

Enhanced substitutional lability of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\eta^2\text{-PhCCPh})]$: facile insertion of CO and organoisocyanides into iron–alkyne bonds

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The η^2 -alkyne complex $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\eta^2\text{-PhCCPh})]$ **1** reacts readily with PR_3 to give $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{PR}_3)(\eta^2\text{-PhCCPh})]$, and then $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2(\eta^2\text{-PhCCPh})]$ ($\text{R} = \text{OMe}$, **2a**; OEt , **2b**; O^nBu , **2c**; Me , **2d**; ^nBu , **2e**; Ph , **2f**). The ability of the alkyne ligand to act as a four-electron donor to a ligand-dissociated 16-electron reaction intermediate promotes site-specific replacement of the axial phosphite ligands; there is no evidence for equatorial CO replacement. Reaction of **1** with CO affords six-coordinate ferracyclopent-3-ene-2,5-dione (maleoyl) complexes $[\text{Fe}(\text{CO})_m\{\text{P}(\text{OPh})_3\}_n\{\eta^1 : \eta^1\text{-C}(\text{O})\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{O})\}]$ ($m = 3, n = 1$, **3**; $m = n = 2$, **4a**) in which CO groups have inserted into each of the Fe–C(alkyne) bonds. Analogues of **4a**, $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OR})_3\}_2\{\eta^1 : \eta^1\text{-C}(\text{O})\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{O})\}]$ ($\text{R} = \text{Me}$, **4b**; Et , **4c**), are similarly obtained as the sole products from the reaction of CO with **2a** and **2b**, respectively. The mechanism proposed for this reaction depends on replacement of an axial phosphite ligand by CO which is then susceptible to migratory attack by C(alkyne), whereas the existing equatorial CO ligands are not. The crystal structure of **3** has been determined: the complex exhibits a distorted octahedral geometry about the iron centre with a facial arrangement of the three CO ligands and the remaining coordination sites occupied by the $\text{P}(\text{OPh})_3$ ligand and by the two C(O) groups of the maleoyl moiety. Reaction of **1** and CNR ($\text{R} = \text{Me}$ and Ph) also proceeds *via* alkyne–CNR coupling to give $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}\{\eta^1 : \eta^1 : \eta^1\text{-C}(\text{=NR})\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{=NR})\}]$ which is proposed to have a square pyramidal geometry on the basis of spectroscopic data.

Introduction

The reactions of alkynes with iron carbonyls have been extensively studied since the first such report¹ in 1953 and a wealth of both mononuclear and cluster derivatives is now known.² However, examples of the simplest type of iron–alkyne interaction *viz.* η^2 -alkyne coordination to a single iron centre, remain relatively rare. Such complexes are plausible reaction intermediates but activation of the metal-bound alkyne towards subsequent coupling and insertion reactions militates against their isolation. Thus, the parent molecule $[\text{Fe}(\text{CO})_4(\eta^2\text{-HCCH})]$ was only reported in 1997 and is unstable to further reaction at temperatures greater than *ca.* -60°C .³ As expected, however, substitution of CO ligands by phosphine or phosphite donors stabilises the $\text{Fe}(\eta^2\text{-alkyne})$ fragment and a few $[\text{Fe}(\text{CO})_2(\text{PR}_3)_2(\eta^2\text{-R'CCR'})]$ complexes are known and crystallographically characterised.⁴ We have recently described the synthesis and structure of the η^2 -diphenylacetylene compound $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\eta^2\text{-PhCCPh})]$ **1**: photolysis of $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_2]$ results in CO loss and the formation of an orthometallated iron hydride $[\text{HFe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{PhO})_2\text{POC}_6\text{H}_4]$ ⁵ which reacts with $\text{PhC}\equiv\text{CPh}$ in the presence of a Lewis acid to afford **1**.⁶ In this paper the extremely facile substitution reactions of **1** with two-electron donor ligands are described and rationalised. Reaction of **1** with carbon monoxide or organo isocyanides affords insertion products; to the best of our knowledge, these are the first examples of CO and CNR insertion into a *pre-existing* iron–alkyne bond.

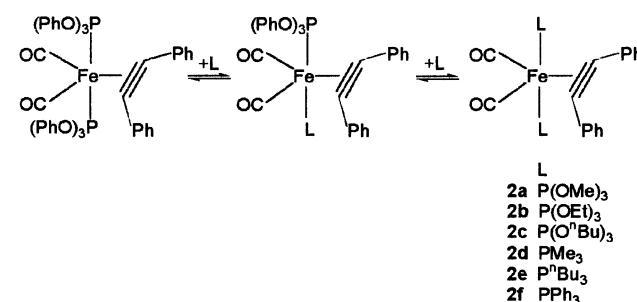
Results and discussion

Reaction with P^{III} ligands

The addition of P^{III} ligands to a solution of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\eta^2\text{-PhCCPh})]$ **1** in toluene at room temperature resulted in a

change from dark orange to bright yellow with $\text{P}(\text{OR})_3$ ($\text{R} = \text{Me}$, Et or ^nBu) or orange with PR_3 ($\text{R} = \text{Me}$ or ^nBu). The reactions were complete within seconds and afforded $[\text{Fe}(\text{CO})_2(\text{L})_2(\eta^2\text{-PhCCPh})]$ **2** in good yield. There was spectroscopic evidence [$\nu(\text{CO})$ bands] for the formation of mixed ligand derivatives $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{L})(\eta^2\text{-PhCCPh})]$ in some reactions, but attempts to isolate these in the pure state failed. The reaction of **1** with PPh_3 followed a similar course, but the reaction is an equilibrium and required a 15-fold excess of PPh_3 to drive it to completion; a pure product could not be isolated.

These observations suggest that the reactions may be described by inter-connecting equilibria (Scheme 1). For most



Scheme 1 Reaction of complex **1** with P^{III} ligands.

of the ligands studied the equilibria lie far to the right. These ligands are either smaller than $\text{P}(\text{OPh})_3$ [*viz.* $\text{P}(\text{OMe})_3$, $\text{P}(\text{OEt})_3$ and $\text{P}(\text{O}^n\text{Bu})_3$ which have cone angles⁷ *ca.* $106\text{--}110^\circ$]; are comparable in size to $\text{P}(\text{OPh})_3$ (cone angle 128°) but are much more nucleophilic (P^nBu_3 , cone angle 132°); or are both smaller and more nucleophilic (PMe_3 , 118°). It is only when $\text{L} = \text{PPh}_3$ (145°) that the incoming ligand is significantly more bulky than $\text{P}(\text{OPh})_3$ and is not particularly nucleophilic. This suggests that

Table 1 Characterisation data for $[\text{Fe}(\text{CO})_2(\text{L})_2(\eta^2\text{-PhCCPh})]$ **1** and **2a–f**

Compound	Analyses ^b (%)				IR ^c		¹³ C NMR ^d			³¹ P NMR ^e		
	L	Yield (%)	Mp ^a	C	H	P	$\nu(\text{CO})$	$\nu(\text{CC})$	$\delta(\text{CO})$	$\delta(\text{CC})$	Other	$\delta(\text{P})$
1	P(OPh) ₃						1984 (8.4) 1917 (10)	1829 (2.1)	217.8 (t, $J_{\text{CP}} = 39.3$)	91.9 (br) J_{CP} unresolved	Ph 151.6–121.1	152.6
2a	P(OMe) ₃	82	119–120	49.4 (49.1)	5.3 (5.3)	11.9 (11.5)	1966 (6.5) 1899 (10)	1825 (1.3)	219.4 (t, $J_{\text{CP}} = 38.8$)	94.9 (t, $J_{\text{CP}} = 12.3$)	Ph 135.7–126.1, Me 51.8 (d, $J_{\text{PC}} = 2.2$)	169.5
2b	P(OEt) ₃	77	146–148	55.3 (54.0)	6.4 (6.5)	8.4 (9.9)	1960 (6.5) 1892 (10)	1822 (1.4)	220.1 (t, $J_{\text{CP}} = 38.7$)	96.3 (t, $J_{\text{CP}} = 13.2$)	Ph 135.8–126.4, CH ₂ 60.9, Me 30.1	165.8
2c	P(O ⁿ Bu) ₃	78	97 (dec.)	61.4 (60.7)	7.8 (8.2)	7.6 (7.8)	1961 (6.3) 1893 (10)	1825 (1.6)	220.1 (t, $J_{\text{CP}} = 38.7$)	95.9 (t, $J_{\text{CP}} = 9.7$)	Ph 135.3–125.6, Bu 68.7, 38.1, 19.1, 14.0	164.8
2d	PMc ₃ ^f	66	101–103	60.3 (59.7)	6.4 (6.4)	12.9 (14.0)	1936 (7.3) 1866 (10)	1797 (1.9)	221.6 ^g (t, $J_{\text{CP}} = 26.9$)	106.3 (t, $J_{\text{CP}} = 9.2$)	Ph 131.8–126.0, Me 17.5 (vt, $N = 12.4$)	22.7 ^g
2e	P ⁿ Bu ₃	76	134–137	68.6 (69.1)	9.4 (9.3)	8.9 (8.0)	1930 (7.0) 1860 (10)	1783 (1.5)	223.4 (t, $J_{\text{CP}} = 26.9$)	106.6 (t, $J_{\text{CP}} = 9.7$)	Ph 136.2–125.5, Bu 26.5 (vt, $N = 10.2$), 25.6, 24.6 (vt, $N = 5.4$), 14.3	47.1
2f	PPh ₃	ca. 55	Oil				1962 (6.5) 1896 (10)	1812 (1.5)	221.3 ^h	103.0 ^h	Ph 132.3–121.8	43.8

^a Melting points in °C. dec. = melts with decomposition. ^b Calculated values in parentheses. Spectra recorded in CH₂Cl₂ solution. ^c Spectra recorded in CDCl₃ solution unless stated otherwise. Chemical shifts in ppm referenced to CDCl₃ as internal standard; multiplicity and coupling constants J (in Hz) in parentheses. ^d Spectra recorded in CDCl₃ solution unless stated otherwise. Chemical shifts in ppm referenced to H₃PO₄ with downfield shifts taken as positive. ^e Complex unstable in CDCl₃; spectrum recorded in d₈-toluene solution. ^f Signals too weak to determine multiplicity.

^a Melting points in °C. dec. = melts with decomposition. ^b Calculated values in parentheses. ^c Peak positions (cm^{−1}) with relative peak heights in parentheses. Spectra recorded in CH₂Cl₂ solution. ^d Spectra recorded in CDCl₃ solution unless stated otherwise. Chemical shifts in ppm referenced to CDCl₃ as internal standard; multiplicity and coupling constants J (in Hz) in parentheses. ^e Spectra recorded in CDCl₃ solution unless stated otherwise. Chemical shifts in ppm referenced to H₃PO₄ with downfield shifts taken as positive. ^f Contains 0.5 Et₂O of crystallisation. ^g Complex unstable in CDCl₃; spectrum recorded in d₈-toluene solution. ^h Signals too weak to determine multiplicity.

the reaction equilibria are controlled in part by steric effects with the smaller ligands replacing the larger, and in part by electronic effects with the stronger nucleophiles replacing the weaker.

Under the same reaction conditions $[\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}_2]$ and the alkene-derivative $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2(\text{C}_2\text{H}_2\text{C}_2\text{O}_3)]$ ($\text{C}_2\text{H}_2\text{C}_2\text{O}_3$ = maleic anhydride) fail to react with any of the above P^{III} ligands.

The yields and characterisation data for complexes **2a–f** are compiled in Table 1; the IR and ¹³C NMR spectroscopic data for compound **1** are included for comparison.

The spectroscopic data for **2** are consistent with the trigonal bipyramidal geometry previously established for the parent complex **1** in which the P^{III} ligands occupy mutually *trans* apical sites and the CO and alkyne moieties are in the equatorial plane of the molecule.⁶ This geometry has been confirmed for **2a** by X-ray crystallographic analysis.^{4b} The IR spectra of **1** and **2** exhibit three absorption bands in the 2000–1750 cm^{−1} region (Table 1): two of these bands are assigned to $\nu(\text{CO})$ vibrations; the third is much weaker and is assigned to the $\nu(\text{CC})$ vibration of the coordinated PhC≡CPh ligand. The frequencies of all three depend on the P^{III} ligand and decrease along the series L = P(OPh)₃ > P(OMe)₃ > P(OⁿBu)₃ > P(OEt)₃ > PPh₃ > PMe₃ > PⁿBu₃. This suggests that the increasing electron-richness of the metal centre in **2** not only brings about increasing back-bonding into the CO π^* orbitals but also into the CC π^* orbitals of the η^2 -alkyne although the frequency changes are greater for the $\nu(\text{CO})$ modes than for $\nu(\text{CC})$. In the strong back-bonding limit the Fe–alkyne interaction is more properly described by a metallacyclopentatriene structure.

The ¹³C NMR spectra of these complexes exhibit the expected triplet resonances for both the carbonyl and acetylenic C atoms (Table 1). The chemical shifts of both groups are a function of L and correlate inversely with the corresponding IR stretching frequencies: thus, $\delta(\text{CO})$ and $\delta(\text{CC})$ increase along the series L = P(OPh)₃ < P(OMe)₃ < P(OⁿBu)₃ \cong P(OEt)₃ < PPh₃ < PMe₃ < PⁿBu₃. The δ values reflect the σ -donor capacity of the phosphane ligand and therefore the extent of π -back-bonding from the iron centre to the CO and alkyne ligands.

Reaction with CO

A solution of **1** in chloroform reacted rapidly with CO to give a mixture of two compounds which were identified by comparison with literature data⁶ as the ferracyclopent-3-ene-2,5-dione complexes $[\text{Fe}(\text{CO})_m\{\text{P}(\text{OPh})_3\}_n\{\eta^1 : \eta^1\text{-C}(\text{O})\text{C}(\text{Ph})\text{-C}(\text{Ph})\text{C}(\text{O})\}]$ (**3**, $m = 3$, $n = 1$; **4a**, $m = 2$, $n = 2$) in which the five-membered maleoyl-type metallacycle arises from CO insertion into the Fe–alkyne bonds of the precursor. When ¹³CO was used in place of normal CO, the same products were obtained but with ¹³CO distributed over all CO sites. Similar reactions occurred between CO and $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OR})_3\}_2(\eta^2\text{-PhCCPh})]$ (R = Me or Et) but only analogues of **4a** were isolated: $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OR})_3\}_2\{\eta^1 : \eta^1\text{-C}(\text{O})\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}(\text{O})\}]$ (**4b**, R = Me; **4c**, R = Et).

The spectroscopic data of **3** and **4** are consistent with the structures shown in Fig. 1; the structure of **3** has also been established by X-ray crystallography (following section). The IR spectra exhibit two $\nu(\text{CO})$ absorption bands the shapes and relative intensities of which are consistent with the presence of a *fac*-M(CO)₃ and a *cis*-M(CO)₂ moiety, respectively. Their frequencies show the expected effects on changing the number and types of phosphite ligands. If the CO ligands are replaced by ¹³CO, the frequencies of these bands decrease by ca. 44–47 cm^{−1} as anticipated.

The IR spectra also show a number of bands at ca. 1600 cm^{−1}. Those complexes which contain a P(OPh)₃ ligand have a band at ca. 1590 cm^{−1} which does not change frequency on replacement of CO by ¹³CO and which is not present in the

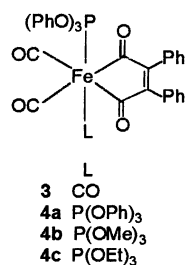


Fig. 1 Structure of the complexes **3** and **4**.

spectra of the P(OMe)₃ and P(OEt)₃ derivatives. It is assigned to an internal vibration of P(OPh)₃. All of the complexes show two absorption bands which are attributed to the $\nu(\text{CO})/\nu(\text{CC})$ vibrations of the $-\text{C}(\text{O})-\text{C}=\text{C}-\text{C}(\text{O})-$ moiety. For **3** they lie at 1651 and 1636 cm^{-1} , and for **4a** at 1642 and 1616 cm^{-1} . If CO is replaced by ^{13}CO these frequencies fall to 1633 and 1604 cm^{-1} , and 1617 and 1578 cm^{-1} , respectively. These observations are consistent with the conclusions that there is mixing of the $\nu(\text{CO})$ and $\nu(\text{CC})$ vibrations of the maleoyl ligand, that the 1651 (**3**) and 1642 cm^{-1} (**4a**) bands have more $\nu(\text{CO})$ character than the 1636 and 1604 cm^{-1} bands, respectively, and that the $-\text{C}(\text{O})-\text{C}(\text{Ph})=\text{C}(\text{Ph})-\text{C}(\text{O})-$ group acts as a π -acceptor ligand whose C=O and C=C bond orders are reduced when the $\text{Fe}(\text{CO})_3\{\text{P}(\text{OPh})_3\}$ moiety is replaced by $\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2$.

All of the anticipated resonances are present in the ^{13}C NMR spectra of **3** and **4** and their all- ^{13}C counterparts, although the latter are complicated by ^{13}C – ^{13}C coupling. The carbonyl region of the ^{13}C NMR spectrum of **4a** comprises a single triplet resonance at δ 205.2 ($J_{\text{CP}} = 22.1$ Hz) whereas that of **3** consists of two doublet signals at δ 205.6 and 202.1 in a 1 : 2 ratio. The less intense resonance exhibits the larger coupling ($J_{\text{CP}} = 30.7$ Hz) and is assigned to the unique CO ligand *trans* to P(OPh)₃; the higher field signal is attributed to the equatorial CO ligands *cis* to P(OPh)₃. In both **3** and **4** the acyl CO groups of the maleoyl ligand are strongly deshielded giving rise to resonances at *ca.* δ 250–262 which couple to the ligated ^{31}P atoms ($J_{\text{CP}} = \text{ca.}$ 31 Hz). Singlet resonances at *ca.* δ 167 are assigned to the central C atoms of the maleoyl ligands.

Crystal structure of complex **3**

Single crystals of **3** were obtained from CDCl_3 –hexane solution and analysed by X-ray diffraction. The molecular structure is shown in Fig. 2 together with selected bond lengths and angles. The coordination geometry about the iron atom is approximately octahedral: the three CO ligands span one face and the remaining coordination sites are occupied by the P(OPh)₃ ligand and by the two C(O) groups of the ferracyclopentenedione moiety. The structure of **3** compares closely with that of $[\text{Fe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}_2\{\eta^1:\eta^1-\text{C}(\text{O})\text{C}(\text{Me})\text{C}[\text{CH}(\text{OEt})_2]\text{C}(\text{O})\}]$ **5** which is obtained directly from the reaction of $[\text{HFe}(\text{CO})_2\{\text{P}(\text{OPh})_3\}(\text{PhO})_2\text{POC}_6\text{H}_4]$ with $\text{MeC}\equiv\text{CCH}(\text{OEt})_2$.⁶ As in **5**, the metallacycle in **3** is essentially planar (r.m.s. deviation from planarity is 0.02 Å) and there is no evidence for bond delocalisation within the ring: C4–C5 [1.356(6) Å] is a typical C–C double bond; C4–C6 [1.496(7) Å] and C5–C7 [1.507(7) Å] are single bonds. The Fe–C(O) bond lengths of 2.017(5) and 2.003(5) Å are slightly, but not significantly, shorter than the average value reported for $\text{Fe}^{\text{II}}-\text{C}(\text{sp}^2)$ bonds (2.05 Å).⁸ The distances C6–O6 [1.215(5) Å] and C7–O7 [1.208(5) Å] are similar to the average C=O bond length of 1.21 Å.⁹ The structural data imply that the π -acceptor function of the maleoyl ligand (deduced above from the IR spectra) must be small.

Distortions from ideal octahedral geometry arise from the constrained bite of the maleoyl ligand which imposes an angle of 81.0(2)° at the metal centre, and results in a correspondingly larger opposite angle C2–Fe–C3 95.6(3)°, and from a significant displacement of the axial ligands in the direction of the ring

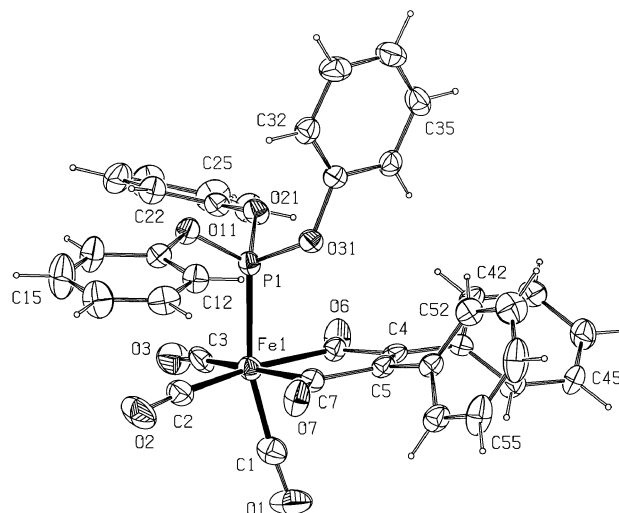


Fig. 2 The molecular structure of complex **3**. Selected bond lengths (Å) and angles (°): Fe–P1 2.1937(19), Fe–C1 1.781(7), Fe–C2 1.859(6), Fe–C3 1.846(6), Fe–C6 2.017(5), Fe–C7 2.003(5), C4–C5 1.356(6), C4–C6 1.496(7), C5–C7 1.507(7), C6–O6 1.215(5), C7–O7 1.208(5), C1–Fe–P1 165.3(2), C2–Fe–C6 171.2(2), C3–Fe–C7 172.7(2), Fe–C1–O1 175.2(6), Fe–C2–O2 175.0(6), Fe–C3–O3 175.0(6), P1–Fe–C2 98.01(19), P1–Fe–C3 94.66(19), P1–Fe–C6 85.15(16), P1–Fe–C7 87.73(16), C1–Fe–C2 93.8(3), C1–Fe–C3 92.9(3), C1–Fe–C6 82.0(2), C1–Fe–C7 83.4(3).

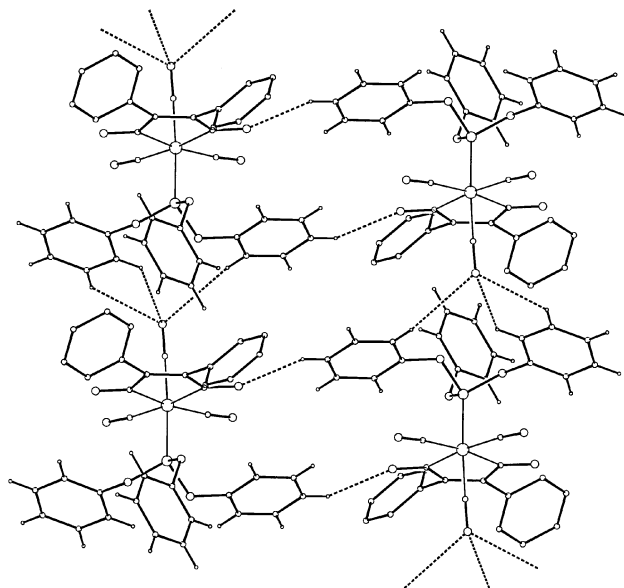


Fig. 3 Packing of the molecules in the crystal structure of complex **3**.

[P1–Fe–C1 165.3(2)°]. The extent of this displacement may be indicated by the angles P1–Fe...Cg1 84.90(9)° and C1–Fe...Cg1 80.7(2)° where Cg1 is the centroid of the metallacycle. This inclination of the axial ligands is also present in complex **5** where the *trans* phosphites make an angle of 167.89(4)° with the iron centre and it has been observed in structural determinations of related metal–maleoyl complexes.⁹

An analysis of the crystal structure of **3** reveals no strong hydrogen bonding interactions; the most significant such intermolecular interaction comprises C14–H14...O7ⁱ ($i = -x, 1 - y, 2 - z$) with $\text{H}\cdots\text{O}$ 2.49 Å and $\text{C}-\text{H}\cdots\text{O}$ 144°. Two molecules of **3** associate about an inversion centre forming a hydrogen bonded motif with graph set $R^2_2(20)$ as depicted in Fig. 3. These pairs stack along the *a*-axis associated through weak $\text{C}-\text{H}\cdots\text{O}$ and $\text{C}-\text{H}\cdots\pi(\text{arene})$ interactions. The latter form through C45–H45... $\pi\{C31, \dots, C36\}^{\text{ii}}$ with $\text{H}\cdots\text{Cg2}^{\text{ii}}$ 2.83 Å and $\text{C}-\text{H}\cdots\text{Cg2}^{\text{ii}}$ 146° where Cg2 is the centroid of the $\{C31, \dots, C36\}$ arene ring system and the symmetry operator

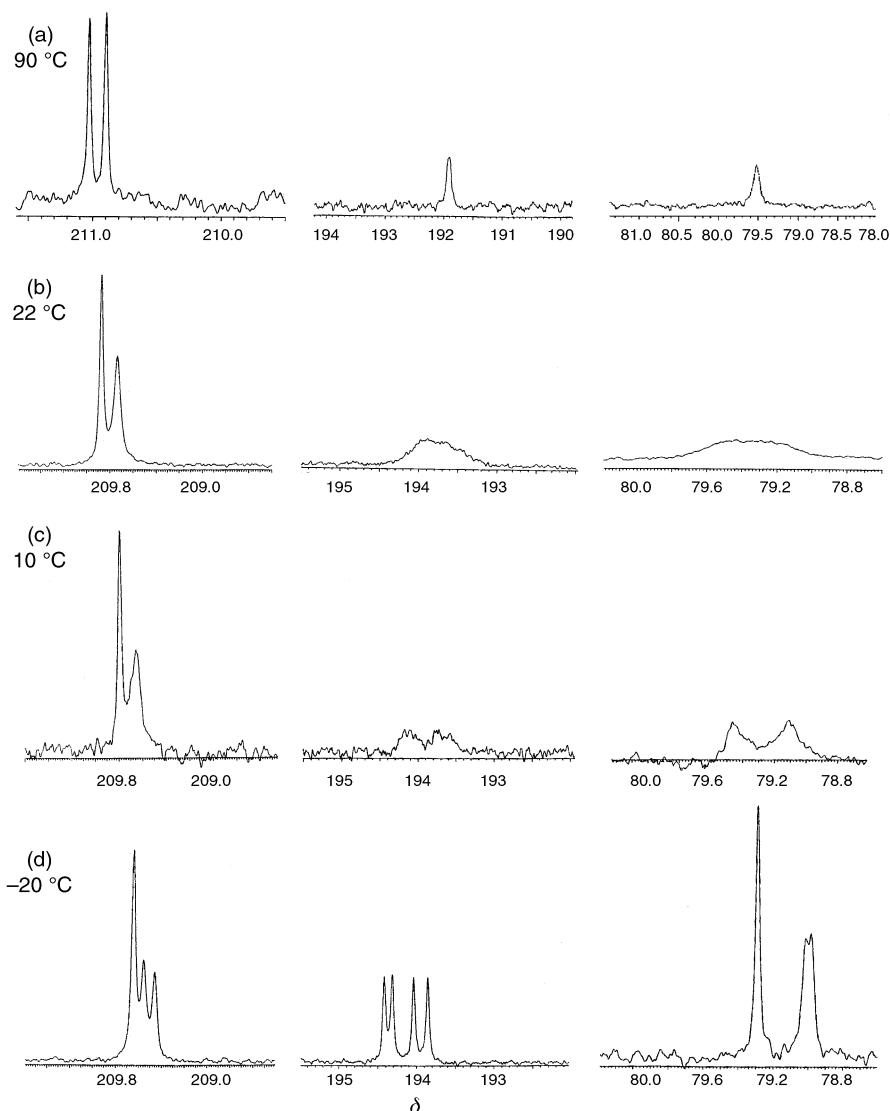


Fig. 4 Variable-temperature ^{13}C NMR spectra for complex **6b**.

ii = ($x - 1, y, z$). This effect results in the two phenyl rings of the maleoyl ligand interacting with a phenoxy ring of a symmetry-related phosphiteⁱⁱ forming what can be described as a triple embrace reminiscent of the hextuple embraces observed in PPh_3 derivatives.¹⁰ The other two phenoxy groups of phosphiteⁱⁱ do not participate in this association. The closest hydrogen bonding interaction involving O1 is $\text{O1} \cdots \text{H35-C35}^{\text{iii}}$ (iii = $x - 1, 1 + y, z$) with $\text{O} \cdots \text{H}$ 2.72 Å and $\text{O} \cdots \text{H-C}$ 138°. However, three other contacts also arise: these are depicted in Fig. 3. The volume element around O1 is such that these contacts, although weak, facilitate bending in the Fe–C1–O1 angle and contribute to the observed deviation from linearity in the direction of the maleoyl group.

Reaction with CNR (R = Me or Ph)

A very rapid reaction occurred on addition of methyl or phenyl isocyanide (CNR) to a toluene solution of **1**. However, the isolated products **6a** (R = Me) and **6b** (R = Ph) were not the expected simple analogues of **3** or **4**. Elemental analysis indicated that both new compounds comprise 2 : 1 adducts of CNR and the fragment $\text{Fe}(\text{CO})_2\{\text{P}(\text{O}^i\text{Ph})_3\}(\text{Ph}_2\text{C}_2)$. The IR spectra of **6a,b** exhibited two $\nu(\text{CO})$ absorption bands but signals attributable to terminal isocyanide ligands or to the $\nu(\text{C}\equiv\text{C})$ stretch of an η^2 -alkyne were not detected. Instead, absorptions at 1715 (**6a**) and 1686 cm^{-1} (**6b**) suggested the presence of imine and/or C=C functionalities. The room-temperature ^{13}C NMR spectrum of **6b** exhibited (in addition

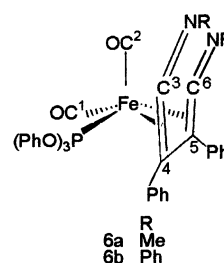


Fig. 5 Proposed structure for complexes **6a** and **b**.

to intense Ph resonances) two signals in the carbonyl region and broad resonances centred at δ 193.8 and 79.4. A variable temperature ^{13}C NMR experiment was therefore undertaken; the data obtained are depicted in Fig. 4. From the above compositional and spectroscopic data and, in particular, the low-temperature ^{13}C NMR spectrum of **6b** [Fig. 4(d)] we propose the structure shown in Fig. 5 in which the iron atom is in a square pyramidal environment and the $\text{RN}=\text{C}=\text{C}(\text{Ph})\text{C}(\text{Ph})\text{C}=\text{NR}$ organic ligand acts as an η^4 , four-electron donor to the metal centre. Such a ligand is not without precedent in the literature: Stone and co-workers have reported¹¹ the crystal structure of the square pyramidal complex $[\text{Fe}(\text{CN}^i\text{Bu})_3\{\eta^1 : \eta^1 : \eta^1 : \eta^1\text{-C}(\text{N}^i\text{Bu})=\text{C}(\text{Ph})\text{C}(\text{Ph})=\text{C}(\text{N}^i\text{Bu})\}]$ which was obtained from the interaction of free diphenylacetylene with pre-coordinated isocyanide ligands in

[Fe(CN^tBu)₅], in opposite sense to the reaction we report here. The room-temperature ¹³C NMR chemical shifts observed for **6b** compare with those reported by Stone and co-workers for the bis(*tert*-butylimino)diphenylbuta-1,3-diene ligand: δ 203.3 [^tBuN=CC(Ph)-] and δ 72.0 [^tBuN=CC(Ph)-].¹¹

The low-temperature ¹³C NMR spectrum of **6b** is consistent with the unsymmetrical structure shown in Fig. 5 in which the phosphite ligand occupies a basal position. In the related complexes [Fe(CO)₂(L)(η^4 -diene)] (L = phosphine or phosphite) the P–CO coupling constants have been shown to have the order $J(\text{P}_{\text{basal}}-\text{CO}_{\text{basal}}) \gg J(\text{P}_{\text{axial}}-\text{CO}_{\text{basal}}) \cong J(\text{P}_{\text{basal}}-\text{CO}_{\text{axial}})$.¹² The doublet resonance at δ 209.5 in the carbonyl region of the low-temperature ¹³C NMR spectrum [Fig. 4(d)] is therefore assigned to C1 [$J(\text{P}_{\text{basal}}-\text{CO}_{\text{basal}}) = 12.3$ Hz] and the singlet at δ 209.7 is assigned to C2 assuming that the smaller $J(\text{P}_{\text{basal}}-\text{CO}_{\text{axial}})$ coupling is not resolved at this temperature. The doublet resonances at δ 194.4 ($J_{\text{CP}} = 13.3$ Hz) and δ 193.9 ($J_{\text{CP}} = 23.1$ Hz) are assigned to C3 and C6, respectively, since C6 is expected to exhibit the larger coupling to the pseudo-*trans* P atom. Similarly, the singlet resonance at δ 79.3 and the doublet at δ 79.0 ($J_{\text{CP}} = 4.8$ Hz) are assigned to C4 and C5, respectively, where P coupling to C4 is not resolved.

On warming to room temperature the ¹³C NMR signals of the organic ligand converge: C3 and C6 coalesce at *ca.* 19 °C and C4 and C5 at *ca.* 22 °C. However, coalescence of the CO resonances is not observed in the temperature range studied. At 90 °C these ligands give rise to two sharp singlets at δ 211.0 and 210.9 whereas the signals due to C3/C6 and C4/C5 appear as somewhat broadened singlets at δ 191.8 and 79.5, respectively. The data suggest a fluxional process which interchanges only the basal phosphite and basal CO ligand. The result is an inversion of chirality at the iron centre which equilibrates the backbone carbon atoms of the bis(phenylimino)diphenylbuta-1,3-diene ligand but does not effect scrambling of the axial and basal CO groups.

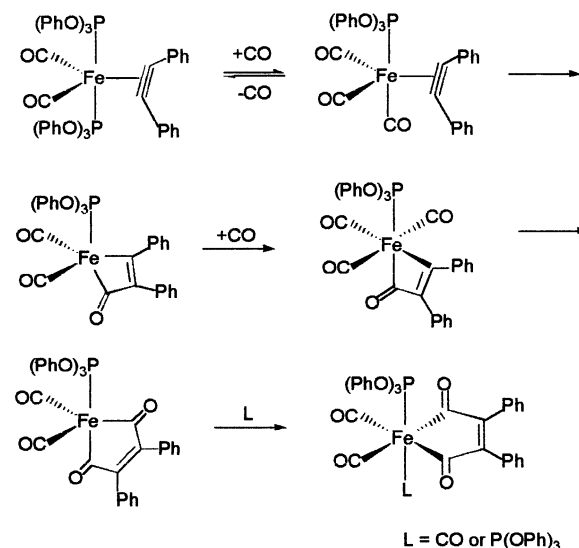
In contrast to **6b**, the variable temperature ¹³C NMR spectra of the methyl derivative **6a** are consistent with a dynamic process which interchanges apical and basal sites and leads to complete CO scrambling in the fast-exchange regime. Such exchange processes are well established for the complexes [Fe(CO)₂(L)(η^4 -diene)] (L = CO, PR₃, CNR) and occur *via* either a sequential Berry pseudorotation or a turnstile rotation of the [Fe(CO)₂(L)] fragment relative to the diene.^{12,13} Thus, at 90 °C the ¹³C NMR spectrum of **6a** exhibits one doublet resonance at δ 213.3 ($J_{\text{CP}} = 14.9$ Hz) attributable to two equivalent CO ligands, and slightly broadened singlets at δ 188.0 and 78.2 assigned to C3/C6 and C4/C5, respectively. On cooling, the CO resonances collapse to a broad singlet which decoalesces at *ca.* 10 °C; the resonances due to the backbone carbon atoms of the organic ligand decoalesce in the range 2–0 °C. At the lowest temperature accessible to us (–20 °C) the gross features of the low temperature spectrum of **6b** are reproduced *i.e.* two signals due to the CO ligands and four signals for the four backbone carbon atoms consistent with the unsymmetrical structure of Fig. 5. However, all resonances are broad and coupling to P is not resolved.

Reaction mechanisms

Complex **1** undergoes facile P(OPh)₃ substitution whereas neither the parent complex [Fe(CO)₃{P(OPh)₃}₂] nor the alkene derivative [Fe(CO)₂{P(OPh)₃}₂(maleic anhydride)] react under the same conditions. We suggest that the ability of the alkyne to act as a four-electron donor as well as a two-electron donor promotes the loss of a P(OPh)₃ ligand by stabilising the formally 16-electron intermediate [Fe(CO)₂{P(OPh)₃}(η^2 -PhCCPh)]. Caulton and co-workers have similarly proposed that four-electron donation from PhCCPh may contribute to the ease of phosphine dissociation in [Ru(CO)₂(P^tBuMe)₂(η^2 -PhCCPh)].¹⁴ Takats and co-workers have observed enhanced

labilisation of the CO ligands in [M(CO)₄(η^2 -alkyne)] (M = Fe, Ru, Os) which undergo substitution reactions at rates that are much greater than those of their [M(CO)₅] precursors.¹⁵ This was attributed to stabilisation of a ligand-dissociated 16-electron intermediate by donation from the filled π_1 alkyne orbital to the vacated metal d_σ orbital [see Fig. 4 in ref. 15(a)]. This suggestion implies that it is an axial ligand which is labilised and our work establishes that this is the case since only the axial P(OPh)₃ ligands of [Fe(CO)₂{P(OPh)₃}₂(η^2 -PhCCPh)] are replaced; no CO substitution is observed. A parallel may be drawn between the substitutional behaviour of **1** and the labilisation of the axial PR₃ ligands in Fe(CO)₂(PR₃)₂(η^2 -CS₂).¹⁶ In these complexes, the CS₂ ligand acts in many respects as though it were an S⁺≡C–S[–] two-electron donor through the S⁺≡C bond.

The reaction of **1** with CO is now explicable. The first step is replacement of the labilised axial phosphite ligand by CO (Scheme 2) followed by migration of one alkyne C atom to



Scheme 2 Proposed mechanism for the reaction of complex **1** with CO.

the axial CO ligand leaving behind a vacant site which is then occupied by a second incoming CO. The second C atom of the alkyne can migrate to this to give an intermediate which may be formulated as a 16-electron species with an η^2 -maleoyl ligand acting as a two-electron donor or a rather labile 18-electron species with the maleoyl ligand acting as an η^4 , four-electron donor. This takes up CO or P(OPh)₃ to give the final products **3** and **4a**, respectively. This scheme accounts for the observed incorporation of ¹³CO into Fe–CO as well as maleoyl CO sites. A similar mechanism may be invoked for the reaction of **1** with organoisocyanides.

The reaction of **1** with CO was monitored by IR spectroscopy in an attempt to detect the intermediates proposed in Scheme 2. The addition of a sub-stoichiometric quantity of CO to a chloroform solution of **1** under nitrogen afforded partial conversion to a species in equilibrium with **1** which was identified as [Fe(CO)₃{P(OPh)₃}(η^2 -PhCCPh)] **7** by comparison of the IR spectrum [$\nu(\text{CO})$ 2043s, 1983m, 1949s; $\nu(\text{CC})$ 1844w cm^{–1}] with that reported for [Os(CO)₃(PMe₃)(η^2 -HCCH)] [$\nu(\text{CO})$ 2056s, 1977m, 1947s cm^{–1}; $\nu(\text{CC})$ not given].^{15b} Complex **7** is unstable in the absence of CO and on a TLC plate and was not isolable: on removal of the solvent or purging the solution with a stream of nitrogen gas, the starting material **1** was cleanly regenerated. However, under a low partial pressure of CO, **7** is long-lived and was observed to decay only slowly (*ca.* hours) to the final products **3** and **4a**. No other intermediates were detected. The isocyanide analogue of **7**, *viz.* [Fe(CO)₂{P(OPh)₃}₂(CNR)(η^2 -PhCCPh)], was not observed in

the reaction of **1** with CNR; for this system, reaction appeared to be complete within the time of mixing and no intermediates were detected by IR spectroscopy.

Complex **1** is stable with respect to CO insertion into the Fe–C(alkyne) bond except in the presence of added CO. This may be rationalised on the basis that the bite angle of the η^2 -alkyne is small and therefore the equatorial CO groups, though formally *cis* to the Fe–C bonds, are actually too distant from them to allow C migration to take place. In the structure of **1** the distance from a C≡C carbon atom to the carbon of the (nearest) equatorial CO ligand is 3.07 Å; the distance to the P atom of the axial phosphite ligands is 2.90 Å.⁶ In complex **7**, [Fe(CO)₃{P(OPh)₃}(η^2 -PhCCPh)], assuming a standard Fe–CO bond distance of 1.78 Å,⁸ the distance to the axial CO carbon is calculated at 2.64 Å. The axial CO ligand is thus *ca.* 0.4 Å closer to the C≡C group and susceptible to migratory attack by C(alkyne).

Conclusions

The stabilisation of the Fe(η^2 -alkyne) fragment by coordination of phosphite donor ligands has enabled a study of the chemistry of the [Fe(CO)₂{P(OPh)₃}₂(η^2 -PhCCPh)] complex. The reactivity of **1** is characterised by rapid phosphite substitution; this is atypical of saturated 18-electron transition-metal complexes, which often tend to be kinetically inert. It is attributed to the capacity of the alkyne ligand to act as a four-electron donor which stabilises the formally 16-electron [Fe(CO)₂{P(OPh)₃}-(η^2 -PhCCPh)] transition state and which specifically promotes labilisation of the *axial* ligands, as observed. When **1** is reacted with excess CO the initial substitution product [Fe(CO)₃-{P(OPh)₃}(η^2 -PhCCPh)] affords ferracyclopentenedione complexes in which CO has inserted into both Fe–alkyne bonds. Since iron–carbonyl mediated alkyne–CO coupling reactions have always been *assumed* to proceed through undetected [Fe(CO)₄(η^2 -alkyne)] intermediates, the above is an important observation. A similar insertion reaction is observed on treatment of **1** with organoisocyanide but here alkyne–CNR coupling affords an unusual bis(imino)buta-1,3-diene ligand which is proposed to act as a four-electron donor to an Fe(CO)₂{P(OPh)₃} fragment.

Experimental

General procedures

[Fe(CO)₂{P(OPh)₃}(η^2 -PhCCPh)] was prepared as described previously.⁶ Other chemicals were purchased from Aldrich and used without further purification. All reactions were carried out at room temperature under an atmosphere of nitrogen in dried and deoxygenated solvents. IR spectra were recorded on a Perkin-Elmer Paragon 1000 FTIR spectra. ¹³C NMR spectra were obtained at 25 °C, unless otherwise stated, on a Varian INOVA 500 MHz spectrometer operating at 125.7 MHz; ³¹P NMR spectra were obtained at 30 °C on a Varian INOVA 300 MHz spectrometer operating at 121.4 MHz. Analyses were determined by the Analytical Laboratory, University College Dublin.

Preparations

[Fe(CO)₂(PR₃)₂(η^2 -PhCCPh)]. The P^{III} exchange products (R = OMe, **2a**; OEt, **2b**; OⁿBu, **2c**; Me, **2d**; ⁿBu, **2e**) were prepared by addition of the appropriate P^{III} ligand to a solution of [Fe(CO)₂{P(OPh)₃}(η^2 -PhCCPh)] (0.25 g, 0.27 mmol) in toluene (20 ml) in a 2 : 1 molar ratio. The resulting mixture was stirred for 15 min and the solvent was then removed at reduced pressure. The residue was recrystallised from dichloromethane–hexane (R = OMe, OEt or OⁿBu) or diethyl ether–methanol (R = Me or ⁿBu) to afford the product as a yellow-orange crystalline solid.

The reaction of [Fe(CO)₂{P(OPh)₃}(η^2 -PhCCPh)] with PPh₃ required a 15-fold excess of the ligand. The reaction mixture was stirred as above and the solvent removed. The residue was extracted with hot pentane to give an orange solution, which was filtered and evaporated to dryness at reduced pressure. Complex **2f** was obtained as an orange oil.

[Fe(CO)₃{P(OPh)₃}(η^1 : η^1 -C(O)C(Ph)C(Ph)C(O))] **3** and [Fe(CO)₂{P(OR)₃}(η^1 : η^1 -C(O)C(Ph)C(Ph)C(O))] (R = Ph, **4a**; Me, **4b**; Et, **4c**). [Fe(CO)₂{P(OPh)₃}(η^2 -PhCCPh)] (0.5 g, 0.55 mmol) was dissolved in chloroform (20 ml) and this solution was injected *via* a rubber septum into a 50 ml flask filled with CO. The flask was shaken for 30 min. The solvent was removed and the residue was purified by column chromatography on silica. Elution with 3 : 1 hexane–chloroform afforded orange [Fe(CO)₃{P(OPh)₃}(η^1 : η^1 -C(O)C(Ph)C(Ph)C(O))] **3** and subsequent elution with 1 : 1 hexane–chloroform gave yellow [Fe(CO)₂{P(OPh)₃}(η^1 : η^1 -C(O)C(Ph)C(Ph)C(O))] **4a**. Both compounds were recrystallised from dichloromethane–hexane.

[Fe(CO)₂{P(OR)₃}(η^1 : η^1 -C(O)C(Ph)C(Ph)C(O))] (**4b**, R = Me; **4c**, R = Et) were similarly obtained as the sole products from the reaction of [Fe(CO)₂{P(OR)₃}(η^2 -PhCCPh)] (R = Me or Et) with CO.

Complex 3. Yield: 41%, mp 126–127 °C. Found: C, 64.8; H, 3.7; P, 4.4. C₃₇H₂₅FeO₈P requires C, 64.9; H, 3.7; P, 4.5%. IR (CH₂Cl₂, cm⁻¹) ν (C=O) 2081vs, 2024vs (br); ν (C=O) 1651w; ν (C=C) 1636m; ν (POPh) 1590m; δ_c (CDCl₃) 251.4 (d, ²J_{CP} = 30.8 Hz, C=O), 205.6 (d, ²J_{CP} = 30.7 Hz, C=O), 202.1 (d, ²J_{CP} = 22.2 Hz, C=O), 167.4 (s, C=C), 151.4–121.1 (Ph); δ_p (CDCl₃) 140.6.

Complex 4a. Yield: 25%, mp 141–142 °C. Found: C, 66.7; H, 4.0; P, 6.3. C₅₄H₄₀FeO₁₀P₂ requires C, 67.1; H, 4.1; P, 6.4%. IR (CH₂Cl₂, cm⁻¹) ν (C=O) 2044vs, 1992s; ν (C=O) 1642w; ν (C=C) 1616m; ν (POPh) 1590m; δ_c (CDCl₃) 259.6 (t, ²J_{CP} = 30.8 Hz, C=O), 205.2 (t, ²J_{CP} = 22.1 Hz, C=O), 168.3 (s, C=C), 151.4–121.2 (Ph); δ_p (CDCl₃) 145.1.

Complex 4b. Yield: 49%, mp 123–124 °C. Found: C, 49.6; H, 4.8; P, 10.8. C₂₄H₂₈FeO₁₀P₂ requires C, 48.6; H, 4.8; P, 10.4%. IR (CH₂Cl₂, cm⁻¹) ν (C=O) 2035vs, 1979s; ν (C=O)/ ν (C=C) 1618m (br); δ_c (CDCl₃) 261.9 (t, ²J_{CP} = 31.0 Hz, C=O), 207.9 (t, ²J_{CP} = 23.8 Hz, C=O), 166.3 (s, C=C), 134.3–127.1 (Ph), 51.8 (vt, N = 2.2 Hz, Me).

Complex 4c. Yield: 51%, mp 122–125 °C. Found: C, 52.9; H, 5.9; P, 8.8. C₃₀H₄₀FeO₁₀P₂ requires C, 53.1; H, 6.0; P, 9.1%. IR (CH₂Cl₂, cm⁻¹) ν (C=O) 2033vs, 1980s; ν (C=O)/ ν (C=C) 1621m (br); δ_c (CDCl₃) 260.9 (t, ²J_{CP} = 30.9 Hz, C=O), 207.6 (t, ²J_{CP} = 22.1 Hz, C=O), 165.9 (s, C=C), 134.3–121.4 (Ph), 62.2 (d, ²J_{CP} = 6.8 Hz, CH₂), 16.1 (d, ³J_{CP} = 5.1 Hz, Me).

[Fe(CO)₂{P(OPh)₃}(η^1 : η^1 : η^1 : η^1 -C(NR)C(Ph)C(Ph)C(NR))] (**6a**, R = Me; **6b**, R = Ph). A 0.1 M solution of methyl or phenyl isocyanide in toluene was added dropwise to a solution of [Fe(CO)₂{P(OPh)₃}(η^2 -PhCCPh)] (0.2 g, 0.22 mmol) in toluene (20 ml). The reaction was monitored by IR spectroscopy and the addition was halted when the IR absorbances of the starting material had disappeared. The solvent was removed and the residue was purified by column chromatography on alumina. Elution with 1 : 1 hexane–dichloromethane removed P(OPh)₃; elution with acetone then afforded a yellow material which was recrystallised from acetone–hexane to give the product as a yellow solid.

Complex 6a. Yield: 53%, mp 129–130 °C. Found: C, 66.4; H, 5.0; N, 3.8; P, 4.7. C₃₈H₃₁FeN₂O₅P requires C, 66.9; H, 4.6; N, 4.1; P, 4.5%. IR (CH₂Cl₂, cm⁻¹) ν (CO) 2006vs, 1957s; ν (C=C)/ ν (C=N) 1715m; ν (POPh) 1591m; δ_c (d-toluene; 90 °C) 213.3 (d, ²J_{CP} = 14.9 Hz, CO), 188.0 (s, N=C=C), 151.4–121.1 (Ph), 78.2 (s, N=C=C), 44.6 (s, Me); δ_c (CD₂Cl₂; -20 °C) 214.6 (br s, CO), 209.4 (br s, CO), 190.7 (br s, N=C=C), 188.9 (br s, N=C=C), 80.1 (br s, N=C=C), 74.9 (br s, N=C=C), 44.6 (m, Me); δ_H (CDCl₃;

30 °C) 7.37–6.97 (25 H, m, Ph), 3.43 (6 H, s, Me); $\delta_{\text{p}}(\text{CDCl}_3; 30\text{ °C})$ 156.7.

Complex 6b. Yield: 47%, mp 163 °C (decomp.). Found: C, 71.1; H, 4.6; N, 3.6; P, 3.6. $\text{C}_{48}\text{H}_{35}\text{FeN}_2\text{O}_5\text{P}$ requires C, 71.5; H, 4.4; N, 3.5; P, 3.8%. IR (CH_2Cl_2 , cm^{-1}) $\nu(\text{CO})$ 2025vs, 1976s; $\nu(\text{C}=\text{C})/\nu(\text{C}=\text{N})$ 1686m; $\nu(\text{POPh})$ 1592m; $\delta_{\text{C}}(\text{d-toluene}; 90\text{ °C})$ 211.0 (s, CO), 210.9 (s, CO), 191.8 (br s, $\text{N}=\text{C}=\text{C}$), 152.0–120.6 (Ph), 79.5 (br s, $\text{N}=\text{C}=\text{C}$); $\delta_{\text{C}}(\text{CDCl}_3; -20\text{ °C})$ 209.7 (s, C^2O), 209.7 (d, $^2J_{\text{CP}} = 12.3\text{ Hz}$, C^1O), 194.4 (d, $^2J_{\text{CP}} = 13.3\text{ Hz}$, $\text{N}=\text{C}^3=\text{C}$), 193.9 (d, $^2J_{\text{CP}} = 23.1\text{ Hz}$, $\text{N}=\text{C}^6=\text{C}$), 151.9–120.0 (Ph), 79.3 (s, $\text{N}=\text{C}=\text{C}^4$), 79.0 (d, $^2J_{\text{CP}} = 4.8\text{ Hz}$, $\text{N}=\text{C}=\text{C}^5$); $\delta_{\text{p}}(\text{CDCl}_3; 30\text{ °C})$ 152.3.

Crystal structure determination of complex 3

X-Ray data were collected on a Bruker P4 diffractometer (Mo-K α radiation, $\lambda = 0.71073\text{ \AA}$) at 294(2) K. $\text{C}_{37}\text{H}_{25}\text{FeO}_8\text{P}$ (yellow plate $0.32 \times 0.30 \times 0.03\text{ mm}$) crystallised in the triclinic space group $P\bar{1}$ with unit cell parameters: $a = 9.508(3)$, $b = 10.766(3)$, $c = 16.973(7)\text{ \AA}$; $\alpha = 83.97(3)$, $\beta = 84.64(2)$, $\gamma = 66.84(2)^\circ$; $V = 1586.0(9)\text{ \AA}^3$; $Z = 2$; $\mu = 0.580\text{ mm}^{-1}$. 5932 reflections were collected in the range $2 \leq \theta \leq 25^\circ$ (h , 0–11; k , –11–12; l , –20–10); 5572 independent reflections [2863 with $I > 2\sigma(I)$] and 424 parameters were used in full-matrix least-squares (SHELXL97^{17a}). Data were not corrected for absorption (four ψ -scan reflections with 5° increments did not afford any significant difference in intensity). In the final refinement cycles (SHELXS97^{17b}) all non-hydrogen atoms were refined with anisotropic displacement parameters. Final $R = 0.068$ [$I > 2\sigma(I)$], $wR_2 = 0.137$ (all data), goodness-of-fit = 0.99. The max./min. residual electron density was $0.30/-0.29\text{ e \AA}^{-3}$ and the final shift/error ratio was <0.001 .

CCDC reference number 154303.

See <http://www.rsc.org/suppdata/dt/b0/b009849n/> for crystallographic data in CIF or other electronic format.

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