Synthesis and Reactivity of Phosphine-substituted Hydrido Silyl Complexes *mer*-$[FeH(SiR_3)(CO)_3\{Ph_2P(CH_2)_nPPh_2\}]$ (n = 1 or 4), *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(PPh_2H)]$ and *mer*-$[FeH\{Si(OMe)_3\}(CO)_3\{Ph_2PCH_2C(O)Ph\}]$. Synthesis of Bimetallic Complexes and Crystal Structure of *mer*-$[(Ph_3P)\overline{Cu(\mu\text{-dppm})Fe}\{Si(OMe)_3\}(CO)_3]$ *

Pierre Braunstein,[a] Michael Knorr,[a] Ulrich Schubert,[b] Maurizio Lanfranchi[c] and Antonio Tiripicchio[c]

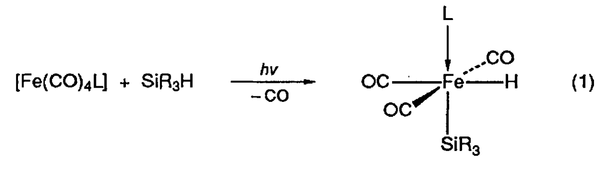
[a] *Laboratoire de Chimie de Coordination, Associé au CNRS (URA 0416), Université Louis Pasteur, 4 rue Blaise Pascal, F-67070 Strasbourg Cédex, France*

[b] *Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-8700 Würzburg, FRG*

[c] *Istituto di Chimica Generale ed Inorganica, Università di Parma, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Viale delle Scienze, I-43100 Parma, Italy*

Phosphine-substituted hydrido silyl complexes $[FeH(SiR_3)(CO)_3L]$ (L = phosphine) have been prepared by carbonyl substitution in *cis*-$[FeH(SiR_3)(CO)_4]$. The reaction of *cis*-$[FeH\{Si(OMe)_3\}(CO)_4]$ **1a** with $Ph_2PCH_2PPh_2$(dppm) in a 1:1 ratio afforded *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]$ **2a**; *mer*-$[FeH\{Si(OEt)_3\}(CO)_3(dppm\text{-}P)]$ **2b** was obtained similarly. The reaction of $[FeH(SiPh_3)(CO)_4]$ with $Ph_2P(CH_2)_4PPh_2$(dppb) afforded *mer*-$[FeH(SiPh_3)(CO)_3(dppb\text{-}P)]$ **3a** and that of **1a** with vinylidenebis(diphenylphosphine) (vdpp) afforded under analogous conditions the chelated complex *cis*-$[FeH\{Si(OMe)_3\}(CO)_2(vdpp\text{-}PP')]$ **3c**. Reaction of **1a** with the functional phosphine $Ph_2PCH_2C(O)Ph$ yielded *mer*-$[FeH\{Si(OMe)_3\}(CO)_3\{Ph_2PCH_2C(O)Ph\}]$ **4** and with PPh_2H, *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(PPh_2H)]$ **5** was obtained. The anionic complexes $K[Fe(SiR_3)(CO)_3(PPh_2X)]$ **6a** (R = OMe, X = CH_2PPh_2), **6b** (R = OEt, X = CH_2PPh_2), **6c** [R = Ph, X = $(CH_2)_4PPh_2$] and **6d** [R = OMe, X = $CH_2C(O)Ph$] were generated from the corresponding hydrido complexes by deprotonation with excess of KH in tetrahydrofuran (thf). They were used to prepare metal–metal bonded heterobinuclear complexes *mer*-$[\overline{LM(\mu\text{-dppm})Fe}\{Si(OMe)_3\}(CO)_3]$ **7b** (M = Cu, L = PPh_3), **7c** (M = Cu, L = MeCN), **8a** (M = Ag, L = $AsPh_3$), **8b** (M = Ag, L = PPh_3) and **10** (M = Au, L = PPh_3). Complex **8a** dissociates $AsPh_3$ in solution with formation of *mer*-$[\overline{Ag(\mu\text{-dppm})Fe\{(MeO})Si(OMe)_2\}(CO)_3]$ **9**, which contains an unusual alkoxysilyl bridge resulting in a AgFeSiO four-membered ring. This very labile complex was also obtained from the reaction of **6a** with $[Ag(MeCN)_2]NO_3$. For comparative purposes, we also prepared *mer*-$[(Ph_3P)AuFe\{Si(OMe)_3\}(CO)_3(PPh_3)]$ **11**. All complexes were characterized by elemental analysis and spectroscopic (IR and ^1H and $^{31}P\text{-}\{^1H\}$ NMR) methods. The crystal structure of compound **7b** has been determined by X-ray diffraction: monoclinic, space group $P2_1/c$, with a = 11.542(5), b = 18.567(7), c = 21.830(7) Å, β = 94.67(2)° and Z = 4. The copper atom is trigonally co-ordinated by two phosphorus atoms from the dppm and PPh_3 ligands and by the Fe atom [Fe–Cu = 2.540(2) Å]. The Fe atom is in an octahedral arrangement determined by three carbon atoms from carbonyl groups, a phosphorus atom of the bridging dppm ligand and by the Si atom of the $Si(OMe)_3$ group.

Phosphine-substituted hydrido silyl complexes of the type $[FeH(SiR_3)(CO)_3L]$ (L = phosphine) are easily prepared by oxidative addition of SiR_3H to a photochemically generated $Fe(CO)_3L$ intermediate. This method applies to a wide range of substituents, both at phosphorus and at silicon [equation (1)].[1]



Another synthetic method consists of the thermal substitution of a CO ligand in $[FeH(SiR_3)(CO)_4]$ by a phosphine. The scope of this method is however limited by possible deprotonation of the hydrido complex in the presence of a basic nucleophile (*e.g.* trialkylphosphine) and by the increased tendency of complexes of the type *cis*-$[FeH(SiR_3)(CO)_3L]$ to eliminate reductively SiR_3H in the presence of nucleophiles, as already noted by Jetz and Graham [equation (2a)].[2] Recent studies have shown that formation of a labile phosphine-substituted hydrido silyl complex with a *trans*-H–Fe–P arrangement precedes reductive elimination of silane.[3,4] Whereas elimination of SiR_3H readily occurs in nucleophilic solvents, the use of hexane allows isolation of *mer*-$[FeH(SiR_3)(CO)_3L]$ with a *trans*-Si–Fe–P arrangement, after isomerization [equation (2b)].

There is current interest in the reactivity of complexes of the

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* μ-Bis(diphenylphosphino)methane-κ*P*:κ*P′*-tricarbonyl-1κ³*C*-trimethoxysilyl-1κ*Si*-triphenylphosphine-2κ*P*-copperiron (*Cu–Fe*).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

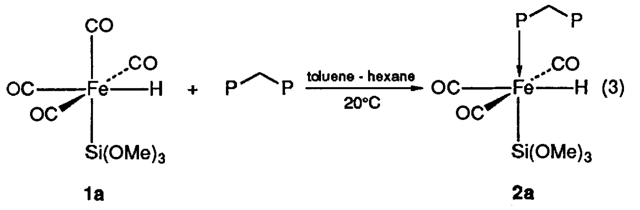
$$cis\text{-}[FeH(SiPh_3)(CO)_4] + PPh_3 \longrightarrow [Fe(CO)_4(PPh_3)] + SiPh_3H \qquad (2a)$$

$$cis\text{-}[FeH(SiPh_3)(CO)_4] + PPh_3 \longrightarrow mer\text{-}[FeH(SiPh_3)(CO)_3(PPh_3)] \qquad (2b)$$

type $[FeH(SiR_3)(CO)_4]$ with diphosphine ligands $Ph_2P(CH_2)_n$-PPh_2[4-6] and we present here our results with the ligands 1,2-bis(diphenylphosphino)methane (dppm, $n = 1$) and 1,2-bis(diphenylphosphino)butane (dppb, $n = 4$), respectively, and vinylidenebis(diphenylphosphine) (vdpp). The former was used with the aim of preparing complexes containing a dangling phosphine ligand which would therefore be suitable for the subsequent synthesis of heterometallic complexes. As an extension of this goal we describe also the synthesis of PPh_2H- and $Ph_2PCH_2C(O)Ph$-substituted hydrido silyl complexes which are potential precursors, respectively, of phosphido- and *P,O*-diphenylphosphinoketone-bridged heterometallic compounds.[7]

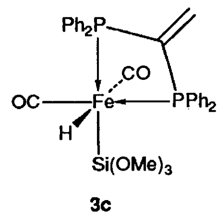
Results and Discussion

Reactions with Diphosphine Ligands.—The reaction of *cis*-$[FeH\{Si(OMe)_3\}(CO)_4]$ **1a** with $Ph_2PCH_2PPh_2$ (dppm) in a 1:1 ratio in a toluene–hexane mixture affords *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(dppm\text{-}P)]$ **2a** in almost quantitative yields [equation (3)]. The three ν(CO) bands in the infrared spectrum



are typical of the *mer* arrangement of the CO ligands and are very similar, both in frequency and intensity, to those of *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(PPh_3)]$.[1] The ^2J(P–Fe–H) coupling constant of 26.5 Hz measured in the ^1H NMR spectrum is indicative of a *cis*-P–Fe–H arrangement of the ligands. The monodentate behaviour of the dppm ligand is confirmed by the AX pattern observed in the ^{31}P-$\{^1H\}$ NMR spectrum in which the doublet for the unco-ordinated phosphorus atom is found at *ca.* δ −25. Pale yellow **2a** is air-stable for a short period of time and is slightly soluble in hexane whereas it is well soluble in aromatic solvents or in CH_2Cl_2. The triethoxysilyl-substituted derivative *mer*-$[FeH\{Si(OEt)_3\}(CO)_3(dppm\text{-}P)]$ **2b** may be obtained in an analogous manner and shows similar spectroscopic properties.

However, the reaction of *cis*-$[FeH\{Si(OMe)_3\}(CO)_4]$ **1a** with vinylidenebis(diphenylphosphine) (vdpp) afforded under analogous conditions the chelated hydrido, silyl complex *cis*-$[FeH\{Si(OMe)_3\}(CO)_2(vdpp\text{-}PP')]$ **3c** as the sole isolated product, despite the known ability of vdpp to form iron complexes with a pendant phosphorus atom.[8] A dynamic

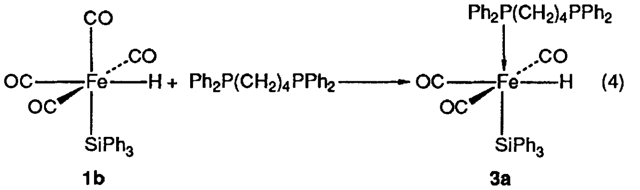


3c

behaviour for this complex accounts for the observation of only a singlet resonance in the ^{31}P-$\{^1H\}$ NMR spectrum at δ 53.0 and a triplet resonance in the ^1H NMR spectrum at δ −7.2 [^2J(PH) = 36.9 Hz] for the hydride ligand. This ligand occupies a *cis* position relative to the two phosphorus atoms, as clearly established in related $Ph_2PCH_2CH_2PPh_2$ (dppe)-substituted hydrido, silyl complexes which also display a fluxional behaviour exchanging the role of the P atoms.[5,6]

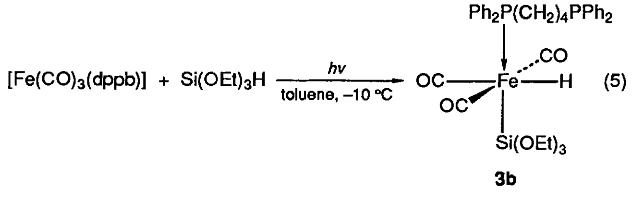
Whereas the chelate complex *cis*-$[FeH(SiMeCl_2)(CO)_2(dppe\text{-}PP')]$ could be obtained from the reaction of *cis*-$[FeH(SiMeCl_2)(CO)_4]$ with dppe, the reaction failed when less-electronegative substituents are attached to silicon, as in *cis*-$[FeH(SiMe_2Ph)(CO)_4]$ or in *cis*-$[FeH(SiPh_3)(CO)_4]$. In these cases, the dihydride all-*cis*-$[FeH_2(CO)_2(dppe\text{-}PP')]$ was obtained, instead of a hydrido silyl complex.[5,6]

However, the reaction of *cis*-$[FeH(SiPh_3)(CO)_4]$ **1b** with $Ph_2P(CH_2)_4PPh_2$ (dppb) in benzene or toluene affords *mer*-$[FeH(SiPh_3)(CO)_3(dppb\text{-}P)]$ **3a** in quantitative spectroscopic yields [equation (4)]. Its ν(CO) IR spectrum is very similar to



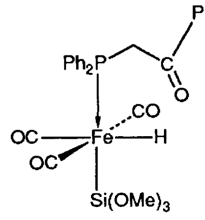
those of complexes **2**. In the ^1H NMR spectrum two doublets with ^2J(PH) = 27 Hz are observed in a 1:1 ratio at δ −9.7 which are separated by *ca.* 1 Hz (measured on a 60 MHz spectrometer). In the ^{31}P-$\{^1H\}$ NMR spectrum recorded at 281 K two signals of similar intensity are observed at δ *ca.* 50.3, which are separated by only 7 Hz (at 36.44 MHz). The resonance of the unco-ordinated phosphorus atom also appears in the form of two lines, slightly broadened, at δ *ca.* −17.4, which are separated by *ca.* 16 Hz. At room temperature the low-field resonance shifts to δ 50.4 and the separation between the lines reduces to 4 Hz. The high-field resonances coalesce into a broad, unresolved signal. The thermal lability of compound **3a** did not allow measurements at higher temperatures. These data would be consistent with the presence at low temperature of two, closely related, conformational isomers for **3a** which, owing to the longer dppb chain, could differ in the orientation of the unco-ordinated phosphorus lone pair. At higher temperatures these isomers undergo rapid exchange. The reduced stability of **3a**, in solution as well as in the solid state, could be due to the possibility of intramolecular nucleophilic attack by the unco-ordinated phosphorus lone pair, therefore facilitating reductive elimination of the silane. We therefore failed to obtain satisfactory elemental analyses for this complex.

The closely related complex *mer*-$[FeH\{Si(OEt)_3\}(CO)_3(dppb\text{-}P)]$ **3b** was observed in the photochemical reaction of $[Fe(CO)_3(dppb\text{-}PP')]$[9] with an excess of $[Si(OEt)_3H]$ in toluene at 263 K [equation (5)]. That opening of the chelate



ring is preferred over carbonyl elimination probably results from steric effects, as also supported by the comparatively facile loss of CO from $[Fe(CO)_3(dppe\text{-}PP')]$ under similar photochemical conditions. A similar steric effect on the competition between CO or phosphine dissociation has previously been noted in the formation of complexes of type $[Mn(\eta\text{-}C_5H_4Me)H(SiR_3)(CO)_2L]$.[10] The similar spectroscopic properites of **3a** and **3b** indicate for the latter complex too the presence of two conformational isomers in solution.

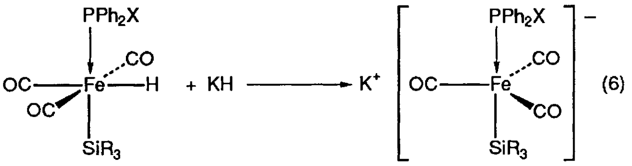
Reaction of Compound **1a** *with the Functional Phosphine* $Ph_2PCH_2C(O)Ph$.—In view of the co-ordinating ability of the keto function of $Ph_2PCH_2C(O)Ph$ and of the rich chemistry of this and related ligands,[11] we investigated its 1:1 reaction with $[FeH\{Si(OMe)_3\}(CO)_4]$ in toluene–hexane. The colourless complex *mer*-$[FeH\{Si(OMe)_3\}(CO)_3\{Ph_2PCH_2C(O)Ph\}]$ **4** was obtained in good yields. Its IR spectrum shows the three typical carbonyl ν(CO) bands together with a medium-intensity absorption at 1675 cm^{-1} assigned to the keto function. The coupling constant $^2J(PH)$ of 26.6 Hz in the ^1H NMR spectrum is again indicative of a *cis*-H–Fe–P arrangement. This complex slowly decomposes at room temperature under an inert atmosphere and its colour darkens within a few days.



4

Reaction of Compound **1** *with* PPh_2H.—After mixing a hexane solution of compound **1a** with a stoichiometric quantity of PPh_2H, vigorous evolution of CO was instantaneously observed. Cream coloured crystals of *mer*-$[FeH\{Si(OMe)_3\}(CO)_3(PPh_2H)]$ **5** were obtained in good yields. The coupling constant $^2J(PH) = 29.2$ Hz in the ^1H NMR spectrum is again indicative of a *cis*-H–Fe–P arrangement. As a consequence of further $^3J(HH)$ coupling with the hydrogen of the PPh_2H ligand, the signal for the hydride ligand at δ −9.21 is split into a doublet of doublets.

Synthesis of the Anionic Complexes $K[Fe(SiR_3)(CO)_3(PR_2X)]$ **6a** (R = OMe, X = CH_2PPh_2), **6b** (R = OEt, X = CH_2PPh_2), **6c** [R = Ph, X = $(CH_2)_4PPh_2$] and **6d** [R = OMe, X = $CH_2C(O)Ph$].—Similar to the other hydrido complexes of type *mer*-$[FeH(SiR_3)(CO)_3(PR_3)]$, complexes **2**–**4** represent convenient sources of carbonylmetalate anions by deprotonation with an excess KH in tetrahydrofuran (thf) [equation (6)]. Although their isolation is not necessary for further reactions, **6a** was precipitated with hexane and kept under nitrogen for days as a colourless, air-sensitive powder. Interactions of K^+ with carbonyl ligand(s) of the anions of **6** were observed in solution, as discussed elsewhere for similar systems.[12–14] Addition of 1 equivalent of 18-crown-6 (1,4,7,10,13,16-hexaoxacyclooctadecane) or of $[N(PPh_3)_2]Cl$ to a thf solution of **6a** or **6c** reduces the number of IR ν(CO) absorptions to a weak A_1 and a very strong E band. As a result, the unperturbed anions have a trigonal-bipyramidal structure with the SiR_3 and PR_2X ligands in the axial positions. In comparison with **2**, the $^{31}P-\{^1H\}$ NMR signal of the phosphorus atom co-ordinated to iron is shifted downfield whereas the chemical shift of the unco-ordinated phosphorus atom remains at δ −24. The value of $^2J(PP)$ is reduced from *ca.* 100 Hz for **2** to *ca.* 80 Hz for **6a** and **6b**.

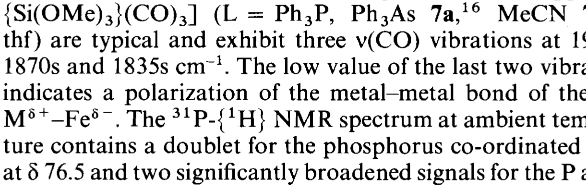


(6)

	X	R
6a	CH_2PPh_2	OMe
6b	CH_2PPh_2	OEt
6c	$(CH_2)_4PPh_2$	Ph
6d	$CH_2C(O)Ph$	OMe

It is noteworthy that stirring compound **2** or **4** with excess of KH in thf for 1 h does not lead to abstraction of a methylene proton of dppm or of an even more acidic methylene proton of $Ph_2PCH_2C(O)Ph$, respectively. In the latter case, this would be easily monitored in the IR spectrum by a further shift towards lower wavenumbers of the vibration assigned to the keto function of **6d** at 1670 cm^{-1}, as observed for the enolato complexes of this ligand.[11]

Reactions of Compound **6a** *with Electrophilic Complexes of* Cu, Ag *and* Au.—We have shown previously that the availability of the phosphorus lone pair of the dppm ligand of **6a** together with the anionic nature of this complex facilitate the synthesis and stabilization of heterometallic complexes containing a dppm backbone.[15–17] A further interesting feature associated with the stabilizing effect of the dppm bridge was the unprecedented formation of MM′SiO four-membered ring systems, which furthermore exhibit oxygen–metal interactions with soft metals such as Rh, Pd and Pt. In order better to understand the conditions for the occurrence of this μ-alkoxysilyl bridging mode, we have now prepared complexes with a L′M–Fe unit where M = Cu, Ag or Au. The reaction of **6a** with a slight excess of $[\{CuCl(PPh_3)\}_4]$ in thf afforded *mer*-$[(Ph_3P)Cu(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **7b** in good yields [equation (7)]. This complex can be exposed to air in the crystalline state for hours without any significant decomposition. The IR spectra for compounds of the type *mer*-$[LM(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ (L = Ph_3P, Ph_3As **7a**,[16] MeCN **7c** or thf) are typical and exhibit three ν(CO) vibrations at 1941m, 1870s and 1835s cm^{-1}. The low value of the last two vibrations indicates a polarization of the metal–metal bond of the type $M^{\delta+}-Fe^{\delta-}$. The $^{31}P-\{^1H\}$ NMR spectrum at ambient temperature contains a doublet for the phosphorus co-ordinated to Fe at δ 76.5 and two significantly broadened signals for the P atoms of PPh_3 and dppm co-ordinated to Cu at δ 0.75 and −10.3, respectively. Cooling the solution to 257 K results in a well resolved ABX spin system with seven lines for the AB part [J(AB) = 144 Hz] and four transitions for the X part [J(AX) = 148, J(BX) = 9 Hz]. The 16e Cu atom has achieved a satisfactory co-ordination in **7b**: it does not react with excess of phosphine and reaction of the iron metalate with $[Cu(PPh_3)_2]NO_3$ similarly affords **7b**.

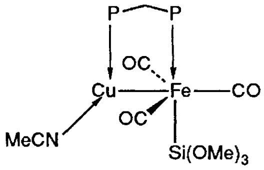


(7)

7b

The less-stable complex *mer*-$[(MeCN)Cu(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **7c** was obtained by the reaction of **6a** with $[Cu(MeCN)_4]BF_4$ in cold thf and was characterized spectroscopically. The very similar IR spectrum and $^{31}P-\{^1H\}$ NMR data [δ 76.8 and −10.3, J(AX) = 142 Hz] indicate a structure analogous to that found for **7b**.

A more complex situation resulted from the reaction of



7c

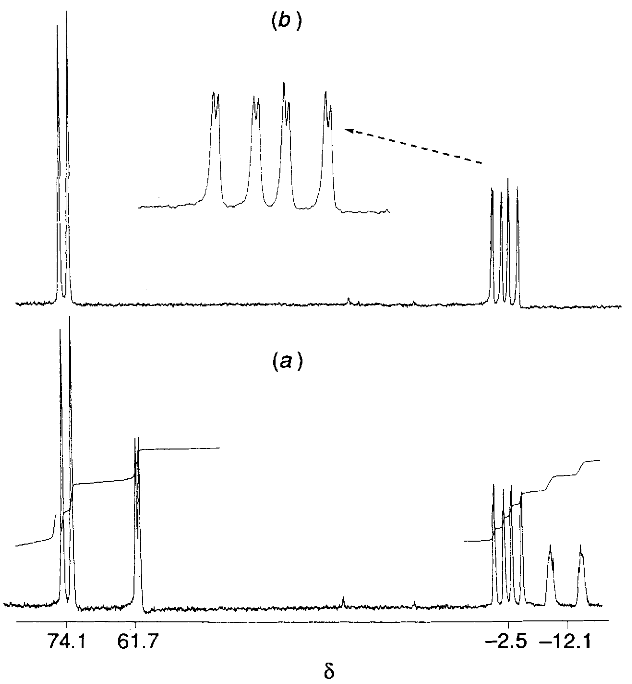
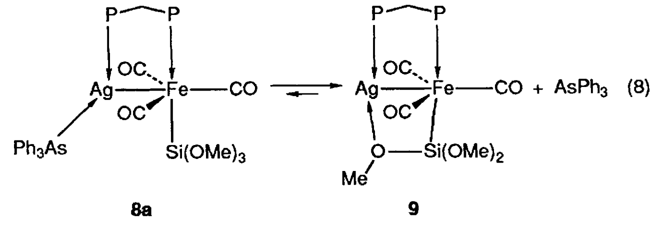


Fig. 1 ^{31}P-{^{1}H} NMR spectra ([$^2H_6$]acetone–CH_2Cl_2, 230 K) of (*a*) the equilibrium mixture between compounds **8a** and **9**, (*b*) after addition of $AsPh_3$, only **8a** being present

compound **6a** with [Ag($AsPh_3$)(NO_3)]. In order to prevent decomposition, the reaction was carried out at 223 K and with exclusion of light. The IR absorptions of **6a** disappeared after 10 min while new absorptions appeared which seemed to represent the superimposition of two different sets. This was confirmed by a ^{31}P-{^{1}H} NMR study of the solution at 230 K, which revealed the presence of two compounds in a *ca.* 60:40 ratio (Fig. 1). A set of signals can be unambiguously attributed to the expected compound *mer*-[(Ph_3As)Ag(μ-dppm)Fe{Si(OMe)$_3$}(CO)$_3$] **8a** since both the chemical shift for the phosphorus co-ordinated to Fe (δ 74.1) and the coupling constant [*J*(PP) = 139 Hz] are in the typical range for this class of compounds.[15–17] Because of the nuclear spin of the silver isotopes ^{107}Ag and ^{109}Ag ($I = \frac{1}{2}$), the resonance of the phosphorus bound to Ag at δ −2.5 is further split into a doublet of doublets [^1J(P–^{109}Ag) = 259, ^1J(P–^{107}Ag) = 227 Hz]. The second set of signals consists of a doublet at δ 61.7 [*J*(PP) = 47 Hz] and a broader doublet of doublets owing to coupling with the silver isotopes at δ −12.1, with an average value for J(^{107,109}AgP) of 438 Hz. In the ^{1}H NMR spectrum two singlets of comparable intensity and assigned to the Si(OMe)$_3$ protons are found at δ 3.42 and 3.57. We propose for the second species a bimetallic structure with a μ-alkoxysilyl bridge, on the basis of the *J*(PP) and chemical shift values for the phosphorus attached to Fe which are close to those found in related Fe–Pd, Fe–Pt and Fe–Rh complexes which display such a μ-alkoxysilyl interaction.[15–17] The observed increase of ^1J(PAg) is furthermore consistent with a decrease in the co-ordination number of silver.[18a,b] The formation of compound **9** may easily be accounted for by partial dissociation of $AsPh_3$ from **8a** [equation (8)]. This equilibrium is instantaneously and completely shifted towards **8a** when an excess of $AsPh_3$ is added to the solution, as monitored by ^{31}P-{^{1}H} and ^{1}H NMR and IR spectroscopic methods (Fig. 1). The IR spectrum of **9** also contains three ν(CO) absorptions consistent with a meridional arrangement about the iron centre, although their shape and positions differ from those of **8a**. Analytically pure compound **9** could be obtained in very low yield by treating a thf solution of **6a** with [Ag(MeCN)$_2$]NO_3, generated *in situ* [equation (9)].



8a **9**

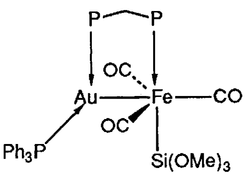
$$[Ag(MeCN)_2]NO_3 + \mathbf{6a} \longrightarrow \mathbf{9} + KNO_3 \qquad (9)$$

Despite the low temperature at which reaction (9) was performed, precipitation of an insoluble dark brown material occurred which could be removed by low-temperature filtration. Elemental analysis of the spectroscopically pure product reveals only the presence of traces of nitrogen. It thus appears that the softer silver(I) ion prefers co-ordination by a siloxy oxygen whereas Cu^{I} prefers to have MeCN in its co-ordination sphere. The lability of the Ag–O bond is consistent with previous observations made when H_2O, [CF_3SO_3]$^-$ or NO_3^- are co-ordinated to Ag$^+$.[19] However, the derivative *mer*-[(Ph_3P)Ag(μ-dppm)Fe{Si(OMe)$_3$}(CO)$_3$] **8b** was obtained in moderate yields as the sole product when using [Ag(PPh_3)(NO_3)]. This colourless compound (solvated by a molecule of toluene) is more stable than **8a** and may be stored under nitrogen for longer periods of time as a solid but decomposes in solution at ambient temperature within a few hours. As in the case of its copper analogue **7b**, the ^{31}P-{^{1}H} NMR spectrum of **8b** shows broadened signals at ambient temperature, indicating partial dissociation of PPh_3. A well resolved ABX pattern, with additional splitting due to coupling with ^{109}Ag and ^{107}Ag, was however obtained at 233 K, which contained a doublet resonance for the phosphorus atom on Fe at δ 75.1 [*J*(AX) = 140, *J*(BX) ≈ 0 Hz] and two symmetric multiplets at δ 10.3 and −5.4 for the PPh_3 and the dppm phosphorus attached to Ag, respectively. For all the silver-containing complexes, we find J(^{107}Ag–P) and J(^{109}Ag–P) coupling constants consistent with the magnetogyric ratios of ^{107}Ag and ^{109}Ag [γ(^{107}Ag): γ(^{109}Ag) = 0.87:1].[18c,d] The IR spectrum contains the same pattern as that for **7b** but is slightly shifted to higher wavenumbers. The ^{1}H NMR spectrum in [$^2H_6$]acetone shows a triplet for the methylene protons of dppm at δ 3.43 and a sharp singlet at δ 3.35 for the methoxy protons. Note that the relative positions are reversed in C_6D_6 where the signal for the methoxy protons appears now at δ 3.84 and the triplet resonance for the methylene protons at δ 3.10 [*J*(PH) = 9.9 Hz]. The SiO interaction suggested for **9** would bear an interesting relevance to the recently discussed side-bonded structure for AgSiO, generated by the reactions of SiO and silver atoms in matrices.[20]

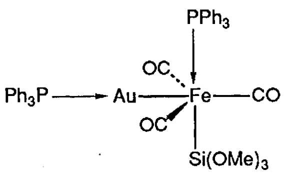
The derivative *mer*-[(Ph_3P)Au(μ-dppm)Fe{Si(OMe)$_3$}(CO)$_3$] **10** was isolated in excellent yields from [Au(PPh_3)Cl] and is stable in solution. As for its homologues **7b** and **8b**, the signals for the phosphorus atom co-ordinated to Au are broadened at ambient temperature in the ^{31}P-{^{1}H} NMR spectrum. At 247 K the doublet resonance [*J*(AX) = 154, *J*(BX) = 0 Hz] of the Fe-bound dppm phosphorus at δ 77.5 represents again the X part, and the two PPh_3 lines at δ 46.0 [*J*(AB) = 203 Hz] and the four lines at δ 37.6 of the Au-bound dppm phosphorus constitute the AB part of a well resolved ABX spectrum. The IR ν(CO) pattern of **10** resembles much those of its copper and silver analogues, the positions being however shifted to higher wavenumbers. Within the series **7b**, **8b** and **10** the following trends are observed: (*i*) the stability decreases from **7b** to **8b** and reaches its maximum with **10**; (*ii*) whereas the general pattern in the IR spectra remains the same, the absorptions are shifted to higher energies when going from Cu to Au (this could be taken as an indication of decreasing polarity of the metal–metal bond along this series); (*iii*) the ^{31}P NMR resonance of the phosphorus on Fe remains nearly unaffected, the signals for the phosphorus atoms attached to the

Table 1 Selected bond distances (Å) and angles (°) for complex **7b**

Fe–Cu	2.540(2)	Fe–C(1)	1.712(12)
Fe–Si	2.271(4)	Fe–C(2)	1.754(13)
Fe–P(1)	2.226(3)	Fe–C(3)	1.748(12)
Cu–P(2)	2.278(3)	Cu–P(3)	2.263(3)
P(1)–C(7)	1.85(1)	P(2)–C(7)	1.84(1)
P(1)–C(8)	1.83(1)	P(2)–C(20)	1.82(1)
P(1)–C(14)	1.81(1)	P(2)–C(26)	1.81(1)
P(3)–C(32)	1.85(1)	Si–O(4)	1.63(1)
P(3)–C(38)	1.81(1)	Si–O(5)	1.58(2)
P(3)–C(44)	1.79(1)	Si–O(6)	1.69(1)
Fe–Cu–P(2)	101.4(1)	C(1)–Fe–C(2)	112.2(6)
Fe–Cu–P(3)	138.6(1)	C(1)–Fe–C(3)	112.0(6)
P(2)–Cu–P(3)	119.9(1)	C(2)–Fe–C(3)	133.2(5)
P(1)–Fe–C(1)	94.5(4)	C(2)–Fe–Cu	64.2(4)
P(1)–Fe–C(2)	95.4(4)	C(3)–Fe–Cu	70.4(4)
P(1)–Fe–C(3)	95.7(4)	C(1)–Fe–Cu	174.0(4)
P(1)–Fe–Cu	90.7(1)	Fe–P(1)–C(7)	113.9(3)
Si–Fe–C(1)	81.8(4)	P(1)–C(7)–P(2)	114.0(5)
Si–Fe–C(2)	86.3(4)	C(7)–P(2)–Cu	107.8(3)
Si–Fe–C(3)	85.5(4)	Fe–Si–O(4)	112.7(3)
Si–Fe–Cu	93.1(1)	Fe–Si–O(5)	116.8(5)
Si–Fe–P(1)	176.3(2)	Fe–Si–O(6)	116.9(4)



10



11

coinage metal being shifted to lower field when going from **7b** to **10**.[21]

For comparative purposes, we prepared *mer*-$[(Ph_3P)AuFe\{Si(OMe)_3\}(CO)_3(PPh_3)]$ **11**, in a manner similar to *mer*-$[(Ph_3P)AuFe(SiMePh_2)(CO)_3(PPh_3)]$ which has a linear Fe–Au–PPh_3 arrangement.[12] The $^{31}P-\{^1H\}$ NMR spectrum contains two weakly coupled signals, for the PPh_3 bound to Fe at δ 67.1 and for the PPh_3 bound to Au at δ 41.1 [$^3J(PP) = 10$ Hz]. When compared with those of *mer*-$[(Ph_3P)Au(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **10**, the carbonyl vibrations of **11** are shifted by about 20 cm^{-1} to higher wavenumbers and exhibit a different pattern. Despite the fact that gold has not achieved its maximim co-ordination number, no μ-alkoxysilyl bridging interaction was evidenced: when cooling a CD_2Cl_2 solution of **11** to 213 K no splitting of the singlet resonance of the methoxy protons was observed in the ^1H NMR spectrum, thus ruling out any significant interaction which would make the methyl groups chemically inequivalent.

In order to establish the detailed molecular geometry of a representative member of this family of complexes, a single-crystal X-ray analysis was performed on **7b**. Preliminary X-ray data indicate that **10** is isostructural with **7b**: $a = 11.447(6)$, $b = 18.534(7)$, $c = 22.094(7)$ Å, $\beta = 94.23(2)°$, $U = 4675(3)$ Å^3 (by least-squares refinement from the θ values of 30 accurately measured reflections on a Siemens AED diffractometer).

Crystal Structure of mer-$[(Ph_3P)Cu(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **7b**.—The structure of compound **7b** is shown in Fig. 2; selected bond distances and angles are given in Table 1. The iron and copper centres are linked by a dppm bridge and a metal–metal bond [Fe–Cu 2.540(2) Å] which falls within the range of values, 2.394–2.580 Å, reported for polynuclear complexes containing this bond (from Cambridge Crystallographic Data Centre). It is equal to the sum of the atomic radii (2.54 Å) and is comparable to the values found in the trinuclear complex $[\{Cu(PPh_3)_2\}_2Fe(CO)_4]$, which contains a nearly linear chain Cu–Fe–Cu [2.499(4) and 2.522(4) Å].[22] The octahedral environment of the Fe atom is determined by the Cu atom, by a phosphorus atom from the dppm ligand [Fe–P(1) 2.226(3) Å], by a Si atom from the $Si(OMe)_3$ ligand [Fe–Si 2.271(4) Å] and by three carbon atoms from terminal carbonyl groups. This environment is similar to that found in $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})PdCl]$ [Fe–P 2.241(2) and Fe–Si 2.275(2) Å],[15] $[(OC)_3\{(MeO)_3Si\}Fe(\mu\text{-dppm})Cu(AsPh_3)]$[16] and *mer*-$[(Ph_3P)AuFe(SiMePh_2)(CO)_3(PPh_3)]$.[12] The trigonal co-ordination around the copper atom involves the Fe atom, a phosphorus atom from the dppm ligand [Cu–P(2) 2.278(3) Å] and the phosphorus atom of the PPh_3 ligand [Cu–P(3) 2.263(3) Å], the Cu atom being displaced by only 0.009(2) Å from the plane passing through the Fe and the two P atoms. A weak interaction between the copper atom and the carbonyls C(2)O(2) and C(3)O(3) may be present in view of the corresponding contacts: Cu–C(2) 2.38(1) and Cu–C(3) 2.55(1) Å . For comparison, semibridging interactions were considered between copper atoms and carbonyl groups in mixed Cu–Fe clusters with Cu–C distances in the range 2.25–2.40 Å[22] and between one of the carbonyl ligands and the copper atom in $[(OC)_2W(\mu\text{-CO})(\mu\text{-dppm})_2(\mu\text{-Cl})Cu]$ with a Cu–C distance of 2.267(8) Å,[21a] or in $[(OC)_2(\eta\text{-}C_5H_5)W(\mu\text{-CO})(\mu\text{-}MeCO_2)_2Cu(mpy)]$ (mpy = 4-methylpyridine) with a Cu–C distance of 2.137(9) Å.[21b]

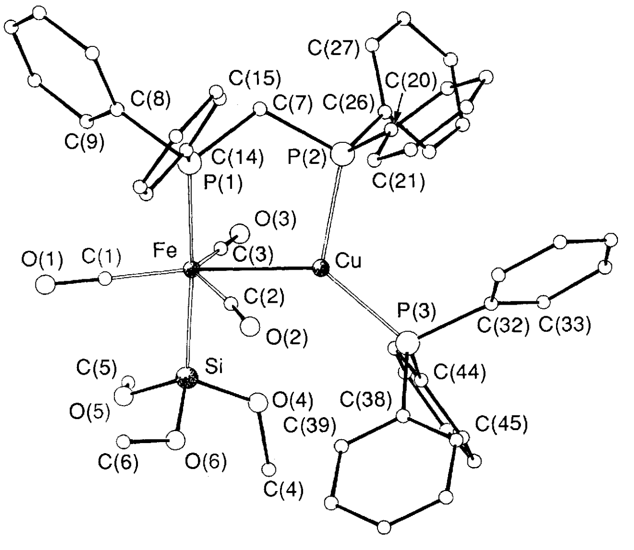


Fig. 2 View of the molecular structure of $[(Ph_3P)Cu(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **7b** with the atom numbering scheme

In contrast to the situation found in $[(OC)_3Fe\{\mu\text{-}Si(OMe)_2(OMe)\}(\mu\text{-dppm})PdCl]$ and in related Fe–Pd, Fe–Pt and Fe–Rh complexes,[15–17] there is no significant bonding interaction in **7b** between the alkoxysilyl ligand and the copper atom, the shortest contact between Cu and an oxygen atom being with O(4) at 3.267(8) Å.

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 starting materials $[FeH(SiPh_3)(CO)_4]$,[2] dppm, dppb[23] and $Ph_2PCH_2C(O)Ph$[11a] were prepared according to the literature; $HSiPh_3$ was a gift from WACKER-Chemie and $Si(OMe)_3H$ was commercially obtained from Aldrich and used as received. Infrared spectra were obtained using a Perkin-Elmer 398 spectrometer, and NMR spectra on Bruker WP 200 SY, WH 90 or Varian T 60 spectrometers (^1H and ^{31}P chemical shifts are positive downfield from $SiMe_4$ and H_3PO_4, respectively). Photochemical reactions were performed in an irradiation vessel using a water- or methanol-cooled high-pressure mercury lamp (180 W, TQ 150, Heraeus).

Preparations.—*cis*-[FeH{Si(OMe)$_3$}(CO)$_4$] **1a**. A magnetically stirred solution of [Fe(CO)$_5$] (1.57 cm^3, 12 mmol) and Si(OMe)$_3$H (3.2 cm^3, 25 mmol) in hexane (300 cm^3) was irradiated with water cooling for 3–4 h. Irradiation was stopped when the ν(CO) absorptions of [Fe(CO)$_5$] had nearly completely disappeared. The resulting pale clear solution was used immediately for further reactions. After evaporation of the solvent under reduced pressure, compound **1a** was obtained as an extremely air-sensitive, bad smelling volatile oil. IR (hexane): ν(CO)/cm^{-1} 2102m, 2047ms (sh), 2033 and 2026vs.

mer-[FeH{Si(OMe)$_3$}(CO)$_3$(dppm-*P*)] **2a**. To a stirred solution of dppm (4.25 g, 11 mmol) in toluene (100 cm^3) was added a hexane solution of compound **1a**, in two portions in order to avoid attack of the dangling phoshorus of **2a** on excess of **1a**. After each addition of **1a** the CO evolved was removed under slightly reduced pressure for 3 min. After keeping the reaction mixture at -20 °C for 2–3 d, compound **2a** crystallized as pale yellow needles. After filtration and washing with hexane (15 cm^3) the crystals were dried for 0.5 h *in vacuo* (4.62 g, 65%), m.p. 66–67 °C (Found: C, 57.30; H, 4.90. Calc. for $C_{31}H_{31}FeO_6P_2Si$: C, 57.60; H, 5.00%). IR (Et$_2$O): ν(CO)/cm^{-1} 2042w, 1982s (sh) and 1975vs. NMR: ^{1}H(C$_6$D$_6$), δ -9.05 [d, FeH, 1 H, ^2J(PH) = 26.5], 3.18 [dd, CH$_2$, 2 H, ^2J(PH) = 9.1, 1.1] and 3.75 (s, 9 H, OCH$_3$); ^{31}P-{^{1}H} ([^{2}H$_6$]acetone), δ 52.1, [d, P(Fe)] and -24.7 [d, P, ^2J(PP) = 104 Hz].

mer-[FeH{Si(OEt)$_3$}(CO)$_3$(dppm-*P*)] **2b**. This compound was prepared in an analogous manner to **2a**, as yellow crystals which melted at room temperature (Found: C, 59.30; H, 5.55. Calc. for $C_{34}H_{38}FeO_6P_2Si$: C, 59.70; H, 5.65%). IR (Et$_2$O): ν(CO)/cm^{-1} 2042w, 1982s (sh) and 1975vs. NMR: ^{1}H(CD$_2$Cl$_2$), δ -9.50 [d, FeH, 1 H, ^2J(PH) = 26.9], 1.21 [t, 9 H, ^3J(HCCH) = 7], 3.27 [dd, CH$_2$, 2 H, ^2J(PH) = 8.9, 2.0], 3.82 [q, 6 H, OCH$_2$, ^3J(HCCH) = 7] and 7.11–7.52 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} (C$_6$D$_6$), δ 52.6 [d, P(Fe), ^2J(PP) = 102] and -24.9 [d, P, ^2J(PP) = 102 Hz].

mer-[FeH(SiPh$_3$)(CO)$_3$(dppb-*P*)] **3a**. To a solution of dppb (0.848 g, 2 mmol) in benzene (30 cm^3) was added solid [FeH(SiPh$_3$)(CO)$_4$] (0.834 g, 2 mmol) at *ca.* 20 °C under dinitrogen purge. The reaction was complete after *ca.* 0.75 h [IR monitoring in the ν(CO) region], affording a light green solution. After removal of the solvent *in vacuo* the residue was extracted with diethyl ether (25 cm^3), the solution was filtered and concentrated to 1/3 and kept at -25 °C. Light yellow microcrystals of the product **3a** precipitated which were collected by filtration and dried *in vacuo* (0.920 g, 55%) (Found: C, 68.90; H, 5.75. Calc. for $C_{49}H_{44}FeO_3P_2Si$: C, 71.20; H, 5.35%). IR (Et$_2$O): ν(CO)/cm^{-1} 2033w, 1988 (sh) and 1969vs. NMR (C$_6$D$_6$): ^{1}H, δ -9.7 [d, FeH, 1 H, ^2J(PH) 27.0 Hz] and 1.1–2.4, (m, br, CH$_2$); ^{31}P-{^{1}H} (281 K), δ 50.3 [s, P(Fe) and -17.4 (s, P). The NMR spectroscopic data for the other species (conformational isomers) observed are nearly identical (see text).

mer-[FeH{Si(OEt)$_3$}(CO)$_3$(dppb-*P*)] **3b**. A solution of [Fe(CO)$_3$(dppb-*PP'*)] (1.13 g, 2 mmol) [^{31}P-{^{1}H}NMR: δ 56.2 (s)] in toluene (150 cm^3) was irradiated with UV light at 263 K in the presence of a four-fold excess of [Si(OEt)$_3$H]. During the course of the irradiation the solution became darker owing to some decomposition. The formation of compound **3b** was observed spectroscopically but attempts to isolate the product failed. IR (toluene): ν(CO)/cm^{-1} 2042w, 1988s (sh) and 1973vs. ^{1}H NMR (C$_6$D$_6$): δ -9.9 [d, ^2J(PH) = 28.0 Hz]; the remaining signals were masked by other products.

cis-[FeH{Si(OMe)$_3$}(CO)$_2${Ph$_2$PC(=CH$_2$)PPh$_2$}] **3c**. This compound was prepared analogously to **2a** in 36% yield as yellow crystals (Found: C, 59.10; H. 5.05. Calc. for $C_{31}H_{32}FeO_5P_2Si$: C, 59.05; H, 5.10%). IR (toluene): ν(CO)/cm^{-1} 1984s and 1942s. NMR: ^{1}H(200 MHz, C$_6$D$_6$), δ -7.21 [t, 1 H, Fe–H, ^2J(PH) = 36.9], 3.71 (s, 9 H, OCH$_3$), 5.11 [dd, 2 H, CH$_2$, ^3J(PH) = 25.1, 36.9 Hz] and 6.89–7.73 (m, 20 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, C$_6$D$_6$–toluene), δ 53.0 (s).

mer-[FeH{Si(OMe)$_3$}(CO)$_3${Ph$_2$PCH$_2$C(O)Ph}] **4**. This compound was prepared analogously to **2a** in 90% yield as a colourless powder (Found: C, 54.50; H, 4.90. Calc. for $C_{26}H_{27}FeO_7PSi$: C, 55.10; H, 4.80%). IR (toluene: ν(CO)/cm^{-1} 2040w, 1988s (sh), 1975vs and 1675m. NMR: ^{1}H(200 MHz, C$_6$D$_6$), δ -9.21 [d, 1 H, Fe–H, ^2J(PH) = 26.6], 3.71 (s, 9 H, OMe), 3.76 [d, 2 H, CH$_2$, ^2J(PH) = 8.5 Hz] and 6.85–7.55 (m, 15 H, C$_6$H$_5$); ^{31}P-{^{1}H} (81.02 MHz, C$_6$D$_6$–toluene), δ 50.5 (s).

mer-[FeH{Si(OMe)$_3$}(CO)$_3$(PPh$_2$H)] **5**. A hexane solution (250 cm^3) of *cis*-[FeH{Si(OMe)$_3$}(CO)$_4$] (10 mmol) was treated with PPh$_2$H (1.86 g, 10 mmol). After the vigorous evolution of CO had stopped, the pale yellow solution was concentrated to about 2/3 of its volume and kept at 253 K. Pale yellow crystals of compound **5** formed which were separated and dried *in vacuo* (3.92 g, 81%), m.p. 26–30 °C (Found: C, 48.00; H, 4.75. Calc. for $C_{18}H_{21}FeO_6PSi$: C, 48.25; H, 4.70%). IR (thf): ν(CO)/cm^{-1} 2052w, 1998s (sh) and 1982vs. NMR (C$_6$D$_6$): ^{1}H (200 MHz), δ -9.21 [dd, 1 H, Fe–H, ^2J(PH) = 29.2, ^3J(HH) = 0.9], 3.71 (s, 9 H, OCH$_3$), 6.21 [d, 1 H, ^1J(PH) = 369] and 6.91–7.38 (m, 10 H, phenyl); ^{31}P (81.02 MHz), δ 30.9 [d, ^1J(PH) = 369 Hz].

Iron metalates. Typically, the hydridoiron complex was dissolved in thf and KH was added in excess. After stirring for 0.75 h, hydrogen evolution had stopped and the clear, pale yellow solution was filtered and used immediately.

K[Fe{Si(OMe)$_3$}(CO)$_3$(dppm-*P*)] **6a**: IR (thf) ν(CO)/cm^{-1} 1928w, 1847vs and 1826s (sh); ^{31}P-{^{1}H} NMR (81.02 MHz, thf–[^{2}H$_6$]acetone) δ 74.2 [d, P(Fe), ^2J(PP) = 79] and -23.8 [d, ^2J(PP) = 79 Hz].

K[Fe{Si(OEt)$_3$}(CO)$_3$(dppm-*P*)] **6b**: IR (thf) ν(CO)/cm^{-1} 1926w, 1844vs and 1812s; ^{31}P-{^{1}H} NMR (81.02 MHz, thf–[^{2}H$_6$]acetone δ 75.1 [d, P(Fe), ^2J(PP) = 80.0] and -23.9 [d, ^2J(PP) = 80.0 Hz].

K[Fe(SiPh$_3$)(CO)$_3$(dppb-*P*)] **6c**: IR (thf) ν(CO)/cm^{-1} 1915w, 1838vs and 1790s (**6c**·18-crown-6: 1915vw and 1830vs).

K[Fe{Si(OMe)$_3$}(CO)$_3${Ph$_2$PCH$_2$C(O)Ph}] **6d**: IR (thf) ν(CO)/cm^{-1} 1917w, 1834s, 1790s and 1670m; ^{31}P-{^{1}H} NMR (81.02 MHz, thf–[^{2}H$_6$]benzene) δ 57.9 (s).

[(Ph$_3$P)Cu(μ-dppm)Fe{Si(OMe)$_3$}(CO)$_3$] **7b**. A solution of compound **6a** (0.685 g, 1 mmol) in thf (30 cm^3) was added at 0 °C to a solution of [Cu(PPh$_3$)$_2$]NO$_3$ (0.649 g, 1 mmol) in thf (5 cm^3). The reaction mixture was stirred for 0.5 h at room temperature, then filtered and concentrated to *ca.* 5 cm^3 under reduced pressure. Addition of hexane (30 cm^3) induced precipitation of the product as a light yellow powder which was collected by filtration and then recrystallized by slow diffusion of hexane into a CH$_2$Cl$_2$ solution. Yellow, air-stable, X-ray-quality crystals formed which were collected and dried *in vacuo* (0.777 g, 80%), m.p. 178–180 °C (decomp.) (Found: C, 60.35; H, 4.55. Calc. for $C_{49}H_{46}CuFeO_6P_3Si$: C, 60.60; H, 4.75%). IR (thf): ν(CO)/cm^{-1} 1941m, 1870s and 1835s. NMR: ^{1}H(200 MHz, CD$_2$Cl$_2$), δ 3.19 [t, 2 H, CH$_2$, ^2J(PH) = 9.6], 3.31 (s, 9 H, OCH$_3$) and 6.95–7.45 (m, 35 H), ^{31}P-{^{1}H} (81.02 MHz, [^{2}H$_6$]acetone–CH$_2$Cl$_2$, 257 K), δ 76.3 [dd, P(Fe), *J*(AX) = 148, *J*(BX) = 9], 0.44 [PPh$_3$(Cu), *J*(AB) = 144, *J*(BX) = 9] and -9.8 [CH$_2$PPh$_2$(Cu), *J*(AB) = 144, *J*(AX) = 148 Hz].

[(MeCN)Cu(μ-dppm)Fe{Si(OMe)$_3$}(CO)$_3$] **7c**. A solution of compound **6a** (0.685 g, 1 mmol) in thf (30 cm^3) was added at 0 °C to a suspension of [Cu(MeCN)$_4$]BF$_4$ (0.346 g, 1.1 mmol) in thf (5 cm^3). A small amount of elemental copper precipitated, which was removed by filtration. Spectroscopic analysis of the concentrated solution indicated the formation of compound **7c** in *ca.* 90% yield. Attempts to crystallize it caused considerable decomposition. IR (thf): ν(CO)/cm^{-1} 1945m, 1870s and 1839s. ^{31}P-{^{1}H} NMR ([^{2}H$_6$]acetone–thf): δ 76.8 [d, P(Fe), ^2J(PP) = 142] and -10.3 [d, P(Cu), ^2J(PP) = 142 Hz].

mer-[(Ph$_3$As)Ag(μ-dppm)Fe{Si(OMe)$_3$}(CO)$_3$] **8a**. To a mixture of [Ag(AsPh$_3$)]NO$_3$ (0.476 g, 1 mmol) and AsPh$_3$ (1 mmol)

Table 2 Fractional atomic coordinates (× 10^4) with estimated standard deviations (e.s.d.s) in parentheses for non-hydrogen atoms of complex **7b**

Atom	*X/a*	*Y/b*	*Z/c*
Cu	2001(1)	2404(1)	1595(1)
Fe	3886(1)	1693(1)	1659(1)
P(1)	4106(2)	1856(1)	2672(1)
P(2)	1564(2)	2393(2)	2593(1)
P(3)	818(2)	2982(2)	877(1)
Si	3772(3)	1485(2)	631(2)
O(1)	6057(8)	932(6)	1611(4)
O(2)	4197(7)	3205(4)	1355(4)
O(3)	1939(8)	706(5)	1683(4)
O(4)	2465(6)	1604(4)	305(3)
O(5)	4304(12)	755(8)	414(6)
O(6)	4541(8)	2041(5)	202(4)
C(1)	5177(10)	1245(7)	1626(5)
C(2)	4001(9)	2608(7)	1473(4)
C(3)	2710(10)	1101(6)	1668(5)
C(4)	2145(12)	1517(7)	−344(7)
C(5)	3656(18)	182(12)	404(9)
C(6)	5731(13)	2194(8)	310(7)
C(7)	2721(8)	1899(5)	3041(4)
C(8)	4828(8)	1127(6)	3120(5)
C(9)	4726(10)	412(7)	2910(5)
C(10)	5205(11)	−151(6)	3249(7)
C(11)	5810(11)	−15(8)	3804(6)
C(12)	5931(11)	670(8)	4030(5)
C(13)	5438(9)	1245(7)	3696(5)
C(14)	4929(9)	2636(6)	2956(5)
C(15)	4663(11)	3044(7)	3453(7)
C(16)	5321(15)	3637(10)	3647(7)
C(17)	6299(16)	3802(9)	3353(8)
C(18)	6601(13)	3392(10)	2868(7)
C(19)	5905(10)	2814(7)	2668(5)
C(20)	1468(10)	3288(5)	2920(4)
C(21)	2297(10)	3785(7)	2779(5)
C(22)	2262(16)	4495(8)	2965(7)
C(23)	1351(21)	4700(8)	3294(7)
C(24)	500(15)	4231(8)	3429(5)
C(25)	555(11)	3510(6)	3240(5)
C(26)	262(9)	1936(5)	2800(5)
C(27)	169(10)	1577(6)	3349(5)
C(28)	−833(13)	1216(7)	3450(7)
C(29)	−1777(13)	1212(8)	2997(8)
C(30)	−1672(12)	1560(9)	2464(8)
C(31)	−651(10)	1926(7)	2357(6)
C(32)	−276(9)	3553(5)	1216(5)
C(33)	−1458(9)	3426(6)	1107(5)
C(34)	−2231(10)	3887(6)	1413(5)
C(35)	−1816(11)	4422(6)	1765(5)
C(36)	−674(10)	4555(6)	1867(5)
C(37)	135(10)	4121(6)	1586(5)
C(38)	1491(8)	3569(5)	349(4)
C(39)	2499(9)	3342(6)	132(5)
C(40)	3120(10)	3771(6)	−272(5)
C(41)	2711(10)	4427(7)	−446(5)
C(42)	1712(12)	4678(8)	−228(6)
C(43)	1091(11)	4248(7)	181(6)
C(44)	−43(9)	2383(6)	387(5)
C(45)	−656(10)	2602(7)	−162(6)
C(46)	−1373(11)	2121(7)	−502(6)
C(47)	−1475(12)	1457(8)	−316(7)
C(48)	−905(12)	1187(9)	228(7)
C(49)	−201(10)	1682(7)	573(6)

in thf (5 cm^3) was added at −50 °C, with exclusion of light, a solution of compound **6a** (0.685 g, 1 mmol) in thf (40 cm^3). The cold solution was filtered rapidly through a Celite-padded filter funnel and concentrated to *ca.* 5 cm^3. Addition of hexane (40 cm^3) led to precipitation of a white powder of the product, which was dried *in vacuo* (0.350 g, 33%) (Found: C, 54.80; H, 4.40. Calc. for $C_{49}H_{46}AgAsFeO_6P_2Si$: C, 55.55; H, 4.40%). IR (thf): ν(CO)/cm^{-1} 1952w, 1880s and 1850s. NMR: ^1H(200 MHz, CD_2Cl_2), δ 3.26 [t, 2 H, CH_2, ^2J(PH) = 9.1], 3.42 (s, 9 H, OCH_3) and 6.90–7.85 (m, 35 H); $^{31}P-\{^1H\}$ (81.02 MHz, $[^2H_6]$acetone–CH_2Cl_2, 230 K), δ 74.1 [d, P(Fe), ^2J(PP) = 139] and −2.5 [ddd, P(Ag), $^1J(P-^{109}Ag)$ = 259, $^1J(P-^{107}Ag)$ = 227, ^2J(PP) = 139 Hz].

$[(Ph_3P)Ag(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **8b**. To a solution of $[Ag(PPh_3)]NO_3$ (0.432 g, 1 mmol) in thf (5 cm^3) was added at −50 °C, with exclusion of light, a solution of compound **6a** (0.685 g, 1 mmol) in thf (40 cm^3). The cold solution was filtered rapidly through a Celite-padded filter funnel and concentrated nearly to dryness. The yellowish oily residue was redissolved in toluene (10 cm^3) and the solution was filtered again. Addition of hexane (40 cm^3) led to precipitation of a white powder of the product, which was dried *in vacuo* (0.521 g, 47%) (Found: C, 60.05; H, 4.40. Calc. for $C_{49}H_{46}AgFeO_6P_3Si{\cdot}C_7H_8$: C, 60.70; H, 4.90%). IR (thf): ν(CO)/cm^{-1} 1949m, 1876s and 1850s. NMR ^1H(200 MHz, $[^2H_6]$benzene), δ 3.10 [t, 2 H, CH_2, ^2J(PH) = 9.9], 3.84 (s, 9 H, OCH_3) and 6.70–7.65 (m, 35 H); $^{31}P-\{^1H\}$ (81.02 MHz, $[^2H_6]$acetone–CH_2Cl_2, 233 K), δ 75.1 [d, P(Fe), J(AX) = 140, J(BX) ≈ 0 Hz], 10.3 [ddd, PPh_3(Ag), $^1J(P-^{109}Ag)$ = 459, $^1J(P-^{107}Ag)$ = 398, J(AB) = 120 and −5.4 [m, P(Ag), $^1J(P-^{109}Ag)$ = 276, $^1J(P-^{107}Ag)$ = 244, J(AB) = 120, J(AX) = 140 Hz].

$[Ag(\mu\text{-dppm})Fe\{(\mu\text{-MeO})Si(OMe)_2\}(CO)_3]$ **9**. To a solution of $[Ag(MeCN)_2]NO_3$, prepared *in situ* by dissolving $AgNO_3$ (0.187 g, 1.1 mmol) in MeCN (2 cm^3)–thf (2 cm^3) was added at −50 °C with exclusion of light a solution of compound **6a** (0.685 g, 1 mmol) in thf (40 cm^3). In order to remove some insoluble products, the cold solution was rapidly filtered through a Celite-padded filter funnel and concentrated nearly to dryness. The remaining yellow oil was dissolved in cold toluene (10 cm^3) and the solution was filtered and concentrated. Addition of cold hexane induced the precipitation of a white powder, which was dried *in vacuo* (0.128 g, 17%) (Found: C, 49.00; 4.35. Calc. for $C_{49}H_{31}AgFeO_6P_2Si$: C, 49.45; H, 4.15%). IR (CH_2Cl_2): ν(CO)/cm^{-1} 1955w, 1890s and 1860vs. NMR: ^1H, see text; $^{31}P-\{^1H\}$ ($[^2H_6]$acetone–CH_2Cl_2, 230 K), δ 61.7 [d, P(Fe), ^2J(PP) = 47] and −12.1 [d, P(Ag), $^1J(P-^{107,109}Ag)$ = 438 Hz].

mer-$[(Ph_3P)Au(\mu\text{-dppm})Fe\{Si(OMe)_3\}(CO)_3]$ **10**. A solution of compound **6a** (0.685 g, 1 mmol) in thf (25 cm^3) was added at 0 °C to a suspension of $[Au(PPh_3)Cl]$ (0.495 g, 1 mmol) in thf (5 cm^3). The yellow reaction mixture was stirred for 0.5 h at room temperature and then filtered to remove KCl. After evaporation of the solvent to dryness the residue was dissolved in CH_2Cl_2 (5 cm^3) and the solution was layered with hexane. Large yellow crystals slowly formed and were collected by decantation and dried *in vacuo*. Keeping the mother-liquor in the cold for 2 d afforded a further crop of yellow microcrystals (0.917 g, 83%), m.p. 162–164 °C (decomp.) (Found: C, 53.55; H, 4.20. Calc. for $C_{49}H_{46}AuFeO_6P_3Si$: C, 53.25; H, 4.20%). IR (thf): ν(CO)/cm^{-1} 1950m, 1886s and 1859s. NMR: ^1H(200 MHz, $[^2H_6]$acetone), δ 3.32 [dt, CH_2, 2 H, ^2J(PH) = 9.6, 1.8], 3.74 (s, 9 H, OCH_3), and 7.16–7.64 (m, 35 H, C_6H_5); $^{31}P-\{^1H\}$ (C_6D_6–CH_2Cl_2, 247 K), δ 77.5 [d, P(Fe), J(BX) = 0, J(AX) = 154], 46.0 [d, Ph_3P(Au), J(AB) = 203] and 37.6 [part A of an ABX spin system, J(AB) = 203, J(AX) = 154 Hz].

$[(Ph_3P)AuFe\{Si(OMe)_3\}(CO)_3(PPh_3)]$ **11**. This colourless compound was prepared in an analogous manner to $[(Ph_3P)AuFe(SiMePh_2)(CO)_3(PPh_3)]$ (yield: 87%) (Found: C, 49.50; H, 3.80. Calc. for $C_{42}H_{39}AuFeO_6P_2Si$: C, 51.35; H, 4.00%). IR (thf): ν(CO)/cm^{-1} 1970m, 1902s (sh) and 1885vs. NMR: ^1H(CD_2Cl_2), δ 3.60 (s, 9 H, OCH_3) and 7.12–7.64 (m, C_6H_5); $^{31}P-\{^1H\}$ ($[^2H_6]$acetone–CH_2Cl_2), δ 67.1 [d, P(Fe), ^3J(PP) = 10] and 41.1 [d, P(Au), ^3J(PP) = 10 Hz].

Crystal Structure Determination of $[(Ph_3P)\overline{Cu(dppm)Fe}\{Si(OMe)_3\}(CO)_3]$ **7b**.—Crystals of compound **7b** were obtained by slow diffusion of hexane into a CH_2Cl_2 solution of the complex. A crystal of approximate dimensions of 0.24 × 0.27 × 0.35 mm was used for the X-ray analysis.

Crystal data. $C_{49}H_{46}CuFeO_6P_3Si$, $M = 971.30$, monoclinic, space group $P2_1/c$, $a = 11.542(5)$, $b = 18.567(7)$, $c = 21.830(7)$ Å, $\beta = 94.67(2)°$, $U = 4663(3)$ Å^3 (by least-squares refinement from the θ values of 28 accurately measured reflections, $\lambda = 0.71073$ Å) $Z = 4$, $D_c = 1.384$ g cm^{-3}, $F(000) = 2008$, μ(Mo-Kα) = 9.40 cm^{-1}.

Data collection and processing. Philips PW 1100 single-crystal diffractometer (θ–2θ scan mode, graphite-monochromated Mo-Kα radiation). All reflections with θ in the range 3–24° were measured; of 7331 independent, 2971 having $I > 2\sigma(I)$ were considered observed and used in the analysis. The individual profiles were analysed according to Lehmann and Larsen.[24] No correction for absorption effects was applied because of the low absorbance of the sample.

Structure solution and refinements. 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 and the carbons of the PPh_3 ligand. All the hydrogen atoms were placed at their calculated positions (C–H 1.08 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 $K = 0.456$ and $g = 0.0033$. Final R and R' values were 0.0563 and 0.0718, respectively. The SHELX-76 and 86 systems of computer programs were used.[25] Atomic scattering factors, corrected for anomalous dispersion, were taken from ref. 26. 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 Diffratometrica del C.N.R., Parma.

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

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