

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

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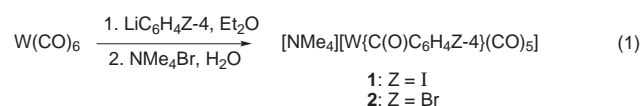
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The synthesis of the 4-iodobenzylidyne and 4-bromobenzylidyne tungsten complexes $[W(CC_6H_4Z-4)X(CO)_2(pic)_2]$ [$Z = I$; $X = Cl$, (**3a**), $Z = I$, $X = Br$ (**3b**); $Z = Br$, $X = Cl$ (**4a**)] was achieved by sequential reaction of $[W(CO)_6]$ with $Li[C_6H_4I-4]$ or $Li[C_6H_4Br-4]$ 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 $[W(CC_6H_4Z-4)X(CO)_2(L_2)]$ [$Z = I$, $L_2 = tmeda$, $X = Cl$ (**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 $[W\{CC_6H_4(CCH-4)\}-Cl(CO)_2(tmeda)]$, **8**. The alkynyl derivatives $[W\{CC_6H_4(CCC_6H_4Y-4)\}Cl(CO)_2(tmeda)]$ ($Y = H$ **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 complexes² are of particular interest³ 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 complexes² are efficient as far as the synthesis of the metal–carbon triple bond⁵ 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.

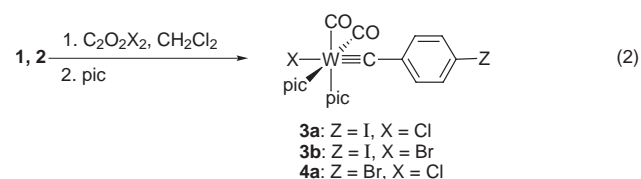
Results and Discussion

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 salt⁹ [equation (1)].

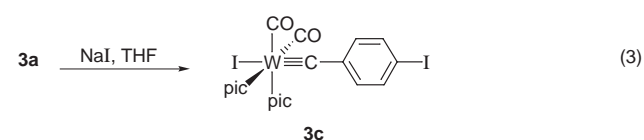


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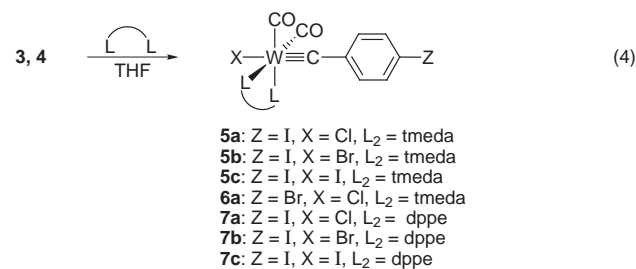
Complexes **1** and **2** are then treated sequentially in methylene chloride with oxalyl halide (either the chloride or bromide) and 4-picoline (4-methylpyridine, pic) to give the 4-picoline-stabilized *trans*-chloro- or *trans*-bromo-tungsten alkylidyne complexes **3a**, **3b** and **4a**, respectively⁵ [equation (2)]. The *trans*-



iodo-substituted analogue **3c** can be obtained from **3a** by treatment with NaI in THF¹⁰ [equation (3)]. The 4-picoline



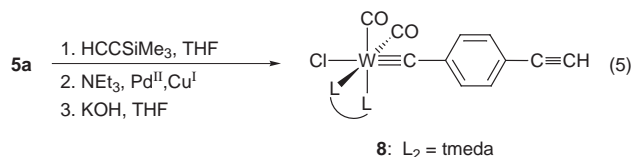
ligands are easily replaced by the chelating ligands *N,N,N',N'*-tetramethylethylenediamine (tmeda) and 1,2-bis(diphenylphosphino)ethane (dppe) to give the complexes **5**, **6** and **7**, respectively [equation (4)]. Palladium-catalyzed cross-coupling



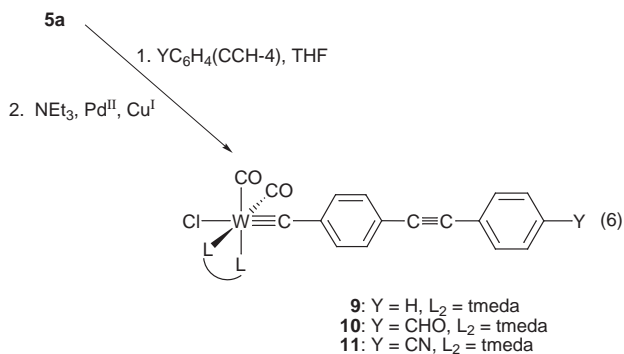
reactions¹¹ of the 4-iodobenzylidyne ligand were demonstrated for complex **5a**, but have not been successful for the bromo derivative **6a**. Thus the 4-ethynylbenzylidyne complex **8** can be obtained by cross-coupling of **5a** with trimethylsilylacetylene, followed by hydrolysis [equation (5)]. Cross-coupling of **5a** with

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

Complex	5a	10
Molecular formula	WClO ₂ N ₂ C ₁₅ H ₂₀	WClO ₃ N ₂ C ₂₄ H ₂₅ ^{1/2} CH ₂ Cl ₂
<i>M</i>	606.54	651.24
Crystal system	Triclinic	Monoclinic
Space group	<i>P</i> $\bar{1}$ (no. 2)	<i>C</i> 2/ <i>c</i> (no. 15)
<i>a</i> /Å	12.89(1)	38.685(4)
<i>b</i> /Å	14.11(2)	8.229(2)
<i>c</i> /Å	12.358(4)	17.228(2)
α /°	90.46(7)	
β /°	109.19(4)	106.43(2)
γ /°	68.0(1)	
<i>U</i> /Å ³	1951(3)	5260(1)
<i>Z</i>	4	8
μ /cm ⁻¹	76.54	46.27
<i>T</i> /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 > 3 σ (<i>I</i>) used in analysis	5541	2768
<i>R</i>	0.035	0.028
<i>R</i> '	0.041	0.034



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



The new alkyldiene 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 alkyne group of complexes **10** and **11**. The substitution of the 4-iodo substituent of the benzylidene ligand by the alkyne groups has virtually no discernible influence on the stretching frequencies of the carbonyl ligands. The introduction of the alkyne groups also exerts very little influence on the ¹³C NMR resonance of the alkyldiene carbon atoms. The alkyne groups of complexes **8–11** give rise to two characteristic ¹³C 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 molecu-

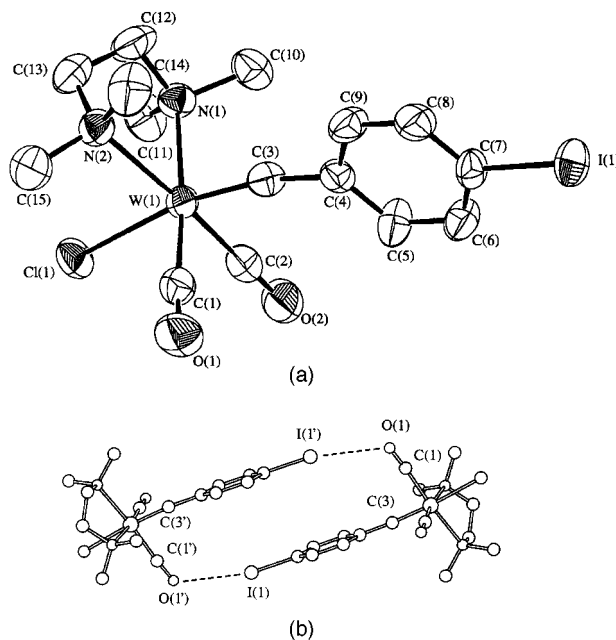


Fig. 1 (a) Molecular structure of complex **5a**. (b) Pairwise arrangement of two molecules **1** in the crystal structure of **5a**

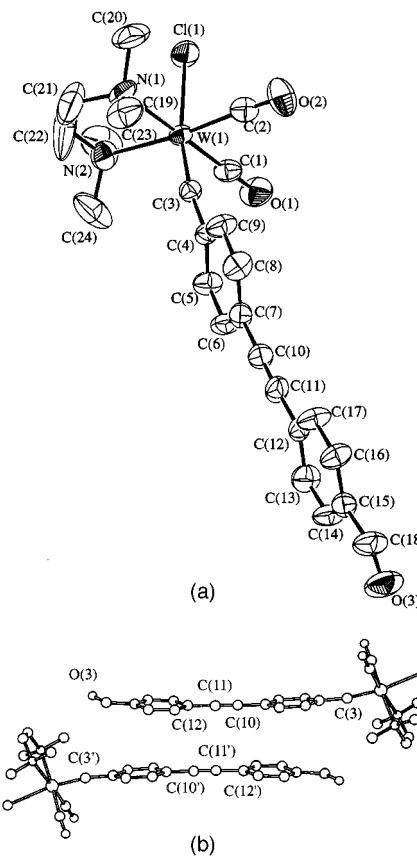


Fig. 2 (a) Molecular structure of complex **10**. (b) Pairwise arrangement of two molecules in the crystal structure of **10**

lar 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 benzylidene ligands. The tungsten–carbon triple bond distance in both structures is about 1.80 Å, which is normal for tungsten alkyldiene complexes.² Thus neither the iodo nor the alkyne substituent in the 4 position of the benzylidene 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-aminobenzylidene tungsten

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

5a					
Molecule 1		Molecule 2		10	
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 alkylidene 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 alkylidene 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 contact¹² 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 contacts¹³ 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-iodobenzylidene ligand as a precursor ligand for extended unsaturated alkylidene ligands. The 4-iodobenzylidene ligand performs well in palladium-catalyzed cross-coupling reactions with unsaturated organic substrates, making extended unsaturated alkylidene ligands

conveniently accessible. In conjunction with facile ligand substitution reactions on pyridine- and tmeda-substituted metal alkylidene complexes, the present work provides a versatile basis for the design of functionalized unsaturated alkylidene 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-ethynylbenzotrile were synthesized according to the reported procedure.^{11d}

Proton, ¹³C and ³¹P 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 ¹H and ¹³C 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

[NMe₄][W₄(CO)₆(C₆H₄I-4)(CO)₅] 1. A solution of Li[C₆H₄I-4] was prepared first by the addition of LiBuⁿ 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, NMe₄Br (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 CH₂Cl₂ 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.). ^1H NMR (CD₃CN): δ 7.70 (d, J = 8.54, 2 H, C₆H₄I), 7.17 (d, J = 8.30 Hz, 2 H, C₆H₄I), 3.07 (s, 12 H, NCH₃). ^{13}C NMR (CD₃CN): δ 278.5 (C=O), 208.6, 204.1 (C \equiv O), 157.5, 137.5, 128.1, 94.9 (C₆H₄I), 56.2 (NCH₃). IR (CH₂Cl₂, cm⁻¹): 2046w (v_{CO}), 1952 (sh) (v_{CO}), 1904s (br) (v_{CO}) [Found (Calc.): C, 30.46 (30.55); H, 2.50 (2.56); N, 2.14 (2.23)%].

[NMe₄][W₄(CO)₆(C₆H₄Br-4)(CO)₅] 2. The synthesis for complex 2 followed the procedure described for 1, whereby *p*-dibromobenzene and 1.1 equivalent LiBuⁿ were used. Red crystals. Yield: 73%, m.p. 140–143 °C (decomp.). ^1H NMR (CD₃CN): δ 7.48 (d, J = 8.54, 2 H, C₆H₄Br), 7.32 (d, J = 8.54 Hz, 2 H, C₆H₄Br), 3.07 (s, 12 H, NCH₃). ^{13}C NMR (CD₃CN): δ 278.2 (C=O), 208.6, 204.1 (C \equiv O), 156.9, 132.3, 131.4, 128.0, 122.7 (C₆H₄Br). IR (CH₂Cl₂, cm⁻¹): 2048w (v_{CO}), 1952 (sh) (v_{CO}), 1904s (v_{CO}) [Found (Calc.): C, 33.02 (33.02); H, 2.50 (2.77); N, 2.48 (2.41)%].

[W(CC₆H₄I-4)Cl(CO)₂(pic)₂] 3a. Complex 1 (2 mmol, 1.258 g) was dissolved in CH₂Cl₂ (60 ml) and the solution was cooled to -78 °C. Oxalyl chloride (2.02 mmol, 0.18 ml) in CH₂Cl₂ (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 CH₂Cl₂. After filtration, hexane was added to the solution to afford orange-red crystals. Yield: 58%, m.p. 153–155 °C (decomp.). ^1H NMR (CDCl₃): δ 8.86 (d, J = 6.59, 4 H, C₅H₄N), 7.59 (d, J = 8.54, 2 H, C₆H₄I), 7.11 (d, J = 6.47, 4 H, C₅H₄N), 7.03 (d, J = 8.55 Hz, 2 H, C₆H₄I), 2.38 (s, 6 H, CH₃). ^{13}C NMR (CDCl₃): δ 259.7 (W \equiv C), 220.7 (CO), 152.3, 150.4, 148.7, 137.0, 130.7, 126.0 (C₆H₄I, C₅H₄N), 21.2 (CH₃). IR (CH₂Cl₂, cm⁻¹): 1989s (v_{CO}), 1902s (v_{CO}) [Found (Calc.): C, 37.34 (37.28); H, 2.85 (2.68); N, 4.17 (4.14)%].

[W(CC₆H₄I-4)Br(CO)₂(pic)₂] 3b. The synthesis for complex 3b followed the procedure described for 3a, whereby C₂O₂Br₂ was used instead of C₂O₂Cl₂. Red-orange crystals. Yield: 43%, m.p. 144–147 °C (decomp.). ^1H NMR (CDCl₃): δ 8.90 (d, J = 6.59, 4 H, C₅H₄N), 7.59 (d, J = 8.30, 2 H, C₆H₄I), 7.11 (d, J = 6.59, 4 H, C₅H₄N), 7.04 (d, J = 8.30 Hz, 2 H, C₆H₄I), 2.39 (s, 6 H, CH₃). ^{13}C NMR (CDCl₃): δ 259.7 (W \equiv C), 220.0 (CO), 152.9, 150.3, 137.1, 130.5, 126.0, 93.1 (C₆H₄I, C₅H₄N), 21.2 (CH₃). IR (CH₂Cl₂, cm⁻¹): 1990s (v_{CO}), 1904s (v_{CO}) [Found (Calc.): C, 35.01 (34.89); H, 2.50 (2.52); N, 3.64 (3.89)%].

[W(CC₆H₄I-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 CH₂Cl₂ 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.). ^1H NMR (CDCl₃): δ 8.97 (d, J = 6.6, 2 H, C₅H₄N), 7.58 (d, J = 8.30, 2 H, C₆H₄I), 7.11 (d, J = 6.35, 2 H, C₅H₄N), 7.06 (d, J = 8.30 Hz, 2 H, C₆H₄I), 2.39 (s, 6 H, NCH₃). ^{13}C NMR (CDCl₃): δ 259.6 (W \equiv C), 218.9 (CO), 154.0, 150.2, 147.5, 137.1, 130.3, 126.0, 93.3 (C₆H₄I, C₅H₄N), 21.2 (CH₃). IR (CH₂Cl₂, cm⁻¹): 1990s (v_{CO}), 1904s (v_{CO}) [Found (Calc.): C, 33.22 (32.84); H, 2.18 (2.36); N, 3.76 (3.65)%].

[W(CC₆H₄Br-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.). ^1H NMR (CDCl₃): δ 8.87 (d, J = 6.59, 4 H, C₅H₄N), 7.38 (d, J = 8.54, 2 H, C₆H₄Br), 7.17 (d, J = 8.30, 2 H, C₆H₄Br), 7.11 (d, J = 6.59 Hz, 4 H, C₅H₄N), 2.38 (s, 6 H, CH₃). ^{13}C NMR (CDCl₃): δ 259.7 (W \equiv C), 220.7 (CO), 152.3, 150.4, 148.2, 131.1, 130.6, 123.0, 121.4 (C₆H₄Br, C₅H₄N), 21.2 (CH₃). IR (CH₂Cl₂, cm⁻¹): 1989s (v_{CO}), 1902s (v_{CO}) [Found (Calc.) (with 0.25 mol hexane): C, 40.94 (41.60); H, 3.25 (3.03); N, 4.26 (4.32)%].

[W(CC₆H₄I-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 CH₂Cl₂. After filtration, hexane was added to the filtrate to afford orange crystals. Yield: 85%, m.p. 170–175 °C (decomp.). ^1H NMR (CDCl₃): δ 7.58 (d, J = 8.55, 2 H, C₆H₄I), 6.95 (d, J = 8.54, 2 H, C₆H₄I), 3.20 (s, 6 H, NCH₃), 2.95–2.85 (br, 4 H, NCH₂), 2.94 (s, 6 H, NCH₃). ^{13}C NMR (CDCl₃): δ 259.5 (W \equiv C), 220.7 (CO), 148.2, 137.1, 130.7, 93.1 (C₆H₄I), 61.0, 58.2, 52.2 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, cm⁻¹): 1989s (v_{CO}), 1898s (v_{CO}) [Found (Calc.): C, 29.93 (29.70); H, 3.30 (3.32); N, 4.58 (4.62)%].

[W(CC₆H₄I-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.). ^1H NMR (CDCl₃): δ 7.58 (d, J = 8.35, 2 H, C₆H₄I), 6.97 (d, J = 8.35 Hz, 2 H, C₆H₄I), 3.24 (d, 6 H, NCH₃), 3.04 (s, 6 H, NCH₃), 2.96–2.92 (m, 4 H, NCH₂). ^{13}C NMR (CDCl₃): δ 259.4 (W \equiv C), 220.0 (CO), 147.6, 137.1, 130.5, 93.3 (C₆H₄I), 61.2, 58.5, 53.6 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, cm⁻¹): 1990s (v_{CO}), 1900s (v_{CO}) [Found (Calc.): C, 27.98 (27.68); H, 3.03 (3.10); N, 4.27 (4.30)%].

[W(CC₆H₄I-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.). ^1H NMR (CDCl₃): δ 7.57 (d, J = 8.55, 2 H, C₆H₄I), 7.00 (d, J = 8.55 Hz, 2 H, C₆H₄I), 3.29 (s, 6 H, NCH₃), 3.22 (s, 6 H, NCH₃), 2.98–2.97 (br, 4 H, NCH₂). ^{13}C NMR (CDCl₃): δ 259.5 (W \equiv C), 218.8 (CO), 146.8, 137.3, 130.3, 93.5 (C₆H₄I), 61.5, 58.8, 56.4 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, cm⁻¹): 1989s (v_{CO}), 1902s (v_{CO}) [Found (Calc.): C, 25.90 (25.81); H, 2.64 (2.89); N, 3.99 (4.01)%].

[W(CC₆H₄Br-4)Cl(CO)₂(tmeda)] 6a. Red-orange crystals. Yield: 82%, m.p. 198–201 °C (decomp.). ^1H NMR (CDCl₃): δ 7.36 (d, J = 8.30, 2 H, C₆H₄Br), 7.08 (d, J = 8.30 Hz, 2 H, C₆H₄Br), 3.20 (s, 6 H, NCH₃), 2.96–2.87 (br, 4 H, NCH₂), 2.94 (s, 6 H, NCH₃). ^{13}C NMR (CDCl₃): δ 259.4 (W \equiv C), 220.7 (CO), 147.7, 131.2, 130.6, 121.5 (C₆H₄Br), 61.0, 58.2, 52.2 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, cm⁻¹): 1989s (v_{CO}), 1898s (v_{CO}) [Found (Calc.): C, 32.53 (32.20); H, 3.23 (3.60); N, 5.18 (5.01)%].

[W(CC₆H₄I-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 CH₂Cl₂. After filtration, hexane was added to the filtrate to afford yellow crystals. Yield: 0.59 g, 66%, m.p. 165–168 °C (decomp.). ¹H NMR (CDCl₃): δ 7.74–7.19 (m, 22 H, PPh₂, C₆H₄I), 6.17 (d, *J* = 8.37 Hz, 2 H, C₆H₄I), 2.99–2.82 (m, 2 H, CH₂PPh₂), 2.73–2.56 (m, 2 H, CH₂PPh₂). ¹³C NMR (CDCl₃): δ 264.1 (W=C), 212.2 (CO, ¹*J*_{PC}^{trans} = 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 (PPh₂, C₆H₄I), 27.5, 27.4, 27.2, 27.0 (CH₂PPh₂). ³¹P NMR (CDCl₃): δ 38.5 (¹*J*_{WP} = 231 Hz). IR (CH₂Cl₂, 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{CC₆H₄I-4}Br(CO)₂(dppe)] 7b. As for **7a** but from **3b**, yellow microcrystals. Yield: 69%, m.p. 175–178 °C (decomp.). ¹H NMR (CDCl₃): δ 7.73–7.20 (22 H, PPh₂, C₆H₄I), 6.32 (d, *J* = 8.34 Hz, 2 H, C₆H₄I), 3.12–2.92 (m, 2 H, CH₂PPh₂), 2.73–2.54 (m, 2 H, CH₂PPh₂). ¹³C NMR (CDCl₃): δ 263.6 (W=C), 211.0 (CO, ¹*J*_{PC}^{cis} = 8, ¹*J*_{PC}^{trans} = 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 (PPh₂, C₆H₄I), 27.5, 27.4, 27.1, 27.0 (CH₂PPh₂). ³¹P NMR (CDCl₃): δ 35.9 (¹*J*_{WP} = 231 Hz). IR (CH₂Cl₂, 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{CC₆H₄I-4}(CO)₂(dppe)] 7c. As for **7a** but from **3c**, yellow microcrystals. Yield: 89%, m.p. 185–188 °C (decomp.). ¹H NMR (CDCl₃): δ 7.72–7.17 (m, 22 H, PPh₂, C₆H₄I), 6.46 (d, *J* = 8.30 Hz, 2 H, C₆H₄I), 3.16–2.99 (m, 2 H, CH₂PPh₂), 2.74–2.56 (m, 2 H, CH₂PPh₂). ¹³C NMR (CDCl₃): δ 262.3 (W=C), 208.9 (CO, ¹*J*_{PC}^{cis} = 8, ¹*J*_{PC}^{trans} = 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 (PPh₂, C₆H₄I), 27.8, 27.6, 27.4, 27.2 (CH₂PPh₂). ³¹P NMR (CDCl₃): δ 30.0 (¹*J*_{WP} = 230 Hz). IR (CH₂Cl₂, 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{CC₆H₄(CCH-4)}Cl(CO)₂(tmdea)] 8. Complex **5a** (1 mmol, 0.607 g) was dissolved in THF (40 ml) and NEt₃ (1 ml) was added. To this solution HCCSiMe₃ (40% excess, 0.2 ml), *cis*-[PdCl₂(PPh₃)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 CH₂Cl₂. After filtration, hexane was added to the filtrate to afford red-orange crystals. Yield: 0.278 g, 55%, m.p. 125–129 °C (decomp.). ¹H NMR (CDCl₃): δ 7.35 (d, *J* = 8.30, 2 H, C₆H₄CCH), 7.16 (d, *J* = 8.55 Hz, 2 H, C₆H₄CCH), 3.21 (s, 6 H, NCH₃), 3.19 (s, 1 H, CCH), 3.00–2.83 (br, 4 H, NCH₂), 2.95 (s, 6 H, NCH₃). ¹³C NMR (CDCl₃): δ 260.2 (W=C), 220.8 (CO), 149.1, 131.8, 129.2, 120.8 (C₆H₄), 83.7 (CCH, ¹*J*_{CH} = 49), 79.2 (CCH, ¹*J*_{CH} = 252 Hz), 61.6, 58.3, 52.3 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, 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{CC₆H₄(CCPh-4)}Cl(CO)₂(tmdea)] 9. Complex **5a** (0.5 mmol, 0.303 g) was dissolved in THF (30 ml) and NEt₃ (1 ml) was added. To this solution HCCC₆H₅ (20% excess, 78 mg), *cis*-PdCl₂(PPh₃)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 CH₂Cl₂. After filtration, hexane was added to the filtrate to afford red-orange crystals. Yield: 76%, m.p. 165–168 °C (decomp.). ¹H NMR (CDCl₃): δ 7.53–7.51 (m, 2 H,

C₆H₅), 7.38 (d, *J* = 8.19, 2 H, C₆H₄C), 7.36–7.25 (m, 3 H, C₆H₅), 7.20 (d, *J* = 8.15 Hz, 2 H, C₆H₄C), 3.22 (s, 6 H, NCH₃), 2.95 (s, 6 H, NCH₃), 2.94–2.89 (br, 4 H, NCH₂). ¹³C NMR (CDCl₃): δ 260.7 (W=C, ¹*J*_{WC} = 199), 220.9 (CO, ¹*J*_{WC} = 174 Hz), 148.5, 131.5, 131.2, 129.2, 128.4, 123.1, 122.0 (C₆H₄C, C₆H₅), 91.6, 89.5 (C≡C), 61.0, 58.2, 52.2 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, 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{CC₆H₄(CCC₆H₄CHO-4)}Cl(CO)₂(tmdea)] 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.). ¹H NMR (CDCl₃): δ 10.02 (s, 1 H, CHO), 7.86 (d, *J* = 8.52, 2 H, C₆H₄CHO), 7.66 (d, *J* = 8.24, 2 H, C₆H₄CHO), 7.41 (d, *J* = 8.52, 2 H, C₆H₄C), 7.22 (d, *J* = 8.51 Hz, 2 H, C₆H₄C), 3.23 (s, 6 H, NCH₃), 2.96 (s, 6 H, NCH₃), 2.95–2.92 (br, 4 H, NCH₂). ¹³C NMR (CDCl₃): δ 260.1 (W=C), 220.8 (CO), 191.4 (CHO), 149.1, 135.4, 132.0, 131.4, 129.6, 121.0 (C₆H₄C, C₆H₄CHO), 93.6, 90.6 (C≡C), 61.1, 58.2, 52.2 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, cm⁻¹): 2214w (ν_{C≡C}), 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.) (with 0.25 mol CH₂Cl₂): C, 45.76 (46.23); H, 3.66 (4.08); N, 4.29 (4.45)%].

[W{CC₆H₄(CCC₆H₄CN-4)}Cl(CO)₂(tmdea)] 11. The synthesis of complex **11** followed the procedure described for **9**, whereby 4-ethynylbenzotrile was used. Red-orange crystals. Yield: 56%, m.p. 160–163 °C (decomp.). ¹H NMR (CDCl₃): δ 7.64 (d, *J* = 8.52, 2 H, C₆H₄CN), 7.59 (d, *J* = 8.51, 2 H, C₆H₄CN), 7.40 (d, *J* = 8.52, 2 H, C₆H₄C), 7.21 (d, *J* = 8.52 Hz, 2 H, C₆H₄C), 3.23 (s, 6 H, NCH₃), 2.96 (s, 6 H, NCH₃), 2.95–2.91 (br, 4 H, NCH₂). ¹³C NMR (CDCl₃): δ 259.8 (W=C), 220.7 (CO), 149.3, 132.1, 131.4, 129.3, 128.1, 120.7, 118.5, 111.5 (C₆H₄C, C₆H₄CN), 93.9, 89.8 (C≡C), 61.1, 58.2, 52.3 [CH₂N(CH₃)₂]. IR (CH₂Cl₂, cm⁻¹): 2214w (ν_{C≡C}), 1989s (ν_{CO}), 1898s (ν_{CO}) [Found (Calc.) (with 0.25 mol CH₂Cl₂): 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 ORTEP¹⁴ 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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References

- W. Beck, B. Niemer and M. Wieser, *Angew. Chem.*, 1993, **105**, 969; *Angew. Chem., Int. Ed. Engl.*, 1993, **33**, 547; H. Lang, *Angew. Chem.*, 1994, **106**, 569; *Angew. Chem., Int. Ed. Engl.*, 1994, **32**, 547; M. B. Sponsler, *Organometallics*, 1995, **14**, 1920; G. Jia, W. F. Wu, R. C. Y. Yeung and H. P. Xia, *J. Organomet. Chem.*, 1997, **539**, 53 and refs. therein.
- E. O. Fischer, *Angew. Chem.*, 1974, **86**, 651; E. O. Fischer, *Adv. Organomet. Chem.*, 1976, **14**, 1; E. O. Fischer and U. Schubert, *J. Organomet. Chem.*, 1975, **100**, 59; R. R. Schrock, *Acc. Chem. Res.*, 1986, **19**, 342; M. A. Gallop and W. R. Roper, *Adv. Organomet. Chem.*, 1986, **25**, 121; H. P. Kim and R. J. Angelici, *Adv. Organomet. Chem.*, 1987, **27**, 51; H. Fischer, P. Hofmann, F. R. Kreissl, R. R. Schrock, U. Schubert and K. Weiss, in *Carbyne Complexes*, VCH Publishers, Weinheim, Germany, 1988; F. G. A. Stone, *Adv. Organomet. Chem.*, 1991, **31**, 53; A. Mayr and H. Hoffmeister, *Adv. Organomet. Chem.*, 1991, **32**, 227; P. F. Engel and M. Pfeiffer, *Chem. Rev.*, 1995, **95**, 2281; A. Mayr and S. Ahn, *Adv. Transition Met. Coord. Chem.*, 1996, **1**, 1; L. McElwee-White, *Synlett.*, 1996, 806.

- 3 T. P. Pollagi, S. J. Geib and M. D. Hopkins, *J. Am. Chem. Soc.*, 1994, **116**, 6051; T. P. Pollagi, J. Manna, S. J. Geib and M. D. Hopkins, *Inorg. Chim. Acta*, 1996, **243**, 177; H. A. Brison, T. A. Pollagi, T. C. Stoner, S. J. Geib and M. D. Hopkins, *Chem. Commun.*, 1997, 1263.
- 4 J. R. Fernandez and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 1988, 3035; S. A. Krouse and R. R. Schrock, *J. Organomet. Chem.*, 1988, **355**, 257; S. J. Davies, A. F. Hill, M. U. Pilotti and F. G. A. Stone, *Polyhedron*, 1989, **8**, 2265; S. A. Krouse and R. R. Schrock, *Macromolecules*, 1989, **22**, 2569; M. H. Chisholm, J. C. Huffman and J. A. Klang, *Polyhedron*, 1990, **9**, 1271; T. M. Gilbert and R. D. Rogers, *J. Organomet. Chem.*, 1991, **421**, C1; W. Weng, J. A. Ramsden, A. M. Arif and J. A. Gladysz, *J. Am. Chem. Soc.*, 1993, **115**, 3824; S. Anderson and A. F. Hill, *J. Chem. Soc., Dalton Trans.*, 1993, 587; B. E. Woodworth and J. L. Templeton, *J. Am. Chem. Soc.*, 1996, **118**, 7418; B. E. Woodworth, P. S. White and J. L. Templeton, *J. Am. Chem. Soc.*, 1997, **119**, 828; S. B. Falloon, W. Weng, A. M. Arif and J. A. Gladysz, *Organometallics*, 1997, **16**, 2008.
- 5 A. Mayr, G. A. McDermott and A. M. Dorries, *Organometallics*, 1985, **3**, 608; A. Mayr, A. M. Dorries, G. A. McDermott and D. Van Engen, *Organometallics*, 1986, **5**, 1504.
- 6 E. O. Fischer, A. Ruhs, F. R. Kreissl, *Chem. Ber.*, 1977, **110**, 805; A. Mayr, M. F. Asaro, M. A. Kjelsberg, K. S. Lee and D. Van Engen, *Organometallics*, 1987, **6**, 432; G. A. McDermott, A. M. Dorries and A. Mayr, *Organometallics*, 1987, **6**, 925; P. Steil and A. Mayr, *Z. Naturforsch. Teil B*, 1992, **47**, 656; A. C. Filippou, D. Wössner, G. Kociok-Köhn, I. Hinz and L. Gruber, *J. Organomet. Chem.*, 1997, **532**, 207.
- 7 E. O. Fischer and G. Kreis, *Chem. Ber.*, 1976, **109**, 1673; H. Fischer and E. O. Fischer, *J. Organomet. Chem.*, 1974, **69**, C1; M. L. Listemann and R. R. Schrock, *Organometallics*, 1985, **4**, 74; S. Anderson and A. F. Hill, *J. Organomet. Chem.*, 1993, **463**, C3; D. S. Williams and R. R. Schrock, *Organometallics*, 1994, **13**, 2101; M. A. Stevenson and M. D. Hopkins, *Organometallics*, 1997, **16**, 3572.
- 8 M. P. Y. Yu, A. Mayr and K.-K. Cheung, *J. Chem. Soc., Dalton Trans.*, 1998, 475.
- 9 E. O. Fischer and A. Maasböl, *Chem. Ber.*, 1967, **100**, 2445.
- 10 E. O. Fischer, T. L. Lindner, F. R. Kreissl and P. Braunstein, *Chem. Ber.*, 1977, **110**, 3139.
- 11 (a) K. Sonogashira, Y. Tohda and N. Hagihara, *Tetrahedron Lett.*, 1975, 4467; (b) L. Cassar, *J. Organomet. Chem.*, 1975, **93**, 253; (c) H. A. Dieck and R. F. Heck, *J. Organomet. Chem.*, 1975, **93**, 259; (d) S. Takahashi, Y. Kuroyama, K. Sonogashira and N. Hagihara, *Synthesis*, 1980, 627.
- 12 P. Murray-Rust and W. D. S. Motherwell, *J. Am. Chem. Soc.*, 1979, **101**, 5525.
- 13 G. R. Desiraju and A. Gavezzotti, *J. Chem. Soc., Chem. Commun.*, 1989, 621.
- 14 C. K. Johnson, ORTEP, Report ORNL-5138, Oak Ridge National Laboratory, Oak Ridge, TN, 1976.

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