

# PROPERTIES OF SILICON DERIVATIVES OF COBALT, MANGANESE AND IRON CARBONYLS

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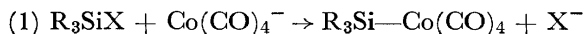
Although the first compound to contain a silicon-transition metal bond,  $\text{Me}_3\text{Si}-\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ , was synthesized by Piper, Lemal and Wilkinson<sup>1</sup> in 1956, it was not until 1965 with the advent of the work by Chalk and Harrod<sup>2</sup> and Aylett and Campbell<sup>3</sup> on silicon cobalt tetracarbonyls that silicon-transition metal chemistry started developing rapidly. The growth of interest in this area of silicon chemistry has been substantial and since the beginning of 1965 approximately thirty-five publications have appeared on this subject.

In this lecture, time is not, of course, available to discuss all of the recent important and interesting advances in silicon-transition metal chemistry. Our research group has been mainly concerned with the structure, and particularly the chemical properties of silicon derivatives of cobalt, manganese and iron carbonyls in which there is a Si-Co, Si-Mn or Si-Fe bond. This lecture will be limited to these derivatives only. In this respect, it might be noted, that in so far as studies of chemical properties are concerned, most investigations to date have been carried out on compounds containing Si-Co, Si-Mn or Si-Fe bonds.

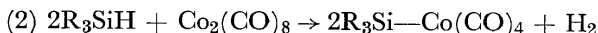
## I. SYNTHESIS

Some of the more common or useful methods for synthesizing silicon derivatives of cobalt, manganese and iron carbonyls are summarized below by means of generalized equations in which X is a halogen and R is a substituent, usually hydrogen or an alkyl or aryl group. The most pertinent references are given in each case.

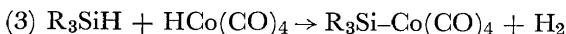
### A. Cobalt Carbonyl Derivatives



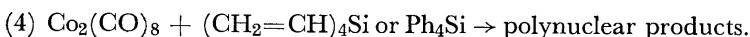
Reaction occurs under mild conditions.<sup>3</sup>



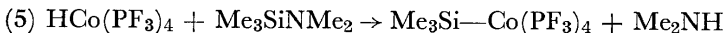
Reaction occurs readily at room temperature.<sup>2, 4, 5</sup>



Reaction occurs readily in the liquid phase at or below room temperature.<sup>4-8</sup>

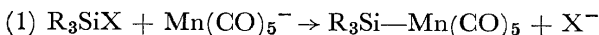


Reaction occurs on refluxing in an appropriate solvent to give species such as  $CH_2=CH-SiCo_3(CO)_9$ <sup>9</sup> and  $[Co_3(CO)_9Si]_2$ <sup>10</sup> respectively.

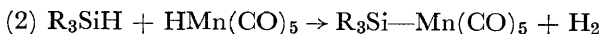


The characterization of the  $Me_3Si-Co(PF_3)_4$  is incomplete and it may well be complexed with the liberated amine.<sup>11</sup>

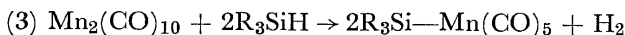
## B. Manganese Carbonyl Derivatives



Reaction proceeds under mild conditions.<sup>12, 13</sup>

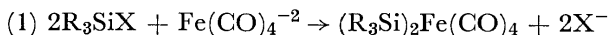


Reaction occurs at 130–135°.<sup>14</sup>

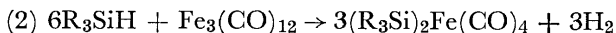


On heating the reactants in the 100–180° range, the reaction proceeds readily<sup>15, 16</sup>.

## C. Iron Carbonyl Derivatives



This type of reaction proceeds readily and it has also been used for attaching the  $-Fe(CO)_2(\pi-C_5H_5)$  group to silicon<sup>1, 17, 18</sup>.



This type of reaction occurs on heating the reagents in the 80–180° range<sup>16, 19</sup>. Cyclic species<sup>16</sup> and compounds such as  $(SiCl_3)_2FeH(CO)(\pi-C_5H_5)$ <sup>20</sup> have also been isolated when  $Fe(CO)_5$  or  $[(\pi-C_5H_5)Fe(CO)]_2$  respectively are used in place of the  $Fe_3(CO)_{12}$ .

## D. Compounds Synthesized in this Study

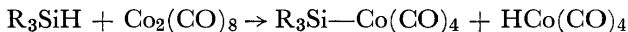
The compounds  $Me_3Si-Co(CO)_4$ ,  $MeSiH_2-Co(CO)_4$  and  $F_3Si-Co(CO)_4$  were synthesized in good yields from the corresponding silane and  $Co_2(CO)_8$  in the absence of solvent at room temperature<sup>5-8, 21</sup>. The species  $MeSiF_2-Co(CO)_4$  was prepared by fluorinating  $MeSiH_2-Co(CO)_4$  with  $PF_5$  at room temperature.<sup>21, 22</sup>

The reaction of  $HCo(CO)_4$  with silanes such as  $Me_3SiH$ ,  $F_3SiH$  and  $Cl_3SiH$  etc. proceeded very rapidly at or below room temperature to give the corresponding silicon cobalt tetracarbonyls<sup>4, 5, 8, 21</sup>. In the case of

$\text{Me}_3\text{SiH}$ , which was the only compound studied under these conditions, no interaction occurred in the gas phase at room temperature during several hours.<sup>7</sup> No reaction took place between  $\text{Me}_3\text{SiH}$  or  $\text{Cl}_3\text{SiH}$  and  $\text{HCo}(\text{CO})_2(\text{PF}_3)_2$  either in solution or in the gas phase at room temperature<sup>21</sup>. It is interesting that this type of reaction could readily be extended to  $\text{Me}_2\text{AsH}$ . Rapid reaction occurred at or below room temperature, *viz.*<sup>5, 7</sup>.



Since  $\text{HCo}(\text{CO})_4$  can be isolated from the reaction of a silane with  $\text{Co}_2(\text{CO})_8$ , *viz.*<sup>4-8, 21</sup>

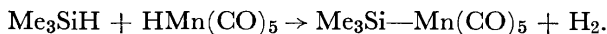


the overall reaction between  $\text{R}_3\text{SiH}$  and  $\text{Co}_2(\text{CO})_8$  may proceed via the intermediate formation of  $\text{HCo}(\text{CO})_4$ ,<sup>4, 5, 7</sup> which then reacts with another molecule of  $\text{R}_3\text{SiH}$ , or partial decomposition of  $\text{HCo}(\text{CO})_4$  might occur, *viz.*



the  $\text{Co}_2(\text{CO})_8$  then reacting with another molecule of  $\text{R}_3\text{SiH}$ . It is likely that both types of reaction sequences occur depending on the silane used.<sup>4</sup>

The manganese derivative,  $\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5$ , was prepared in 68 per cent yield from the reaction of  $\text{Me}_3\text{SiCl}$  with  $\text{NaMn}(\text{CO})_5$  at room temperature and 70 per cent yield by heating  $\text{Me}_3\text{SiH}$  with  $\text{Mn}_2(\text{CO})_{10}$  at 130° for 48 hours<sup>14</sup>. A reaction took place at 130–135° during one day between  $\text{Me}_3\text{SiH}$  and  $\text{HMn}(\text{CO})_5$  giving 23 per cent yields of this compound,<sup>14</sup> *viz.*



The  $\text{Me}_3\text{Si}-\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  was prepared from  $\text{NaFe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  and  $\text{Me}_3\text{SiCl}$  according to the method of Piper *et al.*<sup>1</sup>

## II. THERMOCHEMICAL DATA

Mass spectroscopic appearance potential studies on  $\text{F}_3\text{Si}-\text{Co}(\text{CO})_4$  and  $\text{MeSiF}_2-\text{Co}(\text{CO})_4$  gave Si-Co bond dissociation energies of  $105 \pm 12^{23}$  and  $124 \pm 12^{24}$  kcal/mole respectively†. The corresponding standard heats of formation are  $-489.7 \pm 10$  and  $-433 \pm 12$  kcal/mole respectively<sup>23, 24</sup>. Because of the possibility of excess kinetic energy in the ion fragments, the bond dissociation energies should be regarded as maximum values and the heats of formation as minimum values. Nevertheless, these data indicate that the Si-Co bond is rather strong and it may be compared, for example, with the value of  $82 \pm 2$  kcal/mole reported for the Si-Cl bond dissociation energy in  $\text{Me}_3\text{SiCl}$ .<sup>25</sup>

## III. STRUCTURE

As is well known, some silicon compounds have structures which differ considerably from those of analogous carbon compounds; trimethylamine for example, is a pyramidal molecule whereas the nitrogen and three silicon atoms in  $(\text{SiH}_3)_3\text{N}$  are coplanar.<sup>26</sup> It is therefore of interest to compare the structures of analogous carbon- and silicon-transition metal derivatives where the appropriate data are available.

†If a value of  $-164$  kcal/mole is used for  $\Delta H_f^\circ$  of  $\text{Co}(\text{CO})_4$  (see Bidinosti and McIntyre<sup>22</sup>) these values become 73 and 95 kcal/mole, respectively.

### A. $R_3Si-CO(CO)_4$

Infrared studies in the CO stretching region of compounds of the type  $R_3Si-Co(CO)_4$  [ $R_3Si- = H_3Si-, Me_3Si-, F_3Si-, Cl_3Si-, MeSiH_2-, MeSiF_3-,$  (gas phase)<sup>21, 27</sup> and  $R_3Si- = Et_3Si-, Ph_3Si-, Cl_3Si-, (MeO)_3Si-$  (solution)<sup>28-30</sup>]. are consistent with trigonal bipyramidal configurations about the cobalt with the  $R_3Si-$  group occupying an axial position. No evidence for isomeric species such as one having the  $R_3Si-$  groups in an equatorial position has been obtained. This type of trigonal bipyramidal arrangement is supported by an X-ray single crystal study of  $Cl_3Si-Co(CO)_4$ . The  $SiCl_3-$  group is found in the axial position and the three equatorial CO groups are in staggered conformation with respect to the chlorine atoms which are tetrahedrally disposed about the silicon.<sup>31</sup>

It should be noted that in so far as comparable data are available, the carbon and silicon cobalt tetracarbonyls have similar structures. Thus the infrared spectra of  $H_3C-Co(CO)_4$ ,<sup>32, 33</sup>  $F_3C-Co(CO)_4$ ,<sup>34</sup> and  $Me_3C-Co(CO)_4$ <sup>19</sup> in the CO stretching region are consistent with axially substituted trigonal bipyramidal molecules.

### B. $R_3Si-Mn(CO)_5$

Infrared studies in the CO stretching region of compounds of the type  $R_3Si-Mn(CO)_5$  ( $R_3Si- = Me_3Si-$  (gas phase and solution)<sup>14</sup> and  $R_3Si-_{15, 16, 29, 30} = Ph_3Si-Me_3Si-, Cl_3Si-$  (solution)) are consistent with an octahedral

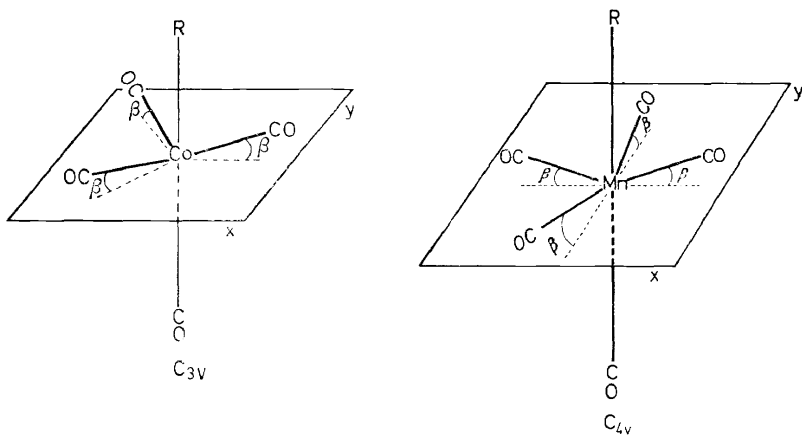


Figure 1. Structure of: (a)  $R-Co(CO)_4$ , (b)  $R-Mn(CO)_5$  where R is hydrogen or a group IV substituent.

conformation about the manganese. This type of configuration is supported by an X-ray single crystal study of  $Me_3Si-Mn(CO)_5$ .<sup>36</sup> The simple alkyl derivatives,  $R_3C-Mn(CO)_5$ , ( $R = H, F, etc.$ ), have similar structures.<sup>35</sup>

### C. $(R_3Si)_2Fe(CO)_4$ and $R_3Si-Fe(CO)_2(\pi-C_5H_5)$

Infrared studies in the CO stretching region of  $(SiH_3)_2Fe(CO)_4$ ,<sup>17</sup>  $(Et_3Si)_2Fe(CO)_4$ <sup>19</sup> and  $SiH_3(H)Fe(CO)_4$ <sup>17</sup> are consistent with octahedral

structures in which the substituent groups are *cis* to each other. It is interesting to note that the isomeric *cis* and *trans* forms of  $(\text{SiCl}_3)_2\text{Fe}(\text{CO})_4$  have been isolated.<sup>19</sup> It might be noted that in  $\text{H}_2\text{Fe}(\text{CO})_4$ <sup>37</sup> and in perfluoroalkyl derivatives such as  $(\text{C}_2\text{F}_5)_2\text{Fe}(\text{CO})_4$ <sup>34</sup> the substituents are *cis* to each other although it has been pointed out that the presence of a *trans* isomer in the latter compound cannot definitely be ruled out.<sup>34</sup>

It is probable that the structures of compounds such as  $\text{Me}_3\text{Si}-\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ <sup>1</sup>,  $\text{Cl}_3\text{Si}-\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$ <sup>16</sup> and  $\text{MeCl}_2\text{Si}-\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  can be regarded, at least to a first approximation, as being derived from an octahedral iron atom with three coordination positions being occupied by the  $\text{C}_5\text{H}_5$  ring, the other three positions being occupied by the two carbonyl groups and by the silicon group. It is interesting to note that the infrared spectrum of  $\text{MeSiCl}_2-\text{Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  strongly suggests the presence of two conformational, isomeric forms for the molecule.<sup>16</sup>

## IV. BONDING

### A. ( $d \rightarrow d$ ) $\pi$ Bonding Between a Transition Metal and Silicon

A number of infrared studies of the CO stretching region of silicon and other Group IV transition metal carbonyls have given evidence for the possible presence of partial ( $d \rightarrow d$ ) $\pi$  double bond character in the Group IV—transition metal bond<sup>19, 21, 27, 29, 38, 39</sup>. Certain of these studies have been correlated with dipole moment measurements<sup>19</sup>. This interaction is depicted diagrammatically in *Figure 2(a)* for  $\text{R}_3\text{Si}-\text{Mn}(\text{CO})_5$  where, for simplicity, the manganese atom and the four equatorial CO groups are shown as being coplanar. Only the ( $d_{zx} \rightarrow d_{zx}$ ) $\pi$  interaction is depicted. An analogous ( $d_{yz} \rightarrow d_{yz}$ ) $\pi$  interaction involving the other two equatorial CO groups would also be present. This type of bonding therefore involves an overlap of filled manganese 3*d* orbitals with the empty silicon 3*d* orbitals. It can be seen that this interaction might be expected to affect the extent of interaction of the type shown in *Figure 2(b)* between the manganese and the empty antibonding  $\pi$  orbitals of the carbonyl groups and hence to affect the CO stretching frequencies. Analogous types of interactions can be postulated for the cobalt and iron carbonyl derivatives.

It is of interest to examine some of the X-ray data available for such compounds in order to ascertain whether or not they are consistent with the ( $d \rightarrow d$ ) $\pi$  bonding hypothesis. A Si—Co bond length of  $2.254 \pm 0.003 \text{ \AA}$  has been determined from a single crystal X-ray study of  $\text{Cl}_3\text{Si}-\text{Co}(\text{CO})_4$ <sup>31</sup>. In view of the uncertainty in assigning an unequivocal value for the covalent radius of cobalt in a compound such as this, considerable care must be exercised in interpreting this datum. However, it appears likely that the covalent radius of cobalt is not less than  $1.22 \text{ \AA}$  in view of the  $1.243 \text{ \AA}$  covalent radius reported for cobalt in  $\text{CoH}$ <sup>40</sup> and the  $1.32 \text{ \AA}$  value found in the penta co-ordinate cobalt compound,  $\text{Co}[\text{Me}_2\text{N}(\text{CH}_2)_2\text{NMe}(\text{CH}_2)_2\text{NMe}_2]\text{Cl}_2$ .<sup>40</sup> A range of values,  $1.22$  to  $1.32 \text{ \AA}$ , for this radius has been found in fifteen assorted cobalt carbonyls<sup>41</sup>.

If the radius for silicon of  $1.15 \text{ \AA}$  from  $\text{Cl}_3\text{Si}-\text{SiCl}_3$ <sup>42</sup> is taken, this then gives a minimum calculated distance for a single Si—Co bond of  $2.37 \text{ \AA}$ . The fact that this calculated value is significantly more ( $0.12 \text{ \AA}$ ) than the

experimental Si—Co bond length is certainly consistent with partial ( $d \rightarrow d$ )  $\pi$  double bond character in this linkage.

A Si—Mn bond length of  $2.497 \pm 0.005 \text{ \AA}$  has been determined from a single crystal X-ray study of  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$ <sup>36</sup>. The calculated Si—Mn single bond length using a value of  $1.46 \text{ \AA}$  for the covalent radius of Mn as recommended by Doedens and Dahl<sup>43</sup> and a value of  $1.17 \text{ \AA}$  for the radius of silicon as determined from  $\text{Me}_3\text{Si—SiMe}_3$ <sup>44</sup> is  $2.63 \text{ \AA}$ . The fact that this value is larger (by  $0.13 \text{ \AA}$ ) than the calculated Si—Mn single bond radius

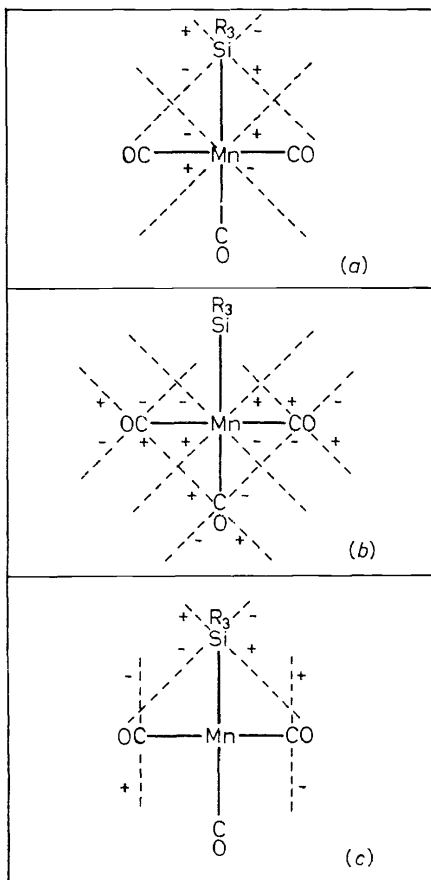


Figure 2. Schematic representation of some of the possible bonding interactions in  $\text{R}_3\text{Si—Mn}(\text{CO})_5$ . (A sideways view along the XY plane which is represented as containing the Mn and the four equatorial CO groups, two of which are shown, is depicted).

is also consistent with partial ( $d \rightarrow d$ )  $\pi$  double bond character in this linkage.

Using this same value for the radius of manganese and a value of  $1.39 \text{ \AA}$  for the radius of tin, as determined from  $(\text{Ph}_2\text{Sn}_6)$ <sup>45</sup>, a similar difference between calculated and experimental Sn—Mn bond lengths can be observed in a

number of compounds, *viz.*,  $\text{Ph}_3\text{Sn—Mn}(\text{CO})_5^{46}$  ( $D_{\text{Sn—Mn}}$  experimental,  $2.674 \pm 0.004\text{\AA}$ ; calculated  $2.85\text{\AA}$ ); *trans*- $\text{Ph}_3\text{Sn—Mn}(\text{CO})_4\text{PPh}_3^{47}$  ( $D_{\text{Sn—Mn}}$  experimental,  $2.627 \pm 0.01\text{\AA}$ );  $\text{Me}_3\text{Sn—Mn}(\text{CO})_5^{48}$  ( $D_{\text{Sn—Mn}}$  experimental,  $2.674\text{\AA}$ ). The transition metal-carbon bond lengths for the equatorial and axial CO groups in the above compounds are either essentially identical or very nearly so. It might be noted, for comparative purposes, that the difference in C—C distances between a carbon-carbon single bond and a carbon-carbon double bond is approximately  $0.2\text{\AA}$ . The percentage shortening is, of course, considerably greater in the carbon-carbon linkage than in the bonds described above.

It appears unlikely that the amount of ionic character in these linkages would cause the observed shortenings. Thus the Allred and Rochow<sup>49</sup> electronegativities for these elements are very similar: Si = 1.74, Sn = 1.72, Co = 1.70 and Mn = 1.60.

It should be stressed that the apparent agreement of these bond length data with the ( $d \rightarrow d$ ) $\pi$  bonding concept suggested from infrared studies may be completely fortuitous since the whole argument is especially dependent on the assignment of an appropriate radius to Co and Mn.

### B. ( $p \rightarrow d$ ) $\pi$ Bonding between axial CO groups and silicon

In discussing interactions other than that of the sigma bond between a Group IV element and a transition metal having attached carbonyl groups, it is of interest to consider whether there is any experimental evidence which is at least qualitatively consistent with a direct "across-space" ( $p \rightarrow d$ ) $\pi$  interaction between the equatorial CO groups and the Group IV element. In the parent compound,  $\text{HCo}(\text{CO})_4$ , from which the Group IV cobalt tetracarbonyls may be considered to be derived, electron diffraction<sup>50</sup> and (vapour phase) infrared<sup>51</sup> data show that the molecule may be regarded as a trigonal bipyramid with the hydrogen in an axial position and the equatorial CO groups raised towards the hydrogen such that the H—Co—CO<sub>(eq.)</sub> angle is approx.  $71^\circ$  (see *Figure 1a*). A distortion in this direction might be expected from simple steric considerations involving the axial hydrogen atom and axial CO group. However, molecular orbital calculations<sup>37,51-54</sup> suggest there may be a strong bonding interaction between the hydrogen 1s orbital and the equatorial CO groups. The question arises whether a somewhat analogous interaction, but involving instead the  $d$  orbitals of the substituent, exists in the Group IV derivatives of  $\text{HCo}(\text{CO})_4$ , and indeed in Group IV derivatives of other transition metal carbonyls.

From simple steric considerations alone, one might expect to find that the equatorial CO groups would be bent *away* from the large Group IV substituent towards the smaller axial CO group *trans* to it. (See also note 1 added in proof on p. 448) Thus, the  $\text{R}_3\text{M—Co—CO}_{(\text{eq.})}$  angle or the  $\text{R}_3\text{M—Mn—CO}_{(\text{eq.})}$  angle (M = Si, Ge, Sn, Pb) would be *greater* than  $90^\circ$ , e.g.  $(90 + \alpha)^\circ$ . However, experimentally, in those compounds investigated to date, the axial CO groups are bent *towards* the larger Group IV substituent and the above angle is, therefore  $(90 - \beta)^\circ$  where  $\beta$  is the angle by which the equatorial carbonyl groups are raised above the plane containing the transition metal. Thus the distortion from the angle expected *only on the basis of simple steric effects* is  $(\alpha + \beta)^\circ$  (see *Figure 1*). The average value

of the  $R_3M-M'-CO_{(eq.)}$  angle ( $M' = Co, Mn$ ) within a given compound is:  $Cl_3Si-Co(CO)_4$  ( $85.2^\circ$ )<sup>31</sup>,  $Me_3Si-Mn(CO)_5$  ( $84.5^\circ$ )<sup>36</sup>,  $Me_3Sn-Mn(CO)_5$  ( $84.3^\circ$ )<sup>48</sup>,  $Ph_3Sn-Mn(CO)_5$  ( $86.7^\circ$ )<sup>46</sup>, *trans*- $Ph_3Sn-Mn(CO)_4(PPh_3)$  ( $85.7^\circ$ )<sup>47</sup>. The distortions for these compounds are therefore, since  $a$  cannot be evaluated, approx.  $\geq 4.8^\circ$ ,  $\geq 5.5^\circ$ ,  $\geq 5.7^\circ$ ,  $\geq 3.3^\circ$  and  $\geq 4.3^\circ$ , respectively. Even in  $Ph_3PAu-Co(CO)_4$  the equatorial CO groups are displaced towards the gold<sup>55</sup>, possibly by an involving the gold  $6d$  orbitals.

Three possible causes for these distortions are (i) intermolecular interactions (distortions) in the crystal lattice, (ii) repulsion of the equatorial CO groups by electron pairs associated with the carbon of the axial CO group and by related effects,<sup>56</sup> and (iii) ( $p \rightarrow d$ ) $\pi$  bonding interaction somewhat analogous to that postulated in  $HCo(CO)_4$ , involving instead, the  $d$  orbitals of the silicon or tin and the  $p$  orbitals of appropriate symmetry on the equatorial CO groups. The magnitudes of the distortion angles are probably greater than that expected on the basis of lattice distortion effects alone, although gas phase structural studies of compounds of appropriate volatility would be most useful in determining the importance of this effect. (see also Note 2 added in proof on p. 448) The fact that the distortion angle is not changed significantly when an axial CO group in  $Ph_3Sn-Mn(CO)_5$  is replaced by a  $Ph_3P$  group suggests that distortion by lone, or  $\pi$ -bonding electron pairs associated with the carbon of the axial CO group may not be an important factor, since the phosphorus of the  $Ph_3P$  has no such electrons.

At least in so far as orbital symmetry is concerned, a direct ( $p \rightarrow d$ ) $\pi$  interaction between the equatorial CO  $p_2$  orbitals and the Group IV element is possible. This is illustrated diagrammatically in *Figure 2 (c)* using  $R_3Si-Mn(CO)_5$  as an example. It might be noted that in  $Cl_3Si-Co(CO)_4$ <sup>31</sup>, for example, the average Si.....C intramolecular distance ( $2.75\text{\AA}$ ) is less than the sum of the Van der Waals radii of silicon and carbon ( $3.54\text{\AA}$ ) but is greater than the sum of the covalent radii of these atoms ( $1.94\text{\AA}$ ). These data, although consistent with a direct Si.....C interaction, cannot be regarded as supporting evidence for such an interaction since atoms which are attached to the same central element frequently approach closer to each other than the sum of their Van der Waals radii. According to this ( $p \rightarrow d$ ) $\pi$  concept, the similarity of the distortion angles in  $Ph_3Sn-Mn(CO)_5$  and *trans*- $Ph_3Sn-Mn(CO)_4(PPh_3)$  would imply that the  $5d$  orbitals of the tin make a better overlap with the  $p$  orbitals of the equatorial CO groups than do the  $3d$  orbitals of the phosphorus. X-ray data on non-fluorinated<sup>57</sup> alkyl or aryl cobalt and manganese carbonyls of these types would be most useful in determining the importance or non-importance of this type of interaction. The distortions could well be due to a combination of the three effects listed above, or, of course, to some completely different effect. It might be noted that during recent years several brief comments have appeared in the literature suggesting the possible existence of some bonding between silicon and an atom (having lone pairs of electrons) from which it is separated by a  $CH_2$  group. Such bonding interactions, as postulated for example, in  $Me_3Si-CH_2-O-Me$ <sup>58</sup>, show some resemblance to the type described above. It is here suggested that, at least a portion of the interaction presently ascribed to ( $d \rightarrow d$ ) $\pi$  bonding between the Group IV



element and the transition metal to which it is attached, may be due to a direct interaction between the *d* orbital of the Group IV element and the equatorial CO groups.

## V. THERMAL STABILITY

There seems little doubt that at least non-fluorinated alkyl silicon derivatives of cobalt, manganese and iron carbonyls are more thermally stable *in vacuo* than their carbon analogues, where these are known. Thus, although  $\text{CH}_3\text{Co}(\text{CO})_4$  decomposes fairly rapidly above  $-30^\circ$ <sup>59</sup>, 30 per cent of a sample of  $\text{H}_3\text{Si}-\text{Co}(\text{CO})_4$  was recovered after heating at  $100^\circ$  for half an hour<sup>3</sup>.

Tertiary alkyl transition metal carbonyls are either very unstable thermally or have defied preparation. They have a very pronounced tendency to decompose to give olefin and transition metal hydride, *e.g.*



It should be noted however, that the infrared spectrum of  $\text{Me}_3\text{C}-\text{Co}(\text{CO})_4$  has recently been studied<sup>19</sup> but that this compound is apparently very unstable<sup>60</sup>. Little meaningful comparative information concerning the thermal stability of perfluoroalkyl cobalt carbonyls is available, although they apparently have greater thermal stability than the non-fluorinated species. Thus,  $\text{F}_3\text{C}-\text{Co}(\text{CO})_4$  and  $\text{C}_2\text{F}_5-\text{Co}(\text{CO})_4$  can be distilled unchanged at their boiling points ( $91^\circ$  and  $110^\circ$ , respectively)<sup>61</sup>.

When silicon cobalt carbonyls are heated *in vacuo*, the thermal decomposition products are found to vary greatly according to the substituents on silicon. Thus,  $\text{H}_3\text{Si}-\text{Co}(\text{CO})_4$  gives some  $\text{SiH}_4$  and  $\text{HCo}(\text{CO})_4$ <sup>3</sup> and although  $\text{Ph}_3\text{Si}-\text{Co}(\text{CO})_4$  yields  $\text{Ph}_6\text{Si}_2$  on pyrolysis,  $\text{Et}_3\text{Si}-\text{Co}(\text{CO})_4$  yields  $(\text{Et}_3\text{Si})_2\text{O}$  at  $190^\circ$ , as the main silicon-containing product<sup>4</sup>. In preliminary experiments, it has been found<sup>7,62</sup> that appreciable quantities of  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  remain even after it has been heated at  $150^\circ$  for several hours *in vacuo*. Approximately 70 per cent of the  $\text{Me}_3\text{Si}$ - groups were recovered as  $(\text{Me}_3\text{Si})_2\text{O}$  after twenty hours at this temperature. It is perhaps fortuitous that the gross composition of the residue corresponds rather closely to  $\text{R}-\text{Co}_3(\text{CO})_9$ , ( $\text{R} = \text{Me}_3\text{SiC} \equiv$ ),<sup>7</sup> *viz.*,

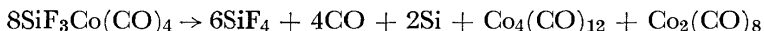


which is analogous to known compounds where  $\text{R} = \text{CH}_2=\text{CHSi} \equiv$ <sup>9</sup>,  $\text{H}_3\text{CC} \equiv$ <sup>41</sup>. It is often noted that a sample of  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$ , which is an essentially colourless solid at room temperature, liberates small quantities of  $(\text{Me}_3\text{Si})_2\text{O}$  within approximately an hour and changes to pink or red. However, after three months *in vacuo* at room temperature, in normal laboratory lighting, 87 per cent of a sample was recovered unchanged<sup>7</sup>.

Both  $\text{MeSiH}_2-\text{Co}(\text{CO})_4$  and  $\text{MeSiF}_2-\text{Co}(\text{CO})_4$  show reasonably good thermal stability<sup>21</sup> although decomposition always appears to proceed fairly rapidly at first and then to slow down. Thus, after five days at room temperature, followed by one day at  $61^\circ$ , a sample of  $\text{MeSiH}_2-\text{Co}(\text{CO})_4$  (neat liquid) showed relatively little decomposition, although small amounts of  $(\text{MeSiH}_2)_2\text{O}$  and  $\text{HCo}(\text{CO})_4$  were formed<sup>21</sup>. Approximately 50 per cent of a sample of  $\text{MeSiF}_2-\text{Co}(\text{CO})_4$  (neat liquid) had decomposed after

twelve hours at room temperature to yield  $(\text{MeSiF}_2)_2\text{O}$  as the only isolable silicon-containing decomposition product<sup>21</sup>.

The fluorinated compound,  $\text{F}_3\text{Si}-\text{Co}(\text{CO})_4$  (neat liquid), undergoes complete decomposition during eighteen hours at room temperature<sup>8</sup>. The decomposition may be represented by the equation:



All the fluorine appears as  $\text{SiF}_4$ <sup>8</sup>. No  $(\text{SiF}_3)_2\text{O}$  or  $\text{Si}_2\text{F}_6$  was formed.

It may be concluded that the major silicon-containing thermal decomposition product of silicon cobalt tetracarbonyls varies greatly according to the substituent on the silicon and the silicon may appear as a silane, disilane or disiloxane, depending on the nature of the substituent.

Hydrides such as  $\text{HMn}(\text{CO})_5$  and organic derivatives such as  $\text{MeMn}(\text{CO})_5$  are generally considerably more stable thermally than the analogous  $-\text{Co}(\text{CO})_4$  species, although  $\text{Me}_3\text{C}-\text{Mn}(\text{CO})_5$  has never been isolated. This is reflected in the greater thermal stability of  $\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5$  as compared to  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$ . Thus, a sample of  $\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5$  (neat liquid) was recovered almost quantitatively after heating at  $160^\circ$  *in vacuo* for two days<sup>14</sup>. Only traces of  $(\text{Me}_3\text{Si})_2\text{O}$  and  $\text{Me}_3\text{SiH}$  were liberated<sup>14</sup>. The parent silicon compound,  $\text{H}_3\text{Si}-\text{Mn}(\text{CO})_5$ , can be stored in an evacuated tube for long periods at room temperature without decomposition<sup>13</sup>.

Although  $\text{Me}_2\text{Fe}(\text{CO})_4$  does not appear to have been synthesized,  $(\text{SiH}_3)_2\text{Fe}(\text{CO})_4$  does not, apparently, decompose rapidly below  $110^\circ$ .<sup>17</sup> The decomposition products include the interesting species  $\text{H}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$  and  $\text{SiH}_4$ <sup>17</sup>. The compound  $\text{Me}_3\text{Si}-\text{Fe}(\text{CO})_2(\pi-\text{C}_5\text{H}_5)$  is also remarkably stable when heated *in vacuo*<sup>63</sup>. No decomposition occurred during one hour at  $160^\circ$  but some  $(\text{Me}_3\text{Si})_2\text{O}$  was evolved after an hour at  $200^\circ$ .

It has been suggested that the greater thermal stability of silicon cobalt carbonyls as compared to the analogous carbon compounds (where known) may be due to the presence of partial ( $d \rightarrow d$ ) $\pi$  double bond character in the silicon-transition element bond<sup>2,3</sup>. Although this may be true, at least in the case of  $\text{Me}_3\text{Si}$ -derivatives, it appears that the greater stability of the silicon compounds could be due to the small tendency of silicon to form ( $p-p$ ) $\pi$  double bonds with carbon. It is interesting to note that those silicon compounds which have, in general, a greater thermal stability than analogous carbon compounds, *e.g.*  $\text{Me}_3\text{Si}-\text{M}$  ( $\text{M} =$  transition metal),  $\text{R}_2\text{Si}(\text{OH})_2$ , and  $\text{R}_2\text{Si}(\text{NH}_2)_2$  give thermal decomposition products which differ considerably in type from those of their carbon analogues. In all cases, the carbon compounds give species containing ( $p-p$ ) $\pi$  double bonds, *viz.*,  $\text{Me}_2\text{C}=\text{CH}$ ,  $\text{R}_2\text{C}=\text{O}$  and  $\text{R}_2\text{C}=\text{NH}$ , respectively. It is therefore not unlikely that the transition state for decomposition of the carbon compounds involves somewhere a partial ( $p-p$ ) $\pi$  double bond between carbon and carbon, carbon and oxygen or carbon and nitrogen, respectively. Since the formation of a partial ( $p-p$ ) $\pi$  double bond between silicon and carbon, silicon and oxygen or silicon and nitrogen is much less likely, this type of reaction mechanism is less probable for the silicon compounds and hence the silicon compounds probably undergo thermal decomposition by a different, higher activation energy process.

## VI. OXIDATIVE STABILITY (TO OXYGEN)

Very few studies of the reaction of *dry* oxygen with silicon derivatives of the transition metals have been performed. The compound  $(\text{SiH}_3)_2\text{Fe}(\text{CO})_4$  explodes in air<sup>17</sup> but this violent oxidation is presumably related to the presence of the Si—H bonds.

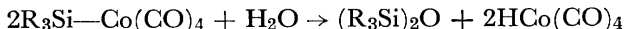
After  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  had been exposed to dry oxygen at 1 atm. pressure at room temperature for forty-five minutes, 81 per cent of the  $\text{Me}_3\text{Si-}$  groups were liberated as  $\text{Me}_3\text{Si}_2\text{O}$ . The reaction was exothermic<sup>64</sup>. The compound,  $\text{Me}_3\text{Si—Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  is very much less reactive. Thus, after ninety-six hours exposure to 0.7 atm. pressure of oxygen, 70 per cent of the compound was recovered unchanged, and some  $(\text{Me}_3\text{Si})_2\text{O}$  was evolved<sup>65</sup>.

## VII. CLEAVAGE OF THE SILICON-TRANSITION METAL BOND

It is convenient to divide the treatment of this topic into several categories, depending on the type of reagent employed.

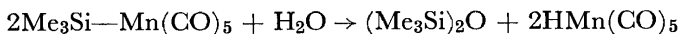
### A. By Protonic Reagents

The Si—Co bond in  $\text{R}_3\text{Si—Co}(\text{CO})_4$  ( $\text{R} = \text{H, Me}$ ) is hydrolytically unstable<sup>3</sup> and it is cleaved at a rapid but measurable rate at or below room temperature on mixing the compounds with water<sup>3,5,7</sup>, *viz.*,



When  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  was held with excess water for fifteen minutes at room temperature, 58 per cent yields of  $(\text{Me}_3\text{Si})_2\text{O}$  were obtained; but hydrolysis was quantitative after two hours. If the reaction had been permitted to occur in a homogeneous liquid phase, hydrolysis might well have proceeded very much more rapidly.

When solid  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$  was permitted to stand with excess water for twenty-four hours at room temperature, 80 per cent of the compound was recovered unchanged<sup>14</sup>. From the products obtained it was evident that some hydrolysis had taken place:

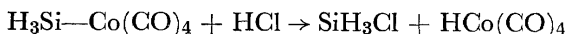


However, the apparent hydrolytic stability is presumably due to the fact that solid  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$  is not wetted by water and when an ethereal solution of the compound was treated with excess water only 9 per cent of the compound was recovered unchanged after five minutes at room temperature; longer reaction times resulted in complete hydrolysis and essentially quantitative recovery of  $(\text{Me}_3\text{Si})_2\text{O}$  and  $\text{HMn}(\text{CO})_5$ .<sup>14</sup>

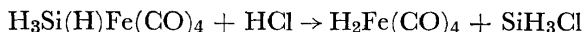
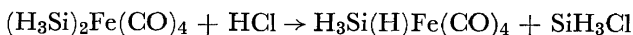
The Si—Fe bond is remarkably resistant to hydrolysis. The parent compound,  $(\text{SiH}_3)_2\text{Fe}(\text{CO})_4$  is reported to react quite slowly with water vapour<sup>17</sup>. Solid  $\text{Me}_3\text{Si—Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  undergoes no reaction whatsoever with liquid water during one day at room temperature<sup>63</sup>. Even when its ethereal solution was treated with excess water for one hour at room temperature, the  $\text{Me}_3\text{Si—Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  was recovered quantitatively<sup>63</sup>. This information indicates that the Si—Fe bond is considerably more stable hydrolytically than the Si—Co and Si—Mn bonds in carbonyl species.

Methanolysis of the Si—Co and Si—Mn bonds in  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  and  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$  occurs rapidly in homogeneous medium at room temperature. Quantitative yields of  $\text{Me}_3\text{SiOMe}$  were obtained from  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  after forty-five minutes<sup>5,7</sup>. Fourteen percent of a sample of  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$  was recovered unchanged from its solution in methanol after five minutes; essentially quantitative yields of  $\text{Me}_3\text{SiOMe}$  were obtained<sup>14</sup>.

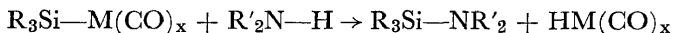
Although gaseous hydrogen chloride readily cleaves the Si—Co bond in  $\text{H}_3\text{Si—Co}(\text{CO})_4$ <sup>3</sup>, *viz.*,



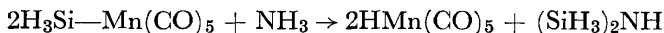
it does not cleave the Si—Mn bond in  $\text{H}_3\text{Si—Mn}(\text{CO})_5$  either at room temperature or at 75°<sup>13</sup>. The Si—Fe bonds in  $(\text{SiH}_3)_2\text{Fe}(\text{CO})_4$  also are not readily cleaved by hydrogen chloride. After ten minutes at 40° only 9 per cent of the Si—Fe bonds were broken, (in a stepwise manner), to yield  $\text{H}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$  and  $\text{H}_2\text{Fe}(\text{CO})_4$ <sup>17</sup>, *viz.*,



The Si—Co and Si—Mn bonds are also cleaved readily at, or below room temperature by N—H bonds to give a mixture of products<sup>7,13</sup>. The chief primary reaction appears to follow the course:



where R = H, Me; R' = H, Me; M = Co, Mn. In the reaction between  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  and  $\text{Me}_2\text{NH}$ , some of the  $\text{Me}_2\text{NH}$  was apparently consumed to form the adduct,  $\text{Me}_3\text{SiCo}(\text{CO})_4 \cdot \text{Me}_2\text{NH}$ . (See Section VII, C)<sup>7</sup>. A clean cut reaction occurred between  $\text{H}_3\text{Si—Mn}(\text{CO})_5$  and  $\text{NH}_3$ <sup>17</sup>:

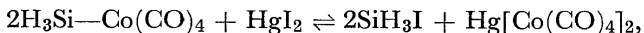


In the analogous reaction with  $\text{H}_3\text{Si—Co}(\text{CO})_4$ , a number of products, including  $\text{SiH}_4$  and  $(\text{SiH}_3)_3\text{N}$  were obtained<sup>13</sup>. The more complex nature of this reaction is believed to be due to the greater acid strength of  $\text{HCo}(\text{CO})_4$  as compared to  $\text{HMn}(\text{CO})_5$ . The  $\text{HCo}(\text{CO})_4$  thus catalyzes the decomposition of the  $(\text{SiH}_3)_2\text{NH}$  first formed<sup>13</sup>.

## B. By Covalent Halides

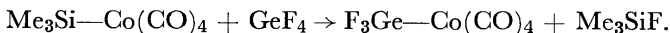
Although a number of covalent or semi-covalent halides have been found to readily cleave the Si—Co bond, it is interesting to find that some such compounds do not attack the bond at all. In those cases where no reaction occurs, it is not clear whether the lack of reactivity is due to thermodynamic or kinetic factors. From the electronegativity data given in Section IV, A, it seems likely that the polarity of the silicon-transition metal bond might be small. This could reduce the ease of nucleophilic attack at silicon in a rate-controlling step. However, it is likely that the rate-controlling step for many reactions might involve electrophilic attack at the transition metal.

It has been observed that mercuric iodide reacts reversibly with  $\text{H}_3\text{Si—Co}(\text{CO})_4$ , *viz.*<sup>3</sup>,

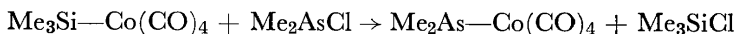


however, no reaction occurred between mercuric iodide and  $\text{F}_3\text{Si}-\text{Co}(\text{CO})_4$  even after heating to  $60^\circ$ <sup>8</sup>. When mercuric chloride, on the other hand, was heated with  $\text{F}_3\text{Si}-\text{Co}(\text{CO})_4$  for three hours at  $60^\circ$ , an analogous reaction did take place and a 90 per cent yield of  $\text{SiF}_3\text{Cl}$  was obtained<sup>8</sup>.

Excess germanium tetrafluoride cleaves the Si—Co bond in  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  after ten minutes at room temperature to give analytically pure  $\text{F}_3\text{Ge}-\text{Co}(\text{CO})_4$ . Quantitative reaction took place according to the equation<sup>5,7</sup>



When  $\text{Me}_2\text{AsCl}$  was mixed with an excess of  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  a rapid reaction took place even at low temperatures<sup>5,7</sup>. A dark red colour developed at  $-23^\circ$  and it is believed that at this temperature the following reaction occurred:



On warming to room temperature, CO was evolved and quantitative yields of analytically pure, polymeric  $[\text{Me}_2\text{As}-\text{Co}(\text{CO})_3]_x$  were isolated, *viz.*,



No reaction occurred between  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  or  $\text{MeSiH}_2-\text{Co}(\text{CO})_4$  and excess boron trifluoride at room temperature<sup>5,7,21</sup>. Similarly, after acetyl chloride and  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  had been held at room temperature for thirty minutes, both materials were recovered essentially quantitatively<sup>7</sup>. When equimolar quantities of  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$ , acetyl chloride and boron trichloride were held at room temperature for thirty minutes, no reaction was observed<sup>64</sup>.

Surprisingly, very little reaction took place between  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  and a large excess of phosphorus pentafluoride at an autogenous gas pressure of approximately 20 atm. during two hours at room temperature. Similarly no reaction occurred between  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  and excess phosphorus trifluoride even when they were heated together at  $100^\circ$  for one hour<sup>7</sup>. Some thermal decomposition of the  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  took place during this period as expected, but most of the phosphorus trifluoride was recovered unchanged. No reaction took place between  $\text{MeSiH}_2-\text{Co}(\text{CO})_4$  and phosphorus trifluoride during one hour at room temperature<sup>21</sup>. When a solution of  $\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5$  and phosphorus trifluoride in pentane was simultaneously heated to approximately  $100^\circ$  for thirty minutes and exposed to ultraviolet radiation, essentially no cleavage of the Si—Mn bond was observed<sup>14</sup>.

A most unexpected and interesting reaction occurred between  $\text{MeSiH}_2-\text{Co}(\text{CO})_4$  and phosphorus pentafluoride in which a net transfer of hydrogen from silicon to cobalt took place<sup>21,65</sup>. Reaction commenced below  $0^\circ$  and was complete after three hours at room temperature. The chief products were:  $\text{MeSiF}_2-\text{Co}(\text{CO})_4$ ,  $\text{MeSiF}_2\text{H}$ ,  $\text{HCo}(\text{CO})_3(\text{PF}_3)$ ,  $\text{HCo}(\text{CO})_2(\text{PF}_3)_2$  and  $\text{HCo}(\text{CO})(\text{PF}_3)_3$ . Exactly the same products were obtained by co-condensing an approximately equimolar mixture of  $\text{MeSiH}_3$  and phosphorus pentafluoride on to  $\text{Co}_2(\text{CO})_8$  and allowing them to stand at room temperature for two and a half hours<sup>21,65</sup>

Since there is no reaction between  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  and phosphorus pentafluoride or between  $\text{MeSiH}_2\text{—Co}(\text{CO})_4$  and phosphorus trifluoride, it appears that a key step in the reaction must have involved reduction of phosphorus pentafluoride by Si—H bonds. Some background experiments were therefore carried out in order to better understand this reaction. After ninety minutes at room temperature, approximately equimolar quantities of  $\text{MeSiH}_3$  and phosphorus pentafluoride underwent the following reaction<sup>21,65</sup>:



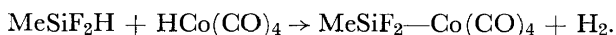
In a somewhat analogous reaction it was found that  $\text{MeSiH}_2\text{Cl}$  and phosphorus pentafluoride yielded, after one hour at room temperature,  $\text{MeSiF}_2\text{H}$ , phosphorus trifluoride and hydrogen chloride, *viz.*<sup>21,65</sup>,



Since the —Cl and — $\text{Co}(\text{CO})_4$  groupings have a number of properties in common, it is believed that the  $\text{MeSiH}_2\text{—Co}(\text{CO})_4$  probably reacts initially in an exactly analogous fashion to  $\text{MeSiH}_2\text{Cl}$ , *viz.*,



Since it is known that Si—H bonds react readily with  $\text{HCo}(\text{CO})_4$  it seems likely that the following reaction would then occur:



Also, since it is known that  $\text{HCo}(\text{CO})_4$  and phosphorus trifluoride react rapidly at low temperatures to give  $\text{HCo}(\text{CO})_x(\text{PF}_3)_{4-x}$ <sup>66</sup> it seems that some of the  $\text{HCo}(\text{CO})_4$  could also react with the phosphorus trifluoride produced to give those carbonyl hydride species which were obtained in the original reaction between  $\text{MeSiH}_2\text{—Co}(\text{CO})_4$  and phosphorus pentafluoride. It seems very probable that the net transfer of hydrogen from silicon to cobalt may occur via this reaction sequence.

### C. By Tertiary Amines

The reactions described in this section may be regarded either as addition reactions to silicon or as reactions involving cleavage of the covalent silicon-transition metal bond.

When  $\text{H}_3\text{Si—Co}(\text{CO})_4$  is treated either with trimethylamine or with pyridine, no carbon monoxide displacement is observed; instead the solid adducts,  $\text{SiH}_3\text{Co}(\text{CO})_4 \cdot 2\text{Base}$  are obtained<sup>12</sup>. Analogous adducts have been obtained from  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  and trimethylamine or pyridine except that in this case the species formed have the composition  $\text{Me}_3\text{SiCo}(\text{CO})_4 \cdot \text{Base}^{64}$ . The CO stretching vibrations for  $\text{H}_3\text{Si—Co}(\text{CO})_4$  and  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  fall in the 2000–2130  $\text{cm}^{-1}$  range, whereas in the corresponding adducts they fall between 1870 and 1890  $\text{cm}^{-1}$ . Since the  $\text{Co}(\text{CO})_4^{-1}$  ion exhibits its chief CO stretching vibration at 1883  $\text{cm}^{-1}$ <sup>67</sup>, it seems likely that these compounds are ionic compounds which could be formulated as  $[(\text{SiH}_3 \cdot 2\text{B})]^+[\text{Co}(\text{CO})_4]^-$  and  $[(\text{Me}_3\text{Si} \cdot \text{B})]^+[\text{Co}(\text{CO})_4]^-$ . The latter species may therefore be regarded as the silicon-substituted quaternary

ammonium salt, *e.g.*  $[\text{Me}_3\text{NSiMe}_3]^+[\text{Co}(\text{CO})_4]^-$ . An analogous compound has been reported for  $\text{H}_3\text{Si}-\text{Mn}(\text{CO})_5$ , *i.e.*  $[(\text{SiH}_3 \cdot 2\text{B})]^+[\text{Mn}(\text{CO})_5]^-$ <sup>12</sup>. It is interesting to find that  $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4$  forms only the 1:2 adduct,  $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4 \cdot 2\text{NMe}_3$ , even with a large excess of trimethylamine<sup>17</sup>. Infrared studies suggest that it is only partly ionic in nature and its chemical properties suggest that one trimethylamine molecule is coordinated to each  $\text{SiH}_3$  group<sup>17</sup>.

These ionic, or partly ionic compounds, appear to be more chemically reactive than the parent compounds. Thus, although hydrogen chloride does not cleave the  $\text{Si}-\text{Mn}$  bond in  $\text{H}_3\text{Si}-\text{Mn}(\text{CO})_5$ , even on warming, it reacts rapidly at  $-80^\circ$  with the pyridine adduct, *viz.*<sup>13</sup>,



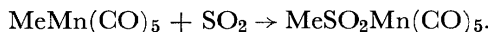
Analogously, when  $[(\text{Me}_3\text{SiNMe}_3)]^+[\text{Co}(\text{CO})_4]^-$  was exposed to dry oxygen at one atm. pressure, an explosion occurred and 85 per cent of the  $\text{Me}_3\text{Si}$ - groups were recovered as  $(\text{Me}_3\text{Si})_2\text{O}$ <sup>64</sup>. This should be compared with the reaction of  $\text{Me}_3\text{Si}-\text{Co}(\text{CO})_4$  with oxygen (Section VI) in which a much less vigorous reaction was observed<sup>64</sup>. When  $[\text{Me}_3\text{SiNMe}_3]^+[\text{Co}(\text{CO})_4]^-$  was heated at  $80^\circ$  for 14 hours *in vacuo*, non-volatile, unidentified species were found together with trace amounts of  $(\text{Me}_3\text{Si})_2\text{O}$ , trimethylamine and carbon monoxide<sup>64</sup>. When excess gaseous hydrogen chloride was permitted to react with  $(\text{H}_3\text{Si})_2\text{Fe}(\text{CO})_4 \cdot 2\text{NMe}_3$ , it was found that  $\text{H}_2\text{Fe}(\text{CO})_4$ , but no  $\text{H}_3\text{Si}(\text{H})\text{Fe}(\text{CO})_4$  was produced<sup>17</sup>.

#### D. Insertion Reactions

It is well known that carbon monoxide will readily insert into carbon-transition metal bonds<sup>68</sup> under relatively mild reaction conditions, *e.g.*,



Sulphur dioxide undergoes an analogous type of reaction. With  $\text{MeMn}(\text{CO})_5$ , for example, reaction occurs at  $-75^\circ$  during one hour<sup>69</sup>:

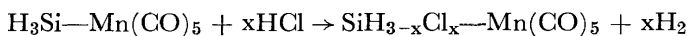


Silicon-transition metal carbonyls however, show no tendency to undergo these types of reactions<sup>4,14</sup>. Neither  $\text{H}_3\text{Si}-\text{Co}(\text{CO})_4$  nor  $\text{H}_3\text{Si}-\text{Mn}(\text{CO})_5$  undergo direct carbonyl insertion into the  $\text{Si}$ -transition metal bond, even with high pressures of carbon monoxide<sup>13</sup>. Likewise, when  $\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5$  was held either at room temperature for forty hours, or at  $100^\circ$  for two and a half hours in the presence of liquid sulphur dioxide, no major reaction occurred, 75 per cent of the  $\text{Me}_3\text{Si}-\text{Mn}(\text{CO})_5$  being recovered in the former experiment and 89 per cent in the latter. No  $\text{SO}_2$ -insertion product was observed<sup>14</sup>. It has been suggested that the reluctance of the  $\text{Si}$ -transition metal bond to undergo insertion reactions may be related to the ( $d \rightarrow d$ ) $\pi$   $\text{Si}$ -metal interaction energy which would thereby be lost<sup>13</sup>.

### VIII. SUBSTITUTION REACTIONS AT SILICON

Very little is known about substitution reactions at silicon during which the silicon-transition metal bond remains intact. However, a remarkable

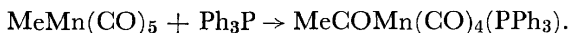
reaction occurs slowly in the gas phase at 75° between  $\text{H}_3\text{Si—Mn}(\text{CO})_5$  and hydrogen chloride in which substitution of hydrogen by chlorine occurs, *viz.*,



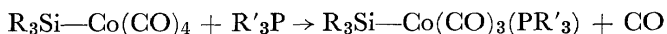
where  $x = 1-3$ . No cleavage of the Si—Mn bond occurs during this process<sup>13</sup>.

## IX. SUBSTITUTION REACTIONS AT THE TRANSITION METAL

Several reactions have been reported in which a CO group in the metal carbonyl portion of the molecule is replaced by a phosphine. The CO grouping is eliminated as carbon monoxide and no evidence has yet been obtained for its insertion into the silicon-transition metal bond as is frequently found with carbon transition metal carbonyls, *e.g.*<sup>70</sup>,



When  $\text{R}_3\text{Si—Co}(\text{CO})_4$  is permitted to react with triphenylphosphine or triethylphosphine, substitution occurs at room temperature, *viz.*,



where  $\text{R} = \text{H}$  and  $\text{R}' = \text{Ph}$ <sup>13</sup> and where  $\text{R} = \text{Et}$  or  $\text{Cl}$  and  $\text{R}' = \text{Et}$ <sup>19</sup>. The  $\text{Et}_3\text{P}$  group enters into the position *trans* to the  $\text{R}_3\text{Si-}$  group<sup>19</sup>.

Ultraviolet irradiation of  $\text{Me}_3\text{Si—Fe}(\text{CO})_2(\pi\text{-C}_5\text{H}_5)$  in the presence of  $\text{Ph}_2\text{PCH}_2\text{CH}_2\text{PPh}_2$  or *cis*- $\text{Ph}_2\text{PCH}=\text{CHPPh}_2$  results in the formation of  $\text{Me}_3\text{SiFe}(\text{diphos})$  ( $\pi\text{-C}_5\text{H}_5$ )<sup>71</sup>.

It was interesting to find that when a pentane solution containing equimolar quantities of  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$  and trifluorophosphine was exposed to ultraviolet radiation for thirty minutes at approximately 100° essentially no cleavage of the Si—Mn bond occurred. Instead, a 90 per cent yield of  $\text{Me}_3\text{Si—Mn}(\text{CO})_4(\text{PF}_3)$  was obtained together with small amounts of more highly  $\text{PF}_3$ -substituted products. The material consisted of the *trans* isomer only<sup>14</sup>.

## X. CONCLUSIONS

In conclusion, it can clearly be seen, even from the small amount of information presently available, that the chemistries of compounds containing Si—Co, Si—Mn and Si—Fe bonds differ considerably from each other in certain respects. Broadly speaking, it appears that the order of increasing thermal stability is  $\text{Si—Co} < \text{Si—Mn} \leq \text{Si—Fe}$  and that the order of decreasing chemical reactivity is  $\text{Si—Co} > \text{Si—Mn} \geq \text{Si—Fe}$ .

It is likely that the most significant advances, in so far as understanding factors which control silicon-transition metal chemistry, will result from (i) a study of analogous carbon, silicon, germanium, tin and lead compounds containing a Group IV element-transition metal bond, *e.g.*,  $\text{Me}_3\text{M—Co}(\text{CO})_4$ , ( $\text{M} = \text{C, Si, Ge, Sn, Pb}$ ) and (ii) a study of similar types of compounds, *e.g.*,  $\text{Me}_3\text{Si—Co}(\text{CO})_4$  and  $\text{Me}_3\text{Si—Mn}(\text{CO})_5$  containing silicon joined to different transition elements. A really meaningful interpretation of the data from studies of type (ii) can, of course, only be presented when comparisons are also made with analogous carbon, germanium, tin and lead compounds.



The number and variety of possible compounds containing even one given silicon-transition metal bond which could be synthesized is already very large. Considering presently known techniques only, one can synthesize compounds having different substituents on the silicon or different substituents, such as CO, phosphines,  $\pi$ -bonded organic groups, etc., on the transition metal. When changes in substituents are then extended to species containing more than one silicon-transition metal bond or to polynuclear species, a number of which are already known, an enormous range of compounds is presented.

It seems very likely that in a relatively few years, the chemistry of compounds containing silicon joined to any one particular transition metal will be as extensive as the chemistry of, for example, compounds containing Si—N bonds. Furthermore, it seems highly probable that the chemistries of classes of compounds containing silicon joined to different transition metals may differ from each other to the extent to which compounds containing Si—O and Si—N bonds, for example, differ from each other.

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### Notes added in proof.

- The conclusions reached in the following discussion would remain unchanged even if it were assumed that that the effective steric requirements of the axially-located groups were such that the equatorial carbonyl groups were, from steric requirements alone, approximately coplanar with the central transition element. In this case,  $\alpha$  would simply be close to zero.
- Since this manuscript was submitted for publication, it has been reported<sup>73</sup> that the Si—Co—CO<sub>eq.</sub> angle, determined on a gaseous sample of H<sub>3</sub>Si—Co(CO)<sub>4</sub>, (electron diffraction) is 81.7°. Distortions are therefore probably not determined chiefly by crystal lattice effects.