REACTION OF THE ALKYLIDYNE COMPLEX [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] WITH PHPh$_2$. SYNTHESIS AND X-RAY STRUCTURES OF THE COMPLEXES [W(CHRPPh$_2$)(CO)$_2$(η-C$_5$H$_5$)] AND [W(CHRCOOPPh$_2$)(PHPh$_2$)(CO)(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4)

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Summary

Treatment of [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4) with PHPh$_2$ gives the complexes [W(CHRPPh$_2$)(CO)$_2$(η-C$_5$H$_5$)] and [W(CHRCOOPPh$_2$)(PHPh$_2$)-(CO)(η-C$_5$H$_5$)], which have been structurally characterised by X-ray diffraction. The former complex may be more conveniently synthesised via treatment of [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] with LiPPh$_2$ followed by addition of NH$_4$Br. The reaction of [W(CHRPPh$_2$)(CO)$_2$(η-C$_5$H$_5$)] with HCl (Et$_2$O) or HBF$_4$ · Et$_2$O (NCMe) gives the "piano-stool" complexes [WCl(PPh$_2$CH$_2$R)(CO)$_2$(η-C$_5$H$_5$)] and [W(NCMe)(PPh$_2$CH$_2$R)(CO)$_2$(η-C$_5$H$_5$)][BF$_4$], respectively.

Introduction

Transition metal alkylidyne complexes such as [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4) are susceptible to nucleophilic attack [1]. Thus treatment of [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] with phosphine ligands affords η^1 or η^2 ketenyl derivatives [2] whilst reaction with [WH(CO)$_5$]$^-$ gives the anionic μ-alkylidene complex [W$_2$(μ-CHR)(CO)$_7$(η-C$_5$H$_5$)]$^-$, a process which involves formal 1,2-addition of W–H to the W≡C triple bond [3]. In order to extend the range of such reactions we have studied the related reactions of [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] with PHPh$_2$ and LiPPh$_2$.

Results and discussion

The tungsten alkylidyne complex [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] undergoes facile reactions with tertiary phosphine ligands giving η^1 or η^2-ketenyl derivatives [2]. In

TABLE 1

ANALYTICAL AND OTHER DATA

Compound	M.p. (°C) [a]	Found (calcd.) (%)			$\nu_{max}(CO)$ (cm^{-1}) [b]
		C	H	N	
[W(CHC$_6$H$_4$Me-4,PPh$_2$)(CO)$_2$(μ-C$_5$H$_5$)] (I)	172	54.7 (54.6)	4.0 (3.9)		1930s, 1845s
[W(CHC$_6$H$_4$Me-4COOPPh$_2$)(PHPh$_2$)(CO)(η-C$_5$H$_5$)] [c] (II)	178	57.9 (58.8)	4.3 (4.3)		1797s, 1724s,br
[WCl(PPh$_2$CH$_2$C$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$) (III)	170	50.3 (51.4)	3.9 (3.8)		1953vs, 1862s
[W(NCMe)(PPh$_2$CH$_2$C$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)][BF$_4$] [d] (IV)	120	47.2 (48.2)	3.9 (3.8)	1.9 (1.9)	1979vs, 1887s

[a] Melts with decomposition. [b] In CH$_2$Cl$_2$ solution. [c] ν(PH) at 2319 cm^{-1}. [d] ν(CN) at 2284vw and ν(BF) at 1025–1086br (Nujol).

TABLE 2

NMR DATA[a]

Compound	$\delta(^1\text{H})$ [b]	$\delta(^{31}\text{P})$ [c]
I	2.13 (s, 3H, Me-4), 3.14 (s, 1H, CH), 5.15 (s, 5H, C_5H_5), 6.68 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8], 7.39 (m,br,10H, C_6H_5).	-31.4 [J(WP) 198].
II	2.62 (s, 3H, Me-4), 3.80 [dd, 1H, CH, J(PH) $\cong J$(P'H) 4], 4.96 (s, 5H, C_5H_5), 5.71 [d, 1H, PHPh$_2$, J(PH) 353], 6.61[(AB)$_2$, 4H, C_6H_4, J(AB) 8], 7.0–7.9 (m, 20H, C_6H_5).	31.5 (d, PHPh$_2$, J(WP) 310), 117.0 (d, Ph$_2$PO, J(WP) 307.8, J(PP) 24.4).
III	2.29, 2.31 (s, 3H, Me-4), 3.82, 3.95 [ABX, 2H, CH$_2$, J(AB) 13, J(AX)±9.6, J(BX)±12.2], 5.24 [d, 5H, C_5H_5 (trans isomer), J(PH) 2.2], 5.26 [s, 5H, C_5H_5 (cis isomer)], 6.82 [br, (AB)$_2$, 4H, C_6H_4, J(AB) 8], 7.44 (m,br, 10H, C_6H_5).	21.1 (s, cis isomer, J(WP) 266), 16.5 (s, trans isomer, J(WP) 266).
IV	2.01, 2.05 (s,br, 3H, MeCN), 2.23, 2.25 (s, 3H, Me-4), 4.13 [br,d, 2H, CH$_2$, J(PH) 10], 5.57 (s, 5H, C_5H_5), $\cong$ 6.87 [2×(AB)$_2$, 4H, C_6H_4, J(AB) 7], 7.5–7.7 (m,br, 10H, C_6H_5).	15.3 [J(WP) 244].

[a] Chemical shifts (δ) in ppm, coupling constants in Hz. [b] Measured in CDCl$_3$, ref. TMS. [c] Proton decoupled in CDCl$_3$, measured to high frequency of external 85% H$_3$PO$_4$.

TABLE 3

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR [$\overline{W(CHRPPh_2)}(CO)_2(\eta\text{-}C_5H_5)$] (I)

W–P	2.378(2)	W–C(1)	1.95(1)	W–C(2)	1.96(1)
W–C(10)	2.333(9)	P–C(10)	1.75(1)	P–C(21)	1.805(6)
P–C(3)	1.822(7)	C(1)–O(1)	1.17(1)	C(2)–O(2)	1.16(1)
C(10)–C(11)	1.54(1)	C(10)–H(1)	0.96(12)		
P–W–C(1)	84.9(3)	P–W–C(2)	102.4(3)	C(1)–W–C(2)	78.6(4)
P–W–C(10)	43.5(2)	C(1)–W–C(10)	120.9(4)	C(2)–W–C(10)	85.8(4)
W–P–C(10)	66.9(3)	W–P–C(21)	120.6(2)	C(10)–P–C(21)	112.5(4)
W–P–C(31)	127.4(2)	C(10)–P–C(31)	117.6(4)	W–C(1)–O(1)	177.1(9)
W–C(2)–O(2)	175.8(9)	W–C(10)–P	69.6(3)	W–C(10)–C(11)	127.9(7)
W–C(10)–H(1)	108(7)	P–C(10)–H(1)	109(7)	C(11)–C(10)–H(1)	112(7)

contrast [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] does not react with the secondary phosphine $PHPh_2$ at room temperature, but under more vigorous conditions (toluene, 111°C) a chromatographically separable mixture of compounds I and II is obtained together with traces of extremely unstable by-products which could not be satisfactorily purified or characterised.

The spectroscopic and analytical data (Tables 1 and 2) for I and II did not resolve the nature of these complexes and they were therefore fully characterised by single crystal X-ray diffraction studies (Tables 3–6).

The structure of I (Fig. 1) reveals that the tungsten atom carries a cyclopentadienyl ring, two carbonyl ligands and a ($CHRPPh_2$), phosphine methanide moiety [4] which formally behaves as a neutral three electron donor to tungsten. Evidently attack of $PHPh_2$ upon [$W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)$] involves both hydrogen migration from phosphorus and P–C bond formation. Moreover, in view of the isolobal relationship between the fragments PPh_2 and [$W(CO)_5$]$^-$ a comparison may be

TABLE 4

SELECTED BOND LENGTHS (Å) AND ANGLES (°) FOR [$\overline{W(CHRCOOPPh_2)}(PHPh_2)(CO)(\eta\text{-}C_5H_5)$] (II)

W(1)–P(1)	2.379(2)	W(1)–P(2)	2.430(2)	W(1)–C(1)	1.908(7)
W(1)–C(10)	2.408(6)	P(1)–O(3)	1.643(5)	P(1)–C(111)	1.830(4)
P(1)–C(121)	1.830(5)	P(2)–C(211)	1.830(5)	P(2)–C(221)	1.843(4)
P(2)–H(2)	1.301(2)	C(1)–O(1)	1.180(8)	C(2)–O(2)	1.192(9)
C(2)–O(3)	1.433(7)	C(2)–C(10)	1.459(9)	C(10)–C(11)	1.533(6)
C(10)–H(10)	1.073(7)				
P(1)–W(1)–P(2)	126.8(1)	P(1)–W(1)–C(1)	80.8(2)	P(2)–W(1)–C(1)	80.5(2)
P(1)–W(1)–C(10)	70.4(1)	P(2)–W(1)–C(10)	78.2(2)	C(10)–W(1)–C(10)	121.5(3)
W(1)–P(1)–O(3)	108.1(2)	W(1)–P(1)–C(111)	118.9(2)	O(3)–P(1)–C(111)	100.9(2)
W(1)–P(1)–C(121)	121.8(2)	O(3)–P(1)–C(121)	101.2(2)	W(1)–P(2)–C(211)	121.7(1)
W(1)–P(2)–C(221)	114.6(2)	W(1)–P(2)–H(2)	117.5(1)	C(211)–P(2)–H(2)	98.8(2)
C(221)–P(2)–H(2)	96.1(1)	W(1)–C(1)–O(1)	174.5(7)	O(2)–C(2)–O(3)	116.1(6)
O(2)–C(2)–C(10)	130.8(6)	O(3)–C(2)–C(10)	113.0(6)	P(1)–O(3)–C(2)	112.1(4)
W(1)–C(10)–C(2)	103.0(4)	W(1)–C(10)–C(11)	121.9(4)	C(2)–C(10)–C(11)	112.5(5)
W(1)–C(10)–H(10)	103.5(4)	C(2)–C(10)–H(10)	108.2(5)	C(11)–C(10)–H(10)	106.9(5)
C(10)–C(11)–C(12)	122.9(3)				

TABLE 5

ATOMIC CO-ORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\text{Å}^2 \times 10^3$) FOR [$\overline{\text{W(CHRPPh}_2)}(CO)_2$($\eta$-C$_5H_5$)] (I)

Atom	x	y	z	U^a
W	1066(1)	3683(1)	3709(1)	35(1)
P	1498(3)	5122(2)	3485(1)	38(1)
C(1)	3348(13)	3617(6)	3791(6)	53(3)
O(1)	4715(10)	3549(6)	3818(6)	79(3)
C(2)	1620(13)	3192(6)	2705(6)	46(3)
O(2)	1947(12)	2854(5)	2132(4)	72(3)
C(10)	−133(11)	4732(6)	2985(5)	38(3)
C(11)	−382(8)	4683(4)	2101(2)	41(3)
C(12)	181	5301	1605	50(3)
C(13)	−129	5260	808	52(4)
C(14)	−1001	4600	507	50(3)
C(15)	−1564	3982	1003	60(4)
C(16)	−1255	4024	1800	51(3)
C(17)	−1145(18)	4504(8)	−387(7)	72(5)
C(21)	963(9)	5881(3)	4211(3)	43(3)
C(22)	1602	5782	4954	59(4)
C(23)	1270	6359	5537	87(6)
C(24)	298	7035	5377	96(7)
C(25)	−341	7135	4635	94(6)
C(26)	−9	6558	4052	62(4)
C(31)	3062(7)	5594(4)	2911(4)	45(3)
C(32)	4009	5097	2440	63(4)
C(33)	5203	5455	1995	79(6)
C(34)	5451	6310	2023	82(5)
C(35)	4505	6808	2495	82(6)
C(36)	3310	6450	2939	63(4)
C(41)	−1485(7)	3395(5)	4196(4)	57(4)
C(42)	−627	3783	4804	62(4)
C(43)	659	3260	5000	61(4)
C(44)	595	2549	4512	68(5)
C(45)	−730	2632	4015	67(4)

^{a} Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

drawn with the reaction between [WH(CO)$_5$]$^-$ and [W($\equiv$CR)(CO)$_2$(η-C$_5$H$_5$)] which affords the alkylidene complex [W$_2$(μ-CHR)(CO)$_7$(η-C$_5$H$_5$)]$^-$ [3].

The $\overline{\text{W(CHRPPh}_2)}$ metallocyclic ring in I is analogous to those found in the complexes [$\overline{\text{Mn(CHRPPh}_2)}(CO)_4$] (R = H or Ph) [5] and [$\overline{\text{Mo\{CH}_2\text{P(NMe}_2)_2\}}$-(CO)$_2$($\eta$-C$_5H_5$)] [6]. The W–P (2.378(2) Å), W–C(10) (2.333(9) Å), and P–C(10) 1.75(1) Å) distances are all comparable or somewhat shorter than the related distances in the complexes II (W(1)–P(1) 2.379(2), and W(1)–C(10) 2.408(6) Å), and [$\overline{\text{Mn(CH}_2\text{PPh}_2)}(CO)_4$] [5] (P–CH$_2$ 1.753(4) Å). In particular, the W–P separation (2.378(2) Å) is significantly shorter than expected for a typical W–PR$_3$ bond such as found for the terminal PHPh$_2$ ligand in II (W(1)–P(2) 2.430(2) Å), and the P–C(10) distance (1.75(1) Å) is close to that expected for a P–C(sp^2) bond [5]. Similarly short Mn–P and P–C distances have been noted in the structure of [$\overline{\text{Mn(CH}_2\text{PPh}_2)}(CO)_4$] and have been discussed in terms of possible descriptions of the bonding of the phosphine methanide moiety to the metal atom [5].

TABLE 6

ATOMIC CO-ORDINATES ($\times 10^4$) AND ISOTROPIC THERMAL PARAMETERS ($\text{Å}^2 \times 10^3$) FOR [$\overline{W(CHRCOOPPh_2)}(PHPh_2)(CO)(\eta\text{-}C_5H_5)$] (II)

Atom	x	y	z	U [a]
W(1)	4681(1)	7327(1)	6271(1)	34(1)
P(1)	5568(1)	8271(1)	7350(1)	36(1)
P(2)	3027(1)	6865(2)	5938(1)	39(1)
C(1)	4730(4)	6241(5)	6995(4)	39(2)
O(1)	4810(4)	5524(4)	7420(3)	63(2)
C(2)	4770(5)	9796(6)	6479(4)	42(3)
O(2)	4912(4)	10557(5)	6143(3)	71(2)
O(3)	5474(3)	9568(3)	7167(2)	42(2)
C(10)	3974(4)	9059(5)	6323(3)	37(2)
C(11)	3131(3)	9463(4)	5693(2)	42(2)
C(12)	3172	9654	4977	56(3)
C(13)	2402	10099	4444	57(3)
C(14)	1591	10352	4628	55(3)
C(15)	1550	10161	5344	64(3)
C(16)	2320	9716	5877	52(3)
C(17)	730(6)	10850(7)	4043(5)	75(4)
C(111)	6844(2)	8110(4)	7665(3)	41(2)
C(112)	7430	8997	7701	55(3)
C(113)	8399	8853	7895	71(4)
C(114)	8782	7823	8053	67(4)
C(115)	8196	6936	8017	79(4)
C(116)	7227	7080	7823	62(3)
C(121)	5265(3)	8219(4)	8216(2)	39(2)
C(122)	5537	7341	8694	48(3)
C(123)	5238	7262	9323	58(3)
C(124)	4666	8062	9474	65(3)
C(125)	4393	8941	8996	63(3)
C(126)	4692	9019	8368	49(3)
C(211)	2378(3)	6912(4)	6616(2)	42(2)
C(212)	2849	7023	7371	60(3)
C(213)	2345	7060	7882	80(4)
C(214)	1369	6986	7638	73(4)
C(215)	897	6875	6883	74(4)
C(216)	1401	6838	6373	61(3)
C(221)	2728(3)	5539(3)	5488(2)	41(2)
C(222)	2138	5502	4759	54(3)
C(223)	1929	4515	4392	65(4)
C(224)	2310	3565	4754	62(4)
C(225)	2900	3602	5483	68(4)
C(226)	3109	4589	5850	62(3)
C(21)	5945(4)	7637(5)	5790(3)	59(3)
C(22)	5880	6530	5962	76(4)
C(23)	5016	6126	5492	88(5)
C(24)	4547	6983	5030	92(5)
C(25)	5120	7917	5214	65(4)

[a] Equivalent isotropic U defined as one third of the trace of the orthogonalised U_{ij} tensor.

Spectroscopic data for I are consistent with the structure determined by X-ray diffraction. The IR spectrum shows two carbonyl stretching bands (1930s and 1845s cm^{-1}) whilst the ^1H NMR spectrum has a resonance at δ 3.14 ppm which may be
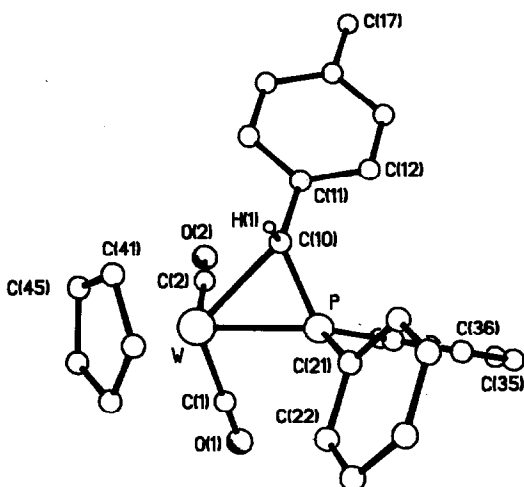
Fig. 1. The molecular structure of [W̄(CHRP̄Ph$_2$)(CO)$_2$(η-C$_5$H$_5$)] (I).

assigned to the RC*H*PPh$_2$ proton. The ^{31}P{^{1}H} NMR spectrum reveals a characteristically shielded resonance at δ -31.4 ppm ($J(^{183}$WP) 198 Hz) for the metallocyclic phosphorus atom [4].

The structure of II (Fig. 2) shows that the tungsten atom carries a cyclopentadienyl ring, a terminal PHPh$_2$ group and a carbonyl ligand. In addition the tungsten atom is σ-bonded via P(1) and C(10), to the ends of a novel (CHRCOOPPh$_2$) ligand. The origin of the C(O)O fragment which links P(1) and C(10) is obscure and it appeared probable that its formation might well involve adventitious incorporation of an oxygen atom during the reaction. However, spectroscopic data revealed that II is formed prior to chromatography, thereby ruling out introduction of oxygen at this stage. Moreover, attempts to increase the yield of II by deliberately introducing dioxygen or by carrying out the synthesis with partially oxidised solutions of PHPh$_2$ were unsuccessful. Thus no firm conclusions may be drawn about the mechanism by which II is formed.
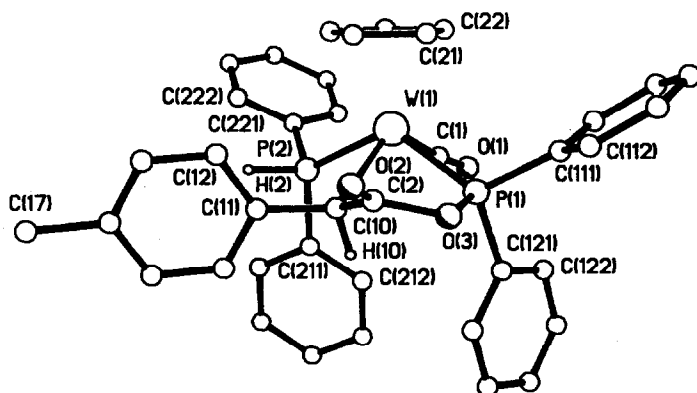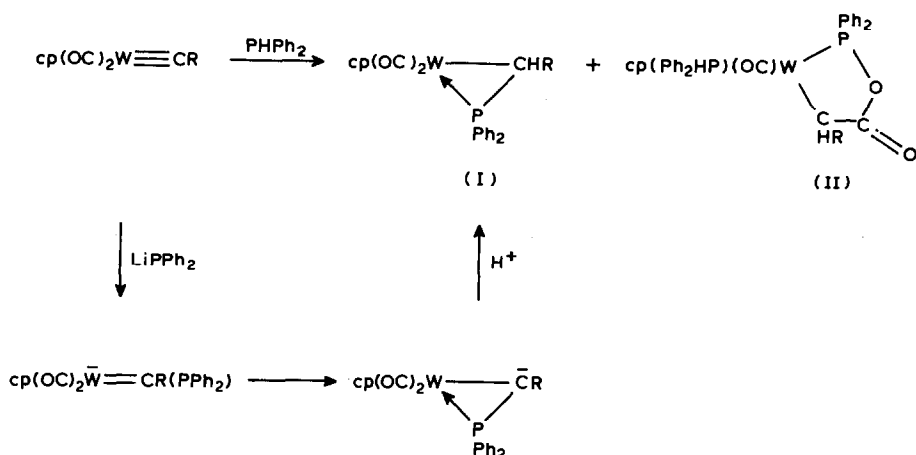

Fig. 2. The molecular structure of [W̄(CHRCOOP̄Ph$_2$)(PHPh$_2$)(CO)(η-C$_5$H$_5$)] (II).

cp(OC)₂W≡CR —PHPh₂→ cp(OC)₂W————CHR + cp(Ph₂HP)(OC)W

(I)

(II)

↓ LiPPh₂   ↑ H⁺

cp(OC)₂W══CR(PPh₂) ————→ cp(OC)₂W————CR

SCHEME 1. (cp = η-C₅H₅, R = C₆H₄Me-4.)

Spectroscopic data for II are, however, consistent with the solid state structure. The IR spectrum shows a carbonyl stretching band at 1797 cm⁻¹ and a low frequency band at 1724 cm⁻¹ which may be attributed to the C=O fragment of the CHRCOOPPh₂ ligand. A characteristic ν(PH) band at 2319 cm⁻¹ is also observed for the PHPh₂ ligand [7]. The ³¹P {¹H} NMR spectrum shows two doublet resonances at δ 31.5 and 117.0 ppm and the latter, comparatively deshielded resonance, is due to the metallocyclic phosphine ligand.

Compound I may also be prepared in high yield (70%) by treating [W(≡CR)(CO)₂(η-C₅H₅)] sequentially with LiPPh₂ and NH₄Br in thf, a process which may involve initial attack of Ph₂P⁻ at the alkylidyne carbon atom [1], as shown in Scheme 1. The expected anionic intermediate [W(CRPPh₂)(CO)₂(η-C₅H₅)]⁻ could not be isolated, and this species is evidently protonated extremely easily to give I.

Treatment of I with HCl in Et₂O leads to opening of the WCHRPPh₂ ring with formation of the red, "piano-stool" complex [WCl(PPh₂CH₂R)(CO)₂(η-C₅H₅)] (III). Spectroscopic data for III reveal that it exists as a mixture of cis and trans isomers (ca. 3/1), a feature which is frequently observed for complexes of the type [MX(CO)₂L(η-C₅H₅)] [8–9]. The ³¹P {¹H} NMR spectrum shows a singlet resonance for each isomer at δ 21.1 (cis) and 16.5 (trans) ppm. Both signals show ¹⁸³W satellites with J(¹⁸³WP) 226 Hz, a value comparable with that found in the related complexes [W(CH₃)(CO)₂L(η-C₅H₅)] [10]. In the ¹H NMR spectrum, resonances for the more abundant cis isomer can be readily identified. The CH₂PPh₂ protons are diastereotopic and appear as an ABX multiplet, which is consistent with the presence of a chiral centre at tungsten in the cis isomer.

Protonation of I with HBF₄ · Et₂O in Et₂O affords an unstable complex [W(BF₄)(PPh₂CH₂R)(CO)₂(η-C₅H₅)] which may have a weakly co-ordinated BF₄⁻ ligand which is readily displaced by MeCN to give the isolable complex [W(NCMe)(PPh₂CH₂R)(CO)₂(η-C₅H₅)][BF₄] (IV). Compound IV may be more conveniently prepared by treating I with HBF₄ · Et₂O in MeCN solution. The IR spectrum shows two carbonyl stretching bands and a weak ν(CN) band at 2284

cm^{-1} for the co-ordinated MeCN ligand)]). The ^{31}P $\{^1H\}$ NMR spectrum at both 30°C and −60°C, showed a single resonance at δ 15.5 ppm ($J(^{183}WP)$ 244 Hz) which suggests that IV exists as a single isomer in solution. In contrast the ^1H NMR spectrum provides evidence for the presence of two isomers in ca. 1/1 ratio. Thus two sets of resonances are observed for the C_6H_4Me-4 ligand and, whilst only one cyclopentadienyl resonance could be observed, the broad pattern of the resonances assigned to the CH$_2$R and MeCN protons is also consistent with overlapping signals from two isomers, although in the latter case coupling with ^{31}P is also possible [12]. It may be that steric congestion within the tungsten co-ordination sphere causes restricted rotation about the W–P or the P–CH$_2$R bond, giving rise to rotamers. Alternatively cis and trans isomers of the type found for III may be present, although it should be noted that the IR spectrum shows an intensity distribution normally associated with the presence of cis carbonyl ligands [9a].

Experimental

All reactions were carried out under dry, oxygen-free argon using Schlenk-tube techniques. The NMR spectra were recorded with JEOL FX 90Q and FX 200 instruments and the IR spectra with a Perkin–Elmer 298 spectrometer. The compound [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] [13] was prepared as described in the literature.

Reaction of [W(≡CC$_4$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] with PHPh$_2$

A mixture of [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.75 g, 1.83 mmol) and PHPh$_2$ (1.5 cm^3, 8.6 mmol) in toluene (20 cm^3) was refluxed for 1 h. The volatiles were removed in vacuo and the resulting oil was dissolved in CH$_2$Cl$_2$ (15 cm^3). Alumina was added to the solution and the mixture was evaporated to dryness. The solid was placed on the top of a water cooled column of alumina and chromatographed. A mixture of diehtyl ether (10%) in hexane eluted a yellow band that gave compound I [W(CHRPPh$_2$)(CO)$_2$(η-C$_5$H$_5$)] as an oil, and this was crystallised from toluene/hexane, to give ca. 0.050 g. A mixture of diethyl ether (20%) in hexane eluted a second band, which gave unstable, unidentified products. Finally, pure diethyl ether eluted a red band that gave compound II [W(CHRCOOPPh$_2$)-(PHPh$_2$)(CO)(η-C$_5$H$_5$)], which was recrystallised from CH$_2$Cl$_2$/hexane as red crystals (0.07 g, 5%).

Preparation of [W(CHRPPh$_2$)(CO)$_2$(η-C$_5$H$_5$)] (I)

A solution of the reagent LiPPh$_2$ was prepared by adding LiBu^n (1 mmol) to a solution of PHPh$_2$ (0.17 cm^3, 1 mmol) in thf (15 cm^3). To this solution was added solid [W(≡CC$_6$H$_4$Me-4)(CO)$_2$(η-C$_5$H$_5$)] (0.41 g, 1 mmol) followed by anhydrous NH$_4$Br (0.099g, 1 mmol). After 4 min the volatiles were removed in vacuo, the residue was extracted with 80% diethyl ether in hexane (5 × 20 cm^3), and the extracts were filtered through Celite. The filtrate was evaporated to 3 cm^3 to give I as a yellow powder. Recrystallization from toluene/hexane, gave yellow crystals of I (0.40 g, 70%).

Preparation of [WCl(PPh$_2$CH$_2$R)(CO)$_2$(η-C$_5$H$_5$)] (III)

Gaseous HCl (1 atm.) was bubbled for 5 min through a solution of I (0.39 g, 0.65

mmol) in diethyl ether (20 cm^3). The resulting solution was evaporated to dryness, the residue extracted with diethyl ether, and the extracts filtered through Celite. The red solution was concentrated to ca. 1 cm^3 and cooled, to give red crystalline III (0.31 g, 69%).

Preparation of [W(NCMe)(Ph$_2$CH$_2$R)(CO)$_2$(η-C$_5$H$_5$)][BF$_4$] (IV)

A solution of HBF$_4$ · Et$_2$O (0.67 mmol) in diethyl ether was added to a solution of I (0.40 g, 0.67 mmol) in MeCN (20 cm^3). The volatiles were evaporated in vacuo and the remaining oil was washed with diethyl ether (2 × 20 cm^3) and extracted with a mixture of 30% CH$_2$Cl$_2$ in hexane (30 cm^3) leaving a greenish residue. The extracts were filtered, concentrated to ca. 8 cm^3, and cooled, then the liquid was decanted and the oily precipitate was stirred with diethyl ether until an orange-yellow powder was formed (0.14 g, 29%). The compound IV was recrystallised from CH$_2$Cl$_2$/diethyl ether as bright orange crystals.

Crystal structure determinations

(a) [W(CHRPPh$_2$)(CO)$_2$(η-C$_5$H$_5$)] (I)

Yellow crystals of I were grown from toluene/hexane. Diffracted intensities were recorded at room temperature from a crystal of dimensions ca. 0.40 × 0.35 × 0.34 mm. Data were collected on a Nicolet P2$_1$ four-circle diffractometer. Of the total 2356 independent intensities collected to $2\theta \leq 50°$ (ω-scans), 2176 had $|F| \geq 5\sigma(F)$, where $\sigma(F)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure, after the data had been corrected for Lorentz, polarisation, and X-ray absorption effects; the latter by an empirical method based upon azimuthal scan data.

Crystal data for I. C$_{27}$H$_{23}$O$_2$PW, Mw. 594.3, orthorhombic, a 8.503(6), b 16.108(7), c 17.171(7) Å, U 2352(2) Å^3, $Z = 4$, D_c 1.68 g cm^{-3}, $F(000) = 1160$, space group $P2_12_12_1$, μ(Mo-K_α) 51.0 cm^{-1}, Mo-K_α X-radiation ($\bar{\lambda}$ 0.71069 Å).

The structure was solved, and all non-hydrogen atoms were located by conventional heavy-atom and difference-Fourier methods. All non-hydrogen atoms were given anisotropic thermal parameters. The position of the important CHRPPh$_2$ hydrogen atom was refined with a fixed isotropic thermal parameter. All remaining hydrogen atoms were included in calculated positions. Chemically related groups of hydrogen atoms were given common refined isotropic thermal parameters except for the Me-4 hydrogen atoms which were given a common fixed isotropic thermal parameter. The cyclopentadienyl and phenyl ligands were treated as rigid groups. Refinement by blocked-cascade least squares led to $R = 0.033$ ($R_w = 0.035$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. A final electron-density difference synthesis showed not peaks ≥ 0.5 e Å^{-3}. Scattering factors were from ref. [14]. All computations were carried out on an 'Eclipse' (Data General) computer with the SHELXTL system of programs [15].

(b) [W(CHRCOOPPh$_2$)(PHPh$_2$)(CO)(η-C$_5$H$_5$)] (II)

Red crystals of II were grown from dichloromethane/hexane. Data collection and refinement were similar to I except as noted below. A crystal of dimensions ca. 0.45 × 0.42 × 0.30 mm gave 5889 independent intensities of which 4507 had $|F| \geq 5\sigma(F)$.

Crystal data for II. $C_{39}H_{34}O_3P_2W$, Mw. 796.5, monoclinic, *a* 14.957(5), *b* 12.399(4), *c* 18.917(5) Å, β 107.59(2)°, *U* 3344(2) Å^3, $Z = 4$, D_c 1.58 g cm^{-3}, $F(000) = 1584$, space group $P2_1/n$, $\mu(\text{Mo-}K_\alpha)$ 36.6 cm^{-1}.

The PHPh$_2$ and CHR hydrogen atoms were refined with fixed isotropic thermal parameters, all remaining hydrogen atoms were not included in the refinement. Final $R = 0.036$ ($R_W = 0.038$) with the weighting scheme $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$. A final electron-density difference synthesis showed no peaks ≥ 1 e Å^{-3}. Lists of thermal parameters and observed and calculated structure factors for both complexes are available from the authors. Any request should be accompanied by the full literature citation for this paper.

Acknowledgements

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