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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,

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 $\text{Mn}_5\text{Si}_3\text{C}$, 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, $\text{Me}_3\text{SiFe(CO)}_2(\eta^5\text{-C}_5\text{H}_5)$, 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 | <i>Nb</i> | Mo | Tc | Ru | Rh | Pd | Ag | Cd |
| La | Hf | <i>Ta</i> | 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 $M(CO)_3(Cp)^-$ ($M = Cr, Mo, W$; $Cp = \eta^5-C_5H_5$), $Mn(CO)_5^-$, $Re(CO)_5^-$, $Fe(CO)_2(Cp)^-$ 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)



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

TABLE I

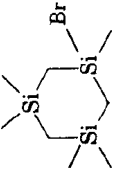
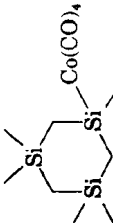
REACTIONS OF ANIONS WITH SILICON HALIDES

| Entry | Anion ^a | Silicon halide | Solvent ^b | Success ^c | Remarks | Ref. |
|-------|-------------------------|----------------------------|-------------------------------------|----------------------|--|-------------|
| 1 | $V(CO)_6^-$ | H_3SiCl | 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_2SiBr | 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_2Si-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 | $Mo(CO)_3(cp)^-$ | $R_2CH_2=CHSiCl$ | Not stated | ✓ | Similarly W | (308) |
| 10 | | R_3Si_2X | Cyclohexane | ✓ | Similarly W ^d | (300) |
| | | $XSIR_2SiR_2X$ | Cyclohexane | ✓ | Forms $XSIR_2SiR_2-Mo$ deriv.; similarly W ^d | (300) |
| 11 | $Mo(CO)_3(C_4H_7)^-$ | Ph_3SiCl | THF | × | Succeeded with Ge, Sn | (255) |
| 12 | $Mo(CO)_4(PPh_3)(Cp)^-$ | Ph_3SiCl | THF | × | — | (138) |
| 13 | $Mn(CO)_5^-$ | H_3SiI | Ether, isopentane | ✓ | Similarly Re | (7, 28, 29) |
| 14 | | H_3SiI_2 | Ether, isopentane | ✓ | Only disubstd. deriv. found; similarly Re | (32) |
| 15 | | H_3SiCl_2 | n-Hexane | ✓ | Mono- and disubstd. derivs. found | (2) |
| 16 | | Me_2SiBr | Pentane | ✓ | — | (194) |
| 17 | | Me_2SiBr | Cyclohexane | ✓ | ^d | (306) |
| 18 | | Me_3SiCl | None | ✓ | — | (62a) |
| 19 | | $Me_{3+n}Si_nX (n = 1, 2)$ | None | ✓ | — | (335) |

| | | | | | | |
|----|--|---|---|---------------------------------|--|-------------------------|
| 20 | $\text{Mn}(\text{CO})_5$ | Me_2SiCl $\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{R})\text{Cl}$ | THF | × | PPh ₃ also present | (146) |
| 21 | $\text{Mn}(\text{CO})_4(\text{PPh}_3)^-$ | R_2SiCl | <i>n</i> -Hexane Ether, CH_2Cl_2 | ✓ | Low yield, much Si-O-Si | (136) |
| 22 | $\text{Mn}(\text{CO})_3\text{L}_2^-$ | Ph_2SiCl PhSiCl R_2SiX | THF | × | Ph ₃ PNPPh ₃ cation, succeeded with Ge, Sn | (151) |
| 23 | $\text{Fe}(\text{CO})_4^+$ | H_2SiI | THF | × | Similarly Re | (138) |
| 24 | | Me_2SiI $\text{ClMe}_2\text{Si}(\text{CH}_2)_3\text{Cl}$ | THF | × | — | (138) |
| 25 | | Me_2SiCl $\text{R}_2\text{Si}^+\text{Cl}$ | THF | × | Similarly Ge, but Sn successful | (350) |
| 26 | | H_2SiI_2 $\text{R}_2(\text{CH}_2=\text{CH})\text{SiCl}$ | Me_2O , isopentane | ✓ | Some $\text{SiH}_2\text{FeH}(\text{CO})_4$ also produced | (38, 39) |
| 27 | | $\text{ClRHSiFe}(\text{CO})_4(\text{Cp})$ $\text{CH}_2(\text{CH}_2)_2\text{Si}(\text{R})\text{Cl}$ $[\text{ClMe}_2\text{SiCH}_2]_2$ | THF Ether | × | Si-O-C derivative formed Cyclic $\text{CH}_2(\text{CH}_2)_2\text{SiMe}_2\text{Fe}(\text{CO})_4$ (I) produced | (54, 331) (132) |
| 28 | $\text{Fe}(\text{CO})_4(\text{Cp})^-$ | Me_2HSiCl $\text{Me}_2\text{Si}(\text{SiMe}_2)_n\text{Cl}$ $\text{Cl}(\text{SiMe}_2)_n\text{Cl}$ $\text{Me}_{n+1}\text{Si}_n\text{Cl}$ $(\text{ClMe}_2\text{Si})_n\text{Si}$ $\text{XSiMe}_2\text{SiMe}_2\text{X}$ | THF THF Benzene, isopentane { Not stated } THF Methylcyclohexane THF THF | ✓ ✓ ✓ ✓ ✓ ✓ ✓ | Optically active MePhNpSi deriv. (Np = 1-naphthyl) Only disubstd. deriv. found | (359) (92) |
| 30 | | | | ✓ | — | (32) |
| 31 | | | | ✓ | — | (123, 308) |
| 32 | | | | ✓ | HRSi[Fe(CO) ₄ (Cp)] ₂ produced | (309) |
| 33 | | | | ✓ | — | (136) |
| 34 | $\text{Fe}(\text{CO})_2(\text{Cp})^-$ | | | ✓ | $[-\text{CH}_2\text{SiMe}_2\text{Fe}(\text{CO})_2(\text{Cp})_2]$ produced | (271, 272) |
| | | | | ✓ | — | (271, 272) |
| | | | | ✓ | — | (271, 272) |
| 35 | | | | ✓ | Disubstd. deriv. formed. $n = 3(i-); n = 4(i-)$ isomer | (271, 272) (335) |
| 36 | | | | ✓ | $\text{SiSiMe}_2\text{Fe}(\text{CO})_2(\text{Cp})_4$ produced $\text{XMe}_2\text{SiSiMe}_2\text{Fe}(\text{CO})_2(\text{Cp})$ formed ^d | (335) (300) |
| 37 | | RSiCl_2 (R = H, Me) Me_2SiBr RMeSiCl_2 (R = H, Me) | Cyclohexane Cyclohexane Cyclohexane | ✓ ✓ ✓ | $\text{Cl}_2\text{RSi}-\text{Fe}$ deriv. formed ^d ^d $\text{ClRMeSi}-\text{Fe}$ deriv. formed ^d | (306) (306) (306) |

(table continues)

TABLE I (Continued)

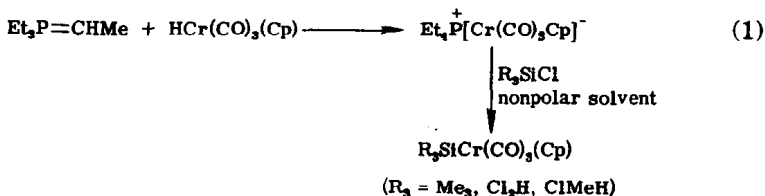
| Entry | Anion ^a | Silicon halide | Solvent ^b | Success ^c | Remarks | Ref. |
|-------|---|---|--------------------------|----------------------|--|----------|
| 38 | Co(CO) ₄ ⁻ | H ₃ SiI | Ether, Me ₂ O | ✓ | — | (26, 29) |
| 39 | Co(CO) ₄ ⁻ | H ₃ SiI ₂ | Ether | ✓ | Disubstd. deriv. only | (29) |
| 40 | Co(CO) ₄ ⁻ | H ₃ SiCl ₂ | Ether | ✓ | Mono- and disubstd. derivs. | (2) |
| | | HSiCl ₃ | Ether | ✓ | Monosubstd. deriv. only | (2) |
| | | Me ₂ HSiCl | Ether | ✓ | — | (2) |
| 41 | | Ph ₃ SiCl | THF | × | (Ph ₃ Si) ₂ O produced | (138) |
| 42 | | Me ₂ SiCl ₂ | Ether | ✓ | — | (336) |
| | | Me ₃ SiCl ₂ | Ether | × | No isolable Si-Co product | (336) |
| | | RSiCl ₃ (R = Me, Cl) | Ether | × | Cl ₃ RSiOCCo ₂ (CO) ₈ formed | (336) |
| | | Me ₂ SiCl _{4-n} (n = 0-3) | THF | × | Cl _{3-n} Me _n SiO(CH ₂) ₄ (CO)Co(CO) ₄ formed | (336) |
| 43 | | SiI ₄ | n-Hexane | ✓ | (OC) ₄ CoSiCo ₂ (CO) ₈ produced | (396) |
| 44 | |  | Methylcyclohexane | ✓ |  | (186) |
| 45 | Co(CO) ₄ (PPh ₃) ⁻ | Ph ₃ SiCl | THF | ✓ | formed, also di- and trisubstd. analogs ^c <i>trans</i> -Ph ₃ SiCo(CO) ₄ (PPh ₃) formed | (138) |
| 46 | Co ₂ (CO) ₈ | R ₃ SiCl (R = Me, Ph) | Ether | × | Me ₃ SiOCCo ₂ (CO) ₈ produced | (312) |
| 47 | Co(POR) ₃] ₂ ⁻ | R ₃ SiCl | Not stated | × | — | (325) |
| 48 | Ir(CO) ₄ ⁻ | H ₃ SiI | Ether | ✓ | — | (37) |
| 49 | M(PF ₃) ₄ ⁻ (M = Rh, Ir) | R ₃ SiCl | Ether | × | Ge analog similar, but Sn analog successful | (51) |

^a Cp = η⁵-C₅H₅.^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)₅(Cp)⁻ (M = Cr, Mo, W), Fe(CO)₄(Cp)⁻, and Mn(CO)₅.

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



and it was concluded that nucleophilic attack by $\text{Co}(\text{CO})_4^-$ 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,

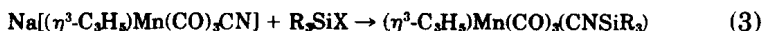


but the second (151) was not.



In the latter case, where $(\text{PNP})^+ = (\text{Ph}_3\text{P}=\text{N}=\text{PPh}_3)^+$, it was shown in a separate experiment that $\text{Me}_3\text{SiMn}(\text{CO})_3$ quickly reacts with $(\text{PNP})^+\text{Cl}^-$ to give $(\text{PNP})^+[\text{Mn}(\text{CO})_4\text{Cl}_2]^-$ 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.,

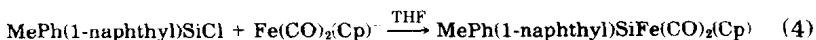


2. The Silicon Halide

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 $\text{Co}(\text{CO})_4^-$ 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.

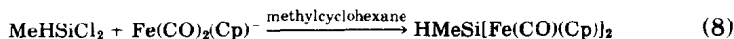
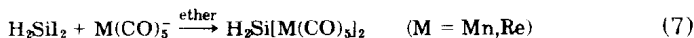
Bulky groups can be tolerated when only one metal group is to be attached to each silicon atom, as for example in the following successful reaction (92):



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),

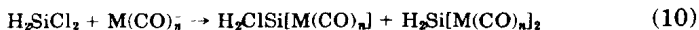
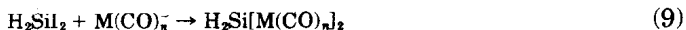


Disubstituted products result only when dihydridosilicon halides are used or in the special case of reactions with $\text{Fe(CO)}_2(\text{Cp})^-$ (2, 29, 32, 309), e.g.,



The sole reported example of a product with more than two metal atoms attached to silicon is the cluster derivative $(\text{OC})_9\text{Co}_3\text{SiCo(CO)}_4$, 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).

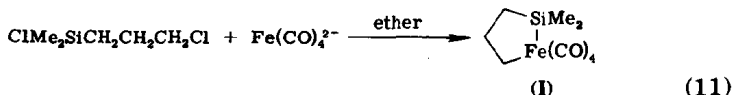
The nature of the halogen attached to silicon also affects the reaction; where comparisons can be made, iodides react more rapidly and completely than chlorides, e.g. (2, 29, 32),



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^- .

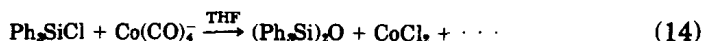
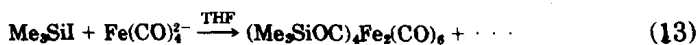
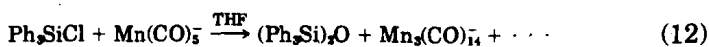
Silicon compounds with both silicon-halogen and carbon-halogen bonds can react using both these functions; an interesting example is the synthesis of the ferrasilacyclopentane (I) (132):



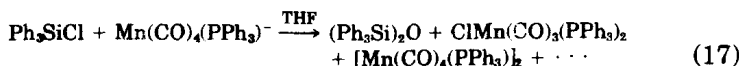
3. The Solvent

In a few cases (Table I, entries 4, 18, and 19), successful syntheses have been carried out by direct reaction between a solid metal carbonate 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.,

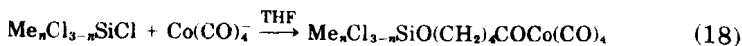


In fact, preparations involving tetrahydrofuran are successful only when using the highly nucleophilic species $\text{Fe}(\text{CO})_2(\text{Cp})^-$ and, in a solitary example, $\text{Co}(\text{CO})_3(\text{PPh}_3)^-$ (138) [which is more nucleophilic than $\text{Co}(\text{CO})_4^-$; note however that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

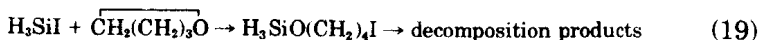


The role of tetrahydrofuran in facilitating silicon transfer from metal to oxygen is further discussed in Section III,F,2.

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.*

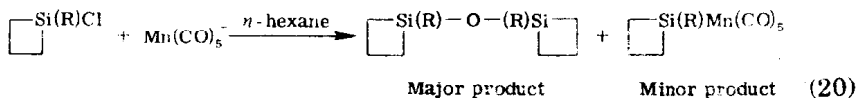


This possibility had been recognized in the case of simple silyl compounds many years ago (20):



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):



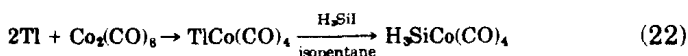
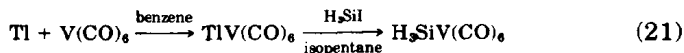
4. Conclusions

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.

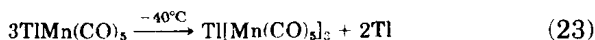
* Additional CO insertion to give an acyl derivative has also occurred in this case.

B. REACTION OF A THALLIUM METAL CARBOXYLATE 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 $\text{TM}(\text{CO})_n$ species. These Tl(I) compounds are slightly soluble in hydrocarbons and react readily with iodosilanes (8, 121):



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



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 $\text{H}_{2n+1}\text{Si}_n$ ($n = 1-5$), $\text{Me}_{2n+1}\text{Si}_n$ ($n = 1, 3, 4$), and $\text{Me}_n\text{Ph}_{3-n}\text{Si}$ ($n = 0-2$), and several dilithium derivatives $\text{Li}(\text{SiPh}_2)_n\text{Li}$ ($n = 4-6$) 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 $\text{R}_3\text{SiM}(\text{CO})_5^-$ ($\text{M} = \text{Cr}, \text{Mo}, \text{W}$) have been prepared in the following way (254):



D. REACTIONS WITH MERCURY SILYL COMPOUNDS

Some applications of the use of substituted disilyl mercury compounds, $\text{Hg}(\text{SiX}_3)_2$ ($\text{X} = \text{Me}, \text{Cl}$), 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 by-product, e.g. (entry 1),



TABLE II
REACTIONS OF SILYL ALKALI METAL COMPOUNDS WITH METAL HALIDES

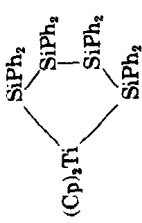
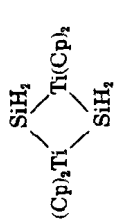
| Entry | Silyl alkali metal derivative/solvent | Metal halide | Product | Ref. |
|-------|--|---|--|----------|
| 1 | $\text{Si}_4\text{Ph}_3\text{Li}_4/\text{THF}$ | $(\text{Cp})_2\text{TiCl}_2$ |  | (239) |
| 2 | $\text{H}_2\text{SiK/glyme}$ | $(\text{Cp})_2\text{TiCl}_2$ |  | (232) |
| 3 | $\text{Ph}_3\text{SiLi}/\text{THF}$ | $(\text{Cp})_2\text{MCl}_2 (\text{M} = \text{Zr, Hf})$ | $\text{Ph}_3\text{SiM}(\text{Cl})(\text{Cp})_2$ | (273) |
| 4 | $\text{Ph}_3\text{SiLi}/\text{THF}$ | $(\text{Cp})_2\text{VCl}_2$ | No Si-V deriv. isolated | (273) |
| 5 | $\text{R}_3\text{SiLi}/\text{THF} (\text{R}_3 = \text{Ph}_3, \text{MePh}_2)$ | $\text{ClM}(\text{CO})_5 (\text{M} = \text{Cr, Mo, W})$ | $\text{R}_3\text{SiM}(\text{CO})_5^-$; similarly, Ge, Sn | (254) |
| 6 | $i\text{-Me}_3\text{Si}_3\text{Li}/\text{THF}$ | $\text{BrMn}(\text{CO})_5$ | $i\text{-Me}_3\text{Si}_3\text{Mn}(\text{CO})_5$ | (335) |
| | $t\text{-Me}_3\text{Si}_4\text{Li}/\text{THF}$ | $\text{BrMn}(\text{CO})_5$ | $t\text{-Me}_3\text{Si}_4\text{Mn}(\text{CO})_5$ | (335) |
| | $t\text{-Me}_3\text{Si}_4\text{Li}/\text{THF}$ | $\text{BrMn}(\text{CO})_4(\text{PPh}_3)$ | $t\text{-Me}_3\text{Si}_4\text{Mn}(\text{CO})_4(\text{PPh}_3)$ | (335) |
| 7 | H_2SiK | $\text{BrFe}(\text{CO})_2(\text{Cp})$ | $\text{H}_2\text{SiFe}(\text{CO})_2(\text{Cp})$ | (9) |
| 8 | R_3SiLi | $\text{Cl}_3\text{Pt}(\text{PMe}_3)\text{Ph}_2$ | $(\text{R}_3\text{Si})_2\text{Pt}(\text{PMe}_3)\text{Ph}_2$ | (97, 98) |
| 9 | PhMe_2SiLi | $\text{CuX} (\text{X} = \text{I, CN})$ | $\text{PhMe}_2\text{SiCu} \cdot \text{LiX}$ } not isolated | (6, 185) |
| 10 | Ph_3SiLi | $\text{ClAu}(\text{PPh}_3)$ | $(\text{PhMe}_2\text{Si})_2\text{CuLi} \cdot \text{LiCN}$ } not isolated $\text{Ph}_3\text{SiAu}(\text{PPh}_3)$ | (43) |

TABLE III
 REACTIONS WITH MERCURY DISILYL DERIVATIVES

| Entry | Mercurial | Metal compound | Silicon-metal product | Ref. |
|-------|-------------------------------------|--|--|------------|
| 1 | Hg(SiMe ₃) ₂ | Mo(CO) ₅ (Cp)Cl | Me ₃ SiMo(CO) ₅ (Cp); similarly W | (306) |
| 2 | Hg(SiCl ₃) ₂ | Mn ₂ (CO) ₁₀ | Cl ₃ SiMn(CO) ₅ | (64) |
| 3 | Hg(SiMe ₃) ₂ | Fe(CO) ₅ ^a | <i>cis</i> -(Me ₃ Si) ₂ Fe(CO) ₄ | (262) |
| 4 | Hg(SiMe ₃) ₂ | Hg[Co(CO) ₄] ₂ | Me ₃ SiCo(CO) ₄ | (293) |
| 5 | Hg(SiMe ₃) ₂ | (Et ₃ P) ₂ Ir(CO)Cl | (Me ₃ Si) ₂ Ir(CO)(HgSiMe ₃)(PEt ₃) ₂ | (241) |
| 6 | Hg(SiMe ₃) ₂ | <i>cis</i> -(Et ₃ P) ₂ PtCl ₂ | <i>trans</i> -(Me ₃ Si)PtCl(PEt ₃) ₂ | (196) |
| 7 | Hg(SiMe ₃) ₂ | <i>cis</i> -(diphos)PtCl ₂ ^b | <i>cis</i> -(Me ₃ Si)PtCl(diphos) + <i>cis</i> -(Me ₃ Si) ₂ Pt(diphos) | (112, 113) |

^a UV irradiation needed; Fe₂(CO)₉ and Fe(CO)₄Br₂ are also effective.

^b diphos = Ph₂PCH₂CH₂PPh₂.

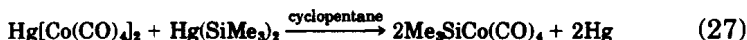
When using the monodentate phosphine derivative shown in entry 6, only one Pt-Cl bond is broken; this is attributed to the high trans influence of the Me₃Si group in the monosubstituted and isomerized product. With a bidentate phosphine (entry 7), however, a change in stereochemistry is prevented and both mono- and disubstituted products are formed.

In the case of reaction with the Ir(I) compound in entry 5, the presumed initial product, (Et₃P)₂Ir(CO)(SiMe₃), undergoes oxidative addition with further Hg(SiMe₃)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,



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.

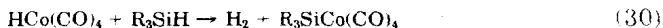
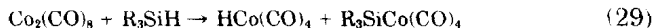


E. REACTIONS OF TRANSITION-METAL CARBONYLS WITH Si-H COMPOUNDS GIVING H₂

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



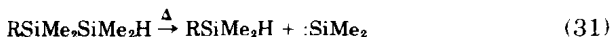
and later work that established that metal carbonyl hydrides may act as intermediates, e.g. (41, 42, 95),



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 $\text{Co}_2(\text{CO})_8$ 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.,

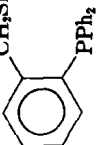

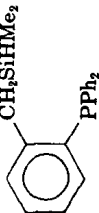
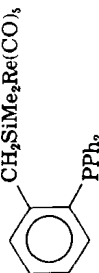
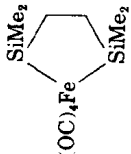


The silylene species may be coordinated to a metal center rather than being free (see Section V,C). When two Si-H groups are separated by $-(\text{CH}_2)_2-$ links, either a cyclic (entry 8) or a linear (entry 26) compound may result: the latter is somewhat unstable thermally. Correspondingly, cyclic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

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

TABLE IV

REACTIONS OF METAL CARBONYL DERIVATIVES WITH SILICON HYDRIDES

| Entry | Metal carbonyl derivative | Silicon hydride | Treatment ^a | Product | Ref. |
|-------|-------------------------------------|--|------------------------|---|------------|
| 1 | $\text{Mn}_2(\text{CO})_{10}$ |  | Δ |  | (13) |
| 2 | HSiF_3 | $\text{HSiPh}_2\text{Cl}_{3-x}$ | Δ | $\text{F}_3\text{SiMn(CO)}_5$ (and Re analog) ^b | (373, 397) |
| 3 | | ($x = 1, 2$) | Δ | $\text{Ph}_2\text{Cl}_{3-x}\text{SiMn(CO)}_5$ | (107) |
| 4 | | HSi_2Me_3 | Δ | $\text{Me}_3\text{Si}_2\text{Mn(CO)}_5$ | (335) |
| | | $\text{HSi}_3\text{Me}_2-i$ | | $i\text{-Me}_3\text{Si}_3\text{Mn(CO)}_5$ | (335) |
| | | $\text{HSi}_4\text{Me}_2-t$ | | $t\text{-Me}_3\text{Si}_4\text{Mn(CO)}_5$ | (335) |
| 5 | HMn(CO)_5 | H_2SiCl_2 | Δ | $\text{Cl}_2\text{SiMn(CO)}_5$ | (2) |
| 6 | $[\text{Mn(CO)}_5(\text{PPh}_3)]_2$ | HSiMe_3 | Δ | $\text{trans-Me}_3\text{SiMn(CO)}_4(\text{PPh}_3)_2$ | (335) |
| 7 | $\text{Re}_2(\text{CO})_{10}$ |  | Δ |  | (13) |
| 8 | Fe(CO)_5 | $[\text{HSiMe}_2\text{CH}_2]_n$ | $h\nu$ |  | (418) |

[Similarly Ru, Os analogs from $\text{M}_3(\text{CO})_{12}$]

(table continues)