Syntheses and Reactions of *ansa*-[2,2-Bis(η-cyclopentadienyl)propane]-tungsten and -molybdenum Compounds†

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Reaction between [MCl_4(dme)] (M = W or Mo; dme = 1,2-dimethoxyethane) with $Li_2[C_5H_4CMe_2C_5H_4]$ gave the *ansa*-bridged metallocene dichlorides [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] (M = W or Mo). Treatment of these with $LiAlH_4$ or $ZnMe_2$ gave respectively the dihydrides [M{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] (M = W or Mo) and the dimethyl derivatives [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2] (M = W or Mo). Treatment of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2] with HX (X = $PhCO_2$ or NH_3I) gave [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me(Y)] with Y = $PhCO_2$ or I, respectively. Both of these react with Na[$AlH_2(OCH_2CH_2OMe)_2$] giving the methylhydride [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me(H)]. The latter is thermally stable in refluxing benzene. Ultraviolet photolysis of [Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] in benzene gave the phenylhydride derivative [Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}Ph(H)]; the corresponding tungsten derivative [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] is not photosensitive. The crystal structures of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2], [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2], (two modifications) and [Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] have been determined by X-ray diffraction. The *ansa*-bridged bis(η-cyclopentadienyl) compounds show marked differences in reactivity compared to non-*ansa* analogues and this is discussed in terms of the modifications of the electronic structure as a consequence of the *ansa* bridge.

ansa-Metallocenes of Group 4 metals have been extensively studied,[1] having been recognised as an important class of compound for the catalytic stereoregular polymerisation of prochiral olefins.[2] They have been synthesised with a variety of bridging groups and substituted cyclopentadienyl and indenyl ligands.[1] Crystallographic studies have shown that the extent of strain, the stereorigidity, in *ansa*-metallocenes is largely dependent on the characteristic of the bridge.[3] It has been reported[4] that titanocene derivatives with an interannular ethylene bridge do not always show the same reactivity previously observed for the unbridged species, normally in processes involving a parallel ring titanocene intermediate. *ansa*-Metallocenes have also been reported for lanthanides,[5] iron(II),[6] ruthenium(II)[7] and chromium(II).[8] The chemistry of the bent bis(η-cyclopentadienyl) derivatives of molybdenum and tungsten is well known and very extensive;[9] we set out to compare the chemistry of analogous derivatives containing the *ansa*-CR_2 system, for example derivatives of the moiety M[(η-C_5H_4)CMe_2(η-C_5H_4)], where M = Mo or W. A preliminary communication of part of this work has been made.[10] Very recently a report of the synthesis of the *ansa* derivatives [M{(η-C_5H_4)$SiMe_2OSiMe_2$(η-C_5H_4)}X_2], M = Mo or W, has been published.[11]

Results and Discussion

The *ansa*-tungstenocene and -molybdocene dichloride compounds [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2], M = W **1** or Mo **2**, have been prepared from [MCl_4(dmpe)] (M = W or Mo, dme = 1,2-dimethoxyethane) and $Li_2[C_5H_4CMe_2C_5H_4]$ in equimolar amounts, in Et_2O. This route is an adaptation of that recently reported for the synthesis of [W(η-C_5H_5)$_2Cl_2$].[12] The products of these apparently heterogeneous reactions were insoluble in diethyl ether and after washing with dme, tetrahydrofuran (thf), EtOH and finally diethyl ether gave satisfactory elemental analyses. However, a Soxhlet extraction using dichloromethane revealed they had inhomogeneous compositions and apart from [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2], which have low solubility in dichloromethane, there were also insoluble materials. Preliminary data suggest that they may be polymers; attempts to characterise them are in progress.[13] The soluble [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] compounds constitute about 60% (for W) and about 20% (for Mo) of the initial reaction products. Typically compounds **1** and **2** were prepared on a 4–8 g scale and were available as synthons for the development of the chemistry of the *ansa*-M[(η-C_5H_4)CMe_2(η-C_5H_4)] moiety. They are red-brown and have been characterised by analytical and spectroscopic data, and by the crystal structure of **1**. The data for **1** and **2** and for all the other new compounds described are given in Table 1. The ^1H NMR spectra of the cyclopentadienyl protons of the [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] fragment consist of a pair of pseudo-triplets, since the *ansa* bridge creates equivalent sets of four α and four β protons, respectively.

Treatment of [M{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2], M = W or Mo, with $LiAlH_4$ in diethyl ether, or $NaBH_4$ in thf, gave, after hydrolysis, the corresponding dihydrides [M{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2], where M = W **3** or Mo **4**, in 25 and 13% yields (from [MCl_4(dme)], respectively. The dihydrides form yellow air-sensitive crystals which are very soluble in most organic solvents and slightly soluble in pentane. They sublime at *ca.* 120 °C at 10^{-3} mmHg (*ca.* 0.133 Pa). The ^1H NMR spectrum of the unpurified product of the $LiAlH_4$ reduction of **1** showed the presence of a trace of another tungsten hydride compound which has not yet been identified. This was readily removed by washing with pentane.

Treatment of a suspension of complexes **1** and **2** in toluene with dimethylzinc gave the expected dimethyl derivatives [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2] **5** and [Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2] **6** in *ca.* 45 and 25% yields, respectively. We note that the corresponding non-*ansa* dimethyl derivatives [Mn(η-C_5H_5)$_2Me_2$] were prepared by a reaction of the

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Table 1 Analytical and spectroscopic data

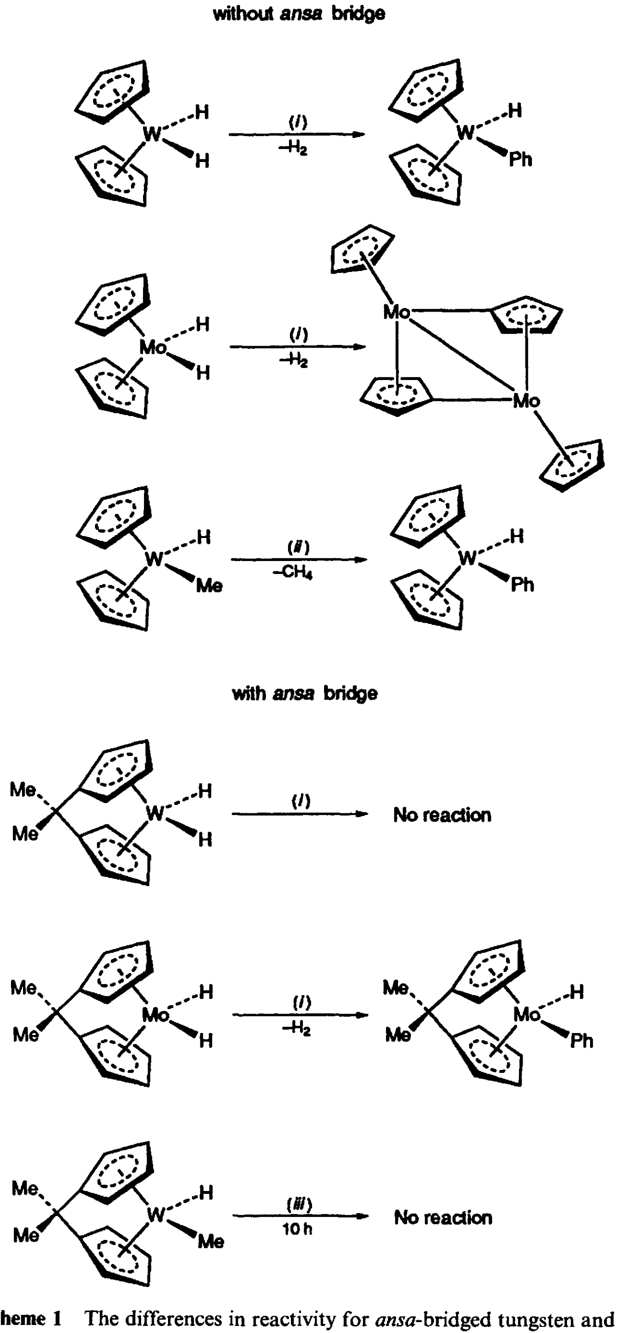
Compound[a]	Spectroscopic data[b]
1 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ C, 36.5 (36.7); H, 3.2 (3.3); Cl, 15.6 (16.7)	^1H:[c] 5.93 (4 H, m, C_5H_4), 5.43 (4 H, m, C_5H_4), 0.83 (6 H, s, CH_3) Mass: *m/z* 426 (M^+), 389 ($M^+ - Cl$) IR: ν(W–Cl) 320m, 300m, 270m
2 $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ C, 46.3 (46.3); H, 4.6 (4.2)	^1H:[c] 6.24 (4 H, m, C_5H_4), 5.02 (4 H, m, C_5H_4), 0.89 (6 H, s, CH_3) IR: ν(Mo–Cl) 320m, 300m, 270m
3 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ C, 44.2 (43.8); H, 4.7 (4.5)	^1H:[d] 4.89 (4 H, m, C_5H_4), 4.02 (4 H, m, C_5H_4), 0.46 (6 H, s, CH_3), −7.33 (2 H, s, J_{WH} = 92) ^{13}C:[d] 86.6 (s, C_5H_4), 64.8 (s, C_5H_4), 43.3 (s, C_5H_4, C_{ipso}), 33.2 [s, $C(CH_3)_2$], 22.1 (s, CH_3) Mass: *m/z* 355 ($M^+ - H_2$) IR: ν(W–H) 1833s, 1823s
4 $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ C, 58.4 (58.2); H, 6.4 (6.0)	^1H:[d] 4.96 (4 H, m, C_5H_4), 4.08 (4 H, m, C_5H_4), 0.54 (6 H, s, CH_3), −4.77 (2 H, s) ^{13}C:[d] 88.6 (s, C_5H_4), 70.7 (s, C_5H_4), 5.13 (s, C_5H_4, C_{ipso}), 33.7 [s, $C(CH_3)_2$], 21.7 (s, CH_3) IR: ν(Mo–H) 1760s, 1750s
5 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me_2]$ C, 47.5 (46.9); H, 5.3 (5.2)	^1H:[d] 4.46 (4 H, m, C_5H_4), 4.10 (4 H, m, C_5H_4), 0.44 [6 H, s, $C(CH_3)_2$], 0.17 (6 H, s, CH_3) ^{13}C:[d] 104.8 (s, C_5H_4), 67.8 (s, C_5H_4), 52.2 (s, C_5H_4, C_{ipso}), 30.9 [s, $C(CH_3)_2$], 22.5 [s, $C(CH_3)_2$], −22.7 (s, CH_3) Mass: 386 (M^+), 371 ($M^+ - CH_3$)
6 $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me_2]$ C, 60.8 (60.8); H, 6.7 (6.8)	^1H:[d] 4.48 (4 H, m, C_5H_4), 4.11 (4 H, m, C_5H_4), 0.51 [6 H, s, $C(CH_3)_2$], 0.13 (6 H, s, CH_3) ^{13}C:[d] 106.3 (s, C_5H_4), 73.4 (s, C_5H_4), 59.2 (s, C_5H_4, C_{ipso}), 31.6 [s, $C(CH_3)_2$], 21.9 [s, $C(CH_3)_2$], −10.7 (s, CH_3)
7 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me(O_2CPh)]$ C, 51.4 (51.4); H, 4.5 (4.5)	^1H:[d] 8.48 (2 H, d, C_6H_5), 7.20 (3 H, m, C_6H_5), 5.32 (2 H, m, C_5H_4), 5.15 (2 H, m, C_5H_4), 4.82 (2 H, m, C_5H_4), 3.99 (2 H, m, C_5H_4), 0.55 [3 H, s, $C(CH_3)_2$], 0.46 [3 H, s, $C(CH_3)_2$], −0.01 (3 H, s, CH_3) ^{13}C:[d] 173.5 (s, CO_2Ph); 135.6 (s, C_6H_5), 130.7 (s, C_6H_5), 130.4 (s, C_6H_5), 130.2 (s, C_6H_5), 114.1 (s, C_5H_4), 106.7 (s, C_5H_4), 74.7 (s, C_5H_4), 70.1 (s, C_5H_4), 59.5 (s, C_5H_4, C_{ipso}), 29.9 [s, $C(CH_3)_2$], 22.4 [s, $C(CH_3)_2$], 21.6 [s, $C(CH_3)_2$], −20.5 (s, CH_3) IR: 1638s, 1626s, 1617s, 1578s, 1405w, 1319s, 1300s, 1267s
8 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me(I)]$ C, 34.5 (33.9); H, 3.4 (3.4); I, 24.3 (25.6)	^1H:[d] 5.60 (2 H, m, C_5H_4), 4.50 (2 H, m, C_5H_4), 4.39 (2 H, m, C_5H_4), 3.71 (2 H, m, C_5H_4), 0.86 (3 H, s, CH_3), 0.23 [3 H, s, $C(CH_3)_2$], 0.09 [3 H, s, $C(CH_3)_2$] ^{13}C:[d] 111.8 (s, C_5H_4), 105.3 (s, C_5H_4), 70.6 (s, C_5H_4), 68.9 (s, C_5H_4), 57.2 (s, C_5H_4, C_{ipso}), 29.5 [s, $C(CH_3)_2$], 22.1 [s, $C(CH_3)_2$], 21.6 [s, $C(CH_3)_2$], −27.8 (s, CH_3)
9 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me(H)]$ C, 45.6 (45.4); H, 5.1 (4.9)	^1H:[d] 5.13 (2 H, m, C_5H_4), 4.41 (4 H, m, C_5H_4), 3.79 (2 H, m, C_5H_4), 0.57 [3 H, s, $C(CH_3)_2$], 0.28 [3 H, s, $C(CH_3)_2$], 0.12 (3 H, s, CH_3), −6.30 (1 H, s, J_{WH} = 97) ^{13}C:[d] 104.5 (s, C_5H_4), 86.6 (s, C_5H_4), 70.5 (s, C_5H_4), 63.3 (s, C_5H_4), 47.7 (s, C_5H_4, C_{ipso}), 31.9 [s, $C(CH_3)_2$], 22.4 [s, $C(CH_3)_2$], 22.3 [s, $C(CH_3)_2$], −37.1 (s, CH_3) Mass: *m/z* 370 (M^+), 354 ($M^+ - CH_4$, base)
10 $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Ph(H)]$ C, 66.7 (66.3); H, 6.3 (5.9)	^1H:[d] 7.59 (2 H, d, C_6H_5), 7.36 (1 H, m, C_6H_5), 6.67 (2 H, m, C_6H_5), 5.48 (2 H, m, C_5H_4), 5.13 (2 H, m, C_5H_4), 4.45 (2 H, m, C_5H_4), 4.27 (2 H, m, C_5H_4), 1.20 [3 H, s, $C(CH_3)_2$], 0.87 [3 H, s, $C(CH_3)_2$], −4.60 (1 H, s) ^{13}C:[d] 148.8 (s, C_6H_5), 129.1 (s, C_6H_5), 125.9 (s, C_6H_5), 123.2 (s, C_6H_5), 107.6 (s, C_5H_4), 90.2 (s, C_5H_4), 76.6 (s, C_5H_4), 71.2 (s, C_5H_4), 58.6 (s, C_5H_4, C_{ipso}), 22.3 [s, $C(CH_3)_2$], 22.3 [s, $C(CH_3)_2$] Mass: *m/z* 343 (M^+), 268 ($M^+ - C_6H_6$), 78 (C_6H_6, base) IR: ν(Mo–H) 1790ms

[a] Analytical data given as found (calculated) in %. [b] Given as: chemical shift (δ) [relative intensity, multiplicity (*J* in Hz), assignment]. IR data (cm^{-1}) determined in Nujol mulls. [c] In CD_2Cl_2. [d] In C_6D_6.

corresponding dichlorides with MgMeBr;[14] however, the reactions between **1** or **2** and MgMeBr gave a complex mixture of products. The dimethyl *ansa*-bridged derivatives **5** and **6** form orange crystals which are very soluble in pentane. They can be prepared, as for the dihydrides, without isolating the intermediate dichlorides. The dimethyltungsten compound **5** was treated with benzoic acid in refluxing light petroleum (b.p. 100–120 °C) giving $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me(O_2CPh)]$ **7**. We note that $[W(\eta-C_5H_5)_2Me_2]$ reacts rapidly with benzoic acid at 60 °C,[15] but **5** in the presence of benzoic acid at 60 °C for 8 h showed no evolution of methane. Treatment of **6** with NH_4I in refluxing thf gave the methyl iodide $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me(I)]$ **8**. The compound **7** was treated with $Na[AlH_2(OCH_2CH_2OMe)_2]$ to give, after hydrolysis, the methyl hydride $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Me(H)]$ **9**, in a procedure analogous to that used for the preparation of $[W(\eta-C_5H_5)_2Me(H)]$.[15] Alternatively, treatment of **8** with $Na[AlH_2(OCH_2CH_2OMe)_2]$ gave **9**. The latter synthesis of **9** gave an improved yield (50%). A solution of **9** in benzene was refluxed for 10 h at 80 °C and the ^1H NMR spectrum showed that no reaction occurred.

It was thought particularly interesting to explore the photochemistry of complexes **3** and **4** since photolysis of the unsubstituted tungsten derivative $[W(\eta-C_5H_5)_2H_2]$ generates tungstenocene, $[W(\eta-C_5H_5)_2]$,[16] which is capable of inserting into mildly activated C–H bonds, *e.g*.. those of $SiMe_4$.[17] In principle, it was hoped that photolysis of **3** might give rise to reactions with saturated hydrocarbons. However, a prolonged photolysis of **3** in benzene for 100 h, monitored by ^1H NMR spectroscopy, showed no reaction. In contrast, photolysis of a solution of $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ in benzene using a medium-pressure mercury lamp for 100 h gave a high yield (*ca*. 80%) of the phenyl hydride $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Ph(H)]$ **10**.

There are three striking differences between the reactions of the *ansa*-bridged compounds described above and those of the non-bridged bis(η-cyclopentadienyl) analogues. First, photolysis of the non-*ansa* $[Mo(\eta-C_5H_5)_2H_2]$ in benzene has been previously shown to give the dimer $[\{Mo(\eta-C_5H_5)(\mu-\kappa,\eta-C_5H_4)\}_2]$.[18] Unlike the formation of **10** from **4**, the phenyl hydride $[Mo(\eta-C_5H_5)_2Ph(H)]$ is not formed, neither can this compound be made by alternative routes available to the tungsten analogue. Also, there are only two examples of alkylhydride derivatives of bis(η-cyclopentadienyl)molybdenum, namely $[Mo(\eta-C_5H_5)_2\{C(CO_2Me){=}CH(CO_2Me)\}H]$[19] and $[Mo(\eta-C_5H_5)_2(CHCNCH_2CN)H]$.[20] Secondly, photolysis of the non-*ansa* [W(η-C_5H_5)$_2$$H_2$] in benzene readily gives the phenyl hydride [W(η-C_5H_5)$_2$Ph(H)][16] whilst under the same conditions **3** is completely unreactive. The higher reactivity to photolysis of **4** with respect to **3** is consistent with the observation[21] that the quantum yield for extrusion of H_2 from [W(η-C_5H_5)$_2$$H_2$] is about one-tenth that for [Mo(η-C_5H_5)$_2$$H_2$]. Thirdly, in contrast to the thermally stable **9**, the methyl hydride [W(η-C_5H_5)$_2$Me(H)] is thermally unstable above *ca.* 40 °C with respect to the reductive elimination of methane. It appears that this methane elimination proceeds by an intramolecular mechanism and tungstenocene is formed as a reactive intermediate.[15] The resulting tungstenocene can insert into many carbon–hydrogen bonds.[15,16] The above observations are summarised in Scheme 1 and it is clear that the *ansa*-bridged compounds [M{(η-C_5H_4)CMe$_2$(η-C_5H_4)}X(Y)] (M = Mo, XY = H_2 **3** or PhH **5**; M = W, XY = H_2 **4** or MeH **9**) have a much greater stability towards reductive elimination of XY, under either thermal or photochemical conditions as appropriate, than do the corresponding non-bridged bis(η-cyclopentadienyl) analogues [M(η-C_5H_5)$_2$X(Y)].



Scheme 1 The differences in reactivity for *ansa*-bridged tungsten and molybdenum metallocene derivatives in comparison with the unbridged analogues. (*i*) *hv*, C_6H_6; (*ii*) 60 °C, C_6H_6; (*iii*) C_6H_6, reflux

The crystal structures of [W{(η-C_5H_4)CMe$_2$(η-C_5H_4)}Cl$_2$] **1**, [W{(η-C_5H_4)CMe$_2$(η-C_5H_4)}H_2] **3**, (two polymorph modifications, **3a** and **3b**) and [Mo{(η-C_5H_4)CMe$_2$(η-C_5H_4)}H_2] **4** have been determined and selected distances and angles are given in Tables 2–4. The structures of **1** and **4** are given in Figs. 1 and 2. The complex [W{(η-C_5H_4)CMe$_2$(η-C_5H_4)}H_2] crystallises in two different space groups; the two forms can be distinguished by their different colours, **3a** being yellow and **3b** orange. The bond distances and angles for the W[(η-C_5H_4)CMe$_2$(η-C_5H_4)] moiety in the two structure solutions are similar; in **3a** all hydrogen atoms were located in the Fourier-difference maps, in **3b** the hydrogens bonded to tungsten were not located. We note that **3b** is isostructural with **4**. The M–X distances (X = Cl or H) in the *ansa*-bridged derivatives are quite similar to those observed in non-bridged analogues, see Table 5 in which selected bond distances and angles of the *ansa*-bridged derivatives are compared with those of the analogous unbridged derivatives. The data in Table 5 also show the metal to ring-normal distances vary from 1.97–1.98 Å in the non-*ansa* [Mo(η-C_5H_5)$_2$Cl$_2$][22] to 1.95 Å in the *ansa*-bridged derivative, and from 1.94–1.95 Å in [Mo(η-C_5H_5)$_2$$H_2$][23] to 1.91 Å in **4**. This suggests there is a compressing effect by the *ansa*-carbon bridge. The most striking structural effect of the *ansa* bridge is in the significant decrease in the bending angle θ, namely the angle between the normals to the rings (θ is defined in Scheme 2). Thus for [M{(η-C_5H_4)CMe$_2$(η-C_5H_4)}Cl$_2$] θ is 114.6° compared to 130.2–130.9° in [Mo(η-C_5H_5)$_2$Cl$_2$], and θ = 121.1° for **4** whilst for

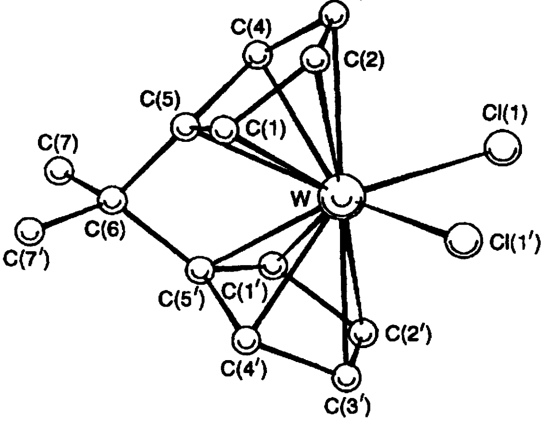


Fig. 1 Molecular structure of [W{(η-C_5H_4)CMe$_2$(η-C_5H_4)}Cl$_2$] **1**

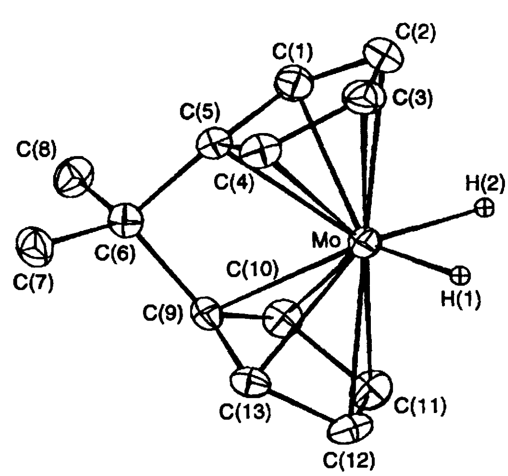


Fig. 2 Molecular structure of [Mo{(η-C_5H_4)CMe$_2$(η-C_5H_4)}H_2] **4**

$[Mo(\eta\text{-}C_5H_5)_2H_2]$ it is 145.8°. It is noteworthy that in the dichloride derivatives the metal–carbon distances of the C_5 rings are somewhat elongated and the bending angles are smaller than for the dihydride derivatives. In all the *ansa* structures the angles at the bridging carbon atom C(6) lie in the range *ca.* 94–97° a significant decrease from the regular tetrahedral value.

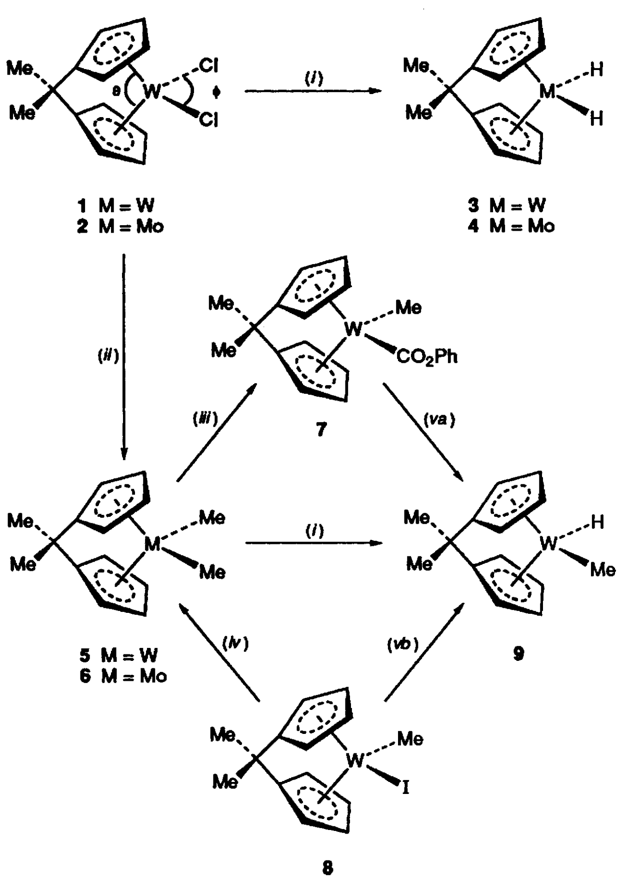
The photoelectron spectrum of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$ has been determined and shows that the ionisation energy associated with the d^2 electron is 6.47 eV (*ca.* 1.03×10^{-18} J), closely similar to that of the non-bridged analogue.[25] These electrons occupy the essentially non-bonding a_1 orbital and calculations show that the energy of this orbital is

Table 2 Selected distances (Å) for complex **3a**

W–X	1.75(6)	C(1)–C(5)	1.457(6)
W–C(1)	2.252(5)	C(2)–C(3)	1.41(1)
W–C(2)	2.348(6)	C(3)–C(4)	1.428(8)
W–C(3)	2.342(6)	C(4)–C(5)	1.441(7)
W–C(4)	2.244(4)	C(5)–C(6)	1.529(6)
W–C(5)	2.196(4)	C(6)–C(7)	1.528(7)
C(1)–C(2)	1.418(7)		

Table 3 Selected distances (Å) for complex **4**

Mo–H	1.66(5), 1.72(7)	C(2)–C(3)	1.399(7)
Mo–C(1)	2.246(4)	C(3)–C(4)	1.411(7)
Mo–C(2)	2.329(4)	C(4)–C(5)	1.451(6)
Mo–C(3)	2.336(5)	C(5)–C(6)	1.534(6)
Mo–C(4)	2.246(4)	C(6)–C(7)	1.516(6)
Mo–C(5)	2.189(4)	C(6)–C(8)	1.529(5)
Mo–C(9)	2.198(4)	C(6)–C(9)	1.542(6)
Mo–C(10)	2.247(4)	C(9)–C(10)	1.437(6)
Mo–C(11)	2.323(4)	C(9)–C(13)	1.444(6)
Mo–C(12)	2.329(4)	C(10)–C(11)	1.423(6)
Mo–C(13)	2.246(4)	C(11)–C(12)	1.429(7)
C(1)–C(2)	1.408(7)	C(12)–C(13)	1.408(6)
C(1)–C(5)	1.450(6)		



Scheme 2 (*i*) $LiAlH_4$ in Et_2O, yield 25 (W) or 13% (Mo); (*ii*) $ZnMe_2$ in toluene, 43 (W) or 24% (Mo); (*iii*) benzoic acid in light petroleum (100–120 °C), reflux, 76%; (*iv*) NH_4I in thf, reflux, 71%; (*v*) sodium dihydridobis(2-methoxyethoxo)aluminate in benzene, 50 (*a*) or 22% (*b*)

Table 4 Comparison of selected structural data for complexes **1**, **3a**, **3b** and **4***

	1	**3a**	**3b**	**4**
M–cp(cent)/Å	1.948	1.924	1.923, 1.920	1.920, 1.917
M–cp(⊥)/Å	1.939	1.917	1.916, 1.915	1.913, 1.912
C(cp)–C(bridge)/Å	1.526(7)	1.529(6)	1.529(6), 1.523(6)	1.534(6), 1.542(6)
X–M–X (φ)/Å	81.85(8)	95.5(4.0)		80.3(2.8)
X–M–cp(cent)/Å	110.7, 109.4	105.2, 107.6		107.3, 103.5, 111.3, 113.1
cp(cent)–M–cp(cent)/°	126.0	130.3	130.0	130.1
Bending angle (θ)/°	115.2	120.3	120.8	121
cp–C_{br}–cp/°	93.8(6)	96.9(5)	96.9(3)	96.0(3)

* cp indicates a η-C_5 ring. Unless otherwise indicated the e.s.d.s are 0.005 Å or 0.05°.

Table 5 Comparison of selected crystallographic data between *ansa* and non-*ansa* analogous derivatives*

Compound	X–M–X (φ)/°	θ/°	M–X/Å	M–cp(⊥)	Ref.
$[Mo(\eta\text{-}C_5H_5)_2Cl_2]$	82.0(2) 82.0(2)	130.9 130.2	2.464(6), 2.470(5) 2.473(5), 2.477(5)	1.98, 1.97 1.97, 1.98	22
$[Mo(\eta\text{-}C_5H_5)_2H_2]$	75.5(3)	145.8	1.685(3)	1.942 1.946	23
$[Mo\{(\eta\text{-}C_5H_4)C(C_4H_8)(\eta\text{-}C_5H_4)\}Cl_2]$	82.6(2)	114.6	2.4621(4) 2.4694(4)	1.949 1.950	10
$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$	80.3(2.8)	121	1.66(5), 1.72(7)	1.913 1.912	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$	81.85(8)	115.2	2.452(2)	1.948	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$	95.4(4.0)	120.3	1.75(6)	1.924	This work
$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(Cl)]$	79.9(3)	116.1	W–Cl 2.466(3) W–C 2.25	1.928	24

* The e.s.d.s are calculated to be better than ± 0.01 Å for M–cp(⊥) (the metal to ring perpendicular distance) and ± 1° for θ.

Table 6 Selected spectroscopic data for selected bis(η-cyclopentadienyl) dihydrides of tungsten and molybdenum

Compound	δ^a	J_{WH}/Hz	$\tilde{\nu}$(M–H)^b/cm^{-1}	M–H/Å	Ref.
[W(η-$C_5Me_5)_2H_2$]	−11.27	85	1919		30
[W(η-$C_5H_5)_2H_2$]	−12.28	69	1896		31
[W{(η-C_5H_4)$SiMe_2OSiMe_2$(η-C_5H_4)}H_2]	−11.82				11
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2]	−7.33	92	1833, 1823	1.75(6)	This work
[Mo(η-$C_5Me_5)_2H_2$]	−8.18		1862		30
[Mo(η-$C_5H_4Me)_2H_2$]	−8.25		1840, 1835^c		30
[Mo(η-$C_5H_5)_2H_2$]	−8.76		1847, 1826^c	1.685(3)	23., 32
[Mo{(η-C_5H_4)$SiMe_2OSiMe_2$(η-C_5H_4)}X_2]	−8.70		1818^c		11
[Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2]	−4.77		1760, 1750	1.66(5), 1.72(7)	This work

[a] Hydride peak in deuteriobenzene. [b] Ir in Nujol. [c] Ir in CH_2Cl_2.

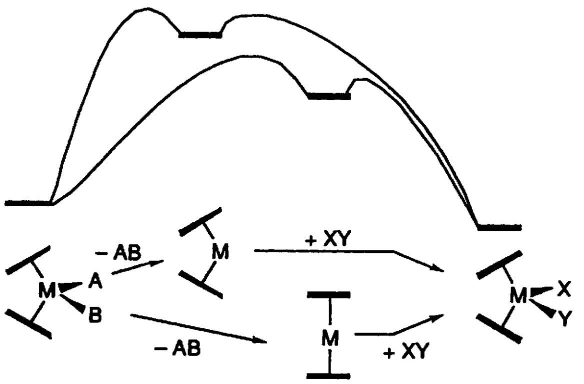


Fig. 3 Proposed energetics for the reaction pathways for reductive elimination of AB from *ansa*- and non-*ansa* bent metallocenes

insensitive to changes of θ.[26] Further, it appears that the changes in θ do not substantially affect the bonding in the X–M–X grouping since the Cl–M–Cl angles (φ) for **1** and [Mo(η-$C_5H_5)_2Cl_2$] are closely similar. However, in the compound [Ti{(η-C_5H_4)CH_2(η-C_5H_4)}Cl_2] the Cl–Ti–Cl angle of 97.1(0.1)° is significantly enlarged compared to the 94.4° in [Ti(η-$C_5H_5)_2Cl_2$].[3a,27]

The single-carbon *ansa* bridge causes both structural and consequently electronic changes for the cyclopentadienyl rings. Structural parameters associated with the cyclopentadienyl rings are presented in Tables 2 and 3. In particular, the M–C distances are shorter for C(1) and substantially longer for C(3) and C(4). In the present system, the C(3)–C(4) bond distance does not show a shortening which could be associated with a η^3-allyl, η^2-olefin structure.[4,28] In the *ansa*-metallocene derivatives [M{(η-C_5H_4)CMe_2(η-C_5H_4)}X_2] the chemical shift of the bridgehead carbon (*ipso*-carbon) of the cyclopentadienyl ligands is strongly shifted to high field compared to that for analogous Group 4 derivatives.[29] A similar upfield shift has been observed for the SiR_2 *ansa* bridge for Group 4 metals[28] and in this case was attributed to a build-up of π-electron density at the bridgehead carbon due to an electron-withdrawing effect of the SiR_2 bridge.

The infrared data in Table 6 show doublets for the stretching frequencies of the MH_2 group of the dihydrides **3** and **4**. This is to be expected from the C_{2v} symmetry but usually only a singlet is observed for *cis*-dihydride systems. Evidence that the one-carbon *ansa*-bridge ligand imposes an electronic effect can be inferred. Thus the ν(Mo–H) stretching frequencies of **3** and **4** are substantially lower than for the non-*ansa* analogues [M(η-$C_5R_5)_2H_2$], R = H. Simple substitution of the C_5 ring of non-*ansa* analogues does not cause a substantial shift of ν(Mo–H) and when R_5 = H_4Me or Me_5 the M–H stretching frequencies are higher than for R_5 = H_5. Further, the compound [Mo{(η-C_5H_4)$SiMe_2OSiMe_2$(η-C_5H_4)}H_2], in which the three-atom *ansa* bridge would cause little strain in the metallocene moiety, has a normal Mo–H stretching frequency. Further, the chemical shifts of the hydride resonances for **3** and **4** are considerably lower than for the non-*ansa* analogues.

It seems likely that the marked increase of stability towards reductive elimination of the *ansa*-bridged compounds **3**–**5** and **9** compared to the related non-bridged compounds may be associated with the inability of the 16-electron systems M[(η-$C_5H_4CMe_2$(η-C_5H_4)] (M = Cr, Mo or W) to adopt a parallel ring structure, which is the ground-state structure of the 16-electron compounds [M(η-$C_5H_5)_2$] (M = Cr or W) (in an argon matrix).[33] A schematic representation of the proposed energetics for reductive-elimination reactions of *ansa* and non-*ansa* metallocenes is given in Fig. 3. The higher energy of the bent matallocene compared to the parallel structure may be associated with the increase in energy of the electrons in the b_2 molecular orbitals as θ decreases from 180° to the typical *ansa* angles shown in Table 4.[34]

In conclusion, we have described convenient syntheses of *ansa*-bridged bis(η-cyclopentadienyl) compounds of molybdenum and tungsten. The reactions and the structures proposed for the new compounds are shown in Schemes 1 and 2. There are substantial differences between the reactivities of *ansa*-bridged bis(η-cyclopentadienyl) derivatives of molybdenum and tungsten compared to those of the non-bridged analogues which we attribute mainly to the structural constraints arising from the *ansa* bridge.

Experimental

All the reactions and manipulations were carried out under dinitrogen using standard Schlenk techniques, or in a dry-box under dinitrogen. Light petroleum (b.p. 40–60 °C), pentane, toluene, benzene, diethyl ether or tetrahydrofuran were dried over molecular sieves prior to refluxing over and subsequent distillation (under dinitrogen) from molten sodium or sodium–potassium alloy as appropriate, and then stored over freshly activated molecular sieves (4 Å). 1,2-Dimethoxyethane was distilled from calcium hydride, and dichloromethane from phosphorus pentaoxide. The compounds [WCl_4(dme)][35] and [$MoCl_4$(dme)][35] and the lithium salt of 2,2-bis(cyclopentadienyl)propane[36] were prepared as described. The compounds lithium aluminium tetrahydride, sodium tetrahydroborate, dimethylzinc (2 mol dm^{-3} toluene solution), benzoic acid, sodium dihydridobis(2-methoxyethoxo)aluminate (3.4 mol dm^{-3} solution in toluene), and ammonium iodide were obtained from Aldrich. Photolysis experiments were carried out in a standard Pyrex-glass apparatus cooled by water, with 500 W medium-pressure mercury lamps supplied by Hanovia. The NMR data were recorded using a Bruker AM 300 spectrometer, at 300 (^1H) or 75 MHz (^{13}C-{^1H}) and given as δ relative to $SiMe_4$, relative intensity, multiplicity, coupling constant (in Hz) and assignment. Mass spectra were measured using electron-impact techniques. The IR spectra were recorded as Nujol mulls on CsI plates using a Perkin-Elmer 1510 FT interferometer or, in the region 400–250 cm^{-1}, a Perkin-Elmer 457 grating spectrometer. Elemental analyses were performed by the analytical department of this laboratory.

Preparations.—$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1**. A mixture of $[WCl_4(dme)]$ (5.4 g, 13.1 mmol) and $Li_2[C_5H_4CMe_2C_5H_4]$ (2.4 g, 13.1 mmol) was stirred for 1 h in the absence of solvent. Diethyl ether (200 cm^3) was then added with vigorous stirring. The suspension was stirred for 48 h. The liquid phase was decanted away and dme (40 cm^3) added. After stirring for 1 h, a dark brown solid was separated and dried. It was washed with thf (30 cm^3), EtOH (60 cm^3) and finally diethyl ether (3 × 30 cm^3). The resulting red-brown solid was then dried (yield 3.2 g, 58%). Though this solid had a satisfactory elemental analysis for complex **1**, it did not have an homogeneous composition, further purification being obtained by Soxhlet extraction with CH_2Cl_2. Final yield 1.9 g, 35%. Crystals suitable for X-ray diffraction were obtained by vapour diffusion of diethyl ether in a dichloromethane solution.

$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **2**. A procedure similar to that for the tungsten derivative was followed. The complex $[MoCl_4(dme)]$ (20.18 g, 61 mmol) and $Li_2[C_5H_4CMe_2C_5H_4]$ (11.33 g, 61 mmol) were used. After washing the product with dme, thf, EtOH and Et_2O, a red-brown solid with a satisfactory elemental analysis for complex **2** was recovered (yield 10.89 g, 53%); after Soxhlet extraction in dichloromethane, yield 1.53 g (8%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$ **3**. A mixture of $[WCl_4(dme)]$ (12.66 g, 30.4 mmol) and $Li_2[C_5H_4CMe_2C_5H_4]$ (5.61 g, 30.4 mmol) was stirred for 1 h in the absence of solvent. After addition of diethyl ether the suspension was stirred for 24 h. The liquid phase was removed, ethanol (*ca.* 250 cm^3) was added and the suspension stirred for 1 h. The solid phase was then separated and washed several times with diethyl ether. To a suspension of this solid in diethyl ether (300 cm^3), cooled at −78 °C, $LiAlH_4$ (6.1 g, 161 mmol) was added slowly (2 h) with vigorous stirring. On completion of the addition the bath temperature was allowed to reach room temperature and the mixture stirred for 48 h; the liquid phase became orange-yellow. The suspension was then filtered, and the filtrate hydrolysed at 0 °C by dropwise addition of a diethyl ether solution (*ca.* 300 cm^3) saturated with water, and then water (100 cm^3). The resulting biphasic suspension was stirred for 1 h at room temperature, then the organic phase was separated. The aqueous phase was washed with diethyl ether (2 × 50 cm^3). The combined organic phases were washed with water (100 cm^3) and then evaporated *in vacuo*. The residue was left to dry overnight and extracted in toluene (100 cm^3). The solvent was removed *in vacuo* and the residue washed with pentane (2 × 20 cm^3) and recrystallised from acetone at −78 °C. Yield, 2.73 g, 25.2%, from $[WCl_4(dme)]$. Alternatively the compound can be purified by sublimation at 120 °C *in vacuo* (10^{-3} Torr, *ca.* 0.133 Pa).

$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$ **4**. A procedure similar to that for the tungsten derivative was followed, using $[MoCl_4(dme)]$ (1.85 g, 5.7 mmol) and $Li_2[C_5H_4CMe_2C_5H_4]$ (1.05 g, 5.7 mmol). After reduction with $LiAlH_4$ (0.89 g, 23 mmol) and hydrolysis, yellow crystals of complex **4** were recovered after recrystallisation from acetone. Yield 0.2 g, 13%.

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **5**. To a suspension of crude $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ (4.4 g, 10.3 mmol) (not extracted into dichloromethane) in toluene (300 cm^3) was added a 2 mol dm^{-3} solution of $ZnMe_2$ in toluene (20.7 cm^3, 41.4 mmol) at −78 °C. The temperature was allowed to reach room temperature (r.t.), and the suspension became dark red and was stirred vigorously for 1 d. The mixture was cooled to 0 °C and water (10 cm^3) added; this mixture was warmed to r.t. and more water (10 cm^3) was added. After stirring for 1 h the suspension was filtered, the residual solid was washed with toluene (3 × 20 cm^3), and the filtrate evaporated to dryness. The residue was extracted into light petroleum (b.p. 40–60 °C), and the extract concentrated to a small volume and left overnight at −78 °C. Orange crystals of complex **5** separated; they were filtered off and dried *in vacuo*. Yield 1.69 g, 42.7%.

$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **6**. A procedure similar to that for the tungsten derivative **5** was followed using the crude (not extracted in dichloromethane) $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ (0.87 g, 2.6 mmol). Yield 0.18 g, 23.5%.

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(O_2CPh)]$ **7**. A mixture of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ (2.47 g, 6.43 mmol) and $PhCO_2H$ (0.78 g, 6.39 mmol) was refluxed in light petroleum (b.p. 100–120 °C, 350 cm^3) for 18 h. The solution turned dark red. Once the reaction was complete, as verified by proton NMR spectroscopy, the product was crystallised from light petroleum (b.p. 100–120 °C) at −78 °C. Yield 2.4 g, 76.2%.

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(I)]$ **8**. A mixture of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ (0.5 g, 1.3 mmol) and NH_4I (0.19 g, 1.3 mmol) was refluxed in thf (70 cm^3) for 18 h. The solution changed from orange to red-purple. When the reaction was complete, as verified by proton NMR spectroscopy, the mixture was filtered and the solvent removed from the filtrate under reduced pressure. The residue was washed with light petroleum, to remove traces of the unreacted dimethyl compound, and then extracted into toluene (2 × 20 cm^3). The resulting solution was concentrated to small volume and, after addition of light petroleum, was cooled to −78 °C. Red-purple crystals of complex **8** separated and were dried *in vacuo*. Yield 0.46 g, 71.3%.

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(H)]$ **9**. *Method* (*a*) *from* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(I)]$. To a solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)Me(I)]$ (0.2 g, 0.4 mmol) in benzene (100 cm^3) was added a 3.4 mol dm^{-3} solution of sodium dihydridobis(2-methoxyethoxo)aluminate in toluene (1 cm^3, 3.4 mmol). The solution became pale yellow. After stirring for 2 d at r.t., water (10 cm^3) was added cautiously at 0 °C; the suspension stirred for 1 h at r.t. and the organic phase separated. The solvent was removed under reduced pressure and the residue extracted into pentane. The extract was cooled at −78 °C giving yellow crystals. A small amount of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$ was removed by a further recrystallisation from the minimum volume of pentane giving a final yellow product. Yield 0.08 g, *ca.* 50%.

Method (*b*) *from* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(O_2CPh)]$. To a solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(O_2CPh)]$ (0.3 g, 0.6 mmol) in benzene (100 cm^3) was added a 3.4 mol dm^{-3} solution of sodium dihydridobis(2-methoxyethoxo)aluminate in toluene (1 cm^3, 3.4 mmol). The solution became pale yellow. After stirring for 2 d at r.t., water (10 cm^3) was added cautiously at 0 °C; the suspension was stirred for 1 h at r.t. and the organic phase separated. The solvent was removed under reduced pressure, and the residue extracted with light petroleum. The extract was cooled to −78 °C and the yellow precipitate recrystallised twice from pentane. Yield 0.05 g, 22.5%.

Photolyses.—$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$. A solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$ (0.1 g, 0.3 mmol) in benzene (300 cm^3) was irradiated with a 500 W medium-pressure mercury lamp for 100 h at room temperature. No reaction occurred, as confirmed by proton NMR spectroscopy on the sample recovered after irradiation.

$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$. A solution of $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$ (0.2 g, 0.7 mmol) in benzene 300 cm^3) was irradiated as above. It became darker yellow and traces of a black insoluble decomposition product appeared. After initial filtration, the solvent was removed *in vacuo*, and the product was recrystallised from light petroleum at −78 °C giving $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Ph(H)]$, which was filtered off and dried *in vacuo*. Yield 0.19 g, 79%.

Thermolysis of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(H)]$. The complex $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(H)]$ (0.2 g, 0.52

Table 7 Crystal data, data collection and processing parameters for complexes **3a**, **3b** and **4**[a,b]

	3a	**3b**	**4**
Formula	$C_{13}H_{16}W$	$C_{13}H_{16}W$	$C_{13}H_{16}Mo$
M	356.12	356.12	268.21
Space group	$C2/c$	$P2_1/n$	$P2_1/n$
a/Å	11.132(1)	7.9901(5)	7.9989(7)
b/Å	11.9584(8)	14.260(1)	14.288(2)
c/Å	8.2409(9)	9.5638(6)	9.5690(9)
β/°	105.22(1)	100.53(1)	100.59(1)
U/Å^3	1058.5(2)	1071.4(1)	1075.0(2)
D_c/g cm^{-3}	2.24	2.21	1.66
μ/cm^{-1}	111.06	109.73	11.48(?)
F(000)	672	672	544
Crystal size/mm	0.16 × 0.25 × 0.78	0.25 × 0.37 × 0.43	0.06 × 0.19 × 0.28
θ_{max}/° for data	34	30	27
No. of reflections:			
total	2611	4143	3056
unique	2162	3114	2345
in refinement [$I > 3\sigma(I)$]	1953	2005	1331
R_{merge}	0.097	0.022	0.023
No. of variables	69	127	136
Observations/variables	28.3	15.8	9.8
Weighting coefficients	52.7 −40.5, 40.8	36.3, −27.9, 29.8	7.5, −1.5, 6.2
Maximum, minimum peaks in the final difference map/e Å^{-3}	0.96, 1.49	0.92, −1.73	0.65, −0.75
R	0.047	0.027	0.031
R'	0.052	0.030	0.037

[a] Details in common: monoclinic; $Z = 4$; lattice segment $-h$ to h, $-k$ to k, $-l$ to l; $R = \Sigma(|F_o - F_c|)/\Sigma|F_o|$; $R' = [\Sigma w(|F_o - F_c)^2/\Sigma w|F_o|^2]^{\frac{1}{2}}$. [b] Data for complex **1** are given in ref. 10.

Table 8 Fractional atomic coordinates ($\times 10^4$) for complex **3a** with estimated standard deviations (e.s.d.s) in parentheses

Atom	X/a	Y/b	Z/c
W	0.5	0.328 95(2)	0.75
C(1)	0.579 3(4)	0.234 9(4)	0.991 0(6)
C(2)	0.525 4(7)	0.331 7(4)	1.041 9(8)
C(3)	0.396 3(7)	0.332 8(4)	0.963 2(9)
C(4)	0.365 9(4)	0.235 2(4)	0.860 8(6)
C(5)	0.479 0(5)	0.172 2(3)	0.878 7(6)
C(6)	0.5	0.087 3(5)	0.75
C(7)	0.614 2(6)	0.013 8(5)	0.819 3(9)
H(1)	0.617(6)	0.427(5)	0.826(8)

Table 9 Fractional atomic coordinates ($\times 10^4$) for complex **4** with e.s.d.s in parentheses

Atom	X/a	Y/b	Z/c
Mo	0.284 76(4)	−0.001 79(3)	0.211 96(3)
C(1)	0.423 7(6)	−0.136 2(3)	0.275 7(5)
C(2)	0.474 5(6)	−0.110 2(3)	0.147 8(6)
C(3)	0.332 8(7)	−0.107 7(3)	0.037 6(5)
C(4)	0.186 9(6)	−0.132 0(3)	0.093 0(4)
C(5)	0.241 3(5)	−0.151 0(3)	0.243 5(4)
C(6)	0.123 3(5)	−0.146 8(3)	0.352 8(4)
C(7)	−0.049 2(6)	−0.190 2(3)	0.297 8(5)
C(8)	0.205 5(6)	−0.191 2(3)	0.494 3(5)
C(9)	0.116 9(5)	−0.039 1(3)	0.361 3(4)
C(10)	0.251 9(6)	0.017 1(3)	0.438 4(4)
C(11)	0.235 9(6)	0.108 4(3)	0.378 3(5)
C(12)	0.092 0(7)	0.109 0(3)	0.265 0(5)
C(13)	0.019 3(5)	0.019 0(3)	0.252 3(5)
H(1)	0.261(6)	0.063(3)	0.065(5)
H(2)	0.481(8)	0.052(6)	0.237(7)

mmol) was dissolved in benzene (200 cm^3). No reaction occurred after prolonged (10 h) heating at 80 °C as confirmed by proton NMR spectroscopy.

Crystal Structure Determinations.—Data were collected at room temperature on an Enraf–Nonius CAD4 diffractometer (ω–2θ mode with ω scan width = 0.77–0.79 + 0.34 tan θ, ω scan speed 1.4–10.1° min^{-1}, ratio of scanning rates $\omega:\theta = 1.2:1$, graphite-monochromated Mo-Kα radiation, $\lambda = 0.710\,69$ Å). Details are given in Table 7. For all structures, corrections for Lorentz and polarisation effects as well as empirical correction for absorption[37] based on azimuthal scan data were applied. All the structures were solved by direct methods (**3b** is isostructural to **4**) and refined by full-matrix least-squares techniques with all non-hydrogen atoms in anisotropic approximation. In **4** all hydrogen atoms were located in the Fourier-difference maps, in **3b** only H atoms connected to W were not located, in **3a** only half the hydrogen atoms were located and the positions of the remainder calculated, and in **1** all H atoms were placed geometrically. For all structures, hydrogen atoms were included in the refinement with the fixed positional and thermal parameters. Only H(1) and H(2) atoms, attached to Mo in complex **4**, and H(1) atom, attached to W in **3a**, were refined isotropically. Chebyshev weighting schemes[38] were applied. Anomalous-dispersion contributions were included in the calculated structure factors. An empirical absorption correction using the DIFABS[39] program was applied after isotropic convergence. Crystallographic calculations were carried out using the CRYSTALS[40] program package on a MicroVAX 3800 computer. Neutral atom scattering factors were taken from the usual sources.[40,41] Fractional atomic coordinates for **3a** and **4** are given in Tables 8 and 9.

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

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