The Synthesis and Reactions of Palladium–Iron Carbonyl Complexes containing Bridging $Ph_2PCH_2PPh_2$ Ligands

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Treatment of a tetrahydrofuran solution of FeI_2 with two equivalents of $Ph_2PCH_2PPh_2$ (dppm), under an atmosphere of CO, gave *trans,mer*-[FeI_2(CO)(dppm-*PP′*)(dppm-*P*)] (**1b**) in high yield. The bromide analogue was prepared similarly but was unstable. Treatment of compound (**1b**) with [$Pd(dba)_2$] (dba = dibenzylideneacetone) in benzene, under an atmosphere of CO, gave the bimetallic iron(I)–palladium(I) complex [$IFe(CO)_2(\mu$-dppm$)_2$PdI] (**2c**). Complex (**2c**) was protonated by $HBF_4 \cdot OEt_2$ to give the cationic hydride [$IFe(CO)_2(\mu$-dppm$)_2(\mu$-H)PdI]BF_4, which was characterised only in solution. Treatment of (**2c**) with MeNC caused displacement of both iodide and carbonyl ligands from iron to give [$(MeNC)_3Fe(\mu$-dppm$)_2$PdI]I, whereas treatment of (**2c**) with the bulky isocyanide Bu^tNC displaced only iodide to give [$(Bu^tNC)(OC)_2Fe(\mu$-dppm$)_2$PdI]I. N.m.r. (^1H- and ^{31}P-{^1H}) and i.r. data are reported.

The chemistry of iron(II) carbonyl phosphine halides has been relatively unexplored.[1] Booth and Chatt[2] described a convenient, mild, synthesis of complexes of the type [$FeCl_2(CO)_2(PEt_nPh_{3-n})_2$] ($n$ = 1, 2, or 3) by treating dichlorobis(tertiary phosphine)iron(II) complexes with carbon monoxide. This approach was also used to prepare the $Ph_2PCH_2CH_2PPh_2$ (dppe) analogue, [$FeCl_2(CO)_2$(dppe-*PP′*)], by reacting iron(II) chloride with dppe followed by treatment with carbon monoxide. Reduction of this complex provided a route to a tricarbonylbis(tertiary phosphine)-iron(0) compound.[3] Bancroft and Libbey[4] have also described a range of Fe^{II} complexes of types [$FeX_2(CO)_2(PPh_2Me)_2$] (X = Cl, Br, or I), [$FeI_2(CO)_3(PPh_3)$], and *cis*- and *trans*-[$FeI_2(CO)_2(PMe_3)_2$]. Other examples include [$FeI_2(CO)_2(PH_3)_2$][5] and the hydride [$FeH(I)(CO)(PMe_3)_3$].[6] There do not appear to be any reports of iron(II) complexes containing the ligand $Ph_2PCH_2PPh_2$ (dppm). We now report the simple, high yield, synthesis of an iron(II) iodocarbonyl complex containing dppm ligands and its use in the synthesis of heterobimetallic complexes with palladium.

Results and Discussion

Treatment of a tetrahydrofuran solution of iron(II) iodide with two equivalents of dppm, under an atmosphere of carbon monoxide, gave the iron(II) complex *trans,mer*-[FeI_2(CO)(dppm-*PP′*)(dppm-*P*)] (**1b**) in 84% yield. This formulation followed from elemental analysis (Table 1) and spectroscopic evidence. The ^{31}P-{^1H} n.m.r. spectrum consisted of four resonances. The high-field resonance at −25.9 p.p.m. is assigned to the unco-ordinated phosphorus atom the chemical shift being similar to that of free dppm (−22.1 p.p.m.). The large value of $^2J(P_BP_C)$ of 170 Hz suggests the presence of *trans* phosphines and so we formulate (**1b**) with meridional stereochemistry (see Table 2 for data and the Scheme for assignments). The ^1H-{^{31}P} n.m.r. spectrum of (**1b**) (Table 3) showed an AB pattern for the resonance assigned to the methylene protons of the monodentate dppm ligand. Additionally, the resonance of the methylene protons of the chelating dppm occurred as a single line, their equivalence being good evidence for the mutually *trans* arrangement of the two iodide ligands. The i.r. spectrum of (**1b**) consisted of a single absorption, assigned to ν(CO), at 1 960 cm^{-1} (CH_2Cl_2 solution). The corresponding dibromide (**1a**) was prepared in an analogous fashion using iron(II) bromide; however it decomposed in solution to give uncharacterised products, and pure products were not isolated. The di-iodide (**1b**) appeared to be stable in the solid state at ambient temperatures for several months, but dichloromethane solutions decomposed over a period of hours.

In recent publications[7–11] we have shown how metal complexes containing both chelating and monodentate dppm ligands can undergo ring-opening reactions with other metal fragments to give heterobimetallic complexes. Particularly useful in this regard have been the Group 6 metal carbonyl derivatives of the type *fac*- or *mer*-[$M(CO)_3$(dppm-*PP′*)(dppm-

Table 1. Infrared[a] and analytical[b] data

Complex	ν(C≡O)/cm^{-1}	ν(C≡N)/cm^{-1}	Analysis (%) C	H	N	X
(**1a**)	1 968s					
(**1b**)	1 960s		55.2 (55.35)	4.15 (4.0)	—	22.6 (22.95)
(**2a**)	1 912s, 1 824m		59.5 (59.05)	4.15 (4.2)	—	6.35 (6.7)
(**2b**)	1 912s, 1 820m					
(**2c**)	1 905s, 1 828m		51.05 (50.35)	4.1 (3.5)	—	20.2 (20.45)
(**3c**)	2 052s, 1 996s					
(**4**)[c]		2 180s, 2 145 (sh), 2 125s	51.2 (51.4)	4.2 (4.1)	3.15 (3.2)	19.45 (19.4)
(**5a**)[d]	1 952s, 1 880m	2 124m	51.55 (51.7)	3.85 (4.05)	1.0 (1.05)	19.0 (19.15)
(**5b**)	1 965s, 1 885m	2 110m				

[a] As solutions in dichloromethane; s = strong, m = medium, and sh = shoulder. [b] Calculated values in parentheses. [c] Λ = 105 ohm^{-1} cm^2 mol^{-1}, 10^{-3} mol dm^{-3} acetone solution. [d] Λ = 140 ohm^{-1} cm^2 mol^{-1}, 10^{-3} mol dm^{-3} acetone solution.

P)]$^{7-10}$ and the manganese complexes *cis,mer*-[MnX(CO)$_2$(dppm-*PP'*)(dppm-*P*)] (X = Cl or Br).^{11} It seemed likely that the iron(II) complex (**1b**) might also undergo similar ring-opening reactions and thus be a useful precursor to hetero-bimetallic complexes. Treatment of (**1b**) with one equivalent of [Pd(dba)$_2$] (dba = dibenzylideneacetone) in benzene, under an atmosphere of carbon monoxide, gave the iron(I)–palladium(I) complex [IFe(CO)$_2$(μ-dppm)$_2$PdI] (**2c**) in 29% yield by a combined ring-opening/redox process. The formulation followed from elemental analysis and spectroscopic evidence. The ^{31}P-{^{1}H} n.m.r. spectrum showed a typical AA'XX' pattern. The ^{1}H-{^{31}P} n.m.r. spectrum showed an AB pattern for the methylene protons of the dppm ligands at *ca.* 20 °C, indicating

Table 2. ^{31}P-{^{1}H} N.m.r. data[a]

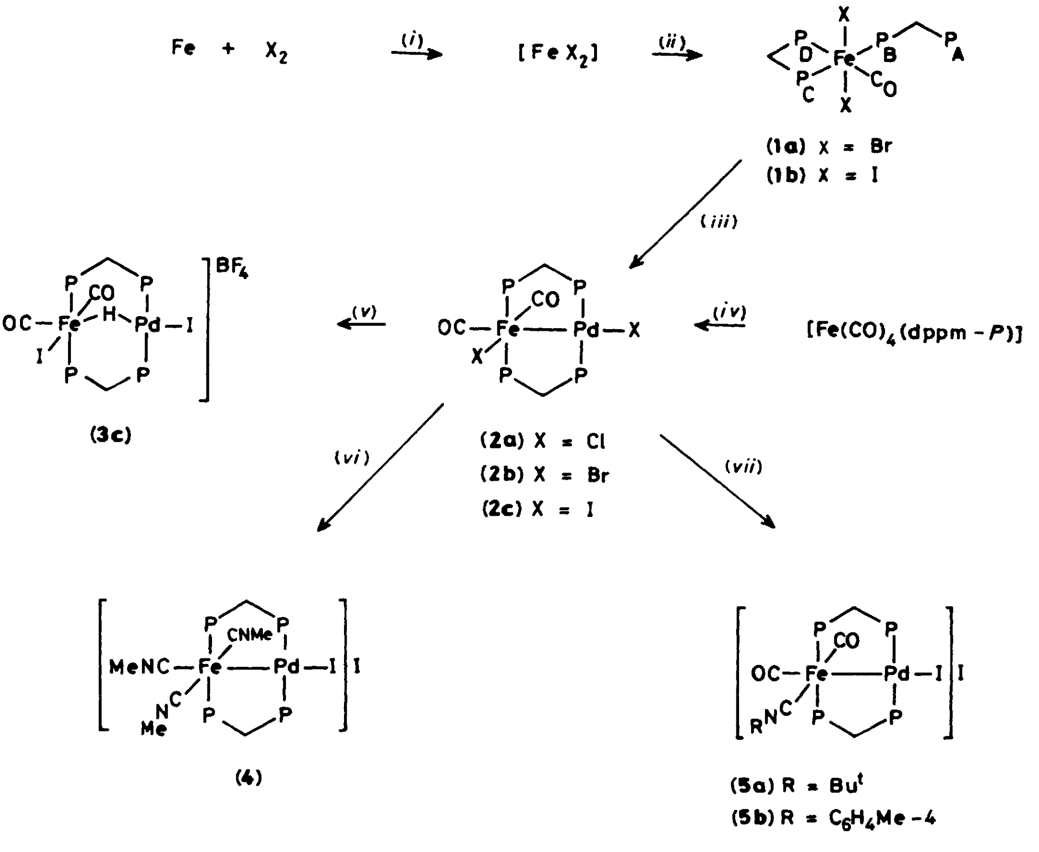
Complex	^{31}P-{^{1}H} (δ)[c]		
(**1a**)[b]	−27.1 (br, P_A)		
	0.6 [d of d, P_C, $J(P_CP_B)$ 200, $J(P_CP_D)$ 54]		
	17.0 [d of d, P_D, $J(P_DP_B)$ 46, $J(P_DP_C)$ 54]		
	33.5 [d of d, P_B, $J(P_BP_C)$ 200, $J(P_BP_D)$ 46]		
(**1b**)[b]	−25.9 [d of d, P_A, $J(P_AP_B)$ 24, $J(P_AP_C)$ 6]		
	0.6 [d of d of d, P_C, $J(P_CP_A)$ 6, $J(P_CP_B)$ 170, $J(P_CP_D)$ 46]		
	24.3 [d of d, P_D, $J(P_DP_B)$ 46, $J(P_DP_C)$ 46]		
	31.2 [d of d of d, P_B, $J(P_BP_A)$ 24, $J(P_BP_C)$ 170, $J(P_BP_D)$ 46]		
(**2a**)	14.9 (PPd)	55.6 (PFe)	*N* 90
(**2b**)	13.2 (PPd)	54.2 (PFe)	*N* 90
(**2c**)	7.5 (PPd)	53.9 (PFe)	*N* 85
(**3c**)	4.2 (PPd)	42.0 (PFe)	*N* 58
(**4**)	1.6 (PPd)	53.7 (PFe)	*N* 85
(**5a**)	13.0 (PPd)	63.0 (PFe)	*N* 95
(**5b**)	12.6 (PPd)	63.8 (PFe)	*N* 98

[a] Recorded at 40.3 MHz in CD$_2$Cl$_2$ solution at 20 °C. Positive shifts (± 0.1 p.p.m.) to high frequency of external 85% H$_3$PO$_4$. Coupling constants (*J*) in Hz (± 3 Hz). [b] See the Scheme for the assignments of P_A, P_B, P_C, and P_D. [c] $N = |^2J(P_{Fe}P_{Pd}) + {}^4J(P_{Fe}P_{Pd}')|$.

Table 3. Selected ^{1}H-{^{31}P} n.m.r. data[a]

Complex	^{1}H (δ)
(**1b**)[b]	2.97 [AB, 1 H, CH$_2$, *J*(HH) 16]
	4.18 [AB, 1 H, CH$_2$, *J*(HH) 16]
	5.17 (s, 2 H, CH$_2$)
(**2a**)[b]	3.87 [AB, 2 H, CH$_2$, *J*(HH) 14]
	4.66 [AB, 2 H, CH$_2$ *J*(HH) 14]
(**2c**)[b]	4.48 [AB, 2 H, CH$_2$, *J*(HH) 14]
	5.05 [AB, 2 H, CH$_2$, *J*(HH) 14]
(**3c**)[b]	−12.50 [t of t, 1 H, μ-H, $J(P_{Fe}H)$ 27, $J(P_{Pd}H)$ 6]
	4.45 [AB, 2 H, CH$_2$, *J*(HH) 14]
	4.90 [AB, 2 H, CH$_2$, *J*(HH) 14]
(**4**)[c]	2.12 [t, 3 H, CH$_3$, *J*(PH) 1]
	2.65 [t, 6 H, CH$_3$, *J*(PH) 2]
	4.41 (s, 4 H, CH$_2$)
(**5a**)[c]	1.00 (s, 9 H, Bu^t)
	4.02 [AB, 2 H, CH$_2$, *J*(HH) 15]
	4.34 [AB, 2 H, CH$_2$, *J*(HH) 15]
(**5b**)[c]	2.40 (s, 3 H, CH$_3$)
	3.96 [AB, 2 H, CH$_2$, *J*(HH) 15]
	4.32 [AB, 2 H, CH$_2$, *J*(HH) 15]
	5.85 [AX, 2 H, C$_6$H$_4$, *J*(HH) 8]
	7.05 [AX, 2 H, C$_6$H$_4$, *J*(HH) 8]

[a] Recorded in CD$_2$Cl$_2$ solution at 20 °C. Chemical shifts (δ) in p.p.m. (±0.01 p.p.m.) relative to SiMe$_4$, coupling constants (*J*) in Hz (±0.3 Hz). [b] 100-MHz spectra. [c] 400-MHz spectra.



Scheme. (*i*) thf, 65 °C; (*ii*) CO, dppm; (*iii*) [Pd(dba)$_2$], CO; (*iv*) [Pd$_2$X$_2$(η^3-C$_3$H$_5$)$_2$]; (*v*) HBF$_4$·Et$_2$O; (*vi*) MeNC; (*vii*) RNC (R = Bu^t or C$_6$H$_4$Me-4) the presence of *cis* carbonyl ligands and the structure as shown in the Scheme. This assignment was further substantiated by the i.r. spectrum (CH_2Cl_2 solution) which showed two absorptions attributable to ν(CO). The lower frequency band (1 828 cm^{-1}) suggested the possibility of a semibridging carbonyl ligand. The intense green colour of the complex also suggested the presence of a strong metal–metal interaction. The chloride (**2a**) and bromide (**2b**) analogues of (**2c**) could be prepared, in low yields, by treating $[Fe(CO)_4(dppm\text{-}P)]$ with $[Pd_2X_2(\eta^3\text{-}C_3H_5)_2]$ (X = Cl or Br). The mechanisms of these reactions are obviously complex and were not studied in any detail. However, spectroscopic evidence (Tables 1—3) suggested that (**2a**) and (**2b**) were entirely structurally analogous to (**2c**).

Complexes (**2a**)—(**2c**) are stable, intensely coloured crystalline solids. In solution (benzene or dichloromethane) however, they decompose over several hours to give the dipalladium(I) complexes $[Pd_2X_2(\mu\text{-dppm})_2]$[12] ($^{31}P\text{-}\{^1H\}$ evidence). This, in part, accounts for the rather low isolated yields and, on some occasions, made the isolation of pure materials difficult.

The iron(I)–palladium(I) bimetallics are isoelectronic with the previously reported manganese–palladium and –platinum complexes $[(OC)_3Mn(\mu\text{-dppm})_2MX]$ (M = Pd or Pt; X = Cl or Br).[11,13,14] The palladium complex (X = Cl) was shown by *X*-ray crystallography to have a semibridging carbonyl ligand.[13] Attempts to extend our reactions to include the preparation of iron–platinum bimetallics, using $[Pt(PPh_3)_4]$ or $[Pt(C_2H_4)(PPh_3)_2]$ as labile sources of Pt^0 were unsuccessful; no Fe–Pt bimetallics could be isolated.

It has been reported[13] that the manganese–palladium complexes of the type $[(OC)_3Mn(\mu\text{-dppm})_2PdX]$ reacted with strong acids (*e.g.* $HBF_4\cdot OEt_2$ or CF_3CO_2H) to give cationic hydrides $[(OC)_3Mn(\mu\text{-dppm})_2PdH(X)]^+$ which were very unstable and only partially characterised in solution. The nature of the hydride ligand was not resolved. Recently we reported the *X*-ray crystal structure of the protonated manganese–platinum complex $[(OC)_3Mn(\mu\text{-dppm})_2PtH(Br)]BF_4$.[11] Although the hydride ligand was not located directly, the large coupling to ^{195}Pt of 975 Hz suggested it was strongly bonded to platinum.

Treatment of $[IFe(CO)_2(\mu\text{-dppm})_2PdI]$ (**2c**) with an excess of $HBF_4\cdot OEt_2$ immediately gave a yellow-brown solution of the cationic hydride $[IFe(CO)_2(\mu\text{-dppm})_2(\mu\text{-}H)PdI]BF_4$ (**3c**). The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum showed an AA′XX′ pattern, and the ^1H n.m.r. spectrum showed a well resolved triplet of triplet hydride resonance at −12.50 p.p.m. Selective decoupling experiments indicated that these couplings arose from both sets of phosphorus nuclei, the larger (27 Hz) from the phosphorus nuclei on iron and the smaller (6 Hz) from the phosphorus nuclei on palladium. These data suggest a bridging hydride ligand, possibly with a stronger interaction to the iron centre than to palladium. The i.r. spectrum of (**3c**) showed a considerable shift of the carbonyl absorption bands to a higher frequency, as expected for a cationic species. Attempts to isolate pure samples of (**3c**) from the reaction solution resulted in partial decomposition back to the starting material (**2c**) (i.r. evidence).

The displacement of the iodide ligands from complex (**2c**) by isocyanides was also investigated. Treatment of (**2c**) with an excess of methyl isocyanide rapidly gave the cationic complex $[(MeNC)_3Fe(\mu\text{-dppm})_2PdI]I$ (**4**) in high yield. The formulation followed from elemental analysis, a conductivity measurement in acetone which indicated a 1:1 electrolyte (Table 1), and spectroscopic evidence. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum was a typical AA′XX′ pattern while the ^1H n.m.r. spectrum showed the presence of two different types of isocyanide ligands in a ratio of 2:1. Both isocyanide (CH_3) resonances also showed small $^5J(PH)$ couplings. Selective decoupling experiments indicated that these couplings arose from the phosphorus nuclei on iron, thus establishing that all three isocyanide ligands are bonded to this atom. Additionally, the resonance due to PCH_2P was a singlet at *ca.* 20 °C. The i.r. spectrum of (**4**) showed three absorptions attributable to ν(CN) whereas no ν(CO) absorptions were present. These data are in agreement with the structure proposed in the Scheme. Thus, methyl isocyanide has preferentially displaced iodide from the iron centre rather than from the palladium centre.

Treatment of (**2c**) with bulky isocyanides such as t-butyl isocyanide or *p*-tolyl isocyanide gave the bimetallic complexes (**5a**) and (**5b**), respectively.

The formulation of (**5a**) as $[(Bu^tNC)(OC)_2Fe(\mu\text{-dppm})_2PdI]I$ followed from elemental analysis, a conductivity measurement in acetone which indicated a 1:1 electrolyte, and spectroscopic evidence. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum consisted of an AA′XX′ pattern and the ^1H n.m.r. spectrum showed an AB pattern for the PCH_2P resonance suggesting the presence of *cis* carbonyl ligands. The i.r. spectrum further substantiated this by showing two ν(CO) absorptions and a single absorption assigned to ν(CN). Presumably, the bulky nature of t-butyl isocyanide relative to methyl isocyanide accounts for the formation of (**5a**) and not of an analogue of (**4**). *p*-Tolyl isocyanide appeared to react with (**2c**) in a similar manner to give an analogous complex (**5b**) ($^{31}P\text{-}\{^1H\}$, ^1H, and i.r. evidence). However, further reactions occurred, presumably involving substitution of carbonyl ligands and a pure product of (**5b**) was not isolated.

Experimental

General methods were as previously described in recent papers from this laboratory.[11] Complexes $[Pd(dba)_2]$[15] and $[Fe(CO)_4(dppm\text{-}P)]$[16] were prepared by previously described methods. The complex $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ was prepared by a literature method[17] and the bromide analogue by metathesis with LiBr in acetone.

Preparations.—*trans,mer*-$[FeI_2(CO)(dppm\text{-}PP')(dppm\text{-}P)]$ (**1b**). Electrolytic iron (0.279 g, 5 mmol) and iodine (0.635 g, 2.5 mmol) were refluxed in tetrahydrofuran (thf) (15 cm^3) for 2 h. The solution was cooled to *ca.* 20 °C, the excess of iron removed with a magnet, and carbon monoxide bubbled through the solution. The ligand dppm (1.92 g, 5 mmol) was added and the mixture stirred under carbon monoxide for 0.5 h. A dark red-brown microcrystalline solid precipitated. Diethyl ether (25 cm^3) was added and the solid isolated by filtration, washed with thf–Et_2O (1:1) (50 cm^3) then Et_2O (50 cm^3), and dried *in vacuo.* Yield: 2.31 g (84%). The corresponding dibromide (**1a**) was prepared similarly using bromine. However, an analytically pure sample was not obtained because of decomposition.

$[IFe(CO)_2(\mu\text{-dppm})_2PdI]$ (**2c**) *from* (**1b**), $[Pd(dba)_2]$, *and* CO. *trans,mer*-$[FeI_2(CO)(dppm\text{-}PP')(dppm\text{-}P)]$ (0.552 g, 0.5 mmol) and $[Pd(dba)_2]$ (0.289 g, 0.5 mmol) were stirred together in benzene (50 cm^3), with carbon monoxide bubbling through the solution, for 3 h. The dark green solution was filtered and excess diethyl ether was added to the filtrate. Refrigeration (5 °C) overnight gave the required product as dark green prisms. Yield: 0.182 g (29%). Often, samples were contaminated with an orange complex identified as $[Pd_2I_2(\mu\text{-dppm})_2]$ by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. Manual separation of the products was relatively straightforward in these cases.

$[ClFe(CO)_2(\mu\text{-dppm})_2PdCl]$ (**2a**) *from* $[Fe(CO)_4(dppm\text{-}P)]$ *and* $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$. A solution of $[Fe(CO)_4(dppm\text{-}P)]$ (0.552 g, 1 mmol) and $[Pd_2Cl_2(\eta^3\text{-}C_3H_5)_2]$ (0.183 g, 0.5 mmol) in benzene (5 cm^3) was put aside at *ca.* 20 °C for 10 d. The dark precipitate which formed was isolated by filtration and washed with diethyl ether (1 cm^3). The solid was recrystallised twice from benzene–diethyl ether to give the desired product as dark violet prisms. Yield: 0.035 g (3%). The dark blue dibromide analogue (**2b**) was prepared in a similar manner using [$Pd_2Br_2(\eta^3-C_3H_5)_2$] in *ca.* 5% yield. However, analytically pure samples could not be obtained.

Protonation of (**2c**) *to give* [$IFe(CO)_2(\mu$-dppm$)_2(\mu$-H)PdI]BF_4 (**3c**). An excess of $HBF_4 \cdot OEt_2$ (10 µl) was added to a solution of [$IFe(CO)_2(\mu$-dppm$)_2$PdI] (0.02 g, 0.016 mmol) in CD_2Cl_2 (0.5 cm^3). The solution changed from dark green to yellow-brown immediately. This solution was examined by $^{31}P-\{^1H\}$ and ^1H n.m.r. spectroscopy which indicated the formation of a single heterobimetallic species. Attempts to isolate the complex resulted in partial decomposition to the starting material (**2c**).

[$(MeNC)_3Fe(\mu$-dppm$)_2$PdI]I (**4**). Methyl isocyanide (55 µl, 1 mmol) was added to a solution of [$IFe(CO)_2(\mu$-dppm$)_2$PdI] (0.250 g, 0.2 mmol) in dichloromethane (25 cm^3). After 10 min the solvent was removed from the orange solution under reduced pressure and the residue recrystallised from dichloromethane–diethyl ether at 5 °C to give the required product as red-brown needles. Yield: 0.19 g (72%).

[$(Bu^tNC)(OC)_2Fe(\mu$-dppm$)_2$PdI]I (**5a**). t-Butyl isocyanide (85 µl, 0.8 mmol) was added to a solution of [$IFe(CO)_2(\mu$-dppm$)_2$PdI] (0.200 g, 0.16 mmol) in dichloromethane (25 cm^3). After 15 min the orange solution was filtered and the filtrate evaporated under reduced pressure to *ca.* 10 cm^3. Addition of diethyl ether (50 cm^3) and refrigeration at 5 °C gave the required product as red-brown needles. Yield: 0.195 g (91%). The *p*-tolyl isocyanide complex (**5b**) was prepared analogously; however, analytically pure samples were not obtained.

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