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# Bimetallic alkoxy-silyl complexes with bis(diphenylphosphino)methane, 2-(diphenylphosphino)pyridine or (diphenylphosphino)acetophenone ligands: crystal structure of $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\overline{\text{OMe}})\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{C}\equiv\text{NR})][\text{PF}_6]$ ( $\text{R} = 2,6\text{-xylyl}$ ) \*

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## Abstract

The heterobimetallic carbene complexes  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\overline{\text{OMe}})\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}\{\overline{\text{C}}(\text{CH}_2)_2\text{CH}(\text{R})\text{O}\}][\text{PF}_6]$  ( $\text{R} = \text{H}$  (2a), Me (2b)) and isonitrile complexes  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\overline{\text{OMe}})\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{C}\equiv\text{N-R})][\text{PF}_6]$  ( $\text{R} = 2,6\text{-xylyl}$  (3a), or *t*-butyl (3b)) have been prepared by the reaction of  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\overline{\text{OMe}})\}(\text{CO})_3(\mu\text{-dppm})\text{PtCl}]$  with 3-butyn-1-ol or ( $\pm$ )-4-pentyn-2-ol or  $\text{R-N}\equiv\text{C}$  respectively, in the presence of  $\text{TlPF}_6$ . The (trimethoxy)silyl ligand bridges the two metals, as a result of a Si-O  $\rightarrow$  Pt interaction. The structure of 3a was refined to  $R = 0.029$  and  $R_w = 0.041$  on the basis of 5764 reflections having  $F_o^2 > 3\sigma(F_o^2)$ . Upon reaction of *cis*- $[\text{MCl}(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)]\{\text{P}(\text{OPh})_3\}$  ( $\text{M} = \text{Pt}$  (5a), or Pd (5b)) with  $\text{K}[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\eta^1\text{-dppm})\}]$  (K1a) the *ortho*-metalated heterobimetallic complexes *cis*- $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-dppm})\text{Pt}\{\text{P}(\text{OPh})_2(\text{OC}_6\text{H}_4)\}\}]$  (6a) and *trans*- $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-dppm})\text{Pd}\{\text{P}(\text{OPh})_2(\text{OC}_6\text{H}_4)\}\}]$  (6b) were formed. The phosphinopyridine- and ketophosphine-bridged complexes  $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-Ph}_2\text{Ppy})\text{Pd}(8\text{-mq})\}]$  (8) and  $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3\{\mu\text{-Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph}\}\text{Pd}(8\text{-mq})\}]$  (10) are described. We also discuss the preparation, dynamic behaviour and spectroscopic properties of heterobimetallic allyl-type complexes  $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-dppm})\text{Ni}(\eta^3\text{-C}_3\text{H}_5)\}]$  (11),  $[\text{Fe}\{\text{Si}(\text{OSiMe}_3)_3(\text{CO})_3(\mu\text{-dppm})\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}]$  (12a),  $[\text{Fe}\{\text{SiMe}(\text{OSiMe}_3)_2(\mu\text{-dppm})\text{Pd}(\eta^3\text{-C}_3\text{H}_5)\}]$  (12b),  $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-Ph}_2\text{Ppy})\text{Pd}(\eta^3\text{-RC}_3\text{H}_4)\}]$  ( $\text{R} = \text{H}$  (13a) or Me (13b)) and  $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\eta^3\text{-C}_8\text{H}_{13})\}]$  (14). Treatment of  $[\text{NiCp}(\text{PPh}_3)\text{Br}]$  with  $[\text{NEt}_3\text{H}]\text{1a}$  yielded the heterobimetallic complex  $[\text{Fe}\{\text{Si}(\text{OMe})_3(\text{CO})_3(\mu\text{-dppm})\text{NiCp}\}]$  (15).

## 1. Introduction

We have recently investigated the potential of functional metallates  $\text{K}[\text{Fe}\{\text{Si}(\text{OR})_3(\text{CO})_3(\eta^1\text{-Ph}_2\text{P} \sim \text{Y})\}]$  (K1) and of their corresponding hydrides  $[\text{FeH}\{\text{Si}(\text{OR})_3(\text{CO})_3(\eta^1\text{-Ph}_2\text{P} \sim \text{Y})\}]$  (H1) for the synthesis of bimetallic complexes of iron with main group or

transition metals (Table 1). When  $\text{Y} = \text{CH}_2\text{PPh}_2$ , the pendant phosphorus donor of the Fe-bound dppm ligand was found to assist the formation of the Fe-M

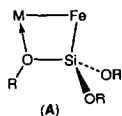
TABLE 1. Functional metallates  $[\text{Fe}(\text{CO})_3\{\text{Si}(\text{OR})_3(\eta^1\text{-Ph}_2\text{P} \sim \text{Y})\}]^-$  (1<sup>-</sup>)

Compound	R	Y
1a	Me	$\text{CH}_2\text{PPh}_2$
1b	Me	$\text{C}_3\text{H}_4\text{N}$
1c	Me	$\text{CH}_2\text{C}(\text{=O})\text{Ph}$
1d	$\text{SiMe}_3$	$\text{CH}_2\text{PPh}_2$

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\* Dedicated to Professor M.F. Lappert on the occasion of his 65th birthday, with our sincere congratulations and warmest wishes.

bond and lead to stable five-membered ring structures of the type  $\overline{\text{Fe}(\mu\text{-dppm})\text{M}}$ . In the case where  $\text{M} = \text{Ag}, \text{Zn}, \text{In}, \text{Pd}, \text{Pt}$  or  $\text{Rh}$ , this has enabled an unprecedented event to occur, namely the formation of a  $\mu_2\text{-}\eta^2\text{-Si-O}$  bridge of type A between the metals [1]:



The labile character of the dative oxygen  $\rightarrow$  metal interaction shown by variable-temperature  $^1\text{H}$  nuclear magnetic resonance (NMR) spectroscopy and chemical reactivity studies, offers possibilities for the attachment of small molecules to a potentially vacant coordination site. In view of the relevance of such processes to substrate activation, it seemed desirable to obtain more information about the factors which govern the occurrence and strength of the dative  $\text{O} \rightarrow \text{M}$  interaction. We describe here the synthesis and properties of a series of  $\text{Fe-Pt}$ ,  $\text{Fe-Pd}$  and  $\text{Fe-Ni}$  complexes, in which this feature is combined with the presence of different types of organic ligand.

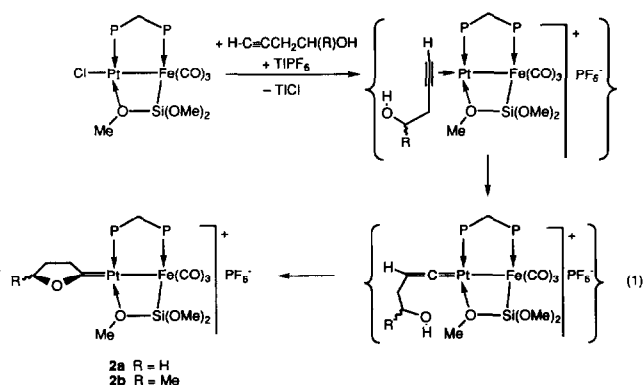
## 2. Results and discussion

### 2.1. Synthesis of a bimetallic Fe-Pt carbene complex

Heterobimetallic complexes containing a terminal carbene ligand are relatively rare [2], in contrast with those where the carbene ligand bridges two metals [3]. With the aim of preparing a bimetallic  $\text{Fe-Pt}$  complex bearing a terminal carbene ligand at the platinum centre, we used two different strategies. The first was the nucleophilic attack of  $\text{K}[\text{Fe}(\text{Si}(\text{OMe})_2)(\text{CO})_3(\eta^1\text{-dppm})]$  (**K1a**) on the carbene complex  $[\text{PtCl}_2(\text{PPh}_3)_2(\text{C}(\text{NHR})(\text{NCH}_2\text{CH}_2\text{CH}_2))]$  ( $\text{R} = \text{t-butyl}$  or  $2,6\text{-xylyl}$ ) which was expected to lead to the formation of at least one  $\text{Fe-Pt}$  bond. However, stirring the reaction mixture for several days at room temperature did not yield a heterobimetallic carbene complex.

In contrast, the reaction of the bimetallic complex  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{PtCl}]$  with 3-butyn-1-ol in tetrahydrofuran (THF) in the presence of  $\text{Ti}[\text{PF}_6]$  led to  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{C}(\text{CH}_2)_3\text{O})][\text{PF}_6]$  (**2a**) which contains the cyclic carbene ligand 2-oxacyclopentylidene. This reaction is likely to proceed by coordination of the alkyne  $\text{C}\equiv\text{C}$  triple bond to the platinum centre, followed by formation of a vinylidene intermediate, intramolecular nu-

cleophilic attack of the oxygen atom and proton migration [4]:



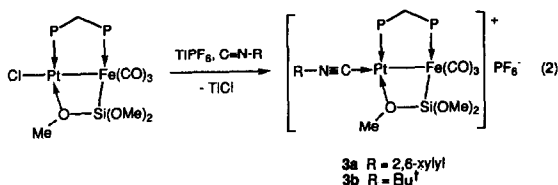
One of the proposed intermediates in the reaction sequence (1) exhibits  $\nu(\text{CO})$  vibrations at 1968s, 1910vs and 1880s  $\text{cm}^{-1}$ , which are replaced by those of **2a** (1992m, 1937s and 1912s  $\text{cm}^{-1}$ ) after 4 h. In the  $^1\text{H}$  NMR spectrum, the methoxy protons give rise to two resonances at  $\delta$  3.84 and 3.76 in a 1:2 ratio. The former resonance shows coupling both with the *trans* phosphorus ( $^4J(\text{PH}) = 1.6$  Hz) and the  $^{195}\text{Pt}$  nucleus ( $^3J(\text{PtH}) = 22.7$  Hz), consistent with a  $\mu_2\text{-}\eta^2\text{-Si-O}$  bridge [1]. The presence of non-equivalent methoxy groups is further supported by the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum where two signals in a 1:2 ratio at  $\delta$  60.4 and 51.1 were observed. The carbonyl groups give rise to two doublets in a 2:1 ratio ( $^2J(\text{PC}) = 17$  and 14 Hz) at  $\delta$  213.2 and 210.0. The chemical shifts of the three methylene groups of the carbene ligand ( $\delta$  19.4, 55.8 and 90.0) are similar to those reported for related mononuclear  $\text{Pt}$  [5] and dinuclear  $\text{Mn-Pt}$  [6] carbene complexes. Unfortunately the  $^{13}\text{C}$  carbene signal could not be detected. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **2a** contains two doublets, one at  $\delta$  3.3 ( $^{2+3}J(\text{PP}) = 44$  Hz) with  $\text{Pt}$  satellites ( $^1J(\text{PtP}) = 4437$  Hz) and the other at  $\delta$  52.3 which is assigned to the  $\text{Fe}$ -bound  $\text{P}$  nucleus. Relatively low values for the  $^{2+3}J(\text{PP})$  coupling may be a consequence of increased electron withdrawal from the  $\text{P-C-P}$  unit by the bimetallic part of the skeleton and appear to be diagnostic for a  $\mu_2\text{-}\eta^2\text{-Si-O}$  bridge [1].

In an analogous manner, we prepared the racemic carbene complex  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{C}(\text{CH}_2)_2\text{CH}(\text{Me})\text{O})][\text{PF}_6]$  (**2b**) with a quantitative spectroscopic yield by using racemic ( $\pm$ )-4-pentyn-2-ol. The presence of an additional methyl group appears to accelerate the transformation at the platinum centre since no intermediate could be detected. Except for the resonances due to the carbene ligand, all other spectroscopic data are almost identical

with those of **2a**. Our tentative assignments of the  $^1\text{H}$  NMR resonances for the carbene ligand result from comparison with **2a** and homodecoupling experiments (see Section 3). As in **2a**, the FAB $^+$  mass spectrum of **2b** exhibits a peak for the molecular ion and an intense peak for the fragment having lost the carbene ligand. This synthetic route has previously been used for the synthesis of mononuclear carbene complexes of platinum [5b,7] and ruthenium [4b–d]. To our knowledge, the only other examples of heterobimetallic complexes bearing the terminal carbene ligand 2-oxacyclopentylidene are  $[\text{Mn}(\text{CO})_4(\mu\text{-I})\text{Pt}(\text{C}(\text{CH}_2)_3\text{O})(\text{P}^t\text{Bu}_2\text{Me})]$  [6] and  $[\text{MoCp}(\text{CO})_2(\mu\text{-PR}_2)(\mu\text{-H})\text{Pt}(\text{C}(\text{CH}_2)_3\text{O})(\text{PCy}_3)]$  [8]. Both compounds were obtained by carbene transfer from the mononuclear complexes  $[\text{Mn}(\text{CO})_4(\text{C}(\text{CH}_2)_3\text{O})\text{I}]$  or  $[\text{MoCp}(\text{CO})_2(\text{C}(\text{CH}_2)_3\text{O})(\text{PR}_2\text{H})\text{BPh}_4]$  upon reaction with  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{P}^t\text{Bu}_2\text{Me})]$  or  $[\text{Pt}(\text{C}_2\text{H}_4)_2(\text{PCy}_3)]$  respectively.

## 2.2. Synthesis of bimetallic Fe–Pt isonitrile complexes

Since coordination of isonitrile ligands to transition metals may provide convenient access to amino-carbene complexes, we were also interested in the synthesis of bimetallic isonitrile complexes [9]. The cationic complexes  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{C}\equiv\text{N-R})][\text{PF}_6^-]$  (R = 2,6-xylyl (**3a**), t-butyl (**3b**)) were obtained as pale-yellow solids by the reaction (2).

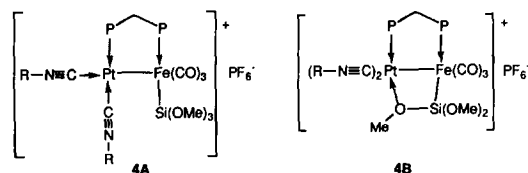


In addition to the three carbonyl vibrations, their IR spectrum exhibits a strong  $\nu(\text{C}\equiv\text{N})$  band, at  $2170\text{ cm}^{-1}$  for **3a** and at  $2199\text{ cm}^{-1}$  for **3b**. The  $\mu_2\text{-}\eta^2\text{-Si-O}$  bridge is maintained in solution since the proton NMR spectrum shows two distinct signals for the methoxy groups, in a 2:1 ratio at  $\delta$  3.83 and 4.18 for **3a**, and at  $\delta$  3.79 and 4.13 for **3b**. It is interesting to compare the IR spectra of **3a** or **3b** and the cationic complex  $[\text{Fe}(\text{Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{CO})][\text{PF}_6^-]$  (**3c**), which was obtained by purging a THF solution of  $[\text{Fe}(\text{Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{PtCl}]$  with CO in the presence of  $\text{Tl}[\text{PF}_6]$  [10]. The terminal CO on platinum absorbs at  $2091\text{ cm}^{-1}$  whereas the Fe-bound carbonyl groups give rise to three absorptions at  $2020\text{m}$ ,  $1970\text{s}$  and  $1953\text{vs cm}^{-1}$ . There are at higher wavenumbers than in  $[\text{Fe}(\text{Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{PtCl}]$  (about  $40\text{ cm}^{-1}$ ) or in **3a** or **3b** (about  $15\text{ cm}^{-1}$ ) owing to the cationic nature of the complex and the better

$\pi$ -acceptor properties of CO vs. isonitrile ligands. The crystal structure of **3a** has been determined by X-ray diffraction (see below).

The addition of  $p\text{-MeC}_6\text{H}_4\text{C}\equiv\text{N}$  to a solution of **3a** did not alter the  $^{31}\text{P}$  NMR signals nor the IR spectrum. It therefore appears that the dative  $\text{O} \rightarrow \text{Pt}$  interaction in **3a** is not broken by  $p$ -tolynitrile, which contrasts with the greater lability of the coordinated ether function in the cationic complex  $[\text{PtCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})]^+$  which was found to be readily displaced by benzonitrile to give  $[\text{PtCl}(\text{Ph}_2\text{PCH}_2\text{CH}_2\text{OMe})_2(\text{NPh})]^+$  [11].

However, the addition of a second equivalent of 2,6-xylyl isonitrile to a solution of **3a** led instantaneously to the bis(isonitrile) complex  $\text{mer-}[\text{Fe}(\text{Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{C}\equiv\text{N-R})_2][\text{PF}_6^-]$  (**4**). In addition to the three  $\nu(\text{CO})$  bands ( $2018\text{m}$ ,  $1960\text{m}$  and  $1928\text{s cm}^{-1}$ ), which are at higher wavenumbers than in the mono(isonitrile) complexes, strong and medium  $\nu(\text{CN})$  bands ( $2180\text{s}$  and  $2145\text{m cm}^{-1}$ ) indicate two isonitrile ligands on platinum. The  $^1\text{H}$  NMR spectrum exhibits only one resonance for the methoxy protons at 3.14 (9H) ppm which would be consistent with a structure of type **4A** in which the  $\text{O} \rightarrow \text{Pt}$



bond has been broken by the second isonitrile, which is obviously a better donor than  $p$ -tolynitrile (see above). Despite the non-equivalence of the two isonitrile ligands in such a structure, only one signal is observed at  $\delta$  2.32 (12 H) for the four methyl groups. This could result from rapid exchange between the isonitrile ligand and since at low temperature (243 K) this signal splits in two singlets. In the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum the doublet for the phosphorus atom on platinum is shifted significantly downfield on going from **3a** ( $\delta$  4.8) to **4** ( $\delta$  22.3), while the  $^{2+3}\text{J}(\text{PP})$  coupling constant increases slightly from 45 to 54 Hz. This is consistent either with a rapid exchange between the methoxy and the isonitrile donors on platinum, or with a pentacoordinate platinum centre. In the latter case (**4B**), trigonal bipyramidal Pt would account for the equivalence of the isonitrile ligands and the small  $^{2+3}\text{J}(\text{PP})$  coupling of 54 Hz observed in the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum. Note that mononuclear pentacoordinate bis(isonitrile) complexes of Pd are intermediates in insertion reactions of isonitriles into M–C bonds [12a]. Stable cationic pentacoordinate bis(isonitrile) complexes of Pt have been reported by Treichel and Knebel [12b].

### 2.3. Crystal structure of $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}\text{-(CO)}_3(\mu\text{-dppm})\text{Pt}(\text{C}\equiv\text{N-R})][\text{PF}_6] \cdot \text{CH}_2\text{Cl}_2$ (R = 2,6-xylyl) (**3a**)

Details are summarized in the Section 3. Selected intramolecular bond lengths and angles are given in Table 2. The molecular structure of **3a** is illustrated in Fig. 1 and consists of a dppm-bridged iron-platinum complex, with a Fe-Pt distance of 2.5818(8) Å and P(1)-Pt and P(2)-Fe distances of 2.206(5) Å and 2.22(2) Å respectively. These distances lie in the ranges found for these bonds in similar complexes [1h, 13]. The environment of the Fe atom is composed by the Si atom from the  $\text{Si}(\text{OMe})_3$  ligand, which is *trans* to P(2), and by three carbon atoms from terminal, meridional carbonyl ligands. Steric effects due to the phenyl rings at P(2) seem to be responsible for the Pt-Fe-C(6) angle of only 164.6(4)°. The C(4)-Fe-C(5) angle of 151.0(5)° lies between the values expected for octahedral and trigonal bipyramidal Fe coordination. In re-

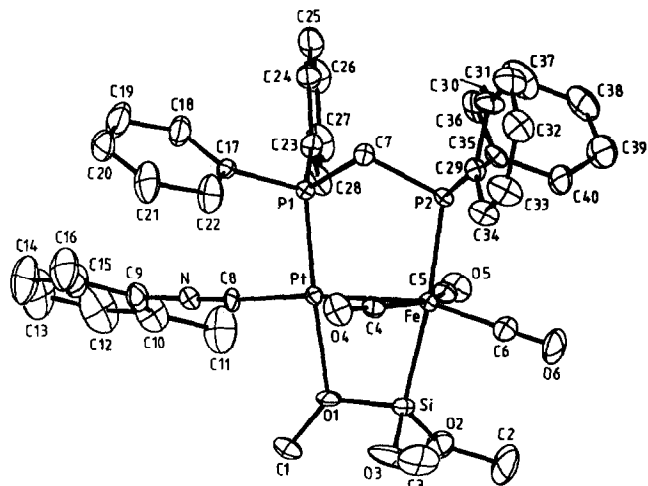


Fig. 1. ORTEP view of the cationic complex  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}\text{-(CO)}_3(\mu\text{-dppm})\text{Pt}(\text{C}\equiv\text{N}-(2,6\text{-xylyl}))]^+$  in **3a**.

TABLE 2. Selected bond distances (Å) and angles (deg) in **3a**

Bond distances			
Pt-Fe	2.5818(8)	P(2)-C(29)	1.81(2)
Pt-P(1)	2.206(5)	P(2)-C(35)	1.82(2)
Pt-O(1)	2.13(1)	Si-O(1)	1.681(8)
Pt-C(8)	1.977(6)	Si-O(2)	1.619(9)
Fe-P(2)	2.22(2)	Si-O(3)	1.60(1)
Fe-Si	2.263(2)	O(1)-C(1)	1.43(1)
Fe-C(4)	1.76(2)	O(2)-C(2)	1.39(1)
Fe-C(5)	1.78(1)	O(3)-C(3)	1.38(1)
Fe-C(6)	1.78(1)	O(4)-C(4)	1.15(2)
P(1)-C(7)	1.83(1)	O(5)-C(5)	1.13(1)
P(1)-C(17)	1.81(2)	O(6)-C(6)	1.14(1)
P(1)-C(23)	1.81(1)	N-C(8)	1.125(8)
P(2)-C(7)	1.84(2)	N-C(9)	1.396(8)
Bond angles			
Fe-Pt-P(1)	94.6(1)	Pt-P(1)-C(7)	113.8(4)
Fe-Pt-O(1)	80.4(2)	Pt-P(1)-C(17)	110.1(6)
Fe-Pt-C(8)	171.0(1)	Pt-P(1)-C(23)	114.5(4)
P(1)-Pt-O(1)	174.4(3)	P(1)-C(7)-P(2)	113.4(9)
P(1)-Pt-C(8)	91.5(2)	Pt-C(8)-N	171.3(6)
O(1)-Pt-C(8)	93.8(2)	Fe-Si-O(1)	100.8(3)
Pt-Fe-P(2)	98.0(4)	Fe-Si-O(2)	119.7(5)
Pt-Fe-Si	76.01(4)	Fe-Si-O(3)	121.0(3)
Pt-Fe-C(4)	74.7(4)	O(1)-Si-O(2)	100.4(7)
Pt-Fe-C(5)	76.3(3)	O(1)-Si-O(3)	104.5(5)
Pt-Fe-C(6)	164.6(4)	O(2)-Si-O(3)	106.8(6)
P(2)-Fe-Si	174.0(4)	Pt-O(1)-Si	102.8(4)
P(2)-Fe-C(4)	92.4(7)	Pt-O(1)-C(1)	129.8(6)
P(2)-Fe-C(5)	90.6(5)	Fe-P(2)-C(7)	109.4(8)
P(2)-Fe-C(6)	97.3(5)	Fe-P(2)-C(29)	118.5(8)
Si-Fe-C(4)	86.5(5)	Fe-P(2)-C(35)	116.0(9)
Si-Fe-C(5)	87.6(2)	C(8)-N-C(9)	179.6(6)
Si-Fe-C(6)	88.6(4)	Fe-C(4)-O(4)	179.1(1)
C(4)-Fe-C(5)	151.0(5)	Fe-C(5)-O(5)	179.0(8)
C(4)-Fe-C(6)	105.5(6)	Fe-C(6)-O(6)	179.1(1)
C(5)-Fe-C(6)	102.7(5)		

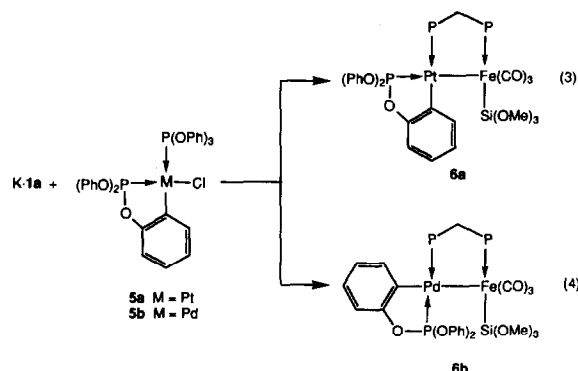
lated Fe-Pd or Fe-Pt complexes in which iron has a similar environment, the latter description was favoured, corresponding to a formal dative  $\text{Fe } d^8 \rightarrow \text{Pt } d^8$  interaction.

The most interesting feature of **3a** is the dative  $\text{O} \rightarrow \text{Pt}$  bond involving the  $\mu_2\text{-}\eta^2\text{-Si-O}$  bridge and resulting in a four-membered Pt-O-Si-Fe ring. Although it is similar to the Pd-O-Si-Fe rings first described in 1989 [1a], it is now structurally characterized for the first time in the case of Pt. This  $\mu_2\text{-}\eta^2\text{-Si-O}$  interaction is responsible for the significant lengthening of the Si-O(1) bond compared with Si-O(2) or Si-O(3) (Table 2). The  $\text{O} \rightarrow \text{Pt}$  distance of 2.13(1) Å is comparable with the corresponding  $\text{O} \rightarrow \text{Pd}$  distance of 2.100(4) Å in  $[(\text{OC})_3\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}\{\mu\text{-dppm}\}\text{PdCl}]$  [1a] and is, as expected, slightly longer than the covalent O-Pt distances of 2.013(4) and 2.034(3) Å in the bis(alkoxo) complex  $\text{cis-}[\text{Pt}(\text{Ph}_2\text{PCH}_2\text{CMe}_2\text{O})_2]$  [14]. The square-planar coordination around the platinum atom also involves a linear terminal isonitrile ( $\text{Fe-Pt-C}(8)$ , 171.0(1)°). The Pt-C(8) distance of 1.977(6) Å compares with those found in other platinum 2,6-xylyl isonitrile complexes [15a]. It is significantly longer than in  $\text{cis-}[\text{PtCl}_2(\text{C}\equiv\text{NPh})_2]$  (1.896(16) Å) [15b], possibly because of the *trans* influence of the metal-metal bond in **3a**.

### 2.4. Synthesis of cyclometallated bimetallic Fe-Pt and Fe-Pd complexes

In 1973 Robinson and coworkers [16] described the preparation of cyclometallated complexes of the type  $[\text{MCl}\{(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)\}\{\text{P}(\text{OPh})_3\}]$  (M = Pt (**5a**) or Pd (**5b**)) by thermal elimination of HCl from the corresponding  $[\text{MCl}_2\{\text{P}(\text{OPh})_3\}_2]$  precursors. In order to obtain bimetallic complexes containing such a metal-

carbon  $\sigma$  bond, we allowed **K1a** to react with **5** in THF (eqns. (3) and (4)).

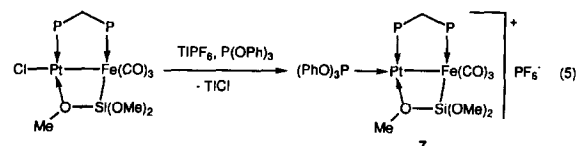


Whereas the reaction with **5a** took 5–6 h at ambient temperature, the reaction with **5b** was complete after 2.5 h at room temperature (about 5 h at  $-30^\circ\text{C}$ ) and afforded stable yellow–orange complexes after work-up. In each case the IR spectrum showed the pattern typical of a meridional arrangement of the carbonyl ligand. In the  $^1\text{H}$  NMR spectra, only a sharp singlet for the three equivalent methoxy groups was observed at 3.39 ppm (**6a**) and 3.98 ppm (**6b**), ruling out any  $\mu_2\text{-}\eta^2\text{-Si-O}$  interaction at ambient temperature. However,  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy revealed two different structures for **6a** and **6b**.

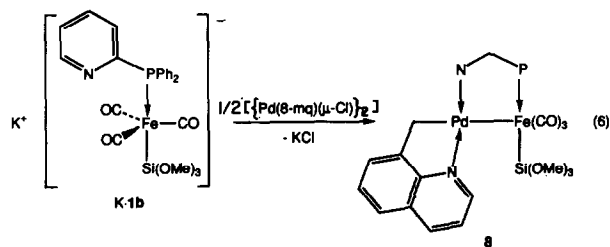
In the spectrum of **6a** a low field doublet ( $^2J(\text{PP}_{cis}) = 9$  Hz) is found at  $\delta$  114.5 with platinum satellites ( $^1J(\text{PPt}) = 5205$  Hz) for the *ortho*-metallated phosphorus ligand. The dppm ligand gives rise to a doublet for the phosphorus on iron at  $\delta$  53.1 ( $^{2+3}J(\text{PP}) = 89$  Hz) with platinum satellites ( $^{2+3}J(\text{Ppt}) = 79$  Hz), and a doublet of doublets at  $\delta$  1.75 ( $^{2+3}J(\text{PP}) = 89$  and  $^2J(\text{PP}_{cis}) = 9$  Hz) for the phosphorus on platinum. The smallness of 9 Hz is characteristic of a *cis* arrangement of two mutually coupled phosphorus nuclei coordinated to platinum and is similar to that found for  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{P}(\text{OPh})_3)]\text{-}[\text{PF}_6]^-$  (**7**) (see below). The resonance for the *ortho*-metallated phosphorus of **6b** appears further downfield (134.9 ppm) as a doublet of doublets, with a very large coupling constant ( $^2J(\text{PP}_{trans}) = 681$  Hz), consistent with other  $^2J(\text{PP})$  phosphite–phosphine *trans*-coupling constants [17], and a further coupling with the dppm-phosphorus coordinated to iron of  $^{3+4}J(\text{PP}) = 25$  Hz. The doublet of doublets for the palladium-bound dppm phosphorus atoms demonstrates the same strong *trans* coupling and a further coupling of 96 Hz with the other dppm phosphorus atoms. The presence of two different structures with respect to the P–M–P arrangement in **6a** and **6b** contrasts with the situation in complexes of type **5** where only *cis* isomers were observed.

Complex  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\text{P}(\text{OPh})_3)]\text{-}[\text{PF}_6]^-$  (**7**) was prepared for comparative purposes by the reaction (5). The  $\mu_2\text{-}\eta^2\text{-Si-O}$  interaction found in the precursor is maintained in this cationic complex, as shown by spectroscopy. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** exhibits a triplet at 115.4 ppm with platinum satellites ( $^1J(\text{PPt}) = 4796$  Hz) for the phosphite ligand. The dppm ligand gives rise to a doublet of doublets for the phosphorus on iron at  $\delta$  44.9 ( $^{2+3}J(\text{PP}) = 40$  Hz,  $^{3+4}J(\text{PP}(\text{OPh})_3) = 23$  Hz) and a doublet of doublets at  $\delta$  6.7 ( $^{2+3}J(\text{PP}) = 40$  Hz and  $^2J(\text{PP}(\text{OPh})_3) = 22$  Hz) for the phosphorus on platinum.

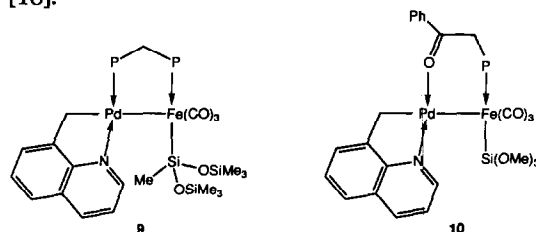
We felt it of interest to compare the situation in **6b** with that in complexes containing a cyclometallated 8-methylquinoline ligand in place of the cyclometallated phosphite ligand. We have recently found that such complexes are accessible and that the palladium–carbon  $\sigma$  bond is *trans* to the metal–metal bond, as in **6b** [10,18]. We have now extended this study by using the  $\text{Ph}_2\text{Ppy}$  ligand in place of dppm and obtained, with an almost quantitative spectroscopic yield (IR monitoring), the bright-yellow complex  $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-Ph}_2\text{Ppy})\text{Pd}(8\text{-mq})]\text{-}[\text{PF}_6]^-$  (**8**) in which two nitrogen donor atoms are bound to Pd (eqn. (6)):



Complex  $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-dppm})\text{Pd}(\text{P}(\text{OPh})_3)]\text{-}[\text{PF}_6]^-$  (**7**) was prepared for comparative purposes by the reaction (5). The  $\mu_2\text{-}\eta^2\text{-Si-O}$  interaction found in the precursor is maintained in this cationic complex, as shown by spectroscopy. The  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum of **7** exhibits a triplet at 115.4 ppm with platinum satellites ( $^1J(\text{PPt}) = 4796$  Hz) for the phosphite ligand. The dppm ligand gives rise to a doublet of doublets for the phosphorus on iron at  $\delta$  44.9 ( $^{2+3}J(\text{PP}) = 40$  Hz,  $^{3+4}J(\text{PP}(\text{OPh})_3) = 23$  Hz) and a doublet of doublets at  $\delta$  6.7 ( $^{2+3}J(\text{PP}) = 40$  Hz and  $^2J(\text{PP}(\text{OPh})_3) = 22$  Hz) for the phosphorus on platinum.

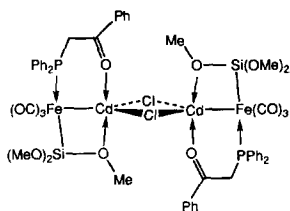


The absence of any significant  $\text{MeO} \rightarrow \text{Pd}$  interaction in solution is revealed by  $^1\text{H}$  NMR spectroscopy in  $\text{CDCl}_3$  which shows only one sharp singlet at  $\delta$  3.73 for the nine equivalent methoxy protons and a singlet at  $\delta$  3.68 for the two equivalent  $\text{CH}_2$  protons of the quinoline ring even at 243 K. The retention of the five membered chelate ring with a dative  $\text{N} \rightarrow \text{Pd}$  bond is similar to the situation recently encountered with **9** [18].



The relatively low value found for  $\nu(\text{CO})$  1959, 1900 and  $1842\text{ cm}^{-1}$  could indicate a semibridging contact between two carbonyl groups on iron and Pd.

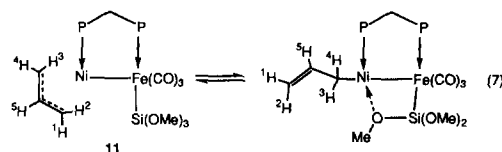
The stability of complex **9** encouraged us to attempt the synthesis of a bimetallic Fe–Pd complex with a ligand less stabilizing than dppm or  $\text{Ph}_2\text{Ppy}$ . In view of our interest in functional phosphine ligands containing oxygen donors [1f,19], we treated  $\text{K}[\text{Fe}(\text{Si}(\text{OMe})_3)(\text{CO})_3(\mu\text{-Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph})]$  (**K1c**) with  $[\{\text{Pd}(\text{8-mq})(\mu\text{-Cl})_2\}]$  in THF. A rapid reaction afforded high yields of yellow  $[\text{Fe}(\text{Si}(\text{OMe})_3)(\text{CO})_3(\mu\text{-Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph})\text{Pd}(\text{8-mq})]$  (**10**) after precipitation with hexane. Although the product had poor elemental analyses, its spectroscopic data are consistent with the structure shown. The IR spectrum of **10** in Nujol displays three  $\nu(\text{CO})$  bands at 1950, 1872 and  $1858\text{ cm}^{-1}$ , which are similar to those of **8** and are typical of a meridional arrangement of the carbonyl groups. An additional medium intensity CO stretch at  $1620\text{ cm}^{-1}$  is also observed. The last is diagnostic of a ketone–metal interaction and a comparable value of  $1630\text{ cm}^{-1}$  has been recently observed for  $[\text{Fe}\{\text{Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph})\text{Cd}(\mu\text{-Cl})_2]$ , the first bimetallic complex in which the unprecedented bridging mode for this type of functional phosphine was established by X-ray diffraction [1f]:



The frequencies of the  $\nu(\text{C}=\text{O})$  bands are intermediate between those observed for the mononuclear 8-mq-substituted complexes  $[(\text{8-mq})\text{PdCl}(\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph})]$  (with an uncoordinated keto function at  $1677\text{ cm}^{-1}$ ) and  $[(\text{8-mq})\text{Pd}(\text{Ph}_2\text{PCH}_2\text{C}(\text{O})\text{Ph})][\text{CF}_3\text{SO}_3]$ , which contains a chelating  $\beta$ -keto phosphine ( $1570\text{ cm}^{-1}$ ) [19c]. The proton NMR spectrum of **10** shows a singlet for the methoxy groups at  $\delta$  3.65 and for the Pd-bound  $\text{CH}_2$  group at 3.78 ppm, and a doublet for the  $\text{PCH}_2$  group at  $\delta$  3.89 with  $^2J(\text{PH}) = 1.5\text{ Hz}$ . This complex may be stored in the solid state for some weeks at a low temperature and is stable in donor solvents such as THF or acetone for short periods (about 0.5 h) but decomposes rapidly in chlorinated solvents. Thus the  $\beta$ -keto phosphine complex is markedly less stable than its dppm analogue. Note that unsupported heterobimetallic complexes containing a cyclopalladated moiety were reported to be labile [20].

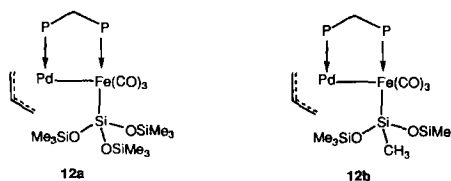
## 2.5. Synthesis of bimetallic Fe–Ni and Fe–Pd allyl complexes

Because of the promising catalytic activity of  $[\text{Fe}(\text{Si}(\text{OMe})_3)(\text{CO})_3(\mu\text{-dppm})\text{Pd}(\eta^3\text{-allyl})]$  in dehydrocoupling reactions [1c], we were interested in preparing related complexes with different steric and electronic environments. The Fe–Ni complex  $[\text{Fe}(\text{Si}(\text{OMe})_3)(\text{CO})_3(\mu\text{-dppm})\text{Ni}(\eta^3\text{-C}_3\text{H}_5)]$  (**11**) was isolated as red microcrystals by the reaction of **K1a** with  $[\{\text{Ni}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2\}]$  in THF at a low temperature with a satisfactory yield. It is less stable in solution than its palladium analogue, but it can be manipulated in air for short periods. The broadening observed at ambient temperature in  $\text{C}_6\text{D}_6$  for the  $^1\text{H}$  NMR resonances of the allylic protons H(2), H(3) and H(4) can be interpreted in terms of a dynamic behaviour involving a rapid  $\eta^3 \rightarrow \eta^1 \rightarrow \eta^3$  rearrangement which exchanges the protons H(3) and H(4). This exchange might be assisted through stabilization of an unsaturated nickel centre by an  $\text{MeO} \rightarrow \text{Ni}$  interaction, as suggested by eqn. (7).



A similar situation has been discussed for  $[\text{Fe}(\text{Si}(\text{OMe})_3)(\text{CO})_3(\mu\text{-dppm})\text{Pd}(\eta^3\text{-allyl})]$  [1c] and is detailed further below. Raising the temperature to 323 K sharpened the allylic resonances of **11** only slightly. Low temperature studies were hampered by poor resolution and solubility.

With the additional aim of introducing a siloxane chain in these complexes, we allowed  $\text{K}[\text{Fe}(\text{Si}(\text{OSiMe}_3)_3)(\text{CO})_3(\eta^1\text{-dppm})]$  (**K1d**) (obtained by deprotonation of  $[\text{FeH}(\text{Si}(\text{OSiMe}_3)_3)(\text{CO})_3(\eta^1\text{-dppm})]$  with KH in THF) to react with  $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})_2\}]$  in THF at a low temperature [18]. The desired bimetallic complex  $[\text{Fe}\{\text{Si}(\text{OSiMe}_3)_3\}(\text{CO})_3(\mu\text{-dppm})\text{Pd}(\eta^3\text{-C}_3\text{H}_5)]$  (**12a**) was isolated as air-stable yellow crystals with a satisfactory yield.



The  $^{31}\text{P}$  NMR data ( $\delta$  66.2 for P on Fe and  $\delta$  26.9 for P on Pd with  $^{2+3}J(\text{PP}) = 109\text{ Hz}$ ) and the IR  $\nu(\text{CO})$  frequencies are very similar to those of  $[\text{Fe}(\text{Si}(\text{OMe})_3)-$

(CO)<sub>3</sub>(μ-dppm)Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>), despite the greater bulk of the siloxane moiety. The allylic resonances H(1) (δ 5.34), H(5) (δ 5.13) and H(2) (δ 3.71) in the <sup>1</sup>H NMR spectrum of **12a** (in C<sub>6</sub>D<sub>6</sub>) appear with the same pattern and nearly identical chemical shifts as in the Si(OMe)<sub>3</sub> derivative [1c]. However there are still two distinct resonances for H(4) (partially masked by the dppm protons at δ 3.43 at ambient temperature but well identified at 253 K) and H(3) at δ 2.55, the latter being a broad doublet due to a <sup>3</sup>J(HH) of 11.6 Hz with H(5). In contrast, in the Si(OMe)<sub>3</sub>-derivative, coalescence of the signals for H(3) and H(4) due to a rapid η<sup>3</sup> → η<sup>1</sup> → η<sup>3</sup> isomerization of the allylic ligand was already observed at room temperature with a doublet at δ 2.91. For **12a** coalescence of H(3) and H(4) occurs at 314 K in CDCl<sub>3</sub> to give a broad signal at δ 3.25, which corresponds to the averaged value for the two chemical shifts found for H(3) (δ 2.65) and H(4) (δ 3.78) at 253 K. The nine methyl groups of the siloxane ligand give rise to a singlet resonance at δ 0.16.

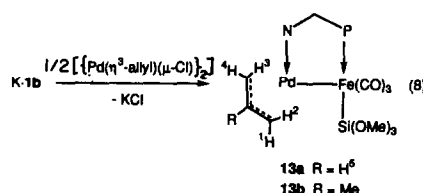
We also synthesized [Fe{SiMe(OSiMe<sub>3</sub>)<sub>2</sub>}(μ-dppm)Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (**12b**) in which the more electron-donating -Si{Me(OSiMe<sub>3</sub>)<sub>2</sub>} siloxane moiety causes a slight shift in the ν(CO) values to lower wavenumbers compared with those for **12a**. Apart from the signals of the siloxane ligand, which consist of a singlet at δ 0.45 for the two OSiMe<sub>3</sub> groups and a second singlet at 1.16 ppm for the silicon-bound methyl group (in benzene), the other resonances in the <sup>1</sup>H NMR spectrum of **12b** are nearly identical with those of **12a**.

Note that the <sup>1</sup>H NMR spectra are solvent dependent. For example, the positions of the allylic resonances H(5) and H(1) of **12b** in CDCl<sub>3</sub> are reversed compared with the situation in C<sub>6</sub>D<sub>6</sub>, as are the resonances of the dppm protons and H(2). In **12b** the protons H(3) and H(4) give rise to two distinct signals, in both C<sub>6</sub>D<sub>6</sub> and CDCl<sub>3</sub> (H(4) as in **12a**, is partially masked by the dppm protons). The doublet centred at 2.70 ppm for H(3) at 298 K collapses to a very broad resonance at 2.78 ppm at 323 K (in CDCl<sub>3</sub>). The resonance for H(4) also collapses, so that the dppm protons now give rise to a sharp triplet. Studies at higher temperatures aimed at observing an averaged signal for H(3) and H(4) were prevented by sample decomposition.

Another important feature in the <sup>1</sup>H NMR spectrum of **12b** in CDCl<sub>3</sub> is the observation of two singlets at δ 0.11 and 0.12 for the OSiMe<sub>3</sub> groups at 298 K which merge into a singlet at 323 K (see Section 3). However, in the room-temperature <sup>13</sup>C{<sup>1</sup>H} NMR spectrum (in CDCl<sub>3</sub>), only one resonance is observed (δ 2.1) for the OSiMe<sub>3</sub> groups. The SiMe carbon atom appears as a doublet at δ 13.5 owing to a *trans* <sup>3</sup>J(PC) coupling of 5 Hz. The three allylic carbon atoms C(1),

C(3) and C(2) appear as doublets at δ 69.3, 80.7 and 115.9, with <sup>3</sup>J(PC) couplings of 5, 37 and 7 Hz respectively. The larger *J*(PC) coupling is always found for the *trans*-carbon C(3). Only a broad resonance at 217 ppm could be detected for the carbonyl groups on Fe.

By using the bridging phosphino-pyridine ligand in place of dppm, related and stable dinuclear complexes could also be obtained with excellent yields (eqn. (8)):



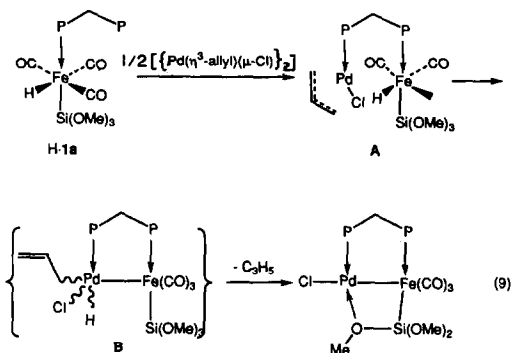
Replacement of a P donor with a harder N donor does not seem to modify the high stability of such complexes, and **13a** and **13b** can also be manipulated in air without decomposition. The meridional arrangement of the carbonyl groups found for the dppm analogues is maintained in **13a** and **13b**, as indicated by their three CO vibrations, at 1961m, 1901s and 1877vs cm<sup>-1</sup>. However, the resonances of the allylic protons in the <sup>1</sup>H NMR spectrum are now significantly altered when compared with the -Si(OMe)<sub>3</sub> dppm-bridged counterparts. The allylic hydrogen H(5) atom of **13a** is coupled to all the allylic protons and appears as a multiplet at δ 5.42. The major difference is now the two distinct high field resonances for the *anti* protons H(2) and H(3) and the two resonances at a lower field for the two *syn* protons H(1) and H(4). The latter appear as a doublet of doublets at δ 4.36 and a multiplet centered at 4.16 ppm respectively, whereas H(2) and H(3) appear as a doublet at δ 3.69 and a broadened doublet of doublets at δ 2.83 respectively.

Selective irradiation of H(5) simplifies the spectrum, so that now the two *syn* protons appear as broad "singlets" and the resonance at δ 2.83 for the *anti* proton H(3) is now simplified to a doublet (geminal coupling with H(4)). (The second *anti* proton is masked by the intense methoxy signal.) This pattern resembles those described in the literature for complexes of the type [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(R)(L)] [21a] in which no σ-π allyl interconversion occurs. In the corresponding dppm complexes [Fe{Si(OMe)<sub>3</sub>}(CO)<sub>3</sub>(μ-dppm)Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)], this interconversion was taking place in CDCl<sub>3</sub> at 323 K, as indicated by the merging at δ 3.25 of the resonances due to H(3) and H(4), whereas those for H(1) and H(2) remained almost unaffected [1c]. This type of dynamic situation has been described for the equilibrium resulting from addition of PPh<sub>3</sub> to [Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(C<sub>6</sub>F<sub>5</sub>)(PPh<sub>3</sub>)] [21b]. We are therefore led to suggest that a methoxy group acts as an intramolecular donor toward the adjacent palladium centre, inducing

dynamic behaviour of the allylic ligand that otherwise requires the addition of an excess of external nucleophile [21d].

The  $^1\text{H}$  NMR spectrum of the (2-methyl)allyl derivative **13b** contains a singlet for the  $\text{CH}_3$  group at  $\delta$  1.71, a doublet at  $\delta$  4.13 and a broad singlet at  $\delta$  3.99 for the *syn* protons H(1) and H(4) respectively, and a sharp singlet at  $\delta$  3.54 and a doublet at  $\delta$  2.86 for the *anti* protons H(2) and H(3) respectively. In both **13a** and **13b** there is a low field doublet at  $\delta$  9.08 due to the proton in the *ortho* position of the pyridine ring, and a sharp singlet at  $\delta$  3.66 for the methoxy protons. In the  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum of **13b** the allylic carbon atoms appear as singlets at  $\delta$  60.8, 76.2 and 124.8 and a further signal for the methyl group at  $\delta$  22.1. Similar chemical shifts are reported for  $[\text{Pd}(\eta^3\text{-MeC}_3\text{H}_4)(\text{py})(\text{PPh}_3)][\text{BF}_4]$  [21c]. These data indicate that, at room temperature, **13a** and **13b** do not display the dynamic behaviour noted above for **12**. This difference is obviously related to the electronic effects resulting from the replacement of the dppm ligand by the phosphinopyridine ligand.

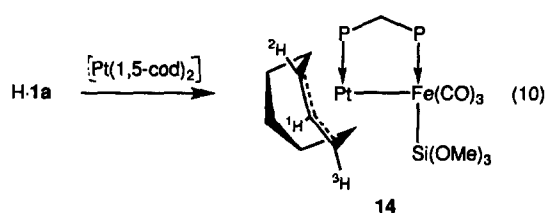
When  $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})\}_2]$  was added to the hydrido-silyl complex **H1a** in cold  $\text{CH}_2\text{Cl}_2$  the solution rapidly turned deep red and only  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{PdCl}]$  could be isolated. Monitoring the reaction by  $^{31}\text{P}$  NMR spectroscopy of the cold reaction mixture reveals instantaneous formation of an intermediate displaying an AX-type doublet ( $^{2+3}J(\text{PP}) = 44$  Hz) at  $\delta$  49.9 for a phosphorus atom coordinated to Fe and at  $\delta$  19.6 for a phosphorus atom on Pd. The signals due to this intermediate progressively disappear while only the resonances of  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{PdCl}]$  [1a] remain detectable after about 40 min. This reaction is likely to proceed by cleavage of the chloride bridges of  $[\{\text{Pd}(\eta^3\text{-C}_3\text{H}_5)(\mu\text{-Cl})\}_2]$  by the pendant phosphorus atom of **H1a** followed by oxidative addition of the Fe–H bond to the Pd. Reductive elimination of propene from a formally  $\text{Pd}^{\text{IV}}$  should lead finally to  $[\text{Fe}(\mu\text{-Si}(\text{OMe})_2(\text{OMe}))(\text{CO})_3(\mu\text{-dppm})\text{PdCl}]$  as tentatively illustrated in reaction (9). We recently isolated the heterobimetallic allylic compound  $[(\eta^5\text{-MeC}_5\text{H}_4)(\text{OC})_2\text{Mn}(\mu\text{-dppm})\text{Pd}(\eta^3\text{-MeC}_3\text{H}_4)\text{Cl}]$  which has a geometry comparable with that of the first intermediate suggested. In this Mn–Pd complex, the absence of a metal–metal interaction resulted in a weak  $^2J(\text{PP})$  coupling of 9 Hz [22]. Since the observed P–P coupling for the intermediate is 44 Hz, we favour a species displaying a metal–metal bond for intermediate **B**.



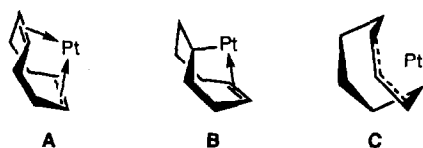
## 2.6. Synthesis of $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\eta^3\text{-C}_8\text{H}_{13})]$ (**14**)

The bimetallic Fe–Pt allyl complex  $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\mu\text{-dppm})\text{Pt}(\eta^3\text{-C}_3\text{H}_5)]$  was recently obtained [1c] by reaction of the iron metallate **K1a** with  $[\{\text{PtCl}(\eta^3\text{-C}_3\text{H}_5)_4\}]$ . We describe here an alternative route to bimetallic Fe–Pt allyl-type complexes. Treatment of the Pt(0) complex  $[\text{Pt}(1,5\text{-cod})_2]$  with the iron hydride  $[\text{FeH}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\eta^1\text{-dppm})]$  (**H1a**) in toluene yielded the yellow complex  $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}(\eta^3\text{-C}_8\text{H}_{13})]$  (**14**) (eqn. (10)). Its IR spectrum ( $1959\text{s}, 1894\text{s}, 1859\text{s}$   $\text{cm}^{-1}$ ) is consistent with a meridional arrangement of the three carbonyl groups. The  $^{13}\text{C}\{^1\text{H}\}$  NMR spectrum indicates the presence of a  $\eta^3$ -cyclooctenyl ligand; it exhibits five signals ( $\delta$  23.6–31.3) for its  $\text{CH}_2$  groups and three resonances at  $\delta$  75.7 ( $^1J(\text{PtC}) = 170$  Hz), 88.4 ( $^1J(\text{PtC}) = 90$  Hz) and 104.4 ( $^1J(\text{PtC}) = 9$  Hz) for the allylic carbon atoms C(1), C(3) and C(2) respectively. The signals at  $\delta$  39.8 (dd,  $^1J(\text{PC}) = 17$  and 30 Hz,  $^2J(\text{PtC}) = 58$  Hz) and  $\delta$  50.2 (s) are assigned to the  $\text{CH}_2$  of the dppm and to the methoxy carbons respectively. The allylic  $^1\text{H}$  NMR resonances are tentatively assigned as follows:  $\delta$  5.95 (H(1)), 5.07 (H(2)), 3.4 (H(3)), overlap with the signal for the dppm  $\text{CH}_2$ ). The  $^{31}\text{P}\{^1\text{H}\}$  NMR resonances at  $\delta$  23.9 (d, P(Pt),  $^1J(\text{PtP}) = 4184$  Hz) and  $\delta$  68.4 (d, P(Fe),  $^2J(\text{PtP}) = 92$  Hz) with a  $^{2+3}J(\text{PP}) = 107$  Hz are almost the same as those of the  $(\eta^3\text{-C}_3\text{H}_5)$  analogue [ $\delta$  (22.8 (d, P(Pt),  $^1J(\text{PtP}) = 4146$  Hz); 68.2 (d, P(Fe),  $^2J(\text{PtP}) = 99$  Hz) and  $^{2+3}J(\text{PP}) = 101$  Hz] [1c]. These  $^1\text{H}$  NMR and  $^{13}\text{C}\{^1\text{H}\}$  NMR assignments are consistent with those for other Pt allyl complexes [1c,23] or  $\eta^3$ -cyclooctenyl ligands in Co [24], Rh [25] or Fe [26] mononuclear complexes. These ligands were derived from 1,5-cod, from the reaction of 1,3-cod with a rhodium hydride complex, and by protonation of a  $\eta^4$ -(1,3-cod) Fe complex respectively.



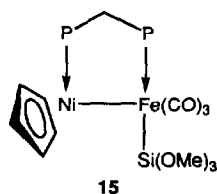


Hydride transfer from a iron-bound hydride to the chelating 1,5-cod moiety **A** could lead to a  $\sigma$ - $\pi$  intermediate **B**, not observed, which would rearrange by 1,3-migration of a proton to **C** observed in the final complex **14** [27]. Such a  $\eta^1$ - $\eta^2$ -cyclooctenyl ligand **B** has already been isolated for instance in Pd mononuclear [28a] or in Cr-Pt dinuclear [28b] complexes.



### 2.7. Synthesis of $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{NiCp}]$ (**15**)

We also examined the reaction between  $[\text{NiCp}(\text{PPh}_3)\text{Br}]$  and **H1a** in toluene. Since the expected HBr elimination with formation of a metal-metal bond did not take place after stirring for 2 h, we generated  $[\text{NEt}_3\text{H}]\mathbf{1a}$  *in situ* by adding  $\text{NEt}_3$  to the reaction mixture. A rapid colour change from violet to red-brown was observed and the dark-brown complex  $[\text{Fe}\{\text{Si}(\text{OMe})_3\}(\text{CO})_3(\mu\text{-dppm})\text{NiCp}]$  (**15**) was isolated with a good yield. The bimetallic structure was deduced unambiguously from the  $^{31}\text{P}\{^1\text{H}\}$  NMR spectrum, which exhibits a doublet at  $\delta$  62.7 for the phosphorus coordinated to iron and a doublet at  $\delta$  37.2 for the phosphorus bound to nickel ( $^{2+3}J(\text{PP}) = 100$  Hz). The  $^1\text{H}$  NMR spectrum is consistent with the proposed structure, as it contains a triplet for the dppm protons at  $\delta$  3.35, a singlet for the methoxy protons at  $\delta$  3.93 and a further singlet for the cyclopentadienyl protons at  $\delta$  5.42. The relatively high value of  $^{2+3}J(\text{PP})$  is consistent with no significant  $\text{MeO} \rightarrow \text{Ni}$  interaction [1].



In conclusion, we have prepared new alkoxysilyl functionalized heterobimetallic Fe-M complexes, in

which an unusual  $\mu_2$ - $\eta^2$ -Si-O bridge may occur, depending upon the stereoelectronic requirements of the organic ligand attached to M. The stabilizing role of dppm and  $\text{Ph}_2\text{P-py}$  used as assembling ligands was further demonstrated and found to be much larger than that of a bridging phosphino-ketone ligand. Studies are in progress to evaluate the reactivity of the metal-carbon bond *cis* to the labile oxygen-metal bond ( $\text{MeO} \rightarrow \text{M}$ ) and probe whether insertion or coupling reactions may occur more readily owing to the existence of a masked coordination site on M.

### 3. Experimental details

All reactions were performed under dry dinitrogen using standard Schlenk techniques. Solvents were freshly distilled under dinitrogen from the usual drying agents prior to use. IR spectra were recorded on Perkin-Elmer 398 and Bruker IFS66 spectrometers, NMR spectra on Bruker WP 200 SY, AC 300 or AM 400 spectrometers ( $^1\text{H}$ ,  $^{13}\text{C}$  and  $^{31}\text{P}$  chemical shifts are positive downfield from external tetramethylsilane (TMS) and  $\text{H}_3\text{PO}_4$  respectively) and FAB<sup>+</sup> mass spectra on a Fisons ZAB-HF spectrometer. Photochemical reactions were performed in an irradiation vessel using a water-cooled high pressure mercury lamp (180 W; Heraeus TQ 150). 3-Butyn-1-ol and ( $\pm$ )-4-pentyn-2-ol were obtained from Aldrich, *t*-butyl isonitrile and 2,6-xylyl isonitrile from Fluka, and used as received. The starting materials  $[\text{FeH}\{\text{Si}(\text{OR})_3\}(\text{CO})_3(\eta^1\text{-Ph}_2\text{P} \sim \text{Y})]$  (**H1**) [1d,18],  $[\text{K}\{\text{Fe}\{\text{Si}(\text{OR})_3\}(\text{CO})_3(\eta^1\text{-Ph}_2\text{P} \sim \text{Y})\}]$  (**K1**) [1d,18],  $[\text{Fe}\{\text{Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-dppm})\text{PtCl}]$  [1a],  $[\text{MCl}(\text{PhO})_2\text{P}(\text{OC}_6\text{H}_4)]\{\text{P}(\text{OPh})_3\}$  ( $\text{M} = \text{Pt}$  (**5a**), Pd (**5b**)) [16],  $[\{\text{Pd}(8\text{-mq})(\mu\text{-Cl})_2\}]$  [29],  $[\text{NiCp}(\text{PPh}_3)\text{Br}]$  [30] and  $[\text{PtCl}_2(\text{PPh}_3)_2(\text{C}(\text{NHR})(\text{NCH}_2\text{CH}_2\text{CH}_2))]$  ( $\text{R} = \textit{t}$ -butyl or 2,6-xylyl) [31] were prepared according to the procedures described in the literature. The synthesis of **3a** has been described in a preliminary communication [9].

#### 3.1. Synthesis of $[\text{Fe}\{\mu\text{-Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-dppm})\text{Pt}\{\text{C}(\text{CH}_2)_2\text{CH}(\text{R})\text{O}\}][\text{PF}_6]_2$ (**2**)

$\text{TIPF}_6$  (0.420 g, 1.2 mmol) was added to a solution of  $[\text{Fe}\{\text{Si}(\text{OMe})_2(\text{OMe})\}(\text{CO})_3(\mu\text{-dppm})\text{PtCl}]$  (0.877 g, 1.0 mmol) in THF (30  $\text{cm}^3$ ). After stirring for 2–3 min, a solution of 3-butyn-1-ol (0.100  $\text{cm}^3$ , 1.3 mmol) in THF (5  $\text{cm}^3$ ) was added in several portions. The reaction was monitored by IR spectroscopy. After further stirring for 4.5 h at room temperature, the solvent was removed under vacuum. The crude product was dissolved in  $\text{CH}_2\text{Cl}_2$  (20  $\text{cm}^3$ ). The solution was filtered and the volume reduced under vacuum to about 5  $\text{cm}^3$ . The brown-yellow product was precipitated with hexane (about 20  $\text{cm}^3$ ), washed twice with diethyl ether (about 20  $\text{cm}^3$ ) and dried under vacuum.

**2a** (R = H): yield, 0.919 g, 0.87 mmol (87%). Anal. Found: C, 39.68; H, 3.62.  $C_{35}H_{37}F_6FeO_7P_3PtSi$  ( $M = 1055.6$ ) calc.: C, 39.83; H, 3.53%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1997m, 1942m, 1912s  $cm^{-1}$ , IR (THF):  $\nu(CO)$  1992m, 1937s, 1912s  $cm^{-1}$ .  $^1H$  NMR (200 MHz, 303 K,  $CD_2Cl_2$ ):  $\delta$  1.59 (qnt, 2H,  $CH_2$ ,  $^3J(HH) = 7.8$  Hz); 2.56 (t, 2H,  $CH_2C=Pt$ ,  $^3J(HH) = 7.7$  Hz); 3.76 (s, 6H,  $(MeO)_2Si$ ); 3.84 (d, 3H, MeOPt,  $^4J(PH) = 1.6$  Hz,  $^3J(PtH) = 22.7$  Hz); 4.04 (dd, 2H,  $PCH_2P$ ,  $^2J(PH) = 9.8$ , 11.5 Hz,  $^3J(PtH) = 64$  Hz); 4.66 (t, 2H,  $CH_2O$ ,  $^3J(HH) = 7.8$  Hz); 7.28–7.75 (m, 20H,  $C_6H_5$ ).  $^{31}P\{^1H\}$  NMR (81.02 MHz, 303 K,  $CDCl_3-CH_2Cl_2$ ):  $\delta$  -143.9 (spt,  $PF_6$ ,  $^1J(PF) = 712$  Hz); 3.3 (d, P(Pt),  $^{2+3}J(PP) = 44$  Hz,  $^1J(PtP) = 4437$  Hz); 52.3 (d, P(Fe),  $^{2+3}J(PP) = 44$  Hz,  $^2J(PtP) = 58$  Hz).  $^{13}C$  NMR (100.6 MHz, 298 K,  $CDCl_3$ ):  $\delta$  19.4 (s, 1C,  $CH_2$ ); 45.9 (m,  $PCH_2P$ ); 51.1 (s, 2C,  $(MeO)_2Si$ ); 55.8 (s, 1C,  $CH_2-C=Pt$ ); 60.4 (s, MeOPt); 90.0 (s, 1C,  $CH_2O$ ); 125.2–133.7 (m, aromatic); 210.0 (m, CO,  $^2J(CP) = 14$  Hz); 213.2 (s, 2CO,  $^2J(CP) = 17$  Hz). Mass spectrum (FAB<sup>+</sup>): 910.1 ( $M^+$ , 15%), 840.1 ( $M^+ - C_4H_6O$ , 35%), 826.1 ( $M^+ - 3CO$ , 50%), 756.1 ( $M^+ - C_4H_6O - 3CO$ , 100%).

**2b** (R = Me): this complex was prepared in a manner similar to **2a** by using ( $\pm$ )-4-pentyn-2-ol. The reaction went to completion faster, with a comparable yield. Anal. Found: C, 41.79; H, 3.45.  $C_{36}H_{39}F_6FeO_7P_3PtSi$  ( $M = 1069.6$ ) calc.: C, 40.43; H, 3.68%. IR ( $CH_2Cl_2$ ):  $\nu(CO)$  1995m, 1939s, 1913s  $cm^{-1}$ . IR (THF):  $\nu(CO)$  1992m, 1937s, 1911s  $cm^{-1}$ .  $^1H$  NMR (300 MHz, 300 K,  $CD_2Cl_2$ ):  $\delta$  1.01 (qnt, 1H,  $CH_2$ ,  $^3J(HH) = 10$  Hz); 1.26 (d, 3H,  $CH_3$ ,  $^3J(HH) = 5.5$  Hz); 1.97 (m, 1H,  $CH_2$ ); 2.36 (dt, 1H,  $CH_2C=Pt$ ,  $^2J(HH) = 22$  Hz,  $^3J(HH) = 10$  Hz); 2.89 (ddd, 1H,  $CH_2C=Pt$ ,  $^2J(HH) = 22$  Hz,  $^3J(HH) = 10$  Hz,  $^3J(HH) = 3$  Hz); 3.77 (s, 6H,  $(MeO)_2Si$ ); 3.82 (s, 3H, MeOPt,  $^3J(PtH) = 20$  Hz); 4.04 (t, 2H,  $PCH_2P$ ,  $^2J(PH) = 10$  Hz,  $^3J(PtH) = 58$  Hz); 5.04 (sxt, 1H,  $CH-O$ ,  $^3J(HH) = 5$  Hz); 7.22–7.77 (m, 20H,  $C_6H_5$ ).  $^{31}P\{^1H\}$  NMR (121.50 MHz, 300 K,  $CD_2Cl_2$ ):  $\delta$  -143.2 (spt,  $PF_6$ ,  $^1J(PF) = 711$  Hz); 3.5 (d, P(Pt),  $^{2+3}J(PP) = 45$  Hz,  $^1J(PtP) = 4459$  Hz); 52.4 (d, P(Fe),  $^{2+3}J(PP) = 45$  Hz). Mass spectrum (FAB<sup>+</sup>): 924.1 ( $M^+$ , 25%), 840.1 ( $M^+ - C_5H_8O$  and  $M^+ - 3CO$ , 100%), 756.1 ( $M^+ - C_5H_8O - 3CO$ , 35%).

### 3.2. Synthesis of $[Fe\{\mu-Si(OMe)_2(OMe)\}(CO)_3(\mu-dppm)Pt(C\equiv N^tBu)] [PF_6]$ (**3b**)

TIPF<sub>6</sub> (0.600 g, 1.72 mmol) was added to a solution of  $[Fe(CO)_3\{\mu-Si(OMe)_2(OMe)(\mu-dppm)PtCl\}]$  (0.802 g, 0.92 mmol) in  $CH_2Cl_2$  (15 cm<sup>3</sup>). After stirring for 2–3 min, the temperature was lowered to 0°C. A solution of *t*-butyl isonitrile (0.105 cm<sup>3</sup>, 0.95 mmol) in cold  $CH_2Cl_2$  (5 cm<sup>3</sup>) was added in several fractions. The reaction mixture was allowed to warm to room temperature. The solution was filtered and some solvent removed

under vacuum. After 10 min the solution was again filtered and rest of the solvent removed under reduced pressure. The product, washed with about 10 cm<sup>3</sup> of hexane and about 20 cm<sup>3</sup> of diethyl ether, was recrystallized from THF–diethyl ether (yield, 0.614 g (62%)).

Anal. Found: C, 39.56; H, 3.55.  $C_{36}H_{40}F_6FeNO_6P_3PtSi$  ( $M = 1068.6$ ) calc.: C, 40.46; H, 3.77%. IR ( $CH_2Cl_2$ ):  $\nu(CN)$  2199s,  $\nu(CO)$  2009s, 1955s, 1929s  $cm^{-1}$ .  $^1H$  NMR (200 MHz, 300 K,  $CDCl_3$ ):  $\delta$  1.09 (s, 9H, <sup>t</sup>Bu), 3.79 (s, 6H,  $(MeO)_2Si$ ); 4.13 (d, 3H, MeOPt,  $^4J(PH) = 1.75$  Hz,  $^3J(PtH) = 21$  Hz); 4.19 (dd, 2H,  $PCH_2P$ ,  $^2J(PH) = 9.9$  and 12 Hz,  $^3J(PtH) = 63$  Hz); 7.3–7.8 (m, 20H,  $C_6H_5$ ).  $^{31}P\{^1H\}$  NMR (81 MHz,  $CDCl_3-CH_2Cl_2$ ):  $\delta$  -143.8 (spt,  $PF_6$ ,  $^1J(PF) = 712$  Hz); 5.1 (d, P(Pt),  $^{2+3}J(PP) = 45$  Hz,  $^1J(PtP) = 4209$  Hz); 47.5 (d, P(Fe),  $^{2+3}J(PP) = 45$  Hz,  $^{2+3}J(PtP) = 35$  Hz). Mass spectrum (FAB<sup>+</sup>): 923.1 ( $M^+$ , 20%), 839.1 ( $M^+ - 3CO$ , 100%), 756.0 ( $M^+ - CN^tBu - 3CO$ , 55%).

### 3.3. Synthesis of $[Fe\{\mu-Si(OMe)_2(OMe)\}(CO)_3(\mu-dppm)Pt(C\equiv N-2,6-xylyl)_2] [PF_6]$ (**4**)

TIPF<sub>6</sub> (0.80 g, 0.23 mmol) was added to a red solution of  $[Fe(CO)_3\{\mu-Si(OMe)_2(OMe)(\mu-dppm)PtCl\}]$  (0.151 g, 0.172 mmol) in  $CH_2Cl_2$  (6 cm<sup>3</sup>). After stirring for 3 min, a solution of 2,6-xylyl isonitrile (0.049 g, 0.37 mmol) in  $CH_2Cl_2$  (5 cm<sup>3</sup>) was slowly added over 30 min. After elimination of the fine white precipitate by centrifugation and decantation, the pale-yellow solution was concentrated under reduced pressure. Further addition of hexane (10 cm<sup>3</sup>) precipitated the product, which was filtered off, washed with hexane (5 cm<sup>3</sup>) and dried under vacuum (yield, 0.167 g (78%)).

Anal. Found: C, 47.98; H, 3.97; N, 2.68.  $C_{49}H_{49}F_6FeN_2O_6P_3PtSi$  ( $M = 1247.9$ ) calc.: C, 47.16; H, 3.96; N, 2.25%. IR ( $CH_2Cl_2$ ):  $\nu(CN)$  2180s, 2145m,  $\nu(CO)$  2018m, 1960m, 1928s  $cm^{-1}$ .  $^1H$  NMR (300 MHz, 300 K,  $CD_2Cl_2$ ):  $\delta$  2.32 (s, 12H,  $CH_3$ ); 3.14 (s, 9H,  $(MeO)_3Si$ ); 3.88 (t, 2H,  $PCH_2P$ ,  $^2J(PH) = 11$  Hz,  $^3J(PtH) = 31$  Hz); 6.9–7.8 (m, 26H, aromatic).  $^1H$  NMR (300 MHz, 243 K,  $CD_2Cl_2$ ):  $\delta$  2.26 (s, 6H,  $CH_3$ ); 2.24 (s, 6H,  $CH_3$ ); 3.06 (s, 9H,  $(MeO)_3Si$ ); 3.83 (t, 2H,  $PCH_2P$ ,  $^2J(PH) = 11$  Hz); 6.8–7.8 (m, 26H, aromatic).  $^{31}P\{^1H\}$  NMR (121.5 MHz, 300 K,  $CD_2Cl_2$ ):  $\delta$  -142.5 (spt,  $PF_6$ ,  $^1J(PF) = 711$  Hz); 22.3 (d, P(Pt),  $^{2+3}J(PP) = 54$  Hz,  $^1J(PtP) = 3365$  Hz); 65.0 (d, P(Fe),  $^{2+3}J(PP) = 54$  Hz).

### 3.4. Synthesis of $cis-[Fe\{Si(OMe)_3\}(CO)_3(\mu-dppm)Pt\{P(OPh)_2(OC_6H_4)\}]$ (**6a**)

To a stirred suspension of **5a** (0.440 g, 0.52 mmol) in THF (10 cm<sup>3</sup>) was added dropwise a THF solution (30 cm<sup>3</sup>) of **K1a** (0.55 mmol) over 1.5 h. The reaction mixture gradually turned orange. After 5 h, the solution was filtered and concentrated under vacuum. Ad-

dition of pentane (15 cm<sup>3</sup>) caused precipitation of a yellow solid which was filtered off and dried *in vacuo*. <sup>31</sup>P NMR examination of the crude residue revealed the presence of free P(OPh)<sub>3</sub> and unreacted **5a** together with the bimetallic complex **6a**. After recrystallization from THF–hexane, **6a** was spectroscopically characterized. Impurities prevented satisfactory elemental analysis.

IR (THF):  $\nu(\text{CO})$  1963m, 1899s, 1867s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, 300 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  3.39 (s, 9H, Si(OMe)<sub>3</sub>); 4.43 (t, 2H, PCH<sub>2</sub>P, <sup>2</sup>J(PH) = 10 Hz); 6.74–7.72 (m, 34H, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, 300 K, CDCl<sub>3</sub>–CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  1.75 (dd, P(Pt), <sup>2+3</sup>J(PP) = 89 Hz, <sup>2</sup>J(PP<sub>cis</sub>) = 9 Hz, <sup>1</sup>J(PtP) = 1795 Hz); 53.1 (d, P(Fe), <sup>2+3</sup>J(PP) = 89 Hz, <sup>2+3</sup>J(PtP) = 79 Hz), 114.5 (d, (PhO)<sub>2</sub>P(Pt), <sup>2</sup>J(PP<sub>cis</sub>) = 9 Hz, <sup>1</sup>J(PtP) = 5205 Hz).

### 3.5. Synthesis of *trans*-[Fe{Si(OMe)<sub>3</sub>}(CO)<sub>3</sub>( $\mu$ -dppm)-Pd{P(OPh)<sub>2</sub>(OC<sub>6</sub>H<sub>4</sub>)}] (**6b**)

To a stirred suspension of **5b** (0.380 g, 0.5 mmol) in THF (10 cm<sup>3</sup>) at –30°C was added dropwise a THF solution (30 cm<sup>3</sup>) of **K1a** (0.5 mmol) over 1 h. The reaction mixture gradually turned red (5 h; IR monitoring). The solvent was removed under vacuum at –20°C and the solution was allowed to warm to room temperature. The solution was then filtered. The addition of pentane (15 cm<sup>3</sup>) caused precipitation of a yellow–orange solid which was filtered off and dried *in vacuo*. Slow decomposition occurred during recrystallization from THF–pentane and prevented satisfactory elemental analysis. Nevertheless **6b** was unambiguously characterized by spectroscopy.

IR (THF):  $\nu(\text{CO})$  1957m, 1892s, 1868s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>):  $\delta$  3.43 (dt, 2H, PCH<sub>2</sub>P, <sup>2</sup>J(HP) = 10 Hz, <sup>3</sup>J(HP<sub>trans</sub>) = 4 Hz); 3.98 (s, 9H, Si(OMe)<sub>3</sub>); 5.87–7.78 (m, 34H, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, C<sub>6</sub>D<sub>6</sub>–CH<sub>2</sub>Cl<sub>2</sub>):  $\delta$  28.5 (dd, P(Pd), <sup>2+3</sup>J(PP) = 95 Hz, <sup>2</sup>J(PP<sub>trans</sub>) = 681 Hz); 62.4 (dd, P(Fe), <sup>2+3</sup>J(PP) = 95 Hz, <sup>3+4</sup>J(PP) = 25 Hz); 134.9 (dd, (PhO)<sub>2</sub>P(Pd), <sup>2</sup>J(PP<sub>trans</sub>) = 681 Hz, <sup>3+4</sup>J(PP) = 25 Hz).

### 3.6. Synthesis of [Fe{ $\mu$ -Si(OMe)<sub>2</sub>(OMe)}(CO)<sub>3</sub>( $\mu$ -dppm)Pt{P(OPh)<sub>3</sub>}]PF<sub>6</sub> (**7**)

TIPF<sub>6</sub> (0.065 g, 1.44 equivalents) was added to a red solution of [Fe(CO)<sub>3</sub>{ $\mu$ -Si(OMe)<sub>2</sub>(OMe)( $\mu$ -dppm)PtCl}] (0.113 g, 0.129 mmol) in CH<sub>2</sub>Cl<sub>2</sub> (6 cm<sup>3</sup>). A solution of P(OPh)<sub>3</sub> (0.045 g, 0.145 mmol, 112 equivalents) in CH<sub>2</sub>Cl<sub>2</sub> (3 cm<sup>3</sup>) was then added with stirring over 15 min. After elimination of the fine white precipitate by centrifugation and decantation, the yellow solution was concentrated under reduced pressure. Further addition of hexane (about 5 cm<sup>3</sup>) precipitated the product, which was filtered off, washed with hexane (about 5 cm<sup>3</sup>) and dried under vacuum (yield, 0.150 g (90%)).

IR (CH<sub>2</sub>Cl<sub>2</sub>):  $\nu(\text{CO})$  2008s, 1957s, 1928s cm<sup>-1</sup>. <sup>1</sup>H

NMR (300 MHz, 300 K, CD<sub>2</sub>Cl<sub>2</sub>):  $\delta$  3.83 (s, 6H, Si(OMe)<sub>2</sub>); 3.92 (d, 3H, MeO → Pt, <sup>4</sup>J(HP) = 1.7 Hz, <sup>3</sup>J(HPt) = 16 Hz); 4.11 (t, 2H, PCH<sub>2</sub>P, <sup>2</sup>J(PH) = 11 Hz, <sup>3</sup>J(HPt) = 60 Hz); 6.85–7.82 (m, 35H, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (81 MHz, 300 K, THF–C<sub>6</sub>D<sub>6</sub>):  $\delta$  –143.5 (spt, PF<sub>6</sub>, <sup>1</sup>J(PF) = 712 Hz); 6.7 (dd, P(Pt), <sup>2+3</sup>J(PP) = 40 Hz, <sup>2</sup>J(PP<sub>cis</sub>) = 22 Hz, <sup>1</sup>J(PtP) = 2943 Hz); 44.9 (dd, P(Fe), <sup>2+3</sup>J(PP) = 40 Hz, <sup>3+4</sup>J(PP) = 23 Hz); 115.4 (t, (PhO)<sub>3</sub>P(Pt), <sup>1</sup>J(PP) = 22 Hz, <sup>1</sup>J(PtP) = 4796 Hz).

### 3.7. Synthesis of [Fe{Si(OMe)<sub>3</sub>}(CO)<sub>3</sub>( $\mu$ -Ph<sub>2</sub>Ppy)Pd(8-mq)] (**8**)

A solution of **K1b** (0.565 g, 1.0 mmol) in THF (35 cm<sup>3</sup>) was added at –25°C to a slurry of [(Pd(8-mq)( $\mu$ -Cl))<sub>2</sub>] (0.285 g, 0.5 mmol) in THF (5 cm<sup>3</sup>). After completion of the reaction (15 min; IR monitoring), the yellow–brown solution was filtered and evaporated to dryness. The residue was extracted with warm CH<sub>2</sub>Cl<sub>2</sub> (about 35 cm<sup>3</sup>). After the addition of hexane (10 cm<sup>3</sup>) to the filtered solution and slow concentration *in vacuo*, yellow **8** precipitated (yield, 0.603 (78%) isolated).

Anal. Found: C, 51.80; H, 4.50; N, 3.50. C<sub>33</sub>H<sub>31</sub>FeNO<sub>6</sub>PPdSi (*M* = 772.95) calc.: C, 51.28; H, 4.04; N, 3.62%. IR (KBr):  $\nu(\text{SiOC-H})$  2828w,  $\nu(\text{CO})$  1959s, 1900vs, 1842s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 298 K):  $\delta$  3.68 (s, 2H, PdCH<sub>2</sub>); 3.73 (s, 9H, Si(OMe)<sub>3</sub>); 7.26–8.94 (m, 20H, aromatic). <sup>1</sup>H NMR (acetone-*d*<sub>6</sub>):  $\delta$  3.63 (s, 9H, Si(OMe)<sub>3</sub>); 3.74 (s, 2H, PdCH<sub>2</sub>); 7.03–9.00 (m, 20H, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, CH<sub>2</sub>Cl<sub>2</sub>–acetone-*d*<sub>6</sub>):  $\delta$  68.4 (s, P(Fe)).

### 3.8. Synthesis of [Fe{Si(OMe)<sub>3</sub>}(CO)<sub>3</sub>{ $\mu$ -Ph<sub>2</sub>PCH<sub>2</sub>C(=O)Ph}Pd(8-mq)] (**10**)

A solution of **K1c** (0.606 g, 1.0 mmol) in THF (35 cm<sup>3</sup>) was added at –25°C to a slurry of [(Pd(8-mq)( $\mu$ -Cl))<sub>2</sub>] (0.285 g, 0.5 mmol) in THF (5 cm<sup>3</sup>). After completion of the reaction (15 min; IR monitoring), the yellow–brown solution was filtered and hexane (10 cm<sup>3</sup>) was added. Upon slow concentration *in vacuo*, yellow **10** precipitated (yield, 0.618 g, (76%)).

IR (Nujol):  $\nu(\text{CO})$  1950m, 1872s, 1858s cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, acetone-*d*<sub>6</sub>):  $\delta$  3.65 (s, 9H, Si(OMe)<sub>3</sub>); 3.78 (s, 2H, PdCH<sub>2</sub>); 3.89 (d, 2H, PCH<sub>2</sub>, <sup>2</sup>J(PH) = 1.5 Hz); 7.03–9.00 (m, 20H, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, CH<sub>2</sub>Cl<sub>2</sub>–acetone-*d*<sub>6</sub>):  $\delta$  46.7 (s, P(Fe)).

### 3.9. Synthesis of [Fe{Si(OMe)<sub>3</sub>}(CO)<sub>3</sub>( $\mu$ -dppm)Ni( $\eta$ <sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (**11**)

A solution of **K1a** (0.685 g, 1 mmol) in THF (25 cm<sup>3</sup>) was added at –25°C to a slurry of [(Ni( $\eta$ <sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)( $\mu$ -Cl))<sub>2</sub>] (0.135 g, 0.5 mmol) in THF (5 cm<sup>3</sup>). After completion of the reaction (10 min; IR monitoring of the disappearance of the  $\nu(\text{CO})$  bands due to **K1a**, the red solution was filtered and evaporated to

dryness. The residue was extracted with warm Et<sub>2</sub>O (about 45 cm<sup>3</sup>). After the addition of hexane (10 cm<sup>3</sup>) to the filtered solution and slow concentration *in vacuo*, red **11** precipitated. The concentration of the mother liquor afforded a further crop of the air-stable product (overall isolated yield, 0.500 g (67%)).

Anal. Found: C, 53.92; H, 4.73. C<sub>34</sub>H<sub>36</sub>FeNiO<sub>6</sub>P<sub>2</sub>Si (M = 745.27) calc.: C, 54.79; H, 4.87%. IR (THF): ν(CO) 1952m, 1881s, 1847vs cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 323 K): δ 2.45 (br, 2H, allyl H(3) and H(4)); 3.23 (t, 2H, PCH<sub>2</sub>P, <sup>2</sup>J(PH) = 10.2 Hz); 3.41 (t, br, 1H, allyl H(2)), 3.98 (s, 9H, OCH<sub>3</sub>); 5.21 (overlapping signals, m, 2H, allyl H(5) and H(1)); 6.91–7.70 (m, 20H, C<sub>6</sub>H<sub>5</sub>). <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, 298 K): 3.25 (d, 2H, <sup>3</sup>J(HH<sup>5</sup>) = 9.2 Hz, allyl H(3) and H(4)); 3.43–3.77 (overlapping signals, 12H, OCH<sub>3</sub>, PCH<sub>2</sub>P, allyl H(2)); 4.72 (br, 1H, allyl H(1)); 5.36 (m, 1H, allyl H(5)); 7.17–7.75 (m, 20H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, CH<sub>2</sub>Cl<sub>2</sub>-acetone-*d*<sub>6</sub>): δ 29.8 (d, P(Ni), <sup>2+3</sup>J(P–P) = 119 Hz); 72.1 (d, P(Fe), <sup>2+3</sup>J(PP) = 119 Hz).

### 3.10. Synthesis of [Fe{Si(OSiMe<sub>3</sub>)<sub>3</sub>}<sub>3</sub>](CO)<sub>3</sub>(μ-dppm)-Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (**12a**)

A solution of **K1d** (0.860 g, 1.0 mmol) in THF (25 cm<sup>3</sup>) was added at –25°C to a slurry of [(Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(μ-Cl))<sub>2</sub>] (0.182 g, 0.5 mmol) in THF (5 cm<sup>3</sup>). After completion of the reaction (15 min; IR monitoring of the disappearance of the ν(CO) bands at 1928w, 1840vs and 1808s cm<sup>-1</sup> due to **K1d**), the yellow solution was filtered and evaporated to dryness. The residue was extracted with warm Et<sub>2</sub>O (about 35 cm<sup>3</sup>). After the addition of hexane (15 cm<sup>3</sup>) to the filtered solution and slow concentration *in vacuo*, yellow **12a** precipitated. Yellow crystals slowly formed at –20°C, which were collected by filtration and dried *in vacuo*. The concentration of the mother liquor afforded a further crop of the air-stable product (overall isolated yield, 0.745 g (77%)).

Anal. Found: C, 49.63; H, 5.34%. C<sub>40</sub>H<sub>54</sub>FeO<sub>6</sub>P<sub>2</sub>-PdSi<sub>4</sub> (M = 967.42) calc.: C, 49.66; H, 5.62%. IR (THF): ν(CO) 1952m, 1881s, 1857vs cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K): δ 0.16 (s, 27H, OSiCH<sub>3</sub>); 2.55 (d, 1H, <sup>3</sup>J(HH(5)) = 11.6 Hz, allyl H(3)); 3.43 (m, 3H, PCH<sub>2</sub>P and H(4)); 3.71 (t, br, 1H, <sup>3</sup>J(HH(5)) ≈ <sup>3</sup>J(PH) = 12.3 Hz, allyl H(2)); 5.13 (m, 1H, allyl H(5)); 5.34 (t, 1H, <sup>3</sup>J(HH(5)) ≈ <sup>3</sup>J(PH) = 7.3 Hz, allyl H(1)); 6.88–7.84 (m, 20H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, C<sub>6</sub>D<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub>): δ 26.9 (d, P(Pd), <sup>2+3</sup>J(PP) = 109 Hz); 66.2 (d, P(Fe), <sup>2+3</sup>J(PP) = 109 Hz).

### 3.11. Synthesis of [Fe{SiMe(OSiMe<sub>3</sub>)<sub>2</sub>}<sub>2</sub>](CO)<sub>3</sub>(μ-dppm)-Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (**12b**)

This complex was prepared in a manner similar to **12a** using K[Fe{Si(CH<sub>3</sub>)(OSiMe<sub>3</sub>)<sub>2</sub>}(CO)<sub>3</sub>(η<sup>3</sup>-dppm)] (yield, 0.651 g (73%)).

Anal. Found: C, 51.99; H, 5.53. C<sub>38</sub>H<sub>48</sub>FeO<sub>5</sub>P<sub>2</sub>PdSi<sub>3</sub> (M = 893.27) calc.: C, 51.10; H, 5.42%. IR (THF): ν(CO) 1950m, 1878s, 1855vs cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, 298 K, C<sub>6</sub>D<sub>6</sub>): δ 0.45 (s, 18H, OSiCH<sub>3</sub>); 1.16 (s, 3H, SiCH<sub>3</sub>); 2.54 (d, br, 1H, <sup>3</sup>J(HH(5)) = 12.4 Hz, allyl H(3)); 3.43 (m, 3H, PCH<sub>2</sub>P, and H(4)); 3.63 (t, br, 1H, <sup>3</sup>J(HH(5)) ≈ <sup>3</sup>J(PH) = 12.5 Hz, allyl H(2)); 5.09 (m, 1H, allyl H(5)); 5.31 (t, 1H, <sup>3</sup>J(HH(5)) ≈ <sup>3</sup>J(PH) = 7.5 Hz, allyl H(1)); 6.89–7.85 (m, 20H, C<sub>6</sub>H<sub>5</sub>). <sup>1</sup>H NMR (200 MHz, 298 K, CDCl<sub>3</sub>): δ 0.11 (s, 9H, OSiCH<sub>3</sub>); 0.12 (s, 9H, OSiCH<sub>3</sub>); 0.61 (s, 3H, SiCH<sub>3</sub>); 2.70 (d, br, 1H, <sup>3</sup>J(HH(5)) = 12.4 Hz, allyl H(3)); 3.44 (t, br, 1H, <sup>3</sup>J(HH(5)) ≈ <sup>3</sup>J(PH) = 12.0 Hz, allyl H(2)); 3.68 (m, 2H, PCH<sub>2</sub>P and allyl H(4)); 5.00 (t, br, 1H, <sup>3</sup>J(HH(5)) ≈ <sup>3</sup>J(PH) = 7.7 Hz, allyl H(1)); 5.31 (m, 1H, allyl H(5)); 7.09–7.51 (m, 20H, C<sub>6</sub>H<sub>5</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, C<sub>6</sub>D<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub>): δ 27.1 (d, P(Pd), <sup>2+3</sup>J(PP) = 107 Hz); 64.9 (d, P(Fe), <sup>2+3</sup>J(PP) = 107 Hz). <sup>13</sup>C{<sup>1</sup>H} NMR (100.6 MHz, CDCl<sub>3</sub>): δ 2.1 (s, OSiC); 13.5 (d, SiC, <sup>3</sup>J(PC) = 5 Hz); 41.2 (dd, PCP, <sup>1</sup>J(PC) = 16 and 23 Hz); 69.3 (d, allyl C(1), <sup>1</sup>J(PC) = 5 Hz); 80.7 (d, allyl C(3), <sup>1</sup>J(PC) = 37 Hz); 115.9 (d, allyl C(2), <sup>1</sup>J(PC) = 7 Hz); 127.8–137.9 (m, aromatic); 217.0 (br, CO).

### 3.12. Synthesis of [Fe{Si(OMe)<sub>3</sub>}<sub>3</sub>](CO)<sub>3</sub>(μ-Ph<sub>2</sub>Ppy)-Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)] (**13a**)

A solution of **K1b** (0.565 g, 1.0 mmol) in THF (25 cm<sup>3</sup>) was added at –25°C to a slurry of [(Pd(η<sup>3</sup>-C<sub>3</sub>H<sub>5</sub>)(μ-Cl))<sub>2</sub>] (0.182 g, 0.5 mmol) in THF (5 cm<sup>3</sup>). After completion of the reaction (15 min; IR monitoring), the yellow solution was filtered and evaporated to dryness. The residue was extracted with warm Et<sub>2</sub>O (about 45 cm<sup>3</sup>). After the addition of hexane (15 cm<sup>3</sup>) to the filtered solution and slow concentration *in vacuo*, yellow **13a** precipitated. Yellow crystals formed slowly at –20°C and were collected by filtration and dried *in vacuo*. Concentration of the mother liquor afforded a further crop of the air-stable product (overall isolated yield, 0.530 g (79%)).

Anal. Found: C, 46.32; H, 4.01; N, 2.02. C<sub>26</sub>H<sub>28</sub>FeNO<sub>6</sub>PPdSi (M = 671.84) calc.: C, 46.48; H, 4.20; N, 2.08%. IR (THF): ν(CO) 1961m, 1901s, 1877vs cm<sup>-1</sup>. <sup>1</sup>H NMR (200 MHz, 303 K, CDCl<sub>3</sub>): δ 2.83 (dd, 1H, <sup>3</sup>J(HH(5)) = 12.4 Hz, <sup>2</sup>J(HH(4)) = 1.1 Hz, allyl H(3)); 3.66 (s, 9H, Si(OMe)<sub>3</sub>); 3.69 (d, partially masked, 1H, allyl H(2)); 4.16 (m, 1H, allyl H(4)); 4.36 (dd, 1H, <sup>3</sup>J(HH(5)) = 6.1 Hz, <sup>4</sup>J(HH(4)) = 1.2 Hz, allyl H(1)); 5.42 (m, 1H, allyl H(5)); 6.99–9.08 (m, 14H, aromatic). <sup>31</sup>P{<sup>1</sup>H} NMR (81.02 MHz, C<sub>6</sub>D<sub>6</sub>-CH<sub>2</sub>Cl<sub>2</sub>): δ 76.7 (s, P(Fe)).

### 3.13. Synthesis of [Fe{Si(OMe)<sub>3</sub>}<sub>3</sub>](CO)<sub>3</sub>(μ-Ph<sub>2</sub>Ppy)-Pd(η<sup>3</sup>-2-MeC<sub>3</sub>H<sub>4</sub>)] (**13b**)

This complex was prepared in a manner similar to **13a** but using [(Pd(η<sup>3</sup>-2-MeC<sub>3</sub>H<sub>4</sub>)(μ-Cl))<sub>2</sub>] (yield, 0.610 g (89%)).

Anal. Found: C, 47.03; H, 4.46; N, 1.84.  $C_{27}H_{30}FeNO_6PPdSi$  ( $M = 685.87$ ) calc.: C, 47.30; H, 4.41; N, 2.04%. IR (THF):  $\nu(CO)$  1961m, 1901s, 1877vs  $cm^{-1}$ .  $^1H$  NMR (200 MHz, 303 K,  $CDCl_3$ ):  $\delta$  1.71 (s, 3H,  $CH_3$ ); 2.86 (d, 1H,  $^2J(HH(4)) = 1.8$  Hz, allyl H(3)); 3.54 (s, 1H, allyl H(2)); 3.66 (s, 9H,  $(MeO)_3Si$ ); 3.99 (s, br, 1H, allyl H(4)); 4.13 (d, 1H,  $^4J(HH(4)) = 1.8$  Hz, allyl H(1)); 6.95–9.08 (m, 14H, aromatic).  $^{31}P\{^1H\}$  NMR (81.02 MHz,  $C_6D_6-CH_2Cl_2$ ):  $\delta$  75.5 (s, P(Fe)).  $^{13}C\{^1H\}$  NMR (75.47 MHz,  $CDCl_3$ ):  $\delta$  22.1 (s,  $CH_3$ ); 50.6 (s, SiOC); 60.8 (s, allyl C(1)); 76.2 (s, allyl C(3)); 124.8 (s, allyl C(2)); 128.8–155.6 (m, aromatic); 216.0 (br, CO).

### 3.14. Synthesis of $[Fe\{Si(OMe)_3\}(CO)_3(\mu-dppm)Pt(\eta^3-C_8H_{13})]$ (14)

A solution of H1a (0.957 g, 1.48 mmol) in toluene (20  $cm^3$ ) was added to a solution of  $[Pt(1,5-cod)_2]$  (0.558 g, 1.36 mmol) in toluene (15  $cm^3$ ) at  $-15^\circ C$ . The red–orange solution was warmed to ambient temperature and concentrated to 5  $cm^3$  under reduced pressure. The addition of hexane (10  $cm^3$ ) induced precipitation of the yellow product, which was filtered off and dried *in vacuo* (yield, 0.500 g (39%)).

Anal. Found: C, 49.53; H, 4.44.  $C_{39}H_{44}FeO_6P_2PtSi$  ( $M = 949.7$ ) calc.: C, 49.32; H, 4.67%. IR (toluene):  $\nu(CO)$  1959s, 1894s, 1859s  $cm^{-1}$ .  $^1H$  NMR (200 MHz, 303 K,  $C_6D_6$ ):  $\delta$  1.0–1.5 (m, br, 5H,  $CH_2$ ); 1.78 (m, br, 1H,  $CH_2$ ); 1.95 (m br, 1H,  $CH_2$ ); 2.34 (m br, 1H,  $CH_2$ ); 3.03 (m br, 1H,  $CH_2$ ); 3.4 (t and m, br, partly overlapped, 3H,  $PCH_2P$  and allyl H(3),  $^2J(PH) = 10$  Hz); 4.01 (s, 9H,  $(MeO)_3Si$ ); 5.07 (t, 1H, allyl H(2),  $J(HH) = 7.9$  Hz,  $^2J(PtH) = 56$  Hz); 5.95 (t, 1H, allyl H(1),  $J(HH) = 8.2$  Hz,  $^2J(PtH) = 16$  Hz); 6.62–7.60 (m, 20H, aromatic).  $^{31}P\{^1H\}$  NMR (81 MHz, 303 K, THF–acetone- $d_6$ ):  $\delta$  23.9 (d, P(Pt),  $^{2+3}J(PP) = 107$  Hz,  $^1J(PtP) = 4184$  Hz); 68.4 (d, P(Fe),  $^{2+3}J(PP) = 108$  Hz,  $^{2+3}J(PtP) = 92$  Hz).  $^{13}C\{^1H\}$  NMR (100 MHz, 300 K,  $CDCl_3$ ):  $\delta$  23.6 (s,  $CH_2$ ); 28.4 (d,  $CH_2$ ,  $J(PC) = 8$  Hz); 29.0 (s,  $CH_2$ ,  $J(PtC) = 21$  Hz); 31.0 (d,  $CH_2$ ,  $J(PC) = 5$  Hz); 31.3 (s,  $CH_2$ ,  $J(PtC) = 29$  Hz); 39.8 (dd,  $PCH_2P$ ,  $^1J(PC) = 17$  and 30 Hz,  $^2J(PtC) = 58$  Hz); 50.2 (s, Si(OMe) $_3$ ); 75.7 (s, allyl C(1),  $^1J(PtC) = 170$  Hz); 88.4 (dd, allyl C(3),  $^2J(PC) = 37$  Hz,  $^4J(PC) = 3$  Hz,  $^1J(PtC) = 90$  Hz); 104.4 (d, allyl C(2),  $^2J(PC) = 3$  Hz,  $^1J(PtC) = 9$  Hz); 127.9–137.6 (m, aromatic); 215.0 (br, CO).

### 3.15. Synthesis of $[Fe\{Si(OMe)_3\}(CO)_3(\mu-dppm)NiCp]$ (15)

To a violet solution of  $[NiCp(PPh_3)Br]$  (0.500 g, 1.0 mmol) in toluene (20  $cm^3$ ) at  $-20^\circ C$  was added H1a (0.646 g, 1.0 mmol). After the solution was stirred for 2 h without any change in the IR spectrum,  $NEt_3$  (0.07

$cm^3$ , 1 mmol) was added. The colour became rapidly dark-red–brown and the solution was allowed to warm slowly to room temperature. The solvent was removed under vacuum, and the dark crude product washed with hexane (about 20  $cm^3$ ). Further recrystallization from toluene/hexane yielded 15 (0.200 g (26%)).

Anal. Found: C, 56.02; p H, 4.58.  $C_{36}H_{36}FeNiO_6P_2Si$  ( $M = 769.2$ ) calc.: C, 56.21; H, 4.72%. IR ( $CH_2Cl_2$ ): 1956s, 1891vs, 1875sh  $cm^{-1}$ .  $^1H$  NMR (200 MHz, 300 K,  $C_6D_6$ ):  $\delta$  3.35 (t, 2H,  $PCH_2P$ ,  $^2J(PH) = 10.4$  Hz); 3.93 (s, 9H,  $(MeO)_3Si$ ); 5.42 (s, 5H,  $C_5H_5$ ); 6.86–7.89 (m, 20H, aromatic) ppm.  $^{31}P\{^1H\}$  NMR (81.0 MHz, 300 K, THF– $C_6D_6$ ): 37.2 (d, P(Ni),  $^{2+3}J(PP) = 100$  Hz); 62.7 (d, P(Fe),  $^{2+3}J(PP) = 100$  Hz).

TABLE 3. Crystal data and data collection for 3a

Formula	$C_{40}H_{41}F_6FeNO_6P_3PtSi \cdot CH_2Cl_2$
Molecular weight	1200.63
Crystal system	Triclinic
Space group	$P\bar{1}$
$a$ (Å)	10.843(3)
$b$ (Å)	11.156(6)
$c$ (Å)	20.022(4)
$\alpha$ (°)	93.47(3)
$\beta$ (°)	98.66(3)
$\gamma$ (°)	95.66(3)
$V$ (Å $^3$ )	2375
$Z$	2
$\rho_{calc}$ (g $cm^{-3}$ )	1.679
Crystal dimensions (mm $\times$ mm $\times$ mm)	0.31 $\times$ 0.28 $\times$ 0.16
$F(000)$	1190
Systematic absences	None
Diffractometer	Enraf–Nonius CAD4
Radiation (graphite monochromator)	Mo ( $\lambda_{K\alpha} = 0.70930$ Å)
Linear absorption coefficient ( $cm^{-1}$ )	35.80
Scan type	$\omega-2\theta$
Scan range (°)	1 + 0.35 tan $\theta$
$\theta$ limits (°)	1–25
Octants collected	(+ $h$ , $\pm k$ , $\pm l$ )
Number of data collected	8465
Number of unique data used	6021 ( $F_o^2 > 6\sigma F_o^2$ )
Number of variables	369
Decay (%)	5
$R_{int} = \Sigma(F_o^2 \langle F_o^2 \rangle) / \Sigma F_o^2$	0.028
$R = \Sigma( F_o  -  F_c ) / \Sigma  F_o $	0.037
$R_w = [\Sigma w( F_o  -  F_c )^2 / \Sigma  F_o ^2]^{1/2}$	0.050
Goodness of fit $[\Sigma w( F_o  -  F_c )^2 / (N_{observ} - N_{params})]^{1/2}$	1.158
Largest shift estimated standard deviation, final cycle	0.01
Largest peak (electrons Å $^{-3}$ )	1.046
Fudge factor	0.08
Correction factors; Maximum; minimum	1.503; 0.773

TABLE 4. Positional parameters and estimated standard deviations

Atom	x	y	z	B (Å <sup>2</sup> )
Pt	0.88056(2)	0.21881(2)	0.19996(1)	1.755(4)
Fe	0.74648(8)	0.31284(7)	0.10320(4)	1.74(2)
P(1)	0.8270(1)	0.3360(1)	0.28122(7)	1.78(3)
P(2)	0.6605(1)	0.4419(1)	0.16656(7)	1.74(3)
P(3)	0.4298(2)	0.3059(2)	0.6002(1)	4.48(5)
Si	0.8434(2)	0.1746(2)	0.04893(8)	2.40(3)
F(1)	0.4326(7)	0.2317(7)	0.6654(3)	9.3(2)
F(2)	0.3126(7)	0.3646(6)	0.6167(4)	10.6(2)
F(3)	0.4199(7)	0.3681(8)	0.5345(3)	13.3(2)
F(4)	0.5578(7)	0.2637(9)	0.5892(4)	14.4(3)
F(5)	0.505(1)	0.413(1)	0.6443(7)	18.4(4)
F(6)	0.355(1)	0.1974(7)	0.5616(5)	17.1(4)
O(1)	0.9284(4)	0.1192(4)	0.1150(2)	3.3(1)
O(2)	0.7632(6)	0.0517(5)	0.0125(3)	5.4(1)
O(3)	0.9432(6)	0.2152(5)	0.0013(3)	7.6(1)
O(4)	0.9867(5)	0.4628(5)	0.1273(3)	4.1(1)
O(5)	0.5769(5)	0.1132(4)	0.1352(3)	4.0(1)
O(6)	0.6227(6)	0.3719(6)	-0.0289(3)	6.0(2)
N	1.0083(5)	0.0615(5)	0.3063(3)	2.8(1)
C(1)	1.0077(8)	0.0238(7)	0.1128(4)	5.1(2)
C(2)	0.671(1)	0.036(1)	-0.0445(5)	7.5(3)
C(3)	0.958(1)	0.3146(9)	-0.0356(4)	6.5(2)
C(4)	0.8922(6)	0.4027(6)	0.1176(3)	2.6(1)
C(5)	0.6437(6)	0.1907(5)	0.1232(3)	2.7(1)
C(6)	0.6703(7)	0.3486(6)	0.0227(4)	3.2(1)
C(7)	0.7568(6)	0.4693(5)	0.2512(3)	2.4(1)
C(8)	0.9712(6)	0.1220(5)	0.2668(3)	2.3(1)
C(9)	1.0536(7)	-0.0141(7)	0.3552(4)	3.6(2)
C(10)	0.9885(9)	-0.1299(8)	0.3526(5)	5.5(2)
C(11)	0.873(1)	-0.169(1)	0.2999(7)	7.9(3)
C(12)	1.034(1)	-0.2013(9)	0.4033(6)	8.4(3)
C(13)	1.139(1)	-0.160(1)	0.4487(6)	9.8(3)
C(14)	1.204(1)	-0.045(1)	0.4490(5)	9.0(3)
C(15)	1.1597(9)	0.0303(8)	0.4017(4)	5.3(2)
C(16)	1.228(1)	0.151(1)	0.3972(6)	7.4(3)
C(17)	0.9651(6)	0.3976(6)	0.3402(3)	2.4(1)
C(18)	0.9846(8)	0.3756(9)	0.4084(4)	4.9(2)
C(19)	1.0970(9)	0.420(1)	0.4499(4)	6.4(3)
C(20)	1.1890(8)	0.4868(8)	0.4239(5)	5.3(2)
C(21)	1.1735(9)	0.5107(9)	0.3583(5)	6.2(2)
C(22)	1.0589(8)	0.4661(8)	0.3150(5)	5.2(2)
C(23)	0.7222(6)	0.2599(6)	0.3314(3)	2.6(1)
C(24)	0.6802(7)	0.3296(7)	0.3828(3)	3.6(2)
C(25)	0.6017(7)	0.2693(9)	0.4232(4)	4.7(2)
C(26)	0.5702(8)	0.1489(9)	0.4122(4)	5.4(2)
C(27)	0.6098(8)	0.0807(8)	0.3617(4)	5.0(2)
C(28)	0.6876(7)	0.1383(6)	0.3188(4)	3.7(2)
C(29)	0.6560(6)	0.5956(5)	0.1427(3)	2.4(1)
C(30)	0.5942(7)	0.6748(6)	0.1799(4)	3.5(2)
C(31)	0.5976(8)	0.7963(6)	0.1639(5)	4.7(2)
C(32)	0.6584(8)	0.8342(7)	0.1109(4)	4.6(2)
C(33)	0.7175(8)	0.7559(7)	0.0756(4)	4.7(2)
C(34)	0.7167(7)	0.6369(6)	0.0901(4)	3.4(2)
C(35)	0.4994(6)	0.3965(5)	0.1781(3)	2.3(1)
C(36)	0.4638(7)	0.3800(9)	0.2389(4)	4.8(2)
C(37)	0.3383(9)	0.341(1)	0.2426(5)	7.4(3)
C(38)	0.2507(8)	0.3190(9)	0.1845(5)	6.0(3)
C(39)	0.2882(8)	0.341(1)	0.1246(5)	6.9(3)

TABLE 4 (continued)

Atom	x	y	z	B (Å <sup>2</sup> )
C(40)	0.4108(7)	0.376(1)	0.1194(4)	5.4(2)
C(1A)	0.281(1)	0.816(1)	0.2714(6)	10.0(4)
Cl(1)	0.3048(4)	0.9593(5)	0.2393(2)	11.8(1)
Cl(2A)	0.235(1)	0.700(1)	0.2111(5)	15.3(4)
Cl(2B)	0.145(1)	0.741(1)	0.2193(5)	13.9(3)

Anisotropically refined atoms are given in the form of the isotropic equivalent displacement parameter defined as:  $\frac{4}{3} [a^2B_{1,1} + b^2B_{2,2} + c^2B_{3,3} + ab(\cos \gamma)B_{1,2} + ac(\cos \beta)B_{1,3} + bc(\cos \alpha)B_{2,3}]$ .

### 3.16. Crystallographic data, structure solution and refinement of 3a

Suitable pale-yellow crystals of **3a** were obtained by slow crystallization from a dichloromethane solution layered with hexane, at  $-10^\circ\text{C}$ . Diffraction measurements were carried out at room temperature on a Enraf–Nonius CAD-4 four-circle diffractometer using graphite monochromated Mo K $\alpha$  radiation. Unit-cell parameters were calculated from the setting angles of 25 carefully centred reflections. The intensities of three reflections ( $\bar{1}2\bar{8}$ ,  $42\bar{2}$  and  $02\bar{1}0$ ) were monitored after every hour of exposure and showed slight crystal decay. Corrections were made for this decay. Intensities were corrected for Lorentz–polarization effects. The Enraf–Nonius SDP package was used for all computations. The method of Walker and Stuart was used for the absorption corrections. The crystal structure was solved by direct methods using MULTAN 82 and successive Fourier difference syntheses and refined by the full-matrix least-squares method with anisotropic thermal parameters for all non-hydrogen atoms. The function minimized was  $\Sigma(w|F_o| - |F_c|)^2$ , where the weight  $w$  is  $4F_o^2 / [\sigma^2(F_o^2) + (0.08F_o^2)^2]$ . The neutral-atom scattering factors used for all atoms and anomalous dispersion coefficients for all non-hydrogen atoms were obtained from standard sources [32]. The crystal data and data collection are summarized in Table 3 and the positional parameters obtained from the last cycle of refinement are listed in Table 4, with the corresponding standard deviations.

### 4. Supplementary material available

Temperature factors for anisotropic atoms (Table S-I), a complete set of bond distances (Table S-II), a complete set of bond angles (Table S-III) (six pages), and observed and calculated structure factors amplitude for all observed reflections (Table S-IV) have been deposited with the Cambridge Crystallographic Data Centre (36 pages).

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