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Reactions of Group VIII Metal Carbonyl Anions with 1,2-Dichlorotetramethyldisilane

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*Reactions of 1,2-dichlorotetramethyldisilane with transition metal carbonyl anions, $NaCo(CO)_4$ and $Na_2Fe(CO)_4$, proceed easily to give monodisplacement products. Thus, reaction with $NaCo(CO)_4$ yields a neutral chlorodisilanyl cobalt complex, $Cl(CH_3)_2Si(CH_3)_2SiCo(CO)_4$, and the analogous reaction with $Na_2Fe(CO)_4$ in diethyl ether gives an ionic chlorodisilanyltetracarbonylferrate salt, $[Cl(CH_3)_2Si(CH_3)_2SiFe(CO)_4]^-Na^+$. The β-chloride of $Cl(CH_3)_2Si(CH_3)_2SiCo(CO)_4$ was unreactive toward BCl_3. Prolonged reaction with $NaCo(CO)_4$ resulted in formation of the cluster compound, $(CO)_9Co_3COSi(CH_3)_2Si(CH_3)_2Co(CO)_4$ and of bis(μ-dimethylsilylene)bis(tricarbonylcobalt)(*Co–Co*).

Introduction

1,2-Dihaloalkanes react with transition metal anions with loss of both halides, giving either free alkenes [1] or alkene–metal complexes [2], depending on the stability of the alkene. Thus, dechlorination of 3,4-dihalocyclobutenes by $Na_2Fe(CO)_4$ yields the stable cyclobutadienetricarbonyliron [2a]. Our interest in transition metal complexes containing a tetramethyldisilene moiety [3] led us to study similar reactions of 1,2-dichloro-1,1,2,2-tetramethyldisilane, *1*, which may be expected to react similarly, to give a transition metal complex [4]. However, dichlorodisilane *1*, unlike 1,2-dichloroalkanes, did not react at all with neutral metal carbonyls [$Fe(CO)_5$ under thermal and photolytic conditions, $Fe_2(CO)_9$, or $Co_2(CO)_8$], perhaps due to the enhanced Si-Cl bond strength as compared to C–Cl.

Therefore an investigation of reactions of *1* with some Group VIII metal carbonyl anions was undertaken. Reactions of *1* with cyclopentadienyl carbonyl anions [5] have been found to give $Cl(CH_3)_2Si(CH_3)_2M(CO)_nCp$ (M = Fe, n = 2; M = Cr, Mo, W, n = 3) as the principal products. Only the very nucleophilic $NaFe(CO)_2Cp$ has been found able to displace the second halide, to form the disubstituted product $[CpFe(CO)_2Si(CH_3)_2-]_2$ [5a]. $NaCo(CO)_4$ and $Na_2Fe(CO)_4$ were chosen for detailed study due to their differences in nucleophilicity and metallic charge and for comparison with the results of our previous studies with 1,1,2,2-tetramethyldisilane and uncharged metal carbonyls [6].

Results

Stirring *1* with $NaCo(CO)_4$ for one day yielded a light-yellow high boiling liquid, *2*, which was isolated by vacuum distillation. The infrared spectrum of *2* exhibited four strong metal carbonyl absorptions at 2093(s), 2033(s), 2000(sh), 1995(vs) and 1962(w, ^{13}CO) cm^{-1}, suggesting the product to be $ClSi(CH_3)_2Si(CH_3)_2Co(CO)_4$ with C_{3v} local symmetry of the $Co(CO)_4$ group. The shoulder at 2000 cm^{-1} is probably an indication of a slight distortion due to the asymmetric nature of the disilanyl ligand. The ^1H NMR and ^{13}C NMR spectra of *2* both showed two high field resonances of equal intensity in agreement with the structure $Cl[Si(CH_3)_2]_2Co(CO)_4$. The 70 eV mass spectrum of *2* did not show the molecular ion at m/e 322; however, the series of ions corresponding to $(CO)_nCoSi_2(CH_3)_4Cl^+$ (n = 3–0) was observed. The isotope ratio of all major fragments indicated tenacious retention of the chlorine.

The β-chlorine atom of *2* was also chemically unreactive. After more than two weeks dissolved in BCl_3 at room temperature, *2* gave no sign of chloride ionization; only small amounts of *1* and $HCo(CO)_4$ were detectable.

Attack of nucleophiles at the β-Si of *2*, though hindered, could be observed. Thus, on prolonged stirring of *1* with $NaCo(CO)_4$ (in a 1:2 mol ratio) or *2* with $NaCo(CO)_4$, two new carbonyl bands at 2101 and 2048 cm^{-1} appeared in the IR. After stirring for 8–9 days at room temperature the reaction mixtures, although still showing the presence of *2*, were worked up to yield the known compound $Co_2(CO)_6[Si(CH_3)_2]_2$, *3*, [6] and a new cobalt cluster compound, $Co_4(CO)_{14}[Si(CH_3)_2]_2$, *4*, in a ratio of 1:6.

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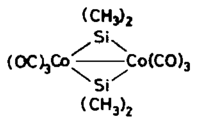
TABLE I. Infrared Spectra of Silyltetracarbonylferrate Salts.

Compound	Carbonyl Bands, cm^{-1}	Medium
$ClSi(CH_3)_2Si(CH_3)_2Fe(CO)_4^-Na^+$ [a]	1994(s), 1914(s), 1892(s), 1805(s)	ether
$(C_6H_5)_3SiFe(CO)_4^-Li^+$ [b]	2002, 1925, 1891, 1825	KBr
$(C_6H_5)_3SiFe(CO)_4^-N(C_2H_5)_4^+$ [c]	1995(s), 1907(m), 1879(vs), 1865(sh)	CH_2Cl_2
$Cl_3SiFe(CO)_4^-N(C_2H_5)_4^+$ [c]	2031(s), 1950(m), 1916(vs), 1904(sh)	CH_2Cl_2

[a] This work. [b] Ref. 9. [c] Ref. 10.



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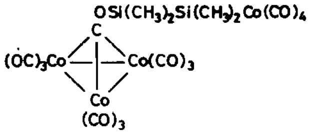

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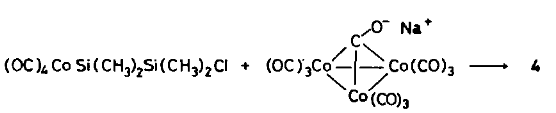
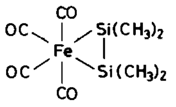
3 was identified by NMR, MS and TLC comparison with previously obtained material [6]. *4* was characterized by means of its IR spectrum (2101(w), 2048(s), 2036(m) and 2013(m) cm^{-1} which compared closely with those reported for two similar silyl clusters $(CO)_9Co_3COSiR_2Co(CO)_4$ (R = Et, Ph) [7]), and its ^1H NMR spectrum in benzene (two singlets at δ 0.53 and 0.50 ppm) and by preparing a sample through reaction of *2* with the known $NaCo_3(CO)_{10}$ [8].



The reaction produced $Co_4(CO)_{14}[Si(CH_3)_2]_2$, *4*, which was identical by IR and NMR with the material previously obtained.

Reaction of *1* with $Na_2Fe(CO)_4 \cdot 1.5$ dioxane in diethyl ether gave as the main product an insoluble red-yellow salt, *6*, in a 45% yield. When heated above 140 °C in a closed capillary tube, *6* decomposed with darkening. It dissolved readily in polar organic solvents, but not in nonpolar hydrocarbon solvents. The infrared spectrum of *6* in diethyl ether showed four strong terminal metal carbonyl bands at 1994, 1914, 1892 and 1805 cm^{-1}, suggesting the ionic structure $[Cl(CH_3)_2Si(CH_3)_2SiFe(CO)_4]^-Na^+$. The spectrum is in good agreement with those of analogous silyltetracarbonylferrate salts (see Table I).

6 revealed two silyl methyl resonances, at δ 0.47 and 0.51, of equal intensity, and a singlet at 3.65 ppm due to dioxane, the integral corresponding to a molecular formula of $[Cl(CH_3)_2Si(CH_3)_2SiFe(CO)_4]^- Na^+ \cdot 1.5$ dioxane. The mass spectrum obtained from *6* by heating the mass spectrometer direct inlet above 100 °C exhibited significant peaks at m/e 284, 228, 200 and 172, corresponding to ions $Fe(CO)_n[Si(CH_3)_2]_2^+$ (n = 4, 2, 1 and 0). These fragments appear to derive from a disilene complex, *7*.



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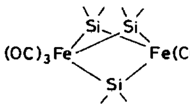
Most significantly, *no* mass spectral peaks containing chlorine are discernible in the mass spectrum obtained from *6*. The spectrum differs in this sense from those of *2* and analogous chlorodisilanyl metal complexes [5]. For example, *all* major peaks in the mass spectrum of the analogous cobalt compound *2* clearly showed retention of the chlorine atom. The absence of any chlorine-containing peaks in the spectrum of *6* indicates that the volatile material produced from *6* in the direct inlet has already lost its chlorine in a thermal intramolecular displacement reaction to form *7* before entering the ionization chamber. The mass spectrum also contained fragments at m/e 88, 58 and 43, confirming the presence of dioxane in the crystal lattice of *6*.

Reaction of *1* with $Na_2Fe(CO)_4$ also produced several minor products which were separated from *6* by extraction into hexane. The known bis(μ-dimethylsilylene)-μ-carbonylbis(tricarbonyliron)(*Fe–Fe*), *8*, [6, 11] was identified by means of IR, ^1H NMR and mass spectra. Two other products, *tris*(μ-dimethylsilylene)bis(tricarbonyl iron)(*Fe–Fe*), *9*, and bis(μ-tetramethyldisilano)bis(tricarbonyliron), *10*, were suggested by series of peaks in the mass spectra of soluble product mixtures.



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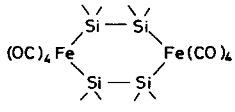

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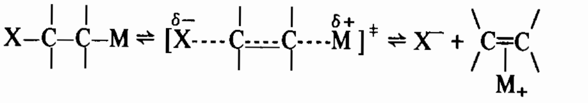
Discussion

Reactions of 1,2-dichlorotetramethyldisilane with $NaCo(CO)_4$ and $Na_2Fe(CO)_4 \cdot 1.5$ dioxane proceed reasonably quickly and in similar ways to yield the new chlorodisilanyl complexes *2* and *6*, respectively. In the iron case, however, the results are very dependent on the preparation of the salt and on the solvent used. *6* was not formed in attempts using different preparations of $Na_2Fe(CO)_4$ or in THF or hydrocarbon solutions.

The β-chlorine of *2* showed no tendency to ionize upon prolonged treatment with BCl_3. This low ionicity has previously been observed in other β-halodisilanylmetal compounds, $X\text{-}SiMe_2SiMe_2\text{-}M$ [X = Br, Cl, F; M = $Fe(CO)_2Cp$, $Cr(CO)_3Cp$, $Mo(CO)_3Cp$, $W(CO)_3Cp$] which have failed to give detectible cations by chloride loss in presence of Ag^+, $AlCl_3$, and $SbCl_5$ or even in the mass spectrometer [5a]. This behavior contrasts sharply with carbon systems, X–C–C–M, which manifest very high ionicity.

The origin of this unreactivity must lie at least in part in the greater strength of Si–X bonds compared to C–X; moreover, no trivalent silicenium ion, R_3Si^+, has yet been detected [12]. Failure of the metal to induce ionic reactivity in the chlorodisilanes, in contrast to the carbon analogues, is most consistent with hyperconjugative interactions in the latter transition states, which are inhibited in the disilanes by the well-known [3]

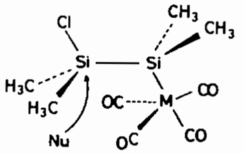


$$X{-}C{-}C{-}M \rightleftharpoons [\overset{\delta-}{X}\cdots C\cdots C\cdots \overset{\delta+}{M}]^{\ddagger} \rightleftharpoons X^- + C{=}C\ M_+$$

reluctance of Si to engage in pπ–pπ bonding.

The metal group in *6*, having a negative charge, may be expected to be considerably more nucleophilic than that in *2* or the other previously studied (chlorodisilanyl) metal compounds [5]. Indeed, intramolecular displacement appears to occur thermally at about 100 °C, in the direct inlet of the mass spectrometer. Further study of this reaction under more accessible conditions is a high priority.

Isolation of *2* and *6*, and of related compounds in reaction of *1* with other transition metal anions, attests to the comparative unreactivity of the β-chloride to attack by external nucleophiles, probably as a consequence of steric interactions.



2, M = Co

6, M = Fe^-

Nevertheless, in the reaction of *2* with $NaCo(CO)_4$, *3* and *4* were found to form very slowly in a rather unexpected ratio of 1:6. Competitive nucleophilic attack of $Co(CO)_4^-$ and $Co_3(CO)_{10}^-$ on *2* are the most likely pathways for production of *3* and *4* respectively [13]. Relative steric requirements of the two nucleophiles are unclear, but may favor attack by $Co_3(CO)_{10}^-$ to give *4*. A further rationale for predominance of *4* in the absence of major amounts of $Co_3(CO)_{10}^-$ lies in the difference in the nucleophilicity of these anions. In a study in which relative nucleophiliciities of various metal carbonyl anions toward methyl iodide were evaluated, $Co(CO)_4^-$ was found to be the least nucleophilic [14]. The relative nucleophilicity of $Co_3(CO)_{10}^-$ has not been reported, but insofar as it resembles an alkoxide ion, its nucleophilicity toward Si may be expected to be very high, making formation of *4* more facile.

The origin of $Co_3(CO)_{10}^-$ in sufficient quantity is unclear, although infrared analysis of our $NaCo(CO)_4$ does indicate minor amounts of $NaCo_3(CO)_{10}$ present as an impurity. Several previous examples of halosilanes reacting with transition-metal anions to give metal-cluster-derived products [15] and products with Si–O bonds [16] have been reported, although mechanisms of these complex reactions remain obscure.

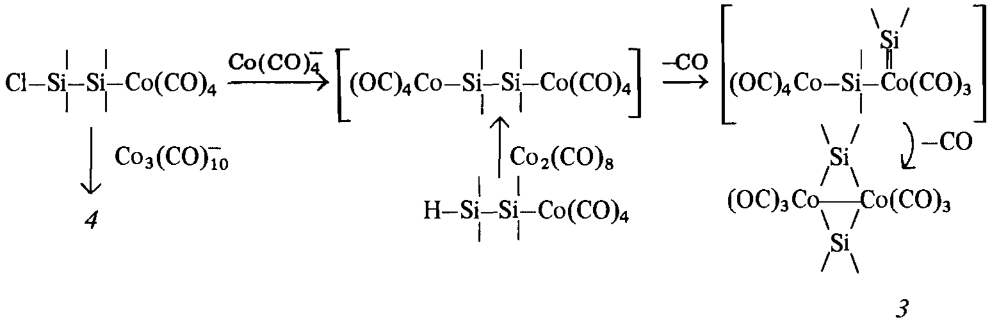
Formation of *6* is also accompanied by formation of products containing two iron atoms per molecule. The known compound *8* (identified by IR, NMR and mass spectroscopy) probably arises by a path analogous to that which produces *3*, (see below). Formation of *9* and *10* are reminiscent of results reported by Triplett and Curtis, [17] who obtained analogous products on reaction of 1,2-dichloro-1,1,2,2-tetramethyldigermane with $Na_2Fe(CO)_4$ in petroleum ether.

The production of small amounts of dimetallic products in reactions of *1* with $Co(CO)_4^-$ (*3*) and $Fe(CO)_4^=$ (*8, 9, 10*) suggests that a second displacement does proceed to some extent, often with subsequent fission of the Si–Si bond of the initial μ-disilanodimetal product. Previous results on reactions of 1,1,2,2-tetramethyldisilane with $Fe_2(CO)_9$ and $Co_2(CO)_8$ led us to conclude that such μ-disilanodimetal compounds spontaneously rearrange, with CO loss, to the μ(dimethylsilylene) compounds, *3* and *8* [6]. Formation of the same compounds in these nucleophilic displacement reactions buttresses this conclusion. In the Co case, for example, the path suggested is that of Scheme I.

Experimental

Materials

1 was prepared from hexamethyldisilane [18] using acetyl chloride and freshly sublimed $AlCl_3$ [19], purified by distillation and assayed by NMR. $NaCo(CO)_4$ was prepared by reaction of freshly sublimed $Co_2(CO)_8$ and NaOH dried at 150 °C/1 mm for 20 hr [20]. $NaCo_3(CO)_{10}$ was prepared by sodium reduction of $Co_2(CO)_8$ [8]. $Na_2Fe(CO)_4\cdot$ 1.5 dioxane was used as obtained from Alfa-Ventron. Solvents were dried over appropriate drying agents, distilled and saturated with nitrogen before use. All experiments were conducted under a dry nitrogen atmosphere using Schlenk and syringe techniques. Spectroscopic samples were prepared in a Vacuum



Scheme I

Atmospheres Model DL-001-SP dry box nominally at ⩽1 ppm O_2.

Reaction of 1 *with NaCo(CO)*$_4$ *in Hexane*

In a dry box, 1.1 g (5.0 mmol) of $NaCo(CO)_4$ was placed in a round-bottomed flask equipped with a stopcock gas adapter and a septum. The flask was removed from the dry box. Hexane (26 ml) and *1*, $Si_2Cl_2(CH_3)_4$, (0.40 ml, 2.2 mmol) were added by syringe. The reaction mixture was stirred at room temperature for 24 hours. The initially colorless solution turned slowly dark red-brown. No gas evolution was observed. The reaction mixture was vacuum filtered, and the solvent was stripped from the filtrate at reduced pressure. The involatile dark-red liquid was transferred to microdistillation apparatus in the dry box. A yellow-brown liquid distilled at 0.005 mm Hg and room temperature. The IR spectrum of the distillate in hexane exhibited carbonyl bands at 2098(m), 2032(s), 2000(sh) and 1996(s) cm^{-1}, as well as peaks due to small amounts of $HCo(CO)_4$ (at 2117, 2054, 2032 cm^{-1}) and $Co_2(CO)_8$ (at 2017, 2044, 1866 and 1859 cm^{-1}). The ^{1}H NMR spectrum in C_6D_6 showed resonances at δ 0.58 ppm and 0.46 ppm. The mass spectrum confirmed the identity of this compound, which could be obtained pure by distillation at 85 °C/0.3 mm, as $(CO)_4CoSi(CH_3)_2Si(CH_3)_2Cl$, *2*. The molecular ion at m/e 322 was not observed; however, all the ions formed by successive loss of four carbonyls from the molecular ion (at m/e 294, 266, 238 and 210) were present, along with major peaks at 208, 192, and 151 (all containing Cl). The proton-decoupled ^{13}C NMR spectrum of *2* in C_6D_6 showed two resonances of almost equal intensity at δ 4.00 and 2.67 ppm.

The pot residue of the distillation contained, according to NMR, mostly additional *2* (resonances at δ 0.46 and 0.57 ppm). Smaller resonances at δ 0.74 (*3*), 0.68, 0.51 and 0.48 (*4*), 0.36 and 0.28 ppm (siloxane) were also present. In the IR spectrum of the pot residue, carbonyl bands due to *2* (2093, 2032, 1996 and 1962 cm^{-1}), $Co_2(CO)_8$ (2071, 1867 and 1859 cm^{-1}) and $Co_4(CO)_{12}$ (2064 and 1867 cm^{-1}) were observed. Bands at 2101 and 2048 cm^{-1} were due to *4* (see below).

Prolonged Reaction of 1 *with NaCo(CO)*$_4$ *in Hexane*

The reaction was run as above, using 0.83 g (4.3 mmol) of $NaCo(CO)_4$, hexane (20 ml), and *1* (0.5 ml, 2.7 mmol). The color of the reaction mixture turned slowly to red, but no significant gas evolution was observed. After one day stirring at room temperature an IR sample showed strong absorption due to *2* at 2093, 2032 and 1996 cm^{-1}, and a strong carbonyl band at 2048 cm^{-1}. The new peak at 2048 cm^{-1} continued to grow slowly while the bands at 2093 and 1996 cm^{-1} due to *2* diminished in intensity. After eight days the reaction mixture was vacuum-filtered. Potentiometric titration of the solid dissolved in distilled water revealed 4.4 mmol of Cl^- (80%). The volatile material was removed from the filtrate under vacuum. The involatile dark oily residue was distilled at 0.005 mm Hg and room temperature, to give a brown distillate, which according to NMR contained mostly *2*, along with two singlet resonances at δ 0.28 and 0.16 ppm. The resonance at 0.28 ppm was due to octamethyltetrasila-1,4-dioxane, as confirmed by GC (OV-17 column, 100 °C) comparison with an authentic sample.

The pot residue was analyzed by NMR and mass spectra. It exhibited proton resonances in benzene at δ 0.76, 0.63, 0.60, 0.53, 0.50, 0.48 and 0.38 ppm, with approximate relative intensities 1:2:2.5:3:3:2.5:2. The resonances at 0.60 and 0.48 ppm are due to *2*. The peak at 0.76 ppm was identified as *3* by TLC comparison with an authentic sample [6]. A direct inlet mass spectroscopic study showed *2* and *3* as the principal volatile components. A 30 eV mass spectrum of the less volatile material in the region m/e 300 - 640 revealed two carbonyl fragmentation series, apparently deriving from $Co_4(CO)_{14}[Si(CH_3)_2]_2$, *4*, (the series $Co_4(CO)_x[Si(CH_3)_2]_2$ (x = 9–1) being observed) and from $Co_4(CO)_{14}[Si(CH_3)_2]$ (the series $Co_4(CO)_y[Si(CH_3)_2]$ (y = 9–1) being observed). Similarly, ions corresponding to $Co_4(CO)_z[Si(CH_3)_2]_2O$ (z = 8–1) suggested the presence of $Co_4(CO)_{14}[Si(CH_3)_2]_2O$. Prolonged distillation of the pot residue yielded some further *2*, identified by NMR, which distilled over at 0.005 mm Hg and 60–70 °C. The remaining pot residue exhibited carbonyl bands at 2101(w), 2093(m), 2090(m), 2048(s), 2036(s), 2013(m) and 1996(s) cm^{-1} in the IR. The peaks at 2093 and 1996 are due to residual *2*. The remaining bands at 2101, 2090, 2048, 2036 and 2013, are assigned to cluster compound *4*. The ^1H NMR spectrum in benzene showed singlet resonances at δ 0.73, 0.60, 0.57, 0.50 and 0.48, 0.46 and 0.35 ppm at approximate relative intensities 1:2:1:3:3:1:2 and a broad multiplet at 0.27 ppm. The resonance at 0.73 ppm is due to *3*. The singlets at 0.57 and 0.46 ppm are due to *2*. The resonances at 0.50 and 0.48 ppm of equal intensity are assigned to *4*. The remaining two singlets, at 0.60 and 0.35 ppm, are assigned to the other cluster $Co_4(CO)_{14}[Si(CH_3)_2]_2O$, which results from a contaminant in the starting *1*. Separation of these cluster compounds by column chromatography on silica or preparative TLC failed. *3* could be obtained in fairly pure form in the fastest moving material. The other compounds did not move significantly due to apparent decomposition.

Reaction of 2 *with* $NaCo_3(CO)_{10}$ *in Hexane*

A sample (0.80 g, 1.7 mmol)of $NaCo_3(CO)_{10}$ was placed in a round-bottomed flask equipped with a gas adapter and a septum, followed by hexane (25 ml) and *2* (0.60 g, 1.9 mmol). After the reaction mixture had been stirred under nitrogen for 30 hours, the color of the reaction mixture had turned dark brown. An IR spectrum exhibited carbonyl bands at 2093, 2033, 1999 and 1962 cm^{-1} due to *2*, at 2064, 2056 and 1868 cm^{-1} due to $Co_4(CO)_{12}$, and a shoulder at 2048 cm^{-1} due to *4*. As stirring at room temperature was continued, new carbonyl bands at 2101(w) and 2048(s) cm^{-1} increased slowly in size, while the bands due to *2* slowly decreased. After stirring for 9 days the reaction was stopped, although the mixture still contained some *2* according to IR. The reaction mixture was filtered under nitrogen, and the solid titrated for Cl^- indicating 1.13 mmol (60%). All volatile material was pumped from the filtrate under vacuum. The volatile fraction exhibited carbonyl bands at 2117(w), 2101, 2055(m) 2045(w), 2032(s), 2020(w), 2003(w), 1996(w) cm^{-1}; the major bands at 2117, 2055, 2032 and 1996 cm^{-1} were identified as $HCo(CO)_4$. The involatile dark red residue in hexane showed transition metal carbonyl bands at 2101(w), 2094(m), 2065(w), 2048(s), 2035(s), 2014(sh), 1996(s), 1963(w) and 1868(w) cm^{-1}. The bands at 2065 and 1868 cm^{-1} were identified as $Co_4(CO)_{12}$, the bands at 2094, 1996 and 1963 cm^{-1} as *2*, and the remainder as *4*. The ^1H NMR spectrum in benzene contained resonances at δ 0.71 ppm due to *3*, at 0.60 and 0.48 ppm (of equal intensity) due to *2* and at 0.55 and 0.52 ppm (of equal intensity) due to *4*. The relative quantities of *3*, *2* and *4* were approximately 1:4:5, respectively. A broad multiplet at 0.28 ppm, probably due to a polysiloxane, was also present.

Attempted Reaction of $(CO)_4CoSi(CH_3)_2Si(CH_3)_2Cl$ *with* BCl_3

In the dry box about 0.4 ml of *2* was placed in a NMR tube equipped with a female joint. The NMR tube was closed with a stopcock gas adapter and removed from the dry box. About 1 ml of BCl_3 was condensed from a vacuum line into the tube at −80 °C, and the tube was then sealed and allowed to warm to room temperature. The NMR spectrum exhibited two singlet resonances at δ 0.54 and 0.43 ppm (*vs.* external TMS reference) of equal intensity. After one day at room temperature, a new resonance at 0.34 ppm was observed, and some precipitate had collected on the bottom of the NMR tube. After two more weeks at room temperature, only a slight increase in size of the signal at 0.34 ppm was observed. The tube was opened under nitrogen, and unreacted BCl_3 was allowed to evaporate. The mixture was filtered in the dry box, giving a light blue solid (presumably an inorganic cobalt salt) and a red-brown liquid phase. The ^1H NMR spectrum of the latter (in benzene) exhibited singlet resonances at δ 0.60 ppm, 0.48 ppm and 0.35 ppm of approximate relative intensities 3:3:1. The resonances at 0.60 and 0.48 ppm are due to unchanged *2*. The peak at 0.35 ppm was identified as *1* by adding a small amount and observing it to increase in size.

After a similar run, an IR spectrum showed peaks due to *2* and a small amount of $HCo(CO)_4$. Thus, the only apparent reaction was cleavage of the Si–Co bond of *2* by adventitious HCl.

Reaction of $Na_2Fe(CO)_4$ *with* 1 *in Diethyl Ether*

In a dry box, 1.1 g (3.3 mmol) of $Na_2Fe(CO)_4 \cdot 1.5$ dioxane was placed in a flask equipped with a gas adapter and a septum, followed by diethyl ether (50 ml) and *1* (0.80 ml, 4.3 mmol). While the reaction mixture was stirred at room temperature for 16 hours, no gas evolution was observed, and the color turned slowly from colorless to yellow-brown. The reaction mixture was filtered under nitrogen. Silver titration of the residue in distilled water indicated 4.4 mmol of ionic Cl^-. Volatile material which was removed from the filtrate at 0.1 mm Hg exhibited ^1H NMR resonances and singlet resonances at 0.56, 0.26 and 0.19 ppm. The peaks at 0.56 and 0.19 ppm are due to *1* and the hydrolysis product, octamethyltetrasila-1,4-dioxane, respectively.

During removal of volatiles a yellow solid started to precipitate from the solution. The involatile residue was transferred to the dry box, where the residue was extracted with hexane, leaving an insoluble red-yellow solid (0.7 g), m.p. > 140 °C (dec.) which exhibited transition metal carbonyl bands at 2000 (s, br), 1910(s, br) and 1850 (s, br) cm^{-1} in Nujol. The ^{1}H NMR spectrum of the solid in CD_3COCD_3 showed singlet resonances at δ 3.65 ppm (dioxane), 0.51 ppm, 0.47 ppm, 0.35 ppm and 0.25 ppm. The major resonances at 3.65, 0.51 and 0.47 ppm appear at approximate relative intensities 2.2:1:1, respectively. These peaks suggest a salt structure of $[Cl(CH_3)_2Si(CH_3)_2SiFe(CO)_4]^-Na^+\cdot 1.5$ dioxane for *6*. The solid dissolved in water forming a red solution. When a few drops of $AgNO_3$ solution were added a heavy white precipitate formed, indicating the presence of Cl^- in the water solution. The mass spectrum of the solid, obtained using the solid probe at *ca.* 50 °C showed sequences of ions corresponding in mass to $[Si(CH_3)_2]_4Fe_2(CO)_x$, x = 7–2, 0, presumably from *10*, $[Si(CH_3)_2]_3Fe_2(CO)_y$, y = 6–3, 1, 0, presumably from *9*, and $[Si(CH_3)_2]_2Fe_2(CO)_z$, z = 7, 5–0, from the known compound *8* [6]. Further heating to *ca.* 100 °C gave a clean spectrum which showed ions at m/e 43, 58, and 88 due to dioxane and at m/e 284, 228, 200 and 172 corresponding to the fragments $Fe[Si(CH_3)_2]_2(CO)_n$, n = 4, 2, 1, 0. Removal of the hexane under vacuum from the extracts left a brown oily residue, which exhibited NMR singlet resonances at δ 1.07 ppm due to *8* [6, 11] and unidentified resonances at 0.56, 0.45, 0.25 and 0.06 ppm with approximate relative intensities 1:1:1:2:3, respectively, in CH_2Cl_2. Transition metal carbonyl bands in hexane solution appeared at 2065(sh), 2061(w), 2041(w), 2031(sh), 2025(m), 2002(s), and 1976(s) cm^{-1}. The bands at 2061, 2041, and 2031 cm^{-1} correspond to those of *8* [6, 11]. The mass spectrum of the soluble material contained ion series at m/e 424, 396, 368, 340, 312, 284 and 256, due to *8*. Similarly, ions at m/e 454, 426, 398, 370, 342, 314, and 286 indicated *9*.

No reaction occurred (based on IR and NMR) on stirring $Na_2Fe(CO)_4\cdot 1.5$ dioxane with $Si_2(CH_3)_4Cl_2$ for four days in hexane.

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