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Studies of *ansa*-bis(cyclopentadienyl)tungsten derivatives

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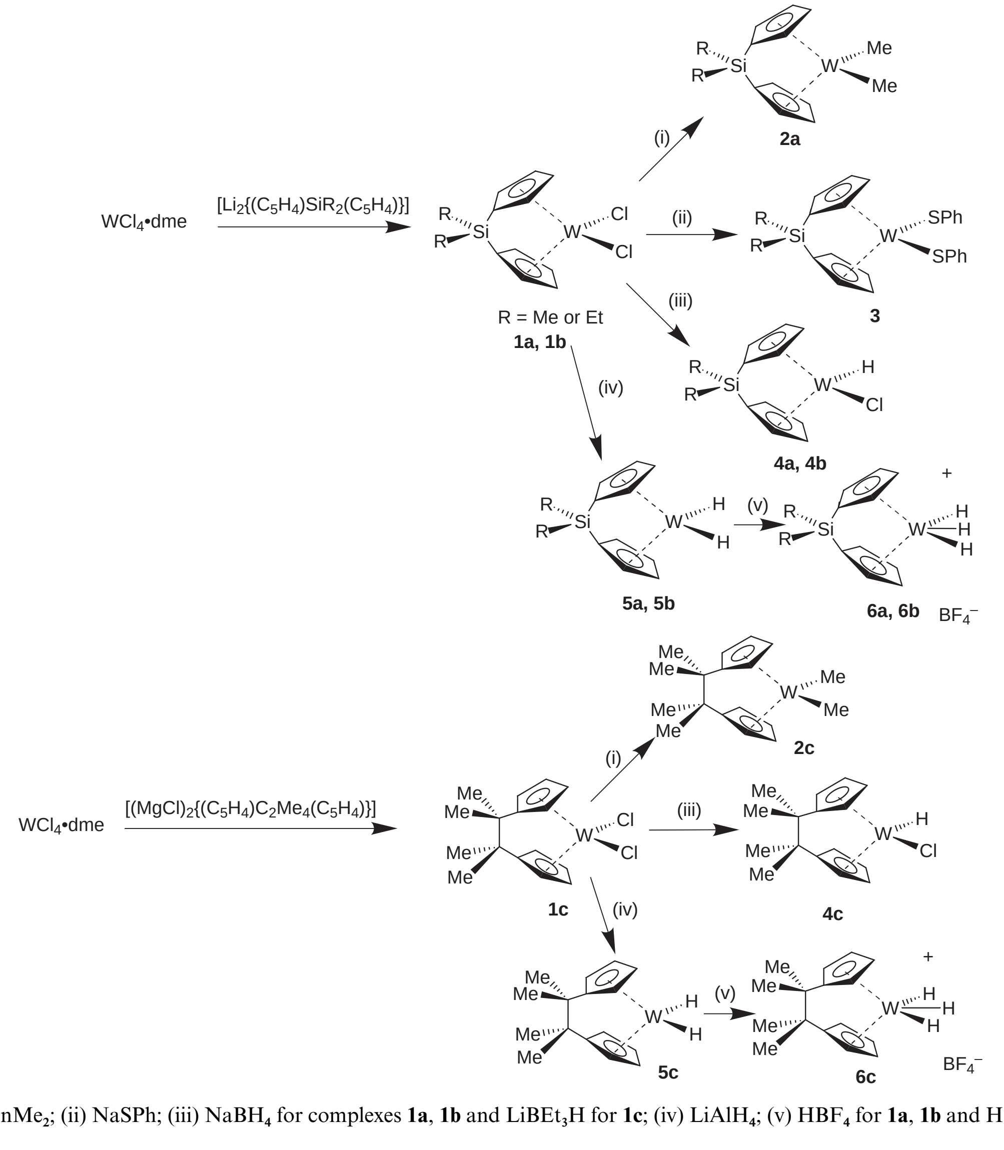
The new compounds [W{(η-C_5H_4)X(η-C_5H_4)}Cl_2] **1**, [W{(η-C_5H_4)X(η-C_5H_4)}Me_2] **2**, [W{(η-C_5H_4)$SiMe_2$-(η-C_5H_4)}$(SPh)_2$] **3**, [W{(η-C_5H_4)X(η-C_5H_4)}H(Cl)] **4**, [W{(η-C_5H_4)X(η-C_5H_4)}H_2] **5** and [W{(η-C_5H_4)-X(η-C_5H_4)}H_3]$^+$Y$^-$ **6**, where X = $SiMe_2$, $SiEt_2$ or CMe_2CMe_2, and Y = BF_4 or Cl, have been prepared. The crystal structures of [W{(η-C_5H_4)X(η-C_5H_4)}Me_2] (X = $SiMe_2$ or CMe_2CMe_2) have been determined.

Recently we have described *ansa*-metallocenes of tungsten and molybdenum and shown that their properties are significantly different from non-*ansa* analogues.[1,2] In particular we noted that the complex [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_3]$^+$$PF_6^-$ displays exceptional highly temperature variable ^{1}H NMR spectroscopic data with ^2J(HH) of *ca.* 16 000 Hz at −70 °C attributed to quantum mechanical exchange coupling. By comparison, [W(η-C_5H_5)$_2$$H_3$]$^+$$BF_4^-$ shows very different temperature independent behaviour.[3] We have prepared a number of related *ansa*-tungstenocene complexes to investigate the effect that changes in the bridging ring substituents have upon their properties.

Results and Discussion

The new dichloride compounds [W{(η-C_5H_4)X(η-C_5H_4)}Cl_2] (X = $SiMe_2$ **1a**, $SiEt_2$ **1b** or CMe_2CMe_2 **1c**) were prepared by reaction between [WCl_4(dme)] and the lithium salts [Li_2{(C_5H_4)X(C_5H_4)}] (X = $SiMe_2$ or $SiEt_2$) or [(C_5H_4)CMe_2CMe_2(C_5H_4)$(MgCl)_2$] respectively (Scheme 1).[1,2] The hydrolytic



Scheme 1 (i) $ZnMe_2$; (ii) NaSPh; (iii) $NaBH_4$ for complexes **1a**, **1b** and $LiBEt_3H$ for **1c**; (iv) $LiAlH_4$; (v) HBF_4 for **1a**, **1b** and HCl for **1c**

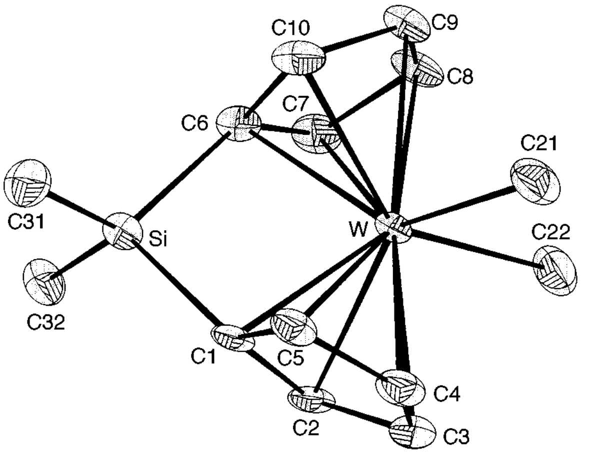


Fig. 1 Molecular structure of [W{(η-C_5H_4)$SiMe_2$(η-C_5H_4)}Me_2] **2a**

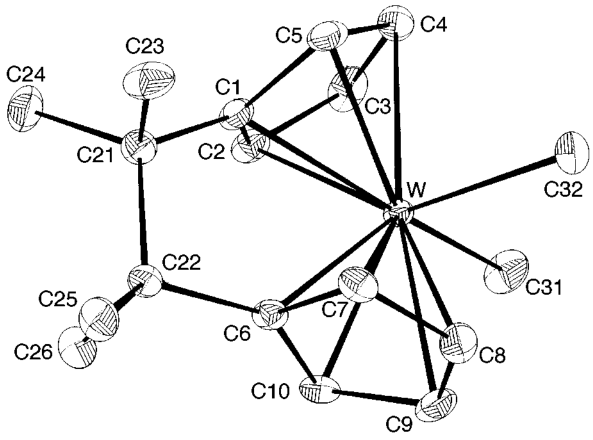


Fig. 2 Molecular structure of [W{(η-C_5H_4)CMe_2CMe_2(η-C_5H_4)}Me_2] **2c**

instability of **1a**, **1b** and the greater solubility of **1b**, **1c**, compared with [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2], required a modified work-up procedure in which the products were Soxhlet extracted with either CH_2Cl_2 (**1a**, **1b**) or toluene (**1c**). It is believed that the insoluble residues formed in these reactions may contain a large proportion of polymeric metallocene material. Indeed, reaction between the compound [WCl_4(dme)] and [Li_2{(C_5H_4)CMe_2CMe_2(C_5H_4)}] gave only polymeric product. It is interesting that a sample of **1a** stored under N_2 for several months in a clear glass vessel was converted into a polymeric form, becoming insoluble in all common solvents but maintaining identical elemental analysis to that of **1a**. For compounds **1a**, **1b** crude material that had only been washed with dme and Et_2O was used for their further reactions.

The analytical and spectroscopic data characterising compounds **1a**–**1c** and the other new compounds are in Table 1. They will not be discussed further except where interpretation is not straightforward. During the course of this work the preparation of **1a**, but not **1b** or **1c**, was reported and characterised purely by ^1H NMR spectroscopy and elemental analysis.[4]

Treatment of compounds **1a**, **1c** with an excess of dimethylzinc gave the orange dimethyl derivatives [W{(η-C_5H_4)X(η-C_5H_4)}Me_2] (X = $SiMe_2$ **2a** or CMe_2CMe_2 **2c**) in high yields. Crystals of **2a** and **2c** suitable for X-ray diffraction studies were grown by slow cooling of a pentane saturated solution. The crystal structures of **2a** and **2c** have been determined and are shown in Figs. 1 and 2 respectively. Selected interatomic distances and angles are listed in Table 2. The data show little variation in the bond lengths by comparison with the carbon-bridged analogue, [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2].[2] The only significant difference is the larger angles subtended by the cyclopentadienyl–tungsten bond vectors for **2a**. For instance, the angle θ defined as Cp_{cent}–W–Cp_{cent} decreases in the order 138.1, 136.6 and 128.4° for **2a**, **2c** and [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Me_2] respectively. A similar trend has been noted previously in some related titanium complexes listed in Table 3.

The reaction of complex **1a** with NaSPh gave the expected dithiolato complex [W{(η-C_5H_4)$SiMe_2$(η-C_5H_4)}$(SPh)_2$] **3** as a red solid. In contrast, the reaction of **1a** with NaSMe gave a mixture of products which the ^1H NMR spectroscopic data suggested included both [W{(η-C_5H_4)$SiMe_2$(η-C_5H_4)}$(SMe)_2$] and [W(η-C_5H_5)$_2$$(SMe)_2$] but no further studies were made.

Treatment of the compounds **1a**, **1b** with $NaBH_4$ gave the light orange chlorohydride complexes [W{(η-C_5H_4)X(η-C_5H_4)}H(Cl)] (X = $SiMe_2$ **4a** or $SiEt_2$ **4b**) in moderate yields. The compound [W{(η-C_5H_4)CMe_2CMe_2(η-C_5H_4)}H(Cl)] **4c** was also prepared, from the reaction between **1c** and $LiBEt_3H$. We note that treatment of [W(η-C_5H_5)$_2$$Cl_2$] and [W{(η-$C_5H_4$)$CMe_2$(η-$C_5H_4$)}$Cl_2$] with $NaBH_4$ gave the chlorohydride [W(η^5-C_5H_5)$_2$H(Cl)] and the dihydride complex [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] respectively.[1,8] Treatment of **1a**, **1b** with $LiBEt_3H$ gave only [W(η^5-C_5H_5)$_2$$H_2$], in moderate yields.

The yellow dihydride compounds [W{(η-C_5H_4)X(η-C_5H_4)}H_2] (X = $SiMe_2$ **5a**, $SiEt_2$ **5b** or CMe_2CMe_2 **5c**) were prepared by treatment of **1a**–**1c** with $LiAlH_4$. In the case of the silicon compounds care must be taken to separate the co-product of [W(η-C_5H_5)$_2$$H_2$] by extraction with pentane at −100 °C. The compounds **5a**–**5c** could be sublimed at approximately 100 °C and 10^{-2} Torr (Torr ≈ 133 Pa). Compounds **5a**–**5c** and **4a**–**4c** display very similar behaviour, with no discernible internal order, but intermediate between that of [W(η^5-C_5H_5)$_2$$H_2$] and [W{(η-$C_5H_4$)$CMe_2$(η-$C_5H_4$)}$H_2$] as evidenced by their ν(W–H) (*ca.* 1870 and *ca.* 1890 cm^{-1}) stretches and ^1J(HW) (*ca.* 80 and 67 Hz) (Table 4).[1] The PE spectra of **5a** and [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] are shown in Fig. 3 and vertical ionisation energies (IE) listed in Table 5. That of [W(η-C_5H_5)$_2$$H_2$] has been published previously.[12] Band A is assigned to ionisation of the two d electrons. Band B comprises ionisations from both the highest occupied orbitals of the cyclopentadienyl rings and the tungsten–hydrogen bonding electrons. Band C is associated with ionisations of the bridging group and occurs at a lower ionisation energy in the Si bridged compound than the C bridged compound. Similar bands have been found in the PE spectra of C and Si bridged ferrocenophanes.[9] The IE of the d band, A, varies little between the three compounds; the small stabilisation in the carbon bridged compound with the smaller θ value borders on significant. There are changes in the profile of band B which comprises six ionisations but overall the energy spread of this band is very similar for all three compounds. The principal difference in the three spectra is the presence and position of the bridge ionisation mentioned above. We therefore conclude that any changes in the WH_2 system on forming the *ansa* bridge are too subtle to be detected by PE spectroscopy.

It has previously been noted that [W{(η-C_5H_4)CMe_2(η-C_5H_4)}H_2] is unchanged by photolysis or thermolysis in benzene, whereas [W(η^5-C_5H_5)$_2$$H_2$] is converted into [W(η^5-C_5H_5)$_2$Ph(H)] under identical conditions.[1] We found evidence for intermediate behaviour for complex **5c**. Thus photolysis of **5c** in benzene was monitored by ^1H NMR spectroscopy and showed a decrease in the intensity of the hydride resonance at δ −10.0 and the growth of both a new hydride resonance at δ −9.4 [^1J(WH) = 80 Hz] together with associated *ansa*-metallocene-backbone resonances. Comparison of δ(^1H) and ^1J(WH) values with those of the compound [W(η-C_5H_5)$_2$Ph(H)] suggest that [W{(η-C_5H_4)CMe_2CMe_2(η-C_5H_4)}Ph(H)] was formed.[1] Integration of the hydride resonance indicated that only half of **5c** was consumed after 125 h of photolysis whereas [W(η-C_5H_5)$_2$$H_2$] had been fully consumed within 100 h. These differences can be associated with relative ease of distortion of the 16 valence electron tungstenocene intermediates to form a parallel ring structure.

Table 1 Analytical and spectroscopic data

Compound and analysis[a]	Spectroscopic data[b]
1a [W{(η-C_5H_4)SiMe$_2$(η-C_5H_4)}Cl$_2$] Green C, 28.7 (28.7); H, 3.7 (3.3)	^{1}H:[c] 6.12 (4 H, m, C_5H_4), 5.81 (4 H, m, C_5H_4), 0.09 (6 H, s, Me$_2$Si) ^{13}C-{^{1}H}:[c] 125.9 (s, C_5H_4), 78.7 (s, C_5H_4), 66.0 (s, C_5H_4, C_{ipso}), −5.9 (s, SiMe$_2$) Mass (FAB): *m*/*z* 442 (M^+), 405 ($M^+ - \mathrm{Cl}$)
1b [W{(η-C_5H_4)SiEt$_2$(η-C_5H_4)}Cl$_2$] Green	^{1}H:[c] 6.12 (4 H, br m, C_5H_4), 5.8 (4 H, br m, C_5H_4), 1.02 [6 H, t, ^3J(HH) 8, Me], 0.60 [4 H, q, ^3J(HH) 8, SiCH$_2$] ^{13}C-{^{1}H}:[c] 125.9 (s, C_5H_4), 79.3 (s, C_5H_4), 65.7 (s, C_5H_4, C_{ipso}), 5.7 (s, Me), 0.9 (s, SiCH$_2$)
1c [W{(η-C_5H_4)CMe$_2$CMe$_2$(η-C_5H_4)}Cl$_2$] Green C, 41.83 (41.14); H, 4.22 (4.32)	^{1}H:[c] 6.27 (4 H, m, C_5H_4), 5.97 (4 H, m, C_5H_4), 0.99 (12 H, s, C_2Me_4) ^{13}C-{^{1}H}:[c] 120.8 (s, C_5H_4, C_{ipso}), 119.7 (s, C_5H_4), 78.2 (s, C_5H_4), 46.2 (s, C_2Me_4), 28.9 (s, C_2Me_4) IR:[d] 3098s, 2972s (br), 2945m, 2878m, 1558w, 1456m, 1452m, 1398w, 1391s, 1252m, 1060m (br), 894w, 862s, 858 (sh), 844m, 812s and 288m [ν(W–Cl)] Mass (FAB): *m*/*z* 467 (M^+), 431 ($M^+ - \mathrm{Cl}$), 213 ($M^+ - \mathrm{W} - \mathrm{Cl}_2$)
2a [W{(η-C_5H_4)SiMe$_2$(η-C_5H_4)}Me$_2$] Orange C, 42.0 (42.0); H, 5.6 (5.0)	^{1}H:[e] 4.53 (4 H, m, C_5H_4), 4.12 (4 H, m, C_5H_4), 0.09 (6 H, s, WMe$_2$), −0.32 (6 H, s, Me$_2$Si) ^{13}C-{^{1}H}:[e] 110.8 (s, C_5H_4), 71.6 (s, C_5H_4), 45.3 (s, C_5H_4, C_{ipso}), −7.6 (s, SiMe$_2$), −27.9 (s, WMe$_2$) Mass (FAB): *m*/*z* 400 (M^+), 387 ($M^+ - \mathrm{Me}$), 371 ($M^+ - \mathrm{Me}_2$), 344 ($M^+ - \mathrm{SiMe}_2$), 327 ($M^+ - \mathrm{SiMe}_3$)
2c [W{(η-C_5H_4)CMe$_2$CMe$_2$(η-C_5H_4)}Me$_2$] Orange	^{1}H:[e] 4.96 (4 H, m, C_5H_4), 4.17 (4 H, m, C_5H_4), 0.66 (12 H, s, C_2Me_4), 20.9 (6 H, s, WMe$_2$) ^{13}C-{^{1}H}:[e] 105.7 (s, C_5H_4, C_{ipso}), 104.4 (s, C_5H_4), 72.1 (s, C_5H_4), 47.1 (s, C_2Me_4), 27.6 (s, C_2Me_4), −26.1 [s, WMe$_2$] Mass (FAB): *m*/*z* 426 (M^+), 411 ($M^+ - \mathrm{Me}$), 395 ($M^+ - \mathrm{Me}_2$), 213 ($M^+ - \mathrm{W} - 2\mathrm{Me}$)
3 [W{(η-C_5H_4)SiMe$_2$(η-C_5H_4)}(SPh)$_2$] Red	^{1}H:[c] 7.5 (br m, SPh), 7.3 (br m, SPh), 7.1 (br m, SPh), 6.9 (br m, SPh), 5.76 (4 H, m, C_5H_4), 5.16 (4 H, m, C_5H_4), 0.13 (6 H, s, Me$_2$Si) ^{13}C-{^{1}H}:[c] 135.0 (s, SPh), 133.5 (s, SPh), 128.3 (s, SPh), 124.7 (s, SPh), 119.9 (s, C_5H_4), 79.6 (s, C_5H_4), 66.0 (s, C_5H_4, C_{ipso}), −5.9 (s, SiMe$_2$)
4a [W{(η-C_5H_4)SiMe$_2$(η-C_5H_4)}H(Cl)] Yellow-orange C, 36.9 (37.1); H, 4.4 (4.1)	^{1}H:[e] 5.65 (2 H, m, C_5H_4), 5.33 (2 H, m, C_5H_4), 5.24 (2 H, m, C_5H_4), 3.62 (2H, m, C_5H_4), −0.25 (6 H, s, Me$_2$Si), −0.76 (6 H, s, Me$_2$Si), −9.49 [1 H, s, ^1J(WH) 67, WH] ^{13}C-{^{1}H}:[e] 121.1 (s, C_5H_4), 92.1 (s, C_5H_4), 77.1 (s, C_5H_4), 69.0 (s, C_5H_4), 46.2 (s, C_5H_4, C_{ipso}), −7.7 (s, SiMe$_2$), −8.2 (s, SiMe$_2$) IR:[f] 1906 [ν(W–H)]
4b [W{(η-C_5H_4)SiEt$_2$(η-C_5H_4)}H(Cl)] Yellow	^{1}H:[e] 5.67 (2 H, m, C_5H_4), 5.35 (2 H, m, C_5H_4), 5.24 (2 H, m, C_5H_4), 3.67 (2 H, m, C_5H_4), 0.76 [3 H, t, ^3J(HH) 8, Me], 0.51 [3 H, t, ^3J(HH) 8, Me], 0.34 [2 H, q, ^3J(HH] 8, SiCH$_2$], 0.22 [2 H, q, ^3J(HH) 8, SiCH$_2$], −9.54 [1 H, s, ^1J(WH) 67, WH] ^{13}C-{^{1}H}:[e] 121.2 (s, C_5H_4), 92.2 (s, C_5H_4), 77.5 (s, C_5H_4), 69.5 (s, C_5H_4), 45.7 (s, C_5H_4, C_{ipso}), 4.3 (s, Me), 3.8 (s, Me), −0.75 (s, SiCH$_2$), −0.85 (s, SiCH$_2$) IR:[f] 1899 [ν(W–H)] Mass (FAB): *m*/*z* 435 (M^+), 400 ($M^+ - \mathrm{Cl}$)
4c [W{(η-C_5H_4)CMe$_2$CMe$_2$(η-C_5H_4)}H(Cl)] Yellow Cl, 8.17 (8.15)	^{1}H:[e] 5.71 (2 H, s, C_5H_4), 5.23 (2 H, s, C_5H_4), 4.81 (2 H, s, C_5H_4), 4.26 (2 H, s, C_5H_4), 0.57 (6 H, s, C_2Me_4), 0.23 (6 H, s, C_2Me_4), −10.22 [1 H, s, *J*(WH) 67, WH] ^{13}C-{^{1}H}:[e] 113.96 (s, C_5H_4), 95.10 (s, C_5H_4, C_{ipso}), 86.87 (s, C_5H_4), 78.38 (s, C_5H_4), 69.01 (s, C_5H_4), 45.67 (s, C_2Me_4), 27.46 (s, C_2Me_4), 26.93 (s, C_2Me_4) IR:[d] 3098m, 3075m, 2964s, 2869m, 1883m [ν(W–H)], 1703m, 1456s, 1262s, 1102s, 1036s, 891w, 865m, 802s Mass (FAB): *m*/*z* 433 (M^+), 431 ($M^+ - \mathrm{H}$), 396 ($M^+ - \mathrm{H} - \mathrm{Cl}$)
5a [W{(η-C_5H_4)SiMe$_2$(η-C_5H_4)}H$_2$] Yellow	^{1}H:[e] 4.97 (4 H, m, C_5H_4), 4.21 (4 H, m, C_5H_4), −0.22 (6 H, s, Me$_2$Si), −10.14 [2 H, s, ^1J(WH) 79, WH$_2$] ^{13}C-{^{1}H}:[e] 88.3 (s, C_5H_4), 66.2 (s, C_5H_4), 61.4 (s, C_5H_4, C_{ipso}), −7.5 (s, SiMe$_2$) IR:[f] 1865 [ν(W–H)]
5b [W{(η-C_5H_4)SiEt$_2$(η-C_5H_4)}H$_2$] Yellow C, 42.9 (43.0); H, 5.5 (5.4)	^{1}H:[e] 4.97 (4 H, m, C_5H_4), 4.24 (4 H, m, C_5H_4), 0.84 [6 H, t, ^3J(HH) 8, Me], 0.34 [4 H, q, ^3J(HH) 8, SiCH$_2$], −10.18 [2 H, s, ^1J(WH) 79, WH$_2$] ^{13}C-{^{1}H}:[e] 88.3 (s, C_5H_4), 66.9 (s, C_5H_4), 61.9 (s, C_5H_4, C_{ipso}), 5.4 (s, Me), 0.5 (s, SiCH$_2$) IR:[f] 1881 [ν(W − H)], 1870 [ν(W − H)] Mass (FAB): *m*/*z* 400 (M^+)
5c [W{(η-C_5H_4)CMe$_2$CMe$_2$(η-C_5H_4)}H$_2$] Yellow C, 49.85 (48.26); H, 5.57 (6.46)	^{1}H:[e] 4.99 (4 H, s, C_5H_4), 4.62 (4 H, s, C_5H_4), 0.70 (12 H, s, C_2Me_4), −10.06 [2 H, s, ^1J(WH) 80, WH$_2$] ^{13}C-{^{1}H}:[e] 99.53 (s, C_5H_4, C_{ipso}), 82.18 (s, C_5H_4), 68.00 (s, C_5H_4), 45.93 (s, C_5H_4), 27.59 (s, C_2Me_4) IR:[d] 1941s, 1875s [ν(W–H)], 1860s [ν(W–H)], 1805s, 1785 (sh), 1738m, 1636m, 1608s (br)
6a [W{(η-C_5H_4)SiMe$_2$(η-C_5H_4)}H$_3$][BF$_4$] White	^{1}H:[g] 5.64 (4 H, m, C_5H_4), 5.39 (4 H, m, C_5H_4), −0.18 (6 H, s, Me$_2$Si), −4.3 (1 H, m, WH), −5.7 (2 H, m, WH$_2$) ^{13}C-{^{1}H}:[g] 93.6 (s, C_5H_4), 89.8 (s, C_5H_4), 84.6 (s, C_5H_4, C_{ipso}), −6.0 (s, SiMe$_2$) IR:[f] 1946 [ν(W–H)], 1919 [ν(W–H)]
6b [W{(η-C_5H_4)SiEt$_2$(η-C_5H_4)}H$_3$][BF$_4$] White C, 30.9 (31.3); H, 3.8 (4.2)	^{1}H:[c] 5.82 (4 H, m, C_5H_4), 5.73 (4 H, m, C_5H_4), 1.27 [6 H, t, ^3J(HH) 8, Me], 1.18 [4 H, q, ^3J(HH) 8, SiCH$_2$], −4.0 (1 H, m, WH), −5.3 (2 H, m, WH$_2$) ^{13}C-{^{1}H}:[c] 96.2 (s, C_5H_4), 92.3 (s, C_5H_4), 66.0 (s, C_5H_4, C_{ipso}), 3.5 (s, Me), −1.8 (s, SiCH$_2$) IR:[f] 1952 [ν(W–H)], 1928 [ν(W–H)]
6c [W{(η-C_5H_4)CMe$_2$CMe$_2$(η-C_5H_4)}H$_3$]Cl White	^{1}H:[c] 6.60 (4 H, s, C_5H_4), 5.40 (4 H, s, C_5H_4), 1.40 (12 H, s, C_2Me_4), −4.43 (3 H, s, WH$_3$) ^{13}C-{^{1}H}:[g] 118.02 (s, C_5H_4, C_{ipso}), 85.58 (s, C_5H_4), 83.92 (s, C_5H_4), 45.78 (s, C_2Me_4), 26.38 (s, C_2Me_4) IR:[f] 1913m [ν(W–H)], 1864w, 1751w, 1403m

[a] Elemental analyses (%) are reported as found (required). For complexes **1a**, **4a** and **5b** the formulations were $C_{12}H_{14}Cl_2SiW\cdot CH_2Cl_2\cdot H_2O$, $C_{12}H_{15}ClSiW\cdot 0.5C_5H_{12}$ and $C_{14}H_{20}SiW\cdot 0.25OEt_2$. [b] The NMR data recorded at room temperature are given as: chemical shift (δ) (multiplicity, relative intensity, assignment, *J*/Hz). Where necessary assignments were confirmed using ^{1}H–^{1}H and ^{1}H–^{13}C shift correlation experiments. The ^{13}C-{^{1}H} NMR assignments of the C_{ipso} are given for **1b**, **1c**, **2a**, **2c**, **3**, **4c**, **6a**, **6c**; it was not possible to observe the *ipso*-cyclopentadienyl carbon atoms for the other compounds probably due to the associated problems of long relaxation times and lack of NOE enhancement. The ^{1}H NMR spectra for **1**–**3**, **5** and **6** all include the expected two virtual triplets assignable to the substituted cyclopentadienyl ring protons. The upfield chemical shift of the silicon analogues has previously been noted and ascribed to a build-up of π-electron density at this carbon atom due to the electron-withdrawing effect of the SiR$_2$ group. [c] In CD_2Cl_2. [d] KBr Disc. [e] In C_6D_6. [f] Selected IR data (cm^{-1}) determined in Nujol mulls. [g] In $CDFCl_2$.

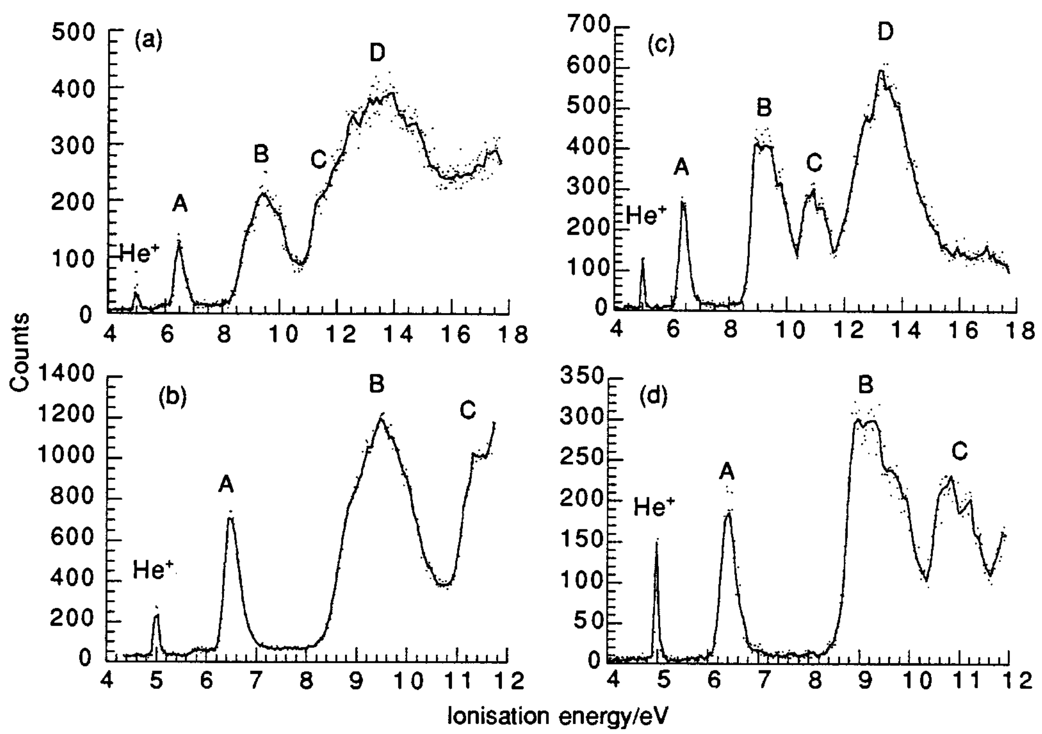


Fig. 3 The He I PE spectra of $[W\{(\eta\text{-}C_5H_4)X(\eta\text{-}C_5H_4)\}H_2]$, (a) and (b) X = CMe_2 and (c) and (d) X = $SiMe_2$ (**5a**)

Table 2 Selected interatomic distances (Å) and angles (°) for $[W\{(\eta\text{-}C_5H_4)X(\eta\text{-}C_5H_4)\}Me_2]$ X = $SiMe_2$ **2a** or CMe_2CMe_2 **2c**

	2a	**2c**		**2a**	**2c**
W–Me average	2.242	2.244	Me–W–Me	77.1(2)	77.76(11)
W–Cp^1_{cent}	1.963(5)	1.961(3)	C(1)–Si–C(6)	91.2(3)	—
W–Cp^1 average	2.313	2.305	C(31)–Si–C(32)	114.7(3)	—
W–C(1)	2.264(5)	2.236(3)	Cp^1_{cent}–W–Cp^2_{cent}	138.1	136.60
W–Cp^2_{cent}	1.965(5)	1.954(3)	Cp^1_{cent}–C(1)–X*	158.1	176.24
W–Cp^2 average	2.310	2.300	Cp^2_{cent}–C(6)–X	159.3	176.73
W–C(6)	2.248(7)	2.240(2)	C(1)–W–C(6)	72.23(18)	71.21(9)

* Cp^1 = Ring C(1)–C(5), Cp^2 = Ring C(6)–C(10), X = Si for **2a** and C(21) or C(22) where appropriate for **2c**.

Table 3 Comparison of selected structural data for complexes **2a**, **2c** and related compounds

Compound	θ/°[a]	φ/°[b]	Ref.
$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **2a**	138.1	77.1	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2CMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **2c**	136.6	77.8	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Me_2]$	128.4	66.2	2
$[Mo\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$	128.0	76.4	2
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Et_2]$	128.1	76.8	2
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(CD_3)I]$	127.5	78.7	2
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$	115.2	81.8	2
$[Ti(\eta\text{-}C_5H_5)_2Cl_2]$	131	94.4	6
$[Ti\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Cl_2]$	128.7	95.8	5
$[Ti\{(\eta\text{-}C_5H_4)C_2H_4(\eta\text{-}C_5H_4)\}Cl_2]$	128.0	94.8	7
$[Ti\{(\eta\text{-}C_5H_4)CH_2(\eta\text{-}C_5H_4)\}Cl_2]$	121.5	97.1	7

[a] Defined as Cp_{cent}–M–Cp_{cent} angle. [b] Defined as the X–M–X angle. To the best of our knowledge the crystal structure of $[W(\eta\text{-}C_5H_4)_2Me_2]$ has not been reported.

Table 3 shows trends in the θ angles for some related complexes and indicates that metallocene derivatives containing the C_2Me_4 bridge should have a similar θ and exert a similar influence to the non-bridged analogue.

Treatment of the dihydrides **5a**–**5c** with HCl or HBF_4 in Et_2O produced the trihydride cations $[W\{(\eta\text{-}C_5H_4)X(\eta\text{-}C_5H_4)\}H_3]^+Y^-$ (X = $SiMe_2$, Y = BF_4 **6a**; X = $SiEt_2$, Y = BF_4 **6b**; X = CMe_2CMe_2, Y = Cl **6c**). Use of a relatively non-co-ordinating anion such as BF_4 helped stabilise the product, whereas **6c** decomposed at room temperature. The variable temperature ^1H NMR spectra of **6a**–**6c** show, in addition to the low field temperature invariant resonances for the $(\eta\text{-}C_5H_4)X(\eta\text{-}C_5H_4)$ (X = $SiMe_2$ **6a**, $SiEt_2$ **6b** or CMe_2CMe_2 **6c**) backbone group, a second order AB_2X spin system (X = ^{183}W, 14%) for the WH_3 moiety with $J(H_AH_B)$ values that vary with temperature (Table 6 and Fig. 4). The values for δ(A), δ(B) and $J(H_AH_B)$ were obtained either directly from the ^1H NMR spectra, when the system approached the first order behaviour, or indirectly by modelling with the spectral spin simulation program gNMR.[13] The first order temperature invariant coupling to ^{183}W had values of $^1J(WH_A) = 70 \pm 2$ Hz and $^1J(WH_B) = 52 \pm 2$ Hz for all three systems. Experimental spectra below −90 °C were obtained using $CDFCl_2$ as solvent. For compounds **6a**–**6c** the magnitudes of $J(H_AH_B)$ were found to vary over a range 8–75 Hz between −140 and 0 °C. Overall, the behaviour of these compounds is intermediate between that observed for $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3]^+$ for which $J(H_AH_B)$ varies between 16 000 Hz at −70 °C and 2900 Hz at −130 °C and for $[W(\eta\text{-}C_5H_5)_2H_3]^+$ for which $J(H_AH_B) = 8.5$ Hz at all temperatures.[2,3]

As previously reported, the coupling mechanism is best explained in terms of two contributions to $J(H_AH_B)$, $^2J_{mag} - 2J_{ex}$ where J_{mag} is the conventional two-bond Fermi contact coupling constant and J_{ex} the quantum mechanical exchange coupling constant. The former is independent of temperature and generally takes a very small value of *ca.* 18–22 Hz, whereas the latter value exponentially increases with temperature due to thermal occupation of higher vibrational states each with a larger J_{ex}.[2] As proposed by Heinekey,[3] this vibration principally consists of the WH_AH_B wag and, as a result of substantial

Table 4 Comparison of selected ν(W–X) stretches in the IR spectrum and ^{1}J(HW) in the ^{1}H NMR spectrum

Compound	$\tilde{\nu}$(W–H)/cm^{-1}	^{1}J(HW)/Hz	Ref.
$[W(\eta\text{-}C_5H_5)_2H(Cl)]$	1968[a]	62	9
$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}H(Cl)]$ **4a**	1906[a]	67	This work
$[W\{(\eta\text{-}C_5H_4)SiEt_2(\eta\text{-}C_5H_4)\}H(Cl)]$ **4b**	1899[a]	67	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2CMe_2(\eta\text{-}C_5H_4)\}H(Cl)]$ **4c**	1883[b]	67	This work
$[W(\eta\text{-}C_5H_5)_2H_2]$	1896[a]	73	1, 10
$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}H_2]$ **5a**	1865[a]	79	This work
$[W\{(\eta\text{-}C_5H_4)SiEt_2(\eta\text{-}C_5H_4)\}H_2]$ **5b**	1881, 1870[a]	79	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2CMe_2(\eta\text{-}C_5H_4)\}H_2]$ **5c**	1875, 1860[b]	80	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$	1833, 1823[a]	92	1
$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}H_3]^+$ **6a**	1946, 1919[a]	71, 52	This work
$[W\{(\eta\text{-}C_5H_4)SiEt_2(\eta\text{-}C_5H_4)\}H_3]^+$ **6b**	1952, 1928[a]	71, 52	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2CMe_2(\eta\text{-}C_5H_4)\}H_3]^+$ **6c**	1913[a]	69, 52	This work
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3]^+$	1913[a]	76, 57	This work
$[W(\eta\text{-}C_5H_5)_2H_3]^+$	1932	69, 47	11, This work

[a] Determined as a Nujol mull. [b] Determined as a KBr disc.

Table 5 Vertical ionisation energies (in eV; *ca.* 1.60 × 10^{-19} J) for $[W(\eta\text{-}C_5H_4)X(\eta\text{-}C_5H_4)H_2]$ (X = CMe$_2$ or SiMe$_2$ **5a**) and $[W(\eta\text{-}C_5H_5)_2H_2]$

Band	X = CMe$_2$	X = SiMe$_2$	$[W(\eta\text{-}C_5H_5)_2H_2]$	Assignment
A	6.45	6.39	6.4	W d
B	8.85	8.89	8.9	W–H
	9.41	9.31	9.6	C$_5$H$_4$ π
	9.91	9.97		
C	11.30	10.61		X
		10.90		
		11.15		
D	12.53	12.69	12.6	
	13.5	13.20	13.7	

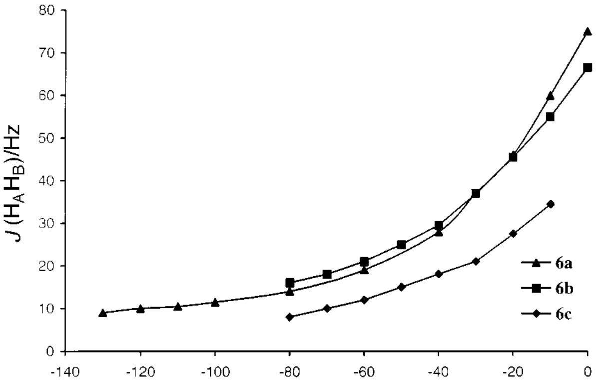


Fig. 4 Variation with temperature of $J(H_AH_B)$ in the ^{1}H NMR spectrum of complexes **6a**–**6c**

delocalisation of the hydride wavefunctions, allows tunnelling to occur and gives rise to large couplings. The principal factors that seem to result in larger J_{ex} include low electron density at the metal centre, close proximity of the hydrogen atoms and lower frequency wags (and hence weaker bonds). The contrast between the small temperature dependent $J(H_AH_B)$ for **6a**–**6c** and the extremely large value for methylene-bridged $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3]^+$ is especially notable. Previously we have associated $J(H_AH_B)$ trends with those for ν(W–H) stretches assuming that the trend in stretches mirrored the trend in bending frequencies (Table 4).[2] However, the new data for **6a**–**6c** suggest that this relationship is tenuous. The small changes between **6a** and **6b** may partly be due to solvent effects, which have previously been noted for $[Nb(\eta\text{-}C_5H_5)_2H_3]$ in CDFCl$_2$ and [^{2}H$_{14}$]methylcyclohexane.[3]

At temperatures above 20 °C, the hydride peaks for complexes **6a**–**6c** begin to broaden due to the hydride chemical exchange occurring on a similar timescale to that of the ^{1}H NMR spectrum. This has previously been observed for both $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_3]^+$ and $[W(\eta\text{-}C_5H_4)_2H_3]^+$ at similar temperatures.[2,3]

In conclusion we have found that the properties of the new *ansa*-silicon or *ansa*-ethylene compounds described above are intermediate between those of the *ansa* CMe$_2$-bridged and non-bridged compounds.

Experimental

General

All manipulations of air- and/or moisture-sensitive materials were performed in an inert atmosphere using either a dual vacuum/nitrogen line and standard Schlenk techniques, or in an inert atmosphere dry-box containing nitrogen. In each case the nitrogen was purified by passage over 4 Å molecular sieves, and either BASF catalyst for the dry-box or MnO for the Schlenk line. Solvents and solutions were transferred through stainless steel cannulae using a positive pressure of nitrogen. Filtrations were generally performed using modified stainless steel cannulae which had been fitted with glass fibre filter discs. All glassware and cannulae were dried overnight at 150 °C before use.

Physical measurements

The ^{1}H and ^{13}C NMR spectra were recorded using a Varian UNITY plus (^{1}H 500 MHz, ^{13}C 125 MHz) spectrometer and are at room temperature unless otherwise stated. Spectra were referenced internally using the residual protio solvent (^{1}H) and solvent (^{13}C) resonances relative to tetramethylsilane (δ 0). The NMR simulations were carried out using the program gNMR for Windows.[13] Infrared spectra were recorded on either a Mattson-Polaris or a Perkin-Elmer 1710 FT interferometer or, in the region below 400 cm^{-1}, on a Perkin-Elmer grating spectrometer, mass spectra (FAB) by the EPSRC Mass Spectrometry Service at Swansea. Elemental analyses were performed by the Microanalytical Department of the Inorganic Chemistry Laboratory, Oxford. The He I photoelectron spectra were measured on a PES Laboratories 0078 PE spectrometer and calibrated with N$_2$, Xe and He.

Solvents were pre-dried by standing over 4 Å Linde molecular sieves and then refluxed and distilled under a nitrogen atmosphere from phosphorus pentaoxide or calcium hydride (dichloromethane), potassium (thf), sodium (toluene) or sodium–potassium alloy (1 : 3 w/w) [light petroleum (b.p. 40–60 °C), diethyl ether, pentane]. Deuteriated solvents (Aldrich) for NMR studies were stored in Young's ampoules over 4 Å molecular sieves under nitrogen after having been refluxed with potassium metal (C$_6$D$_6$) or calcium hydride (CD$_2$Cl$_2$). The compounds ZnMe$_2$, NaBH$_4$, LiBEt$_3$H, LiAlH$_4$, 85% HBF$_4$ in Et$_2$O and HCl in Et$_2$O were used as purchased; [WCl$_4$(dme)],[14]

Table 6 High field ^{1}H NMR spectroscopic data for $[W\{(\eta\text{-}C_5H_4)X(\eta\text{-}C_5H_4)\}H_3]^+$ **6a**–**6c**

	6a[a]			**6b**[b]			**6c**[a]		
T/°C	δ(H_A)	δ(H_B)	*J*(H_AH_B)/Hz	δ(H_A)	δ(H_B)	*J*(H_AH_B)/Hz	δ(H_A)	δ(H_B)	*J*(H_AH_B)/Hz
0	−4.27	−5.67	75	−4.01	−5.37	66.5			
−10	−4.30	−5.68	60	−4.04	−5.38	55	−4.25	−4.63	34.5
−20	−4.31	−5.69	46	−4.07	−5.40	45.5	−4.26	−4.65	27.5
−30	−4.34	−5.70	37	−4.10	−5.41	37	−4.28	−4.66	21
−40	−4.37	−5.72	28	−4.13	−5.42	29.5	−4.31	−4.68	18
−50				−4.16	−5.44	25	−4.36	−4.72	15
−60	−4.42	−5.75	19	−4.19	−5.46	21	−4.38	−4.73	12
−70				−4.21	−5.48	18	−4.42	−4.75	10
−80	−4.47	−5.76	14	−4.25	−5.50	16	−4.46	−4.78	8
−100	−4.52	−5.79	11.5						
−110	−4.55	−5.81	10.5						
−120	−4.58	−5.82	10						
−130	−4.60	−5.83	9						

[a] In $CDFCl_2$. [b] In CD_2Cl_2.

$[Li_2\{(\eta\text{-}C_5H_4)_2SiR_2\}]$ (R = Me or Et),[5] $[(MgCl)_2\{(C_5H_4)C_2Me_4(C_5H_4)\}]\cdot4thf$,[15] $CDFCl_2$[16] and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}H_2]$[1] were prepared using standard literature methods.

Preparations

$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ 1a. The two solids $[WCl_4(dme)]$ (6.43 g, 15.5 mmol) and $[Li_2\{(C_5H_4)_2SiMe_2\}]$ (3.1 g, 15.5 mmol) were stirred in the absence of solvent to give a good admixture. Diethyl ether (100 cm^3) was added and the resulting brown suspension stirred for 4 d. The mother-liquor was decanted off and the solid washed with dme (8 × 30 cm^3) and Et_2O (2 × 20 cm^3) and pumped to dryness to yield crude $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1a** as a green solid. Pure **1a** was obtained by Soxhlet extraction into CH_2Cl_2 for 4 h followed by washing with pentane (3 × 10 cm^3). Yield 1.35 g, 20%. For subsequent reactions it was possible to use crude **1a** that had not been Soxhlet extracted.

$[W\{(\eta\text{-}C_5H_4)SiEt_2(\eta\text{-}C_5H_4)\}Cl_2]$ 1b. The two solids $[WCl_4(dme)]$ (4.20 g, 10.0 mmol) and $[Li_2\{(C_5H_4)_2SiEt_2\}]$ (3.1 g, 10.8 mmol) were stirred in the absence of solvent to give a good admixture. Diethyl ether (75 cm^3) was added and the resulting brown suspension stirred for 6 d. The mixture was pumped to dryness, extracted with CH_2Cl_2 (4 × 30 cm^3) and washed with pentane (3 × 10 cm^3). Yield 3.6 g, 72%. For subsequent reactions it was possible to use crude **1b** that had not been Soxhlet extracted.

$[W\{(\eta\text{-}C_5H_4)C_2Me_4(\eta\text{-}C_5H_4)\}Cl_2]$ 1c. The two solids $[WCl_4(dme)]$ (5.44 g, 13.1 mmol) and $[(MgCl)_2\{(C_5H_4)C_2Me_4(C_5H_4)\}]\cdot4thf$ (8.13 g, 13.1 mmol) were stirred in the absence of solvent to give a good admixture. Diethyl ether (200 cm^3) was added and the resulting brown suspension stirred for 3 d. The volatiles were removed under reduced pressure and the resulting pale brown solid was Soxhlet extracted with toluene for 5 h to yield a deep red-brown solution. The solvent was removed under reduced pressure, yielding a dark oily solid which was washed with pentane (2 × 50 cm^3). The resulting dark grey solid was dried under reduced pressure. An analytically pure sample of **1c** was obtained by dissolving the solid in toluene, concentrating the solution under reduced pressure and cooling to −80 °C. The compound **1** was isolated by filtration, prior to drying under reduced pressure and obtained as a grey powder. Yield 1.73 g, 28%.

$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Me_2]$ 2a. To a suspension of crude $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1a** (0.4 g, 0.9 mmol) in toluene (70 cm^3) at −78 °C was added dropwise a solution of $ZnMe_2$ in toluene (2 M, 5 cm^3, 2 mmol) and the resulting mixture stirred overnight at room temperature. The orange suspension was then cooled to 0 °C and the excess of $ZnMe_2$ hydrolysed by addition of distilled water (1 cm^3). After stirring for 30 min at room temperature the suspension was filtered and the residual solid extracted with light petroleum (2 × 15 cm^3). The extracts were combined, concentrated and cooled to −20 °C to yield orange crystals of $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Me_2]$ **2a**. Yield 0.050 g, 14%. The complex $[W\{(\eta\text{-}C_5H_4)C_2Me_4(\eta\text{-}C_5H_4)\}Me_2]$ **2c** was prepared in a similar fashion. Yield 0.09 g, 47%.

$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}(SPh)_2]$ 3. A mixture of the two solids NaSPh (0.42 g, 3 mmol) and crude $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1a** (0.67 g, 0.15 mmol) was stirred until homogenous and then thf (50 cm^3) added and the resulting orange solution stirred for 1 d and refluxed for 6 h. The mixture was then filtered and washed with thf (2 × 15 cm^3) and the extracts were combined and pumped to dryness. Extraction into CH_2Cl_2, pumping to dryness, and recrystallisation from acetone–pentane at −80 °C yielded $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}(SPh)_2]$ **3** as an orange solid. Yield 0.142 g, 16%.

$[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}H(Cl)]$ 4a. To a stirred brown suspension of crude $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ **1a** (0.146 g, 0.33 mmol) in dme (40 cm^3) at −50 °C was added solid $NaBH_4$ (0.056 g, 1.5 mmol). The reaction mixture was stirred at −50 °C for 3 h and then filtered. Volatiles were removed under reduced pressure and the sticky orange solid was extracted with toluene (25 cm^3) and pumped to dryness. Subsequent washing with pentane (3 × 10 cm^3) yielded $[W\{(\eta\text{-}C_5H_4)SiMe_2(\eta\text{-}C_5H_4)\}H(Cl)]$ **4a** as an orange powder. Yield 0.02 g, 15%. The complex $[W\{(\eta\text{-}C_5H_4)SiEt_2(\eta\text{-}C_5H_4)\}H(Cl)]$ **4b** was prepared in a similar fashion to that of **4a** except extraction with benzene, as opposed to toluene, was used. Yield 0.08 g, 14%.

$[W\{(\eta\text{-}C_5H_4)C_2Me_4(\eta\text{-}C_5H_4)\}H(Cl)]$ 4c. To a stirred brown suspension of $[W\{(\eta\text{-}C_5H_4)C_2Me_4(\eta\text{-}C_5H_4)\}Cl_2]$ **1c** (0.130 g, 0.27 mmol) in toluene (50 cm^3) at −78 °C was added dropwise a solution of $LiBEt_3H$ in thf (1 M, 1.5 cm^3, 1.5 mmol). The reaction mixture was allowed slowly to warm to room temperature and stirred for 2 h. Unchanged $LiBEt_3H$ was hydrolysed by cautious addition of distilled water (2 cm^3) to the yellow-orange solution at room temperature. Volatiles were removed under reduced pressure to leave a brown solid which was extracted with toluene (50 cm^3). Toluene was removed under reduced pressure and the resulting solid extracted with light petroleum. The orange solution was concentrated under reduced pressure and cooled to −80 °C to yield $[W\{(\eta\text{-}C_5H_4)C_2Me_4(\eta\text{-}C_5H_4)\}H(Cl)]$ **4c** as an orange powder which could be isolated by filtration and dried under reduced pressure. Yield 0.150 g, 35%.

[W{(η-C$_5$H$_4$)SiMe$_2$(η-C$_5$H$_4$)}H$_2$] 5a. A suspension of LiAlH$_4$ (0.27 g, 7.21 mmol) in diethyl ether (20 cm^3) at −78 °C was added dropwise to a suspension of [W{(η-C$_5$H$_4$)SiMe$_2$(η-C$_5$H$_4$)}Cl$_2$] **1** (0.636 g, 1.44 mmol) in diethyl ether (50 cm^3) at −78 °C. The resulting yellow suspension was allowed slowly to warm to room temperature and stirred for 10 h. The suspension was filtered and the residual solid extracted into diethyl ether (3 × 50 cm^3). The diethyl ether extracts were combined and unchanged LiAlH$_4$ was hydrolysed by cautious addition of diethyl ether saturated with distilled water (20 cm^3) and then distilled water (10 cm^3) at 0 °C. After stirring for 30 min the organic phase was decantered off and the aqueous phase extracted with diethyl ether (3 × 20 cm^3). The yellow ether extracts were combined, washed with distilled water (10 cm^3) and pumped to dryness under reduced pressure to leave a yellow oily solid. The solid was extracted with benzene, pumped to dryness, washed with pentane (2 × 10 cm^3) at −100 °C and dried under reduced pressure to yield [W{(η-C$_5$H$_4$)SiMe$_2$-(η-C$_5$H$_4$)}H$_2$] **5a** as a yellow powder. Yield 0.106 g, 20%. The complexes [W{(η-C$_5$H$_4$)SiEt$_2$(η-C$_5$H$_4$)}H$_2$] **5b** and [W{(η-C$_5$H$_4$)C$_2$Me$_4$(η-C$_5$H$_4$)}H$_2$] **5c** were prepared in a similar fashion. Yield 0.080 g, 22% and 0.220 g, 42.2% respectively.

[W{(η-C$_5$H$_4$)C$_2$Me$_4$(η-C$_5$H$_4$)}H$_3$]Cl 6c. A yellow solution of [W{(η-C$_5$H$_4$)C$_2$Me$_4$(η-C$_5$H$_4$)}H$_2$] **5c** (0.075 g, 0.188 mmol) in diethyl ether (20 cm^3) was treated with a solution of HCl in diethyl ether (1 M, 2 cm^3, 2 mmol). The resulting pale grey suspension was stirred for 30 min. The complex [W{(η-C$_5$H$_4$)-C$_2$Me$_4$(η-C$_5$H$_4$)}H$_3$]Cl **6c** was isolated as a white powder by filtration and washing with diethyl ether (2 × 20 cm^3) and then dried under reduced pressure. Yield, 0.052 g, 64%. The complexes [W{(η-C$_5$H$_4$)SiMe$_2$(η-C$_5$H$_4$)}H$_3$][BF$_4$] **6a** and [W{(η-C$_5$H$_4$)SiEt$_2$(η-C$_5$H$_4$)}H$_3$][BF$_4$] **6b** were prepared in a similar manner to that of **6c** except that HBF$_4$ in Et$_2$O was used in place of HCl in Et$_2$O.

Crystallography

Crystals of complexes **2a** and **2c** were both grown from a saturated pentane solution at *ca.* 193 K and isolated by filtration. A specimen was chosen under an inert atmosphere, covered with paratone-N oil, and mounted on the end of a glass fibre.

Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.710 69 Å). The images were processed with the DENZO and SCALEPACK programs.[17] Corrections for Lorentz-polarisation effects were performed.

All solution, refinement, and graphical calculations were performed using the CRYSTALS[18] and CAMERON[19] software packages. The crystal structure was solved by direct methods using the SIR 92 program[20] and was refined by full-matrix least squares on *F*. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. A Chebychev weighting scheme with the parameters 4.80, 0.569 and 3.64 (**2a**) or 2.32, 0.530 and 1.82 (**2c**) was applied as well as an empirical absorption correction.[21]

Crystal data. For **2a**, C$_{14}$H$_{20}$SiW, $M = 400.25$, monoclinic, space group $P2_1/n$, 0.2 × 0.1 × 0.5 mm, $a = 8.064(2)$, $b = 14.808(3)$, $c = 11.212(3)$ Å, $\beta = 98.54(2)°$, $U = 1324.0(6)$ Å^3, $T = 100$ K, $Z = 4$, μ(Mo-Kα) = 8.98 mm^{-1}, 5956 reflections measured, 2715 unique, $R = 0.034$, $R' = 0.041$. For **2c**, C$_{18}$H$_{26}$W, $M = 426.26$, monoclinic, space group $P2_1/c$, 0.35 × 0.35 × 0.3 mm, $a = 9.350(3)$, $b = 13.145(3)$, $c = 12.739(4)$ Å, $\beta = 105.042(2)°$, $U = 1512.1(8)$ Å^3, $T = 125$ K, $Z = 4$, μ(Mo-Kα) = 7.79 mm^{-1}, 7382 reflections measured, 3097 unique, $R = 0.0199$, $R' = 0.026$.

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See http://www.rsc.org/suppdata/dt/1998/2689/ for crystallographic files in .cif format.

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