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VIII*. SYNTHESIS OF TRIMETHYLSILYLIRON COMPOUNDS USING BIS(TRIMETHYLSILYL)MERCURY

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Summary

The synthesis of *cis*-$(OC)_4Fe(SiMe_3)_2$ and $Hg[Fe(CO)_4SiMe_3]_2$ by the photochemical reaction of $Hg(SiMe_3)_2$ with $Fe(CO)_5$ is described. The spectroscopic properties of the new compounds are discussed.

Introduction

Reactions of metal carbonyl anions with organometallic halides of germanium, tin, and lead provide a useful route to transition metal derivatives of these elements. However, complications often arise when the same reaction is attempted with organosilicon halides. This problem first arose in the attempted synthesis of $Ph_3SiMn(CO)_5$ from $NaMn(CO)_5$ and Ph_3SiCl in tetrahydrofuran [1], although an alternative route to the desired compound was later found [2].

The present work was prompted by complications in the reaction of $Na_2Fe(CO)_4$ with Me_3SiI in tetrahydrofuran [3,4], which did not afford the expected $(OC)_4Fe(SiMe_3)_2$. Instead, a quite different compound was obtained. Originally formulated as the dimer $[(OC)_4Fe(SiMe_3)_2]_2$ [3,4], it has now been shown to have the formula $(Me_3Si)_4Fe_2(CO)_{10}$ and to possess no iron—silicon bonds [5]. In view of our interest in the spectra and stereochemistry of compounds of the $(OC)_4M(ER_3)_2$ type (M = Fe, Ru, Os; E = C, Si, Ge, Sn, Pb; R = halogen or organic group) [6,7], we sought an alternative route to $(OC)_4Fe(SiMe_3)_2$. The reagent which came to mind was bis(trimethylsilyl)mercury, and we describe here its use in the preparation of the desired compound, as well as a novel mercury-containing silyliron derivative formed in the same reactions.

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[*] For Part VII see ref. 21.

Results and discussion

Bis(trimethylsilyl)mercury reacts under irradiation with $Fe(CO)_5$, or with $Fe_2(CO)_9$, or, less desirably, with $(OC)_4FeBr_2$, to form the new compounds *cis*-$(OC)_4Fe(SiMe_3)_2$ (I) and Hg[*cis*-$Fe(CO)_4SiMe_3]_2$ (II). Reaction with excess $Fe(CO)_5$ in sunlight is the preferred method, and each compound is obtained in 25—35% yield on the basis of $Hg(SiMe_3)_2$.

Compound I may be handled in air for short periods. Heating in a sealed tube with *n*-pentane for several days resulted in slight darkening but there was no change in the infrared spectrum. After a further 12 h at 120°, the solution was black but infrared band intensities suggested that ca. 80% of the compound had survived; new bands attributable to $Fe(CO)_5$ were observed at this stage.

The infrared spectrum of I (Fig. 1a) shows five carbonyl stretching bands in addition to a shoulder. For a *cis* isomer of idealized C_{2v} symmetry, only four bands are expected. The separation of the two pairs of bands at higher frequency is 6—7 cm^{-1}, the same magnitude we have often observed for conformational splitting in other cases [8], and may be due to this effect. On the other hand, some *trans*-$(OC)_4Fe(SiMe_3)_2$ may be present in equilibrium, as is the case with $(OC)_4Os(SiMe_3)_2$ [6,9,10]. A single absorption in the proton magnetic resonance spectrum does not exclude the presence of both *cis* and *trans* isomers since the forms may by interconverting rapidly [6]. An X-ray structure of I by Bennett and Smith [22] confirms the *cis* geometry, but indicates marked deviation from regular octahedral geometry.

Compound II is a pale yellow solid obtained by crystallization from pentane or by sublimation at 90° in vacuum; the sublimation is accompanied by thermal decomposition. There are three possible geometrical isomers for II, assuming linearity at mercury and octahedral coordination at iron: *trans—trans*, *cis—trans*, and *cis—cis*. The complexity of the infrared spectrum (Fig. 1b) excludes the *trans—trans* possibility, since for idealized D_{4h} or D_{4d} symmetry, only

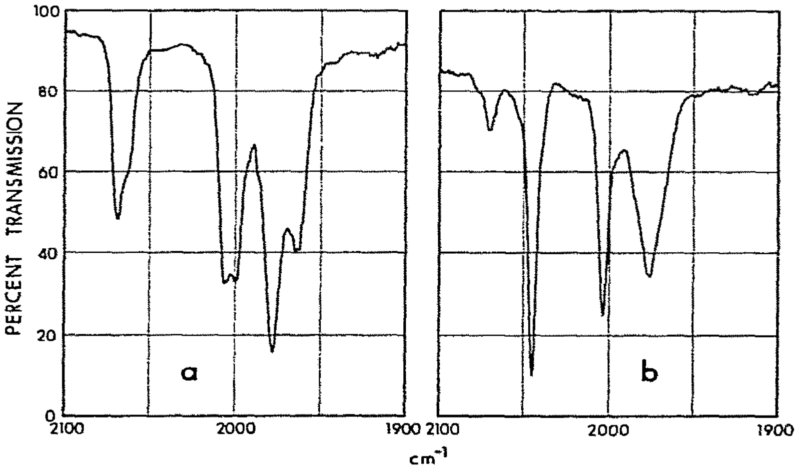
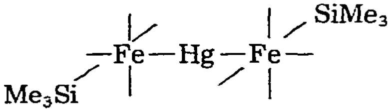


Fig. 1. Infrared spectra in the carbonyl stretching region of (a) $(OC)_4Fe(SiMe_3)_2$ (I) and (b) $Hg[Fe(CO)_4SiMe_3]_2$ (II). The solvent is n-heptane.

two infrared active carbonyl stretching modes are expected. The single NMR signal for the Me_3Si groups makes a *cis—trans* isomer unlikely (unless stereochemical nonrigidity is involved). The remaining and most likely possibility is the *cis—cis*, or bis-radially substituted form, for which four infrared bands are expected.



(II) (*cis—cis* form)

The mass spectrum of I was straightforward, dominated by the series $Fe(CO)_m Si_2Me_n$ (m = 0—4); n = 5 or 6). The most noteworthy features of the mass spectrum of the mercury derivative II are the ions $HgFe_2(CO)_8Si_2Me_{5,6}$, $HgFe_2(CO)_7Si_2Me_6$, $HgFe(CO)_{3,4}SiMe_3$ and the series $Fe_2(CO)_m Si_2Me_n$ (n = 6, m = 0—6; n = 5, m = 1—5). Binuclear ions without mercury have previously been observed in the mass spectra of bis(transition metal)mercury compounds [11,12], and have been attributed in one case to pyrolysis of the sample in the mass spectrometer [12]. A similar explanation may apply in the present case, since $Hg[Fe(CO)_4SiMe_3]_2$ is not particularly stable thermally and could well decompose slowly at the 50° source temperature used in this work.

Bis(trimethylsilyl)mercury is a highly reactive species which has been used in the preparation of several other transition metal derivatives of silicon [13]. Its reaction with $(OC)_4FeBr_2$ is formally of the same type as that with $(Et_3P)_2PtCl_2$ [14], involving exchange of halogen for a trimethylsilyl group.

The smooth reaction with $Fe_2(CO)_9$ (often regarded as a source of $Fe(CO)_4$) suggested to us that the process could be regarded as insertion of $Fe(CO)_4$ into Hg—Si bonds, or alternatively as the addition of Hg—Si to the coordinately unsaturated intermediate (compare the addition to $(Et_3P)_2IrCOCl$ [15]). The following reactions may be involved:

$$Hg(SiMe_3)_2 + \text{“}Fe(CO)_4\text{”} \rightarrow Me_3SiHgFe(CO)_4SiMe_3 \tag{1}$$

$$Me_3SiHgFe(CO)_4SiMe_3 + \text{“}Fe(CO)_4\text{”} \rightarrow Hg[Fe(CO)_4SiMe_3]_2 \tag{2}$$

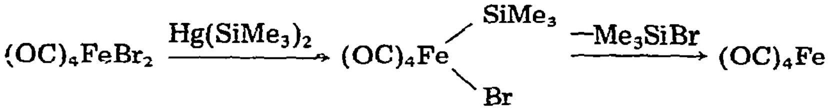
$$Hg[Fe(CO)_4SiMe_3]_2 + Hg(SiMe_3)_2 \rightarrow 2Hg + (OC)_4Fe(SiMe_3)_2 \tag{3}$$

Reaction (2) represents the insertion of a second $Fe(CO)_4$ moiety to form II. Reaction (3) is similar to the facile reaction reported [16] between $Hg[Co(CO)_4]_2$ and $Hg(SiMe_3)_2$ to form $Me_3SiCo(CO)_4$. We have shown in a separate experiment that II reacts with $Hg(SiMe_3)_2$ as shown in reaction (3). In reactions involving photochemical generation of $Fe(CO)_4$ from $Fe(CO)_5$, the relative yields of I and II would depend upon the rate of generation of $Fe(CO)_4$, and hence upon the intensity of the illumination. This was qualitatively observed in some experiments sunlight was used as the light source, and the yield of I relative to II was higher on a slightly more hazy day, as the above sequence would lead one to expect.

Another possible reaction step which cannot be excluded is (4), which would parallel the observed behavior of unsymmetrical organic derivatives of trimethylsilylmercury [17].

$$Me_3SiHgFe(CO)_4SiMe_3 \rightarrow Hg + (OC)_4Fe(SiMe_3)_2 \tag{4}$$

As noted, I and II can be isolated from the reaction of $(OC)_4FeBr_2$ with $Hg(SiMe_3)_2$, but the yields are quite low. It may be that the initial reaction in this case serves only to generate $Fe(CO)_4$ in a wasteful fashion (reaction 5).



$$(\mathrm{OC})_4\mathrm{FeBr}_2 \xrightarrow{\mathrm{Hg(SiMe_3)_2}} (\mathrm{OC})_4\mathrm{Fe}\begin{matrix}\mathrm{SiMe_3}\\ \mathrm{Br}\end{matrix} \xrightarrow{-\mathrm{Me_3SiBr}} (\mathrm{OC})_4\mathrm{Fe} \qquad (5)$$

This is of course speculative, but it is similar to a sequence postulated recently in the unusual reaction of $(diphos)PtCl_2$ with $Hg(SiMe_3)_2$ [18].

The stability and properties of $(OC)_4Fe(SiMe_3)_2$ shed some light on the nature of the complicated reaction between $[Fe(CO)_4]^{2-}$ and Me_3SiBr or Me_3SiI. One possibility was that the latter reaction formed the expected I, which was transformed under reaction conditions to $[Me_3Si(OC)_4Fe_2(CO)_6]$. It is known, for instance, that $Me_3SiCo(CO)_4$ is converted thermally to the siloxy derivatives $(Me_3SiOC)_4Co_2(CO)_4$ and $Me_3SiOCCo_3(CO)_9$, and that the latter is also formed in a room temperature reaction of $Me_3SiCo(CO)_4$ with tetrahydrofuran (THF) [19].

As noted above, I is reasonably stable thermally when heated at 120° in a hydrocarbon solvent, and no infrared bands due to $[Me_3Si(OC)_4Fe_2(CO)_6]$ were detected. However, a rapid reaction of I occurs with THF at room temperature, forming a deep red solution. The complex products from this remarkable reaction have not yet been characterized, but we infer from the infrared spectrum of the mixture that $(Me_3SiOC)_4Fe_2(CO)_6$ is not among them. Our conclusion, then, is that I is probably not an intermediate leading to $(Me_3SiOC)_4Fe_2(CO)_6$ in the reaction of $[Fe(CO)_4]^{2-}$ with Me_3SiX.

Experimental

All reactions were carried out in Schlenk apparatus under a nitrogen atmosphere. Mass spectra were measured using an Associated Electrical Industries MS-9 spectrometer with direct probe and a source temperature of 50°. Bis(trimethylsilyl)mercury was prepared by a modification of the method described by Wiberg et al. [20].

Reaction of $Hg(SiMe_3)_2$ and $Fe(CO)_5$

A sample of $Hg(SiMe_3)_2$ (3.00 g, 8.65 mmol) was placed in a 100-ml quartz round-bottom flask. The flask was evacuated on a vacuum system and $Fe(CO)_5$ (5.0 ml, 37 mmol) and 65 ml Skelly B (a mixture of hexane isomers) was distilled in at —196°. The reaction mixture was warmed to room temperature and exposed to intense Alberta sunlight for one afternoon. The flask was vented using an oil-filled bubbler during irradiation; CO was rather rapidly evolved. The reaction mixture was filtered into an evacuated Schlenk tube, and the filtrate kept at —10° overnight, resulting in a voluminous mass of yellow needle-shaped crystals. The mother liquor was decanted and the crystals dried under vacuum, affording 1.36 g $Hg[Fe(CO)_4SiMe_3]_2$ (II). The filtrate was concentrated under vacuum to half its volume, and again cooled to afford an additional 0.28 g II (total yield, 1.64 g, 2.4 mmol, 28%). The analytical sample was obtained by two recrystallizations from n-pentane as pale yellow crystals, m.p. 106—107° (sealed capillary under nitrogen). (Found: C, 24.55; H, 2.88. $C_{14}H_{18}O_8Fe_2HgSi_2$ calcd.: C, 24.62; H, 2.66%.) NMR (C_6D_{12})τ9.42, singlet. IR (n-heptane) 2070w, 2045vs, 2003s, 1976s (cf. Fig. 1b).

The filtrate from above was taken to dryness under vacuum and the dark brown residue sublimed at 35° (0.01 mm) onto a water-cooled probe. Yield, 0.97 g colorless crystalline $(OC)_4Fe(SiMe_3)_2$ (I) (3.1 mmol, 36%). A second sublimation afforded the analytical sample as coarse colorless crystals, m.p. 68.0—68.5° (sealed capillary) (Found: C, 38.06; H, 5.78. $C_{10}H_{18}O_4FeSi_2$ calcd.: C, 38.22; H, 5.77%.) NMR (C_6D_6)τ 9.53, singlet. IR (n-heptane) 2069 m, 2061 m(sh), 2006 s, 2000 s, 1979 vs, 1964 m (cf. Fig. 1a).

Reaction of $Hg(SiMe_3)_2$ and $Hg[Fe(CO)_4SiMe_3]_2$

Samples of $Hg(SiMe_3)_2$ (0.91 g, 2.61 mmol) and $Hg[Fe(CO)_4SiMe_3]_2$ (1.69 g, 2.47 mmol) were placed in a Schlenk tube. The tube was evacuated and isopentane (40 ml) was distilled into it. The reaction mixture was warmed to room temperature and stirred magnetically for 2 h, then cooled to —10° for 48 h. The clear brown supernatant liquid was decanted from the fine grey precipitate into a sublimation apparatus, where solvent was removed; sublimation at 35° (0.01 mm) afforded $(OC)_4Fe(SiMe_3)_2$ (I) (1.20 g, 3.82 mmol, 78%), identified by IR and mass spectrum. The grey precipitate was washed with acetone and dried, and was recognized as metallic mercury (0.800 g, 4.0 mmol, 82%).

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