

Formation of Substituted Cyclopentadienyl Ligands on Tungsten *via* Reactions Between the Alkyne Complexes $[W(CO)(R^1C_2R^2)_3]$ ($R^1 = R^2 = Ph$ or Et ; $R^1 = Me$, $R^2 = Ph$) and the Alkylidyne Compounds $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$ or Me); X-Ray Crystal Structures of $[W_2(\mu-CO)_2(CO)(\eta-PhC_2Ph)(\eta-C_5Ph_4R)-(\eta-C_5H_5)]$ and $[W_2(\mu-EtC_2Et)(CO)_4(\eta-C_5Et_4R)(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$)*

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In octane under reflux the compounds $[W(CO)(R^1C_2R^2)_3]$ ($R^1 = R^2 = Ph$ or Et) react with $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ to give the ditungsten complexes $[W_2(\mu-CO)_2(CO)(\eta-PhC_2Ph)-\{\eta-C_5Ph_4(C_6H_4Me-4)\}(\eta-C_5H_5)]$ and $[W_2(\mu-EtC_2Et)(CO)_4\{\eta-C_5Et_4(C_6H_4Me-4)\}(\eta-C_5H_5)]$, respectively. The structures of these products have been established by X-ray diffraction studies. In the former species a short W–W bond [2.586(1) Å] is asymmetrically bridged by two CO groups, and a PhC_2Ph ligand is terminally bound to one tungsten atom. In the latter molecule a hex-3-yne ligand transversely bridges a W–W vector [3.003(1) Å]; three carbonyl groups are terminally attached to the tungsten atoms and one is semi-bridging. Reaction of $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$ with $[W(CO)(PhC_2Ph)_3]$ also affords an alkyne-bridged ditungsten compound $[W_2(\mu-PhC_2Ph)-(CO)_4(\eta-C_5MePh_4)(\eta-C_5H_5)]$. The species $[W(CO)(MeC_2Ph)_3]$, containing an unsymmetrical alkyne, reacts in octane under reflux with $[W(\equiv CC_6H_4Me-4)(CO)_2(\eta-C_5H_5)]$ to give the complex $[W_2(\mu-MeC_2Ph)(CO)_4\{\eta-C_5Me_2Ph_2(C_6H_4Me-4)\}(\eta-C_5H_5)]$, produced as an isomeric mixture. The spectroscopic data (i.r. and n.m.r.) for the new compounds are reported and discussed and a possible mechanism for their formation suggested.

The compound $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$) reacts with a variety of low-valent metal species to afford complexes with metal–metal bonds and bridging CR or RC_2R groups.¹ However, the only compounds with W–W bonds prepared in this manner so far are the tritungsten compounds $[W_3-(\mu_3-CR)(CO)_6(\eta-C_5H_5)_3]$ ² and $[W_3(\mu-CO)_2(\mu-CR)_2(CO)_4(\eta-C_5H_5)_2]$.³ The former, with a trimetallatetrahedrane core structure, is prepared by refluxing $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ with $[W_2(CO)_4(\eta-C_5H_5)_2]$ in toluene; the latter is obtained by treating $[W(CO)_3(NCMe)_3]$ with $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ in hexane under reflux and has an open metal-chain structure. In addition, the 'dimer' of the tolylmethylidyne complex, $[W_2(\mu-RC_2R)(CO)_4\eta-C_5H_5]$, forms as a by-product in several reactions.^{2,4} In order to extend our studies in this area, we have examined reactions between the tris(alkyne)tungsten complexes $[W(CO)(R^1C_2R^2)_3]$ [$R^1 = R^2 = Ph$ (**1a**); $R^1 = R^2 = Et$ (**1b**); $R^1 = Me$, $R^2 = Ph$ (**1c**)]^{5,6} and $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$, and we have also investigated the reaction between (**1a**) and the methylmethylidyne tungsten species $[W(\equiv CMe)(CO)_2(\eta-C_5H_5)]$.

The pseudo-tetrahedral molecules $[W(CO)(R^1C_2R^2)_3]$ involve a situation in which two of the alkyne ligands can be considered to function as four-electron donors.⁶ The molecular structure of (**1a**) has been established by an X-ray diffraction study.⁷ Little is known about the reactivity of the tris-

(alkyne)monocarbonyltungsten compounds (**1**), or other complexes of this class.^{8–10}

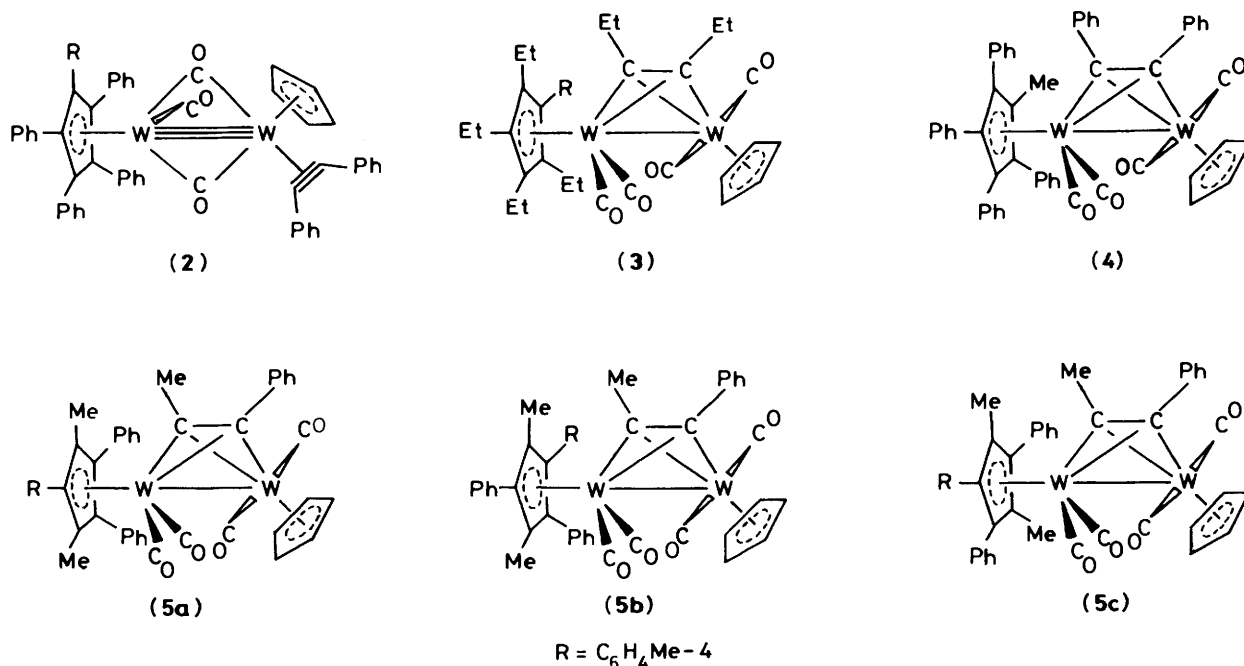
Results and Discussion

Although no reaction occurred at room temperature between the compounds (**1**) and $[W(\equiv CR)(CO)_2(\eta-C_5H_5)]$ ($R = C_6H_4Me-4$ or Me) in organic solvents, when the reactants were refluxed in octane ditungsten complexes were formed. Thus, the tolylmethylidyne tungsten compound with (**1a**) and with (**1b**) afforded the species (**2**) and (**3**), respectively. The spectroscopic properties of these two products were very different, thus indicating that the molecular structures were not similar. The i.r. spectrum of (**2**) had carbonyl stretching bands in the bridging region, whereas that of (**3**) did not (Table 1). Moreover, the pattern of bands observed in the spectrum of the latter was very similar to those shown by the compound $[W_2(\mu-RC_2R)(CO)_4(\eta-C_5H_5)_2]$, mentioned above, thus suggesting a similar structure. The ¹³C-{¹H} n.m.r. spectra of both (**2**) and (**3**) showed that the CO groups undergo an exchange process at room temperature on the n.m.r. time-scale and this is discussed below. The spectra (Table 2) also established that neither complex contained a μ - or μ_3 -CR ligand. The ligated carbon atoms of bridging tolylmethylidyne ligands resonate in the range ca. 330–430 p.p.m. for dimetal species,¹¹ and ca. 225–330 p.p.m. for trimetal clusters in which the carbyne group is spanning three metal atoms.^{2,11,12} No such resonances are present in the spectra of (**2**) or (**3**). In order to resolve the structures of these compounds single-crystal X-ray diffraction studies were carried out on both species. The results are summarised in Tables 3 and 4, and the molecular structures are shown in Figures 1 and 2.

The tungsten–tungsten bond in (**2**) (Figure 1) is asymmetrically bridged by two carbonyl groups C(01)O(01) [$W(1)-C(01)-O(01)$ 167.4(11), $W(2)-C(01)-O(01)$ 121.9(8)°] and C(9)O(9) [$W(1)-C(9)-O(9)$ 121.9(8), $W(2)-C(9)-O(9)$ 167.0(9)°].

* Di- μ -carbonyl-2-carbonyl-1- η -cyclopentadienyl-1- η^2 -diphenylacetylene-2-[η^5 -tetraphenyl(*p*-tolyl)cyclopentadienyl]ditungsten ($3W-W$) and 1,1,2,2-tetracarboxyl-1- η -cyclopentadienyl- μ -[hex-3-yne- $C^3, C^4(W^1)$, $C^3, C^4(W^2)$]-2-[η^5 -tetraethyl(*p*-tolyl)cyclopentadienyl]ditungsten ($W-W$) respectively.

Supplementary data available (No. SUP 56154, 13 pp.): full listing of bond distances and angles, thermal parameters, H-atom co-ordinates. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xviii–xix. Structure factors are available from the editorial office.

**Table 1.** Analytical^a and physical data for the ditungsten compounds

Compound	M.p. (θ _c /°C) ^b	Colour	Yield (%)	ν _{max.} (CO) ^c /cm ⁻¹	Analysis (%)	
					C	H
(2) [W ₂ (μ-CO) ₂ (CO)(η-PhC ₂ Ph){η-C ₅ Ph ₄ (C ₆ H ₄ Me-4)}(η-C ₅ H ₅)]	194	Red-brown	26	1 912s, 1 830m, 1 788vs, 1 690vw,br	56.8 (57.2)	3.5 (3.5)
(3) [W ₂ (μ-EtC ₂ Et)(CO) ₄ {η-C ₅ Et ₄ (C ₆ H ₄ Me-4)}(η-C ₅ H ₅)]	161	Red	30	1 964s, 1 892vs, 1 800m	47.2 (47.0)	4.9 (4.7)
(4) [W ₂ (μ-PhC ₂ Ph)(CO) ₄ (η-C ₅ MePh ₄)(η-C ₅ H ₅)]	129	Red-brown	84	1 975s, 1 914vs, 1 803m	57.9 (57.5)	4.0 (3.5)
(5a) [W ₂ (μ-MeC ₂ Ph)(CO) ₄ {η-C ₅ Me ₂ Ph ₂ (C ₆ H ₄ Me-4)}(η-C ₅ H ₅)]	102	Red	30	1 971s, 1 906vs, 1 804m,br	53.5 (53.0)	4.5 (3.6)
(5b), (5c) [W ₂ (μ-MeC ₂ Ph)(CO) ₄ {η-C ₅ Me ₂ Ph ₂ (C ₆ H ₄ Me-4)}(η-C ₅ H ₅)]	214	Red	14	1 971s, 1 906vs, 1 807m	52.4 (53.0)	4.0 (3.6)

^a Calculated values are given in parentheses. ^b With decomposition. ^c In CH₂Cl₂.

The appearance of bridging CO bands in the i.r. spectrum of (2) (Table 1) is thus explained. A third CO ligand in (2) is terminally bonded to W(1) [W(1)-C(8)-O(8) 177.6(11)°], and this atom also carries a cyclopentadienyl ring having a tolyl and four phenyl substituents. However, the Me-4 group was refined at two positions [C(24A) and C(44A)] owing to a 50:50 disorder of the tolyl group on the substituted cyclopentadienyl ligand.

The tungsten atom W(2) is ligated by an η-C₅H₅ group, and by a PhC₂Ph molecule. The metal-metal separation [2.586(1) Å] is relatively short, and may be regarded as indicating the presence of a W≡W triple bond, a feature consistent with an electron count of 18 at each tungsten atom. The W(1)-W(2) distance may be compared with the metal-metal separation in [W₂(CO)₆(η-C₅H₅)₂] [3.222(1) Å],¹³ where the two halves of the molecule are generally regarded as being held together by a single W-W bond. A more relevant comparison for the metal-metal distance in (2) may be with that observed [2.448(1) Å] in the dimolybdenum compound [Mo₂(CO)₄(η-C₅H₅)₂], which formally contains a metal-metal triple bond.¹⁴ The covalent radii of molybdenum and tungsten are essentially the same.

In compound (3) (Figure 2), an EtC₂Et group spans the W-W bond [3.003(1) Å] so that the atoms W(1), W(2), C(33), and C(34) form a dimetallatetrahedrane core, very similar to that found¹⁵

in the related complex [W₂(μ-HC₂H)(CO)₄(η-C₅H₅)₂] [W-W 2.987(1) Å]. The μ-C-C separation in the latter [1.33(3) Å] is also similar to the corresponding distance [C(33)-C(34) 1.361(14) Å] in (3). In the dimolybdenum complex [Mo₂(μ-EtC₂Et)(CO)₄(η-C₅H₅)₂] the μ-C-C distance is 1.335(8) Å,¹⁶ virtually identical with C(33)-C(34). Each tungsten atom carries two CO ligands, one of which on W(1) is semi-bridging [W(1)-C(1)-O(1) 168.6(8)°]. Interestingly, in [W₂(μ-HC₂H)(CO)₄(η-C₅H₅)₂]¹⁵ and in [Mo₂(μ-EtC₂Et)(CO)₄(η-C₅H₅)₂]¹⁶ one CO group is also semi-bridging, with W-C-O and Mo-C-O bond angles of 167(2) and 168.1(5)°, respectively. The semi-bridging CO ligand in (3) accounts for the observation of a band in the i.r. spectrum at 1 800 cm⁻¹ (Table 1).

Whereas W(2) carries an η-C₅H₅ ligand, W(1) has attached to it a C₅Et₄(C₆H₄Me-4) group, akin to the related C₅Ph₄(C₆H₄Me-4) ligand in (2). In the pentasubstituted cyclopentadienyl group in (3), the four Et groups lie on the same side of the C₅ ring, opposite to W(1), thus minimising steric interactions with the remainder of the molecule. The phenyl groups in the C₅Ph₄(C₆H₄Me-4) ring of (2) are unable to bend away from the tungsten atom to which this ring is attached to the same extent as the Et substituents bend away in (3).

Having established the molecular structures of compounds

Table 2. Hydrogen-1 and carbon-13 n.m.r. data^a for the ditungsten complexes

Complex	¹ H (δ) ^b	¹³ C (δ) ^c
(2)	2.22 (s, 3 H, Me-4), 5.55 (s, 5 H, C ₅ H ₅), 6.68—7.83 (m, 34 H, C ₆ H ₄ and Ph)	233.0 (br, CO), 145.8—127.4 (C ₆ H ₄ , Ph, C ₂ Ph ₂), 111.7, 111.3, 111.0 [C ₃ Ph ₄ (C ₆ H ₄ Me-4)], 97.0 (C ₅ H ₅), 21.3 (Me-4)
(3)	0.99 [t, 6 H, Me, <i>J</i> (HH) 4], 1.01 [t, 6 H, Me, <i>J</i> (HH) 4], 1.24 [t, 6 H, Me, <i>J</i> (HH) 4], 2.35 (s, 3 H, Me-4), 2.3—2.5 (m, br, 8 H, CH ₂), 2.99 (m, br, 4 H, CH ₂), 5.24 (s, 5 H, C ₅ H ₅), 7.17 [(AB) ₂ , 4 H, C ₆ H ₄ , <i>J</i> (AB) 6]	221.8, 220.7 (br, CO), 137.4 [C ¹ (C ₆ H ₄)], 132.8, 130.1, 129.0 (C ₆ H ₄), 109.3, 109.1, 108.5 [C ₃ Et ₄ (C ₆ H ₄ Me-4)], 89.9 (C ₅ H ₅), 27.5 [br, CH ₂ (μ-C ₂ Et ₂)], 21.2 (Me-4), 19.5, 19.3 (CH ₂), 17.1 [Me (μ-C ₂ Et ₂)], 16.6, 16.3 (Me)
(4)	1.21 (s, 3 H, Me), 5.26 (s, 5 H, C ₅ H ₅), 6.75—7.18 (m, 30 H, Ph)	227.0, 221.2, 218.8, 218.1 (CO), 144.6, 141.0 [C ¹ (Ph)], 133.2—124.1 (Ph), 111.7, 110.7, 109.7, 109.1 (C ₄ Ph ₄), 96.0 (CMe), 92.8 (C ₅ H ₅), 91.1, 89.8 (μ-C ₂), 12.4 (Me)
(5a)	2.07 (s, 6 H, C ₅ Me ₂), 2.23 (s, 3 H, Me-4), 2.72 (s, 3 H, ≡CMe), 5.28 (s, 5 H, C ₅ H ₅), 6.96—7.24 (m, 19 H, C ₆ H ₄ and Ph)	224.6, 219.5, 218.6, 217.0 (CO), 137.3—124.5 (C ₆ H ₄ , Ph), 109.4, 109.2, 108.8, 95.8, 95.5 (C ₅ Me ₂ Ph ₂ R), 91.5 (C ₅ H ₅), 89.6 (≡CMe), 89.2 (≡CPh), 21.1 (Me-4), 20.5 (≡CMe), 12.5 (C ₅ Me ₂)
(5b), (5c)	2.06 (s, br, 6 H, C ₅ Me ₂), 2.16 (s, 6 H, Me-4), 2.29 (s, br, 6 H, C ₅ Me ₂), 2.54 (s, br, 6 H, ≡CMe), 5.29 (s, 5 H, C ₅ H ₅), 5.30 (s, 5 H, C ₅ H ₅), 6.74—7.25 (m, 38 H, C ₆ H ₄ and Ph)	^d 226.6, 221.7, 221.6, 217.1 (CO), 144.4, 137.2 [C ¹ (Ph, C ₆ H ₄)], 133.5—124.8 (Ph, C ₆ H ₄), 112.8, 110.4, 108.3, 108.0, 107.2, 106.0 (C ₅ Me ₂ Ph ₂ R), 91.9 (C ₅ H ₅), 90.8 (≡CMe), 87.8 (≡CPh), 21.2 (Me-4), 19.5 (≡CMe), 12.7, 12.1 (C ₅ Me ₂)

^a Chemical shifts (δ) in p.p.m., coupling constants in Hz. ^b Measured in CDCl₃. ^c Hydrogen-1 decoupled, to high frequency of SiMe₄, measured in CD₂Cl₂-CH₂Cl₂. ^d Measured at -40 °C.

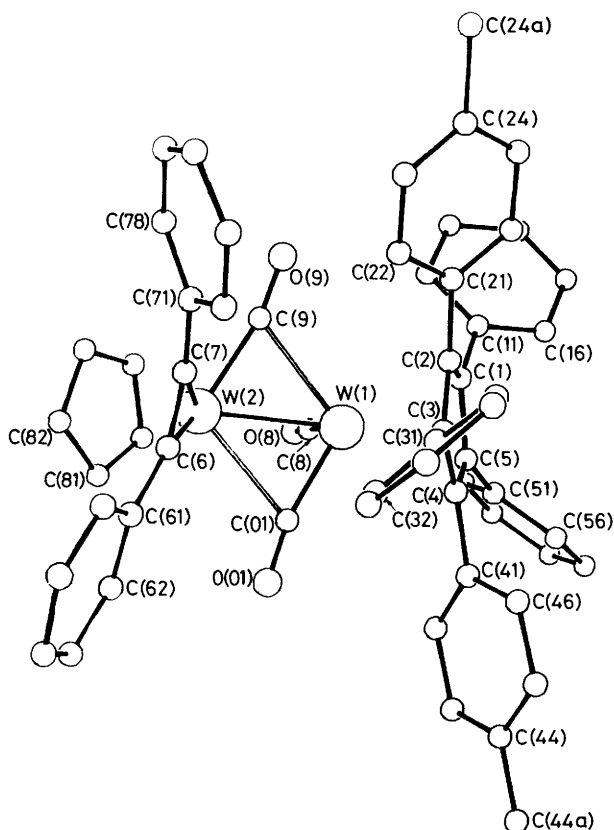


Figure 1. The molecular structure of [W₂(μ-CO)₂(CO)(η-PhC₂Ph){η-C₃Ph₄(C₆H₄Me-4)}(η-C₅H₅)] (2) showing the atom numbering scheme

(2) and (3), it is possible to account for the n.m.r. data (Table 2). The ¹H n.m.r. spectra are as expected and call for no comment. As mentioned earlier, the complexes undergo dynamic behaviour in solution. At room temperature, one broad CO peak is seen in the ¹³C-¹H n.m.r. spectrum of (2) but at

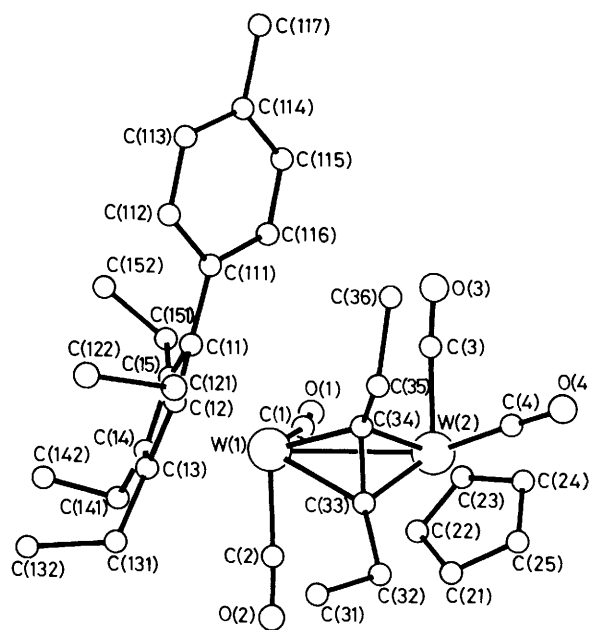
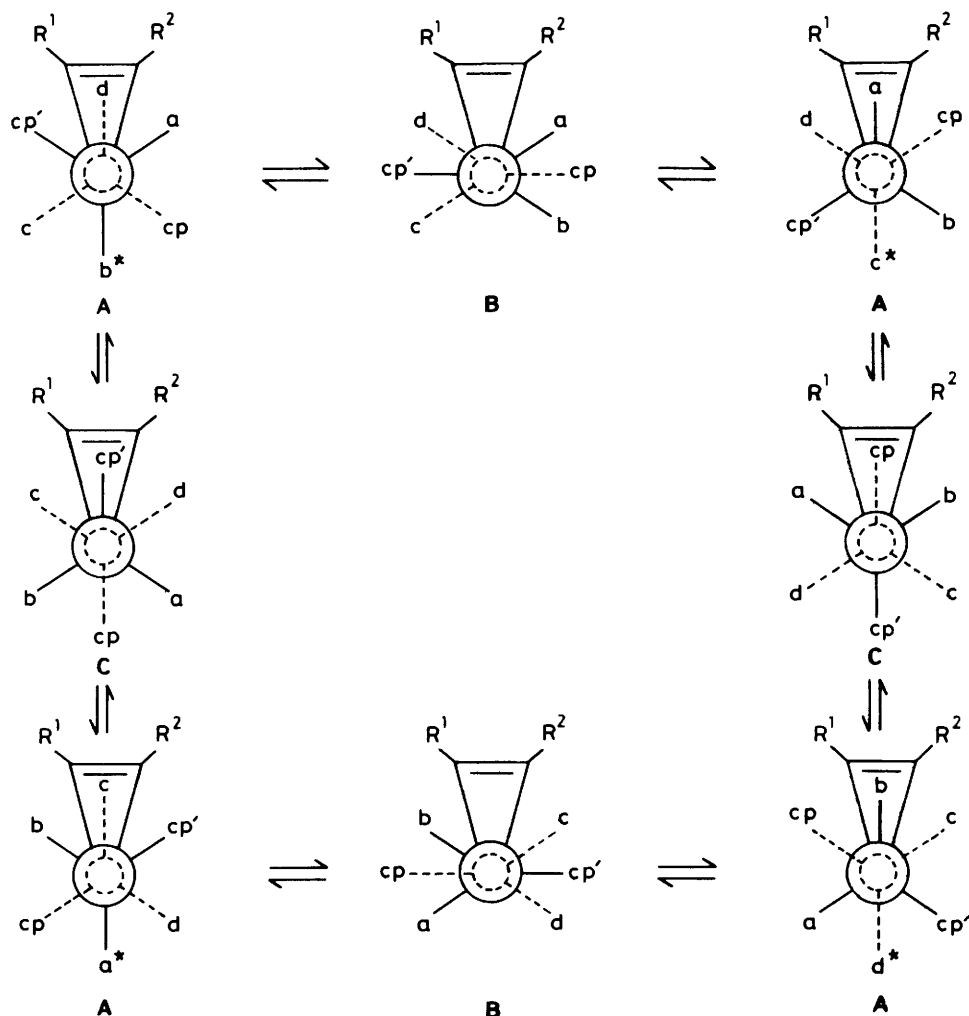


Figure 2. The molecular structure of [W₂(μ-EtC₂Et)(CO)₄{η-C₅Et₄(C₆H₄Me-4)}(η-C₅H₅)] (3) showing the atom numbering scheme

-90 °C three resonances occur (δ 255.2, 223.4, and 222.9 p.p.m.), in accord with the three chemically different environments for the CO ligands as established by the X-ray study. Compound (3) has a ¹³C-¹H n.m.r. spectrum with two broad CO resonances at room temperature, but at -40 °C the limiting spectrum is reached with four signals at δ 224.5, 223.4, 222.2, and 220.6 p.p.m., as expected from the structure found in the solid state.

Several alkyne-bridged dimolybdenum compounds with structures similar to (3) have been studied, but in all cases unsubstituted cyclopentadienyl rings have been present in the molecules.^{16,17} Variable-temperature n.m.r. measurements



Scheme 1. cp = η -C₅H₅, cp' = substituted cp ring; a—d are the CO ligands, with an asterisk (*) denoting a semi-bridging CO. For compounds (3) and (4), R¹ = R²; for the isomeric mixture (5), R¹ = Me, R² = Ph

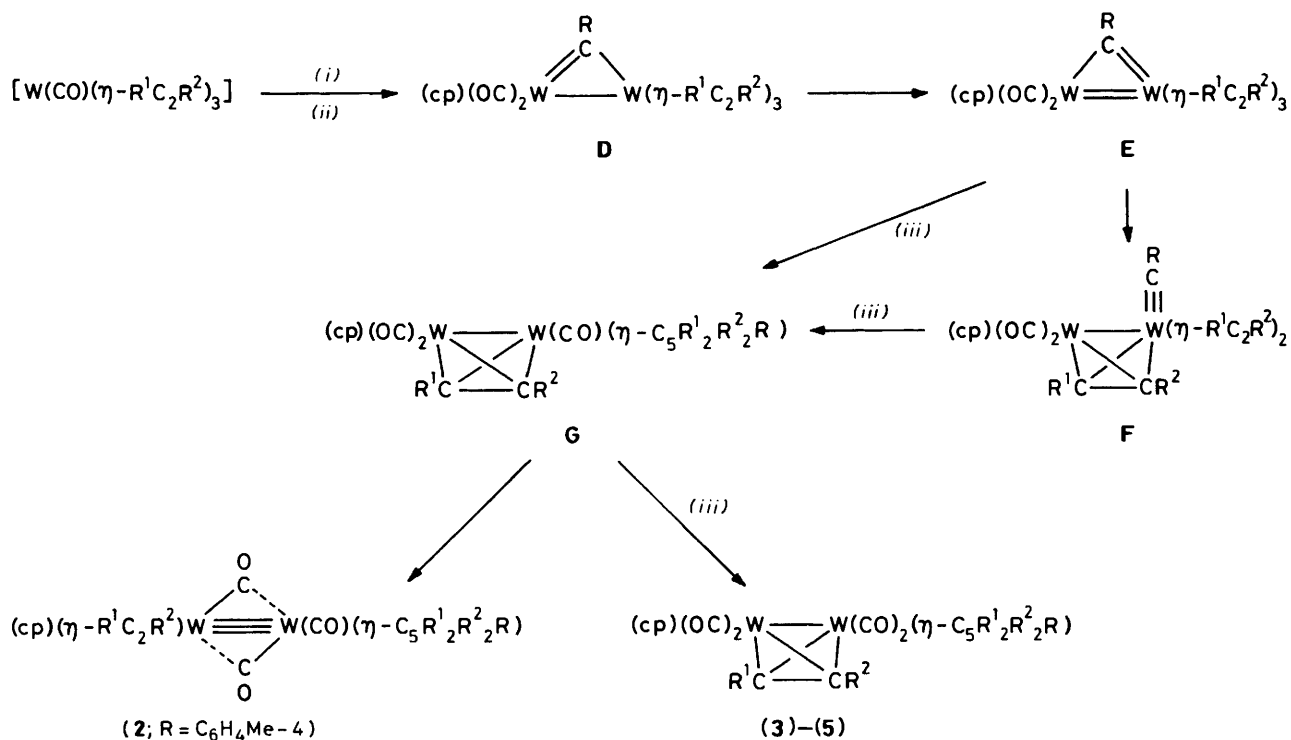
have revealed two major dynamic processes (Scheme 1). The lowest energy process ($A \rightleftharpoons B \rightleftharpoons A$) interconverts isomers of type **A** via an intermediate **B** with C_2 symmetry, whilst a higher energy process ($A \rightleftharpoons C \rightleftharpoons A$, $> ca. -40^\circ C$) occurs which involves a sterically more hindered intermediate **C** having mirror symmetry. It seems probable that the same fluxional processes are occurring in compound (3). However, the presence of a substituted cyclopentadienyl ring on one of the tungsten atoms destroys the C_2 symmetry of intermediate **B**. Thus in the absence of CO scrambling between the two tungsten atoms, a process not favoured in these species,¹⁶ the low-energy process $A \rightleftharpoons B \rightleftharpoons A$ no longer renders the pairs of carbonyl ligands equivalent on what, in this system, are two chemically distinct tungsten atoms. The room-temperature spectrum of (3) thus shows two CO resonances whereas at $-40^\circ C$, when the exchange process $A \rightleftharpoons C \rightleftharpoons A$ is frozen out, four signals are observed. In contrast, in the upper temperature limiting spectrum of [Mo₂(μ -PhC₂Ph)(CO)₄(η -C₅H₅)₂] a single CO peak is observed and at low temperatures four resonances are seen.¹⁶ With (3) we cannot rule out the likely possibility that two closely related isomers of type **A** are present at $-40^\circ C$ but are interconverted by the process $A \rightleftharpoons B \rightleftharpoons A$ (Scheme 1).

In the ¹³C-¹H} n.m.r. spectrum of (3) at room temperature three resonances for the C₅Et₄(C₆H₄Me-4) nuclei were observed (Table 2). However, when the spectrum was measured

at $-40^\circ C$ five resonances are seen (δ 109.8, 109.2, 108.8, 107.6, and 107.3 p.p.m.) in accord with chirality at the tungsten centre, a situation which results when the process $A \rightleftharpoons C \rightleftharpoons A$ becomes slow on the n.m.r. time-scale. Similar behaviour is shown by the signals for the CH₂CH₃ groups, there being six peaks in the room-temperature spectrum and 12 in the spectrum measured at $-40^\circ C$.

No resonances were seen in the ¹³C-¹H} n.m.r. spectra of (2) or (3) which could be assigned to the ligated acetylenic carbon atoms. In (2) it is probable that these signals lie in the aromatic region, where many resonances were observed (Table 2). For a bridging μ -C₂R₂ group the resonances generally appear near the signal for the C₅H₅ group but are often not observed.

The reaction between (1a) and the methylmethylidyne-tungsten compound [W(\equiv CMe)(CO)₂(η -C₅H₅)] was also studied. The product (4) proved to be isostructural with (3), based on the spectroscopic properties. In the i.r. spectrum the pattern of bands in the CO stretching region for (4) is identical with that for (3). The ¹³C-¹H} n.m.r. spectrum (room temperature) of (4) revealed that it does not undergo a process which interconverts the pairs of CO ligands on each metal centre ($A \rightleftharpoons C \rightleftharpoons A$, Scheme 1). There are four CO resonances and five signals for the C₅MePh₄ ring in the room-temperature spectrum. Moreover, in the spectrum of (4) peaks at 91.1 and 89.8 p.p.m. are tentatively assigned to the μ -C₂



Scheme 2. cp = η -C₅H₅. (i) + [W(\equiv CR)(CO)₂(cp)] (R = C₆H₄Me-4 or Me); (ii) -CO; (iii) +CO

Table 3. Selected internuclear distances (Å) and angles (°) for [W₂(μ -CO)₂(CO)(η -PhC₂Ph){ η -C₅Ph₄(C₆H₄Me-4)}(η -C₅H₅)] (2), with estimated standard deviations in parentheses

W(1)–W(2)	2.586(1)	W(2)–C(01)	2.467(15)
W(1)–C(01)	1.949(12)	W(2)–C(9)	1.988(11)
W(1)–C(9)	2.446(15)	C(9)–O(9)	1.160(15)
C(01)–O(01)	1.17(2)	C(8)–O(8)	1.16(2)
W(1)–C(8)	1.964(14)	W(2)–C(7)	2.15(2)
W(2)–C(6)	2.120(14)		
C(6)–C(7)	1.31(2)		
W(2)–W(1)–C(8)	85.5(3)	W(1)–W(2)–C(6)	110.2(3)
W(2)–W(1)–C(9)	46.4(2)	W(1)–W(2)–C(7)	106.7(3)
W(2)–W(1)–C(01)	64.1(4)	C(9)–W(2)–C(01)	107.9(4)
C(8)–W(1)–C(9)	90.1(6)	C(9)–W(2)–C(6)	115.0(5)
C(8)–W(1)–C(01)	92.3(5)	C(9)–W(2)–C(7)	81.6(5)
C(9)–W(1)–C(01)	110.0(5)	C(01)–W(2)–C(6)	86.2(5)
W(1)–W(2)–C(9)	63.1(4)	C(01)–W(2)–C(7)	108.5(5)
W(1)–W(2)–C(01)	45.3(2)	C(6)–W(2)–C(7)	35.6(5)
W(1)–C(8)–O(8)	177.6(11)	W(1)–C(9)–O(9)	121.9(8)
W(1)–C(01)–O(01)	167.4(11)	W(2)–C(9)–O(9)	167.0(9)
W(2)–C(01)–O(01)	121.9(8)		
W(2)–C(7)–C(6)	70.8(10)	W(2)–C(6)–C(7)	73.6(9)
W(2)–C(6)–C(61)	142.8(12)	W(2)–C(7)–C(71)	144.4(9)

nuclei. A possible explanation for the absence of the higher-energy exchange process in (4) in solution is steric interaction between the C₅MePh₄ ring and the μ -RC₂R ligand in the sterically hindered intermediate C (Scheme 1).¹⁷

The reaction between [W(\equiv CC₆H₄Me-4)(CO)₂(η -C₅H₅)] and compound (1c), containing the unsymmetrical alkyne ligand MeC \equiv CPh, was also investigated. It was anticipated that a mixture of isomeric species would be formed, arising from different arrangements of the Me, Ph, and C₆H₄Me-4 substituents on the pentasubstituted cyclopentadienyl ligand. Two products could be separated based on differences in solubility

Table 4. Selected internuclear distances (Å) and angles (°) for [W₂(μ -EtC₂Et)(CO)₄{ η -C₅Et₄(C₆H₄Me-4)}(η -C₅H₅)] (3), with estimated standard deviations in parentheses

W(1)–W(1)	3.003(1)	W(2)–C(33)	2.160(9)
W(1)–C(33)	2.169(9)	W(2)–C(34)	2.273(10)
W(1)–C(34)	2.161(9)	W(2)–C(3)	1.969(10)
W(1)–C(1)	1.976(9)	W(2)–C(4)	1.974(14)
W(1)–C(2)	1.970(11)	C(3)–O(3)	1.141(13)
C(1)–O(1)	1.150(11)	C(4)–O(4)	1.152(16)
C(2)–O(2)	1.134(13)	C(34)–C(35)	1.460(14)
C(31)–C(32)	1.515(15)	C(35)–C(36)	1.510(17)
C(32)–C(33)	1.511(13)		
C(33)–C(34)	1.361(14)		
W(2)–W(1)–C(33)	45.9(2)	W(1)–W(2)–C(33)	46.9(2)
W(2)–W(1)–C(34)	49.0(3)	W(1)–W(2)–C(34)	45.8(2)
W(2)–W(1)–C(1)	65.1(3)	W(1)–W(2)–C(4)	122.4(3)
W(2)–W(1)–C(2)	86.0(3)	W(1)–W(2)–C(3)	89.2(3)
C(33)–W(1)–C(34)	36.4(4)	C(33)–W(2)–C(34)	35.6(4)
C(1)–W(1)–C(2)	91.5(4)	C(3)–W(2)–C(4)	82.8(4)
C(1)–W(1)–C(33)	108.4(4)	C(3)–W(2)–C(33)	119.3(4)
C(1)–W(1)–C(34)	108.4(4)	C(3)–W(2)–C(34)	84.5(4)
C(2)–W(1)–C(33)	69.7(4)	C(4)–W(2)–C(33)	89.3(4)
C(2)–W(1)–C(34)	106.1(4)	C(4)–W(2)–C(34)	76.6(4)
W(1)–C(1)–O(1)	168.6(8)	W(2)–C(3)–O(3)	174.0(9)
W(1)–C(2)–O(2)	176.4(9)	W(2)–C(4)–O(4)	175.1(10)

and chromatographic behaviour. Structural assignments are made on the basis of i.r. and n.m.r. data and must be regarded as tentative in view of the many possible isomers which could be formed. The more soluble fraction is assigned structure (5a), and less soluble as a mixture of the diastereomeric pair (5b) and (5c). The i.r. spectra in the CO region (Table 1) were very similar to that of (3), indicating a similarity in structure, *i.e.* a C₂W₂ core involving a bridging MeC₂Ph ligand.

Isomer (5a) shows dynamic behaviour (A \rightleftharpoons C \rightleftharpoons A,

Table 5. Atomic positional (fractional co-ordinates) parameters ($\times 10^4$), with estimated standard deviations in parentheses, for compound (2)

Atom	x	y	z	Atom	x	y	z
W(1)	3 373(1)	1 464(1)	1 903(1)	C(56)	3 657(9)	2 942(10)	5 220(8)
W(2)	2 601(1)	259(1)	-37(1)	C(51)	3 826(8)	2 116(9)	4 413(7)
C(1)	4 758(8)	2 473(9)	3 493(8)	C(6)	1 752(9)	1 255(10)	-753(9)
C(12)	6 103(10)	1 253(10)	3 368(10)	C(62)	-79(10)	810(12)	-1 335(10)
C(13)	7 023(10)	982(11)	3 847(10)	C(63)	-1 054(11)	916(15)	-1 883(13)
C(14)	7 531(10)	1 485(13)	4 919(11)	C(64)	-1 267(12)	1 597(16)	-2 390(13)
C(15)	7 140(11)	2 249(12)	5 494(10)	C(65)	-454(14)	2 181(19)	-2 344(16)
C(16)	6 182(10)	2 524(10)	5 000(9)	C(66)	529(11)	2 085(14)	-1 820(12)
C(11)	5 694(8)	2 066(9)	3 951(8)	C(61)	736(9)	1 414(11)	-1 270(9)
C(2)	4 616(8)	3 145(9)	2 944(8)	C(7)	2 658(9)	1 441(10)	-646(9)
C(21)	5 399(8)	3 514(8)	2 712(8)	C(72)	3 194(10)	3 205(11)	-684(9)
C(22)	5 186(10)	3 545(9)	1 805(9)	C(73)	3 788(12)	3 789(13)	-878(11)
C(23)	5 909(10)	3 939(9)	1 651(9)	C(74)	4 472(11)	3 237(12)	-1 233(10)
C(24)	6 873(10)	4 325(10)	2 374(10)	C(75)	4 611(10)	2 130(13)	-1 340(10)
C(25)	7 121(10)	4 317(11)	3 287(10)	C(76)	4 036(9)	1 530(11)	-1 117(9)
C(26)	6 388(8)	3 912(9)	3 477(8)	C(71)	3 300(8)	2 057(10)	-817(8)
C(24a)	7 786(38)	4 619(42)	2 223(37)	C(81)	1 366(11)	-1 463(12)	-1 090(12)
C(3)	3 669(8)	3 493(10)	2 740(8)	C(82)	1 664(11)	-1 307(11)	-1 752(10)
C(32)	2 321(10)	4 050(11)	1 472(9)	C(83)	2 666(11)	-1 395(11)	-1 432(11)
C(33)	1 977(12)	4 812(13)	1 065(11)	C(84)	2 971(11)	-1 607(10)	-613(11)
C(34)	2 551(15)	5 867(15)	1 405(13)	C(85)	2 203(15)	-1 664(11)	-387(11)
C(35)	3 499(13)	6 125(13)	2 188(13)	C(8)	3 436(9)	-45(10)	1 943(9)
C(36)	3 874(11)	5 383(10)	2 622(10)	C(9)	4 068(9)	795(9)	673(8)
C(31)	3 265(9)	4 295(10)	2 248(9)	O(8)	3 487(7)	-914(7)	2 004(7)
C(4)	3 208(8)	3 136(10)	3 209(8)	O(9)	4 920(5)	950(7)	917(6)
C(42)	1 619(9)	2 642(12)	3 255(9)	C(01)	1 919(9)	1 159(10)	1 209(9)
C(43)	774(10)	3 003(14)	3 449(10)	O(01)	1 058(6)	1 116(7)	966(6)
C(44)	649(12)	4 154(16)	3 733(12)	Cl(1)	9 599(7)	3 383(8)	202(7)
C(45)	1 312(11)	4 947(14)	3 822(11)	Cl(2)	8 853(10)	4 952(10)	1 557(10)
C(46)	2 134(10)	4 597(11)	3 630(9)	C(a)	9 892(33)	4 337(36)	1 394(32)
C(41)	2 299(9)	3 454(10)	3 352(8)	C(b)	1 086(28)	1 427(30)	5 074(27)
C(44a)	-173(31)	4 438(35)	3 902(31)	Cl(3)	1 548(17)	1 666(19)	6 310(17)
C(5)	3 868(8)	2 483(10)	3 683(9)	Cl(4)	101(17)	580(19)	4 123(16)
C(52)	3 966(10)	1 051(11)	4 399(9)	Cl(5)	770(33)	2 709(35)	5 821(31)
C(53)	3 972(12)	785(11)	5 138(10)	Cl(6)	-225(21)	1 176(23)	4 333(20)
C(54)	3 808(11)	1 595(12)	5 938(10)	Cl(7)	-156(21)	1 963(23)	4 805(21)
C(55)	3 683(11)	2 702(11)	5 977(10)	Cl(8)	1 516(24)	2 220(26)	6 376(23)

Scheme 1) similar to that found for (3), but the presence of two different substituents on the transversely bridged alkyne destroys the mirror symmetry of the intermediate C. Thus in the room-temperature $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum four CO resonances are observed instead of the two seen in the spectrum of (3). However, when the spectrum is measured at -40°C four additional signals due to CO groups appear. Moreover, the C_5H_5 nuclei gave rise to one peak in the room-temperature spectrum and two resonances in the -40°C spectrum as one might expect for the 'freezing' out of the process $\text{A} \rightleftharpoons \text{C} \rightleftharpoons \text{A}$, which when the R groups on the alkyne are not identical affords two non-equivalent species of type A.

The ^1H n.m.r. spectrum of (5b) and (5c) as expected showed two C_5H_5 resonances (relative intensity ca. 2:3). These signals, however, were barely resolved from one another, and not surprisingly only one Me-4 group peak was seen. Four resonances due to the C_5Me_2 protons and two signals for the bridging alkyne methyl group might have been expected for two diastereoisomers whereas two and one were observed, respectively. However, all three peaks were broad, presumably reflecting structural similarity of the two isomers resulting in a lack of resolution of these bands. The poorly resolved $^{13}\text{C}\{-^1\text{H}\}$ n.m.r. spectrum (Table 2) showed four strong CO resonances and a number of inadequately resolved weaker signals precluding any definite analysis of the species present at low temperature.

The reactions which afford compounds (2)–(5) evidently involve cleavage of $\text{W}=\text{C}$ bonds and cyclisation of alkyne and

alkylidyne groups on a tungsten or ditungsten centre. It has been shown previously¹⁸ that the reaction of certain mononuclear tungsten alkylidyne complexes with alkynes results in the formation of co-ordinated cyclopentadienyl ligands, and it has been suggested that these cyclisation reactions occur *via* tungstacyclobutadiene ring systems.

The mechanism for formation of (2)–(5) is not known but one possible pathway is shown in Scheme 2. Formation of intermediate D involves displacement of CO, a step which has precedent in the reaction of $[\text{W}(\text{CO})\{\text{PhC}_2\text{C}_6\text{H}_3(\text{OMe})_{2-3,4}\}_3]$ with PMe_2Ph to give $[\text{W}(\text{PMe}_2\text{Ph})\{\text{PhC}_2\text{C}_6\text{H}_3(\text{OMe})_{2-3,4}\}_3]$,⁹ and in the formation of numerous dimetal compounds with bridging alkylidyne ligands.¹ The conversion of D into F involves transfer of a bridging alkylidyne ligand to a terminal bonding mode, a process which also has precedent in the reaction of $[\text{W}_3(\mu\text{-CC}_6\text{H}_4\text{Me-4})_2(\mu\text{-CO})_2(\text{CO})_4(\eta\text{-C}_5\text{H}_5)_2]$ with CO to give $[\text{W}_2(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_7(\eta\text{-C}_5\text{H}_5)]$.³ The pathway from D to F would be facilitated by the ability of the alkyne ligands to function as variable electron donors, contributing either two or four electrons to tungsten,¹⁹ and the ability of tungsten to form multiple metal–metal bonds. These properties would allow the tungsten centres to maintain 18-electron shells. In this context, the previously observed²⁰ oligomerisation of alkynes at a dimolybdenum centre may be relevant, since in these processes intermediates of variable metal–metal bond multiplicity have been characterised. The conversion of F into G may involve the intermediacy of a tungstacyclobutadiene structure,¹⁸ or possibly G might form from E *via* C–C bond

Table 6. Atomic positional (fractional co-ordinates) parameters ($\times 10^4$), with estimated standard deviations in parentheses, for compound (3)

Atom	x	y	z	Atom	x	y	z
W(1)	3 301(1)	1 393(1)	3 265(1)	C(32)	1 510(9)	-166(7)	2 193(5)
W(2)	1 650(1)	251(1)	3 941(1)	C(33)	1 896(8)	458(7)	2 840(5)
O(1)	4 202(6)	1 013(5)	4 883(3)	C(34)	1 499(8)	1 317(7)	3 021(6)
O(2)	4 177(6)	-534(5)	2 771(4)	C(35)	552(8)	1 864(8)	2 654(6)
O(3)	1 228(7)	1 959(5)	4 911(4)	C(36)	143(10)	2 661(8)	3 083(8)
O(4)	-938(7)	378(6)	3 482(4)	C(111)	2 875(7)	3 841(7)	3 532(5)
C(1)	3 777(8)	1 093(6)	4 294(5)	C(112)	2 650(8)	4 710(7)	3 195(6)
C(2)	3 858(8)	158(7)	2 974(5)	C(113)	2 101(9)	5 443(8)	3 498(6)
C(3)	1 406(8)	1 366(7)	4 531(5)	C(114)	1 768(9)	5 324(7)	4 159(6)
C(4)	22(12)	358(7)	3 626(6)	C(115)	1 981(9)	4 466(7)	4 505(5)
C(11)	3 506(7)	3 092(7)	3 233(4)	C(116)	2 505(8)	3 731(7)	4 203(5)
C(12)	3 335(7)	2 736(7)	2 504(5)	C(117)	1 208(10)	6 112(8)	4 498(7)
C(13)	4 231(8)	2 113(6)	2 416(5)	C(121)	2 469(8)	3 085(7)	1 891(5)
C(14)	4 990(7)	2 080(6)	3 100(5)	C(122)	2 959(9)	3 787(7)	1 408(5)
C(15)	4 548(8)	2 698(6)	3 585(5)	C(131)	4 451(9)	1 648(7)	1 731(5)
C(21)	2 254(8)	-1 334(7)	3 808(5)	C(132)	5 380(10)	2 131(8)	1 417(6)
C(22)	3 020(9)	-911(7)	4 365(5)	C(141)	6 086(8)	1 571(7)	3 245(6)
C(23)	2 426(10)	-656(7)	4 909(5)	C(142)	7 094(8)	2 234(8)	3 240(7)
C(24)	1 324(10)	-928(7)	4 708(6)	C(151)	5 140(8)	2 990(7)	4 319(5)
C(25)	1 229(10)	-1 338(7)	4 012(6)	C(152)	5 628(10)	4 000(8)	4 320(6)
C(31)	1 702(11)	250(8)	1 480(6)				

formation on the dimetal centre.²⁰ It is suggested that G is a common intermediate for affording products with either a structure like that of (2), or complexes with a structure like those of (3)–(5). The two structural types differ in number of CO ligands and in whether there is a bridging or a terminal alkyne ligand present. Pyrolysis of compound (3), however, did not result in loss of CO and a rearrangement to a structure similar to that of (2). The bridged alkyne–ditungsten compounds are thermally very stable. Moreover, although (2) was observed to react with CO, it did not convert to a tetracarbonyl alkyne-bridged ditungsten species akin to (3). Monitoring of the reaction by i.r. suggested that (2) was converted into the hexacarbonyl ditungsten compound $[\text{W}_2(\text{CO})_6\{\eta\text{-C}_5\text{Ph}_4(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)]$. This reaction is complex and requires further study, but it is evident that (3)–(5) are not formed *via* an intermediate with a structure similar to that of (2).

It is difficult to suggest a reason why the reaction between (1a) and $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ affords (2), whereas all the other reactions studied give products in which an alkyne molecule transversely bridges the metal–metal bond. Excess CO is required in the formation of (3)–(5), and its source may be *via* thermal decomposition of the reactants $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (R = $\text{C}_6\text{H}_4\text{Me-4}$ or Me). It is noteworthy that compound (4) is the species formed in highest yield (Table 1) in a reaction using an excess of the methylmethylidynetungsten compound which is thermally less stable than its tolylmethylidyne analogue. Steric factors may also determine the structural character of the final products.

Experimental

Light petroleum refers to that fraction of b.p. 40–60 °C. Experiments were carried out using Schlenk-tube techniques, under a dry oxygen-free nitrogen atmosphere. The i.r. spectra were measured with Nicolet MX-10 and MX-5 spectrophotometers and n.m.r. spectra with JNM FX 90Q and FX 200 spectrometers. Alumina used in chromatography was BDH aluminium oxide (Brockman activity II). The compounds $[\text{W}(\equiv\text{CR})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (R = Me or $\text{C}_6\text{H}_4\text{Me-4}$)²¹ and $[\text{W}(\text{CO})(\text{R}^1\text{C}_2\text{R}^2)_3]$ (R¹ = R² = Ph or Et; R¹ = Me, R² = Ph)^{5,7} were prepared by literature methods. Analytical and other data for the new compounds are given in Table 1.

Reactions of the Compound $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$.—(a) *With $[\text{W}(\text{CO})(\text{PhC}_2\text{Ph})_3]$.* A mixture of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (0.25 g, 0.60 mmol) and $[\text{W}(\text{CO})(\text{PhC}_2\text{Ph})_3]$ (0.46 g, 0.60 mmol) in octane (20 cm³) was refluxed for 1 h. Upon cooling to room temperature, solvent was decanted and the dark residue washed with light petroleum (7 × 20 cm³) and extracted with dichloromethane (5 cm³). The extract was chromatographed (20 × 2 cm column) and elution with diethyl ether gave a red solution which afforded, on concentration *in vacuo* and cooling to -20 °C, red-brown microcrystals of $[\text{W}_2(\mu\text{-CO})_2(\text{CO})(\eta\text{-PhC}_2\text{Ph})\{\eta\text{-C}_5\text{Ph}_4(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)]$ (2) (0.18 g).

(b) *With $[\text{W}(\text{CO})(\text{EtC}_2\text{Et})_3]$.* An octane (30 cm³) solution of $[\text{W}(\text{CO})(\text{EtC}_2\text{Et})_3]$ (0.54 g, 1.2 mmol) and $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (0.48 g, 1.2 mmol) was refluxed for 1 h. Solvent was removed *in vacuo* and the residue extracted with light petroleum (5 × 30 cm³) and the extracts chromatographed. Elution with light petroleum–diethyl ether (4:1) gave a red solution which upon removal of solvent *in vacuo* afforded red microcrystals of $[\text{W}_2(\mu\text{-EtC}_2\text{Et})(\text{CO})_4\{\eta\text{-C}_5\text{Et}_4(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)]$ (3) (0.32 g).

(c) *With $[\text{W}(\text{CO})(\text{MeC}_2\text{Ph})_3]$.* A mixture of $[\text{W}(\equiv\text{CC}_6\text{H}_4\text{Me-4})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (0.49 g, 1.2 mmol) and $[\text{W}(\text{CO})(\text{MeC}_2\text{Ph})_3]$ (0.67 g, 1.2 mmol) was refluxed (1 h) in octane (30 cm³). Solvent was removed *in vacuo*, and the residue was extracted with light petroleum (5 × 30 cm³) and the extracts chromatographed. Elution with light petroleum–diethyl ether (1:1) gave a dark red eluate which on removal of solvent *in vacuo* afforded dark red microcrystals of $[\text{W}_2(\mu\text{-MeC}_2\text{Ph})(\text{CO})_4\{\eta\text{-C}_5\text{Me}_2\text{Ph}_2(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)]$ (5a) (0.13 g).

The remaining less soluble residue from the reaction was extracted with dichloromethane and the extracts chromatographed. Elution with the same solvent gave, after removal of solvent *in vacuo*, red microcrystals of a mixture of the two isomers $[\text{W}_2(\mu\text{-MeC}_2\text{Ph})(\text{CO})_4\{\eta\text{-C}_5\text{Me}_2\text{Ph}_2(\text{C}_6\text{H}_4\text{Me-4})\}(\eta\text{-C}_5\text{H}_5)]$ (5b) and (5c) (0.06 g).

Reaction of the Compound $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ with $[\text{W}(\text{CO})(\text{PhC}_2\text{Ph})_3]$.—A mixture of $[\text{W}(\text{CO})(\text{PhC}_2\text{Ph})_3]$ (0.45 g, 0.60 mmol) and $[\text{W}(\equiv\text{CMe})(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ (0.25 g, 0.75 mmol) in octane (20 cm³) was refluxed for 1 h. Solvent was removed *in vacuo*, and the residue extracted with light petroleum (5 × 30

cm³). Chromatography of the extracts, eluting with light petroleum–diethyl ether (1:1), gave a red solution. Removal of solvent *in vacuo* gave red-brown microcrystals of [W₂(μ-PhC₂Ph)(CO)₄(η-C₅MePh₄)(η-C₅H₅)] (4) (0.56 g).

Crystal Structure Determinations.—(a) [W₂(μ-CO)₂(CO)(η-PhC₂Ph){η-C₅Ph₄(C₆H₄Me-4)}(η-C₅H₅)] (2). Crystals of (2) grow as red-brown needles from dichloromethane–light petroleum. Diffracted intensities were recorded at 200 K on a Nicolet P3m four-circle automated diffractometer. Of the total 7 283 independent reflections, measured to 2θ ≤ 50°, 5 704 had $I \geq 2\sigma(I)$ where $\sigma(I)$ is the estimated standard deviation based on counting statistics, and only these were used in the refinement of the structure. The intensity data were corrected for Lorentz, polarisation, and X-ray absorption effects; the last by numerical methods (crystal size ca. 0.4 × 0.1 × 0.1 mm, faces indexed <0 1 1> and <1 0 0>).

Crystal data. C₅₈H₄₂O₃W₂·CH₂Cl₂, $M = 1\,238.6$, triclinic, $a = 14.895(9)$, $b = 12.852(7)$, $c = 16.228(8)$ Å, $\alpha = 114.90(4)$, $\beta = 114.33(4)$, $\gamma = 87.70(5)^\circ$, $U = 2\,534$ Å³, $Z = 2$, $D_c = 1.63$ g cm⁻³, $F(000) = 1\,158$, space group $P\bar{1}$ (no. 2), Mo- K_α X-radiation (graphite monochromator), $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 47.3$ cm⁻¹.

(b) [W₂(μ-EtC₂Et)(CO)₄{η-C₅Et₄(C₆H₄Me-4)}(η-C₅H₅)] (3). Crystals of (3) grow as red prisms from cold light petroleum solutions. That chosen for data collection was of dimensions ca. 0.1 × 0.5 × 0.5 mm. Data were collected as for (2). Of the total 4 315 independent reflections (2θ ≤ 45°), 3 461 with $I \geq 2\sigma(I)$ were used for structure solution and refinement, after corrections for Lorentz, polarisation, and absorption effects; the last by an empirical method based on an ellipsoidal model with azimuthal scan data.²²

Crystal data. C₃₅H₄₂O₄W₂, $M = 894.4$, monoclinic, $a = 12.124(4)$, $b = 14.033(8)$, $c = 18.82(1)$ Å, $\beta = 99.29(4)^\circ$, $U = 3\,160(2)$ Å³, $Z = 4$, $D_c = 1.88$ g cm⁻³, $F(000) = 1\,727$, space group $P2_1/c$ (no. 14), $\mu(\text{Mo-}K_\alpha) = 74.69$ cm⁻¹.

Structure solution and refinement for (2) and (3). Both structures were solved by conventional heavy-atom and electron-density difference methods and refined by blocked-cascade least squares.²² Anisotropic thermal parameters were used for all non-hydrogen atoms, except for the disordered Me-4 group [C(24a) and C(44a)] in (2), which was refined isotropically using a 50:50 disordered model. In (2), a dichloromethane molecule of crystallisation was found to occupy equally two different lattice sites. While one of the solvent molecules of half occupancy was well ordered and refined anisotropically, the other was found to have an orientational disorder, with the chlorine atoms being isotropically refined as equally occupying six different positions. Hydrogen atoms in both structures were incorporated in calculated positions (C–H 0.96 Å) with isotropic thermal parameters equal to 1.2 times the equivalent isotropic thermal parameter of the attached carbon atom. For (2), refinement converged at $R\,0.048$ ($R'\,0.047$); with weights applied according to the scheme $w = [\sigma^2(F_o) + 0.000\,7|F_o|^2]^{-1}$ giving a satisfactory weight analysis in terms of $|F_o|$ and $\sin\theta/\lambda$. For (3), refinement led to $R\,0.040$ ($R'\,0.041$), with weights applied according to the scheme $w = [\sigma^2(F_o) + 0.000\,3|F_o|^2]^{-1}$. All computations were carried out on an Eclipse S230 (Data General) computer with the SHELXTL system of programs.²² Atomic scattering factors were taken from ref. 23, as were the anomalous dispersion corrections and mass absorption

coefficients. Atomic co-ordinates for the two structures are given in Tables 5 and 6.

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