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4-Iodobenzylidyne as a precursor ligand for extended unsaturated alkylidyne ligands

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The synthesis of the 4-iodobenzylidyne and 4-bromobenzylidyne tungsten complexes $[W(CC_6H_4Z\text{-}4)X(CO)_2(pic)_2]$ [Z = I; X = Cl, (**3a**), Z = I, X = Br (**3b**); Z = Br, X = Cl (**4a**)] was achieved by sequential reaction of $[W(CO)_6]$ with $Li[C_6H_4I\text{-}4]$ or $Li[C_6H_4Br\text{-}4]$ in diethyl ether and $C_2O_2Cl_2$ or $C_2O_2Br_2$ and 4-picoline (pic, 4-methylpyridine) in CH_2Cl_2. The chloro ligand in **3a** could be replaced by the iodo ligand to give **3c** (X = I) by reaction with NaI in THF. Substitution of the picoline ligands by *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and dppe afforded the complexes $[W(CC_6H_4Z\text{-}4)X(CO)_2(L_2)]$ [Z = I, L_2 = tmeda, X = Cl (**5a**), X = Br (**5b**), X = I (**5c**); Z = Br, L_2 = tmeda, X = Cl (**6a**); Z = I, L_2 = dppe, X = Cl (**7a**), X = Br (**7b**), X = I (**7c**)]. The iodo group of the new alkylidyne complexes underwent Pd^{II} catalyzed cross-coupling reactions effectively. Thus coupling of complexes **5a** with trimethylsilylacetylene, followed by hydrolysis, afforded the acetylide derivative $[W\{CC_6H_4(CCH\text{-}4)\}Cl(CO)_2(tmeda)]$, **8**. The alkynyl derivatives $[W\{CC_6H_4(CCC_6H_4Y)\text{-}4\}Cl(CO)_2(tmeda)]$ (Y = H **9**, CHO **10** or CN **11**) were obtained by reactions of complex **5a** with the respective aromatic acetylenes. The molecular structures of complexes **5a** and **10** have been determined by X-ray crystallography.

Molecular systems featuring strong electronic coupling between transition-metal centers and unsaturated organic systems are attracting increasing interest as potential components for molecular materials.[1] In this context, metal alkylidyne complexes[2] are of particular interest[3] since they contain one of the strongest metal–ligand π interactions, the metal–carbon triple bond. The development of metal alkylidyne complexes as functional components in molecular materials requires procedures for the synthesis of extended unsaturated alkylidyne ligands.[4] Currently available methods for the synthesis of alkylidyne metal complexes[2] are efficient as far as the synthesis of the metal–carbon triple bond[5] and the modification of the ancillary ligands are concerned,[6] but provide only limited direct access to functionalized unsaturated alkylidyne ligands, since they involve highly reactive intermediates or reagents which would interfere with the presence of a variety of functional groups.[7] It is therefore necessary to devise procedures which allow the elaboration of unsaturated alkylidyne ligands *after* formation of the metal–carbon triple bond. In pursuit of this goal, we have recently developed a route to tungsten complexes of the 4-aminobenzylidyne ligand, a versatile precursor for extended unsaturated alkylidyne ligands.[8] In a continuation of this effort, we present here tungsten complexes of the 4-iodobenzylidyne and 4-bromobenzylidyne ligands and demonstrate the convenient replacement of the iodo substituent by alkynyl groups *via* palladium-catalyzed cross-coupling reactions.

Results and Discussion

The synthesis of the 4-iodobenzylidyne and 4-bromobenzylidyne ligands follows established procedures.[5] In the first step, tungsten hexacarbonyl is allowed to react with (4-iodophenyl)lithium and (4-bromophenyl)lithium in diethyl ether to afford the anionic acyl complexes **1** and **2**, respectively, which are isolated as the tetramethylammonium salt[9] [equation (1)].

$$W(CO)_6 \xrightarrow[2.\ NMe_4Br,\ H_2O]{1.\ LiC_6H_4Z\text{-}4,\ Et_2O} [NMe_4][W\{C(O)C_6H_4Z\text{-}4\}(CO)_5] \quad (1)$$

1: Z = I
2: Z = Br

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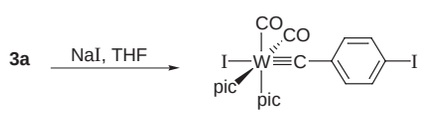
Complexes **1** and **2** are then treated sequentially in methylene chloride with oxalyl halide (either the chloride or bromide) and 4-picoline (4-methylpyridine, pic) to give the 4-picoline-stabilized *trans*-chloro- or *trans*-bromo-tungsten alkylidyne complexes **3a**, **3b** and **4a**, respectively[5] [equation (2)]. The *trans*-

(2)

3a: Z = I, X = Cl
3b: Z = I, X = Br
4a: Z = Br, X = Cl

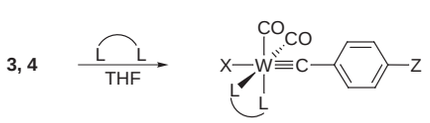
iodo-substituted analogue **3c** can be obtained from **3a** by treatment with NaI in THF[10] [equation (3)]. The 4-picoline



(3)

3c

ligands are easily replaced by the chelating ligands *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (tmeda) and 1,2-bis(diphenylphosphino)ethane (dppe) to give the complexes **5**, **6** and **7**, respectively [equation (4)]. Palladium-catalyzed cross-coupling



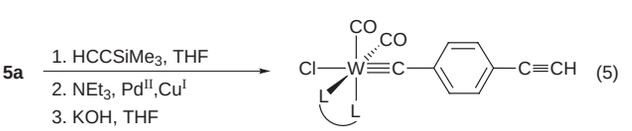
(4)

5a: Z = I, X = Cl, L_2 = tmeda
5b: Z = I, X = Br, L_2 = tmeda
5c: Z = I, X = I, L_2 = tmeda
6a: Z = Br, X = Cl, L_2 = tmeda
7a: Z = I, X = Cl, L_2 = dppe
7b: Z = I, X = Br, L_2 = dppe
7c: Z = I, X = I, L_2 = dppe

reactions[11] of the 4-iodobenzylidyne ligand were demonstrated for complex **5a**, but have not been successful for the bromo derivative **6a**. Thus the 4-ethynylbenzylidyne complex **8** can be obtained by cross-coupling of **5a** with trimethylsilylacetylene, followed by hydrolysis [equation (5)]. Cross-coupling of **5a** with

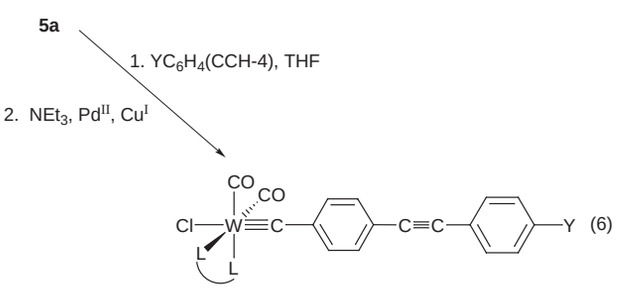
Table 1 Crystal data and collection parameters for complexes **5a** and **10**

Complex	**5a**	**10**
Molecular formula	$WIClO_2N_2C_{15}H_{20}$	$WClO_3N_2C_{24}H_{25}\cdot\frac{1}{2}CH_2Cl_2$
M	606.54	651.24
Crystal system	Triclinic	Monoclinic
Space group	$P\bar{1}$ (no. 2)	*C*2/*c* (no. 15)
a/Å	12.89(1)	38.685(4)
b/Å	14.11(2)	8.229(2)
c/Å	12.358(4)	17.228(2)
α/°	90.46(7)	
β/°	109.19(4)	106.43(2)
γ/°	68.0(1)	
U/Å^3	1951(3)	5260(1)
Z	4	8
μ/cm^{-1}	76.54	46.27
T/K	301	301
Crystal color	Orange	Orange
Crystal dimensions/mm	0.15 × 0.10 × 0.25	0.35 × 0.15 × 0.10
Total reflections measured	7992	5057
Unique reflections	7632	4987
Reflections > 3σ(*I*) used in analysis	5541	2768
R	0.035	0.028
R′	0.041	0.034



8: L_2 = tmeda

phenylacetylene as well as 4-ethynylbenzonitrile and 4-ethynylbenzaldehyde affords the complexes **9**–**11** containing functionalized extended unsaturated alkylidyne ligands [equation (6)].



9: Y = H, L_2 = tmeda
10: Y = CHO, L_2 = tmeda
11: Y = CN, L_2 = tmeda

The new alkylidyne tungsten complexes **3**–**11** exhibit two IR absorptions for the two carbonyl ligands. The carbonyl stretching frequencies of complexes **3** and **4** shift to slightly lower energies upon substitution of the 4-picoline ligands by tmeda and to higher energies by about 30 cm^{-1} upon substitution by dppe. A weak absorption at 2214 cm^{-1} was observed for the alkynyl group of complexes **10** and **11**. The substitution of the 4-iodo substituent of the benzylidyne ligand by the alkynyl groups has virtually no discernible influence on the stretching frequencies of the carbonyl ligands. The introduction of the alkynyl groups also exerts very little influence on the ^{13}C NMR resonance of the alkylidyne carbon atoms. The alkynyl groups of complexes **8**–**11** give rise to two characteristic ^{13}C NMR resonances in the range δ 79–94.

The molecular structures of complexes **5a** and **10** were determined by X-ray crystallography. The crystallographic information is summarized in Table 1. Selected bond distances and bond angles are listed in Table 2. Drawings of the molecular structures of **5a** and **10** are shown in Fig. 1(a) and 2(a). The molecules of **5a** and **10** differ only in the respective substituents at the 4 position of the benzylidyne ligands. The tungsten–carbon triple bond distance in both structures is about 1.80 Å, which is normal for tungsten alkylidyne complexes.[2] Thus neither the iodo nor the alkynyl substituent in the 4 position of the benzylidyne ligand exerts any discernible influence on the length of the metal–carbon triple bond. This result was expected, since several electronically more consequential transformations of the amino group in 4-aminobenzylidyne tungsten

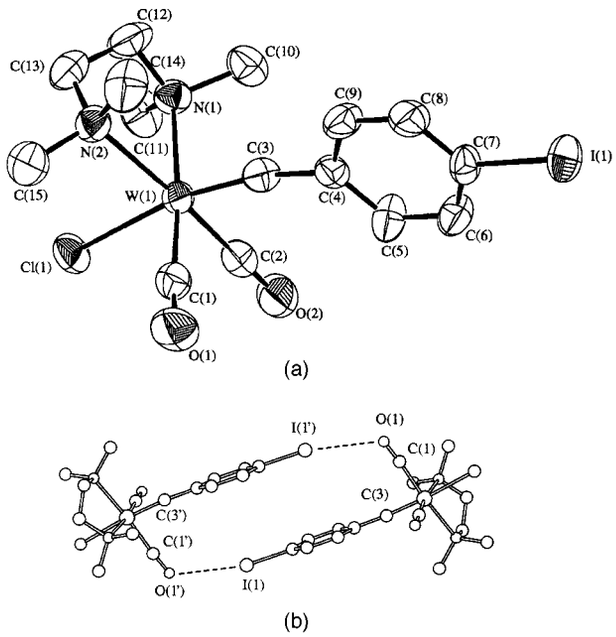


Fig. 1 (a) Molecular structure of complex **5a**. (b) Pairwise arrangement of two molecules 1 in the crystal structure of **5a**

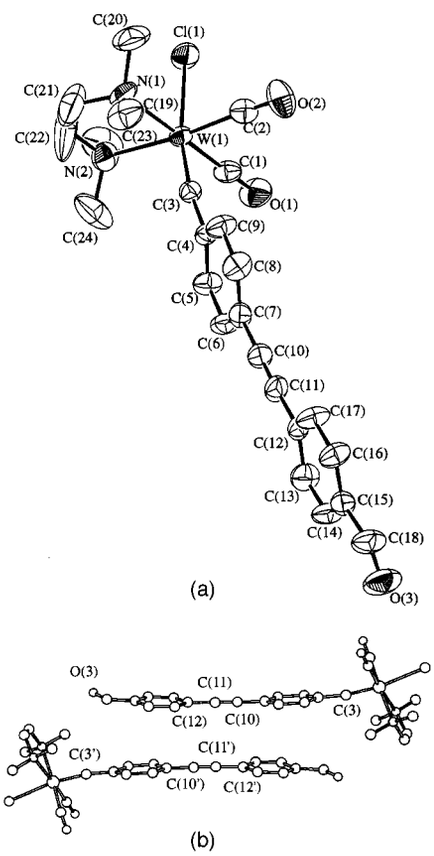


Fig. 2 (a) Molecular structure of complex **10**. (b) Pairwise arrangement of two molecules in the crystal structure of **10**

Table 2 Selected bond lengths (Å) and angles (°) for complexes **5a** and **10**

5a				**10**	
Molecule 1		Molecule 2			
W(1)–Cl(1)	2.536(2)	W(2)–Cl(2)	2.534(2)	W(1)–Cl(1)	2.583(2)
W(1)–N(2)	2.312(7)	W(2)–N(4)	2.300(7)	W(1)–N(2)	2.294(6)
W(1)–C(2)	1.94(1)	W(2)–C(17)	1.958(10)	W(1)–C(2)	1.982(9)
W(1)–N(1)	2.317(7)	W(2)–N(3)	2.320(7)	W(1)–N(1)	2.320(6)
W(1)–C(1)	1.990(10)	W(2)–C(16)	1.98(1)	W(1)–C(1)	1.994(8)
W(1)–C(3)	1.807(8)	W(2)–C(18)	1.818(8)	W(1)–C(3)	1.800(7)
I(1)–C(7)	2.088(7)	I(2)–C(22)	2.082(8)	Cl(2)–C(25)	1.64(1)
C(3)–C(4)	1.46(1)	C(18)–C(19)	1.45(1)	O(3)–C(18)	1.175(10)
C(4)–C(5)	1.38(1)	C(19)–C(20)	1.39(1)	C(3)–C(4)	1.454(9)
C(4)–C(9)	1.40(1)	C(19)–C(24)	1.39(1)	C(4)–C(5)	1.380(9)
C(5)–C(6)	1.39(1)	C(20)–C(21)	1.38(1)	C(4)–C(9)	1.400(10)
C(6)–C(7)	1.36(1)	C(21)–C(22)	1.38(1)	C(5)–C(6)	1.395(10)
C(7)–C(8)	1.38(1)	C(22)–C(23)	1.36(1)	C(6)–C(7)	1.38(1)
C(8)–C(9)	1.39(1)	C(23)–C(24)	1.38(1)	C(7)–C(8)	1.38(1)
				C(7)–C(10)	1.440(10)
				C(8)–C(9)	1.364(10)
				C(10)–C(11)	1.171(9)
				C(11)–C(12)	1.451(9)
				C(12)–C(13)	1.38(1)
				C(12)–C(17)	1.37(1)
				C(13)–C(14)	1.37(1)
				C(14)–C(15)	1.36(1)
				C(15)–C(16)	1.38(1)
				C(15)–C(18)	1.49(1)
				C(16)–C(17)	1.38(1)
Cl(1)–W(1)–N(1)	88.9(2)	Cl(2)–W(2)–N(3)	88.0(2)	Cl(1)–W(1)–N(1)	88.3(2)
Cl(1)–W(1)–N(2)	87.0(2)	Cl(2)–W(2)–N(4)	89.0(2)	Cl(1)–W(1)–N(2)	88.2(2)
Cl(1)–W(1)–C(1)	88.3(3)	Cl(2)–W(2)–C(16)	85.9(3)	Cl(1)–W(1)–C(1)	89.5(2)
Cl(1)–W(1)–C(2)	85.7(3)	Cl(2)–W(2)–C(17)	86.4(3)	Cl(1)–W(1)–C(2)	87.1(2)
Cl(1)–W(1)–C(3)	168.7(3)	Cl(2)–W(2)–C(18)	167.9(2)	Cl(1)–W(1)–C(3)	169.6(2)
N(1)–W(1)–N(2)	78.0(3)	N(3)–W(2)–N(4)	78.1(3)	N(1)–W(1)–N(2)	78.5(3)
N(1)–W(1)–C(1)	174.9(3)	N(3)–W(2)–C(16)	172.1(3)	N(1)–W(1)–C(1)	176.4(3)
N(1)–W(1)–C(2)	97.7(3)	N(3)–W(2)–C(17)	96.9(4)	N(1)–W(1)–C(2)	97.3(3)
N(1)–W(1)–C(3)	99.1(3)	N(3)–W(2)–C(18)	99.5(3)	N(1)–W(1)–C(3)	98.4(3)
N(2)–W(1)–C(1)	97.6(3)	N(4)–W(2)–C(16)	96.7(3)	N(2)–W(1)–C(1)	98.7(3)
N(2)–W(1)–C(2)	171.6(3)	N(4)–W(2)–C(17)	173.3(4)	N(2)–W(1)–C(2)	173.8(3)
N(2)–W(1)–C(3)	102.4(3)	N(4)–W(2)–C(18)	101.8(3)	N(2)–W(1)–C(3)	100.9(3)
C(1)–W(1)–C(2)	86.4(4)	C(16)–W(2)–C(17)	87.8(4)	C(1)–W(1)–C(2)	85.3(3)
C(1)–W(1)–C(3)	84.2(4)	C(16)–W(2)–C(18)	87.3(4)	C(1)–W(1)–C(3)	84.3(3)
C(2)–W(1)–C(3)	85.3(4)	C(17)–W(2)–C(18)	83.3(4)	C(2)–W(1)–C(3)	84.1(3)
W(1)–C(3)–C(4)	169.1(6)	W(2)–C(18)–C(19)	170.1(6)	W(1)–C(3)–C(4)	171.0(6)
				C(7)–C(10)–C(11)	179.9(9)
				C(10)–C(11)–C(12)	177.1(9)
				O(3)–C(18)–C(15)	125.6(9)

complexes failed to significantly affect the bond distances beyond the immediate vicinity of the amino group.[8] The structures of complexes **5a** and **10** exhibit some noteworthy deviations in the bond angles from the idealised geometry of octahedral alkylidyne metal complexes. The Cl(1)–W(1)–C(3) and the W(1)–C(3)–C(4) bond angles are smaller than 180° (by 9–12°) and the co-ordination angles between the carbonyl and alkylidyne ligands are, in part, significantly smaller than 90° (by up to 6°). These structural features are presumably the consequence of crystal packing forces. As special intermolecular interactions which may, at least in part, be responsible for these features, we were able to identify a short iodine–oxygen contact[12] in **5a**, [I(1)···O(1′) of molecule 1 3.381(8) Å] [no corresponding short contacts were found for I(2) of molecule 2] and short π–π contacts[13] in **10** [C(10)···C(11′) 3.67(1), C(10)···C(12′) 3.53(1), C(11)···C(11′) 3.47(1) Å]. These short intermolecular contacts are illustrated in Figs. 1(b) and 2(b).

The present work establishes the 4-iodobenzylidyne ligand as a precursor ligand for extended unsaturated alkylidyne ligands. The 4-iodobenzylidyne ligand performs well in palladium-catalyzed cross-coupling reactions with unsaturated organic substrates, making extended unsaturated alkylidyne ligands conveniently accessible. In conjunction with facile ligand substitution reactions on pyridine- and tmeda-substituted metal alkylidyne complexes, the present work provides a versatile basis for the design of functionalized unsaturated alkylidyne metal complexes.

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 under nitrogen. Tungsten hexacarbonyl, oxalyl chloride, oxalyl bromide, 4-picoline, tmeda, dppe, *p*-diiodobenzene, *p*-dibromobenzene, trimethylsilylacetylene and phenylacetylene were obtained from commercial sources and used as received. 4-Ethynylbenzaldehyde and 4-ethynylbenzonitrile were synthesized according to the reported procedure.[11d]

Proton, ^{13}C and ^{31}P NMR spectra were recorded on 270 MHz JEOL JNMGSX270 FT-NMR, 300 MHz BRUKER DPX300 FT-NMR and 500 MHz BRUKER DRX500 FT-NMR spectrometers. Chemical shifts of ^{1}H and ^{13}C spectra are given in

parts per million (δ) relative to tetramethylsilane, ^{31}P NMR spectra are referenced to 85% H_3PO_4 and are proton decoupled. Infrared spectra were recorded on a Shimadzu FTIR-8201PC spectrometer, melting points on a Stuart Scientific SMP1 instrument under nitrogen. Elemental analysis were performed by Butterworth Laboratories Ltd.

Preparations

[NMe_4][W{C(O)C_6H_4I-4}$(CO)_5$] 1. A solution of Li[C_6H_4I-4] was prepared first by the addition of $LiBu^n$ in hexane (0.95 equivalent, 1.6 M, 8.9 ml) to *p*-diiodobenzene (15 mmol, 4.95 g) in diethyl ether (50 ml) and stirred for 1 h at room temperature (r.t.). The resulting solution was transferred to a suspension of $W(CO)_6$ (12.8 mmol, 4.52 g) in ether (30 ml) at r.t., the solvent was removed *in vacuo* after stirring the mixture for 1 h. The solid residue was redissolved in degassed deionized water (100 ml). After filtration, NMe_4Br (2.8 g) in deionized water (20 ml) was added. The mixture was stirred at 0 °C for 5 min and the precipitate filtered off and dried *in vacuo*. The precipitate was dissolved in CH_2Cl_2 and dried with magnesium sulfate. After filtration hexane was added to the solution to afford red crystals. Yield: 58%, m.p. 160–165 °C (decomp.). ^{1}H NMR (CD_3CN): δ 7.70 (d, J = 8.54, 2 H, C_6H_4I), 7.17 (d, J = 8.30 Hz, 2 H, C_6H_4I), 3.07 (s, 12 H, NCH_3). ^{13}C NMR (CD_3CN): δ 278.5 (C=O), 208.6, 204.1 (C≡O), 157.5, 137.5, 128.1, 94.9 (C_6H_4I), 56.2 (NCH_3). IR (CH_2Cl_2, cm^{-1}): 2046w (ν_{CO}), 1952 (sh) (ν_{CO}), 1904s (br) (ν_{CO}) [Found (Calc.): C, 30.46 (30.55); H, 2.50 (2.56); N, 2.14 (2.23)%].

[NMe_4][W{C(O)C_6H_4Br-4}$(CO)_5$] 2. The synthesis for complex **2** followed the procedure described for **1**, whereby *p*-dibromobenzene and 1.1 equivalent $LiBu^n$ were used. Red crystals. Yield: 73%, m.p. 140–143 °C (decomp.). ^{1}H NMR (CD_3CN): δ 7.48 (d, J = 8.54, 2 H, C_6H_4Br), 7.32 (d, J = 8.54 Hz, 2 H, C_6H_4Br), 3.07 (s, 12 H, NCH_3). ^{13}C NMR (CD_3CN): δ 278.2 (C=O), 208.6, 204.1 (C≡O), 156.9, 132.3, 131.4, 128.0, 122.7 (C_6H_4Br). IR (CH_2Cl_2, cm^{-1}): 2048w (ν_{CO}), 1952 (sh) (ν_{CO}), 1904s (ν_{CO}) [Found (Calc.): C, 33.02 (33.02); H, 2.50 (2.77); N, 2.48 (2.41)%].

[W(CC_6H_4I-4)Cl$(CO)_2$(pic)$_2$] 3a. Complex **1** (2 mmol, 1.258 g) was dissolved in CH_2Cl_2 (60 ml) and the solution was cooled to −78 °C. Oxalyl chloride (2.02 mmol, 0.18 ml) in CH_2Cl_2 (10 ml) was added. The resulting solution was allowed to warm up to −20 °C and 4-picoline (2 ml) was added. The mixture was stirred at r.t. for 2 h, the solvent was 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-red crystals. Yield: 58%, m.p. 153–155 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.86 (d, J = 6.59, 4 H, C_5H_4N), 7.59 (d, J = 8.54, 2 H, C_6H_4I), 7.11 (d, J = 6.47, 4 H, C_5H_4N), 7.03 (d, J = 8.55 Hz, 2 H, C_6H_4I), 2.38 (s, 6 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 259.7 (W≡C), 220.7 (CO), 152.3, 150.4, 148.7, 137.0, 130.7, 126.0 (C_6H_4I, C_5H_4N), 21.2 (CH_3). IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1902s (ν_{CO}) [Found (Calc.): C, 37.34 (37.28); H, 2.85 (2.68); N, 4.17 (4.14)%].

[W(CC_6H_4I-4)Br$(CO)_2$(pic)$_2$] 3b. The synthesis for complex **3b** followed the procedure described for **3a**, whereby $C_2O_2Br_2$ was used instead of $C_2O_2Cl_2$. Red-orange crystals. Yield: 43%, m.p. 144–147 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.90 (d, J = 6.59, 4 H, C_5H_4N), 7.59 (d, J = 8.30, 2 H, C_6H_4I), 7.11 (d, J = 6.59, 4 H, C_5H_4N), 7.04 (d, J = 8.30 Hz, 2 H, C_6H_4I), 2.39 (s, 6 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 259.7 (W≡C), 220.0 (CO), 152.9, 150.3, 137.1, 130.5, 126.0, 93.1 (C_6H_4I, C_5H_4N), 21.2 (CH_3). IR (CH_2Cl_2, cm^{-1}): 1990s (ν_{CO}), 1904s (ν_{CO}) [Found (Calc.): C, 35.01 (34.89); H, 2.50 (2.52); N, 3.64 (3.89)%].

[W(CC_6H_4I-4)I$(CO)_2$(pic)$_2$] 3c. Complex **3a** (0.5 mmol, 0.3383 g) was dissolved in THF (30 ml), a few drops of 4-picoline and NaI (1 g) were added. The resulting mixture was stirred at 50 °C for 2 h. The solvent was then removed *in vacuo*. The residue was dissolved in CH_2Cl_2 and filtered. After filtration, hexane was added to the filtrate to afford red-orange microcrystals. Yield: 0.272 g, 71%, m.p. 138–140 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.97 (d, J = 6.6, 2 H, C_5H_4N), 7.58 (d, J = 8.30, 2 H, C_6H_4I), 7.11 (d, J = 6.35, 2 H, C_5H_4N), 7.06 (d, J = 8.30 Hz, 2 H, C_6H_4I), 2.39 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 259.6 (W≡C), 218.9 (CO), 154.0, 150.2, 147.5, 137.1, 130.3, 126.0, 93.3 (C_6H_4I, C_5H_4N), 21.2 (CH_3). IR (CH_2Cl_2, cm^{-1}): 1990s (ν_{CO}), 1904s (ν_{CO}) [Found (Calc.): C, 33.22 (32.84); H, 2.18 (2.36); N, 3.76 (3.65)%].

[W(CC_6H_4Br-4)Cl$(CO)_2$(pic)$_2$] 4a. The synthesis for complex **4a** followed the procedure described for **3a**, whereby complex **2** was used. Orange-red crystals. Yield: 71%, m.p. 150–153 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 8.87 (d, J = 6.59, 4 H, C_5H_4N), 7.38 (d, J = 8.54, 2 H, C_6H_4Br), 7.17 (d, J = 8.30, 2 H, C_6H_4Br), 7.11 (d, J = 6.59 Hz, 4 H, C_5H_4N), 2.38 (s, 6 H, CH_3). ^{13}C NMR ($CDCl_3$): δ 259.7 (W≡C), 220.7 (CO), 152.3, 150.4, 148.2, 131.1, 130.6, 123.0, 121.4 (C_6H_4Br, C_5H_4N), 21.2 (CH_3). IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1902s (ν_{CO}) [Found (Calc.) (with 0.25 mol hexane): C, 40.94 (41.60); H, 3.25 (3.03); N, 4.26 (4.32)%].

[W(CC_6H_4I-4)Cl$(CO)_2$(tmeda)] 5a. Complex **3a** (1 mmol, 0.677 g) was dissolved in THF (40 ml), and tmeda (1 ml) was added. The resulting mixture was stirred at 50 °C for 2 h, the solvent was then removed *in vacuo*. The residue was washed with hexane, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the filtrate to afford orange crystals. Yield: 85%, m.p. 170–175 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.58 (d, J = 8.55, 2 H, C_6H_4I), 6.95 (d, J = 8.54, 2 H, C_6H_4I), 3.20 (s, 6 H, NCH_3), 2.95–2.85 (br, 4 H, NCH_2), 2.94 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 259.5 (W≡C), 220.7 (CO), 148.2, 137.1, 130.7, 93.1 (C_6H_4I), 61.0, 58.2, 52.2 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.): C, 29.93 (29.70); H, 3.30 (3.32); N, 4.58 (4.62)%].

[W(CC_6H_4I-4)Br$(CO)_2$(tmeda)] 5b. The synthesis of complex **5b** used the procedure given for **5a** but starting from **3b**. Yellow-orange microcrystals. Yield: 57%, m.p. 180–183 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.58 (d, J = 8.35, 2 H, C_6H_4I), 6.97 (d, J = 8.35 Hz, 2 H, C_6H_4I), 3.24 (d, 6 H, NCH_3), 3.04 (s, 6 H, NCH_3), 2.96–2.92 (m, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 259.4 (W≡C), 220.0 (CO), 147.6, 137.1, 130.5, 93.3 (C_6H_4I), 61.2, 58.5, 53.6 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1990s (ν_{CO}), 1900s (ν_{CO}) [Found (Calc.): C, 27.98 (27.68); H, 3.03 (3.10); N, 4.27 (4.30)%].

[W(CC_6H_4I-4)I$(CO)_2$(tmeda)] 5c. The synthesis of complex **5c** used the procedure given for **5a** but starting from **3c**. Orange-yellow microcrystals. Yield: 70%, m.p. 190–193 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.57 (d, J = 8.55, 2 H, C_6H_4I), 7.00 (d, J = 8.55 Hz, 2 H, C_6H_4I), 3.29 (s, 6 H, NCH_3), 3.22 (s, 6 H, NCH_3), 2.98–2.97 (br, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 259.5 (W≡C), 218.8 (CO), 146.8, 137.3, 130.3, 93.5 (C_6H_4I), 61.5, 58.8, 56.4 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1902s (ν_{CO}) [Found (Calc.): C, 25.90 (25.81); H, 2.64 (2.89); N, 3.99 (4.01)%].

[W(CC_6H_4Br-4)Cl$(CO)_2$(tmeda)] 6a. Red-orange crystals. Yield: 82%, m.p. 198–201 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.36 (d, J = 8.30, 2 H, C_6H_4Br), 7.08 (d, J = 8.30 Hz, 2 H, C_6H_4Br), 3.20 (s, 6 H, NCH_3), 2.96–2.87 (br, 4 H, NCH_2), 2.94 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 259.4 (W≡C), 220.7 (CO), 147.7, 131.2, 130.6, 121.5 (C_6H_4Br), 61.0, 58.2, 52.2 [$CH_2N(CH_3)_2$]. IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.): C, 32.53 (32.20); H, 3.23 (3.60); N, 5.18 (5.01)%].

[W(CC_6H_4I-4)Cl$(CO)_2$(dppe)] 7a. Complex **3a** (1 mmol,

0.667 g) was dissolved in THF (40 ml) and dppe (1.05 mmol, 0.418 g) was added. The resulting mixture was stirred at 50 °C for 2 h, the solvent was then removed *in vacuo*. The residue was washed with hexane, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the filtrate to afford yellow crystals. Yield: 0.59 g, 66%, m.p. 165–168 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.74–7.19 (m, 22 H, PPh_2, C_6H_4I), 6.17 (d, J = 8.37 Hz, 2 H, C_6H_4I), 2.99–2.82 (m, 2 H, CH_2PPh$_2$), 2.73–2.56 (m, 2 H, CH_2PPh$_2$). ^{13}C NMR ($CDCl_3$): δ 264.1 (W≡C), 212.2 (CO, $^1J^{trans}_{PC}$ = 46 Hz), 148.3, 136.4, 135.89, 135.3, 133.0, 132.9, 132.8, 132.6, 132.5, 132.1, 130.8, 130.3, 130.1, 128.6, 128.5, 128.4, 93.2 (PPh_2, C_6H_4I), 27.5, 27.4, 27.2, 27.0 (*C*H$_2$PPh$_2$). ^{31}P NMR ($CDCl_3$): δ 38.5 ($^1J_{WP}$ = 231 Hz). IR (CH_2Cl_2, cm^{-1}): 2008s (ν_{CO}), 1940s (ν_{CO}) [Found (Calc.): C, 47.33 (47.30); H, 3.10 (3.18); N, <0.3 (0)%].

[W(CC$_6$H$_4$I-4)Br(CO)$_2$(dppe)] 7b. As for **7a** but from **3b**, yellow microcrystals. Yield: 69%, m.p. 175–178 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.73–7.20 (22 H, PPh_2, C_6H_4I), 6.32 (d, J = 8.34 Hz, 2 H, C_6H_4I), 3.12–2.92 (m, 2 H, CH_2PPh$_2$), 2.73–2.54 (m, 2 H, CH_2PPh$_2$). ^{13}C NMR ($CDCl_3$): δ 263.6 (W≡C), 211.0 (CO, $^1J^{cis}_{PC}$ = 8, $^1J^{trans}_{PC}$ = 44 Hz), 148.0, 136.5, 136.0, 135.3, 132.9, 132.8, 132.7, 132.6, 132.3, 130.7, 130.0, 128.6, 128.5, 128.4, 93.4 (PPh_2, C_6H_4I), 27.5, 27.4, 27.1, 27.0 (*C*H$_2$PPh$_2$). ^{31}P NMR ($CDCl_3$): δ 35.9 ($^1J_{WP}$ = 231 Hz). IR (CH_2Cl_2, cm^{-1}): 2010s (ν_{CO}), 1942s (ν_{CO}) [Found (Calc.): C, 45.49 (45.05); H, 2.89 (3.02); N, <0.3 (0)%].

[W(CC$_6$H$_4$I-4)I(CO)$_2$(dppe)] 7c. As for **7a** but from **3c**, yellow microcrystals. Yield: 89%, m.p. 185–188 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.72–7.17 (m, 22 H, PPh_2, C_6H_4I), 6.46 (d, J = 8.30 Hz, 2 H, C_6H_4I), 3.16–2.99 (m, 2 H, CH_2PPh$_2$), 2.74–2.56 (m, 2 H, CH_2PPh$_2$). ^{13}C NMR ($CDCl_3$): δ 262.3 (W≡C), 208.9 (CO, $^1J^{cis}_{PC}$ = 8, $^1J^{trans}_{PC}$ = 41 Hz), 147.5, 136.7, 135.9, 135.3, 134.1, 133.4, 132.8, 132.7, 132.6, 132.5, 132.4, 130.5, 130.2, 128.5, 128.4, 128.3, 93.6 (PPh_2, C_6H_4I), 27.8, 27.6, 27.4, 27.2 (*C*H$_2$PPh$_2$). ^{31}P NMR ($CDCl_3$): δ 30.0 ($^1J_{WP}$ = 230 Hz). IR (CH_2Cl_2, cm^{-1}): 2006s (ν_{CO}), 1940s (ν_{CO}) [Found (Calc.): C, 43.16 (42.89); H, 2.51 (2.88); N, <0.3 (0)%].

[W{CC$_6$H$_4$(CCH-4)}Cl(CO)$_2$(tmeda)] 8. Complex **5a** (1 mmol, 0.607 g) was dissolved in THF (40 ml) and NEt_3 (1 ml) was added. To this solution $HCCSiMe_3$ (40% excess, 0.2 ml), *cis*-[$PdCl_2(PPh_3)_2$] (10 mg) and CuI (20 mg) were added. The resulting mixture was stirred at 50 °C for 3 h, the solvent was then removed *in vacuo*. The residue was redissolved in THF (40 ml), KOH powder (0.4 g) was added and the solution stirred at r.t. for 4 h. The solution was then filtered, and the solvent was removed *in vacuo*. The residue was washed with hexane, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the filtrate to afford red-orange crystals. Yield: 0.278 g, 55%, m.p. 125–129 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.35 (d, J = 8.30, 2 H, C_6H_4CCH), 7.16 (d, J = 8.55 Hz, 2 H, C_6H_4-CCH), 3.21 (s, 6 H, NCH_3), 3.19 (s, 1 H, CCH), 3.00–2.83 (br, 4 H, NCH_2), 2.95 (s, 6 H, NCH_3). ^{13}C NMR ($CDCl_3$): δ 260.2 (W≡C), 220.8 (CO), 149.1, 131.8, 129.2, 120.8 (C_6H_4), 83.7 (*C*CH, $^1J_{CH}$ = 49), 79.2 (C*C*H, $^1J_{CH}$ = 252 Hz), 61.6, 58.3, 52.3 [*C*H$_2$N(*C*H$_3$)$_2$]. IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.): C, 40.85 (40.46); H, 4.00 (4.19); N, 5.46 (5.55)%].

[W{CC$_6$H$_4$(CCPh)-4}Cl(CO)$_2$(tmdea)] 9. Complex **5a** (0.5 mmol, 0.303 g) was dissolved in THF (30 ml) and NEt_3 (1 ml) was added. To this solution $HCCC_6H_5$ (20% excess, 78 mg), *cis*-$PdCl_2(PPh_3)_2$ (10 mg) and CuI (20 mg) were added. The resulting mixture was stirred at r.t. overnight. The solvent was removed *in vacuo*. The residue was washed with hexane, dried, and redissolved in CH_2Cl_2. After filtration, hexane was added to the filtrate to afford red-orange crystals. Yield: 76%, m.p. 165–168 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.53–7.51 (m, 2 H, C_6H_5), 7.38 (d, J = 8.19, 2 H, C_6H_4C), 7.36–7.25 (m, 3 H, C_6H_5), 7.20 (d, J = 8.15 Hz, 2 H, C_6H_4C), 3.22 (s, 6 H, NCH_3), 2.95 (s, 6 H, NCH_3), 2.94–2.89 (br, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 260.7 (W≡C, $^1J_{WC}$ = 199), 220.9 (CO, $^1J_{WC}$ = 174 Hz), 148.5, 131.5, 131.2, 129.2, 128.4, 123.1, 122.0 (C_6H_4C, C_6H_5), 91.6, 89.5 (C≡C), 61.0, 58.2, 52.2 [*C*H$_2$N(*C*H$_3$)$_2$]. IR (CH_2Cl_2, cm^{-1}): 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.): C, 47.34 (47.57); H, 4.08 (4.34); N, 4.96 (4.82)%].

[W{CC$_6$H$_4$(CCC$_6$H$_4$CHO-4}Cl(CO)$_2$(tmeda)] 10. The synthesis of complex **10** followed the procedure described for **9**, whereby 4-ethynylbenzaldehyde was used. Orange crystals. Yield: 76%, m.p. 175–180 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 10.02 (s, 1 H, CHO), 7.86 (d, J = 8.52, 2 H, C_6H_4CHO), 7.66 (d, J = 8.24, 2 H, C_6H_4CHO), 7.41 (d, J = 8.52, 2 H, C_6H_4C), 7.22 (d, J = 8.51 Hz, 2 H, C_6H_4C), 3.23 (s, 6 H, NCH_3), 2.96 (s, 6 H, NCH_3), 2.95–2.92 (br, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 260.1 (W≡C), 220.8 (CO), 191.4 (CHO), 149.1, 135.4, 132.0, 131.4, 129.6, 121.0 (C_6H_4C, C_6H_4CHO), 93.6, 90.6 (C≡C), 61.1, 58.2, 52.2 [*C*H$_2$N(*C*H$_3$)$_2$]. IR (CH_2Cl_2, cm^{-1}): 2214w ($\nu_{C\equiv C}$), 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.) (with 0.25 mol CH_2Cl_2): C, 45.76 (46.23); H, 3.66 (4.08); N, 4.29 (4.45)%].

[W{CC$_6$H$_4$(CCC$_6$H$_4$CN-4)}Cl(CO)$_2$(tmeda)] 11. The synthesis of complex **11** followed the procedure described for **9**, whereby 4-ethynylbenzonitrile was used. Red-orange crystals. Yield: 56%, m.p. 160–163 °C (decomp.). ^{1}H NMR ($CDCl_3$): δ 7.64 (d, J = 8.52, 2 H, C_6H_4CN), 7.59 (d, J = 8.51, 2 H, C_6H_4CN), 7.40 (d, J = 8.52, 2 H, C_6H_4C), 7.21 (d, J = 8.52 Hz, 2 H, C_6H_4C), 3.23 (s, 6 H, NCH_3), 2.96 (s, 6 H, NCH_3), 2.95–2.91 (br, 4 H, NCH_2). ^{13}C NMR ($CDCl_3$): δ 259.8 (W≡C), 220.7 (CO), 149.3, 132.1, 131.4, 129.3, 128.1, 120.7, 118.5, 111.5 (C_6H_4C, C_6H_4CN), 93.9, 89.8 (C≡C), 61.1, 58.2, 52.3 [*C*H$_2$N-(*C*H$_3$)$_2$]. IR (CH_2Cl_2, cm^{-1}): 2214w ($\nu_{C\equiv C}$), 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.) (with 0.25 mol CH_2Cl_2): 46.03 (46.45); H, 3.62 (3.94); N, 6.43 (6.70)%].

Crystallography

Details of the structure analyses for complexes **5a** and **10** are given in Table 1. The thermal ellipsoids in the ORTEP[14] drawings of Figs. 1 and 2 are drawn at the 40% probability level.

CCDC reference number 186/1020.

See http://www.rsc.org/suppdata/dt/1998/2373/ for crystallographic files in .cif format.

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