New *ansa*-2,2-bis(η-cyclopentadienyl)propane molybdenum and tungsten compounds and intramolecular hydrogen–deuterium exchange in methyl-hydride and ethyl-hydride derivatives†

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The new compounds $[Mo_2Cl_4(OEt)_4(EtOH)_2]$, $[Mo\{(\eta\text{-}C_5H_4)C(C_5H_{10})(\eta\text{-}C_5H_4)\}Cl_2]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)Cl_2][BF_4]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(SPh)_2]$,* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(SPr^i)_2]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(SPr^i)(NCMe)][BF_4]$, $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$ (M = Mo or W),* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(PPh_3)Cl][PF_6]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CNC_6H_3Me_2\text{-}2,6)Cl][PF_6]$,* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(\eta^2\text{-}C_2H_4)H][B(C_6F_5)_4]$,* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(NCMe)][B(C_6F_5)_4]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(Cl)]$,* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(Cl)][BF_4]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3][PF_6]$,* $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$ (M = Mo or W),* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(I)]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(O_2CPh)]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(X)]$ (X = H or D), $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)_2]$, $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$,* $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)H]$ and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ have been prepared. The asterisk indicates the crystal structure has been determined. Evidence is presented for intramolecular hydrogen–deuterium scrambling processes in the methyl- and ethyl-hydride compounds. Preliminary variable-temperature ^1H NMR studies on $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_A(H_B)_2][PF_6]$ give a value for $J(AB)$ of 16 000 Hz at −70 °C.

ansa-Metallocenes of the Group 4 transition metals have become of special interest as precursors for homogeneous catalysts for olefin polymerisation.[1–4] It has been shown that the presence of the *ansa* bridge can give rise to reactivities and structural features which are markedly different to those of non-*ansa* analogues. Recently we described the synthesis and reactions of *ansa*-metallocenes of molybdenum and tungsten and found unexpected and interesting observations such as a substantially increased stability of the methylhydride $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(H)]$ towards reductive elimination of methane compared to the non-*ansa* analogue $[W(\eta\text{-}C_5H_5)_2Me(H)]$.[5,6] Here we describe further studies on the synthesis and reactions of *ansa*-metallocene derivatives of molybdenum and tungsten.

Results and Discussion

The synthons for the chemistry described below are the previously described compounds $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ (M = Mo **1** or W **2**) which were prepared from the reaction between $[MCl_4(dme)]$ (dme = 1,2-dimethoxyethane) and $Li_2[(C_5H_4)CMe_2(C_5H_4)]$.[6] Owing to the especially low yields for **1**, most of the reactions described below were undertaken purely for **2**. During the work-up of the reaction mixtures the first formed solids of the reaction mixture were washed with ethanol. From these ethanol washings green crystals of $[W_2Cl_4(OEt)_4(EtOH)_2]$ **3** or purple crystals of $[Mo_2Cl_4(OEt)_4(EtOH)_2]$ **4** could be isolated, as described in the Experimental section. The compound **3** was first reported by Klejnot[7] and can be prepared *via* a number of routes including alcoholysis of WCl_4.[8–11] The analogous molybdenum compound $[Mo_2Cl_4(OEt)_4(EtOH)_2]$ **4** has not been reported before and was characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR and infrared spectroscopies and microanalysis. All the characterising data for the new compounds described in this paper are summarised in Table 1 and will not be further discussed except where assignments are not straightforward. The ^1H NMR spectrum of **4** in CD_2Cl_2 exhibited methyl triplets at δ 1.27 and 1.37 and methylene quartets at δ 4.52 and 5.42. In each case the lower-field resonance was half the intensity of the one at higher field and is attributed to the OEt bridges. A broad singlet at δ 8.24 was assigned to the hydroxyl protons. The infrared spectrum showed ν(Mo−Cl) modes at 340, 309 and 285 cm^{-1}. Observation of only a single set of resonances for the terminal ethoxy and ethanol ligands is probably due to a rapid migration of the proton between these terminal ligands; analogous behaviour has been observed for $[W_2Cl_4(OEt)_4(EtOH)_2]$.[12]

In an attempt to circumvent problems associated with the low solubility of compound **1**, the analogous fused cyclohexyl *ansa* system was prepared. Thus the reaction between $[MoCl_4(dme)]$ and $Li_2[(C_5H_{10})C(C_5H_4)_2]$ gave the 1,1-bis(η-cyclopentadienyl)cyclohexane derivative $[Mo\{(\eta\text{-}C_5H_4)C(C_5H_{10})(\eta\text{-}C_5H_4)\}Cl_2]$ **5** in 21% yield. The greater solubility of **5** enabled the $^{13}C\text{-}\{^1H\}$ NMR spectrum to be determined easily (see Table 1).

A number of alternative synthetic routes to compound **1** were also attempted in order to improve upon the low yields achieved using the previously reported method.[6] Altering the established protocol by changing the solvent to dme or the ordering of addition of reagents and solvent together led to either intractable oils or even more modest yields. However, reaction of the compound $Mo(NMe_2)_4$ with the neutral *ansa*-bis(cyclopentadiene) ligand $Me_2C(C_5H_5)_2$ gave an uncharacterised solid which, after treatment with HCl, gave the dichloride, **1** in 55% yield.[13] Interestingly, unlike the original method of synthesis of **1**, this procedure gave no polymeric metallocene material, however the pure starting complex $Mo(NMe_2)_4$ can only be prepared conveniently on a relatively small scale (up to 10 g) as compared with $[MoCl_4(dme)]$ (50 g easily).[14]

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† Dedicated to the memory of Sir Geoffrey Wilkinson, a great mentor and friend.

Table 1 Analytical and spectroscopic data

Compound and analysis[a]	Spectroscopic data[b]
4 $[Mo_2Cl_4(OEt)_4(EtOH)_2]$ Purple C, 24.9 (23.8); H, 5.8 (5.3); Cl, 23.8 (23.4)	^{1}H:^{c} 8.24 (2 H, br s, OH), 5.42 [4 H, q, *J*(HH) 7, CH_2 (bridging)], 4.52 [8 H, q, *J*(HH) 7, CH_2 (terminal)], 1.37 [6 H, t, *J*(HH) 7, CH_3 (bridging)], 1.27 [12 H, t, *J*(HH) 7, CH_3 (terminal)] ^{13}C-{^{1}H}:^{c} 79.1 [s, CH_2 (bridging)], 76.8 [s, CH_2 (terminal)], 16.9 [s, CH_3 (bridging)], 16.8 [s, CH_3 (terminal)] Mass (FAB): *m/z* 603 (M^+)
5 $[Mo\{(\eta\text{-}C_5H_4)C(C_5H_{10})\text{-}(\eta\text{-}C_5H_4)\}Cl_2]$ Green C, 51.0 (51.0); H, 5.8 (4.8); Cl, 18.3 (18.2)	^{1}H:^{c} 6.32 (4 H, m, C_5H_4), 5.04 (4 H, m, C_5H_4), 1.49 [4 H, br m, $C(C_5H_{10})$], 1.25 [2 H, s, $C(C_5H_{10})$], 1.20 [4 H, br m, $C(C_5H_{10})$] ^{13}C-{^{1}H}:^{c} 123.0 (s, C_5H_4), 78.8 (s, C_5H_4), 30.5 [s, $C(C_5H_{10})$], 25.2 [s, $C(C_5H_{10})$], 20.6 [s, $C(C_5H_{10})$] Mass (FAB): *m/z* 308 ($M^+ - Cl_2$, base) IR:^{d} ν(Mo–Cl) 295, 270
6 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\text{-}Cl_2][BF_4]$ Green C, 31.0 (30.5); H, 2.9 (2.8); Cl, 12.5 (13.9)	Mass (FAB): *m/z* 425 ($M^+ - BF_4$), 387 ($M^+ - BF_4 - Cl$) IR:^{d} ν(W–Cl) 355, 310
7 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}(SPh)_2]$ Orange C, 52.6 (52.5); H, 4.5 (4.2); S, 11.3 (11.2)	^{1}H:^{c} 7.42 [4 H, d, *J*(HH) 5, C_6H_5, H_o], 7.23 (4 H, m, C_6H_5, H_m), 7.09 [2 H, t, *J*(HH) 5, C_6H_5, H_p], 5.61 (4 H, m, C_5H_4), 4.70 (4 H, m, C_5H_4), 0.77 [6 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{c} 133.6 (s, C_6H_5, C_o), 128.2 (s, C_6H_5, C_m), 124.9 (s, C_6H_5, C_p), 114.7 (s, C_5H_4), 73.0 (s, C_5H_4), 51.7 (s, C_5H_4, C_{ipso}), 30.1 [s, $\mathit{C}(CH_3)_2$], 22.1 [s, $C(\mathit{C}H_3)_2$] Mass (FAB): *m/z* 572 (M^+), 463 ($M^+ - SPh$, base), 386 ($M^+ - SPh - Ph$), 354 ($M^+ - 2SPh$) IR:^{d} ν(W–S) 495w, 480
8 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}(SPr^i)_2]$ Orange-yellow C, 45.1 (45.2); H, 5.6 (5.6); S, 12.6 (12.7)	^{1}H:^{c} 5.44 (4 H, m, C_5H_4), 5.20 (4 H, m, C_5H_4), 2.81 [2 H, spt, *J*(HH) 5, $C\mathit{H}(CH_3)_2$], 1.27 [12 H, d, *J*(HH) 6, $CH(C\mathit{H}_3)_2$], 0.95 [s, 6 H, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{e} 113.8 (s, C_5H_4), 70.3 (s, C_5H_4), 58.9 (s, C_5H_4, C_{ipso}), 38.7 [s, $\mathit{C}H(CH_3)_2$], 29.7 [s, $\mathit{C}(CH_3)_2$], 29.0 [s, $CH(\mathit{C}H_3)_2$], 22.2 [s, $C(\mathit{C}H_3)_2$] Mass (FAB): *m/z* 503 (M^+), 461 ($M^+ - Pr^i$), 429 ($M^+ - SPr^i$), 387 ($M^+ - SPr^i - Pr^i$), 355 ($M^+ - 2SPr^i$)
9 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}(SPr^i)(NCMe)][BF_4]$ Orange	^{1}H:^{f} 5.95 (2 H, m, C_5H_4), 5.83 (2 H, m, C_5H_4), 5.73 (2 H, m, C_5H_4), 5.41 (2 H, m, C_5H_4), 2.80 [1 H, spt, *J*(HH) 5, $CH(CH_3)_2$], 2.13 (3 H, s, CH_3CN), 1.61 [6 H, d, *J*(HH) 6, $CH(CH_3)_2$], 0.99 [3 H, s, $C(CH_3)_2$], 0.91 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 121.9 (s, C_5H_4), 109.2 (s, C_5H_4), 77.3 (s, C_5H_4), 73.1 (s, C_5H_4), 72.1 (s, C_5H_4, C_{ipso}), 40.7 [$\mathit{C}H(CH_3)_2$], 30.8 [s, $\mathit{C}(CH_3)_2$], 28.3 [$CH(\mathit{C}H_3)_2$], 22.8 [s, $C(\mathit{C}H_3)_2$], 21.7 [s, $C(\mathit{C}H_3)_2$] IR:^{d} ν(C–C) and $\delta(CH_3)$ 2362m, ν(CN) 2339s
10 $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$ Red-brown C, 41.6 (42.0); H, 3.8 (3.9); N, 3.4 (3.3); Cl, 9.2 (8.3)	^{1}H:^{f} 6.57 (2 H, m, C_5H_4), 6.39 (2 H, m, C_5H_4), 5.43 (2 H, m, C_5H_4), 5.15 (2 H, m, C_5H_4), 2.50 (3 H, s, MeCN), 1.00 [3 H, s, $C(CH_3)_2$], 0.83 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 127.4 (s, C_5H_4), 116.8 (s, C_5H_4), 83.3 (s, C_5H_4), 79.3 (s, C_5H_4), 77.6 (s, C_5H_4, C_{ipso}), 31.5 [s, $\mathit{C}(CH_3)_2$], 21.3 [s, $C(\mathit{C}H_3)_2$], 20.6 [s, $C(\mathit{C}H_3)_2$] IR:^{g} ν(C–C) and $\delta(CH_3)$ 2318, ν(CN) 2291, ν(Mo–Cl) 285
11 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$ Red-brown C, 31.3 (31.3); H, 3.3 (3.0); N, 2.9 (2.4); Cl, 5.6 (6.2)	^{1}H:^{f} 6.24 (2 H, m, C_5H_4), 6.13 (2 H, m, C_5H_4), 5.76 (2 H, m, C_5H_4), 5.59 (2 H, m, C_5H_4), 2.59 (3 H, s, MeCN), 0.97 [3 H, s, $C(CH_3)_2$], 0.78 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 124.6 (s, C_5H_4), 112.1 (s, C_5H_4), 77.6 (s, C_5H_4), 72.8 (s, C_5H_4), 71.8 (s, C_5H_4, C_{ipso}), 30.8 [s, $\mathit{C}(CH_3)_2$], 22.3 [s, $C(\mathit{C}H_3)_2$], 21.6 [s, $C(\mathit{C}H_3)_2$] Mass (FAB): *m/z* 430 ($M^+ - PF_6$), 389 ($M^+ - PF_6 - MeCN$, base) IR:^{g} ν(C–C) and $\delta(CH_3)$ 2321, ν(CN) 2293
11a $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][BF_4]$ Pink C, 34.9 (34.8); H, 3.2 (3.3); N, 2.7 (2.7)	^{1}H:^{f} 6.25 (2 H, m, C_5H_4), 6.14 (2 H, m, C_5H_4), 5.77 (2 H, m, C_5H_4), 5.60 (2 H, m, C_5H_4), 2.14 (3 H, s, MeCN), 0.98 [3 H, s, $C(CH_3)_2$], 0.79 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 124.6 (s, C_5H_4), 112.1 (s, C_5H_4), 77.6 (s, C_5H_4), 72.8 (s, C_5H_4), 71.8 (s, C_5H_4, C_{ipso}), 30.8 [s, $\mathit{C}(CH_3)_2$], 22.3 [s, $C(\mathit{C}H_3)_2$], 21.6 [s, $C(\mathit{C}H_3)_2$] Mass (FAB): *m/z* 430 ($M^+ - BF_4$), 389 ($M^+ - BF_4 - MeCN$, base), 353 ($M^+ - BF_4 - MeCN - Cl$) IR:^{d} ν(C–C) and $\delta(CH_3)$ 2322m, ν(CN) 2285s, ν(W–Cl) 285w
12 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}(PPh_3)Cl][PF_6]$ Red C, 46.2 (46.6); H, 4.3 (3.9)	^{1}H:^{f} 7.56 (6 H, m, PPh_3, H_o), 7.54 (9 H, m, PPh_3, H_m and H_p), 5.99 (2 H, m, C_5H_4), 5.97 (2 H, m, C_5H_4), 5.92 (2 H, m, C_5H_4), 4.06 (2 H, m, C_5H_4), 1.15 [3 H, s, $C(CH_3)_2$], 0.57 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 134.1 [d, ^{2}*J*(PC) 11, PPh_3, C_o], 132.6 (s, PPh_3, C_p), 130.1 [d, ^{3}*J*(PC) 10, PPh_3, C_m], 120.4 (s, C_5H_4), 109.5 (s, C_5H_4), 77.5 (s, C_5H_4), 73.1 (s, C_5H_4), 69.5 (s, C_5H_4, C_{ipso}), 30.0 [s, $\mathit{C}(CH_3)_2$], 22.1 [s, $C(\mathit{C}H_3)_2$], 21.3 [s, $C(\mathit{C}H_3)_2$] Mass (FAB): *m/z* 651 ($M^+ - PF_6$), 391 ($M^+ - PF_6 - PPh_3$)
13 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}(CNC_6H_3Me_2\text{-}2,6)Cl][PF_6]$ Orange C, 39.9 (39.7); H, 3.9 (3.5); N, 2.3 (2.1); Cl, 5.0 (5.3)	^{1}H:^{f} 7.39 [2 H, d, *J*(HH) 4, $C_6H_3Me_2$, H_m], 7.30 (1 H, m, $C_6H_3Me_2$, H_p), 6.44 (2 H, m, C_5H_4), 6.12 (2 H, m, C_5H_4), 5.97 (2 H, m, C_5H_4), 5.28 (2 H, m, C_5H_4), 2.51 (6 H, s, $C_6H_3\mathit{Me}_2$-2,6), 1.31 [3 H, s, $C(CH_3)_2$], 0.80 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 131.9 (s, CNC_6H_3, C_p), 129.3 (s, CNC_6H_3, C_m), 125.2 (s, C_5H_4), 101.6 (s, C_5H_4), 83.2 (s, C_5H_4), 71.2 (s, C_5H_4), 69.6 (s, C_5H_4, C_{ipso}), 32.0 [s, $\mathit{C}(CH_3)_2$], 22.8 [s, $C(\mathit{C}H_3)_2$], 21.1 [s, $C(\mathit{C}H_3)_2$], 18.9 (s, $C_6H_3\mathit{Me}_2$-2,6) Mass (FAB): *m/z* 520 ($M^+ - PF_6$, base), 389 ($M^+ - PF_6 - CNC_6H_3Me\text{-}2,6$), 353 ($M^+ - PF_6 - CNC_6H_3Me_2\text{-}2,6 - Cl$) IR:^{d} ν(CN) 2151s, ν(M–Cl) 305w
15 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}(\eta^2\text{-}C_2H_4)H][B(C_6F_5)_4]$ Red-orange	Mass (FAB): *m/z* 384 [$M^+ - B(C_6F_5)_4$], 354 [$M^+ - B(C_6F_5)_4 - C_2H_5$] IR:^{g} ν(W–H) 1823w, $\nu(C_6F_5)$ 1543s, 1518s, ν(C=C) 1483m, $\nu(C_6F_5)$ 1093s, 980s
16 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}Et(NCMe)][B(C_6F_5)_4]$ Green C, 44.4 (44.6); H, 1.8 (2.1); N, 1.3 (1.3)	^{1}H:^{f} 5.54 (4 H, m, C_5H_4), 5.46 (4 H, m, C_5H_4), 5.28 (4 H, m, C_5H_4), 5.05 (4 H, m, C_5H_4), 2.34 (3 H, s, CH_3CN), 1.39 [3 H, t, *J*(HH) 8, $CH_2C\mathit{H}_3$], 0.70 [3 H, q, *J*(HH) 7, $C\mathit{H}_2CH_3$], 0.94 [3 H, s, $C(CH_3)_2$], 0.83 [3 H, s, $C(CH_3)_2$] ^{13}C-{^{1}H}:^{f} 149.1 [d, *J*(CF) 262, C_6F_5], 139.2 [d, *J*(CF) 288, C_6F_5], 137.3 [d, *J*(CF) 244, C_6F_5], 111.6 (s, C_5H_4), 109.6 (s, C_5H_4), 75.1 (s, C_5H_4), 71.2 (s, C_5H_4), 62.8 (s, C_5H_4, C_{ipso}), 31.9 [s, $\mathit{C}(CH_3)_2$], 22.5 [s, $C(\mathit{C}H_3)_2$], 22.1 [s, $C(\mathit{C}H_3)_2$], 20.7 (s, $CH_2\mathit{C}H_3$), 5.1 (s, $\mathit{C}H_3CN$), −10.8 (s, $\mathit{C}H_2CH_3$) Mass (FAB): *m/z* 424 [$M^+ - B(C_6F_5)_4$], 383 [$M^+ - B(C_6F_5)_4 - MeCN$], 354 [$M^+ - B(C_6F_5)_4 - MeCN - Et$] IR:^{d} ν(C–C) and $\delta(CH_3)$ 2361w, ν(CN) 2315w
16a $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(NCMe)][PF_6]$ Green C, 35.6 (35.9); H, 3.7 (3.9); N, 2.2 (2.4)	^{1}H:^{h} 5.77 (4 H, m, C_5H_4), 5.59 (4 H, m, C_5H_4), 5.49 (4 H, m, C_5H_4), 5.26 (4 H, m, C_5H_4), 2.65 (3 H, s, MeCN), 1.42 [3 H, t, *J*(HH) 8, $CH_2C\mathit{H}_3$], 1.03 [3 H, s, $C(CH_3)_2$], 0.93 [3 H, s, $C(CH_3)_2$], 0.78 [2 H, q, *J*(HH) 7, $C\mathit{H}_2CH_3$] ^{13}C-{^{1}H}:^{h} 111.6 (s, C_5H_4), 109.7 (s, C_5H_4), 75.0 (s, C_5H_4), 71.4 (s, C_5H_4), 62.8 (s, C_5H_4, C_{ipso}), 31.7 [s, $\mathit{C}(CH_3)_2$], 22.5 (s, $CH_2\mathit{C}H_3$), 22.1 [s, $C(\mathit{C}H_3)_2$], 20.6 [s, $C(\mathit{C}H_3)_2$], 4.4 (s, $NC\mathit{C}H_3$), −10.9 (WCH_2) Mass (FAB): *m/z* 424 ($M^+ - PF_6$), 383 ($M^+ - PF_6 - NCMe$), 358 ($M^+ - PF_6 - Et$, base) IR:^{d} ν(CN) 2297w

Table 1 (*Continued*)

Compound and analysis[a]	Spectroscopic data[b]
17 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(Cl)]$ Red C, 43.0 (43.0); H, 4.5 (4.6); Cl, 8.8 (8.5)	^1H:[h] 5.26 (2 H, m, C_5H_4), 5.18 (2 H, m, C_5H_4), 5.09 (2 H, m, C_5H_4), 4.60 (2 H, m, C_5H_4), 1.41 [3 H, t, *J*(HH) 8, $\mathrm{CH_2C}\mathit{H}_3$], 1.02 [3 H, s, $C(CH_3)_2$], 0.84 [2 H, q, *J*(HH) 7, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 0.73 [s, 3 H, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[i] 116.7 (s, C_5H_4), 107.4 (s, C_5H_4), 71.1 (s, C_5H_4), 70.5 (s, C_5H_4), 30.5 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.7 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 20.6 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], −6.8 (s, WCH_2) Mass (EI): *m/z* 389 ($M^+ - Et$), 354 ($M^+ - Cl - Et$) IR:[d] ν(M−Cl) 291m
18 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(Cl)][BF_4]$ Purple C, 35.5 (35.6); H, 4.1 (3.9)	Mass (FAB): *m/z* 418 ($M^+ - BF_4$), 389 ($M^+ - BF_4 - Et$, base peak), 353 ($M^+ - BF_4 - Et - Cl$) IR:[d] ν(W−Cl) 280w
20 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3][PF_6]$ Colourless C, 31.1 (31.1); H, 3.4 (3.4)	^1H:[f] 5.70 (4 H, m, C_5H_4), 5.59 (4 H, m, C_5H_4), 1.41 [6 H, s, $C(CH_3)_2$], −3.28 (3 H, br s, WH_3) $^{13}C\text{-}\{^1H\}$:[c] 118.7 (s, C_5H_4), 95.8 (s, C_5H_4), 84.1 (s, C_5H_4, C_{ipso}), 38.1 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 22.4 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$] IR:[g] ν(W−H) 1913 (br) w
21 $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$ Orange C, 63.0 (63.0); H, 7.6 (7.5)	^1H:[e] 4.34 (4 H, m, C_5H_4), 4.20 (4 H, m, C_5H_4), 1.46 [3 H, t, *J*(HH) 8, $\mathrm{CH_2C}\mathit{H}_3$], 0.79 [2 H, q, *J*(HH) 7, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 0.50 [6 H, s, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[e] 106.2 (s, C_5H_4), 73.0 (s, C_5H_4), 59.6 (s, C_5H_4, C_{ipso}), 31.7 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 21.9 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 21.2 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 6.3 (s, $\mathit{C}\mathrm{H_2CH_3}$) Mass (EI): *m/z* 328 ($M^+$), 298 ($M^+ - Et$), 270 ($M^+ - Et_2$, base)
22 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$ Orange C, 49.5 (49.5); H, 5.5 (5.9)	^1H:[e] 4.31 (4 H, m, C_5H_4), 4.23 (4 H, m, C_5H_4), 1.62 [3 H, t, *J*(HH) 8, $\mathrm{CH_2C}\mathit{H}_3$], 0.63 [2 H, q, *J*(HH) 7, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 0.41 [6 H, s, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[e] 104.7 (s, C_5H_4), 67.5 (s, C_5H_4), 52.1 (s, C_5H_4, C_{ipso}), 31.1 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 21.7 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 21.5 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], −6.5 (s, $\mathit{C}\mathrm{H_2CH_3}$) Mass (EI): *m/z* 413 ($M^+$), 383 ($M^+ - Et$), 355 ($M^+ - Et_2$)
23 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(I)]$ Purple C, 35.4 (35.3); H, 3.1 (3.7)	^1H:[e] 5.56 (2 H, m, C_5H_4), 4.39 (2 H, m, C_5H_4), 4.37 (2 H, m, C_5H_4), 3.64 (2 H, m, C_5H_4), 1.60 [2 H, q, *J*(HH) 9, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 1.39 [3 H, t, *J*(HH) 7, $\mathrm{CH_2C}\mathit{H}_3$], 0.20 [3 H, s, $C(CH_3)_2$], 0.08 [3 H, s, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[e] 111.4 (s, C_5H_4), 105.3 (s, C_5H_4), 57.0 (s, C_5H_4, C_{ipso}), 29.6 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 22.5 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.2 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 21.5 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], −12.5 (s, $\mathit{C}\mathrm{H_2CH_3}$) Mass (EI): *m/z* 511 ($M^+$, base), 481 ($M^+ - Et$), 354 ($M^+ - Et - I$)
24 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(O_2CPh)]$ Orange C, 52.5 (52.4); H, 4.8 (4.8)	^1H:[j] 7.79 [2 H, d, C_6H_5, *J*(HH) 6, H_o], 7.36 [1 H, t, *J*(HH) 5, C_6H_5, H_p], 7.26 (2 H, m, C_6H_5, H_m), 5.50 (2 H, m, C_5H_4), 5.41 (2 H, m, C_5H_4), 5.32 (2 H, m, C_5H_4), 4.68 (2 H, m, C_5H_4), 1.48 [3 H, t, *J*(HH) 9, $\mathrm{CH_2C}\mathit{H}_3$], 1.13 [3 H, s, $C(CH_3)_2$], 1.01 [3 H, q, *J*(HH) 7, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 0.64 [3 H, s, $C(CH_3)_2$], 0.47 [3 H, s, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[j] 173.4 (s, $\mathit{C}\mathrm{O_2C_6H_5}$), 130.6 (s, C_6H_5, C_o), 129.4 (s, C_6H_5, C_p), 129.1 (s, C_6H_5, C_{ipso}), 127.8 (s, C_6H_5, C_m), 113.6 (s, C_5H_4), 107.3 (s, C_5H_4), 75.9 (s, C_5H_4), 73.6 (s, C_5H_4), 59.5 (s, C_5H_4, C_{ipso}), 30.4 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 22.8 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 22.1 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 19.5 ($\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), −6.6 ($\mathit{C}\mathrm{H_2CH_3}$) Mass (FAB): *m/z* 504 (M^+), 475 ($M^+ - Et$, base), 383 ($M^+ - O_2CPh$), 355 ($M^+ - Et - O_2CPh$)
25 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(H)]$ Yellow C, 46.9 (46.9); H, 5.3 (5.3)	^1H:[e] 5.12 (2 H, m, C_5H_4), 4.50 (2 H, m, C_5H_4), 4.31 (2 H, m, C_5H_4), 3.78 (2 H, m, C_5H_4), 1.58 [3 H, t, *J*(HH) 7, $\mathrm{CH_2C}\mathit{H}_3$], 1.14 [2 H, q, *J*(HH) 7, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 0.55 [3 H, s, $C(CH_3)_2$], 0.28 [3 H, s, $C(CH_3)_2$], −6.46 [1 H, s, *J*(WH) 31, WH] $^{13}C\text{-}\{^1H\}$:[e] 104.1 (s, C_5H_4), 87.3 (s, C_5H_4), 70.5 (s, C_5H_4), 63.0 (s, C_5H_4), 47.8 (s, C_5H_4, C_{ipso}), 32.0 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 23.6 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.4 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 22.2 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 20.2 (s, WCH_2) Mass (EI): *m/z* 413 (M^+), 383 ($M^+ - Et$), 355 ($M^+ - EtH$) IR:[d] ν(W−H) 1797m
26 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(D)]$ Yellow C, 47.1 (46.8); H/D, 5.2 (5.5)	^1H:[e] 5.12 (2 H, m, C_5H_4), 4.50 (2 H, m, C_5H_4), 4.30 (2 H, m, C_5H_4), 3.79 (2 H, m, C_5H_4), 1.58 [3 H, t, *J*(HH) 7, $\mathrm{CH_2C}\mathit{H}_3$], 1.14 [2 H, q, *J*(HH) 7, $\mathrm{C}\mathit{H}_2\mathrm{CH_3}$], 0.54 [3 H, s, $C(CH_3)_2$], 0.28 [3 H, s, $C(CH_3)_2$] ^2H:[k] 5.09 (s, C_5H_3D), 4.28 (s, C_5H_3D), −6.48 (s, WD) $^{13}C\text{-}\{^1H\}$:[e] 104.1 (s, C_5H_4), 87.3 (s, C_5H_4), 70.5 (s, C_5H_4), 63.1 (s, C_5H_4), 47.9 (s, C_5H_4, C_{ipso}), 32.0 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 23.6 (s, $\mathrm{CH_2}\mathit{C}\mathrm{H_3}$), 22.4 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 22.3 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], −20.2 (s, $\mathit{C}\mathrm{H_2CH_3}$) Mass (EI): *m/z* 384 ($M^+ - H$), 383 ($M^+ - D$), 355 ($M^+ - Et$) IR:[d] ν(W−D) 1298m
27 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)_2]$ Orange C, 46.5 (46.2); H/D, 6.1 (6.7)	^1H:[e] 4.44 (4 H, m, C_5H_4), 4.10 (4 H, m, C_5H_4), 0.29 [6 H, s, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[e] 104.7 (s, C_5H_4), 67.9 (s, C_5H_4), 52.0 (s, C_5H_4, C_{ipso}), 31.1 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 22.6 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$] Mass (EI): *m/z* 391 ($M^+$), 372 ($M^+ - CD_3$), 354 ($M^+ - CD_3 - CD_3$, base) IR:[d] ν(C−D) 2191m, 2093m, 2047m
28 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$ Purple C, 33.6 (33.7); H/D, 3.3 (3.4)	^1H:[e] 5.58 (2 H, m, C_5H_4), 4.46 (2 H, m, C_5H_4), 4.36 (2 H, m, C_5H_4), 3.68 (2 H, m, C_5H_4), 0.23 [3 H, s, $C(CH_3)_2$], 0.09 [3 H, s, $C(CH_3)_2$] $^{13}C\text{-}\{^1H\}$:[e] 111.9 (s, C_5H_4), 105.1 (s, C_5H_4), 70.5 (s, C_5H_4), 68.9 (s, C_5H_4), 57.1 (s, C_5H_4, C_{ipso}), 22.1 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 21.6 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$] Mass (FAB): *m/z* 511 (M^+, base), 481 ($M^+ - CD_3$), 372 ($M^+ - I$), 355 ($M^+ - I - CD_3$) IR:[d] ν(C−D) 2096m, 2044m, ν(W−I) 328m
29 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)H]$ Yellow	^1H:[e] 5.13 (2 H, m, C_5H_4), 4.40 (4 H, m, C_5H_4), 3.78 (2 H, m, C_5H_4), 0.58 [3 H, s, $C(CH_3)_2$], 0.29 [3 H, s, $C(CH_3)_2$], −6.31 [1 H, s, *J*(WH) 62, WH] ^2H:[k] −0.09 (s, 1 D, WD) $^{13}C\text{-}\{^1H\}$:[e] 104.3 (s, C_5H_4), 86.7 (s, C_5H_4), 70.5 (s, C_5H_4), 63.4 (s, C_5H_4), 47.6 (s, C_5H_4, C_{ipso}), 31.9 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 22.4 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 22.3 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$] Mass (EI): *m/z* 374 ($M^+$), 373 ($M^+ - H$), 354 ($M^+ - H - CD_3$) IR:[d] ν(C−D) 2092m, 2052m, ν(W−H) 1786s
30 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ Yellow C, 45.3 (45.3); H/D, 5.1 (5.2)	^1H:[e] 5.12 (2 H, m, C_5H_4), 4.40 (4 H, m, C_5H_4), 3.77 (2 H, m, C_5H_4), 0.57 [3 H, s, $C(CH_3)_2$], 0.28 [3 H, s, $C(CH_3)_2$] ^2H:[k] 5.09 (s, C_5H_3D), 4.36 (s, C_5H_3D), −6.31 (s, 1 D, WD) $^{13}C\text{-}\{^1H\}$:[e] 104.5 (s, C_5H_4), 86.7 (s, C_5H_4), 70.5 (s, C_5H_4), 63.4 (s, C_5H_4), 47.7 (s, C_5H_4, C_{ipso}), 31.7 [s, $\mathit{C}\mathrm{(CH_3)_2}$], 22.3 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], 22.1 [s, $\mathrm{C(}\mathit{C}\mathrm{H_3)_2}$], −37.2 (s, WCH_3) Mass (EI): *m/z* 376 (M^+), 375 ($M^+ - H$), 357–354 ($M^+ - D - CH_3$, base) IR:[d] ν(C−D) 2336w, ν(W−D) 1264m

[a] Analytical data are given as found (calculated) in %. For compounds **9**, **15** and **29** satisfactory in-house analyses could not be obtained due to their air sensitivity. [b] NMR data given as: chemical shift (δ) (multiplicity, relative intensity, assignment, *J*/Hz]. Where necessary assignments were confirmed using ^1H–^1H and ^1H–^{13}C shift correlation experiments. [c] In CD_2Cl_2. [d] Data (cm^{-1}) determined in KBr disc. [e] In C_6D_6. [f] In CD_3CN. [g] Data (cm^{-1}) determined in Nujol mull. [h] In $(CD_3)_2CO$. [i] In C_4D_8O. [j] In $CDCl_3$. [k] In $C_6H_6 + C_6D_6$.

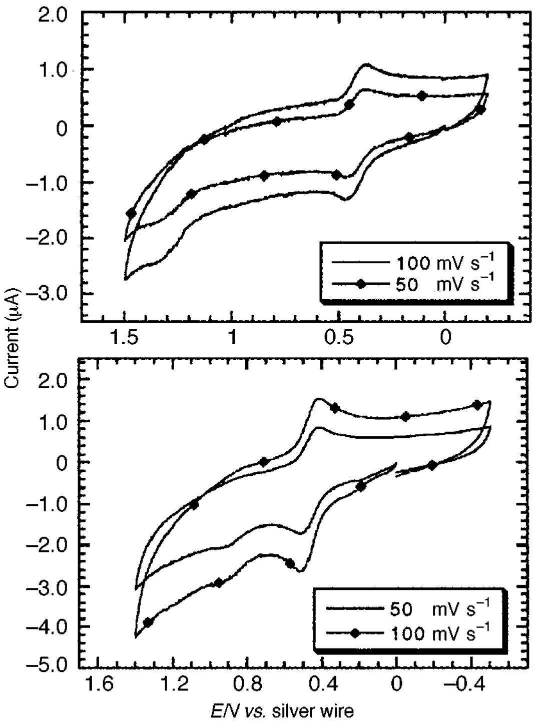


Fig. 1 Cyclic voltammograms of 1 mM solutions of compounds **1** (upper) and **2** (lower) in MeCN containing 0.1 M NBu_4PF_6

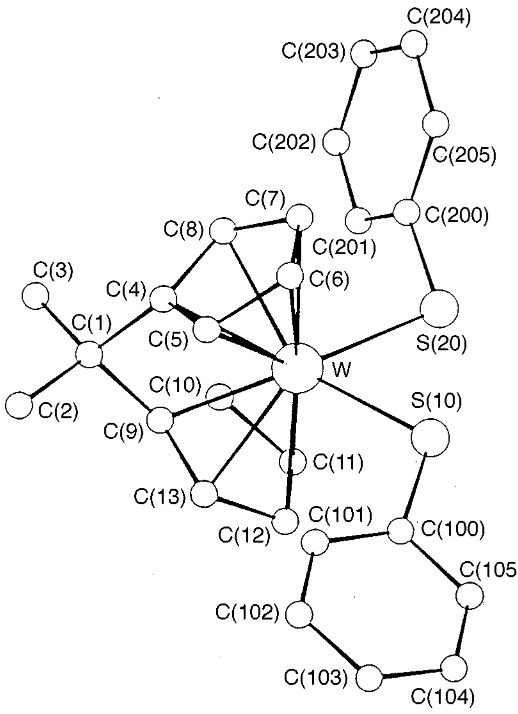


Fig. 2 Molecular structure of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}$(SPh)_2$] **7**

The electrochemical behaviour of compounds **1** and **2** has been studied in acetonitrile solutions with tetrabutylammonium hexafluorophosphate as supporting electrolyte. The voltammograms obtained are illustrated in Fig. 1 and show that **1** and **2** undergo a reversible oxidation in the range 0.4 to 0.6 V, equation (1). The electrochemical behaviour of **2** suggested that

$$[M]^{IV}Cl_2 \rightleftharpoons [M]^{V}Cl_2^{+} + e^{-} \qquad (1)$$

the cation [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2]$^+$ may be isolable. Indeed, treatment of **2** with $NOBF_4$ in dichloromethane gave the expected d^1 paramagnetic compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2][BF_4] **6.**

Table 2 Selected interatomic distances (Å) and angles (°)

[W{(η-C_5H_4)CMe_2(η-C_5H_4)}$(SPh)_2$] **7**			
W–S	2.467	S–W–S	73.47(3)
		Ph–S–W	114.1(1)
[Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}(NCMe)Cl][PF_6] **10**			
Mo–Cl	2.444(2)	Cl–Mo–N	83.4(2)
Mo–N	2.143(5)	Mo–N–CMe	176.0(6)
Mo–Cp_{cent}	1.942	N–Mo–Cp_{cent}	108.6
		Cl–Mo–Cp_{cent}	110.1
		Cp_{cent}–Mo–Cp_{cent}	126.0
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}(NCMe)Cl][PF_6] **11**			
W–Cl	2.432(3)	Cl–W–N	82.4(4)
W–N	2.12(1)	W–N–CMe	175.1(11)
W–Cp_{cent}	1.94	N–W–Cp_{cent}	109.2
MeC–N	1.16(1)	Cl–W–Cp_{cent}	110.0
		Cp_{cent}–W–Cp_{cent}	126.7
		Cp_{cent}–W–Cp_{cent}	115.79
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}($CNC_6H_3Me_2$-2,6)Cl][PF_6] **13**			
W–Cl	2.430(2)	Cl–W–CN	85.0(3)
W–CN	2.06(1)	W–C–N	174.8(7)
C–N	1.16(1)	Cp_{cent}–W–Cp_{cent}	115.79
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2] **14**			
W–Me	2.19(3)	Me–W–Me	66.2(19)
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}(η^2-C_2H_4)H][B$(C_6F_5)_4$] **15**			
H_2C–CH_2	1.51	Cp_{cent}–W–Cp_{cent}	126.31
W–C_2H_{4cent}	2.16	Cp_{cent}–W–C_2H_{4cent}	112.41
W–Cp_{cent}	1.96		
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(Cl)] **17**			
W–Cl	2.4711(9)	CH_2–W–Cp_{cent}	109.31
CH_2–CH_2	1.511(6)	Et–W–Cl	78.1(2)
W–Cp_{cent}	1.942		
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_3][PF_6] **20**			
W–Cp_{cent}	1.963	Cp_{cent}–W–Cp_{cent}	127.08
[Mo{(η-C_5H_4)CMe_2(η-C_5H_4)}Et_2] **21**			
Mo–Et	2.245(2)	Et–Mo–Cp_{cent}	110.15
Mo–Cp_{cent}	1.9419		
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et_2] **22**			
W–Et	2.240(5)	Et–W–Cp_{cent}	110.06
W–Cp_{cent}	1.9464	Me_2C–W–Cp_{cent}	64.09
[W{(η-C_5H_4)CMe_2(η-C_5H_4)}(CD_3)I] **28**			
W–I	2.796(1)	I–W–CD_3	78.7(3)
W–CD_3	2.44(2)	I–W–Cp_{cent}	110.02
W–Cp_{cent}	1.95	Cp_{cent}–W–Cp_{cent}	127.5

It proved possible to substitute both the chloride ligands in compound **2** with thiolate groups by treatment with $^-$SPh and $^-$SPr^i to give the compounds [W{(η-C_5H_4)CMe_2(η-C_5H_4)}X_2], where X = SPh **7** or SPr^i **8** respectively. By analogy with the IR spectrum of [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}$(SPh)_2$], bands corresponding to the deformation modes of the SPh ligands in **7** are seen at 1575, 1020 and 702 cm^{-1} and to the ν(W–S) stretch at 495 and 480 cm^{-1}.[15] Crystals of **7** suitable for structure determination were obtained by the slow diffusion of diethyl ether into a concentrated acetonitrile solution of **7**. The molecular structure is shown in Fig. 2 with selected interatomic distances and bond angles listed in Table 2. The S–W–S angle of 73.47(3)° is similar to the value of 71.1° observed in the related complex [Mo(η-C_5H_5)$_2$(SBu^t)$_2$].[16] The average W–S bond length of 2.467 Å is in accordance with the values of 2.419 and 2.421 Å observed for [W(η-C_5H_5)$_2$$S_4$] and [W(η-$C_5H_5$)$_2$($S_2C_6H_4$)] respectively.[17,18] Addition of $NOBF_4$ to a solution of **8** gave orange crystals of diamagnetic [W{(η-C_5H_4)-

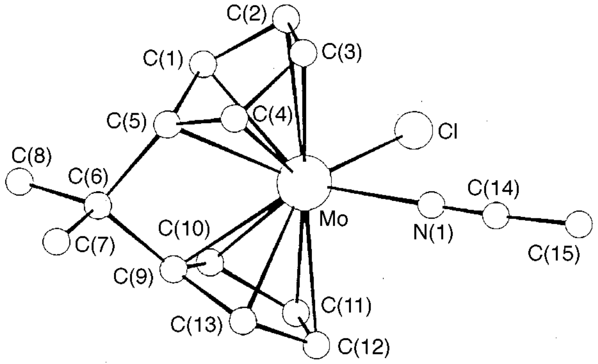


Fig. 3 Molecular structure of $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl]^+$ **10**

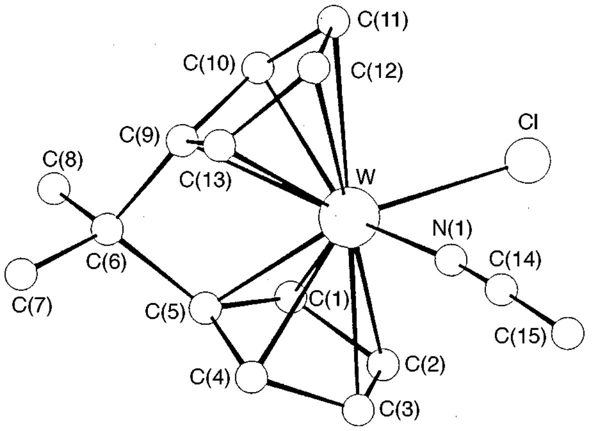


Fig. 4 Molecular structure of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl]^+$ **11**

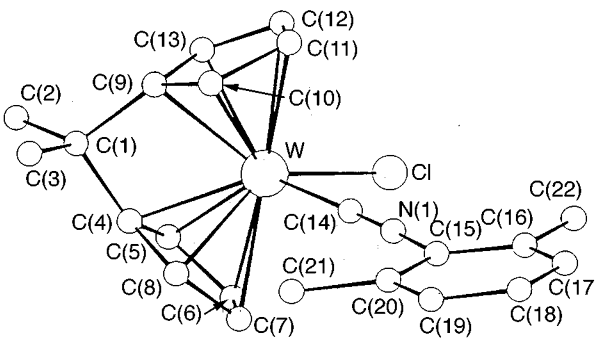


Fig. 5 Molecular structure of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CNC_6H_3\text{-}Me_2\text{-}2,6)Cl]^+$ **13**

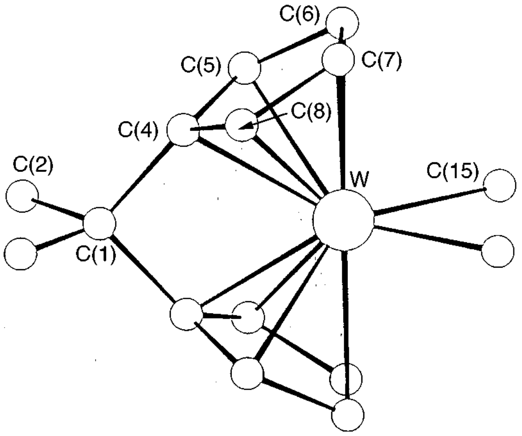


Fig. 6 Molecular structure of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **14**

$CMe_2(\eta\text{-}C_5H_4)\}(SPr^i)(NCMe)][BF_4]$ **9**. The infrared spectrum showed a characteristic band at 2339 cm^{-1} assignable to the $\nu(CN)$ stretch.

Treatment of compound **1** or **2** with 1 equivalent of $TlPF_6$ or $NOBF_4$ in acetonitrile afforded $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$ (M = Mo **10** or W **11**) in high yields. Single crystals of **10** and **11** suitable for an X-ray analysis were grown from concentrated acetonitrile solutions. Both compounds crystallise in the orthorhombic space group $P2_12_12_1$. The almost identical molecular structures are shown in Figs. 3 and 4; selected interatomic distances and angles are listed in Table 2. The co-ordination geometry about the central metal atom is comparable to that found in $[W(\eta\text{-}C_5H_5)_2(NCMe)Et][PF_6]$ and the M–Cl bond lengths [2.442(2) for **10**, 2.432(3) Å for **11**] are within the usual range for M^{IV}–Cl bonds.[19] The M–N–CMe groups have angles of 176.0° for **10** and 175.1° for **11**. The angle between the ring centroids of 126.0° in **10** and 126.7° in **11** is small when compared to values of 140.2 and 133.8(3)° for the non-*ansa* complexes $[W(\eta\text{-}C_5H_5)_2(NCMe)Et][PF_6]$ and $[Mo(\eta\text{-}C_5H_5)_2(NCMe)Cl][PF_6]$ respectively, and is indicative of the highly strained nature of *ansa* systems.[19,20]

The compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$ **11** is an excellent precursor for other *ansa*-bridged compounds. When acetone was added to a powdered mixture of **11** and triphenylphosphine red crystals of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(PPh_3)Cl][PF_6]$ **12** were formed. Similarly, addition of acetonitrile to a mixture of **11** and $CNC_6H_3Me_2$-2,6 gave orange crystalline $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CNC_6H_3Me_2\text{-}2,6)Cl][PF_6]$ **13**. Crystals of **13** suitable for X-ray analysis were grown by slow diffusion of diethyl ether into a concentrated acetonitrile solution. Compound **13** crystallises in the triclinic space group $P\bar{1}$ and the molecular structure is shown in Fig. 5 with selected interatomic distances and angles listed in Table 2. As for compounds **10** and **11**, the angle between the ring centroids of the cation is small (116°) compared to the values of 139 and 137° observed for $[W(\eta\text{-}C_5H_5)_2Br(CNMe)]^+$ and $[W(\eta\text{-}C_5H_5)_2Cl(CNEt)]^+$.[21,22] The angle between the equatorial ligands (φ) in **13** of 85.0° is typical for $[M(\eta\text{-}C_5H_5)_2X(L)]^+$ complexes such as 83.3° found for $[W(\eta\text{-}C_5H_5)_2Br(CNMe)]^+$.[22] The W–C distance of 2.06(1) Å is rather small when compared to those of other tungsten isocyanide complexes. Although, the $^{13}C\text{-}\{^1H\}$ NMR spectrum of **13** was consistent with the proposed structure, a signal for the quaternary metal-bound isocyanide carbon could not be detected due to its long relaxation times.

As reported previously, reaction between $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **2** and dimethylzinc in toluene followed by hydrolysis gave $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **14** in 45% yield.[6] Single crystals, from which the molecular structure illustrated in Fig. 6 could be determined, were grown by the slow cooling of a saturated pentane solution of **14**. Selected interatomic distances and angles are listed in Table 2. The two methyl ligands lie in a mirror plane and have similar geometries and bond lengths to those of the *ansa*-bridged diethyl compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$ discussed below. Treatment of **14** with a toluene solution of $[CPh_3][B(C_6F_5)_4]$ at low temperature formed orange crystals of the ethylene hydride compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(\eta^2\text{-}C_2H_4)H][B(C_6F_5)_4]$ **15**. In the IR spectrum weak bands at 1823 and 1483 cm^{-1} were tentatively assigned to the ν(W–H) and ν(C=C) stretches. The molecular structure of **15** has been determined and is shown in Fig. 7 with selected interatomic distances and angles listed in Table 2. Although the WH hydrogen atom was not located in the difference maps its presence may be inferred from the spatial position of the ethylene group. Whilst **15** is stable in the crystalline state it reacts upon dissolution in co-ordinating solvents with the insertion of the ethylene ligand into the tungsten–hydride bond. Thus, when acetonitrile was added to **15** there was an immediate change to green and the new cationic ethyl compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(NCMe)][B(C_6F_5)_4]$ **16** was formed.

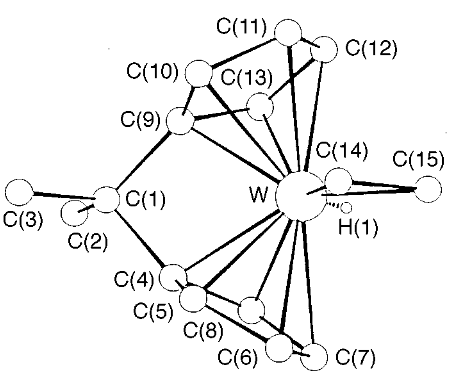


Fig. 7 Molecular structure of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(η-C_2H_4)-H]$^+$ **15**. The dashed line indicates a bond to a H atom whose position was inferred only and could not be located in the difference map

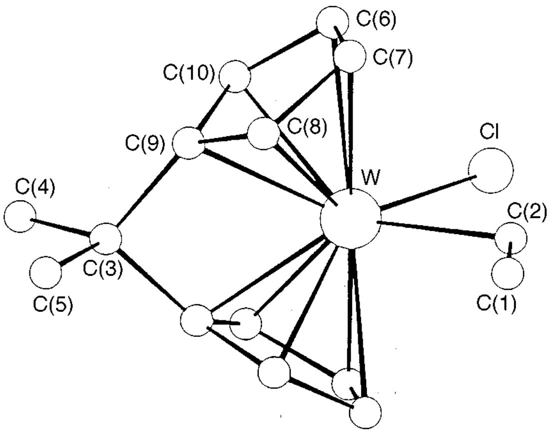


Fig. 8 Molecular structure of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(Cl)] **17**

Insertion of an ethene ligand into a tungsten–hydride bond has been observed previously including formation of [W(η-C_5H_5)$_2$Et(NCMe)][PF_6].[19]

Ethylaluminium dichloride (in excess or 1 mole equivalent) was also found to react with compound **2** to yield, after work-up, red crystals of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(Cl)] **17**. In contrast to the reaction of an excess of ethylaluminium dichloride with the dichlorides [M(η-C_5H_4)$_2$$Cl_2$] (M = Mo or W) to give the cationic hydrido-η-ethylene complexes [M{(η-C_5H_5)$_2$-(η-C_2H_4)H]$^+$ (M = Mo or W), no hydridoethylene cation was formed in the case of **17**.[23] It seems likely that the *ansa* bridge stabilises **17** towards β-hydride elimination. Single crystals of **17** suitable for an X-ray analysis were obtained from a concentrated tetrahydrofuran (thf) solution at −20 °C. The compound **17** crystallises in the monoclinic space group $P2_1/m$ and the molecular structure is shown in Fig. 8 with selected interatomic distances and angles listed in Table 2. The ethyl and chloride groups lie on a crystallographic mirror plane and have a geometry similar to that found for [Mo(η-C_5H_5)$_2$Et(Cl)].[24] The W–C bond length of 2.233(4) Å is comparable to the values of 2.240(5) and 2.284(10) Å observed in [W(η-C_5H_4)CMe_2-(η-C_5H_4)Et_2] and [Mo(η-C_5H_5)$_2$Et(Cl)] respectively.[24]

The reaction of compound **17** with 1 equivalent of $TlPF_6$ in acetonitrile gave, after 2 weeks at 80 °C, [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(NCMe)][PF_6] **16a** as a green solid. Addition of $NOBF_4$ to **17** produced an instant change to pink and addition of diethyl ether to the solution followed by cooling to −20 °C produced a mixture of long pink needle-like crystals and a smaller quantity of purple blocks. The two types of crystals were separated by hand. The ^{1}H and ^{13}C-{^{1}H} NMR spectra of the pink needles were identical to those of the complex [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(NCMe)Cl][PF_6] **11**, suggesting that one of the products formed in the reaction was [W{(η-C_5H_4)-CMe_2(η-C_5H_4)}(NCMe)Cl][BF_4] **11a**. The infrared and mass spectrum and microanalysis data were entirely consistent with the proposed formulation. The purple blocks were found to be paramagnetic and the microanalytical data and mass spectrum suggested the d^1 compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-Et(Cl)][BF_4] **18**. The infrared spectrum showed a band at 280 cm^{-1} assigned to ν(W–Cl).

It has been shown that treatment of compound **2** with $LiAlH_4$ in diethyl ether gives the dihydride [W{(η-C_5H_4)CMe_2-(η-C_5H_4)}H_2] **19** in low yields.[25] We have found that treatment of a suspension of **2** in thf with a four-fold excess of $LiBEt_3H$ gave **19** free from side products in acceptable yields (*ca.* 62%).

Treatment of an aqueous suspension of compound **19** with 6 M hydrochloric acid at 0 °C followed by addition of aqueous ammonium hexafluorophosphate gave a flocculent white precipitate of the trihydride cation [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_3][PF_6] **20**. This trihydride cation can be readily deprotonated by the addition of aqueous potassium hydroxide to regenerate **19** quantitatively. Crystals of **20** suitable for X-ray diffraction could be precipitated from an aqueous solution and selected interatomic distances and angles are listed in Table 2. The compound **20** crystallises in the monoclinic space group $P2_1/m$. The Fourier-difference map was dominated by the tungsten peak with additional problems associated with the presence of diffraction ripples resulting from series termination errors and therefore the metal-bound hydrogen atoms could not be located. More certain location of the hydrogen positions would require neutron diffraction studies. The structure of **20** is very similar in geometry to that for [Nb(η-C_5H_5)$_2$$H_3$] and [W($\eta$-$C_5H_5$)$_2$$H_3$]Cl.[26] For **20** the angle between the ring centroids of 127.08° is much smaller than those of 148.2 and 141.6° for [W(η-C_5H_5)$_2$$H_3$]Cl and [Nb($\eta$-$C_5H_5$)$_2$$H_3$] respectively.[26] As is usually found in ions having nearly spherical symmetry the fluorine atoms in **20** have large thermal parameters indicating considerable disorder in the PF_6^- anion.

The variable-temperature ^{1}H NMR spectrum of the trihydride **20** has been studied and found to exhibit very unusual behaviour. The lower-field region ($\delta > 0$) shows the expected pattern for the W{(η-C_5H_4)CMe_2(η-C_5H_4)} backbone and does not change significantly on cooling to −140 °C. However, in the WH_3 region at room temperature a broad peak at δ −3.28 decoalesces and splits into a number of sharp lines below −70 °C consistent with an AB_2X spin system (X = ^{183}W, 14%) as illustrated in Fig. 9.[27] Two processes are responsible for this behaviour; higher-temperature chemical exchange and lower-temperature quantum-mechanical exchange coupling, and both will be discussed below. Similar behaviour has been found for [Mo(η-C_5H_5)$_2$$H_3$]$^+$.[28]

Chemical exchange resulting from thermally activated A/B site exchange is responsible for the broad hydride signal above 10 °C. Such behaviour has been noted before for many trihydride systems such as [Ir(η-C_5Me_5)LH_3]$^+$ (L = PR_3) and [Mo(η-C_5H_5)$_2$$H_3$]$^+$.[28,29] Interestingly, [W(η-C_5H_5)$_2$$H_3$]$^+$ displays a static AB_2X pattern invariant with temperature.[30]

At temperatures below −70 °C this exchange is frozen out and sharp signals are seen. The resulting spectrum is a highly second-order AB_2X (X = ^{183}W, 14%) system and values for δ(A), δ(B) and *J*(AB) could only be obtained indirectly by modelling with the spectral spin-simulation program gNMR.[27] This yielded values of δ(A) −1.1, δ(B) −4.1 and *J*(AB) = 16 000 Hz at −70 °C. This exceptionally large value for J_{AB} was also found to be highly temperature dependent and, with the use of modelling, was found to decrease to 2300 Hz by −140 °C. It was only possible to simulate the NMR spectra below −70 °C, which are also illustrated in Fig. 9, as thermally activated site exchange occurred above this temperature and resulted in line broadening and coalescence of the resonances. Experimental spectra below −90 °C were obtained using $CDFCl_2$ as solvent with low solubility and solvent freezing preventing spectra being obtained at temperatures lower than −140 °C. First-order temperature-invariant coupling to ^{183}W was also observed and modelled with *J*(WA) = 76 and *J*(WB) = 57 Hz.

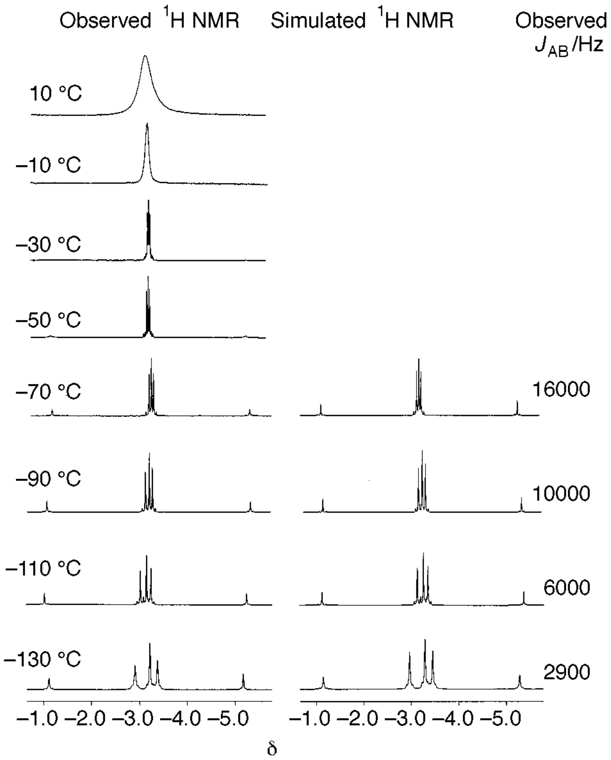


Fig. 9 Variable-temperature ^{1}H NMR spectra of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3][PF_6]$ **20** and the simulated spectra in the hydride region

There have been a number of documented cases of very large temperature-dependent ^2J(HH) couplings in the last 10 years, with many instances of couplings being larger than for H_2 itself [^1J(HH) = 280 Hz].[29,31,32] Systems found tended to be based on either $[M(\eta\text{-}C_5H_5)_2H_3]^{n+}$ (M = Nb, $n = 0$; M = Mo, $n = 1$) or $[M(\eta\text{-}C_5H_5)LH_3]^{n+}$ (M = Ru, $n = 0$, L = PR_3; M = Ir, $n = 1$, L = PR_3) with varying substituents on the cyclopentadienyl and phosphine ligands resulting in different observed couplings. These unusual J values have been rationalised in terms of two distinct contributions to the observed coupling J_{obs} which equals $-2J_{ex} + J_m$ where J_m is the magnetic component and J_{ex} the exchange component; J_m is the result of coupling mediated by the conventional Fermi-contact mechanism, is independent of temperature and generally takes a very small value of *ca.* 18–22 Hz.[28,29] An observable J_{ex}, which can often be of the order of hundreds of Hz, is well known in the ESR spectra of biradicals but is rarely observed for heavy particle couplings like protons. The exact details of the mechanism are still open to debate but Heineky's proposals[28,29] seem most consistent with all available data. In this approach a soft vibrational potential, principally consisting of the WH_AH_B wag, allows substantial delocalisation of the hydrides wavefunction which allows tunelling to occur and gives rise to large couplings. The well documented exponential increase in J_{ex} at elevated temperatures results from thermal occupation of higher vibrational states each with an increasingly larger J_{ex}.[32,33] Principal factors that seem to result in larger J_{ex} include low electron density at the metal centre, closeness of hydrogen atoms and lower-frequency wags (and hence weaker bonds). The contrast between the large J_{ex} for **20** and the lack of exchange coupling for the non-bridged analogue $[W(\eta\text{-}C_5H_5)_2H_3]^+$ is notable and can be partly rationalised on the basis of the above factors. Although it was not possible to identify any WH wags in **20**, the ν(W–H) stretch at 1913 cm^{-1} of **20** is *ca.* 21 cm^{-1} lower than for $[W(\eta\text{-}C_5H_5)_2H_3]^+$ and various studies have concluded that lowering ν(M–H) by 100 cm^{-1} can increase J_{ex} by two orders of magnitude.[28,33,34] A comparison of ν(M–H) stretching frequencies for a series of *ansa*- and non-*ansa*-bridged complexes has been reported and in each case ν(M–H) was lower for the *ansa*-bridged complexes due to the difference in the electronic effects caused by the presence of the bridge.[25] The observed geometries of the M–X moieties of *ansa*-bridged compounds of the type $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}X_2]$ are very similar to those of the related unbridged compounds $[M(\eta\text{-}C_5H_5)_2X_2]$, and only θ, the bending angle between the two cyclopentadienyl rings, changes significantly (Table 3).

Table 3 Angles θ and φ for some *ansa*-metallocenes

Compound	φ^a/°	θ^b/°
2 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]^c$	81.85(8)	115.2
7 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(SPh)_2]$	73.47(3)	
10 $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$	83.4(2)	126.0
11 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(NCMe)Cl][PF_6]$	82.4(4)	126.7
13 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CNC_6H_3Me_2\text{-}2,6)Cl][PF_6]$	85.0(3)	115.8
14 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$	66.2(19)	
17 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(Cl)]$	78.1(1)	
21 $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$	76.41(7)	128.0
22 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$	76.8(2)	128.1
28 $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$	78.7(3)	127.5

[a] Defined as the angle between the two non-cyclopentadienyl ligands. [b] Defined as the angle between normals to the two cyclopentadienyl ligands. [c] Ref. 25.

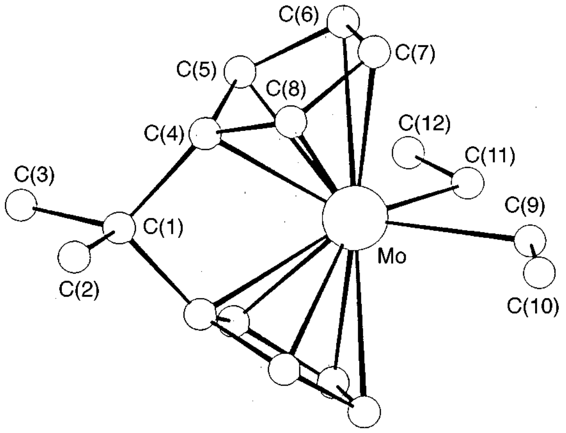


Fig. 10 Molecular structure of $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$ **21**

The value of J_{ex} at the highest temperature at which it is possible to model (−70 °C, J_{ex} = 16 000 Hz) is the biggest two-bond coupling so far reported. Other large values are found for $[Ir(\eta\text{-}C_5H_5)(mtpb)H_3]^+$ (mtpb = 1-methyl-4-phospha-3,6,8-trioxabicyclo[2.2.2]octane)[31] at temperatures below −77 °C, although Heineky[35] has recently observed a value of 45 000 Hz in a related iridium system. The striking difference in behaviour between **20** and $[W(\eta\text{-}C_5H_5)_2H_3]^+$ clearly merits further investigation.

We note that a study on the mechanism of protonation of $[M(\eta\text{-}C_5H_5)_2H_2]$ (M = Mo or W) has suggested that in the tungsten system the protonation involves an initial attack by a proton on a hydride ligand, to generate the dihydrogen ligand in $[W(\eta\text{-}C_5H_5)_2(\eta^2\text{-}H_2)H]^+$ and this intermediate subsequently undergoes an intramolecular oxidative addition of the dihydrogen ligand to give the trihydride $[W(\eta\text{-}C_5H_5)_2H_3]^+$.[36] In the same study, an equilibrium between $[W(\eta\text{-}C_5H_5)_2(\eta^2\text{-}H_2)H]^+$ and $[W(\eta\text{-}C_5H_5)_2H_3]^+$ was proposed and it is believed that the two tautomers interconvert *via* a transition state in which the η^2-dihydrogen ligand has an elongated H–H bond.

Treatment of compound **1** or **2** with an excess of diethylzinc at low temperature gave the diethyl compounds $[M\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$ (M = Mo **21** or W **22**) as orange solids. Crystals suitable for a structure determination were obtained by the slow cooling of concentrated pentane solutions to −80 °C. The resulting crystal structures are shown in Figs. 10 and 11 with selected bond lengths and angles shown in Table 2. As expected for more strained systems the angle between the ring

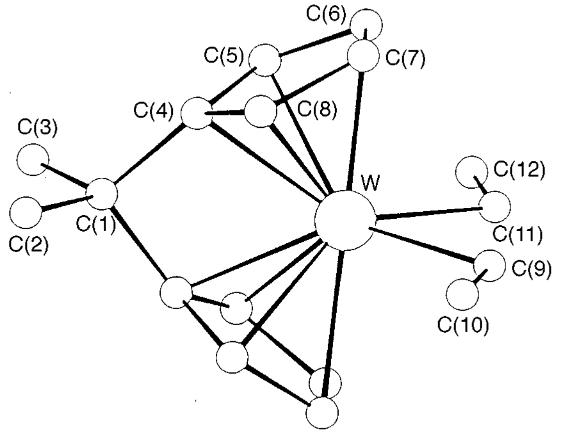


Fig. 11 Molecular structure of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et_2] **22**

centroids is very similar in both but is less than the value (135.2°) observed in the complex [Mo(η-C_5H_5)$_2$$Bu_2$].[37] The ease of preparation and thermal stability of **21** and **22** is of interest when compared with the non-bridged systems, which cannot be synthesized by reaction of the dichlorides with $ZnEt_2$. It seems likely that **21** and **22** are relatively thermally stable with respect to β-hydride elimination when compared to other Group 6 alkyl compounds possessing β-hydrogens.[37–40]

Attempts were made to synthesize the ethyl hydride/deuteride analogue of compound **2** in order to investigate the nature of any reactions undergone on heating. The compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et_2] **22** proved to be an excellent initial precursor and treatment with 1 equivalent of the weak acids NH_4I or $PhCO_2H$ yielded [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(I)] **23** or [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(O_2CPh)] **24** respectively. The infrared spectrum of **23** showed a sharp peak at 330 cm^{-1} assigned to the W–I stretch. When the compounds [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(X)] (X = Cl, **17**, I **23** or O_2CPh **24**) were treated with Na[$(MeOCH_2CH_2O)_2AlH_2$] and subsequently hydrolysed the desired ethylhydride [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(H)] **25** was produced as an air-sensitive yellow powder. It was soluble in alkanes and could be purified by recrystallisation from pentane at low temperature or by vacuum sublimation at 125 °C. Attempts to prepare the deuteride analogue were only partially successful when a toluene solution of **17** was treated with an excess of freshly prepared Li[$(MeOCH_2CH_2O)_2AlD_2$].[41] Upon work-up the resulting orange powder was shown to consist mainly of the expected compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(D)] **26** together with some C_5-ring-deuteriated products such as [W{(η-C_5H_3D)CMe_2(η-C_5H_4)}Et(H)]. The mass spectrum showed a parent ion for **26** with an appropriate isotope pattern as well as a fragment ion corresponding to [W{(η-C_5H_4)CMe_2(η-C_5H_3D)}]$^+$. The inferred presence of a monodeuteriated C_5H_3D ligand is supported by the observation of a weak ν(C–D) stretch in the infrared spectrum at 2336 cm^{-1} and two bands in the ^2H NMR spectrum at δ 5.09 and 4.28 corresponding to deuterium on the cyclopentadienyl rings. An alternative synthetic strategy for pure **26** by reaction of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(H)] with $LiBu^n$ and subsequent quenching with D_2O was unsuccessful. Incorporation of deuterium in η-C_5 rings has been noted previously. For example, reactions between [W(η-C_5H_5)$_2$Me(I)] and Li[$(MeOCH_2CH_2O)_2AlD_2$] and also [BEt_3D]$^-$ with [Fe(η-C_5H_5)(CO)(PPh_3)($MeCCO_2Et$)]$^+$ yield η-C_5H_4D-containing products.[6,41,42]

The perdeuteriomethyl hydride could also be synthesized easily using an analogous route to compound **25**. Treatment of a toluene suspension of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] **2** with an excess of $Zn(CD_3)_2$ resulted in a red suspension from which [W{(η-C_5H_4)CMe_2(η-C_5H_4)}$(CD_3)_2$] **27** could be isolated.[43,44] The ^{13}C-{^1H} NMR spectrum showed no resonances due to the perdeuteriated methyl carbons as expected for reduction of intensity by coupling to the three quadrupolar deuterium nuclei. The infrared spectrum showed a band at 2047 cm^{-1} due to ν(C–D) of the perdeuteriated methyl ligands. Subsequent reaction of **27** with NH_4I in tetrahydrofuran at 60 °C for 48 h gave purple crystals of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-(CD_3)I] **28**. The infrared spectrum showed peaks at 2197, 2096 and 2044 cm^{-1} attributed to ν(C–D) of the CD_3 group and a peak at 328 cm^{-1} assigned to the W–I stretching mode. Crystals of **28** suitable for X-ray analysis were grown by slow diffusion of pentane into a concentrated toluene solution of **28**. The compound crystallises in the monoclinic space group $P2_1/m$. The molecular structure is shown in Fig. 12 and the primed atoms are generated from the asymmetric unit using the mirror plane *m*. Selected interatomic distances and bond angles are listed in Table 2. The geometry is similar to that found for other single-carbon *ansa*-bridged metallocenes, the W–I bond distance of 2.796(1) Å being slightly shorter than values usually found for this type of bond which vary between 2.83 and 2.86 Å.[45] The I–W–CD_3 angle of 78.7(3)° is larger than Cl–W–CH_3 observed in the analogous compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me(Cl)].[46] This larger angle can be rationalised in terms of the larger atomic radius of the iodide atom compared to that of chloride. All other bond lengths and angles are of similar magnitudes to those expected for this class of compound.

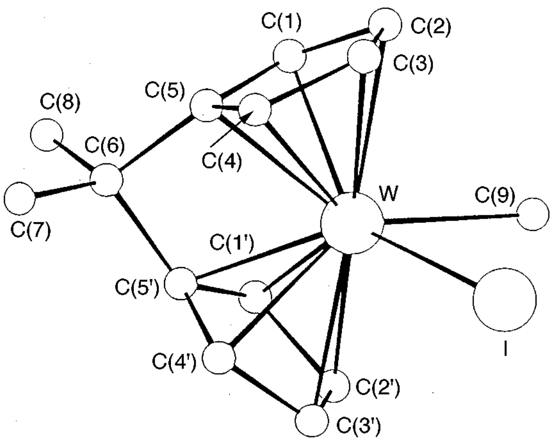


Fig. 12 Molecular structure of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(CD_3)I] **28**

Addition of an excess of sodium bis(2-methoxyethoxy)-aluminium hydride to a purple solution of compound **28** finally gave, after hydrolysis, yellow crystals of [W{(η-C_5H_4)CMe_2-(η-C_5H_4)}(CD_3)H] **29**. As for **27**, there was no observable signal for the CD_3 group in the ^{13}C-{^1H} NMR spectrum, however its presence was confirmed by the ^2H NMR spectrum which showed only a singlet at δ −0.091 and the infrared spectrum which contained bands at 2195, 2092 and 2052 cm^{-1} due to the CD_3 group.

In an analogous procedure to the preparation of compound **26**, [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me(I)] was treated with an excess of Li[$(MeOCH_2CH_2O)_2AlD_2$] to give the expected compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me(D)] **30**. Again the cyclopentadienyl rings become partially deuteriated as a consequence of the *exo* attack of deuteride on the cyclopentadienyl rings.

We have investigated hydrogen–deuterium exchange processes in the partially deuteriated compounds **26**, **29** and **30** and have found some interesting differences from the non-*ansa* analogues. First, in a preliminary experiment, a sealed NMR tube containing a solution of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-Me(D)] **30** in benzene was heated at 75 °C over a period of 6 weeks and ^2H NMR spectra were recorded periodically. As illustrated in Fig. 13, the δ(WD) signal was found to decrease and a signal due to δ(WCD_3) appeared. Differences in zero-point energies between C–H and C–D causing deuterium preferentially to bond to the carbon atom as opposed to the tung-

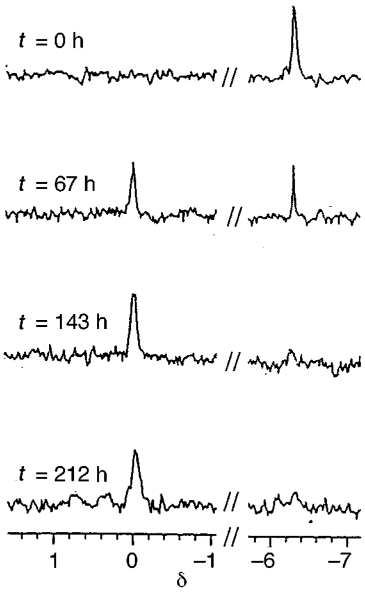


Fig. 13 High-field ^2H NMR spectra of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-Me(D)] **30** in benzene as a function of time

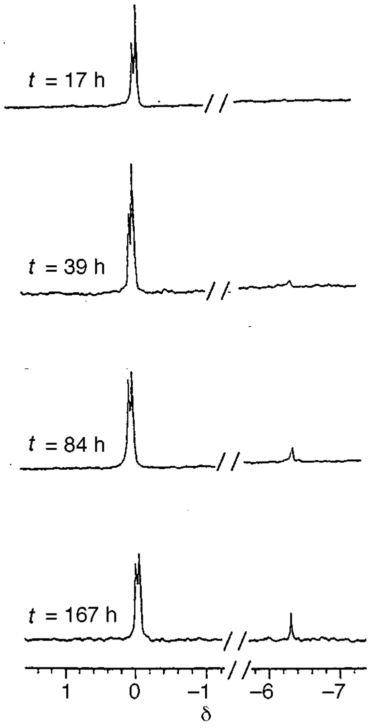


Fig. 14 High-field ^2H NMR spectra of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-(CD_3)H] **29** in C_6H_6 as a function of time

sten atom result in non-statistical relative intensities for the δ(WD) and δ(WCD_3) peaks. Although ring to metal hydride-transfer reactions are common in bis(η-cyclopentadienyl)metal chemistry, it is probable that in the above exchange the deuterium on the cyclopentadienyl ring does not participate in the scrambling process seen above.[47] Ambiguity in the initial percentage of deuteriation at the tungsten centre prevented accurate kinetic data from being obtained. Further studies were therefore undertaken on **28** and **29**.

Two samples of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(CD_3)H] **29** were prepared in C_6D_6, one of lower concentration (10 mM) and one of higher concentration (100 mM). Each sample contained toluene as an internal standard and was frozen at −196 °C prior to the start of the experiment. The samples were heated to 75 °C; the ^1H and ^2H NMR spectra were recorded periodically and the hydride NMR signal was integrated against the intensity of the internal standard. Fig. 14 shows a partial ^2H NMR spectrum of **29** (100 mM) and the growth of the δ(WD) signal due to exchange is clear. The exponential decay of the δ(WCD_3) signal for both samples of **29**, as shown in Fig. 15, confirms that the exchange process is first order. There is no evidence for sample decomposition. For first-order reactions the approach of reactant concentrations to the equilibrium value is described by expression (2) where $[A]_t$ = concentration of reactant at time t, $[A]_0$ = concentration of reactant time $t = 0$, k_{-1} = rate of replenishing reaction and k = rate of forward reaction.

$$\frac{[A]_t}{[A]_0} = \frac{k_{-1} + k e^{-(k + k_{-1})t}}{k + k_{-1}} \qquad (2)$$

Table 4 Kinetic data derived from the exponential decay of intensities of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(CD_3)H] **29**

Concentration/ mM	Parameter	Value	Error
10	k	2.50×10^{-6} s^{-1}	1.4×10^{-7} s^{-1}
	k_{-1}	1.25×10^{-6} s^{-1}	9.7×10^{-8} s^{-1}
	K	2	0.29
100	k	2.42×10^{-6} s^{-1}	1.1×10^{-7} s^{-1}
	k_{-1}	9.77×10^{-7} s^{-1}	8.1×10^{-8} s^{-1}
	K	2.48	0.34

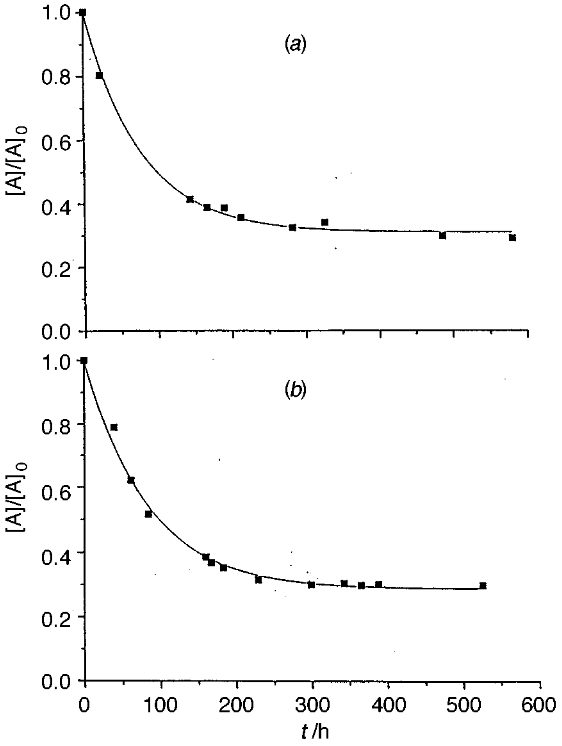


Fig. 15 Plots of the exponential decay of [W{(C_5H_4)CMe_2(η-C_5H_4)}-(CD_3)H] **29**: (a) 10 mM sample, (b) 100 mM sample

The data obtained for the intramolecular scrambling observed in **29** for both lower and higher concentrations were fitted well by equation (2) and the values so obtained for the rate constants k and k_{-1} and the equilibrium constant ($K = k/k_{-1}$) are shown in Table 4. The small errors between the calculated curve and observed points for the 10 and 100 mM samples ($\chi^2 = 2.5 \times 10^{-4}$ and 4.4×10^{-4} respectively) indicate that the scrambling in both dilute and concentrated solutions occurs through an intramolecular mechanism. This is in contrast to the findings of Norton and co-workers[41] where at higher concentration [W(η-C_5H_5)$_2$(CD_3)H] scrambles through a combination of inter- and intra-molecular processes. The rate constants (k) obtained for **29** (2.5×10^{-6} s^{-1} at 10 mM, 2.42×10^{-6}

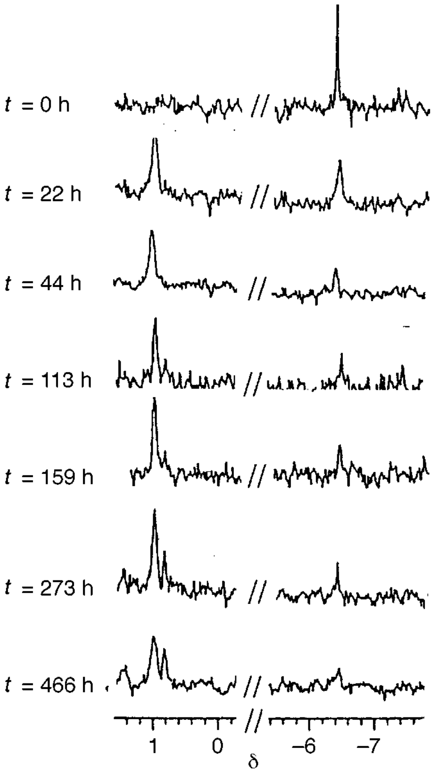


Fig. 16 High-field ^{2}H NMR spectrum of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(D)] **26** in benzene

s^{-1} at 100 mM) are an order of magnitude smaller than that obtained for the intramolecular scrambling in [W(η-C_5H_5)$_2$-(CD_3)H] (2.5 × 10^{-5} s^{-1}). This reduced reactivity for *ansa* as compared with non-*ansa* analogues is well established and is attributed to changes in the stability of the transition state. The values for the equilibrium isotope constant K obtained from k/k_{-1} for the 10 and 100 mM concentrations were 2.0 ± 0.29 and 2.48 ± 0.34 respectively. As for **30**, these values are lower than the purely statistical value (3) due to the difference in zero-point energies of a hydrogen or deuterium atom bound to a carbon or metal atom resulting in deuterium preferentially bonding to a carbon.

Similar exchange studies were undertaken with the ethyldeuteride derivative [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(D)] **26**. Although samples of **26** were contaminated with small amounts of the partially ring-deuteriated compound, as described previously, it is believed that this will not significantly affect the exchange process occurring at the metal centre in [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(D)]. The signals corresponding to the methyl and methylene protons in the ^{1}H NMR spectrum of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(D)] occur as a triplet at δ 1.58 and a quartet at δ 1.14 respectively; in the ^{2}H NMR spectrum the signals appear as two broad singlets at δ 0.969 and 0.805 respectively. This assignment was based upon the relative intensities of the signals upon approach to equilibrium which was approximately 3:2, that is the statistical value for the distribution of deuterium for methyl and methylene bound sites. Fig. 16 shows the partial ^{2}H NMR spectra of **26**, and the decrease in intensity of the W−D signal with time can clearly be seen as the scrambling occurs. It is interesting that the deuterium migrates more rapidly to the β-methyl group and exchange with the α-methyl hydrogens is only detected after *ca.* 200 h at 75 °C. This result is in contrast to Bergman's findings on the isomerisation of [Rh(η-C_5Me_5)(PMe_3)Et(D)] where the deuterium migrates primarily with the α-methylene hydrogens; only when the temperature is raised, scrambling into the β position is observed.[48]

The question arises as to the mechanism of hydrogen–deuterium scrambling in compounds **26** and **29**. We will briefly consider mechanisms involving agostic intermediates (also called σ complexes) and mechanisms which proceed *via* α- or β-elimination processes. These alternatives are outlined in Scheme 1. In the case of **29**, as illustrated in Scheme 1(*a*), scrambling could occur *via* agostic species **A** and **B** or *via* a methylidene mechanism. The η^1-methane species **A**, with a formal electron count of 18, would likely be intermediate while the η^2-methane species **B**, which has a 20-electron count, could be either a transition state or more likely an intermediate. The methylidene mechanism also proceeds *via* a 20-electron intermediate/transition state, **C**. For **26** there are two pathways, as shown in Scheme 1(*b*) for migration of the deuterium from the metal atom to the (β) methyl group of the ethyl ligand. One mechanism involves β elimination to form the 20-electron count η-ethenedihydride system **D**, the other involves reductive elimination to form successively **E** (18 electron, monoagostic), **F** (20 electron, diagostic) and **E** again.

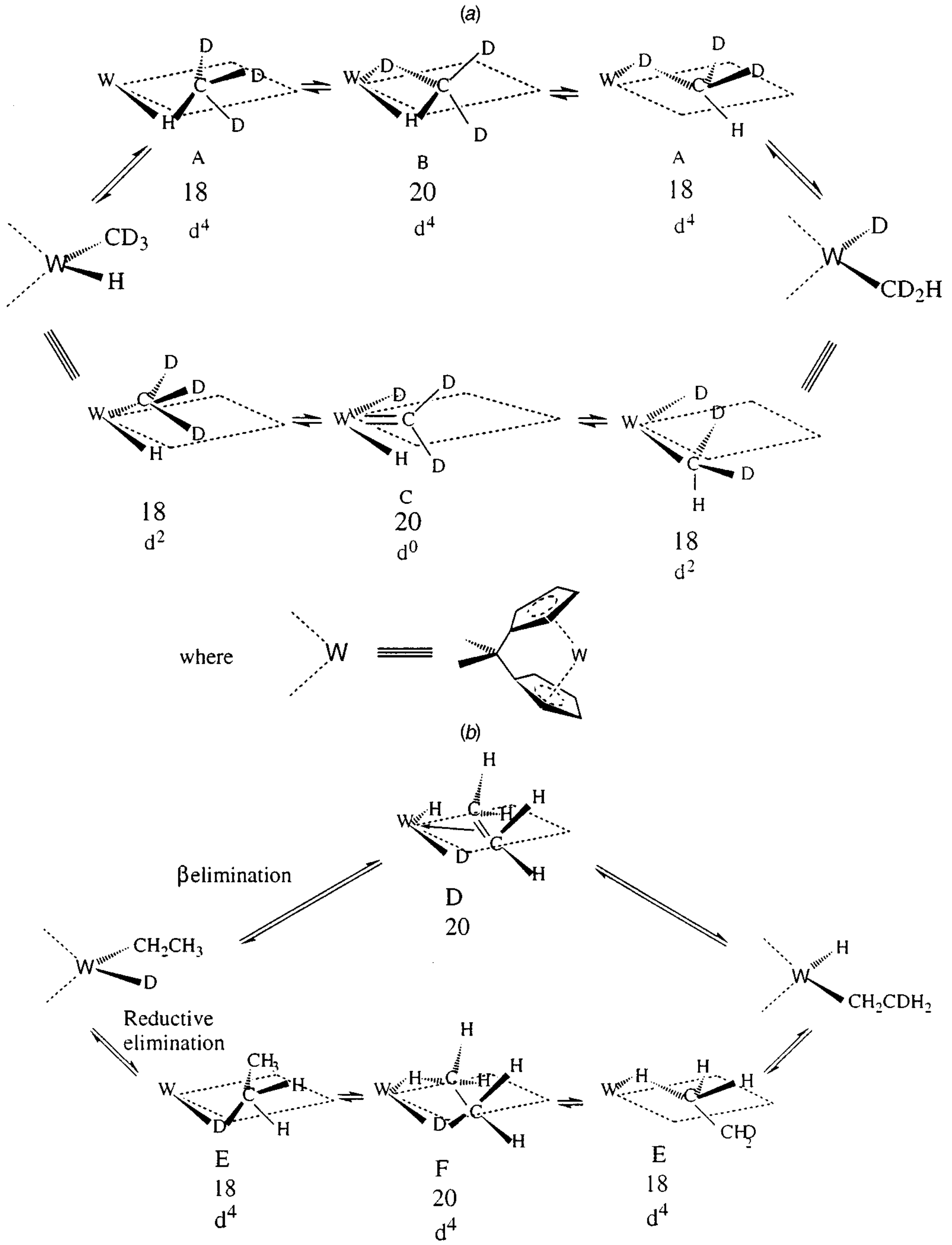
The NMR data for compounds **26** and **29** do not allow distinction to be made between the two mechanisms shown in Scheme 1(*a*) and (*b*). For **29** we note that the symmetries of **B** and **C** are identical and they differ only in the interatomic distances. Very recent theoretical calculations suggest that structure **B** is favoured and similar calculations on **D**, **E** and **F** are currently underway.[49] We do note for **26** that the observation of faster H/D exchange in the β position as compared to the α (methylene) site suggests that the β-elimination mechanism *via* **D** is favoured.[50] Previous reports of H/D scrambling in methyl compounds have all invoked agostic, as opposed to methylidene, intermediates. For instance, Norton and co-workers[41] proposed agostic methane intermediates for the intramolecular scrambling process observed in [W(η-C_5H_5)$_2$Me(H)] and [W(η-C_5H_5)$_2$Me(D)]. Furthermore in the case of the latter it was suggested that the alternative alkylidene mechanism was inconsistent with the observed ease of methane elimination. Studies on the permethyltungstenocene system, [W(η-C_5Me_5)$_2$-Me(D)] by Bercaw and Parkin also led to the proposal that intramolecular H/D exchange of the WMe(D) groupings proceeded *via* an agostic methane. Bergman and co-workers[51] provided elegant evidence in support of agostic alkane intermediates in similar exchange processes in complexes [Ir(η-C_5Me_5)-(PMe_3)R(H)], where R = methyl, cyclohexyl or cyclopropyl.

In conclusion, the new compounds and reactions are shown in Schemes 2 and 3. The thermal stability of the methylhydride **29** and ethylhydride **26** are sufficient to allow hydrogen–deuterium scrambling without reductive elimination of alkane. This scrambling occurs *via* intramolecular processes. Variable-temperature NMR studies on the trihydride cation **20** show a very large temperature-dependent J(HH) coupling (*ca.* 16 000 Hz at −70 °C) between the WH_3 hydrogen atoms, explicable in terms of a quantum-mechanical exchange-coupling mechanism.

Experimental

All preparations and manipulations of air- and/or moisture-sensitive materials were carried out under an inert atmosphere of dinitrogen, using standard Schlenk-line techniques, or in an inert-atmosphere dry-box containing dinitrogen.[52] Inert gases were purified by passage through columns filled with molecular sieves (4 Å) and either manganese(II) oxide suspended on vermiculite, for the vacuum line, or a BASF catalyst, for the dry-box. All glassware and cannulae were thoroughly cleaned and then dried at 150 °C before use.

All solvents were deoxygenated before use, either by repeated evacuation followed by admission of dinitrogen, or by bubbling dinitrogen through the solvent for approximately 15 min. Solvents were pre-dried over activated 4 Å molecular sieves and then distilled over sodium [toluene, diglyme, light petroleum ether (b.p. 100–120 °C)], sodium–potassium alloy [diethyl ether, *n*-pentane, light petroleum (b.p. 40–60 °C)], potassium (thf, ben-

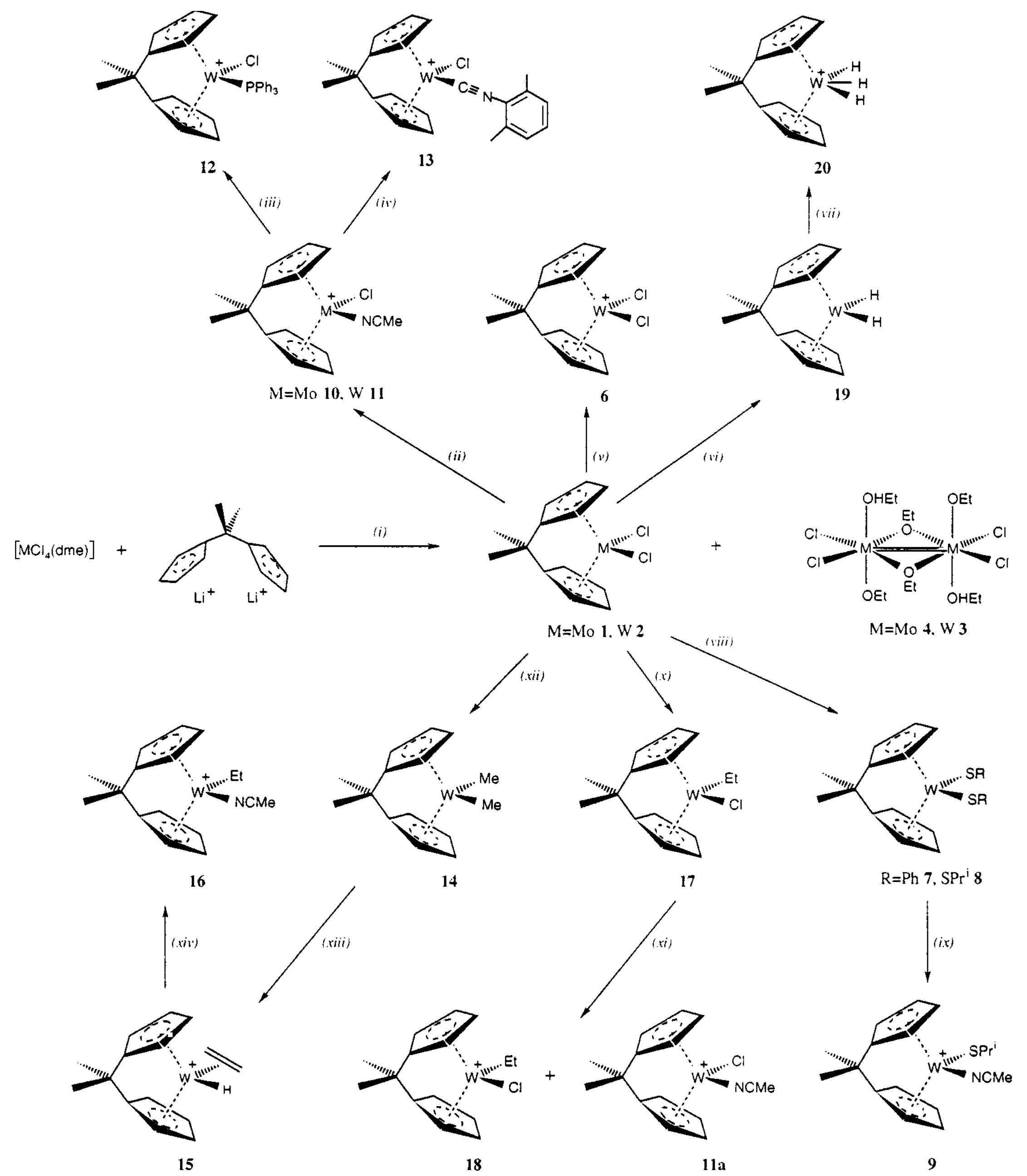


Scheme 1 Possible pathways for H/D scrambing in (*a*) [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(CD_3)H] **29** and (*b*) [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Et(D)] **26** showing the number of valence electrons and d^n configuration

zene), P_2O_5 (dichloromethane) or calcium hydride (acetonitrile) under a slow continuous stream of dinitrogen. Distilled water and D_2O (Aldrich) were deoxygenated before use by bubbling dinitrogen through the solvent for approximately 15 min. Deuteriated solvents for NMR spectroscopy were deoxygenated and dried over calcium hydride (dichloromethane) or potassium (benzene, thf and toluene) and then distilled before use.

The compounds WCl_6 (99%), $MoCl_5$ (98%), $LiAlH_4$ (95%), $LiAlD_4$ (96%), $PhCO_2H$ (99%), $NOBF_4$, $TlPF_6$, Super-Hydride ($LiBEt_3H$) and Super-Deuteride ($LiBEt_3D$) (1.0 M in thf), dimethylzinc (2.0 M in toluene), diethylzinc (1.0 M in hexanes), Na[$(MeOCH_2CH_2O)_2AlH_2$] (>65% w/w in toluene) were from Aldrich and used as received, C_5H_8 (97%), $H_2C{=}CHCH_2SiMe_3$ (99%), 2-methoxyethanol (99%) from Aldrich and further purified by distillation and NH_4I (Aldrich, 99%) was recrystallised from thf. The following compounds were prepared by literature methods: [$MoCl_4$(dme)],[14] [WCl_4(dme)],[14] 6,6-dimethylfulvene,[53] cyclohexylfulvene,[53] (C_5H_5)CMe_2(C_5H_5),[54] perdeuteriated methyl iodide,[55] perdeuteriated dimethylzinc[43] and lithium bis(2-methoxyethoxy)aluminium deuteride.[47]

The NMR spectra were recorded on either a Varian Unity-Plus 500 MHz (^1H, ^{13}C and ^2H at 499.868, 125.704, and 76.13 MHz respectively) or a Bruker AM300 spectrometer (^1H and ^{13}C at 300.1 and 75.5 MHz respectively), referenced internally using the residual protio solvent (^1H) and solvent (^{13}C) resonances and measured relative to $SiMe_4$ (^1H and ^{13}C δ 0) or to an internal standard (C_6D_6 or $C_6D_5CD_3$). The NMR simulations were carried out using the program gNMR for windows.[27] Mass spectra (electron impact, EI), were recorded on an AEI MS 302 mass spectrometer, updated by a data-handling system supplied by Mass Spectrometry Services Ltd.; FAB mass spectra were obtained by the EPSRC mass spectrometry service. The *m/z* values quoted are based on the most abundant isotope of each element. Electrochemical studies were performed using an EG & G Princeton Applied Research Potentiostat, model 273. The cell consisted



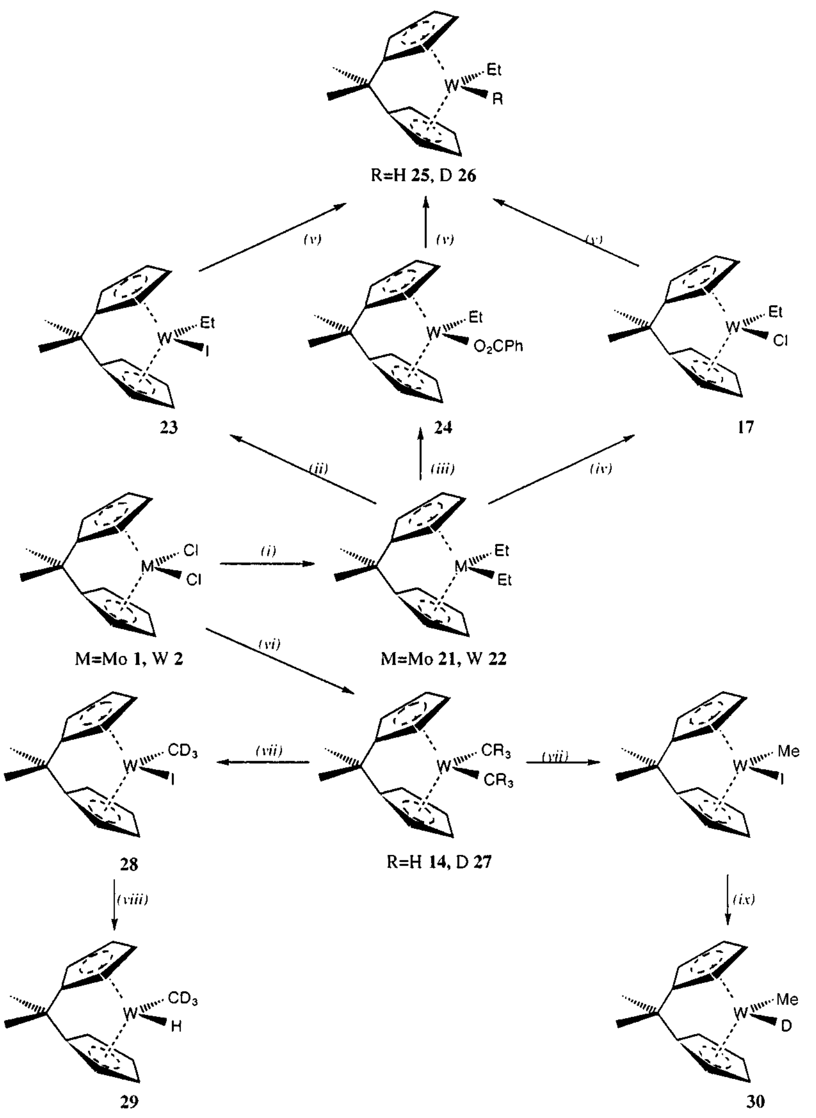
Scheme 2 Summary of reactions leading to the preparation of compounds **1**–**20**. (*i*) Et_2O; (*ii*) $TlPF_6$ or $NOBF_4$, MeCN; (*iii*) PPh_3, Me_2CO; (*iv*) $CNC_6H_3Me_2$-2,6, MeCN; (*v*) $NOBF_4$, CH_2Cl_2; (*vi*) $LiBEt_3H$, thf; (*vii*) HCl, NH_4PF_6; (*viii*) NaSR, EtOH; (*ix*) $NOBF_4$, MeCN; (*x*) $(AlEtCl_2)_2$, C_6H_5Me; (*xi*) $NOBF_4$, MeCN; (*xii*) $ZnMe_2$, C_6H_5Me; (*xiii*) $[CPh_3][B(C_6F_5)_4]$; (*xiv*) MeCN

of a vacuum-tight chamber fitted with inlets for a glassy carbon (GC) working electrode, a platinum-gauze auxiliary electrode and a silver-wire pseudo-reference electrode. Typically experiments were carried out using *ca.* 35 cm^3 of a 0.1 M tetrabutylammonium hexafluorophosphate in acetonitrile solution containing 1–2 M of sample under dinitrogen at ambient temperature. The potentials were referenced to the ferrocenium–ferrocene couple at +0.3770 V relative to silver wire; the reversibility was judged by comparison of ΔE at various scan rates with that of the ferrocene internal standard. Infrared spectra were recorded on either a Perkin-Elmer 1710 FTIR or a Mattson instruments Galaxy series FT-IR 6020 spectrometer in the range 500 to 4000 cm^{-1} and a Perkin-Elmer 580B spectrometer in the range 500 to 200 cm^{-1}. Samples were either prepared as Nujol mulls between KBr plates or as KBr discs. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford.

Preparations

$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ 1. A mixture of the two solids $[MoCl_4(dme)]$ (40.36 g, 122 mmol) and $Li_2[(C_5H_4)CMe_2(C_5H_4)]$ (22.66 g, 122 mmol) was stirred in the absence of solvent until a homogeneous mixture formed. Diethyl ether (1000 cm^3) was added with vigorous stirring. The resulting purple suspension was stirred for 3 d. The liquid phase was then decanted and dme (80 cm^3) added to the remaining solid. After stirring for 1 h a dark brown solid was filtered off and dried *in vacuo*. The solid was then washed with ethanol (100 cm^3) and transferred to a frit where it was washed with diethyl ether (5 × 30 cm^3) until the washings were colourless. A Soxhlet extraction of the resulting air- and moisture-stable brown solid with CH_2Cl_2 over 24 h gave $[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1** as a green solid. Final yield 3.07 g (8%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ 2. A mixture of the two



Scheme 3 Summary of reactions leading to the preparation of compounds **21**–**30**. (*i*) $ZnEt_2$, C_6H_5Me; (*ii*) NH_4I, diglyme (2,5,8-trioxanonane); (*iii*) $PhCO_2H$ light petroleum, (b.p. 100–120 °C), $(AlEtCl_2)_2$, C_6H_5Me; (*iv*) $Na[AlR(OCH_2CH_2OMe)_2]$, C_6H_5Me; (*v*) $Zn(CR_3)_2$, C_6H_5Me; (*vi*) NH_4I, thf; (*vii*) $Na[AlH_2(OCH_2CH_2OMe)_2]$, C_6H_5Me; (*viii*) $Na[AlD_2(OCH_2CH_2OMe)_2]$, C_6H_5Me; (*ix*) $Li[AlD(OCH_2CH_2OMe)_2]$

solids $[WCl_4(dme)]$ (30 g, 70.59 mmol) and $Li_2[(C_5H_4)CMe_2(C_5H_4)]$ (13.35 g, 72.50 mmol) was stirred in the absence of solvent until a homogeneous mixture formed. Diethyl ether (1000 cm^3) was added with vigorous stirring. The resulting brown suspension was stirred for 3 d. The liquid phase was then decanted and dme (225 cm^3) was added to the remaining solid. After stirring for 1 h a dark brown solid was filtered off and dried *in vacuo*. It was then washed with ethanol (300 cm^3) and transferred to a frit and washed with diethyl ether (6 × 30 cm^3) until the washings were colourless. A Soxhlet extraction of the resulting air- and moisture-stable brown solid with CH_2Cl_2 over 24 h gave $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **2** as a purple solid. Final yield 10.5 g (35%).

$[W_2Cl_4(OEt)_4(EtOH)_2]$ 3. Compound **3** was isolated as a by-product during the purification of **2**. The unchanged starting material $[WCl_4(dme)]$ was hydrolysed by the addition of ethanol to give an air- and moisture-stable solid. Compound **3** was isolated as green crystals from the ethanol washings, purified by washing with diethyl ether (4 × 10 cm^3) and characterised by ^1H and $^{13}C\text{-}\{^1H\}$ NMR spectroscopy, mass spectrometry and microanalysis. The unit cell of the crystal was found to be the same as that of an authentic sample.[12]

$[Mo_2Cl_4(OEt)_4(EtOH)_2]$ 4. Compound **4** was isolated as a by-product during the purification of **1**. The unchanged starting material $[MoCl_4(dme)]$ was hydrolysed by the addition of ethanol to give a moisture-stable solid. The product was isolated as purple crystals which were washed with diethyl ether (2 × 10 cm^3) then dried *in vacuo*.

$[Mo\{(\eta\text{-}C_5H_4)C(C_5H_{10})(\eta\text{-}C_5H_4)\}Cl_2]$ 5. A mixture of the two solids $[MoCl_4(dme)]$ (4 g, 12.2 mmol) and $Li_2[(C_5H_4)C(C_5H_{10})(C_5H_4)]$ (2.74 g, 12.2 mmol) was thoroughly mixed in the absence of solvent. Diethyl ether (300 cm^3) was added with vigorous stirring. The resulting purple suspension was stirred for 3 d. The liquid phase was then decanted and dme (20 cm^3) added to the remaining solid. After stirring for 1 h a dark brown solid was filtered off and dried *in vacuo*. It was then washed with ethanol (25 cm^3), transferred onto a glass frit and washed with diethyl ether (3 × 10 cm^3) until the washings were colourless. A Soxhlet extraction of the resulting air- and moisture-stable brown solid with CH_2Cl_2 over 24 h gave $[Mo\{(\eta\text{-}C_5H_4)C(C_5H_{10})(\eta\text{-}C_5H_4)\}Cl_2]$ **5** as a green powder. Yield 0.97 g (21%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2][BF_4]$ 6. The compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1** (0.3 g, 0.69 mmol) in CH_2Cl_2 (100 cm^3) was treated dropwise with a solution of $NOBF_4$ (0.08 g, 0.69 mmol) in CH_2Cl_2 (50 cm^3). The initial purple solution slowly turned green; the reaction was continued for 12 h. The volatiles were removed under reduced pressure and the residual green solid washed with diethyl ether (3 × 10 cm^3) giving [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$][BF$_4$] **6** as a green solid. Yield 0.29 g, 82%.

[Mo{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(NCMe)Cl][PF$_6$] 10. A mixture of [Mo{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **1** (0.4 g, 1.19 mmol) and TlPF$_6$ (0.41 g, 1.19 mmol) in acetonitrile (60 cm^3) was heated at 100 °C for 48 h in a Rotoflo ampoule. The reaction mixture changed from a green-brown suspension to a red-brown solution. The solution was filtered and the volatiles removed under reduced pressure to leave a brown solid which was washed with diethyl ether (3 × 10 cm^3). After drying the residue was recrystallised from acetonitrile–diethyl ether (1:5) at −20 °C. Yield 0.09 g (16%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(SPh)$_2$] 7. A mixture of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **2** (0.5 g, 1.18 mmol) and NaSPh (0.62 g, 4.7 mmol) was heated at 80 °C in ethanol (200 cm^3) for 3 d. The resulting orange solution was filtered through a bed of Celite whilst warm. Small orange crystals of [W{(η-C$_5$H$_4$)-CMe$_2$(η-C$_5$H$_4$)}(SPh)$_2$] **7** were precipitated on cooling to room temperature. The mother-liquor was concentrated under reduced pressure and a second crop of crystals was isolated by cooling to −20 °C. Overall yield 0.42 g (62%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(SPr^i)$_2$] 8. A mixture of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **2** (0.21 g, 0.49 mmol) and NaSCHMe$_2$ (0.62 g, 4.7 mmol) was heated at 80 °C in ethanol (100 cm^3) for 5 d. The resulting orange solution was filtered away from the unchanged NaSCHMe$_2$ and the volatiles were removed under reduced pressure to give an orange solid which was then extracted into diethyl ether (3 × 20 cm^3). Concentration of the diethyl ether solution under reduced pressure, followed by cooling to −78 °C, gave [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(SPr^i)$_2$] **8** as orange crystals. Yield 0.09 g (38%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(SPr^i)(NCMe)][BF$_4$] 9. To an orange solution of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(SPr^i)$_2$] **8** (0.04 g, 0.08 mmol) in MeCN (20 cm^3) was added a solution of NOBF$_4$ (0.01 g, 0.09 mmol) in MeCN (20 cm^3). The colour changed from green to orange. The reaction was left to stir for 1 h at room temperature. The solution was filtered and the volatiles were removed under reduced pressure to give an orange solid which was washed with diethyl ether (2 × 20 cm^3) to give [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(SPr^i)(NCMe)][BF$_4$] **20** as an orange powder. Yield 0.016 g (36%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)(NCMe)Cl][PF$_6$] 11. A mixture of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **2** (0.3 g, 0.69 mmol) and TlPF$_6$ (0.24 g, 0.69 mmol) in acetonitrile (100 cm^3) was heated at 100 °C for 48 h in a Rotoflo ampoule. The reaction mixture changed from a purple suspension to a red-brown solution. The solution was filtered and the volatiles removed under reduced pressure to leave a brown solid which was washed with diethyl ether (3 × 10 cm^3). After drying the residue was essentially pure, by NMR spectroscopy. An analytically pure sample was obtained by recrystallisation from acetonitrile–diethyl ether (1:5) at −20 °C. Yield 0.31 g (78%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(PPh$_3$)Cl][PF$_6$] 12. A mixture of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(NCMe)Cl][PF$_6$] **11** (0.1 g, 0.17 mmol) and triphenylphosphine (0.046 g, 0.17 mmol) was dissolved in acetone (75 cm^3) and heated at 60 °C for 36 h. The resultant red solution was filtered to separate it from a small amount of white solid. The volatiles were then removed under reduced pressure to leave a red-orange solid. Recrystallisation from acetone–diethyl ether (1:5) at −20 °C gave [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(PPh$_3$)Cl][PF$_6$] **12** as orange crystals. Yield 0.06 g (46%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(CNC$_6$H$_3$Me$_2$-2,6)Cl][PF$_6$] 13. A mixture of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(NCMe)Cl][PF$_6$] **11** (0.1 g, 0.17 mmol) and 2,6-dimethylphenyl isocyanide (0.23 g, 0.17 mmol) in acetonitrile (30 cm^3) was heated at 60 °C for 3 d. The orange solution was filtered and the volatiles removed under reduced pressure to leave a crystalline solid which was washed with diethyl ether (2 × 20 cm^3). Recrystallisation from a concentrated acetonitrile solution at −20 °C gave [W{(η-C$_5$H$_4$)-CMe$_2$(η-C$_5$H$_4$)}(CNC$_6$H$_3$Me$_2$-2,6)Cl][PF$_6$] **13** as orange crystals. Yield 0.081 g (72%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Me$_2$] 14. To a suspension of crude [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **2** (4.4 g, 10.3 mmol) in toluene (300 cm^3) was added a 2 M solution of ZnMe$_2$ in toluene (20.7 cm^3, 41.4 mmol) at −78 °C. The reaction was allowed to reach room temperature slowly and was then stirred for 24 h. The dark red suspension was then cooled to 0 °C and water (10 cm^3) was added. After stirring for 1 h the suspension was filtered, the residual solid 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) which was then concentrated under reduced pressure and cooled to −78 °C. Orange crystals of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Me$_2$] **14** separated which were filtered off and dried *in vacuo*. Yield 1.69 g (43%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(η^2-C$_2$H$_4$)H][B(C$_6$F$_5$)$_4$] 15. To a vigorously stirred orange solution of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Me$_2$] **14** (0.1 g, 0.26 mmol) in toluene (30 cm^3) at −78 °C was added dropwise a solution of [CPh$_3$][B(C$_6$F$_5$)$_4$] (0.24 g, 0.26 mmol) in toluene (40 cm^3) that had also been cooled to −78 °C. A red oil formed on addition. Upon slow warming to room temperature this dissolved and the stirring was stopped. The solution was left to stand overnight during which time orange crystals of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(η^2-C$_2$H$_4$)H][B(C$_6$F$_5$)$_4$] **15** separated and were filtered off. Yield 0.12 g (43%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Et(NCMe)][B(C$_6$F$_5$)$_4$] 16. Acetonitrile (30 cm^3) was added to an orange crystalline sample of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}(η^2-C$_2$H$_4$)H][B(C$_6$F$_5$)$_4$] **15** (0.6 g, 0.56 mmol). The solid dissolved to give a dark green solution. The solvent was removed under reduced pressure and the resulting green solid was washed with diethyl ether (2 × 20 cm^3). Recrystallisation from acetonitrile–diethyl ether (1:5) at −20 °C gave dark green [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}-Et(NCMe)][B(C$_6$F$_5$)$_4$] **16**. Yield 0.57 g (92%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Et(Cl)] 17. Crude (*i.e.* non-Soxhlet extracted) [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **2** (3 g, 7 mmol) was added slowly to a stirred 1 M solution of [(AlEtCl$_2$)$_2$] in toluene (200 cm^3) *via* a solid-addition funnel. As the solid was added a dark oil formed below a copper-coloured solution. The reaction mixture was allowed to stir for 12 h and the copper-coloured supernatant was then decanted from the oil, which was dried *in vacuo*. The dark oil was then cooled to −196 °C and cautiously hydrolysed by the dropwise addition of ethanol (40 cm^3). The reaction mixture was allowed to warm to room temperature and the solvent removed under reduced pressure to leave a red-brown solid. The solid was washed with water (3 × 50 cm^3), dried *in vacuo* and then extracted into toluene (3 × 50 cm^3) to give an orange filtrate. The toluene solution was concentrated by slow removal of the solvent under reduced pressure, light petroleum (b.p. 40–60 °C) was added and the mixture cooled to −80 °C giving red crystals of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Et(Cl)] **17**. Yield 0.67 g (23%).

[W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Et(NCMe)][PF$_6$] 16a. A mixture of [W{(η-C$_5$H$_4$)CMe$_2$(η-C$_5$H$_4$)}Et(Cl)] **17** (0.15 g, 0.36 mmol) and TlPF$_6$ (0.126 g, 0.36 mmol) in acetonitrile (100 cm^3) was stirred at room temperature for 2 d. The orange reaction mixture was then heated at 80 °C for 1 week during which time it darkened. The solvent was removed under reduced pressure and the remaining brown solid was washed with toluene (2 × 20

cm^3) to remove any unchanged **17**. The tan coloured solid was then recrystallised from acetonitrile–diethyl ether (1:5) to give a pale green powder of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(NCMe)][PF_6]$. Yield 0.1 g (49%).

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(NCMe)Cl][BF_4]$ 11a and $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(Cl)][BF_4]$ 18. To a stirred solution of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(Cl)]$ **17** (0.05 g, 0.12 mmol) in acetonitrile (30 cm^3) was added a solution of $NOBF_4$ (0.014 g, 0.12 mmol) in acetonitrile (20 cm^3). The colour changed immediately from orange to pink. After 24 h the volume of solvent was reduced to *ca.* 15 cm^3 and diethyl ether (20 cm^3) was added; the solution was then cooled to −20 °C. The compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(NCMe)Cl][BF_4]$ **11a** was isolated as long, pink needles and $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(Cl)][BF_4]$ **18** was isolated as purple crystals.

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ 19. To a stirred purple suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ **2** (1.4 g, 2.82 mmol) in thf (300 cm^3) at −78 °C was added $LiBEt_3H$ (10.1 cm^3 of a 1 M solution in thf, 10.1 mmol). The reaction was allowed to warm slowly to room temperature during which time it changed to orange. The mixture was stirred for 2 h after which time distilled water (5 cm^3) was cautiously added to hydrolyse the unchanged $LiBEt_3H$. The reaction mixture was then freed from volatiles under reduced pressure and the resulting brown solid was extracted into toluene (3 × 50 cm^3). The solvent was then removed under reduced pressure and the solid recrystallised from acetone at −78 °C to give yellow crystals of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ **19**. Yield 0.62 g (62%).

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_3][PF_6]$ 20. To a stirred suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ **19** (0.11 g, 0.31 mmol) in distilled water (5 cm^3) was added slowly HCl (24 cm^3 of a 6 M solution) at 0 °C. The solution was filtered after 10 min to remove a small amount of insoluble $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ **2**. The yellow filtrate was added dropwise to a solution of NH_4PF_6 (0.13 g, 0.46 mmol) in water (20 cm^3). A white precipitate of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_3][PF_6]$ **20** formed which was filtered off and washed with water (1 × 5 cm^3) and diethyl ether (2 × 10 cm^3) prior to drying *in vacuo*. Yield 0.05 g (31%).

Deprotonation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_3]Cl$. To a stirred suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ **19** (0.11 g, 0.31 mmol) in water (5 cm^3) at 0 °C was added HCl (24 cm^3 of a 6 M solution). The yellow solution of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_3]Cl$ was filtered from a small amount of grey solid. The solution was stirred at 0 °C and NaOH (6 cm^3 of a 12 M solution) was added dropwise. A yellow precipitate formed, which was filtered off and washed with water (1 × 5 cm^3) and diethyl ether (2 × 10 cm^3) before being dried *in vacuo*. Comparison of the ^1H NMR spectrum with that of an authentic sample showed the product to be $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ **19**.

$[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et_2]$ 21. To a suspension of $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ **1** (1 g, 2.96 mmol) in toluene (100 cm^3) was added a solution of diethylzinc in hexanes (25 cm^3 of a 0.84 M solution, 21 mmol) at −78 °C. The reaction was allowed to warm to ambient temperature and then stirred for 2 d. The red suspension was hydrolysed at 0 °C by dropwise addition of water (20 cm^3). After stirring for 2 h the solution was filtered and the remaining solid washed with toluene (3 × 20 cm^3). All extracts were combined and evaporated to dryness. The residue was extracted in pentane (2 × 50 cm^3) and cooled to −78 °C to afford $[Mo\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et_2]$ **21** as an orange powder. The product was further purified by sublimation at 80 °C (10^{-1} Torr, ≈13.3 Pa). Yield 0.16 g (17%).

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et_2]$ 22. To a suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ **2** (5 g, 11.75 mmol) in toluene (150 cm^3) was added a solution of diethylzinc in hexanes (55.9 cm^3 of a 0.84 M solution, 47 mmol) at −78 °C. The reaction was then allowed to warm to ambient temperature and stirred for 2 d. The red suspension was hydrolysed at 0 °C by dropwise addition of water (30 cm^3). After stirring for 2 h the solution was filtered and the remaining solid washed with toluene (3 × 20 cm^3). All extracts were combined and evaporated to dryness. The residue was extracted in pentane (3 × 25 cm^3). The solution was then cooled to −78 °C to afford $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et_2]$ **22** as orange crystals. The filtrate was concentrated and cooled again to give a second crop of product. Combined yield 2.03 g (42%).

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(I)]$ 23. A mixture of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et_2]$ **22** (0.1 g, 0.25 mmol) and powdered NH_4I (0.04 g, 0.30 mmol) in diglyme (100 cm^3) was heated at 120 °C for 4 d in a Rotoflo ampoule. The colour gradually turned from orange to purple. The solution was filtered and volatiles removed under reduced pressure. The purple solid was washed with pentane (2 × 20 cm^3) to remove trace amounts of **22**. The solid obtained after drying was recrystallised from toluene–pentane (1:5) at −78 °C giving purple crystals of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(I)]$ **23**. Yield 0.09 g (69%).

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(O_2CPh)]$ 24. A mixture of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et_2]$ **22** (0.35 g, 0.84 mmol) and benzoic acid (0.1 g, 0.84 mmol) was refluxed in light petroleum (b.p. 100–120 °C) (100 cm^3) in a Rotoflo ampoule. The colour gradually turned from orange to yellow over the course of 11 d. The solution was filtered and concentrated under reduced pressure. Recrystallisation from light petroleum (b.p. 100–120 °C) at −78 °C gave $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(O_2CPh)]$ **24** as orange crystals. Yield 0.11 g (26%).

$[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(H)]$ 25. *Method* (*a*) *from* $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(Cl)]$. To a solution of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(Cl)]$ **17** (0.05 g, 0.12 mmol) in toluene (50 cm^3) was added sodium bis(2-methoxyethoxy)aluminium hydride in toluene (1 cm^3 of a 3.4 M solution, 3.4 mmol). The colour changed from orange to yellow during the course of the addition. After stirring for 24 h at room temperature, water (10 cm^3) was added dropwise. The organic phase was decanted, the volatiles were removed under reduced pressure and the yellow solid was extracted into pentane (2 × 10 cm^3). After filtration, the yellow solution was cooled to −78 °C to remove trace amounts of the less soluble $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H_2]$ **19**. The filtrate was then concentrated under reduced pressure and cooled to −78 °C to give $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(H)]$ **25**. Yield 0.018 g (36%).

Method (*b*) *from* $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(I)]$. A solution of sodium bis(2-methoxyethoxy)aluminium hydride in toluene (1 cm^3 of a 3.4 M solution, 3.4 mmol) was added to a solution of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(I)]$ **23** (0.1 g, 0.20 mmol) in toluene (50 cm^3). The colour changed from purple to yellow after 12 h, the reaction was continued for 12 h then the solution was hydrolysed at 0 °C by dropwise addition of water (10 cm^3). The organic phase was decanted, the volatiles were removed under reduced pressure and the orange-yellow solid was extracted into pentane (2 × 10 cm^3). After filtration, the yellow solution was cooled to −78 °C which removed trace amounts of **19**. The filtrate was then concentrated under reduced pressure and cooled to −78 °C giving yellow crystals of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(H)]$ **25**. Yield 0.032 g (41%).

Method (*c*) *from* $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(O_2CPh)]$. A solution of sodium bis(2-methoxyethoxy)aluminium hydride in toluene (1 cm^3 of a 3.4 M solution, 3.4 mmol) was added to a solution of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Et(O_2CPh)]$ **24** (0.15 g, 0.30 mmol) in toluene (100 cm^3). The colour changed from orange to yellow during the course of the addition. After stirring for 24 h at room temperature the solution was hydrolysed at 0 °C by slow addition of water (10 cm^3). The organic phase was decanted and the volatiles removed under reduced pressure before the yellow solid was extracted into pentane (2 × 10 cm^3). After filtration, the yellow solution was cooled to −78 °C which removed trace amounts of **17**. The filtrate was then concentrated under reduced pressure and cooled to −78 °C producing a yellow crystalline compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(H)]$ **25**. Yield 0.028 g (24%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(D)]$ 26. To a solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(Cl)]$ **17** (0.10 g, 0.24 mmol) dissolved in toluene (50 cm^3) was added a solution of lithium bis(2-methoxyethoxy)aluminium deuteride in toluene (3.3 cm^3 of a 0.72 M solution, 2.4 mmol). The colour changed from orange to yellow during the course of the addition. After stirring for 24 h at room temperature the solution was hydrolysed at 0 °C by dropwise addition of D_2O (10 cm^3). The organic phase was decanted, the volatiles were removed under reduced pressure and the yellow solid was extracted into pentane (2 × 10 cm^3). After filtration, the yellow solution was cooled to −78 °C to remove trace amounts of the less soluble **19**. The filtrate was then concentrated under reduced pressure and cooled to −78 °C, giving yellow crystals of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(D)]$ **26**. Yield 0.033 g (36%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)_2]$ 27. To a suspension of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **2** (2 g, 4.7 mmol) in toluene (150 cm^3) at −78 °C was added a solution of perdeuteriated dimethylzinc (31 cm^3 of a 0.5 M solution, 18.8 mmol). The reaction mixture was allowed to warm to room temperature and then stirred for 2 d. The red suspension was hydrolysed at 0 °C by dropwise addition of D_2O (10 cm^3). After stirring for 2 h the solution was filtered and the remaining solid washed with toluene (2 × 20 cm^3). All extracts were combined and evaporated to dryness. The residue was extracted in pentane (25 cm^3). The solution was then cooled to −78 °C to afford the product $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)_2]$ **27** as orange crystals. The filtrate was concentrated under reduced pressure and cooled to give a second crop of product. Combined yield 0.77 g (42%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$ 28. A mixture of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)_2]$ **27** (0.12 g, 0.31 mmol) and powdered NH_4I (0.044 g, 0.31 mmol) in thf (50 cm^3) was heated at 60 °C for 48 h. The solution was then filtered and volatiles removed under reduced pressure to leave a purple solid which was subsequently washed with pentane (3 × 10 cm^3) to remove any trace amounts of **27**. The solid obtained after drying was recrystallised from toluene–pentane (1 : 5) at −78 °C to give purple crystals of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$ **28**. Yield 0.11 g (68%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)(CD_3)H]$ 29. To a solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$ **28** (0.1 g, 0.2 mmol) in toluene (50 cm^3) was added a solution of sodium bis(2-methoxyethoxy)aluminium hydride in toluene (0.5 cm^3 of a 3.4 M solution, 1.7 mmol). The colour changed from purple to bright yellow during the course of the addition. After stirring for 24 h at room temperature the solution was hydrolysed at 0 °C by dropwise addition of D_2O (5 cm^3). The organic phase was decanted and the volatiles were removed under reduced pressure. The orange solid was then extracted into pentane (2 × 20 cm^3). After filtration, the resultant yellow solution was cooled to −78 °C to remove trace amounts of the less soluble $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$. After removal of the volatiles, sublimation at 59 °C (10^{-2} Torr) gave $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)H]$ **29** as a yellow powder. Yield 0.027 g (36%).

$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ 30. A solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(I)]$ (0.1 g, 0.2 mmol) in benzene (50 cm^3) was treated with a solution of lithium bis(2-methoxyethoxy)aluminium deuteride in toluene (2.4 cm^3 of a 0.72 M solution, 1.7 mmol).[6] The colour changed from orange to yellow during the course of the addition. After stirring for 24 h at room temperature the solution was hydrolysed at 0 °C by dropwise addition of D_2O (5 cm^3). The organic phase was decanted, the volatiles removed under reduced pressure and the yellow solid was extracted into pentane (3 × 10 cm^3). After filtration, the yellow solution was cooled to −78 °C to remove trace amounts of the less soluble **16**. The filtrate was then concentrated under reduced pressure and cooled to −78 °C, causing precipitation of yellow crystals of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ **30**. Yield 0.023 g (31%).

Thermolysis studies on $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(D)]$

Stock solutions of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ **30** and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et(D)]$ **26** *ca.* 100 mM in C_6H_6 containing 1% $[^2H_8]$toluene were prepared. Aliquots of 0.6 cm^3 were pipetted into two 5 mm NMR tubes which had been sealed onto vacuum-line adaptors. The contents of the tubes were then degassed by three freeze–pump–thaw cycles and the tubes sealed under vacuum. The samples were stored at −196 °C prior to use. The thermal decompositions were carried out in a constant-temperature oil-bath (75 ± 0.5 °C). Samples were removed from the oil-baths at intervals and cooled to room temperature for analysis by ^2H NMR spectroscopy.

Kinetics of hydrogen/deuterium exchange in the compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)H]$ 29

Two solutions of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)H]$ **29** were prepared of differing concentrations, one (10 mM; 0.002 g, 0.005 mmol) in C_6D_6 (0.6 cm^3) containing $C_6H_5CH_3$ (5 µl) as an internal standard and one of increased concentration (100 mM; 0.02 g, 0.05 mmol) in C_6H_6 (0.6 cm^3) containing $C_6H_5CH_3$ (5 µl) as an internal standard. The samples were pipetted into two 5 mm NMR tubes which had been sealed onto vacuum-line adaptors. The contents of the tubes were then degassed by three freeze–pump–thaw cycles and the tubes sealed under vacuum. The samples were stored at −196 °C prior to use. The thermal decompositions were carried out in a constant-temperature oil-bath (75 ± 0.5 °C). Samples were removed from the oil-baths at intervals and cooled to room temperature prior to analysis by ^1H NMR spectroscopy. The extent of the reaction was determined by comparing the peak height of the hydride ligand resonance in $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)H]$ with that of the toluene internal standard.

Thermolysis of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ 30 under an atmosphere of CH_4 (g)

A solution of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me(D)]$ **30** was prepared by dissolving it (0.04 g, 0.11 mmol) in C_6H_6 (0.6 cm^3) containing one drop of C_6D_6. It was transferred to a 5 mm NMR tube which had been sealed onto a vacuum-line adaptor. The contents of the tube were then degassed by three freeze–pump–thaw cycles and the tube filled with CH_4 (g) and sealed under a positive pressure (2.57 atm; atm = 101 325 Pa). The thermal decomposition was carried out in a constant-temperature oil-bath (75 ± 0.5 °C).

Crystallography

All crystals were mounted in Lindemann glass capillaries under nitrogen. Crystal data, data collection and refinement parameters for all compounds are given in Tables 5 and 6. For compounds **7**, **11**, **13**, **14**, **15**, **17**, **20**, **21** and **22** crystals were transferred to the goniometer head of an Enraf-Nonius CAD4 diffractometer. Unit-cell parameters were calculated from the

Table 5 Crystal data, data collection and refinement for compounds **7**, **10**, **11**, **13**–**15**, **17** and **20**

	7	**10**	**11**	**13**	**14**	**15**	**17**	**20**
Formula	$C_{25}H_{24}S_2W$	$C_{15}H_{17}ClF_6MoNP$	$C_{15}H_{17}ClF_6NPW$	$C_{22}H_{23}ClF_6NPW$	$C_{15}H_{20}W$	$C_{39}H_{19}BF_{20}W$	$C_{15}H_{19}ClW$	$C_{13}H_{17}F_6PW$
M	572.44	487.66	575.57	665.70	384.17	1062.23	418.62	502.09
Crystal size/mm	0.24 × 0.24 × 0.34	0.2 × 0.3 × 0.3	0.4 × 0.6 × 0.6	0.50 × 0.50 × 0.80	0.09 × 0.11 × 0.12	0.37 × 0.50 × 1.02	0.84 × 0.47 × 0.34	0.27 × 0.27 × 0.30
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic	Triclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	*Pcan*	$P2_12_12_1$	$P2_12_12_1$	$P\bar{1}$	*C*2/*c*	$P\bar{1}$	$P2_1/m$	$P2_1/m$
a/Å	13.137(2)	7.9010(4)	7.949(4)	8.804(2)	11.60(3)	10.405(5)	7.1961(5)	8.4748(7)
b/Å	13.166(2)	14.6690(8)	14.732(3)	9.572(2)	13.22(1)	14.16(1)	8.147(1)	8.7330(7)
c/Å	24.033(2)	14.957(7)	15.037(3)	15.365(5)	8.45(6)	15.850(7)	11.176(1)	10.422(1)
α/°				93.82(3)		111.20(5)		
β/°				103.49(2)	103.53(4)	92.29(4)	92.828(8)	98.612(9)
γ/°				87.62(2)		105.72(5)		
U/Å^3	4147.44	1733.5	1760.8	1139.91	1260.60	2071.18	654.41	765.18
Z	8	4	4	2	4	2	2	2
D_c/g cm^{-3}	1.83	1.87	2.17	1.88	2.02	1.73	2.12	2.17
F(000)	2199.56	968	1096	1330	730	1028	397	746
μ/cm^{-1}	123.53	10.42	70.01	54.21	93.33	32.31	91.58	78.61
X-Radiation (λ/Å)	Cu-Kα (1.541 80)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)	Mo-Kα (0.710 69)
Scan mode	ω–2θ	ω	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ	ω–2θ
θ_{min}, θ_{max}/°	0, 75	1.0, 26.0	1.0, 25.0	1.0, 20.0	1.0, 24.0	1.0, 30.0	1.0, 30.0	1.0, 30.0
Minimum, maximum *h*, *k*, *l*	0, 16; 0, 16; 0, 30	−*h*, *h*; −*k*, *k*; −*l*, *l*	−1, *h*; −1, *k*; −1, *l*	−7, 7; −8, 8; −1, 14	−9, 9; −10, 10; −1, 10	−14, 12; −16, 15; −1, 18	−10, 10; −1, 11; −1, 15	−11, 11; −1, 12; −1, 14
Reflections measured	5088	15 824	3045	2419	2400	8387	2462	2847
Independent reflections	4172	2025	2311	2083	985	7517	2042	2366
Total observed data [$I > 3\sigma(I)$]	3977	1752	2013	1995	468	5902	1977	1574
Merging *R*	0.020	0.053	0.042	0.025	0.074	0.017	0.026	0.056
Absorption correction	DIFABS		DIFABS	DIFABS	DIFABS	DIFABS	DIFABS	DIFABS
minimum, maximum	0.304, 1.175			0.81, 1.31	0.97, 1.00	0.82, 1.22	0.83, 1.27	0.77, 1.43
No. parameters	254	226	226	361	74	220	129	147
Data : parameters	16 : 1	8 : 1	10 : 1	6 : 1	6 : 1	11 : 1	15 : 1	11 : 1
Weighting scheme	Chebychev	Chebychev	Chebychev	Chebychev	Chebychev	Chebychev	Chebychev	Chebychev
Minimum, maximum residual peak/e Å^{-3}	−1.40, 0.88	−0.57, 0.94	−1.70, 1.48	−1.23, 0.67	−2.01, 2.59	−0.81, 3.76	−1.66, 0.66	−1.86, 0.13
R	0.034	0.036	0.040	0.032	0.053	0.059	0.020	0.067
R′	0.041	0.039	0.046	0.036	0.065	0.057	0.023	0.080
T/K	298	193	298	298	298	298	298	298

Table 6 Crystal data, data collection and refinement for compounds **21**, **22** and **28** *

	21	**22**	**28**
Formula	$C_{17}H_{24}Mo$	$C_{17}H_{24}W$	$C_{14}H_{14}D_3IW$
M	324.32	412.22	499.02
Crystal size/mm	0.43 × 0.65 × 0.71	0.25 × 0.56 × 0.62	0.2 × 0.2 × 0.3
a/Å	8.707(2)	8.703(1)	7.2640(2)
b/Å	8.1253(8)	8.1243(9)	8.4750(5)
c/Å	10.474(1)	10.480(1)	10.731(3)
β/°	91.02(1)	91.12(1)	91.508(4)
U/Å^3	740.89	740.93	660.4
D_c/g cm^{-3}	1.45	1.85	2.51
F(000)	336	400	456
μ/cm^{-1}	8.45	79.58	112.23
Scan mode	ω–2θ	ω–2θ	ω
θ_{min}, θ_{max}/°	1.0, 30.0	1.0, 36.0	1.0, 26.0
Minimum, maximum, h, k, l	−12, 12; −1, 11; −1, 14	−14, 14; −1, 13; −1, 17	$-h$, h; $-k$, k; $-l$, l
Reflections measured	2970	4607	8033
Independent reflections	2257	3678	1379
Total observed data [$I > 3\sigma(I)$]	2163	3210	1371
Merging R	0.026	0.045	0.057
Absorption correction	DIFABS	DIFABS	
minimum, maximum	0.90, 1.07	0.80, 1.16	
No. parameters	100	100	82
Data : parameters	22 : 1	32 : 1	17 : 1
Minimum, maximum residual peak/e Å^{-3}	−0.58, 0.61	−2.89, 1.50	−5.47, 2.81
R	0.020	0.032	0.063
R'	0.021	0.036	0.067

* Details in common: monoclinic, space group $P2_1/m$; $Z = 2$; Mo-Kα radiation (λ 0.710 69 Å); Chebychev weighting scheme; 298 K.

setting of 25 carefully centred reflections. Three reflections were chosen as intensity standards and were measured every 3600 s of X-ray exposure time and three orientation controls were measured every 250 reflections. Data were corrected for the effects of absorption using DIFABS.[56] For compounds **10** and **28** crystals were transferred to the goniometer head of an Enraf-Nonius DIP2020 diffractomer. Absorption effects and crystal decay were corrected by multiframe scaling of the image-plate data.[57] All data were corrected for Lorentz-polarisation effects.

The structures of compounds **7**, **10**, **11**, **13**, **20** and **28** were solved by direct methods giving non-hydrogen atom positions.[58] For **14**, **15**, **17**, **21** and **22** the non-hydrogen atoms were located by Patterson and Fourier-difference synthesis.[58] The structures were refined using full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. For **20** the hydrogen atoms bound to the tungsten could not be located; the ring and methyl hydrogens were placed in calculated positions and not included in the refinement. For the remaining structures hydrogen atoms were placed in calculated positions during the final cycles of refinement. Three-parameter Chebychev weighting schemes and corrections for anomalous dispersion were applied to all data. All crystallographic calculations were carried out using CRYSTALS[59] on a PC/AT-486 computer. Neutral atom scattering factors were taken from ref. 60.

For compound **14** the quality of the data obtained was poor as the crystal slowly decomposed in the X-ray beam (40% decay in intensity). Owing to the low ratio of data : parameters (6 : 1) two non-hydrogen atoms remained isotropic during the final cycles of refinement; it is believed however that the connectivity between the atoms can be trusted. For **15** and **28** the residual electron density remained high. The peaks were located close to the heavy atoms W and I and are therefore not likely to indicate missing atom positions.

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