a single example of an anionic species: $Cl_3SiFe(CO)_4^-$ (entry 22) has a trigonal bipyramidal arrangement analogous to structure (**XXXV**), and a very short Si–Fe bond.

Among the iron compounds, several of the type $(R_3Si)_2FeH(CO)(Cp)$ (entries 23, 24, and 29) possess the structure shown in (**XLIV**), with trans R_3Si groups. In the case when $R_3 = MeF_2$, d(Fe–H) is about 150 pm, while the Si· · ·H distance (206 pm) is not thought to correspond to significant interaction.



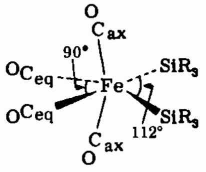
(**XLIV**)



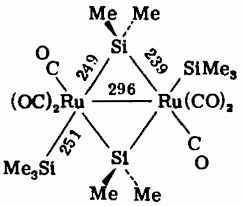
(**XLV**)

Examples of both *trans*- and *cis*-$(R_3Si)_2Fe(CO)_4$ structures are known, (**XLV**) and (**XLVI**), shown in entries 28 and 32 respectively. The *cis*-bis(trimethylsilyl) compound is considerably distorted, to the extent that the $C_{ax}FeC_{ax}$ angle is only 141°. The authors attribute this both to the bulk and the excellent σ-donor characteristics of the Me_3Si groups, and they point out that calculations have suggested that very good σ-donors can stabilize a bicapped tetrahedral geometry (*234*). It is significant that a related compound with less steric congestion and poorly σ-donating ligands, *cis*-$(Cl_3Ge)_2Ru(CO)_4$, adopts an almost regular octahedral arrangement (*45*).

An interesting diruthenium compound (entry 33) has the structure shown in (**XLVII**); the ring is planar, bisected by a metal–metal bond, and the Si–Ru distances vary noticeably according to their bridging or terminal position and, in the former case, whether they are trans to carbonyl or silicon. The remaining ruthenium derivatives in entries

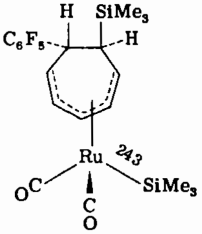


(XLVI)

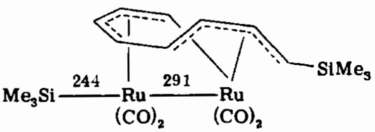


(XLVII)

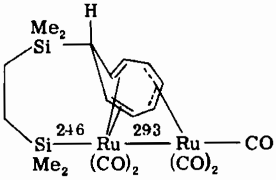
34–37 will not be discussed in detail, since their main interest lies in the arrangement of the organic portion, but they are depicted in formulas (**XLVIII**)–(**LI**).



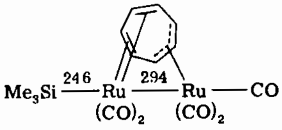
(XLVIII)



(IL)



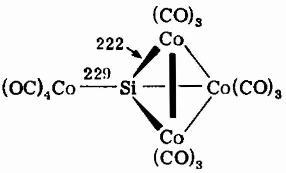
(L)



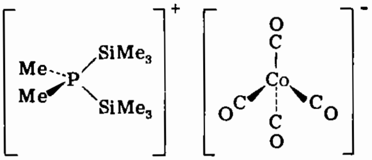
(LI)

It will be seen that the Si–Ru and (where appropriate) Ru–Ru bond lengths are remarkably constant.

When SiI_4 and $NaCo(CO)_4$ are warmed and irradiated together in *n*-hexane, the cluster compound $(OC)_4CoSiCo_3(CO)_9$ (entry 38) is produced, probably through the intermediacy of $ISiCo_3(CO)_9$. Its structure is shown in formula (LII) and the differing Si–Co(cluster) and Si–Co(*exo*) bond lengths should be noted.

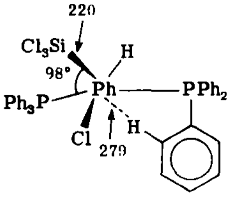


(LII)

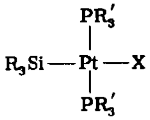


(LIII)

Compound (**LIII**) (entry 41), made from $Me_3SiCo(CO)_4$ and $Me_2P(SiMe_3)$, consists of separated ions, the anion being tetrahedral and the cation approximately so; there is no Si–Co interaction (cf. Section III,D). The coordination around Rh(III) in compound (**LIV**) (entry 42) is approximately trigonal bipyramidal, with phosphines in axial positions. However, an *ortho* hydrogen of one triphenylphosphine ligand molecule is sufficiently close to the metal to raise the coordination number arguably to six; the angle $\widehat{PRhP}$ is only 162°.



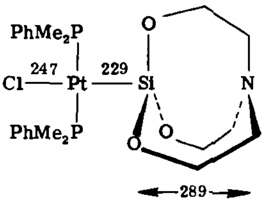
(**LIV**)



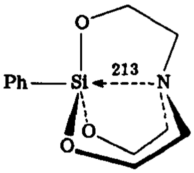
(**LV**)

Entries 46 and 48 are examples of trans square-planar Pt(II) derivatives (**LV**; X = Cl, R'_3 = $PhMe_2$); the latter, with R_3 = MePh(1-naphthyl), is chiral at silicon, and its structure is particularly significant because it establishes the absolute stereochemistry of the (+)-enantiomer as (*S*). The long Pt–Cl bond (245 pm in each case) should be noted: it is attributed to the large trans influence of silicon (*97, 98, 229*). The simple silyl derivative in entry 50 [**LV**; X = H, R'_3 = $(cyclohexyl)_3$] is prepared from monosilane and $PtH_2[P(cyclohexyl)_3]_2$; the Si–Pt distance is appreciably greater than that in other members of this class.

In compound (**LVI**) (entry 45), the silicon is part of a silatrane cage (*24*): in contrast to simple silatranes such as (**LVII**) (*356*), in which there is substantial Si· · ·N interaction, the platinum-substituted version has essentially none, and the coordination about nitrogen is trigonal planar. It is suggested that these effects are a result of electron release from platinum, which provides sufficient negative charge on silicon to discourage electron donation. Again, the Pt–Cl bond trans to silicon is very long.

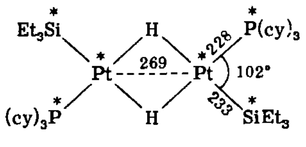


(**LVI**)



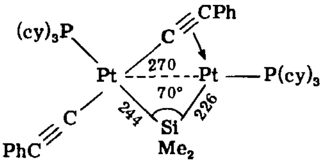
(**LVII**)

Another compound containing the tricyclohexylphosphine ligand is the novel hydrogen-bridged species (**LVIII**, cy = cyclohexyl) (entry 49) made from $Pt(C_2H_4)_2[P(cyclohexyl)_3]$ and $HSiEt_3$ at room temperature. The starred atoms in the diagram are nonplanar; they lie in two planes intersecting along the H · · · H axis, with a dihedral angle of 21°. This compound acts as a potent catalyst for hydrosilation reactions (*205, 206, 415*).



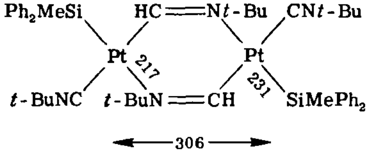
(LVIII)

(cy = cyclohexyl)



(LIX)

A more complicated structure (**LIX**) (entry 44) results from the reaction of $Pt(C_2H_4)[P(cyclohexyl)_3]_2$ with $Me_2Si(C{\equiv}CPh)_2$; the $SiMe_2$ bridging group is markedly asymmetric. Entry 47 (**LX**) is an example of an isocyanide complex with bridging substituted methyleneimine groups; the central diplatina six-membered ring is in a boat conformation, with no Pt · · · Pt interaction, and the Pt–N bonds trans to silicon are unusually long.

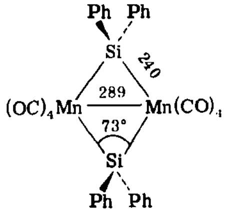


(LX)

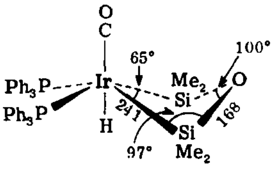
Two interesting cyclic compounds are listed as entries 9 and 43. The first (**LXI**) contains a metal–metal bond and a planar Mn_2Si_2 ring, and should be compared with structure (**XXXIX**). The second, (**LXII**), has a four-membered $IrSi_2O$ ring, bent about the Si · · · Si axis, while the iridium atom is some 26 pm above the P_2Si_2 plane. The Si$\hat{O}$Si bond angle is much less than the normal range (130–180°), and it is clear that the ring is highly strained; this fact may well be related to the compound's ability to catalyze the disproportionation reaction (*139, 207*) of Eq. (122).

$$(Me_2SiH)_2O \rightarrow Me_2SiH_2 + \frac{1}{x}(Me_2SiO)_x \qquad (122)$$

Three other cyclic compounds are depicted in Table XVII as entries 25–27: the first two compounds show a skew-boat conformation, while the last approximates to a chair form.



(LXI)



(LXII)

B. Vibrational Spectroscopy

Although routine reports of infrared spectra have often been published, there have been few recent accounts of more complete studies involving Raman measurements, isotopic substitution, or force-constant calculations. Table XVIII also shows that relatively few different types of compounds have received this degree of attention.

It is now clear that some coupling may occur in these molecules between ν(Si–M), ν(CO), and Si–X modes. Thus, intense polarized Raman bands assigned to ν(Si–M) occur at the following frequencies (cm^{-1}): $Me_3SiRe(CO)_5$, 297 (*82*); $H_3SiRe(CO)_5$, 297; $D_3SiRe(CO)_5$, 284 (*121*). In $H_2Si[Re(CO)_5]_2$, a similar band occurs at 250 cm^{-1} (*32*). Also, carbonyl stretching frequencies in the infrared spectra of $H_2Si[M(CO)_5]_2$ (M = Mn, Re) shift by 1–6 cm^{-1} on deuteration (*32*). It may be noted that there is strong vibrational coupling between the two $M(CO)_5$ units in these compounds. This suggests that a correlation with the established vibrational modes of the parent carbonyls $(OC)_5M$—$M(CO)_5$ may be made, and indeed bands of the silanediyl compounds have been satisfactorily assigned on this basis.

Very low values of the Si–H stretching frequency are found in some H_2SiM_2 derivatives; the value found for $H_2Si[Fe(CO)_2(Cp)]_2$ of 2042 cm^{-1} (*32*) compares quite closely with the value of 2037 cm^{-1} predicted from simple additivity considerations (*235*). These low values are consistent with very low effective electronegativities for metal carbonylate groups (*32, 235*).

Two quantitative applications may be noted: in the first (entries 12 and 14), infrared intensity measurements are related to the angle of tilt, θ, between equatorial CO groups and the metal–silicon bond [see formulas (**XXXIV**) and (**XXXV**)]. Thus in the series $Me_3MCo(CO)_4$ the

TABLE XVIII

Vibrational Spectroscopy of Silicon–Metal Compounds[a]

Entry	Compound	Information[b]	Ref.
1	$H_3SiMn(CO)_5$ [c]	IR/R; AFCC	(*7, 30, 299*)
2	$Me_3SiMn(CO)_5$ [d]	IR/R; AFCC	(*81*)
3	$R_3SiMn(CO)_5$ (R = H, Me)	NCA	(*349*)
4	$Cl_3SiMn(CO)_5$ [e]	IR; NCA	(*347, 348*)
5	$H_2Si[Mn(CO)_5]_2$ [c]	IR/R; D	(*32*)
6	$(Ph_2Si)Re_2(CO)_8H_2$ [f]	R; D	(*12*)
7	$Me_3SiRe(CO)_5$ [d]	IR/R; AFCC	(*82*)
8	$Cl_3SiFe(CO)_4^-NEt_4^+$	IR/R	(*61*)
9	$Cl_2MeSiFe(CO)_2(Cp)$[g]	VT/IR; AFCC; isomers	(*141, 142*)
10	$R_3SiFe(CO)_2(Cp)$[g] (R = alkyl, aryl, etc.)	IR	(*354*)
11	$Cl_3SiCo(CO)_4$ [d]	IR/R; FFC; NCA	(*60–62, 148, 424*)
12	$X_3SiCo(CO)_4$ (X = Cl, Ph)	IR; intensity/angles	(*143*)
13	$X_3SiCo(CO)_4$ (X = H, F)	IR/R; FFC	(*61*)
14	$Me_3SiCo(CO)_4$ [d]	IR/R; intensity/angles	(*73, 152*)

[a] Routine reports of infrared spectra are generally excluded.

[b] IR = infrared; R = Raman; AFCC = approximate force-constant calculations; NCA = normal coordinate analysis; D = deuterium substitution; VT = variable temperature; FFC = force-field calculations; intensity/angles = infrared intensity measurements used to calculate angles between CO groups.

[c] Also Re.

[d] Also Ge and Sn analogs.

[e] Also X_3Ge (X = Cl, Br); X_3Sn (X = Cl, Br, I).

[f] See Section IV,A for a discussion of these results in connection with possible Re–H · · · Si bridging.

[g] Cp = $(\eta^5\text{-}C_5H_5)$.

angles are estimated to be: M=Si, 82½°; Ge, 94°; Sn, 98° (*73*). In the second (entry 9), substitution of carbonyl groups by ^{13}CO led to the calculation of force constants for the two rotational conformers of $Cl_2MeSiFe(CO)_2(Cp)$, which arise because of hindered rotation about the Si–Fe bond. Variable-temperature infrared studies on the same compound also led to rough estimates of the small enthalpy and entropy differences between the two forms. In this connection, it has also been reported that more than two carbonyl stretching bands are present in the infrared spectra of $ClMe_2SiFe(CO)_2(Cp)$ and $ClMe(n\text{-}Pr)SiFe(CO)_2(Cp)$, implying that these too exist as different conformers (*136*).

Continuing attempts have been made to relate vibrational spectra to the bonding in these compounds. In some cases [e.g., entries 11 and 13

(*60, 61*)], the role of d_π–d_π Si–M interactions has been emphasized, while in others (e.g., entry 10), observed effects have been related chiefly to the high σ-donor ability of R_3Si groups. No decision can yet be made as to which is the more realistic of these approaches.

C. NMR SPECTROSCOPY

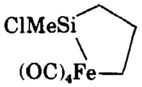
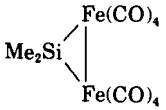
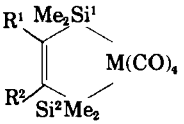
Developments in instrumental techniques have made possible the direct observation of ^{29}Si-NMR spectra (e.g., *90, 218–220*), and the first results for silicon–transition-metal compounds have now been reported (Table XIXA). The sign convention is such that positive values of δ denote shifts to lower fields (or higher frequencies) with respect to the standard, so that the silicon becomes less shielded. The wide range of values of δ should be noted: the order of decreasing shielding seen in entries 2, 1, 3, and 14, respectively, parallels that observed for tin nuclei in analogous tin compounds, but the factors determining the size of δ are not yet clear, and it certainly cannot be correlated directly with, for example, the extent of d_π–d_π interaction. Entries 11 and 12 show that increasing ring strain is associated with a dramatic increase in δ values.

Measurements of ^{13}C-NMR spectra have provided much useful information concerning the number and proportions of isomers in solution, and their rates of interconversion (Table XIXB). It is generally true that in octahedral derivatives $R_3SiM(CO)_5$ of the type shown in formula (**XXXIV**), the carbon atom of the axial carbonyl group (trans to silicon) is more shielded (i.e., resonates at higher field) than carbon atoms in the equatorial CO groups (entry 7). For disubstituted octahedral compounds $(R_3M)_2M'(CO)_4$ (entry 9), the carbon atoms trans to M [e.g., C_{eq} in (**XLVI**)] are more shielded than the remaining two, except in the solitary case of $(Me_3Sn)_2Fe(CO)_4$ (*420*).

Graham and his colleagues have examined a wide range of compounds (entry 9) to determine the preferred stereochemistry and rates of interconversion of isomers. Some of their results relating to silicon derivatives are shown in Table XX. In certain cases, samples enriched with ^{13}CO were used, while sometimes the presence of the minor isomer was established by infrared methods. For *cis*-$(Me_3Si)_2Fe(CO)_4$, the ^{13}C-NMR spectrum at very low temperatures shows separate resonances for axial and equatorial carbonyl groups (**XLVI**), but at higher temperatures the molecule is fluxional, with a coalescence temperature of −55°. Because $^1J(^{13}CO–^{57}Fe)$ and $^2J(^{13}CO–^{29}Si)$ spin–spin coupling is preserved in the high-temperature limiting spectrum, carbonyl ex-

TABLE XIXA

NMR SPECTROSCOPY OF SILICON–TRANSITION-METAL COMPOUNDS: ^{29}Si MEASUREMENTS

Entry	Compound	δ Value[a]	Ref.
1	$Me_3SiMn(CO)_5$	+17.6	(*295*)
2	$Me_3SiRe(CO)_5$	−14.4	(*295*)
3	$Me_3SiFe(CO)_2(Cp)^b$	+41.0	(*295*)
		+40.8	(*283*)
		+41.9	(*451*)
4	$Me_3Si^2Me_2Si^1Fe(CO)_2(Cp)^b$	+17.6 (Si^1)	(*451*)
		−11.1 (Si^2)	(*451*)
5	$MeClHSiFe(CO)_2(Cp)^b$	+65.9	(*302*)
6	$MeF_2SiFe(CO)_2(Cp)^b$	+68.3	(*302*)
7	$MeHSi[Fe(CO)_2(Cp)]_2{}^b$	+62.5	(*302*)
8	$ClHSi[Fe(CO)_2(Cp)]_2{}^b$	+110.7	(*302*)
9	$MeClSi[Fe(CO)_2(Cp)]_2{}^b$	+142.0	(*302*)
10	$Cl_2Si[Fe(CO)_2(Cp)]_2{}^b$	+146.7	(*302*)
11		+96	(*290*)
12		+173	(*68*)
13			(*451*)
	M = Fe; $R^1 = R^2 = Ph$	+48.2	
	M = Fe; $R^1 = Ph$, $R^2 = Me_3Si^3$	+48.8, +45.4 (Si^1, Si^2) −7.6 (Si^3)	
	M = Ru; $R^1 = Ph$, $R^2 = Me_3Si^3$	+34.7, +32.4 (Si^1, Si^2) −7.9 (Si^3)	
14	$Me_3SiCo(CO)_4$	+44.0	(*295*)
15	$F_3SiCo(CO)_4$	−29.1[c]	(*263a*)

[a] Referred to Me_4Si standard.

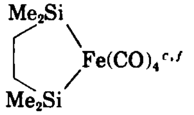
[b] $Cp = (\eta^5\text{-}C_5H_5)$.

[c] Value obtained from ^{19}F double resonance experiments (*263a*).

change is considered to be a nondissociative, intramolecular process. One possible route would involve rapid cis ⇄ trans ⇄ cis′ equilibria, but other pathways such as a trigonal twist or a tetrahedral jump are not excluded (*419*). The activation parameters for the positional inter-

TABLE XIXB

NMR SPECTROSCOPY OF SILICON–TRANSITION-METAL COMPOUNDS: ^{13}C MEASUREMENTS AND OTHER NUCLEI

Entry	Compound	Comments	Ref.
^{13}C Measurements			
7	$X_3SiRe(CO)_5$ [a] ($X = Cl, Me$)	*trans*-CO more shielded than *cis*-CO	*(425)*
8	$R_3SiFe(CO)_2(Cp)$ [b] ($R = Me, Ph$)	d_π–d_π Si–Fe interaction assumed	*(188)*
9	$(Cl_nMe_{3-n}Si)_2Fe(CO)_4$ [a,c,d] ($n = 0$–3)	VT[e]; fluxional (see text)	*(361, 362 419, 420)*
10		VT; nonfluxional	*(418)*
11	$(Cl_3Si)_2Ru(CO)[\eta^6\text{-}C_6H_4(t\text{-}Bu)_2\text{-}p]$	VT; restricted rotation	*(363)*
12	$X_3SiCo(CO)_4$ [f] ($X = F, Cl, Ph$)	VT; fluxional	*(296)*
Other nuclei			
13	$X_3SiMn(CO)_5$ [g] ($X = Cl, Ph, C_6F_5$)	^{55}Mn	*(47)*
14	$(\mu\text{-}SiMe_2)_2Fe_2(CO)_7$	^1H; fluxional	*(289)*
15	$(\mu\text{-}SiHMe)Fe_2(CO)_3(Cp)_2$ [b]	^1H; isomers	*(309)*
16	$Ph_3SiPt(C_6H_4F)(PMe_2Ph)_2$ and related compounds	^{19}F	*(155)*
17	*trans*-$R_3SiPtX(PR'_3)_2$	^1H, ^{31}P, ^{195}Pt	*(11)*

[a] Also Ge, Sn analogs.
[b] Cp = (η^5-C_5H_5).
[c] Also Ru, Os analogs.
[d] Also ^1H study of some Si–Ru, Si–Os derivatives.
[e] VT = Variable-temperature study.
[f] Also ^1H study.
[g] Also Ge, Sn, Pb analogs.

change of carbonyl groups in this compound are $\Delta H^\ddagger$, 43.5 ± 2.5 kJ mol^{-1}, and $\Delta S^\ddagger$, -9.5 ± 11.0 J K^{-1} mol^{-1}, and it appears that the barrier heights increase in the orders Fe < Ru < Os and $Me_3Si < ClMe_2Si < Cl_2MeSi < Cl_3Si$.

Consistent with the idea outlined above, the cyclic compounds in entry 10 are anchored in the cis position, and are shown by ^{13}C- and ^1H-NMR measurements to be stereochemically rigid, even at 90°.

The ruthenium compound in entry 11 has a piano-stool structure (**LXIII**), and hindered rotation about the Ru–aromatic ring bond may

TABLE XX

POSITION OF Cis–Trans EQUILIBRIA FOR COMPOUNDS $(R_3Si)_2M(CO)_4$ (M = Fe, Ru, Os)[a]

Compound	% Trans isomer	T(K)	Solvent
$(Me_3Si)_2Fe(CO)_4$	0	183	CD_2Cl_2
$(ClMe_2Si)_2Fe(CO)_4$	0	253	Toluene-d_8
$(Cl_2MeSi)_2Fe(CO)_4$	8	253	Toluene-d_8
$(Cl_3Si)_2Fe(CO)_4$	19	300	Toluene-d_8
$(Me_3Si)_2Ru(CO)_4$	0	253	Toluene-d_8
$(ClMe_2Si)_2Ru(CO)_4$	0	303	Toluene-d_8
$(Cl_2MeSi)_2Ru(CO)_4$	12	305	Toluene-d_8
$(Cl_3Si)_2Ru(CO)_4$	[b,c]	—	CD_2Cl_2
$(Me_3Si)_2Os(CO)_4$	63[d]	303	Toluene-d_8
$(ClMe_2Si)_2Os(CO)_4$	60	303	Toluene-d_8
$(Cl_2MeSi)_2Os(CO)_4$	[b]	—	CD_2Cl_2
$(Cl_3Si)_2Os(CO)_4$	100[e]	303	CD_2Cl_2

[a] Data from Refs. (*419*) and (*420*).

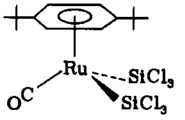
[b] Cis and trans isomers both isolable; isomerization is negligible at room temperature.

[c] Above 70°C, isomerization proceeds to give equilibrium mixture with 70% trans form.

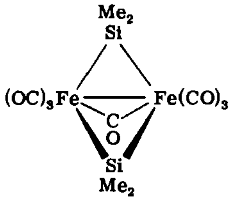
[d] For cis $\rightleftharpoons$ trans equilibrium, $\Delta H^\circ = 3.5$ kJ mol^{-1}; $\Delta S^\circ = 16$ J K^{-1} mol^{-1}.

[e] Above 120°C, cis isomer isomerizes to 100% trans.

be demonstrated by variable-temperature NMR methods. The least hindered position is that in which the line joining the two bulky *t*-butyl groups bisects the angle between the two $SiCl_3$ groups.



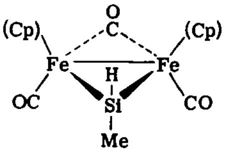
(LXIII)



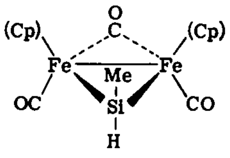
(LXIV)

Another example of a fluxional species is $R_3SiCo(CO)_4$, given in entry 12; exchange of axial and equatorial carbonyl groups is easy even at low temperatures, as shown by the low observed coalescence temperatures for R = F, −144°C; Cl, −85°C; and Ph, −61°C. Again the process is seen as intramolecular, with exchange rates chiefly determined by steric factors: the derived free energy of activation when R = F is 29; Cl, 35; and Ph, 40 kJ mol^{-1}. Either Berry pseudorotation or "turnstile" rotation could provide a reasonable pathway for the exchange.

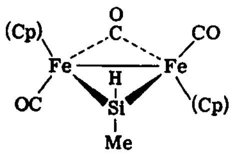
The compound (**LXIV**) (entry 14) provided an early example of a stereochemically nonrigid bridged system. Variable-temperature ^{1}H-NMR spectra showed it to be fluxional at room temperature. A number of related systems have now been studied, including $(OC)_3Co(\mu\text{-}GeMe_2)_2Co(CO)_3$ (*5*), $(Cp)(CO)Fe(\mu\text{-}CO)(\mu\text{-}GeMe_2)Fe(CO)(Cp)$ (*4*), and $(OC)_3Fe(\mu\text{-}CO)(\mu\text{-}SnR_2)_2Fe(CO)_3$ (*213*). All are fluxional, although the second becomes so only above about 90°C.



(**LXVa**)



(**LXVb**)



(**LXVc**)

When compound (**LXV**) is prepared by the reaction

$$MeHSi[Fe(CO)_2(Cp)]_2 \xrightarrow{h\nu} \underset{\textbf{(LXV)}}{(Cp)(CO)Fe(\mu\text{-}CO)(\mu\text{-}SiHMe)Fe(CO)(Cp)} + CO \qquad (123)$$

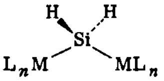
its solution initially contains the two cis isomers (**LXVa**) and (**LXVb**); however, after a time all three isomers can be detected by ^{1}H-NMR spectroscopy (entry 15).

It was inferred from ^{55}Mn-NMR chemical shift data for the compounds in entry 13 that the ability of the X_3M groups to function as σ-donors increases in the order $M = Ge < Sn < Si$. It is interesting that this order, presumably also one of increasing M–Mn bond strength, agrees with the orders of force constants for group IV–transition-metal bonds derived from vibrational spectra of $Me_3MMn(CO)_5$ (*81*) and $Cl_3MCo(CO)_4$ (*424*). Orders of bond dissociation energy derived from appearance potentials are sometimes different, however (see Section IV,D).

The same conclusion, that the Ph_3Si group is a good σ-donor, was drawn from ^{19}F-NMR experiments on fluorophenyl derivatives of Si–Pt compounds (entry 16); additionally, it was concluded that Ph_3Si attached to Pt was a good π-acceptor. A wide range of chemical shifts and coupling constants involving ^{1}H, ^{31}P, and ^{195}Pt nuclei were determined by double-resonance experiments on a large number of Si–Pt derivatives (entry 17).

Useful information can sometimes be obtained from $^1J(^{29}Si\text{–}^1H)$ coupling constants. It has been shown that their magnitude depends chiefly on the Fermi contact term, and hence on the degree of s character in the Si–H bond (*149*). Exceptionally low values of the $(^{29}Si\text{–}H)$

coupling constant are observed for compounds of the type $H_2Si(ML_n)_2$: for $ML_n = Re(CO)_5$, it is only 165 Hz (*32*). This implies that the s character of the Si–H bonds is very small and hence, from Bent's rule (*55*), that the (ML_n) groups have very low effective electronegativities. Similar conclusions have been reached from measurements of Si–H stretching frequencies in these compounds (see Section IV,B) and of $^2J(^{119}Sn–C–H)$ coupling constants in compounds such as $Me_2Sn[Re(CO)_5]_2$ (*413*). In pictorial terms, this effect is equivalent to a structure (**LXVI**); the bulky (ML_n) groups are as far apart as possible, and the Si–M bonds have essentially sp character. Diffraction experiments are needed to confirm this.



(LXVI)

D. Mass Spectrometry and Appearance Potentials

In Table XXI are listed those compounds which have been studied in some detail by the use of this technique.

The normal fragmentation pattern for a compound $R_3SiM(CO)_5$ involves loss of CO and concomitant loss of R (especially when R = H); although Si–M cleavage may occur, SiM^+ is always an abundant species. For the compounds $H_2Si[M(CO)_5]_2$ (M = Mn, Re; entry 6), the following pattern has been established, where x = 0–2 and y = 0–10:

$$\begin{tikzcd}
SiH_2M_2(CO)_{10}^+ \arrow[r] & SiH_xM_2(CO)_y^+ \arrow[r] & SiM_2^+ \arrow[r] \arrow[d] & SiM^+ \arrow[r] \arrow[d] & Si^+ \\
& & M_2^+ \arrow[r] & M^+ &
\end{tikzcd} \qquad (124)$$

Other processes (all established by the observation of enhanced metastable peaks) include elimination of R–R, SiR_2, and $M(CO)_5$, e.g. (*32*),

$$SiR_2Re_2(CO)_9^+ \rightarrow SiRe_2(CO)_9^+ + R_2 \qquad (R = H, D) \qquad (125)$$

$$SiF_2Mn_2(CO)_5^+ \rightarrow Mn_2(CO)_5^+ + SiF_2 \qquad (126)$$

$$SiF_2M_2(CO)_{10}^+ \rightarrow SiF_2M(CO)_5^+ + M(CO)_5 \qquad (M = Mn, Re) \qquad (127)$$

The cationic product in Eq. (127) is a substituted silicenium ion; attempts to produce a corresponding species chemically by abstraction of R^- from $R_3SiM(CO)_n$ or $R_2Si[M(CO)_n]_2$ have all been unsuccessful [see Section III,C and Ref. (*24*)]. Thus addition of the chloride-ion acceptor $SbCl_5$ to $Cl_3SiRe(CO)_5$ results in Si–Re bond cleavage (*32*).

TABLE XXI

MASS SPECTROSCOPIC STUDIES OF SILICON–TRANSITION-METAL COMPOUNDS

Entry	Compound	Ref.
1	$R_3SiCr(CO)_3(Cp)$ ($R_3 = F_xMe_{3-x}$; $x = 0-3$)	*(304)*
2	$R_3SiMn(CO)_5$ (R = H)	*(30)*
3	$R_3SiMn(CO)_5$ (R = Me)[a] AP[b]	*(81, 410)*
4	$R_3SiMn(CO)_5$ [$R_3 = (C_6F_5)_xPh_{3-x}$; $x = 0-3$)[a] AP[b]	*(108)*
5	$Me_3SiMn(CO)_n(PF_3)_{5-n}$ ($n = 2-5$)	*(378)*
6	$R_2Si[Mn(CO)_5]_2$ (R = H)[c]	*(2, 32)*
7	$R_2Si[Mn(CO)_5]_2$ (R = Cl)	*(2)*
8	$Me_3SiRe(CO)_5^a$ AP[b]	*(82)*
9	$R_3SiFe(CO)_2(Cp)$ ($R_3 = H_3, Br_3, I_3, Br_2OMe$, . . .)	*(237)*
10	$R_3SiFe(CO)_2(Cp)$ (R = Me)[d] AP[b]	*(253, 410)*
11	$R_3SiFe(CO)_2(Cp)$ [$R_3 = Cl_x(OR)_{3-x}$; $x = 0-3$)	*(236)*
12	$R_3SiFe(CO)_2(Cp)$ ($R_3 = F_xMe_{3-x}$; $x = 0-3$)	*(304)*
13	$Me_3SiFe(CO)(PPh_3)(Cp)$ AP[b]	*(410)*
14	$R_2Si[Fe(CO)_2(Cp)]_2$ (R = H)	*(32)*
15	$R_2Si[Fe(CO)_2(Cp)]_2$ (R = HCl, HMe, Cl_2, ClMe, F_2)	*(309)*
16	$R_3SiCo(CO)_4$ (R = H)	*(29)*
17	$R_3SiCo(CO)_4$ ($R_3 = Cl_3, F_3, Me_3, MeF_2$) AP[b]	*(379, 380)*
18	$R_3SiCo(CO)_4$ (R = Me)[a] AP[b]	*(82)*
19	$R_3SiCo(CO)_4$ ($R = C_6F_5$)	*(398)*
20	$Cl_3SiCo(CO)_n(PF_3)_{4-n}$ ($n = 2, 3$)	*(381)*
21	$H_2Si[Co(CO)_4]_2$	*(2)*
22	$Cl_2SiCo_2(CO)_7$	*(2)*

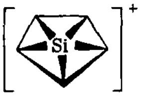
[a] Also Ge, Sn analogs.
[b] AP = appearance potential measurements.
[c] Also Re analog.
[d] Also Ge, Sn, Pb analogs.

$$Cl_3SiRe(CO)_5 + 2SbCl_5 \rightarrow Re(CO)_5Cl \cdot SbCl_5 + SiCl_4 + SbCl_3 \qquad (128)$$

Fragmentation of compounds with metal–cyclopentadienyl bonds has been observed to give rise to very abundant $C_5H_5Si^+$ ions (e.g., entries 9, 14, and 15). In Eq. (129), they correspond to the base peak *(32)*.

$$X_2Si[Fe(CO)_2(Cp)]_2 \rightarrow C_5H_5Si^+ + \cdots \qquad (X = H, Cl) \qquad (129)$$

It was suggested that this ion might have the penta-*hapto* arrangement (**LXVII**): calculations have since shown that this arrangement is favored energetically over alternative likely structures *(287)*, while X-ray studies of the solid compound $C_5Me_5Sn^+BF_4^-$ reveal that $C_5Me_5Sn^+$ adopts a similar geometry *(267)*.



(LXVII)

Other processes established include the migration of halogen from silicon to metal (e.g., entries 1, 9, and 12) and of fluorine from carbon to metal (entry 4). Ions containing silicon and oxygen are sometimes found (e.g., entries 2 and 16); while they may arise from adventitious hydrolysis, it seems probable that they are also the result of migration of silicon from metal to carbonyl oxygen (see Section III,F,2).

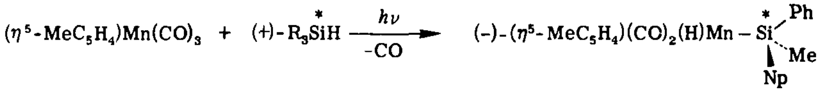
Measurements of appearance potentials can, in favorable circumstances, provide estimates of silicon–transition-metal bond dissociation energies. Thus D(Si–M) in $Me_3SiM(CO)_5$ is 240 kJ mol^{-1} (M = Mn) (*81, 108*) and 300 kJ mol^{-1} (M = Re) (*82*). This illustrates the general point that the heavier transition metals in a group form the strongest bonds with silicon; other group IV elements do the same (*87*). Confirmation of these high values for D(Si–M) comes from measurements of the dissociation of the diatomic molecule AuSi at high temperatures in the gas phase, from which a value of 318 ± 17 kJ mol^{-1} for D(Au–Si) was inferred (*192*).

For a series of compounds $Me_3MMn(CO)_5$, the dissociation energy D(M–Mn) remains similar or falls slightly on passing from M = Si to Ge to Sn, while estimates of force constants from vibrational spectra also suggest that the Si–Mn bond is a little stronger than the Ge–Mn linkage (*129, 410*). In the case of $Me_3MRe(CO)_5$, however, the bond dissociation energies increase in the order $M = Si < Ge < Sn$ (*82*). Although an exact value for D(Si–Co) in $Me_3SiCo(CO)_4$ could not be obtained, it appears to be greater than 230 kJ mol^{-1} and less than the corresponding value for D(Sn–Co) (*82*). It is interesting that the value of D(Si–Fe) rises from 190 kJ mol^{-1} in $Me_3SiFe(CO)_2(Cp)$ to 215 kJ mol^{-1} in the phosphine-substituted derivative $Me_3SiFe(CO)(PPh_3)(Cp)$. In corresponding pairs of compounds, D(Si–Fe) is again less than D(Sn–Fe) (*410*), and bonds to Cr, Mo, and W probably become stronger on passing from Si to Ge to Sn (*87*).

E. OPTICAL ACTIVITY IN SILICON–TRANSITION-METAL COMPOUNDS

The synthesis of a number of compounds of the type $R^1R^2R^3SiM(L)_n$, with a chiral silicon atom, has made it possible to examine the stereochemistry of reactions of silicon in some detail. Table XXII shows that compounds with silicon linked to Mn, Fe, Co, and Pt have been studied.

Compound (**LXVIII**) in entries 1–6 is readily made by the oxidative addition–elimination reaction:



$$(\eta^5\text{-MeC}_5\text{H}_4)\text{Mn(CO)}_3 + (+)\text{-R}_3\overset{*}{\text{Si}}\text{H} \xrightarrow[-\text{CO}]{h\nu} (-)\text{-}(\eta^5\text{-MeC}_5\text{H}_4)(\text{CO})_2(\text{H})\text{Mn}-\overset{*}{\text{Si}}(\text{Ph})(\text{Me})(\text{Np})$$

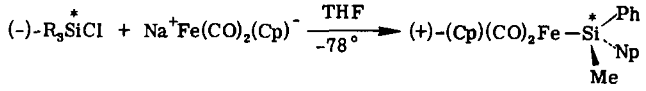
(LXVIII)

(130)

It is assumed, in common with other reactions involving metal insertion into Si–H bonds (see below), that this reaction proceeds with retention of configuration at silicon.

Its reactions fall into two chief categories. In the first (entries 1–3), nucleophiles attack the silicon atom with inversion at silicon: this is consistent with the manganese-containing unit behaving as a good leaving group (*24, 406*). In the second type, either nucleophilic (entries 4 and 5) or electrophilic (entry 6) attack leads to reductive elimination of the original silane, with retention of configuration; this process is termed "de-insertion" by the original authors, and is related to the M—H· · ·Si interaction already present in the molecule of (**LXVIII**), evidenced by a Si· · ·H distance of only 176 pm in $Ph_3SiMnH(CO)(Cp)$ (*248, 251*) (see Sections III,G,2 and IV,A).

Compound (**LXIX**) results from the reaction of the appropriate chlorosilane with $[Fe(CO)_2(\eta^5\text{-}C_5H_5)]^-$ anions (*91, 92, 123*); such reactions proceed with inversion of configuration (*406*):



$$(-)\text{-R}_3\overset{*}{\text{Si}}\text{Cl} + \text{Na}^+\text{Fe(CO)}_2(\text{Cp})^- \xrightarrow[-78°]{\text{THF}} (+)\text{-(Cp)(CO)}_2\text{Fe}-\overset{*}{\text{Si}}(\text{Ph})(\text{Np})(\text{Me})$$

(LXIX) (131)

Reaction with nucleophiles is difficult (entries 8 and 9), and proceeds with retention in each case; this is consistent with the known behavior of the $Fe(CO)_2(Cp)$ unit as a good nucleophile and a poor leaving group (*147*). Electrophilic attack by chlorine also involves retention (entry 10).

In contrast to the behavior of the manganese derivative (**LXVIII**), the iron compound undergoes carbonyl substitution without cleavage of the Si–M bond (entry 7).

$$(+)\text{-R}_3\text{Si}^*\text{Fe(CO)}_2(\text{Cp}) + \text{PPh}_3 \xrightarrow[-\text{CO}]{h\nu} (\pm)\text{-R}_3\text{Si}^*\text{Fe}^*(\text{CO})(\text{PPh}_3)(\text{Cp}) \qquad (132)$$

(LXX)

The product (**LXX**) contains an additional chiral center at iron (with four different attached groups), and is consequently formed as a pair of

TABLE XXII

Optically Active Silicon–Metal Compounds and Their Reactions

Entry	Compound	Reagent	Silicon product[a]	Reference
1	(−)-$R_3Si^*MnH(CO)_2(Cp')$[b,c] **(LXVIII)**	H_2O	(−)-R_3Si^*OH[d] (I)	(*117, 118*)
2		$MeOH/NEt_3$	(−)-R_3Si^*OMe[d] (I)	(*117, 118*)
3		$LiAlH_4$	(−)-R_3Si^*H (I)	(*117, 118*)
4		PR_3 (R = Ph, OPh)	(+)-R_3Si^*H[e] (R)	(*117, 118*)
5		LiMe	(+)-R_3Si^*H (R)	(*117, 118*)
6		Cl_2 or CCl_4	(+)-R_3Si^*H (R)	(*117, 118*)
7	(*R*)-(+)-$R_3Si^*Fe(CO)_2(Cp)$[b,f] **(LXIX)**	$PPh_3/h\nu$	(±)-$R_3Si^*Fe^*(CO)(PPh_3)(Cp)$[g]	(*91, 92*)
8		H_2O	$(R_3Si^*)_2O$[d] (R)	(*91, 92*)
9		$LiAlH_4$	(−)-R_3Si^*H (R)	(*91, 92*)
10		Cl_2	R_3Si^*Cl[h] (R)	(*91, 92*)
11		$P(OPh)_3$	(−)-R_3Si^*H (R)	(*93*)
12	(−)-$R_3Si^*Fe^*(CO)(PPh_3)(Cp)$[b,f] **(LXX)**	$LiAlH_4$	(−)-R_3Si^*H (R)	(*91, 92*)
13		Cl_2	R_3Si^*Cl[h] (R)	(*91, 92*)
14		Cl_2/PPh_3	R_3Si^*Cl[h] (I)	(*91, 92*)
15	(*S*)-(+)-$R_3Si^*Co(CO)_4$[b] **(LXXI)**	Et_3SiH	(+)-R_3Si^*H (R)	(*407, 408*)
16		R'OH (R = H, Me)[i]	(−)-R_3Si^*OR' (I)	(*114, 115, 407, 408*)
17		$LiAlH_4$	(−)-R_3Si^*H (I)	(*114, 115*)
18		$Hg(OAc)_2$	(−)-R_3Si^*OAc (I)	(*114, 115*)
19		$NMe_3(CH_2Ph)^+F^-$	(±)-R_3Si^*F (rac)	(*114, 115*)
20		X_2 (X = Cl, Br)	(−)-R_3Si^*X[h] (R)	(*114, 115*)

21		Cl_2/PPh_3	(±)-R_3Si^*Cl (rac)	(*114, 115*)
22		LiMe (excess)[j]	R_3Si^*Li[k] (R)	(*114, 115*)
23		LiPh (1 mole)	*trans*-$[R_3Si^*Co(CO)_3COPh]^-Li^+$[l]	(*120*)
24	*trans*-(*S*)-(+)-$R_3Si^*PtCl(L)_2$ **(LXXII)** (L = PMe_2Ph)	$LiAlH_4$	(+)-R_3Si^*H (R)	(*157, 163, 164*)
25		PhSH	(+)-R_3Si^*H (R)	(*157, 163, 164*)
26		Et_3SiH	(+)-R_3Si^*H (R)	(*157, 163, 164*)
27		X_2 (X = Br, I)	R_3Si^*Cl (R)	(*157, 163, 164*)
28	*trans*-(−)-$R_3Si^*PtH(L)_2$ **(LXXIII)** (L = PPh_3)	$LiAlH_4$	(−)-R_3Si^*H (R)	(*163, 164*)
29		PhSH	(−)-R_3Si^*H (R)	(*163, 164*)
30		PhCOCl	(−)-R_3Si^*H (R)	(*163, 164*)
31		$PhC\equiv CH$	(−)-R_3Si^*H (R)	(*163, 164*)

[a] R = retention, I = inversion, rac = racemization.

[b] R_3Si^* = MePh(1-naphthyl)Si.

[c] Cp′ = η^5-MeC_5H_4.

[d] Converted into R_3Si^*H by $LiAlH_4$, with retention, to estimate optical purity.

[e] Also (Cp′)$Mn(CO)_2(PR_3)$.

[f] Cp = η^5-C_5H_5.

[g] Similar mixtures of diastereoisomers result using $P(cyclohexyl)_3$ and $P(OEt)_3$.

[h] Converted into R_3Si^*H by $LiAlH_4$, with inversion, to estimate optical purity.

[i] With NEt_3.

[j] MeMgBr behaves similarly but with lower stereospecificity.

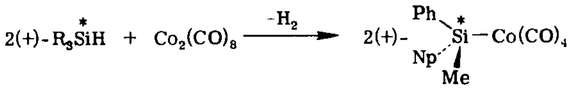
[k] Converted by water into R_3Si^*H, with retention, to estimate optical purity.

[l] On heating, gives R_3Si^*COPh, with retention.

diastereoisomers. These can be separated by fractional crystallization, and their reactions have been studied. The (−) isomer behaves similarly to the parent compound (**LXIX**) in its reactions with $LiAlH_4$ or Cl_2 (entries 12 and 13), but predominant inversion of configuration occurs with Cl_2 and PPh_3 together (entry 14). The reasons for this behavior are not yet clearly understood.

An interesting reaction occurs between compound (**LXIX**) and $P(OPh)_3$ (entry 11); R_3Si^*H is eliminated in a process reminiscent of reductive elimination, with retention of configuration; the proposed mechanism, involving *ortho*-hydrogen elimination from a phenyl group of the ligand, has already been outlined in Section III,B,4, and the observed retention underlines the similarity of this reaction to that of $R_3Si^*MnH(CO)_2(\eta^5\text{-}MeC_5H_4)$ in entry 4.

The cobalt compound $R_3Si^*Co(CO)_4$ (**LXXI**) was historically the first optically active silicon–transition-metal derivative to be prepared (*407*), using the route of Eq. (133).



(133)

(LXXI)

An exactly similar reaction is observed in the case of (+)-R_3Ge^*H, and the product, (+)-$R_3Ge^*Co(CO)_4$, has been shown by X-ray diffraction techniques to have the absolute configuration (*S*) (*115*). In the same way, diffraction studies show the absolute configuration of (+)-R_3Si^*H to be (*R*), and (+)-R_3Ge^*H is known to be the same (*116*). It may therefore be deduced that the product of reaction (133) is (*S*)-(+)-$R_3Si^*Co(CO)_4$, and that the reaction follows the general rule of retention at silicon for reactions involving substitution or metal insertion at a Si–H bond (*164, 406*).

Attack of nucleophiles on $R_3SiCo(CO)_4$ generally proceeds readily with Si–Co bond cleavage and inversion at silicon (entries 16–18); this is consistent with $Co(CO)_4$ being a good leaving group. Entry 15 shows a substitution reaction of the Si–H bond, which goes with retention. This is clearly related to the fact that $R_3Si^*Co(CO)_4$ acts as a catalyst for Si*–H/Si*–D exchange with complete retention of configuration (*407*).

$$(+)\text{-}R_3Si^*H + PhEtMeSiD \xrightleftharpoons{\text{catalyst}} (+)\text{-}R_3Si^*D + PhEtMeSiH \qquad (134)$$

Electrophilic attack by Cl_2 causes cleavage with retention (entry 20); a number of other compounds either do not react (e.g., alkyl, aryl, and acyl halides, BF_3) or cause racemization (entries 19 and 21) (*115*).

Organolithium compounds can yield more than one product with $R_3Si^*Co(CO)_4$; equimolar amounts give an adduct resulting from nucleophilic attack by $R^{\delta-}$ on oxygen of a *trans*-carbonyl group (entry 23; compare Sections III,B,7 and III,F,1).

$$\begin{tikzcd}
(+)\text{-}R_3Si^*Co(CO)_4 + LiPh \arrow[r] & \textit{trans}\text{-}[R_3Si^*Co(CO)_3(COPh)]^-Li^+ \arrow[dl, "\text{heat}"'] \arrow[d, "(Ph_3P)_2N^+Cl^-"] \\
(-)\text{-}R_3Si^*COPh & (+)\text{-}[(Ph_3P)_2N]^+\{\textit{trans}\text{-}[R_3SiCo(CO)_3(COPh)]\}^-
\end{tikzcd} \tag{135}$$

The anion can be isolated as its salt with the large cation, $[(Ph_3P)_2N]^+$; on heating, the lithium salt decomposes to give a benzoylsilane with retention. With an excess of organolithium reagent, the optically active silylanion derivative R_3Si^*Li is produced (entry 22), possibly via an adduct of the type shown above. It may be noted that the analogous germyl anion reagents, R_3Ge^*Li, have been used to prepare optically active Ge–Ni, Ge–Mo, and Ge–W derivatives (*116*), and the silicon analog could also prove to be a useful synthetic agent.

Two methods have been used to make optically active silicon–platinum compounds (*157, 163, 164*):

$$\begin{array}{ccc} (+)\text{-}R_3Si^*H + \textit{cis}\text{-}PtCl_2(L)_2 & \xrightarrow{NEt_3} & \textit{trans}\text{-}(+)\text{-}R_3SiPtCl(L)_2 \\ (L = PMe_2Ph) & & \textbf{(LXXII)} \end{array} \tag{136}$$

$$\begin{array}{ccc} (+)\text{-}R_3Si^*H + Pt(C_2H_4)(L)_2 & \longrightarrow & (-)\text{-}R_3SiPtH(L)_2 \\ (L = PPh_3) & & \textbf{(LXXIII)} \end{array} \tag{137}$$

Both reactions are thought to proceed with retention of configuration. This has been confirmed in the first case by an X-ray diffraction study of compound **(LXXII)** (*156*), which has an absolute configuration of (*S*), corresponding to that of its precursor (*R*)-(+)-R_3Si^*H [compare Section IV,A, formula **(LV)**]. It will be seen that all the reactions in entries 24–31 proceed with retention, and it has been suggested (*163, 164*) that this is the norm for Si–Pt compounds, and that the reactions all involve six-coordinate intermediates, with successive steps of oxidative addition and reductive elimination. It is possible to demonstrate stereochemical cycles with a high degree of retention of optical activity [93% in reaction (138)].

$$\begin{tikzcd}
(+)\text{-}R_3Si^*H \arrow[r, "\textit{cis}\text{-}PtCl_2(L)_2"] & \textit{trans}\text{-}(+)\text{-}R_3SiPtCl(L)_2 \arrow[l, bend left, "LiAlH_4"]
\end{tikzcd} \tag{138}$$

F. OTHER TECHNIQUES

1. *Kinetic Measurements*

Several kinetic determinations have been performed with silicon–transition-metal compounds. These include the rates of cleavage of $R_3SiFe(CO)_2(Cp)$ and $Me_3SiMn(CO)_5$ by $HgBr_2$ or iodine (*102, 103*). In both cases the rates for corresponding group IV compounds increased in the order Si < Ge ≪ Sn, and it was suggested that the reactions proceed via an S_E2 open and a cyclic transition state respectively. Investigations of the kinetics of oxidative addition to Ir(I) compounds by R_3SiH have already been discussed in Section II,F (*179, 221, 222, 224*), while the kinetics of reductive elimination of R_3SiH have been investigated for systems such as

$$Ph_3SiMnH(CO)_2(Cp) + PPh_3 \rightarrow Ph_3SiH + Mn(CO)_2(PPh_3)(Cp) \qquad (139)$$

It was concluded that $HSiPh_3$ is lost in a concerted unimolecular process (*225*).

A recent investigation of the hydrosilation of alkynes by Et_3SiH in the presence of the bridged derivative $\{(PhCH_2)Me_2SiPt[P(cyclohexyl)_3](\mu\text{-}H)\}_2$, analogous to (**LVIII**), has shown that the rate increases as the π-acceptor power of the alkyne increases, consistent with the formation of Si–Pt–alkyne complexes as intermediates (*416*). This complements earlier kinetic studies on the hydrosilation of alkenes catalyzed by Co, Rh, and Pt compounds, in which similar Si–metal–alkene intermediates were postulated (*85, 134*).

2. *Photoelectron and Mössbauer Spectroscopy*

Photoelectron spectra using ultraviolet excitation have been reported for $H_3SiMn(CO)_5$ (*129, 369*), $F_3SiMn(CO)_5$ (*371*), $Me_3SiMn(CO)_5$ (*319*), $H_3SiRe(CO)_5$ (*129*), and $H_3SiCo(CO)_4$ (*129*). In a number of cases, comparisons have been made with similar carbon and germanium derivatives, and attempts have been made to relate the inferred ordering of molecular-orbital energy levels to observed electronic spectra (*319*). Although it is hard to draw firm conclusions from the results, it seems likely that the σ-acceptor power of the MR_3 groups increases in the order M = C < Ge < Si. There is no clear evidence for d_π–d_π interaction between silicon and the transition metal, and in particular a decrease in Si–M bond length (and hence an increase in bond energy) on passing from $H_3SiMn(CO)_5$ to $F_3SiMn(CO)_5$ is attributed to stronger σ-interaction in the latter compound (*371*).

The X-ray–excited O(1s) photoelectron spectra of various compounds of the type $RMn(CO)_5$ have been correlated with infrared carbonyl stretching frequencies, and conclusions have been drawn about the extent of π-donation from metal to ligands; in particular, it is inferred that the $SiCl_3$ group in $Cl_3SiMn(CO)_5$ is a rather poor π-acceptor (*265*).

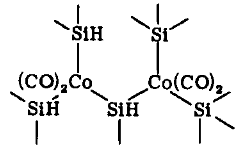
Measurements of Mössbauer spectra have been confined to a number of silicon–iron derivatives (^{57}Fe spectra). Compounds studied include $(H_3Si)_2Fe(CO)_4$ and $H_3SiFeH(CO)_4$ (*48*); $Ph_nX_{3-n}SiFe(CO)_2(Cp)$ (X = Cl, C_6F_5) (*107*); $Cl_3SiFeH(diphos)_2$ and $(R_3Si)_2Fe(diphos)_2$ (R = Cl, OEt; diphos = $Ph_2PCH_2CH_2PPh_2$) (*355*); $[ClMeSiFe(CO)_4]_2$ (*395*); and a range of derivatives $RFe(CO)_2(Cp)$ in which R = $Ph_nMe_{3-n}Si$ (n = 0–3), Et_3Si, Me_5Si_2, Me_7Si_3, or various organo groups (*354*). In the last case, it was shown that the silyl compounds had greater s-electron density at iron than their alkyl analogs, and the authors suggested that this was related to the superior σ-donor ability of silyl groups rather than to significant silicon–metal π-interaction (*354*). The dimeric character of the compound $[ClMeSiFe(CO)_4]_2$, with a four-membered $\overline{\mathrm{FeSiFeSi}}$ ring, was confirmed by its Mössbauer spectrum, typical of that expected for six-coordinate iron (*395*). There appear to have been no instances of NQR spectra since the early work on a range of group IV compounds of general type $X_3MCo(CO)_4$ (M = Si, Ge, Sn, Pb) (*78, 341*); in the case of $Cl_3SiCo(CO)_4$, the ^{59}Co, ^{35}Cl, and ^{37}Cl resonances were observed, and some evidence was adduced for Si–Cl π-bonding.

V. Topics of Special Interest

A. PYROLYSIS AND CHEMICAL VAPOR DEPOSITION: METAL SILICIDES

Silicon–transition-metal compounds vary widely in their resistance to thermal degradation; in the case of the hydrido derivatives, some approximate decomposition temperatures are: $H_3SiV(CO)_6$, 25°C; $H_3SiFeH(CO)_4$, 70°C; $H_3SiCo(CO)_4$, 100°C; $H_3SiMn(CO)_5$, 130°C; $(H_3Si)_2Fe(CO)_4$, 150°C; $H_2Si[Re(CO)_5]_2$, 180°C (*25*). Where comparisons are possible, they are all more stable thermally than their carbon analogs. Although reports of corresponding temperatures for organo- and halogenosilyl derivatives are sparse (*42, 213a, 215, 235, 306*), it appears that most of these compounds begin to decompose below 200°C.

Early studies on $H_3SiCo(CO)_4$ and $H_3SiMn(CO)_5$ showed that H_2 and CO were important volatile decomposition products, and it was at first supposed that the dark residual solid consisted of a highly cross-linked network of SiH_x and $M(CO)_y$ units, linked by silicon–metal bonds (*29*, *30*), like (**LXXIV**).



(LXXIV)

It soon became clear, however, that other processes, such as Si–O bond formation and disproportionation, were occurring, as already discussed in Sections III,F,2 and III,G,1.

A more detailed study of the pyrolysis of $H_3SiMn(CO)_5$ in a sealed tube for various periods of time at 450°C showed that the volatile products were H_2, CO, SiH_4, and CH_4; a metallic-looking brown film covered the walls of the tube, and an apparently amorphous grey powder was also present (*33*). Figure 5 shows that hydrogen and methane are produced in increasing amounts as the reaction proceeds, while CO reaches a steady concentration after about 10 min. Silane reaches a maximum concentration after about 5 min, then decreases to zero after 60 min.; silane is known to decompose to silicon and hydrogen above about 425°C (*368*), and its presence is readily accounted for by the disproportionation reaction (109).

Any disiloxane, $(SiH_3)_2O$, produced as a result of silicon migration from metal to oxygen (Section III,F,2) will rapidly decompose at 450°C

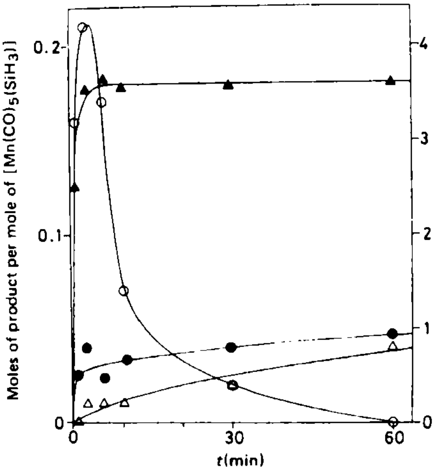


FIG. 5. Volatile products from the static pyrolysis of $H_3SiMn(CO)_5$. Key: left-hand scale, SiH_4 ○, CH_4 △; right-hand scale, H_2 ●, CO ▲.

to yield SiH_4 and polymeric solids containing silicon, oxygen, and possibly hydrogen (*22*). Carbon monoxide is an inevitable breakdown product of metal carbonyl derivatives, and its slow reaction with hydrogen, possibly catalyzed by the solid metal-containing products, accounts for the formation of methane.

$$CO + 3H_2 \rightarrow CH_4 + H_2O \tag{140}$$

Water will be removed by reaction with Si–H bonds.

After 60 min at 450°C, the inferred composition of the residual solid is $Si_{1.00}Mn_{1.00}C_{1.36}O_{1.40}H_{0.97}$; it will be seen that nearly 30% of the original oxygen and carbon is retained. Bearing in mind the vigorous conditions, this suggests that these elements are present not as residual carbonyl groups but combined with silicon and manganese respectively. It is significant that the decomposition of $Cr(CO)_6$ at 630°C leads to as little as 40% of the chromium as free metal, the remainder being present as carbide and oxide (*351*). As a route to pure metal silicides, pyrolysis under these conditions offers little hope of success; uv photolysis gives similar unpromising products (*80, 83*).

Much more promising results have been obtained with a flow system shown diagrammatically in Fig. 6; this allows the vapor of a silyl metal-carbonyl derivative to be rapidly pyrolyzed in a stream of helium

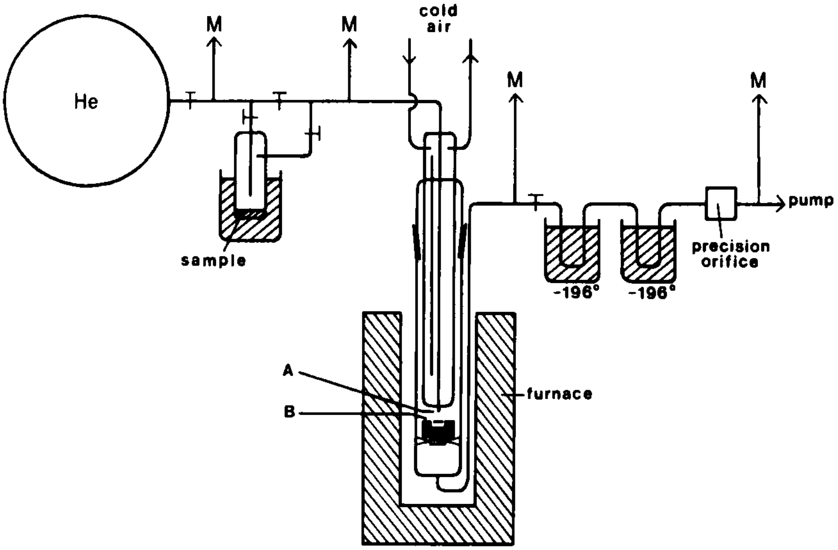


FIG. 6. Chemical vapor deposition apparatus for deposition of metal silicides. Key: A, vapor exit nozzle from cooled inlet tube; B, substrate plate (e.g., Si, SiO_2, metals), with metal support.

as carrier gas at low pressure. Chemical vapor deposition (c.v.d.) processes of this kind are being used increasingly for the production of pure materials needed for electronics applications (*366*), although their use to prepare metal silicides has until now been limited to the coreduction of $SiCl_4$ and a volatile transition metal halide, heated together in the vapor phase in a stream of hydrogen (*339*).

In the present case, conditions are adjusted so that helium and silyl metal-carbonyl vapor (typically with a mole ratio of 30 : 1) have a total pressure of about 1 mmHg. Decomposition is very rapid on entering the furnace: crystalline solids may form around the exit nozzle, while a matt grey or mirror-like thin film is deposited on a small plate about 5 mm from the nozzle. These thin films have been analyzed by X-ray powder and electron microprobe methods, and directly by atomic absorption spectroscopy (*33, 121, 187*).

Silyl cobalt tetracarbonyl decomposes in a straightforward way to give a single phase:

$$H_3SiCo(CO)_4 \xrightarrow{500°C} CoSi\ (+\ H_2 + CO) \qquad (141)$$

Similarly, disilyl iron tetracarbonyl gives as a single product the low-temperature (β) form of iron disilicide, a semiconductor; on annealing at 1000°C for 4 days, the β form decomposes to give a mixture of the iron-deficient high-temperature (α) form, together with FeSi.

$$(H_3Si)_2Fe(CO)_4 \xrightarrow{500°C} \beta\text{-}FeSi_2 \xrightarrow{1000°C} \alpha\text{-}FeSi_2 + FeSi \qquad (142)$$

Silyl manganese pentacarbonyl decomposes in a more complex way to give a mixture of two phases, "MnSi" (actually a silicon-rich nonstoichiometric phase of approximate composition $MnSi_{1.25}$) and stoichiometric Mn_5Si_3, such that the overall metal : silicon ratio is 1 : 1. The analogous rhenium system behaves similarly.

$$H_3SiMn(CO)_5 \xrightarrow{500°C} \text{"MnSi"} + Mn_5Si_3 \qquad (143)$$

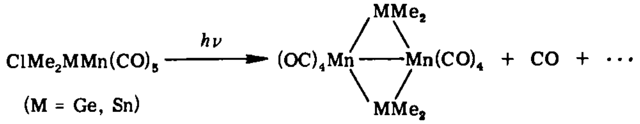
These examples illustrate the important general point that the metal : silicon ratio of the silicide film is always the same as that in the volatile precursor.

These reactions appear to involve a rapid stripping process, reminiscent of that occurring in a mass spectrometer (Section IV,D). Hydrogen and CO are lost before the system is able to reach equilibrium: the products are therefore different from those formed in sealed-tube reactions and favored thermodynamically. Provided that it is possible to synthesize sufficiently volatile precursors with the desired metal : silicon ratio, this c.v.d. process affords a route to thin films of a range of pure metal silicides, using relatively low temperatures. In contrast, other methods of preparation usually involve heating silicon–metal mixtures to high temperatures, and often produce a number of different phases (*18, 59, 187*).

B. Silicon–Transition-Metal Cluster Compounds

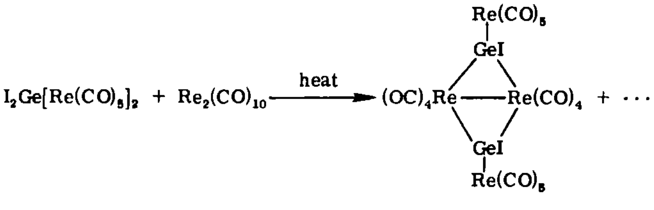
Following the many recent developments in the chemistry of metal carbonyl clusters and other metal–metal bonded species, interest has developed in silicon–transition-metal clusters. These will be defined for the present purpose as compounds containing (1) at least one metal–metal bond and (2) at least one silicon atom directly linked to two or more metal atoms. Thus compounds such as $Me_3SiOs(CO)_4Os(CO)_4$-$SiMe_3$ and $R_3SiOCCo_3(CO)_9$ are excluded; examples of compounds that meet these criteria are shown in Table XXIII.

Structural features of the compounds in entries 1–6 have already been discussed in Section IV,A. The manganese compound in entry 2 (and its rhenium analog) were prepared by heating Ph_2SiH_2 with the metal carbonyl $M_2(CO)_{10}$; similar germanium- and tin–manganese derivatives have been made via Eq. (144) (*263, 414*).



(144)

Related compounds with exocyclic group IV–metal bonds can also be made, e.g. (*282, 367*),



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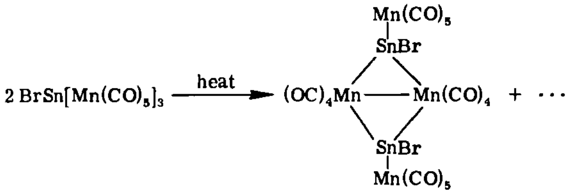
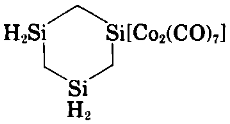


(146)

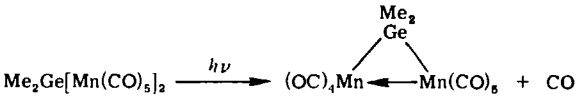
TABLE XXIII

SILICON–TRANSITION-METAL CLUSTER COMPOUNDS

Entry	Compound	M–M bridging groups	Ref.
1	$(Et_2Si)_2W_2(CO)_8H_2$ **(XLII)**	$2(Si \cdots H)$	(*52*)
2	$[Ph_2SiMn(CO)_4]_2$ **(LXI)**	2Si	(*402*)
3	$[Ph_2SiRe(CO)_4]_2$ **(XXXIX)**	2Si	(*53, 127*)
4	$(Ph_2Si)Re_2(CO)_8H_2$ **(XXXVIII)**	Si	(*173*)
5	$(Et_2Si)_2Re_2(CO)_7H_2$ **(XL)**	2Si	(*128*)
6	$(Et_2Si)_2Re_2(CO)_6H_4$ **(XLI)**	2Si	(*127*)
7	$(Me_2Si)Fe_2(CO)_8$ **(LXXVIII)**	Si	(*68*)
8	$(Ph_2Si)Fe_2(CO)_3(Cp)_2$[a] **(LXXVI)**	Si,CO	(*110*)
9	$(MeRSi)Fe_2(CO)_3(Cp)_2$[a,b] **(LXXVI)**	Si,CO	(*309*)
10	$(Me_2Si)_2Fe_2(CO)_7$ **(LXXVII)**	2Si,CO	(*268, 289, 395*)
11	$(ClMeSi)_2Fe_2(CO)_7$ **(LXXVII)**	2Si,CO	(*395*)
12	$(Cl_2Si)_2Fe_2(CO)_7$ **(LXXVII)**	2Si,CO	(*391*)
13	$(Me_3Si)_2(Me_2Si)_2Ru_2(CO)_6$[c] **(XLVII)**	2Si	(*76, 130*)
14	$(Me_2Si)_3Ru_2(CO)_6$ like **(LXXIX)**	3Si	(*76*)
15	$(Me_2Si)_3Os_3(CO)_9$ **(LXXXI)**	Si	(*76*)
16	$(R_2Si)Co_2(CO)_7$[d] **(LXXXII)**	Si,CO	(*181, 268*)
17	$(Cl_2Si)Co_2(CO)_7$ **(LXXXII)**	Si,CO	(*2*)
18	$[(OC)_4Co]PhSiCo_2(CO)_7$ **(LXXXII)**	Si,CO	(*46*)
19	$[(OC)_5Mn]ClSiCo_2(CO)_7$ **(LXXXII)**	Si,CO	(*2*)
20	 **(LXXXII)**	Si,CO	(*186*)
21	$(Me_2Si)_2Co_2(CO)_6$ **(LXXXIII)**	2Si	(*268*)
22	$[(OC)_4Co]SiCo_3(CO)_9$ **(LII)**	Si	(*389, 396*)
23	$(OC)_9Co_3SiSiCo_3(CO)_9$	Si	(*269, 278*)
24	$(Me_2Si)Pt_2[P(cyclohexyl)_3]_2(C{\equiv}CPh)_2$ **(LIX)**	$Si,C{\equiv}C$	(*105*)

[a] Cp = η^5-C_5H_5.
[b] R = H, Cl.
[c] Also Os analog.
[d] R = Me, Et, Ph.

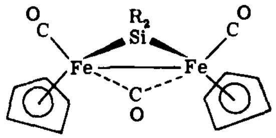
On the other hand, the photolysis of $Me_2Ge[Mn(CO)_5]_2$ leads to a compound first formulated as **(LXXV)** with no bridging CO groups (*263*), but now known to be $(OC)_4Mn(\mu\text{-}CO)(\mu\text{-}GeMe_2)Mn(CO)_4$ (*413a*).



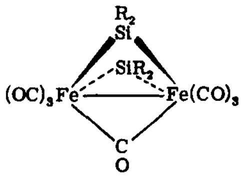
(LXXV)

(147)

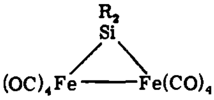
The iron derivatives in Table XXIII fall into three categories based on the structures (**LXXVI**) (entries 8 and 9), (**LXXVII**) (entries 10–12), and (**LXXVIII**) (entry 17).



(**LXXVI**; and corresponding trans form)

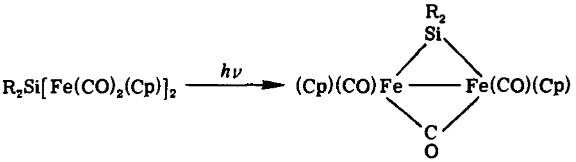


(**LXXVII**)

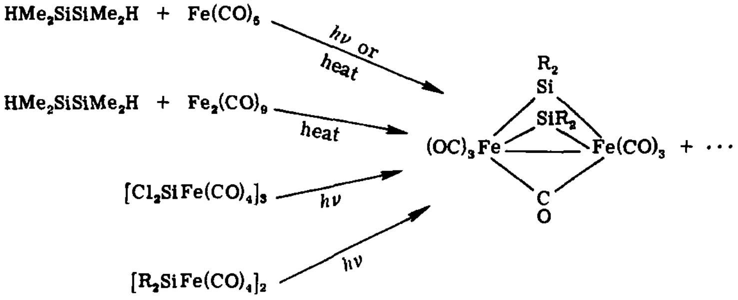


(**LXXVIII**)

They have been prepared by the following reactions:



(148)

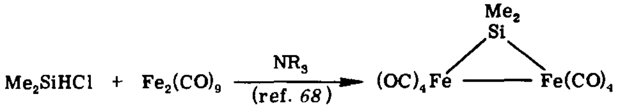


$R_2 = Me_2$, HMe

R = Me; refs. (*268, 289*)
R = Cl; ref. (*391*)
$R_2 = Me_2$, HMe; ref. (*395*)

(149)

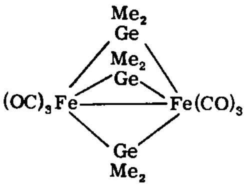
where R = Me (Refs. *268, 289*), R = Cl (Ref. *391*), or $R_2 = Me_2$ or HMe (Ref. *395*).



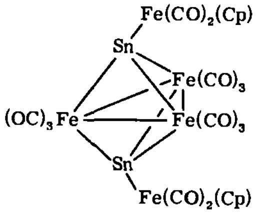
(150)

NMR studies of the cis–trans isomerism of (**LXXVI**; R_2 = HMe) (*309*), the fluxionality of (**LXXVII**; R = Me) (*289*), and the ^{29}Si chemical shift of (**LXXVIII**; R = Me) (*68*) have already been discussed in Section IV,C.

Germanium and tin analogs of structures (**LXXVI**) and (**LXXVII**) are known (*172, 213, 263, 414*), and some of them are fluxional (*4, 213*); a germanium analog of compound (**LXXVIII**) has also been reported (*77*; see also Ref. *324*). No silicon–iron example of the structural types represented by (**LXXIX**) (*77*) or (**LXXX**) (*320*) has yet been prepared,

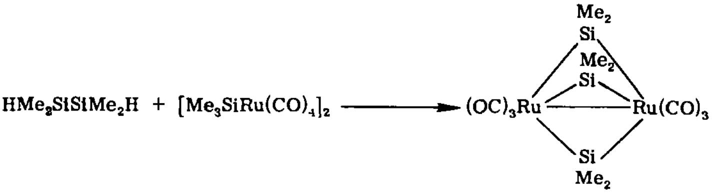


(LXXIX)



(**LXXX**)

although the Si–Ru analog of (**LXXIX**) is known (entry 14); the disilicon bridged Ru and Os derivatives (entry 13) also have no Si–Fe counterpart. They and the interesting trinuclear osmium cluster (**LXXXI**) (entry 15) are prepared by the extrusion of silylene units from disilanes in the presence of metal carbonyl compounds (*76*) (cf. reactions 149 and 157).



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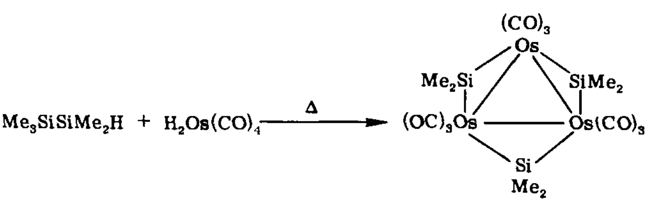
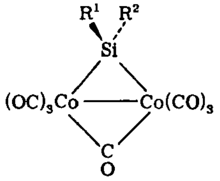


(**LXXXI**)

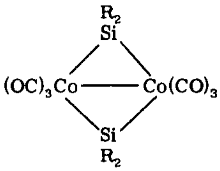
(152)

The chemistry of silicon–cobalt clusters is more complicated because of the ready elimination of CO from proximate $Co(CO)_4$ groups (*208*) to give $Co_2(CO)_7$ or $Co_3(CO)_9$ units. This elimination is generally easier for silicon–cobalt compounds than for corresponding germanium and tin derivatives, so that, for example, no stable silicon analogs of $Sn[Co(CO)_4]_4$ (*178, 393*) or $RM[Co(CO)_4]_3$ (M = Ge, Sn) (*178, 190, 334*) are known.

Structures of compounds in entries 16–20 are all based on the type (**LXXXII**), in which R^1 and R^2 can be alkyl, aryl, halogen, a metal carbonyl group, or part of a cyclic system.



(LXXXII)



(LXXXIII)

They are usually readily prepared by reactions such as Eq. (153) (*2, 181*), where R = Ph, Et, Cl, or Eq. (154) (*46*).

$$R_2SiH_2 + Co_2(CO)_8 \rightarrow R_2SiCo_2(CO)_7 + CO + H_2 \tag{153}$$

$$2PhSiH_3 + 3Co_2(CO)_8 \rightarrow 2[(OC)_4Co]PhSiCo_2(CO)_7 + 2CO + 3H_2 \tag{154}$$

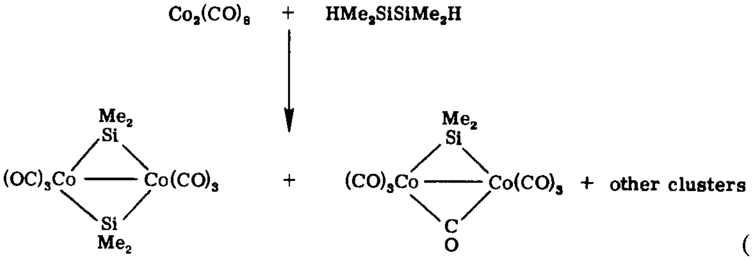
There is no evidence that they will react with CO to form an open silanediyl derivative, although germanium analogs undergo the following reversible change (*49, 263*):

$$R_2GeCo_2(CO)_7 \underset{h\nu}{\overset{CO}{\rightleftharpoons}} R_2Ge[Co(CO)_4]_2 \tag{155}$$

Again, the germanium analog of the product from reaction (154) can gain or lose CO to form an open germanetriyl or a closed tricobalt cluster derivative, but the silicon compound apparently undergoes neither of these reactions (*46, 178*).

$$\underset{(R = Me, Ph)}{RGeCo_3(CO)_9} \xleftarrow{\Delta} [(OC)_4Co]RGeCo_2(CO)_7 \xrightarrow[300\ atm]{CO} \underset{(R = Ph)}{RGe[Co(CO)_4]_3} \tag{156}$$

Structure (**LXXXIII**) is represented by the compound in entry 21; it is one product from the following reaction (*268*):



(157)

Both germanium (*5*) and tin (*414*) analogs are known, and their ready fluxionality (down to below −50°C) has been studied in detail (*5*).

The compound in entry 22, $(OC)_4CoSiCo_3(CO)_9$ (LII), results when a mixture of SiI_4 and $Na^+Co(CO)_4^-$ in hexane is warmed and irradiated; probably $ISiCo_3(CO)_9$ is formed as an intermediate (*396*). The tetrahedral $SiCo_3$ unit parallels that found in many methylidyne tricobalt clusters of the type $RCCo_3(CO)_9$ (*358, 401*); a germanium analog of compound (LII) is known, but apparently not one with tin (*71, 389*). One of the first reported $SiCo_3$ cluster derivatives was the silicon–silicon bonded species in entry 23 (*269*).

$$Co_2(CO)_8 + SiPh_4 \xrightarrow[\text{pet. ether}]{\text{reflux}} (OC)_9Co_3Si{-}SiCo_3(CO)_9 \qquad (158)$$

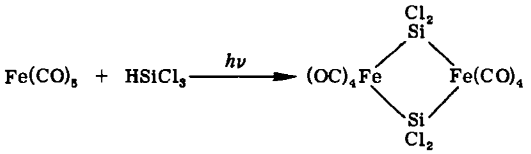
From subsequent work, however, it appears that the product isolated was $ClCCo_3(CO)_9$ (*278*). Silicon compounds of the type $RSiCo_3(CO)_9$, corresponding to one of the germanium–cobalt products of reactions (156), have not yet been made; neither has an analog of the spiroderivative $Ge[Co_2(CO)_7]_2$ (*191*). Synthetic efforts directed towards these systems would be valuable.

The sole example of a silicon–platinum cluster is the compound in entry 24: its structure has been noted in Section IV,A. It seems very likely that many further cluster systems await discovery, particularly with iridium, platinum, and gold, and that this represents an important future area of research. One obvious application is as precursors to metal silicides with high metal : silicon ratios using c.v.d. techniques (compare Section V,A).

C. METAL-COMPLEXED SILYLENE DERIVATIVES

There are a number of successful examples of the stabilization of a short-lived species by coordination to a metal center (*388*), and to these can now be added the silylene (SiR_2) group, which normally exists only as a transient intermediate (*332*).

Attempts to produce compounds of the type $R_2SiM(CO)_n$, in which the silylene is acting as a two-electron donor, normally lead to isolation of oligomers (*258, 391, 392, 395*).



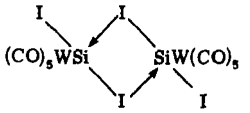
(159)

$$Et_4N^+[R^1R^2ClSiFe(CO)_4]^- \xrightarrow{AlCl_3} [R^1R^2SiFe(CO)_4]_n + AlCl_4^- \qquad (160)$$

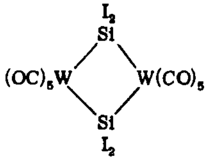
where $n = 3$ for $R^1 = R^2 = Cl$; or $n = 2$ for $R^1R^2 = Me_2$, MeCl, (cyclohexyl)Cl.

$$W(CO)_6 + Si_2I_6 \xrightarrow{h\nu} [I_2SiW(CO)_5]_2 \qquad (161)$$

The original authors suggested that the products of reactions (160) and (161) might be halogen-bridged [e.g., (**LXXXIVa**)], but a directly bonded ring such as (**LXXXIVb**) and the product of reaction (159) seem



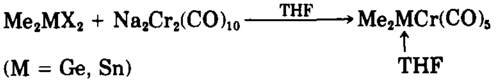
(LXXXIVa)



(LXXXIVb)

at least as likely.

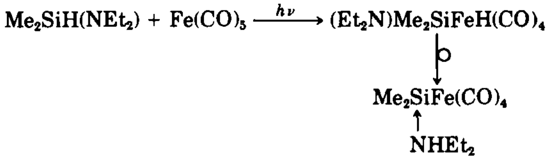
In the case of germanium and tin, reactions such as (162) lead to the production of $GeMe_2$– or $SnMe_2$–metal complexes, stabilized by electron donation from the Lewis base, tetrahydrofuran (*315*).



$$\underset{(M = Ge, Sn)}{Me_2MX_2 + Na_2Cr_2(CO)_{10}} \xrightarrow{THF} \underset{\overset{\uparrow}{THF}}{Me_2MCr(CO)_5} \qquad (162)$$

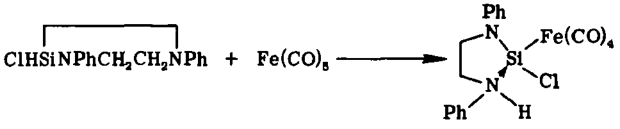
Furthermore, if the groups attached to the group IV atom are large, unsolvated derivatives such as $R_2GeCr(CO)_5$ [$R = CH(SiMe_3)_2$, $N(SiMe_3)_2$, or mesityl] can be isolated (*266*, *292*).

With silicon, no exactly analogous products have been reported. A base-stabilized Me_2Si–iron derivative has been produced, however, by the following ingenious reaction (*394*).



$$Me_2SiH(NEt_2) + Fe(CO)_5 \xrightarrow{h\nu} (Et_2N)Me_2SiFeH(CO)_4 \rightarrow \underset{\overset{\uparrow}{NHEt_2}}{Me_2SiFe(CO)_4} \qquad (163)$$

It is stable only below −20°C. Attempts to produce an unsupported silylene–iron complex by the removal of HCl from compound (**LXXXV**) were unsuccessful (*394*).



(LXXXV) (164)

The first silylene–metal complex with no base stabilization was prepared by extrusion of $SiMe_2$ from a substituted disilane (*384*), as in Eq. (165) where R is H or Me.

$$Fe_2(CO)_9 + HMe_2SiSiMe_2R \xrightarrow[25°C;\ 15\ h]{benzene} Me_2SiFeH(CO)_3(SiMe_2R) \qquad (165)$$

The product is a barely volatile liquid at room temperature; with PPh_3, both silicon atoms are displaced from iron, leaving $Fe(CO)_3(PPh_3)_2$.

Silylene–metal complexes, $R_2SiM(L)_n$, have often been invoked as possible intermediates in metal-catalyzed reactions of silicon compounds. Some examples of M include Ni (reaction of organodisilanes with alkynes) (*345*); Pt (disproportionation of methyldisilanes) (*431*); Rh (formation of organodisilanes and trisilanes from substituted hydridosilanes) (*342*); and Pd (reaction of substituted silacyclopropenes with alkynes) (*383*). Iron–silylene intermediates may also be involved in the decomposition of η^3-silaallyl derivatives* such as $(CH_2CHSiMe_2)Fe(CO)_3SiR_3$ (*385*) or of (η^4-disilahexadiene)–$Fe(CO)_3$ complexes (*328*); in both cases, SiR_2 species appear as products. It may finally be noted that the proposed di(silylene)–platinum complex $(Ph_3P)_2Pt(SiCl_2)_2$ (*390*) should now be re-formulated as a cyclic platinadisiloxane $(Ph_3P)_2\overline{PtSiCl_2OSiCl_2}$ (*197*) (see Section III,B,8).

Appendix

Since this review was written, a number of significant new papers have appeared; they are briefly noted here in relation to the most relevant section of the text.

Section II,A,3. The harmful effect of cyclic ethers as solvents is emphasised by a recent study of their reaction with $Me_3SiMn(CO)_5$ (cf. Section III,B,3) (*437*):

$$\begin{array}{lcl} Me_3SiMn(CO)_5 + \overline{CH_2[CH_2]_nO} & \longrightarrow & (OC)_5Mn[CH_2]_{n+1}OSiMe_3 \\ (n = 2\text{–}4) & & \quad\big\downarrow\ CO \\ & & (OC)_5MnC(O)[CH_2]_{n+1}OSiMe_3 \end{array}$$

Acyclic ethers R_2O also attack $(Me_3Si)_2Fe(CO)_4$, giving Me_3SiOR and $Me_3SiFe(R)(CO)_4$ as initial products (*435, 436*).

Section II,D. Reaction between $Hg(SiMe_3)_2$ and $(Cp)_2ZrCl_2$ gives $Me_3SiZr(Cp)_2Cl$ and $(Me_3Si)_2Zr(Cp)_2$ (*434*). Also, the novel reagent

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* But see footnote, p. 37, and Appendix.

$(Me_3Si)_3Al$ reacts with $(Cp)_2TiCl_2$ to give $Me_3SiTi(Cp)_2Cl$ (*449*). It has previously been reported that Me_3SiLi yielded no Si–Ti product with $(Cp)_2TiCl_2$, although with $TiCl_4$ some evidence for $(Me_3Si)_4Ti$ and $(Me_3Si)_2Ti \cdot n THF$ was obtained (*447*).

Sections II,E and II,F. The first examples of silylation of metal clusters are reported, using both anionic clusters with H_2 evolution (*454*):

$$HRu_3(CO)_{11}^- + 2Et_3SiH \rightarrow HRu_3(CO)_{10}(SiEt_3)_2^- + H_2 + CO$$

and neutral clusters with oxidative addition (*456*):

$$M_3(CO)_{12} + 3HSiCl_2X \rightarrow (XCl_2Si)_3M_3H_3(CO)_9 + 3CO \qquad (M = Ru, Os;\ X = Me, Cl)$$

Oxidative addition has also been used to prepare the bicyclic cis derivative $Pt(\leftarrow PPh_2[CH_2]_2SiMe_2)_2$ from Pt(cycloocta-1,5-diene)$_2$ and $Ph_2P[CH_2]_2SiHMe_2$ (*443*), and a range of cyclic compounds $SiF_2C(t\text{-}Bu){=}CHSiF_2ML_n$ [ML_n = $Mo(CO)_5$, $Mn(CO)_2(Cp)$, and $Fe(CO)_4$] from $SiF_2C(t\text{-}Bu){=}CHSiF_2$ and appropriate metal carbonyls (compare Table V, entry 39, probably an $Ni(CO)_3$ adduct) (*458*). NMR studies (*440*) of the oxidative addition of SiH_3Q (Q = H, Me, halogen, etc.) to $IrH(CO)(PPh_3)_2$, yielding $QH_2SiIrH_2(CO)(PPh_3)_2$, have shown that the stereochemistry is more complex than that postulated earlier (*179, 180*). For related studies with $IrI(CO)(PEt_3)_2$, see (*439*).

Section II,G,4,c. It is now clear (*446, 450, 451*) that the products from the reaction of $Fe_2(CO)_9$ with vinyl disilanes are not (η^3-silaallyl)-$Fe(CO)_3$ species, as previously proposed (*382, 385*), but rather η^2-vinyl adducts of $Fe(CO)_4$[e.g., (η^2-$CH_2{=}CHSiR_2X$)$Fe(CO)_4$]. All attempts to remove X as X^- have proved fruitless (cf. Section III,G,2).

Section III,E,3. All metal ligands except SiR_3 are substituted when *trans*-$Ph_3SiPtCl(PMe_2Ph)_2$ reacts with KCN and 18-crown-6 in CH_2Cl_2 solution, giving $[K(18\text{-crown-}6)]_2^+[Ph_3SiPt(CN)_3]^{2-}$ (*432*).

Section III,G,2. Sequential oxidative addition, halogenation at Si, and reductive elimination provide an elegant route to pure R_2SiHX derivatives (cf. Section III,C,1 and Table XII, entry 14) (*453*):

$$\begin{tikzcd}
(Cp')Mn(CO)_3 + Ph_2SiH_2 \arrow[r] & (Cp')Mn(H)(CO)_2SiHPh_2 \arrow[d, "\text{halogenation}"] \\
(Cp')Mn(CO)_3 + Ph_2SiHX & (Cp')Mn(H)(CO)_2SiXPh_2 \arrow[l, "CO"']
\end{tikzcd}$$

$(Cp' = \eta^5\text{-}MeC_5H_4)$

Section IV,A. Some recently determined bond lengths (from X ray, in picometers) are: d(Si–Ti) in $Me_3SiTi(Cp)_2Cl$, 267 (*449*); d(Si–Mo) in $\overline{SiF_2C(t\text{-}Bu){=}CHSiF_2Mo}(CO)_5$, 261 (*444*); d(Si–Fe) in (*cyclo*-Si_5Me_9)-$SiMe_2Fe(CO)_2(Cp)$, 235 (*438*).

Section IV,F,2. Further X-ray excited photoelectron spectra (ESCA) of $RMn(CO)_5$ (R = $SiCl_3$, SiF_3, Me, halogens, etc.) have yielded Mn, C, and O binding energies, reinforcing the earlier conclusion (*265*) that π effects vary little with change in R (*433*).

Section V,B. The first silicon–iridium cluster, $MeSiIr_3(CO)_9$, results from the reaction between $NaIr(CO)_4$ and $MeSiCl_3$ (*445*). Also, substituted tricobalt clusters of the type $MeSi[Co(CO)_3]_2[M(CO)_3(Cp)]$ (M = Mo, W) have been prepared by heating $H_2MeSiM(CO)_3(Cp)$ with $Co_2(CO)_8$ (*455*).

Section V,C. A development of the highest significance is the characterization of stable Ge=Mn derivatives (*442*); analogous silicon compounds are eagerly awaited.

Finally, recent catalytic studies in which silicon–metal intermediates have been implicated include the photocatalysis of hydrosilation (Si–Fe, *452*; Si–Co, *448*; Si–Rh, *441*) and the double silylation of alkynes with disilanes (Si–Pd, *457*).

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