DALTON

Mixed iron–silicon–tin complexes stabilized by a phosphinoenolate bridging ligand. Crystal structure of $[(OC)_3\{(MeO)_3Si\}Fe\{\mu\text{-}Ph_2PCH{=}C(O)Ph\}SnBu^n{}_2]$

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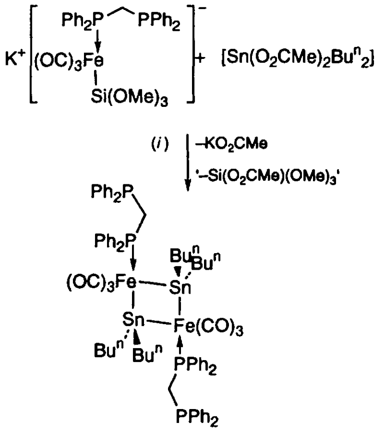
Interesting differences have been observed in the reactivity of *mer*-$[FeH(CO)_3\{Si(OMe)_3\}\{Ph_2PCH_2C(O)Ph\}]$ and *mer*-$[FeH(CO)_3\{Si(OMe)_3\}\{Ph_2PCH_2C(O)NPh_2\}]$ toward tin derivatives of the type $[SnX_2R_2]$. Whereas the former which contains a diphenylphosphino ketone ligand reacted with $[SnCl_2Bu^n{}_2]$, $[SnBr_2Bu^n{}_2]$, $[Sn(O_2CMe)_2Bu^n{}_2]$ or $[SnCl_2Ph_2]$ to yield only one type of complex $[(OC)_3\{(MeO)_3Si\}Fe\{\mu\text{-}Ph_2PCH{=}C(O)Ph\}SnR_2]$ (R = Bu^n or Ph), respectively, the latter with the *N*,*N*-diphenyl-2-diphenylphosphinoacetamide ligand afforded different products depending upon the nature of X in $[SnX_2Bu^n{}_2]$. With $[SnCl_2Bu^n{}_2]$ or $[SnBr_2Bu^n{}_2]$ the product obtained was $[(OC)_3\{(MeO)_3Si\}Fe\{\mu\text{-}Ph_2PCH{=}C(O)NPh_2\}SnBu^n{}_2]$, but with $[Sn(O_2CMe)_2Bu^n{}_2]$ no reaction was observed. The halides appear to be better leaving groups than acetate and this, associated with the different acidity of the PCH_2 protons between the two phosphine ligands, is responsible for the formation or not of the six-membered ring (Fe–Sn–phosphinoenolate) complex the stability of which constitutes the driving force in the reaction.

As part of our current studies on the synthesis and reactivity of heterometallic complexes containing a Fe–Si bond,[1] we have recently found that the alkoxysilyl Fe–Pd complex $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})Pd(SnPh_3)]$ catalyses the dehydrogenative coupling of the tertiary stannane $SnPh_3H$.[2] This has stimulated our interest in the synthesis and characterization of well defined complexes containing Fe–Si and Fe–Sn bonds which could be relevant to this chemistry. In order to assist the formation of metal–metal bonded complexes, we have used $Ph_2PCH_2PPh_2$ (dppm) as an assembling ligand. However, the reaction in Scheme 1 led to the formation of a tetranuclear complex containing pendant phosphorus groups while the silyl ligand was lost.[3] This latter observation may be related to the known use of $[Sn(O_2CMe)_2Bu^n{}_2]$ as a Lewis-acid catalyst in sol-gel chemistry involving alkoxysilyl groups.

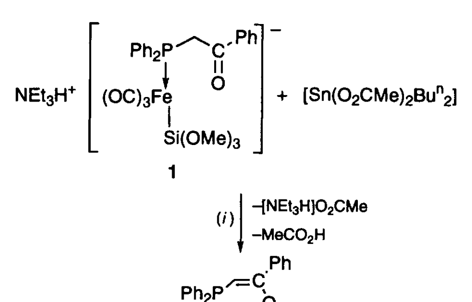


Scheme 1 (*i*) Tetrahydrofuran

Following previous studies on the co-ordination chemistry of the functional phosphine ligands $Ph_2PCH_2C(O)Ph$ and $Ph_2PCH_2C(O)NPh_2$,[4] we felt it interesting to investigate whether the oxophilicity of tin would be sufficient to promote a bridging behaviour for these P,O ligands, a situation encountered so far only in Fe–Cd and Fe–In systems.[5]

Results and Discussion

The iron metalate $[Fe(CO)_3\{Si(OMe)_3\}\{Ph_2PCH_2C(O)Ph\}]^-$, obtained *in situ* as its $[NEt_3H]^+$ salt **1** by deprotonation of the corresponding hydride *mer*-$[FeH(CO)_3\{Si(OMe)_3\}\{Ph_2PCH_2C(O)Ph\}]$ **2** with NEt_3 (see Experimental section) was treated with 1 equivalent of $[Sn(O_2CMe)_2Bu^n{}_2]$ in CH_2Cl_2. The reaction was monitored by IR spectroscopy, following the disappearance of the ν(C≡O) absorptions of the metalate (1826s, 1842vs and 1929w cm^{-1}). A yellow complex was isolated which displayed an absorption at 1537 cm^{-1} in CH_2Cl_2, in addition to the ν(C≡O) stretches. The considerable shift from 1685 cm^{-1} in **2** in CH_2Cl_2 clearly indicated that the keto function was no longer pendant. For comparison, oxygen co-ordination in the Fe–Cd complex $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}[\mu\text{-}Ph_2PCH_2C(O)Ph](\mu\text{-}Cl)Cd\}_2](Fe\text{–}Cd)$ resulted in a shift of only *ca.* 45 cm^{-1}.[5b] Furthermore, examination of the ^1H NMR spectrum revealed a resonance at δ 5.18 (d, 1 H) against 4.22 for the PCH_2 protons of **2**. These data are consistent with the formation of an enolate system[4] and the occurrence of a bridging phosphinoenolate ligand (Scheme 2). The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **3** contains a singlet at δ 24.0 with satellites due to a $^2J(P^{117,119}Sn)$ coupling of 133 Hz. It is interesting that a similar upfield shift has been observed for *mer*-$[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-}SnCl_2)(\mu\text{-dppm})PtCl(PEt_3)]$[6] in which the dppm ligand is also part of a six-membered ring (δ 37.0). Two $^{13}C\text{-}\{^1H\}$ resonances were observed at δ 87.2 [d, $^1J(PC)$ = 62.6 Hz] and at δ 172.7 (s) which belong to the ligand phosphine enolate. The former is shifted downfield when



Scheme 2 (*i*) CH$_2$Cl$_2$

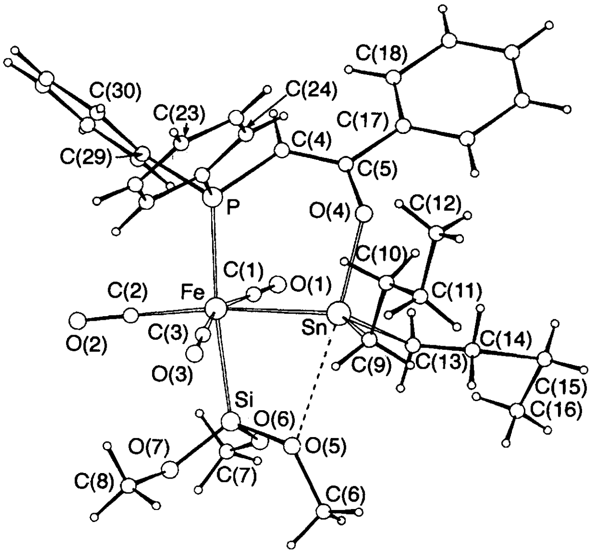


Fig. 1 View of the molecular structure of complex **3**. Selected bond distances (Å) and angles (°): Fe–Sn 2.567(3), Fe–P 2.287(4), Fe–Si 2.317(4), Fe–C(1) 1.747(7), Fe–C(2) 1.796(7), Fe–C(3) 1.777(8), Sn–O(4) 2.075(7), Sn–C(9) 2.071(8), Sn–C(13) 2.111(6), P–C(4) 1.783(6), C(4)–C(5) 1.310(7), C(5)–O(4) 1.340(9), Si–O(5) 1.606(7), Si–O(6) 1.616(7) and Si–O(7) 1.592(6); Sn–Fe–P 90.8(1), Sn–Fe–Si 83.9(1), Fe–Sn–O(4) 101.8(2), Fe–Sn–C(9) 124.5(2) and Fe–Sn–C(13) 115.5(2)

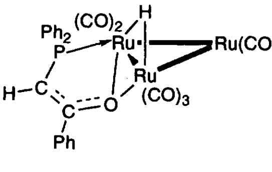
compared with that for **1** {δ 43.9 [d, ^1J(PC) = 12.2 Hz]} whereas the latter is upfield shifted [δ 196.4 (s) for **1**]. The crystal structure of **3**, determined by an X-ray diffraction study, confirmed the presence of the bridging phosphinoenolate ligand.

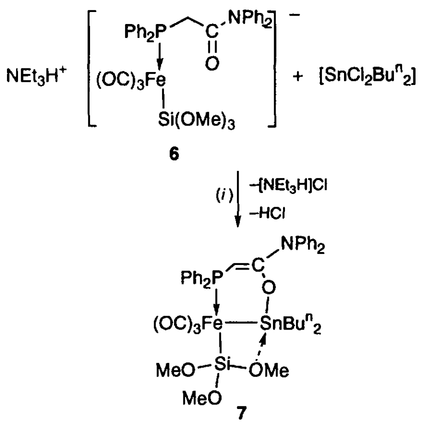
A view of the molecular structure of compound **3** is given in Fig. 1. The phosphinoenolate ligand acts as a bridge, through the P and O(4) atoms, between the Fe and Sn atoms which are linked by a metal–metal bond. The octahedral co-ordination around Fe involves the Sn atom, the P atom [Fe–P 2.287(4) Å], three carbon atoms from terminal carbonyl groups, and a Si atom of the alkoxysilyl ligand [Fe–Si 2.317(4) Å]. The Sn atom displays a severely distorted tetrahedral co-ordination [bond angles range from 97.5(3) to 124.5(2)°] involving the Fe atom, the O(4) atom [Sn–O(4) 2.075(7) Å] and two carbons from butyl groups. The Fe–Sn bond distance [2.567(3) Å] is shorter than those found in [{Fe(CO)$_3$(dppm-*P*)(μ-SnBu$^n{}_2$)}$_2$], 2.674(1) and 2.645(1) Å,[3] and in [Fe(CO)$_3$(dppm)(SnClPh$_2$)$_2$], 2.603(1) and 2.608(1) Å,[1e] but is very close to that found in the complex *mer*-[(OC)$_3${(MeO)$_3$Si}Fe(μ-SnCl$_2$)(μ-dppm)PtCl(PEt$_3$)], 2.568(2) Å,[6] and to the mean value found in complexes in which Fe–Sn bonds were present (2.562 Å, from Cambridge Crystallographic Data Base). There is a weak bonding interaction between the alkoxysilyl ligand and the Sn atom, the separation between the Sn atom and the O(5) atom being 2.811(5) Å. This short contact does not affect the Si–O(5) bond distance, which is very close to the other two, but could be responsible for the narrower Fe–Si–O(5) and Si–O(5)–C(6) angles (with respect to the corresponding angles with the other oxygen atoms) and for the larger Fe–Sn–C(9) and Fe–Sn–C(13) angles (with respect to the other in the tetrahedral co-ordination). The tetrahedral co-ordination around the tin is significantly distorted toward trigonal bipyramidal with atoms O(4) and O(5) occupying the axial positions [O(5)–Sn–O(4) 173.8(3)°]. In the phosphinoenolate ligand the PC(4)C(5)O(4)C(17) moiety is practically planar and the values of the C(4)–C(5) and C(5)–O(4) distances are in agreement with a significant double-bond character for the C–C bond, more pronounced than in several complexes in which this ligand forms five-membered chelates with extensive electron delocalization.[4a,b]

Using [SnCl$_2$Bu$^n{}_2$] as precursor led to the same bimetallic complex in better yields (see Experimental section), indicating in this case no influence of the leaving group on tin upon the nature of the reaction product.[7] Reaction of **1**, previously dried under vacuum to eliminate any NEt$_3$ present, with [SnCl$_2$Bu$^n{}_2$] also led to complex **3**. Thus, the deprotonation of the ketophosphine ligand does not result from the excess of NEt$_3$. When KH was used as a base instead of NEt$_3$ in the reaction with **2**, deprotonation of both the metal centre and the ketophosphine ligand occurred, to form K$_2$[Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$\overset{\cdots}{-}$C($\overset{\cdots}{-}$O)Ph}] **4**. This was evidenced in the IR spectrum by a shift of the ν(CO) absorption toward lower wavenumbers and the appearence of a ν(C$\overset{\cdots}{-}$C) + ν(C$\overset{\cdots}{-}$O) absorption due to the enolate moiety at 1514 cm^{-1} in thf. A singlet resonance was observed in the ^{31}P-{^{1}H} NMR spectrum at δ 57.9, a value which has been previously erroneously assigned to monoanion K[Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}]$^-$.[8] This resonance is shifted upfield compared with that of **1** (δ 74.9). The ^{13}C-{^{1}H} NMR spectrum contains a resonance at δ 181.0 (s) which is assigned to the enolate C(O) carbon. For comparison, this resonance was observed at δ 197.2 [d, ^2J(PC) = 9.2 Hz] for free Ph$_2$PCH$_2$C(O)Ph, at δ 196.4 for **1**, at δ 188.7 in **2**, and at δ 173.0 [d, ^2J(PC) = 22.3 Hz] for K[Ph$_2$PCH$\overset{\cdots}{-}$C($\overset{\cdots}{-}$O)Ph].[9] Reaction of **4** with [Sn(O$_2$CMe)$_2$Bu$^n{}_2$] or [SnCl$_2$Bu$^n{}_2$] afforded **3** instantaneously. Similarly, its reaction with [SnCl$_2$Ph$_2$] afforded [(OC)$_3${(MeO)$_3$Si}Fe{μ-Ph$_2$PCH=C(O)Ph}SnPh$_2$] **5**, similar to **3**.

Particularly noteworthy is the 'spontaneous' deprotonation of the functional phosphine which leads to the enolate ligand.[4b] In view of the weak basicity of the chloride or acetate ions liberated in the reaction, it must be related to the strong propensity of the tin centre to form a covalent Sn–O bond. In previous studies phosphinoenolate ligands have always been found as five-membered chelates,[4] with the exception of the Ru$_3$ cluster shown.[10] The stability of the six-membered ring unit is nicely illustrated by the occurrence in the mass spectrum of **3** of a fragment at *m*/*z* 325 which corresponds to the ring FePCCOSn plus a phenyl group (either on P or C).

With the related compound Ph$_2$PCH$_2$C(O)NPh$_2$ interesting differences were observed. Although deprotonation of the hydrido complex *mer*-[FeH(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)NPh$_2$}] **6** by NEt$_3$ in CH$_2$Cl$_2$, followed by addition of [SnCl$_2$Bu$^n{}_2$] rapidly afforded **7**, which is similar to **3** (Scheme





Scheme 3 (*i*) CH_2Cl_2

3), reaction with [Sn(O_2CMe)$_2$Bu$^n{}_2$] did not lead to **7**, and most of the metalate remained unchanged. The spectroscopic features of **7** are similar to those of **3** and indicate a similar structure (see Experimental section).

It is surprising that the 'spontaneous' deprotonation of the phosphinoacetamide ligand occurs so readily with [SnCl$_2$Bu$^n{}_2$] and not with [Sn(O_2CMe)$_2$Bu$^n{}_2$]. The different behaviour between **1** and [NEt$_3$H][FeH(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)NPh$_2$}] could be explained by the combined effects of a binding of the acetate to the tin centre being stronger than that of the chloride and of the electron-donating properties of the NPh$_2$ group which renders the PCH$_2$ protons less acidic. This disfavours or prevents formation of the six-membered ring (Fe–Sn–phosphinoenolate) complex the stability of which constitutes the driving force in the reaction. Even when KH was used to deprotonate **6** in thf no **7** was observed upon reaction with [Sn(O_2CMe)$_2$Bu$^n{}_2$].

The reactivity of these complexes is currently investigated and will be compared to that of mononuclear compounds containing these phosphinoenolate ligands in a chelating mode.

Experimental

All experiments were carried out using Schlenk-tube techniques under purified nitrogen. Solvents were dried and distilled under nitrogen before use. Elemental C, H and N analyses were performed by the service Central de Microanalyses du CNRS. Infrared spectra were recorded on a Bruker IFS66 (4000–400 cm^{-1}) spectrometer, proton, ^{31}P-{^{1}H} and ^{13}C-{^{1}H} NMR spectra on a Bruker SY 300 spectrometer at 300.13, 121.49 and 75.75 MHz respectively. The ^{1}H, ^{13}C and ^{31}P chemical shifts are given relative to external SiMe$_4$ and H$_3$PO$_4$ respectively. Mass spectra were measured on a Fisons ZAB-HF spectrometer (Université Louis Pasteur). All reactions were monitored by infrared spectroscopy [ν(CO) region].

Preparations

***mer*-[FeH(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}] 2.** This complex was prepared in 90% yield as detailed previously.[5a] IR (thf): ν(C≡O) 2050w, 1986s and 1977vs; ν(C=O) 1685 cm^{-1}. NMR: ^{1}H (CDCl$_3$); δ −9.56 [d, FeH, 1 H, ^{2}*J*(PH) 24.4], 3.64 (s, 9 H, OCH$_3$) and 4.22 [d, 2 H, PCH$_2$, ^{2}*J*(PH) 6.8]; ^{31}P-{^{1}H} (CDCl$_3$); δ 49.6 (s, PFe); ^{13}C-{^{1}H} (C$_6$D$_6$); δ 37.9 [d, PCH$_2$, ^{1}*J*(PC) 22.5 Hz], 45.6 (s, OCH$_3$), 120.7–132.6 (m, aromatics), 188.7 [s, C(O)], 205.3 (s, 1 CO) and 205.4 (s, 2 CO).

***mer*-[FeH(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)NPh$_2$}] 6.** This complex was prepared using a similar procedure, starting from [Fe(CO)$_5$] (10 mmol) and *N*,*N*-diphenyl-2-diphenylphosphinoacetamide (3.95 g, 10 mmol). Yield: 85%. IR (thf): ν(C≡O) 2051w, 1988s and 1976vs; ν(C=O) 1493 cm^{-1}. NMR: ^{1}H (CD$_2$Cl$_2$), δ −9.68 [d, FeH, 1 H, ^{2}*J*(PH) 26.8], 3.55 [d, 2 H, P-CH$_2$, ^{2}*J*(PH) 5.3 Hz] and 3.58 (s, 9 H, OCH$_3$); ^{31}P-{^{1}H} (CDCl$_3$); δ 52.8 (s, PFe).

[NEt$_3$H][Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}] 1. The hydrido complex **2** was deprotonated using NEt$_3$ as a base. Typically, **2** was dissolved in CH$_2$Cl$_2$ (*ca.* 30 cm^3) and a slight excess of NEt$_3$ was added to the solution. Immediately, the yellow solution turned bright orange. After stirring for 15 min the solvent was evaporated under vacuum and an orange solid was obtained. IR (CH$_2$Cl$_2$): ν(C≡O) 1929w, 1842vs and 1826s; ν(C=O) 1671 cm^{-1}. NMR (CD$_2$Cl$_2$): ^{1}H, δ 1.17 (t, 9 H, C*H*$_3$CH$_2$), 2.84 (q, 6 H, C*H*$_2$CH$_3$), 3.48 (s, 9 H, OCH$_3$), 3.58 (s, 1 H, *H*NEt$_3$), 4.29 (d, 2 H, PCH$_2$) and 7.2–7.9 (m, Ph); ^{31}P-{^{1}H}, δ 74.9 (s, PFe); ^{13}C-{^{1}H}, δ 9.9 (s, NCH$_2$*C*H$_3$), 43.9 [d, PCH$_2$, ^{1}*J*(PC) 12.2 Hz], 46.8 (s, N*C*H$_2$CH$_3$), 50.4 (s, OCH$_3$), 128.0–140.7 (m, Ph), 196.4 [s, C(O)], 217.3 (s, 2 CO) and 217.5 (s, CO).

K$_2$[Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH⋯C(⋯O)Ph}] 4. The hydridoiron complex **2** (1 mmol) was dissolved in thf (*ca.* 30 cm^3) and a large excess of KH was added to the solution. The mixture was stirred for 1.5 h until no gas evolution was observed. The pale yellow solution first turned orange and then pale yellow again. Then, the mixture was filtered in order to eliminate the excess of KH and the solution was concentrated. IR (thf): ν(C≡O) 1919w, 1832vs and 1804s cm^{-1}; ν(C⋯C) + ν(C⋯O) 1514 cm^{-1}. NMR (thf–C$_6$D$_6$): ^{31}P-{^{1}H}, δ 57.9 (s, PFe); ^{13}C-{^{1}H}, δ 44.9 (s, OCH$_3$), 121.4–140.9 (m, aromatics), 181.0 (s, C⋯O), 215.3 (s, 1 CO) and 215.7 (s, 2 CO); the PCH resonance could not be observed, perhaps overlapped by the strong signal of thf at δ 67.7.

[(OC)$_3${(MeO)$_3$Si}Fe{μ-Ph$_2$PCH=C(O)Ph}SnBu$^n{}_2$] 3. *Method* 1. To a stirred solution of [NEt$_3$H[Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}] prepared *in situ* from the corresponding hydride (0.566 g, 1.0 mmol) and excess of NEt$_3$ (0.28 cm^3) in CH$_2$Cl$_2$ was added [Sn(O_2CMe)$_2$Bu$^n{}_2$] (0.27 cm^3, 1.0 mmol). Rapidly, a yellow solution was obtained, the reaction mixture was stirred for 30 min and the solution was concentrated. The product was precipitated by addition of a large excess of hexane. The yellow residue was purified by washing with hexane.

Method 2. To a stirred solution of K$_2$[Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH⋯C(⋯O)Ph}] prepared as described above (from 0.566 g, 1.0 mmol of the corresponding hydride and 0.09 g KH) was added [SnCl$_2$Bu$^n{}_2$] (0.304 g, 1.0 mmol). Immediately, a white precipitate was formed. The solution was stirred for 15 min and then slowly concentrated. It was filtered in order to eliminate KCl and the product was isolated by precipitation upon addition of hexane. An excess of [SnCl$_2$Bu$^n{}_2$] did not perturb the reaction. The complex was crystallized from a very concentrated thf solution at −30 ° C. Yield: 89% (Found: C, 51.3; H, 5.40. Calc: C, 51.15; H, 5.55%). IR (thf): ν(C≡O) 2023w, 1969s and 1954vs; IR ν(CO) 1537 cm^{-1}. NMR: ^{1}H (CD$_2$Cl$_2$); δ 0.84 [t, 6 H, CH$_3$, ^{3}*J*(HH) 7.3], 1.27–1.67 (m, 12 H, CH$_2$), 3.63 (s, 9 H, OCH$_3$), 5.18 [d, 1 H, PCH=, ^{2}*J*(PH) 7.12] and 7.33–7.46 (m, 15 H, Ph); ^{31}P-{^{1}H} (CD$_2$Cl$_2$), δ 24.0 [s, PFe, ^{2}*J*(P^{117,119}Sn) 133]; ^{13}C-{^{1}H} (CDCl$_3$), δ 13.5 (s, CH$_2$*C*H$_3$), 20.9 (s, *C*H$_2$CH$_3$), 26.8 [s, SnCH$_2$, ^{1}*J*(C^{117,119}Sn) 32], 28.3 (s, CH$_2$), 51.2 (s, OCH$_3$), 87.2 [d, PCH$_2$, ^{1}*J*(PC) 62.6 Hz], 125.9–139.9 (m, Ph), 172.7 (s, COSn), 209.4 (s, 2 CO) and 210.5 (s, CO). Mass spectrum (FAB$^+$): 799 (M^+, 34), 741 (M^+ − Bu, 50), 713 (M^+ − Bu − CO, 57), 685 (M^+ − Bu − 2CO, 5), 600 (M^+ − 2Bu − 3CO, 28), 479 [M^+ − 2Bu − 3CO − Si(OMe)$_3$, 100%], 402 [M^+ − 2Bu − 3CO − Si(OMe)$_3$ − Ph, 21] and 325 [M^+ − 2Bu − 3CO − Si(OMe)$_3$ − 2Ph, 61%].

[(OC)$_3${(MeO)$_3$Si}Fe{μ-Ph$_2$PCH=C(O)Ph}SnPh$_2$] 5. The procedure used was similar to that described for complex **3** according to method 2, adding $[SnCl_2Ph_2]$ (0.344 g, 1.0 mmol) to a solution of $K_2[Fe(CO)_3\{Si(OMe)_3\}\{Ph_2PCH\overset{..}{-}C(\overset{..}{-}O)Ph\}]$ prepared *in situ* from **2** (0.566 g, 1.0 mmol) and an excess of KH (0.09 g) in thf. Yield: 74% (Found: C, 53.7; H, 4.40. Calc: C, 54.5; H, 4.20%). IR (thf): ν(C≡O): 2037w, 1985s and 1971vs; ν(CO) 1537 cm^{-1}. NMR (CD_2Cl_2): ^1H, δ 3.62 (s, 9 H, OCH_3), 5.27 [d, 1 H, PCH=, ^2J(PH) 7.2] and 7.28–7.75 (m, 25 H, Ph); $^{31}P-\{^1H\}$, δ 20.1 [s, PFe, $^2J(P^{117,119}Sn)$ 183 Hz].

$[(OC)_3\{(MeO)_3Si\}Fe\{\mu-Ph_2PCH=C(O)NPh_2\}SnBu^n_2$ 7. The procedure used was similar to that described for complex **3** according to method 1, adding $[SnCl_2Bu^n_2]$ (0.304 g, 1.0 mmol) to a solution of $[NEt_3H][Fe(CO)_3\{Si(OMe)_3\}\{Ph_2PCH_2-C(O)NPh_2\}]$ prepared *in situ* from the corresponding hydride (0.657 g, 1.0 mmol) with an excess of NEt_3 (0.30 cm^3) in CH_2Cl_2. Yield: 82%. IR (thf): ν(C≡O) 2023w, 1969s and 1954vs cm^{-1}. NMR ($CDCl_3$): ^1H, δ 0.84 (t, 6 H, CH_3), 0.90–1.50 (m, 12 H, CH_2), 3.63 (s, 9 H, OCH_3), 4.18 [d, 1 H, PCH=, ^2J(PH) 9.6]; $^{31}P-\{^1H\}$, δ 26.95 [s, PFe, $^2J(P^{117,119}Sn)$ 122 Hz].

X-Ray crystallography

Crystal data for complex 3. $C_{34}H_{43}FeO_7PSiSn$, $M = 797.31$, monoclinic, space group $P2_1/n$, $a = 20.271(4)$, $b = 18.242(3)$, $c = 10.695(3)$ Å, $\beta = 105.21(2)°$, $U = 3816(1)$ Å^3, $Z = 4$, $D_c = 1.388$ g cm^{-3}, $F(000) = 1632$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,73$ Å, $\mu = 11.49$ cm^{-1}.

The crystals were of poor quality and diffracted weakly. A crystal of 0.22 × 0.25 × 0.30 mm was used for the X-ray analysis. No correction for absorption was applied. The intensity data were collected on a Philips PW 1100 diffractometer, using the θ–2θ scan technique at room temperature. 9184 Unique reflections were measured with θ in the range 3–28°; only 2193, having $I > 2\sigma(I)$, were used in the refinement. The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares procedures (based on F), with anisotropic thermal parameters in the last cycles of refinement for all non-hydrogen atoms except the carbons of the phenyl and butyl groups. In the final cycles of refinement, a weighting scheme $w = k[\sigma^2(F_o) + gF_o^2]^{-1}$ was used; at convergence g values were 0.672 and 0.0032, respectively. All hydrogen atoms were placed at their geometrically calculated positions in the final ΔF map and refined, 'riding' on the corresponding carbon atoms, isotropically. The SHELX 76 and SHELXS 86 systems of computer programs were used.[11] The R and R' values were 0.0500 and 0.0525.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/237.

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