Synthesis of dppm-Stabilized Si–Fe–M (M = Zn, Cd, Hg or Tl) Complexes and Crystal Structure of a Heterotetranuclear Fe_2Cd_2 Complex (dppm = $Ph_2PCH_2PPh_2$) *

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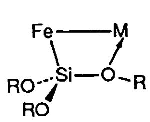
Treatment of $K[Fe(CO)_3\{Si(OMe)_3\}(dppm\text{-}P)]$ (dppm = $Ph_2PCH_2PPh_2$) with CdX_2 (X = Cl or Br) in tetrahydrofuran (thf) in a 1:1 ratio afforded the tetranuclear iron–cadmium complexes *mer*-$[\{[(MeO)_3Si](OC)_3Fe(\mu\text{-dppm})Cd(\mu\text{-}X)\}_2]$ **2a** (X = Cl) and **2b** (X = Br) in 78 and 65% isolated yield, respectively. Each Fe–Cd bond is supported by a dppm ligand. The reaction of the ketophosphine-substituted metalate $K[Fe(CO)_3\{Si(OMe)_3\}\{Ph_2PCH_2C(O)Ph\}]$ with $CdCl_2$ in a 1:1 ratio similarly afforded *mer*-$[\{[(MeO)_3Si](OC)_3Fe[\mu\text{-}Ph_2PCH_2C(O)Ph]Cd(\mu\text{-}Cl)\}_2]$ **2c**, in which a bridging mode for the functional (*P,O*) ligand is assumed for the first time. Reaction of $K[Fe(CO)_3\{Si(OMe)_3\}(dppm\text{-}P)]$ with $ZnCl_2$ afforded the Fe–Zn analogue **3**, which is very labile. Similarly, Fe–Hg complexes of the type *mer*-$[\{(MeO)_3Si\}(OC)_3Fe(\mu\text{-dppm})HgX]$ (R = Et, X = Ph; R = Me, X = C_6Cl_5 or Cl) were prepared. The chloride bridges of **2a** are easily split by nucleophiles. Using $Ph_2PCH_2C(O)Ph$, *mer*-$[\{(MeO)_3Si\}(OC)_3Fe(\mu\text{-dppm})CdCl\{Ph_2PCH_2C(O)Ph\}]$ and *mer*-$[\{(MeO)_3Si\}(OC)_3Fe(\mu\text{- dppm})HgCl\text{-}\{Ph_2PCH_2C(O)Ph\}]$ were obtained. They reacted with $Tl[PF_6]$ to yield cationic complexes in which the ketophosphine acts as a chelating ligand. The synthesis of the Fe–Tl^{III} complex *mer*-$[\{(MeO)_3Si\}(OC)_3Fe(\mu\text{-dppm})Tl(C_6F_5)_2]$ **9** is also described. The $^{31}P\text{-}\{^1H\}$ NMR resonance due to the phosphorus bound to thallium consists of a doublet of doublets at δ −14.0 with $^1J(P\text{–}^{203}Tl/^{205}Tl)$ = 6765 Hz. The molecular structure of complex **2a** was determined by X-ray diffraction. Crystals of the hexane solvate are orthorhombic, space group *Pbcn*, with $a = 23.498(9)$, $b = 16.856(8)$, $c = 18.220(8)$ Å, and $Z = 4$. The structure has been solved from diffractometer data by Patterson and Fourier methods and refined by full-matrix least squares to $R = 0.0653$ for 2906 observed reflections. In the dimeric complex, having an imposed C_2 symmetry, the two Fe–Cd distances, 2.624(2) Å, are indicative of metal–metal bonds and the two Cd atoms are joined by a double nearly symmetrical chloride bridge. A phosphorus atom of the dppm ligand completes the co-ordination of the Cd atom. Each Fe atom is octahedrally co-ordinated by three carbonyl groups in a meridional arrangement, by a phosphorus atom of the dppm ligand, by the Si atom of the $Si(OMe)_3$ ligand and by the Cd atom.

We have recently investigated reactions of the trigonal-bipyramidal anion $[Fe(CO)_3\{Si(OMe)_3\}(dppm\text{-}P)]^-$ $\mathbf{1}^-$ (dppm = $Ph_2PCH_2PPh_2$) with complexes of Pd, Pt, Rh and Ag which have resulted in the synthesis of heterodinuclear complexes containing an unprecedented μ-SiO bridge, of type **A**, between iron and the adjacent transition metal.[1] The lone pair on the pendant phosphorus ligand of $\mathbf{1}^-$ led to easy formation of a dppm bridge between the metal centres and thus to additional stabilization. In order to explore the possibility of generating novel MFeSiO four-membered ring structures and evaluate the stabilising role of dppm by comparison with heterometallic complexes containing an analogous, though unsupported M–Fe–Si array,[2] we have sought to extend this type of chemistry to the synthesis of Fe–Zn, Fe–Cd, Fe–Hg and Fe–Tl complexes. We describe here such new complexes and report the crystal structure of $[\{[(MeO)_3Si](OC)_3Fe(\mu\text{-dppm})Cd(\mu\text{-}Cl)\}_2]$ **2a**.



A

Results and Discussion

The reaction of the potassium salt of $\mathbf{1}^-$ with an excess of CdX_2 (X = Cl or Br) in tetrahydrofuran (thf) afforded the iron–cadmium tetranuclear complexes *mer*-$[\{[(MeO)_3Si](OC)_3Fe(\mu\text{-dppm})Cd(\mu\text{-}X)\}_2]$ **2a** (X = Cl) and **2b** (X = Br) in 78 and 65% isolated yield, respectively [equation (1)] The new compounds were characterized by elemental analysis and IR, ^1H and $^{31}P\text{-}\{^1H\}$ NMR spectroscopy; preparative details are given in the Experimental section. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of **2a** consisted of two resonances, a low-field doublet at δ 67.1 [$^{2+3}J(P\text{–}P)$ = 107 Hz, with cadmium satellites since both ^{111}Cd and ^{113}Cd, in 12.75 and 12.26% abundance, respectively, have $I = \frac{1}{2}$] assigned to the P atom of the dppm ligand bonded to Fe, and a doublet at δ −14.9, assigned to the

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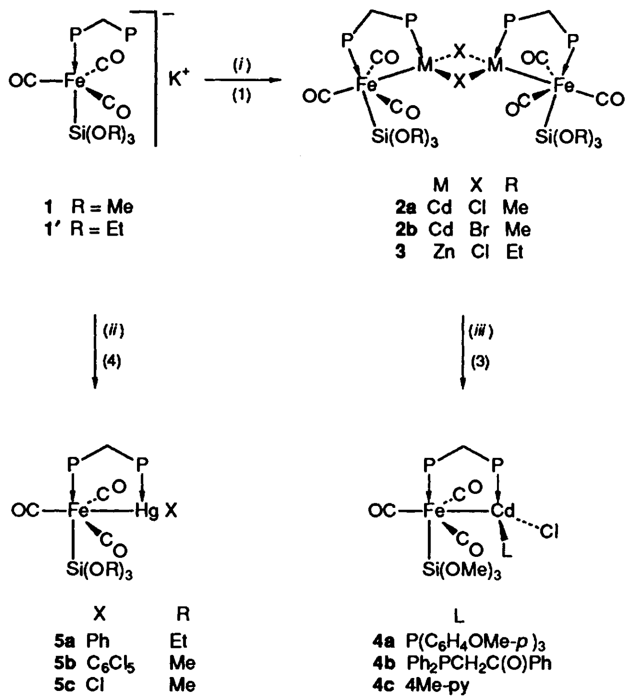
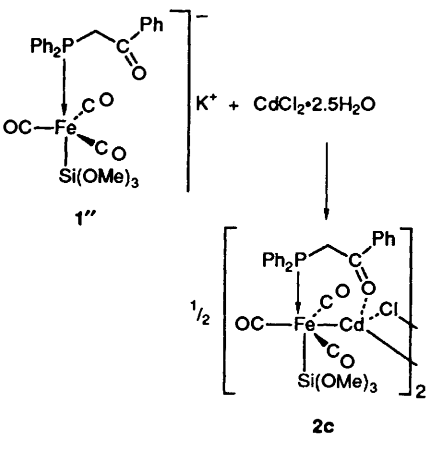
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 (*i*) CdX$_2$–thf, −KX; (*ii*) Hg(X)Cl–thf, −KX; (*iii*) L–CH$_2$Cl$_2$

Cd-bound P atom, although the $^1J(^{113}\text{Cd–P})$ and $^1J(^{111}\text{Cd–P})$ couplings were not observed, even at −30 °C. This could be ascribed to the lability of the Cd–P(2) bond, which is also supported by the rather long Cd–P(2) distance found in the solid-state structure of **2a** (see below). In other cases where $^1J(^{113}\text{Cd–P})$ and $^1J(^{111}\text{Cd–P})$ were observed (in **4** and **7**), the ratio of these coupling constants was close to the expected value of 1.046.[3] The ^{1}H NMR spectrum of **2a** in CD_2Cl_2 showed a triplet for the PCH_2P protons at δ 3.06 [^2J(P–H) = 9.5 Hz] and only one resonance at δ 3.49 for the OMe protons. Similar data were obtained for **2b**. The triplet pattern results from an accidentally equal coupling with the two chemically different P nuclei. The dimeric nature of these complexes [ν(Cd–Cl) 215, 202; ν(Cd–Br) 160(br) cm^{-1}] was established by an X-ray diffraction study of **2a**.

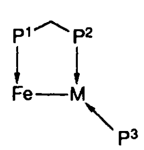
For comparison and in view of the observed lability of the Cd–P(2) bond in complexes **2**, we thought that the functional phosphine $Ph_2PCH_2C(O)Ph$, which would give rise to a strong Fe–P and a weaker (if at all) O→Cd interaction, might also allow the stabilization of a related dimeric complex. Thus, we treated K[Fe(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}][1d] with $CdCl_2$ in thf in a 1 : 1 ratio [equation (2)]. A stable complex was formed and isolated in high yields, whose analytical and spectroscopic data [*e.g.* ν(Cd–Cl) 229 cm^{-1}] are consistent with the dimeric formulation *mer*-[{[(MeO)$_3$Si](OC)$_3$Fe[μ-Ph$_2$PCH$_2$C(O)Ph]Cd(μ-Cl)}$_2$] **2c**. The shift of the ketonic ν(CO) vibration from 1675 cm^{-1} for *mer*-[FeH(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}] to 1630 cm^{-1} for **2c** is indicative of an O→Cd interaction. A crystal structure determination should confirm the first occurrence of a bridging mode for the (diphenylphosphino)acetophenone ligand.



2c (2)

The zinc analogue of complex **2a** was prepared at −30 °C in nearly quantitative yields by using a similar procedure but *mer*-[{[(EtO)$_3$Si](OC)$_3$Fe(μ-dppm)Zn(μ-Cl)}$_2$] **3** was too labile to be isolated analytically pure, owing to its tendency to decompose, probably *via* radical processes, with formation of *mer*-[FeH(CO)$_3${Si(OEt)$_3$}(dppm-*P*)]. The stabilizing effect of dppm is notable, although not quite sufficient, since attempts to prepare related Fe–Zn complexes with PPh$_3$ in place of dppm have failed, and resulted exclusively in the formation of *mer*-[FeH(CO)$_3$(SiMePh$_2$)(PPh$_3$)].[2b,c] The similarity between the spectroscopic data for **2a** and **3** is also consistent with a dimeric structure for **3**. Chloride-bridged bimetallic Zn–Mo complexes have also been reported.[4]

The halide bridges of complex **2** are easily split by nucleophiles and reaction with 2 mol equivalents of the phosphine ligands P(C$_6$H$_4$OMe-*p*)$_3$ or Ph$_2$PCH$_2$C(O)Ph afforded *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl{P(C$_6$H$_4$-OMe-*p*)$_3$}] **4a** and *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl{Ph$_2$PCH$_2$C(O)Ph}] **4b**, respectively [equation (3)]. In the latter complex, no significant O→Cd interaction, involving either a methoxy group or the keto function, was observed despite the ability of this functional phosphine ligand to act as a chelate, even with typical soft metal ions.[5] The halide bridges of **2** are also instantaneously split by 4-methylpyridine (4Me-py) to afford quantitatively *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl(4Me-py)] **4c**. The affinity of Cd^{II} in bimetallic Cd–Fe complexes for *N*-donor ligands has been observed before.[6] The addition of an excess of the base did not alter the IR spectrum significantly whereas, in the case of **3**, partial heterolytic cleavage of the Fe–Zn bond resulted, with liberation of [Fe(CO)$_3${Si(OEt)$_3$}(dppm-*P*)]$^-$. This is consistent with a more polar character of the Fe–Zn bond, compared to the Fe–Cd bond. The monomeric nature of these Fe–Cd complexes is evidenced by the value of the ν(Cd–Cl) IR absorption observed in the range 245–261 cm^{-1},[3] and by mass spectroscopy (fast atom bombardment, FAB) for **4b**.



A static structure is observed for **4a** at 233 K and the resonance for P^3, the phosphorus atom of the monodentate phosphine, appears as a doublet at δ −6.1, owing to a $^2J(P^2–P^3)$ coupling of 77 Hz, and shows in addition cadmium satellites with $^1J(\text{P–}^{111}\text{Cd}/^{113}\text{Cd})$ = 1186/1238 Hz. In comparison, [CdCl$_2${P(C$_6$H$_4$OMe-*p*)$_3$}$_2$] shows δ −3.22 and $^1J(\text{P–}^{111}\text{Cd}/^{113}\text{Cd})$ = 1475/1543 Hz.[3] Similarly, a static structure is observed for **4b** at 233 K and $^2J(P^2–P^3)$ = 50 Hz (Fig. 1). The $^1J(\text{P}^3\text{–}^{111}\text{Cd}/^{113}\text{Cd})$ coupling of 965/1020 Hz is in the normal range,[7] whereas ^1J(P^2–Cd) is quite small (*ca.* 100 Hz), similar to the corresponding value for **4c** (83 Hz) which is observed only at low temperature. This would be consistent with some lability of the Cd–P(2) bond, as also noted in other cases.[7a] The ^{31}P-{^{1}H} NMR spectra of **4a** and **4b** are temperature-dependent. The broadening observed at room temperature is indicative of a dynamic behaviour. For **4b** the resonance at δ −20.6 due to the phosphorus atom of the

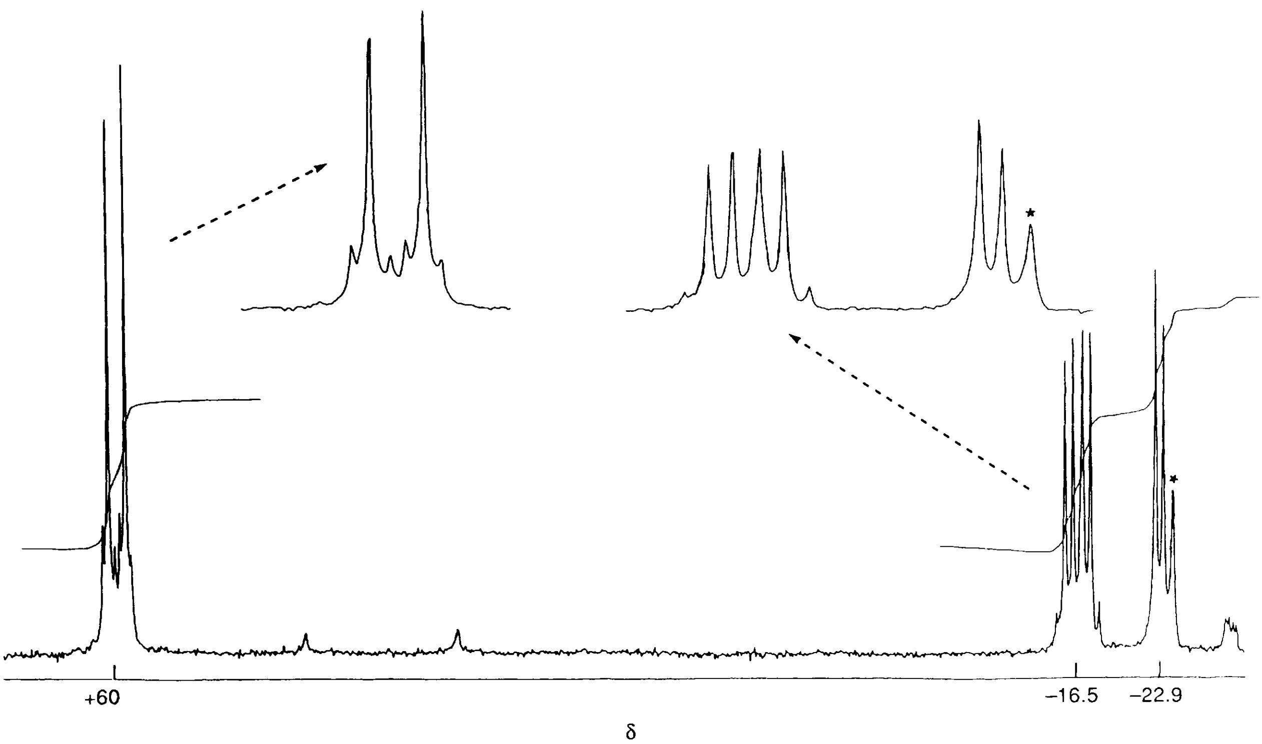
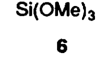


Fig. 1 $^{31}P-\{^1H\}$ NMR spectrum of *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl{$Ph_2PCH_2C(O)Ph$}] **4b** at 233 K in CH_2Cl_2–CD_2Cl_2. The asterisk denotes the presence of an impurity

functional phosphine appears as a broad singlet, with no resolved coupling with the dppm phosphorus atoms. Its chemical shift lies between that for the free ligand (δ −17.1) and the value found in the low-temperature spectrum (δ −22.9). Cooling a solution of **4b** in CD_2Cl_2 resulted in the progressive appearance of three sets of well resolved signals with their corresponding satellites (see Experimental section). Complex **4a** displays a similar dynamic behaviour. Note that the lability of the Cd–P(2) bond was even greater in the dimeric complexes **2** (see above).

The reaction of the potassium salt of **1′**$^-$ or **1**$^-$ with [HgPhCl] or [$Hg(C_6Cl_5)Cl$] in thf [equation (4)] afforded in high yields the stable complexes *mer*-[{(EtO)$_3$Si}(OC)$_3$Fe(μ-dppm)HgPh] **5a** or *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Hg(C_6Cl_5)] **5b**, respectively, which are similar to the complex *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)HgCl] **5c** obtained from $HgCl_2$.[1b] The ^1H NMR spectra of complexes **5** always contain the expected doublet of doublets for the PCH_2 protons. The nature of the substituent X bound to Hg has a notable effect on the magnitude of the *J*(P–Hg) coupling constants. Thus at 298 K, the values of ^1J(P–Hg) and ^{2+3}J(P–Hg) for **5a** are respectively 360 and 29 Hz, whereas for **5c** these become 1745 and 460 Hz.[1b] The situation in **5b** is somewhat intermediate with ^1J(P–Hg) = 600 Hz and ^{2+3}J(P–Hg) = 244 Hz. The values of the chemical shifts for the Hg-bound P nucleus vary from δ − 0.5 for **5c**[1b] to −20.9 for **5a**. Addition of 1 equivalent of $Ph_2PCH_2C(O)Ph$ to **5c** afforded *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)HgCl{$Ph_2PCH_2C(O)Ph$}] **6**, the Fe–Hg analogue of **4b** [equation (5)]. It also exhibits dynamic behaviour and the $^{31}P-\{^1H\}$ NMR resonance due to the functional phosphine is shifted from *ca.* δ −2.0 at 298 K to δ 24.9 at 243 K. At this temperature all the expected *J*(P–P) and *J*(P–Hg) couplings are resolved. The IR spectrum of **6** in thf is consistent with the lability of the ketophosphine ligand since it shows superimposition of the ν(CO) absorptions due to **5c** and **6** in the solid state.



(5)

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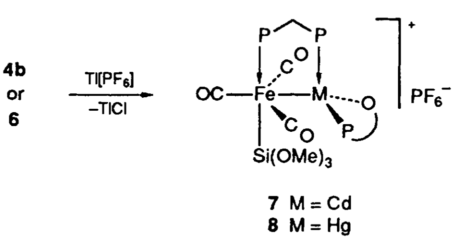
The lability of the M–P(3) bond is significantly reduced in the cationic complexes *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Cd{$Ph_2PCH_2C(O)Ph$}][PF_6] **7** and *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Hg{$Ph_2PCH_2C(O)Ph$}][PF_6] **8**, prepared respectively from **4b** or **6** by chloride abstraction [equation (6)], as shown by the presence of only one species in solution. Furthermore, their $^{31}P-\{^1H\}$ NMR spectra are well resolved, with all the expected couplings, and the δ value for the co-ordinated ketophosphine is shifted from −22.9 to −12.4 on going from **4b** to **7**, and from 24.9 to 48.9 on going from **6** to **8**.



(6)

7 M = Cd
8 M = Hg

Since it is known that in compounds of the type [$TlX(C_6F_5)_2$] the thallium can increase its co-ordination number to five in the presence of donor ligands L [PPh_3, $AsPh_3$, $OPPh_3$, 2,2′-bipyridine (bipy) *etc.*][8a,b] we decided to treat **1**$^-$ with [$TlBr(C_6F_5)_2$] in order to obtain a dppm-bridged Fe–Tl bimetallic complex which could possibly display a μ-SiO bridge. Dative O→Tl^{III} interactions are present in *e.g.* [{$TlMe_2$(μ-$OSiMe_3$)}$_2$].[8c] Addition of the potassium salt of **1**$^-$ to a thf solution of [$TlBr(C_6F_5)_2$] afforded in almost quantitative yield the stable yellow compound *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Tl(C_6F_5)$_2$] **9** [equation (7)]. The structure depicted

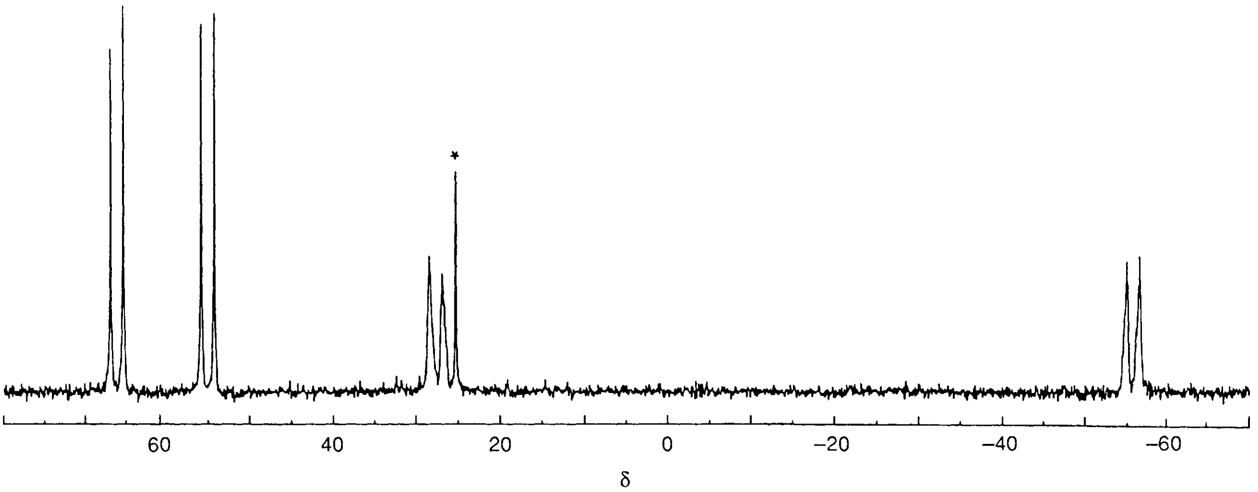
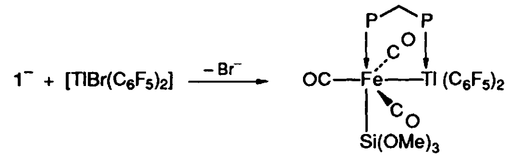


Fig. 2 ^{31}P-{^{1}H} NMR spectrum at 298 K in CH_2Cl_2–C_6D_6 of the reaction mixture containing *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Tl(C_6F_5)$_2$] **9**. The asterisk denotes the presence of $Ph_2P(O)CH_2P(O)Ph_2$ as an impurity



(7)

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Table 1 Selected bond distances (Å) and angles (°) in complex **2a** *

Cd–Fe	2.624(2)	Fe–P(1)	2.251(4)
Cd–Cl	2.546(3)	Fe–Si	2.286(5)
Cd–Cl′	2.570(4)	Fe–C(1)	1.743(16)
Cd–P(2)	2.796(4)	Fe–C(2)	1.772(15)
		Fe–C(3)	1.761(16)
P(2)–Cd–Fe	95.5(1)	Si–Fe–C(1)	85.9(5)
P(2)–Cd–Cl	100.2(1)	Si–Fe–C(2)	81.4(5)
P(2)–Cd–Cl′	104.2(1)	Si–Fe–C(3)	82.9(5)
Cl–Cd–Cl′	86.4(1)	C(1)–Fe–C(2)	101.8(6)
Cl–Cd–Fe	131.1(1)	C(1)–Fe–C(3)	102.4(7)
Cl′–Cd–Fe	133.6(1)	Cd–Fe–C(2)	77.1(5)
Cd–Fe–P(1)	90.3(1)	Cd–Fe–C(3)	77.0(5)
Cd–Fe–Si	88.2(1)	Cd–Cl–Cd′	92.6(1)
P(1)–Fe–C(1)	95.6(5)	Fe–C(1)–O(1)	177.4(14)
P(1)–Fe–C(2)	104.0(5)	Fe–C(2)–O(2)	174.1(12)
P(1)–Fe–C(3)	91.0(5)	Fe–C(3)–O(3)	175.0(13)

* Primed atoms are related to unprimed ones by the transformation $-x, y, \frac{1}{2} - z$

may be unambiguously deduced from the spectroscopic data. The meridional arrangement of the CO ligands is once again indicated by the presence of three ν(CO) vibrations at 2028, 1969 and 1962 cm^{-1}. The very informative ^{31}P-{^{1}H} NMR spectrum shows for the phosphorus atom co-ordinated to iron a doublet of doublets at δ 60.6 due to ^{2+3}J(P–P) 126 Hz and a coupling with the NMR-active Tl nuclei (^{203}Tl/^{205}Tl, $I = \frac{1}{2}$, natural abundance 29.52 and 70.48%, respectively) with ^{2+3}J(P–Tl) = 895 Hz (Fig. 2). The resonance due to the phosphorus bound to Tl consists of a doublet of doublets centred at δ −14.0 with ^1J(P–Tl) = 6765 Hz, each signal being further split into a multiplet owing to coupling with the fluorine nuclei on the phenyl groups. This rare value of a ^1J(P–Tl) coupling is much larger than for the dimeric dialkylthallium(III) phosphides (R_2Tl–PR′$_2$)$_2$ (*ca.* 3200 Hz).[9] Despite the fact that Tl has not achieved its maximum co-ordination number, no μ-SiO interaction was evidenced: upon cooling a CD_2Cl_2 solution of **9** to 213 K, no splitting of the singlet resonance of the methoxy protons was observed in the ^{1}H NMR spectrum, thus ruling out any significant interaction which would make the methyl groups chemically inequivalent. The methylenic protons of the dppm ligand appear to be involved in a dynamic process because at room temperature only a broad resonance was seen. Heating the solution to 328 K showed the expected doublet of triplets pattern at δ 3.40, owing to ^3J(H–Tl) = 58.1 Hz and ^2J(H–P) = 10.1 Hz. To the best of our knowledge,[10] **9** represents the first dppm-bridged Fe–Tl complex.

Crystal Structure of mer-[{[(MeO)$_3$Si](OC)$_3$Fe(μ-dppm)Cd(μ-Cl)}$_2$]·C_6H_{14} **2a** C_6H_{14}.—The structure of complex **2a** is shown in Fig. 3 and selected bond distances and angles are given in Table 1. The tetranuclear complex, having an imposed crystallographic C_2 symmetry, consists of two Fe–Cd dinuclear units with the Cd atoms joined by a double, nearly symmetric chloride bridge [Cd–Cl 2.546(3) and 2.570(4) Å]. The two $CdCl_2$ triangles of the Cd(μ-Cl)$_2$Cd system make a dihedral angle of 165.3(1)°. The iron and cadmium centres are linked by a dppm bridge and a metal–metal bond [Fe–Cd 2.624(2) Å]. The latter distance is comparable to those in the only other two structures reported until now for complexes containing Fe–Cd bonds, [{CdFe(CO)$_4$}$_4$] [2.559(2)–2.565(2) Å][6a] and [{(bipy)CdFe(CO)$_4$}$_3$] [2.631(4)–2.653(5) Å].[6b] The octahedral environment about the Fe atom is determined by the Cd atom, a phosphorus atom of the dppm ligand [Fe–P(1) 2.251(4) Å], the Si atom of the Si(OMe)$_3$ ligand [Fe–Si 2.286(5) Å] and by three carbon atoms of terminal carbonyl groups. It is similar to that found in the related complexes *mer*-[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl] [Fe–P 2.241(2) and Fe–Si 2.275(2) Å],[1a] *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Cu(AsPh$_3$)][1b] and *mer*-[(Ph$_2$MeSi)(Ph$_3$P)(OC)$_3$FeAu(PPh$_3$)].[2a] The flattened tetrahedral co-ordination about the cadmium atom involves the Fe atom, a phosphorus atom of the dppm ligand [Cd–P(2) 2.796(4) Å] and the two Cl atoms [the Cd atom is displaced out of the plane passing through the Fe and the two Cl atoms by 0.424(1) Å towards the phosphorus atom]. In **2a** the Cd–Cl distances of 2.546(3) and 2.570(4) Å are shorter than generally observed,[11] and consistent with the cadmium ion being four-co-ordinated. The Cd–P bond distance of 2.796(4) Å is surprisingly long in view of the values reported until now for these distances which fall in a narrow range 2.524–2.646 Å (from Cambridge Crystallographic Data Centre) consistent with the sum of the Pauling covalent radii (1.48 + 1.10 = 2.58 Å). Moreover the values for the Cd–P distance do not seem to be influenced significantly by the cadmium environments, the

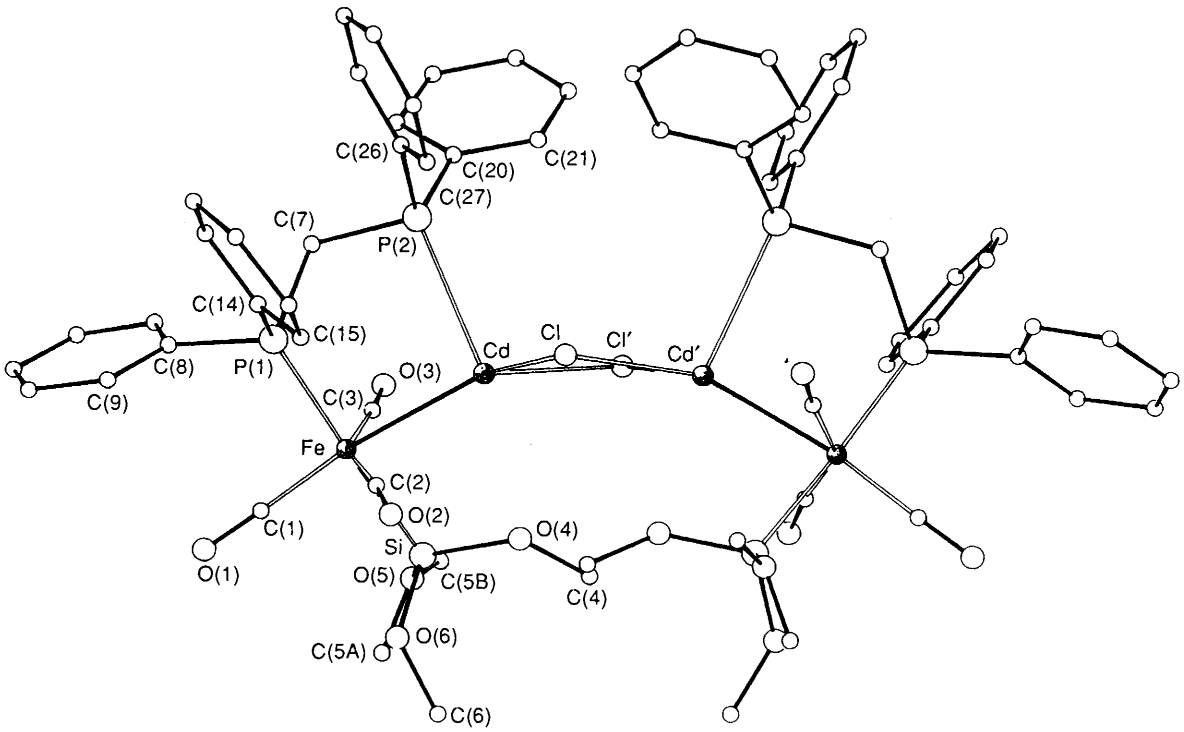

Fig. 3 View of the structure of the complex *mer*-[{[(MeO)$_3$Si](OC)$_3$Fe(μ-dppm)Cd(μ-Cl)}$_2$] **2a** showing the numbering scheme used

longest distances having been found in the tetrahedral complex [CdCl$_2$(PPh$_3$)$_2$] (2.633 and 2.646 Å)[12] and in the five-co-ordinated complex [{CdCl$_2$(Ph$_2$PC$_2$H$_4$NEt$_2$)}$_2$] [2.563(1) and 2.617(1) Å in two independent molecules].[13] It is noteworthy that very few complexes containing cadmium atoms bonded to phosphorus atoms (in particular of phosphine ligands) have been structurally characterized and **2a** appears to be the first complex in which the Cd atom is involved in such a bond with the dppm ligand. Heterodinuclear complexes with bridging dppm ligands between Pt and Cd have been reported but structural data are not available.[14] The reasons for the unusually long Cd–P distance are not known at this stage but steric factors may play an important role as the bulky phosphine ligands are situated in the same portion of space with respect to the [Fe–Cd(μ-Cl)]$_2$ unit.

In contrast to the situation found in *mer*-[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl] and in related Fe–Pt and Fe–Rh complexes,[1a,c,e] there is no significant bonding interaction in **2a** between the alkoxysilyl ligand and the cadmium atom, despite the harder character of the Cd^{2+} ion. In other words, cadmium prefers intermolecular co-ordination by Cl over intramolecular μ-SiO bridge formation. When taking into account the contact observed between the Cd atom and one oxygen atom of the alkoxysilyl group [Cd ··· O(4) 2.950(13) Å], that may reflect a weak interaction, the co-ordination about the cadmium atom could be described also as an elongated, and strongly distorted, trigonal bipyramid with the phosphorus and the oxygen atoms occupying the apical sites.

Experimental

All experiments were carried out using Schlenk-tube techniques, under oxygen-free nitrogen. The NMR spectra were recorded using a Bruker WP200 instrument with proton chemical shifts measured relative to tetramethylsilane and phosphorus chemical shifts relative to phosphoric acid. Unless otherwise specified, the pure complexes are air-stable in the solid state for prolonged periods.

Syntheses.—*mer*-[{[(MeO)$_3$Si](OC)$_3$Fe(μ-dppm)Cd(μ-Cl)}$_2$] **2a**. A solution of K[Fe(CO)$_3${Si(OMe)$_3$}(dppm-*P*)][1] (0.685 g, 1 mmol) in thf (25 cm^3) was slowly added at 25 °C over 1 h *via* a dropping funnel to a suspension of dehydrated CdCl$_2$ (0.275 g, 1.5 mmol) in thf (5 cm^3). After the end of the reaction (2.5 h, IR monitoring) the yellowish clear solution was filtered and evaporated to dryness. The residue was dissolved in CH$_2$Cl$_2$ (*ca.* 10 cm^3), the solution filtered through Celite and the filtrate was layered with hexane. Colourless crystals slowly formed at −15 °C, and were collected by filtration and dried *in vacuo*. Concentration of the mother-liquor afforded a further crop of the product (overall yield: 0.620 g, 78%) [Found: C, 46.65; H, 4.10. Calc. for $C_{62}H_{62}Cd_2Cl_2Fe_2O_{12}P_4Si_2$ (*M* = 1586.74): C, 46.95; H, 3.95%]. IR (CH$_2$Cl$_2$): ν(CO) 1985m, 1918s, 1900vs; FTIR (polyethylene) ν(CdCl) 215s(br) and 202s(br) cm^{-1}. NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 3.06 [t, 2 H, CH$_2$, ^2J(P–H) = 9.5], 3.49 (s, 9 H, OCH$_3$) and 7.11–7.51 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} [81.02 MHz, (CD$_3$)$_2$CO–CH$_2$Cl$_2$, 293 K], δ −14.9 [d, P(Cd), ^{2+3}J(P–P) = 107, ^1J(P–^{111}Cd/^{113}Cd) not observed] and 67.1 [d, P(Fe), ^{2+3}J(P–P) = 107, ^{2+3}J(P–^{111}Cd/^{113}Cd) = 84 Hz (when the satellites due to coupling to cadmium are broad, the coupling quoted is the average for ^{111}Cd and ^{113}Cd)]. The ^1J(P–^{111}Cd/^{113}Cd) satellites were also not observed at 243 K.

mer-[{[(MeO)$_3$Si](OC)$_3$Fe(μ-dppm)Cd(μ-Br)}$_2$] **2b**. This complex was prepared similarly to **2a** by using CdBr$_2$·4H$_2$O. Yield: 0.546 g, 65% [Found: C, 44.05; H, 3.85. Calc. for $C_{62}H_{62}Br_2Cd_2Fe_2O_{12}P_4Si_2$ (*M* = 1677.26): C, 44.40; H, 3.75%]. IR (CH$_2$Cl$_2$): ν(CO) 1985m, 1919s, 1900vs; FTIR (polyethylene) ν(CdBr) 160s cm^{-1}. NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 3.09 [t, 2 H, CH$_2$, ^2J(P–H) = 9.5], 3.44 (s, 9 H, OCH$_3$) and 7.11–7.51 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} [81.02 MHz, (CD$_3$)$_2$CO–CH$_2$Cl$_2$], δ −16.3 [d, P(Cd), ^{2+3}J(P–P) = 110, ^1J(P–^{111}Cd/^{113}Cd) not observed] and 66.9 [d, P(Fe), ^{2+3}J(P–P) = 110, ^{2+3}J(P–^{111}Cd/^{113}Cd) = 82 Hz].

mer-[{[(MeO)$_3$Si](OC)$_3$Fe[μ-Ph$_2$PCH$_2$C(O)Ph]Cd(μ-Cl)}$_2$] **2c**. This yellow microcrystalline complex was prepared in a manner similar to **2a**, by using the potassium salt of **1**$''^-$

[prepared from *mer*-[FeH(CO)$_3${Si(OMe)$_3$}{Ph$_2$PCH$_2$C(O)Ph}]^{1d} (1.145 g, 2.02 mmol) and excess of KH] in thf (20 cm^3) and CdCl$_2$·2.5H$_2$O (0.643 g, 2.82 mmol) in thf (5 cm^3) (0.985 g, 69%) [Found: C, 44.45; H, 4.10. Calc. for C$_{52}$H$_{52}$Cd$_2$Cl$_2$Fe$_2$O$_{14}$P$_2$Si$_2$ (*M* = 1426.5): C, 43.80; H, 3.65%]. IR (KBr): ν(CO) 1989s, 1924vs, 1907(sh), 1630m; (thf) 1988m, 1928s, 1907vs, 1641w; (CH$_2$Cl$_2$) 1991m, 1928(sh), 1911vs, 1637mw; FTIR (polyethylene) ν(CdCl) 229vs (br) cm^{-1} NMR: ^{1}H (200 MHz, C$_6$D$_6$), δ 3.81 (s, 9 H, OCH$_3$), 3.91 [d, 2 H, PCH$_2$, ^{2}*J*(P–H) = 10.5] and 6.54–7.54 (m, 15 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, thf–C$_6$D$_6$), δ 63.5 [s with Cd satellites, P(Fe), ^{2}*J*(P–^{111}Cd/^{113}Cd) = 55 Hz].

mer-[{[(EtO)$_3$Si](OC)$_3$Fe(μ-dppm)Zn(μ-Cl)}$_2$] **3**. This complex was prepared at −30 °C in a manner similar to that used for **2a** by using K[Fe(CO)$_3${Si(OEt)$_3$}(dppm-*P*)] and ZnCl$_2$. The reaction was instantaneous and the spectroscopic yield (IR and ^{31}P-{^{1}H} NMR spectroscopy) was quantitative. Progressive formation of the hydrido complex *mer*-[FeH(CO)$_3${Si(OEt)$_3$}(dppm-*P*)] occurred at ambient temperature. Addition of pentane to the filtered solution led to precipitation of a white powder of the product. IR (thf): ν(CO) 1984m, 1924s, 1898vs; FTIR (polyethylene) ν(ZnCl) 297(br) cm^{-1}. NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 1.24 [t, 9 H, CH$_3$, ^{3}*J*(H–H) = 6.9], 3.21 [t, 2 H, CH$_2$, ^{2}*J*(P–H) = 9.9], 3.92 [q, 6 H, OCH$_2$, ^{3}*J*(H–H) = 6.9] and 7.23–7.67 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} [81.02 MHz, (CD$_3$)$_2$CO–CH$_2$Cl$_2$], δ −21.2 [d, P(Zn), $^{2+3}$*J*(P–P) = 120] and 66.9 [d, P(Fe), $^{2+3}$*J*(P–P) = 120 Hz].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl{P(C$_6$H$_4$OMe-*p*)$_3$}] **4a**. This complex was prepared as detailed for **4b** by using P(C$_6$H$_4$OMe-*p*)$_3$. Colourless microcrystals were obtained in 69% yield [Found: C, 54.25; H, 4.65. Calc. for C$_{52}$H$_{52}$CdClFeO$_9$P$_3$Si (*M* = 1445.7): C, 54.50; H, 4.55%]. IR (CH$_2$Cl$_2$): ν(CO) 1983m, 1923s, 1897vs; FTIR (polyethylene) ν(CdCl) 245s(br) cm^{-1}. NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 3.37 [br t, 2 H, CH$_2$, ^{2}*J*(P–H) = 9.5], 3.44 (s, 9 H, OCH$_3$), 3.77 (s, 9 H, PhOMe), 6.79–7.59 (m, 32 H, aromatic protons); ^{31}P-{^{1}H} (81.02 MHz, CH$_2$Cl$_2$–CD$_2$Cl$_2$, 233 K), δ −18.1 [dd, P^2(Cd), $^{2+3}$*J*(P^1–P^2) = 107, ^{2}*J*(P^2–P^3) = 77], −6.1 [d, P^3(Cd), ^{2}*J*(P^2–P^3) = 77, ^{1}*J*(P–^{111}Cd/^{113}Cd) = 1186/1238] and 60.0 [d, P^1(Fe), $^{2+3}$*J*(P^1–P^2) = 107, $^{2+3}$*J*(P–Cd) = 76 Hz].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl{Ph$_2$PCH$_2$C(O)Ph}] **4b**. Solid Ph$_2$PCH$_2$C(O)Ph (0.304 g, 1 mmol) was added to a stirred solution of complex **2a** (0.794 g, 0.5 mmol) in CH$_2$Cl$_2$ (15 cm^3). After stirring for 1 h, the clear yellowish solution was concentrated to half volume and an equivalent volume of hexane added. Yellow microcrystals of solvated **4b**·CH$_2$Cl$_2$ formed at −30 °C, which were collected by filtration and dried under vacuum (0.957 g, 81%) [Found: C, 52.40; H, 4.15. Calc. for C$_{51}$H$_{48}$CdClFeO$_7$P$_3$Si·CH$_2$Cl$_2$ (*M* = 1182.58): C, 52.80; H, 4.25%]. IR (CH$_2$Cl$_2$): ν(CO) 1982m, 1912s (sh), 1897vs, 1673m; (thf) 1982m, 1921m, 1896vs; FTIR (polyethylene) ν(CdCl) 250 (br) cm^{-1} NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 3.27 [t, 2 H, PCH$_2$, ^{2}*J*(P–H) = 9.8], 3.47 (s, 9 H, OCH$_3$), 4.02 [d, 2 H, CH$_2$C(O), ^{2}*J*(P–H) = 1.4] and 7.03–7.97 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, CH$_2$Cl$_2$–CD$_2$Cl$_2$, 233 K), δ −22.9 [d, P^3(Cd), ^{2}*J*(P^2–P^3) = 50, ^{1}*J*(P–^{111}Cd/^{113}Cd) = 965/1020], −16.5 [dd, P^2(Cd), $^{2+3}$*J*(P^1–P^2) = 110, ^{2}*J*(P^2–P^3) = 50, ^{1}*J*(P–Cd) ≈ 110] and 60.0 [d, P^1(Fe), $^{2+3}$*J*(P^1–P^2) = 110, $^{2+3}$*J*(P–Cd) = 75]; (CD$_2$Cl$_2$, 298 K) δ −20.6 [s, P^3(Cd)], −17.4 [d, P^2(Cd), $^{2+3}$*J*(P^1–P^2) = 108] and 60.5 [br d, P^1(Fe), $^{2+3}$*J*(P^1–P^2) = 108 Hz]. Mass spectrum (fast atom bombardment, FAB): (positive ion) *m*/*z* 1063.0 (*M*$^+$ − CH$_2$Cl$_2$ − Cl); (negative ion) 1097.1 (*M*$^-$ − CH$_2$Cl$_2$) and 793 [*M*$^-$ − CH$_2$Cl$_2$ − Ph$_2$PCH$_2$C(O)Ph].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)CdCl(4-Me-py)] **4c**. This complex was prepared as detailed for **4b** by adding 4Me-py (0.058 cm^3, 0.6 mmol) *via* a microsyringe to a solution of **2a** (0.397 g, 0.25 mmol) in CH$_2$Cl$_2$ (12 cm^3). A colourless powder was obtained (0.405 g, 93%) [Found: C, 51.00; H, 4.50; N, 2.20. Calc. for C$_{37}$H$_{38}$CdClFeNO$_6$P$_2$Si (*M* = 872.4): C, 50.95; H, 4.40; N, 1.60%]. IR (CH$_2$Cl$_2$): ν(CO) 1980m, 1918s, 1884vs; FTIR (polyethylene) ν(CdCl) 261s(br) cm^{-1} NMR: ^{1}H (200 MHz, CDCl$_3$), δ 2.35 (s, *Me*-py, a slight excess of 4Me-py is present, which accounts also for the high value found for the N analysis), 3.04 [t, 2 H, CH$_2$, ^{2}*J*(P–H) = 9.1], 3.64 (s, 9 H, OCH$_3$) and 7.10–8.57 (m, 24 H, aromatic protons); ^{31}P-{^{1}H} (81.02 MHz, CH$_2$Cl$_2$–CD$_2$Cl$_2$, 243 K), δ −16.2 [d, P(Cd), $^{2+3}$*J*(P–P) = 102, ^{1}*J*(P–Cd) = 83] and 67.4 [d, P(Fe), $^{2+3}$*J*(P–P) = 102, $^{2+3}$*J*(P–Cd) = 60 Hz].

mer-[{(EtO)$_3$Si}(OC)$_3$Fe(μ-dppm)HgPh] **5a**. A solution of the potassium salt of **1**′$^-$ (0.727 g, 1 mmol) in thf (25 cm^3) was added at 0 °C to a solution of [HgPhCl] (0.313 g, 1 mmol) in thf (5 cm^3). The reaction mixture was stirred for 0.5 h. The yellow solution was filtered and evaporated to dryness under reduced pressure. The oily residue was dissolved in a mixture of Et$_2$O–hexane. After a few days at −20 °C yellow microcrystals of the product were formed and collected (0.704 g, 73%) [Found: C, 50.00; H, 4.45. Calc. for C$_{40}$H$_{42}$FeHgO$_6$P$_2$Si (*M* = 965.24): C, 49.75; H, 4.40%]. IR (CH$_2$Cl$_2$): ν(CO) 2003m, 1941(sh) and 1923vs cm^{-1} NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 1.25 [t, 9 H, CH$_3$, ^{3}*J*(H–H) = 7.0], 3.30 [dd, 2 H, PCH$_2$, ^{2}*J*(P–H) = 9.4 and 3.3], 3.97 [q, 6 H, OCH$_2$, ^{3}*J*(H–H) = 7.0] and 7.10–7.53 (m, 25 H, C$_6$H$_5$); ^{31}P-{^{1}H} [81.02 MHz, toluene–(CD$_3$)$_2$CO, 243 K], δ −19.4 [d, P(Hg), ^{1}*J*(P–Hg) = 480, $^{2+3}$*J*(P–P) = 116], 57.6 [d, P(Fe), $^{2+3}$*J*(P^1–P^2) = 116, ^{2}*J*(P–Hg) = not resolved]; (298 K) δ −20.9 [d, P(Hg), ^{1}*J*(P–Hg) = 360, $^{2+3}$*J*(P–P) = 115] and 56.7 [d, P(Fe), $^{2+3}$*J*(P–P) = 115, $^{2+3}$*J*(P–Hg) = 29 Hz).

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Hg(C$_6$Cl$_5$)] **5b**. The synthesis was similar to that described for complex **5a**, starting from [Hg(C$_6$Cl$_5$)Cl] and the potassium salt of **1**$^-$ [Found: C, 40.75; H, 3.00. Calc. for C$_{37}$H$_{31}$Cl$_5$FeHgO$_6$P$_2$Si (*M* = 1095.39): C, 40.55; H, 2.85%]. IR (CH$_2$Cl$_2$): ν(CO) 2015m, 1953(sh) and 1944vs(br) cm^{-1}. NMR: ^{1}H (200 MHz, CDCl$_3$, 320 K), δ 3.16 [dd, 2 H, PCH$_2$, ^{2}*J*(PH) = 9.9 and 3.2], 3.69 (s, 9 H, CH$_3$) and 7.10–7.53 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} [81.02 MHz, CH$_2$Cl$_2$–(CD$_3$)$_2$CO], δ −10.9 [d, P(Hg), ^{1}*J*(P–^{199}Hg) = 600, $^{2+3}$*J*(P–P) = 133] and 67.1 [d, P(Fe), $^{2+3}$*J*(P–P) = 133, $^{2+3}$*J*(P–^{199}Hg) = 244 Hz].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)HgCl{Ph$_2$PCH$_2$C(O)Ph}] **6**. Solid Ph$_2$PCH$_2$C(O)Ph (0.304 g, 1 mmol) was added to a stirred solution of *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)HgCl] (0.882 g, 1 mmol) in CH$_2$Cl$_2$ (15 cm^3). After being stirred for 1 h, the clear, pale yellow solution was concentrated and hexane was added. Pale yellow microcrystals of solvated complex **6** formed at −30 °C, which were collected by filtration and dried under vacuum (0.805 g, 68%) [Found: C, 52.25; H, 4.35. Calc. for C$_{51}$H$_{48}$ClFeHgO$_7$P$_3$Si (*M* = 1185.83): C, 51.65; H, 4.10%]. IR (KBr): ν(CO) 2006ms, 1944s, 1914s and 1673m cm^{-1}. NMR: ^{1}H (200 MHz, CD$_2$Cl$_2$), δ 3.41 [dd, 2 H, PCH$_2$, ^{2}*J*(P–H) = 10.4 and 7.1], 3.48 (s, 9 H, OCH$_3$), 4.42 [br s, 2 H, CH$_2$C(O)] and 7.07–7.83 (m, 35 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, CH$_2$Cl$_2$–CD$_2$Cl$_2$, 243 K), δ 3.9 [dd, P^2(Hg), $^{2+3}$*J*(P^1–P^2) = 135, ^{2}*J*(P^2–P^3) = 45, ^{1}*J*(P–Hg) = 1490], 24.9 [d, P^3(Hg), ^{2}*J*(P^2–P^3) = 45, ^{1}*J*(P–Hg) = 1615] and 58.1 [d, P^1(Fe), $^{2+3}$*J*(P^1–P^2) = 135, ^{2}*J*(P–Hg) = 297]; (298 K) δ −2.8 [d, P^2(Hg), $^{2+3}$*J*(P^1–P^2) = 134, ^{1}*J*(P–Hg) = 1670], −2.0 [br, P^3(Hg)] and 54.2 [d, P^1(Fe), $^{2+3}$*J*(P^1–P^2) = 134, $^{2+3}$*J*(P–Hg) = 397 Hz].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Cd{Ph$_2$PCH$_2$C(O)Ph}][PF$_6$] **7**. Solid Tl[PF$_6$] (0.074 g, 0.21 mmol) was added to a solution of complex **4b** (0.211 g, 0.19 mmol) in CH$_2$Cl$_2$ (5 cm^3). After being stirred for 4 h the clear, pale yellow solution was filtered, concentrated and pentane was added. Pale yellow microcrystals of complex **7** formed at −30 °C, which were collected by filtration and dried under vacuum (0.204 g, 89%) [Found: C, 50.70; H, 3.80. Calc. for C$_{51}$H$_{48}$CdF$_6$FeO$_7$P$_4$Si (*M* = 1207.2): C, 50.75; H, 4.00%]. IR (CH$_2$Cl$_2$): ν(CO) 1991s, 1925s, 1894vs and 1627m cm^{-1}. NMR: ^{1}H (200 MHz, CDCl$_3$), δ 3.29 [t, 2 H, PCH$_2$, ^{2}*J*(P–H) = 9.5], 3.44 (s, 9 H,

Table 2 Fractional atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for the non-hydrogen atoms of complex **2a**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cd	691(1)	2015(1)	2016(1)
Fe	1553(1)	2789(1)	1444(1)
Cl	362(1)	1874(2)	3340(2)
P(1)	2114(2)	1718(2)	1592(2)
P(2)	1147(1)	505(2)	1779(2)
Si	942(2)	3808(3)	1193(3)
O(1)	2417(4)	3803(7)	801(6)
O(2)	1496(4)	3516(6)	2896(6)
O(3)	1051(5)	2071(7)	137(5)
O(4)	328(5)	3617(8)	1562(7)
O(5)	849(10)	4023(14)	281(13)
O(6)	1163(6)	4652(8)	1564(7)
C(1)	2077(7)	3384(9)	1049(7)
C(2)	1502(6)	3197(7)	2338(8)
C(3)	1227(6)	2357(8)	672(9)
C(4)	−228(10)	3979(15)	1435(14)
C(5A)	1095(43)	4581(60)	131(52)
C(5B)	551(31)	3750(45)	−304(44)
C(6)	892(16)	5444(24)	1516(23)
C(7)	1789(5)	792(7)	1275(6)
C(8)	2743(5)	1762(7)	1004(7)
C(9)	3216(8)	2144(9)	1245(10)
C(10)	3674(7)	2258(10)	773(12)
C(11)	3663(9)	1996(11)	72(11)
C(12)	3196(9)	1645(12)	−155(10)
C(13)	2741(7)	1535(11)	295(8)
C(14)	2406(6)	1426(8)	2485(7)
C(15)	2227(7)	1765(9)	3135(7)
C(16)	2446(9)	1516(11)	3802(8)
C(17)	2791(9)	872(12)	3809(9)
C(18)	2970(8)	517(11)	3173(9)
C(19)	2780(7)	782(8)	2514(8)
C(20)	789(6)	−158(7)	1148(7)
C(21)	241(7)	−344(10)	1253(9)
C(22)	−62(7)	−836(11)	789(10)
C(23)	196(8)	−1154(10)	214(10)
C(24)	741(9)	−990(8)	82(8)
C(25)	1064(7)	−485(8)	528(7)
C(26)	1404(5)	−153(7)	2479(6)
C(27)	1356(7)	27(9)	3196(7)
C(28)	1565(8)	−466(12)	3742(8)
C(29)	1817(8)	−1163(10)	3561(11)
C(30)	1889(8)	−1374(10)	2853(9)
C(31)	1677(7)	−852(8)	2311(8)
C(32)	862(26)	3063(34)	−1769(35)
C(33)	330(17)	2804(27)	−2056(26)
C(34)	361(16)	2127(25)	−2557(25)

OCH$_3$), 4.46 [d, 2 H, CH$_2$C(O), ^2J(P–H) = 8.0] and 7.11–8.19 (m, 35 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, CH$_2$Cl$_2$–CD$_2$Cl$_2$, 233 K), δ −147.9 [spt, PF$_6^-$, ^1J(P–F) = 712], −12.4 [d, P^3(Cd), ^2J(P^2–P^3) = 46, ^1J(P–^{111}Cd/^{113}Cd) = 1344], −6.7 [dd, P^2-(Cd), ^{2+3}J(P^1–P^2) = 102, ^2J(P^2–P^3) = 46] and 63.5 [d, P^1(Fe), ^{2+3}J(P^1–P^2) = 106]; (298 K) δ −143.4 [spt, PF$_6^-$, ^1J(P–F) = 713], −9.7 [br s, P^3(Cd)], −4.2 [d, P^2(Cd), ^{2+3}J(P^1–P^2) = 100] and 67.3 [d, P^1(Fe), ^{2+3}J(P^1–P^2) = 106 Hz].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Hg{Ph$_2$PCH$_2$C(O)-Ph}][PF$_6$] **8**. Solid Tl[PF$_6$] (0.078 g, 0.2 mmol) was added to a solution of complex **6** (0.118 g, 0.1 mmol) in CH$_2$Cl$_2$ (5 cm^3). After vigorous stirring for 4 h the IR spectrum of the filtered solution showed a shift of all the ν(CO) absorptions: 2025m, 1959vs(br) and 1664m cm^{-1}. The yellow product was isolated in 90% yield. ^{31}P-{^{1}H} NMR (81.02 MHz, CH$_2$Cl$_2$–CD$_2$Cl$_2$, 298 K): δ −147.6 [spt, PF$_6^-$, ^1J(P–F) = 712], 15.8 [dd, P^2(Hg), ^{2+3}J(P^1–P^2) = 142, ^2J(P^2–P^3) = 58, ^1J(P–Hg) = 1924], 48.9 [slightly broadened dd, P^3(Hg), ^{3+4}J(P^1–P^3) = 9, ^2J(P^2–P^3) = 58, ^1J(P–Hg) = 590] and 58.8 [dd, P^1(Fe), ^{2+3}J(P^1–P^2) = 142, ^{3+4}J(P^1–P^3) = 9, ^{2+3}J(P–Hg) = 354 Hz].

mer-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Tl(C$_6$F$_5$)$_2$] **9**. A solution of the potassium salt of **1**$^{-1}$ (0.685 g, 1 mmol) in thf (25 cm^3) was slowly added at 25 °C over 1 h *via* a dropping funnel to a thf solution of [TlBr(C$_6$F$_5$)$_2$] (0.620 g, 1 mmol). After the reaction was completed (1 h, IR monitoring), the yellowish clear solution was filtered and evaporated to dryness. The product formed an oily residue which was triturated in Et$_2$O to produce a yellow powder (1.006 g, 85%) [Found: C, 44.35; H, 2.65. Calc. for C$_{43}$H$_{31}$F$_{10}$FeO$_6$P$_2$SiTl (*M* = 1183.97): C, 43.60; H, 2.65%]. IR (thf): ν(CO) 2028m, 1969(sh) and 1962vs(br) cm^{-1} NMR: ^{1}H (200 MHz, CDCl$_3$, 328 K), δ 3.40 [dt, 2 H, PCH$_2$, ^2J(P–H) = 10.1, ^3J(H–^{203}Tl/^{205}Tl) = 58.1], 3.68 (s, 9 H, CH$_3$) and 6.8–7.5 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, CH$_2$Cl$_2$–C$_6$D$_6$), δ −14.0 [dd, P(Tl), ^1J(P–^{203}Tl/^{205}Tl) = 6765, ^{2+3}J(P–P) = 126] and 60.6 [dd, P(Fe), ^{2+3}J(P–P) = 126, ^{2+3}J(P–^{203}Tl/^{205}Tl) = 895 Hz].

Crystal Structure Determination of mer-[{[(MeO)$_3$Si](OC)$_3$-Fe(μ-dppm)Cd(μ-Cl)}$_2$]·C$_6$H$_{14}$ **2a**·C$_6$H$_{14}$.—Crystals of complex **2a**·C$_6$H$_{14}$ were obtained by slow recrystallization from CH$_2$Cl$_2$–hexane. A crystal of approximate dimensions 0.20 × 0.24 × 0.26 mm was used for the X-ray analysis.

Crystal data. C$_{62}$H$_{62}$Cd$_2$Cl$_2$Fe$_2$O$_{12}$P$_4$Si$_2$·C$_6$H$_{14}$, *M* = 1672.80, orthorhombic, space group *Pbcn*, *a* = 23.498(9), *b* = 16.856(8), *c* = 18.220(8) Å, *U* = 7217(5) Å^3 (by least-squares refinement from the θ values of 28 accurately measured reflections, λ = 0.710 73 Å), *Z* = 4, D_c = 1.540 g cm^{-3}, *F*(000) = 3400, μ(Mo-Kα) = 12.24 cm^{-1}.

Data collection and processing. Siemens AED single-crystal diffractometer (θ–2θ scan mode, niobium-filtered Mo-Kα radiation). All reflections with θ in the range 3–25° were measured; of 7555 independent reflections, 2906 having $I > 2\sigma(I)$, were considered observed and used in the analyses. The individual profiles were analysed according to Lehmann and Larsen.[15] No correction for absorption effects was applied because of the low absorbance of the sample.

Structure solution and refinement. Patterson and Fourier methods, full-matrix least-squares refinements with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except those of the methoxy groups, one of which was found disordered and distributed in two positions [C(5A) and C(5B)] of equal occupancy factors. In the final ΔF map a hexane molecule of solvation, having crystallographically C_2 symmetry, was found and refined isotropically. All the hydrogen atoms, except those of the very agitated methyl groups and of the hexane molecule, were placed at their calculated positions (C–H 1.00 Å) and refined 'riding' on the corresponding carbon atoms. A weighting scheme $w = K[\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with *K* = 0.685 and *g* = 0.0052. Final *R* and *R′* values were 0.0653 and 0.0716 respectively. The SHELX 76 and SHELXS 86 systems of computer programs were used.[16] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 17. Final atomic coordinates for the non-hydrogen atoms are given in Table 2.

All calculations were carried out on the CRAY X-MP/12 computer of the Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale, Bologna and on the Gould Powernode 6040 of the Centro di Studio per la Strutturistica Diffrattometrica del C.N.R., Parma.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

Acknowledgements

We are grateful to Professor U. Schubert (University Würzburg, Germany) for fruitful discussions. Financial support from the Centre National de la Recherche Scientifique (Paris), the Alexander von Humboldt-Stiftung (Bad-Godesberg) (to P. B.), the 'Deutsche Forschungsgemeinschaft' (Bonn) (to M. K.), and the Commission of the European Communities (Contract No. ST2J-0479) is gratefully acknowledged.

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Received 29*th July* 1991; *Paper* 1/03886I