Protonation of the Alkylidynetungsten Complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-2, $C_6H_3Me_2$-2,6 or C_6H_4OMe-2) *

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The complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-2 or $C_6H_3Me_2$-2,6) react with 2 equivalents of CF_3CO_2H in CH_2Cl_2 to afford $[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2R)(\eta\text{-}C_5H_5)]$, and with 2 equivalents of $HBF_4{\cdot}Et_2O$ in NCMe to give the salts $[W(CO)(NCMe)_2(\eta^2\text{-}COCH_2R)(\eta\text{-}C_5H_5)][BF_4]_2$. Treatment of $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ with *ca.* 0.5 equivalent of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at *ca.* −78 °C gives the salt $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$. However, if the reaction of $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2\text{-}(\eta\text{-}C_5H_5)]$ with 1 equivalent of $HBF_4{\cdot}Et_2O$ is carried out in the presence of PPh_3 or $Ph_2PCH_2PPh_2$ the complexes $[W\{\sigma,\eta^2\text{-}CH(PPh_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ and $[W\{CH(C_6H_4OMe\text{-}2)PPh_2CH_2PPh_2\}\text{-}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, respectively, are obtained. The structure of the former has been established by X-ray diffraction. In the cation the tungsten atom is ligated by the cyclopentadienyl group, two CO molecules (W–C–O average 176°), and by a $CH(PPh_3)C_6H_4OMe$-2 fragment. The latter is attached to the metal in a σ,η^2-bonding mode *via* a W–CH(PPh_3) linkage [2.16(3) Å] and connectivities to two carbon atoms of the C_6H_4OMe-2 ring [W–C^1 2.31(3) and W–C^6 2.65(4) Å].

The protonation of alkylidynemetal complexes is of considerable interest on account of the varied nature of the compounds formed, and mechanistic aspects of the reactions observed.[1] This is illustrated by studies on the complex $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ **1a**. Treatment of the latter with an excess of $HBF_4{\cdot}Et_2O$ affords an unstable complex formulated as $[WH(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, whereas with *ca.* 0.5 equivalents of $HBF_4{\cdot}Et_2O$ the ditungsten salt $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ **2a** is obtained *via* a reaction which involves coupling of two alkylidyne fragments.[2] It is very probable that the reaction leading to compound **2a** involves the intermediacy of the alkylidenetungsten species $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3a**, which whilst not isolable might readily form from an hydrido precursor such as $[WH(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$. Strong support for this proposal comes from the synthesis of complexes structurally related to **3a**. Thus treatment of the reagent **1a** with aqueous HI affords the stable alkylidenetungsten complex $[W\{=C(H)C_6H_4Me\text{-}4\}I(CO)_2(\eta\text{-}C_5H_5)]$ **4**;[2] while protonation of $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2\{HB(pz)_3\}]$ [$HB(pz)_3$ = hydrotris(pyrazol-1-yl)borate] with $HBF_4{\cdot}Et_2O$ gives the alkylidenetungsten salt $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2\{HB(pz)_3\}][BF_4]$ **3b**, which unlike the species **3a** can be isolated.[3] Moreover, it has been shown by Geoffroy and co-workers[4] that if the reagent **1a** is treated with $HBF_4{\cdot}Et_2O$ in the presence of PhC≡CPh a stable vinylalkylidene complex $[W\{=C(Ph)C(Ph)=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ is formed. This result also supports the idea of a transient intermediate **3a**, the alkylidene group of which adds to the substrate PhC≡CPh.

The purpose of the work described in this paper was to extend the scope of protonation studies on complexes of the type $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = aryl), by investigating reactions of species having a substituent in the *ortho* position on the arene ring. It was anticipated that by steric or electronic effects such a substituent could stabilise the 16-electron tungsten centre of an initially formed $[W\{=C(H)R\}(CO)_2(\eta\text{-}C_5H_5)]^+$ complex. As mentioned above, compound **3b** can be isolated, although its stability may be due more to the protective influence of the bulky $HB(pz)_3$ ligand (cone angle 180°) than to donation of an electron pair from the nearby OMe group to the tungsten centre to give the metal atom an 18-electron closed shell.

Results and Discussion

Studies were initiated with the complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-2 **1b** or $C_6H_3Me_2$-2,6 **1c**). Treatment of CH_2Cl_2 solutions of these reagents with 2 mol equivalents of CF_3CO_2H affords the η^2-acyl complexes $[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2R)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-2 **5a** or $C_6H_3Me_2$-2,6 **5b**) characterised by the data given in Tables 1 and 2. Use of less than 2 equivalents of acid gave the same species together with unchanged starting material.

As expected, the IR spectra of both compounds **5a** and **5b** display a single CO stretching band for the terminal carbonyl ligand. The $^{13}C\text{-}\{^1H\}$ NMR spectra are informative. Resonances for η^2-acyl groups are seen at δ 276.8 [**5a**, with *J*(WC) 64 Hz] and 277.0 (**5b**), and peaks for the terminal CO ligands are observed at δ 201.4 [**5a**, with *J*(WC) 136 Hz] and 201.7 (**5b**). Kreissl *et al.*[5] have reported that treatment of **1a** with CF_3CO_2H affords the complex $[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ **5c**, closely related to compounds **5a** and **5b**. As expected, **5c** has spectroscopic properties [ν_{max}(CO) 2052vs cm^{-1}; $^{13}C\text{-}\{^1H\}$ NMR, δ 276.3 (η^2-CO) and 200.7 (CO)] very similar to those of **5a** and **5b**. Another member of this family of complexes is **5d** obtained by treating the reagent **1a** with HCl.[5] An X-ray crystallographic study[5] on the related compound $[WCl_2(CO)(\eta^2\text{-}COCH_2Me)(\eta\text{-}C_5H_5)]$ has fully confirmed the existence of the η^2-acyl ligand in species of this class, a feature which allows the tungsten atoms to acquire an 18-electron filled shell.

Reactions between compound **1b** or **1c** and *ca.* 2 equivalents of $HBF_4{\cdot}Et_2O$ using NCMe as solvent were next investigated and found to give the salts $[W(CO)(NCMe)_2(\eta^2\text{-}COCH_2R)(\eta\text{-}C_5H_5)][BF_4]_2$ (R = C_6H_4Me-2 **6a** or $C_6H_3Me_2$-2,6 **6b**). Use of less than 2 equivalents of the acid in these reactions failed to give

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* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.

Table 1 Analytical[a] and physical data for the complexes

Compound		Colour	Yield (%)	ν_{max}(CO)[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
3c	$[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$	Yellow	90	2046vs, 1987vs	34.7 (35.2)	2.8 (2.6)
5a	$[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)]$	Orange-red	73	[c]2049vs	36.2 (35.9)	2.3 (2.2)
5b	$[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2C_6H_3Me_2\text{-}2,6)(\eta\text{-}C_5H_5)]$	Yellow	78	[d]2048vs	37.0 (37.0)	2.5 (2.5)
6a	$[W(CO)(NCMe)_2(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)][BF_4]_2$	Orange-red	63	[e]2091vs	[f]33.1 (34.3)	3.1 (3.0)
6b	$[W(CO)(NCMe)_2(\eta^2\text{-}COCH_2C_6H_3Me_2\text{-}2,6)(\eta\text{-}C_5H_5)][BF_4]_2$	Yellow	68	[e]2088vs	[g]34.4 (35.3)	3.6 (3.3)
6c	$[W(NCMe)_3(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)][BF_4]_2$[h]	Orange	82			
6d	$[W(NCMe)_3(\eta^2\text{-}COCH_2C_6H_3Me_2\text{-}2,6)(\eta\text{-}C_5H_5)][BF_4]_2$[h]	Orange	82			
7a	$[W\{\sigma,\eta^2\text{-}CH(PPh_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$	Orange-red	99	1954vs, 1866vs	52.0 (51.2)	4.1 (3.7)
8	$[W\{CH(C_6H_4OMe\text{-}2)PPh_2CH_2PPh_2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$	Yellow	80	1948vs, 1866vs	52.9 (53.6)	4.5 (3.9)

[a] Calculated values given in parentheses. [b] Measured in CH_2Cl_2 unless otherwise stated. [c] Peaks at 1701vs and 1710 (sh) cm^{-1} due to CF_3CO_2 groups. [d] Peaks at 1702vs and 1710 (sh) cm^{-1} due to CF_3CO_2 groups. [e] Measured in NCMe. [f] N, 3.7 (4.2)%. [g] N, 3.3 (4.1)%. [h] Satisfactory microanalytical data not obtained, see text.

Table 2 Hydrogen-1 and carbon-13 NMR data[a] for the new tungsten compounds

Compound	$\delta(^1H)$[b]	$\delta(^{13}C)$[c]
3c	3.72 (s, 3 H, OMe), 5.99 (s, 5 H, C_5H_5), 6.87–7.53 (m, 4 H, C_6H_4), 13.08 [s, 1 H, W=CH, *J*(WH) 25]	263.6 (W=CH), 215.2 (CO), 157.8, [$C^2(C_6H_4)$], 133.1–110.8 (C_6H_4), 97.8 (C_5H_5), 56.0 (OMe)
5a	2.35 (s, 3 H, Me-2), 4.85, 4.97 [AB, 2 H, CH_2, *J*(AB) 17], 5.54 (s, 5 H, C_5H_5), 7.28–7.37 (m, 4 H, C_6H_4)	276.8 [W(η^2-CO), *J*(WC) 64], 201.4 [CO, *J*(WC) 136], 162.3 [q, $\mathit{C}O_2CF_3$, *J*(FC) 39], 161.7 [q, $\mathit{C}O_2CF_3$, *J*(FC) 39], 137.7, 131.5, 131.4, 131.1, 129.3, 127.2 (C_6H_4), 115.7 [q, $CO_2\mathit{C}F_3$, *J*(FC) 289], 115.2 [q, $CO_2\mathit{C}F_3$, *J*(FC) 289], 96.5 (C_5H_5), 47.3 (CH_2), 19.7 (Me-2)
5b	2.31 (s, 6 H, Me_2-2,6), 4.92 (s, 2 H, CH_2), 5.63 (s, 5 H, C_5H_5), 7.12–7.21 (m, 3 H, C_6H_3)	277.0 [W(η^2-CO)], 201.7 (CO), 161.8 [q, $\mathit{C}O_2CF_3$, *J*(FC) 39], 161.7 [q, $\mathit{C}O_2CF_3$, *J*(FC) 39], 137.7, 130.7, 129.1, 128.9 (C_6H_3), 115.7 [q, $CO_2\mathit{C}F_3$, *J*(FC) 290], 115.2 [q, $CO_2\mathit{C}F_3$, *J*(FC) 288], 96.4 (C_5H_5), 44.4 (CH_2), 20.6 (Me_2-2,6)
6a[d]	1.98 (s, 3 H, NCMe), 2.25 (s, 3 H, NCMe), 2.43 (s, 3 H, Me-2), 5.07 (s, 2 H, CH_2), 5.77 (s, 5 H, C_5H_5), 7.17–7.33 (m, 4 H, C_6H_4)	[e] 274.0 [W(η^2-CO)], 138.2, 132.6 [C^1, $C^2(C_6H_4)$], 131.8, 131.6, 129.6 127.6 (C_6H_4), 119.8 (N*C*Me), 99.4 (C_5H_5), 48.1 (CH_2), 19.9 (Me-2), 4.7 (NC*Me*), 1.8 (NC*Me*)
6b[d]	1.97 (s, 6 H, NCMe), 2.23 (s, 6 H, Me_2-2,6), 5.18, 5.20 (AB, br, 2 H, CH_2), 6.21 (s, 5 H, C_5H_5), 6.96–7.24 (m, 3 H, C_6H_3)	[e] 274.9 [W(η^2-CO)], 138.2, 132.5, 132.0, 129.4 (C_6H_3), 118.4 (N*C*Me), 99.5 (C_5H_5), 45.3 (CH_2), 20.7 (Me_2-2,6), 1.7 (NC*Me*)
6c[d]	2.25 (s, 3 H, Me-2), 2.43 (s, 6 H, NCMe), 2.69 (s, 3 H, NCMe), 5.07 (s, 2 H, CH_2), 5.77 (s, 5 H, C_5H_5), 7.27–7.33 (m, 4 H, C_6H_4)	[e] 274.1 [W(η^2-CO)], 138.2, 132.7 [C^1, $C^2(C_6H_4)$], 131.8, 131.7, 129.6, 127.6 (C_6H_4), 118.5 (N*C*Me), 99.4 (C_5H_5), 48.1 (CH_2), 19.9 (Me-2), 4.7 (NC*Me*), 1.8 (NC*Me*)
6d[d]	2.21 (s, 6 H, Me_2-2,6), 2.47 (s, 6 H, NCMe), 2.69 (s, 3 H, NCMe), 5.10 (s, 2 H, CH_2), 5.80 (s, 5 H, C_5H_5), 7.14–7.23 (m, 3 H, C_6H_3)	[e] 275.0 [W(η^2-CO)], 138.2, 132.6, 132.0, 129.3 (C_6H_3), 118.5 (N*C*Me), 99.5 (C_5H_5), 45.3 (CH_2), 20.8 (Me_2-2,6), 4.8 (NC*Me*), 1.8 (NC*Me*)
7a	3.84 [d, 1 H, PCH, *J*(PH) 7], 4.18 (s, 3 H, OMe), 5.08 [d, 1 H, $C^6H(C_6H_4)$, *J*(HH) 1], 5.24 (s, 5 H, C_5H_5), 6.55 [t, 1 H, C_6H_4, *J*(HH) 7], 6.78 [d, 1 H, C_6H_4, *J*(HH) 7], 7.35–7.80 (m, 16 H, Ph, C_6H_4)	234.6 (CO), 231.0 [d, CO, *J*(PC) 9], 159.7 [d, $C^2(C_6H_4)$, *J*(PC) 3], 135.4–129.0, 122.7, 107.2 (Ph, C_6H_4), 93.8 (C_5H_5), 83.9 [$C^6(C_6H_4)$], 56.5 (OMe), 9.3 [d, PCH, *J*(PC) 69]
8[f]	3.82 (s, 3 H, OMe), 3.93 (s, 3 H, OMe), 4.07 [d of d, 1 H, PCH, *J*(PH) 7 and 16], 4.07 [d of d, 1 H, PCH, *J*(PH) 15 and 24], 4.68 (br, 4 H, PCH_2P), 5.26 (s, 10 H, C_5H_5), 6.57–7.75 (m, 48 H, C_6H_4, Ph)	239.0 [CO, *J*(PC) 22], 235.1, 231.8 (CO), 154.0, 153.9 [$C^2(C_6H_4)$], 135.6–129.3 (Ph, C_6H_4), 127.3, 126.8, 121.6, 120.2, 111.3, 110.0 (C_6H_4), 92.3, 91.8 (C_5H_5), 55.6 (OMe), 36.7 [PCH_2P, *J*(PC) 72 and 19], −5.5 [PCH, *J*(PC) 39], −6.6 [PCH, *J*(PC) 19]

[a] Chemical shifts (δ) in ppm, coupling constants (*J*) in Hz. [b] Measured at ambient temperatures in CD_2Cl_2 unless otherwise stated. [c] Hydrogen-1 decoupled, measured at ambient temperatures in CD_2Cl_2 unless otherwise stated. Chemical shifts are positive to high frequency of $SiMe_4$. [d] Measured in $NCCD_3$. [e] Resonances for the NCMe ligands are difficult to assign, see text. [f] Peaks are duplicated due to presence of two isomers (*ca.* 1:1), see text.

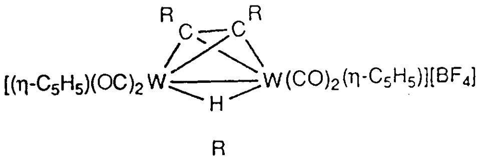
isolable products. Both salts **6a** and **6b** are relatively unstable, decomposing slowly at *ca.* −15 °C in the solid state, making it difficult to obtain good microanalytical data. However, as expected, they display a single CO stretching band in their IR spectra (**6a** 2091, **6b** 2088 cm^{-1}). Diagnostic resonances for η^2-CO groups are seen in the $^{13}C\text{-}\{^1H\}$ NMR spectra at δ 274.0 (**6a**) and 274.9 (**6b**). Because these salts are insoluble in most organic solvents, except Me_2CO or NCMe, and since they decomposed in the former solvent it was necessary to record their NMR spectra in $NCCD_3$. In this solvent CO is readily lost to give complexes **6c** and **6d**, respectively (see below), and consequently resonances for the carbonyl ligands were not observed. Moreover, with the spectra measured in $NCCD_3$, resonances for the NCMe ligands in **6a** and **6b** were difficult to assign.

If the reactions between compound **1b** or **1c** and $HBF_4{\cdot}Et_2O$ are carried out at −78 °C with CH_2Cl_2 as solvent unstable red-brown solutions are obtained, which show a strong broad CO stretching band at *ca.* 2055 cm^{-1}. A similar absorption is displayed at *ca.* 2051 cm^{-1} by an unstable complex formulated as $[WH(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, and obtained by treating the reagent **1a** with an excess of $HBF_4{\cdot}Et_2O$.[2] As mentioned earlier, if compound **1a** is treated with *ca.* 0.5 equivalent of $HBF_4{\cdot}Et_2O$ the ditungsten complex **2a** is formed.

Refluxing compound **6a** or **6b** in NCMe for *ca.* 30 min affords the tris(acetonitrile) complexes $[W(NCMe)_3(\eta^2\text{-}COCH_2R)(\eta\text{-}C_5H_5)][BF_4]_2$ (R = C_6H_4Me-2 **6c** or $C_6H_3Me_2$-2,6 **6d**). Instability prevented satisfactory microanalysis. However, NMR data were obtained (Table 2) with resonances very similar to those of **6a** and **6b**, respectively, as expected. Also

$[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$

	R
1a	C_6H_4Me-4
1b	C_6H_4Me-2
1c	$C_6H_3Me_2$-2,6
1d	C_6H_4OMe-2



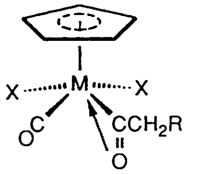
	R
2a	C_6H_4Me-4
2b	C_6H_4OMe-2

$[W\{=C(H)R\}(CO)_2L][BF_4]$

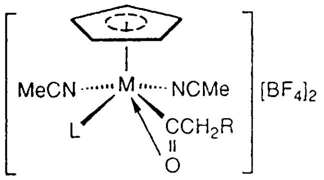
	R	L
3a	C_6H_4Me-4	$\eta\text{-}C_5H_5$
3b	C_6H_4OMe-2	$\eta\text{-}HB(pz)_3$
3c	C_6H_4OMe-2	$\eta\text{-}C_5H_5$

$[W\{=C(H)C_6H_4Me\text{-}4\}I(CO)_2(\eta\text{-}C_5H_5)]$

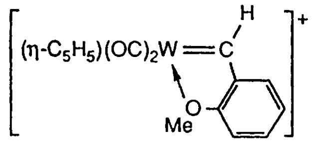
4



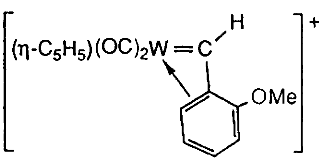
	R	X
5a	C_6H_4Me-2	O_2CCF_3
5b	$C_6H_3Me_2$-2,6	O_2CCF_3
5c	C_6H_4Me-4	O_2CCF_3
5d	C_6H_4Me-4	Cl



	R	L
6a	C_6H_4Me-2	CO
6b	$C_6H_3Me_2$-2,6	CO
6c	C_6H_4Me-2	NCMe
6d	$C_6H_3Me_2$-2,6	NCMe



A



B

as expected, the IR spectra of **6c** and **6d** showed no CO stretching bands.

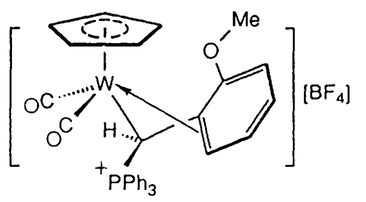
The successful isolation of the alkylidenetungsten complex **3b**, in which the aryl ring carries an *ortho* OMe substituent, led to a study of the reaction of compound **1d** with *ca.* 0.5 equivalent of $HBF_4{\cdot}Et_2O$. In CH_2Cl_2 at −78 °C these two reagents afforded $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3c**, characterised by the data given in Tables 1 and 2. Although **3c** slowly decomposes, especially in solution in the presence of an excess of $HBF_4{\cdot}Et_2O$, it is possible to obtain good NMR data. In the ^1H NMR spectrum a resonance at δ 13.08, with *J*(WH) 25 Hz, and equivalent in intensity to a single proton, is diagnostic for the presence of the W=CH group. Correspondingly, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum there is a peak at δ 263.6 which may be attributed to the ligated carbon atom of the alkylidene ligand W=*C*(H)C_6H_4OMe-2. These ^1H and $^{13}C\text{-}\{^1H\}$ NMR data compare well with those for the *C*(*H*)C_6H_4Me-4 group in compound **4** (^1H, δ 13.08; $^{13}C\text{-}\{^1H\}$, δ 267.4), the structure of which has been established by X-ray crystallography.[2]

The isolation of **3c** contrasts with the failure to obtain the salt **3a**, and the existence of the former species must be due to the presence of the OMe group. This stabilisation could occur by donation of an electron pair from the oxygen of the OMe substituent to the tungsten atom, as in **A**, thereby allowing the latter to attain a filled valence shell, and inhibiting decomposition. Alternatively, but perhaps less likely, the metal atom could attain an 18-electron configuration by formulation **B** which is structurally related to the vinylalkylidenetungsten complex $[\overline{W\{=C(Ph)C(Ph)}{=}C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)]^+$ mentioned above.[4] Moreover, **B** also resembles a structure of another complex described below.

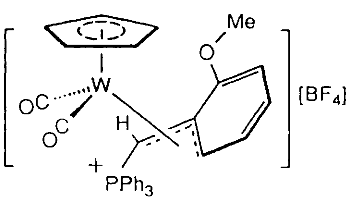
Signals for two minor species can be observed in the NMR spectra of complex **3c** due to its decomposition. A weak resonance at δ −16.57 with $^{183}W\text{-}^1H$ coupling (33 Hz) suggested the formation of a ditungsten complex **2b**. In the ^1H NMR spectrum of the analogue **2a** the resonance for the hydrido ligand is at δ −17.0 with *J*(WH) 33 Hz. Another minor species present may be $[W(CO)_3(\eta^2\text{-}COCH_2C_6H_4OMe\text{-}2)(\eta\text{-}C_5H_5)][BF_4]_2$, structurally related to the compounds **6**, since in the ^1H NMR spectrum of impure **3c** there is a peak at δ 5.15 for a CH_2 group, and resonances in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 46.3 and 282.1 which may be assigned to the *C*H_2 and *C*OCH_2 nuclei, respectively. Similar values are observed for the compounds **6**.

Protonation of compound **1d** with 1 equivalent of $HBF_4{\cdot}Et_2O$ did not give a pure product, and the mixture decomposed rapidly. Also no pure product was isolated when CO saturated solutions of **1d** were treated with 1 equivalent of $HBF_4{\cdot}Et_2O$, conditions which might have favoured the formation of the above-mentioned species $[W(CO)_3(\eta^2\text{-}COCH_2C_6H_4OMe\text{-}2)(\eta\text{-}C_5H_5)][BF_4]_2$.

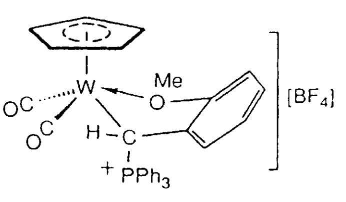
Protonation of the reagent **1d** in CH_2Cl_2 at −78 °C in the presence of PPh_3 was next investigated. Based on studies reported elsewhere,[6] it was anticipated that under these conditions a stable salt $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)][BF_4]$ would be obtained. In practice the reaction followed a different pathway affording a species $[W\{\sigma,\eta^2\text{-}CH(PPh_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **7**, the nature of which was not apparent until an X-ray diffraction study had



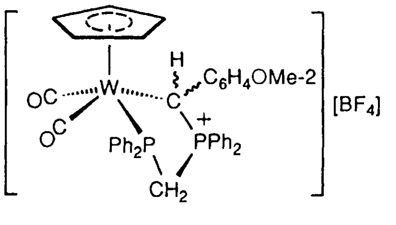
7a



7b



7c



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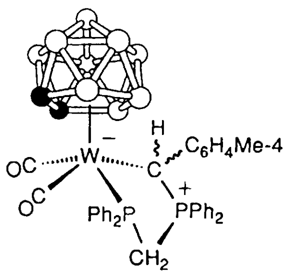

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Table 3 Selected bond lengths (Å) and angles (°) for $[W\{\sigma,\eta^2\text{-CH(PPh}_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **7a** (one of two independent cations), with estimated standard deviations in parentheses

W(1)–C(106)	1.98(3)	W(1)–C(107)	1.97(5)	W(1)–C(108)	2.16(3)	W(1)–C(111)	2.31(3)
W(1)–C(116)	2.65(4)	P(1)–C(108)	1.82(3)	P(1)–C(121)	1.74(3)	P(1)–C(131)	1.82(3)
P(1)–C(141)	1.79(3)	C(106)–O(106)	1.09(4)	C(107)–O(107)	1.18(6)	C(108)–C(111)	1.34(5)
C(111)–C(112)	1.43(5)	C(112)–C(113)	1.37(6)	C(113)–C(114)	1.46(6)	C(114)–C(115)	1.37(5)
C(115)–C(116)	1.38(6)	C(111)–C(116)	1.56(6)	W(1)–C(C_5H_5)	2.33(3)*		

C(106)–W(1)–C(107)	76(2)	C(106)–W(1)–C(108)	90(1)	C(107)–W(1)–C(108)	122(2)
C(108)–P(1)–C(121)	110(1)	C(108)–P(1)–C(131)	112(1)	C(121)–P(1)–C(131)	108(1)
C(108)–P(1)–C(141)	111(1)	C(121)–P(1)–C(141)	110(1)	C(131)–P(1)–C(141)	105(1)
W(1)–C(106)–O(106)	174(3)	W(1)–C(107)–O(107)	178(3)	W(1)–C(108)–P(1)	132(2)
W(1)–C(108)–C(111)	79(2)	P(1)–C(108)–C(111)	120(3)	W(1)–C(111)–C(108)	67(2)
W(1)–C(111)–C(112)	117(2)	C(108)–C(111)–C(112)	125(4)	W(1)–C(111)–C(116)	84(2)
C(108)–C(111)–C(116)	122(3)	C(112)–C(111)–C(116)	113(3)	C(111)–C(112)–C(113)	125(4)
C(111)–C(112)–O(117)	114(4)	C(114)–C(115)–C(116)	122(4)	W(1)–C(116)–C(111)	60(2)
W(1)–C(116)–C(115)	124(3)	C(111)–C(116)–C(115)	121(3)	P(1)–C(121)–C(122)	117.9(7)
P(1)–C(121)–C(126)	121.8(7)	P(1)–C(131)–C(132)	118.0(7)	P(1)–C(131)–C(136)	121.9(7)
P(1)–C(141)–C(142)	120.3(7)	P(1)–C(141)–C(146)	119.5(7)		

* Average distance from W to ligated C atoms of C_5H_5 ring.

been carried out. Although crystals were relatively small, and there were two structurally similar but crystallographically independent ion pairs in the asymmetric unit, the structure was unambiguously established.

One of the cations is shown in Fig. 1, and selected internuclear distances and angles are given in Table 3. It is immediately apparent that the cation has a novel structure resulting from addition of the proton and a PPh_3 group to the ligated carbon atom of the alkylidyne group of the precursor **1d**. As a result the tungsten atom is co-ordinated by atoms C(108), C(111) and C(116), but with different metal–carbon separations [W(1)–C(108) 2.16(3), W(1)–C(111) 2.31(3) and W(1)–C(116) 2.65(4) Å]. The attachment of C(111) and C(116) to the metal atom results in a C(111)–C(116) distance of 1.56(6) Å, appreciably longer than the remaining C–C bonds in the C_6 ring (average 1.40 Å). The W atom carries, as expected, the C_5H_5 group and two essentially linearly bound CO ligands [W–C–O average 176(3)°].

The η^3 or σ,η^2-bonding of the C_3 fragment to the metal atom is similar to that found in several other structures including the species $[M(CO)_2\{\eta^3\text{-CH(R)}C_6H_4Me\text{-}4\}(\eta\text{-}C_5H_5)]$ (M = Mo, R = H;[7] M = W, R = Ph[8a]) and $[W(CO)_2\{\eta^3\text{-CH}(BC_8H_{14})C_6H_4Me\text{-}4\}(\eta\text{-}C_5H_5)]$.[8b] An interesting feature of the structure of **7** is the aforementioned long W(1)–C(116) separation. Allylic bonding of three carbon atoms to tungsten usually results in metal–carbon separations of 2.240–2.303 Å.[9] Only W(1)–C(111) in complex **7** falls in this range. In the complex $[W(CO)_2\{\eta^3\text{-CH(Ph)}C_6H_4Me\text{-}4\}(\eta\text{-}C_5H_5)]$ the W–C distances to the $C(H)C_6H_4Me\text{-}4$ group are 2.32(3), 2.35(3) and 2.41(3) Å.[8a] However, in $[W(CO)_2\{\eta^3\text{-CH}(BC_8H_{14})C_6H_4Me\text{-}4\}(\eta\text{-}C_5H_5)]$ the bonding is more asymmetric, as in **7**, with corresponding distances of 2.275(8), 2.355(8) and 2.613(8) Å.[8b]

The hydrogen atom attached to C(108) was not found in the X-ray diffraction study, but its presence was apparent from NMR data discussed below. The C(108)–P(1) distance [1.82(3) Å] is as expected,[9] and with the P atom 1.44 Å outside the plane defined by C(108), C(111) and C(116) it can be inferred that C(108) has appreciable sp^3 character. The bonding of the $CH(PPh_3)C_6H_4OMe\text{-}2$ fragment is thus best described as σ,η^2 (**7a**) rather than η^3 (**7b**). An unexpected feature of the structure

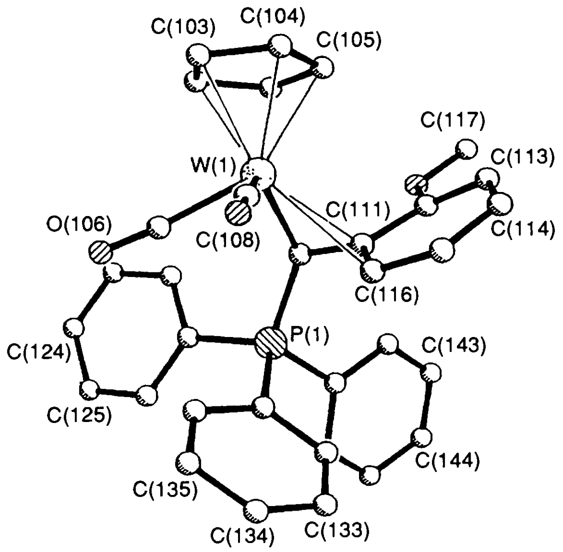
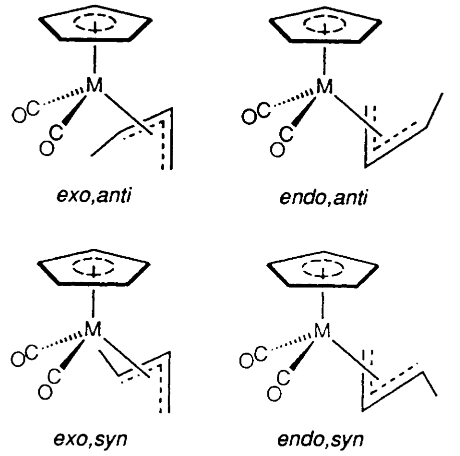


Fig. 1 Structure of one of the cations of [W{σ,η^2-CH(PPh$_3$)C$_6$H$_4$OMe-2}(CO)$_2$(η-C$_5$H$_5$)][BF$_4$] **7a**, showing the crystallographic atom labelling scheme


exo,anti *endo,anti*

exo,syn *endo,syn*

Scheme 1 Possible conformations for allyl complexes

of the cation of **7** is the spectator role played by the OMe substituent on the C$_6$ ring, and there is no evidence for bonding of type **7c**, even in solution as deduced from NMR data, discussed below.

Notwithstanding the distortions from η^3 allylic geometry noted above, the complex **7** may be conveniently described as having an *exo,anti*-allylic conformation (Scheme 1). Interestingly, extended Hückel molecular orbital (EHMO) calculations by Hoffmann and co-workers[10] on the model complex [Mo(CO)$_2$(η-C$_3$H$_5$)(η-C$_5$H$_5$)] suggest a small preference for the *endo* geometry. Presumably complex **7** adopts an *exo* conformation because in an *endo,anti* conformation severe steric congestion would arise between the PPh$_3$ substituent and the cyclopentadienyl ring. A similar argument has been invoked to explain the *exo* stereochemistry observed in the solid-state structure of the complex [Mo(CO)(PEt$_3$)(η^3-*anti*-1-MeC$_3$H$_4$)(η^5-C$_9$H$_7$)] (C$_9$H$_7$ = indenyl)[11] and we have previously shown that [W(CO)$_2${η^3-CH(BC$_8$H$_{14}$)C$_6$H$_4$Me-4}(η-C$_5$H$_5$)], which has a bulky *anti*-BC$_8$H$_{14}$ substituent, also has an *exo,anti* geometry in the solid state.[8b] In contrast, the complexes [M(CO)$_2${η^3-CH(R)C$_6$H$_4$Me-4}(η-C$_5$H$_5$)] (M = Mo, R = H;[7] M = W, R = Ph[8a]) adopt the theoretically preferred *endo* conformations and it is noteworthy that in [W(CO)$_2${η^3-CH(Ph)C$_6$H$_4$Me-4}(η-C$_5$H$_5$)] the Ph substituent adopts a *syn* position. For **7** a *syn* geometry would result in steric hindrance between the PPh$_3$ ligand and the methoxy substituent of the C$_6$H$_4$OMe-2 ring, thus it seems clear that the observed *exo,anti* geometry observed in the crystal of **7** is primarily determined by the steric constraints imposed by the bulky PPh$_3$ ligand.

Having established the structure of compound **7** as **7a** the spectroscopic data are readily interpretable. There are, as expected, two CO stretching bands (1954 and 1866 cm^{-1}). Interestingly, these absorptions are at considerably lower frequencies than those for the neutral precursor **1d** (1985 and 1907 cm^{-1}) suggesting that the positive charge resides on the phosphorus atom rather than on the metal centre. In the ^{1}H NMR spectrum of **7a** there is a doublet at δ 3.84 [*J*(PH) 7 Hz] due to the PCH moiety. Correspondingly, the ^{13}C-{^{1}H} NMR spectrum shows a doublet for this fragment at δ 9.3 [*J*(PC) 69 Hz]. A resonance at δ 5.08 in the ^{1}H NMR spectrum is ascribed to the hydrogen attached to C(116) (Fig. 1) since this proton is expected to be more shielded than the other protons in the C$_6$H$_4$ ring. Similarly, a signal at δ 83.9 in the ^{13}C-{^{1}H} NMR spectrum is attributed to C(116). The two non-equivalent CO ligands give rise to two resonances at δ 234.6 and 231.0 [*J*(PC) 9 Hz]. The doublet signal must be due to C(107)O(107) which is transoid to the phosphorus atom. The ^{31}P-{^{1}H} NMR spectrum [chemical shifts (δ) are positive to high frequency of 85% H$_3$PO$_4$ (external)] shows only a single resonance at δ 30.0, and as expected no ^{183}W satellite peaks are observed, since there is no P–W bond.

Protonation of the reagent **1d** in CH$_2$Cl$_2$ at −78 °C with 1 equivalent of HBF$_4$·Et$_2$O in the presence of dppm (Ph$_2$PCH$_2$PPh$_2$) yields the complex [W{CH(C$_6$H$_4$OMe-2)PPh$_2$CH$_2$PPh$_2$}(CO)$_2$(η-C$_5$H$_5$)][BF$_4$] **8**, data for which are given in Tables 1 and 2. The spectroscopic properties are in complete accord with the structure proposed. There are two CO stretching bands (1948 and 1866 cm^{-1}) in the IR spectrum, similar to those of the salt **7a**. Examination of the NMR spectra of compound **8** revealed that in solution it exhibited dynamic behaviour involving equilibration between two isomers present in approximately equal amounts, based on relative peak intensities. It seems likely that this isomerism involves two different orientations of the C(H)C$_6$H$_4$OMe-2 group with respect to the remainder of the cation.[12]

The ^{31}P-{^{1}H} NMR spectrum was especially informative. At ambient temperatures only broad signals are observed. However, at −80 °C two pairs of doublets are seen in 1:1 ratio, with one signal in each pair showing strong ^{183}W–^{31}P coupling for the PW group in each isomer: δ 43.7 [*J*(PP) 36, *J*(WP) 264] and 41.6 [*J*(PP) 36 Hz] for one isomer, and δ 34.5 [*J*(PP) 36] and 23.6 [*J*(PP) 36, *J*(WP) 260 Hz] for the other.

In the ^{1}H NMR spectrum of compound **8** the two isomers give rise to resonances for the OMe groups at δ 3.82 and 3.93. An apparent sextet results from coincidence of signals due to the C*H*PPh$_2$ groups of the two isomers, with each CHP group giving rise to a doublet of doublets signal. Thus for one isomer there is a resonance pattern centred at δ 4.07 with *J*(PH) 16 and 7 Hz, and similarly for the other isomer there is also a resonance at δ 4.07 but with *J*(PH) 24 and 15 Hz. In addition, in the ^{1}H NMR spectrum there is a broad signal at *ca.* δ 4.68 due to the overlap of signals due to the PCH$_2$P group of the two isomers.

The ^{13}C-{^{1}H} NMR spectrum of compound **8** shows a doublet of relative intensity two at δ 239.0 with ^{31}P–^{13}C coupling [*J*(PC) 22 Hz] and two signals at δ 235.1 and 231.8 for the four carbonyl groups of the two isomers. The doublet resonance results from coincidence of the signals due to the carbonyl ligand of each isomer which is *trans* to the phosphorus atom directly bonded to the tungsten. A resonance at δ 36.7 with ^{31}P–^{13}C coupling [*J*(PC) 72 and 19 Hz] is assigned to the PCH$_2$P groups for both isomers. Interestingly, the CHP groups are extremely shielded. One isomer has a resonance at δ −5.5 with ^{31}P–^{13}C coupling [*J*(PC) 39 Hz], with the signal for the other being at δ −6.6 with *J*(PC) 19 Hz. These values are acceptable if we recall that the chemical shift for the CHP group of **7a** is also shielded [δ 9.3 with *J*(PC) 69 Hz].

The cation of **8** is isolobal with the recently described complex $[W\{CH(C_6H_4Me\text{-}4)PPh_2CH_2PPh_2\}(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ **9**, prepared by treating $[PPh_4][W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta^5\text{-}C_2B_9H_9Me_2)]$ with $HBF_4{\cdot}Et_2O$ in the presence of dppm.[12] The structure of compound **9** has been established by X-ray diffraction, but like **8** in solution it exists as a mixture of isomers, the latter being attributed to different orientations of the $C(H)C_6H_4Me\text{-}4$ group with respect to the remainder of the molecule.

Formation of the salts **7a** and **8** on protonation of **1d** in the presence of the phosphines evidently proceeds *via* the alkylidene complex **3c**. Indeed, **7a** can be prepared sequentially by first isolating **3c**, and then treating the latter with PPh_3. Reactions between alkylidenetungsten compounds and tertiary phosphines have been extensively studied,[13] and it is evident that one of two pathways is followed. Either the alkylidene ligand is displaced by the phosphine, or the latter adds to the ligated carbon atom of the co-ordinated alkylidene fragment to yield ylide type structures. Evidently the latter pathway is favoured in the formation of compounds **7a**, **8** and **9**.

As mentioned in the Introduction, the object of the work described herein was to investigate the influence on the protonation pathways followed by reagents of type **1** when the aryl rings present in the latter carry an *ortho* substituent. It is evident from the results obtained that the presence of Me groups, as in **1b** or **1c**, does not lead to isolable alkylidenetungsten complexes. Instead, the only products which could be isolated resulted from the addition of 2 equivalents of acid, *e.g.* complexes **5a**, **5b** and **6**. With the alkylidynetungsten compound **1d**, however, it was possible to isolate the alkylidenetungsten salt **3c**. Synthesis of the latter in the presence of PPh_3 or dppm afforded the novel compounds **7a** and **8**.

Experimental

All experiments were carried out under nitrogen, using Schlenk-tube techniques. Solvents were rigorously dried and freshly distilled before use. Light petroleum refers to that fraction of b.p. 40–60 °C. The NMR spectra were recorded with JEOL JNM GX270 and GX400 spectrometers and the IR spectra with a Perkin-Elmer FT1600 spectrometer. Chromatography columns (*ca.* 20 cm in length and 3 cm in diameter) were charged with Aldrich aluminium oxide (Brockman activity III). The reagent $HBF_4{\cdot}Et_2O$ consisted of an 85% solution in diethyl ether. The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}2$, $C_6H_3Me_2\text{-}2,6$ or $C_6H_4OMe\text{-}2$) have been obtained previously by treating the species $[W(\equiv CR)Br(CO)_4]$ with NaC_5H_5.[14] For the work described herein they were more conveniently obtained by a procedure developed by Mayr and co-workers[15] which involves the direct syntheses of the species $[W(\equiv CR)(O_2CCF_3)(CO)_2(py)_2]$ (py = pyridine) from $[W(CO)_6]$, followed by treatment of these trifluoroacetate reagents with NaC_5H_5. The route to the acetate complexes is exemplified by the preparation of the new compound $[W(\equiv CC_6H_4OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$.

To a suspension of $[W(CO)_6]$ (9.0 g, 25.6 mmol) in Et_2O (150 cm^3) was added dropwise 1 equivalent of (2-methoxyphenyl)-lithium, monitored by IR spectroscopy, to generate $Li[W\{C(O)C_6H_4OMe\text{-}2\}(CO)_5]$ *in situ*. The resulting orange solution was cooled to −78 °C, and $(CF_3CO)_2O$ (4.0 cm^3, 28.3 mmol) in Et_2O (50 cm^3) was added dropwise over 1 h. After warming to −20 °C, pyridine (14.5 cm^3, 179 mmol) was added, and the mixture was stirred overnight at room temperature, CO being released. Solvent was removed *in vacuo*, and the orange residue was dissolved in CH_2Cl_2 (50 cm^3) and chromatographed at −20 °C. Elution with CH_2Cl_2 gave an orange eluate from which solvent was removed *in vacuo*. Crystallisation of the solid from CH_2Cl_2–light petroleum (*ca.* 60 cm^3, 1:5) afforded orange-red *microcrystals* of $[W(\equiv CC_6H_4OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$ (8.50 g, 53% yield) (Found: C, 40.6; H, 2.9; N, 4.7. $C_{22}H_{17}F_3N_2O_5W$ requires C, 41.9; H, 2.7; N, 4.5%); $\nu_{max}(CO)$ at 1986vs and 1899vs cm^{-1} (in CH_2Cl_2). NMR ($CDCl_3$): ^1H, δ 3.86 (s, 3 H, OMe), 6.79–6.88 (m, 2 H, C_6H_4), 7.23–7.35 (m, 6 H, py), 7.73–7.80 (m, 2 H, C_6H_4) and 9.21–9.27 (m, 4 H, py); $^{13}C-\{^1H\}$, δ 259.7 [C≡W, J(WC) 209], 220.5 [CO, J(WC) 170], 160.4 (O_2CCF_3), 160.2–110.7 (C_6H_4 and py), 130.7 [q, CF_3, J(FC) 269 Hz] and 55.5 (OMe).

Protonation of the Compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ ($R = C_6H_4Me\text{-}2$ *or* $C_6H_3Me_2\text{-}2,6$).—(*i*) Compound **1b** (0.30 g, 0.74 mmol) in CH_2Cl_2 (30 cm^3) was treated with CF_3CO_2H (0.15 cm^3, 1.95 mmol) at room temperature for *ca.* 5 min. Solvent was removed *in vacuo* and the residue was dissolved in CH_2Cl_2–light petroleum (20 cm^3, 1:1). The volume was reduced *in vacuo* to *ca.* 5 cm^3 giving orange-red *microcrystals* of $[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)]$ **5a** (0.34 g).

(*ii*) In a similar experiment, compound **1c** (0.60 g, 1.42 mmol) and CF_3CO_2H (0.25 cm^3, 3.25 mmol) gave yellow *microcrystals* of $[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2C_6H_3Me_2\text{-}2,6)(\eta\text{-}C_5H_5)]$ **5b** (0.72 g).

(*iii*) The reagent **1b** (0.30 g, 0.74 mmol) in NCMe (20 cm^3) was treated with $HBF_4{\cdot}Et_2O$ (0.21 cm^3, 1.6 mmol) at room temperature, and the mixture was stirred for 5 min. Solvent was removed *in vacuo*, the residue was dissolved in NCMe (3 cm^3), and Et_2O (*ca.* 12 cm^3) was added dropwise with vigorous stirring. The yellow solid thus obtained was washed with Et_2O (2 × 5 cm^3) and dried *in vacuo* to give orange-red *microcrystals* of $[W(CO)(NCMe)_2(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)][BF_4]_2$ **6a** (0.30 g).

(*iv*) As in the synthesis of **6a**, compound **1c** (0.60 g, 1.42 mmol) in NCMe (20 cm^3) on treatment with $HBF_4{\cdot}Et_2O$ (0.40 cm^3, 3.1 mmol) afforded yellow *microcrystals* of $[W(CO)(NCMe)_2(\eta^2\text{-}COCH_2C_6H_3Me_2\text{-}2,6)(\eta\text{-}C_5H_5)][BF_4]_2$ **6b** (0.66 g).

Synthesis of the Salts $[W(NCMe)_3(\eta^2\text{-}COCH_2R)(\eta\text{-}C_5H_5)][BF_4]_2$ ($R = C_6H_4Me\text{-}2$ *or* $C_6H_3Me_2\text{-}2,6$).—(*i*) The salt **6a** (0.26 g, 0.38 mmol) was dissolved in NCMe (20 cm^3), and the mixture was refluxed for 30 min. After cooling to room temperature, solvent was removed *in vacuo*. The residue was dissolved in NCMe (3 cm^3), and Et_2O (*ca.* 10 cm^3) was added dropwise with rigorous stirring to give orange *microcrystals* of $[W(NCMe)_3(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)][BF_4]_2$ **6c** (0.21 g), after washing with Et_2O (2 × 5 cm^3) and drying *in vacuo*.

(*ii*) Similarly, compound **6b** (0.25 g, 0.37 mmol) in NCMe (20 cm^3) after refluxing the mixture yielded orange *microcrystals* of $[W(NCMe)_3(\eta^2\text{-}COCH_2C_6H_3Me_2\text{-}2,6)(\eta\text{-}C_5H_5)][BF_4]_2$ **6d** (0.21 g).

Protonation of the Compound $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$.—(*i*) The compound **1d** (0.20 g, 0.47 mmol) was dissolved in CH_2Cl_2 (20 cm^3), treated with $HBF_4{\cdot}Et_2O$ (0.03 cm^3, 0.23 mmol) and stirred at −78 °C for 10 min. After warming to room temperature the solvent was removed *in vacuo*. The residue was crystallised from CH_2Cl_2–Et_2O (*ca.* 35 cm^3, 1:8) to give a yellow powder, which was washed once with Et_2O (10 cm^3) and dried *in vacuo* to give yellow *microcrystals* of $[W\{{=}C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3c** (0.11 g).

(*ii*) A CH_2Cl_2 (20 cm^3) solution of compound **1d** (0.10 g, 0.24 mmol) and PPh_3 (0.13 g, 0.50 mmol) was treated with $HBF_4{\cdot}Et_2O$ (0.03 cm^3, 0.23 mmol) and the mixture was stirred at −78 °C for 10 min. After warming to room temperature, solvent was removed *in vacuo*. The residue was crystallised from CH_2Cl_2–Et_2O (*ca.* 35 cm^3, 1:6) and the powder thus obtained was washed with Et_2O (10 cm^3) and dried *in vacuo* to yield orange-red *microcrystals* of $[W\{\sigma,\eta^2\text{-}CH(PPh_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **7a** (0.18 g).

(*iii*) As in the synthesis of **7a**, the reagent **1d** (0.10 g, 0.24 mmol) and dppm (0.10 g, 0.26 mmol) in CH_2Cl_2 (20 cm^3) was treated with $HBF_4{\cdot}Et_2O$ (0.03 cm^3, 0.23 mmol) and stirred at −78 °C for 10 min to afford yellow *microcrystals* of $[W\{CH(C_6H_4OMe\text{-}2)PPh_2CH_2PPh_2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$

Table 4 Atomic positional parameters (fractional coordinates, × 10^4) with estimated standard deviations in parentheses for complex **7a**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	8 398(1)	9 152(1)	10 000	W(2)	4 185(1)	15 922(1)	13 316(1)
P(1)	6 919(5)	10 503(7)	10 497(5)	P(2)	5 671(5)	14 556(7)	12 830(5)
C(101)	9 237(15)	9 363(16)	10 698(11)	C(201)	2 986(14)	15 566(17)	13 238(13)
C(102)	9 036	8 384	10 702	C(202)	3 081	16 536	13 414
C(103)	9 229	7 973	10 147	C(203)	3 405	17 028	12 937
C(104)	9 547	8 699	9 800	C(204)	3 512	16 362	12 467
C(105)	9 552	9 558	10 141	C(205)	3 252	15 459	12 652
C(106)	7 625(15)	8 284(22)	10 171(13)	C(206)	4 920(24)	16 754(34)	12 993(21)
O(106)	7 238(15)	7 744(21)	10 265(13)	O(206)	5 320(18)	17 330(26)	12 917(16)
C(107)	8 179(23)	8 579(32)	9 218(22)	C(207)	4 467(22)	16 609(35)	14 044(9)
O(107)	8 023(17)	8 239(23)	8 754(15)	O(207)	4 556(19)	16 944(26)	14 501(8)
C(108)	7 825(16)	10 341(24)	10 363(15)	C(208)	4 763(19)	14 670(26)	12 858(16)
C(111)	8 122(15)	10 755(25)	9 893(16)	C(211)	4 488(15)	14 220(19)	13 394(12)
C(112)	8 674(20)	11 424(28)	9 921(23)	C(212)	3 888(16)	13 778(21)	13 397(16)
C(113)	9 088(20)	11 666(26)	9 451(18)	C(213)	3 585(23)	13 421(34)	13 993(22)
C(114)	8 875(19)	11 387(27)	8 853(18)	C(214)	3 795(24)	13 848(30)	14 529(22)
C(115)	8 320(17)	10 809(27)	8 769(15)	C(215)	4 308(20)	14 480(29)	14 584(20)
C(116)	7 944(21)	10 461(29)	9 241(20)	C(216)	4 648(19)	14 616(26)	13 979(16)
O(117)	8 854(14)	11 692(20)	10 510(13)	O(217)	3 767(14)	13 308(20)	12 938(13)
C(117)	9 378(21)	12 330(30)	10 662(20)	C(217)	3 243(20)	12 581(28)	12 852(19)
C(121)	6 653	9 778	11 085	C(221)	5 931	15 347	12 213
C(122)	7 139(10)	9 495(19)	11 503(12)	C(222)	5 479(10)	15 680(19)	11 779(12)
C(123)	6 939	9 000	12 015	C(223)	5 715	16 259	11 316
C(124)	6 252	8 787	12 108	C(224)	6 403	16 506	11 286
C(125)	5 766	9 070	11 689	C(225)	6 855	16 173	11 719
C(126)	5 967	9 565	11 177	C(226)	6 619	15 593	12 183
C(131)	6 409	10 206	9 843	C(231)	6 169	14 813	13 466
C(132)	6 250(13)	10 943(13)	9 446(11)	C(232)	6 322(12)	14 038(13)	13 836(11)
C(133)	5 893	10 740	8 923	C(233)	6 640	14 194	14 385
C(134)	5 694	9 800	8 797	C(234)	6 803	15 125	14 563
C(135)	5 853	9 063	9 195	C(235)	6 650	15 900	14 193
C(136)	6 210	9 266	9 718	C(236)	6 332	15 744	13 644
C(141)	6 735	11 736	10 654	C(241)	5 862	13 367	12 590
C(142)	7 263(9)	12 383(18)	10 763(12)	C(242)	5 343(10)	12 702(19)	12 489(13)
C(143)	7 114	13 327	10 926	C(243)	5 504	11 767	12 318
C(144)	6 438	13 623	10 978	C(244)	6 184	11 496	12 249
C(145)	5 910	12 976	10 869	C(245)	6 703	12 161	12 350
C(146)	6 059	12 032	10 706	C(246)	6 542	13 097	12 521
B(1)	6 068(9)	15 572(12)	16 039(9)	B(2)	3 695(10)	19 483(14)	12 236(9)
F(11)	6 242(15)	14 630(18)	16 120(14)	F(21)	3 825(16)	20 415(20)	12 142(15)
F(12)	5 587(14)	15 639(22)	15 599(13)	F(22)	3 193(16)	19 397(22)	12 639(13)
F(13)	5 809(14)	15 934(21)	16 560(12)	F(23)	3 503(15)	19 071(22)	11 723(13)
F(14)	6 634(14)	16 085(20)	15 878(13)	F(24)	4 257(14)	19 050(22)	12 442(14)

8 (0.17 g), after crystallisation from CH_2Cl_2–hexane (15 cm^3, 1 : 2) and washing once with hexane (20 cm^3).

Crystal Structure Determination of Compound **7a**.—Small crystals were grown from CH_2Cl_2–hexane (1 : 5) as orange prisms. The complex crystallised with two chemically identical and crystallographically independent ion pairs in the asymmetric unit. Data were collected at 298 K on a Siemens R3m/V four-circle diffractometer from a crystal of dimensions *ca.* 0.50 × 0.20 × 0.02 mm which was sealed under nitrogen in a glass capillary. The small crystal diffracted poorly and of the 6016 unique reflections collected (Wyckoff ω scans, $2\theta \leqslant 50°$) 2763 had $F \geqslant 4\sigma(F)$, and only these were used for structure solution and refinement, after corrections for Lorentz, polarisation and X-ray absorption effects, the latter by an empirical method.[16]

Crystal data. $C_{33}H_{28}BF_4O_3PW$, $M = 774.2$, orthorhombic, space group $Pca2_1$, $a = 19.623(5)$, $b = 13.936(4)$, $c = 22.413(7)$ Å, $U = 6129(3)$ Å^3, $Z = 8$, $D_c = 1.68$ g cm^{-3}, $F(000) = 3040$, Mo-Kα X-radiation (graphite monochromator), $\bar{\lambda} = 0.710\,69$ Å, μ(Mo-Kα) = 39.6 cm^{-1}.

The observed systematic absences and unit-cell parameters were consistent with the orthorhombic space groups $Pca2_1$ (acentric) or *Pbcm* (centric). In *Pbcm* the calculated density suggests one ion pair per asymmetric unit but attempts to solve the structure in this space group revealed two half molecules lying on special positions with imposed mirror symmetry. Since the cation is chiral it would necessarily be disordered in this space group. In the lower-symmetry space group $Pca2_1$ refinement was more successful and revealed two ordered and crystallographically independent ion pairs per asymmetric unit. Unfortunately these were related by a strong pseudo-centre of symmetry and this feature together with the poor quality of the data set seriously compromises the quality of the structure determination. Thus whilst the structure of the cation is qualitatively correct the structural parameters should be treated with due caution.

The structure was solved by conventional heavy-atom methods and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. The tungsten and phosphorus atoms were refined with anisotropic thermal parameters. All other non-hydrogen atoms were refined with isotropic thermal parameters because of the limited amount of observed data. The atoms C(111) and C(211) were refined with fixed thermal parameters ($U_{iso} = 0.03$ Å^2 for both). All the phenyl rings bonded to phosphorus, and the cyclopentadienyl group, were treated as rigid groups. The BF_4^- groups in both ion pairs of the asymmetric unit, and atoms C(207), O(207), C(208), C(211) and C(216), were refined with bond-length restraints (DFIX).[16] All hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2). Refinement by blocked-cascade least squares led to $R = 0.076$ ($R' = 0.069$) with a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.001|F|^2]$ giving a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 2.83 or < -1.37 e Å^{-3}.

All calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[16] Scattering factors with corrections for anomalous dispersion were taken from ref. 17. Atom coordinates are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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