Formation of the Alkoxyalkyl Complexes $[M\{CHMe(OMe)\}(CO)_2(\eta-C_5H_4R)]$ (M = Mo, R = H; M = W, R = H or Me) and their Transformations by Loss of MeOH into η^3-Propenoyl or Vinyl Complexes. Crystal Structures of $[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta-C_5H_5)]BF_4$, $[Mo(\eta^3-CH_2CHC{=}O)(CO)(PPh_3)(\eta-C_5H_5)]$ and $[W(\sigma-CH{=}CH_2)(CO)_2(PPh_3)(\eta-C_5H_4Me)]$†

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Addition of $MeSO_3F$ or $[Me_3O]BF_4$ followed by PPh_3 to the aldehyde complex $[Mo(MeCHO)(CO)_2(\eta-C_5H_5)]^-$ results in formation of the methoxyalkyl complex *trans*-$[Mo\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta-C_5H_5)]$ in a reaction that proceeds *via* the unstable $[Mo\{\eta^2-CHMe(OMe)\}(CO)_2(\eta-C_5H_5)]$. A by-product of this reaction is the ylide *trans*-$[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta-C_5H_5)]X$ ($X = BF_4^-$ or SO_3F^-), a species ($X = BF_4$) better prepared by treatment of *trans*-$[Mo\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta-C_5H_5)]$ with HBF_4 in the presence of PPh_3. The crystalline ylide *trans*-$[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta-C_5H_5)]BF_4$ is monoclinic, with $a = 11.378(34)$, $b = 18.903(35)$, $c = 20.17(8)$ Å, $\beta = 115.28(31)°$ and for the 3918 independent reflections with $I/\sigma(I) > 3.0$, $R = 0.0510$. In solution, *trans*-$[Mo\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta-C_5H_5)]$ either degrades to $[MoH(CO)_2(PPh_3)(\eta-C_5H_5)]$ or loses MeOH to form the η^3-propenoyl $[Mo(\eta^3-CH_2CHC{=}O)(CO)(PPh_3)(\eta-C_5H_5)]$. This molecule is monoclinic, with $a = 17.231(50)$, $b = 8.189(14)$, $c = 16.727(36)$ Å, $\beta = 106.79(22)°$ and for the 1654 independent reflections for which $|F|/\sigma(|F|) > 4.0$, $R = 0.100$. The proposed mechanism for its formation is based on isotopic tracking experiments and includes a vinyl to carbonyl migration. Treatment of $[WMe(CO)_3(\eta-C_5H_4R)]$ (R = H or Me) with PPh_3 in MeCN gives the acyl $[W(\sigma-COMe)(CO)_2(PPh_3)(\eta-C_5H_4R)]$. These react with $[Me_3O][BF_4]$ to form the cationic carbenes $[W\{{=}CMe(OMe)\}(CO)_2(PPh_3)(\eta-C_5H_4R)]BF_4$, which in turn react with $LiBHEt_3$ to give the alkoxyalkyls *trans*-$[W\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta-C_5H_4R)]$. The alkoxyalkyls *trans*-$[W\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta-C_5H_4R)]$ react with traces of acid to form the σ-vinyls *trans*-$[W(\sigma-CH{=}CH_2)(CO)_2(PPh_3)(\eta-C_5H_4R)]$, the methylcyclopentadienyl species of which is crystalline, monoclinic, with $a = 36.952(40)$, $b = 10.971(13)$, $c = 25.148(23)$ Å and $\beta = 103.60(8)°$. For the 2542 independent reflections for which $|F|/\sigma(|F|) > 5.0$, R converged to 0.0750.

One of our interests concerns the reactions of nucleophiles with complexes containing an alkyl function.[1] For instance, the alkyl complexes $[M\{(CH_2)_3Br\}(CO)_3(\eta-C_5H_5)]$ react with nucleophiles such as iodide[2] or transition-metal anions[3] to form carbene complexes.

We showed earlier that the reaction of $LiBHEt_3$ with $[MoMe(CO)_3(\eta-C_5H_5)]$ **1** leads to the acetaldehyde anion $[Mo(MeCHO)(CO)_2(\eta-C_5H_5)]^-$ **2** *via* intermediate formyl and hydride species (Scheme 1).[4] The reaction of anion **2** with MeI under a CO atmosphere is significant in that MeCHO is evolved together with $[MoMe(CO)_3(\eta-C_5H_5)]$ **1**, effectively completing a cycle which produces acetaldehyde from MeI, CO and $LiBHEt_3$. The first stage of the reaction of the anion **2** with MeI is probably formation of a new Mo–Me bond by alkylation at the metal to give an intermediate, **3**, from which MeCHO is displaced by incoming CO. In this paper we examine the reactions of the alternative methylating agents $[Me_3O]BF_4$ and $MeSO_3F$ with anion **3**. We demonstrate that these alkylating agents attack a different site of **2** with interesting consequences.

Results and Discussion

Methylation of $Li[Mo(MeCHO)(CO)_2(\eta-C_5H_5)]$ **2** *to form* $[Mo\{\eta^2-CHMe(OMe)\}(CO)_2(\eta-C_5H_5)]$ **5**.—Addition of $MeSO_3F$ to a tetrahydrofuran (thf) solution containing anion **2** at ambient temperature promptly gives a yellow solution whose carbonyl IR spectrum indicates a neutral *cis*-dicarbonyl of the type *cis*-$[Mo(A)(B)(CO)_2(\eta-C_5H_5)]$ as the only product. Unfortunately, this product is extremely sensitive to air and moisture and all attempts to isolate it failed. It changes colour and binds strongly to alumina on attempted chromatography. Significantly, its two bands in the carbonyl IR spectrum [ν_{CO}/cm^{-1} (thf) 1930s and 1833s] are virtually identical in position and relative intensity to those of the previously characterised $[Mo\{\overline{CH(CH_2)_3O}\}(CO)_2(\eta-C_5H_5)]$ **4** [ν_{CO}/cm^{-1}(thf) 1926s and 1827s] (Scheme 2).[5] The context of the chemistry and these IR data strongly suggest that the product is $[Mo\{\eta^2-CHMe(OMe)\}(CO)_2(\eta-C_5H_5)]$ **5**. Complex **5** arises through alkylation at the ligated aldehyde oxygen rather than at molybdenum as when using MeI as the alkylating agent (Scheme 1). Chemical corroboration of this structure comes from its reaction with PPh_3 which provides the phosphine complex **6**.

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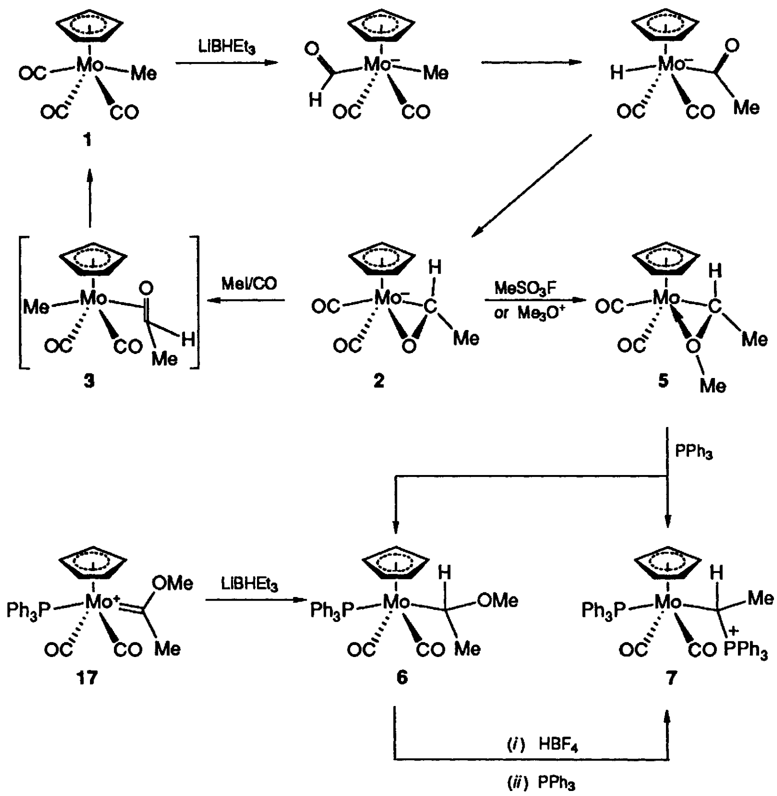
† *trans*-Dicarbonyl(η^5-cyclopentadienyl)[(1-triphenylphosphonio)ethyl-$\kappa C'$]molybdenum(II) tetrafluoroborate, carbonyl(η^5-cyclopentadienyl)(propen-1-oyl-C^{1-3})(triphenylphosphine)molybdenum and *trans*-dicarbonyl(η^5-cyclopentadienyl)(triphenylphosphine)vinyl tungsten.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

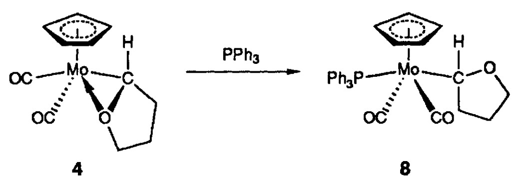


Scheme 1

Table 1 Physical and other data for the complexes

Complex	Colour	IR[b]/cm^{-1}	Decomp. point[c]/°C	Mass spectrum[d]	Analysis (%)[a] C	H
6	Yellow	1934m, 1847s	68–70	$[M - CO]^+$, 512 (512)	62.65 (62.5)	5.2 (5.05)
17	Yellow	1989m, 1911s	156–158	$[M]^+$, 539 (539)	54.0 (53.9)	4.1 (4.2)
7[e]	Yellow	1954m, 1866s	118–120	$[M]^+$, 771 (771)	62.9 (63.1)	4.9 (4.6)
20	Yellow	1888s, 1837 (sh), 1688m	149–152	$[M + H]^+$, 509 (509)	64.3 (64.0)	4.9 (4.6)
29	Yellow	1981m, 1901s	176–178	$[M]^+$, 625 (625)	47.4 (47.2)	3.6 (3.7)
30	Yellow	1926m, 1835s	*f*	$[M - OMe]^+$, 595 (595)	*f*	*f*
31	Yellow	1927m, 1837s, 1591w	146–148	$[M + H]^+$, 625 (625)	53.9 (53.9)	4.0 (4.0)
32	Yellow	1977m, 1896s	132–134	$[M]^+$, 639 (639)	47.2 (48.0)[g]	3.95 (3.9)[g]
33	Yellow	1925m, 1831s	72–74	$[M - OMe]^+$, 609 (609)	54.55 (54.4)	4.65 (4.6)
34	Yellow	1940m, 1853s	95–97	$[M]^+$, 594 (594)	53.1 (53.2)[h]	3.8 (3.85)[h]
35	Orange	1934m, 1847s	102–104	$[M]^+$, 608 (608)	54.9 (55.3)	4.5 (4.1)

[a] Calculated values are in parentheses. [b] In CH_2Cl_2 solution. [c] Decomposition point. [d] From the ^{98}Mo or ^{184}W molecular ion in the mass spectrum. [e] As BF_4^- salt. [f] Not obtained pure since always obtained containing a little complex **18**. [g] Rapid hydrolysis in air prevents accurate analysis. [h] Crystallized with 0.25 molecules CH_2Cl_2.



Scheme 2

Formation of $[Mo\{\sigma\text{-}CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **6**.—If addition of $MeSO_3F$ to a solution of **2** to give a solution containing **5** is followed promptly by addition of PPh_3, then a yellow reaction mixture is formed whose strongest signals in the IR spectrum [ν_{CO}/cm^{-1}(thf) 1935m and 1855s] indicate a neutral *trans*-dicarbonyl. The major product of this reaction is an air-stable neutral product characterized spectroscopically as $[Mo\{\sigma\text{-}CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **6**. A cationic compound $[Mo\{\sigma\text{-}CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$-$SO_3F$ **7** (X = SO_3F) is also isolated in varying yields in this reaction depending on the reaction conditions and work-up (see below). Compound **6** is formed by the cleavage of the labile O→Mo donor bond in **5** by PPh_3. This behaviour closely resembles the cleavage of the corresponding bond in **4** by PPh_3 which gives the tetrahydrofuranyl compound **8** (Scheme 2).[5]

The ^1H NMR spectrum of **6** (Table 2) contains a particularly characteristic quartet of doublets assigned to the proton α to the metal. The multiplicity is a result of coupling to the adjacent methyl and to phosphorus. Compound **6** possesses a chiral centre α to the metal, but of course it is isolated as a racemate. The chiral centre causes an interesting effect in the ^{13}C NMR spectrum. The asymmetric centre renders the environments of the two carbonyl ligands inequivalent, that is, diastereotopic. Hence, although in achiral *trans*-$[MR(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (R = alkyl) systems only one carbonyl peak is expected, two are

Table 2 Proton and ^{13}C NMR spectra of the complexes[a]

Complex	$\delta(^1H)$	$\delta(^{13}C)$(ppm)
6	[b] 7.68–7.47 (6 H, m, *o*-Ph), 7.06–6.91 (9 H, m, *m*- and *p*-Ph), 5.40 [1 H, d of q, *J*(HH) 6.5, *J*(PH) 3, CH], 4.76 [5 H, d, *J*(PH) 1, C_5H_5], 3.38 (3 H, s, OMe), 2.24 [3 H, d, *J*(HH) 6.5, CHMe]	[c] 240.8 [d, *J*(PC) 23, CO], 237.9 [d, *J*(PC) 25, CO], 136.9–128.0 (Ph), 93.1 (C_5H_5), 75.1 [d, *J*(PC) 12, CH], 58.5 (OMe), 26.2 (CH*Me*)
6–D	[b] 7.71–7.50 (6 H, m, *o*-Ph), 7.06–6.91 (9 H, m, *m*- and *p*-Ph), 4.76 [5 H, d, *J*(PH) 1, C_5H_5], 3.38 (3 H, s, OMe), 2.22 (3 H, s, CDMe)	[c] 240.7 [d, *J*(PC) 22, CO], 237.9 [d, *J*(PC) 25, CO], 136.8–127.4 (Ph), 93.0 (C_5H_5), 74.6 (br, CD), 58.4 (OMe), 26.1 (CD*Me*)
6–D$_3$	[b] 7.61–7.49 (6 H, m, *o*-Ph), 7.04–6.91 (9 H, m, *m*- and *p*-Ph), 5.38 [1 H, d, *J*(PH) 3.5, CH], 4.76 [5 H, d, *J*(PH) 1, C_5H_5], 3.38 (3 H, s, OMe)	[c,e] 240.9 [d, *J*(PC) 22, CO], 237.8 [d, *J*(PC) 25, CO], 136.9–128.0 (Ph), 93.1 (C_5H_5), 75.0 [d, *J*(PC) 11, CH], 58.5 (OMe)
17	[f] 7.67–7.51 (9 H, m, *m*- and *p*-Ph), 7.32 (6 H, s, br, *o*-Ph), 5.47 [5 H, d, *J*(PH) 1, C_5H_5], 4.35 (3 H, s, OMe), 3.12 (3 H, s, =CMe)	[g] 337.0 [d, *J*(PC) 11, Mo=C], 231.9 [d, *J*(PC) 26, CO], 133.4–129.5 (Ph), 98.6 (C_5H_5), 66.2 (OMe), 46.3 (=C*Me*)
17–D$_3$	[f] 7.66–7.50 (9 H, m, *m*- and *p*-Ph), 7.32 (6 H, s, br, *o*-Ph), 5.46 [5 H, d, *J*(PH) 1, C_5H_5], 4.36 (3 H, s, OMe)	[g,e] 337.4 [d, *J*(PC) 11, Mo=C], 231.8 [d, *J*(PC) 26, CO], 133.7–129.5 (Ph), 98.6 (C_5H_5), 66.2 (OMe)
7[k]	[l] 7.68–6.95 (30 H, m, Ph), 4.86 [5 H, d, *J*(PH) 2, C_5H_5], 3.10 [1 H, d of d of q, *J*(HH) 7.5, *J*(PH) 18, 4.5, CH], 1.71 [3 H, d of d, *J*(HH) 7.5, *J*(PH) 21, CHMe]	
20	[c] 7.50–7.18 (15 H, m, Ph), 5.11 (5 H, s, C_5H_5), 3.23 [1 H, d of d, *J*(HH) 10, *J*(PH) 1, CH_2], 1.83 [1 H, d of d, *J*(HH) 7, *J*(PH) 10, CH_2], 1.56 [1 H, d of d, *J*(HH) 10, 7, CH]	[c] 266.5 [d, *J*(PC) 6, CH_2CH*C*O], 238.5 [d, *J*(PC) 16, CO], 134.1–128.2 (Ph), 89.9 (C_5H_5), 34.9 (CH_2), 28.8 (CH)
20-D	[c,h] 7.58–7.10 (15 H, m, Ph), 5.02 (5 H, s, C_5H_5), 3.15 (1 H, s, CH_2), 1.85 [1 H, d, *J*(PH) 10, CH_2]	[c] 266.6 [d, *J*(PC) 6, CH_2CD*C*O], 238.5 [d, *J*(PC) 16, CO], 134.1–128.1 (Ph), 89.9 (C_5H_5), 35.0 (CH_2), 28.6 (br, CD)
20-D$_2$	[c,i] 7.58–7.21 (15 H, m, Ph), 5.11 (5 H, s, C_5H_5), 1.54 (1 H, s, CH)	[c] 266.2 [d, *J*(PC) 5, CD_2CH*C*O], 238.4 [d, *J*(PC) 16, CO], 132.8–127.2 (Ph), 90.0 (C_5H_5), 34.6 (br, CD_2), 28.6 (CH)
27-D$_3$	7.50–7.25 (15 H, m, Ph), 4.98 (5 H, s, C_5H_5)	[c,e] 270.2 [d, *J*(PC) 11, *C*OCD_3], 238.0 [d, *J*(PC) 23, CO], 135.1–128.3 (Ph), 96.7 (C_5H_5)
29	[f] 7.65–7.51 (9 H, m, *m*- and *p*-Ph), 7.30 (6 H, s, br, *o*-Ph), 5.58 [5 H, d, *J*(PH) 1.5, C_5H_5], 4.27 (3 H, s, OMe), 3.12 (3 H, s, =CMe)	[g] 313.6 [d, *J*(PC) 10.5, W=C], 224.9 [d, *J*(PC) 21, CO], 133.6–129.6 (Ph), 97.7 (C_5H_5), 65.2 (OMe), 42.8 (=C*Me*)
30	[b] 7.62–7.40 (6 H, m, *o*-Ph), 7.18–6.90 (9 H, m, *m*- and *p*-Ph), 5.34 [1 H, d of q, *J*(HH) 6.5, *J*(PH) 4.5, CH], 4.77 [5 H, d, *J*(PH) 1.5, C_5H_5], 3.38 (3 H, s, OMe), 2.30 [3 H, d, *J*(HH) 6.5, *J*(WH) 4, CHMe]	[c] 232.5 [d, *J*(PC) 18, CO], 230.9 [d, *J*(PC) 19, CO], 136.0–128.0 (Ph), 91.6 (C_5H_5), 62.1 [d, *J*(PC) 11, CH], 58.6 (OMe), 26.6 (CH*Me*)
31	7.48–7.30 (15 H, m, Ph), 4.95 (2 H, m, $C_5\mathit{H}_4$Me), 4.69 (2 H, m, $C_5\mathit{H}_4$Me), 2.61 (3 H, s, COMe), 2.13 (3 H, s, C_5H_4*Me*)	[c] 255.6 [d, *J*(PC) 8, *C*OMe], 232.6 [d, *J*(PC) 17, CO], 135.5–128.3 (Ph), 110.8 (C_5H_4Me), 98.3 (C_5H_4Me), 92.2 (C_5H_4Me), 54.7 (CO*Me*), 13.3 (C_5H_4*Me*)
32	[f] 7.65–7.49 (9 H, m, *m*- and *p*-Ph), 7.34 (6 H, s, br, *o*-Ph), 5.41 (2 H, m, $C_5\mathit{H}_4$Me), 5.34 (2 H, m, $C_5\mathit{H}_4$Me), 4.33 (3 H, s, OMe), 3.15 (3 H, s, =CMe), 2.12 (3 H, s, C_5H_4*Me*)	[g] 313.8 [d, *J*(PC) 8, W=C], 226.0 [d, *J*(PC) 21, CO], 133.8–129.7 (Ph), 114.1 (C_5H_4Me), 99.5 (C_5H_4Me), 95.4 (C_5H_4Me), 65.4 (OMe), 47.8 (=C*Me*), 12.7 (C_5H_4*Me*)
33	[b] 7.66–7.52 (6 H, m, *o*-Ph), 7.06–6.90 (9 H, m, *m*- and *p*-Ph), 5.27 [1 H, d of q, *J*(HH) 6.5, *J*(PH) 3, CH], 4.78 (2 H, m, $C_5\mathit{H}_4$Me), 4.37 (2 H, m, $C_5\mathit{H}_4$Me), 3.37 [3 H, d, *J*(HH) 6.5, *J*(WH) 4.5, CH*Me*], 2.14 (3 H, s, C_5H_4*Me*)	[c] 235.2 [d, *J*(PC) 16, CO], 232.1 [d, *J*(PC) 19, CO], 137.8–128.0 (Ph), 105.4 (C_5H_4Me), 98.6 (C_5H_4Me), 91.7 (C_5H_4Me), 88.5 (C_5H_4Me), 88.2 (C_5H_4Me), 63.4 (br, CH), 58.4 (OMe), 26.2 (CH*Me*), 13.3 (C_5H_4*Me*)
33-D	[b] 7.65–7.52 (6 H, m, *o*-Ph), 7.06–6.91 (9 H, m, *m*- and *p*-Ph), 4.79 (2 H, m, $C_5\mathit{H}_4$Me), 4.37 (2 H, m, $C_5\mathit{H}_4$Me), 3.37 (3 H, s, OMe), 2.37 [3 H, s, *J*(WH) 4.5, CH*Me*], 2.14 (3 H, s, C_5H_4*Me*)	[c] 235.2 [d, *J*(PC) 16, CO], 232.1 [d, *J*(PC) 19, CO], 137.7–128.0 (Ph), 105.3 (C_5H_4Me), 98.5 (C_5H_4Me), 91.1 (C_5H_4Me), 88.4 (C_5H_4Me), 88.1 (C_5H_4Me), 63.1 (br, CD), 58.3 (OMe), 26.1 (CD*Me*), 13.3 (C_5H_4*Me*)
34	7.87 [1 H, d of d, *J*(HH) 17.5, 11, CH], 7.45–7.33 (15 H, m, Ph), 6.48 [1 H, d of d, *J*(HH) 11, 3, CH_2], 5.67 [1 H, d of d, *J*(HH) 17.5, 3, CH_2], 4.95 [5 H, d, *J*(PH) 1.5, C_5H_5]	[d] 218.2 [d, *J*(PC) 20, CO], 136.8–128.4 (Ph), 92.0 (C_5H_5)
35	7.75 [1 H, d of d, *J*(HH) 18, 11, CH], 7.45–7.35 (15 H, m, Ph), 6.54 [1 H, d of d, *J*(HH) 11, 3, CH_2], 5.71 [1 H, d of d, *J*(HH) 18, 3, CH_2], 4.79 (2 H, m, $C_5\mathit{H}_4$Me), 4.66 (2 H, m, $C_5\mathit{H}_4$Me), 2.10 (3 H, s, C_5H_4*Me*)	[c] 229.0 [d, *J*(PC) 18, CO], 140.5 [d, *J*(PC) 10, CH], 136.1–128.1 (Ph), 126.8 (CH_2), 107.2 (C_5H_4Me), 93.1 (C_5H_4Me), 89.1 (C_5H_4Me), 13.3 (C_5H_4*Me*)
35-D	[j] 7.45–7.34 (15 H, m, Ph), 6.54 [1 H, d, *J*(HH) 3, CH_2], 5.70 [1 H, d, *J*(HH) 3, CH_2], 4.79 (2 H, m, $C_5\mathit{H}_4$Me), 4.66 (2 H, m, $C_5\mathit{H}_4$Me), 2.10 (3 H, s, C_5H_4*Me*)	[c] 229.0 [d, *J*(PC) 18, CO], 140.0 (br, CD), 136.0–128.1 (Ph), 126.6 (CH_2), 107.1 (C_5H_4Me), 93.0 (C_5H_4Me), 89.0 (C_5H_4Me), 13.2 (C_5H_4*Me*)

[a] In $CDCl_3$ and at ambient temperature unless stated otherwise. Coupling constants in Hz throughout. [b] In C_6D_6 at ambient temperature. [c] In $CDCl_3$ at −50 °C. [d] In CD_2Cl_2 at ambient temperature, no CH=CH_2 group apparent. [e] No CD_3 group apparent at the signal-to-noise level in the spectrum. [f] In CD_3CN at ambient temperature. [g] In CD_3CN at −40 °C. [h] ^2H NMR data in $CHCl_3$ at ambient temperature; δ_D 1.68 (1 D, s, br, CD). [i] ^2H NMR data recorded in $CHCl_3$ at ambient temperature; δ_D 3.22 (1 D, s, br, CD_2), 1.93 (1 D, s, br, CD_2). [j] ^2H NMR data recorded in $CHCl_3$ at ambient temperature; δ_D 7.79 (1 D, s, br, CD). [k] As BF_4^- salt. [l] In CD_2Cl_2 at ambient temperature. Complex **7** (X = BF_4) is insufficiently soluble for a ^{13}C NMR spectrum to be recorded.

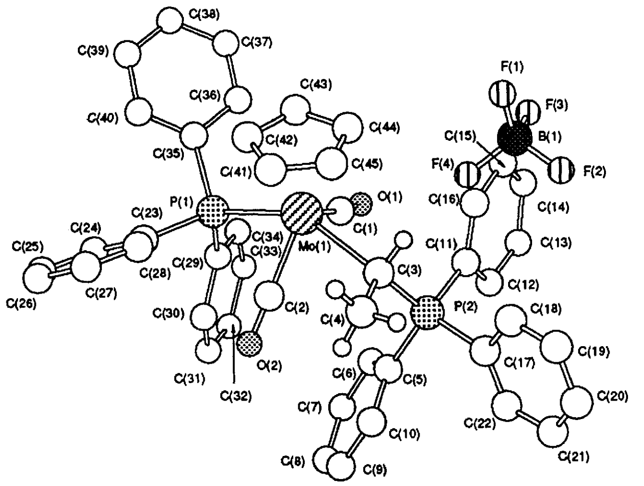
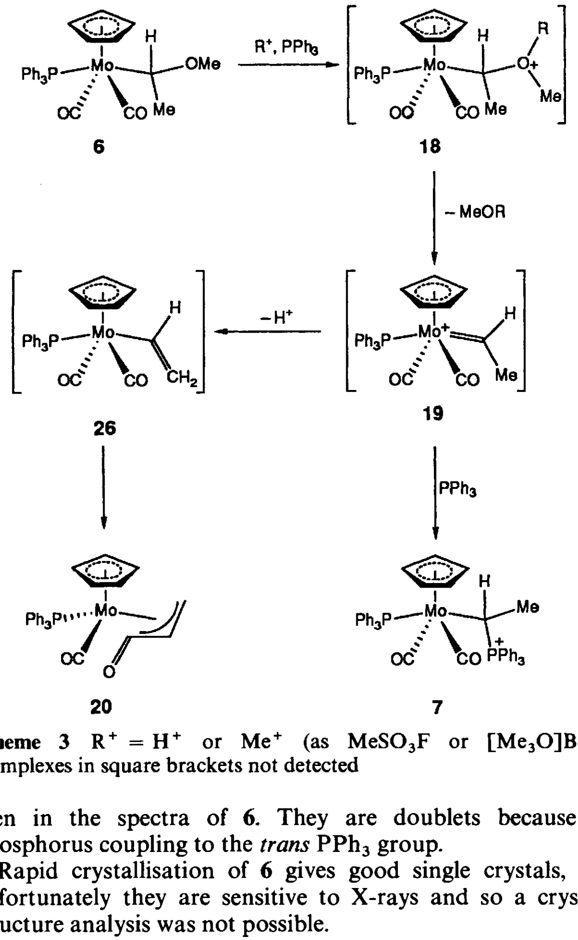


Fig. 1 Structure of the cation 7 with atom labelling



Scheme 3 $R^+ = H^+$ or Me^+ (as $MeSO_3F$ or $[Me_3O]BF_4$). Complexes in square brackets not detected

seen in the spectra of 6. They are doublets because of phosphorus coupling to the *trans* PPh_3 group.

Rapid crystallisation of 6 gives good single crystals, but unfortunately they are sensitive to X-rays and so a crystal-structure analysis was not possible.

The same products are seen when $[Me_3O]BF_4$ is used in place of $MeSO_3F$ as the alkylating agent. The yields are similar with either of the two reagents. In both cases, reasonably prompt work-up is required because of the tendency of these alkylating agents to polymerize thf.

Complexes of the type $[M\{CHMe(OR)\}L_n]$ are comparatively rare but known examples include $[Fe\{CHMe(OMe)\}(CO)(L)(\eta\text{-}C_5H_5)]$ **9** (L = CO), **10** ($L = PPh_3$)[6] or **11** [$L = P(OPh)_3$]. The ^1H NMR spectroscopic properties of the CHMe(OMe) ligands in **9**, **10** and **11** are rather similar to those of **6**. In addition, the complexes $[M(CH_2OMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **12** (M = Mo), **13** (M = W),[7] $[M(CH_2OMe)(CO)_3(\eta\text{-}C_5H_5)]$ **14** (M = Mo), **15** (M = W)[8] and $[Fe\{CMe_2(OMe)\}(CO)_2(\eta\text{-}C_5H_5)]$ **16**[9] are known. Attempts to synthesise $[W\{CHMe(OMe)\}(CO)_3(\eta\text{-}C_5H_5)]$ by the reaction of the carbene cation $[W\{=CMe(OMe)\}(CO)_3(\eta\text{-}C_5H_5)]^+$ with hydride led only to $[WEt(CO)_3(\eta\text{-}C_5H_5)]$.[8] Complex **12** undergoes hydride abstraction on treatment with $[CPh_3]^+$ to give the cationic carbene $[Mo\{=CH(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ together with $[MoMe(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$.[8] It is expected that cationic carbenes of this type will undergo the reverse reaction, that is, attack by hydride to form methoxy alkyl complexes. As an example, treatment of $[Fe\{=CMe(OEt)\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]^+$ with $NaBH_4$ is known to give the ethoxyalkyl $[Fe\{CH(Me)OEt\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$.[10] The carbene complex $[Mo\{=CMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ **17** is known and readily available through treatment of $[Mo(\sigma\text{-}COMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ with $[Me_3O]BF_4$.[10] We find that **17** does indeed undergo reaction with $LiBHEt_3$ to form **6** (Scheme 1), and in a reasonable yield.

Formation and Structure of the Cation $[Mo\{\sigma\text{-}CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ **7**.—When compound **2** is treated with either $MeSO_3F$ or $[Me_3O]BF_4$ followed by PPh_3, a cationic product **7** is frequently isolated in variable quantities in addition to compound **6** (see above). The cation is the same in each case, but, of course, its counterion varies (BF_4^- or SO_3F^-). Integration of the ^1H NMR spectrum of this material (Table 2) shows it to contain two PPh_3 units per $Mo(\eta\text{-}C_5H_5)$ unit, while the double doublet and double quartet structures confirm that a CHMe unit is present which is coupled to phosphorus. These data suggest structure **7** ($X = BF_4$) and **7** ($X = SO_3F$) respectively. This conclusion is reinforced by an X-ray crystal analysis on **7** ($X = BF_4$). The molecular structure is shown in Fig. 1, while Tables 3 and 4 give details of atom positions, bond lengths and bond angles.

The geometry of the molybdenum atom in **7** ($X = BF_4$) is square-based pyramidal ('four-legged piano stool') with an apical cyclopentadienyl group. The geometry of the mutually *trans*-basal carbonyl ligands, the PPh_3 ligand and the cyclopentadienyl ligand are all normal. The remaining group is a 1-(triphenylphosphine)ethyl ligand. The crystal structure is completed by an extensively disordered BF_4^- anion. The molybdenum–alkyl bond [Mo–C(3)] is long at 2.35 Å and the hydrogen atom carried by C(3) is only 2.62 Å from the molybdenum. The molybdenum atom is 2.01 Å from the mean cyclopentadienyl plane. The torsion angles P(1)–Mo(1)–C(3)–X are 54 [X = P(2)], −84 [X = C(4)] and 160 [X = H(3)], which places the hydrogen substituent on C(3) nearest to the cyclopentadienyl ligand.

A reasonable mechanism of formation of **7** from **6** is shown in Scheme 3. It relies on excess methylating reagent attacking **6** at the OMe group to form intermediate **18**, abstracting methoxide and thus eliminating MeOMe. The resulting intermediate alkylidene cation **19** is then attacked by excess PPh_3 at the alkylidene atom to give **7**. The conditions for this process typically occur during work-up of the reaction (see Experimental section) if the reaction mixture is not filtered prior to stripping the solvent. That is, concentration of the reaction mixture prior to filtration through alumina provides the conditions for $\mathbf{6} \longrightarrow \mathbf{18} \longrightarrow \mathbf{19} \longrightarrow \mathbf{7}$. On the other hand, filtration prior to solvent removal disposes of the excess alkylating agent and prevents formation of **7**, favouring isolation of **6**.

Alkylidene complexes related to the intermediate **19** are known. The somewhat unstable cations $[M(=CHR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ (M = Mo, R = H; M = W, R = H or Ph) are formed in the reactions of $[Mo(CH_2OR)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ ($R = Me$, CH_2Ph or $COBu^t$) with $Me_3SiOSO_2CF_3$ and of $[W(CH_2R)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ (R = H or Ph) with $[CPh_3]^+$ respectively.[7] Attempts were not made to isolate or further identify the alkylidene cation **19**.

Complex **7** is an ylide. However attempts to deprotonate, **7** at the α position by reaction with LiBu in a manner related to the well known deprotonation of the Wittig reagent $[PPh_3Me]I$ were not successful. A few other related complexes are known. The NMR data for **7** are very similar to those reported for the

Table 3 Atomic coordinates (× 10^4) for $[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]BF_4$ **7**

Atom	*x*	*y*	*z*
Mo	1635(1)	1853(1)	556(1)
P(1)	1241(2)	3109(1)	124(1)
P(2)	4727(2)	986(1)	1448(1)
O(1)	3396(6)	2666(3)	1944(3)
O(2)	2993(6)	2016(3)	−501(3)
C(1)	2808(7)	2347(4)	1429(4)
C(2)	2511(7)	1962(4)	−102(4)
C(3)	3082(7)	896(4)	832(4)
C(4)	2944(8)	440(4)	166(4)
C(5)	5553(7)	1600(4)	1107(4)
C(6)	5830(7)	2296(4)	1347(4)
C(7)	6468(8)	2725(5)	1060(5)
C(8)	6813(7)	2497(5)	520(5)
C(9)	6499(8)	1816(6)	261(5)
C(10)	5880(7)	1364(4)	546(4)
C(11)	4870(7)	1249(4)	2331(4)
C(12)	5988(8)	1591(5)	2822(4)
C(13)	6067(10)	1804(6)	3494(4)
C(14)	5066(10)	1695(5)	3688(5)
C(15)	3992(9)	1328(5)	3224(5)
C(16)	3904(8)	1103(4)	2549(4)
C(17)	5580(7)	150(4)	1599(4)
C(18)	4935(8)	−460(4)	1667(5)
C(19)	5556(11)	−1111(4)	1803(5)
C(20)	6810(10)	−1150(5)	1882(5)
C(21)	7448(9)	−558(6)	1834(5)
C(22)	6826(9)	93(5)	1688(5)
C(23)	545(7)	3232(4)	−867(4)
C(24)	499(9)	3906(5)	−1165(5)
C(25)	−45(9)	3998(5)	−1918(4)
C(26)	−578(9)	3429(5)	−2369(5)
C(27)	−549(9)	2765(5)	−2080(4)
C(28)	−7(8)	2672(4)	−1334(4)
C(29)	2654(7)	3693(4)	428(4)
C(30)	3427(8)	3714(4)	45(5)
C(31)	4494(8)	4137(5)	277(5)
C(32)	4870(8)	4529(4)	902(5)
C(33)	4129(9)	4506(4)	1288(5)
C(34)	3025(8)	4098(4)	1052(4)
C(35)	116(7)	3580(4)	405(4)
C(36)	334(8)	3583(4)	1144(4)
C(37)	−486(9)	3922(4)	1372(5)
C(38)	−1564(8)	4269(4)	878(6)
C(39)	−1801(9)	4267(4)	156(6)
C(40)	−961(7)	3926(4)	−76(5)
C(41)	−296(8)	1226(5)	−153(5)
C(42)	−593(7)	1883(5)	54(4)
C(43)	−150(7)	1894(5)	825(4)
C(44)	458(7)	1244(4)	1086(4)
C(45)	341(7)	840(4)	479(4)
B(1)	1784(14)	−664(6)	2183(9)
F(1)	573(12)	−918(12)	1986(12)
F(2)	2615(21)	−1218(9)	2373(15)
F(3)	2075(22)	−205(12)	2751(10)
F(4)	1880(26)	−309(12)	1622(11)
B(2)	1633(35)	−569(21)	2140(22)
F(5)	1496(59)	−1280(21)	2129(31)
F(6)	2540(47)	−377(34)	2810(30)
F(7)	476(43)	−266(30)	2000(31)
F(8)	2029(71)	−373(38)	1622(38)
B(3)	1588(15)	−558(9)	2148(8)
F(9)	2109(29)	−371(16)	1681(14)
F(10)	1591(27)	−1(11)	2568(13)
F(11)	2297(24)	−1088(12)	2592(11)
F(12)	362(16)	−787(17)	1755(14)

Table 4 Selected bond lengths (Å) and angles (°) for $[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]BF_4$ **7**

Mo–P(1)	2.502(8)	Mo–C(1)	1.935(9)
Mo–C(2)	1.982(11)	Mo–C(3)	2.349(10)
Mo–C(41)	2.365(10)	Mo–C(42)	2.294(10)
Mo–C(43)	2.316(12)	Mo–C(44)	2.341(12)
Mo–C(45)	2.380(11)	P(1)–C(23)	1.825(9)
P(1)–C(29)	1.827(9)	P(1)–C(35)	1.837(11)
P(2)–C(3)	1.757(8)	P(2)–C(5)	1.804(10)
P(2)–C(11)	1.788(10)	P(2)–C(17)	1.810(10)
O(1)–C(1)	1.139(9)	O(2)–C(2)	1.154(13)
C(3)–C(4)	1.545(12)	Mo · · · H(3)	2.62
P(1)–Mo–C(1)	79.1(3)	P(1)–Mo–C(2)	74.6(3)
C(1)–Mo–C(2)	102.1(4)	P(1)–Mo–C(3)	144.8(3)
C(1)–Mo–C(3)	90.8(3)	C(2)–Mo–C(3)	74.7(3)
Mo–P(1)–C(23)	115.6(3)	Mo–P(1)–C(29)	117.1(3)
C(23)–P(1)–C(29)	101.4(4)	Mo–P(1)–C(35)	113.4(3)
C(23)–P(1)–C(35)	104.0(4)	C(29)–P(1)–C(35)	103.4(4)
C(3)–P(2)–C(5)	111.4(4)	C(3)–P(2)–C(11)	110.3(4)
C(5)–P(2)–C(11)	111.1(4)	C(3)–P(2)–C(17)	111.5(4)
C(5)–P(2)–C(17)	107.2(4)	C(11)–P(2)–C(17)	105.1(4)
Mo–C(1)–O(1)	173.5(8)	Mo–C(2)–O(2)	178.1(6)
Mo–C(3)–P(2)	121.3(4)	Mo–C(3)–C(4)	115.0(4)
P(2)–C(3)–C(4)	110.5(6)	Mo–C(3)–H(3)	95.2
P(2)–C(3)–H(3)	101.5	C(4)–C(3)–H(3)	110.7

neutral diastereotopic pairs of rhenium complexes $[Re\{CHMe(PPh_3)\}(NO)(PPh_3)(\eta\text{-}C_5H_5)]$.[11]

The above postulated mechanism for the formation of **7** is supported by experiments conducted on isolated **6**. Addition of $HBF_4{\cdot}OEt_2$ to a thf solution of **6** (Scheme 1) followed rapidly by PPh_3 gives near quantitative yields of the ylide **7** ($X = BF_4$). The counterion is BF_4^-, and the role of the acid is to remove methoxide as MeOH.

Formation of the η^3*-Propenoyl* $[Mo\{\eta^3\text{-}CH_2CHC{=}O\}(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ **20**.—Complex **6** is somewhat unstable, in the sense that it rearranges under certain conditions when stirred in solution. Compound **6** is stable in clean dry CH_2Cl_2 or $CHCl_3$. However, when stirred in $CHCl_3$ (used as supplied and so containing a little HCl) the IR bands of **6** are replaced by a broad envelope of bands [ν_{CO}/cm^{-1}($CHCl_3$) 1885]. In addition a low-frequency absorption in the region expected for organic ketonic stretches [ν_{CO}/cm^{-1}($CHCl_3$) 1685] is evident. These features were traced to the complex $[Mo(\eta^3\text{-}CH_2CHC{=}O)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ **20**. A similar rearrangement is observed when a little Al_2O_3 is added to a solution of **6** in clean dry CH_2Cl_2 or $CHCl_3$.

Complex **20** is unusual. Although a monocarbonyl, the IR spectrum consists of a broad envelope of overlapping bands. The ^1H NMR spectrum (Table 2) in $CDCl_3$ shows a cyclopentadienyl ring, a PPh_3 ligand and a three-proton spin system showing phosphorus coupling. The ^{13}C NMR spectrum is informative. There are two phosphorus coupled carbonyl signals. One at δ_C 238.5 is in a position characteristic of a terminal metal–carbonyl while the chemical shift of the other at δ_C 266.5 is indicative of an sp^2 hybridised carbonyl bound to molybdenum. These spectroscopic data are consistent with the η^3-propenoyl (acryloyl) complex **20**.

The structure of **20** was confirmed by X-ray crystallography. The molecular structure and atom labelling are shown in Fig. 2 while Tables 5 and 6 gives details of atom positions, bond lengths and bond angles.

The molecular structure comprises a conventional $Mo(CO)_2(\eta\text{-}C_5H_5)$ fragment co-ordinated to a η^3-propenoyl ligand. The η^3-propenoyl ligand bonds to the molybdenum in an allylic mode through the three carbon atoms at distances of 2.35, 2.34 and 2.11 Å; the shortest distance is to the carbon bearing the oxygen atom. The oxygen atom is at a non-bonding distance of 3.12 Å from the metal. The hydrogen atoms on this

Table 5 Atom coordinates (× 10^4) for [Mo(η^3-$CH_2CHC{=}O$)(CO)(PPh_3)(η-C_5H_5)] **20**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Mo	1756(1)	1814(3)	679(1)	C(13)	4266(9)	4042(19)	802(10)
P	2641(4)	3222(10)	−64(4)	C(14)	3217(9)	1826(18)	−552(9)
O(1)	3343(12)	652(27)	1966(11)	C(15)	3227(9)	2046(18)	−1376(9)
O(2)	1304(16)	−1828(28)	983(13)	C(16)	3644(9)	946(18)	−1738(9)
C(1)	2780(15)	1070(31)	1442(17)	C(17)	4053(9)	−373(18)	−1275(9)
C(2)	2153(10)	4726(19)	−880(10)	C(18)	4043(9)	−592(18)	−451(9)
C(3)	1310(10)	4761(19)	−1181(10)	C(19)	3626(9)	508(18)	−89(9)
C(4)	928(10)	5896(19)	−1790(10)	C(20)	1127(11)	4330(20)	802(11)
C(5)	1390(10)	6996(19)	−2098(10)	C(21)	1598(11)	3799(20)	1604(11)
C(6)	2234(10)	6961(19)	−1796(10)	C(22)	1261(11)	2310(20)	1786(11)
C(7)	2615(10)	5826(19)	−1188(10)	C(23)	583(11)	1922(20)	1097(11)
C(8)	3451(9)	4475(19)	623(10)	C(24)	501(11)	3171(20)	489(11)
C(9)	3228(9)	5860(19)	990(10)	C(25)	1308(16)	747(36)	−681(17)
C(10)	3821(9)	6811(19)	1537(10)	C(26)	1702(15)	−492(33)	−162(15)
C(11)	4636(9)	6377(19)	1716(10)	C(27)	1454(15)	−683(33)	576(16)
C(12)	4859(9)	4993(19)	1348(10)				

Table 6 Selected bond lengths (Å) and angles (°) for [Mo(η^3-$CH_2CHC{=}O$)(CO)(PPh_3)(η-C_5H_5)] **20**

Mo–P	2.509(10)	Mo–C(1)	1.952(24)
Mo–C(20)	2.365(18)	Mo–C(21)	2.314(19)
Mo–C(22)	2.288(21)	Mo–C(23)	2.323(21)
Mo–C(24)	2.371(19)	Mo–C(25)	2.349(28)
Mo–C(26)	2.339(28)	Mo–C(27)	2.105(28)
P–C(2)	1.850(17)	P–C(8)	1.842(16)
P–C(14)	1.851(19)	O(1)–C(1)	1.156(29)
O(2)–C(27)	1.229(37)	C(25)–C(26)	1.380(37)
C(26)–C(27)	1.425(41)		
P–Mo–C(1)	84.5(9)	Mo–C(1)–O(1)	172.1(27)
P–Mo–C(25)	76.6(8)	C(1)–Mo–C(25)	120.0(11)
P–Mo–C(26)	89.9(7)	C(1)–Mo–C(26)	90.7(10)
P–Mo–C(27)	125.3(8)	C(1)–Mo–C(27)	84.6(10)
Mo–P–C(2)	117.4(6)	Mo–P–C(8)	113.9(6)
C(2)–P–C(8)	101.0(8)	Mo–P–C(14)	114.5(6)
C(2)–P–C(14)	105.9(8)	C(8)–P–C(14)	102.3(8)
C(25)–C(26)–C(27)	114.2(26)	O(2)–C(27)–C(26)	136.6(28)

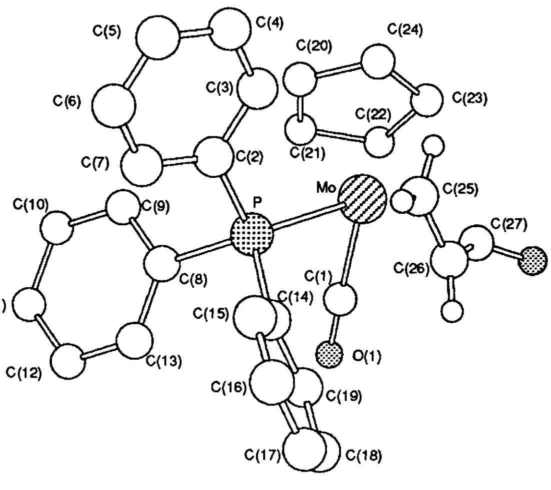


Fig. 2 Molecular structure of **20** with atom labelling

ligand are placed in positions coplanar with the skeleton and one hydrogen atom on C(25) therefore makes a short contact to the molybdenum of 2.36 Å. The molybdenum atom lies 1.99 Å from the cyclopentadienyl plane and 1.68 Å from the allyl plane, from which the oxygen atom deviates by 0.56 Å in a direction away from the metal. There are no significant intermolecular contacts.

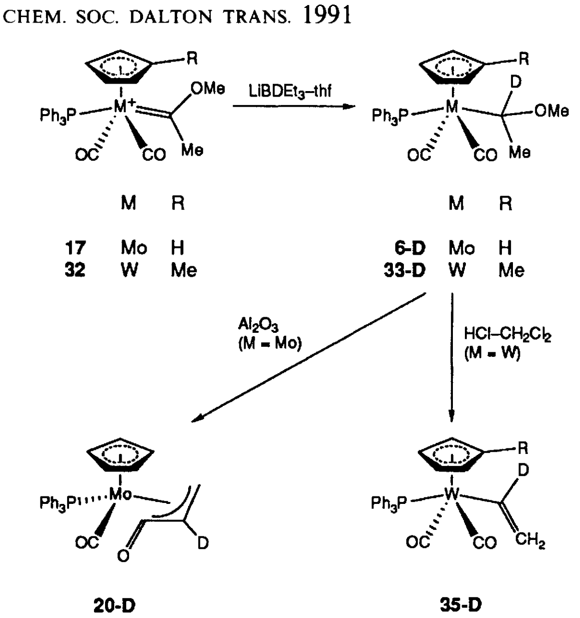
In the solid state, there is only one orientation for the propenoyl group. In solution, the multiplicity of IR signals and the broadness of the ^1H NMR spectrum indicate that there may be fluxional processes associated with reorientations of the propenoyl ligand both relative to the η-C_5H_5 ligand and relative to the Mo(CO)(PPh_3) unit. Any such processes are not yet characterised. However, it seems reasonable that propenoyl reorientations could take place in a fashion related to those of η^3-allyl rotations in [Mo(η^3-allyl)$(CO)_2$(η-C_5H_5)] type complexes.[12]

The complexes [M({η^3-$CH_2C(NR_2)C{=}O$}$(CO)_2$(η-C_5H_5)] (M = Mo or W; R = Me or Et) are related to **20** and prepared by addition of activated alkynes to [MH$(CO)_3$(η-C_5H_5)].[13] None is structurally characterised, but their spectroscopic properties are similar to **20**. Further, the complexes [W{η^3-$CH(CF_3)C(CF_3)C{=}O$}(CO)(PR_3)(η-C_5H_5)] **21**–**24** and [W{η^3-$CH(CF_3)C(CF_3)C{=}O$$(CO)_2$($\eta$-$C_5H_5$)] **25** are also known and the crystal structures of those analysed are clearly related to that of complex **20**.[14] It is clear that in these cases the propenoyl ligands are formed by vinyl to carbonyl migration reactions. A number of other propenoyl derivatives are known and the implication is that these also are formed by similar migratory processes.[15] In addition, the σ-propenoyl compounds [Fe{$CO(CH{=}CH_2)$}$(CO)_2$(η-C_5H_5)] and [W{$CO(CH{=}CH_2)$}$(CO)_3$(η-C_5H_5)] are known. Decarbonylation of such species affords metal vinyl complexes and *not* η^3-propenoyl complexes.[16] The results of labelling experiments (see below) are fully consistent with a process involving a vinyl to carbonyl migration for the conversion of **6** into **20** (Scheme 3).

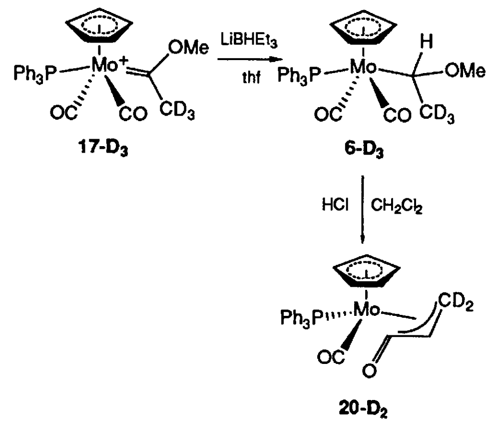
A second product in addition to compound **20** is sometimes found when **6** is maintained in solution over prolonged periods. This is the known hydride *cis*- and *trans*-[MoH$(CO)_2$(PPh_3)(η-C_5H_5)],[17] presumably produced through a β-elimination pathway. We isolated this during attempts to crystallize **6** from CH_2Cl_2 and hexane. Its spectroscopic data are comparable with those of samples prepared independently.

Mechanism of Formation of [Mo(η^3-$CH_2CHC{=}O$)(CO)(PPh_3)(η-C_5H_5)] **20** *from* **6**.—The mechanism of formation of **20** is clearly of some interest. We executed a series of isotopic probe experiments to trace the movements of key atoms during the formation of **20** as a way to provide mechanistic information.

Treatment of the cation **17** with $LiBDEt_3$ (Scheme 4) leads to [Mo{σ-CDMe(OMe)}$(CO)_2$(PPh_3)(η-C_5H_5)] **6-D**. After work-up, the extent of deuterium incorporation at the α position is estimated as >99% from the lack of signals due to the α-hydrogen atom of **6** in the ^1H NMR spectrum of **6-D** and from the molecular-ion isotope pattern of **6-D**. Treatment of **6-D** with neutral alumina gives [Mo(η^3-CH_2CDCO)(CO)(PPh_3)(η-C_5H_5)] **20-D**. The ^1H, ^2H and ^{13}C NMR spectra of **20-D** indicate that deuterium is *only* present in the *central* allyl position.



Scheme 4



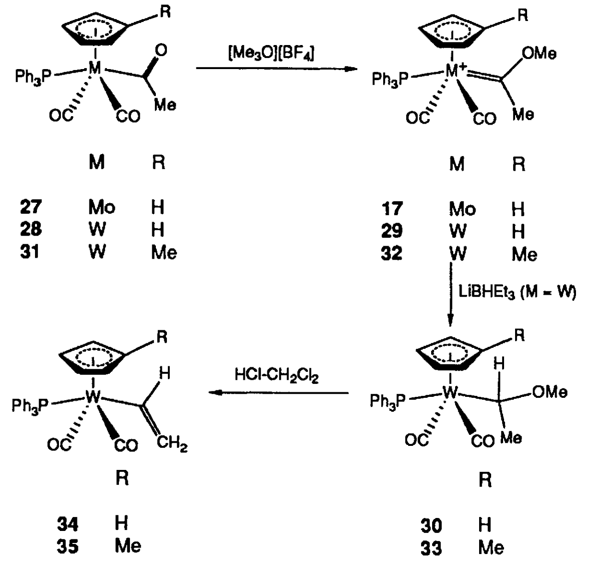
Scheme 5

The complex $[Mo\{\sigma\text{-}CH(CD_3)(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **6-D$_3$** is obtained by addition of $LiBHEt_3$ to the deuteriated cation $[Mo\{=C(CD_3)(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **17-D$_3$** (Scheme 5). The latter species is made by successive treatment of the readily available $[Mo(CD_3)(CO)_3(\eta\text{-}C_5H_5)]$ **1-D$_3$** with PPh_3 and $[Me_3O]BF_4$. A little surprisingly, **6-D$_3$** shows no sign of loss of MeOD on treatment with Al_2O_3, but the reaction of $HCl–CHCl_3$ with **6-D$_3$** is successful and the product is **20-D$_2$**. The ^1H, ^2H and ^{13}C NMR and mass spectra are completely consistent with *both* deuterium atoms being sited at the *terminal* carbon.

The rearrangement of **20** to **6** is acid catalysed. Addition of very small amounts of acid to **6** are sufficient to cause the reaction to proceed virtually instantaneously. Such small amounts of acid can be in the form of trace amounts of HCl dissolved in commercially available CH_2Cl_2 or $CHCl_3$ when used without purification. Alternatively, simply filtering solutions of **6** through a little acidic or neutral Al_2O_3 provides enough acid. Addition of any of the bases Na_2CO_3, NEt_3 or NaOH to a solution of **6** in dry distilled $CHCl_3$ results in no formation of **20** over several hours. It is apparent that the role of the acid is to catalytically remove MeOH as shown in Scheme 3. The result of methanol loss is the undetected vinyl intermediate complex $[Mo(CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **26**. Migration of the vinyl to an adjacent carbonyl and co-ordination of the double bond to the metal results in formation of the η^3-propenoyl ligand. The mechanism illustrated in Scheme 3 is consistent with the isotopic probes discussed above.

Formation of trans-$[W\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4R)]$ **30** *(R = H) and* **33** *(R = Me).*—We were naturally keen to examine tungsten chemistry corresponding to the above. However, while the reaction of **1** with $LiBHEt_3$ gives anion **2**, the hydrido acyl $[WH(COMe)(CO)_2(\eta\text{-}C_5H_5)]^-$ is formed in the corresponding reaction of $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ with $LiBHEt_3$.[18] Therefore a different approach to a tungsten analogue of **6** was required.

This is outlined in Scheme 6. Treatment of the molybdenum acyl $[Mo(COMe)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **27** with $[Me_3O]BF_4$ is known to give the cationic carbene **17**.[19] The analogous tungsten acyl **28** is apparently unreported but is available in the reaction of $[WMe(CO)_3(\eta\text{-}C_5H_5)]$ with PPh_3 using MeCN as solvent. This reaction is unremarkable other than to point out that it takes some time to complete, 100 h in MeCN at reflux against 8 h at ambient temperature for the molybdenum species. The reaction of the tungsten acyl **28** with $[Me_3O]BF_4$ gives the cationic carbene $[W\{=CMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]^+$ **29** in a straight-forward reaction. The spectroscopic properties of **29** (Tables 1 and 2) require little comment.



Scheme 6

Addition of $LiBHEt_3$ to a suspension of **29** in thf leads smoothly to the alkyl **30**. Its spectroscopic properties (Tables 1 and 2) are comparable to those of its molybdenum analogue **6**.

For reasons detailed below it was necessary to synthesize the corresponding methylcyclopentadienyl complexes. The sequence of Scheme 6 starting from compound **31** gives, in sequence, **32** and **33**. Their spectroscopic properties are gathered in Tables 1 and 2.

Compound **30** is noticeably more prone to reaction with acid than the molybdenum compound **6**. Rearrangements as detailed below occur even in really rather pure $CHCl_3$ or CH_2Cl_2.

Formation and Structure of the Vinyl Complexes $[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_4R)]$ **34** *(R = H) and* **35** *(R = Me).*—Addition of traces of acid to solutions of **30** result in loss of MeOH and formation of the new vinyl complex *trans*-$[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **34**. The ^1H NMR properties of **34** are quite characteristic of metal vinyl complexes reported elsewhere.[20] Unfortunately the solubility properties of **34** are such that the signal-to-noise ratio in the ^{13}C NMR spectrum is sufficiently high to render the vinyl signal unassignable.

It is a fact that in many cases methylcyclopentadienyl complexes are more soluble than their cyclopentadienyl analogues. Compound **35** was prepared by reacting traces of acid with **33** and this is sufficiently soluble to allow acquisition of good ^{13}C NMR data. A bonus was the formation of good single crystals.

Table 7 Atomic coordinates (× 10^4) for $[W(\sigma\text{-}CH{=}CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **35**

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
W(1)	3020(1)	1256(2)	1711(1)	C(27)	2842(6)	800(25)	2547(10)
W(1a)	749(1)	1290(2)	1657(1)	C(28)	3019(6)	−178(25)	2953(10)
P(1)	2833(2)	−318(8)	1004(3)	C(1a)	1164(9)	2246(34)	1575(13)
P(1a)	451(2)	2734(8)	937(3)	C(2a)	670(10)	188(30)	1037(11)
O(1)	3716(7)	−282(28)	1938(10)	C(3a)	488(5)	2436(17)	235(6)
O(2)	3005(8)	2813(24)	703(10)	C(4a)	176(5)	2382(17)	−202(6)
O(1a)	1435(6)	2782(22)	1571(9)	C(5a)	217(5)	2133(17)	−728(6)
O(2a)	599(7)	−473(23)	665(9)	C(6a)	571(5)	1937(17)	−817(6)
C(1)	3439(10)	277(36)	1823(14)	C(7a)	884(5)	1990(17)	−380(6)
C(2)	3019(10)	2228(38)	1081(16)	C(8a)	842(5)	2240(17)	146(6)
C(3)	2968(5)	−1888(15)	1200(9)	C(9a)	605(5)	4295(15)	1013(9)
C(4)	2976(5)	−2244(15)	1735(9)	C(10a)	750(5)	4721(15)	1543(9)
C(5)	3069(5)	−3440(15)	1901(9)	C(11a)	879(5)	5917(15)	1627(9)
C(6)	3153(5)	−4280(15)	1532(9)	C(12a)	864(5)	6686(15)	1180(9)
C(7)	3145(5)	−3924(15)	996(9)	C(13a)	719(5)	6260(15)	650(9)
C(8)	3052(5)	−2728(15)	830(9)	C(14a)	590(5)	5064(15)	567(9)
C(9)	2327(4)	−486(21)	740(7)	C(15a)	−49(4)	2810(21)	859(7)
C(10)	2138(4)	584(21)	545(7)	C(16a)	−226(4)	3879(21)	960(7)
C(11)	1753(4)	563(21)	338(7)	C(17a)	−606(4)	3867(21)	948(7)
C(12)	1557(4)	−528(21)	326(7)	C(18a)	−808(4)	2786(21)	835(7)
C(13)	1747(4)	−1598(21)	520(7)	C(19a)	−631(4)	1717(21)	733(7)
C(14)	2132(4)	−1577(21)	728(7)	C(20a)	−252(4)	1729(21)	745(7)
C(15)	3004(5)	−134(18)	390(7)	C(21a)	1206(9)	68(36)	1823(14)
C(16)	2766(5)	−108(18)	−131(7)	C(22a)	1502(10)	−143(43)	1685(14)
C(17)	2909(5)	98(18)	−589(7)	C(23a)	791(4)	855(22)	2605(7)
C(18)	3291(5)	278(18)	−526(7)	C(24a)	706(4)	2118(22)	2545(7)
C(19)	3529(5)	251(18)	−6(7)	C(25a)	354(4)	2242(22)	2171(7)
C(20)	3385(5)	45(18)	452(7)	C(26a)	221(4)	1056(22)	2001(7)
C(21)	3493(9)	2449(35)	1917(15)	C(27a)	491(4)	199(22)	2269(7)
C(22)	3771(11)	2712(38)	1713(17)	C(28a)	457(4)	−1182(22)	2224(7)
C(23)	2948(6)	2046(25)	2564(10)	Cl(1)	375(13)	−4368(43)	2785(18)
C(24)	2701(6)	2657(25)	2126(10)	Cl(2)	−213(13)	−3713(43)	1956(18)
C(25)	2443(6)	1788(25)	1839(10)	C(Cl)	−58(13)	−4754(43)	2447(18)
C(26)	2530(6)	641(25)	2099(10)				

Atoms W(1), P(1), O(1), O(2), C(1)–C(28) comprise molecule 1; atoms W(1a), P(1a), O(1a), O(2a), C(1a)–C(28a) comprise molecule 2; atoms Cl(1), Cl(2), C(Cl) comprise the dichloromethane solvent molecule.

Table 8 Bond lengths (Å) and angles (°) for $[W(\sigma\text{-}CH{=}CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **35**

	Molecule 1	Molecule 2		Molecule 1	Molecule 2
W(1)–P(1)	2.457(9)	2.462(9)	P(1)–C(9)	1.841(16)	1.801(19)
W(1)–C(1)	1.851(38)	1.910(36)	P(1)–C(15)	1.813(21)	1.815(16)
W(1)–C(2)	1.909(41)	1.941(29)	O(1)–C(1)	1.170(46)	1.163(42)
W(1)–C(21)	2.148(35)	2.120(35)	O(2)–C(2)	1.139(48)	1.162(37)
W(1)–C(23)	2.385(25)	2.401(19)	C(21)–C(22)	1.283(60)	1.243(54)
W(1)–C(24)	2.327(26)	2.450(20)	C(27)–C(28)	1.520(2)	1.523(2)
W(1)–C(25)	2.304(24)	2.406(20)	Cl–C(Cl)	1.680(2)	
W(1)–C(26)	2.349(25)	2.328(19)	C–C(phenyl)	1.395	
W(1)–C(27)	2.399(26)	2.325(21)	C–C(cp)	1.420	
P(1)–C(3)	1.828(19)	1.831(19)			
P(1)–W(1)–C(1)	77.6(11)	78.4(10)	W(1)–C(2)–O(2)	177.7(28)	175.9(34)
P(1)–W(1)–C(2)	81.2(12)	81.5(9)	P(1)–C(3)–C(4)	117.8(8)	122.2(6)
C(1)–W(1)–C(2)	106.9(17)	103.2(15)	P(1)–C(3)–C(8)	122.2(8)	117.8(6)
P(1)–W(1)–C(21)	132.6(11)	138.5(10)	P(1)–C(9)–C(10)	115.2(8)	117.4(8)
C(1)–W(1)–C(21)	73.3(15)	75.2(15)	P(1)–C(9)–C(14)	124.8(8)	122.6(8)
C(2)–W(1)–C(21)	72.7(15)	74.2(14)	P(1)–C(15)–C(16)	122.3(6)	121.9(8)
W(1)–P(1)–C(3)	117.1(7)	118.2(7)	P(1)–C(15)–C(20)	117.6(6)	117.8(8)
W(1)–P(1)–C(9)	114.8(8)	117.3(7)	W(1)–C(21)–C(22)	136.2(31)	140.8(33)
C(3)–P(1)–C(9)	101.1(10)	100.3(10)	C(23)–C(27)–C(28)	126.0(1)	126.0(1)
W(1)–P(1)–C(15)	116.3(7)	112.1(8)	C(26)–C(27)–C(28)	126.0(1)	125.9(1)
C(3)–P(1)–C(15)	101.9(11)	102.0(9)	Cl(1)–C(Cl)–Cl(2)	108.7(1)	
C(9)–P(1)–C(15)	103.3(9)	104.9(10)	C–C–C(phenyl)	120.0	
W(1)–C(1)–O(1)	173.8(34)	173.6(27)	C–C–C(cp)	108.0	

The X-ray crystal structure of **35** is displayed in Fig. 3 while Tables 7 and 8 give details of atom positions, bond lengths and bond angles. The molecule is based on a conventional square-based pyramidal geometry with an apical cyclopentadienyl group. The two crystallographically independent molecules are chemically very similar and all differences can be ascribed to crystal packing effects. In both molecules, an η^5-methylcyclopentadienyl ligand is attached fairly symmetrically to the tungsten at perpendicular distances of 2.018 and 2.049 Å. The apparently different sites for the methyl substituent (compared

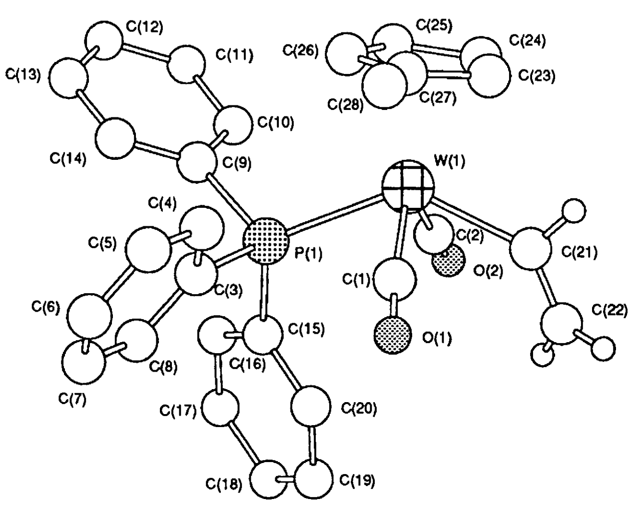
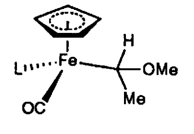
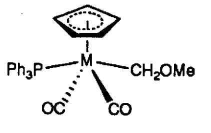


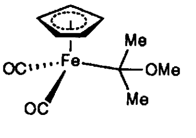
Fig. 3 Molecular structure of **35** with atom labelling



	L
9	CO
10	PPh$_3$
11	P(OPh)$_3$



	M	L
12	Mo	PPh$_3$
13	W	PPh$_3$
14	Mo	CO
15	W	CO



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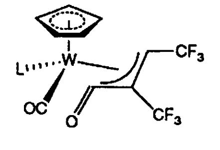

	L
21	PPh$_3$
22	PMe$_3$
23	PMe$_2$Ph
24	PPh$_2$H
25	CO

to the basal ligands) must be considered in the light of the possible disorder of this atom in both molecules, although the illustrated site seems to be the one of substantially highest occupancy. The ligands in the basal sites are two *trans* carbonyls, a PPh$_3$ and a vinyl group (mean C–C 1.26 Å) which is bent away from the cyclopentadienyl ring. The tungsten–carbon bond lengths are similar (mean value 2.13 Å) as are the W–C–C angles (138°).

In some reactions related to those here, the complexes [Fe{CHMe(OMe)}(CO)(L)(η-C$_5$H$_5$)] [L = CO, PPh$_3$ or P(OPh)$_3$] lose MeOH in CHCl$_3$ containing HCl to form [Fe(σ-CH=CH$_2$)(CO)(L)(η-C$_5$H$_5$)][21] while [Fe{CMe$_2$(OMe)}(CO)$_2$(η-C$_5$H$_5$)] forms [Fe(σ-CMe=CH$_2$)(CO)$_2$(η-C$_5$H$_5$)] after heating for 8 h at 60 °C.[22] Metal vinyls are not particularly common. Other synthetic procedures for their preparation include the reaction of [MH(CO)$_3$(η-C$_5$H$_5$)] (M = Mo or W) with activated cyanoalkynes to give cyanovinyls, the photochemical decarbonylation of σ-propenoyls, proton abstraction from cationic carbenes in the presence of base, attack of nucleophiles on co-ordinated alkyne complexes or the protonation of vinylidenes such as [Rh(=C=CH$_2$)(PPr$^i_3$)(η-C$_5$H$_5$)] with HX, which affords the vinyl complexes [RhX(σ-CH=CH$_2$)(PPr$^i_3$)(η-C$_5$H$_5$)].[23]

Mechanism of Formation of the Tungsten Vinyl Complexes [W(σ-CH=CH$_2$)(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$R)] **34** (R = H) *and* **35** (R = Me).—A single isotopic probe was used to investigate the formation of the the tungsten vinyl complexes. The reaction of the carbene cation **31** with LiBDEt$_3$ affords the labelled alkyl complex [W{CDMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)] **33-D** in good yield. This reacts with traces of HCl in CH$_2$Cl$_2$ to form the labelled vinyl complex [W(σ-CD=CH$_2$)(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)] **35-D** (Scheme 4). There is no sign of any deuterium in any other position. This result is consistent with the mechanism in Scheme 4.

Conclusion

The isolation of the tungsten vinyl complexes **34** and **35** on treatment of the alkyl complexes **30** and **33** with acid provides strong circumstantial evidence supporting the formation of a molybdenum vinyl intermediate **26** in the reaction of the alkoxyalkyl complex **6** with acid whose ultimate product is the η^3-propenoyl complex **20**. The tendency of tungsten compounds to undergo insertion reactions far more slowly than their molybdenum analogues because of the strength of the tungsten–carbon bond is well known. In this case, the strength of the tungsten–vinyl bond seems sufficient to prevent the isomerization of the vinyls **34** or **35** to a tungsten analogue of **20**.

Experimental

Infrared spectra were recorded using a Perkin-Elmer 257 instrument, calibrated using the 1601.4 cm^{-1} absorption of polystyrene film, or on a Perkin-Elmer 1700 Fourier-Transform instrument linked to a Perkin-Elmer 4600 Data Station. Proton NMR spectra were recorded using JEOL PFT-100 (100 MHz), Perkin-Elmer R34 (220 MHz), Bruker AM-250 (250 MHz) or Bruker WH-400 (400 MHz) instruments. Carbon-13 NMR spectra were obtained using JEOL PFT-100 (25.2 MHz) and Bruker AM-250 (62.9 MHz) spectrometers. Mass spectra were recorded using either Kratos MS25 (electron impact mode), or Kratos MS80 (fast atom bombardment mode) instruments.

All reactions were performed under a nitrogen or argon atmosphere using deoxygenated solvents dried with an appropriate agent: tetrahydrofuran (thf) from sodium–benzophenone, CH$_2$Cl$_2$ from CaH$_2$ and light petroleum (b.p. 40–60 °C throughout) from LiAlH$_4$. All other materials were used as supplied.

The compounds [MoMe(CO)$_3$(η-C$_5$H$_5$)] **1**, [WMe(CO)$_3$(η-C$_5$H$_5$)], [WMe(CO)$_3$(η-C$_5$H$_4$Me)] and *trans*-[Mo(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **27**,[10] were prepared by literature procedures or minor variations thereof. The deuteriated compounds [Mo(CD$_3$)(CO)$_3$(η-C$_5$H$_5$)] **1-D** and *trans*-[Mo{=C(OMe)CD$_3$}(CO)(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17-D$_3$** were prepared analogously to their unlabelled analogues by use of the appropriate deuteriated materials.

Preparations.—*trans*-[Mo{σ-CHMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **6**. *Method* 1. The hydride LiBHEt$_3$ (1.0 cm^3, 1.0 mol dm^{-3} in thf, 1.0 mmol) was added to a stirred suspension of *trans*-[Mo{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17** (0.50 g, 0.80 mmol) in thf (40 cm^3). The carbene dissolved to give a yellow solution with an IR spectrum [ν_{CO}/cm^{-1}(thf) 1933m and 1851s] assigned to complex **6**. The solution was filtered rapidly through Al$_2$O$_3$ (2 × 2 cm) and the solvent removed. Rapid chromatography on Al$_2$O$_3$ (5 × 2 cm) yielded only **6** as a yellow powder (0.26 g, 61%) upon elution with light petroleum–Et$_2$O (1:1). Rapid recrystallization of this material from Et$_2$O–hexane afforded orange crystals (0.19 g, 44%). In a separate experiment, slow recrystallisation of a 0.22 g sample of **6** from CH$_2$Cl$_2$ and hexane (−30 °C) gave only the *cis*- and *trans*-hydride [MoH(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] (55 mg, 28%) as a first crop and some impure **6** (95 mg) as a second crop.

Method 2. Solid [Me$_3$O]BF$_4$ (0.35 g, 2.36 mmol) was added to a cold (−80 °C) solution of the anion [Mo(MeCHO)(CO)$_2$(η-C$_5$H$_5$)]$^-$ **2** [prepared according to the literature method from the alkyl **1** (0.50 g, 1.92 mmol) and LiBHEt$_3$ (2.3 cm^3, 1.0

mol dm^{-3}, 2.3 mmol) in thf (100 cm^3)]. The mixture was allowed to warm to ambient temperature (1 h) during which time it darkened and the IR spectrum indicated formation of the *cis* dicarbonyl complex **5** [ν_{CO}/cm^{-1}(thf) 1930s and 1833s]. The solution was recooled to −80 °C and PPh$_3$ (1.24 g, 4.72 mmol) was added. The reaction was allowed to come to room temperature (1 h) during which time the final product **6** formed. The solution was filtered through alumina (1 × 2 cm) and then chromatographed rapidly on alumina (5 × 2 cm). This gave PPh$_3$ on elution with light petroleum and *trans*-[Mo{CHMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **6** as a yellow solid (0.60 g, 58%) on elution with dichloromethane–light petroleum (1:1). A similar yield was obtained when MeSO$_3$F was used as the alkylating agent.

trans-[Mo{σ-CDMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **6-D**. Application of a similar method for the synthesis of **6** using *trans*-[Mo{=C(OMe)Me}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17** (0.86 g, 0.96 mmol) and LiBDEt$_3$ (1.2 cm^3, 1.2 mmol) in thf (40 cm^3) afforded **6-D** as a yellow solid (0.54 g, 73%). Found: *m*/*z* 510, [*M* − OMe]$^+$.

trans-[Mo{σ-CH(CD$_3$)(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **6-D$_3$**. Application of the above method for the synthesis of **6** using *trans*-[Mo{=C(OMe)CD$_3$}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17-D$_3$** (0.42 g, 0.88 mmol) and LiBHEt$_3$ (0.9 cm^3, 0.9 mmol) in thf (30 cm^3) afforded **6-D$_3$** as a yellow solid (0.18 g, 39%). Found: *m*/*z* 515, [*M* − CO]$^+$.

trans-[Mo{CHMe(PPh$_3$)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **7**. *Method* 1. Solid [Me$_3$O]BF$_4$ (0.6 g, 4.05 mmol) and PPh$_3$ (1.04 g, 4.0 mmol) were added to a solution of the anion [Mo(MeCHO)(CO)$_2$(η-C$_5$H$_5$)]$^-$ **2** [prepared according to the literature[4] from the alkyl **1** (0.52 g, 2.00 mmol) and LiBHEt$_3$ (2.3 cm^3, 2.3 mmol) in thf (100 cm^3)]. The reaction was stirred at ambient temperature (5 min) during which time the solution changed from orange-brown to red and the IR spectrum indicated the presence of **6** and traces of **1**. Solvent was removed under vacuum until a yellow precipitate formed. The solid was collected by filtration, washed with Et$_2$O (2 × 10 cm^3) and dried to give *trans*-[Mo{CHMe(PPh$_3$)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **7** as a yellow powder (0.41 g, 25%).

Method 2. A cold (−90 °C) solution of complex **6** (0.15 g, 0.28 mmol) and PPh$_3$ (0.3 g, 1.15 mmol) in thf (10 cm^3) was treated with HBF$_4$·OEt$_2$ (0.045 g, 0.28 mmol) and the solution warmed to room temperature (1 h), by which time a yellow powder had precipitated. Diethyl ether (30 cm^3) was added to ensure complete precipitation and the product was collected by filtration. Washing with diethyl ether (2 × 15 cm^3) and drying under vacuum afforded **7** as a lemon yellow powder (0.21 g, 97%).

trans-[Mo{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17**. This was prepared by modification of literature procedures. An excess of [Me$_3$O]BF$_4$ (1.60 g, 10.81 mmol) was added to a solution of *trans*-[Mo(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **27** (2.00 g, 3.83 mmol) in dry CH$_2$Cl$_2$ (20 cm^3). The solution was stirred (16 h) after which time the IR spectrum indicated the carbene **17** to be the only product. Prompt filtration through Kieselguhr (3 × 2 cm, twice) followed by dropwise addition of Et$_2$O to the resulting solution afforded *trans*-[Mo{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17** as a yellow powder (1.90 g, 79%).

trans-[Mo{=C(CD$_3$)(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17-D$_3$**. In a similar fashion to the synthesis of **17**, [Me$_3$O]BF$_4$ (1.20 g, 8.11 mmol) and the acyl **27-D$_3$** (0.70 g, 1.33 mmol) in dry CH$_2$Cl$_2$ (10 cm^3) gave *trans*-[Mo{=C(CD$_3$)(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **17-D$_3$** as a yellow powder (0.48 g, 66%). Found: *m*/*z* 542, [*M*$^+$].

[Mo(η^3-CH$_2$CHC=O)(CO)(PPh$_3$)(η-C$_5$H$_5$)] **20**. *Method* 1. The methoxyalkyl **6** (0.60 g, 1.11 mmol) was dissolved in CHCl$_3$ (50 cm^3) and passed through Al$_2$O$_3$ (4 × 2 cm) several times. The IR spectrum of the yellow solution [ν_{CO}/cm^{-1}(CHCl$_3$) 1971w, 1943w, 1885s, 1865s and 1683m] indicated the formation of the propenoyl complex **20**. The solvent was removed and the residue chromatographed on Al$_2$O$_3$ (7 × 2 cm) at −50 °C. Elution with CHCl$_3$ afforded the propenoyl **20** which was isolated from CH$_2$Cl$_2$–hexane as a yellow powder (0.33 g, 58%).

Method 2. The methoxyalkyl **6** (0.20 g, 0.37 mmol) was dissolved in distilled CHCl$_3$ (30 cm^3) and treated with three drops of a HCl(g)-saturated CHCl$_3$ solution. The IR and ^{1}H NMR spectrum of the reaction mixture indicated immediate formation of the propenoyl **20**. Chromatography on alumina (4 × 2 cm) at −50 °C gave **20** on elution with chloroform. Crystallization from dichloromethane–hexane afforded **20** as a yellow powder (0.063 g, 34%).

[Mo(η^3-CH$_2$CDC=O)(CO)(PPh$_3$)(η-C$_5$H$_5$)] **20-D**. By application of Method 1 above for the synthesis of complex **20** to [Mo{CDMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **6-D** (0.54 g, 1.00 mmol) the complex [Mo{η^3-CH$_2$CDC=O}(CO)(PPh$_3$)(η-C$_5$H$_5$)] **20-D** was obtained as a yellow powder (0.3 g, 60%). Found: *m*/*z* 510, [*M* + 1]$^+$.

[Mo(η^3-CD$_2$CHC=O)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **20-D$_2$**. By application of Method 2 above for the synthesis of complex **20** to [Mo{CH(CD$_3$)(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **6-D$_3$** (0.081 g, 0.15 mmol), the complex [Mo{η^3-CD$_2$CHCO}(CO)(PPh$_3$)(η-C$_5$H$_5$)] **20-D$_2$** was obtained as a yellow powder (0.074 g, 97%). Found: *m*/*z* 511, [*M* + 1]$^+$. In an attempted alternative preparation, the alkyl **6-D$_3$** (0.18 g, 0.27 mmol) was treated with alumina as in the above synthesis of **20**, but no reaction was observed. Prolonged stirring (10 h) in CHCl$_3$ (2 cm^3) in the presence of Al$_2$O$_3$ (0.4 g) was necessary to consume the starting material but only PPh$_3$, [MoCl(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] and [Mo(COCD$_3$)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **22-D$_3$** could be detected (IR and ^{1}H NMR spectroscopy) in the largely decomposed reaction mixture.

trans-[Mo(COCD$_3$)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **27-D$_3$**. This compound was prepared from [Mo(CD$_3$)(CO)$_3$(η-C$_5$H$_5$)] **1-D$_3$** in a method based on the literature method for *trans*-[Mo(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)].[10] Solid PPh$_3$ (0.60 g, 2.29 mmol) was added to [Mo(CD$_3$)(CO)$_3$(η-C$_5$H$_5$)] **1-D$_3$** (0.50 g, 1.90 mmol) in MeCN (30 cm^3) and the reaction mixture stirred (10 h). The solvent was evaporated at reduced pressure and the residue chromatographed on Al$_2$O$_3$ (11 × 2 cm). Elution with light petroleum afforded PPh$_3$. Elution with CH$_2$Cl$_2$ provided *trans*-[Mo(COCD$_3$)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **27-D$_3$** which was isolated from CH$_2$Cl$_2$–light petroleum as a yellow powder (0.84 g, 85%). Found: *m*/*z* 528, [*M* + 1]$^+$.

trans-[W{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **29**. A similar method to the synthesis of **17** above was applied but using a mixture of [Me$_3$O]BF$_4$ (1.97 g, 13.31 mmol) and *trans*-[W(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **28**[10] (1.22 g, 2.00 mmol) in CH$_2$Cl$_2$ (25 cm^3). Stirring (60 h) gave *trans*-[W{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **29** as a yellow powder (0.95 g, 76%).

trans-[W{σ-CHMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **30**. Application of a similar method to that of the synthesis of **6** using *trans*-[W{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)]BF$_4$ **29** (0.95 g, 1.52 mmol) and LiBHEt$_3$ (1.7 cm^3, 1.7 mmol) in thf (5 cm^3) afforded **30** as a yellow solid (0.73 g, 77%). This compound was never obtained completely pure as samples always contained small amounts of the vinyl **34**.

trans-[W(σ-COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)] **31**. The compound was prepared from [WMe(CO)$_3$(η-C$_5$H$_4$Me)] by a method based on a literature synthesis of *trans*-[W(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_5$)] **28**. A mixture of PPh$_3$ (4.00 g, 15.27 mmol) and [WMe(CO)$_3$(η-C$_5$H$_4$Me)] (2.00 g, 5.52 mmol) in MeCN (40 cm^3) was heated at reflux (120 h). The solvent was removed under reduced pressure and the residue chromatographed on Al$_2$O$_3$ (15 × 2 cm). Elution with light petroleum–CH$_2$Cl$_2$ (2:1) gave PPh$_3$, unreacted [WMe(CO)$_3$(η-C$_5$H$_4$Me)] and some *trans*-[WMe(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)]. Development with CH$_2$Cl$_2$ provided *trans*-[W(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)] **31** which was crystallized from CH$_2$Cl$_2$–light petroleum as yellow prisms (1.57 g, 46%).

trans-[W{=CMe(OMe)}(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)]BF$_4$ **32**. In a similar fashion to the synthesis of **17**, [Me$_3$O]BF$_4$ (2.64 g, 17.84 mmol) and *trans*-[W(COMe)(CO)$_2$(PPh$_3$)(η-C$_5$H$_4$Me)]

31 (1.40 g, 2.24 mmol) in dry CH_2Cl_2 (25 cm^3) gave *trans*-$[W\{=CMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]BF_4$ **32** as a yellow powder (1.30 g, 80%). This material, assayed pure by spectroscopic techniques, gave unacceptable elemental analyses because of its rapid hydrolysis in air.

trans-$[W\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **33**. Application of a similar method to that of the synthesis of **30** to a mixture of $LiBHEt_3$ (0.5 cm^3, 1.0 mol dm^{-3} in thf, 0.5 mmol) and *trans*-$[W\{=CMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]BF_4$ **32** (0.35 g, 0.48 mmol) in thf (25 cm^3) afforded **33** as a yellow solid (0.25 g, 81%).

trans-$[W\{CDMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **33-D**. Using a similar method to that of the synthesis of **30**, the reaction of $LiBDEt_3$ (0.5 cm^3, 1.0 mol dm^{-3} in thf, 0.5 mmol) with *trans*-$[W\{=CMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]BF_4$ **32** (0.35 g, 0.48 mmol) in thf (25 cm^3) gave **33-D** as a yellow solid (0.30 g, 97%). Found: *m*/*z* 610, $[M - OMe]^+$.

$[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **34**. By application of the above method for the synthesis of **20** but utilizing $[W\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **30** (0.6 g, 0.95 mmol), the vinyl complex $[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **34** was obtained as a pale yellow powder (0.39 g, 69%).

trans-$[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **35**. Use of a similar synthetic route as for **34**, but starting with the alkyl *trans*-$[W\{CHMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **33** (0.16 g, 0.24 mmol) afforded the vinyl **35** as orange crystals (0.12 g, 79%).

trans-$[W(\sigma\text{-}CD=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **35-D**. Using a similar method to that of the synthesis of **34**, but starting with the alkyl *trans*-$[W\{CDMe(OMe)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]$ **33-D** (0.14 g, 0.22 mmol) gave the vinyl **35-D** as orange crystals (0.10 g, 77%). Found: *m*/*z* 609, $[M]^+$.

Attempted Vinyl to Carbonyl Migration of trans-$[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]$ **34**.—A solution of the vinyl **34** (0.25 g, 0.42 mmol) in MeCN (10 cm^3) was heated at reflux (100 h). The IR spectrum indicated unchanged starting material and a 44% recovery was made. In a separate experiment, photolysis of a solution of the vinyl **34** (0.10 g, 0.17 mmol) in thf (15 cm^3) resulted in no reaction other than decomposition over 6 h.

Crystal-structure Determinations.—Crystal data for $[Mo\{CHMe(PPh_3)\}(CO)_2(PPh_3)(\eta\text{-}C_5H_5)]BF_4$ **7**. $C_{45}H_{39}BF_4MoO_2P_2$, *M* = 856.45 [crystallises from dichloromethane–hexane as parallelepipeds with well formed (100) and (001) faces; dimensions 0.123 × 0.262 × 0.531 mm], monoclinic, *a* = 11.378(34), *b* = 18.903(35), *c* = 20.17(8) Å, β = 115.28(31)°, *U* = 3922(19) Å^3 (from 61 scans with $6.5 < 2\theta < 24°$), D_m = 1.42, *Z* = 4, D_c = 1.451 g cm^{-3}, space group $P2_1/c$ (C^5_{2h}, no. 14), Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 4.61 cm^{-1}, *F*(000) = 1751.65. Data were collected on a Stoe Stadi-2 diffractometer in the range $6.5 < 2\theta < 50°$ by the ω-scan method giving 3918 independent reflections with $I/\sigma(I) > 3.0$. Absorption corrections were applied. The structure was solved by Patterson and Fourier methods; refinement was by blocked-cascade least squares. Hydrogen atoms were detected and placed in predicted positions with thermal parameters 1.2 times greater than the attached atom. Final *R* 0.0510. Thermal anisotropy for all but hydrogen atoms and the lowest population BF_4 component. Anomalous scattering for Mo and P, a unit weighting scheme was used. Scattering factors were taken from the SHELXTL program package.[24] The BF_4^- ion was disordered into three components centred on approximately the same position with occupancies of 0.45, 0.39 and 0.16; each component was given a constrained approximate tetrahedral geometry, but with refinement of an approximately common B–F length permitted.

Crystal data for $[Mo(\eta^3\text{-}CH_2CHC=O)(CO)(PPh_3)(\eta\text{-}C_5H_5)]$ **20**. $C_{27}H_{23}MoO_2P$, *M* = 506.35 (crystallizes from dichloromethane–hexane as red prisms, dimensions 0.28 × 0.15 × 0.08 mm), monoclinic, *a* = 17.231(50), *b* = 8.189(14), *c* = 16.727(36) Å, β = 106.79(22)°, *U* = 2259(9) Å^3 (from 17 scans with $5.0 < 2\theta < 20°$), *Z* = 4, D_c = 1.489 g cm^{-3}, space group $P2_1/c$ (C^5_{2h}, no. 14), Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 6.56 cm^{-1}, *F*(000) = 1031.73.

Weak three-dimensional X-ray diffraction data were collected from a small crystal in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The 1654 independent reflections for which $|F|/\sigma(|F|) > 4.0$ were corrected for Lorentz and polarisation effects and for absorption. The structure was solved by Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. Geometrical constraints were applied to the three phenyl rings, to the cyclopentadienyl ring and to the CH_2 fragment based on C(25). Hydrogen atoms were placed in calculated positions with U_{iso} 1.2 greater than the supporting atom and were refined in riding mode. Refinement converged at *R* 0.100 with allowance for anisotropic thermal motion of molybdenum, phosphorus and oxygen only, and for the anomalous scattering of molybdenum and phosphorus. Computer programs used were those of the SHELXTL package[24] as implemented on the NOVA-3 computer: scattering factors were taken from the program package; unit weights were used throughout the refinement.

Crystal data for $[W(\sigma\text{-}CH=CH_2)(CO)_2(PPh_3)(\eta\text{-}C_5H_4Me)]\cdot 0.25CH_2Cl_2$ **35**. $C_{28.25}H_{25.5}Cl_{0.5}O_2PW$, *M* = 629.51 (crystallizes from dichloromethane–hexane as yellow prisms; crystal dimensions 0.35 × 0.25 × 0.18 mm), monoclinic, *a* = 36.952(40), *b* = 10.971(13), *c* = 25.148(23) Å, β = 103.60(8)°, *U* = 9909(18) Å^3 (from 20 scans with $6.0 < 2\theta < 22°$), *Z* = 16, D_c = 1.688 g cm^{-3}, space group $C2/c$ (C^6_{2h}, no. 15), Mo-Kα radiation (λ = 0.710 69 Å), μ(Mo-Kα) = 49.03 cm^{-1}, *F*(000) = 4934.82.

Three-dimensional, room-temperature X-ray data were collected in the range $3.5 < 2\theta < 50°$ on a Nicolet R3 diffractometer by the ω-scan method. The 2542 independent reflections for which $|F|/\sigma(|F|) > 5.0$ were corrected for Lorentz and polarisation effects, and for absorption by analysis of azimuthal scans. The structure was solved by standard Patterson and Fourier techniques and refined by blocked-cascade least-squares methods. The geometries of the five- and six-membered rings were constrained to be planar (D_{5h} and D_{6h} respectively). The methyl substituents on the cyclopentadienyl rings seem to be disordered amongst several sites although, in each case, one site was strongly preferred and this was included with full occupancy. Hydrogen atoms were placed in predicted positions with isotropic thermal parameters related to those of the supporting atoms. A molecule of dichloromethane was found to be disordered near to the crystallographic C_2 axis and it was refined with constraints on its geometry. The refinement converged at a final *R* of 0.0750 (*R'* = 0.0647) with allowance for the thermal anisotropy of tungsten, phosphorus and oxygen only. A weighting scheme with $w^{-1} = [\sigma^2(F) + g(F)^2]$ with *g* = 0.000 30 was used in the later stages of refinement. Complex scattering factors were taken from ref. 25 and from the program package SHELXTL,[24] as implemented on the Data General NOVA 3 computer, which was used throughout the refinement.

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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