Synthesis and Reactions of Binuclear Molybdenocene and Tungstenocene Derivatives

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The tetramer $[\{Mo(\eta\text{-}C_5H_5)_2HLi\}_4]$ reacts with N_2O giving the yellow dimers *cis*- and *trans*-$[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta\text{-}C_5H_4)_2]$. These thermally rearrange to the green dimer $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$. Protonation of the latter gives $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}H)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][PF_6]$. Photolysis of $[Mo(\eta\text{-}C_5H_5)_2H_2]$ or the yellow dimers gives a red dimer $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$. Prolonged treatment of the four neutral dimers with aqueous acid gives $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][PF_6]_2$. The red and yellow dimers react with iodine giving $[\{Mo(\eta\text{-}C_5H_5)I\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ and the corresponding reaction with the green dimer yields $[\{Mo(\eta\text{-}C_5H_5)I\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$. The red dimer also adds to methyl bromide giving $[\{Mo(\eta\text{-}C_5H_5)Me\}\{Mo(\eta\text{-}C_5H_5)Br\}(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$, whereas the yellow dimer reacts with methyl iodide to give $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$. Photolysis of $[W(\eta\text{-}C_5H_5)_2H_2]$ in diethyl ether gives *cis*- and *trans*-$[\{W(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$ and the cation $[W(\eta\text{-}C_5H_5)_2(\eta\text{-}C_2H_4)H]^+$. Thermal decomposition of $[W(\eta\text{-}C_5H_5)_2MeH]$ in cyclohexane gives isomers of the compound $[\{W(\eta\text{-}C_5H_5)_2Me\}\{W(\eta\text{-}C_5H_5)H\}(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$.

THE electron-rich compound $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (1) has been shown to form derivatives which contain covalent bonds between the molybdenum and electrophilic ligand atoms such as Li,[1] Mg,[2] and Al.[3] Indeed the radical $[Mo(\eta\text{-}C_5H_5)_2H]^\cdot$ has been likened to a simple alkyl radical,[1] so that the tetramer $[\{Mo(\eta\text{-}C_5H_5)_2HLi\}_4]$ may be regarded as analogous to an alkyl-lithium compound and reacts, for example, with carbon dioxide giving the monocarbonyl, $[Mo(\eta\text{-}C_5H_5)_2(CO)]$, in very high yield.

Nitrous oxide N_2O is isoelectronic with CO_2 and we therefore explored the reaction between N_2O and the tetramer $[\{Mo(\eta\text{-}C_5H_5)_2HLi\}_4]$ in an attempt to prepare the dinitrogen derivative, $[Mo(\eta\text{-}C_5H_5)_2(N_2)]$. However, this study led to an extensive chemistry of binuclear molybdenum derivatives which has been briefly communicated [4] and which we now present in full below.

RESULTS

Treatment of a suspension of the tetramer $[\{Mo(\eta\text{-}C_5H_5)_2HLi\}_4]$ in toluene or light petroleum–diethyl ether with nitrous oxide results in an exothermic reaction giving a red solution from which, after removal of solvent, a red solid was obtained. Washing this with cold methanol and acetone gave a lemon-yellow solid (2). This was slightly soluble in toluene, acetone, 1,2-dimethoxyethane, and tetrahydrofuran.

Recrystallisation of (2) from these solutions gave another yellow compound (3) which was similar to compound (2). The differences in the i.r. spectra of (2) and (3) are slight, but are sufficient to enable identification of greater than 20% of (2) in (3) and *vice versa*. Both (2) and (3) are oxidised in air within a few minutes, but appear to be stable at 0 °C under a dinitrogen atmosphere. Solutions of (2) and (3) turn green after a few hours at room temperature (see below). The low solubility of (2) and (3) and their thermal instability in solution necessitated the use of large volumes of solvent and maintaining the temperature below 0 °C when exploring their chemistry.

When solutions of (2) or (3) are stirred at 70 °C for 1 h the solids dissolve and the initially light yellow solutions turn dark green, yielding excellent dark green crystals (4). Compound (4) is rapidly oxidised by air both in solution and as the pure crystalline material. It readily reacts with moisture (see below) and rigorously dry solvents were essential when handling the compound.

When the conversion of (2) or (3) to (4) was carried out under vacuum, g.l.c. analysis showed that no cyclopentadiene was evolved during the reaction and Töepler pump measurements showed that no gas such as dihydrogen was evolved. When the conversion was monitored in a sealed ^1H n.m.r. tube there was no evidence at any time for the presence of species other than (2)—(4).

Treatment of (4) with aqueous hexafluorophosphoric acid gave red-brown air-sensitive microcrystals (5). Compound (5) is soluble in acetone, acetonitrile, and dimethyl sulphoxide. Prolonged treatment of a solution of (4) in acetone with aqueous HPF_6 gave yellow-brown crystals (6). Reduction of (6) with $Na[AlH_2(OCH_2CH_2OMe)_2]$ in benzene gave the parent compound (4) in good yield. The cation (5) could also be deprotonated with aqueous potassium hydroxide to give (4).

The ^1H n.m.r. spectrum of (4) shows the presence of Mo–H groups, $\eta\text{-}C_5H_5$ groups, and four protons which constitute an AA′BB′ coupling system and which can be assigned to a C_5H_4 group. The AA′BB′ protons appear as two triplets and have similar coupling constants to those observed in the spectrum of bis(fulvalene)di-iron.[5] There was no observable change in the ^1H n.m.r. spectrum of (4) when the sample was cooled to −90 °C. The i.r. spectrum of (4) shows a band at 1 795 cm^{-1} which may be assigned to a terminal Mo–H stretching mode. No other unambiguously assignable bands were noted in the complex i.r. spectrum, and the spectrum is consistent with a number of possible structures.

The low solubility of compounds (2) and (3) coupled with their thermal instability caused severe problems in the determination of the ^1H n.m.r. spectra. It was, however, possible to determine the spectra of a mixture of the compounds using pulse Fourier-transform techniques. The data obtained are given in the Table. There are bands at τ 18.55 and 18.65, assignable to metal–hydrogen groups. There are also sharp bands at τ 5.32 and 5.35 assignable to $\eta\text{-}C_5H_5$ groups. The relative intensity of these bands changes as compounds (2) and (3) rearrange to (4). These changes suggest that the band at τ 5.35 corresponds to the resonance at τ 18.55, whilst the resonance at τ 5.32 changes intensity in the same manner as that of at τ 18.65. The spectra may be interpreted in terms of the initial species (2) changing to (3) whilst either one or both of these are converted into (4) at a rate similar to that at which (2) is converted into (3). The mass spectra of (2)—(4) are identical, the highest observed principal peak of *m/e* 450 corresponding to the stoicheiometry $[C_{20}H_{18}Mo_2]^+$. This stoicheiometry is at variance with the number of hydrogens clearly indicated to be present by the ^1H n.m.r. data for (4), *i.e.* in ratio corresponding to η-C_5H_5 : η-C_5H_4 : Mo–H. We assume, therefore, that the peak at *m/e* 450 corresponds to the parent ion less dihydrogen. The lack of the parent-ion peak is not surprising when it is noted that the elimination of dihydrogen from metal hydrides may occur very readily and even the thermally stable dihydride $[Mo(\eta\text{-}C_5H_5)_2H_2]$ (1) shows only a very weak parent-ion peak in the mass spectrum compared to the intense band arising from the $P^+ - 2$ ion. The mass spectrum of (3) also shows peaks assignable to the fragments $[C_{20}H_{16}Mo_2]^+$ and $[C_{20}H_{16}Mo_2]_2{}^+$.

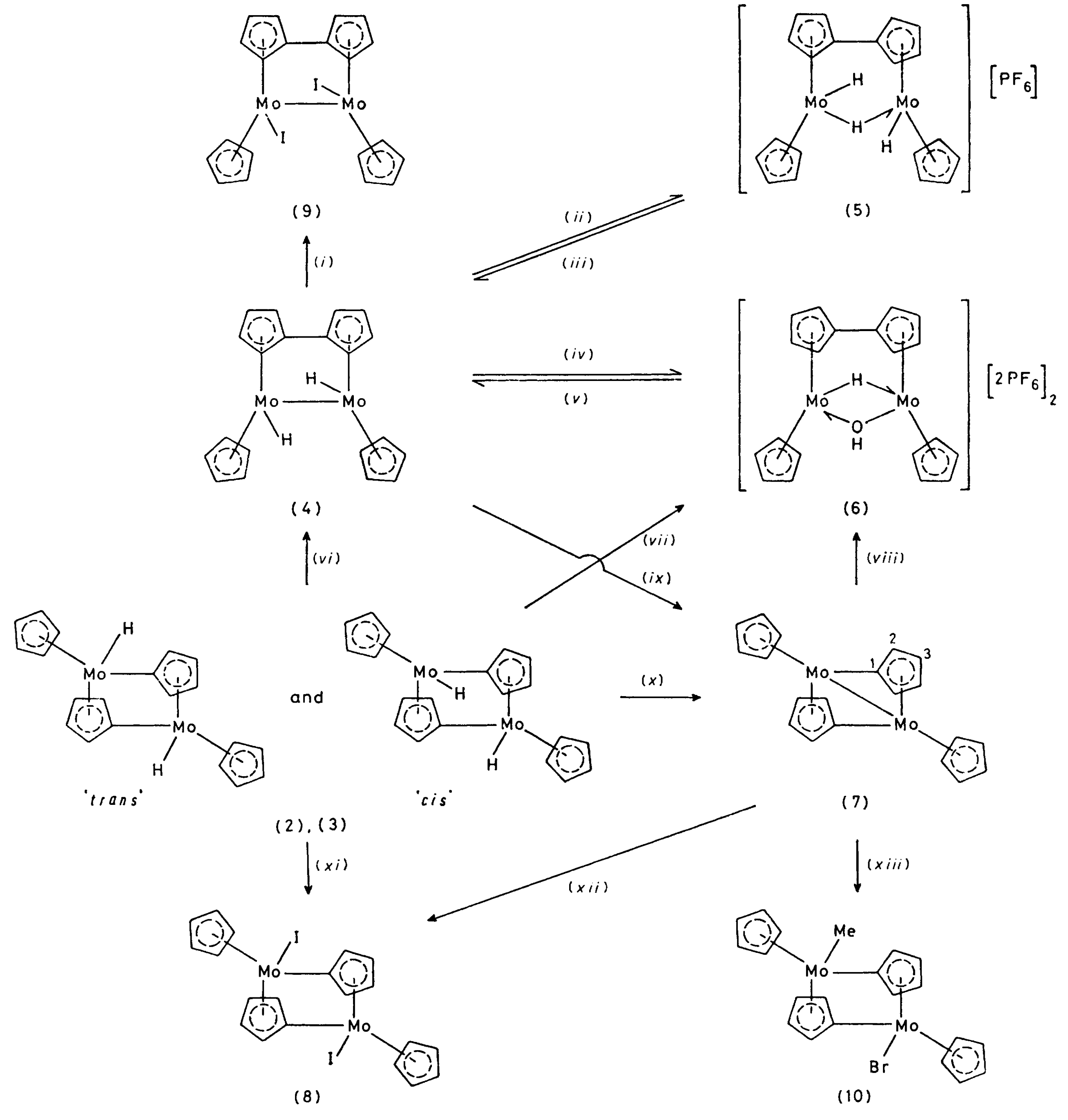
Analytical and spectroscopic data

Compound	Colour	Analytical data (%) [a]			N.m.r. data [b]
		C	H	I,Br	
(2) cis- or *trans*-$[\{Mo(C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Yellow	53.1 (53.1)	4.5 (4.4)		5.35, *s*, C_5H_5; 18.55, *s*, Mo–H; other complex bands around τ 5—6 [c,d]
(3)	Yellow	53.1 (53.1)	4.6 (4.4)		5.32, *s*, C_5H_5; 18.65, *s*, Mo–H; other complex bands around τ 5—6 [c,d]
(4) $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$	Green	53.0 (53.1)	4.5 (4.4)		5.47, **10**, *s*, $2C_5H_5$; 6.01, **4**, *t* (J = 2.2), $2(H_A,H_{A'})$; 6.53, **4**, *t* (J = 2.2), $2(H_B,H_{B'})$; 19.81, **2**, *s*, 2Mo–H. ^{13}C n.m.r. (δ): 81.43, C^1; 77.59, C_5H_5; 69.21, C^2 or C^3; 67.84, C^3 or C^2 [e]
(5) $[\{Mo(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}H)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)][PF_6]$	Red	40.7 (40.1)	3.4 (3.5)		4.94, **10**, *s*, $2C_5H_5$; 5.03, **4**, *t* (J = 2.4), $2(H_A,H_{A'})$; 5.11, **4**, *t* (J = 2.4), $2(H_B,H_{B'})$; 22.22, **3**, *s*, MoH_3Mo [f]
(6) $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}H)(\mu\text{-}OH)(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]\text{-}[PF_6]_2$	Yellow-brown	31.6 (31.7)	2.7 (2.6)		2.67, **1**, *s*, OH; 3.10, **2**, *c*, $2H_A$; 4.03, **10**, *s*, $2C_5H_5$; 4.11, **2**, *c*, $2H_C$; 4.30, **2**, *c*, $2H_C$; 4.99, **2**, *c*, 2H; 21.15, **1**, *s*, MoHMo [c]
(7) $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Dark red	53.4 (53.3)	4.5 (4.1)		4.48, **2**, *c*, $2H_A$; 5.03, **2**, *c*, $2H_B$; 5.30, **10**, *s*, $2C_5H_5$; 5.81, **2**, *c*, $2H_C$; 6.74, **2**, *c*, $2H_D$
(8) $[\{Mo(\eta\text{-}C_5H_5)I\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Dark brown	33.9 (34.1)	2.6 (2.6)	36.6 (36.1)	4.16, **2**, *c*, $2H_A$; 4.76, **10**, *s*, $2C_5H_5$; 5.40, **2**, *c*, $2H_B$; 5.50, **2**, *c*, $2H_C$; 5.64, **2**, *c*, $2H_D$ [g]
(9) $[\{Mo(\eta\text{-}C_5H_5)I\}_2(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$	Light brown	34.0 (34.1)	2.7 (2.7)	35.9 (36.1)	Insoluble
(10) $[\{Mo(\eta\text{-}C_5H_5)Me\}\{Mo(\eta\text{-}C_5H_5)Br\}(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Yellow-brown	46.1 (46.2)	4.2 (3.9)	14.9 (14.7)	5.28, **1**, *c*, H^1; 5.41, *ca.* **5**, *s*, (C_5H_5); 5.46, *ca.* **5**, *s*, C_5H_5; 5.67, **2**, *c*, $H^2 + H^3$; 5.98, **1**, *c*, H^4; 6.84, **1**, *c*, H^5; 6.95, **1**, *c*, H^6; 7.11, **1**, *c*, H^7; 11.58, **3**, *s*, CH_3 [f,g]
(12) *trans*-$[\{W(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Yellow	37.9 (38.2)	3.2 (3.2)		4.91, **2**, *c*, $2H_A$; 5.23, **2**, *c*, $2H_B$; 5.36, **12**, *s*, $2H_C + 2C_5H_5$; 6.28, **2**, *c*, $2H_D$; 20.51, **2**, *s*, 2W–H
(13) *cis*-$[\{W(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Yellow	38.5 (38.2)	3.1 (3.2)		4.81, **2**, *c*, $2H_A$; 5.32, **14**, *d* (J = 0.7), $2H_B + 2H_C + 2C_5H_5$; 6.27, **2**, *c*, $2H_D$; 20.59, **2**, *c*, 2W–H
(15) *cis-* or *trans-* $[\{W(\eta\text{-}C_5H_5)H\}\{W(\eta\text{-}C_5H_5)Me\}(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2]$	Yellow	39.6 (39.3)	3.3 (3.4)		4.54, **1**, *c*, H^1; 5.01, **1**, *c*, H^2; 5.26, **1**, *c*, H^3; 5.43, *ca.* **5**, *d* (J = 0.6), C_5H_5; 5.52, *ca.* **5**, *s*, C_5H_5; 5.65, **1**, *c*, H^4; 6.17, **1**, *c*, H^5; 6.24, **1**, *c*, H^6; 6.39, **1**, *c*, H^7; 9.73, **3**, *s* [$J(^{183}W\text{–}^1H)$ = 2.5], W–Me; 21.48, **1**, *s*, W–H [h]
(16)	Yellow				4.88, **1**, *c*, H^1; 5.05, **1**, *c*, H^2; 5.26, **1**, *c*, H^3; 5.46, *ca.* **5**, *d* (J = 0.6), C_5H_5; 5.55, *ca.* **5**, *s*, C_5H_5; 5.79, **1**, *c*, H^4; 6.09, **1**, *c*, H^5; 6.18, **1**, *c*, H^6; 6.31, *c*, H^7; 9.59, **3**, *s* [$J(^{183}W\text{–}^1H)$ = 2.5], W–Me; 21.41, **1**, *s*, W–H [h,i]
(17) $[\{Mo(\eta\text{-}C_5H_5)\}_2(\mu\text{-}OEt)(\mu\text{-}\sigma:\eta^5\text{-}C_5H_4)_2][PF_6]$	Dark red	41.6 (41.3)	3.9 (3.6)		3.71, **2**, *c*, $2H_A$; 4.85, **10**, *s*, $2C_5H_5$; 5.29, **2**, *c*, $2H_B$; 5.63, **2**, *c*, $2H_C$; 6.41, **2**, *c*, $2H_D$; 7.06, **2**, *q* (J = 7), $-CH_2-$; 9.44, **3**, *t* (J = 7), CH_3 [f]

[a] Calculated values are given in parentheses. [b] 90 MHz in C_6D_6 unless otherwise indicated. Data given as: chemical shift, **relative intensity**, *multiplicity* (J in Hz), assignment. [c] In $(CD_3)_2CO$. [d] Determined by pulse Fourier-transform ^1H n.m.r., from analysis after 500, 2 000, and 2 330 scans, ending 4 h after the initial preparation of the solution. [e] Broad-band decoupled; C^1, C^2, and C^3 are assigned to carbons of a C_5H_5 group. Assignment of C^2 and C^3 is uncertain. [f] In CD_3CN. [g] In $(CD_3)_2SO$. [h] H^1—H^7 are the ABCD hydrogens of two C_5H_4 groups. H^8 is presumed to be hidden within the resonances of the two C_5H_5 groups. [i] The spectrum was obtained by subtraction of that of pure (16) from that of a mixture of (15) and (16).

We conclude that (2)—(4) are closely related and probably isomers and that the analytical, mass spectral, and ^1H n.m.r. data taken together indicate that the compounds are dimers of stoicheiometry $C_{20}H_{20}Mo_2$.

The ^1H n.m.r. spectrum of (5) shows a sharp singlet at τ 4.94 assignable to η-C_5H_5 protons. There is a complex band centred at τ 4.0 with the appearance characteristic of an AA′BB′ system. In addition there is a sharp singlet at τ 22.22 of intensity corresponding to three hydrogens. The



SCHEME 1 (*i*) I_2 in MeCN, 85%; (*ii*) HPF_6 (aq), 5 min, 65%; (*iii*) K[OH], 70%; (*iv*) HPF_6 (aq) 48 h, 55%; (*v*) Na[AlH_2($OCH_2CH_2OCH_3$)$_2$], 65%; (*vi*) 70 °C in toluene, 30 min, >95%; (*vii*) HPF_6 (aq), 48 h, 50%; (*viii*) HPF_6 (aq), 48 h, 70%; (*ix*) irradiation in toluene, 20 h, 85%; (*x*) irradiation in toluene, −10 °C, 20 h, 80%; (*xi*) I_2 or MeI, *ca.* 60%; (*xii*) I_2 in MeCN, 90%; (*xiii*) MeBr, 80%. Percentages are yields throughout

i.r. spectrum of (5) shows a broad band at 1 861 cm^{-1} and a sharp band at 1 262 cm^{-1}. These bands were reduced in relative intensity in a deuteriated sample of (5) prepared by treating (4) with deuteriohydrochloric acid. We assign these bands to terminal metal–hydrogen and bridging metal–hydrogen–metal modes respectively. The ^1H n.m.r. spectrum of (6) may be interpreted in terms of the presence of two equivalent η-C_5H_5 groups and two equivalent groups of four protons giving rise to an ABCD spectrum. There is also a band at τ 2.67 assignable to an OH group and a band at τ 21.15 due to a metal–hydrogen group.

The crystal structure of (6) has been determined [4] and is shown in Scheme 1. The compound is a $\eta^5:\eta^5$-bicyclopentadienyl derivative, *i.e.* [{Mo(η-C_5H_5)}$_2$(μ-OH)(μ-H)-{μ-(η^5-C_5H_4-η^5-C_5H_4)}][PF_6]$_2$. This structure is entirely in accord with the ^1H n.m.r. spectrum as discussed above.

We have shown the sequences of events (4) + HPF_6(aq) $\longrightarrow$ (5) $\longrightarrow$ (6) and (6) $\longrightarrow$ (4), which suggests that these three compounds would be expected to have closely related structures. Given this assumption we may interpret the spectroscopic data given above for (4) and (5) in terms of the structures shown in Scheme 1. We must assume that the metal hydrogens in these compounds exchange positions, so that they appear equivalent on the n.m.r. time scale. There are many precedents for fluxional metal hydride systems, including rapid exchange between terminal and bridging hydrogens.

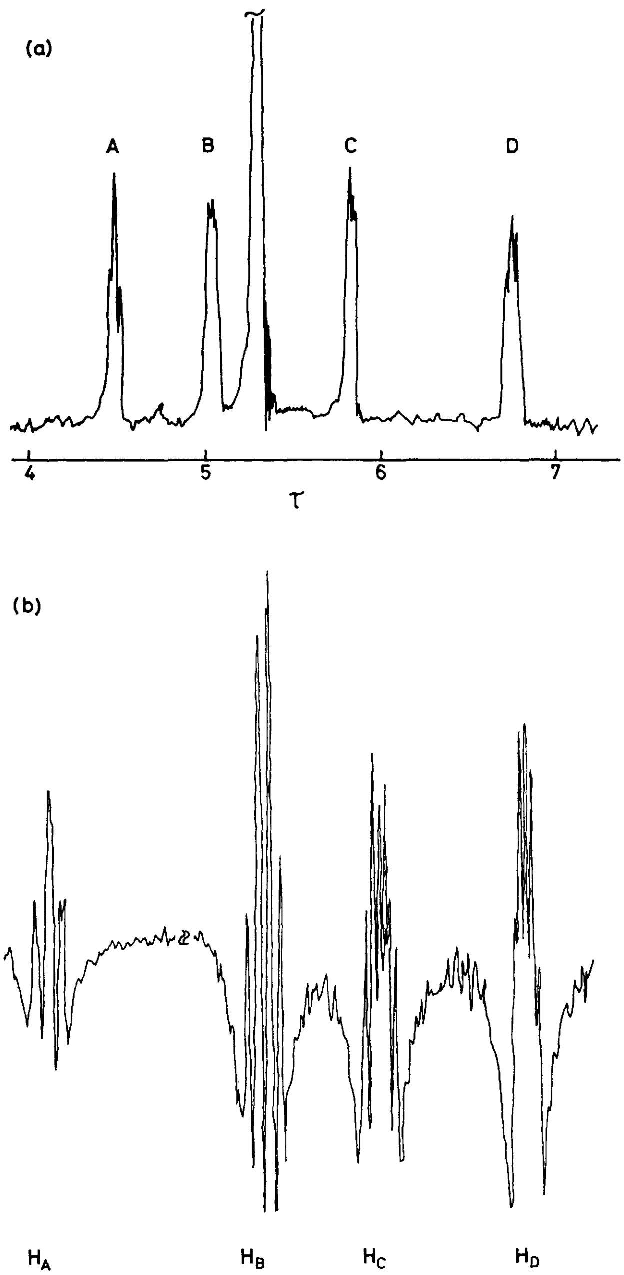


FIGURE 1 (a) ^{1}H n.m.r. spectrum of (7) showing the typical ABCD pattern for a μ-σ : η^5-C_5H_4 ligand system; (b) 270 MHz ^{1}H n.m.r. spectrum of (8) after deconvolution, showing the fine structure of an ABCD spin system

Davison and Wreford[6] have examined the question of the structure of the green form of titanocene, where there was a need to distinguish between the bridging η^5-C_5H_4-η^5-C_5H_4 ligands and two σ : η^5-C_5H_4 ligands. By use of crystallographically characterised compounds which also exhibit an AA′BB′ system for these ligands, they proposed the ^{13}C n.m.r. criterion that the chemical-shift difference between $C_{AA'}$ and $C_{BB'}$ was *ca.* 20 p.p.m. for the σ : η^5-C_5H_4 ligand and *ca.* 2 p.p.m. for the η^5-C_5H_4-η^5-C_5H_4 ligand. The ^{13}C n.m.r. spectrum of (4) with broad-band decoupling shows a chemical-shift difference, $C_{AA'} - C_{BB'}$, or *vice versa*, of 1.4 p.p.m., which further supports the proposal of the presence of a η^5-C_5H_4-η^5-C_5H_4 ligand in (4) as suggested by the protonation–deprotonation–reduction sequence involving (4), (5), and (6).

We now consider the structure of the yellow dimers (2) and (3). We have shown that these are readily and irreversibly converted into the green dimer (4). Prolonged treatment of (9) and (3) with aqueous HPF_6 gives (6). These observations constrain us to propose structures for (2) and (3) which may be seen to be suitable precursors for (4) and (6). Also, we draw attention to the structures of related binuclear metallocene systems. For example, we have characterised from the crystal structures the compounds *cis*- and *trans*-[{W(η-C_5H_5)H}{W(η-C_5H_5)(CH_2SiMe_3)}(μ-σ : η^5-C_5H_4)$_2$] [7,8] and we have shown that there are two isomers of stoicheiometry $C_{20}H_{20}W_2$, one of which has been shown from the crystal-structure determination to be *trans*-[{W(η-C_5H_5)H}$_2$(μ-σ : η^5-C_5H_4)$_2$],[8] see below.

By analogy, we propose that the yellow compounds (2) and (3) are the *cis* and *trans* isomers of the compounds [{Mo(η-C_5H_5)H}$_2$(μ-σ : η^5-C_5H_4)$_2$] although we cannot distinguish which compound is which isomer.

Irradiation of the compound [Mo(η-C_5H_5)$_2$$H_2$] (1) in ethanol, benzene, or mesitylene gives red crystals (7), which microanalysis and ^{1}H n.m.r. show to have the stoicheiometry $C_{20}H_{18}Mo_2$. The photolysis of (1) in ethanol also gave, after addition of hexafluorophosphate, a red crystalline compound which will be discussed later.

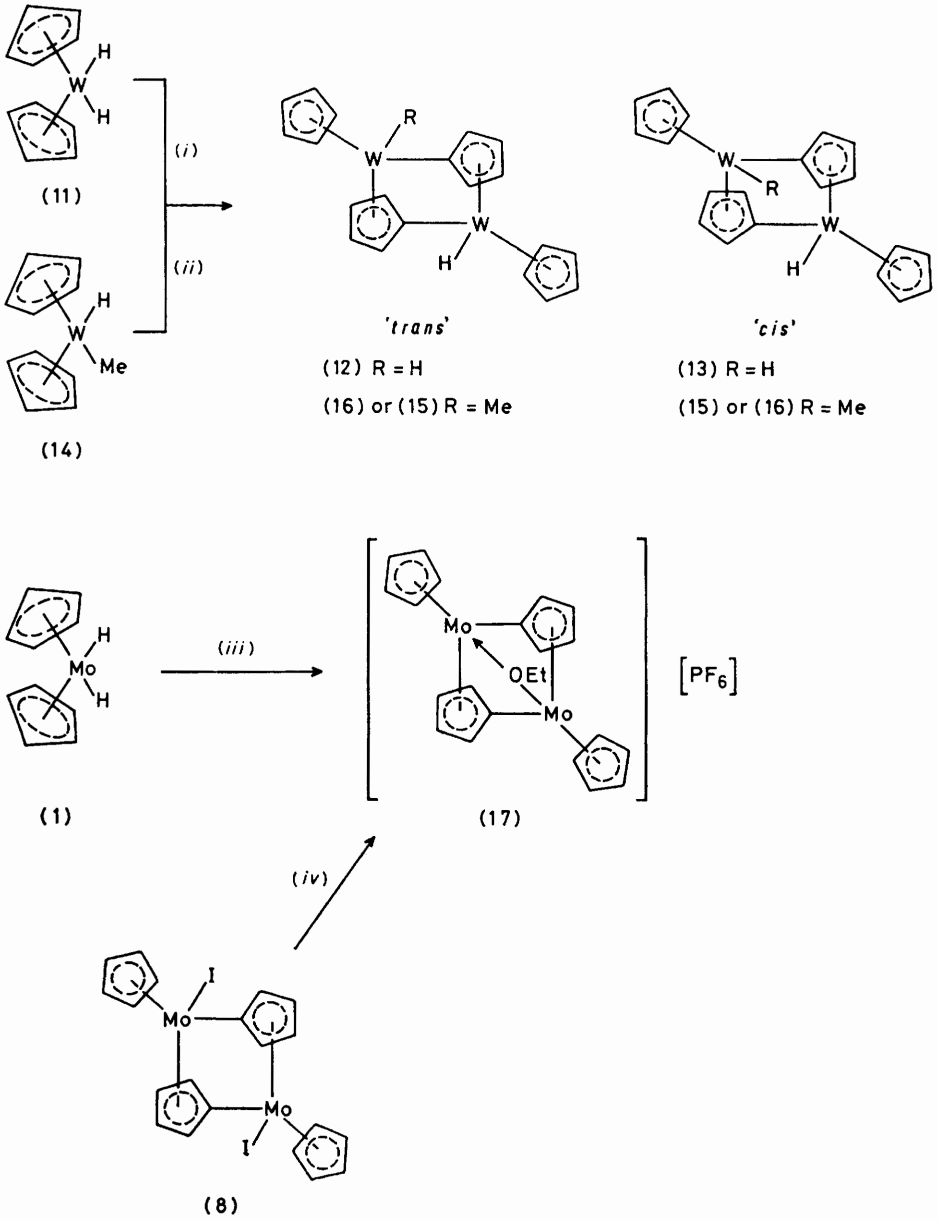
The ^{1}H n.m.r. spectrum of (7) indicates the presence of two equivalent η-C_5H_5 groups and two C_5H_4 groups, occurring as an ABCD system, only. The spectrum, which is typical for unsymmetrical η-C_5H_4 groups, is shown in Figure 1. The ^{13}C n.m.r. spectrum of (7) shows that the carbon bonded to molybdenum (C^1) has a chemical shift of 144.8 p.p.m. This is the first example of the observation of this resonance in a σ : η^5-C_5H_4 system. The corresponding resonance could not be detected for the compounds [M(η-C_5H_5)(CO)][Mn(CO)$_4$] (M = Mo or W) even in the presence of [Cr(acac)$_3$] (acac = acetylacetonate). This (C^1) resonance occurs at a considerably higher chemical shift than that observed for a normal η^5-C_5H_5 group, *ca.* 80 p.p.m.,[9] and indeed the value approaches that found for metal carbenes, *ca.* 200—350 p.p.m.[10]

Compound (7) can also be isolated by irradiation of toluene solutions of (2)—(4). We note that thermal decomposition of (4) up to 160 °C does not form (7). A determination of the crystal structure of (7) shows it to be the compound [{Mo(η-C_5H_5)}$_2$(μ-σ : η^5-C_5H_4)$_2$] rather than [{Mo(η-C_5H_5)}$_2$(μ-η^5-C_5H_4-η^5-C_5H_4)] which might have been expected.[11]

Treatment of (2) with methyl iodide or iodine gives brown crystals of stoicheiometry $C_{20}H_{18}I_2Mo_2$ (8). This compound is also formed by treatment of (7) with iodine. The ^{1}H n.m.r. spectrum of (8) shows a singlet at τ 4.76 corresponding to two equivalent η-C_5H_5 groups. There are four other complex bands at τ 4.16, 5.40, 5.50, and 5.64, which may be assigned to an ABCD system for the C_5H_4 ligands.

Reaction of (4) with 1 equivalent of iodine gives light brown crystals (9), which were shown by analysis to have the stoicheiometry $C_{20}H_{18}I_2Mo_2$. Treatment of (9) with excess of I_2 gives the known compound $[\{Mo(\eta\text{-}C_5H_5)I_2\}_2\text{-}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$ [12] and we can therefore confidently assign to compound (9) the structure $[\{Mo(\eta\text{-}C_5H_5)I\}_2\text{-}(\mu\text{-}\eta^5\text{-}C_5H_4\text{-}\eta^5\text{-}C_5H_4)]$. The i.r. spectrum and solubility properties of (9) differ significantly from those of (8), for which we propose the structure shown in Scheme 1. We note that attempts to abstract halogens from both (8) and (9) using sodium amalgam do not lead to isolation of (7), but only to intractable solids.

The red dimer (7) gives the dication (6) on prolonged treatment with aqueous acid. Treatment of the red dimer (7) with methyl bromide leads to the formation of the yellow-brown crystalline product (10) which on the basis of the data in the Table we assign as the compound $[\{Mo(\eta\text{-}C_5H_5)Me\}\{Mo(\eta\text{-}C_5H_5)Br\}(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)_2]$.



SCHEME 2 (*i*) Photolysis in diethyl ether, 40%; (*ii*) thermolysis in cyclohexane, 30%; (*iii*) photolysis in ethanol, 7%; (*iv*) Na(OEt)–$[PF_6]^-$ (aq), 75%. Percentages are yields throughout

Photolysis of $[W(\eta\text{-}C_5H_5)_2H_2]$ (11) in diethyl ether followed by chromatography of the reaction mixture gave three components. The first component consisted of small yellow crystals which are only slightly soluble in most organic solvents. The mass spectrum showed a highest principal peak at *m/e* 626 corresponding to the dimer $[C_{20}H_{18}W_2]^+$. However, the i.r. and ^1H n.m.r. spectra clearly indicate the presence of W–H. Therefore we deduce that the molecular formula of the compound corresponds to $C_{20}H_{20}W_2$, and that the mass spectrum shows as the highest peak the parent ion less two mass units. The crystal structure together with the ^1H n.m.r. data show this compound to be *trans*-[{W(η-C_5H_5)H}$_2$(μ-σ : η^5-C_5H_4)$_2$] (12) (Scheme 2).

The second component of the reaction mixture was a yellow powder. It was rather more soluble than (12) and was also moderately air sensitive. The mass spectrum showed a highest principal peak at *m/e* 626, but as for (12) both the i.r. and ^1H n.m.r. spectra clearly indicate the presence of only one type of W–H and we again deduce a molecular formula of $C_{20}H_{20}W_2$, the mass spectrum showing only the parent ion less two mass units. The ^1H n.m.r. spectrum is very similar to that of (12), showing a doublet at τ 5.32 (*J* = 0.7 Hz) and a band at τ 20.59 corresponding to a W(η-C_5H_5)H system. There were in addition, two complex bands centred at τ 4.81 and 6.27 and the presence of a shoulder indicated further bands partially obscured by that due to the η-C_5H_5 groups. The i.r. spectrum is generally very similar to that of (12). We conclude that the second component is the *cis* isomer of (12), *cis*-[{W(η-C_5H_5)H}$_2$(μ-σ : η^5-C_5H_4)$_2$] (13).

The third component, which was eluted with methanol and treated with dilute hydrochloric acid and aqueous ammonium hexafluorophosphate gave the known ethylene hydride compound [W(η-C_5H_5)$_2$(η-C_2H_4)H][PF_6].[13]

Compounds (12) and (13) are also formed by photolysis of (11) in cyclohexane.

The thermal decomposition of [W(η-C_5H_5)$_2$MeH] [14] (14) in tetramethylsilane or cyclohexane at 70 °C gave an orange solid. Chromatography gave two components, first a yellow solid and secondly [W(η-C_5H_5)$_2H_2$] (11). The yellow solid was soluble in light petroleum and was moderately air sensitive. The ^1H n.m.r. spectrum was strongly reminiscent of the spectrum of the mixture of the isomers (12) and (13), and showed that there were two compounds present. Further lengthy chromatography of the first component gave yellow crystals (15) which the ^1H n.m.r. spectrum showed to be a pure sample of one of the components of the original mixture. The spectrum showed two bands at τ 5.43 and 5.52 assignable to two different η-C_5H_5 groups. The lower resonance was a sharp singlet whereas the band at τ 5.52 was a doublet (*J* = 0.6 Hz), showing the presence of the system W(η-C_5H_5)H. The presence of W–H was confirmed by a band at τ 21.48. There was also a sharp singlet at τ 9.72 with satellites (*J* = 2.5 Hz) showing the presence of a ^{183}W–CH_3 system. In addition, there were seven complex bands in the region τ 4.5—6.4 and if it is assumed that there is an eighth band obscured by the η-C_5H_5 resonances at τ 5.43 and 5.52 then the eight bands can be assigned to two different ABCD systems of C_5H_4 groups. The mass spectrum of these yellow crystals showed a highest principal peak at *m/e* 642 indicating the molecular formula [{W(η-C_5H_5)H}{W(η-C_5H_5)-Me}(μ-σ : η^5-C_5H_4)$_2$]. We conclude that (15) is the *cis* or *trans* isomer of this compound (see Scheme 2).

The ^1H n.m.r. spectrum of the second component of the mixture can be deduced in part by subtraction from the spectrum of the mixture those bands known to arise from the pure compound (15). The resulting spectrum strongly suggests that this compound (16), is very similar to pure (15). For example there are two bands assignable to η-C_5H_5 groups at τ 5.45 and 5.50. The lower band is a doublet (*J* = 0.6 Hz) indicating a W(η-C_5H_5)H group, with the W–H resonance occurring at τ 21.41, and there is a band at τ 9.59 with satellites (*J* = 2.5 Hz) assignable to a ^{183}W–CH_3 system. The spectrum also exhibits seven complex resonances in the region τ 4.8—6.3 and we can assume an eighth band obscured by the resonances due to the η-C_5H_5 groups. These bands can be assigned to two sets of ABCD systems of different C_5H_4 groups. We conclude that this second component (16) is also the *trans* or *cis* isomer of [{W(η-C_5H_5)H}{W(η-C_5H_5)Me}(μ-σ : η^5-C_5H_4)$_2$]. The data do not permit the *cis* or *trans* configuration to be assigned to a particular component (15) or (16).

The red hexafluorophosphate salt isolated from the photolysis of [Mo(η-C_5H_5)$_2H_2$] in ethanol has the stoicheiometry corresponding to [{Mo(η-C_5H_5)}$_2$(μ-σ : η^5-C_5H_4)$_2$-(μ-OEt)][PF_6] (17). Treatment of (8) with sodium ethoxide gives (17) in good yield. The ^1H n.m.r. spectrum of (17) shows only a single sharp band at τ 4.85 assignable to two equivalent η-C_5H_5 groups. There is a triplet at τ 9.44 (*J* = 7 Hz) and quartet at τ 7.06 (*J* = 7 Hz) assignable to an ethyl group. The remaining bands occur as a set of four peaks, each of intensity two, assignable to two η-C_5H_4 groups behaving as ABCD systems. No band assignable to Mo–H was observed in the ^1H n.m.r. or i.r. spectra. We, therefore, propose a structure for compound (17) which has a (μ-σ : η^5-C_5H_4)$_2$ system rather than a μ-η^5-C_5H_4-η^5-C_5H_4 group (Scheme 2).

DISCUSSION

On the basis of the evidence presented above we have proposed the structures shown in Schemes 1 and 2 for the new compounds reported in this work. The representations of the structures are in fact simplified for purposes of clarity and do not reveal accurately the stereoisomerism of compounds of this type. The crystal structure of *trans*-[{W(η-C_5H_5)H}$_2$(μ-σ : η^5-C_5H_4)$_2$] shows it to have a centre of symmetry and an *RS* configuration.[8] The *cis* isomer of this compound can occur in both *SS* and *RR* configurations (see Figure 2). For most of the new compounds described in this paper we do not have sufficient evidence to distinguish between possible optical or geometrical (*cis* and *trans*) isomers. The solution structures proposed for (6) and (7) are confirmed by the determination of the solid-state structures in single-crystal *X*-ray diffraction studies.[4,11] The structures of some of the other compounds do, however, require some discussion.

If the structures proposed for (4) and (5) are to account satisfactorily for the equivalence of the metal hydrides in the ^1H n.m.r. spectra and for the appearance of the C_5H_4 groups as AA′BB′ rather than ABCD coupling systems, we must assume that the molecules are fluxional. The ^1H n.m.r. spectra of (4) and (5) were examined at temperatures from 25 to −90 °C, but we were unable to observe any temperature dependence of the spectra such as would provide evidence in support of fluxionality. We were, however, able to rule out possible symmetric structures such as those shown in Figure 3 on the basis of the i.r. spectra which unambiguously showed that the hydride ligands in (4) are terminal rather than bridging and that (5) contains both bridging and terminal hydride ligands. These symmetric structures are also implausible on the grounds that they would involve 20-electron valence shells [or possibly 19 e$^-$ for (I) without a Mo–Mo bond] which are previously unobserved configurations for bis(η-cyclopentadienyl) complexes of Mo or W. The electron-counting procedure is discussed below.

At least two simple mechanisms can be envisaged for the transfer of hydrogens between the molybdenum atoms in (4). Examination of models suggests that synchronous transfer (Figure 3) requires minimal rearrangement of the hydrocarbon and molybdenum framework of the molecule, but it does involve the occupation of two antibonding orbitals in the preceding transition state and simultaneous movement of both hydrogen nuclei. Sequential migration of the hydrogen nuclei (Figure 4), which proceeds by reductive elimination of Mo–H [(i)—(ii)] followed by oxidative addition of Mo–H [(iii)—(iv)], could well be a lower-energy process, and has the added attraction of involving the 18-electron intermediate (A). The ready accessibility of such an intermediate in this system could account elegantly for the reaction of (4) with CO reported by Smart [15] and for the photochemical conversion of (4) to (7) (Figure 4). Loss of dihydrogen from (B) would be a closely related reaction to the well established photoinduced evolution of dihydrogen from $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W).[16] Alternatively, there may be direct photoevolution of H_2 from the binuclear compound (4) to an intermediate such as (C) (Figure 4). Such a conversion of a M–H–M–H group into the M=M group as in the intermediate (D) would constitute a previously unobserved binuclear mechanism for the reductive elimination of H_2 which is formally forbidden as a thermal reaction. The formation of (7) from intermediate (C) could occur by a four-centre state similar to that proposed for the formation of (4) from (2) or (3) (see below and Figure 4).

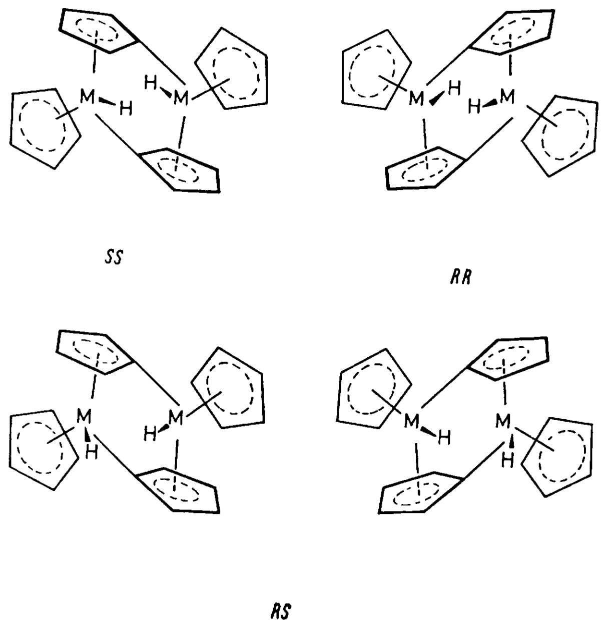


FIGURE 2 Stereoisomers of *cis*- and *trans*-$[\{M(\eta\text{-}C_5H_5)H\}_2(\mu\text{-}\sigma : \eta^5\text{-}C_5H_4)_2]$ (M = Mo or W)

The fluxionality of the trihydride (5) can be accounted for by a similar sequential transfer of hydrogens between the molybdenum atoms (Figure 5).

The bridging hydride ligands in (5) and (6) must clearly be bonded to the molybdenum atoms through a three-centre two-electron molecular orbital of the type so commonly met in the chemistry of the boranes. Such electron-deficient bonding can give rise to problems when one attempts to ' count the electrons ' in novel polynuclear structures, as a consequence of the two-centre two-electron valence-bond model which is frequently used when representing such structures on paper.[17] Accordingly, we would like to introduce the convention of representing such bridging hydrides as illustrated in Figure 6(a) for diborane. This convention emphasises that there is an important distinction between the number of valence pairs in a molecule and the number of occupied valence orbitals and enables us to indicate both numbers in a simple manner even for a complex bonding situation. Indeed, it enables us to evaluate both numbers at a glance for complex polynuclear species in which the occurrence of electron-deficient bonding means that there are fewer valence electron pairs than occupied orbitals, and hence to apply the 18-electron rule (which is in fact the nine occupied orbitals rule) to such situations. Some examples are illustrated in Figure 6(c)—(g). The structure of $[Ru_4(CO)_{12}H_4]$ is an interesting case, since this molecule was only recently shown to have the structure shown in Figure 6(f) rather than that in 6(e).[18] Using our convention it is immediately clear that the latter structure implies a 19-electron configuration for each Ru atom. The extension of the convention to a hydride bridging three centres is straightforward and is again analogous to the conventional representation of a three-way bridging halide ligand. Similarly, the symmetrical structures, such as are shown for (4) and (5) in Figure 3, may be immediately

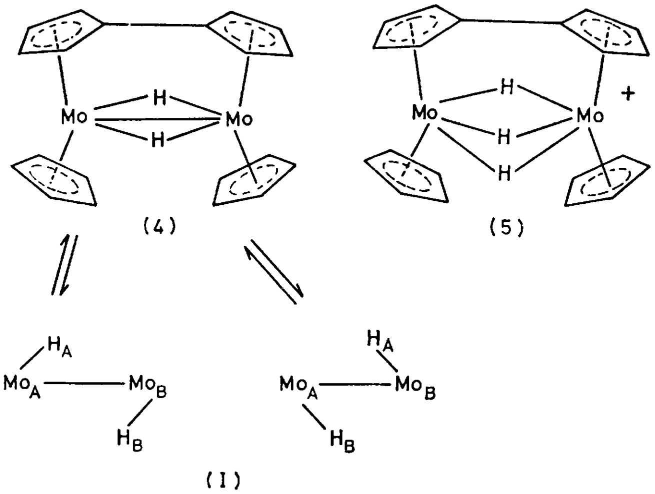


FIGURE 3 Symmetrical intermediates of (4) and (5) which would be required for a synchronous intramolecular exchange process, as shown in (I)

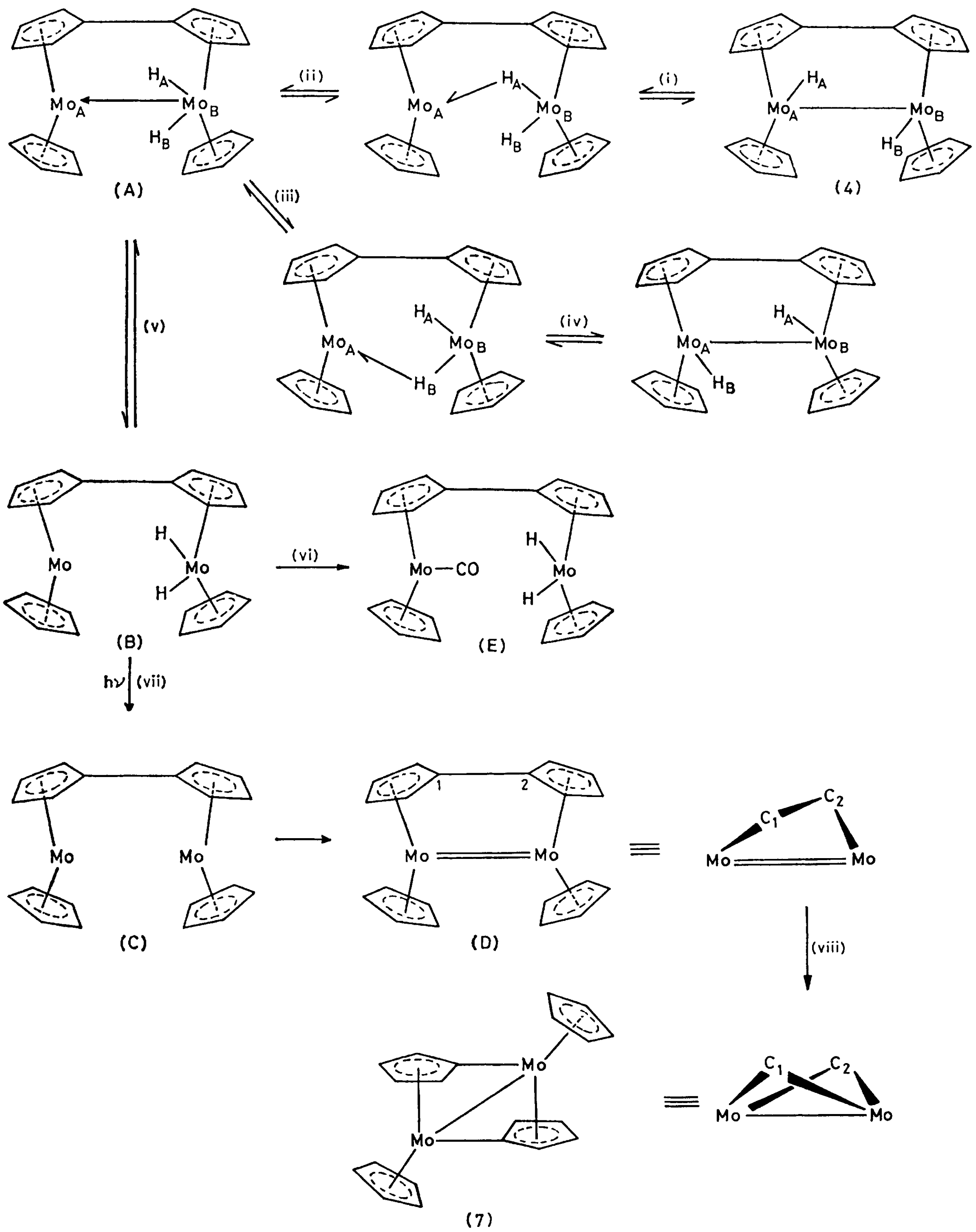


FIGURE 4 (i)—(iv) Proposed mechanism for the sequential equilibration of Mo–H in (4); (i), (ii), (v), (vi) proposed mechanism for formation of carbonyl (E); (i), (ii), (v), (vii), (viii) proposed mechanism for photochemical formation of (7) from (4) discarded by use of the —H⇀ representation which shows the molybdenum centres to have 20-electron environments.

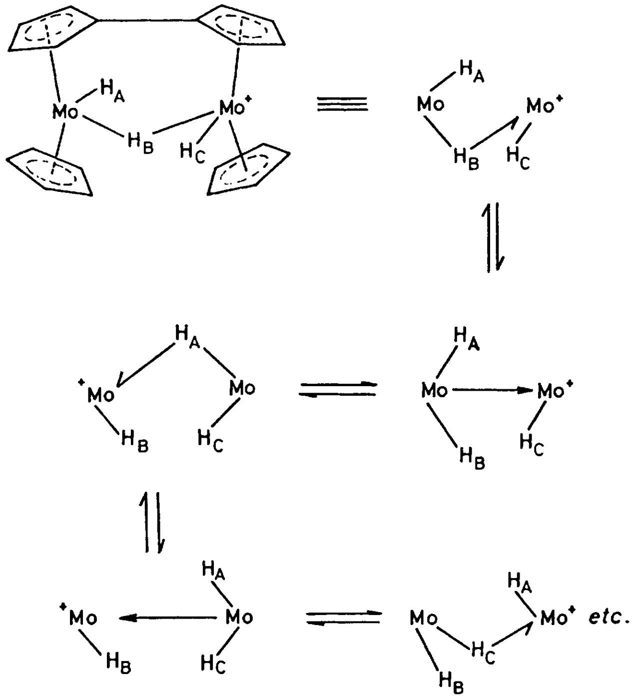


FIGURE 5 Representation of the cycle of a mechanism for sequential intramolecular equilibration of the Mo–H in (5)

Finally, the thermally induced rearrangement of (2) and/or (3) to (4) may be envisaged to proceed *via* a four-centre transition state, which can arise when the two halves of the molecule are twisted in a manner that causes C^1 to approach C^2 (see Figure 7).

EXPERIMENTAL

All reactions and manipulations were carried out under dinitrogen or *in vacuo*. All solvents were dried and distilled. Hydrogen-1 n.m.r. spectra were determined using a Bruker (90 MHz) or JEOL (60 MHz) instrument. Microanalyses were by A. Bernhardt or by the microanalytical laboratory of this department. Infrared spectra were recorded as mulls on a Perkin-Elmer 457 instrument and were calibrated with polystyrene film. Mass spectra were determined using an A.E.I. M.S. 9 spectrometer.

The compounds $[\mathrm{Mo}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{H}_2]$ and $[\mathrm{W}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{H}_2]$ were prepared as described previously.[20]

cis- *and* trans-*Bis*(μ-σ : 1—5-η-*cyclopentadienediyl*)-*bis*-[(η-*cyclopentadienyl*)*hydridomolybdenum*], (2) *and* (3).—The freshly prepared tetramer $[\{\mathrm{Mo}(\eta\text{-C}_5\mathrm{H}_5)_2\mathrm{HLi}\}_4]$ [1] (5.0 g, 5.3 mmol) was suspended in dry distilled toluene and dry nitrous oxide was slowly bubbled through the solution for 15 min. The mixture was vigorously shaken during this period and kept cool (below 30 °C) by periodically placing the reaction vessel in liquid dinitrogen. An immediate reaction was observed giving a dark red solution. The passage of N_2O was stopped after all the initial solid had dissolved. The mixture was left for 30 min at 0 °C and then the solvent was removed under reduced pressure at 0 °C. The residual red solid was cooled to −196 °C and methanol (50 cm³) was added. The mixture was allowed to warm to 0 °C giving a red solid and a brown solution. The mixture was filtered and the residue was washed with methanol (6 × 10 cm³) at 0 °C. The now light brown residue was washed with dry acetone (20 cm³) at 0 °C giving a lemon-yellow solid (2.30 g, 45%) (2). The yellow solid could be recrystallised from toluene, acetone, 1,2-dimethoxyethane, or tetrahydrofuran giving yellow microcrystals which were shown to be (3). It was also found that if the red toluene solution, as above, was placed briefly under vacuum until the toluene ceased to froth a red solid and a yellow solid precipitated. These were filtered off and the red solid removed by washing with methanol to leave pure (2) (0.24 g, 5%).

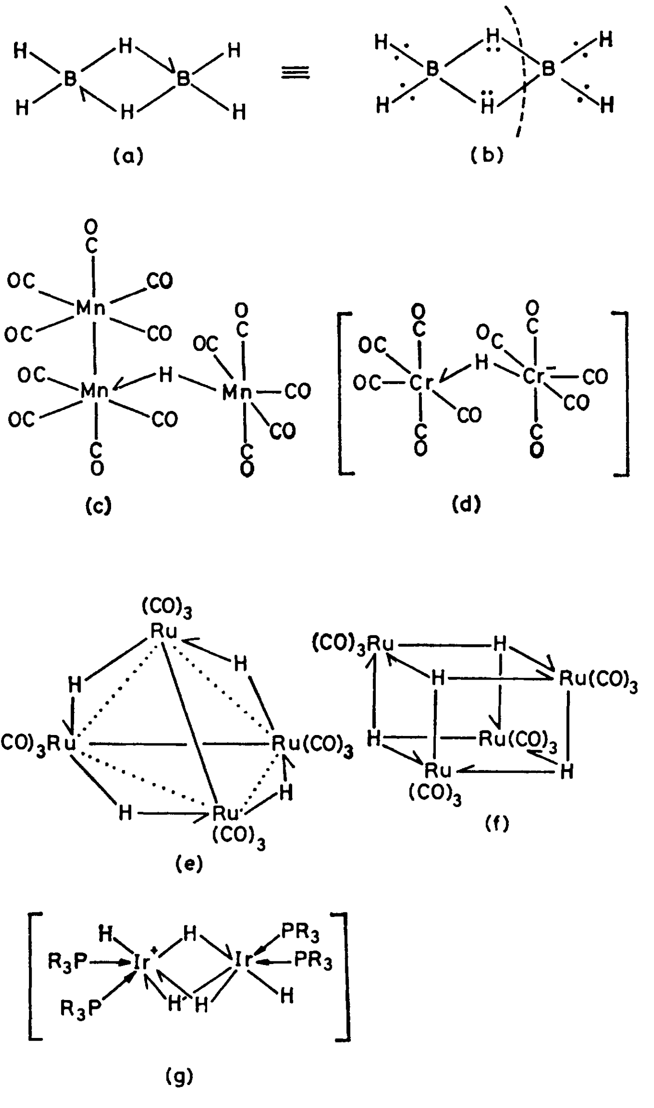


FIGURE 6 (a) Representation of diborane showing the bridging hydrogens as —H⇀, where ⇀ indicates a two-electron donation from hydrogen to the boron (as in bridging halides, *e.g.* — Cl→); (b) a simple picture of diborane showing that each boron has a filled-shell eight-electron count; (c) and (d) ref. 17), (e) and (f) (ref. 18), and (g) (ref. 19) showing in each case that the metals attain the 18-electron count

In addition, when the reaction between the tetramer and N_2O was carried out as described above using light petroleum–diethyl ether instead of toluene, and the isolation procedure using methanol was followed, the resulting yellow crystalline product was found (from i.r. spectra) to be a mixture of (2) and (3).

μ-1—5-η : 1—5-*η-Bicyclopentadienyl-bis*[(*η-cyclopentadienyl*)*hydridomolybdenum*], (4).—Pure (2) (0.6 g, 1.3 mmol) in toluene (50 cm^3) was warmed to 70 °C for 1 h. The initially yellow solution became dark green. The solvent was removed under reduced pressure, the residue was extracted with dry acetone (40 cm^3), and the dark green extract was concentrated under reduced pressure and cooled to −78 °C. After 14 h dark green crystals separated. These were collected, washed with light petroleum, and dried *in vacuo* (0.35 g, 60%). The *compound* could be recrystallised from benzene–light petroleum (b.p. 100—120 °C) at −70 °C and from acetonitrile at 70 °C. The same compound could be obtained in a similar manner from (3).

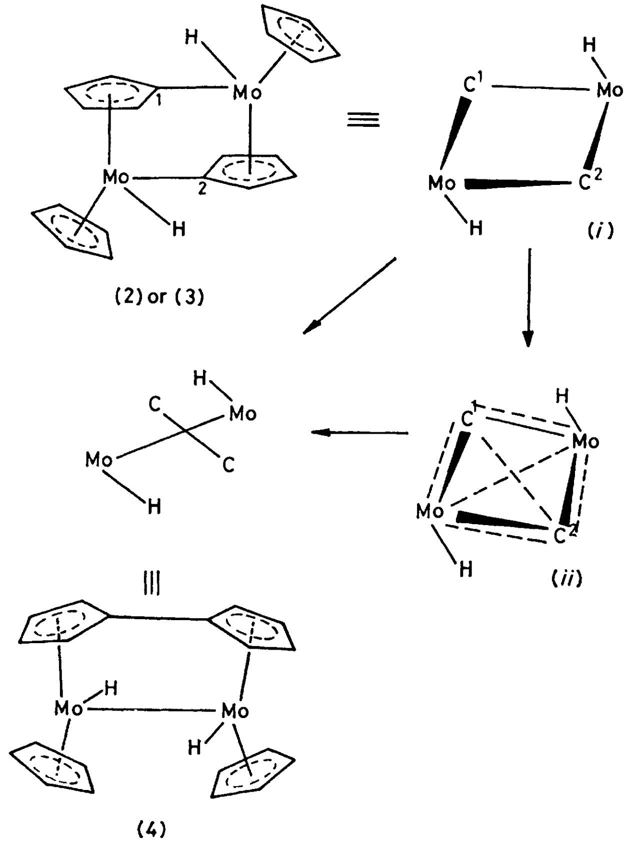


FIGURE 7 Mechanism of formation of (4) from (2) or (3) showing (*i*) tetrahedral disposition of Mo–C^1–C^2 system, (*ii*) four-centre transition state

μ-1—5-η : 1—5-*η-Bicyclopentadienyl-μ-hydrido-bis*[(*η-cyclopentadienyl*)*hydridomolybdenum*] *Hexafluorophosphate*, (5).—Compound (4) (0.5 g, 1.1 mmol) in acetone (20 cm^3) was treated with hexafluorophosphoric acid (0.5 cm^3 of 60% aqueous solution). An immediate reaction gave a red-brown solution. Water (10 cm^3) and aqueous ammonium hexafluorophosphate (0.2 g in 2 cm^3 of water) were added. Slow concentration of the solution under reduced pressure gave red-purple microcrystals. These were collected, washed with water (2 × 20 cm^3), and dried *in vacuo* (0.13 g, 65%). The product was recrystallised from acetone–water.

Bis(μ-σ : 1—5-*η-cyclopentadienediyl*)-*bis*[(*η-cyclopentadienyl*)*iodomolybdenum*], (8).—(*a*) *From* (2). Pure (2) (0.12 g, 0.27 mmol) was suspended in acetonitrile (15 cm^3) at 0 °C and methyl iodide (23 g, 160 mmol) was added. The yellow solid dissolved within 2 min giving a dark brown solution. The mixture was left to stand for 12 h during which period a brown solid precipitated. The mother-liquor was filtered and concentrated under reduced pressure to 3 cm^3. After 1 h dark brown microcrystals separated which were collected, washed with acetonitrile, and dried *in vacuo*. The initially formed brown solid and the brown crystals were combined and recrystallised from acetonitrile giving brown crystals (0.11 g, 60%).

The above reaction was repeated at −25 °C with (2) (0.1 g, 0.26 mmol) using iodine (0.065 g, 0.26 mmol) instead of methyl iodide. The identical product could be isolated as before but in reduced yield (0.07 g, 37%).

(*b*) *From* (7). Pure (7) (0.16 g, 0.36 mmol) in dry acetonitrile (20 cm^3) was treated with iodine (0.09, 0.36 mmol) in acetonitrile (10 cm^3). The initially dark red solution became brown and after a few minutes dark brown crystals separated. The mixture was allowed to stand for 12 h, the crystals were then filtered off, washed with acetonitrile, and dried *in vacuo* (0.23 g, 92%). The i.r. spectrum showed the product to be identical to that prepared in (*a*).

μ-1—5-η : 1—5-*η-Bicyclopentadienyl-μ-hydrido-μ-hydroxo-bis*[(*η-cyclopentadienyl*)*molybdenum*], (6).—(*a*) *From* (2). Pure (2) (0.26 g, 0.58 mmol) was suspended in acetone (40 cm^3) and treated with aqueous HPF_6 (20 cm^3 of a 2% solution). The solid rapidly dissolved giving a red solution which slowly changed to brown over 36 h. The solvent was then slowly removed under reduced pressure giving golden brown plates. These were collected, washed with water (2 cm^3), and dried *in vacuo* (0.1 g, 20%). A second crop of the product could be obtained by pumping the mother liquor to dryness, extracting the product with acetone (5 cm^3), and recrystallising it by adding 2% aqueous HPF_6 (3 cm^3) and concentrating the solution under reduced pressure. It was observed that dark brown needles were obtained under these conditions as well as golden brown plates. Yield 0.22 g (50%). The compound could also be obtained in a third crystal form as fine yellow-brown needles by recrystallisation from very dilute solutions in acetone–2% aqueous HPF_6. The i.r. and ^1H n.m.r. spectra of the three types of crystal were identical and the crystal types appeared to differ only in the number of molecules of water of crystallisation present. The same product could be obtained in a similar manner from (3).

(*b*) *From* (4). The above reaction was repeated using (4) (0.15 g, 0.33 mmol). The identical product was obtained as golden brown plates (0.14 g, 56%).

(*c*) *From* (7). Pure (7) (0.1 g, 0.22 mmol) was dissolved in a 1 : 1 mixture of benzene and acetone (50 cm^3) and treated with aqueous HPF_6 (10 cm^3 of a 3% solution). The solution was allowed to stand for 12 h, during which time a brown solid precipitated out. The solid was recrystallised from acetone–aqueous hexafluorophosphoric acid solution. After removal of solvent under reduced pressure, the brown crystals were washed with distilled water (2 × 2 cm^3) and dried *in vacuo* (0.12 g, 69%).

Bis(μ-σ : 1—5-*η-cyclopentadienediyl*)-[*bromo*(*η-cyclopentadienyl*)*molybdenum*][(*η-cyclopentadienyl*)*methylmolybdenum*], (10).—Pure (7) (0.05 g, 0.11 mmol) in dry benzene was treated with an excess of methyl bromide (1.5 g, 0.14 mmol). The solution was kept at room temperature for 17 h during which time the initial dark red colour changed to yellow-brown. The solvent was removed under reduced pressure and the residue was extracted with benzene. After filtration the yellow-brown filtrate was concentrated and treated with light petroleum (b.p. 100—120 °C) giving yellow-brown microcrystals. These were collected and washed with light petroleum and finally dried *in vacuo* (0.05 g, 83%).

Bis(μ-σ : 1—5-η-*cyclopentadienediyl*)-*bis*[(η-*cyclopentadienyl*)*molybdenum*](Mo–Mo), (7), *and Bis*(μ-σ : 1—5-η-*cyclopentadienediyl*)-μ-*ethoxo-bis*[(η-*cyclopentadienyl*)*molybdenum*] *Hexafluorophosphate*, (17).—(*a*) *From ethanol.* The compound [Mo(η-C_5H_5)$_2$$H_2$] (1) (1.5 g, 6.6 mmol) in dry ethanol (1 l) was irradiated for 72 h at room temperature, using a water-cooled medium-pressure mercury lamp in Pyrex apparatus. The solution turned dark red and small deep red crystals were deposited which are unidentified. After filtration of the reaction mixture the solvent was removed from the filtrate giving a dark red solid. This was extracted with benzene and the extract filtered and concentrated. On addition of light petroleum (b.p. 100—120 °C) dark red needles of the pure compound (7) were obtained (0.5 g, 34%). The residue left after the extraction with benzene was re-extracted with ethanol giving a dark red solution. Addition of an excess of aqueous [NH_4][PF_6] gave a red-brown precipitate. This was collected and recrystallised from acetone–water giving dark red microcrystals (0.15 g, 75%) of the pure compound (17).

(*b*) *From benzene.* Pure (1) (0.6 g, 2.6 mmol) was irradiated in dry benzene (200 cm^3) for 20 h. The resulting deep red solution was filtered from a brown flocculent precipitate and the solvent was removed from the filtrate under reduced pressure giving a dark red oil. Extraction with dry benzene at 80 °C gave a dark red solution which was concentrated until near saturation. Light petroleum (b.p. 100—120 °C) was added and the solution was left to cool for 12 h. Dark red rectangular crystals of (7) separated. These were washed with light petroleum (b.p. 30—40 °C) and dried *in vacuo* (0.4 g, 66%).

(*c*) *From mesitylene.* The above procedure was repeated using (1) (0.7 g, 3.1 mmol) in mesitylene (200 cm^3) to give (7) (0.5 g, 71%), which was purified and isolated as described in (*b*).

μ-1—5-η : 1—5-η-*Bicyclopentadienyl-bis*[(η-*cyclopentadienyl*)*iodomolybdenum*], (9).—Pure (4) (0.31 g, 0.71 mmol) in refluxing acetonitrile (50 cm^3) was treated with an acetonitrile solution of iodine (0.18 g, 0.70 mmol). The initially dark green solution turned dark brown. After warming the solution to 80 °C for 10 min the dark brown solution was filtered and concentrated under reduced pressure (to 30 cm^3). On cooling over 12 h light brown needles separated which were washed with acetonitrile (2 × 3 cm^3) then light petroleum and finally dried *in vacuo* (0.42 g, 85%).

cis- *and* trans-*Bis*(μ-σ : 1—5-η-*cyclopentadienediyl*)-*bis*-[(η-*cyclopentadienyl*)*hydridotungsten*], (12) *and* (13). Pure [W(η-C_5H_5)$_2$$H_2$] (1.0 g, 3.2 mmol) in diethyl ether (900 cm^3) was irradiated for 52 h. The resulting orange solution was filtered from dark decomposition products and the solvent was removed from the filtrate under reduced pressure. The residual red solid was extracted with toluene and chromatographed on an alumina column. Elution with toluene–light petroleum (b.p. 60—80 °C), 7 : 3, gave a yellow band which was collected. The solvent was removed from the eluate and the resulting yellow solid was crystallised from hot toluene as yellow crystals of (12) (0.22 g, 22%). Elution of a second band with pure toluene gave a yellow solid which was crystallised from hot toluene–light petroleum as a microcrystalline powder (13) which was dried *in vacuo* (0.18 g, 18%).

Finally, elution of the column with methanol gave a third red band. This was collected and the solvent was removed under reduced pressure, giving a red oil. This was extracted with dilute hydrochloric acid and [NH_4][PF_6] was added to the extract giving a white precipitate. This was collected and recrystallised from acetone–water giving white crystals which were shown to be [W(η-C_5H_5)$_2$(C_2H_4)H][PF_6] by comparison of the i.r. and ^{1}H n.m.r. spectra with those of an authentic sample (0.25 g, 16%).

cis- *and* trans-*Bis*(μ-σ : 1—5-η-*cyclopentadienediyl*)-[(η-*cyclopentadienyl*)*hydridotungsten*][(η-*cyclopentadienyl*)*methyltungsten*], (15) *and* (16).—Pure [W(η-C_5H_5)$_2$MeH] (0.2 g, 0.6 mmol) was heated in cyclohexane (200 cm^3) at 70 °C for 12 h. The reaction mixture was evaporated to dryness and a toluene extract was chromatographed on an alumina column. Elution with toluene–light petroleum (b.p. 60—80 °C), 3 : 2, gave a yellow band which was collected. The solvent was removed under reduced pressure giving a yellow solid. This was recrystallised from light petroleum at −78 °C. The resulting bright orange needles were washed with light petroleum (b.p. 30—40 °C) and dried *in vacuo* (0.06 g, 31%). They were found to be a mixture of (15) and (16).

A second yellow band eluted with toluene–diethyl ether (1 : 1) was shown to be (11) by comparison of its i.r. spectrum with that of an authentic sample. The orange crystals crystals obtained from the first band were rechromatographed on an alumina column. Elution with toluene–light petroleum (b.p. 60—80 °C), 1 : 10, separated two components. The first band was collected but the second band decomposed on the column. The first eluate gave a yellow solid which was recrystallised from light petroleum (b.p. 60—80 °C) at −78 °C as yellow needles. These were washed with light petroleum and dried *in vacuo.* They were shown by the i.r. and ^{1}H n.m.r. spectra to be pure (15) (0.02 g, 10%).

Reaction of (5) *with Potassium Hydroxide.*—Pure (5) (0.20 g, 0.34 mmol) was suspended in a benzene–water mixture (50 cm^3, 1 : 1). Aqueous potassium hydroxide (2 mol dm^{-3}, 1.5 cm^3) was added and the mixture was shaken for 10 min. After filtration the dark green benzene layer was separated. Removal of the solvent under reduced pressure gave green crystals which were recrystallised from toluene–light petroleum (b.p. 60–80 °C) at −78 °C. The resulting green crystals were identified as pure (4) from the i.r. spectrum (0.11 g, 70%).

Reaction of (6) *with* Na[$AlH_2(OCH_2CH_2OMe)_2$].—Pure (6) (0.21 g, 0.27 mmol) was suspended in benzene (50 cm^3). An excess of Na[$AlH_2(OCH_2CH_2OMe)_2$] (2 cm^3 of 70% benzene solution) was added and the solution was stirred. The solid dissolved and reacted giving a dark green solution during 30 min. The solution was cooled to 0 °C and aqueous sodium hydrogencarbonate solution (20 cm^3, 15%) was added. The mixture was passed rapidly through Celite 545 (1 cm column) and the dark green benzene layer was separated from the aqueous layer. Removal of the solvent under reduced pressure and recrystallisation of the resulting dark green solid from toluene–light petroleum at −78 °C gave dark green microcrystals. These were shown to be

(4) by comparison of their i.r. spectrum with that of an authentic sample (0.08 g, 64%).

Reaction of (8) *with Sodium Ethoxide*.—Sodium ethoxide (from 0.2 g, 8.7 mmol of sodium) in ethanol (30 cm^3) was added to a suspension of (8) (0.1 g, 0.14 mmol) in ethanol (40 cm^3). The mixture was stirred at 60 °C for 1 h. The solvent was removed from the resulting deep red solution obtained under reduced pressure. The residue was vigorously shaken with aqueous sodium hexafluorophosphate (0.15 g, 0.92 mmol in 25 cm^3 water) and acetone (60 cm^3). The deep green extract was filtered and slowly concentrated under reduced pressure. Dark green crystals precipitated which were washed with distilled water and dried *in vacuo*. Comparison of their i.r. and ^{1}H n.m.r. spectra with those of an authentic sample showed them to be (17) (0.65 g, 74%).

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