Journal of Organometallic Chemistry, 479 (1994) 117–124

Cyclometallation of 2-halogenobenzaldehyde mixed azine phosphines of type $PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4X\text{-}2)$ (X = I, Br or Cl) involving facile C–X bond fission at tungsten(0)

Sarath D. Perera and Bernard L. Shaw

School of Chemistry, University of Leeds, Leeds LS2 9JT (UK)

(Received November 15, 1993)

Abstract

Condensation of *Z*-$PPh_2CH_2C(^tBu)=NNH_2$ with 2-halobenzaldehydes gave mixed azines of the type *ZE*-$PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4X\text{-}2)$ (X = I, **2a**; Br, **2b**; Cl, **2c**; or F, **2e**, respectively). **2a**, **2b**, or **2c** reacted with *fac*-$[W(CO)_3(NCEt)_3]$ to give tungsten(0) complexes $[W(CO)_3(NCEt)\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4X\text{-}2)\}]$ **(3a–3c)**, which rapidly underwent oxidative addition to give seven-coordinate tungsten(II) complexes of the type $[WX(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4)\}]$ **(4a–4c)**. The fluoro-mixed azine $Ph_2PCH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)$ **(2e)** with *fac*-$[W(CO)_3(NCEt)_3]$ gave $[W(CO)_3(NCEt)\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)\}]$ **(3e)** which did not undergo C–F oxidative addition, but when treated with CO or CN^tBu gave tungsten(0) complexes of the type $[W(CO)_3L\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)\}]$ (L = CO, **5a** or CN^tBu, **5b**). The mixed azine from 2-chloro-6-fluorobenzaldehyde and **1** *i.e.* $PPh_2CH_2C(^tBu)=N-N=CH(C_6H_3Cl\text{-}2,\text{-}F\text{-}6)$ **(2d)** with *fac*-$[W(CO)_3(NCEt)_3]$ underwent oxidative addition at the C–Cl bond to give $[WCl(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_3F\text{-}6)\}]$ **(4d)** *via* a tungsten(0) complex **3d**. Treatment of the aryl-tungsten(II) complex $[WBr(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4)\}]$ **(4b)** with $NaBH_4$/CO caused aryl–tungsten bond fission (reductive elimination) and C=N reduction to give the benzylhydrazone–phosphine complex $[W(CO)_4\{PPh_2CH_2C(^tBu)=NNHCH_2Ph\}]$ **(6)** which was also formed by reducing the benzaldehyde mixed azine phosphine tungsten(0) complex $[W(CO)_4\{PPh_2CH_2C(^tBu)=N-N=CHPh\}]$ **(8)** with $NaBH_4$.

Key words: Tungsten; Cyclometallation; Azine; Phosphine; Oxidative addition

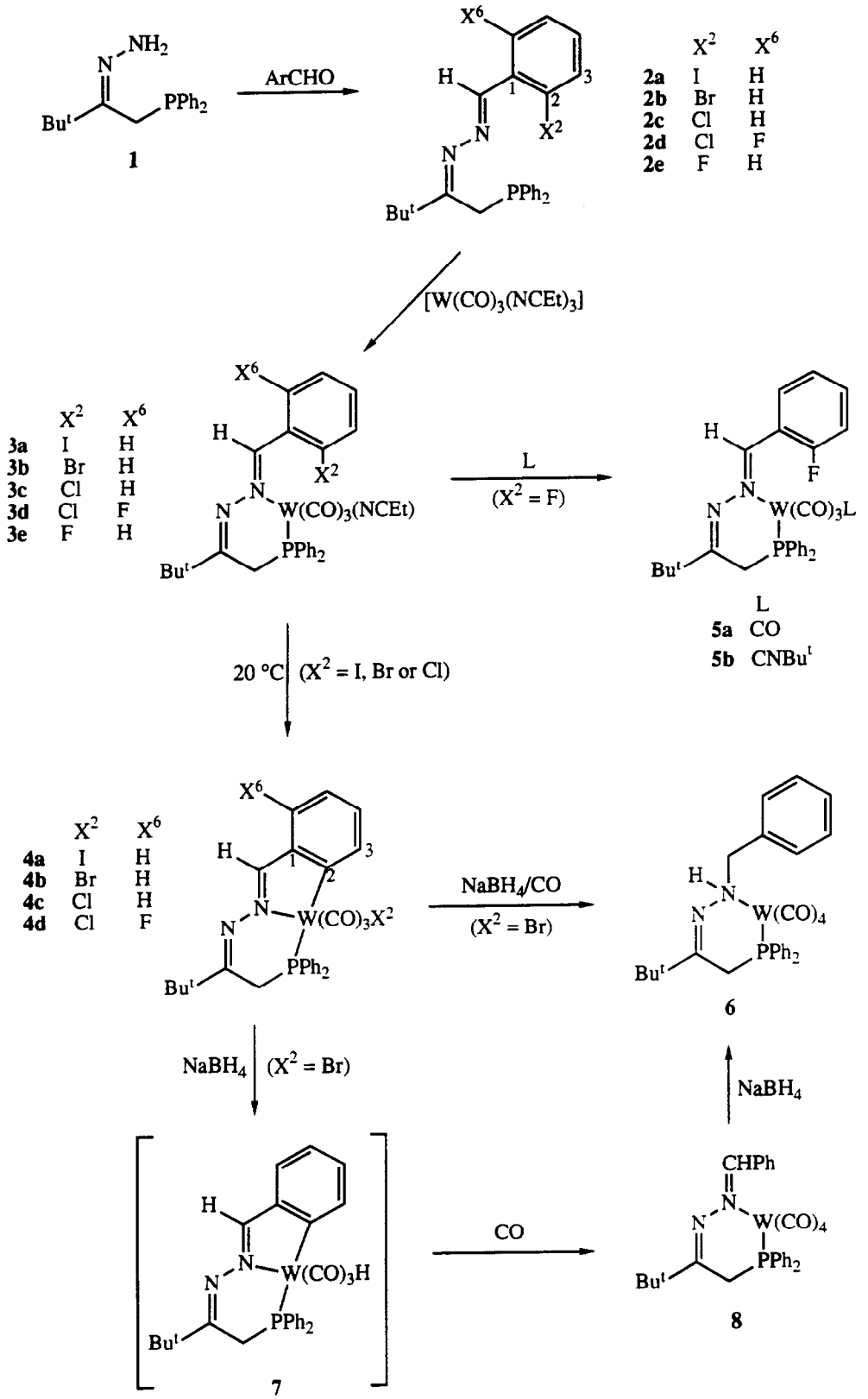
1. Introduction

Oxidative addition reactions are very important in organo-transition metal chemistry and in some areas of catalysis. Commonly, they are carried out with organic iodides, bromides or chlorides, where the organic group can be alkyl, alkenyl or aryl, with metals such as platinum(0), platinum(II), palladium(0), rhodium(I), iridium(I), nickel(0) *etc.* [1,2]. In the present work we have developed a method of activating the C–X (X = Cl, Br or I) bond of some mixed azines formed from 2-halobenzaldehydes. We have described the phosphino-hydrazone $PPh_2CH_2C(^tBu)=NNH_2$ which has the *Z*-configuration **1** [3]. Hydrazones (=NNH_2) are very nucleophilic and usually condense rapidly and completely with aldehydes or ketones to give azines [4].

We anticipated that **1** would condense rapidly with 2-halo-benzaldehydes to give mixed azines, $Ph_2PCH_2C(^tBu)=N-N=CH(C_6H_4X\text{-}2)$, which from steric considerations would have the *ZE*-configuration **2**. Hence, a mixed azine of type **2** would chelate to a metal through *P* and *N*=$CH(C_6H_4X)$ to give a six-membered chelate ring, thus forcing the 2-haloaryl moiety against the metal and promoting cyclometallation. We have investigated such a reaction with tungsten(0) and find that cyclometallation does indeed occur under mild conditions. Richmond reported the first example of aryl C–X bond activation (cyclometallation) by tungsten(0) using symmetrical Schiff base ligands of the type $(2\text{-}XC_6H_4)CH=NCH_2CH_2N=CH(C_6H_4X\text{-}2)$ (X = Cl, Br or I) [5]. Such ethylenediamine derivatives reacted with $[W(CO)_3(NCEt)_3]$ to give 7-coordinate aryl-tungsten complexes $[WX(CO)_3\{(C_6H_4)CH=NCH_2CH_2N=CH(C_6H_4X\text{-}2)\}]$ [5,6].

Correspondence to: Professor B.L. Shaw.

0022-328X/94/$7.00
SSDI 0022-328X(93)24395-L


NH2
N
Bu^t
PPh2
1
ArCHO
X6
H
1
2
3
X2
N
N
Bu^t
PPh2
2a I H
2b Br H
2c Cl H
2d Cl F
2e F H
[W(CO)3(NCEt)3]
3a I H
3b Br H
3c Cl H
3d Cl F
3e F H
W(CO)3(NCEt)
L
(X2 = F)
W(CO)3L
5a CO
5b CNBu^t
20 °C (X2 = I, Br or Cl)
4a I H
4b Br H
4c Cl H
4d Cl F
W(CO)3X2
NaBH4/CO
(X2 = Br)
W(CO)4
6
NaBH4 (X2 = Br)
NaBH4
CHPh
CO
W(CO)3H
7
8

2. Results and discussion

The mixed azines and the complexes prepared from them are shown in Scheme 1. Elemental analytical and mass spectral data are given in the Experimental section and phosphorus-31 and proton NMR data are in Table 1; carbon-13 NMR data in Table 2, and IR data in Table 3. Carbon-13 spectra were assigned by use of an Attached Proton Test (APT) for some key compounds, and by comparison with published data for 2-fluorobenzaldehyde [7] and fluorobenzene [8]. Some of the compounds were too labile to characterise and **7** is a postulated intermediate. The iodo-analogue **2a** was prepared *in situ* and characterised by phosphorus-31 NMR spectroscopy, whereas the other haloazine phosphines of type **2** were isolated and characterised.

Treatment of the mixed azine **2a**, prepared *in situ* from 2-iodobenzaldehyde and **1**, with the labile tungsten(0) complex $[W(CO)_3(NCEt)_3]$ [9] gave an intermediate complex, detected by phosphorus-31 NMR spectroscopy showing a singlet at $\delta P = 43.3$ ppm with $^1J(^{183}WP) = 257$ Hz, typical of a W(0) complex [1,10,11]. We formulate the complex as $[W(CO)_3(NCEt)\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4I\text{-}2)\}]$ (**3a**). This was not isolated but rapidly converted into the 7-coordinate tungsten(II) complex $[WI(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4)\}]$ (**4a**) isolated in 77% yield. This complex **4a** had δP at 5.6 ppm and a much smaller value of $^1J(^{183}WP)$ (191 Hz) than the tungsten(0) complex **3a**. Such a value for $^1J(^{183}WP)$ is typical for tungsten(II) [10,12,13]. Interestingly, in the proton NMR spectrum of **4a** (Table 1) $CH(C_6H_4)$ was coupled to both phosphorus and tungsten-183, $^4J(PH) = 1.5$ Hz, $^3J(WH) = 5.5$ Hz. The CH_2 protons were not equivalent, in agreement with a 7-coordinate complex. The IR data (Table 3) with values for $\nu(C{\equiv}O)$ of 2025, 1945 and 1895 cm^{-1} are typical for tungsten(II) and not tungsten(0) [5,6]. In the carbon-13 spectrum (Table 2) a resonance of 163.1 ppm with $^2J(PC) = 2.5$ Hz is assigned to the carbon directly bonded to tungsten *i.e.*

TABLE 1. $^{31}P\{^1H\}$ NMR data [a] and Proton NMR data [b]. {[c] ^2J(HH), [d] ^2J(PH), [e] ^3J(HH), [f] ^3J(WH) and [g] ^4J(PH)}

	δ(P)	^1J(WP)	δ(^{t}Bu)	δ(CH_2)	δ(CH=N)
1	−22.6	–	0.98(9H, s)	3.10(2H, d, 2.2 [d])	–
2a	−10.1 [h]	–	–	–	–
2b	−10.8	–	1.24(9H, s)	3.49(2H, d, 2.5 [d])	8.33(1H, s)
2c	−10.7	–	1.24(9H, s)	3.50(2H, d, 2.7 [d])	8.39(1H, s)
2d	−11.6	–	1.29(9H, s)	3.53(2H, d, 2.2 [d])	8.01(1H, s)
2e	−10.7	–	1.24(9H, s)	3.50(2H, d, 2.7 [d])	8.24(1H, s)
3a	43.3 [h]	257	–	–	–
3b	43.4 [h]	257	–	–	–
3c	43.6 [h]	259	–	–	–
3d	42.4 [h]	259	–	–	–
3e [i,j]	44.1 [h]	259	0.87(9H, s)	2.58(1H, dd, 12.8 [c], 9.5 [d]) 3.36(1H, dd, 12.8 [c], 9.7 [d])	8.35(1H, s) [k]
4a [i]	5.6 [h]	191	1.31(9H, s)	3.15(1H, dd, 17.0 [c], 13.2 [d]) 4.06(1H, dd, 17.0 [c], 9.9 [d])	8.94(1H, d, 1.5 [g], 5.5 [f])
4b [i]	12.9 [h]	189	1.26(9H, s)	3.00(1H, dd, 16.8 [c], 13.2 [d]) 3.97(1H, dd, 16.8 [c], 10.3 [d])	8.9(1H, d, 1.7 [g], 5.1 [f])
4c [i]	17.4 [h]	187	1.23(9H, s)	2.93(1H, dd, 16.6 [c], 13.2 [d]) 3.88(1H, dd, 16.6 [c], 10.3 [d])	8.89(1H, d, 1.5 [g], 5.1 [f])
4d [i]	18.7 [h]	190	1.22(9H, s)	2.91(1H, dd, 16.4 [c], 13.2 [d]) 3.85(1H, dd, 16.4 [c], 10.6 [d])	9.16(1H, d, 1.7 [g], 5.7 [f])
5a [i]	41.8	259	0.85(9H, s)	3.11(2H, d, 10.5 [d]) [l]	8.54(1H, s) [k]
5b [i]	40.2	255	0.84(9H, s) 1.15(9H, s)	2.68(1H, dd, 12.5 [c], 9.7 [d]) 3.32(1H, dd, 12.5 [c], 9.8 [d])	8.49(1H, s) [k]
6 [i,m]	46.0	266	0.71(9H, s)	2.62(1H, dd, 14.1 [c], 8.0 [d], CH_2P) 3.68(1H, dd, 14.1 [c], 10.7 [d], CH_2P) 4.50(1H, dd, 13.6 [c], 2.0 [g], CH_2N) 4.82(1H, dd, 13.6 [c], 9.9 [g], CH_2N)	
8	42.9	263	0.92(9H, s)	3.00(2H, d, 10.2 [d])	8.27(1H, d, 1.7 [g])

[a] Recorded at 36.2 MHz, chemical shifts δ(P) are in ppm relative to 85% H_3PO_4, ^1J(WP) values are in Hz, solvent $CDCl_3$ unless otherwise stated. [b] Recorded at 100 MHz, chemical shifts are in ppm relative to $SiMe_4$, J values are in Hz, solvent $CDCl_3$ unless otherwise stated, s = singlet, d = doublet, t = triplet, dd = doublet of doublets, ddq = double doublet of quartets, br = broad; resonances due to aryl protons appeared between 6.5 and 8.0 ppm. [h] In THF (external lock C_6D_6). [i] In CD_2Cl_2. [j] 0.91[3H, t, 7.5 [e], CH_2Me], 2.05[2H, ddq, 7.5 [e], ^5J(PH) 1.8, CH_2Me]. [k] Observed weak four bond coupling to phosphorus. [l] At −65°C, CH_2 protons gave an ABX pattern absorbing at 2.61(1H, dd, 12.9 [c], 11.0 [d]) and 3.51(1H, dd, 12.9 [c], 11.7 [d]). [m] 5.17[1H, t, br, ^3J(HH) = ^3J(PH) 8.3, NH], this was recorded at 400 MHz.

C^2. This chemical shift value is as expected for carbon bonded to tungsten(II) [5,14], thus in $NEt_4[WPh(CO)_5]$ the phenyl carbon bonded to tungsten *i.e.* the *ipso*-carbon was reported to have a δC value of 163.3 ppm [14]. Similarly, treatment of $[W(CO)_3(NCEt)_3]$ with **2b** or **2c** gave the corresponding 7-coordinate tungsten(II)

TABLE 2. $^{13}C\{^1H\}$ NMR data [a]

Complex	δ_C
1	26.2 [1C, d, ^1J(PC) 22.7, CH_2], 28.6 (3C, s, C*Me*$_3$), 38.1 [1C, d, ^3J(PC) 1.4, *C*Me$_3$], 156.6 (1C, s, C=N). PPh_2 group—128.5 [4C, d, ^3J(PC) 7.0, 4 × C_m], 129.0 (2C, s, 2 × C_p), 132.8 [4C, d, ^2J(PC) 19.7, 4 × C_o], 137.6 [2C, d, ^1J(PC) 14.9, 2 × C_i]
2b	28.7 [3C, d, ^4J(PC) 2.0, C*Me*$_3$], 28.9 [1C, d, ^1J(PC) 22.9, CH_2], 38.8 (1C, s, *C*Me$_3$), 155.6 [1C, d, ^5J(PC) 1.6, HC=N], 175.7 [1C, d, ^2J(PC) 4.5, ^{t}Bu*C*=N]. Aryl group—125.1 (1C, s, C^2), 127.0s, 128.6s, 131.1s, 132.8s (=CH*Ar*), 133.3 (1C, s, C^1). PPh_2 group—128.2 [4C, d, ^3J(PC) 7.0, 4 × C_m], 128.6 (2C, s, 2 × C_p), 132.8 [4C, d, ^2J(PC) 21.2, 4 × C_o], 138.8 [2C, d, ^1J(PC) 17.2, 2 × C_i].
2c	28.8 [3C, d, ^4J(PC) 1.9, C*Me*$_3$], 29.0 [1C, d, ^1J(PC) 22.8, CH_2], 38.8 (1C, s, *C*Me$_3$), 153.4 [1C, d, ^5J(PC) 1.6, HC=N], 175.7 [1C, d, ^2J(PC) 4.4, ^{t}Bu*C*=N] Aryl group—126.5s, 129.6s, 130.9s, 132.1s (=CH*Ar*), 131.9 (1C, s, C^2), 135.0 (1C, s, C^1). PPh_2 group—128.3 [4C, d, ^3J(PC) 6.8, 4 × C_m], 128.6 (2C, s, 2 × C_p), 132.9 [4C, d, ^2J(PC) 20.3, 4 × C_o], 138.8 [2C, d, ^1J(PC) 17.1, 2 × C_i].
2e	28.8 [3C, d, ^4J(PC) 2.0, C*Me*$_3$], 29.0 [1C, d, ^1J(PC) 22.8, CH_2], 38.8 (1C, s, *C*Me$_3$), 150.1 [1C, dd, ^5J(PC) 1.9, ^3J(FC) 4.3, HC=N], 175.5 [1C, d, ^2J(PC) 4.5, ^{t}Bu*C*=N]. Aryl group—115.4 [1C, d, ^2J(FC) 21.2, C^3], 122.4 [1C, d, ^2J(FC) 9.5, C^1], 123.9 [1C, d, J(FC) 3.5, =CH*Ar*], 127.7 [1C, d, J(FC) 2.7, =CH*Ar*], 131.6 [1C, d, J(FC) 3.5, =CH*Ar*], 161.8 [1C, d, ^1J(FC) 253.0, C^2]. PPh_2 group—128.3 [4C, d, ^3J(PC) 7.0, 4 × C_m], 128.6 [2C, s, 2 × C_p], 132.9 [4C, d, ^2J(PC) 20.2, 4 × C_o], 138.9 [2C, d, ^1J(PC) 17.2, 2 × C_i].
3e [b]	9.9 (1C, s, MeCH_2), 12.4 (1C, s, *Me*CH_2), 24.8 [1C, d, ^1J(PC) 8.6, CH_2], 27.5 (3C, s, C*Me*$_3$), 39.4 [1C, d, ^3J(PC) 1.8, *C*Me$_3$], 148.7 [1C, dd, ^5J(PC) 5.0, ^3J(FC) 9.1, HC=N], 170.6 (1C, s, ^{t}Bu*C*=N), 214.7 [1C, d, ^2J(PC) 6.9, CO], 215.2 [1C, d, ^2J(PC) 45.7, CO (*trans* to P)], 218.1 [1C, d, ^2J(PC) 4.6, CO]. Aryl group—116.2 [1C, d, ^2J(FC) 21.2, C^3], 119.9[1C, d, ^2J(FC) 9.5, C^1], 124.4[1C, d, J(FC) 3.6, =CH*Ar*], 129.1 (1C, s, =CH*Ar*), 133.4 [1C, d, J(FC) 9.1, =CH*Ar*], 161.4[1C, d, ^1J(FC) 253.7, C^2]. PPh_2 groups—128.9 [2C, d, ^3J(PC) 9.1, 2 × C_m], 129.0 [2C, d, ^3J(PC) 8.8, 2 × C_m], 130.9 [1C, d, ^4J(PC) 2.1, C_p], 131.4 (1C, s, C_p), 132.0 [2C, d, ^2J(PC) 11.8, 2 × C_o], 135.2 [2C, d, ^2J(PC) 13.7, 2 × C_o], 134.5 [1C, d, ^1J(PC) 47.6, C_i].
4a [b,c]	28.9 (3C, s, C*Me*$_3$), 29.0 [1C, d, ^1J(PC) 24.2, CH_2], 41.3 [1C, d, ^3J(PC) 5.5, *C*Me$_3$], 171.7 [1C, d, ^3J(PC) 4.1, HC=N], 173.8 [1C, d, ^2J(PC) 3.0, ^{t}Bu*C*=N]. Aryl group—124.5 (1C, s, *Ar*), 131.6 (1C, s, *Ar*), 131.8 (1C, s, *Ar*), 143.5 (1C, s, C^1), 144.2 (1C, s, *Ar*), 163.1 [1C, d, ^2J(PC) 2.5, C^2]. PPh_2 groups—128.8 [2C, d, ^3J(PC) 9.3, 2 × C_m], 129.2 [2C, d, ^3J(PC) 10.3, 2 × C_m], 130.5 [1C, d, ^4J(PC) 2.0, C_p], 131.1 [1C, d, ^1J(PC) 44.8, C_i], 131.4 [2C, d, ^2J(PC) 9.3, 2 × C_o], 132.0 [1C, d, ^4J(PC) 2.2, C_p], 134.2 [2C, d, ^2J(PC) 11.3, 2 × C_o], 134.4 [1C, d, ^1J(PC) 46.9, C_i].
4b [b,c]	26.6 [1C, d, ^1J(PC) 22.7, CH_2], 28.7 (3C, s, C*Me*$_3$), 41.1 [1C, d, ^3J(PC) 5.3, *C*Me$_3$], 170.9 [1C, d, ^3J(PC) 4.1, HC=N], 173.5 [1C, d, ^2J(PC) 3.1, ^{t}Bu*C*=N]. Aryl group—124.4 (1C, s, *Ar*), 131.5 (1C, s, *Ar*), 131.9 (1C, s, *Ar*), 143.1 (1C, s, C^1), 144.1 (1C, s, *Ar*), 165.9 [1C, d, ^2J(PC) 2.0, C^2]. PPh_2 groups—128.9 [2C, d, ^3J(PC) 9.4, 2 × C_m], 129.3 [2C, d, ^3J(PC) 10.1, 2 × C_m], 130.6 [1C, d, ^1J(PC) 43.7, C_i], 130.7 [1C, d, ^4J(PC) 2.0, C_p], 131.6 [2C, d, ^2J(PC) 9.6, 2 × C_o], 132.0 [1C, d, ^4J(PC) 2.4, C_p], 134.1 [2C, d, 2J(PC) 11.4, 2 × C_o], 133.7 [1C, d, ^1J(PC) 48.0, C_i].
4d [b,c,d]	25.6 [1C, d, ^1J(PC) 21.6, CH_2], 28.6 (3C, s, C*Me*$_3$), 41.0 [1C, d, ^3J(PC) 5.8, *C*Me$_3$], 164.0 [1C, d, ^3J(PC) or ^3J(FC) 3.2, HC=N], 173.8 [1C, d, ^2J(PC) 3.1 ^{t}Bu*C*=N]. Aryl group—109.5 [1C, d, ^2J(FC) 19.3, C^5], 133.0 [1C, d, ^3J(FC) 8.0, C^4], 139.5 [1C, d, ^4J(FC) 2.8, C^3], 164.0 [1C, d, ^2J(FC) 241.3, C^6]. PPh_2 groups—128.9 [2C, d, ^3J(PC) 9.3, 2 × C_m], 129.3 [2C, d, ^3J(PC) 10.1, 2 × C_m], 130.2 [1C, d, ^1J(PC) 43.2, C_j], 130.9 [1C, d, ^4J(PC) 2.0, C_p], 131.7 [2C, d, ^2J(PC) 9.6, 2 × C_o], 132.0 [1C, d, ^4J(PC) 2.3, C_p], 133.7 [1C, d, ^1J(PC) 37.5, C_i], 134.0 [2C, d, ^2J(PC) 11.4, 2 × C_o].
5a [b]	25.3 [1C, d, ^1J(PC) 11.1, CH_2], 27.3 (3C, s, C*Me*$_3$), 39.5 [1C, d, ^3J(PC) 1.9, *C*Me$_3$], 153.2 [1C, dd, ^5J(PC) 4.9, ^3J(FC) 7.9, HC=N], 172.2 [1C, s, ^{t}Bu*C*=N], 203.6 [2C, d, ^2J(PC) 7.3, 2 × CO], 208.9 [1C, d, ^2J(PC) 35.1, CO (*trans* to P)], 210.0 [1C, d, ^2J(PC) 3.8, CO]. Aryl group—116.4 [1C, d, ^2J(FC) 21.8, C^3], 119.9 [1C, d, ^2J(FC) 9.4, C^1], 124.4 [1C, d, J(FC) 3.6, =CH*Ar*], 130.9 (1C, s, =CH*Ar*), 133.0 [1C, d, J(FC) 8.9, =CH*Ar*], 161.4 [1C, d, ^1J(FC) 254.6, C^2]. PPh_2 groups—129.2 [4C, d, ^2J(PC) 9.8, 4 × C_m], 131.2 [2C, s, 2 × C_p], 132.9 [4C, br, d, ^2J(PC) 8.9, 4 × C_o], 135.9 [2C, br, d, ^1J(PC) 32.4, 2 × C_i].

TABLE 2 (continued)

Complex	δ_C
5b [b]	24.9 [1C, d, ^1J(PC) 9.2, CH_2P], 27.5 (3C, s, CMe_3), 30.6 (3C, s, CMe_3), 39.3 [1C, d, ^3J(PC) 2.0, CMe_3], 56.7 [1C, s, CMe_3], 150.6 [1C, dd, ^3J(PC) 5.0, ^3J(FC) 8.8, HC=N], 157.0 (1C, s, br, C≡N), 170.5 (1C, s, ^{t}BuC=N), 210.8 [1C, d, ^2J(PC) 7.9, CO], 212.9 [1C, d, ^2J(PC) 38.9, CO (*trans* to P)], 215.4 [1C, d, ^2J(PC) 4.4, CO]. Aryl group—116.2 [1C, d, ^2J(FC) 21.8, C^3], 120.1 [1C, d, ^2J(FC) 10.0, C^1], 124.4 [1C, d, J(FC) 3.6, =CH*Ar*, 131.4 [1C, s, =CH*Ar*], 133.3 [1C, d, J(FC) 9.2, =CH*Ar*], 161.5 [1C, d, ^1J(FC) 253.9, C^2], PPh_2 groups—128.7 [2C, d, ^3J(PC) 9.9, 2 × C_m], 128.9 [2C, d, ^3J(PC) 9.1, 2 × C_m], 129.9 (1C, s, C_p), 130.7 [1C, d, ^4J(PC) 2.0, C_p], 132.0 [2C, d, ^2J(PC) 12.5, 2 × C_o], 134.4 [2C, d, ^2J(PC) 9.2, 2 × C_o], 135.8 [1C, d, ^1J(PC) 35.8, C_i], 138.6 [1C, d, ^1J(PC) 33.1, C_i].
6 [b]	24.1 [1C, d, ^1J(PC) 10.3, CH_2P], 27.7 (3C, s, CMe_3), 39.4 (1C, s, CMe_3), 168.1 (1C, s, C=N), 203.0 [1C, d, ^2J(PC) 5.1, CO], 204.4 [1C, d, ^2J(PC) 9.3, CO], 209.4 [1C, d, ^2J(PC) 35.1, CO (*trans* to P)], 209.6 [1C, d, ^2J(PC) 3.0, CO]. Benzyl group—69.4 [1C, d, ^3J(PC) 4.0, CH_2N], 128.6 (1C, s, C^4 of CH_2Ph), 128.8 (2C, s, CH_2Ph), 129.7 (2C, s, CH_2Ph), 138.3 (1C, s, C^1 of CH_2Ph), PPh_2 groups—129.1 [2C, d, ^3J(PC) 10.5, 2 × C_m], 129.2 [2C, d, ^3J(PC) 9.2, 2 × C_m], 130.3 (1C, s, C_p), 131.6 [1C, d, ^4J(PC) 1.9, C_p], 131.1 [2C, d, ^2J(PC) 11.6, 2 × C_o], 134.9 [2C, d, ^2J(PC) 14.0, 2 × C_o], 133.7 [1C, d, ^1J(PC) 36.5, C_i], 138.0 [1C, d, ^1J(PC) 40.5, C_i].
8	24.9 [1C, d, ^1J(PC) 10.5, CH_2P], 27.2 (3C, s, CMe_3), 39.1 [1C, d, ^3J(PC) 1.9, CMe_3], 170.7 (1C, s, ^{t}BuC=N), 203.3 [2C, d, ^2J(PC) 7.4, 2 × CO], 208.6 [1C, d, ^2J(PC) 35.5, CO (*trans* to P)], 209.7 [1C, d, ^2J(PC) 3.5, CO (*trans* to N)]. Benzylidene group—158.8 [1C, d, ^3J(PC) 4.7, HC=N], 128.3 (1C, s, C^4 of Ph), 130.5 (2C, s, =CH*Ph*), 131.2 (1C, s, C^1 of Ph), 131.8 (2C, s, =CH*Ph*). PPh_2 groups—128.7 [4C, d, ^3J(PC) 9.7, 4 × C_m], 131.4 [2C, s, 2 × C_p], 132.6 [4C, br, 4 × C_o], 135.6 [2C, br, 2 × C_i].

[a] Recorded at 100.6 MHz, chemical shifts (δ) are in ppm, coupling constants J in Hz, solvent $CDCl_3$ unless otherwise stated. The aryl group not bonded to phosphorus is referred to as *Ar* and the carbons that could be assigned are numbered (C^1, C^2 etc.) as in formulae; carbons that were not assigned are referred to as *Ar*. The carbons of the PPh_2 groups are labelled C_i, C_o, C_m and C_p and refer to *ipso*, *ortho*, *meta* and *para* carbons. [b] In CD_2Cl_2. [c] Resonances due to carbonyl ligands were not observed. [d] C^1 and C^2 were not resolved.

complexes, **4b** or **4c** respectively; we detected an intermediate in each of these reactions and formulate these as **3b** and **3c**. The tungsten(II) complexes **4b** and **4c** showed similar NMR (Tables 1 and 2) and IR data (Table 3) to **4a**. The mixed azine from 2-chloro-6-fluoro-benzaldehyde gave **4d** in which the C–Cl of **2d** has added oxidatively to tungsten; the carbon-13 data for **4d** (Table 2) clearly show that the aryl ring has retained its fluoro-substituent in the 6-position. Treatment of the mixed azine **2e**, from 2-fluorobenzaldehyde, with $[W(CO)_3(NCEt)_3]$ gave the monopropionitrile tungsten(0) complex **3e** in 71% yield in which the C–F (or C–H) bond has not oxidatively added to the tungsten(0)

TABLE 3. IR data [a]

Complex	ν(C≡O)/cm^{-1}
3e	1920, 1815, 1790
4a	2025, 1945, 1895
4b	2025, 1945, 1895
4c	2025, 1945, 1895
4d	2025, 1945, 1900
5a	2015, 1890, 1845
5b [b]	1925, 1840, 1810
6 [c]	2015, 1890, 1845
8	2015, 1890, 1850

[a] Recorded in CH_2Cl_2, all carbonyl bands are strong. [b] ν(C≡N^{t}Bu) = 2115 cm^{-1}. [c] ν(N–H)(KBr disc) = 3200 cm^{-1}.

and showed no tendency to do so even at 60°C; at this temperature some disproportionation took place giving tetracarbonyl tungsten(0) complex **5a**. The factors which influence the tendency for C–X bonds to add oxidatively to a metal are complex but for the tungsten(0) complexes studied in this paper there is good correlation with C–X bond strengths, *i.e.* the C–I adds the fastest followed by the C–Br and C–Cl, whilst the two strongest bonds, C–F or C–H, do not add. Average values of Ph–X bond strengths are as follows — for X = I, 66; X = Br, 82; X = Cl, 97; X = H, 112 and X = F, 127 kcal mol^{-1} [15]. The mono-propionitrile tungsten(0) complex **3e** was characterised and the NMR and IR data indicate a *fac*-stereochemistry. The treatment of monofluoro-imine ligand, $Me_2NCH_2CH_2N$=CH(C_6H_4F-2), with $W(CO)_3(NCEt)_3$ gave the tetracarbonyl tungsten(0) complex $[W(CO)_4\{Me_2NCH_2CH_2N$=CH(C_6H_4F-2)$\}]$ and some cyclometallated tungsten(II) complex $[WF(CO)_3\{Me_2NCH_2CH_2N$=CH($C_6H_4$)$\}]$ [16]. When $[W(CO)_3(NCEt)_3]$ was treated with Ph_2PCH_2C(^{t}Bu)=N–N=CH(C_6H_4F-2) in the presence of carbon monoxide or **3e** was treated with carbon monoxide, the tetracarbonyl complex **5a** was formed and characterised. As reported in Table 1, the CH_2P protons are equivalent at 20°C but at −65°C form the AB-part of an ABX-spin system (X = phosphorus). This is because the six-membered chelate ring is flexible and the flux-

ionality at 20°C renders the methylene protons equivalent but at −65°C the two methylene protons have become inequivalent with one probably *pseudo*-equatorial and the other *pseudo*-axial. Treatment of **3e** with CN^tBu displaced the NCEt and gave the hoped for mono *t*-butyl isocyanide complex **5b**. The phosphorus-31 and proton NMR data indicated that only one isomer, of composition $[W(CO_3)(CN^tBu)\{Ph_2PCH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2\}]$ was formed; the carbon-13 NMR data (Table 2) show that the CO ligands are *fac* and the CO ligand *trans* to phosphorus is easily identified from the large value of $^2J(PC)$ of 38.9 Hz. In the proton NMR spectrum the CH_2 protons are non-equivalent, as expected for a *fac*-geometry.

We found that on treatment with sodium borohydride and carbon monoxide the aryl–tungsten bond was broken and the C=N bond was reduced to give the benzylhydrazone tetracarbonyl derivative **6**. The $^{31}P\text{-}\{^1H\}$ NMR data are in agreement with **6** being tungsten(0). The proton NMR data and the IR data show the presence of NH and there are two AB-patterns for the methylene protons in the $^1H\text{-}\{^{31}P\}$ NMR spectrum, one due to CH_2P and the other due to CH_2N. The carbon-13 NMR spectrum shows four non-equivalent carbonyl groups, as expected. We suggest that this conversion of **4** to **6** goes *via* the intermediates **7** and **8**. We did not identify the hydride **7** which we suggest reacts rapidly with carbon monoxide to give the mixed azine tetracarbonyl benzylidene complex **8** by reductive elimination and this is then reduced to **6**. Consistent with this hypothesis we now find that **8**, which we have made previously [3], is rapidly reduced by sodium borohydride to give **6**. Recently, Richmond and co-workers have reported reductive elimination processes involving aryl–tungsten bonds in some tungsten(II) alkoxide complexes [17].

3. Experimental section

All the reactions were carried out in under dry nitrogen or dry argon. Tetrahydrofuran (THF) was distilled from sodium and benzophenone under nitrogen immediately before use. Infra-red spectra were recorded using a Perkin-Elmer model 457 grating spectrometer. NMR spectra were recorded using a JEOL FX-90Q spectrometer (operating frequencies for ^1H and ^{31}P of 89.5 and 36.2 MHz respectively), a JEOL FX-100 spectrometer (operating frequencies for ^1H and ^{31}P of 99.5 and 40.25 MHz respectively) or a Bruker AM400 spectrometer (operating frequencies for ^1H, ^{31}P and ^{13}C of 400.13, 161.9 and 100.6 MHz respectively). ^1H and ^{13}C chemical shifts are relative to tetramethylsilane and ^{31}P shifts are relative to 85% phosphoric acids, and all coupling constants are in Hz. Mass spectra were recorded using a VG Autospec spectrometer with 8 kV acceleration.

$PPh_2CH_2C(^tBu)=NNH_2$ **1** was prepared according to our published procedure [3].

$PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4I\text{-}2)$ (**2a**) was prepared *in situ* by treating 2-iodobenzaldehyde with $PPh_2CH_2C(^tBu)=NNH_2$ (**1**) in dry THF.

$PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4Br\text{-}2)$ (**2b**). 2-Bromobenzaldehyde (0.28 g, 0.18 ml, 1.5 mmol) was added to a solution of phosphino hydrazone (**1**) (0.4 g, 1.35 mmol) in ethanol (*ca.* 4 ml), and the resultant yellow solution was put aside for 24 h. The required mixed azine phosphine **2b** was obtained as a pale yellow crystalline solid (0.43 g, 68%). (Found: C, 64.35; H, 5.7; N, 6.05. $C_{25}H_{26}BrN_2P$ requires C, 64.5; H, 5.6; N 6.0%). *m/z* (EI): 409 and 407 ($M - {}^tBu$).

$PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4Cl-2)$ (**2c**). The azine phosphine **2c** was prepared by condensing **1** with 2-chlorobenzaldehyde and isolated in a similar manner to **2b**. Yield 69%. (Found: C, 70.9; H, 6.2; Cl, 8.5; N, 6.5. $C_{25}H_{26}ClN_2P$ requires C, 71.3; H, 6.2; Cl, 8.4; N, 6.65%). *m/z* (EI) 364 ($M - {}^tBu$).

$PPh_2CH_2C(^tBu)=N-N=CH(C_6H_3Cl\text{-}2,F\text{-}6)$ (**2d**). The azine phosphine **2d** was prepared by condensing **1** with 2-chloro-6-fluorobenzaldehyde and isolated in a similar manner to **2b**. Yield 56%. (Found: C, 68.5; H, 5.85; Cl, 7.95; N, 6.45. $C_{25}H_{25}ClFN_2P$ requires C, 68.4; H, 5.75; Cl, 8.1; N, 6.4%). *m/z* (EI): 437 ($M - 1$) and 381 ($M - {}^tBu$).

$PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)$ (**2e**). The azine phosphine **2e** was prepared by condensing **1** with fluorobenzaldehyde and isolated in a similar manner to **2b**. Yield 81%. (Found: C, 73.85; H, 6.25; N, 7.15. $C_{25}H_{26}FN_2P$ requires C, 74.25; H, 6.5; N, 6.9%). *m/z* (EI): 404 (M^+) and 347 ($M - {}^tBu$).

$[W(CO)_3(NCEt)\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)\}]$ (**3e**). A solution containing $[W(CO)_3(NCEt)_3]$ [9] (0.18 g, 0.41 mmol) and the azine phosphine **2e** (0.17 g, 0.42 mmol) in dry THF (*ca.* 8 ml) was put aside for 30 min at *ca.* 20°C. The resulting dark brown solution was filtered and the solvent removed under reduced pressure. The residue was then triturated with methanol to give the propionitrile-tungsten(0) complex **3e** as brown microcrystals (0.22 g, 71%). (Found: C, 51.0; H, 4.25; N, 5.75, $C_{31}H_{31}FN_3O_3PW$ requires C, 51.2; H, 4.3; N, 5.75%). *m/z* (FAB) 727 (M^+), 672 ($M - NCEt$), 644 ($M - NCEt - CO$) and 588 ($M - NCEt - 3CO$).

$[WI(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4)\}]$ (**4a**). 2-Iodobenzaldehyde (35 mg, 0.15 mmol) was added to a solution containing phosphino hydrazone (**1**) (45 mg, 0.15 mmol) in dry THF (3 ml). After 5 min the $^{31}P\text{-}\{^1H\}$ NMR spectrum of the resulting pale yellow solution showed a singlet at −10.1 ppm, which we assigned to the azine phosphine **2a**. To this solution

$[W(CO)_3(NCEt)_3]$ (65 mg, 0.15 mmol) was then added. After 20 min the resulting solution was filtered and concentrated to a low volume (*ca.* 0.2 ml) under reduced pressure. Addition of hexane to the residue gave the tricarbonyl tungsten(II) complex **4a** as yellow microcrystals (90 mg, 77%). An analytical sample was recrystallised from dichloromethane/methanol. (Found: C, 42.8; H, 3.45; N, 3.85. $C_{28}H_{26}IN_2O_3PW$ requires C, 43.1; H, 3.35; N, 3.6%). *m/z* (FAB) 752 (M − CO), 724 (M − 2CO) and 696 (M − 3CO).

$[WBr(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4)\}]$ (**4b**). A solution containing $[W(CO)_3(NCEt)_3]$ (0.10 g, 0.23 mmol) and the azine phosphine **2b** (0.11 g, 0.23 mmol) in dry THF (*ca.* 4 ml) was stirred for 45 min at *ca.* 20°C. The resulting dark brown solution was filtered and the solvent removed under reduced pressure. The residue was then recrystallised from dichloromethane/methanol to give the tricarbonyl tungsten(II) complex **4b** as yellow microcrystals (0.12 g, 71%). (Found: C, 45.65; H, 3.55; Br, 10.7; N, 3.8. $C_{28}H_{26}BrN_2O_3PW$ requires C, 45.85; H, 3.55; Br, 10.9; N, 3.8%). *m/z* (FAB) 706 and 704 (M − CO), 678 and 676 (M − 2CO), 650 and 648 (M − 3CO).

$[WCl(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4)\}]$ (**4c**). The chloro-complex **4c** was prepared from **2c** with a reaction time of 7 h and isolated in a similar manner to **4b** as yellow microcrystals. Yield 62%. (Found: C, 48.5; H, 3.7; Cl, 5.1; N, 4.0. $C_{28}H_{26}ClN_2O_3PW$ requires C, 48.8; H, 3.8; Cl, 5.15; N, 4.05%). *m/z* (FAB) 662 and 660 (M − CO), 634 and 632 (M − 2CO), 606 and 604 (M − 3CO).

$[WCl(CO)_3\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_3F\text{-}6)\}]$ (**4d**). The chloro-complex **4d** was prepared from **2d** with a reaction time of 45 min and isolated in a similar manner to **4b** as yellow microcrystals. Yield 48%. (Found: C, 47.4; H, 3.6; Cl, 4.95; N, 4.0. $C_{28}H_{25}ClFN_2O_3PW$ requires C, 47.6; H, 3.55; Cl, 5.0; N, 3.95%). *m/z* (FAB) 707 (M + 1), 678 (M − CO), 650 (M − 2CO) and 622 (M − 3CO).

$[W(CO)_4\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)\}]$ (**5a**). Carbon monoxide was bubbled through a solution containing $[W(CO)_3(NCEt)_3]$ (60 mg, 0.14 mmol) and the azine phosphine **2e** (56 mg, 0.14 mmol) in dry THF (*ca.* 3 ml) for 1 h. The solution was then filtered and concentrated to a low volume (*ca.* 0.2 ml) under reduced pressure. Addition of methanol to the residue gave the tetracarbonyl tungsten(0) complex **5a** as red microcrystals (50 mg, 52%). An analytical sample was recrystallised from dichloromethane/methanol. (Found: C, 47.5; H, 3.25; N, 4.05. $C_{29}H_{26}FN_2O_4PW \cdot 0.5CH_2Cl_2$ requires C, 47.7; H, 3.65; N, 3.75%). *m/z* (FAB) 700 (M^+), 672 (M − CO), 644 (M − 2CO) and 588 (M − 4CO).

$[W(CO)_3(CN^tBu)\{PPh_2CH_2C(^tBu)=N-N=CH(C_6H_4F\text{-}2)\}]$ (**5b**). An excess of *t*-butyl isonitrile (30 μl) was added to a solution of **3e** (60 mg, 0.08 mmol) in dichloromethane (2 ml). After 1 h, the solution was filtered and concentrated to a low volume (*ca.* 0.2 ml) under reduced pressure. The residue was then triturated with methanol to give the isonitrile tungsten(0) complex **5b** as red microcrystals (48 mg, 77%). (Found: C, 52.4; H, 4.65; N, 5.5. $C_{33}H_{35}FN_3O_3PW$ requires C, 52.45; H, 4.65; N, 5.55%). *m/z* (FAB) 755 (M^+), 727 (M − CO) and 588 (M − CN^tBu − 3CO).

$[W(CO)_4\{PPh_2CH_2C(^tBu)=N-NHCH_2Ph\}]$ **6**. (i) *From the aryl-tungsten complex* **4b**. An excess of $NaBH_4$ (30 mg) and the tricarbonyl tungsten(II) complex **4b** (40 mg, 0.054 mmol) were allowed to stir in THF (2 ml) and ethanol (0.25 ml) in an atmosphere of carbon monoxide for 30 min. The solution was then evaporated to dryness under reduced pressure and the residue extracted into CH_2Cl_2 (3 × 1 ml). The solvent was then removed under reduced pressure and the residue recrystallised from dichloromethane/methanol to give the tetracarbonyl tungsten(0) complex **6** as yellow microcrystals (19 mg, 51%).

(ii) *From complex* **8**. An excess of $NaBH_4$ (50 mg) was added to a stirred solution of **8** (44 mg, 0.063 mmol) in THF (2 ml) and ethanol (0.25 ml). After 30 min, the solution was worked up as described in method (i) to give the tetracarbonyl tungsten(0) complex **6** as yellow microcrystals (32 mg, 73%). (Found: C, 50.15; H, 4.15; N, 4.05. $C_{29}H_{26}N_2O_4PW \cdot 0.2CH_2Cl_2$ requires C, 50.15; H, 4.15; N, 4.05%). *m/z* (FAB) 684 (M^+), 656 (M − CO), 600 (M − 3CO) and 572 (M − 4CO).

Acknowledgements

We thank the SERC for a fellowship (to S.D.P.) and for other support.

References

1 J.P. Collman, L.S. Hegedus, J.R. Norton and R.G. Finke, *Principles and Applications of Organotransition Metal Chemistry*, University Science Books, Mill Valley, CA, 1987 and refs. therein.
2 G. Wilkinson, F.G.A. Stone and E.W. Abel (eds.), *Comprehensive Organometallic Chemistry* Pergamon, Oxford, 1982 and refs. therein.
3 K.K. Hii, S.D. Perera, B.L. Shaw and M. Thomton-Pett, *J. Chem. Soc., Dalton Trans.*, (1992) 2361.
4 J. March, *Advanced Organic Chemistry* 4th edition, Wiley, New York, 1992, 904.
5 T.G. Richmond, M.A. King, E.P. Kelson and A.M. Arif, *Organometallics*, *6* (1987) 1995.
6 For a review see: T.G. Richmond, *Coord. Chem. Rev.*, *105* (1990) 221.
7 S. Mohanty and P. Venkateswarlu, *Mol. Phys.*, *12* (1967) 277.
8 F.J. Weigert and J.D. Roberts, *J. Am. Chem. Soc.*, *91* (1969) 4940.
9 G.J. Kubas, *Inorg. Chem.*, *22* (1983) 692.

10 S.D. Perera, B.L. Shaw and M. Thornton-Pett, *J. Chem. Soc., Dalton Trans.*, (1992) 1469.
11 A. Breque, C.C. Santini, F. Mathey, J. Fischer and A. Mitschler, *Inorg. Chem.*, *23* (1984) 3463.
12 B.J. Brisdon, *J. Organomet. Chem.*, *125* (1977) 225.
13 S.W. Lee and W.C. Trogler, *Organometallics*, *9* (1990) 1470.
14 C.P. Casey and S.W. Polichnowski, *J. Am. Chem. Soc.*, *100* (1978) 7565.
15 *Handbook of Chemistry and Physics*, The Chemical Rubber Company, Cleveland, Ohio, U.S.A., 52nd edition, page F-186, and references therein.
16 B.L. Lucht, M.J. Poss, M.A. King and T.G. Richmond, *J. Chem. Soc., Chem. Commun.*, (1991) 400.
17 B.P. Buffin, A.M. Arif and T.G. Richmond, *J. Chem. Soc., Chem. Commun.*, (1993) 1432.