Proton-induced Dimerisation and Related Reactions of Mononuclear Tungsten Carbyne Complexes. Crystal Structures of the Compounds $[W\{=C(H)(C_6H_4Me\text{-}4)\}(I)(CO)_2(\eta\text{-}C_5H_5)]$ and $[W\{\eta^2\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][BF_4]\cdot(Me_2CO)$

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Abstract

Protonation of the compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) with *ca.* 0.5 mol equivalents of the reagent $HBF_4\cdot Et_2O$ affords the ditungsten salts $[W_2(\mu\text{-}H)(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ formed via a coupling of the carbyne groups in the precursors. These compounds are readily deprotonated to give the bridged alkyne complexes $[W_2(\mu\text{-}RC_2R)(CO)_4(\eta\text{-}C_5H_5)_2]$, a process which is reversed with acid. Aqueous HI with $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ affords the iodo carbene complexes $[W(=CHR)(I)(CO)_2(\eta\text{-}C_5H_5)]$. The structure of the species with R = C_6H_4Me-4 has been established by X-ray diffraction [W=C 2.05(2) Å]. The tolyl substituent on the alkylidene carbon atom is *transoid* to the $\eta\text{-}C_5H_5$ ligand, and the alkylidene group is *transoid* to the iodine atom. Protonation of the ketenyl–tungsten complexes $[W\{=C(R)\cdot\dot{C}:O\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4, PR'_3 = PMe_3, PPr^i_3 or $PMePh_2$; R = Me, PR'_3 = PMe_3) affords the salts $[W\{\eta^2\text{-}C_2(OH)(R)\}(CO)(PR'_3)(\eta\text{-}C_5H_5)][BF_4]$ containing hydroxy–alkyne ligands. The structure of the species with R = C_6H_4Me-4 and PR'_3 = PMe_3 has been established by X-ray diffraction. It contains an acetone molecule of crystallisation which is hydrogen bonded to the proton of the hydroxyl group on the alkyne. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra of the new compounds are reported and discussed.

Introduction

It is rapidly becoming apparent that the alkylidyne–tungsten complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (**1a**, R = C_6H_4Me-4; **1b**, R = Me) [1, 2] are useful precursors to a variety of organotungsten compounds. For example, reactions with low-valent metal species afford cluster compounds containing bonds between tungsten and other transition elements [3]. Reactions with tertiary phosphines yield either tungsten-substituted ketenes $[W\{C(R):C:O\}(CO)(PR'_3)_2(\eta\text{-}C_5H_5)]$ or η^2-ketenyl complexes $[W\{=C(R)\cdot\dot{C}:O\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (R' = alkyl or aryl) [2, 4, 5]. Hydrogen chloride in ethereal solution promotes a novel C–C coupling reaction to give η^2-acyl complexes $[WCl_2\{\eta^2\text{-}C(CH_2R):O\}(CO)(\eta\text{-}C_5H_5)]$ [6], while $[W(\equiv CMe)(CO)_2(\eta\text{-}C_5H_5)]$ with $BH_3\cdot$thf (thf = tetrahydrofuran) affords the ditungsten complex $[W_2\{\mu\text{-}MeCB(H)CH_2Me\}(CO)_4(\eta\text{-}C_5H_5)_2]$ [7]. In this paper we describe reactions of the species $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ with $HBF_4\cdot Et_2O$ and with aqueous HI, as well as alkylation and protonation studies on the η^2-ketenyl complexes $[W\{=C(R)\cdot\dot{C}:O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$. A preliminary account of some of the work has been given [8].

Results and Discussion

Protonation of (**1a**) with 0.4 equivalents of $HBF_4\cdot Et_2O$, thus ensuring that the tolylmethylidyne–tungsten complex is present in excess, affords a yellow salt, characterised as the ditungsten complex (**2a**) by microanalysis and by its spectroscopic properties (Tables I and II). The ^1H NMR spectrum shows a resonance for the hydrido ligand at δ −17.0 p.p.m. with ^{183}W satellite peaks. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum there is no resonance corresponding to a terminal or bridging $C\text{-}C_6H_4Me$-4 ligand. Two peaks at δ 209.1 and 203.3 p.p.m. can be assigned to CO ligands, from which it is assumed that the observed spectrum is not the limiting one, and that the cation of (**2a**) is undergoing dynamic behaviour via a low energy process similar to that described in detail

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TABLE I. Analytical[a] and Other Data for the Tungsten Complexes.

	Compound	M.p. (°C)	Colour	Yield (%)	ν_{max} (CO) (cm^{-1})[c]	Analysis	
						C	H
(2a)	$[W_2(\mu\text{-H})\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$	[b]178	Yellow	95	2024s, 1976s	39.3(39.9)	2.8(2.8)
(2b)	$[W_2(\mu\text{-H})(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$	[b]157	Yellow	75	2060sh, 2035s, 1973s	28.0(28.8)	2.3(2.3)
(3b)	$[W_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]\cdot CH_2Cl_2$	[b]210–212	Red	60	1973m, 1902s, 1813m	31.4(30.5)	2.6(2.4)
(4a)	$[W\{=C(H)C_6H_4Me\text{-}4\}(I)(CO)_2(\eta\text{-}C_5H_5)]$	90–94	Red	42	2004w, 1934s	[d]33.6(33.5)	2.5(2.4)
(4b)	$[W\{=C(H)Me\}(I)(CO)_2(\eta\text{-}C_5H_5)]$[e]	–	Red	–	2018m, 1954s	22.5(23.5)	2.4(2.0)
(5)	$[W(\equiv CC_6H_4Me\text{-}4)(H)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$	[b]102	Yellow	98	2051s(br)	36.5(36.3)	2.6(2.6)
(7a)	$[W\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][BF_4]\cdot Me_2CO$	92	Red	90	1975s	40.6(40.1)	4.3(4.3)
(7b)	$[W\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PPr^i_3)(\eta\text{-}C_5H_5)][BF_4]$	96	Red	98	1965s	44.1(43.9)	5.1(5.2)
(7c)	$[W\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMePh_2)(\eta\text{-}C_5H_5)][BF_4]$	95	Red	80	1973s	47.9(48.4)	3.7(3.7)
(8)	$[W\{\eta\text{-}C_2(OH)(Me)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][BF_4]$	124	Red	98	1970s	28.6(28.2)	3.6(3.5)
(9a)	$[W\{\eta\text{-}C_2(OMe)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][SO_3CF_3]$	122	Red	98	1977s	36.5(37.0)	3.7(3.7)
(9b)	$[W\{\eta\text{-}C_2(OMe)(Me)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][SO_3CF_3]$	86	Yellow	98	1975s	29.3(28.8)	3.5(3.5)

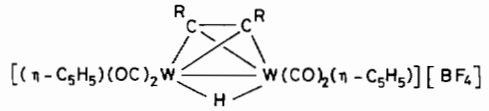
[a]Calculated values in parentheses. [b]With decomposition. [c]In CH_2Cl_2. [d]I, 23.3(23.6); Mass spec. m/e 536(536). [e]Unstable, see text.

TABLE II. NMR Data[a] for the Tungsten Complexes.

Compound	^1H (δ)	^{13}C (δ)[b]
(2a)[c]	−17.00 [s, 1 H, μ-H, J(WH) 33], 2.42 (s, 6 H, Me-4), 5.53 (s, 10 H, C_5H_5), 7.21 (m, 8 H, C_6H_4).	209.1 [CO, J(WC) 153], 203.3 [CO, J(WC) 154], 139.3 [$C^1(C_6H_4)$], 137.4, 130.3, 129.1 (C_6H_4), 91.8 (C_5H_5), 60.7 (μ-C_2), 21.3 (Me-4).
(2b)[d,e]	−18.50 [s, 1 H, μ-H, J(WH) 32], 3.01 (s, 6 H, Me), 5.91 (s, 10 H, C_5H_5).	209.8 [CO, J(WC) 150], 202.5 [CO, J(WC) 159], 90.1 (C_5H_5), 64.9 (μ-C_2), 22.9 (Me-4).
(3b)[f,g]	2.60 (s, 6 H, Me), 5.15 (s, 10 H, C_5H_5), 5.35 (s, 2 H, CH_2Cl_2).	218.5 [CO, J(WC) 171], 89.4 (C_5H_5), 21.4 (Me).
(4a)[h]	2.23 (s, 3 H, Me-4), 6.01 (s, 5 H, C_5H_5), 7.23 and 7.62 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 13.08 (s, 1 H, C*H*R).	267.4 [*C*HR, J(WC) 75], 206.5 [CO, J(WC) 161], 146.9–129.2 (C_6H_4), 96.6 (C_5H_5), 21.1 (Me-4).
(4b)[i]	2.66 [d, 3 H, Me, J(HH) 8], 5.95 (s, 5 H, C_5H_5), 13.42 [q, 1 H, C*H*Me, J(HH) 8].	287.2 (*C*HMe0, 206.4 (CO), 97.9 (C_5H_5), 36.6 (Me).
(7a)[j,k]	1.68 [d, 9 H, MeP, J(PH) 9], 2.39 (s, 3 H, Me-4), 6.30 [d, 5 H, C_5H_5, J(PH) 2], 7.44 and 7.86 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8], 13.90 (s, br, 1 H, OH).	226.7 [d, *C*OH, J(PC) 7, J(WC) 80], 224.6 [d, CO, J(PC) 5, J(WC) 130], 191.7 [*C*R, J(WC) 75], 142.1–130.8 (C_6H_4), 95.3 (C_5H_5), 21.6 [d, MeP, J(PC) 39], 21.7 (Me-4).
(7b)[l]	1.10 (m, 21 H, Pr^i), 2.40 (s, 3 H, Me-4), 6.10 (s, 5 H, C_5H_5), 7.20–7.70 (m, 4 H, C_6H_4).	
(7c)[l]	2.35 (s, 3 H, Me-4), 2.40 [d, 3 H, MeP, J(PH) 10], 6.12 [d, 5 H, C_5H_5, J(PH) 2], 7.20–7.70 (m, 14 H, C_6H_4 and Ph).	
(8)[j,m]	1.64 [d, 9 H, MeP, J(PH) 11], 2.80 [d, 3 H, Me, J(PH) 2], 6.10 [d, 5 H, C_5H_5, J(PH) 2], 13.50 (s, br, 1 H, OH).	222.5 [*C*OH, J(WC) 50], 222.2 [d, CO, J(PC) 10], 197.2 [*C*Me, J(WC) 41], 92.3 (C_5H_5), 21.4 [d, MeP, J(PC) 37], 20.1 (Me).
(9a)[j]	1.67 [d, 9 H, MeP, J(PH) 11], 2.38 (s, 3 H, Me), 4.54 (s, 3 H, OMe), 6.24 [d, 5 H, C_5H_5, J(PH) 2], 7.39 and 7.77 [$(AB)_2$, 4 H, C_6H_4, J(AB) 8].	230.8 [*C*OMe, J(WC) 72], 224.0 [CO, J(WC) 142], 193.4 [*C*R, J(WC) 51], 141.5–129.7 (C_6H_4), 121.6 [q, CF_3SO_3, J(FC) 322], 94.0 (C_5H_5), 66.7 (OMe), 21.7 [d, MeP, J(PC) 37], 21.1 (Me-4).
(9b)[j,m]	1.67 [d, 9 H, MeP, J(PH) 11], 2.97 (s, 3 H, Me), 4.40 (s, 3 H, OMe), 6.23 (s, 5 H, C_5H_5).	227.1 [*C*OMe, J(WC) 70], 222.9 [d, CO, J(PC) 4, J(WC) 143], 197.6 [d, *C*Me, J(PC) 7, J(WC) 55], 121.5 [q, CF_3SO_3, J(FC) 322], 94.2 (C_5H_5), 66.3 (OMe), 21.1 [d, MeP, J(PC) 37], 19.9 (Me).

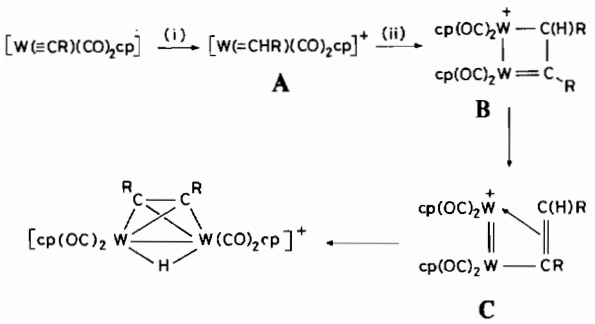
[a]Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at room temperature unless otherwise stated. [b]Hydrogen-1 decoupled, measured to high frequency of $SiMe_4$. [c] ^1H spectrum measured in CD_2Cl_2, ^{13}C-{^1H} spectrum in CD_2Cl_2–CH_2Cl_2. [d] ^1H spectrum measured in $(CD_3)_2CO$, ^{13}C-{^1H}spectrum in CD_2Cl_2–CH_2Cl_2. [e]Spectra measured at −10 °C. [f]Spectra measured in $CDCl_3$. [g] ^{13}C-{^1H}spectrum measured at −20 °C. [h] ^1H spectrum measured in $CDCl_3$, ^{13}C-{^1H} spectrum in $CDCl_3$–$CHCl_3$. [i] ^1H spectrum measured in $CDCl_3$, ^{13}C-{^1H} spectrum in CD_2Cl_2–CH_2Cl_2. [j] ^1H spectrum measured in $(CD_3)_2CO$, ^{13}C-{^1H} spectrum in $(CD_3)_2CO$–Me_2CO. [k] ^1H spectrum measured at −50 °C. [l] ^1H spectrum measured in $(CD_3)_2CO$, hence O*H* not observed. [m]Spectra measured at −20 °C.

elsewhere for the neutral complexes $[W_2(\mu\text{-alkyne})(CO)_4(\eta\text{-}C_5H_5)_2]$ [9].



(2a) R = C_6H_4Me-4
(2b) R = Me

Protonation of **(1b)** under similar conditions to those for **(1a)** afforded the ditungsten salt **(2b)**. The analytical and spectroscopic data (Tables I and II) were again in accord with the structure proposed. Evidently in these protonation reactions the carbyne ligands in the mononuclear tungsten compounds **(1)** undergo a C–C coupling reaction, perhaps via the pathway shown in Scheme 1.



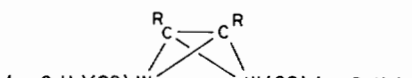
R = C_6H_4Me-4 or Me; cp = η-C_5H_5.
(i) + $HBF_4 \cdot Et_2O$, (ii) + $[W(\equiv CR)(CO)_2cp]$.

Scheme 1.

It is reasonable to assume that the initial proton of **(1)** occurs at the alkylidyne carbon atom to give a cationic 16-electron tungsten intermediate $[W(=CHR)(CO)_2(\eta\text{-}C_5H_5)]^+$, possibly stabilised by co-ordination of a solvent molecule or the $[BF_4]^-$ anion [10] to the metal centre. There is considerable precedent for initial attack of the proton at an alkylidyne carbon atom. Thus, as described below, the compounds **(1)** react with aqueous HI to give the iodotungsten carbene complexes **(4)**. As mentioned earlier, HCl in diethyl ether reacts with the complexes **(1)** to give η^2-acyl complexes which are obviously formed via addition of protons to the carbyne–carbon atoms [6]. Recently it has been shown that protonation of the compound $[W(\equiv CSMe)(CO)_2(HBpz_3)]$ affords the salt $[W\{\eta^2\text{-}C(H)SMe\}(CO)_2(HBpz_3)][SO_3CF_3]$ [$HBpz_3$ = tris(pyrazolylborato)] [11], a reaction also involving protonation at the alkylidyne carbon. Moreover, protonation of the molybdenum carbyne complex $[Mo(\equiv CCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]$ is believed to afford initially the cation $[Mo(=CHCH_2Bu^t)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$ which subsequently rearranges to the thermodynamically controlled product $[Mo(\equiv CCH_2Bu^t)(H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)]^+$ [12]. These protonation reactions are evidently charge controlled, since theoretical work [13] suggests that in neutral carbyne–metal complexes the carbyne–carbon is the most negative ligand site.

It is proposed that the intermediate **A**, shown in Scheme 1, reacts rapidly with the excess of **(1a)** or **(1b)** present to afford the dimetallacyclobutene intermediate **B**, which rearranges to the final products **(2)** via the bridged-vinyl species **C**. Intermediate **B**, bearing in mind the isolobal relationship between the compounds **(1)** and alkynes [3], is similar to alkyne adducts of tungsten carbenes observed by G. L. Geoffroy *et al.* [14]. Intermediate **C** is modelled on the known dimolybdenum vinyl bridged complex $[Mo_2(\mu\text{-}\sigma,\eta^2\text{-}CH{:}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$ formed by protonation of $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$ [15, 16]. In this process the first step is believed to involve an intermediate with a structure similar to those of the compounds **(2)**, but in the case of molybdenum the vinyl-bridged species is thermodynamically the most stable.

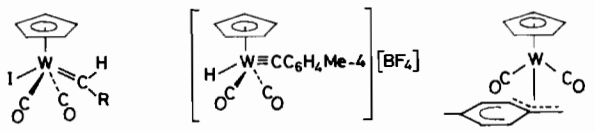
Treatment of compound **(2a)** with PMe_3 or $K[BH(CHMeEt)_3]$, or chromatography of solutions of the salt on basic alumina, results in deprotonation to give the known complex **(3a)** [17]. Compound **(2b)** is also readily deprotonated with PMe_3 or upon treatment with LiMe yielding the bridged alkyne complex **(3b)** (Tables I and II). In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of the latter the signals for the ligated carbons of the alkyne could not be unambiguously assigned. However, this is not an unusual feature of the spectra of this class of complex where the chemical shifts occur over a wide range [9]. The IR spectrum of **(3b)** (Table I), with three bands in the CO stretching region, with one at *ca.* 1800 cm^{-1} due to a semi-bridging ligand, is typical for compounds of this type. Formation of the complexes **(3)** from **(2)** can be reversed by protonation of the former with the reagent $HBF_4 \cdot Et_2O$, but the reaction proceeds more readily with **(3b)** than with **(3a)**. It is interesting to compare these results with the protonation of $[Mo_2(\mu\text{-}HC_2H)(CO)_4(\eta\text{-}C_5H_5)_2]$, mentioned earlier, which gives $[Mo_2(\mu\text{-}\sigma,\eta^2\text{-}CH{:}CH_2)(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$.



(3a) R = C_6H_4Me-4
(3b) R = Me

As described above, the syntheses of the compounds **(2)** were carried out using a deficiency of

the reagent $HBF_4 \cdot Et_2O$. It was therefore of interest to establish whether the same pathway was followed when excess of the acid was employed. Unfortunately under these conditions the results were not reproducible. Using (**1a**), formation of a new compound (**5**) was observed, but generally (**2a**) was also produced, and separation of the two species was not then possible. However, (**5**) was sometimes formed cleanly, and this allowed the data listed in Table I to be obtained. It was thought initially that (**5**) was $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, the intermediate invoked in Scheme 1, but the $^{13}C\text{-}\{^1H\}$ NMR spectrum was not consistent with this formulation. There was a CO resonance at δ 203.3 p.p.m. [J(WC) 156 Hz] and a peak at 282.4 p.p.m. in the region expected for a tungsten ligated alkylidene group W=*C*(H)R. However, in a fully coupled ^{13}C spectrum this resonance showed only very weak (5 Hz) $^1H-^{13}C$ coupling, whereas typically such couplings are over 100 Hz. For example, in $[W\{=C(H)NEt_2\}Cl(CO)_2(\eta\text{-}C_5H_5)]$ $J(^1H-^{13}C)$ is 138.5 Hz [18]. The weak $^1H-^{13}C$ coupling on the signal at δ 282.4 p.p.m. in the ^{13}C NMR spectrum of (**5**) suggests that it is the hydrido(alkylidyne) species $[W(\equiv CC_6H_4Me\text{-}4)(H)(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, formed by rearrangement of the initially produced $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ (compare the formation of $[Mo(\equiv CCH_2Bu^t)(H)\{P(OMe)_3\}_2(\eta\text{-}C_5H_5)][BF_4]$, described above). In accord with this proposal, (**5**) was found not to react with (**1a**) on stirring mixtures of the two compounds in CH_2Cl_2 for several hours. Addition of CH_2Cl_2 solutions of (**5**) to $K[BH(CHMeEt)_3]$ in tetrahydrofuran gives the known η^3-benzyl complex (**6**) [19]. Treatment of (**5**) with Et_4NI in CH_2Cl_2 followed by chromatography on alumina affords compound (**4a**). This reaction may proceed by deprotonation of (**5**) yielding (**1a**), with subsequent addition of HI to the latter to give (**4a**), or by rearrangement of an initially formed species $[W\{=C(I)C_6H_4Me\text{-}4\}(H)(CO)_2(\eta\text{-}C_5H_5)]$. However, these suggestions assume that (**5**) is correctly formulated as a hydrido(tolylmethylidyne)tungsten complex. We were unable to detect a high-field resonance in the ^1H NMR spectrum of (**5**) and hence the presence of a hydrido ligand could not be confirmed, and so the exact nature of the species must remain unresolved



(**4a**) R = C_6H_4Me-4 (**5**) (**6**)

(**4b**) R = Me

Compound (**4a**), and its analogue (**4b**) may be prepared by reacting the compounds (**1**) with aqueous HI, and data for these species are summarised in Tables I and II. Compound (**4b**) is relatively unstable. Treatment of (**4a**) with $K[BH(CHMeEt)_3]$ gives (**6**) and not the hydrido(tolylmethylidene) species $[W\{=CH(C_6H_4Me\text{-}4)\}(H)(CO)_2(\eta\text{-}C_5H_5)]$.

In order to establish fully the nature of compound (**4a**), a single crystal X-ray diffraction study was carried out. The results are summarised in Table III and the molecule is shown in Fig. 1. The molecule as a whole possesses a *pseudo*-mirror plane defined by the tolyl ring, and the W and I atoms. The structure has a close resemblance to that of the recently reported [20] compound $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$ with the $SnPh_3$ group in the latter replaced by an iodide ligand in (**4a**). In the tin–tungsten complex the W=C distance is 2.032(7) Å compared with 2.054(16) Å in (**4a**), and these values may themselves be compared with the W=C separations in $[W(=CPh_2)(CO)_5]$ [2.14(2) Å] [21] and in $[W(=CHPh)(\eta\text{-}C_5H_5)_2]$ [2.05(2) Å] [22]. The penta-

TABLE III. Selected Internuclear Distances (Å) and Angles (°) for $[W\{=C(H)C_6H_4Me\text{-}4\}(I)(CO)_2(\eta\text{-}C_5H_5)]$ (**4a**).

W–I	2.847(2)	W–C	2.05(2)
W–C(7)	2.02(2)	W–C(8)	1.96(2)
C–C(1)	1.42(3)	C(7)–O(7)	1.10(2)
C(8)–O(8)	1.22(2)	W–C(O1)	2.42(2)
W–C(O2)	2.36(2)	W–C(O3)	2.34(2)
W–C(O4)	2.36(3)	W–C(O5)	2.40(2)
I–W–C	142.8(5)	I–W–C(7)	75.1(5)
C–W–C(7)	79.5(7)	I–W–C(8)	77.5(5)
C–W–C(8)	78.6(7)	C(7)–W–C(8)	96.3(8)
W–C–C(1)	139(1)	W–C(7)–O(7)	175(2)
W–C(8)–O(8)	176(2)		

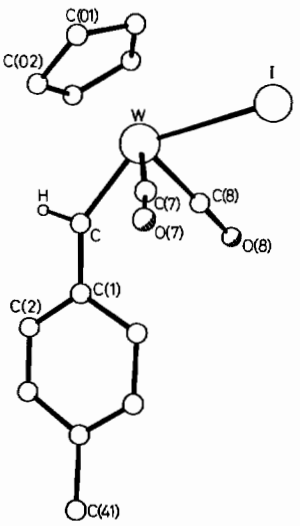


Fig. 1. Molecular structure of $[W\{=C(H)C_6H_4Me\text{-}4\}(I)(CO)_2(\eta\text{-}C_5H_5)]$ (**4a**) showing the atom numbering scheme.

TABLE IV. Selected Internuclear Distances (Å) and Angles (°) for $[W\{\eta^2\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][BF_4]\cdot OCMe_2$ (7a).

W–P	2.449(2)	W–C(4)	2.000(7)
W–C(5)	2.059(6)	W–C(6)	1.992(7)
W–C(11)	2.289(6)	W–C(12)	2.350(5)
W–C(13)	2.430(6)	W–C(14)	2.369(8)
W–C(15)	2.300(7)	P–C(1)	1.805(8)
P–C(2)	1.809(15)	P–C(3)	1.796(8)
C(4)–O(4)	1.325(9)	C(4)–C(5)	1.365(7)
C(5)–C(21)	1.440(7)	C(6)–O(6)	1.152(8)
C(7)–C(9)	1.45(2)	C(8)–C(9)	1.493(9)
C(9)–O(9)	1.200(9)	O(4)–H	1.00*
O(9)–H	1.63[a]	mean B–F	1.32
P–W–C(4)	97.4(2)	P–W–C(5)	96.3(2)
C(4)–W–C(5)	39.3(2)	P–W–C(6)	87.3(2)
C(4)–W–C(6)	120.3(2)	C(5)–W–C(6)	81.0(3)
W–P–C(1)	110.5(3)	W–P–C(2)	116.8(4)
W–P–C(3)	117.2(3)	C(1)–P–C(2)	104.7(5)
C(1)–P–C(3)	101.9(5)	C(2)–P–C(3)	104.0(5)
W–C(4)–O(4)	153.5(4)	W–C(4)–C(5)	72.7(4)
O(4)–C(4)–C(5)	133.0(5)	W–C(5)–C(4)	68.0(3)
W–C(5)–C(21)	156.9(5)	C(4)–C(5)–C(21)	135.1(7)
C(7)–C(9)–C(8)	118.5(7)	C(7)–C(9)–O(9)	121.5(7)
C(8)–C(9)–O(9)	119.9(8)		

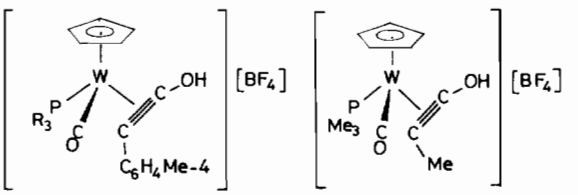
[a]Hydrogen atom parameters were not refined, hence no e.s.d.

carbonyl species is a W(0) complex and hence the W=C distance would be expected to be longer than in the other three compounds which involve W(II).

In both (**4a**) and in $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$ the $\eta\text{-}C_5H_5$ and C_6H_4Me-4 groups are *transoid* to each other to avoid steric repulsions between these bulky groups. Although the H atom on C in (**4a**) was not located by the X-ray study its presence was clearly revealed in the ^1H NMR spectrum (Table II). Moreover, the W–C–C(1) angle [139(1)°] indicates the presence of the hydrogen atom bound to C. The plane defined by W·C(7)·C(8) is approximately perpendicular to the $\eta\text{-}C_5$ plane and the W·C·I plane with dihedral angles of 89.9 and 91.1°, respectively.

The W–C–O groups deviate only slightly from linearity. The W–I distance [2.847(2) Å] is very similar to that found [2.845(5) Å] in $[W(\equiv CPh)(I)(CO)_4]$ [23]. The C–W–I angle of 142.8(5)° compares with 137.8(2)° for the C–W–Sn angle in $[W\{=C(H)C_6H_4Me\text{-}4\}(SnPh_3)(CO)_2(\eta\text{-}C_5H_5)]$.

During the course of our work we carried out protonation and methylation studies on the η^2-ketenyl complexes $[W\{=C(R)\cdot C{:}O\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me; R′ = alkyl or aryl) [2, 4, 5] in order to compare the nature of the products formed with those produced by treating the alkylidynetungsten compounds (**1**) with $HBF_4\cdot Et_2O$ or HI. Treatment of the complexes $[W\{=C(C_6H_4Me\text{-}4)\cdot C{:}O\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (PR'_3 = PMe_3, PPr^i_3 or $PMePh_2$) with $HBF_4\cdot Et_2O$ afforded the red crystalline salts (**7a**)–(**7c**), data for which are given in Tables I and II. An analogous salt (**8**) was obtained from $[W\{=C(Me)\cdot C{:}O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$. It was thought possible that these protonation reactions



(**7a**) PR_3 = PMe_3
(**7b**) PR_3 = PPr^i_3
(**7c**) PR_3 = $PMePh_2$

(**8**)

might produce alkylidene–tungsten complexes $[W(=CHR)(CO)_2(PR_3)(\eta\text{-}C_5H_5)][BF_4]$ (R = C_6H_4-Me-4 or Me) similar to the compound $[W(=CHPh)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)][AsF_6]$ prepared by Brookhart *et al.* [24] from $[W(CH_2Ph)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ and $[CPh_3][AsF_6]$. However, none of the species (**7**) or (**8**) showed in their $^{13}C\text{-}\{^1H\}$ NMR spectra a resonance characteristic for a W=*C*HR group. Consequently, to establish the structure of this class of compound, an X-ray diffraction study was carried out on (**7a**) for which suitable crystals were available.

The results of the X-ray diffraction work are summarized in Table IV and the molecular structure of the cation, which is associated with a molecule of acetone of crystallisation, is shown in Fig. 2. It is immediately apparent that the molecule contains a co-ordinated hydroxy–alkyne ligand, which is bound slightly asymmetrically to the tungsten

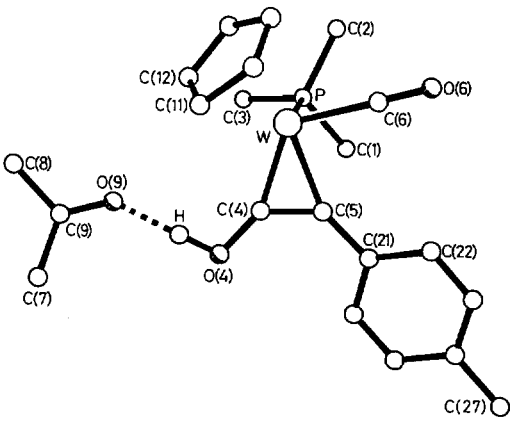


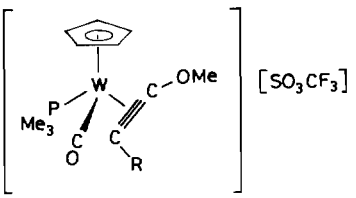
Fig. 2. Molecular structure of the cation $[W\{\eta^2\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]^+$ showing the acetone molecule of crystallisation, and the atom numbering scheme.

atom [W–C(4) 2.000(7), W–C(5) 2.059(6) Å]. In the symmetrically bonded alkyne complex $[WCl(acac)\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)_2]$ the tungsten–carbon (alkyne) distances are 2.04(2) Å [25]. The tungsten atom in (**7a**) is also ligated by CO, PMe_3 and $\eta\text{-}C_5H_5$ groups. As is usual in metal–alkyne complexes, the substituents on the C(4) and C(5) atoms are bent back away from the metal [C(5)–C(4)–O(4) 133.0(5), C(4)–C(5)–C(21) 135.1(7)°]. The C(4)–C(5) distance [1.365(7) Å] is more than the corresponding separation [1.32(2) Å] in $[WCl(acac)\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)_2]$. This difference may possibly be due to the alkyne in the latter compound formally acting as a two-electron donor whereas in (**7a**) it functions as a four-electron donor, a feature discussed further below.

In (**7a**) the acetone molecule is hydrogen bonded to the proton on the hydroxyl substituent of the alkyne group. The O(4)–O(9) separation [2.63 Å] indicates a strong O–H···O interaction. The acidic nature of the hydroxyl proton is readily demonstrated by its deprotonation with $K[BH(CHMeEt)_3]$ regenerating the ketenyl complex $[W\{=C(C_6H_4\text{-}Me\text{-}4)\cdot C{:}O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$.

Having established the structure of (**7a**), its NMR spectra and those of the related compounds (**7b**), (**7c**), and (**8**) are readily interpreted. In the ^1H spectrum of (**7a**), measured at −50 °C (Table II), a resonance at δ 13.90 may be ascribed to the O*H* group. In the $^{13}C\text{-}\{^1H\}$ spectrum there are three relatively low-field signals at δ 226.7 [d, *J*(PC), 7, *J*(WC) 80 Hz], 224.6 [d, *J*(PC) 5, *J*(WC) 130 Hz] and 191.7 p.p.m. [*J*(WC) 75 Hz] which may be assigned to the *C*OH, *C*O, and *C*C_6H_4Me-4 nuclei, respectively. The resonances for the ligated carbon atoms of the alkyne are in the chemical shift region for this type of ligand when functioning as a four rather than a two electron donor [26]. In view of the established structure of (**7a**) this NMR result is not surprising, since if the alkyne group contributed only two electrons to the tungsten, the metal atom would be electronically unsaturated with 16 electrons in the valence shell. In the $^{13}C\text{-}\{^1H\}$ NMR spectrum of (**8**) the alkyne carbon atoms also resonate at low field corresponding to the MeC≡C(OH) group acting as a four-electron donor.

Treatment of the complexes $[W\{=C(R)\cdot C{:}O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (R = C_6H_4Me-4 or Me) with $MeSO_3CF_3$ affords the salts (**9**) (Tables I and II) which contain the methoxyalkyne ligands MeOC≡CR. The ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra are in accord with the structures proposed, with the alkynes donating four electrons to the tungsten centres in (**9a**) and (**9b**). Kreissl and co-workers [27] have independently prepared these compounds.



(**9a**) R = C_6H_4Me-4
(**9b**) R = Me

Experimental

All experiments were carried out under an atmosphere of oxygen-free nitrogen, using Schlenk tube techniques. All solvents were dried and deoxygenated before use. Infrared spectra were measured on Nicolet FT 10-MX or 5-MX spectrometers. All NMR spectra were recorded on JEOL FX 90Q or FX 200 instruments. Chromatography was carried out on alumina (Brockman Activity II unless otherwise stated) or Florisil columns. Light petroleum refers to that fraction of b.p. 40–60 °C. The reagent $HBF_4\cdot Et_2O$ consisted of a 54% solution of HBF_4 in diethyl ether. The compounds $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = Me or C_6H_4Me-4) [1, 2] and $[W\{=C(R)\cdot C{:}O\}(CO)(PR'_3)(\eta\text{-}C_5H_5)]$ (R = Me, PR'_3 = PMe_3 [2]; R = C_6H_4Me-4, PR'_3 = PMe_3 [4], PPr^i_3 or $PMePh_2$ [5]) were prepared by literature methods. Analytical and other data for the new compounds are given in Table I.

Protonation of the Complexes [W(≡CR)(CO)$_2$(η-C$_5$H$_5$)] (R = C$_6$H$_4$Me-4 or Me)

A CH_2Cl_2 (10 cm^3) solution of (**1a**) (0.41 g, 1.0 mmol) at −50 °C was treated with $HBF_4 \cdot Et_2O$ (0.4 mmol). The resultant yellow solution was allowed to warm to room temperature, and stirred for 15 min. Solvent was removed *in vacuo*, and the yellow powder obtained washed with Et_2O (4 × 10 cm^3). Recrystallisation from CH_2Cl_2–light petroleum (8 cm^3, 1:3) at −20 °C gave bright yellow crystals of $[W_2(\mu\text{-H})\{\mu\text{-C}_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ $[BF_4]$ (**2a**) (0.43 g).

The compound $[W_2(\mu\text{-H})(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ $[BF_4]$ (**2b**) (0.11 g) was similarly prepared from (**1b**) (0.13 g, 0.4 mmol), and recrystallised from MeCN–Et_2O–light petroleum (5 cm^3, 1:2:2) at −20 °C. Solutions of (**2b**) in CH_2Cl_2 or thf are unstable.

A diethyl ether solution (10 cm^3) of (**1a**) (0.22 g, 0.5 mmol) was treated with an excess of $HBF_4 \cdot Et_2O$ (*ca.* 2 mmol) at room temperature. The resulting yellow mixture was stirred for 20 min. The precipitate was removed and washed with diethyl ether (4 × 10 cm^3), affording the yellow microcrystalline product $[W(\equiv CC_6H_4Me\text{-}4)(H)(CO)_2(\eta\text{-}C_5H_5)]$ $[BF_4]$ (**5**) (0.24 g). This product is stable for several hours in CH_2Cl_2 but decomposes rapidly in thf. Moreover, as described earlier, the preparation of (**5**) is often accompanied by (**2a**).

Deprotonation of the Compounds [W$_2$(μ-H)(μ-RC$_2$R)(CO)$_4$(η-C$_5$H$_5$)$_2$]

A light petroleum (5 cm^3) solution of PMe_3 (0.33 mmol) was added to a stirred CH_2Cl_2 (8 cm^3) solution of (**2a**) (0.30 g, 0.33 mmol) at −30 °C. The yellow solution was allowed to warm to room temperature with stirring for a further 2 h. The resulting red solution was evaporated *in vacuo*. Extraction of the residue with CH_2Cl_2–light petroleum (3:7) gave a deep red solution which was chromatographed on an alumina column (1 × 10 cm). Elution with CH_2Cl_2–light petroleum (3:1) gave a red eluate. Removal of solvent *in vacuo* afforded red microcrystals of the known compound $[W_2\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2]$ (**3a**) (0.24 g), identified spectroscopically (IR and NMR) [17]. The buff coloured residue remaining after extraction of (**3a**) was identified as $[PHMe_3]$ $[BF_4]$.

A sample of (**2a**) (0.23 g, 0.25 mmol) in CH_2Cl_2 (0.5 cm^3) was chromatographed on basic alumina (Brockman Activity I). Elution with Me_2CO developed a yellow band which turned deep red. Evaporation of the red eluate yielded (**3a**) (0.16 g). Compound (**3a**) was also produced in virtually quantitative yield by treating a thf solution of (**2a**) with one equivalent of K[BH(CHMeEt)$_3$].

Treatment of (**2b**) (0.25 g, 0.33 mmol) in CH_2Cl_2 with PMe_3 (0.33 mmol) in light petroleum gave the cherry red complex $[W_2(\mu\text{-}C_2Me_2)(CO)_4(\eta\text{-}C_5H_5)_2]$ (**3b**) (0.13 g) and $[PHMe_3]$ $[BF_4]$. Compound (**3b**) could also be obtained by treating (**2b**) in thf with 1 equivalent of MeLi (1.25 molar solution in Et_2O). Immediate gas evolution was observed with a colour change from yellow to red.

Synthesis of the Complexes [W(=CHR)(I)(CO)$_2$(η-C$_5$H$_5$)]

A CH_2Cl_2 (15 cm^3) solution of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (0.97 g, 2.38 mmol) was treated with 0.36 cm^3 of HI (constant boiling solution, *ca.* 50% HI). After 45 min stirring, solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (1:4) and applied to the top of an alumina column (2 × 20 cm). Elution with the same solvent mixture, increasing to 2:1, afforded a trace of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ followed by a yellow band. Solvent was removed *in vacuo* affording dark red microcrystals of $[W\{=C(H)C_6H_4Me\text{-}4\}(I)(CO)_2(\eta\text{-}C_5H_5)]$ (**4a**) (0.85 g). Compound (**4b**) was similarly prepared but in low yield.

A sample of (**4a**) (0.23 g, 0.43 mmol) was treated with K[BH(CHMeEt)$_3$] (0.5 cm^3 solution in thf, 0.50 mmol) and the mixture stirred (20 min). After filtration through an alumina plug (1 × 3 cm), solvent was removed *in vacuo*, and the residue dissolved in CH_2Cl_2–light petroleum (2 cm^3, 1:7) and chromatographed. Elution with the same solvent mixture gave after removal of solvent orange microcrystals of $[W(\eta^3\text{-}CH_2C_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ (**6**) (0.07 g, 40%), identified spectroscopically [19].

Preparation of the Salts [W{η-C$_2$(OH)R}(CO)(PR$_3$)(η-C$_5$H$_5$)][BF$_4$]

Compounds (**7a**)–(**7c**) were prepared in an analogous manner, and hence only the synthesis of (**7a**) is described. A purple CH_2Cl_2 (10 cm^3) solution of $[W\{=C(C_6H_4Me\text{-}4)\cdot C{:}O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (0.24 g, 0.5 mmol) at −50 °C was treated with $HBF_4 \cdot Et_2O$ (0.5 mmol) in CH_2Cl_2 (1 cm^3). The resultant red solution was stirred (10 min) at −50 °C and then allowed to warm to room temperature. Solvent was removed *in vacuo* affording a pink solid which was washed with Et_2O (3 × 10 cm^3). Crystallisation from Me_2CO and Et_2O, using vapour diffusion, gave red crystals of $[W\{\eta\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ $[BF_4] \cdot Me_2CO$ (**7a**) (0.28 g).

Treatment of $[W\{=C(Me)\cdot C{:}O\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (0.21 g, 0.5 mmol) with an equivalent of $HBF_4 \cdot Et_2O$ as described for the synthesis of (**7a**), gave red crystals of $[W\{\eta\text{-}C_2(OH)(Me)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ $[BF_4]$ (**8**) (0.21 g).

Preparation of the Salts [W{η-C$_2$(OMe)R}(CO)(PMe$_3$)(η-C$_5$H$_5$)][SO$_3$CF$_3$]

The reagent CF_3SO_3Me (0.25 mmol) was added to a purple CH_2Cl_2 (8 cm^3) solution of $[W\{=C(C_6\text{-}$

$\overline{H_4Me\text{-}4)\cdot C:O}\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ (0.12 g, 0.25 mmol) at 0 °C. After warming to room temperature, solvent was removed *in vacuo*. The orange residue was washed with Et_2O (3 × 10 cm^3) and dried *in vacuo*. Recrystallisation from CH_2Cl_2–Et_2O–light petroleum (1:2:2) afforded pale red crystals of $[W\{\eta\text{-}C_2(OMe)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ $[SO_3CF_3]$ (**9a**) (0.16 g). The related compound $[W\{\eta\text{-}C_2(OMe)(Me)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ $[SO_3CF_3]$ (**9b**) (0.13 g) was similarly prepared as yellow needles from $[\overline{W\{=C(Me)\cdot C:O\}}(CO)(PMe_3)(\eta\text{-}C_5H_5)]$ and CF_3SO_3Me.

Crystal Structure Determinations

(a) Crystals of (**4a**) were grown from CH_2Cl_2–light petroleum. That for data collection was of dimensions *ca.* 0.75 × 0.5 × 0.4 mm. Intensities were collected at 298 K to $2\theta \leqslant 50°$ (θ–2θ scans) on a Nicolet *P3m* four-circle diffractometer. Of the 2659 reflections, 1943 satisfied the criterion $I \geqslant 3\sigma(I)$, where $\sigma(I)$ is the standard deviation based on counting statistics, and only these were used in the solution and refinement of the structure after corrections for Lorentz, polarisation and X-ray absorption effects, the latter by an empirical method based on azimuthal scan data [28].

Crystal data: $C_{15}H_{13}IO_2W$, M = 536.0, monoclinic, a = 17.14(1), b = 7.171(4), c = 13.183(8) Å, β = 106.38(5)°, U = 1544(1) Å^3, Z = 4, D_m = 2.33 g cm^{-3}, D_c = 2.29 g cm^{-3}, $F(000)$ = 984, space group $P2_1/c$, Mo-K_α X-radiation (graphite monochromator), $\bar{\lambda}$ = 0.71069 Å, μ(Mo-K_α) = 95.5 cm^{-1}.

The structure was solved, and all non-hydrogen atoms located, by conventional heavy-atom and electron-density difference methods. Hydrogen atoms of the C_5H_5 and C_6H_4Me groups were incorporated to ride on their attached carbon atoms with C–H 0.96 Å and $U_H = 1.2\ U_c$ (equivalent), and refined isotropically. The W=C*H*R hydrogen atom was not located in the difference density maps, but was included in a calculated position. All other atoms were ascribed anisotropic temperature parameters. Refinement by blocked-cascade least squares converged at R 0.067 (R_w 0.067) with weights applied according to the scheme $w = [\sigma^2(F_o) + 0.004|F_o|^2]^{-1}$. The final electron-density difference synthesis showed a peak of almost 5 eÅ^{-3} in the region of the W atom, and this is attributed to limitations of the absorption correction. Scattering factors and corrections for anomalous dispersion were from ref. 29. All calculations were carried out on a 'Eclipse' Data General computer with the SHELXTL system of programs [28]. The final atom co-ordinates for (**4a**) are listed in Table V.

(b) Crystals of (**7a**) were grown from Me_2CO–Et_2O as red prisms, that for data collection having dimensions *ca.* 0.25 × 0.30 × 0.55 mm. Data collection was similar to that for (**4a**) except in the following respects: range $2\theta \leqslant 50°$ (ω scans), 4754 intensities with 3887 meeting the criterion $I \geqslant 2.5\sigma(I)$. Data were corrected for Lorentz and polarisation effects, and an X-ray absorption correction was applied [28].

TABLE V. Atomic Positional (Fractional Co-ordinates) Parameters (×10^4) for $[W\{=C(H)C_6H_4Me\text{-}4\}(I)(CO)_2(\eta\text{-}C_5H_5)]$ (**4a**).

Atom	*x*	*y*	*z*
W	8094(1)	5341(1)	2721(1)
I	8703(1)	2556(2)	4283(1)
C	7036(11)	6497(23)	1793(12)
C(1)	6186(10)	6320(20)	1618(10)
C(2)	5656(10)	7418(22)	833(12)
C(3)	4845(12)	7287(24)	624(13)
C(4)	4448(12)	5963(24)	1136(12)
C(5)	4951(12)	4836(25)	1883(15)
C(6)	5809(11)	4918(22)	2115(12)
C(41)	3529(11)	5853(28)	885(14)
C(O1)	9223(14)	7495(28)	3273(18)
C(O2)	8660(14)	8133(31)	2295(21)
C(O3)	8668(13)	6789(38)	1514(16)
C(O4)	9199(14)	5310(30)	1983(16)
C(O5)	9528(12)	5760(35)	3029(16)
C(7)	7481(10)	5736(24)	3808(12)
C(8)	7493(12)	3113(27)	2073(13)
O(7)	7156(9)	6081(23)	4390(9)
O(8)	7125(10)	1772(17)	1605(10)

Crystal data: $C_{18}H_{22}BF_4O_2PW\cdot(OCMe_2)$, M = 630.1, triclinic, a = 8.018(5), b = 13.676(7), c = 12.728(7) Å, α = 69.04(4), β = 71.52(5), γ = 89.53(5)°, U = 1227(1) Å^3, Z = 2, D_c = 1.71 g cm^{-3}, $F(000)$ = 616, space group $P\bar{1}$, Mo-K_α = 49.2 cm^{-1}.

The structure was solved in a similar manner to that of (**4a**) with hydrogen atoms included in calculated positions and given isotropic thermal parameters. The hydroxyl [O(4)–H] hydrogen atom was located in a final difference map but was not refined. All remaining atoms were refined with anisotropic thermal parameters. Convergence occurred with R 0.033 (R_w 0.034) with a weighting scheme of the form $w = [\sigma^2(F_o) + 0.001|F_o|^2]^{-1}$ giving a satisfactory weight analysis. The final electron-density difference synthesis showed no peaks $\geqslant$ or $\leqslant$0.5 eÅ^{-3} except in the region of the W where peaks of *ca.* 1.5 eÅ^{-3} were observed. Scattering factors and corrections for anomalous dispersion were made as for (**4a**). Atom co-ordinates for (**7a**) are listed in Table VI.

For both structures, a complete listing of bond distances and angles, structure factors, thermal parameters, and hydrogen atom co-ordinates, are available from the authors upon request.

TABLE VI. Atomic Positional (Fractional Co-ordinates) Parameters for $[W\{\eta^2\text{-}C_2(OH)(C_6H_4Me\text{-}4)\}(CO)(PMe_3)(\eta\text{-}C_5H_5)][BF_4]\cdot(Me_2CO)$ (7a).

Atom	x	y	z
W	0.48804(2)	0.21453(1)	0.16228(2)
P	0.7750(2)	0.14718(12)	0.14878(14)
C(1)	0.7469(12)	0.0048(6)	0.2108(11)
C(2)	0.9015(13)	0.1848(9)	0.2262(11)
C(3)	0.9313(12)	0.1752(10)	0.0018(8)
C(4)	0.4031(7)	0.1298(5)	0.0857(5)
O(4)	0.3708(7)	0.1170(4)	−0.0047(4)
C(5)	0.3460(8)	0.0726(5)	0.2057(5)
C(6)	0.4319(9)	0.1591(5)	0.3388(6)
O(6)	0.3983(9)	0.1302(5)	0.4408(5)
C(7)	0.425(2)	0.2837(9)	−0.3467(12)
C(8)	0.6340(12)	0.4346(6)	−0.3720(7)
C(9)	0.5274(9)	0.3296(5)	−0.2963(6)
O(9)	0.5232(8)	0.2868(4)	−0.1950(5)
C(11)	0.4175(10)	0.3653(5)	0.0400(7)
C(12)	0.6019(10)	0.3696(5)	−0.0083(6)
C(13)	0.6806(10)	0.3802(5)	0.0713(7)
C(14)	0.5432(18)	0.3796(5)	0.1738(7)
C(15)	0.3784(10)	0.3719(5)	0.1544(8)
C(21)	0.2429(8)	−0.0278(5)	0.2826(5)
C(22)	0.1699(14)	−0.0607(7)	0.4066(7)
C(23)	0.0638(14)	−0.1538(7)	0.4750(7)
C(24)	0.0338(9)	−0.2249(5)	0.4257(6)
C(25)	0.1047(10)	−0.1929(5)	0.3040(6)
C(26)	0.2067(9)	−0.0974(5)	0.2345(6)
C(27)	−0.0788(11)	−0.3281(6)	0.5013(7)
B	0.8961(10)	0.5141(7)	0.2299(8)
F(1)	1.0124(10)	0.5659(6)	0.2516(7)
F(2)	0.7606(9)	0.4606(9)	0.3212(6)
F(3)	0.8502(11)	0.5706(6)	0.1379(7)
F(4)	0.9822(11)	0.4391(7)	0.1945(9)

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