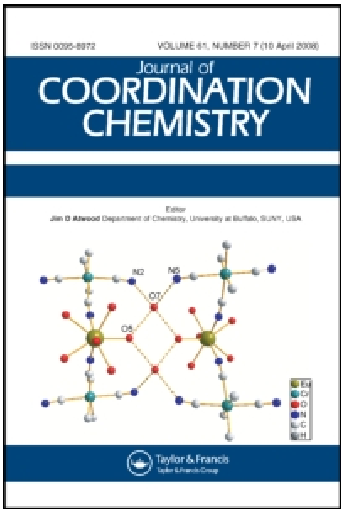

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ORGANOMETALLOIDAL DERIVATIVES OF THE TRANSITION METALS I

Bis-Trimethylsilylacetylene and *Bis*-Trimethylsilylbutadiyne Complexes of the Transition Metals[1]

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The reactions of *bis*-trimethylsilylacetylene and *bis*-trimethylsilylbutadiyne with various transition metal carbonyls have been studied. Both form stable complexes of iron, cobalt and manganese. The infrared spectral data indicates that for the group IV substituted ligands the pi-accepting ability increases in the order $C < Si < Sn$. Mass spectral data provides evidence for the existence of novel *bis*-cyclobutadiene iron fragments and also the unknown tetrasilylcyclobutadiene.

INTRODUCTION

In 1959 Hubel and coworkers published the first in a series of papers outlining the complex reactions between acetylenes and various transition metal carbonyls.[2] In this and a subsequent paper[3] were tabulated five iron carbonyl complexes for the mono-silylacetylenes, Me_3SiC_2H and Me_3SiC_2Ph of unreported structure, and it was stated that the *bis*-trimethylsilylacetylene failed to react because of its steric requirements. This was subsequently modified by a report[4] that an unstable complex of the type (acetylene)$Fe(CO)_4$ seemed to form; however, no details have appeared. Cobalt carbonyl complexes of *bis*-(phenylethynyl) dimethylsilane and other silylacetylenes have been reported,[5] but the general lack of silylacetylenic metal complexes may be due to the facile cleavage of the silicon sp-carbon linkage catalysed by transition metals, as observed by Kraihanzel during attempts to prepare π-silylacetylene platinum complexes.[6] In the course of studies of the interactions of silylacetylenes with transition metal complexes, we have used both *bis*-trimethylsilylacetylene (I) and *bis*-trimethylsilylbutadiyne(II) as bonding ligands and report some results of these studies in the present paper.

EXPERIMENTAL

All reactions were performed in an atmosphere of dry nitrogen using dry degassed solvents. Infrared spectra of the carbonyl regions were recorded in cyclohexane on a Perkin Elmer 421 spectrometer, pmr spectra were recorded on either a Varian A-60 or Perkin Elmer R-12A, and mass spectra were recorded on either a Hitachi RMU 6E or an A.E.I. MS 9. Ultraviolet irradiations were performed using a Hanovia 500 watt immersion type lamp with a quartz window.

REACTIONS OF SILYLACETYLENES WITH IRON CARBONYLS

Bis-trimethylsilylacetylene and $Fe_3(CO)_{12}$

A mixture of 1.1 g $Fe_3(CO)_{12}$ (1.1 g, 2.2×10^{-3} m) and $Me_3SiC_2SiMe_3$ (0.33 g, 1.9×10^{-3} m) was irradiated in benzene for 24 h. After removal of solvent the oily residue was dissolved in the minimum of petroleum-ether (40–60°) and placed upon an alumina column. A single yellow band was eluted with the same solvent, the resulting solid purified by sublimation at 35°/0.5 mm of Hg, to yield 0.5 g (1.47×10^{-3} m, 77%) of yellow crystalline product, m.p. 37°C, $(Me_3SiC_2SiMe_3)Fe(CO)_4$.

Anal. Calcd. %C 42.6, %H 5.32, %O 18.9; Found %C 42.4, %H 5.72, %0 15.9.

Infrared. ν ($C{\equiv}O$), 2078(m), 2001(s), 1970(s), 1872(wbd) cm^{-1}. No band for $C{\equiv}C$.

PMR (τ) 9.65(s).

Other reactions performed with *bis*-trimethylsilylacetylene are tabulated below with reaction conditions and product yields, only $(Me_3SiC_2SiMe_3)Fe(CO)_4$ being isolated.

1. $+Fe(CO)_5$. Refluxing hexane, 50% yield.
2. $+Fe(CO)_5$. Irradiation in hexane at 26°, 75% yield.
3. $+Fe_2(CO)_9$. Stir in hexane at 26°, 80% yield.

Bis-trimethylsilybutadiyne and $Fe_3\ (CO)_{12}$

A mixture of $Fe_3(CO)_{12}$ (lg, 2.0×10^{-3} m) and $Me_3SiC_4SiMe_3$ (0.5 g, 2.6×10^{-3} m) was irradiated in benzene for 48 hours. The red solution was filtered and the solvent removed under reduced pressure, leaving an oily residue. The residue was dissolved in the minimum of petroleum ether (40–60°) and placed upon an alumina column. Eluting with the same solvent resulted in two distinct bands. An initial yellow band produced a small quantity of unstable semi-crystalline material that could not be properly characterized. An infrared spectrum indicated terminal carbonyl bands at 2066(m), 2041(s), 2002(s), 1991(m) and 1949(w). Further elution of a second pink band yielded 0.085 g (1.6×10^{-4} m) of red crystalline $(Me_3SiC_4SiMe_3)_2Fe_2(CO)_8$,(III), mp. 85–7°.

Anal. Calcd. %C 46.4, %H 4.97; Found %C 47.2, %H 5.38.

Infrared. ν (C≡O) cm^{-1}, 2073(m), 2047(m-s), 2018(s). ν (C=O) 1652(m).

PMR (τ). 9.81(s).

Reactions using $Fe_2(CO)_9$ and $Fe(CO)_5$ as starting iron carbonyl led to essentially similar reaction products and yields.

REACTIONS OF SILYLACETYLENES WITH COBALT OCTACARBONYL

Bis-trimethylsilylacetylene

A mixture of the carbonyl (2.0 g, 5.9×10^{-3} m) and the acetylene (1.0 g, 5.9×10^{-3} m) was stirred in hexane for 3 h. After removal of the solvent the residue was eluted on an alumina column. The single brown band was collected and yielded 2.3 g (5.1×10^{-3} m, 86%) of $(Me_3SiC_2SiMe_3)Co_2(CO)_6$,mp. 150° (decomp).

Anal. Calcd. %C 36.8, %H 3.95; Found. %C 36.7, %H 4.05.

Infrared. ν (C≡O) cm^{-1}. 2080(m), 2043(m-s), 2021(s), 2013(s).

PMR. (τ) 9.95(s).

Bis-trimethylsilybutadiyne

A mixture of the carbonyl (0.6 g, 1.77×10^{-3} m) and the butadiyne (II) (0.25 g, 1.29×10^{-3} m) was stirred in hexane for 2 h. After removal of solvent the residue was eluted with hexane upon an alumina column. Two bands formed, an initial red band followed by a green band. The red band, eluted with hexane, yielded a red oil $Co_2(CO)_6$(II), (0.40 g, 8.4×10^{-4} m, 65%).,

Anal. Calcd. %C 40.0, %H 3.76; Found %C 40.1, %H 3.86.

Infrared. ν (C≡O) cm^{1}. 2083(m), 2051(m-s), 2024(s).

PMR (τ) 9.67(s), 9.80(s).

Further elution with a 80:20 hexane/methylene chloride mixture yielded 0.2 g (2.6×10^{-4} m, 26%) of green crystalline $Co_4(CO)_{12}$(II), mp. 180° (decomp).

Anal. Calcd. %C 34.4, %H 2.59; Found %C 34.7, %H 2.34.

Infrared. ν (C≡O) cm^{-1}. 2070(m-s), 2051(s), 2022(s-m), 2011(m).

PMR (τ) 9.65 (s).

Reaction between $Co_2(CO)_6(Me_3SiC_4SiMe_3)$ *and* $Co_2(CO)_8$

An excess of cobalt octacarbonyl and $Co_2(CO)_6(Me_3S\,C_4SiMe_3)$,(0.2 g, 4.2×10^{-4} m) was stirred for 1 h in hexane. Work up as in the above experiment yielded 0.27 (85%) of $Co_4(CO)_{12}$(II).

REACTION OF BIS-TRIMETHYLSILYLACETYLENE WITH Π-CYCLOPENTADIENYLMANGANESETRICARBONYL.

A mixture of $CpMn(CO)_3$ (1.0 g, 4.9×10^{-3} m) and $Me_3SiC_2SiMe_3$ (0.85 g, 5.0×10^{-3} m) was irradiated in hexane for 24 h. Removal of the solvent left a yellow wax which was sublimed at 60°C onto an ice-cooled probe at a pressure of 0.5 mm Hg to form a pale yellow crystalline material, 0.43 g (1.3×10^{-3} m, 26%), mp. 48–53°.

Anal. Calcd. %C 52.1, %H 6.64; Found. %C 52.2 %H 7.02.

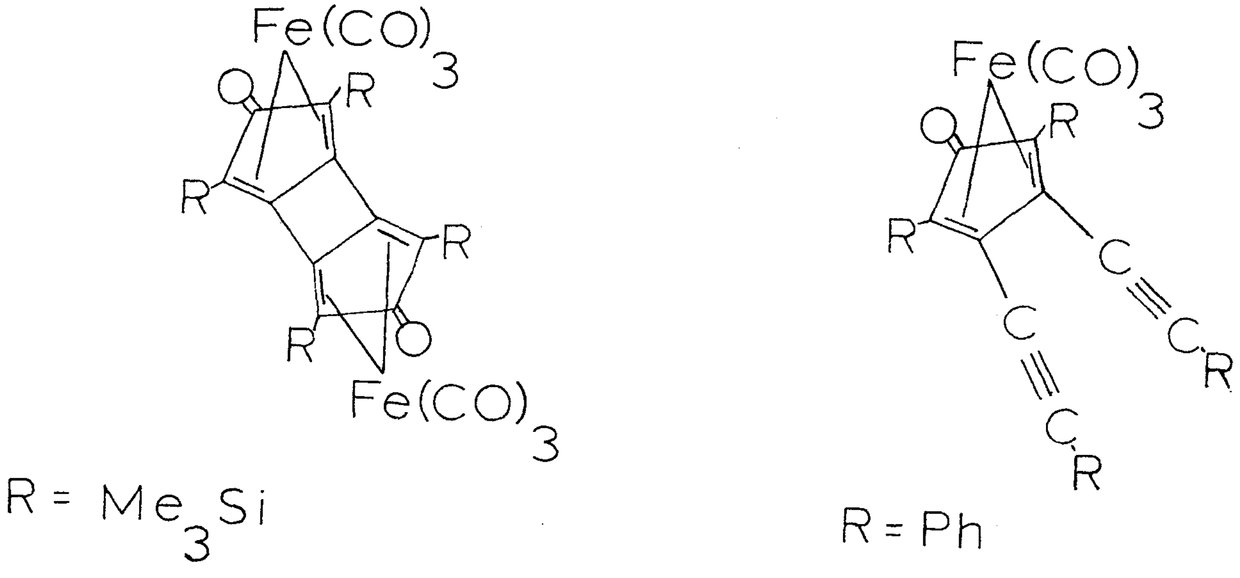
Infrared. ν (C≡O) cm^{-1}. 1995(s), 1925(s).

PMR (τ). 5.2(s), 9.68(s).

RESULTS AND DISCUSSION

Both *bis*-trimethylsilylacetylene (I) and *bis*-trimethylsilylbutadiyne (II) react readily with the various iron carbonyls to form stable crystalline complexes. *I* reacts with the carbonyls under varying conditions to form the yellow crystalline $Fe(CO)_4$ $(Me_3SiC_2SiMe_3)$ in recovered yields varying from 50–80%. The complex is stable indefinitely in an inert atmosphere at —15°, but slowly decomposes under the same conditions at room temperature. The infrared spectrum exhibits four terminal carbonyl stretching frequencies (2078, 2001, 1970, 1872 cm^{-1}) but no band attributable to the complexed acetylenic linkage. The pmr spectrum exhibits one single resonance at 9.65 τ compared to 9.85 τ for the free ligand reflecting the decrease in electron density in the pi system upon coordination to the iron. The mass spectrum is in accord with that expected for an iron tetracarbonyl derivative and is recorded in Scheme 1a. The parent ion, m/e 338, is observed as are the ions associated with the stepwise loss of carbonyl groups. The base ion is that of the carbonyl free acetylene iron fragment, m/e 226, indicating that under the conditions of the mass spectrometer the acetylene iron bond is stronger than the carbonyl iron bonds. Attempts to illustrate this chemically were unsuccessful; treatment of the complex under mild conditions with triphenylphosphine produced only high yields of *t*-*bis*-triphenylphosphine tricarbonyl iron.

II reacts with the iron carbonyls to form the unusual 2,5, *bis*-trimethylsilylcyclopentadienone iron tricarbonyl dimer (III), Figure 1. The infrared spectrum of *III* exhibits three terminal carbonyl stretching frequences (2073, 2047, 2018 cm^{-1}) and a ketonic carbonyl stretching frequency at 1652 cm^{-1}, while the pmr spectrum exhibits one single resonance at 9.84 τ indicating all the trimethylsilyl groups to be equivalent. The mass spectrum of the complex is of particular interest and the disintegration pattern is recorded in Scheme 1b. The spectrum exhibits a parent ion, m/e 724, followed by rapid loss of two methyl groups from the silicon atoms. Peaks corresponding to the stepwise loss of the six terminal carbonyl groups from this ion are observed, with large populations resulting from the ions having lost three and six such groups, i.e. complete decarbonylation of the two iron atoms. Subsequent to the loss of the terminal carbonyl groups, the loss of the ketonic carbonyl groups is observed and the base peak corresponds to a *bis*-iron butadienyl or *bis*-iron cyclobutadienyl fragment, m/e 470. Bruce has reported that the fragmentation pattern of cyclopentadienone tricarbonyl iron $(C_5H_4O)Fe(CO)_3$ indicates a similar carbon monoxide elimination from the *free* cyclopentadienone ligand producing cyclobutadiene.[7] The mass spectrum reported here is the first to note the



III IV

FIGURE 1

expulsion of carbon monoxide from a complexed cyclopentadienone ligand and the formation of what may be novel cyclobutadiene iron fragments. There is an absence of any meaningful disintegration pattern to this ion. The complex *III* is related to the product obtained from the reaction of *bis*-phenylbutadiyne with iron carbonyl, $Fe(CO)_4PhC_4Ph$,[8] (IV), Figure 1, where the two free acetylenic groups have further reacted to form a second cyclopentadienone iron tricarbonyl system. In the absence of any established mechanism for the pentadienone formation, this further reactivity of the silyl substituted system is not readily explained.

A second very unstable complex was observed from the reaction of $Me_3SiC_4SiMe_3$ with the iron carbonyls. The infrared spectrum exhibits five bands in the terminal carbonyl region (2066, 2041, 2002, 1991, 1949 cm^{-1}). This spectrum closely resembles that of $Fe(CO)_4(Me_3SiC_2SiMe_3)$ where the extra band at 1991 cm^{-1} can be attributed to the complexed acetylenic linkage which in this case is nonsymmetrical. The yellow semi-solid decomposes under very mild conditions to liberate the free butadiyne, and appears to be the *bis*-*tetra*-carbonyl iron butadiyne species, $[Fe(CO)_4]_2(Me_3SiC_4SiMe_3)$.

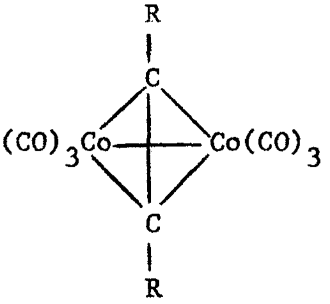
Both *I* and *II* react readily with cobalt octacarbonyl to form the familiar bridging acetylenic complexes.[9] As expected the silylbutadiyne forms a pair of complexes in which either one or both of the acetylene linkages have reacted. The red monosubstituted complex is readily converted to the green di-substituted complex on treatment with more cobalt octacarbonyl. A characteristic reaction of terminal acetylenic cobalt complexes, $(RC_2H)Co_2(CO)_6$, is their acid rearrangement to $RCH_2C(Co(CO)_3)_3$.[10] Since the relationship between deprotonation and de-silylation has often been observed we attempted to effect a related rearrangement for the *bis*-silylacetylene cobalt complex. Treatment of the complex, $(Me_3SiC_2SiMe_3)Co_2(CO)_6$, with acid under the conditions reported to cause the rearrangement resulted in no reaction and the complex was recovered intact. Such treatment would have destroyed the free ligand,[11] hence it is clear that the nature of the acetylene is much altered in the complex. By way of comparison we treated the *mono*-silylacetylene cobalt complex, $(Me_3SiC_2H)Co_2(CO)_6$, to the same acid conditions, since this contains a terminal acetylenic hydrogen. The reaction resulted in complete decomposition and no organometallic products were isolated. Since it is reasonable that the first step in the rearrangement process is protonation of the complexed acetylene, it seems that for the *bis*-silylacetylenic complex steric factors retard this protonation.

The reaction between *I* and cyclopentadienylmanganese tricarbonyl was investigated and led to the formation of a yellow crystalline product which is stable only when stored in an inert atmosphere at −15°C. The pmr and analytical data indicated the compound to be the cyclopentadienylmanganese dicarbonyl acetylene complex, $CpMn(CO)_2(Me_3SiC_2SiMe_3)$; however, the infrared spectrum exhibits a band at 1616 cm^{-1} indicative of a ketonic carbonyl group, together with the expected bands for the terminal carbonyl groups at 1995, 1929 cm^{-1}. The mass spectrum, Scheme lc, contains those peaks expected for the acetylene dicarbonyl complex, i.e. parent ion m/e 346, and a band due to loss of two carbonyls, m/e 290, the monocarbonyl ion typically not being observed for complexes of the type $CpMn(CO)_2L$, L = olefin.[12] However, there is also a series of peaks indicating the presence of the hitherto unknown *tetra*-trimethylsilylcylopentadienone as a free ligand, i.e. parent m/e 368 and the fragment resulting in loss of the ketonic carbonyl, probably the *tetra*-silyl cyclobutadiene, m/e 340. *Tetra*-phenylcyclopentadienone was found as a side product in the reaction of diphenylacetylene with cyclopentadienyl manganese tricarbonyl, the complex $CpMn(CO)(PhC_2Ph)_2$ being proposed as an intermediate in its formation.[13] We have at the present time found no evidence for the formation of this type of complex during our studies. Attempts to separate the complex from the trace amounts of the *tetra*-silyl cyclopentadienone have not met with success, and it appears that the organosilyl compound may result from decomposition of the dicarbonyl complex. We are continuing studies on this aspect of the work in order to isolate the *tetra*-silyl cyclopentadienone and investigate the chemistry of the new system. Attempts at decarbonylation will be performed in the hope of obtaining the novel crowded *tetra*-trimethylsilylcyclobutadiene, as observed in the mass spectrum reported above.

The carbonyl stretching frequencies of the various group IV substituted acetylene cobalt complexes are recorded in Table I. A very definite increase in the carbonyl stretching frequency may be observed as one changes from C → Si → Sn → H. This implies a corresponding increase in the pi-accepting ability of the acetylene ligands $C < Si < Sn < H$. The group IV trimethyl derivatives are well established as inductively electron-releasing and such an effect will raise the energy of the pi antibonding orbitals of the acetylene, reducing their potential to participate in retrodative bonding with the metal atom. However, both tin and silicon possess empty d-orbitals which can remove electron density from the acetylene pi system thereby lowering the antibonding energy level, partly counteracting the inductive effect. Thus, the overall pi-accepting ability of the carbon derivative will be less than that of the other two group IV systems; the relationship between these is due to a combination of inductive electron-release and dπ-pπ interaction which is impossible to separate.

TABLE I

Carbonyl stretching frequencies for acetylenic cobalt complexes



R	ν cm^{-1}			
H[14]	2099	2059	2034	2028
Me_3Sn[15]	2088	2048	2024	2015
Me_3Si	2080	2043	2021	2013
Me_3C[16]	2070	2032	2008	

SCHEME I

Mass spectral fragmentation patterns

1a.

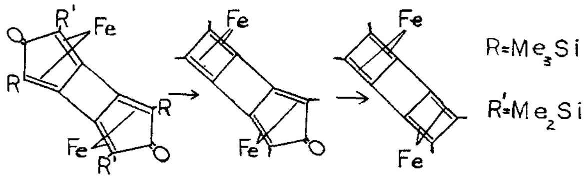
338(6) $[(Me_3SiC_2SiMe_3)Fe(CO)_4] \xrightarrow{-(CO)}$ 310(8) $\xrightarrow{-(CO)}$ 282(12) $\xrightarrow{-(CO)}$ 254(20) $\xrightarrow{-(CO)}$ 226(100) $[Me_3SiC_2SiMe_3(Fe)]$

*

1b.

724(1) $[Me_3SiC_4SiMe_3Fe_2(CO)_8] \xrightarrow{-2(CH_3)}$ 694(15) $\xrightarrow{-(CO)}$ 666(2) $\xrightarrow{-(CO)}$ 638(8) $\xrightarrow{-(CO)}$ 610(78) $\xrightarrow{-(CO)}$ 582(2) $\xrightarrow{-(CO)}$ 554(20) $\xrightarrow{-(CO)}$ 526(72) $\xrightarrow{-(CO)}$ 498(8) $\xrightarrow{-(CO)}$ 470(100)

Other ions observed. 416(32); 398(26); 306(32); 262(28) 179(12) $[Me_2SiC_4SiMe_3]$; 73(68) $[Me_3Si]$

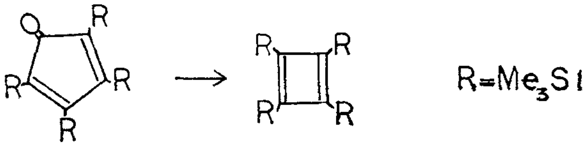


m/e 526(72) m/e 498(8) m/e 470(100)

1c.

346(4) $[CpMn(CO)_2SiMe_3C_2SiMe_3] \xrightarrow{-2(CO)}$ 290(50) $\xrightarrow{-(Me_3SiC)_2}$ 120(27)

Second fragmentation pattern observed; 368(2) $\xrightarrow{-(CO)}$ 340(5)



m/e 368(2) m/e 340(5)

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