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Reactions of 1,1,2,2-Tetramethyldisilane with Group VIII Metal Carbonyls

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1,1,2,2-Tetramethyldisilane reacts with $Fe_2(CO)_9$ *to yield bis(*μ*-dimethylsilylene)-*μ*-carbonyl bis(tricarbonyliron)(*Fe–Fe*). Reaction with octacarbonyldicobalt analogously gives bis(*μ*-dimethylsilylene)bis(tricarbonylcobalt)(*Co–Co*) as stable product; spectroscopic results also indicate* inter alia *the formation of (tetramethyldisilyl)tetracarbonylcobalt,* μ*-(dimethylsilylene)-*μ*-carbonyl-bis(tricarbonyl)cobalt(*Co–Co*), and cobalt cluster compounds. Reactivity of zerovalent transition metal compounds toward Si–Si bonds seems to be greatest for the nickel triad and to decrease as one moves from right to left across the transition series.*

Introduction

Silanes containing Si–H bonds frequently react with low-valent transition metal compounds, generating new silyl–transition metal compounds [1]. Our interest in transition metal complexes containing the tetramethyldisilene moiety led us therefore to investigate reactions of 1,1,2,2-tetramethyldisilane, *1* [2], with some transition metal carbonyls.

The only such reaction reported, that of *1* with $Fe(CO)_5$ at 120 °C or photochemically at 30 °C, has been reported to yield bis(μ-dimethylsilylene)-μ-carbonyl-bis(tricarbonyliron)(*Fe–Fe*), *2* [3a]. We therefore decided first to study the reaction of *1* with diiron enneacarbonyl under mild conditions. Then a more extensive study of reaction of *1* with octacarbonyldicobalt was undertaken.

Results

Reaction of *1* with 2 equivalents of $Fe_2(CO)_9$ in cyclohexane gave *2* as the principal product. *2* was isolated by low-temperature crystallization from toluene and characterized by IR, ^{1}H NMR (δ 0.76 in toluene and 1.07 ppm in methylene chloride) and mass spectrometry. The mass spectrum showed a prominent molecular ion at m/e 424 and series of ions corresponding to $(Me_2Si)_2Fe_2(CO)_{7-0}$, $(Me_2Si)Fe_2(CO)_{6-2,0}$, $Fe_2(CO)_{4-0}$, and $CH_2SiFe_2(CO)_{2-0}$.

Sakurai [3b] has recently reported formation of a very sensitive dimethylsilylene complex on reaction of *1* with $Fe_2(CO)_9$ in benzene. We have not detected this compound in our work, but believe that it may be an intermediate in formation of *2* under our conditions (*vide infra*).

Reaction of *1* with $Co_2(CO)_8$ proceeds readily at room temperature, initially with gas evolution, to give a complex mixture of products, as indicated by the presence of eight well-defined resonances in the δ 0–1.5 region of the NMR spectrum and a very complex carbonyl region in the IR.

Only one of the several products has proven, however, to be isolable. It was obtained by chromatography on silica gel. Voluminous gas evolution from the column indicated extensive decomposition of other products. The stable product, *3*, was obtained in 15% yield as light yellow crystals, mp 92–4 °C, by chromatography and recrystallization from pentane. The mass spectrum of *3* revealed a parent ion at m/e 402, suggesting the compound *3* to be bis(μ-dimethylsilylene)-bis(tricarbonylcobalt)(*Co–Co*); this composition was confirmed by precise mass measurement. The entire sequence of fragments $(Me_2Si)_2Co_2(CO)_{6-0}$ was observed, along with series of fragments $(Me_2Si)_2Co(CO)_{4-0}$ [4], $(Me_2Si)Co_2(CO)_{2,1}$ and $(Si_2C_4H_{10})Co_2(CO)_{3-1}$. The infrared spectrum of *3* showed five strong peaks, at 2087, 2030, 2005, 1999, and 1993 (sh) cm^{-1}, in good agreement with the IR data for the known bis(μ-dimethylgermylene)bis(tricarbonylcobalt)(*Co–Co*) [5]. The ^{1}H NMR spectrum in benzene at room temperature shows a sharp singlet at δ 0.65. These data confirm the structure *3* for the stable product from $Co_2(CO)_8$ and tetramethyldisilane.

The only other product which was invariably isolated from the reaction mixtures was dodecacarbonyltetracobalt. Small amounts were evident in most reaction mixtures by IR, and up to 41% yields were obtained by chromatography. Some of the latter probably arose by decomposition of primary products on the columns.

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Isolation and purification of additional products have proven difficult due to their lability. However, a number have been tentatively identified by spectroscopic means. One such product, easily removed from the reaction mixture by virtue of its volatility and identified spectroscopically, was hydridotetracarbonylcobalt. This product was formed in greater amounts when the initial ratio of *1*:$Co_2(CO)_8$ was low. A second volatile product was a liquid which could be distilled from 1:1 reaction mixtures at 5 millitorr after solvent removal at 1 torr. This product, *4*, was not obtained in pure form but was identified as (1,1,2,2-tetramethyldisilyl)tetracarbonylcobalt by means of its NMR spectrum in benzene-d_6: δ 4.03 (1H, sept., J = 4.5 Hz), 0.48 (6H, s), and 0.10 (6H, d, J = 4.5 Hz) and its IR spectrum: strong carbonyl bands at 2093, 2031, 2003, and 1995 cm^{-1}, in good agreement with analogous silyltetracarbonylcobalt compounds [1]. NMR spectra of mixtures resulting from reaction of $Co_2(CO)_8$ and *1* in 2:1 ratio showed little *4*, in contrast to 1:1 mixtures, suggesting facile reaction of *4* with excess $Co_2(CO)_8$. The expected product of this reaction, μ-(1,1,2,2-tetramethyldisilane-1,2-diyl)bis(tetracarbonylcobalt), *5*, was not isolable, but was in the most volatile fraction from 2:1 $Co_2(CO)_8$–*1* reaction mixtures. This material showed a sharp NMR resonance at δ 0.40 (benzene solution) and strong IR peaks at 2092, 2030, and 1995 cm^{-1}, consistent with $Co(CO)_4$ groups (the IR also showed peaks due to $HCo(CO)_4$ and $Co_2(CO)_8$.) The only known analog of *5*, μ-(1,1,2,2-tetramethyldisilane-1,2-diyl)bis(cyclopentadienyldicarbonyliron), shows its methyl resonance at δ 0.45 [6]. Solutions of *5* decompose slowly due to adventitious air, giving rise to a singlet at δ 0.13, suggestive of octamethyltetrasila-1,4-dioxane (δ 0.14) or a related oligomer.

The infrared spectra of both 1:1 and 1:2 reaction mixtures showed a band at 1842 cm^{-1}, clearly a bridging carbonyl group. Its appearance was associated with a nmr resonance at δ 0.51, which was usually be strongest in the nmr spectrum. Comparison with the spectra of $(SiCl_2)Co_2(CO)_7$ (ν_{CO} 1835) [7], $(SiPh_2)Co_2(CO)_7$(ν_{CO} 1837) [8], and $(GeMe_2)Co_2(CO)_7$(ν_{CO} 1844, δ_{CH_3} 0.63) [9] strongly suggests the formation of *6*, $(SiMe_2)Co_2(CO)_7$, in which one bridging carbonyl of $Co_2(CO)_8$ is replaced by a bridging dimethylsilylene group. Unfortunately, isolation of *6* proved impossible because of its lability and low volatility. Its thermal instability mimics that of the germanium analog, which decomposes rapidly above 25 °C [9].

The nmr spectra of product mixtures from reactions run with excess $Co_2(CO)_8$ showed a prominent low-field resonance at δ 1.44. The component which gave rise to this resonance showed very low volatility and solubility. Recrystallization of a product mixture from pentane at −78 °C gave a brown solid whose IR showed peaks at 2058, 1848, and 1836 cm^{-1}, as well as peaks due to *3* and $Co_2(CO)_8$. The NMR revealed *3* and the δ 1.44 material in comparable amounts, along with a smaller peak. The data suggest formation of a product $Co_4(CO)_{12-x}(SiMe_2)_x$, (x = 1 or 2), *7*, in which one or two bridging carbonyl groups of $Co_4(CO)_{12}$ have been replaced by dimethylsilylene moieties.

Further evidence of cluster products was obtained upon chromatography of a product mixture from a reaction involving excess $Co_2(CO)_8$. Early fractions contained mixtures of *3* with a very unstable deep red substance, *8*, having IR bands at 2100(w), 2053(s), 2045(m), 2038(m), 2015(w), and 2003(w). The similarity of the infrared spectrum to those reported for $(OC)_4CoSiR_2OCCo_3(CO)_9$ compounds [8] (R = C_2H_5, C_6H_5) suggests the formation of an analogous compound $(OC)_4Co(SiMe_2)_yOCCo_3(CO)_9$ (y = 1 or 2) in our reactions. However the instability of this material precluded identification.

Discussion

The stable products from reaction of tetramethyldisilane, *1*, with $Fe_2(CO)_9$ or $Co_2(CO)_8$, have, in both cases, two dimethylsilylene bridges replacing two bridging carbonyls in the parent dinuclear carbonyl. Thus, both reactions proceed with eventual fission of the Si–Si bond of the disilane as well as the Si–H bonds.

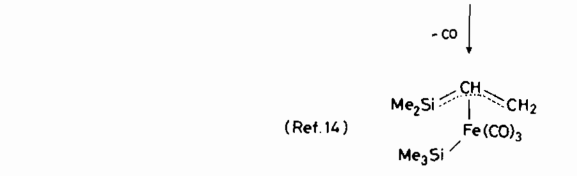
Compounds of the nickel triad metals and Vaska's compound, *trans*-$(Ph_3P)_2Ir(CO)Cl$, have been found in many cases to undergo oxidative addition to Si–Si bonds [10], for example:

$$Pt(PPh_3)_4 + X_3SiSiX_3 \longrightarrow (Ph_3P)_2Pt(SiX_3)_2 + 2PPh_3$$

$$X = Cl, Br$$

Such reactions are of considerable importance in catalytic processes such as disilane redistributions [11], bis-silylation of multiple bonds [10b, 12], and silodehalogenation of aryl halides [13].

Group VIII metals of the iron triad cleave Si–Si bonds less commonly, usually in intramolecular reactions:



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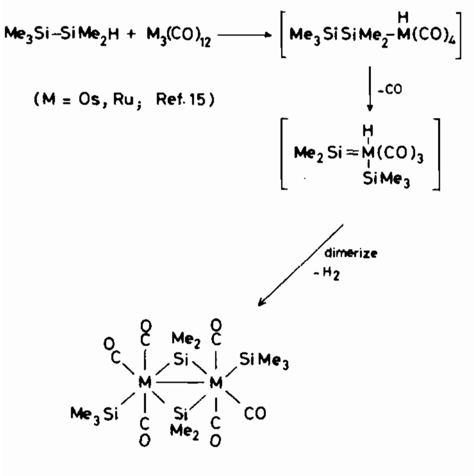
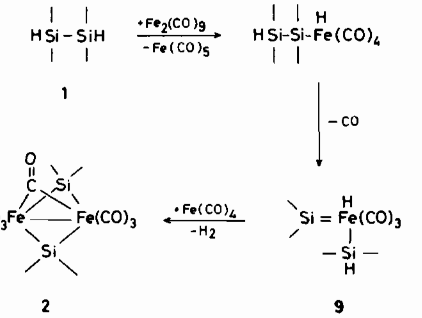


The formation of *2* is probably another example of such a process:



Compound *9*, here proposed as an intermediate, has been isolated from the reaction under different conditions [3b].

The formation of *3* appears to be the first report of oxidative addition of cobalt to a Si–Si bond. As with the iron triad, the reaction probably occurs intramolecularly in *4* or *5*, since neither 1,2-dichloro-1,1,2,2-tetramethyldisilane nor 1,2-dimethyl-1,1,2,2-tetrachlorodisilane reacts with $Co_2(CO)_8$ under these conditions, despite the tendency of halogens to increase reactivity of Si–Si bonds toward oxidative addition [1, 10]. But for the unreactivity of the dichloro- and tetrachlorodisilanes, formation of (dimethylsilyl)tetracarbonylcobalt from *1* would be an attractive route to *6* and *8*.

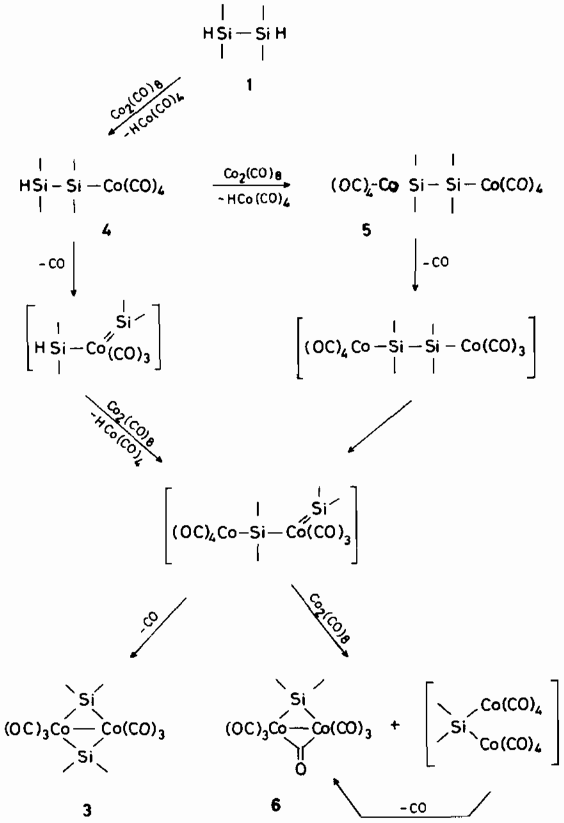
It is noteworthy that the group VII metals undergo reaction with Si–H bonds of disilanes without disrupting the Si–Si bonds [16]:

$$Me_3Si{-}SiMe_2H + M'_2(CO)_{10} \longrightarrow Me_3Si{-}SiMe_2M'(CO)_5 + HM'(CO)_5$$
$$M' = Mn, Re$$

Thus, as one moves from right to left in the transition series, the tendency for zerovalent transition metal species to disrupt the Si–Si bond by oxidative addition appears to decrease. This is consistent with the decreasing stability of silyl–transition metal compounds in general on moving from right to left in a transition series [1]. Both phenomena probably reflect the weakening strength of silicon–transition metal bonds in the same sense [1, 17].

The stable product *3* is the first example of a cobalt complex containing two silylene bridges. Analogous bis(dimethylgermylene)- and bis(dimethylstannylene)hexacarbonyldicobalt compounds have been prepared by reaction of dimethylgermane and dimethylstannane with octacarbonyldicobalt [5]. Formation of *3* from the disilane *1* is mechanistically more problematical. However, not only *3*, but also *6* and *7* appear to possess single dimethylsilylene groups extracted from *1*. It seems most reasonable to assume that these products arise via the straightforward 'hydrogen elimination' products *4* and *5*. A possible scheme appears below:

Possible Scheme for Reaction of Tetramethyldisilane with Dicobalt Octacarbonyl



Experimental

Reaction of Tetramethyldisilane, 1, *with Diiron Enneacarbonyl*

Diiron enneacarbonyl (1.85 g, 5.1 mmol), *1* [2] (0.40 ml, 2.4 mmol) and cyclohexane (20 ml) in a 50 ml Erlenmeyer flask were stirred together for 20 hours in a nitrogen-filled Vacuum Atmospheres glove box nominally at 1 ppm O_2. The mixture was filtered to remove a yellow inorganic precipitate, and the volatile material ($Fe(CO)_5$ and cyclohexane by IR) was pumped from the filtrate at *ca.* 1 torr and room temperature. The residue, a red oil, was dissolved in a minimum amount of toluene and cooled to –80 °C, whereupon red-brown crystals formed. The liquid was removed by syringe, and the air-sensitive crystals were dried in vacuum. Spectroscopic samples were prepared in the glove box. The infrared showed carbonyl bands at 2063, 2041, 2031, 2002, 1982, and 1843 cm^{-1} due to *2* [3a], bis(μ-dimethylsilylene)-μ-carbonyl-bis(tricarbonyliron)(*Fe–Fe*), and weaker bands at 2093, 2087, 2023 and 2013 cm^{-1} due to impurities. The most prominent mass spectroscopic peaks (Hewlett-Packard 5982, direct inlet, 70 eV) were at m/e 312 (100%, $Fe_2(CO)_3(SiMe_2)_2^+$), 256 (58%, $Fe_2(CO)(SiMe_2)_2^+$), 284 (54%, $Fe_2(CO)_2(SiMe_2)_2^+$) and 228 (40%, $Fe_2(SiMe_2)_2^+$).

An NMR spectrum of the crude reaction mixture indicated two unknown products in addition to *2*, with resonances at δ 1.03 and 0.66 ppm (toluene). Thermal reaction of *1* with $Fe(CO)_5$ in refluxing toluene or octane gave no *2* in our hands.

Photochemical Reaction of 1 *with Iron Pentacarbonyl*

A 20 cm long by 2.5 cm diameter quartz tube was charged with 70 ml of degassed cyclohexane, then fitted with a gas outlet tube connected to a Nujol bubbler. Iron pentacarbonyl (0.95 ml, 7.1 mmol) and *1* (0.50 ml, 2.7 mmol) were introduced by syringe through a rubber cap. The solution was photolyzed in a Rayonet photoreactor at 300 nm for 3 hours. The mixture was filtered under nitrogen, and the volatiles pumped off, leaving a dark red solid which was shown to be *2* by IR and NMR comparisons with the previous material.

Reaction of 1 *with Octacarbonyldicobalt in 1:2 Ratio*

a) A small round-bottom flask fitted with stopcock gas outlet and a rubber septum was charged with freshly sublimed $Co_2(CO)_8$ (1.3 g, 3.7 mmol), then evacuated and refilled several times with nitrogen. Benzene (10 ml) and tetramethyldisilane (0.32 ml, 1.9 mmol) were added by syringe. Gas evolution ensued for several minutes, after which a sample was removed by syringe and analyzed by nmr, which showed eight well-defined resonances, at δ 1.47, 0.70, 0.68, 0.65, 0.53, 0.40, 0.15 and 0.08. The volatile material (benzene and unreacted starting materials by IR and NMR) was pumped off at *ca.* 1 torr. The residue was chromatographed on Florisil. Partial decomposition was indicated by copious gas evolution. Hexane eluted a mixture of *3* and $Co_4(CO)_{12}$. Recrystallization from pentane at –80 °C gave first $Co_4(CO)_{12}$ then *3*, mp 92–94 °C. The four largest peaks in the mass spectrum of *3* were at m/e 290 (100%, $Co_2(CO)_2(SiMe_2)_2^+$, 259 (96%, $Co(CO)_3(SiMe_2)_2^+$), 288 (86%, $Co_2(CO)_2(Si_2C_4H_{10})^+$, and 175 (65%, $Co(SiMe_2)_2^+$). High resolution MS data (AEI MS-30): Calcd for $^{12}C_{10}$ $^{1}H_{12}$ $^{59}Co_2$ $^{16}O_6$ $^{28}Si_2$: 401.8836; Found: 401.8845. IR and NMR data: see text.

b) Similarly, 1.416 g (4.14 mmol) of $Co_2(CO)_8$ and 0.35 ml (2.1 mmol) of *1* in 20 ml hexane were allowed to react for 4 hr at 5–25 °C. The volatiles were removed under vacuum, giving a solution of $HCo(CO)_4$ in hexane (IR:2112(m), 2049(s), 2026(vs), 1986(m)). The residue, 1.56 g of red oil, was dissolved in 2 ml pentane and cooled to –78 °C, giving a brown solid. NMR of this solid (in benzene) showed three singlets of δ 1.46, 0.66 and 0.19 in a 6:13:5 ratio. The main component was thus *3*. IR showed three singlets at δ 1.46, 0.66 and 0.19 in a 2058, 1848, and 1836 cm^{-1} attributable to the δ 1.46 species, *7*, believed to be a derivative of $Co_4(CO)_{12}$ with one or two bridging dimethylsilylene groups replacing carbonyl groups. Further purification of *7* was not achieved.

c) Octacarbonyldicobalt (2.060 g, 6.00 mmol) and tetramethyldisilane (0.47 ml, 2.8 mmol) were allowed to react in benzene as before, for 18 hours. The volatile material was removed from the product mixture at room temperature and 1 torr, giving a liquid solution (benzene, unreacted tetramethyldisilane and $HCo(CO)_4$) and a brown solid which collected in the inlet tube of a –78 °C trap. The solid, *5*, had nmr and IR properties as described in the text.

The residue was chromatographed on silica gel. Elution with hexane gave mixtures of *3* with an unstable dark red solid, whose IR was consistent with a structure $(OC)_4Co(SiMe_2)_yOCCo_3(CO)_9$ (y = 1 or 2) [8]. The nmr showed a singlet at δ 1.50, which had not been visible in the unchromatographed mixture. The material decomposed, with complete loss of the deep red color, within two hours at room temperature under nitrogen. Recrystallization of the combined fractions from hexane then gave *3*, mp 92 – 4 °C.

Reaction of 1 *with Octacarbonyldicobalt in 1.3:1 Ratio*

Tetramethyldisilane, *1* (0.58 ml, 3.5 mmol) and $Co_2(CO)_8$ (0.90 g, 2.6 mmol) were allowed to react for 18 hours in 15 ml cyclohexane. The volatile material was then pumped off at *ca.* 1 torr. IR and nmr spectroscopy revealed $HCo(CO)_4$ (δ – 11.4), unreacted *1*, and cyclohexane. Distillation of the residue at 30–60 °C and 5 millitorr gave a yellow-brown liquid. IR and nmr spectra revealed *4* as the principal component of this liquid (see text), along with some $Co_4(CO)_{12}$ and *6*. The pot residue proved to contain principally *3* and *6*.

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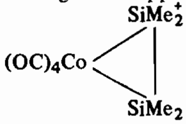
4 These fragments appear to derive from the closed-shell ion , a complexed disilene. Analogous fragments do not appear in the mass spectrum of *2.*

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