Chemistry of Polynuclear Metal Complexes with Bridging Carbene or Carbyne Ligands. Part 69.[1] Reactions of [MoW(≡CC$_6$H$_4$Me-4)(CO)$_7$(η-C$_5$H$_5$)] with But-2-yne; Crystal Structures of [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$-(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] and [MoW{μ-C(C$_6$H$_4$Me-4)C(=CH$_2$)C(H)MeC(O)}(CO)$_6$-(η-C$_5$H$_5$)]·0.5CH$_2$Cl$_2$ *

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Treatment of [MoW(≡CC$_6$H$_4$Me-4)(CO)$_7$(η-C$_5$H$_5$)] with but-2-yne in refluxing thf (tetrahydrofuran) affords the compound [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)]. In contrast, at room temperature in thf these reagents yield the complex [MoW{μ-C(C$_6$H$_4$Me-4)C(=CH$_2$)C(H)MeC(O)}(CO)$_6$(η-C$_5$H$_5$)]. The structures of both products have been established by X-ray diffraction. That of [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] has a Mo-W bond [2.971(2) Å] spanned by the μ-C(C$_6$H$_4$Me-4)C(Me)C(Me) group. The molybdenum atom carries a cyclopentadienyl and two carbonyl groups, while the tungsten atom is ligated by a carbonyl and two MeC≡CMe groups. In the other dimetal compound the Mo-W bond [3.131(1) Å] is bridged by a novel C$_4$ fragment in such a manner that there is a MoC(C$_6$H$_4$Me-4)C(=CH$_2$)C(H)MeC(O) ring system, the C(C$_6$H$_4$Me-4)C=CH$_2$ moiety of which is η^3-co-ordinated to the tungsten. The latter carries four essentially orthogonal carbonyl groups, and the molybdenum centre is ligated by two carbonyl groups and the C$_5$H$_5$ ring. The ^{1}H and ^{13}C-{^{1}H} n.m.r. spectra of the new compounds are reported and discussed, as are their possible modes of formation. Reaction between [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] and PMe$_3$ affords a simple substitution product containing a W(PMe$_3$)(η-MeC$_2$Me)$_2$ fragment.

The family of dimetal compounds [MW(≡CC$_6$H$_4$Me-4)-(CO)$_4$L$_n$] [ML$_n$ = Re(CO)$_5$ (1a), Mo(CO)$_3$(η-C$_5$H$_5$) (1b), or Co(CO)$_4$ (1c)] are potentially useful reagents for further syntheses. Thus the W≡C bonds present in these species combine with low-valent metal–ligand fragments to afford a variety of tri-, tetra-, or penta-nuclear metal compounds.[2] Moreover, the alkylidyne-carbon centre in (1a) is attacked by the nucleophiles PMe$_3$ or H$^-$ to afford the dimetal ligand-bridged compounds [ReW{μ-C(C$_6$H$_4$Me-4)(PMe$_3$)}(μ-CO)-(CO)$_8$][3] and [N(PPh$_3$)$_2$][ReW{μ-CH(C$_6$H$_4$Me-4)}(CO)$_9$],[4] respectively. In view of these results we have investigated reactions of the compounds (1) with alkynes. From the nature of the products obtained from (1a) and PMe$_3$ or H$^-$, it was anticipated that alkynes would attack at the alkylidyne-carbon centres to afford complexes containing a bridging C$_3$ fragment. In practice (1a) was inert to PhC≡CPh or MeC≡CMe even at elevated temperatures. However, but-2-yne reacted readily with (1b) and (1c). The results obtained with the molybdenum–tungsten compound (1b) are described in this paper. The products obtained from reactions between (1c) and alkynes proved to be of several different structural types, and these will be reported in a subsequent paper.

Results and Discussion

Compound (1b) reacts readily with but-2-yne in thf (tetrahydrofuran), but the nature of the product obtained

ML$_n$
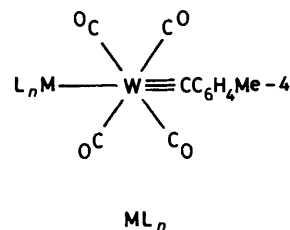
(1a)   Re(CO)$_5$

(1b)   Mo(CO)$_3$(η-C$_5$H$_5$)

(1c)   Co(CO)$_4$

depends critically on whether the process is carried out under reflux conditions or whether the reactants are stirred together at ambient temperature. When the two reagents are heated together the product is the yellow crystalline compound [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] (2a), formed in *ca.* 70% yield. If, however, (1b) in thf is treated with but-2-yne at room temperature, the product is the red crystalline compound [MoW{μ-C(C$_6$H$_4$Me-4)C(=CH$_2$)-C(H)MeC(O)}(CO)$_6$(η-C$_5$H$_5$)] (3), also obtained in *ca.* 70% yield. Both (2a) and (3) are readily purified by column chromatography, the former on alumina and the latter on Florisil, and satisfactory microanalytical data were obtained.

The n.m.r. data (^{1}H and ^{13}C-{^{1}H}) for (2a) and (3) (Table 1) are in accord with the formulations of these species, but discussion of the spectra is deferred until the results of X-ray diffraction studies are described. The structure of (2a) is shown in Figure 1, and selected bond distances and angles are listed in Table 2. Data for (3) are given in Table 3, and the structure is shown in Figure 2.

Table 1. Hydrogen-1 and carbon-13 n.m.r. data[a] for the molybdenum–tungsten complexes

Complex	^{1}H(δ)[b]	^{13}C(δ)[c]
(2a)	[d] 1.64 (s, 3 H, Me), 2.31 (s, 3 H, Me), 2.35 (s, 3 H, Me), 2.63 (s, 3 H, Me), 2.68 (s, 3 H, Me), 2.90 (s, 3 H, Me), 3.11 (s, 3 H, Me), 5.05 (s, 5 H, C_5H_5), 6.53, 7.04 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8]	[d] 246.7, 241.9 (MoCO), 217.9 (WCO), 173.5 (CMe), 162.8 (CMe), 154.3 (CMe), 152.7 (CMe), 148.7 [$C^1(C_6H_4)$], 145.7 (μ-CMe), 133.0, 128.4, 128.0 (C_6H_4), 100.0, 99.8 (μ-CC_6H_4Me-4 and μ-CMe), 90.6 (C_5H_5), 26.9 (Me), 21.1 (Me-4), 17.2, 16.7, 15.4, 15.1, 11.9 (Me)
(2b)[e]	[f] 1.27 [d, 9 H, MeP, J(PH) 8], 1.46 (s, 3 H, Me), 2.10 (s, 3 H, Me), 2.35 (s, 3 H, Me), 2.38 (s, 3 H, Me), 2.68 (s, 3 H, Me), 2.99 (s, 3 H, Me), 3.04 (s, 3 H, Me), 4.92 (s, 5 H, C_5H_5), 6.71, 6.98 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8]	250.4, 245.6 (MoCO), 190.3 (CMe), 186.3 [d, CMe, J(PC) 9], 161.1 [d, CMe, J(PC) 21], 157.0 [d, CMe, J(PC) 25], 148.1 [$C^1(C_6H_4)$], 145.2 (μ-CMe), 133.0, 130.5, 127.9 (C_6H_4), 106.2 [d, μ-CC_6H_4Me-4, J(PC) 6], 101.6 (μ-CMe), 91.4 (C_5H_5), 27.7 (Me), 20.9 (Me-4), 18.3 [d, MeP, J(PC) 24], 16.8, 16.5, 16.1, 15.7, 10.1 (Me)
(3)	[d] 1.03 [d, 3 H, C(H)Me, J(HH) 7], 2.33 (s, 3 H, Me-4), 2.85 (s, 1 H, CH$_2$), 3.70 (s, 1 H, CH$_2$), 4.38 [q, 1 H, C(H)Me, J(HH), 7], 4.99 (s, 5 H, C_5H_5), 6.81 [d of d, 1 H, C_6H_4, J(HH) 8, 2], 6.97 [d of d, 1 H, C_6H_4, J(HH) 8, 2], 7.19 [d of d, 1 H, C_6H_4, J(HH) 8, 2], 7.74 [d of d, 1 H, C_6H_4, J(HH) 8, 2]	259.8 (C=O), 226.7, 224.2 (MoCO), 209.3, 205.7, 201.6, 201.2 (WCO), 191.7 (μ-CC_6H_4Me-4), 152.5 [$C^1(C_6H_4)$], 137.8, 129.2, 127.9 (C_6H_4), 119.5 (C=CH$_2$), 92.9 (C_5H_5), 70.4 [C(H)Me], 48.8 (CH$_2$), 21.2 (Me-4), 11.6 (Me)
(6)	[g] 0.93 [d, 3 H, C(H)Me, J(HH) 7], 1.38 [t of t, 12 H, MeCH$_2$N, J(HH) 7, J(NH) 2], 2.18 (s, 3 H, Me-4), 2.85 [q, 1 H, C(H)Me, J(HH) 7], 3.48 [q, 8 H, MeCH_2N, J(HH) 7], 3.80 (s, 3 H, CMe), 4.71 (s, 5 H, C_5H_5), 6.87, 7.38 [(AB)$_2$, 4 H, C_6H_4, J(AB) 8]	[g] 251.3 (C=O)*, 247.3, 247.2 (MoCO)*, ca. 209 (WCO)*, 196.0 (μ-CC_6H_4Me-4), 146.2 [$C^1(C_6H_4)$], 130.2, 128.3, 125.2 (C_6H_4, μ-CMe*), 92.3 (C_5H_5), 64.7 [C(H)Me], 53.0 (NCH_2Me), 21.1 (Me-4), 20.7, 18.4 (Me), 7.7 (N$CH_2$$Me$)

[a] Chemical shifts (δ) in p.p.m., coupling constants in Hz. Measurements at ambient temperatures unless otherwise stated. [b] Measured in CD_2Cl_2, unless otherwise stated. [c] Hydrogen-1 decoupled, chemical shifts are positive to high frequency of SiMe$_4$. Measurements in CD_2Cl_2–CH_2Cl_2 unless otherwise stated. [d] Measured at -50 °C. [e] Phosphorus-31, δ -22.5 p.p.m. [J(WP) 132 Hz], to high frequency of 85% H_3PO_4 (external). [f] In CDCl$_3$. [g] In $(CD_3)_2$CO, signals marked with an asterisk are partially obscured by solvent or CC_6H_4Me-4 peaks and assignments are tentative.

(2a) CO

(2b) PMe$_3$

(3)
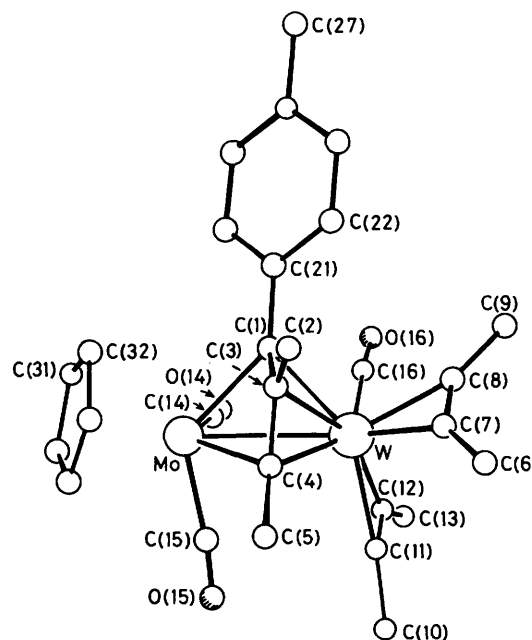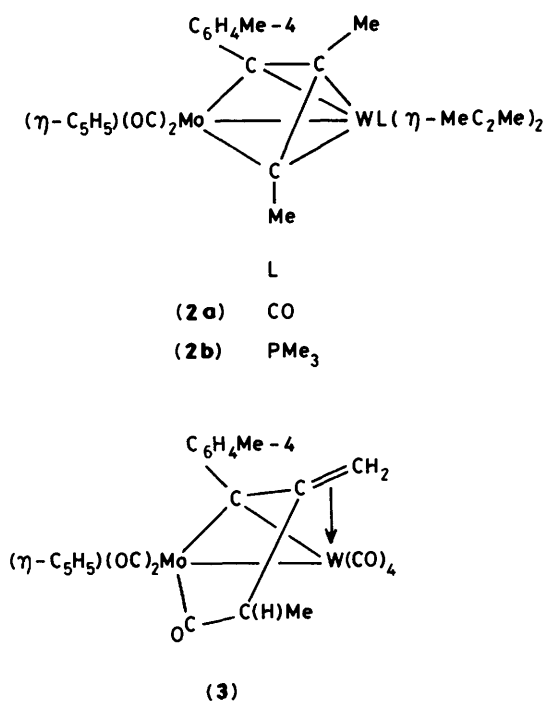
Figure 1. The molecular structure of [MoW{μ-C(C$_6$H$_4$Me-4)C(Me)-C(Me)}(CO)$_3$(η-MeC$_2$Me)$_2$(η-C$_5$H$_5$)] (2a), showing the crystallographic numbering scheme

In (2a) a Mo–W bond [2.971(2) Å] is transversely spanned by a C(C$_6$H$_4$Me-4)C(Me)C(Me) fragment. The molybdenum atom carries the η-C$_5$H$_5$ ring and two terminally bonded CO groups. The tungsten atom is co-ordinated by one carbonyl group and two but-2-yne molecules. Features of the structure of (2a) have been observed previously in other complexes. Thus the μ-C(C$_6$H$_4$Me-4)C(Me)C(Me) fragment occurs in the compounds [MW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_2$L$_n$(η-C$_5$H$_5$)] [ML$_n$ = Fe(CO)$_3$ (4a), Co(η-C$_5$Me$_5$) (4b), or Rh(η^5-C$_9$H$_7$)

(4c)][5] and [FeW{μ-C(C$_6$H$_4$Me-4)C(Me)C(Me)}(CO)$_5$(η-C$_5$Me$_5$)] (5).[6] In (2a) the C(1)–C(3) [1.44(1) Å] and C(3)–C(4) [1.40(1) Å] distances are very similar to those found for corresponding distances in (4a) [1.440(8) and 1.435(8) Å, respectively].[5]

The ligating carbon atoms of the two but-2-yne molecules in (2a) are 2.09 Å (mean) from the tungsten. This value may be compared with the tungsten to alkyne-carbon atom distances in

Table 2. Selected internuclear distances (Å) and angles (°) for [MoW{μ-C(C₆H₄Me-4)C(Me)C(Me)}(CO)₃(η-MeC₂Me)₂(η-C₅H₅)] (**2a**) with estimated standard deviations in parentheses

Mo–W	2.971(2)	W–C(1)	2.211(8)	W–C(3)	2.478(8)	W–C(4)	2.214(8)
W–C(7)	2.071(7)	W–C(8)	2.103(7)	W–C(11)	2.090(8)	W–C(12)	2.077(8)
W–C(16)	2.029(8)	Mo–C(1)	2.243(8)	Mo···C(3)	2.64	Mo–C(4)	2.236(8)
Mo–C(14)	1.976(9)	Mo–C(15)	1.990(9)	C(1)–C(3)	1.44(1)	C(1)–C(21)	1.49(1)
C(2)–C(3)	1.51(1)	C(3)–C(4)	1.40(1)	C(4)–C(5)	1.52(1)	C(6)–C(7)	1.51(1)
C(7)–C(8)	1.29(1)	C(8)–C(9)	1.50(1)	C(10)–C(11)	1.50(1)	C(11)–C(12)	1.29(1)
C(12)–C(13)	1.50(1)	C(14)–O(14)	1.17(1)	C(15)–O(15)	1.13(1)	C(16)–O(16)	1.13(1)
C(1)–W–C(3)	35.1(3)	C(1)–W–C(4)	60.9(3)	C(3)–W–C(4)	34.1(3)	Mo–W–C(7)	139.5(2)
Mo–W–C(8)	149.7(2)	C(7)–W–C(8)	36.0(3)	Mo–W–C(11)	101.6(2)	C(7)–W–C(11)	91.7(3)
C(8)–W–C(11)	108.1(3)	Mo–W–C(12)	107.5(2)	C(7)–W–C(12)	105.6(3)	C(8)–W–C(12)	100.0(3)
C(11)–W–C(12)	36.0(3)	Mo–W–C(16)	98.1(2)	C(7)–W–C(16)	110.7(3)	C(8)–W–C(16)	74.6(3)
C(11)–W–C(16)	115.0(3)	C(12)–W–C(16)	79.1(3)	C(1)–Mo–C(4)	60.1(3)	W–Mo–C(14)	77.5(3)
W–Mo–C(15)	80.4(3)	C(14)–Mo–C(15)	79.6(4)	W–C(1)–Mo	83.7(3)	W–C(1)–C(21)	126.6(5)
Mo–C(1)–C(21)	133.3(5)	C(3)–C(1)–C(21)	125.4(7)	W–C(3)–C(2)	138.8(6)	C(1)–C(3)–C(2)	128.8(8)
C(1)–C(3)–C(4)	104.3(6)	C(2)–C(3)–C(4)	126.9(8)	W–C(4)–Mo	83.8(3)	W–C(4)–C(5)	133.7(6)
Mo–C(4)–C(5)	127.0(6)	C(3)–C(4)–C(5)	124.1(7)	C(6)–C(7)–C(8)	144.1(8)	C(7)–C(8)–C(9)	143.2(7)
C(10)–C(11)–C(12)	141.5(8)	C(11)–C(12)–C(13)	142.0(9)	Mo–C(14)–O(14)	173.1(8)	Mo–C(15)–O(15)	175.4(8)
W–C(16)–O(16)	177.0(8)						
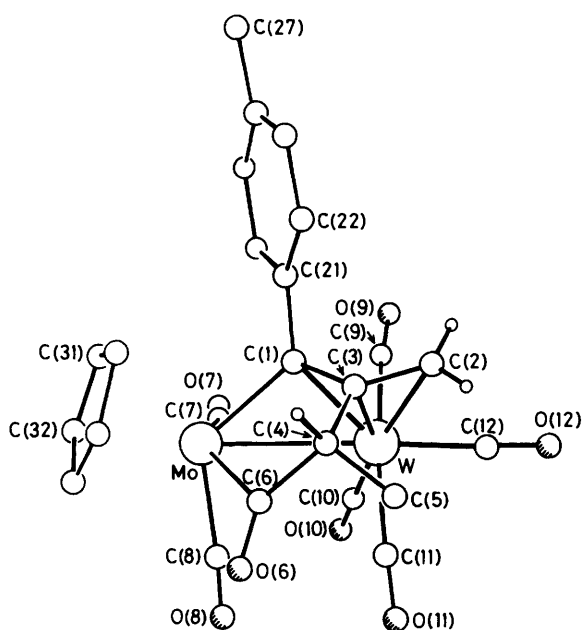
Figure 2. The molecular structure of [MoW{μ-C(C₆H₄Me-4)C(= CH₂)C(H)MeC(O)}(CO)₆(η-C₅H₅)]·0.5CH₂Cl₂ (**3**), showing the crystallographic numbering scheme
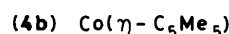

MLₙ

(**4a**)   Fe(CO)₃

(**4b**)   Co(η-C₅Me₅)

(**4c**)   Rh(η⁵-C₉H₇)

(**5**)
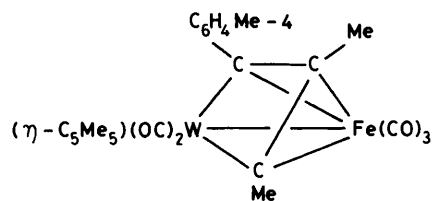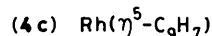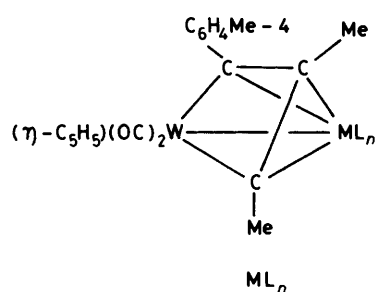
[W₂(μ-CO)₂(CO)(η-PhC₂Ph){η-C₅Ph₄(C₆H₄Me-4)}(η-C₅H₅)] (mean 2.14 Å)[7] and in [PtW{μ-CH(C₆H₄Me-4)}(μ-CO)(PMe₃)₂(η-MeC₂Me)(η-C₅H₅)][BF₄] (mean 2.033 Å).[8] The Mo–W distance [2.971(2) Å] in (**2a**) is similar to that found in [MoW₂(μ-CC₆H₄Me-4)₂(μ-CO)₂(CO)₄(η-C₅H₅)₂] [2.938(1) Å][9] and would appear to correspond to that of a single bond. In contrast, in the unsaturated dimetal complex [MoW(μ-CC₆H₄Me-4)(CO)₃(η⁵-C₉H₇)(η⁵-C₂B₉H₉Me₂)] the Mo–W separation [2.657(2) Å] is appreciably shorter.[10]

In compound (**3**) (Figure 2) it is immediately apparent that the Mo–W bond [3.131(1) Å] is spanned by five carbon atoms, four of which form a five-membered ring with the molybdenum atom, while the C(C₆H₄Me-4)C=CH₂ moiety is η³-co-ordinated to the tungsten. The organic fragment C(C₆H₄Me-4)C(= CH₂)CHMeC(O) is derived from the p-tolylmethylidyne

group in the precursor (**1b**), a molecule of but-2-yne which has undergone rearrangement, and a molecule of carbon monoxide. In addition to being ligated by the C=CH₂ group [W–C(2) 2.466(7), W–C(3) 2.320(6) Å], the tungsten centre also carries four essentially orthogonally disposed carbonyl groups. The molybdenum atom is bonded by two carbonyl groups and the cyclopentadienyl group.

The spectroscopic data for (**2a**) and (**3**) are in accord with the structures found in the solid state by X-ray diffraction. The i.r. spectrum of (**2a**) shows three terminal CO bands at 2 045, 1 946, and 1 869 cm⁻¹, while that of (**3**) has five such bands at 2 051, 1 994, 1 968, 1 956, and 1 944 cm⁻¹. In addition, in the spectrum of (**3**) there is a band at 1 651 cm⁻¹ attributable to the acyl group C(6)O(6) (Figure 2).

Examination of the ¹H and ¹³C-{¹H} n.m.r. spectra of (**2a**) at

Table 3. Selected internuclear distances (Å) and angles (°) for [MoW{μ-C(C₆H₄Me-4)C(=CH₂)C(H)MeC(O)}(CO)₆(η-C₅H₅)]·0.5CH₂Cl₂ (3) with estimated standard deviations in parentheses

Mo–W	3.131(1)	W–C(1)	2.290(6)	W–C(2)	2.466(7)	W–C(3)	2.320(6)
W···C(4)	3.28	W–C(9)	2.019(7)	W–C(10)	2.002(7)	W–C(11)	2.071(7)
W–C(12)	1.972(7)	Mo–C(1)	2.167(6)	Mo···C(4)	3.24	Mo–C(6)	2.264(6)
Mo–C(7)	2.020(7)	Mo–C(8)	2.041(7)	C(1)–C(3)	1.461(9)	C(1)–C(21)	1.493(9)
C(2)–C(3)	1.377(9)	C(3)–C(4)	1.508(9)	C(4)–C(5)	1.538(10)	C(4)–C(6)	1.561(9)
C(6)–O(6)	1.200(8)	C(7)–O(7)	1.150(8)	C(8)–O(8)	1.121(9)	C(9)–O(9)	1.133(9)
C(10)–O(10)	1.137(8)	C(11)–O(11)	1.120(9)	C(12)–O(12)	1.157(9)		
C(1)–W–C(2)	61.8(2)	C(1)–W–C(3)	36.9(2)	C(2)–W–C(3)	33.3(2)	Mo–W–C(9)	102.6(2)
Mo–W–C(10)	89.4(2)	C(9)–W–C(10)	85.1(3)	Mo–W–C(11)	87.7(2)	C(9)–W–C(11)	165.0(3)
C(10)–W–C(11)	84.1(3)	Mo–W–C(12)	174.5(2)	C(9)–W–C(12)	82.1(3)	C(10)–W–C(12)	93.8(3)
C(11)–W–C(12)	88.3(3)	W–Mo–C(6)	74.6(2)	C(1)–Mo–C(6)	76.7(2)	W–Mo–C(7)	72.0(2)
C(6)–Mo–C(7)	144.9(3)	W–Mo–C(8)	80.0(2)	C(6)–Mo–C(8)	78.6(3)	C(7)–Mo–C(8)	85.2(3)
W–C(1)–Mo	89.2(2)	W–C(1)–C(3)	72.6(3)	Mo–C(1)–C(3)	115.6(4)	W–C(1)–C(21)	126.0(4)
Mo–C(1)–C(21)	123.1(4)	C(3)–C(1)–C(21)	116.9(5)	W–C(2)–C(3)	67.5(4)	W–C(3)–C(1)	70.4(3)
W–C(3)–C(2)	79.2(4)	C(1)–C(3)–C(2)	119.1(6)	W–C(3)–C(4)	116.4(4)	C(1)–C(3)–C(4)	116.5(5)
C(2)–C(3)–C(4)	124.2(6)	C(3)–C(4)–C(5)	118.2(6)	C(3)–C(4)–C(6)	107.0(5)	C(5)–C(4)–C(6)	113.4(6)
Mo–C(6)–C(4)	114.5(4)	Mo–C(6)–O(6)	124.4(5)	C(4)–C(6)–O(6)	121.0(6)	Mo–C(7)–O(7)	172.6(6)
Mo–C(8)–O(8)	176.4(6)	W–C(9)–O(9)	172.0(6)	W–C(10)–O(10)	179.6(6)	W–C(11)–O(11)	172.1(6)
W–C(12)–O(12)	176.9(7)						

room temperature revealed the existence of dynamic behaviour, but limiting spectra were obtained at −50 °C (Table 1). The ¹H spectrum showed the expected seven Me group resonances. The ¹³C-{¹H} spectrum was more informative with resonances at δ 246.7 and 241.9 p.p.m. due to the CO ligands attached to the molybdenum, and a peak at 217.9 p.p.m. for the tungsten co-ordinated carbonyl group. There are seven Me group signals as expected, but of more interest are the resonances due to the metal-ligating carbon atoms of the μ-C₃ and η-MeC₂Me fragments. The signals at δ 99.8 and 100.0 p.p.m. may be attributed to the μ-C(C₆H₄Me-4)C(Me)CMe nuclei, although a specific assignment is not possible, while that at δ 145.7 p.p.m. is due to the μ-C(C₆H₄Me-4)C(Me)C(Me) nucleus. These assignments are based on the signals observed earlier for this group in the ¹³C-{¹H} n.m.r. spectra of the compounds (4) and (5).[5,6] The peaks in the spectrum of (2a) at δ 152.7, 154.3, 162.8, and 173.5 p.p.m. must be due to the ligating carbon atoms of the two η-MeC₂Me groups. Moreover, the chemical shifts are relatively deshielded and lie in the range expected for alkyne ligands functioning formally as three-electron donors to a metal centre.[11] If the but-2-yne molecules in (2a) each donate three electrons to the tungsten atom the latter attains an eighteen electron filled shell configuration.

The ¹H n.m.r. spectrum of (3) shows all the expected resonances (Table 1) and calls for no comment. The ¹³C-{¹H} n.m.r. spectrum, measured at ambient temperature, revealed six CO resonances indicating the absence of any site-exchange of carbonyl groups. A peak at δ 259.8 p.p.m. is assigned to the molybdenum-bound acyl carbonyl group. Measurement of a fully-coupled ¹³C spectrum (−50 °C) confirmed the assignments (Table 1) for the carbon nuclei of the C=CH₂ and C(H)Me groups. Thus the signal at δ 119.5 p.p.m. (μ-C=CH₂) remained a singlet while those at δ 70.4 [C(H)Me, J(HC) 122 Hz], 48.8 [C=CH₂, J(HC) 162 Hz], and 11.6 p.p.m. [C(H)Me, J(HC) 122 Hz] became a doublet, a triplet, and a quartet, respectively.
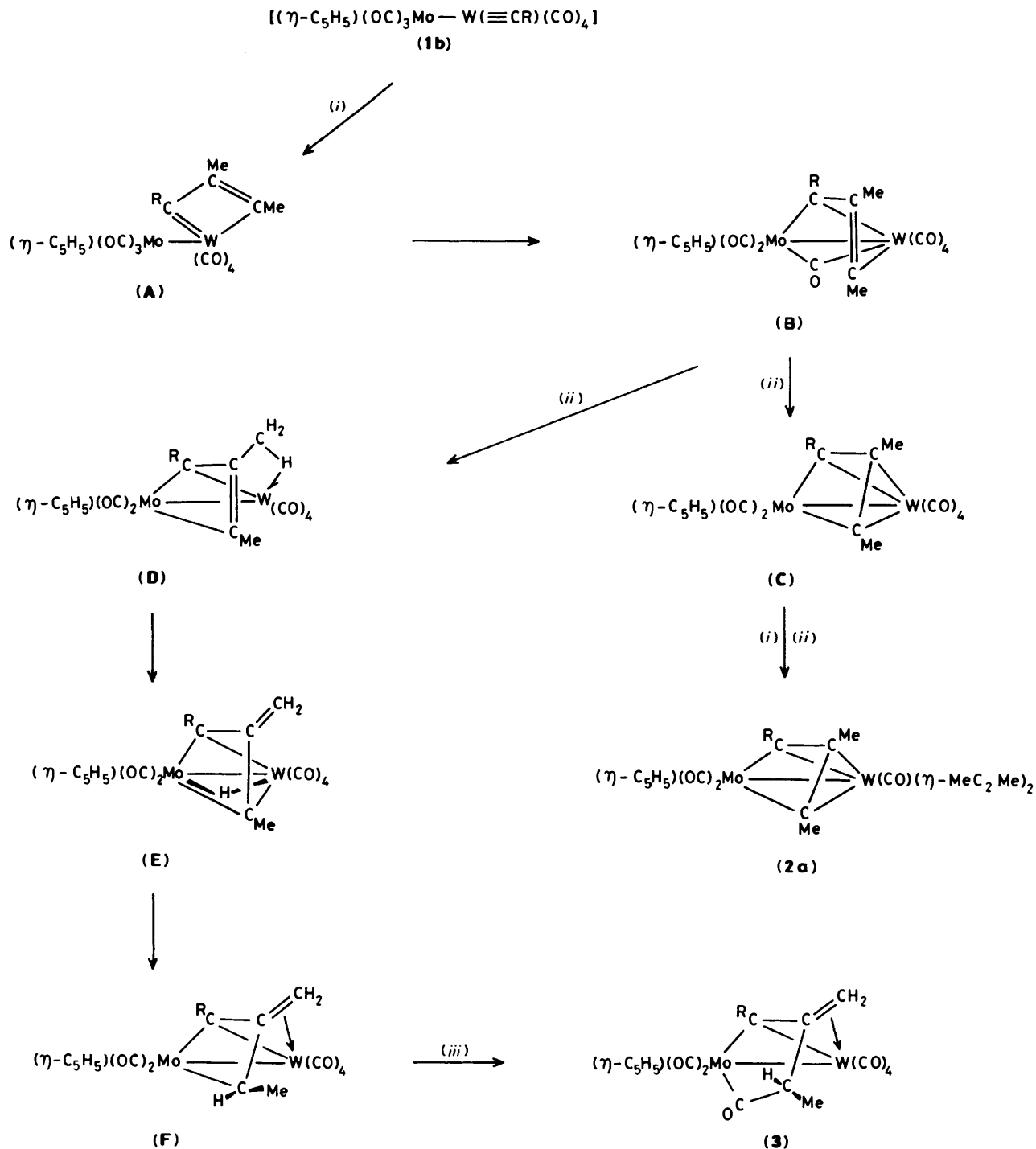
The pathways leading to compounds (2a) and (3) are obscure on present evidence, but possible routes are shown in the Scheme. As mentioned in the Introduction, nucleophilic attack by PMe₃ or H⁻ on (1a) occurs at the alkylidyne-carbon atom to produce bridging ligands C(C₆H₄Me-4)(PMe₃) and CH(C₆H₄-Me-4), respectively. A similar process involving (1b) and MeC≡CMe could give initially intermediate (A) followed by (B).

The tungstacyclobutadiene ring in the former is of the type invoked in alkyne metathesis[12,13] and has been structurally identified in the compounds [W{C(Buᵗ)C(Me)C(Me)}Cl₃], [W{C(Et)C(Et)C(Et)}(C₆H₃Prⁱ₂-2,3)₃], [W{C(Et)C(Et)C-(Et)}{OCH(CF₃)₂}₃], and [W{C(Buᵗ)C(H)C(Buᵗ)}{OCH-(CF₃)₂}₃].[14]

Intermediate (B) in the presence of excess but-2-yne in refluxing thf could afford compound (2a) via (C). Under these conditions (2a) is the only product. A possible route to (3) is via the common intermediate (B), leading through (D), (E), and (F) to the product. It seems likely that the rearrangement of the MeC₂Me fragment to C(=CH₂)C(H)Me is metal assisted [(D) ⟶ (E)]. We have recently described similar hydrogen migrations in reactions of the compounds [FeMo(μ-CC₆H₄-Me-4)(CO)₅L(η-C₅H₅)] (L = CO or PMe₃) with but-2-yne.[15] Carbon monoxide insertion in the final step [(F) ⟶ (3)] has precedent in the reversible reaction of [FeMo{μ-C(C₆H₄Me-4)-C(Et)C(Et)}(CO)₅(η-C₅H₅)] with CO leading to formation of a μ-C(C₆H₄Me-4)C(Et)C(Et)C(O) ligand at the iron–molybdenum centre.[16]

During the course of our work the important observation was made that when compound (3) was heated with but-2-yne in thf, complex (2a) was produced in essentially quantitative yield. This result supports the idea of common intermediates in the formation of these complexes, and demonstrates that the hydrogen migration process leading to (3) is readily reversed. Moreover, the transformation of (3) into (2a) might imply that species like (E) or (F) convert directly to (2a) in the presence of excess but-2-yne. It is evident that whatever pathways are involved in the formation of (2a) and (3), the dimetal systems typified by (1b) have considerable potential for the activation of alkynes.

As part of the studies reported herein, the reaction between (2a) and PMe₃ was investigated. It was hoped that this reaction would promote a combination of a terminally bound η-MeC₂Me group in (2a) with the μ-C₃ fragment to afford an η-C₅Me₄(C₆H₄Me-4) ligand at the tungsten centre. This expectation was based on earlier work[7] in which it was shown that alkyl- or aryl-substituted cyclopentadienyl groups are formed in reactions between the mononuclear tungsten compounds [W(CO)(R¹C₂R²)₃] (R¹ = R² = Ph or Et; R¹ = Me, R² = Ph) and [W(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)]. Thus

$[(\eta\text{-}C_5H_5)(OC)_3Mo\text{—}W(\equiv CR)(CO)_4]$

(1b)

(i)

(A) $(\eta\text{-}C_5H_5)(OC)_3Mo\text{—}W(CO)_4$

(B) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)_4$

(D) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)_4$

(C) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)_4$

(E) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)_4$

(2a) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)(\eta\text{-}MeC_2Me)_2$

(F) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)_4$

(3) $(\eta\text{-}C_5H_5)(OC)_2Mo\text{—}W(CO)_4$

Scheme. $R = C_6H_4Me\text{-}4$: (i) $+MeC\equiv CMe$, (ii) $-CO$, (iii) $+CO$

treatment of the latter with $[W(CO)(\eta\text{-}EtC_2Et)_3]$ affords the complex $[W_2(\mu\text{-}EtC_2Et)(CO)_4\{\eta\text{-}C_5Et_4(C_6H_4Me\text{-}4)\}(\eta\text{-}C_5H_5)].[7]$

The reaction between **(2a)** and PMe_3 in refluxing toluene afforded the compound $[MoW\{\mu\text{-}C(C_6H_4Me\text{-}4)C(Me)C(Me)\}\text{-}(CO)_2(PMe_3)(\eta\text{-}MeC_2Me)_2(\eta\text{-}C_5H_5)]$ **(2b)** in *ca.* 85% yield. The n.m.r. data (Table 1) and i.r. spectrum in the carbonyl stretching region $[\nu_{max.}(CO)$ at 1 932 and 1 845 cm$^{-1}]$ were in accord with the formulation of **(2b)** as a simple derivative of **(2a)** in which a carbonyl group ligating the tungsten in the latter

species had been substituted by PMe_3. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum of **(2b)** showed a characteristic resonance for a $W(PMe_3)$ group at δ -22.5 p.p.m. with $^{183}W\text{-}^{31}P$ satellite peaks $[J(WP)$ 132 Hz]. Thus unfortunately the reaction between **(2a)** and PMe_3 did not promote the desired formation of a $W\{\eta\text{-}C_5Me_4(C_6H_4Me\text{-}4)\}$ group.

It was thought that the vinylidene group present in **(3)** might be susceptible to attack by hydride anion. Treatment of **(3)** with $K[BH(CHMeEt)_3]$ in thf at *ca.* -60 °C followed by addition of NEt_4Cl afforded a yellow salt $[NEt_4][MoW\{\mu\text{-}C(C_6H_4Me\text{-}$

(6)
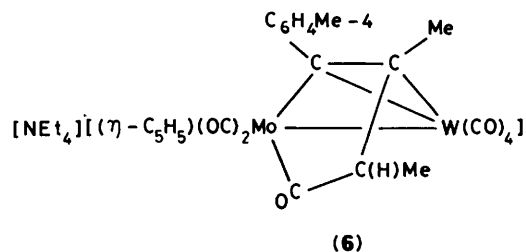
4)C(Me)C(H)MeC(O)}(CO)₆(η-C₅H₅)] (6). However, the instability of this species prevented satisfactory microanalysis, and the formulation rests on the n.m.r. data (Table 1). Attempts to obtain a neutral complex from (6) by protonation led only to decomposition.

Experimental

Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. Light petroleum refers to that fraction of b.p. 40—60 °C. Brockman activity II alumina was used for chromatography. The compound [MoW(≡CC₆H₄Me-4)(CO)₇(η-C₅H₅)] was prepared by treating [W(≡CC₆H₄Me-4)Br(CO)₄] with K[Mo(CO)₃(η-C₅H₅)] using the method reported previously for the synthesis of its phenylmethylidyne analogue.[17]

Reactions between [MoW(≡CC₆H₄Me-4)(CO)₇(η-C₅H₅)] *and But-2-yne.*—(i) A Schlenk tube, to which a condenser was attached, was charged with compound (1b) (0.19 g, 0.30 mmol), thf (30 cm³) as solvent, and excess of but-2-yne (12 mmol). With the condenser maintained at ca. −20 °C, the contents of the Schlenk tube were refluxed for 24 h, the function of the condenser being to return the but-2-yne to the reaction vessel. Solvent was removed in vacuo, and the residue dissolved in CH₂Cl₂–light petroleum (10 cm³, 1:1) and chromatographed on alumina (2 × 30 cm column). Elution with CH₂Cl₂–light petroleum (1:4) removed initially a trace of [Mo(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)] (identified by i.r.), followed by a yellow eluate. Removal of solvent in vacuo from the latter afforded yellow microcrystals of [MoW{μ-C(C₆H₄Me-4)C(Me)C(Me)}-(CO)₃(η-MeC₂Me)₂(η-C₅H₅)] (2a) (0.15 g, 70%) (Found: C, 48.3; H, 4.6. C₂₈H₃₀MoO₃W requires C, 48.4; H, 4.4%); ν_max.(CO) at 2 045s, 1 946vs, and 1 869s cm⁻¹ (light petroleum).

(ii) A thf (20 cm³) solution of (1b) (0.20 g, 0.30 mmol) was treated with a large excess of but-2-yne (ca. 1 cm³) and the mixture stirred at room temperature for 7 h. Solvent was removed in vacuo, and the residue dissolved in CH₂Cl₂–light petroleum (10 cm³, 1:1) and chromatographed on Florisil (2 × 30 cm column). Elution with Et₂O–light petroleum (1:2) removed traces of [Mo(≡CC₆H₄Me-4)(CO)₂(η-C₅H₅)] and (2a), both identified by i.r. Elution of the column with CH₂Cl₂ gave a red eluate. Removal of solvent in vacuo from the latter, and crystallisation of the residue from CH₂Cl₂–Et₂O (1:10) gave red crystals of [MoW{μ-C(C₆H₄Me-4)C(=CH₂)C(H)-MeC(O)}(CO)₆(η-C₅H₅)] (3) (0.15 g, 70%) (Found: C, 41.3; H, 3.1. C₂₄H₁₈MoO₇W requires C, 41.3; H, 2.6%); ν_max.(CO) at 2 051vs, 1 994m, 1 968s, 1 956m, 1 944m, and 1 651w cm⁻¹ (light petroleum).

Reaction of [MoW{μ-C(C₆H₄Me-4)C(Me)C(Me)}(CO)₃(η-MeC₂Me)₂(η-C₅H₅)] *with* PMe₃.—A mixture of (2a) (0.14 g, 0.20 mmol) and PMe₃ (1 cm³, 10 mmol) in toluene (30 cm³) was refluxed (24 h) in a Schlenk tube to the top of which was fitted a condenser cooled to −20 °C. Solvent was removed in vacuo, and the residue was dissolved in CH₂Cl₂–light petroleum (10 cm³, 2:3) and chromatographed at −20 °C on alumina (2 × 15

cm column). Elution with CH₂Cl₂–light petroleum (1:4) gave a trace of (2a) followed by a yellow eluate. Removal of solvent in vacuo from the latter afforded yellow microcrystals of [MoW{μ-C(C₆H₄Me-4)C(Me)C(Me)}(CO)₂(PMe₃)(η-MeC₂-Me)₂(η-C₅H₅)] (2b) (0.13 g, 85%) (Found: C, 48.5; H, 5.6. C₃₀H₃₉MoO₂PW requires C, 48.5; H, 5.3%); ν_max.(CO) at 1 932vs and 1 845s cm⁻¹ (light petroleum).

Reaction of [MoW{μ-C(C₆H₄Me-4)C(=CH₂)C(H)MeC(O)}-(CO)₆(η-C₅H₅)] *with* K[BH(CHMeEt)₃].—A thf (15 cm³) solution of (3) (0.14 g, 0.22 mmol) at −60 °C was treated with K[BH(CHMeEt)₃] (0.22 cm³, 0.22 mmol) in the same solvent. An immediate colour change from red to yellow occurred. The mixture was treated with NEt₄Cl (0.04 g, 0.22 mmol) and allowed to warm to room temperature with stirring (1 h). After filtration through a Celite pad (ca. 5 cm), solvent was removed in vacuo and the residue crystallised from thf–Et₂O (12 cm³, 1:5) at −78 °C to give yellow microcrystals of [NEt₄][MoW{μ-C(C₆H₄Me-4)C(Me)C(H)MeC(O)}(CO)₆(η-C₅H₅)] (6) (0.16 g, 90%).

Crystal Structure Determinations.—(a) [MoW{μ-C(C₆H₄-Me-4)C(Me)C(Me)}(CO)₃(η-MeC₂Me)₂(η-C₅H₅)] (2a). Diffracted intensities were collected at 293 K from a crystal of dimensions ca. 0.45 × 0.30 × 0.22 mm on a Nicolet P3m diffractometer. Of the 4 504 unique data collected (Wyckoff ω scans, 2θ ≤ 50°), 3 503 had I ⩾ 2.5σ(I), and only these were used for structure solution and refinement. The data were corrected for Lorentz and polarisation effects and for X-ray absorption, the latter by an empirical method based on azimuthal scan data.[18]

Crystal data. C₂₈H₃₀MoO₃W, M = 694.3, monoclinic, space group P2₁/n (non-standard setting of P2₁/c, no. 14), a = 8.952(4), b = 20.613(18), c = 14.223(8) Å, β = 99.31(4)°, U = 2 590(3) Å³, Z = 4, D_c = 1.78 g cm⁻³, F(000) = 1 352, Mo-K_α X-radiation (graphite monochromator), λ = 0.710 69 Å, μ(Mo-K_α) = 50.3 cm⁻¹.

The structure was solved by conventional heavy-atom methods and successive difference Fourier syntheses were used to locate all non-hydrogen atoms, which were refined with anisotropic thermal parameters. Hydrogen atoms were included at fixed positions (C–H 0.96 Å) with a common refined isotropic thermal parameter for the methyl hydrogen atoms attached to C(2), C(5), C(6), C(9), C(10), C(13), and C(27), and fixed isotropic thermal parameters (ca. 1.2 × U_equiv of the parent carbon atom) for all remaining hydrogen atoms. Refinement by blocked-cascade least squares led to R = 0.040 (R' = 0.041), with a weighting scheme of the form w⁻¹ = [σ²(F) + 0.000 85|F|²] giving a satisfactory analysis of variance. The final electron density difference synthesis showed no peaks > 1.60 or < −1.17 e Å⁻³, the largest lying close to the metal atoms.

(b)[MoW{μ-C(C₆H₄Me-4)C(=CH₂)C(H)MeC(O)}(CO)₆(η-C₅H₅)]·0.5CH₂Cl₂ (3). Crystals grow as deep red blocks from CH₂Cl₂. Diffracted intensities were collected as for (2a) from a crystal of dimensions ca. 0.25 × 0.55 × 0.30 mm. Of the 4 723 unique data collected (ω—2θ scans, 2θ ≤ 50°), 4 025 had I ⩾ 2.0σ(I) and only these were used in structure solution and refinement. The data were corrected for Lorentz and polaris-ation effects and for X-ray absorption, the latter by an empirical method.[18]

Crystal data. C₂₄H₁₈MoO₇W·0.5CH₂Cl₂, M = 740.7, monoclinic, space group P2₁/n (non-standard setting of P2₁/c. no. 14), a = 9.381(1), b = 20.379(3), c = 13.958(2) Å, β = 91.28(1)°, U = 2 667.9(6) Å³, Z = 4, D_c = 1.84 g cm⁻³, F(000) = 1 420, μ(Mo-K_α) = 50.0 cm⁻¹.

The structure was solved as for (2a), difference Fourier synthesis being used to locate all non-hydrogen atoms (with the

Table 4. Atomic positional parameters (fractional co-ordinates × 10⁴) for compound (2a), with estimated standard deviations in parentheses

Atom	x	y	z
W	576(1)	1 791(1)	2 711(1)
Mo	2 002(1)	514(1)	3 252(1)
C(1)	1 194(8)	978(4)	1 834(5)
C(2)	−1 539(11)	538(5)	1 112(6)
C(3)	−316(9)	766(4)	1 897(6)
C(4)	−416(9)	820(4)	2 867(6)
C(5)	−1 747(10)	581(5)	3 307(7)
C(6)	−3 101(9)	2 142(6)	1 881(7)
C(7)	−1 404(8)	2 164(4)	1 949(5)
C(8)	−300(8)	2 463(4)	1 652(5)
C(9)	59(11)	2 986(5)	992(7)
C(10)	−1 134(11)	2 060(5)	4 676(7)
C(11)	−16(9)	2 099(4)	4 002(5)
C(12)	1 168(9)	2 414(4)	3 859(6)
C(13)	2 236(11)	2 938(5)	4 279(7)
C(14)	3 748(10)	1 112(4)	3 476(6)
O(14)	4 847(7)	1 420(4)	3 674(5)
C(15)	1 810(9)	848(4)	4 539(6)
O(15)	1 751(8)	1 002(4)	5 297(4)
C(16)	2 410(8)	2 240(4)	2 337(6)
O(16)	3 408(7)	2 515(4)	2 137(6)
C(21)	1 846(9)	1 031(4)	941(6)
C(22)	1 009(10)	1 306(4)	130(6)
C(23)	1 572(10)	1 360(5)	−720(6)
C(24)	2 999(11)	1 137(4)	−795(7)
C(25)	3 871(10)	881(5)	12(7)
C(26)	3 320(10)	833(4)	875(7)
C(27)	3 569(13)	1 195(6)	−1 748(8)
C(31)	3 583(13)	−332(5)	2 971(9)
C(32)	2 242(15)	−429(5)	2 322(9)
C(33)	1 068(14)	−544(5)	2 830(8)
C(34)	1 655(15)	−536(5)	3 808(8)
C(35)	3 209(13)	−414(5)	3 893(9)

Table 5. Atomic positional parameters (fractional co-ordinates × 10⁴) for compound (3), with estimated standard deviations in parentheses

Atom	x	y	z
W	2 127(1)	2 154(1)	899(1)
Mo	5 006(1)	1 604(1)	141(1)
C(1)	3 605(7)	2 388(3)	−340(4)
C(2)	1 047(7)	2 560(4)	−616(5)
C(3)	2 237(7)	2 181(3)	−760(4)
C(4)	2 215(7)	1 526(3)	−1 264(5)
C(5)	761(8)	1 204(4)	−1 482(6)
C(6)	3 275(7)	1 069(3)	−703(4)
O(6)	3 197(5)	483(2)	−775(4)
C(7)	5 445(7)	2 139(3)	1 330(5)
O(7)	5 841(5)	2 417(3)	2 002(4)
C(8)	4 487(7)	875(4)	1 073(5)
O(8)	4 261(7)	457(3)	1 569(4)
C(9)	2 654(7)	3 077(4)	1 296(5)
O(9)	2 872(7)	3 579(3)	1 617(4)
C(10)	2 743(7)	1 907(4)	2 233(5)
O(10)	3 099(6)	1 764(3)	2 988(4)
C(11)	1 344(7)	1 205(4)	838(5)
O(11)	882(6)	701(3)	912(4)
C(12)	219(7)	2 447(4)	1 284(5)
O(12)	−879(5)	2 647(3)	1 507(4)
C(21)	4 129(6)	3 053(3)	−610(4)
C(22)	3 737(7)	3 304(3)	−1 500(5)
C(23)	4 314(8)	3 891(4)	−1 840(5)
C(24)	5 285(8)	4 250(4)	−1 298(5)
C(25)	5 648(8)	4 006(4)	−416(5)
C(26)	5 105(7)	3 422(3)	−67(5)
C(27)	5 925(11)	4 887(4)	−1 661(8)
C(31)	7 142(7)	2 025(4)	−373(6)
C(32)	7 406(7)	1 435(4)	136(6)
C(33)	6 784(7)	900(4)	−391(5)
C(34)	6 147(8)	1 178(4)	−1 216(5)
C(35)	6 348(7)	1 872(4)	−1 203(5)
Cl(1)	3 888(13)	626(7)	6 448(7)
Cl(2)	4 314(20)	−403(10)	5 918(19)

exception of the solvent carbon atom), H(2a), H(2b), and H(4). All non-hydrogen atoms were refined with anisotropic thermal parameters, atoms H(2a), H(2b), and H(4) were refined with fixed isotropic thermal parameters ($ca.$ 1.2 × U_{equiv} of the parent carbon atoms). All remaining hydrogen atoms were included at calculated positions (C–H 0.96 Å) with fixed isotropic thermal parameters ($ca.$ 1.2 × U_{equiv} of the parent carbon atoms) for those attached to cyclopentadienyl and phenyl rings, and a common refined isotropic thermal parameter for all hydrogen atoms belonging to methyl groups. During the refinement it became apparent from the presence of large residual peaks in the electron-density difference synthesis [$ca.$ 3.4 e Å⁻³, near the centre of inversion at fractional co-ordinates ($\frac{1}{2}$, 0, $\frac{1}{2}$)] that a poorly defined solvent of crystallisation was present. A ¹H n.m.r. spectrum of the remainder of the sample of crystals indicated the presence of between 0.5 and 1.0 molecule of CH_2Cl_2 per molecule of (3). The final stages of refinement included two chlorine atoms (with site occupancy factors of 0.5 and anisotropic thermal parameters), and this produced a significant improvement in the structure as measured by R indices, residual electron density, and the estimated standard deviations of the molecular parameters. The fact that a suitable position for the carbon atom could not be found, and the short Cl–Cl separation ($ca.$ 2.3 Å) indicated severe disorder. The model corresponded to an average of one molecule of CH_2Cl_2 near each ($\frac{1}{2}$, 0, $\frac{1}{2}$) site. It is possible that more than one molecule could be accommodated at some, or all, of these sites, and an observed crystal decay ($ca.$ 7% over the 80 h of data collection) may be due to partial loss of solvent during data collection.

Refinement by blocked-cascade least squares led to R 0.033 (R' 0.035) and a weighting scheme of the form $w^{-1} = [\sigma^2(F) + 0.000 5|F|^2]$ gave a satisfactory analysis of variance. The final electron-density difference synthesis showed no peaks > 1.36 or < −0.63 e Å⁻³, the largest lying close to the disordered solvent molecule. All calculations were performed on a Data General 'Eclipse' computer with the SHELXTL system of programs.[18] Scattering factors with corrections for anomalous dispersion were taken from reference 19. The atom co-ordinates for (2a) and (3) are given in Tables 4 and 5, respectively.

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