Occurrence of a μ-SiF Interaction in Bimetallic Trifluorosilyl Complexes *

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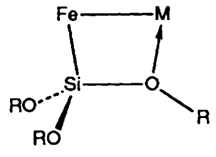
With the aim of inducing a μ-SiF interaction between two metal centres, MeO was replaced by F on the silicon atom involved in μ-SiO bonding with a bimetallic unit by the reaction of *mer*-[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl)] **1** (dppm = Ph$_2$PCH$_2$PPh$_2$) with BF$_3$. However, the desired complex *mer*-[(OC)$_3$Fe{μ-SiF$_2$(F)}(μ-dppm)PdCl] **3** could only be characterised in solution. From the solution structure of the reaction intermediate *mer*-[(OC)$_3$Fe{μ-SiF$_2$(OMe)}(μ-dppm)PdCl] **2** where a MeO→Pd interaction in preference to F→Pd is suggested on the basis of spectroscopic data, it appears that the dative F→Pd interaction is weaker than the corresponding MeO→Pd one. In the presence of an excess of BF$_3$, rupture of the Fe–Si bond of **3** eventually occurred in CH$_2$Cl$_2$, resulting in the formation of [(OC)$_3$Fe(μ-Cl)(μ-dppm)PdCl] **4a**. When the complex *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **5** was treated with BF$_3$·Et$_2$O, the trifluorosilyl derivative *mer*-[(F$_3$Si)(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **6** was obtained and isolated in 87% yield. The structure of its benzene solvate **6**·0.5C$_6$H$_6$ was determined by X-ray diffraction: triclinic, space group $P\bar{1}$, a = 17.692(7), b = 13.084(5), c = 11.031(5) Å, α = 112.16(1), β = 91.31(2), γ = 101.71(1)° and Z = 2. It has been solved by Patterson and Fourier methods and refined by full-matrix least squares to R = 0.0408 for 5870 observed reflections. The Fe and Pt atoms are at a distance of 2.661(1) Å, consistent with a metal–metal bond. The nearly square-planar co-ordination of Pt involves also one P atom from dppm, one PPh$_3$ and a hydride. The co-ordination of Fe is completed by three carbonyl groups, a P atom of the dppm ligand, and the SiF$_3$ ligand. Noteworthy are the weak intramolecular interactions between the hydride and two F atoms from the SiF$_3$ ligand [H ··· F 2.39(7) and 2.50(6) Å]. The IR and NMR (^{1}H, ^{31}P-{^{1}H} and ^{19}F-{^{1}H}) spectra of the new complexes are reported and discussed.

In previous papers we have shown that suitable heterodinuclear cores Fe–M (M = Pd, Pt, Rh or Ag), stabilised by a bridging bis(diphenylphosphino)methane (Ph$_2$PCH$_2$PPh$_2$, dppm) ligand, may give rise to a μ-SiO bonded trialkoxysilyl group which is σ bonded to the iron centre.[1] The O→M donor interaction results in the formation of a stable, but often kinetically labile, four-membered ring system of type **A**.



A

The unprecedented nature of such interactions, together with their possible relevance to surface phenomena,[2] has prompted a study of their scope with respect to the nature of the metals M as well as of the substituents at silicon. Since some successful attempts have been made to transform M–Si–OR linkages in M–Si–F groups in mononuclear transition metal–silicon complexes,[3] we have tried to apply similar methods to heterodinuclear systems. Here we describe our efforts to replace the methoxy groups on the silicon atom by fluorines in Fe–Pd and Fe–Pt complexes and report the crystal structure of the trifluorosilyl bimetallic complex *mer*-[(F$_3$Si)(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **6**.

Results and Discussion

Dropwise addition of a solution of BF$_3$·Et$_2$O in dichloromethane to a solution of *mer*-[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl] **1**[1a] in CH$_2$Cl$_2$ resulted in rapid disappearance of **1** [equation (1)]. Monitoring by IR spectroscopy in the ν(CO) region showed a progressive shift of the absorptions due to **1** at 1995s, 1941vs and 1918s cm^{-1} towards higher frequency, consistent with the formation of structurally related complexes and the stepwise substitution of the methoxy groups by the more electron-withdrawing fluorine atoms. The fully fluorinated complex finally exhibits in CH$_2$Cl$_2$ three absorptions at 2015s, 1960 (sh) and 1947s cm^{-1} with a very similar pattern to the IR spectrum of **1**, thus indicating that the meridional arrangement of the carbonyl ligands has been retained. This red trifluorosilyl derivative is the main reaction

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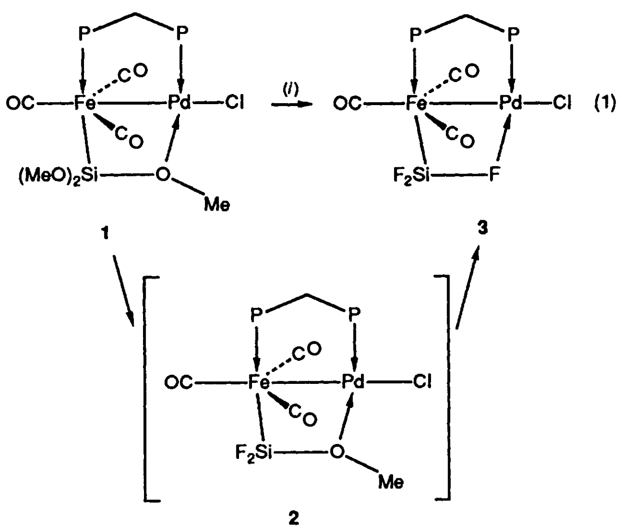
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



Scheme 1 (*i*) $BF_3 \cdot xEt_2O$, $-B(OMe)_3$

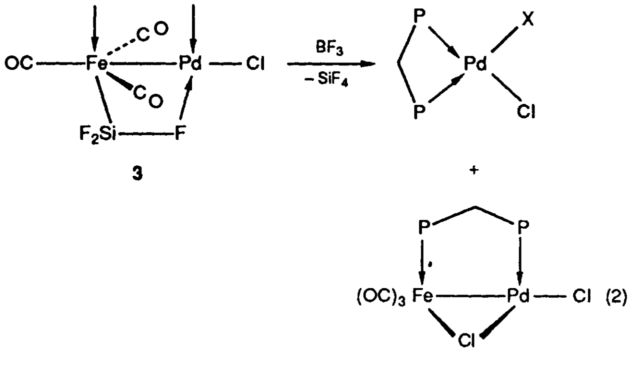
product but could only be characterisd spectroscopically in solution. Its IR and $^{31}P-\{^1H\}$ and $^{19}F-\{^1H\}$ NMR data (see below) are consistent with its formulation as *mer*-$[(OC)_3Fe\{\mu-SiF_2(F)\}(\mu-dppm)PdCl]$ **3**. A deep red intermediate complex **2** could be isolated before completion of the reaction by precipitation with hexane. Its IR absorptions (CH_2Cl_2) at 2008s, 1955vs and 1941 (sh) cm^{-1} are intermediate between those of **1** and **3**. The $^{31}P-\{^1H\}$ NMR spectrum of **2** contains two resonances centred at δ 44.3 (dt) for the phosphorus bound to Fe and at δ 31.9 (d) for that bound to Pd. These chemical shifts as well as the J(PP) coupling constant of 54 Hz are quite similar to those for **1**, but the resonance at δ 44.3 shows further coupling to two equivalent fluorine nuclei which gives rise to a triplet splitting with $^3J(PF) = 21$ Hz. The absence of a $^2J[P(Pd)F]$ coupling is a further indication of a preferred MeO⟶Pd over F⟶Pd interaction, suggesting a weaker F⟶Pd bonding. On the basis of these spectroscopic data, we therefore assign to **2** the structure shown in Scheme 1.

When a *ca.* 10% excess of $BF_3 \cdot Et_2O$ was used in reaction (1) (to ensure completion) very broad $^{31}P-\{^1H\}$ resonances at δ 43.5 and 32.5 were observed at ambient temperature which are indicative of a dynamic phenomenon. This could result from intermolecular interactions between the methoxy group of complex **2**, possibly present in minor amount, and BF_3, a kind of interaction that may well precede the substitution of F for MeO, and/or donor–acceptor interactions between the SiF_3 group of **3** and BF_3. Cooling the solution to 223 K slows this exchange process. Two sets of complex multiplets are then seen for **3** at δ 44.6 and 33.6 for the phosphorus atom bound to Fe or Pd, respectively. These were not analysed further but the presence of a F⟶Pd donor interaction is supported by the observation of ^{2+4}J(PF) couplings for the phosphorus on Pd [note that the ^4J(PF) coupling was not resolved in the spectrum of the partially fluorinated derivative **2**], of ^3J(PF) couplings of *ca.* 20 Hz for the phosphorus on Fe, and a ^{2+4}J(PP) coupling of *ca.* 58 Hz which appears to be characteristic of a dppm ligand bridging a Fe–M unit of type **A**.[1] Further evidence for the structure of complex **3** is provided by the $^{19}F-\{^1H\}$ NMR spectrum of the reaction mixture which showed a set of poorly resolved resonances which contained a doublet at δ −87.3 [$^3J(PF) = 21$ Hz, ^1J(SiF) not resolved] and a less-intense, broader resonance at δ −87.6, a pattern possibly consistent with the presence of chemically different fluorine nuclei. These chemical shifts lie in the range typical of SiF_3-substituted transition-metal complexes.[4a,5] Malisch[4a] has reported that, within a series of complexes, increasing the number of fluorine ligands on silicon leads to a change of the chemical shifts from *ca.* δ −110 to −130 for $SiFR_2$ to *ca.* δ −80 for SiF_3 derivatives.

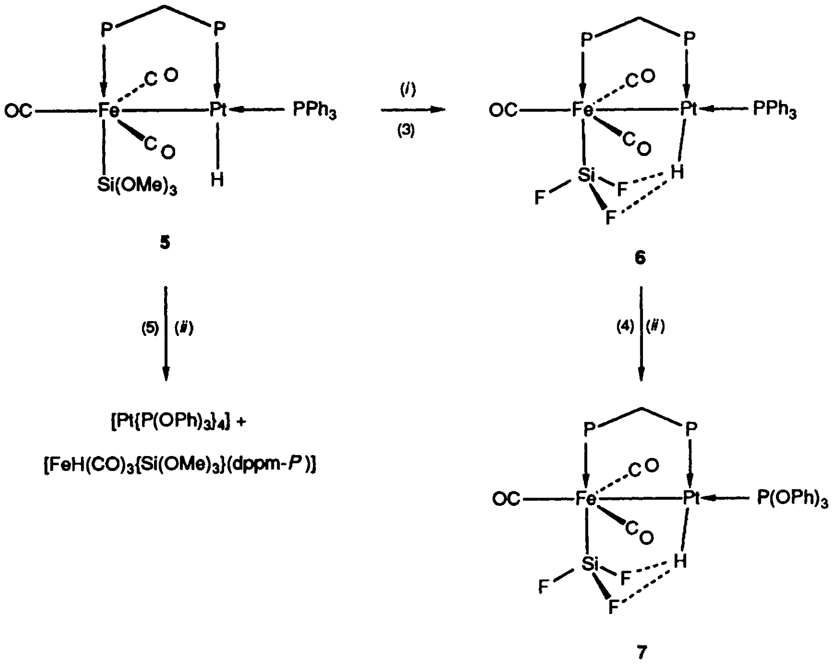
Relatively weak fluorinating agents are also able to replace methoxy groups at Si by fluorine, as observed during the reaction of complex **1** with excess of $AgBF_4$ in CH_2Cl_2, which afforded cationic complexes of the type *mer*-$[(OC)_3Fe\{\mu-SiF_n(OMe)_{3-n}\}(\mu-dppm)Pd(solv)][BF_4]$ [IR evidence: ν(CO) 2010s, 1958vs and 1941s cm^{-1}]. However, no reaction between **1** and a three-fold excess of LiF in tetrahydrofuran–acetone occurred after 30 min.[4a]

The reaction of complex **1** with BF_3, leads readily to replacement of MeO by F on a silicon atom involved in μ-SiO bonding with a bimetallic unit. Previous studies have shown that such a ligand exchange at Si may be performed on mononuclear complexes such as $[Fe(cp)(CO)_2\{Si(OMe)_3\}]$ (cp = η-C_5H_5), leading to $[Fe(cp)(CO)_2(SiF_3)]$.[3b] In this case too, progressive substitution of the methoxy groups was observed in the presence of HPF_6. The occurrence of a μ-SiF interaction in **3** rests at the moment on spectroscopic data, but represents an interesting extension to the recently discovered μ-SiO interactions.[1] In this context, it is worth mentioning that an interaction between a palladium(II) centre and a SiF_3 group of a phoshine ligand was discussed recently for *trans*-$[PdCl_2(Me_2PCH_2CH_2SiF_3)_2]$.[6] Although it was described as occurring solely through the Si atom, the existence of Si–F–Pd interactions of the type found in **3** would represent an interesting alternative consistent with the spectroscopic data reported.

In the presence of excess of BF_3, rupture of the Fe–Si bond of **3** eventually occurred in CH_2Cl_2, resulting in the formation of $[(OC)_3Fe(\mu-Cl)(\mu-dppm)PdCl]$ **4a** [equation (2)]. The $^{31}P-\{^1H\}$ NMR spectrum of **4a** contains an AX pattern with a doublet for the P atom co-ordinated to Fe at δ 62.5 [$^2J(PP) = 22$ Hz] and the corresponding doublet for the Pd-bound P atom at δ 8.8. This complex was unambiguously identified by its transformation [addition of NaI to a tetrahydrofuran (thf) solution of **4a**] to $[(OC)_3Fe(\mu-I)(\mu-dppm)PdI]$ **4b** which was compared with a structurally characterised authentic sample,[7a] which has a similar Fe–Pt analogue.[7b] The Cl ligands present in complex **4a** originate from the solvent (CH_2Cl_2). In addition to the loss of the silicon substituent, which has been observed in similar reactions,[4a] partial fragmentation of the metal–metal bond also occurred as a palladium(II) complex containing a chelated dppm ligand was spectroscopically detected in solution ($^{31}P-\{^1H\}$ NMR: complex multiplet at δ −54.6). A dynamic situation is also observed for this complex, even as low as 243 K. At 223 K, coupling with F and P nuclei is partially resolved, giving rise to a multiplet structure (J *ca.* 20 Hz). This would be consistent with this complex being of the type *cis*-[Pd(dppm-*PP'*)Cl(X)] with X = BF_4 and a rapid dissociation of the Pd–X bond.[8]



Despite the fact that substitution at silicon of alkoxy groups with fluorine atoms should induce a strengthening of the Fe–Si



Scheme 2 (*i*) BF$_3$·*x*Et$_2$O, −B(OMe)$_3$; (*ii*) P(OPh)$_3$

bond[9] {see also below the results of the X-ray structure determination of *mer*-[(F$_3$Si)(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **6**}, the rupture of the Fe–Si bond of **3**, observed above, is favoured by the considerable bonding energy of the newly generated Si–F bond (*ca.* 595 kJ).[10] It has been recently observed that even HBF$_4$ may lead to iron–silicon bond cleavage in phosphido-bridged complexes of the type [(R$_3$Si)(OC)$_3$Fe(μ-PPh$_2$)Pt(PPh$_3$)$_2$] [R$_3$ = MePh$_2$ or (OMe)$_3$] and the resulting fluorosilane SiFR$_3$ could be detected.[11] In addition, mononuclear SiR$_3$-substituted complexes of Cr, W and Fe have been previously shown to react with BF$_3$ with breaking of the M–Si bond.[4]

When the bimetallic hydrido complex *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **5** was treated with BF$_3$·Et$_2$O the new complex *mer*-[(F$_3$Si)(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **6** was obtained and isolated in 87% yield [equation (3), Scheme 2]. Its ^{1}H NMR spectrum contains a triplet for the PCH$_2$P protons at δ 3.42 [^2J(PH) = 10.0 Hz] with platinum satellites [^3J(PtH) = 28.9 Hz]. The hydride resonance, which appears as a doublet of triplets [with the corresponding ^1J(^{195}Pt–H) satellites] for **5**, is further split here into quartets owing to coupling with the F nuclei [^2J(P$_{trans}$H) = 195, ^2J(P$_{cis}$H) ≈ ^3J(PH) = 14, ^4J(FH) = 3 Hz], which thus appear to be equivalent in solution (Fig. 1). The same pattern is observed in the satellites which result from coupling to ^{195}Pt [^1J(PtH) = 685 Hz]. The *J*(FH) coupling constant of 3 Hz may result from ^{3+4}J(HF) through-bond as well as from through-space interactions.[12] The ^{31}P-{^{1}H} NMR spectrum of **6** contains a complex multiplet at δ 72.3, assigned to the Fe-bound P atom. It could not be fully analysed but it exhibits couplings with the other dppm P atom [^{2+3}J(PP) = 114 Hz], the PPh$_3$ ligand, three fluorine nuclei and the platinum atom. The resonance at higher field for the Pt-bound dppm P atom, *ca.* δ 30 with corresponding ^1J(PtP) = 2145 Hz, partially overlaps with the resonance for the PPh$_3$ ligand on Pt, giving rise to a second order-type pattern. Further information is provided by the ^{19}F-{^{1}H} NMR spectrum (Fig. 2), which displays a slightly broadened doublet at δ −87.6 due to a ^3J[FP(Fe)] *trans* coupling of 20 Hz and additional coupling (not resolved) with the other phosphorus nucleus. In addition, ^3J(PtF) and ^1J(SiF) couplings of 58 and 388 Hz result in two sets of satellites having *ca.* 33 and 5% intensities, respectively. Despite the inequivalence between the fluorine nuclei due to the weak interaction found in the solid state (see below) between the hydride ligand and the SiF$_3$ moiety, all fluorine nuclei appear equivalent in the ^{19}F NMR spectrum, even at 183 K in CD$_2$Cl$_2$, since no coupling between fluorine ligands was observed in the low-temperature ^{19}F-{^{1}H} NMR spectrum of **6**.

The shift of the ν(CO) absorptions of complex **6** compared with those in **5** again results from the replacement of the OMe groups by the more electronegative fluorine atoms. The ν(Pt–H) frequency appears at 2101 cm^{-1}, compared to 2149 cm^{-1} for **5**, consistent with the H···F interactions observed in the solid-state structure of **6**. When a two-fold excess of [NEt$_4$]F·4H$_2$O was added to a CH$_2$Cl$_2$–acetone solution of **5** a progressive darkening occurred. However, after 9 h of stirring, the IR and ^{31}P-{^{1}H} NMR spectra of the solution showed only the presence of the starting material.

Complex **6** reacts with a slight excess of P(OPh)$_3$ to give the substitution product **7** [equation (4), Scheme 2]. The spectroscopic features of **7** are similar to those for **6**, indicating a similar structure, with a ^2J(P$_{cis}$H) coupling constant of 14 Hz, greater than for **6**, as expected for a phosphite *vs.* a phosphine complex. It is noteworthy that when its trimethoxysilyl analogue **5** was treated with an equimolar amount of P(OPh)$_3$ we were not able to detect a substitution product, but reductive elimination of Pt^0 and formation of a Fe–H bond occurred instead [equation (5)]. In addition to [FeH(CO)$_3${Si(OMe)$_3$}(dppm-*P*)] and [Pt{P(OPh)$_3$}$_4$] [^{31}P-{^{1}H} NMR: δ 98.8, ^1J(PtP) = 5868 Hz[13]], only unreacted **5** was detected. The latter completely disappears when excess of P(OPh)$_3$ is used. This difference in reactivity may be related to the fact that the platinum centre is more electron rich in **5** than in **6**, thus facilitating the reductive-elimination pathway.

Crystal Structure of mer-[(F$_3$Si)(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)]·0.5C$_6$H$_6$ **6**·0.5C$_6$H$_6$.—In the crystal, molecules of complex **6** and benzene molecules of solvation, having an imposed crystallographic C_i symmetry, are present and separated by normal van der Waals contacts. The structure of the dinuclear complex is shown in Fig. 3 together with the atomic numbering scheme. Selected bond distances and angles are given in Table 1.

The iron and platinum centres are linked by a dppm bridge and a metal–metal bond [Fe–Pt 2.661(1) Å]. This distance is in

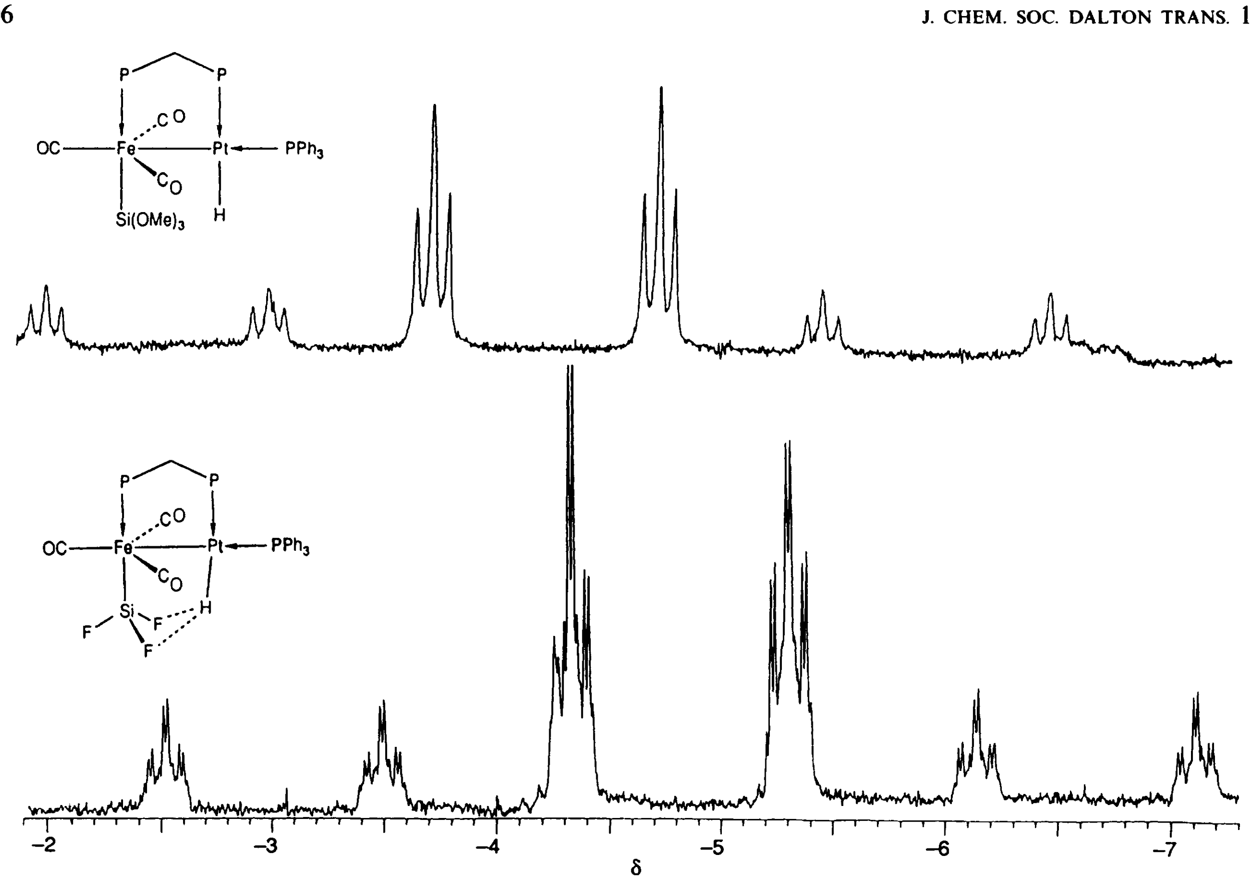


Fig. 1 Proton NMR spectra (200 MHz) in the hydride region of complexes *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$)] **5** (top, in CDCl$_3$) and *mer*-[(F$_3$Si)(OC)$_3$Fe(μ-dppm)PtH(PPh$_3$] **6** (bottom, in CD$_2$Cl$_2$)

Table 1 Selected bond distances (Å) and angles (°) in complex **6**

Pt–Fe	2.661(1)	Fe–C(3)	1.766(8)
Pt–P(2)	2.318(2)	Si–F(1)	1.584(5)
Pt–P(3)	2.225(2)	Si–F(2)	1.578(8)
Pt–H(1)	1.71(8)	Si–F(3)	1.575(7)
Fe–P(1)	2.242(3)	C(1)–O(1)	1.134(11)
Fe–Si	2.249(3)	C(2)–O(2)	1.146(12)
Fe–C(1)	1.756(9)	C(3)–O(3)	1.164(10)
Fe–C(2)	1.776(10)		
Fe–Pt–P(2)	94.9(1)	C(1)–Fe–C(2)	111.0(4)
P(2)–Pt–P(3)	103.9(1)	C(1)–Fe–C(3)	106.9(4)
P(3)–Pt–H(1)	80(3)	Pt–Fe–C(1)	170.8(3)
Fe–Pt–H(1)	81(3)	C(2)–Fe–C(3)	140.8(5)
Pt–Fe–P(1)	94.3(1)	P(1)–Fe–Si	175.8(1)
P(1)–Fe–C(1)	92.8(3)	Fe–Si–F(1)	115.3(3)
P(1)–Fe–C(2)	92.7(3)	Fe–Si–F(2)	119.9(3)
P(1)–Fe–C(3)	95.2(3)	Fe–Si–F(3)	117.8(3)
Pt–Fe–Si	88.2(1)	F(1)–Si–F(2)	98.2(4)
Si–Fe–C(1)	85.0(3)	F(1)–Si–F(3)	100.7(4)
Si–Fe–C(2)	84.8(3)	F(2)–Si–F(3)	101.4(4)
Si–Fe–C(3)	88.8(3)	Fe–C(1)–O(1)	179.6(9)
Pt–Fe–C(2)	74.6(3)	Fe–C(2)–O(2)	177.4(9)
Pt–Fe–C(3)	66.6(3)	Fe–C(3)–O(3)	173.6(8)

the middle of the range reported for bimetallic complexes containing such a bond (2.522–2.799 Å, Cambridge Crystallographic Data Centre). The environment of the Fe atom is determined by the Pt atom, by a phosphorus atom from the dppm ligand [Fe–P(1) 2.242(3) Å], by a Si atom from the SiF$_3$ ligand [Fe–Si 2.249(3) Å] and by three carbon atoms from terminal carbonyl groups. It may be viewed as distorted octahedral, consistent with a formal Fe(d^7)–Pt(d^9) situation, or alternatively as a distorted trigonal bipyramid, corresponding to a formal dative Fe(d^8)→Pt(d^8) interaction. This environment is similar to that found in several other bimetallic complexes in which a trimethoxysilyl group is terminally bound to iron, as in *mer*-[{(MeO)$_3$Si}(OC)$_3$Fe(μ-dppm)Cu(PPh$_3$)] [Fe–P 2.226(3) and Fe–Si 2.271(4)] [1d] or forms a μ-SiO bridge between adjacent metals, as in *mer*-[(OC)$_3$Fe{μ-Si(OMe)$_2$(OMe)}(μ-dppm)PdCl] [1a] [Fe–P 2.241(2) and Fe–Si 2.275(2) Å]. Although one would anticipate a shortening of the Fe–Si bond with increasing the number of F substituents at Si,[9] it is interesting that the Fe–Si distance appears much less sensitive to electronic effects induced by the substituents at Si than are the ν(CO) frequencies of the Fe(CO)$_3$ moiety. The square-planar co-ordination around the platinum atom involves the Fe atom, a phosphorus atom from the dppm ligand [Pt–P(2) 2.318(2) Å], a phosphorus atom from a PPh$_3$ ligand [Pt–P(3) 2.225(2) Å] and a hydride [Pt–H(1) 1.71(8) Å]. The Pt atom is displaced by 0.053(1) Å out of the mean plane passing through the Fe, P(2), P(3) and H(1) atoms. The Pt–P(2) bond length, significantly greater than that of Pt–P(3), indicates the higher *trans* influence of the hydride ligand with respect to the metal–metal (Fe–Pt) bond.

The Si–F distances, 1.575(7), 1.578(8) and 1.584(5) Å, are significantly shorter than those in *e.g.* [Fe(cp)(CO)$_2$(SiFPh$_2$)] [1.624(2) Å] [14a] or [Fe(cp)H(CO)(SiF$_2$Me)$_2$] [1.591(2) and 1.601(2) Å].[14b] The separations between the hydride H(1) and the fluorine atoms F(2) and F(3) [H(1)···F(2) 2.50(6) and H(1)···F(3) 2.39(7) Å] are consistent with weak attractive interactions, being slightly shorter than the sum of the van der Waals radii (1.20 and 1.47 Å).[12a] They should be compared with those in other systems where H···F interactions are present, as in [Ru$_2$(cp)$_2$(CO){CF$_2$=CF(CF$_3$)}(μ-CH$_2$)(μ-CO)] (calc. 2.23 Å) for which incipient H···F formation was discussed.[12b] In contrast, the very strong (and symmetrical) hydrogen bonding encountered in NaHF$_2$ and KHF$_2$ implies distances between the fluorine atoms involved in the F···H···F system of only

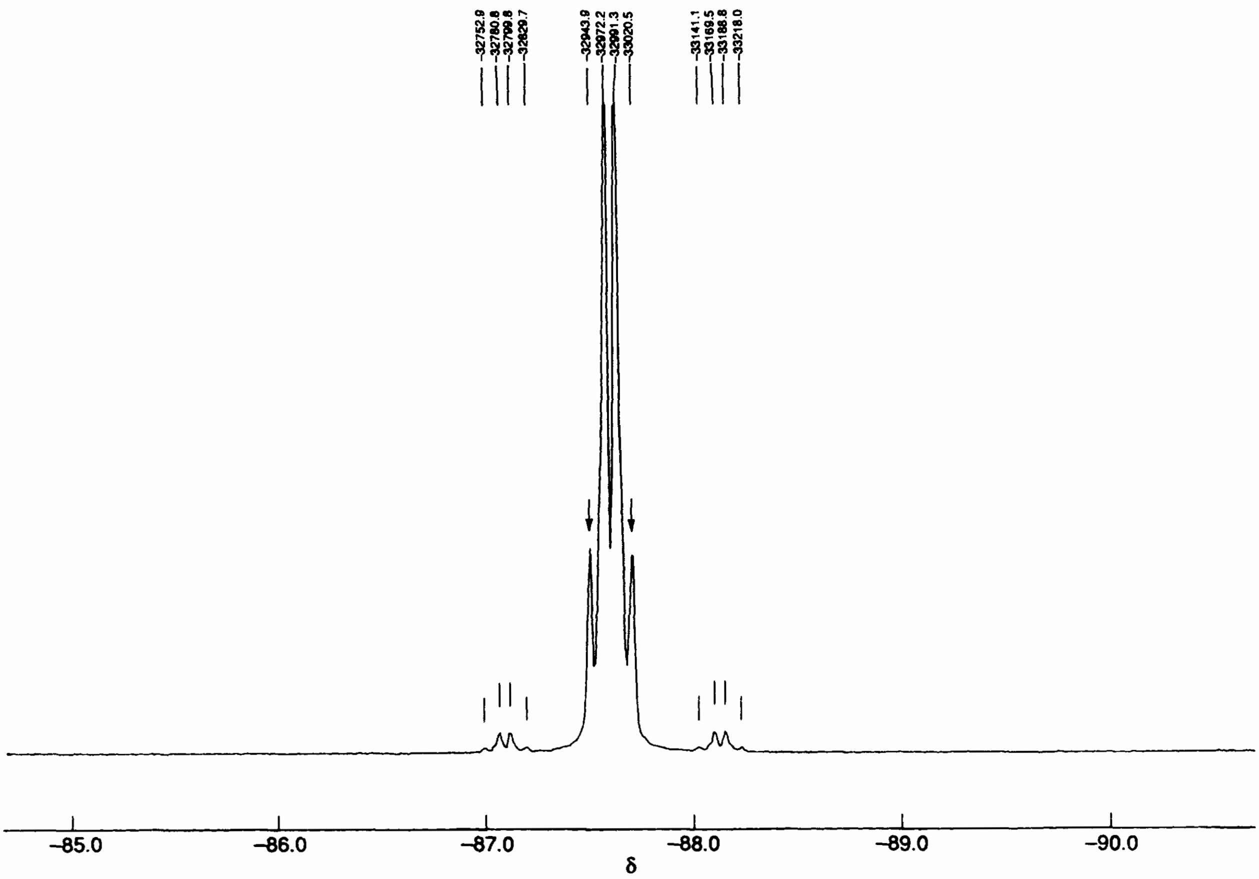


Fig. 2 $^{19}F-\{^1H\}$ NMR spectrum of complex **6** at 303 K in CD_2Cl_2. The resonances marked with an arrow belong to the ^{195}Pt satellites, those with a vertical line to the ^{29}Si satellites

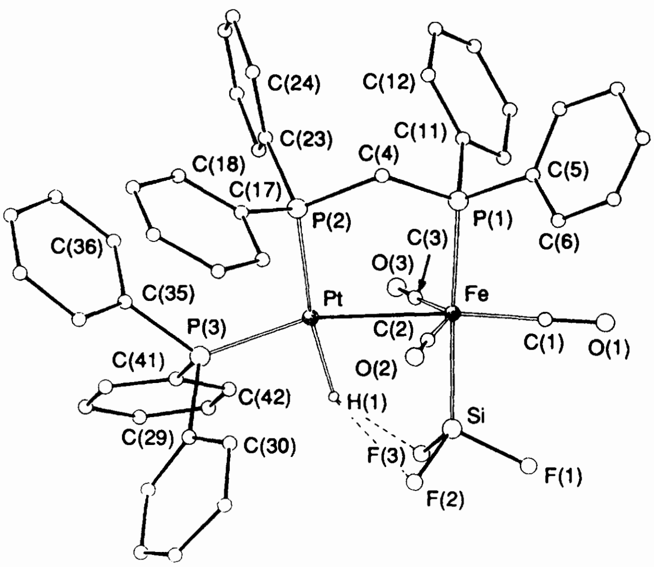


Fig. 3 View of the molecular structure of complex **6** with the atomic numbering scheme

2.27 and 2.292(4) Å; this distance becomes 2.49 and 2.45 Å in crystalline HF and KH_4F_5, respectively.[15] The tilting of the square-planar arrangement around Pt, which brings the hydride towards the two fluorine atoms, as shown in particular by the Fe–Pt–H(1) angle of 81(3)°, is also consistent with a weak H···F interaction. The large P(2)–Pt–P(3) angle of 103.9(1)° probably results from both the attractive H···F interactions and the presence of the bulky PPh_3 ligand *cis* to the Pt–H bond.

Experimental

All reactions were performed under dry nitrogen using standard Schlenk techniques. Solvents were freshly distilled under nitrogen from the usual drying agents prior to use. The complexes **1** and **5** were prepared according to the literature.[1a] Infrared spectra were obtained using a Perkin-Elmer 398 spectrometer, and NMR spectra on a Bruker WP 200 SY or AM 400 FT instrument (^1H, ^{31}P and ^{19}F chemical shifts are positive downfield from $SiMe_4$, H_3PO_4 and $CClF_3$, respectively).

Reaction of mer-$[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})PdCl]$ **1** *with* $BF_3 \cdot Et_2O$.—To a stirred solution of complex **1** (0.394 g, 0.5 mmol) in CH_2Cl_2 (10 cm^3) was added in two portions a solution of $BF_3 \cdot Et_2O$ (65 μl, 0.6 mmol) in CH_2Cl_2 (5 cm^3). The red solution immediately became dark red and the progress of the reaction was monitored by IR and ^{31}P NMR spectroscopy (see data in the text). After stirring for 24 h no complex with a Fe–Si bond was detected and only $[(OC)_3Fe(\mu\text{-}Cl)(\mu\text{-dppm})PdCl]$ **4a** and *cis*-[Pd(dppm-*PP'*)Cl(X)] (X = BF_4) were present in a *ca.* 3:1 ratio. Data for **4a**: IR (CH_2Cl_2) ν(CO) 2060s, 2010vs and 1980m (sh) cm^{-1}; $^{31}P-\{^1H\}$ NMR in the text.

Complex **4a** was transformed into $[(OC)_3Fe(\mu\text{-}I)(\mu\text{-dppm})PdI]$ **4b** by the addition of a three-fold excess of NaI in thf. IR (CH_2Cl_2): ν/cm^{-1}(CO) 2037s, 1990vs and 1973s (sh) cm^{-1}; $^{31}P-\{^1H\}$ NMR [81.02 MHz, $(CD_3)_2CO-CH_2Cl_2$]; δ 62.0 [d, P(Fe), $^{2+3}J(PP)$ = 26] and −10.5 [d, P(Pd), $^{2+3}J(PP)$ = 26 Hz]. These data were compared with those of a structurally characterised authentic sample.[7a]

Synthesis of mer-$[(F_3Si)(OC)_3Fe(\mu\text{-dppm})PtH(PPh_3)]$ **6**.—To a stirred solution of *mer*-$[\{(MeO)_3Si\}(OC)_3Fe(\mu\text{-dppm})PtH(PPh_3)]$ **5** (1.050 g, 0.95 mmol) in CH_2Cl_2 (25

Table 2 Fractional atomic coordinates (× 10^4) with estimated standard deviations in parentheses for complex **6**

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Pt	2536(1)	4908(1)	2226(1)
Fe	2173(1)	2657(1)	1039(1)
P(1)	1987(1)	2385(2)	2909(2)
P(2)	2172(1)	4949(2)	4246(2)
P(3)	2883(1)	6728(2)	2533(2)
Si	2274(2)	2846(2)	−898(2)
F(1)	2043(5)	1700(5)	−2163(6)
F(2)	1753(4)	3531(5)	−1313(6)
F(3)	3100(3)	3372(6)	−1180(6)
O(1)	1978(5)	261(5)	−503(7)
O(2)	695(4)	3312(6)	956(7)
O(3)	3856(3)	3516(6)	1656(7)
C(1)	2053(5)	1202(8)	99(9)
C(2)	1283(5)	3080(7)	1007(8)
C(3)	3182(5)	3237(7)	1446(8)
C(4)	1636(5)	3550(7)	4111(9)
C(5)	1230(5)	1175(7)	2812(8)
C(6)	580(6)	834(9)	1934(11)
C(7)	−34(7)	−60(10)	1904(12)
C(8)	28(8)	−612(12)	2675(14)
C(9)	646(9)	−300(13)	3586(15)
C(10)	1284(8)	637(11)	3640(13)
C(11)	2818(4)	2216(7)	3758(8)
C(12)	2977(5)	2659(8)	5110(10)
C(13)	3629(7)	2479(10)	5702(12)
C(14)	4101(7)	1892(10)	4953(12)
C(15)	3946(7)	1439(10)	3597(12)
C(16)	3316(6)	1618(8)	2989(10)
C(17)	1483(4)	5833(7)	4845(8)
C(18)	1615(5)	6777(8)	6011(10)
C(19)	1090(6)	7495(9)	6335(10)
C(20)	446(6)	7246(9)	5483(10)
C(21)	295(6)	6305(9)	4320(11)
C(22)	809(5)	5596(8)	4005(10)
C(23)	2932(4)	5347(7)	5594(8)
C(24)	2765(6)	5433(8)	6859(9)
C(25)	3369(7)	5652(9)	7830(12)
C(26)	4124(7)	5796(10)	7529(12)
C(27)	4297(6)	5716(9)	6328(11)
C(28)	3702(5)	5477(7)	5314(9)
C(29)	2253(5)	7019(7)	1433(8)
C(30)	1519(8)	6394(12)	1087(13)
C(31)	988(11)	6566(15)	235(16)
C(32)	1241(8)	7415(12)	−204(14)
C(33)	1977(8)	7952(12)	18(14)
C(34)	2507(7)	7760(10)	866(11)
C(35)	2884(5)	7831(7)	4148(8)
C(36)	3426(5)	7934(8)	5163(9)
C(37)	3458(6)	8757(9)	6413(11)
C(38)	2961(6)	9494(10)	6631(12)
C(39)	2448(7)	9416(10)	5673(12)
C(40)	2388(6)	8562(8)	4391(10)
C(41)	3869(4)	7152(7)	2177(8)
C(42)	4264(5)	6346(8)	1449(9)
C(43)	5011(6)	6689(8)	1176(10)
C(44)	5364(6)	7790(9)	1592(10)
C(45)	4986(6)	8601(10)	2337(11)
C(46)	4230(5)	8275(8)	2633(10)
C(47)	4194(8)	−35(13)	54(14)
C(48)	4743(10)	954(14)	565(16)
C(49)	4435(10)	−1046(14)	−502(16)
H(1)	2706(41)	4772(60)	656(71)

cm^3) was added a solution of $BF_3{\cdot}Et_2O$ (126 μl, 1.15 mmol) in CH_2Cl_2 (2 cm^3) in two portions over a period of 30 min. The clear yellow solution was stirred for 45 min and the progress of the reaction was monitored by IR spectroscopy. The solution was then concentrated to *ca.* 5 cm^3 and the crude product was precipitated as a creamy coloured powder by addition of Et_2O (20 cm^3) and dried *in vacuo*. Yield: 0.882 g (87%). Nearly colourless crystals were obtained by layering a concentrated CH_2Cl_2 solution with Et_2O and keeping the Schlenk tube at −10 °C for a few days (Found: C, 51.20; H, 3.70. Calc. for $C_{46}H_{38}F_3FeO_3P_3PtSi$: C, 51.75; H, 3.60%). IR: (CH_2Cl_2) ν(CO) 1982s, 1920s, 1891vs cm^{-1}; (KBr) ν(CO) 1974s, 1911s, 1883vs; ν(PtH) 2101w cm^{-1}. NMR: ^{1}H (200 MHz, CD_2Cl_2); δ −4.81 [dtq, 1 H, PtH, $^2J(P_{trans}H)$ = 195, $^2J(P_{cis}H)$ = ^{3+4}J(PH) = 14, ^4J(FH) = 3, ^1J(PtH) = 685], 3.42 [t, 2 H, CH_2, ^2J(PH) = 10, ^3J(PtH) = 28.9] and 7.05–7.38 (m, 35 H, C_6H_5); ^{31}P-{^{1}H} [81.02 MHz, $(CD_3)_2CO$–CH_2Cl_2], δ 72.3 [dm, P(Fe), ^{2+3}J(PP) = 114], 30.6 [dm, P(Pt), ^{2+3}J(PP) = 114, ^1J(PtP) = 2145] and 29.8 [t, Ph_3P(Pt), ^1J(PtP) = 3602]; ^{19}F-{^{1}H} (376.50 MHz, CD_2Cl_2, external $CFCl_3$), δ −87.60 [br d, $^3J(P_{trans}F)$ = 20, ^3J(PtF) = 58, ^1J(SiF) = 388 Hz].

Synthesis of mer-[$(F_3Si)(OC)_3$Fe(μ-dppm)PtH{$P(OPh)_3$}] **7**.—To a CD_2Cl_2 solution of complex **6** (0.011 g, 0.01 mmol) was added $P(OPh)_3$ (0.009 g, 0.03 mmol). The progress of the reaction was followed by NMR spectroscopy. IR (CH_2Cl_2): ν(CO) 1992s, 1931s and 1903s cm^{-1}. NMR (CD_2Cl_2): ^{1}H (200 MHz), δ −4.10 [ddt, 1 H, PtH, $^2J(P_{trans}H)$ = 196, $^{2+3}J(P_{cis}H)$ = 14, ^4J(FH) = 3, ^1J(PtH) = 733], 3.48 [t, 2 H, CH_2, ^2J(PH) = 10.2, ^3J(PtH) = 30] and 7.05–7.38 (m, 35 H, C_6H_5); ^{19}F-{^{1}H} (376.50 MHz), δ −86.57 [br d, $^3J(PF)_{trans}$ = 20 Hz, ^3J(PtF) = 59, ^1J(SiF) = 379 Hz].

Crystal Structure Determination of mer-[$(F_3Si)(OC)_3$Fe(μ-dppm)PtH(PPh_3)]·$0.5C_6H_6$ **6**·$0.5C_6H_6$.—An X-ray-quality crystal of approximate dimensions 0.23 × 0.25 × 0.32 mm was grown from a CH_2Cl_2–benzene–hexane solution. Unit-cell parameters were obtained by least-squares refinement of the θ values of 30 accurately measured reflections (θ 10.1–18.9°).

Crystal data. $C_{46}H_{38}F_3FeO_3P_3PtSi{\cdot}0.5C_6H_6$, M = 1106.80, triclinic, space group $P\bar{1}$, a = 17.692(7), b = 13.084(5), c = 11.031(5) Å, α = 112.16(1), β = 91.31(2), γ = 101.71(1)°, U = 2302(2) Å^3, Z = 2, D_c = 1.597 g cm^{-3}, $F(000)$ = 1098, μ(Mo-Kα) = 35.62 cm^{-1}.

Data were collected at room temperature on a Siemens AED single-crystal diffractometer using niobium-filtered Mo-Kα radiation (λ = 0.710 73 Å) and the θ–2θ scan mode. All reflections with θ in the range 3–25° were measured; of 8137 independent reflections, 5870, having $I > 2\sigma(I)$, were considered observed and used in the analysis. The individual profiles were analysed according to Lehmann and Larsen.[16] The intensity of one standard reflection was measured after 50 reflections as a general check on crystal and instrument stability. No significant change in the measured intensities was observed during the data collection. A correction for absorption was applied (maximum and minimum transmission factors 1.370 and 0.866).[17] Only the observed reflections were used in the structure solution and refinement.

The structure was solved by Patterson and Fourier methods, and refined by full-matrix least squares first with isotropic and then with anisotropic thermal parameters in the last cycles for all the non-hydrogen atoms except those of the phenyl groups and those of the benzene molecule of solvation. The benzene molecule was found to have an imposed C_i symmetry. The three hydrogen atoms, not belonging to phenyl groups, clearly localised in the final ΔF map, were refined isotropically; the remaining ones, except those of the solvent molecule, were placed at their geometrically calculated positions (C–H 1.08 Å) and refined 'riding' on the corresponding carbon atoms. The final cycles of refinement were carried out on the basis of 372 variables; the largest remaining peak in the final difference map, close to the Pt atom, was equivalent to *ca.* 0.29 e Å^{-3}. A weighting scheme $w = [\sigma^2(F_o) + gF_o^2]^{-1}$ was used in the last cycles of refinement with $g = 0.0026$ at convergence. Final R and R' values were 0.0408 and 0.0509 respectively. The SHELX 76 and SHELXS 86 systems of computer programs were used.[18] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 19. Final atomic coordinates for the non-hydrogen atoms are given in Table 2. All calculations were carried out on the CRAY X-MP/48 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.

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