Organomercury Complexes of Iron, Cobalt, and Tungsten

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The iron complexes *cis*-$[\mathrm{Fe(CO)_4(HgR)_2}]$ [R = $\mathrm{CH_2SiMe_3}$, $\mathrm{CH(SiMe_3)_2}$, or $\mathrm{C(SiMe_3)_3}$] have been prepared. Their spectroscopic properties are reported, and their tendency to symmetrise, *e.g.* $n[\mathrm{Fe(CO)_4(HgR)_2}] \longrightarrow n\mathrm{HgR_2} + [\{\mathrm{HgFe(CO)_4}\}_n]$, has been examined. The complex $[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$ resists thermal symmetrisation; it reacts with $\mathrm{HgBr_2}$ and with $[\mathrm{Fe(CO)_4(HgBr)_2}]$ forming $\mathrm{HgBr[C(SiMe_3)_3]}$ and $[\{\mathrm{HgFe(CO)_4}\}_n]$ probably *via* the intermediate $[\mathrm{Fe(CO)_4(HgBr)\{Hg[C(SiMe_3)_3]\}}]$. At 60 °C the carbonyl groups in *cis*-$[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$ are fluxional, whereas at −55 °C axial and equatorial CO groups can be distinguished. The fluxional behaviour does not involve dissociation, and there is no evidence for the *trans* isomer. At 35 °C this complex shows an anomalous $^{13}\mathrm{CO}$ spectrum. The impure complexes $[\mathrm{Co(CO)_4(HgCH_2SiMe_3)}]$ and $[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)}]$ are also reported.

ALTHOUGH many compounds are known in which mercury is bonded to a transition metal, relatively few organomercury–transition-metal complexes have been studied: the first, $[\mathrm{Fe(CO)_4(HgMe)_2}]$ was prepared over 30 years ago by Hein and Henser.[1] Other transition metals known to form M–HgR complexes are Fe,[2] Co,[3] Mo and W,[4] V, Nb, and Ta,[5,6] Ir and Rh,[7] and Pt.[8] The most notable reaction of these complexes is the ease with which they symmetrise to the dialkyl- or diarylmercury and M–Hg complexes.

The high thermal stability of many trimethylsilylmethylmetal compounds and the fairly high steric requirement of this ligand led us to prepare and examine the following complexes: $[\mathrm{Fe(CO)_4(HgR)_2}]$, $[\mathrm{Co(CO)_4(HgR)}]$, and $[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)(HgR)}]$ (R = $\mathrm{CH_2SiMe_3}$). For comparison we have also prepared the more sterically hindered complexes $[\mathrm{Fe(CO)_4\{Hg[CH(SiMe_3)_2]\}_2}]$ and $[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$.

RESULTS AND DISCUSSION

Each of the octahedral iron complexes $[\mathrm{Fe(CO)_4(HgR)_2}]$, prepared from HgR(Cl) and $[\mathrm{Fe(CO)_4}]^{2-}$, gave i.r. bands in the ν(CO) region consistent with a *cis* (C_{2v}) configuration[9] (Table 1). This is the same configuration as in the methyl and butyl analogues and evidently, even for R groups having a large steric requirement, the *cis* configuration is favoured since it allows a greater degree of π-back bonding from iron to the carbonyl groups. Attempts to obtain a Raman spectrum of $[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$ were unsuccessful because of decomposition in the laser beam. For each of the iron complexes the median value of ν(CO) is lower than that calculated[2] (2 035 cm^{-1}) for zero electron transfer between an iron atom and a group bonded to it; hence, on this criterion HgR acts as an electron donor towards iron.

Symmetrisation of these iron complexes, which presumably proceeds through a series of bimolecular reactions (1), would predictably be influenced by the

$$n[\mathrm{Fe(CO)_4(HgR)_2}] \longrightarrow n\mathrm{HgR_2} + [\{\mathrm{HgFe(CO)_4}\}_n] \quad (1)$$

steric requirement of the R group and this effect was quite marked. For $[\mathrm{Fe(CO)_4(HgCH_2SiMe_3)_2}]$, symmetrisation was slow in $\mathrm{CDCl_3}$ at room temperature, whereas at 100 °C in the absence of solvent it proceeded rapidly. Unexpectedly, the bis(trimethylsilyl)methyl complex $[\mathrm{Fe(CO)_4\{Hg[CH(SiMe_3)_2]\}_2}]$ symmetrised so readily that purification was difficult, and only limited spectroscopic data were obtained. By contrast, $[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$ was stable over 3 months in $\mathrm{CDCl_3}$ at 20 °C; it was unaffected by heating at 110 °C for 7 h or at 150 °C for 4 h. At 200 °C in a nitrogen atmosphere it partly sublimed and partly decomposed to mercury and an unidentified brown solid. This complex also reacted with carbon tetrachloride slowly at room temperature and rapidly at 35 °C with deposition of an orange solid. It was stable to $\mathrm{CF_3CO_2H}$ under conditions that are said to cleave Pt–Hg (or Fe–Hg) bonds,[10] and did not react with $\mathrm{SiMe_3Cl}$ in refluxing benzene or with excess of $\mathrm{PPh_3}$ in benzene at room temperature. With $\mathrm{HgBr_2}$ in tetrahydrofuran(thf) solution it reacted quantitatively at room temperature [equation (2)]. Similarly, the sparingly soluble complex

$$\begin{gathered}[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}] + \mathrm{HgBr_2} \longrightarrow \\ \mathrm{HgBr[C(SiMe_3)_3]} + [\{\mathrm{HgFe(CO)_4}\}_n] \quad (2)\end{gathered}$$

$$\begin{gathered}[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}] + [\mathrm{Fe(CO)_4(HgBr)_2}] \\ \downarrow \\ \mathrm{Hg} + \mathrm{HgBr[C(SiMe_3)_3]} + [\{\mathrm{HgFe(CO)_4}\}_n] \quad (3)\end{gathered}$$

cis-$[\mathrm{Fe(CO)_4(HgBr)_2}]$ slowly dissolved in thf in the presence of 1 mol of $[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$; some

TABLE 1

Carbonyl stretching vibrations (cm^{-1})

cis-$[\mathrm{Fe(CO)_4(HgCH_2SiMe_3)_2}]$ [a]	2 050s	1 994s	1 985m	1 960s
cis-$[\mathrm{Fe(CO)_4\{Hg[CH(SiMe_3)_2]\}_2}]$ [b]	2 058s	1 995s	1 984m(sh)	1962s
cis-$[\mathrm{Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2}]$ [b]	2 060s	1 997s	1 984m	1 966s
$[\mathrm{Co(CO)_4(HgCH_2SiMe_3)}]$ [c]	2 079s	2 015m	1 993s	
$[\mathrm{W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)}]$ [c]	1 982m	1 915m	1 891s	

[a] In Nujol. [b] In Nujol, CsI, and $\mathrm{CCl_4}$. [c] In hexane.

mercury then separated followed by slow precipitation of the polymer [$\{HgFe(CO)_4\}_n$] [equation (3)]. Both these reactions probably proceed through a series of four-centred intermediates and changes in the u.v. spectra provide some evidence for the intermediate, [$Fe(CO)_4\{HgBr\}\{Hg[C(SiMe_3)_3]\}$]. The polymer [$\{HgFe(CO)_4\}_n$] has an i.r. spectrum[11] consistent with the structural unit *cis*-$Hg_2Fe(CO)_4$ and it seemed to us that a cyclic tetramer with linear Fe–Hg–Fe groups might be present in the polymer. However, the brown polymer remained insoluble after Soxhlet extraction with toluene over 3 d, and its mass spectrum at 200 °C contained only ions due to Hg^+ and $[Fe(CO)_n]^+$.

TABLE 2

Hydrogen-1 and ^{13}C n.m.r. data [a]

Complex	^1H δ(CH_3)	^1H δ(CH_2)	^1H δ(CH)	^1H δ(C_5H_5)	^1H ^2J(HgH)	^1H ^4J(HgH)
[$Fe(CO)_4(HgCH_2SiMe_3)_2$] [b]	0.18	0.78			166	6
[$Fe(CO)_4\{Hg[CH(SiMe_3)_2]\}_2$]	0.13		0.85		*d*	*d*
[$Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2$] [c]	0.21					<2
[$Co(CO)_4(HgCH_2SiMe_3)$] [b]	0.13	1.10			189	6
[$W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)$] [b]	0.06	0.49		5.61		

	^{13}C θ$_c$/°C	^{13}C δ($SiMe_3$)	^{13}C δ(HgC)	^{13}C δ(CO)	^{13}C ^1J(HgC)	^{13}C ^2J(CFeHg)	^{13}C ^3J(HgCSiC)	^{13}C ^1J($SiCH_3$)
[$Fe(CO)_4(HgCH_2SiMe_3)_2$] [b]	35	2.4	45.9 [e]	210.8	601.5	117.0	52.9	
[$Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2$] [f,g]	60	6.18	62.0	209.7	234.2	139.2	48.8	34.1
	35	6.10	61.7	209.7, 211.3	238.0		50.6	36.8
f,h	−55	5.80	60.4	208.8, 210.5				

[a] Relative to internal $SiMe_4$; shifts in p.p.m., *J* values in Hz. [b] In $CDCl_3$. [c] In CCl_4. [d] Not measured due to symmetrisation. [e] 50Hz coupling observed, possibly $^1J(^{29}Si–C)$. [f] With [$Fe^{III}(pd)_3$] (pd = pentane-2,4-dionate). [g] At 22.63 MHz. [h] At 45.28 MHz.

The complex [$Co(CO)_4(HgCH_2SiMe_3)$] was isolated as a yellow viscous oil. Its i.r. spectrum in the ν(CO) region contained three bands as expected for a trigonal-bipyramidal molecule with equatorial carbonyl groups (C_{3v} symmetry). The spectrum in this region was practically identical to that of [$Co(CO)_4(HgMe)$] showing that the CH_2SiMe_3 group does not influence the molecular geometry. Comparison of the median ν(CO) frequency at 2 020 cm^{-1} with Kahn and Bigorgne's value[3] of 2 045 cm^{-1} for zero charge transfer to cobalt suggests that $Hg(CH_2SiMe_3)$ is a weak electron donor. Slow symmetrisation of this complex took place in $CDCl_3$ solution (50% over 1 month at 20 °C, 100% over 2 h at 80 °C) [equation (4)].

$$2[Co(CO)_4(HgCH_2SiMe_3)] \longrightarrow Hg(CH_2SiMe_3)_2 + Hg[Co(CO)_4]_2 \quad (4)$$

The complex [$Co(CO)_4(HgMe)$], which has only been prepared in solution, is evidently of similar stability; other [$Co(CO)_4(HgR)$] complexes are much less stable to symmetrisation.

Two methods were used to prepare [$W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)$]: reaction of $Hg(CH_2SiMe_3)Cl$ with the anion [$W(CO)_3(\eta\text{-}C_5H_5)$]$^-$ or with the complex [$W(CO)_3(\eta\text{-}C_5H_5)(SnMe_3)$]. Neither method gave a pure product due to rapid symmetrisation [equation (5)]. The i.r. spectrum of the purified product corresponded to a mixture of all three compounds.

$$2[W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)] \longrightarrow Hg(CH_2SiMe_3)_2 + Hg[W(CO)_3(\eta\text{-}C_5H_5)]_2 \quad (5)$$

In the ν(CO) region bands at 1 994, 1 971, 1 898, and 1 875 cm^{-1} are probably due to $Hg[W(CO)_3(\eta\text{-}C_5H_5)]_2$ and, by comparison with other metal–tungsten complexes, bands at 1 982, 1 915, and 1 891 cm^{-1} may be ascribed to [$W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)$]. A weak band at 1 931 cm^{-1} could not be assigned. Comparison with work on [$W(CO)_3(\eta\text{-}C_5H_5)(HgMe)$] suggests that [$W(CO)_3(\eta\text{-}C_5H_5)(HgCH_2SiMe_3)$] is the more stable in solution, but that in the solid state the reverse is true.

Mass Spectra.—The cobalt and tungsten complexes symmetrised rapidly on the probe, and the recorded spectra corresponded to that of $Hg(CH_2SiMe_3)_2$. The iron complex [$Fe(CO)_4(HgCH_2SiMe_3)_2$] was remarkable in that 12.6% of the ion current was carried by the parent ion. Subsequent fragmentation involved competitive loss of carbonyl, methyl, $SiMe_3$, and CH_2SiMe_3 groups. The presence of HgR_2 (2%) suggests that symmetrisation occurred on the probe, although this does not necessarily follow. Transfer of R groups from mercury to iron was also observed {as in $[Fe(CO)_nR]^+$ (*n* = 0, 1, 3, or 4)}. Processes involving loss of CH_3 were also observed {as in $[P - CH_3]^+$, $[Fe(CO)(CH_2SiMe_2)]^+$, and $[Fe(CH_2SiMe_2)]^+$}. The bis- and tris-(trimethylsilyl)methyl complexes showed essentially the same features with very abundant parent ions.

N.M.R. Spectra.—Proton and ^{13}C n.m.r. data are listed in Table 2. The chemical shift of the methylene protons in the cobalt complex is as low as in $Hg(CH_2SiMe_3)Cl$ and much lower than in the iron complex. Hence, although the electronegativity of the X group in a $Hg(CH_2SiMe_3)X$ compound affects the chemical shifts of both the methylene and methyl protons, a direct relationship is not observed since the electron circulation in neighbouring groups also contributes to the chemical shift. The ^2J and ^4J coupling constants for both the iron and cobalt complexes are greater than in $Hg(CH_2SiMe_3)_2$, but less than those for the alkylmercury halides; this is as expected because the stability of the metal carbonyl anions will increase the *s* character of the Hg–C bond.

The ^{13}C n.m.r. spectrum of *cis*-[$Fe(CO)_4(HgCH_2$-

$SiMe_3)_2$] at 35 °C showed a single ^{13}CO resonance, corresponding to rapid exchange of CO between axial and equatorial sites, flanked by ^{199}Hg satellites. The ^{13}CO signal strength was about a third of the $^{13}CH_2$ signal due to the long relaxation time of ^{13}CO, and coupling to ^{57}Fe was not detected. The tris(trimethylsilyl)methyliron complex, with further quaternary carbon atoms in addition to the carbonyl groups, gave a more complex ^{13}C spectrum. At 35 °C in $CDCl_3$ solution the $^{13}CH_3$ resonance showed the expected coupling to ^{199}Hg and ^{29}Si; the quaternary ^{13}C resonance which also coupled to mercury was of low intensity, whilst the low-field, low-intensity, ^{13}CO resonance appeared as a broad singlet with a suggestion of a further resonance to even lower field. Addition of [$Fe^{III}(pd)_3$] (pentane-2,4-dionate) as a shiftless relaxation reagent considerably enhanced the strength of the quaternary carbon signal; it strengthened the 'main' ^{13}CO resonance, and revealed a further weak, broad, ^{13}CO resonance to low field (intensity ratio *ca.* 8 : 1). At −55 °C these two ^{13}CO signals were sharp and of roughly equal intensity, again with [$Fe^{III}(pd)_3$] present. At 60 °C only one sharp ^{13}CO resonance was present, and this showed coupling to mercury (verified by operating at 45.28 and 22.6 MHz). It therefore appears that at −55 °C the 1 : 1 doublet corresponds to the two axial and two equatorial carbonyl groups, whilst at 60 °C the carbonyl groups are fluxional, and since ^{199}Hg coupling is retained the process is non-dissociative. At the intermediate temperature the intensity difference of the two signals is difficult to explain: it might be due to differences in the relaxation time of axial and equatorial carbonyl groups and the differing effectiveness of the relaxation agent. However, the separation between the two carbonyl signals at 35 °C was essentially independent of spectrometer frequency (69 Hz at 45 MHz, 71 Hz at 22.6 MHz). In complexes of the type [$Fe(CO)_4(MMe_3)_2$] (M = Si, Ge, or Sn), axial–equatorial carbonyl exchange appears to involve *cis–trans–cis* interconversions,[12] but we found no evidence for even a relatively low concentration of *trans* isomers, either from the vibrational or ^1H or ^{13}C n.m.r. spectra.

The large difference between $^1J(HgC)$ for the two iron complexes (Table 2) is even greater than that observed in the corresponding dialkylmercury compounds where the low value observed for $Hg[C(SiMe_3)_3]_2$ has been ascribed to a decrease in the *s* character of the bond between the quaternary carbon atom and mercury.[13] The validity of this conclusion is not supported by closer study of the ^{13}C spectra of the compounds $Hg(CH_2SiMe_3)Cl$ and $Hg[C(SiMe_3)_3]Cl$ where if the low value of $^1J(HgC)$ in $Hg[C(SiMe_3)_3]Cl$ were due to decreased *s* character of the Hg–C bond then a corresponding increase in $^1J(^{29}Si–C)$ would have been expected. In fact, as the following figures show, the opposite trend is observed: $Hg(CH_2SiMe_3)Cl$ [$^1J(^{29}Si–^{13}CH_2)$ 47, $^1J(^{199}Hg–^{13}CH_2)$ 1 174]; $Hg[C(SiMe_3)_3]Cl$ [$^1J(^{29}Si–^{13}C)$ 33, $^1J(^{199}Hg–^{13}C)$ 665 Hz*].

EXPERIMENTAL

Tetracarbonylbis[(*trimethylsilylmethyl*)*mercurio*]*iron*.—Potassium hydroxide (5.0 g) and barium hydroxide (6.5 g) in water (60 cm³) were stirred for 12 h with pentacarbonyliron (5 cm³). The compound $Hg(CH_2SiMe_3)Cl$ [13] (11.3 g) in methanol (50 cm³) was slowly added and the resulting deep red solution extracted with hexane, from which the complex separated as a greenish yellow solid, m.p. 67 °C (70%) (Found: C, 19.2; H, 3.1. $C_{12}H_{22}FeHgO_4Si_2$ requires C, 19.4; H, 3.0%). A 1 mol dm^{-3} solution of the complex in $CDCl_3$ initially showed the expected two ^1H n.m.r. peaks at δ 0.78 and 0.08 p.p.m., each with Hg satellites. After 7 d in the dark at 20 °C a small amount of the orange polymeric complex [$\{HgFe(CO)_4\}_n$] had separated and additional resonances due to $Hg(CH_2SiMe_3)_2$ appeared at 0.10 and 0.04 p.p.m. Over 3 weeks, 50% decomposition had occurred, and thermal decomposition of the complex was almost complete after 2 h at 100 °C yielding $Hg(CH_2SiMe_3)_2$ (95%) and [$\{HgFe(CO)_4\}_n$] (Found: C, 11.5. Calc. for C_4FeHgO_4: C, 13.0%).

The complex [$Fe(CO)_4\{Hg[C(SiMe_3)_3]\}_2$], prepared using $Hg[C(SiMe_3)_3]Cl$ [13] as described in the preceding experiment, formed pale yellow crystals, m.p. 182—184 °C (75%) (Found: C, 28.5; H, 5.6. $C_{24}H_{54}FeHg_2O_4Si_6$ requires C, 27.9; H, 5.3%); [$Fe(CO)_4\{Hg[CH(SiMe_3)_2]\}_2$] was isolated from the reaction of $Hg[CH(SiMe_3)_2]Cl$ [13] with [$Fe(CO)_4$]$^{2-}$ as a viscous oil which could not be purified (Found: C, 25.9; H, 4.6. $C_{18}H_{38}FeHg_2O_4Si$ requires C, 24.4; H, 4.3%).

Tetracarbonyl[(*trimethylsilylmethyl*)*mercurio*]*cobalt*.— The complex [$Co_2(CO)_8$] (5 g) in methanol (50 cm³) was heated at 50 °C until CO evolution had ceased when $Hg(CH_2SiMe_3)Cl$ (6.14 g) in methanol (50 cm³) was added at −45 °C; vacuum distillation gave the complex as a viscous orange solution, b.p. 41 °C (0.15 mmHg) (3.23 g, 37%).† A 1 mol dm^{-3} solution in $CDCl_3$ initially showed two ^1H n.m.r. resonances at 1.1 and 0.13 p.p.m. both with Hg satellites. After 7 d at 20 °C in the dark, 25% decomposition had occurred yielding $Hg(CH_2SiMe_3)_2$ and $Hg[Co(CO)_4]_2$, m.p. 79 °C (decomp.), isolated as an orange solid (Found: C, 17.7. Calc. for $C_8Co_2HgO_8$: C, 17.7%). After 1 month, 45% decomposition had occurred, and the original complex completely decomposed when heated at 80 °C for 2 h to give the same products. Reaction of $Na[Co(CO)_4]$ with $Hg(CH_2SiMe_3)Cl$ gave the same complex in 22% yield.

Tricarbonyl(η-*cyclopentadienyl*)[(*trimethylsilylmethyl*)-*mercurio*]*tungsten*.—The complex [$W(CO)_3(\eta-C_5H_5)(SnMe_3)$] (0.41 g) and $Hg(CH_2SiMe_3)Cl$ (0.32 g) in $CDCl_3$ gave a deep yellow solution from which the crude complex was isolated after shaking with ice–water, as a pale yellow solid (0.28 g), m.p. 75 °C (decomp.) (Found: C, 26.0; H, 2.6. $C_{12}H_{16}HgO_3SiW$ requires C, 23.2; H, 2.6%). This experiment, carried out in an n.m.r. tube, gave data included in the Discussion but after 3 weeks at 20 °C in the dark a yellow solid was present, identified by its i.r. spectrum as $Hg[W(CO)_3(\eta-C_5H_5)]_2$, m.p. 197 °C (decomp.) (Found: C, 21.9; H, 1.1. Calc. for $C_{16}H_{10}HgO_6W_2$: C, 22.1; H, 1.2%). Using $Na[W(CO)_3(\eta-C_5H_5)]$ in diglyme followed by $Hg(CH_2SiMe_3)Cl$ gave, after hydrolysis, the crude complex as a bright yellow solid, m.p. 75 °C (decomp.) (Found: C, 26.9; H, 2.7. $C_{12}H_{16}HgO_3SiW$ requires C, 23.2; H, 2.6%).

Reaction of cis-[$Fe(CO)_4\{Hg[C(SiMe_3)_3]_2\}$] *with* cis-[$Fe(CO)_4(HgBr)_2$] *and with* $HgBr_2$.—The complex [$Fe(CO)_4$-

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* Correction from an earlier value.[13]

† Throughout this paper: 1 mmHg ≃ 13.6 × 9.8 Pa.

{Hg[C(SiMe$_3$)$_3$]}$_2$] (0.1 mmol), [Fe(CO)$_4$(HgBr)$_2$] (0.1 mmol), and tetrahydrofuran (thf) (5 cm^3) were stirred at 20 °C under nitrogen. Aliquots were withdrawn at intervals for u.v. spectral measurements. The initial suspension dissolved over 1—1.5 h to give a clear colourless solution and a small amount of mercury separated. With further stirring the solution turned yellow and polymeric [{HgFe(CO)$_4$}$_n$] gradually deposited (Found: C, 12.7. Calc. for C_4HgFeO_4: C, 13.0%). After 3 d the filtrate yielded by sublimation [80 °C (10^{-3} mmHg)] colourless crystals of HgBr[C(SiMe$_3$)$_3$] (Found: C, 23.8; H, 5.3. $C_{10}H_{27}BrHgSi_3$ requires C, 23.5; H, 5.3%). Mass spectrum: intense peak at 497 corresponding to $[P - Me]^+$. Hydrogen-1 n.m.r. spectrum in C_6D_6: δ(CH$_3$) 0.08 p.p.m.; ^2J(SiH) 6.1; ^1J(CH) 119 Hz.

A similar reaction using HgBr$_2$ was much faster; possibly because both reactants dissolved in thf. No mercury was formed but HgBr[C(SiMe$_3$)$_3$] and [{HgFe(CO)$_4$}$_n$] were isolated.

Two bands were present in the u.v. spectrum of [Fe(CO)$_4${Hg[C(SiMe$_3$)$_3$]}$_2$] [$\lambda_{max.}$ (log ε): 231 (3.2) and 285 nm (2.45 dm^3 mol^{-1} cm^{-1})], and a thf solution of [Fe(CO)$_4$(HgBr)$_2$] also had two bands at 220 and 268 nm. Equimolar mixtures of these complexes and of [Fe(CO)$_4${Hg[C(SiMe$_3$)$_2$]}$_2$] + HgBr$_2$ absorbed at 228 and 273 nm. The intensity of the band at 273 nm, which may be ascribed to the intermediate [Fe(CO)$_4$(HgBr){Hg[C(SiMe$_3$)$_3$]}], diminished with time and was not detectable after 17 h. Both HgBr$_2$ and HgBr[C(SiMe$_3$)$_3$] absorb in the 220—231 nm region (log ε $\simeq$ 4). All absorption bands were broad.

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