DALTON
FULL PAPER

4-Aminobenzylidyne: a versatile precursor for extended unsaturated alkylidyne ligands †

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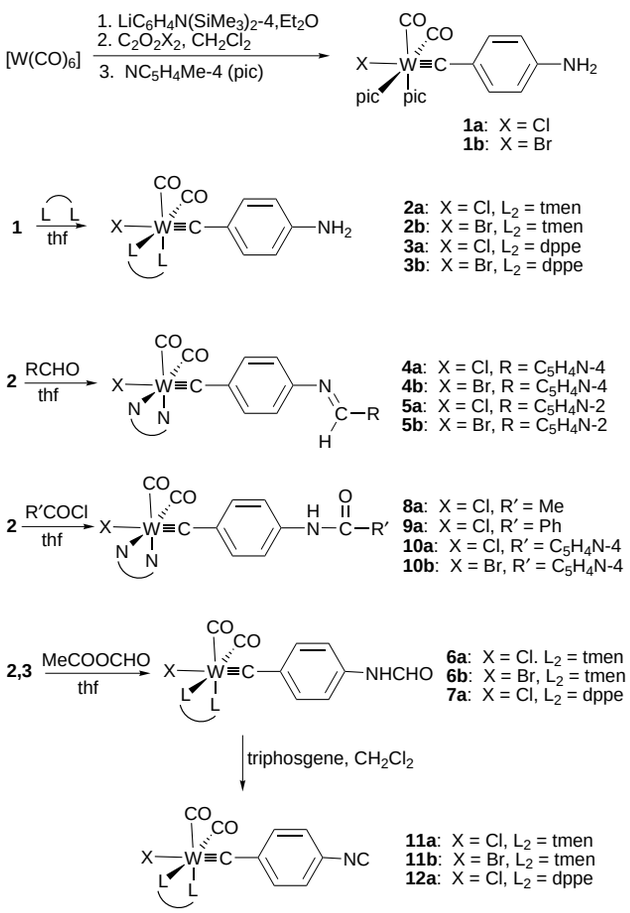
The 4-aminobenzylidyne tungsten complexes $[W(CC_6H_4NH_2\text{-}4)X(CO)_2(pic)_2]$ **1** (X = Cl **a** or Br **b**) have been prepared by sequential reaction of $[W(CO)_6]$ with $LiC_6H_4N(SiMe_3)_2$-4 in diethyl ether and $C_2O_2Cl_2$ or $C_2O_2Br_2$ and 4-methylpyridine (pic) in CH_2Cl_2. Substitution of the picoline ligands by tmen ($Me_2NCH_2CH_2NMe_2$) and dppe ($Ph_2PCH_2CH_2PPh_2$) afforded the complexes $[W(CC_6H_4NH_2\text{-}4)X(CO)_2(L_2)]$ (L_2 = tmen **2**, X = Cl **a** or Br **b**; dppe **3**, X = Cl **a** or Br **b**). The amino group of the new alkylidyne complexes undergoes typical functional group transformations. Treatment of complexes **2** with pyridine-2-carbaldehyde afforded the Schiff-base derivatives $[W\{CC_6H_4(NCHC_5H_4N\text{-}2)\text{-}4\}X(CO)_2(tmen)]$ **5** (X = Cl **a** or Br **b**). Formylation of complexes **2** with acetic formic anhydride afforded the formamides $[W(CC_6H_4NHCHO\text{-}4)X(CO)_2(tmen)]$ **6** (X = Cl **a** or Br **b**). The isocyanide derivatives $[W(CC_6H_4NC\text{-}4)X(CO)_2(tmen)]$ **11** (X = Cl **a** or Br **b**) were obtained by dehydration of complexes **6** with triphosgene–NEt_3. The molecular structures of **3a**, **4b**, **8a**, **9a** and **10b** were determined by X-ray crystallography.

Molecules in which metal complex fragments and extended organic π systems are connected *via* metal–carbon multiple bonds[1] have received increasing attention in recent years. Owing to their special electronic properties, such metalla-π systems are of potential interest as components in molecular materials. In this context, transition-metal alkylidyne complexes[2] are promising candidates[3,4] as they possess strong metal–carbon triple bonds.[5] We are especially interested in exploring the potential of Fischer-type alkylidyne metal complexes.[4,6] Most representatives of this class of compound are electronically and co-ordinatively saturated, which affords them high stability, and the methods for their synthesis are highly developed, at least as far as the generation of the metal–carbon triple bonds and the variation of the ancillary ligands are concerned.[1,7] However, specific methods to extend the π systems of the alkylidyne ligands and to establish conjugated links with other functionalities across unsaturated alkylidyne ligands have not yet been developed. This situation is, at least in part, a consequence of the particular reaction conditions involved in the preparation of the metal–carbon triple bonds. The employment of highly reactive nucleophiles as well as electrophiles at different stages of alkylidyne metal complex synthesis[7,8] precludes the presence of many types of functional group. Owing to these limitations, it is necessary to develop procedures which allow the modification of unsaturated alkylidyne ligands *after* formation of the metal–carbon triple bonds. As a possible system for this endeavor, we have identified the 4-aminobenzylidyne ligand. The presence of the amino group is expected to provide a variety of opportunities to extend the benzylidyne ligand in an electronically conjugated manner.

Results and Discussion

The 4-aminobenzylidyne tungsten complexes **1** are synthesized by reaction of $[W(CO)_6]$ with $LiC_6H_4N(SiMe_3)_2$-4[9] in diethyl ether, followed by addition of oxalyl halide and 4-methylpyridine (pic) in CH_2Cl_2 (Scheme 1). After removal of the solvent from the reaction mixture and recrystallization from methylene chloride–hexane, the products **1** are isolated in 25–40% yield. No special procedures are required for the desilylation of the amino group. Substitution of the two pic ligands in **1** by tmen ($Me_2NCH_2CH_2NMe_2$) and dppe ($Ph_2PCH_2CH_2PPh_2$) affords the derivatives **2** and **3**.



Scheme 1 thf = Tetrahydrofuran

The amino group of the complexes **1**–**3** undergoes typical functional group transformations.[10] For example, Schiff-base formation of complexes **2** with pyridine-4- and -2-carbaldehyde gives the imines **4** and **5** and reaction of **2** and **3** with acetic formic anhydride and with acetyl, benzoyl as well as isonicotinoyl chloride affords the formyl derivatives **6** and **7** and the acyl derivatives **8**–**10**. The isocyano derivatives **11** and **12** form upon

† Dedicated to Professor Walter Siebert on the occasion of his 60th birthday.

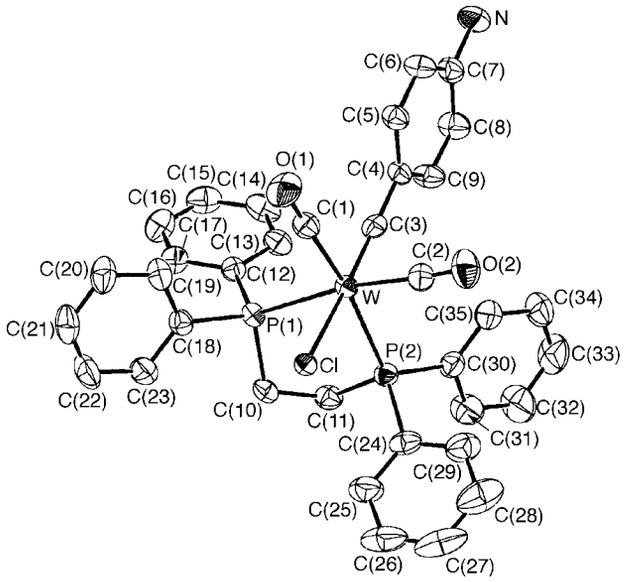


Fig. 1 Molecular structure of complex **3a**

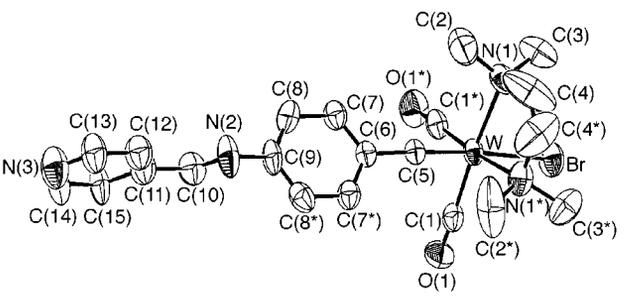


Fig. 2 Molecular structure of complex **4b**

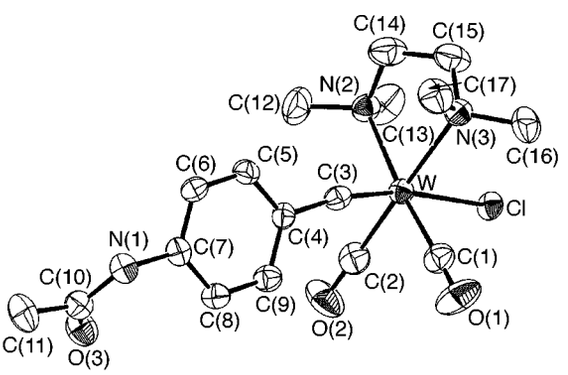


Fig. 3 Molecular structure of complex **8a**

treatment of complexes **6** and **7** with triphosgene $[(Cl_3CO)_2CO]$–NEt_3.[11]

The transformations of the amino group in complexes **2** into imine, amide and isocyanide functionalities are accompanied by noticeable changes of the spectroscopic parameters of the tungsten alkylidyne fragment. For example, the stretching frequencies of the carbonyl ligands, which are sensitive to the electron density of the tungsten center, increase by about 10 wavenumbers upon Schiff-base formation and formylation, and by about 15 wavenumbers upon formation of the isocyanide functionality. Considering that the carbonyl ligands on the tungsten center are primarily interacting with the d orbital which is orthogonal to the metal alkylidyne π system,[4] these data indicate the presence of significant electronic coupling between the tungsten atom and the remote functional groups. The ^{13}C NMR resonances of the alkylidyne carbon atom shift only slightly in response to the functional group transformations taking place on the opposite side of the arene group.

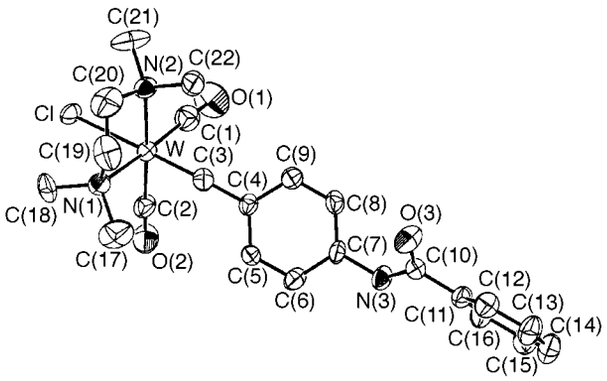


Fig. 4 Molecular structure of complex **9a**

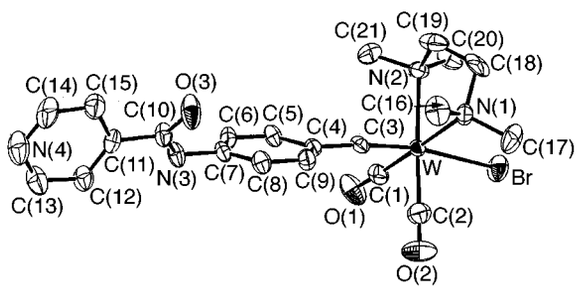


Fig. 5 Molecular structure of complex **10b**

The crystal structures of compounds **3a**, **4b**, **8a**, **9a** and **10b** have been determined by X-ray crystallography. Selected bond distances and angles are listed in Table 1, and the molecular structures are shown in Figs. 1–5, respectively. The amino group in **3a** is strongly conjugated with the phenyl group, as indicated by the short N–C(7) bond length of 1.373(9) Å,[12] but this feature is not mirrored in the bonding parameters of the W–C(3)–C(4) fragment. The W–C(3) distance of 1.812(7) Å and the C(3)–C(4) distance of 1.453(9) Å are within the established range for metal–carbon triple and C(sp)–C(sp^2) bonds.[1,13] There are also no signs of bond localization within the phenyl ring. The same situation is found in the other structures determined in this study. The distances within the W≡C–C fragments and the phenyl rings of compounds **4b**, **8a**, **9a** and **10b** are unexceptional.[1] However, compared with that in **3a**, the N–C (phenyl) distance, N(2)–C(9), has lengthened to 1.41(1) Å in the Schiff-base derivative **4b**, and to almost the same value in the amide derivatives **8a**, **9a** and **10b**, reflecting a reduction or elimination of the π interaction between the nitrogen atom and the phenyl ring in these compounds.[13] Thus, the functional group transformations cause the expected changes of the local bonding parameters, but apparently do not have a significant effect on the bond distances involving the alkylidyne carbon atom.

In conclusion, the 4-aminobenzylidyne ligand is a versatile unit for the design of extended unsaturated alkylidyne ligands. Several of the new alkylidyne ligands derived from it, in particular the isocyanide derivatives, are designed for the attachment of additional metal centers which are spacially separated from, yet electronically conjugated with, the alkylidyne metal center. There is spectroscopic evidence for electronic coupling between the metal center and the nitrogen functionality across the unsaturated alkylidyne π system.

Experimental

General

Standard inert-atmosphere techniques were used throughout. Diethyl ether, hexane and tetrahydrofuran were purified by reflux over sodium and distilled under nitrogen. Methylene chloride was heated to reflux over calcium hydride and distilled

Table 1 Selected bond lengths (Å) and angles (°)

Complex **3a**

W–Cl	2.584(2)	W–C(3)	1.812(7)
W–C(1)	2.013(8)	W–C(2)	1.986(9)
W–P(1)	2.544(2)	W–P(2)	2.537(2)
N–C(7)	1.373(9)	C(3)–C(4)	1.453(9)
C(4)–C(5)	1.376(10)	C(4)–C(9)	1.402(9)
C(5)–C(6)	1.38(1)	C(6)–C(7)	1.39(1)
C(7)–C(8)	1.38(1)	C(8)–C(9)	1.38(1)
Cl–W–C(3)	173.9(2)	W–C(3)–C(4)	170.7(6)
P(1)–W–P(2)	79.91(6)	P(1)–W–C(1)	95.7(2)
P(2)–W–C(2)	93.7(2)	C(1)–W–C(2)	89.9(3)

Complex **4b**

W–C(5)	1.799(9)	W–C(1)	1.986(9)
W–Br	2.696(1)	W–N(1)	2.318(6)
C(1)–O(1)	1.141(8)	C(5)–C(6)	1.45(1)
C(6)–C(7)	1.377(9)	C(7)–C(8)	1.396(10)
C(8)–C(9)	1.373(10)	C(9)–N(2)	1.41(1)
N(2)–C(10)	1.15(1)	C(10)–C(11)	1.52(2)
C(11)–C(12)	1.39(2)	C(12)–C(13)	1.36(2)
C(13)–N(3)	1.28(2)	N(3)–C(15)	1.33(2)
Br–W–C(5)	168.3(3)	W–C(5)–C(6)	173.6(7)
C(1)–W–C(1)	87.6(5)	N(1)–W–N(1)	78.6(4)
C(1)–W–N(1)	96.8(3)	C(9)–N(2)–C(10)	122(1)
N(2)–C(10)–C(11)	124(1)	Br–W–C(1)	87.3(2)
Br–W–N(1)	90.9(2)		

Complex **8a**

W–Cl	2.585(2)	W–C(3)	1.799(7)
W–N(2)	2.312(6)	W–N(3)	2.295(5)
W–C(1)	1.972(9)	W–C(2)	1.980(8)
C(3)–C(4)	1.467(9)	C(4)–C(5)	1.390(9)
C(4)–C(9)	1.398(9)	C(5)–C(6)	1.363(9)
C(6)–C(7)	1.393(9)	C(7)–C(8)	1.380(9)
C(8)–C(9)	1.375(9)	N(1)–C(7)	1.424(9)
N(1)–C(10)	1.340(9)	C(10)–C(11)	1.51(1)
C(10)–O(3)	1.222(8)	C(1)–O(1)	1.143(9)
C(2)–O(2)	1.155(9)		
Cl–W–C(3)	168.4(2)	W–C(3)–C(4)	167.7(5)
C(1)–W–C(2)	85.9(3)	C(1)–W–N(3)	96.3(2)
C(2)–W–N(2)	99.3(3)	N(2)–W–N(3)	78.4(2)
Cl–W–C(1)	88.5(2)	Cl–W–C(2)	88.8(2)
Cl–W–N(2)	89.3(2)	Cl–W–N(3)	87.9(2)
C(3)–W–C(1)	84.8(3)	C(3)–W–C(2)	81.2(3)
C(3)–W–N(2)	98.1(2)	C(3)–W–N(3)	102.3(2)
C(7)–N(1)–C(10)	123.8(6)	N(1)–C(10)–C(11)	114.5(7)
N(1)–C(10)–O(3)	122.8(7)	C(11)–C(10)–O(3)	122.7(7)

Complex **9a**

W–Cl	2.579(2)	W–C(3)	1.810(9)
W–C(1)	2.00(1)	W–C(2)	1.98(1)
W–N(1)	2.292(7)	W–N(2)	2.315(7)
N(3)–C(7)	1.42(1)	N(3)–C(10)	1.35(1)
O(3)–C(10)	1.23(1)	C(3)–C(4)	1.45(1)
C(4)–C(5)	1.40(1)	C(4)–C(9)	1.42(1)
C(5)–C(6)	1.38(1)	C(6)–C(7)	1.39(1)
C(7)–C(8)	1.38(1)	C(8)–C(9)	1.37(1)
C(10)–C(11)	1.49(1)	C(11)–C(12)	1.38(1)
C(11)–C(16)	1.40(1)	C(12)–C(13)	1.39(1)
C(13)–C(14)	1.40(2)	C(14)–C(15)	1.35(2)
C(15)–C(16)	1.40(1)		
Cl–W–C(3)	170.7(3)	W–C(3)–C(4)	173.5(7)
N(3)–C(10)–C(11)	117.2(8)	O(3)–C(10)–N(3)	121.2(9)
O(3)–C(10)–C(11)	121.5(9)	C(7)–N(3)–C(10)	124.9(8)
N(1)–W–N(2)	78.9(3)	N(1)–W–C(2)	98.8(4)
N(2)–W–C(1)	97.2(4)	C(1)–W–C(2)	85.0

Complex **10b**

W–C(3)	1.807(7)	Br–W	2.6975(9)
W–C(1)	1.974(9)	W–C(2)	1.96(1)
W–N(1)	2.292(7)	W–N(2)	2.291(6)
C(1)–O(1)	1.16(1)	C(2)–O(2)	1.14(1)
C(3)–C(4)	1.440(10)	C(4)–C(5)	1.39(1)
C(4)–C(9)	1.39(1)	C(5)–C(6)	1.375(10)
C(6)–C(7)	1.38(1)	C(7)–C(8)	1.37(1)
C(8)–C(9)	1.39(1)	N(3)–C(7)	1.426(9)
N(3)–C(10)	1.339(9)	C(10)–O(3)	1.208(10)
C(10)–C(11)	1.50(1)	C(11)–C(12)	1.37(1)
C(12)–C(13)	1.39(1)	C(13)–C(14)	1.31(1)
N(4)–C(14)	1.33(1)	C(14)–C(15)	1.38(1)
C(15)–C(11)	1.40(1)		
Br–W–C(3)	169.6(2)	W–C(3)–C(4)	173.2(6)
C(1)–W–C(2)	86.2(4)	C(1)–W–N(2)	98.4(3)
N(1)–W–N(2)	78.8(3)	N(1)–W–C(2)	96.6(3)
Br–W–C(1)	89.2(2)	Br–W–C(2)	88.1(3)
Br–W–N(1)	89.2(2)	Br–W–N(2)	91.9(2)
C(7)–N(3)–C(10)	123.9(6)	N(3)–C(10)–O(3)	122.3(7)
O(3)–C(10)–C(11)	120.5(7)	N(3)–C(10)–C(11)	117.2(7)

under nitrogen. Tungsten hexacarbonyl, oxalyl chloride, oxalyl bromide, 4-methylpyridine, *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen) and 1,2-bis(diphenylphosphino)ethane (dppe) were obtained from commercial sources and used as received.

Proton, ^{13}C and ^{31}P NMR spectra were recorded on Fourier-transform 270 MHz JEOL JNMGSX270, 300 MHz Bruker DPX300 and 500 MHz Bruker DRX500 spectrometers. Chemical shifts of ^{1}H and ^{13}C are given in parts per million (δ) relative to tetramethylsilane, ^{31}P to 85% H_3PO_4 and proton decoupled. The IR spectra were recorded on a Shimadzu FTIR-8201PC spectrometer. Melting points were recorded on a Stuart Scientific SMP1 instrument under nitrogen. Elemental analyses were performed by Butterworth Laboratories Ltd.

Preparations

[W(CC$_6$H$_4$NH$_2$-4)Cl(CO)$_2$(pic)$_2$] 1a. A solution of LiC$_6$H$_4$N(SiMe$_3$)$_2$-4 was prepared by the addition of LiBu^n in hexane (1.6 M, 8.625 cm^3) to BrC$_6$H$_4$N(SiMe$_3$)$_2$-4[9] (11.5 mmol, 3.634 g) in ether (30 cm^3) and stirring for 2 h at 0 °C. The resulting solution was transferred to a suspension of [W(CO)$_6$] (10 mmol, 3.52 g) in ether (20 cm^3) at room temperature (r.t). The mixture was stirred for 1 h at r.t., then concentrated (to about 5 cm^3), and hexane added to precipitate the acyltungsten intermediate, which was filtered off and washed with hexane (5 × 20 cm^3). (If the solvent is simply removed at this stage, the product contains up to 10% of the bromo analogue **1b**.) The solid residue was redissolved in CH_2Cl_2 (80 cm^3) and filtered. After cooling to −78 °C, $C_2O_2Cl_2$ (10.1 mmol, 0.88 cm^3) was added. The resulting mixture was allowed to warm up to −20 °C and 4-methylpyridine (5 cm^3) added. The mixture was stirred at r.t. for 2 h and the solvent then removed *in vacuo*. The residue was washed with hexane, dried and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford orange-yellow crystals. Yield: 1.46 g, 26%, m.p. 114–117 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.86 (d, J = 6.48, 4 H, C_5H_4N), 7.17 (d, J = 8.51, 2 H, $C_6H_4NH_2$), 7.06 (d, J = 6.13, 4 H, C_5H_4N), 6.52 (d, J = 8.53 Hz, 2 H, $C_6H_4NH_2$), 3.6 (br, 2 H, NH_2) and 2.35 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 265.2 (W≡C), 221.5 (CO), 152.4, 150.0, 146.4, 140.8, 131.1, 125.8, 114.0 (C_5H_4N, $C_6H_4NH_2$) and 21.1 (NCH_3). IR (CH_2Cl_2, cm^{-1}): 1979s (ν_{CO}) and 1890s (ν_{CO}) [Found (Calc.): C, 44.42 (44.59); H, 3.55 (3.56); N, 6.99 (7.43)%]

[W(CC$_6$H$_4$NH$_2$-4)Br(CO)$_2$(pic)$_2$] 1b. The synthesis followed the procedure described for complex **1a**, whereby $C_2O_2Br_2$ was used instead of $C_2O_2Cl_2$. (The solvent was removed directly from the acyltungsten intermediate.) Orange-yellow crystals. Yield: 37%, m.p. 115–120 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.92 (d, J = 6.35, 4 H, C_5H_4N), 7.18 (d, J = 8.54, 2 H, $C_6H_4NH_2$), 7.07 (d, J = 6.11, 4 H, C_5H_4N), 6.52 (d, J = 8.54 Hz, 2 H, $C_6H_4NH_2$), 3.52 (br, 2 H, NH_2) and 2.36 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 265.1 (W≡C), 220.8 (CO), 153.0, 150.0, 146.4, 140.3, 131.0, 125.8, 114.0 ($C_6H_4NH_2$, C_5H_4N) and 21.2 (CH_3). IR (CH_2Cl_2, cm^{-1}): 1979s (ν_{CO}) and 1890s (ν_{CO}) [Found (Calc.): C, 40.95 (41.34); H, 3.37 (3.30); N, 6.92 (6.89)%].

[W(CC$_6$H$_4$NH$_2$-4)Cl(CO)$_2$(tmen)] 2a. Complex **1a** (1 mmol, 0.565 g) was dissolved in CH_2Cl_2 (50 cm^3) and tmen (1 cm^3) added. The resulting mixture was stirred at 50 °C for 2 h and the solvent then removed *in vacuo*. The residue was washed with hexane, dried and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford orange-yellow crystals. Yield: 0.28 g, 56%, m.p. 160–165 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.09 (d, J = 8.79, 2 H, $C_6H_4NH_2$), 6.50 (d, J = 8.79 Hz, 2 H, $C_6H_4NH_2$), 3.80 (br, 2 H, NH_2), 3.18 (s, 6 H, NCH_3), 3.01–2.81 (br, 4 H, NCH_2) and 2.91 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 264.8 (W≡C), 221.5 (CO), 146.4, 140.3, 131.1, 114.0 ($C_6H_4NH_2$), 60.9, 58.0, 52.0 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1976s (ν_{CO}) and 1884s (ν_{CO}) [Found (Calc.): C, 36.31 (36.35); H, 4.44 (4.47); N, 8.46 (8.48)%].

[W(CC$_6$H$_4$NH$_2$-4)Br(CO)$_2$(tmen)] 2b. Orange-yellow crystals. Yield: 77%, m.p. 150–160 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.11 (d, J = 8.44, 2 H, $C_6H_4NH_2$), 6.50 (d, J = 8.46 Hz, 2 H, $C_6H_4NH_2$), 3.83 (br, 2 H, NH_2), 3.22 (s, 6 H, NCH_3), 3.02 (s, 6 H, NCH_3) and 2.90 (m, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 264.6 (W≡C), 220.8 (CO), 146.4, 139.7, 131.0, 114.0 ($C_6H_4NH_2$), 61.1, 58.3, 53.4 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1979s (ν_{CO}) and 1886s (ν_{CO}) [Found (Calc.): C, 33.58 (33.36); H, 4.03 (4.11); N, 7.78 (7.78)%].

[W(CC$_6$H$_4$NH$_2$-4)Cl(CO)$_2$(dppe)] 3a. Complex **1a** (1 mmol, 0.565 g) was dissolved in CH_2Cl_2 (50 cm^3) and dppe (1.1 mmol, 0.438 g) added. The resulting mixture was stirred at 50 °C for 2 h and the solvent then removed *in vacuo*. The residue was washed with hexane, dried and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford yellow crystals. Yield: 0.46 g, 59%, m.p. 154–160 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.74–7.17 (m, 20 H, PPh_2), 6.36 (d, J = 8.54, 2 H, $C_6H_4NH_2$), 6.20 (d, J = 8.79 Hz, 2 H, $C_6H_4NH_2$), 3.72 (br, 2 H, NH_2) and 2.97–2.50 (4 H, CH_2PPh_2). ^{13}C NMR ($CDCl_3$): δ 270.1 (W≡C, $^1J^{cis}_{PC}$ = 10), 213.1 (CO, $^1J^{cis}_{PC}$ = 7, $^1J^{trans}_{PC}$ = 45 Hz), 146.2, 140.5, 136.0, 135.4, 133.0, 132.8, 132.7, 131.5, 130.0, 129.9, 128.5, 128.4, 113.3 (PPh_2, $C_6H_4NH_2$), 27.6, 27.4, 27.2, 27.0 (CH_2PPh_2). ^{31}P NMR ($CDCl_3$): δ 39.0 ($^1J_{WP}$ = 229 Hz). IR (CH_2Cl_2, cm^{-1}): 1998s (ν_{CO}) and 1929s (ν_{CO}) [Found (Calc.): C, 54.03 (54.04); H, 3.80 (3.89); N, 1.96 (1.80)%].

[W(CC$_6$H$_4$NH$_2$-4)Br(CO)$_2$(dppe)] 3b. Yellow crystals. Yield: 80%, m.p. 175–178 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.72–7.19 (m, 20 H, PPh_2), 6.50 (d, J = 8.46, 2 H, $C_6H_4NH_2$), 6.26 (d, J = 8.51 Hz, 2 H, $C_6H_4NH_2$), 3.70 (br, 2 H, NH_2) and 3.03–2.51 (4 H, CH_2PPh_2). ^{13}C NMR ($CDCl_3$): δ 269.6 (W≡C, $^1J^{cis}_{PC}$ = 10), 211.8 (CO, $^1J^{trans}_{PC}$ = 43, $^1J^{cis}_{PC}$ = 7 Hz), 145.9, 140.3, 135.9, 135.6, 133.2, 132.9, 132.8, 132.7, 131.4, 130.0, 128.4, 128.3, 128.1, 113.6 (PPh_2, $C_6H_4NH_2$), 27.4, 27.3, 27.2, 27.1 (CH_2PPh_2). ^{31}P NMR ($CDCl_3$): δ 36.4 ($^1J_{WP}$ = 229 Hz). IR (CH_2Cl_2, cm^{-1}): 1998s (ν_{CO}) and 1929s (ν_{CO}) [Found (Calc.): C, 50.62 (51.12); H, 3.50 (3.68); N, 1.77 (1.70)%].

[W{CC$_6$H$_4$(NCHC$_5$H$_4$N-4)-4}Cl(CO)$_2$(tmen)] 4a. Complex **2a** (1 mmol, 0.496 g) was dissolved in thf (100 cm^3) and pyridine-4-carbaldehyde (0.2 cm^3) added with tmen (0.5 cm^3). The resulting mixture was stirred under reflux overnight and the solvent then removed *in vacuo*. The residue was washed with hexane, dried and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford light orange crystals. Yield: 0.47 g, 81%, m.p. 180–188 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.76 (d, J = 6.10, 2 H, C_5H_4N), 8.42 (s, 1 H, NCH), 7.74 (d, J = 6.11, 2 H, C_5H_4N), 7.29 (d, J = 8.31, 2 H, C_6H_4NCH), 7.13 (d, J = 8.30 Hz, 2 H, C_6H_4NCH), 3.24 (s, 6 H, NCH_3), 3.06–2.92 (br, 4 H, NCH_2) and 2.96 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 261.0 (W≡C), 220.9 (CO), 157.5 (NCH), 150.6, 149.5, 148.0, 142.7, 130.4, 122.2, 120.9, 114.0 (C_6H_4N, C_5H_4N), 61.0, 58.2, 52.2 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1985s (ν_{CO}) and 1894s (ν_{CO}) [Found (Calc.) (with 0.25 mol CH_2Cl_2): C, 42.02 (42.12); H, 4.20 (4.24); N, 9.18 (9.25)%].

[W{CC$_6$H$_4$(NCHC$_5$H$_4$N-4)-4}Br(CO)$_2$(tmen)] 4b. Red-orange crystals. Yield: 64%, m.p. 185–190 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.76 (d, J = 5.98, 2 H, C_5H_4N), 8.42 (s, 1 H, NCH), 7.74 (d, J = 6.11, 2 H, C_5H_4N), 7.31 (d, J = 8.54, 2 H, C_6H_4NCH), 7.16 (d, J = 8.35 Hz, 2 H, C_6H_4NCH), 3.28 (s, 6 H, NCH_3), 3.07 (s, 6 H, NCH_3) and 2.96 (m, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 260.8 (W≡C), 220.2 (CO), 157.6 (NCH), 150.6, 149.7, 147.4, 142.7, 131.0, 130.3, 122.2, 121.0, 114.0 (C_6H_4NCH, C_5H_4N), 61.2, 58.6, 53.5 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1987s (ν_{CO}) and 1896s (ν_{CO}) [Found (Calc.): C, 39.91 (40.09); H, 3.86 (4.00); N, 8.72 (8.90)%].

[W{CC$_6$H$_4$(NCHC$_5$H$_4$N-2)-4}Cl(CO)$_2$(tmen)] 5a. The synthesis followed the procedure described for complex **4a**, whereby pyridine-2-carbaldehyde was used. Red-orange crystals. Yield: 43%, m.p. 115–120 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.72 (d, J = 4.52, 1 H, 2-C_5H_4N), 8.57 (s, 1 H, NCH), 8.17 (d, J = 7.81, 1 H, 2-C_5H_4N), 7.82 (dt, J = 7.76, 1.47, 1 H, 2-C_5H_4N), 7.39 (ddd, J = 7.51, 4.82, 1.22, 1 H, 2-C_5H_4N), 7.30 (d, J = 8.54, 2 H, C_6H_4NCH), 7.18 (d, J = 8.54 Hz, 2 H, C_6H_4NCH), 3.24 (s, 6 H, CH_3), 3.06–2.87 (br, 4 H, NCH_2) and 2.96 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 261.5 (W≡C), 221.0 (CO), 160.2 (NCH), 154.3, 149.8, 147.7, 136.8, 131.1, 130.5, 125.3, 122.2, 121.1, 114.0 (C_6H_4NCH, C_5H_4N), 61.0, 58.2, 53.5 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1985s (ν_{CO}) and 1894s (ν_{CO}) [Found (Calc.): C, 43.03 (43.13); H, 4.37 (4.31); N, 9.37 (9.58)%].

[W{CC$_6$H$_4$(NCHC$_5$H$_4$N-2)-4}Br(CO)$_2$(tmen)] 5b. Red-orange crystals. Yield: 0.274 g, 24%, m.p. 115–120 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.72 (d, J = 3.91, 1 H, 2-C_5H_4N), 8.57 (s, 1 H, NCH), 8.18 (d, J = 7.81, 1 H, 2-C_5H_4N), 7.82 (td, J = 7.69, 1.22, 1 H, 2-C_5H_4N), 7.39 (ddd, J = 7.39, 4.38, 1.22, 1 H, 2-C_5H_4N), 7.32 (d, J = 8.54, 2 H, C_6H_4NCH), 7.17 (d, J = 8.79 Hz, 2 H, C_6H_4NCH), 3.28 (s, 6 H, NCH_3), 3.06 (s, 6 H, NCH_3) and 2.96 (m, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 261.4 (W≡C), 220.4 (CO), 160.3 (NCH), 154.4, 149.8, 147.1, 136.8, 130.3, 125.3, 122.1, 121.1, 114.0 (C_6H_4NCH, C_5H_4N), 61.2, 58.5, 53.5 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1987s (ν_{CO}) and 1896s (ν_{CO}) [Found (Calc.): C, 39.78 (40.09); H, 3.70 (4.00); N, 8.64 (8.90)%].

[W(CC$_6$H$_4$NHCHO-4)Cl(CO)$_2$(tmen)] 6a. Complex **2a** (6 mmol, 2.974 g) was dissolved in thf (50 cm^3) and acetic formic anhydride (0.6 cm^3) was added at 0 °C. The resulting mixture was stirred at 0 °C for 15 min and the solvent then removed *in vacuo*. The residue was washed with anhydrous ether, dried and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford yellow-orange crystals. Yield: 2.86 g, 91%, m.p. 150–158 °C (decomp.). ^{1}H NMR ($CDCl_3$), two isomers: major isomer, δ 8.36 (d, J = 1.71, 1 H, NHC*H*O), 7.33 (br, 1 H, N*H*CHO), 7.44 (d, J = 8.55, 2 H, C_6H_4NH), 7.21 (d, J = 8.55, 2 H, C_6H_4NH); minor isomer, 8.67 (d, J = 11.47, 1 H, NHC*H*O), 7.55 (d, J = 11.23, 1 H, N*H*CHO), 7.23 (d, J = 8.30, 2 H, C_6H_4NH), 6.94 (d, J = 8.55 Hz, 2 H, C_6H_4NH), 3.21 (s, 6 H, NCH_3), 3.00–2.83 (br, 4 H, NCH_2) and 2.94 (s, 6 H, NCH_3). ^{13}C

NMR ($CDCl_3$), two isomers: major isomer, δ 261.6 (W≡C), 221.0 (CO), 158.8 (NHCHO), 145.7, 136.0, 130.3, 119.4 (C_6H_4NHCHO); minor isomer, 260.1 (W≡C), 220.8 (CO), 161.7 (NHCHO), 146.2, 135.5, 130.9, 118.0 (C_6H_4NHCHO), 61.0, 58.1, 52.5 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1985s (ν_{CO}), 1894s (ν_{CO}) and 1705m ($\nu_{C=O}$) [Found (Calc.) (with 0.25 mol CH_2Cl_2): C, 35.92 (35.82); H, 4.13 (4.16); C, 7.73 (7.71)%].

[W(CC$_6$H$_4$NHCHO-4)Br(CO)$_2$(tmen)] 6b. Orange-yellow crystals. Yield: 76%, m.p. 165–167 °C (decomp.). ^{1}H NMR ($CDCl_3$), two isomers: major isomer, δ 8.37 (d, J = 1.55, 1 H, NHC*H*O), 7.43 (d, J = 8.56, 2 H, C_6H_4NH), 7.25 (d, J = 8.73, 2 H, C_6H_4NH); minor isomer δ 8.69 (d, J = 11.36, 1 H, NHC*H*O), 7.56 (d, J = 9.61, 1 H, C_6H_4NH), 7.23 (d, J = 8.70, 2 H, C_6H_4NH), 6.93 (d, J = 8.51 Hz, 2 H, C_6H_4NH), 3.25 (s, 6 H, NCH_3), 3.04 (s, 6 H, NCH_3) and 2.94 [m, 4 H, CH_2N(CH$_3$)$_2$]. ^{13}C NMR ($CDCl_3$), two isomers: major isomer, δ 261.1 (W≡C), 220.3 (CO), 158.6 (C=O), 136.0, 130.1, 119.4 (C_6H_4NH); minor isomer, 259.8 (W≡C), 220.1 (CO), 161.5 (C=O), 135.5, 130.7, 118.0 (C_6H_4NH), 61.2, 58.5, 53.5 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1987s (ν_{CO}), 1896s (ν_{CO}) and 1707m ($\nu_{C=O}$) [Found (Calc.): C, 34.12 (33.83); H, 3.90 (3.90); N, 7.40 (7.40)%].

[W(CC$_6$H$_4$NHCHO-4)Cl(CO)$_2$(dppe)] 7a. Yellow crystals. Yield: 48%, m.p. 150–152 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.61 (d, J = 11.23 Hz, 1 H, major isomer NHC*H*O), 8.16 (s, 1 H, minor isomer NHC*H*O), 7.74–6.44 (25 H, PPh_2, C_6H_4NHCHO, N*H*CHO), 3.52–2.91 (m, 2 H, CH_2PPh$_2$) and 2.8–2.60 (m, 2 H, CH_2PPh$_2$). ^{13}C NMR ($CDCl_3$): δ 267.1 (W≡C), 212.6 (CO, major isomer, $^1J^{cis}_{PC}$ = 8, $^1J^{trans}_{PC}$ = 44), 212.4 (CO, minor isomer, $^1J^{cis}_{PC}$ = 8, $^1J^{trans}_{PC}$ = 45 Hz), 161.5 (NH*C*HO, major isomer), 158.8 (NH*C*HO, minor isomer), 146.2, 145.9, 145.6, 136.3, 136.1, 136.0, 135.8, 135.3, 135.2, 132.9, 132.8, 132.7, 132.5, 132.2, 132.1, 131.9, 131.5, 131.1, 130.8, 130.7, 130.5, 130.2, 129.2, 128.9, 128.6, 128.5, 128.2, 127.9, 118.5, 118.2, 116.8 (PPh_2, C_6H_4NHCHO), 27.5, 27.3, 27.1, 26.9 (CH_2PPh_2). ^{31}P NMR ($CDCl_3$): δ 38.9 ($^1J_{WP}$ = 230, major isomer) and 38.7 ($^1J_{WP}$ = 231 Hz, minor isomer). IR (CH_2Cl_2, cm^{-1}): 2006s (ν_{CO}), 1936s (ν_{CO}) and 1705m ($\nu_{C=O}$).

[W(CC$_6$H$_4$NHCOMe$_3$-4)Cl(CO)$_2$(tmen)] 8a. Complex **2a** (0.5 mmol, 0.248 g) was dissolved in thf (50 cm^3) and acetyl chloride (1 mmol, 0.07 cm^3) was added at 0 °C. The resulting mixture was stirred at 0 °C for 15 min and the solvent then removed *in vacuo*. The residue was washed with anhydrous ether, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford yellow-orange crystals. Yield: 0.207 g, 77%, m.p. 180–188 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.38 (d, J = 8.54, 2 H, C_6H_4NH), 7.23 (br, 1 H, NH), 7.20 (d, J = 8.54 Hz, 2 H, C_6H_4NH), 3.20 (s, 6 H, NCH_3), 3.04–2.86 (br, 4 H, NCH_2), 2.94 (s, 6 H, NCH_3) and 2.17 (s, 3 H, $COCH_3$). ^{13}C NMR ($CDCl_3$): δ 261.7 (W≡C), 221.0 (CO), 168.1 (NHCO), 136.9, 130.2, 119.1 (C_6H_4NH), 61.0, 58.1, 52.1 [$CH_2N(CH_3)_2$] and 24.7 (CO*C*H$_3$). IR (CH_2Cl_2, cm^{-1}): 1985s (ν_{CO}), 1892s (ν_{CO}) and 1697w ($\nu_{C=O}$) [Found (Calc.) (with 0.25 mol CH_2Cl_2): C, 37.09 (37.07); H, 4.27 (4.42); N, 7.57 (7.52)%].

[W(CC$_6$H$_4$NHCOPh-4)Cl(CO)$_2$(tmen)] 9a. The synthesis followed the procedure described for complex **8a**, whereby benzoyl chloride was used instead of acetyl chloride. Yellow-orange crystals. Yield: 67%, m.p. 195–199 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.78 (br, 1 H, NH), 7.88–7.24 (9 H, C_6H_4NH, Ph), 3.23 (s, 6 H, NCH_3), 3.06–2.88 (br, 4 H, NCH_2) and 2.95 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 261.5 (W≡C), 221.0 (CO), 165.4 (NHCO), 137.0, 134.7, 132.1, 130.3, 128.9, 127.0, 120.0 (C_6H_4NH, Ph), 61.0, 58.2, 52.2 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1985s (ν_{CO}), 1894s (ν_{CO}) and 1682w ($\nu_{C=O}$) [Found (Calc.): C, 43.77 (44.06); H, 4.29 (4.37); N, 6.98 (7.01)%].

[W{CC$_6$H$_4$NHCO(C$_5$H$_4$N-4)-4}Cl(CO)$_2$(tmen)] 10a. Complex **2a** (0.5 mmol, 0.248 g) was dissolved in thf (50 cm^3) and NEt_3 (1 cm^3) added. Then isonicotinoyl chloride hydrochloride (0.1 g) was added. The resulting mixture was stirred at 50 °C for 2 h, then filtered and the solvent removed *in vacuo*. The residue was washed with anhydrous ether, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford yellow-orange crystals. Yield: 0.1636 g, 54%, m.p. 170–175 °C (decomp.). ^{1}H NMR (CD_3CN): δ 8.92 (1 H, s, NHCO), 8.76 (d, J = 6.11, 2 H, C_5H_4N), 7.66 (d, J = 8.63, 2 H, C_6H_4NH), 7.32 (d, J = 8.53 Hz, 2 H, C_6H_4NH), 7.27 (d, J = 5.73, 2 H, C_5H_4N), 3.19 (s, 6 H, CH_3), 2.94 [m, 4 H, CH_2N(CH$_3$)$_2$] and 2.84 (s, 6 H, CH_3). ^{13}C NMR (CD_3CN): δ 263.4 (W≡C), 223.5 (CO), 165.0 (NHCO), 151.5, 150.6, 146.5, 142.9, 138.7, 131.1, 122.3, 120.9 (C_6H_4NH, C_5H_4N) 61.8, 58.6, 53.8 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1985s (ν_{CO}), 1894s (ν_{CO}) and 1686w ($\nu_{C=O}$) [Found (Calc.): C, 41.70 (41.99); H, 4.18 (4.20); N, 9.07 (9.33)%].

[W{CC$_6$H$_4$NHCO(C$_5$H$_4$N-4)-4}Br(CO)$_2$(tmen)] 10b. Yellow-orange crystals. Yield: 72%, m.p. 180–183 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.93 (s, 1 H, NHCO), 8.75 (d, J = 6.08, 2 H, C_5H_4N), 7.76 (d, J = 6.10, 2 H, C_5H_4N), 7.65 (d, J = 8.67, 2 H, C_6H_4NH), 7.34 (d, J = 8.68 Hz, 2 H, C_6H_4NH), 3.22 (s, 6 H, NCH_3), 3.01–2.90 (br, 4 H, NCH_2) and 2.96 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 263.7 (W≡C), 222.6 (CO, $^1J^{cis}_{WC}$ = 171 Hz), 164.9 (NHCO), 151.3, 145.7, 142.7, 138.7, 130.9, 130.8, 122.1, 120.8 (C_6H_4NHCO), 61.6, 58.7, 53.6 (CH_2NCH_3). IR (CH_2Cl_2, cm^{-1}): 1987s (ν_{CO}) and 1896s (ν_{CO}).

[W(CC$_6$H$_4$NC-4)Cl(CO)$_2$(tmen)] 11a. Complex **6a** (1 mmol, 0.524 g) was dissolved in CH_2Cl_2 (50 cm^3) and NEt_3 (0.56 cm^3) added. After cooling to −78 °C, a solution of triphosgene (0.2 g) in CH_2Cl_2 (10 cm^3) was added. The resulting mixture was allowed to warm up to 0 °C and was stirred at 0 °C for 30 min. The solvent was then removed *in vacuo*. The residue was washed with hexane, redissolved in thf (30 cm^3) and then filtered. The solvent was again removed *in vacuo*. The residue was redissolved in CH_2Cl_2. After filtration, hexane was added to the solution to afford red-orange crystals. Yield: 0.20 g, 40%, m.p. 80–86 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.17–7.25 (br, 4 H, C_6H_4NC), 3.21 (s, 6 H, NCH_3), 3.01–2.85 (br, 4 H, NCH_2) and 2.95 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 257.5 (W≡C), 220.5 (CO), 164.3 (NC), 149.6, 130.1, 126.3 (C_6H_4NC), 61.1, 58.2, 52.3 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 2124m (ν_{CN}), 1992s (ν_{CO}) and 1902s (ν_{CO}) [Found (Calc.) (with 0.5 mol CH_2Cl_2): C, 35.95 (36.16), H, 3.80 (3.86); N, 7.62 (7.67)%].

[W(CC$_6$H$_4$NC-4)Br(CO)$_2$(tmen)] 11b. Red-orange crystals. Yield: 54%, m.p. 95–100 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.26 (br, 4 H, C_6H_4NC), 3.25 (s, 6 H, NCH_3), 3.05 (s, 6 H, NCH_3) and 2.95 (m, 4 H, CH_2NMe$_2$). ^{13}C NMR ($CDCl_3$): δ 257.3 (W≡C), 219.7 (CO), 165.6 (NC), 149.1, 129.9, 126.3 (C_6H_4NC), 61.2, 58.6, 53.6 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 2124m (ν_{CN}), 1992s (ν_{CO}) and 1904s (ν_{CO}) [Found (Calc.) (with 0.25 mol CH_2Cl_2): C, 33.96 (34.16); H, 3.60 (3.62); N, 7.03 (7.36)%].

[W(CC$_6$H$_4$NC-4)Cl(CO)$_2$(dppe)] 12a. Yellow microcrystals. Yield 30%, m.p. 115–118 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.74–7.19 (20 H, PPh_2), 6.91 (d, J = 8.56, 2 H, C_6H_4NC), 6.39 (d, J = 8.48 Hz, 2 H, C_6H_4NC), 3.03–2.84 (m, 2 H, CH_2PPh$_2$) and 2.77–2.58 (m, 2 H, CH_2PPh$_2$). ^{13}C NMR ($CDCl_3$): δ 261.7 (W≡C), 212.0 (CO, $^1J^{cis}_{PC}$ = 7, $^1J^{trans}_{PC}$ = 46 Hz), 165.5 (N≡C), 149.7, 135.9, 133.0, 132.9, 132.5, 132.4, 130.4, 130.2, 128.7, 128.6, 128.5, 125.5 (PPh_2, C_6H_4NC), 27.5, 27.4, 27.2, 27.0 (CH_2PPh_2). ^{31}P NMR ($CDCl_3$): δ 38.2 ($^1J_{WP}$ = 230 Hz). IR (CH_2Cl_2, cm^{-1}): 2124w (ν_{CN}), 2010s (ν_{CO}) and 1944s (ν_{CO}) [Found (Calc.): C, 54.66 (54.88); H, 3.22 (3.58); N, 1.82 (1.78)%].

Table 2 Crystal data and collection parameters for complexes **3a**, **4b**, **8a**, **9a** and **10b**

	3a	**4b**	**8a**	**9a**	**10b**
Molecular formula	$C_{35}H_{30}ClNO_2P_2W\cdot CH_2Cl_2$	$C_{21}H_{25}BrN_4O_2W$	$C_{17}H_{24}ClN_3O_3W$	$C_{22}H_{26}ClN_3O_3W$	$C_{21}H_{25}BrN_4O_3W$
M	862.81	629.21	537.70	599.77	645.21
Crystal system	Monoclinic	Orthorhombic	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$ (no. 14)	$Pnma$ (no. 62)	$P2_1/n$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)
a/Å	19.851(2)	15.563(6)	11.756(4)	10.642(5)	10.680(3)
b/Å	9.089(3)	10.855(6)	12.972(5)	13.764(6)	13.549(4)
c/Å	21.874(2)	13.592(4)	14.510(4)	15.915(5)	16.015(4)
β/°	113.16(1)		112.17(2)	95.71(3)	95.73(2)
U/Å^3	3628.6(9)	2296(2)	2049(1)	2320(1)	2305.8(10)
Z	4	4	4	4	4
D_c/g cm^{-3}	1.579	1.820	1.743	1.717	1.858
μ/cm^{-1}	35.28	68.05	57.9	51.28	67.82
F(000)	1704	1216	1048	1176	1248
T/K	301	301	301	301	301
Crystal dimensions/mm	0.25 × 0.15 × 0.45	0.25 × 0.15 × 0.35	0.20 × 0.15 × 0.35	0.20 × 0.15 × 0.40	0.20 × 0.15 × 0.10
Diffractometer	Enraf-Nonius CAD4	Rigaku AFC7R	Rigaku AFC7R	Rigaku AFC7R	Mar IPDS
Total reflections measured	6288	2320	3548	3436	14 592
Unique reflections	6204	2320	3368	3237	4397
Reflections used	4409	1525	2722	2621	3210
Parameters	406	151	230	271	271
R	0.033	0.030	0.029	0.031	0.038
R'	0.041	0.034	0.036	0.046	0.047
Goodness of fit	2.51	1.67	2.13	2.50	1.63
(Δ/σ)	0.03	0.00	0.04	0.01	0.00
Maximum, minimum, peak in final Fourier map/e Å^{-3}	1.30, −0.66	0.79, −0.61	1.13, −1.29	0.98, −0.47	1.07, −2.38

Crystallography

Complex 3a. Enraf-Nonius CAD4 diffractometer with graphite-monochromatized Mo-Kα radiation (λ = 0.71 073 Å), ω–2θ scans, 6288 reflections measured ($2\theta_{max} = 48°$), 6204 independent, 4409 with $I > 3\sigma(I)$ considered observed. Structure solution by Patterson and Fourier methods (PATTY [14]) and refinement using the software package TEXSAN [15] on a Silicon Graphics Indy computer. One formula unit constitutes a crystallographic asymmetric unit. All 45 non-H atoms were refined anisotropically. Atoms H(1) and H(2) bonded to N were located in a Fourier-difference synthesis, and the other 30 H atoms placed at calculated positions with thermal parameters equal to 1.3 times that of the attached C atoms were not refined. Convergence for 406 parameters by full-matrix least-squares refinement on F with $w = 4F_o^2/\sigma^2(F_o^2)$, where $\sigma^2(F_o^2) = [\sigma^2(I) + (0.013F_o^2)^2]$ for 4409 reflections with $I > 3\sigma(I)$, was reached at $R = 0.033$ and $R' = 0.041$ with a goodness of fit of 2.51. $(\Delta/\sigma)_{max} = 0.03$. The final Fourier-difference map was featureless, with maximum positive and negative peaks of 1.30 and 0.66 e Å^{-3}, respectively.

The crystal structures of compounds **4b**, **8a**, **9a** and **10b** were solved by a similar procedure using other diffractometers. Details are given in Table 2. The thermal ellipsoids in the ORTEP [16] drawings of Figs. 1–5 are drawn at the 40% probability level.

CCDC reference number 186/804.

See http://www.rsc.org/suppdata/dt/1998/475/ for crystallographic files in .cif format.

Acknowledgements

Support for this work by the Committee on Research and Conference Grants (CRCG) is gratefully acknowledged. M. P. Y. Y. acknowledges the receipt of a Postgraduate Studentship, administered by The University of Hong Kong.

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Received 20*th October* 1997; *Paper* 7/07519G