Protonation of the Alkylidynetungsten Complex $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ *

John C. Jeffery,[a] **Sihai Li**[a] **and F. Gordon A. Stone**[b]
[a] *School of Chemistry, The University, Bristol BS8 1TS, UK*
[b] *Department of Chemistry, Baylor University, Waco, TX 76798-7348, USA*

The complex $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ has been prepared and its protonation with $HBF_4{\cdot}Et_2O$ and aqueous HI investigated. In CH_2Cl_2 at −78 °C mixtures of the alkylidynetungsten compound and PPh_3 on treatment with $HBF_4{\cdot}Et_2O$ afford the complex $[W(CO)_2\{\eta^4\text{-}C_6H_4(CH_2)[CH(PPh_3)]\text{-}1,2\}(\eta\text{-}C_5H_5)][BF_4]_2$, the structure of which has been established by X-ray crystallography. The $C_6H_4(CH_2)[CH(PPh_3)]$-1,2 ligand is η^4-co-ordinated to the tungsten *via* the carbon atoms of the *ortho* CH and CH_2 substituents of the C_6H_4 group and their respective ring carbons [W–C 2.30(2) to 2.41(2) Å]. The terminal CH fragment carries a PPh_3 group P–C [1.81(2) Å]. The tungsten atom is also ligated by the C_5H_5 ring and two CO groups in the usual manner. Treatment of $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ with aqueous HI affords sequentially the alkylidene complex $[W\{=C(H)C_6H_4CH_2OMe\text{-}2\}I(CO)_2(\eta\text{-}C_5H_5)]$ and the acyl compound $[WI_2(CO)(\eta^2\text{-}COCH_2C_6H_4CH_2OMe\text{-}2)(\eta\text{-}C_5H_5)]$. Possible pathways to the new compounds are discussed, and their ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra are reported.

In the previous paper[1] we reported that protonation of the alkylidynetungsten complex $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ in CH_2Cl_2 at −78 °C with half an equivalent of $HBF_4{\cdot}Et_2O$ affords an isolable but unstable salt $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **1**. If $[W(\equiv CC_6H_4OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ is treated with $HBF_4{\cdot}Et_2O$ in the presence of PPh_3 or dppm ($Ph_2PCH_2PPh_2$) the complexes $[W\{\sigma,\eta^2\text{-}CH(PPh_3)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **2** and $[W\{CH(C_6H_4OMe\text{-}2)PPh_2CH_2PPh_2\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$ **3** are obtained, respectively. The structure of compound **2** was confirmed by an X-ray diffraction study.[1] Compounds **2** and **3** evidently form by addition of a phosphine group to the alkylidene–carbon atom of **1**. This chemistry contrasts with that of $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$. The latter with $HBF_4{\cdot}Et_2O$ affords the ditungsten compound $[W_2(\mu\text{-}H)\{\mu\text{-}C_2(C_6H_4Me\text{-}4)_2\}(CO)_4(\eta\text{-}C_5H_5)_2][BF_4]$, and it is not possible to isolate $[W\{=C(H)C_6H_4Me\text{-}4\}(CO)_2(\eta\text{-}C_5H_5)][BF_4]$, the first product of protonation.[2] Thus the existence of **1** must be due to some electronic or steric effect of the OMe-2 substituent on the C_6H_4 ring, as discussed previously.[1]

In this paper we report further studies on the protonation of complexes of the type $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = aryl) in which there is a potentially active substituent in the *ortho* position on the arene ring. The compound $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$ **4** (py = pyridine) has been prepared and used to synthesise $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ **5**. It was anticipated that the presence of the CH_2OMe-2 substituent would lead to unusual products on protonation of **5**, an idea confirmed by experiment.

Results and Discussion

Treatment of $[W(CO)_6]$ in Et_2O with $LiC_6H_4CH_2OMe$-2, followed by $(CF_3CO)_2O$ in the same solvent at −78 °C, and then pyridine at −20 °C, affords, after column chromatography, the orange-red complex **4**, characterised by the data given in Tables 1 and 2. As expected, the IR spectrum shows two strong CO absorptions at 1992 and 1906 cm^{-1}, and a low-intensity band at 1710 cm^{-1} due to the C=O group of the O_2CCF_3 ligand. The ^1H NMR spectrum shows resonances for the OMe and CH_2 groups at δ 3.32 and 4.69, respectively, and corresponding peaks are seen in the $^{13}C\text{-}\{^1H\}$ NMR spectrum at δ 58.3 (OMe) and 72.3 (CH_2). The latter spectrum also shows a diagnostic signal for the *C*≡W nucleus at δ 273.1. Other peaks in the ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectra are as expected.

Reaction of the reagent **4** with NaC_5H_5 in thf (tetrahydrofuran) affords complex **5**. The spectroscopic properties of the latter (Tables 1 and 2) are in complete accord with its formulation. The $^{13}C\text{-}\{^1H\}$ NMR spectrum shows resonances at δ 296.8 and 220.5 for the C≡W and CO groups, respectively. There are also six peaks for the six non-equivalent carbon atoms of the C_6H_4 ring, as well as the expected signals for the C_5H_5, CH_2 and OMe groups (Table 2). Complex **5** is very soluble in organic solvents and often forms as a red oil, but microcrystals may be obtained by prolonged pumping *in vacuo*.

When compound **5** is treated with 1 equivalent of $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 at −78 °C no stable product is obtained, even when solutions are saturated with CO. It appears that any alkylidene species $[W\{=C(H)C_6H_4CH_2OMe\text{-}2\}(CO)_n(\eta\text{-}C_5H_5)][BF_4]$ (*n* = 2 or 3) have only a fleeting existence, decomposing readily. In an attempt to isolate a complex akin to **2**, compound **5** was treated in CH_2Cl_2 at −78 °C with $HBF_4{\cdot}Et_2O$ in the presence of PPh_3. It was found necessary to add 2 equivalents of the acid to 1 of **5**, otherwise complex inseparable mixtures were obtained. Upon addition of the acid to the mixture of **5** and PPh_3 a red solution is formed but this slowly precipitates a pale red solid identified as the novel complex $[W(CO)_2\{\eta^4\text{-}C_6H_4(CH_2)[CH(PPh_3)]\text{-}1,2\}(\eta\text{-}C_5H_5)][BF_4]_2$ **6**, by a single-crystal X-ray diffraction analysis.

Data from the X-ray study are listed in Table 3, and the structure of the cation is shown in Fig. 1 It is immediately apparent that protonation of the compound **5** in the presence of PPh_3 has resulted in elimination of the OMe group, presumably as MeOH. The tungsten atom is η^4-ligated by a diene fragment C(10)C(11)C(16)C(17) [W–C(10) 2.31(2), W–C(11) 2.41(2), W–C(16) 2.38(2) and W–C(17) 2.30(2) Å]. These distances are within the range (2.263–2.460 Å) found in other η^4 diene–tungsten complexes.[3] Within the ligated C_4 fragment the C–C distances [C(10)–C(11) 1.47(3), C(11)–C(16) 1.42(3) and C(16)–C(17) 1.47(4) Å] are also comparable with those in

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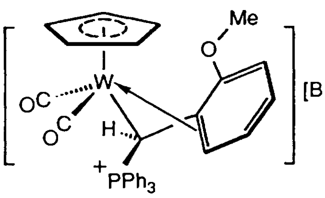
* *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1992, Issue 1, pp. xx–xxv.



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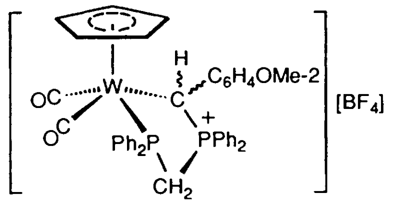

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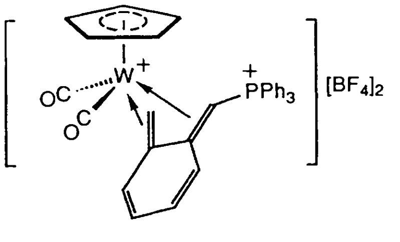

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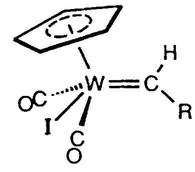
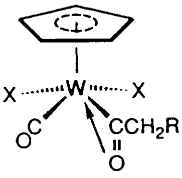


	R
7a	$C_6H_4CH_2OMe$-2
7b	C_6H_4Me-4



	X	R
8a	I	$C_6H_4CH_2OMe$-2
8b	Cl	C_6H_4Me-4

Table 1 Analytical[a] and other data for the tungsten compounds

Compound	Colour	Yield (%)	$\nu_{max}(CO)$[b]/cm^{-1}	Analysis (%) C	Analysis (%) H
4 $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$	Orange-red	87	[c] 1992vs, 1906vs	[d] 42.6 (42.9)	3.0 (3.0)
5 $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$	Orange-red	72	[e] 1994vs, 1924vs	44.3 (43.9)	3.6 (3.2)
6 $[W(CO)_2\{\eta^4\text{-}C_6H_4(CH_2)[CH(PPh_3)]\text{-}1,2\}(\eta\text{-}C_5H_5)][BF_4]_2$	Pale red	71	[f] 2080vs, 2030vs	[g] 44.4 (44.0)	3.3 (3.2)
7a $[W\{=C(H)C_6H_4CH_2OMe\text{-}2\}I(CO)_2(\eta\text{-}C_5H_5)]$[h]	Dark green	29	2006m, 1936vs		
8a $[WI_2(CO)(\eta^2\text{-}COCH_2C_6H_4CH_2OMe\text{-}2)(\eta\text{-}C_5H_5)]$	Brown	76	2040vs	27.5 (27.7)	2.5 (2.3)

[a] Calculated values are in parentheses. [b] Measured in CH_2Cl_2 unless otherwise stated. [c] A band at 1710m cm^{-1} is assigned to the CF_3CO_2 ligand. [d] N, 4.3 (4.4)%. [e] Measured in hexane. [f] Measured in MeCN. [g] Crystallised with 1 molecule of CH_2Cl_2. [h] Oil, 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]
4[d]	3.32 (s, 3 H, OMe), 4.69 (s, 2 H, CH_2), 7.21–8.88 (m, 14 H, C_6H_4, py)	273.1 (W≡C), 220.7 (CO), 153.0, 147.7 [C^1, $C^2(C_6H_4)$], 138.3, 132.2, 128.4, 127.8 (C_6H_4), 151.9, 138.7, 125.3 (py), 72.3 (CH_2), 58.3 (OMe)
5[d]	3.45 (s, 3 H, OMe), 4.70 (s, 2 H, CH_2), 5.69 (s, 5 H, C_5H_5), 7.12–7.41 (m, 4 H, C_6H_4)	296.8 (W≡C), 220.5 [CO, J(WC) 196], 148.4, 137.8 [C^1, $C^2(C_6H_4)$], 130.3, 128.7, 127.2, 126.9 (C_6H_4), 91.5 (C_5H_5), 71.9 (CH_2), 58.5 (OMe)
6[e]	2.29 [d, 1 H, PCH, J(PH) 8], 2.41 [d, 1 H, CH_2, J(HH) 5], 4.16 [d, 1 H, CH_2, J(HH) 5], 5.84 (s, 5 H, C_5H_5), 7.60–7.96 (m, 19 H, Ph, C_6H_4)	198.2, 197.2 (CO), 137.9 (C_6H_4), 137.0 [d, J(PC) 22, Ph], 136.7 (Ph), 135.2 [d, J(PC) 10, Ph], 131.9 [d, J(PC) 12, Ph], 129.0 [d, J(PC) 5, C_6H_4], 120.8, 119.6 (C_6H_4), 110.1 [d, J(PC) 12, C_6H_4], 109.6 (C_6H_4), 91.2 (C_5H_5), 41.7 (CH_2), 30.2 [d, J(PC) 72, C(H)P]
7a	3.31 (s, 3 H, OMe), 4.39 (s, 2 H, CH_2), 6.07 (s, 5 H, C_5H_5), 7.26–8.45 (m, 4 H, C_6H_4), 13.71 (s, 1 H, W=CH)	263.9 (C=W), 208.2 (CO), 148.6, 138.9 [C^1, $C^2(C_6H_4)$], 132.9, 131.7, 130.5, 130.2 (C_6H_4), 98.5 (C_5H_5), 74.0 (CH_2), 58.1 (OMe)
8a	3.40 (s, 3 H, OMe), 4.47, 4.51 [AB, 2 H, CH_2OMe, J(AB) 11], 4.57, 4.70 [AB, 2 H, CCH_2, J(AB) 17], 5.39 (s, 5 H, C_5H_5), 7.40–7.44 (m, 4 H, C_6H_4)	273.2 [W(η^2-CO)], 194.8 (CO), 137.2, 133.0 [C^1, $C^2(C_6H_4)$], 132.1, 131.0, 129.4, 129.1 (C_6H_4), 92.6 (C_5H_5), 74.1 (CH_2OMe), 59.0 (OMe), 45.1 (CCH_2)

[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 $CDCl_3$. [e] Measured in CD_3CN.

Table 3 Selected bond lengths (Å) and angles (°) for $[W(CO)_2\{\eta^4\text{-}C_6H_4(CH_2)[CH(PPh_3)]\text{-}1,2\}(\eta\text{-}C_5H_5)][BF_4]_2\cdot Me_2CO$ **6**, with estimated standard deviations in parentheses

W–C(6)	2.07(3)	W–C(7)	2.06(3)	W–C(10)	2.31(2)	W–C(11)	2.41(2)
W–C(16)	2.38(2)	W–C(17)	2.30(2)	P–C(10)	1.81(2)	P–C(21)	1.78(2)
P–C(31)	1.80(2)	P–C(41)	1.78(1)	C(6)–O(6)	1.11(4)	C(7)–O(7)	1.14(4)
C(10)–C(11)	1.47(3)	C(11)–C(12)	1.47(3)	C(11)–C(16)	1.42(3)	C(12)–C(13)	1.31(4)
C(13)–C(14)	1.38(4)	C(14)–C(15)	1.40(5)	C(15)–C(16)	1.47(4)	C(16)–C(17)	1.47(4)
W–C(C_5H_5)	2.32(2)*						

C(6)–W–C(7)	82(1)	C(10)–W–C(11)	36.4(8)	C(10)–W–C(16)	62.6(7)
C(11)–W–C(16)	34.5(8)	C(10)–W–C(17)	71.7(8)	C(11)–W–C(17)	63.0(9)
C(16)–W–C(17)	37(1)	C(10)–P–C(21)	108.9(8)	C(10)–P–C(31)	109(1)
C(21)–P–C(31)	102.9(8)	C(10)–P–C(41)	114.8(9)	C(21)–P–C(41)	111.0(7)
C(31)–P–C(41)	109.9(7)	W–C(6)–O(6)	177(2)	W–C(7)–O(7)	174(3)
W–C(10)–P	128(1)	W–C(10)–C(11)	76(1)	P–C(10)–C(11)	123(2)
W–C(11)–C(10)	68(1)	W–C(11)–C(12)	129(2)	C(10)–C(11)–C(12)	127(2)
W–C(11)–C(16)	72(1)	C(10)–C(11)–C(16)	115(2)	C(12)–C(11)–C(16)	118(2)
C(11)–C(12)–C(13)	121(2)	C(12)–C(13)–C(14)	123(3)	C(13)–C(14)–C(15)	121(3)
C(14)–C(15)–C(16)	118(3)	W–C(16)–C(11)	74(1)	W–C(16)–C(15)	124(2)
C(11)–C(16)–C(15)	119(3)	W–C(16)–C(17)	69(1)	C(11)–C(16)–C(17)	117(2)
C(15)–C(16)–C(17)	125(2)	W–C(17)–C(16)	75(1)	P–C(21)–C(22)	120.9(5)
P–C(21)–C(26)	118.9(5)				

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

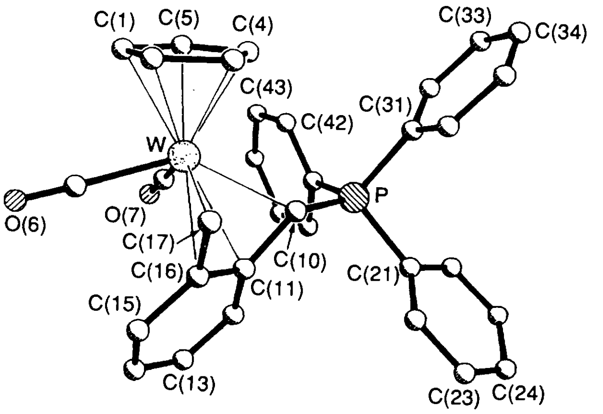


Fig. 1 Structure of the cation of $[W(CO)_2\{\eta^4\text{-}C_6H_4(CH_2)[CH(PPh_3)]\text{-}1,2\}(\eta\text{-}C_5H_5)][BF_4]_2$ **6**, showing the crystallographic atom labelling scheme

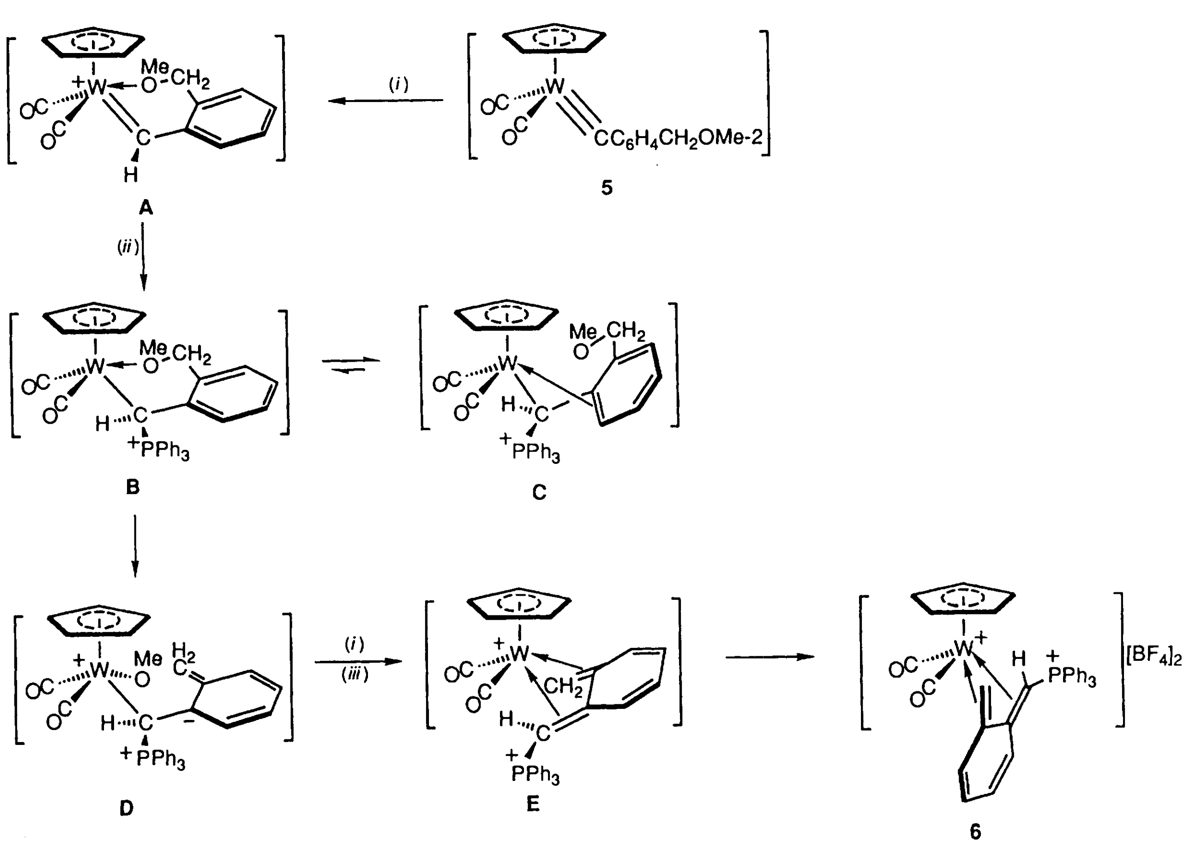
diene–metal complexes. The C(10)–C(11)–C(16) and C(11)–C(16)–C(17) angles are 115(2) and 117(2)°, respectively, being within experimental error not significantly different from the value expected (120°) for a *cis* butadiene group. The hydrogen atom attached to C(10) was not located in the electron-density difference map but its presence was confirmed by the ^1H NMR spectrum discussed below.

The carbon atom C(10) carries a PPh_3 group, with the C(10)–P separation [1.81(2) Å] being similar to those of the other C–P distances [average 1.79(2) Å] in the cation. The phosphorus atom lies in the plane defined by C(10) and the C_6H_4 ring, implying that C(10) is sp^2 hybridised. This is in contrast with the corresponding carbon atom in compound **2** which shows appreciable tetrahedral sp^3 character.[1] As expected, the tungsten atom is ligated by the C_5H_5 ring and two terminally bound CO groups.

Having established the structure of complex **6** the spectroscopic properties are readily interpretable. There are two CO absorptions in the IR spectrum at 2080 and 2030 cm^{-1}, and these relatively high wavenumbers are in accord with the tungsten atom formally carrying a positive charge. Compound **2** displays CO stretches at 1954 and 1866 cm^{-1}. In the ^1H NMR spectrum of **6** there is a doublet resonance at δ 2.29 [*J*(PH) 8 Hz] due to the C(*H*)PPh_3 proton. Doublet signals at δ 2.41 and 4.16 with *J*(HH) 5 Hz can be attributed to the C(17)H_2 group. This assignment is reasonable since the inner *endo* proton is expected to be less deshielded than the outer *exo* proton as observed in other diene–metal complexes.[4]

As expected, the $^{13}C\text{-}\{^1H\}$ NMR spectrum shows resonances (δ 198.2 and 197.2) corresponding to two non-equivalent CO groups. The carbon atoms of the C_6H_4 ring are non-equivalent and so there are six resonances for these nuclei, two of which show small $^{31}P\text{-}^{13}C$ couplings (Table 2). The ligated carbon of the CH_2 moiety resonates at δ 41.7 and the signal for the C(H)P group is a doublet at δ 30.2 [*J*(PC) 72 Hz]. The $^{31}P\text{-}\{^1H\}$ NMR spectrum of complex **6** shows a singlet at δ 26.7 [to high frequency of 85% H_3PO_4 (external)].

The formation of complex **6** is of interest, and a possible mechanism for its formation is shown in Scheme 1. The alkylidene intermediate **A** would form by protonation of the alkylidyne-carbon atom of **5**. As mentioned in the Introduction it is possible to isolate compound **1**, the $[BF_4]^-$ salt of the alkylidenetungsten complex $[W\{=C(H)C_6H_4OMe\text{-}2\}(CO)_2(\eta\text{-}C_5H_5)]^+$ and it seems probable that both **1** and **A** are stabilised by co-ordination of the alkoxy substituents to the metal centre.[1] Addition of tertiary phosphines to alkylidene-carbon atoms has ample precedent,[5] and we have previously shown that the complex **1** with PPh_3 affords **2**.[1] Addition of PPh_3 to intermediate **A** would therefore be expected to give **B** which *via* a facile dissociation of the alkoxyl substituent could readily rearrange to **C** which is structurally closely related to the complex **2**. As mentioned earlier, protonation of the reagent **5** with $HBF_4\cdot Et_2O$ in the presence of PPh_3 results initially in the formation of a transient red species with ν_{max}(CO) at 1956 and 1860 cm^{-1}, values very similar to those displayed by complex **2** (1954 and 1866 cm^{-1}). Unfortunately it was not possible to isolate this intermediate, even when 1 equivalent of $HBF_4\cdot Et_2O$ was used at −78 °C. However, the IR data are consistent with the suggestion that complex **C** is the red transient species observed in this reaction. The latter might react directly with more $HBF_4\cdot Et_2O$ with loss of MeOH to yield **6**, but if the conversion of **B** into **C** is reversible it is perhaps more likely that **6** is formed *via* the intermediate **B**. The latter might cleave to afford a W–OMe intermediate **D** which in the presence of the acid would eliminate MeOH giving **E**. Loss of alkoxy groups by this method has precedent.[6] A simple rotation of the butadiene fragment in **E** would then give **6**. The above mechanism is attractive because it shows how the stereochemistry of PPh_3 addition in **C**, which was firmly established for the methoxy analogue **2**, is preserved during its transformation to the final butadiene product **6**.



Scheme 1 (*i*) $HBF_4{\cdot}Et_2O$, (*ii*) PPh_3, (*iii*) −MeOH

Whatever the mechanism for the formation of compound **6**, as far as we are aware its structure is unprecedented. Clearly further studies on the protonation of complexes $[W(\equiv CR)(CO)_2(\eta\text{-}C_5H_5)]$ (R = aryl) in which the arene ring carries an *ortho* substituent are merited.

The protonation of compound **5** with aqueous HI was investigated. With 1 equivalent of the acid the alkylidene-tungsten complex $[W\{=C(H)C_6H_4CH_2OMe\text{-}2\}I(CO)_2(\eta\text{-}C_5H_5)]$ **7a** is formed. This product is analogous to the compound $[W\{=C(H)C_6H_4Me\text{-}4\}I(CO)_2(\eta\text{-}C_5H_5)]$ **7b**, previously obtained from $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$ and HI, and structurally identified by X-ray diffraction.[2a]

Compound **7a** was characterised spectroscopically since it formed as a dark green oil which failed to crystallise despite persistent efforts to make it do so. Nevertheless, the spectroscopic properties leave no doubt about its formulation. In the IR spectrum there are CO bands at 2006 and 1936 cm^{-1}, which may be compared with those observed in the spectrum of **7b** at 2004 and 1934 cm^{-1}.[2a] The alkylidene ligand in a **7a** reveals itself in the ^1H NMR spectrum with a resonance at δ 13.71 for the $C(H)C_6H_4CH_2OMe\text{-}2$ proton, and in the $^{13}C\text{-}\{^1H\}$ NMR spectrum with a signal at δ 263.9 for the ligated carbon atom of the $C(H)C_6H_4CH_2OMe\text{-}2$ group. The corresponding NMR data for **7b** are δ 13.08 for $C(H)C_6H_4Me\text{-}4$ and δ 267.4 for $C(H)C_6H_4Me\text{-}4$.

Treatment of the reagent **5** with an excess of aqueous HI affords the η^2-acyl complex $[WI_2(CO)(\eta^2\text{-}COCH_2C_6H_4CH_2OMe\text{-}2)(\eta\text{-}C_5H_5)]$ **8a**, characterised by the data given in Tables 1 and 2. This compound shows a single metal carbonyl absorption (2040 cm^{-1}) in its IR spectrum. The NMR data are in complete agreement with the formulation of **8a**. In particular, in the $^{13}C\text{-}\{^1H\}$ NMR spectrum there is a diagnostic resonance for the η^2-acyl group at δ 273.2. Similar peaks for the ligated carbon atoms of the acyl ligands are observed in the $^{13}C\text{-}\{^1H\}$ NMR spectra of related complexes, *e.g.* $[W(O_2CCF_3)_2(CO)(\eta^2\text{-}COCH_2C_6H_4Me\text{-}2)(\eta\text{-}C_5H_5)]$ (δ 276.8).[1]

Compound **8a** is closely related to $[WCl_2(CO)(\eta^2\text{-}COCH_2C_6H_4Me\text{-}4)(\eta\text{-}C_5H_5)]$ **8b**, obtained from the reaction between HCl and $[W(\equiv CC_6H_4Me\text{-}4)(CO)_2(\eta\text{-}C_5H_5)]$.[7] The spectroscopic properties of **8b** [ν_{max}(CO) 2038 cm^{-1}; $^{13}C\text{-}\{^1H\}$, δ 277.9 (η^2-CO)] are very similar to those of **8a**.

Acyl complexes such as **8b**, and several related compounds described in the previous paper,[1] are thought to form by addition of a second equivalent of the acid to the C=W bond of an initially formed but unstable alkylidenemetal species. The synthesis of **7a** and **8a** from the same reaction, depending on the quantity of acid used, supports the proposed mechanism for these reactions.[7]

Experimental

The experimental procedures and the instrumentation used for the spectroscopic studies have been given in the preceding paper.[1] The reagent $HBF_4{\cdot}Et_2O$ consisted of an 85% solution in diethyl ether. Chromatography columns (*ca.* 20 cm in length and 3 cm in diameter) were charged with Aldrich aluminium oxide (Brockman activity III).

Preparation of the Complexes $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$ *and* $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$.—(*i*) A hexane (30 cm^3) solution of 2-bromobenzyl methyl ether (3.0 g, 14.9 mmol) was treated with $LiBu^n$ (10 cm^3 of a 1.5 mol dm^{-3} solution in hexane, 15 mmol), and the mixture was stirred for 30 min. The resulting white precipitate was allowed to settle, solvent was removed with a syringe, and the residue was washed with hexane (2 × 10 cm^3) and dried *in vacuo* to give $LiC_6H_4CH_2OMe\text{-}2$.

To a suspension of $[W(CO)_6]$ (4.5 g, 12.8 mmol) in Et_2O (50 cm^3) was added dropwise a solution containing 1 mol equivalent of the above lithium reagent in Et_2O (20 cm^3). Complete consumption of $[W(CO)_6]$ was monitored by IR spectroscopy. The resulting orange solution was cooled to −78 °C, and $(CF_3CO)_2O$ (2.0 cm^3, 14.2 mmol) in Et_2O (20 cm^3) was added dropwise over 30 min. After warming to −20 °C, pyridine (7.5

Table 4 Atomic positional parameters (fractional coordinates, × 10^4) with estimated standard deviations in parentheses for complex **6**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W	7 833(1)	12 392(1)	3 533(1)	P	6 586(6)	12 682(3)	2 024(2)
C(1)	9 146(25)	13 215(12)	4 126(7)	C(2)	10 154	12 645	3 924
C(3)	10 301	12 730	3 318	C(4)	9 384	13 353	3 146
C(5)	8 670	13 653	3 645	C(6)	7 296(34)	11 992(11)	4 348(16)
O(6)	7 000(33)	11 805(11)	4 789(8)	C(7)	5 738(35)	12 898(15)	3 605(14)
O(7)	4 553(23)	13 133(11)	3 678(9)	C(10)	7 301(31)	12 075(11)	2 590(9)
C(11)	6 320(28)	11 572(13)	2 935(10)	C(12)	4 664(26)	11 513(12)	2 905(10)
C(13)	3 924(37)	11 075(15)	3 265(13)	C(14)	4 625(40)	10 655(14)	3 689(13)
C(15)	6 208(39)	10 639(14)	3 738(12)	C(16)	7 099(35)	11 112(11)	3 343(9)
C(17)	8 760(33)	11 192(13)	3 362(11)	C(22)	5 936(17)	11 317(7)	1 486(7)
C(23)	5 405	10 880	1 027	C(24)	4 710	11 231	557
C(25)	4 546	12 020	547	C(26)	5 077	12 457	1 006
C(21)	5 772	12 105	1 476	C(32)	8 102(16)	13 870(7)	1 470(7)
C(33)	9 288	14 168	1 143	C(34)	10 541	13 716	1 009
C(35)	10 607	12 966	1 203	C(36)	9 421	12 668	1 531
C(31)	8 168	13 120	1 664	C(42)	5 829(13)	14 034(8)	2543(7)
C(43)	4 817	14 588	2 737	C(44)	3 263	14 499	2 645
C(45)	2 721	13 857	2 359	C(46)	3 733	13 303	2 165
C(41)	5 286	13 392	2 257	B(1)	11 050(32)	10 646(22)	2 045(14)
F(11)	11 054(25)	10 126(10)	2 482(9)	F(12)	9 557(20)	10 714(9)	1 848(9)
F(13)	12 005(25)	10 429(13)	1 669(10)	F(14)	11 338(23)	11 368(10)	2 296(10)
B(2)	3 870(95)	9 058(33)	−64(25)	F(21)	3 197(44)	9 074(23)	−495(20)
F(22)	4 256(54)	8 373(14)	32(12)	F(23)	5 180(31)	9 381(14)	−256(11)
F(24)	3 635(37)	9 380(13)	438(13)	*C(50)	3 970(60)	5 002(17)	−375(16)
*C(51)	4 472(42)	4 330(18)	−68(13)	*O(51)	3 953(37)	4 127(13)	399(12)
*C(52)	5 615(82)	3 847(32)	−385(32)				

* Acetone solvent molecule.

cm^3, 92.7 mmol) was added and the mixture was stirred for 2 h at room temperature. Solvent was removed *in vacuo*, and orange residue was dissolved in CH_2Cl_2 (20 cm^3) and chromatographed at −30 °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–hexane (*ca.* 30 cm^3, 1:5) afforded orange-red *microcrystals* of $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(O_2CCF_3)(CO)_2(py)_2]$ **4** (7.20 g).

(*ii*) Compound **4** (2.00 g, 3.10 mmol) was dissolved in thf (30 cm^3) and treated with NaC_5H_5 (*ca.* 1 g, excess) at room temperature. The mixture was stirred overnight to ensure that the reaction was complete. Solvent was removed *in vacuo*, the residue was extracted with CH_2Cl_2–hexane (20 cm^3, 1:1), and the extracts were chromatographed. Elution of the column with the same solvent mixture gave an orange-red eluate. Removal of solvent *in vacuo* afforded an orange-red oil which was sufficiently pure for use in further synthesis. Exposure of the oil to vacuum for *ca.* 5 d gave orange-red *microcrystals* of $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$ **5** (0.98 g).

Protonation of the Complex $[W(\equiv CC_6H_4CH_2OMe\text{-}2)(CO)_2(\eta\text{-}C_5H_5)]$.—(*i*) A CH_2Cl_2 (20 cm^3) solution containing complex **5** (0.10 g, 0.23 mmol) and PPh_3 (0.13 g, 0.50 mmol) was treated with $HBF_4\cdot Et_2O$ (0.06 cm^3, 0.45 mmol) at −78 °C. The IR spectrum of the mixture showed initially the development of two CO stretching bands at 1956vs and 1860vs cm^{-1}. After warming to room temperature, the mixture was stirred overnight. Diethyl ether (10 cm^3) was added with stirring to precipitate the product which was allowed to settle before solvent was carefully removed with a syringe. The residue was washed once with CH_2Cl_2–Et_2O (10 cm^3, 2:3) and dried *in vacuo* to give pale red *microcrystals* of $[W(CO)_2\{\eta^4\text{-}C_6H_4(CH_2)[CH(PPh_3)]\text{-}1,2\}(\eta\text{-}C_5H_5)][BF_4]_2$ **6** (0.15 g).

(*ii*) Complex **5** (0.10 g, 0.23 mmol) was dissolved in CH_2Cl_2 (20 cm^3), treated with HI (aqueous, 57%, 0.03 cm^3, 0.23 mmol) and the mixture was stirred at room temperature for 5 min. Solvent was removed *in vacuo* and the residue was placed under high vacuum for 30 min to remove the remaining HI, and then dissolved in CH_2Cl_2–hexane (10 cm^3, 1:1). Chromatography of the solution, eluting with the same solvent mixture, gave a green eluate. Solvent was removed *in vacuo* to give $[W\{=C(H)C_6H_4CH_2OMe\text{-}2\}I(CO)_2(\eta\text{-}C_5H_5)]$ **7a** as a dark green oil (0.037 g).

(*iii*) In a similar reaction, a CH_2Cl_2 (20 cm^3) solution of complex **5** (0.10 g, 0.23 mmol) was treated with HI (aqueous, 57%, 0.4 cm^3, 3.03 mmol) at room temperature for 1 h. Solvent was removed *in vacuo* and the remaining water was removed with a syringe. The residue was shaken with light petroleum (2 × 10 cm^3) and then dissolved in CH_2Cl_2–hexane (15 cm^3, 1:2). Concentration of the solution to *ca.* 5 cm^3 *in vacuo* afforded brown microcrystals of $[WI_2(CO)(\eta^2\text{-}COCH_2C_6H_4CH_2OMe\text{-}2)(\eta\text{-}C_5H_5)]$ **8a** (0.12 g).

Crystal Structure Determination.—Crystals of complex **6** were obtained from Me_2CO–Et_2O (1:5) as orange cubes, and that chosen for study had dimensions *ca.* 0.25 × 0.25 × 0.08 mm and was sealed under nitrogen in a Lindemann tube. Diffracted intensities were collected with a Siemens R3m/V diffractometer (293 K, Mo-Kα X-radiation, graphite monochromator, $\lambda = 0.710\,69$ Å). Of the 3623 data collected (θ–2θ scans, $2\theta \leqslant 50°$), 2086 unique data had $F \geqslant 5\sigma(F)$, and only these were used for structure solution and refinement. The data were corrected for Lorentz, polarisation and X-ray absorption effects, the latter by a method based upon azimuthal scan data.[8] The compound crystallises with a molecule of acetone in the unit cell.

Crystal data. $C_{33}H_{27}B_2F_8O_2PW\cdot Me_2CO$, $M = 902.1$, orthorhombic, space group $P2_12_12_1$, $a = 8.814(3)$, $b = 17.589(4)$, $c = 23.203(5)$ Å, $U = 3597(2)$ Å^3, $Z = 4$, $D_c = 1.67$ g cm^{-3}, $F(000) = 1776$, μ(Mo-Kα) = 34.0 cm^{-1}.

The structure was solved by conventional heavy-atom methods, and successive Fourier difference syntheses were used to locate all non-hydrogen atoms. All the phenyl rings and the cyclopentadienyl group were treated as rigid groups. All non-hydrogen atoms were refined with anisotropic thermal parameters, except C(12) which was refined isotropically. Hydrogen atoms were included in calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ($U_{iso} = 0.08$ Å^2). Calculations were performed on a DEC micro-Vax II computer with the SHELXTL PLUS system of programs.[8] Refinement by full-matrix least squares converged at $R = 0.057$ ($R' = 0.055$) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.0018 |F|^2]$ gave a satisfactory analysis of variance. Atom coordinates are listed in Table 4. Scattering factors with corrections for anomalous dispersion, included in the programs,[8] were taken from ref. 9. The final electron-density difference synthesis showed no peaks > 1.98 or < -1.06 e Å^{-3}.

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

Acknowledgements

We thank the British Council and the State Education Commission of the People's Republic of China for a studentship (to S. L.) under the Sino-British Friendship Scholarship Scheme, and the Robert A. Welch Foundation for support (to S. L. and F. G. A. S.).

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Received 31*st July* 1991; *Paper* 1/03967I