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Polyhedron 24 (2005) 1388–1403

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Hydrogen/deuterium exchange in alkyl-hydride derivatives of *ansa*-tungstenocene compounds

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Received 22 March 2005; accepted 19 May 2005
Available online 14 July 2005

Abstract

The higher *n*-alkyl hydrides $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(R)H](R = \{(CH_2)_nCH_3\}$, $n = 1–4$) and the isotopically labelled analogues $[W(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}(R)D]$, ($R = \{(CH_2)_nCH_3\}$ ($n = 1–4$) and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{CD_2CD_3\}H]$ have been prepared and the hydrogen/deuterium exchange processes under thermal conditions in these compounds have been investigated by NMR spectroscopy. In every case of all the possible alkyl hydrogens of the alkyl groups R only H/D exchange with the α-CH_2 methylene hydrogens was observed.

Keywords: *Ansa*-metallocene; Alkylhydrides; Hydrogen/deuterium exchange; Tunsten; Intramolecular

1. Introduction

We have reported the hydrogen/deuterium (H/D) exchange process for the *ansa*-methyl-deuteride compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}MeD]$ [1] and shown that this methyl-hydride compound is much more thermally stable towards the reductive elimination of methane than the non-*ansa* analogue $[W\{(\eta\text{-}C_5H_5)_2\}MeH]$ [1]. This enhanced thermal stability of the *ansa*-metallocene towards reductive elimination was attributed to the inability of the bent ansa compound to attain the parallel ring structure which has been previously shown to be the preferred ground state structure of the 16-electron molecule tungstenocene $[W\{(\eta\text{-}C_5H_5)_2\}]$ [2,3]. We have shown that hydrogen/deuterium exchange process for the methyl-deuteride compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}MeD]$ proceeds without observable decomposition. An intramolecular mechanism involving an agostic tungsten-methane system was proposed [2,3].

In the light of this *ansa*-stabilisation effect it was decided to attempt to synthesise and study the thermal stability and H/D exchange reactions of the higher alkyl-hydride derivatives $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}(R)H]$, where $R = \{(CH_2)_nCH_3\}(n = 2–4)$. It was also decided to reinvestigate the previous study of H/D exchange reaction of the ethyl-hydride $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}EtD]$ since preliminary evidence suggested that both α- and β-hydrogens of the ethyl group underwent exchange and that the rate of the β-hydrogen exchange was faster than for the α-hydrogen exchange [2]. This result was in contrast to the report that for H/D exchange of the compounds $[Rh(\eta\text{-}C_5Me_5)PMe_3(^{13}CH_2CH_3)D]$ for which the rate of H/D exchange was faster for the α-hydrogens [4,5].

2. Results and discussion

The dialkyl compounds $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}R_2]$ ($R = \{(CH_2)_nCH_3\}$ (where n = 1, **2**; 2, **3**; or 3, **4**) were prepared by the reaction between the previously

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doi:10.1016/j.poly.2005.05.004

described [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] [1] and the zinc dialkyl compounds [Zn{$(CH_2)_nCH_3$}$_2$] ($n = 1$, 2 or 3) in toluene at low temperatures [2,3]. In a typical reaction, the mixture was stirred at room temperature for 12 h and then the excess of the dialkylzinc reagent was cautiously hydrolysed by the addition of H_2O, prior to passing the toluene soluble mixture down an alumina column and then eluting with toluene. The compounds **2** and **3** were extracted into pentane and isolated as yellow crystalline solids by cooling the solution to −80 °C. The compound **3** is new and has been characterised by elemental analyis, FAB mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The characterising data for **3** and all the other new compounds described in this work are given in Table 1. In most cases assignments of the ^1H NMR spectra were assisted by ^1H–^1H NMR COSY experiments [6].

Treatment of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] with di(*n*-butyl)zinc [Zn{$(CH_2)_3CH_3$}$_2$] in toluene at low temperature affords a mixture of the σ-*n*-butyl compounds [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_3CH_3$}$_2$] (**4**) and [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_3CH_3$}Cl] (**5**). The yellow σ-*n*-butyl compounds **4** and **5** can be separated by fractional recrystallisation from a 1:1 toluene/pentane solution in 16% and 41% yield, respectively. Unexpectedly the NMR data showed the peak due to the hydrogens in the α-CH_2, methylene group relative to the metal is not the highest field resonance of the hydrogens of the *n*-butyl ligand. In the σ-ethyl compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2CH_3$}I] the peak due to the α-CH_2 methylene hydrogens is also found at a lower field relative to the β-methyl hydrogens [2]. The *n*-pentyl-chloride compound [W{(η-C_5H_4)-CMe_2(η-C_5H_4)}{$(CH_2)_4CH_3$}Cl] (**6**) was prepared by the reaction between [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] and [Zn{$(CH_2)_4CH_3$}$_2$]. The compound **6** is obtained as a pale orange/red solid in 29% yield following passage in diethyl ether down an alumina column. The corresponding di-*n*-pentyl compound [W{(η-C_5H_4)CMe_2-(ηC_5H_4)}{$(CH_2)_4CH_3$}$_2$] (**7**) was isolated in the same reaction as a very minor product (ca. 1%). It was characterised by ^1H NMR spectroscopy only. The di-*n*-hexyl compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_5CH_3$}$_2$] (**8**) was prepared by the reaction between [W{(η-C_5H_4)-CMe_2(η-C_5H_4)}Cl_2] and [Zn{$(CH_2)_5CH_3$}$_2$].

Treatment of the di-*n*-propyl compound [W{(η-C_5H_4)-CMe_2(η-C_5H_4)}{$(CH_2)_2CH_3$}$_2$] (**3**) with NH_4I in THF at 65 °C gave the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_2CH_3$}I] (**9**) as a pale red solid in 47% yield. The compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{$(CH_2)_2CH_3$}I] (**9**) was treated with [Na{$AlH_2(OCH_2O$-$CH_2CH_3)_2$}] at low temperature to give, after cautious hydrolysis of excess of [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}], the *n*-propyl-hydride compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_2CH_3$}H] (**10**) as a yellow crystalline solid in ca. 50% yield.

Table 1
Analytical and spectroscopic data

Compound[a]	NMR data[b]
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{$(CH_2)_2CH_3$}$_2$] (**3**). Yellow solid: C, 50.9 (51.8); H, 6.5 (6.4). MS: $m/z = 440$ $(M)^+$ 45%, $m/z = 355$ $(M–2\{(CH_2)_2\text{-} CH_3\})^+$ 100%.	^1H: 4.28 (m., 4H, C_5H_4) 4.19 (m., 4H, C_5H_4) 1.45 (m., 4H, $CH_2C\mathit{H}_2CH_3$) 1.21 (t., 6H, $CH_2CH_2C\mathit{H}_3$) 0.55 (m., 4H, $C\mathit{H}_2CH_2CH_3$) 0.43 (m., 6H, CMe_2) $^{13}C\{^1H\}$: 104.26 (s., C_5H_4) 67.19 (s., C_5H_4) 51.43 (s., C_{ipso} C_5H_4) 31.13 (s., $\mathit{C}Me_2$) 22.32 (s., $C\mathit{Me}_2$) 22.19 (s., $(CH_2)_2CH_3$) 5.83 (s., $(CH_2)_2CH_3$) 1.04 (s., $(CH_2)_2CH_3$)
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{$(CH_2)_3$-CH_3}$_2$] (**4**). Yellow solid: C, 53.6 (53.9); H, 6.7 (6.9). MS: $m/z = 468$ $(M)^+$ 86%, $m/z = 411$ $(M–\{(CH_2)_3CH_3\})^+$ 20%, $m/z = 355$ $(M–2\{(CH_2)_3CH_3\})$ 100%.	^1H: 4.31 (m., 4H, C_5H_4) 4.22 (m., 4H, C_5H_4) 1.52 (m., 8H, $CH_2(C\mathit{H}_2)_2CH_3$) 1.16 (t., 6H, $CH_2(CH_2)_2C\mathit{H}_3$) 0.56 (m., 4H, $C\mathit{H}_2(CH_2)_2CH_3$) 0.42 (s., 6H, CMe_2) $^{13}C\{^1H\}$: 104.29 (s., C_5H_4) 67.20 (s., C_5H_4) 51.70 (s., $C_{ipso}C_5H_4$) 40.72 (s., $(CH_2)_3CH_3$) 30.38 (s.,$\mathit{C}Me_2$) 30.35 (s., $(CH_2)_3CH_3$) 22.20 (s., $C\mathit{Me}_2$) 5.92 (s., $(CH_2)_3CH_3$) 1.73 (s., $(CH_2)_3CH_3$)
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{$(CH_2)_3$-CH_3}Cl] (**5**). Pale red solid: C, 46.2 (45.7); H, 5.5 (5.2). MS: $m/z = 446$ $(M)^+$ 55%, $m/z = 411$ $(M–Cl)^+$ 25%, $m/z = 389$ $(M–\{(CH_2)_3CH_3\})^+$ 100%.	^1H: 5.20 (m., 2H, C_5H_4) 4.71 (m., 2H, C_5H_4) 4.68 (m., 2H, C_5H_4) 3.96 (m., 2H, C_5H_4) 1.55 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_3$) 1.37 (m., 2H, $CH_2C\mathit{H}_2CH_2CH_3$) 1.31 (t., 2H, $C\mathit{H}_2CH_2CH_2CH_3$) 1.15 (t., 3H, $CH_2CH_2CH_2C\mathit{H}_3$) 0.35 (s., 3 H, CMe_2) 0.03 (s., 3H, CMe_2) $^{13}C\{^1H\}$: 115.76 (s., C_5H_4) 106.44 (s., C_5H_4) 70.15 (s., C_5H_4) 69.59 (s., C_5H_4) 57.92 (s., C_{ipso} C_5H_4) 39.69 (s., $(CH_2)_3CH_3$) 29.59 (s., $(CH_2)_3CH_3$) 22.39 (s., $(CH_2)_2CH_3$) 21.76 (s., $C\mathit{Me}_2$) 21.61 (s., $C\mathit{Me}_2$) 14.12 (s., $(CH_2)_3CH_3$)
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{$(CH_2)_4$-CH_3}Cl] (**6**). Pale red solid: C, 46.3 (46.9); H, 5.8 (5.5); Cl, 7.2 (7.7). MS: $m/z = 462$ $(M)^+$ 18%, $m/z = 389$ $(M–\{(CH_2)_4CH_3\})^+$ 100%.	^1H: 5.19 (m., 2H, C_5H_4) 4.70 (m., 4H, C_5H_4) 3.97 (m., 2H, C_5H_4) 1.55 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_3$) 1.53 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_3$) 1.42 (t., 2H, $CH_2C\mathit{H}_2CH_2CH_3$) 1.29 (m., 2H, $C\mathit{H}_2CH_2CH_2CH_2CH_3$) 1.11 (t., 3H, $CH_2CH_2CH_2C\mathit{H}_3$) 0.35 (s., 3H, CMe_2) 0.05 (s., 3H, CMe_2) $^{13}C\{^1H\}$: 115.57 (s., C_5H_4)

(*continued on next page*)

Table 1 (*continued*)

Compound[a]	NMR data[b]
	106.17 (s., C_5H_4) 70.18 (s., C_5H_4) 69.48 (s., C_5H_4) 57.93 (s., C_{ipso} C_5H_4) 39.03 (s., $(CH_2)_4CH_3$) 36.88 (s., $(CH_2)_4CH_3$) 29.42 (s., $\mathit{C}Me_2$) 22.72 (s., $(CH_2)_4CH_3$) 21.78 (s., $C\mathit{Me}_2$) 21.62 (s., $C\mathit{Me}_2$) 14.48 (s., $(CH_2)_4CH_3$) 1.38 (s., $(CH_2)_4CH_3$)
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_5CH_3\}_2]$ (**8**). Yellow solid: C, 56.5 (57.3); H, 7.5 (7.7). MS: *m*/*z* = 524 $(M)^+$ 85%, *m*/*z* = 439 $(M\text{–}\{(CH_2)_5CH_3\})^+$ 17%, *m*/*z* = 355 $(M\text{–}2\{(CH_2)_5CH_3\})^+$ 100%.	^{1}H: 4.35 (m., 4H, C_5H_4) 4.25 (m., 4H, C_5H_4) 1.52 (m., 16H, $CH_2(C\mathit{H}_2)_4CH_3$) 1.06 (t., 6H, $CH_2(CH_2)_4C\mathit{H}_3$) 0.58 (m., 4H, $C\mathit{H}_2(CH_2)_2CH_3$) 0.44 (s., 6H, CMe_2) $^{13}C\{^1H\}$: 104.25 (s., C_5H_4) 67.23 (s., C_5H_4) 51.48 (s., C_{ipso} C_5H_4) 38.08 (s., $(CH_2)_5CH_3$) 37.29 (s., $(CH_2)_5CH_3$) 32.07 (s., $(CH_2)_5CH_3$) 30.78 (s., $\mathit{C}Me_2$) 23.28 (s., $(CH_2)_5CH_3$) 22.19 (s., $C\mathit{Me}_2$) 14.28 (s., $(CH_2)_5CH_3$) 2.15 (s., $(CH_2)_5CH_3$)
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_2CH_3\}I]$ (**9**). Pale red solid: C, 36.8 (36.7); H, 4.3 (4.1). MS: *m*/*z* = 524 $(M)^+$ 62%, *m*/*z* = 481 $(M\text{–}\{(CH_2)_2CH_3\})^+$ 85%.	^{1}H: 5.57 (m., 2H, C_5H_4) 4.39 (m., 2H, C_5H_4) 4.37 (m., 2H, C_5H_4) 3.83 (m., 2H, C_5H_4) 1.53 (m., 2H, $CH_2C\mathit{H}_2CH_3$) 1.18 (m., 2H, $C\mathit{H}_2CH_2CH_3$) 1.15 (t., 3H, $CH_2CH_2C\mathit{H}_3$) 0.22 (s., 3H, CMe_2) 0.09 (s., 3H, CMe_2) $^{13}C\{^1H\}$: 111.55 (s., C_5H_4) 105.58 (s., C_5H_4) 70.62 (s., C_5H_4) 68.38 (s., C_5H_4) 57.32 (s., C_{ipso} C_5H_4) 32.62 (s., $(CH_2)_2CH_3$) 22.39 (s., $(CH_2)_2CH_3$) 22.21 (s., $C\mathit{Me}_2$) 21.83 (s., $C\mathit{Me}_2$) −0.53 (s., $(CH_2)_2CH_3$)
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_2CH_3\}H]$ (**10**). Yellow solid: C, 47.8 (47.3); H, 6.1 (5.6).	^{1}H: 5.10 (m., 2H, C_5H_4) 4.48 (m., 2H, C_5H_4) 4.29 (m., 2H, C_5H_4) 3.78 (m., 2H, C_5H_4) 1.36 (m., 2H, $CH_2C\mathit{H}_2CH_3$) 1.13 (t., 3H, $CH_2CH_2C\mathit{H}_3$) 1.04 (m., 2H, $C\mathit{H}_2CH_2CH_3$) 0.56 (s., 3H, CMe_2) 0.29 (s., 3H, CMe_2) −6.47 (m., $^{1}J_{WH}$ = 50 Hz, 1H, WH_2) $^{13}C\{^1H\}$: C_6D_6 125 MHz 103.79 (s., C_5H_4) 86.89 (s., C_5H_4) 70.21 (s., C_5H_4) 62.82 (s., C_5H_4) 57.32 (s., C_{ipso} C_5H_4) 33.30 (s., $(CH_2)_2CH_3$) 22.35 (s., $(CH_2)_2CH_3$) 22.02 (s., $C\mathit{Me}_2$) 21.96 (s., $C\mathit{Me}_2$) −14.99 (s., $(CH_2)_2CH_3$)
$[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_3CH_3\}H]$ (**11**). Yellow solid: C, 49.5 (49.5); H, 5.9 (5.8).	^{1}H: 5.10 (m., 2H, C_5H_4) 4.48 (m., 2H, C_5H_4) 4.29 (m., 2H, C_5H_4) 3.78 (m., 2H, C_5H_4) 1.45 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_3$) 1.36 (m., 2H, $CH_2C\mathit{H}_2CH_2CH_3$) 1.11 (t., 3H, $CH_2CH_2CH_2C\mathit{H}_3$) 1.02 (m., 2H, $C\mathit{H}_2CH_2CH_2CH_3$) 0.55 (s., 3H, CMe_2) 0.29 (s., 3H, CMe_2) −6.46 (m., $^{1}J_{WH}$ = 50 Hz, 1H, WH_2) $^{13}C\{^1H\}$: C_6D_6 125 MHz 103.94 (s., C_5H_4) 86.81 (s., C_5H_4) 70.25 (s., C_5H_4) 62.77 (s., C_5H_4) 53.88 (s., $C_{ipso}C_5H_4$) 42.75 (s., $(CH_2)_3CH_3$) 30.50 (s., $(CH_2)_2CH_3$) 22.03 (s., $C\mathit{Me}_2$) 21.95 (s., $C\mathit{Me}_2$) 14.08 (s., $(CH_2)_3CH_3$) −12.15 (s., $(CH_2)_3CH_3$)
$[W\{(\eta\text{-}_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_4CH_3\}H]$ (**12**). Yellow solid: C, 49.7 (50.7); H, 5.9 (6.2). MS: *m*/*z* = 426 $(M\text{–}H)^+$25%, *m*/*z* = 355 $(M\text{–}\{(CH_2)_4CH_3\}\text{–}H)^+$ 100%.	^{1}H: 5.12 (m., 2H, C_5H_4) 4.51 (m., 2H, C_5H_4) 4.32 (m., 2H, C_5H_4) 3.80 (m., 2H, C_5H_4) 1.49 (m., 2H, $CH_2CH_2CH_2C\mathit{H}_2CH_3$) 1.38 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_3$) 1.36 (m., 2H, $CH_2C\mathit{H}_2CH_2CH_2CH_3$) 1.07 (t., 3H, $CH_2CH_2CH_2CH_2C\mathit{H}_3$) 1.01 (m., 2H, $C\mathit{H}_2CH_2CH_2CH_2CH_3$) 0.46 (s., 3H, CMe_2) 0.20 (s., 3H, CMe_2) $^{13}C\{^1H\}$: C_6D_6 125 MHz 103.78 (s., C_5H_4) 86.84 (s., C_5H_4) 70.20 (s., C_5H_4) 62.74 (s., C_5H_4) 53.88 (s., C_{ipso} C_5H_4) 40.10 (s., $(CH_2)_4CH_3$) 40.04 (s., $(CH_2)_4CH_3$) 31.70 (s., $\mathit{C}Me_2$) 22.78 (s., $(CH_2)_4CH_3$) 22.05 (s., $C\mathit{Me}_2$) 21.96 (s., $C\mathit{Me}_2$) 14.51 (s., $(CH_2)_4CH_3$) −11.83 (s., $(CH_2)_4CH_3$)
$[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}Cl_2]$ (**13d**). Purple solid	^{2}H: 5.96 (br. s., 4D, C_5D_4) 5.44 (br. s., 4D, C_5D_4) 0.70 (s., 6D, $C(CD_3)_2$)
$[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2CH_3\}_2]$ (**14d**). Yellow solid	^{1}H: 1.59 (t., 6H, $CH_2C\mathit{H}_3$) 0.58 (q., 4H, $C\mathit{H}_2CH_3$) ^{2}H:4.30 (s., 4D, C_5D_4) 4.26 (s., 4D, C_5D_4) 0.33 (s., 6D, $C(CD_3)_2$)

Table 1 (*continued*)

Compound[a]	NMR data[b]
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{CH_2CH_3}I] (**15d**). Pale red solid	^{1}H: 1.59 (q., 2H, $C\mathit{H}_2CH_3$) 1.14 (t., 3H, $CH_2C\mathit{H}_3$) ^{2}H: 5.54 (m., 2D, C_5D_4) 4.39 (m., 2D, C_5D_4) 4.37 (m., 2D, C_5D_4) 3.67 (m., 2D, C_5D_4) 0.20 (s., 3D, $C(CD_3)_2$) 0.07 (s., 3D, $C(CD_3)_2$)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{CH_2CH_3}D] (**16d**). Yellow solid	^{1}H: 1.58 (t., 3H, $CH_2C\mathit{H}_3$) 1.12 (q., 2H, $C\mathit{H}_2CH_3$) ^{2}H: 5.08 (s., 2D, C_5D_4) 4.48 (s., 2D, C_5D_4) 4.28 (s., 2D, C_5D_4) 3.75 (s., 2D, C_5D_4) 0.46 (s., 3D, $C(CD_3)_2$) 0.19 (s., 3D, $C(CD_3)_2$) −6.44 (s., 1D, WD)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_2CH_3$}$_2$] (**3d**). Yellow solid	^{1}H: 1.46 (m., 4H, $CH_2C\mathit{H}_2CH_3$) 1.21 (t., 6H, $CH_2CH_2C\mathit{H}_3$) 0.54 (m., 4H, $C\mathit{H}_2CH_2CH_3$) ^{2}H: 4.24 (br. S., 8D, C_5D_4) 0.42 (s., 6D, $C(CD_3)_2$)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_2CH_3$}I] (**9d**). Pale red solid	^{1}H: 1.52 (m., 2H, $CH_2C\mathit{H}_2CH_3$) 1.17 (m., 2H, $C\mathit{H}_2CH_2CH_3$) 1.14 (t., 3H, $CH_2CH_2C\mathit{H}_3$) ^{2}H: 5.55 (m., 2D, C_5D_4) 4.39 (m., 4D, C_5D_4) 3.82 (m., 2D, C_5D_4) 0.18 (s., 3D, $C(CD_3)_2$) 0.07 (s., 3D, $C(CD_3)_2$)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_2CH_3$}D] (**10d**). Yellow solid	^{1}H: 1.37 (m., 2H, $CH_2C\mathit{H}_2CH_3$) 1.16 (t., 3H, $CH_2CH_2C\mathit{H}_3$) 1.04 (m., 2H, $C\mathit{H}_2CH_2CH_3$) ^{2}H: 5.09 (s., 2D, C_5D_4) 4.51 (s., 2D, C_5D_4) 4.29 (s., 2D, C_5D_4) 3.77 (s., 2D, C_5D_4) 0.52 (s., 3D, $C(CD_3)_2$) 0.26 (s., 3D, $C(CD_3)_2$) −6.44 (s., 1D, WD)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_3CH_3$}Cl] (**5d**). Pale red solid	^{1}H: 1.55 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_3$) 1.37 (m., 2H, $CH_2C\mathit{H}_2CH_2CH_3$) 1.28 (t., 3H, $C\mathit{H}_2CH_2CH_2CH_3$) 1.15 (t., 3H, $CH_2CH_2CH_2C\mathit{H}_3$) ^{2}H: 5.20 (s., 2D, C_5D_4) 4.73 (s., 2D, C_5D_4) 4.68 (s., 2D, C_5D_4) 3.98 (s., 2D, C_5D_4) 0.38 (s., 3D, $C(CD_3)_2$) 0.06 (s., 3D, $C(CD_3)_2$)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_3CH_3$}D] (**11d**). Yellow solid	^{1}H: 1.43 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_3$) 1.35 (m., 2H, $CH_2C\mathit{H}_2CH_2CH_3$) 1.16 (t., 3H, $CH_2CH_2CH_2C\mathit{H}_3$) 1.01 (m., 2H, $C\mathit{H}_2CH_2CH_2CH_3$) ^{2}H: 5.05 (s., 2D, C_5D_4) 4.47 (s., 2D, C_5D_4) 4.26 (s., 2D, C_5D_4) 3.77 (s., 2D, C_5D_4) 0.56 (s., 3D, $C(CD_3)_2$) 0.27 (s., 3D, $C(CD_3)_2$) −6.45 (s., 1D, WD)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_4CH_3$}$_2$] (**7d**). Yellow solid	^{1}H: 1.59 (m., 4H, $CH_2C\mathit{H}_2CH_2CH_2CH_3$) 1.50 (m., 4H, $CH_2CH_2C\mathit{H}_2CH_2CH_3$) 1.42 (m., 4H, $CH_2CH_2CH_2C\mathit{H}_2CH_3$) 1.09 (t., 6H, $CH_2CH_2CH_2CH_2C\mathit{H}_3$) 0.75 (m., 4H, $C\mathit{H}_2CH_2CH_2CH_2CH_3$) ^{2}H: 4.31 (s., 4D, C_5D_4) 4.27 (s., 4D, C_5D_4) 0.38 (s., 3D, $C(CD_3)_2$) 0.19 (s., 3D, $C(CD_3)_2$)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_4CH_3$}I] (**17d**). Pale red solid	^{1}H: 1.56 (m., 2H, $CH_2CH_2CH_2C\mathit{H}_2CH_3$) 1.53 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_3$) 1.40 (t., 2H, $CH_2C\mathit{H}_2CH_2CH_3$) 1.29 (m., 2H, $C\mathit{H}_2CH_2CH_2CH_2CH_3$) 1.09 (t., 3H, $CH_2CH_2CH_2CH_2C\mathit{H}_3$) ^{2}H 5.19 (s., 2D, C_5D_4) 4.70 (s., 4D, C_5D_4) 3.96 (s., 2D, C_5D_4) 0.35 (s., $C(CD_3)_2$) 0.05 (s., $C(CD_3)_2$)
[W{(η-C_5D_4)C$(CD_3)_2$-(η-C_5D_4)}{$(CH_2)_4CH_3$}D] (**12d**). Yellow solid	^{1}H:1.54 (m., 2H, $CH_2CH_2CH_2C\mathit{H}_2CH_3$) 1.42 (m., 2H, $CH_2CH_2C\mathit{H}_2CH_2CH_3$) 1.30 (m., 2H, CH_2 $C\mathit{H}_2CH_2CH_2CH_3$) 1.10 (t., 3H, $CH_2CH_2CH_2CH_2C\mathit{H}_3$) 1.05 (m., 2H, $C\mathit{H}_2CH_2CH_2CH_2CH_3$) ^{2}H: 5.11 (m., 2D, C_5D_4) 4.46 (m., 2D, C_5D_4) 4.32 (m., 2D, C_5D_4) 3.80 (m., 2D, C_5D_4) 0.47 (s., 3D, $C(CD_3)_2$) 0.24 (s., 3D, $C(CD_3)_2$) −6.52 (s. 1D, WD)
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{CD_2CD_3}$_2$] (**18**). Yellow solid	^{1}H: 4.27 (m., 4H, C_5H_4) 4.19 (m., 4H, C_5H_4) 0.44 (s., 6H, CMe_2) ^{2}H: 1.60 (s., 6D, $CD_2C\mathit{D}_3$) 0.62 (s., 4D, $C\mathit{D}_2CD_3$)
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{CD_2CD_3}I] (**19**). Pale red solid	^{1}H: 5.56 (s., 2H, C_5H_4) 4.38 (s., 4H, C_5H_4) 3.84 (s., 2H, C_5H_4) 0.17 (s., 3H, CMe_2) 0.04 (s., 3H, CMe_2) ^{2}H: 1.57 (s., 2D, $C\mathit{D}_2CD_3$) 1.34 (s., 3D, $CD_2C\mathit{D}_3$)
[W{(η-C_5H_4)CMe_2-(η-C_5H_4)}{CD_2CD_3}H] (**20**). Yellow solid	^{1}H: 5.11 (s., 2H, C_5H_4) 4.48 (s., 2H, C_5H_4) 4.29 (s., 2H, C_5H_4) 3.77 (s., 2H, C_5H_4) 0.53 (s., 3H, CMe_2) 0.29 (s., 3H, CMe_2) −6.47 (s. ^{1}H, $^1J_{WH}$ = 31 Hz, WH) ^{2}H: 1.58 (s., 3D, $CD_2C\mathit{D}_3$) 1.13 (s., 2D, $C\mathit{D}_2CD_3$)

All IR data are expressed in wave numbers (cm^{-1}).

For the FAB mass spectrometry data, the characteristic isotope patterns were observed.

[a] Microanalytical data given as: element, found(calc.), %.

[b] NMR data are given as chemical shift (δ) [relative intensity, coupling, multiplicity, assignment] at 298 K unless otherwise stated. In C_6D_6 unless otherwise stated. ^{1}H NMR at 500 MHz, ^{13}C{^{1}H} at 125 MHz and ^{2}H at 76.75 MHz.

The *n*-butyl-hydride and *n*-pentyl-hydride compounds; $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ ($n = 3$, **11**; 4, **12**) were prepared similarly by treatment of the corresponding *n*-alkyl-chloride compounds $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}Cl]$ ($n = 3$, **5**; 4, **6**) with $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ as yellow crystalline solids in 42% and 49% yields, respectively.

The isolation and thermal stability at ambient temperatures of the *n*-alkyl-hydrides $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ ($n = 2$, **10**; 3, **11**; 4, **12**) in both the solid state and in solution confirmed our expectation the there would be an increased stability of Group 6 *ansa*-metallocene alkyl-hydrides with respect to reductive alkane elimination as a consequence of the presence of the single carbon *ansa*-bridge.

In order to study hydrogen exchange processes between alkyl and hydride ligands in *n*-alkyl hydride species it was necessary to prepare appropriately isotopically labelled compounds, namely $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}D]$, where $n = 0$–4. It had been shown previously that treatment of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2CH_3\}I]$ with $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ gave a mixture of the desired ethyl-deuteride $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{CH_2CH_3)\}D]$ together with the mono-deuterated C_5-ring ethyl-hydride species $[W\{(\eta\text{-}C_5H_3D)CMe_2(\eta\text{-}C_5H_4)\}\{CH_2CH_3\}H]$ [2].

A reasonable mechanism for the formation of the mono-deuterated C_5-ring compound has been proposed [7] and is shown in Fig. 1.

When the *n*-alkyl-halide compounds $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}X]$ ($X = I$ and $n = 2$, **9** or $X = Cl$, $n = 3$, **5**; 4, **6**) were reacted with $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ then only the undesired mono-deuterated C_5-ring *n*-alkyl hydride species $[W\{(\eta\text{-}C_5\text{-}H_3D)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ are formed, as shown by ^1H and ^2H NMR spectroscopy. There was no evidence for the desired tungsten alkyl-deuteride species $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4\}\{(CH_2)_n\text{-}CH_3\}D]$. It seems that as the length and effective bulk of the *n*-alkyl chain is increased from ethyl to *n*-propyl and longer, the direct attack of deuteride at the metal centre is increasingly disfavoured compared to *exo* attack at the cyclopentadienyl rings of the equilibrium dissociated cations (see Fig. 1).

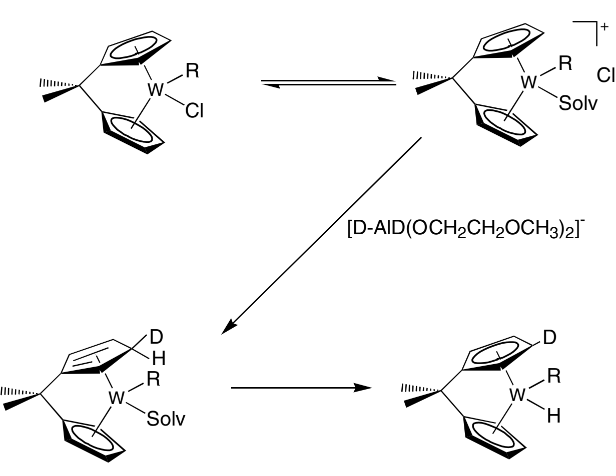


Fig. 1. Mechanism proposed for deuteration of the cyclopentadienyl ring in $[W\{(\eta\text{-}C_5H_{4-x}D_x)CMe_2(\eta\text{-}C_5H_{4-x}D_x)\}(R)H]$ [7].

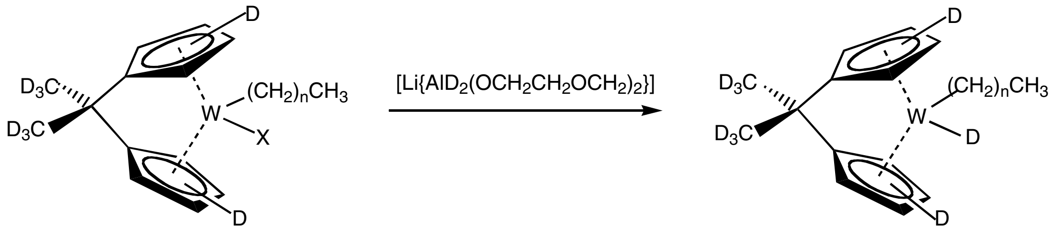
Various alternative routes to the desired compounds $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_nCH_3\}D]$ ($n = 2$–4) were investigated but none were successful. For example, attempts to deprotonate $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}\{(CH_2)_nCH_3\}H]$ using KH in the presence of 18-crown-6, followed by quenching of the anticipated salts $[K(18\text{-crown-6})][W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}\{(CH_2)_nCH_3\}]$ [8] with D_2O, gave no tractable products. Alternative deuteride reagents such as $NaBD_4$ or $LiBEt_3D$ again gave only the ring deuterated *n*-alkyl-hydride compounds. Finally, it was decided to prepare suitable alkyl-deuterides by starting with ring-perdeuterated *ansa*-metallocene alkyl-halides $[W\{(\eta\text{-}C_5D_4)\text{-}C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)_nCH_3\}X]$ ($n = 1$–4; $X = Cl$ or I). Treatment of these with $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ should result in the *exo* attack of D^- and then the *endo*-deuterium should transfer to the tungsten centre to give the desired W–D group (see Fig. 2).

The perdeuterated *ansa*-ligand $[Li_2\{(C_5D_4)C(CD_3)_2\text{-}(C_5D_4)\}]$ and the perdeuterated *ansa*-metallocene dichloride compound $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}Cl_2]$ (**13d**) (where **d** indicates a perdeuterated ansa ligand system) were prepared by a slightly modified procedure to that used for the analogous protio compounds [9] (see Section 3 and Fig. 3).

The compound **13d** was characterised by ^2H NMR spectroscopy and by its subsequent reactions. The extent of deuteration of the metallocene fragment was determined to be >95%.

The deuterated di-*n*-alkyl compounds $[W\{(\eta\text{-}C_5D_4)\text{-}C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)_nCH_3\}_2]$ ($n = 1$, **14d**; 2, **3d**; 4, **6d**) and the corresponding *n*-alkyl-halide compounds $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)_nCH_3\}X]$, ($X = I$, $n = 1$, **15d**; $n = 2$, **9d**; $n = 4$ **7**; $X = Cl$, $n = 3$, **5d**) were then prepared [2]. Due to the small amount of compound **13d** available these deuterated *ansa*-metallocenes were characterised by ^1H and ^2H NMR spectroscopy only. The extent of deuteration of the fragment $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}]$ in all the compounds containing that fragment was shown by NMR data to be 95 ± 2% see Fig. 4.

Addition of $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ to a solution of $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{CH_2CH_3\}I]$ (**15d**) in toluene at low temperature afforded the ethyl-deuteride compound $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\text{-}\{CH_2CH_3\}D]$ (**16d**) as a yellow crystalline solid. Compound **16d** was characterised by ^1H and ^2H NMR spectroscopy. The ^1H NMR spectrum of compound **16d** consists of a triplet and a quartet at δ 1.58 and



n = 1, X = I **(15d)**
n = 2, X = I **(9d)**
n = 3, X = Cl **(5d)**
n = 4, X = I **(17d)**

n = 1 **(16d)**
n = 2 **(10d)**
n = 3 **(11d)**
n = 4 **(12d)**

Fig. 2. Proposed route for the synthesis of the tungsten alkyl-deuterides [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{(CH_2)$_n$$CH_3$}D] where = 1–4.

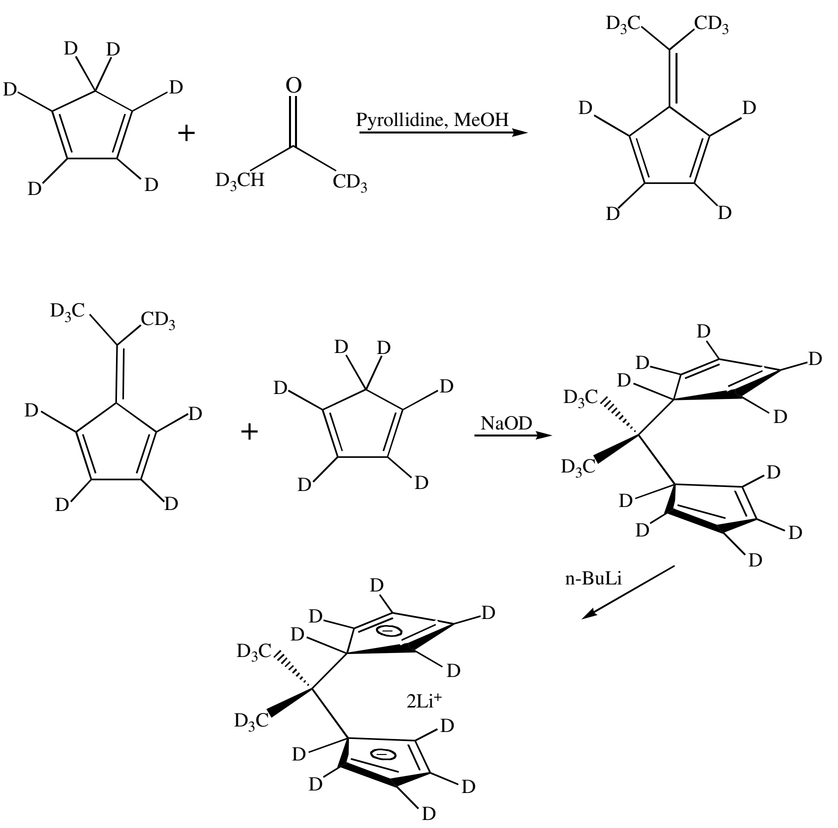


Fig. 3. Synthesis of the perdeuterated ligand precursor {[Li]$_2$[(C_5D_4)C(CD_3)$_2$(C_5D_4)]}.

1.12 ppm, respectively, corresponding to the protons of the ethyl ligand. Residual cyclopentadienyl proton peaks (5% H) are located at δ 5.12, 4.50, 4.31 and 3.78 ppm. The ^2H NMR spectrum of the compound **16d** shows the four deuterium atoms attached to the cyclopentadienyl rings are located at δ 5.08, 4.48 4.28 and 3.75 ppm. Two singlets at δ 0.46 and 0.19 ppm correspond to the deuterium atoms of the C(CD_3)$_2$ bridging unit. A singlet at δ −6.44 ppm is assigned to deuterium attached to the metal. In the ^1H NMR spectrum of the corresponding ethyl-hydride compound [W{(η-C_5H_4)CMe$_2$(η-C_5H_4)}{CH_2CH_3}H] the hydride resonance is found at δ −6.46 ppm [2].

The higher *n*-alkyl-deuteride compounds [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{(CH_2)$_n$$CH_3$}D] (*n* = 2, **10d**; 3, **11d**; 4, **12d**) were prepared by the reaction between [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{(CH_2)$_n$$CH_3$}X] (X = I, *n* = 2, **9d**; 4, **7**; X = Cl, *n* = 3, **5d**) and [Li{AlD_2(OCH$_2$-CH$_2$OCH$_3$)$_2$}]. Again all compounds were obtained as pale yellow solids and characterised by ^1H and ^2H NMR spectroscopy. We note that for all the *n*-alkyl-deuterides there was no evidence for intramolecular

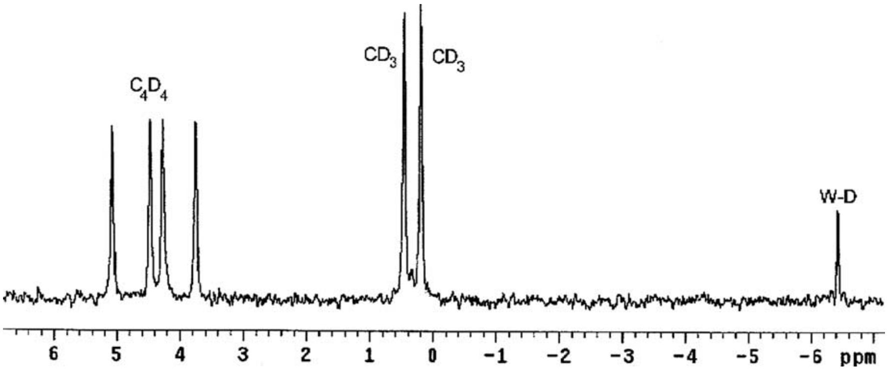


Fig. 4. ^{2}H NMR spectrum of the compound [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{CH_2CH_3}D] (**16d**) in C_6H_6.

H/D scrambling between alkyl and W–D atoms at room temperature even after prolonged storage.

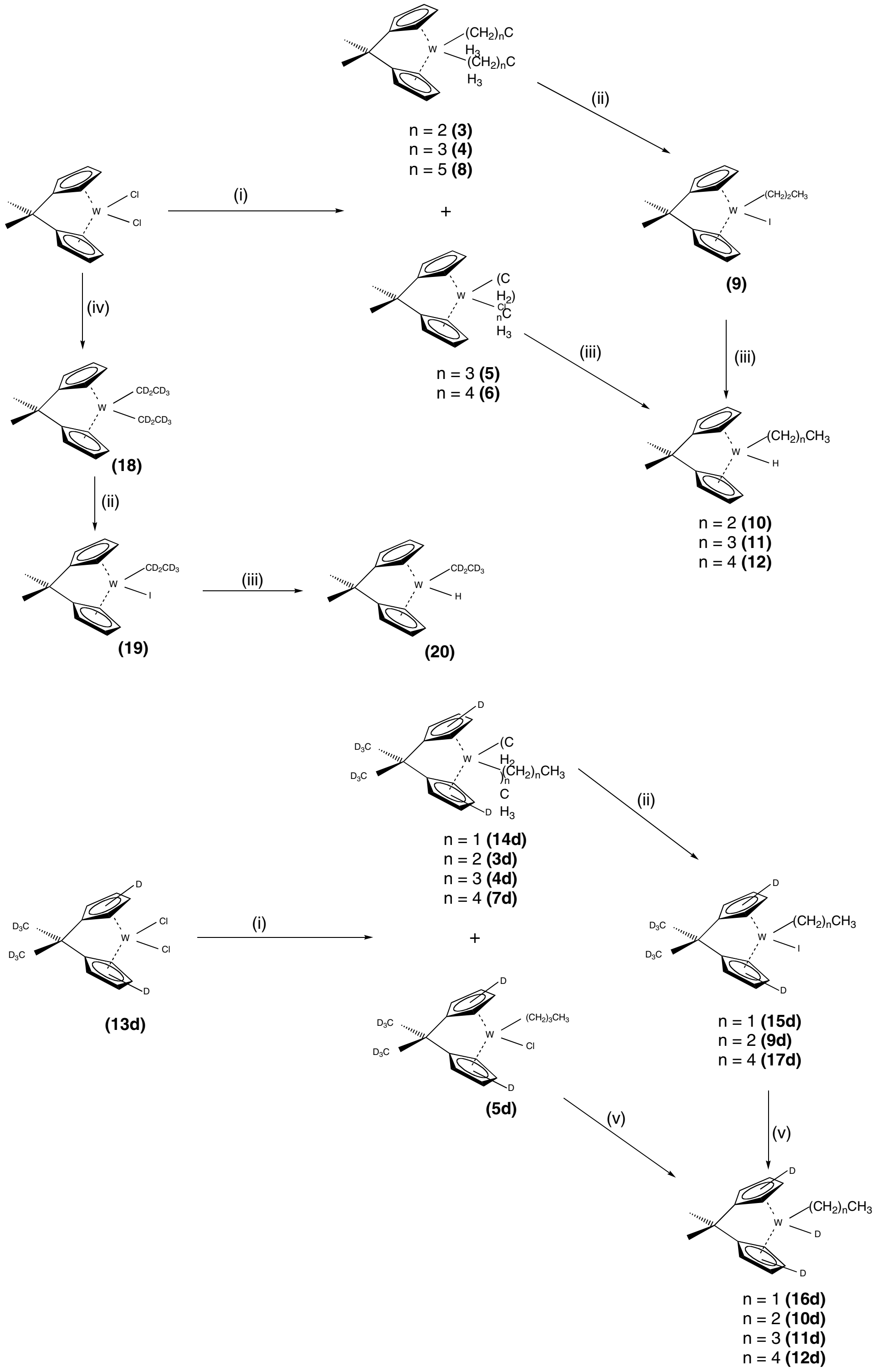
An alternative approach by which to study H/D scrambling in *ansa*-metallocene *n*-alkyl hydride compounds would be to prepare species in which the *n*-alkyl group was deuterated, as in [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{(CD_2)$_n$$CD_3$}]. Indeed the H/D scrambling process in [W{(η-C_5H_4)CMe_2(η-C_5H_4)}(CD_3)H] has been described [2]. Perdeuterated diethylzinc [Zn{CD_2CD_3}$_2$] was prepared by the condensation of d^5-iodoethane onto a Zn/Cu couple in a thick walled-glass tube. The tube was sealed under reduced pressure and heated at 140 °C overnight. [Zn{CD_2CD_3}$_2$] was freed from impurity by low pressure distillation and obtained as a pyrophoric colourless liquid. Treatment of a toluene suspension of the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] with a 0.4 M solution of [Zn{CD_2CD_3}$_2$] in toluene gave a dark red suspension from which the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{CD_2CD_3}$_2$] (**18**) was isolated. The compound **18** was characterised by ^{1}H and ^{2}H NMR spectroscopy. The ^{2}H NMR spectrum shows two peaks at δ 1.60 and 0.62 ppm corresponding to the β-methyl and α-methylene deuterium of the ethyl ligands respectively.

Reaction of the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{CD_2CD_3}$_2$] (**18**) with NH_4I in THF at 65 °C gives the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{CD_2CD_3}I] (**19**), as a pale red solid in 47% yield. The compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{CD_2CD_3}I] (**19**) was reacted with [Na{AlH_2($OCH_2OCH_2CH_3$)$_2$}] at low temperature to give, after cautious hydrolysis of excess [Na{AlH_2($OCH_2CH_2OCH_3$)$_2$}], the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{CD_2CD_3}H] (**20**) as a yellow crystalline solid (see the Scheme 1).

The compound **20** was characterised by ^{1}H and ^{2}H NMR spectroscopy. In the ^{1}H NMR were four singlets at δ 5.11, 4.48, 4.29 and 3.77 ppm corresponding to the hydrogens of the cyclopentadienyl rings and a pair of singlets at δ 0.53 and 0.29 ppm corresponding to the protons of the CMe_2 bridging unit, the singlet at δ −6.47 ppm is assigned to the hydride proton. Associated with this singlet are the characteristic ^{183}W satellites ($^1J_{WH}$ = 31 Hz). The ^{2}H NMR spectrum of the compound **20** shows two peaks at δ 1.58 and 1.13 ppm corresponding to the CD_3 and α-CD_2 groups of the ethyl ligand. The spectroscopic data for the compound **20** are in agreement with that reported for the perprotio compound [W{(η-C_5H_4)CMe_2(η-(C_5H_4)}{CH_2CH_3}H] [2].

The thermolysis of the partially ring deuterated ethyl-deuteride [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{CH_2CH_3}D] has been described previously [2] but quantitative kinetic data for the observed intramolecular hydrogen scrambling processes could not be obtained. Therefore, the perdeutero-*ansa*-tungstenocene ethyl-deuteride [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{CH_2CH_3}D] (**16d**) was prepared and H/D scrambling was reinvestigated. A 8 mM solution of the compound **16d** in C_6H_6 and a 6 mM solution of the compound **16** in C_6D_6 were prepared and sealed in separate NMR tubes. ^{1}H and ^{2}H NMR spectra show that at room temperature there had been no observable scrambling between alkyl and deuterium sites. The samples were heated at 65 °C and ^{1}H and ^{2}H NMR spectra were recorded periodically. After ca. 8 h, the ^{2}H NMR spectra showed a peak at δ 1.10 ppm which grew with time (Fig. 5). Simultaneously, the intensity of the W–D peak at δ −6.44 ppm decreased. The ^{1}H NMR spectra shows there is a decrease in intensity of the quartet at δ 1.12 ppm due to the α-methylene hydrogens compared to the triplet at δ 1.58 ppm corresponding to the β-methyl hydrogens of the ethyl ligand.

Additionally a peak at δ −6.45 ppm corresponding to a tungsten-hydrogen group appeared. These NMR data are fully consistent with H/D exchange between the W–D and the α-CH_2 hydrogens of the ethyl group. No evidence for scrambling of deuterium into the β-methyl hydrogens of the compound **16** was observed. Scrambling of deuterium into this position should be indicated by a peak growing in at, or close to, δ 1.58 ppm, by analogy to the ^{1}H NMR spectrum of the compound **16**. No peak in this region (δ ± 0.15 ppm) was observed. This



Scheme 1. Conditions (i) $[Zn\{(CH_2)_nCH_3\}_2]$ in toluene. (ii) NH_4I in THF, 65 °C. (iii) $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ in toluene. (iv) $[Zn\{CD_2CD_3\}_2]$ in toluene. (v) $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ in toluene. When **d** is placed after a compound number this indicates the ansa-bis-cyclopendadienyl ligand is perdeuterated.

conclusion contrasts with that previously reported for studies on $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{CH_2CH_3\}D]$ where scrambling into the β-position was suggested to occur and further that it occurred at a faster rate than for the α-methylene hydrogens [2]. The quality of the earlier data was significantly worse than for this work and we assume the earlier results were erroneous due to the presence of decomposition products see Fig. 6.

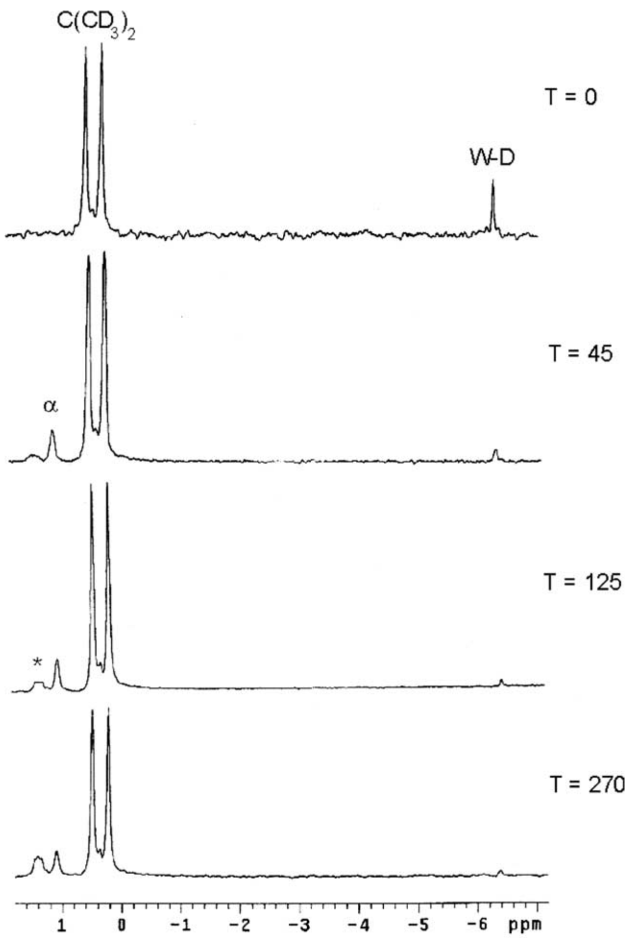


Fig. 5. Partial ^{2}H NMR spectrum of the compound [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{CH_2CH_3}D] (**16d**) in C_6H_6 at 65 °C (*T* in h). The peak marked α corresponds to deuterium in the α-methylene position of the *n*-propyl ligand. * Denotes a decomposition product.

Apart from the H/D scrambling there is evidence for slow thermal decomposition of the compound **16**. After 45 h; the ^{2}H NMR spectra show new peaks in the cyclopentadienyl region δ 6.65–5.32 ppm and broad peaks at δ 2.71 and 1.38 ppm. These new peaks grow in intensity over time while the intensity of all the peaks of the compound **16d** decrease. The ^{1}H NMR spectra of the partially decomposed compound **16** in C_6D_6 showed no ethane was present. Also, there is no evidence in either the ^{1}H or ^{2}H NMR spectra of the partially decomposed solution of compound **16d** for the formation of new W–D or W–H groups. Attempts to identify the nature the new compounds were unsuccessful due to the very small quantity of alkyl-hydride and -deuteride compounds available.

Further, accurate kinetic data for the scrambling of deuterium from the metal to the α-position of the ethyl group in the compound **16** compared to related alkyl-deuteride species could not be obtained due to the presence of the competing decomposition reactions.

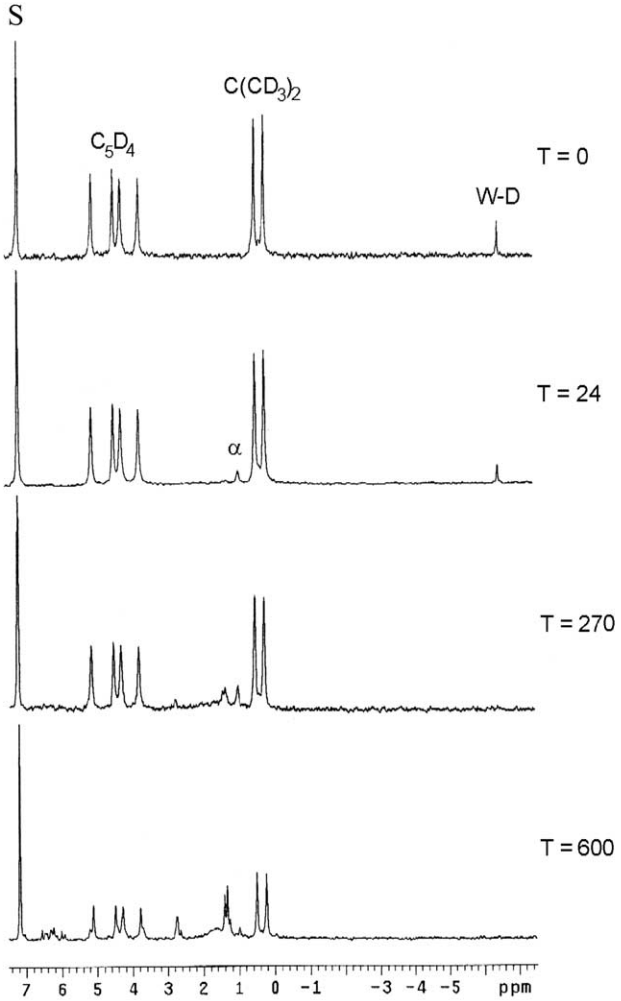


Fig. 6. ^{2}H NMR spectrum of the compound [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{(CH_2)$_2$$CH_3$}D] (**10d**) in C_6H_6 at 65 °C (*T* in h). The peak marked α corresponds to deuterium in the α-methylene position of the *n*-propyl ligand. S denotes the residual solvent peak.

The thermolysis of the d^5-ethyl hydride compound [W{(η-C_5H_4)CMe$_2$(η-C_5H_4)}{CD_2CD_3}$_2$H] (**20**) was studied. A 10 mM solution of the compound **20** in C_6D_6 was sealed in a NMR tube and heated at 65 °C for a prolonged period and the ^{1}H NMR spectra were recorded periodically. After 8 h a peak at δ 1.11 ppm appeared corresponding to hydrogen in the α-methylene group. The increase in the intensity of this resonance was accompanied by a decrease in the intensity of the singlet at δ −6.47 ppm corresponding to the tungsten-hydrogen.

After heating the sample of **20** at 65 °C for 77 h a number of new peaks appeared and grew in intensity in the cyclopentadienyl region of the spectrum together with complex peaks in the region δ 2.65–1.35 ppm. We assign these new peaks to one or more decomposition products. There were no peaks at or close to δ 1.58 ppm implying that H/D scrambling into the β-CD_3

group of the d^5-ethyl ligand does not occur, as found for the studies on **16d**.

A 4 mM solution of the *n*-propyl-deuteride [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}{$(CH_2)_2CH_3$}D] (**10d**) in C_6H_6 and a 3 mM solution of the compound **10a** in C_6D_6 were prepared in separate NMR tubes. The ^{1}H and ^{2}H NMR spectra showed that at room temperature there had been no observable H/D crambling between *n*-propyl and W–D groups. The samples of **10d** were heated at 65 °C and the ^{1}H and ^{2}H NMR spectra recorded periodically. After ca. 12 h the ^{2}H NMR spectrum showed a new and growing peak at δ 1.02 ppm. We note that the compound **10d** has a peak in the ^{1}H NMR spectrum of due to the α-CH_2 hydrogens at δ 1.04 ppm. Also, the ^{2}H NMR spectra showed the peak due to W–D at δ -6.44 ppm decreased. Correspondingly, the relative intensity of the peak due to the α-CH_2 hydrogens in the ^{1}H NMR spectrum of the compound **10d** decreased compared to the resonance due to the β-CH_2 and γ-CH_3 hydrogens of the *n*-propyl group. Additionally, a peak at δ 6.47 ppm corresponding to a W–H group grew in intensity. These spectra are consistent with scrambling of W–D with only the α-CH_2 hydrogens of the *n*-propyl group. The NMR spectra of the thermolysed solutions of **10d** also showed evidence for one or more new compounds and a relative decrease of intensity of all bands associated with **10d**. The rate of scrambling into the α-position is faster than the rate of formation of decomposition products. Attempts to characterise the decomposition products were unsuccessful. Also, attempts to observe C–D coupling in ^{13}C{^{1}H} NMR spectrum of the compound **10d** were thwarted by lack of the of material.

The *n*-butyl-deuteride compound [W{(η-C_5D_4)-$C(CD_3)_2$(η-C_5D_4)}{$(CH_2)_3CH_3$}D] (**11d**) also showed H/D scrambling between the W–D and the α-CH_2 hydrogens of the *n*-butyl group. Thus, an 8 mM solution of the compound **11d** in C_6H_6 and a 5 mM solution of the compound **11d** in C_6D_6 were prepared, sealed in NMR tubes were heated at 65 °C. In the ^{2}H NMR spectra the resonance due to the W–D group at δ -6.45 ppm decreases while a peak at δ 1.01 ppm appears and grows in intensity. In the ^{1}H NMR spectrum the relative intensity of the peak at δ 1.01 ppm corresponding to the hydrogens of the α-CH_2 of the *n*-butyl compound decreases and a peak at δ -6.46 ppm appears and grows in intensity. Again the rate of this α-hydrogen scrambling process was faster than the decomposition reaction which gives rise to one or more new compounds, the nature of which have not been determined. No evidence of scrambling into other positions of the *n*-butyl group was observed.

Scrambling of deuterium into the α-position of the *n*-pentyl compound [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_4CH_3$}D] (**12d**) is observed on heating a 6 mM solution in C_6H_6 and a 4 mM solution in C_6D_6 at 65 °C. In both cases a peak at δ 1.04 ppm appeared in the ^{2}H NMR spectra along with a decrease in the resonance due to the W–D (δ -6.49 ppm). This scrambling process was accompanied by the slow formation of decomposition products. No evidence for scrambling

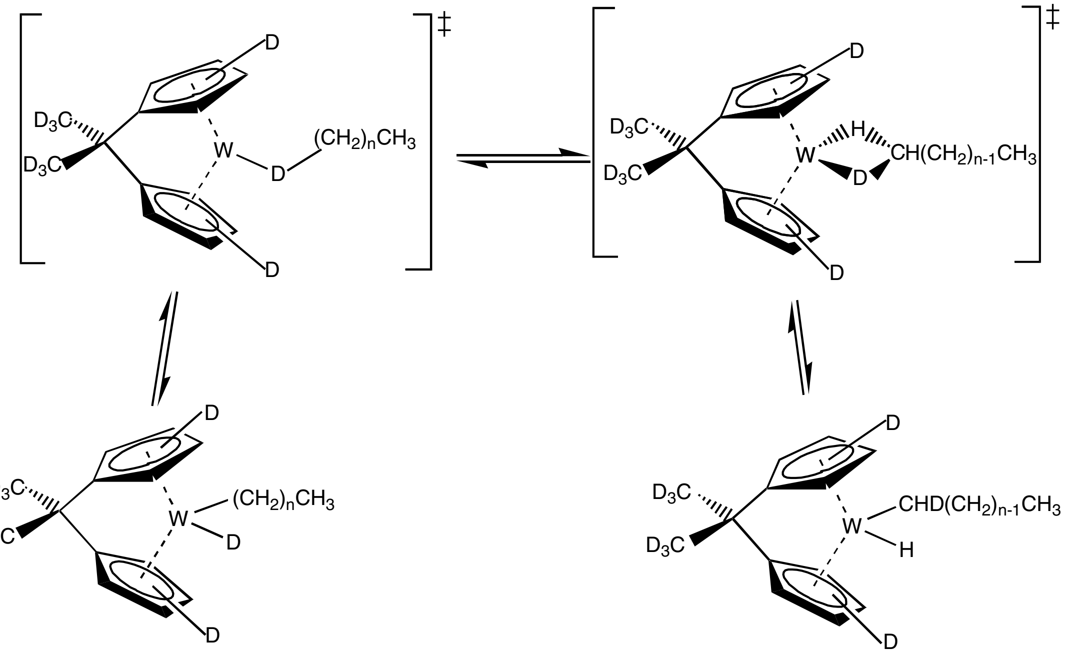


Fig. 7. Intramolecular hydrogen scrambling in the compounds [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}{$(CH_2)_nCH_3$}D] (n = 1–4) via η^1-H and η^2-H,H-σ-complexes.

into other positions of the *n*-pentyl chain was observed by ^1H or ^2H NMR spectroscopy.

In summary, thermolysis of the *n*-alkyl-deuteride compounds $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)_n\text{-}CH_3)_2D\}]$ (n = 1–4) and $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}\{CD_2CD_3)H]\}$ shows intramolecular hydrogen/deuterium exchange between the α-methylene hydrogens of the *n*-alkyl ligand and the W–D group. Exchange into other positions of the *n*-alkyl ligand was not observed for any of the compounds $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)\}_nCH_3)_2D]$ (n = 1–4). Similarly, H/D scrambling onto the α-methylene position was also observed by NMR spectroscopy for the d^5-ethyl-hydride compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}CD_2CD_3)_2H]$. Whereas the methyl-deuteride compound $[W\{(\eta\text{-}_5H_4)\text{-}CMe_2(\eta\text{-}C_5H_4)\}(CH_3)D]$ is stable at 110 °C, the higher *n*-alkyl-deuteride compounds $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{(CH_2)_nCH_3)_2D]\}$ (n = 1–4) decompose slowly above ca. 65 °C.

We propose that the H/D exchange into the α-methylene hydrogens proceeds by an intramolecular mechanism with an intermediate or transition state agostic alkane (see Fig. 7) by analogy with H/D the intermolecular exchange process proposed for the methyl compound $[W\{(\eta\text{-}C_5H_4)C(CH_3)_2(\eta\text{-}C_5H_4)\}\text{-}CH_3D]$ and related studies [2,3,10–26]. Subsequent to this work [6] there have been two reports of migration of transition metal along metal-alkyl chains of the kind hoped for in these studies [27,28]. Also there he been an elegant stdy by Ball et al. [29] in which alkane-σ-transition metal complexes are observed in solution by NMR studies.

3. Experimental

All manipulations of air and/or moisture sensitive materials were performed under an inert atmosphere of dry dinitrogen using standard Schlenk line techniques or in an inert atmosphere dry box containing dinitrogen [30]. Inert gases were purified firstly by passage through columns filled with activated molecular sieves (4 Å) and then either manganese (II) oxide suspended on vermiculite, for the Schlenk line, or BASF catalyst, for the dry box. Celite® filtration aid was purchased from Fluka Chemie and oven-dried at 100 °C prior to use.

Solvents were pre-dried over activated 4 Å molecular sieves and then distilled from Na/K alloy (light petroleum ether (b.p. 40–60 °C), diethyl ether, pentane and DME), from sodium (petroleum ether (b.p. 100–120 °C) and toluene), from potassium (THF) or from calcium hydride (acetonitrile, dichloromethane and TMEDA), under a slow continuous stream of dinitrogen. DMSO and d^1-methanol were used without drying. Deuterated NMR solvents were dried over potassium (benzene, toluene and THF) or calcium hydride (acetone, chloroform, dichloromethane and pyridine), distilled and degassed by the freeze–pump–thaw technique prior to use. $CDFCl_2$ was prepared by the literature method [31]. WCl_6 (99%), $LiAlH_4$ (95%), $LiAlD_4$ (96%), \D4 Super-Hydride® $LiBEt_3H$ (1.0 M solution in THF), dimethylzinc (2.0 M solution in hexanes), diethylzinc (1.0 M solution in hexanes), ^{t}BuLi (1.7 M solution in pentane), ^{n}BuLi (2.5 M solution in light petroleum ether (b.p. 40–60 °C)), $[Na\{AlH_2(OCH_2\text{-}CH_2OCH_3)_2\}]$ (2.5 M solution in toluene), HCl (1.0 M solution in diethyl ether), HBF_4 (54+ wt% solution in diethyl ether), NH_4I, 1-chloro-*n*-propane, 1-chloro-*n*-butane, 1-chloro-*n*-pentane, 1-chloro-*n*-hexane, d^5-ethanol, pyrrolidine, Me_2SiCl_2 and D_2 were purchased from Aldrich Chemical Company and used without further purification. $ZnCl_2$ was bought from Aldrich Chemical Company and dried in refluxing thionyl chloride for 6 h. Magnesium turnings were preactivated by the addition of a small amount (ca. 2 wt%) of dibromoethane to a suspension in THF and then washed with THF.

The compounds $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ [1,2] and $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ [26], were prepared using standard literature methods. NMR spectra were recorded out on a Varian Unity *Plus* 500 spectrometer (^1H, ^2H, and ^{13}C spectra were recorded at 499.868, 76.750, and 125.703 MHz, respectively). The spectra were referenced internally relative to the residual protio-solvent (^1H), residual deutero-solvent (^2H) and solvent (^{13}C) resonances relative to tetramethylsilane (^1H, ^2H, ^{13}C; $\delta = 0$ ppm). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz. Mass spectra (FAB) were recorded by the EPSRC Mass Spectrometry Service at the University College of Swansea.

IR spectra were recorded on a Mattson Polaris FTIR spectrometer or a Perkin–Elmer 1710 FTIR spectrometer. Samples were prepared as a Nujol mull between NaCl plates. Data are quoted in cm^{-1}.

Elemental analysis data were obtained from the Microanalysis Department of the Inorganic Chemistry Laboratory, Oxford.

3.1. Preparation of $[Zn\{CD_2CD_3\}_2]$

A thick-walled glass tube was charged with a finely ground mixture of zinc powder (7 g, 107.1 mmol) and copper powder (1.7 g, 26.8 mmol). Anti-bumping granules were added and the admixture was dried by heating under reduced pressure at 200 °C for 2 h. d^5-Iodoethane (7.9 g, 49.1 mmol) was transferred to the tube via low pressure distillation and the tube was sealed under reduced pressure, prior to heating overnight at 140 °C. The tube was connected to a Schlenk line, carefully scored and then broken. Volatiles were collected and the compound $[Zn\{CD_2CD_3\}_2]$ obtained as an extremely pyrophoric colourless liquid. Yield of $[Zn\{CD_2\text{-}CD_3)\}_2]$ = 0.55 g, 9%.

3.2. The compounds $[Zn\{(CH_2)_nCH_3\}_2]$

1-Chloro-*n*-propane (19.9 g, 250 mmol) was added dropwise to a suspension 3 of activated magnesium turnings (12 g, 490 mmol) in diethyl ether (150 cm^3) at such a rate to maintain a vigorous reaction. The reaction mixture was stirred for 2 h and a colourless solution was then isolated by filtration. Anhydrous $ZnCl_2$ (17 g, 120 mmol) was added to this ethereal solution via a solid addition tube in a slightly exothermic reaction. The resulting white suspension was stirred overnight and a colourless solution was then separated by filtration. Removal of volatiles under reduced pressure yielded $[Zn\{(CH_2)_2CH_3\}_2]$ as a pyrophoric colourless oil. Yield of $[Zn\{(CH_2)_2CH_3\}_2]$ (based on 1-chloro-*n*-propane) = 5.34 g, 28%. The compounds $[Zn\{(CH_2)_3CH_3\}_2]$ (yield [based on 1-chloro-*n*-butane] = 12.06 g, 42%), $[Zn\{(CH_2)_4CH_3\}_2]$ (yield [based on 1-chloro-*n*-pentane] = 14.32 g, 61%) and $[Zn\{(CH_2)_5CH_3\}_2]$ (yield [based on 1-chloro-*n*-hexane] = 25.05 g, 85%) were prepared via an analogous procedure.

3.3. Preparation of d^6-cyclopentadiene

To a flask containing D_2O (560 cm^3) at 3 °C, elemental sodium (65 g, 2.83 mol) was added in small portions over 2 h. A portion of the resulting solution of NaOD in D_2O (85 cm^3) was transferred to a flask containing DMSO (100 cm^3) and stirred vigorously at 0 °C. Freshly distilled cyclopentadiene monomer (125 cm^3, 1.58 mol) was added to the reaction mixture and stirring continued at 0 °C for 1 h. Cyclopentadiene monomer was transferred from the reaction mixture to a Schlenk tube, at −196 °C, under reduced pressure, allowed to warm to −78 °C and then added to a flask containing fresh NaOD in D_2O (85 cm^3) and DMSO (100 cm^3). This procedure was repeated for a total of 5 exchanges. d^6-Cyclopentadiene was stored at −80 °C. Yield of d^6-cyclopentadiene, 46.1 g, 94% D, 40%.

3.4. Preparation of d^{12}-6,6-dimethylfulvene

To a flask containing d^6-acetone (28.4 cm^3, 386 mmol) in d^1-methanol (100 cm^3) at 0 °C was added freshly distilled d^6-cyclopentadiene monomer (27 g, 94% D, 390 mmol). Pyrrolidine (41.7 cm^3, 500 mmol) was added and the reaction mixture immediately turned deep orange. The reaction mixture was stirred at 0 °C for 0.75 h. Glacial acetic acid (50 cm^3) and D_2O (50 cm^3) were added and the organic layer extracted into pentane (3 × 40 cm^3). The organic extracts were combined, washed with D_2O (50 cm^3) and dried over anhydrous $MgSO_4$. A pale orange solution was isolated by filtration and volatiles removed under reduced pressure to afford d^{12}-6, 6-dimethylfulvene as dark orange liquid, which was stored at −80 °C. Yield d^{12}-6, 6-dimethylfulvene, 31.6 g, 95% D, 74%.

3.5. Preparation of $[(C_5D_5)C(CD_3)_2(C_5D_5)]$

THF (350 cm^3) was added to a flask charged with NaOD (20 g, 500 mmol), prepared as described above, and the resulting suspension stirred at room temperature for 1 h. Freshly distilled d^6-cyclopentadiene monomer (15.7 g, 94% D, 232 mmol) was added to the reaction mixture which was stirred for 0.5 h to give a pale pink suspension. A solution of d^{12}-6, 6-dimethylfulvene (26.1 g, 95% D, 232 mmol) in THF (40 cm^3) was added dropwise over 0.5 h and the reaction mixture stirred overnight. An orange solution was isolated by filtration, washed with D_2O (50 cm^3) and dried over $MgSO_4$, prior to separation by filtration. Removal of volatiles under reduced pressure afforded the compound $[(C_5D_5)C(CD_3)_2(C_5D_5)]$ as a pale yellow oil. Yield of $[(C_5D_5)C(CD_3)_2(C_5D_5)]$, 22.7 g, 93% D, 55%.

3.6. Preparation of $[Li_2\{(C_5D_4)C(CD_3)_2(C_5D_4)\}]$

A solution of ^{n}BuLi (40 cm^3, 2.5 M, 100 mmol) in light petroleum ether (b.p. 40–60 °C) was added dropwise to a solution of $[(C_5D_5)C(CD_3)_2(C_5D_5)]$ (11.3 g, 94% D, 62.3 mmol) in light petroleum ether (b.p. 40–60 °C) (100 cm^3) at −78 °C. A flocculent white precipitate immediately formed and the reaction mixture was allowed to warm to room temperature and then stirred overnight. A white solid was isolation by filtration, washed with light petroleum ether (b.p. 40–60 °C) (100 cm^3) and diethyl ether (2 × 50 cm^3) and then dried under reduced pressure. Yield of $[Li_2\{(C_5D_4)C(CD_3)_2(C_5D_4)\}]$,10.8 g, 95% D, 93%.

3.7. Preparation of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_2CH_3\}_2]$ (**3**)

To a suspension of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ (0.6 g, 1.2 mmol) in toluene (40 cm^3) a solution of $[Zn\{(CH_2)_2CH_3\}_2]$ (3.5 cm^3, 1.85 M, 6.5 mmol) in toluene was added slowly at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The dark red suspension was hydrolysed via the cautious addition of H_2O (0.6 cm^3) to remove excess $[Zn\{(CH_2)_2CH_3\}_2]$. The reaction mixture was filtered and the filtrate passed down a column containing activated alumina by elution with toluene. The resulting yellow solution was collected and volatiles removed under reduced pressure to give an oily yellow solid. The residue was extracted into pentane (15 cm^3). The solution was cooled to −80 °C to afford $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{(CH_2)_2CH_3\}_2]$ **3** as a yellow solid. Yield: 0.23 g, 44%.

3.8. Preparation of [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}-{({(CH_2)$_2$$CH_3$}$_2$]} (3d)

The compound [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}{({(CH_2)$_2$$CH_3$}$_2$]} **3d** was prepared by the reaction between the compound **13** (0.44 g, 1.0 mmol) and a solution of [Zn{(CH)$_2$$CH_3$}$_2$](1 cm ^{3}, 1.1 M, 1.10 mmol) in toluene The compound **3d** was obtained as a yellow solid. Yield: 0. 11 g, 23%.

3.9. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{(CH_2)$_3$$CH_3$}$_2$] (4) and [W{(η-$C_5H_4$)$CMe_2$(η-$C_5H_4$)}-{($CH_2$)$_3$$CH_3$}Cl] (5)

To a suspension of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] (0.3 g, 0.6 mmol) in toluene (40 cm^3) a solution of [Zn{(CH_2)$_3$$CH_3$}$_2$] (3.0 cm^3, 1.5 M, 4.5 mmol) in toluene was added slowly at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The dark red suspension was hydrolysed via the cautious addition of H_2O (0.5 cm^3) to remove excess [Zn{(CH_2)$_3$$CH_3$}$_2$]. The reaction mixture was filtered and volatiles removed under reduced pressure. The resulting orange solid was extracted into pentane (15 cm^3) to yield a yellow solution. The residue was extracted into a 1:1 mixture of toluene/pentane (20 cm^3). Cooling of the pentane solution to −80 °C afforded the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{(CH_2)$_3$-CH_3}$_2$] (**4**) as a yellow solid. Yield: 0.045 g, 16%. Cooling of the toluene/pentane solution to −80 °C afforded the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{(CH_2)$_3$-CH_3}Cl] (**5**) as a yellow solid. Yield: 0.11 g, 41%.

3.10. Preparation of [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}-{(CH_2)$_3$$CH_3$}Cl] (5d)

The compound **5d** was prepared by the reaction between the compound **13** (0.24 g, 0.55 mmol) and a solution of [Zn{(CH_2)$_3$$CH_3$}$_2$] (4 cm^3, 1.5 M, 6 mmol) in toluene in a procedure analogous to that used to prepare the compound **5** and was obtained as an yellow solid. Yield: 0.099 g, 39%.

3.11. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{(CH_2)$_4$$CH_3$}Cl] (6) and [W{(η-$C_5H_4$)$CMe_2$(η-$C_5H_4$)}-{($CH_2$)$_4$$CH_3$}$_2$] (7)

To a suspension of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] (1.0 g, 2.34 mmol) in toluene (40 cm^3) a solution of [Zn{(CH_2)$_4$$CH_3$}$_2$] (7.0 cm^3, 1.86 M, 13.0 mmol) in toluene was added slowly at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. The dark red suspension was hydrolysed via the cautious addition of H_2O (0.6 cm^3) to remove excess [Zn{(CH_2)$_4$$CH_3$}$_2$]. The reaction mixture was filtered and the filtrate passed down a column containing activated alumina by elution with toluene to give a yellow solution. Further elution with diethyl ether gave an orange solution which was collected separately. Removal of diethyl ether under reduced pressure afforded the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{(CH_2)$_4$$CH_3$}Cl] (21) (**6**) as a pale red solid. Yield: 0.31 g, 29%.

Removal of volatiles under reduced pressure from the yellow toluene solution yielded a yellow solid. Extraction into pentane (5 cm^3) prior to cooling to −80 °C afforded a yellow solid in very low yield (ca. 0.01 g, 1%) which was characterised by ^{1}H NMR spectroscopy as [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{(CH_2)$_4$-CH_3}$_2$] (**7**).

3.12. Preparation of [W{(η-C_5D_4)C(CD_3)$_2$(η-C_5D_4)}-{(CH_2)$_4$$CH_3$}$_2$] (6d)

To a suspension of the compound **13d** (0.27 g, 95% D, 0.58 mmol) in toluene (50 cm^3) a solution of [Zn-{(CH_2)$_4$$CH_3$}$_2$] (3.0 cm^3, 1.5 M, 4.5 mmol) in toluene was added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Excess [Zn{(CH_2)$_4$$CH_3$}$_2$] was hydrolysed by the cautious addition of D_2O (0.4 cm^3). The resulting solid was extracted into pentane (30 cm^3). Cooling of the pentane solution to −80 °C afforded the compound 6a as a yellow crystalline solid. Yield: 0.098 g, 33%.

3.13. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{(CH_2)$_5$$CH_3$}$_2$] (8)

To a suspension of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] (0.33 g, 0.6 mmol) in toluene (40 cm^3) a solution of [Zn{(CH_2)$_5$$CH_3$}$_2$] (2.0 cm^3, 5.3 M, 10.6 mmol) in toluene was added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Excess [Zn{(CH_2)$_5$$CH_3$}$_2$] was hydrolysed via the cautious addition of H_2O (0.5 cm^3). The reaction mixture was filtered and the filtrate passed down a column containing activated alumina by elution with a 1:1 mixture of diethyl ether/toluene. The resulting yellow solution was collected and volatiles removed under reduced pressure to give an orange/yellow solid, prior to extraction into pentane (15 cm^3) to yield a yellow solution. The residue was extracted into a 1:1 mixture of toluene/pentane (20 cm^3). Cooling of the pentane solution to −80 °C afforded the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{(CH_2)$_5$$CH_3$}$_2$] (**8**) as a yellow solid. Yield: 0.095 g, 18%. Cooling of the toluene/pentane solution to −78 °C afforded a small amount (ca. 0.025 g, 9%) of a pale red solid characterised by ^{1}H NMR spectroscopy as [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{(CH_2)$_5$$CH_3$}Cl].

*3.14. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{$(CH_2)_2CH_3$}I] (**9**)*

A mixture of the compound **3**(0.06 g, 0.13 mmol) and NH_4I (0.05 g, 0.34 mmol) in THF (25 cm^3) was heated at 65 °C for seven days in a Rotaflo® ampoule. A gradual colour change from yellow to pale red was observed. The solution was isolated by filtration and volatiles were removed under reduced pressure. The resulting red–orange solid was washed with pentane (20 cm^3) to remove any unreacted compound **3** prior to extraction into a 1:4 mixture of toluene/pentane. Cooling of the red–orange solution to −80 °C afforded the compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_2CH_3$}I] (**9**) as a pale red solid. Yield: 0.032 g, 47%.

*3.15. Preparation of [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_2CH_3$}I] (**9d**)*

The compound [W{(η-C_5H_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_2CH_3$}I] (**9d**) was prepared by the reaction between the compound **3d** (0.11 g, 0.24 mmol) and NH_4I (0.07 g, 0.48 mmol) in a procedure analogous to that employed to prepare the compound **9** and was obtained as a pale red solid. Yield: 0.057 g, 44%.

3.16. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{$(CH_2)_2CH_3$}H] (10)

To a solution of the compound **23** (0.03 g, 0.06 mmol) in toluene (20 cm^3) was added a solution of [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}] (0.2 cm^3, 2.5 M, 0.5 mmol) in toluene at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight during which time the colour of the solution changed from orange to pale yellow. Excess [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}] was hydrolysed by the cautious addition of H_2O (0.1 cm^3). Volatiles were removed and the reaction mixture dried under reduced pressure for 2 h. The yellow residue was extracted into pentane (2 × 20 cm^3) and the volume subsequently reduced to 10 cm^3 prior to cooling to −80 °C. The compound [W{(η-C_5H_4)CMe_2 (η-C_5H_4)}{$(CH_2)_2CH_3$}H] (**10**) was obtained as a yellow crystalline solid. Yield: 0.012 g, 50%.

*3.17. Preparation of [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_2CH_3$}D] (**10d**)*

The compound [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_2CH_3$}D] (**10d**) was prepared by the reaction between the compound **9d** (0.020 g, 0.04 mmol) and a solution of [Li{$AlD_2(OCH_2CH_2OCH_3)_2$}] (1 cm^3, 1.5 M, 1.5 mmol) in toluene in a procedure analogous to that used to prepare the compound **16** and was obtained as a yellow solid. Since only a small amount of compound was obtained, and in order to utilise all of the compound prepared, the Yield: **10d** was not calculated.

3.18. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{$(CH_2)_3CH_3$}H] (11)

The compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{$(CH_2)_3CH_3$}H] (**11**) was prepared by the reaction between the compound **5** (0.1 g, 0.22 mmol) and a solution of [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}] (2 cm^3, 2.5 M, 5 mmol) in toluene in a procedure analogous to that employed to prepare the compound **10** and was obtained as a yellow solid. Yield: 0.038 g, 42%.

*3.19. Preparation of [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_3CH_3$}D] (**11d**)*

The compound **11d** was prepared by the reaction between the compound **5d** (0.035 g, 0.08 mmol) and a solution of [Li{$AlD_2(OCH_2CH_2OCH_3)_2$}] (1.5 cm^3, 1.0 M, 1.5 mmol) in toluene in a procedure analogous to that used to prepare the compound **16** and was obtained as a yellow solid. Since only a small amount of compound was obtained, and in order to utilise all of the compound prepared, the Yield: **11d** was not determined.

3.20. Preparation of [W{(η-C_5H_4)CMe_2(η-C_5H_4)}-{$(CH_2)_4CH_3$}H] (12)

The compound [W{(η-C_5H_4)CMe_2(η-C_5H_4)}{$(CH_2)_4$-CH_3}H] (**12**) was prepared by the reaction between the chloro compound **6** (0.05 g, 0.11 mmol) and a solution of [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}] (1 cm^3, 2.5 M, 2.5 mmol) in toluene in a procedure analogous to that employed to prepare the compound **11d** and was obtained as a yellow solid. Yield: 0.023 g, 49%.

*3.21. Preparation of [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-{$(CH_2)_4CH_3$}D] (**12d**)*

The compound [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)} {$(CH_2)_4CH_3$}D] (**12d**) was prepared by the reaction between the iodo compound **17d** (0.022 g, 0.05 mmol) and a solution of [Li{$AlD_2(OCH_2CH_2OCH_3)_2$}] (1.0 cm^3, 1.5 M, 1.5 mmol) in toluene in a procedure analogous to that used to prepare the compound **30** and was obtained as a yellow solid. Since only a small amount of compound was obtained and in order to utilise all of the compound prepared the Yield: **12d** was not calculated.

*3.22. Preparation of [W{(η-C_5D_4)$C(CD_3)_2$(η-C_5D_4)}-Cl_2] (**13d**)*

The two solids $WCl_4 \cdot$ DME [32] (10.5 g, 25.2 mmol) and [Li_2{$(C_5D_4)C(CD_3)_2(C_5D_4)$}] (5.5 g, 95%, 27.7 mmol) were stirred together in the absence of solvent to give a good admixture. Diethyl ether (100 cm^3) was added and the resulting brown suspension stirred for two days. The liquid phase was removed by filtration and DME (50 cm^3) was added to the remaining solid. The resulting dark brown suspension was stirred for 0.5 h and a brown solid isolated by filtration. The residue was washed with ethanol (50 cm^3) and then diethyl ether (3×30 cm^3) until the washings were colourless. After drying under reduced pressure, the resulting pale brown solid was extracted into dichloromethane (2×250 cm^3) to give a deep red/brown solution. Removal of volatiles under reduced pressure afforded the compound $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}Cl_2]$ (**13d**) as a purple solid. Yield: 1.25 g, 95% D, 11.3%.

*3.23. Preparation of $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\text{-}\{CH_2CH_3\}_2]$ (**14d**)*

To a suspension of the compound **13d** (0.1 g, 95% D, 0.22 mmol) in toluene (50 cm^3) a solution of $[Zn\{CH_2CH_3\}_2]$ (5.0 cm^3, 1.0 M, 5.0 mmol) in hexanes was added dropwise at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Volatiles were removed under reduced pressure and collected in a trap containing propan-2-ol at −196 °C. Excess $[Zn\{CH_2CH_3\}_2]$ can be readily removed in this way. The resulting solid was extracted into pentane (20 cm^3). Cooling of the pentane solution to −80 °C afforded the compound $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{CH_2CH_3\}_2]$ (**14d**) as a yellow crystalline solid. Yield: 0.042 g, 46%. Preparation of $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{CH_2CH_3\}I]$ (**15d**). The compound $[W\{(\eta\text{-}C_5H_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\{CH_2CH_3\}I]$ (**15d**) was prepared by the reaction between the compound **14d** (0.03 g. 0.07 mmol) and NH_4I (0.02 g, 0.14 mmol) in a procedure analogous to that employed to prepare the compound **2** and was obtained as a pale red solid. Yield: 0.037 g, 67%.

*3.24. Preparation of $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\text{-}\{CH_2CH_3\}D]$ (**16d**)*

To a solution of the compound **15d** (0.03 g, 0.06 mmol) in toluene (20 cm^3) was added a solution of $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ (0.5 cm^3, 1.1 M, 0.55 mmol) in toluene at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight during which time the colour of the solution changed from orange to pale yellow. Excess $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ was hydrolysed by the cautious addition of D_2O (0.35 cm^3). Volatiles were removed, and the reaction mixture dried, under reduced pressure. The yellow residue was extracted into pentane (20 cm^3) and the volume subsequently reduced to 10 cm^3 prior to cooling to −80 °C. The compound **16d** was obtained as a yellow crystalline solid. Since only a small amount of compound was obtained, and in order to utilise all of the compound prepared, the Yield of **16d** was not determined.

*3.25. Preparation of $[W\{(\eta\text{-}C_5D_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\text{-}\{(CH_2)_4CH_3\}I]$ (**17d**)*

The compound $[W\{(\eta\text{-}C_5H_4)C(CD_3)_2(\eta\text{-}C_5D_4)\}\text{-}\{(CH_2)_4CH_3\}I]$ (**17d**) was prepared by the reaction between the compound **7d** (0.05 g, 0.098 mmol) and NH_4I (0.015 g, 0.11 mmol) in a procedure analogous to that employed to prepare the compound **9** and was obtained as a pale red solid. Yield: 0.026 g, 47%.

*3.26. Preparation of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}\{CD_2CD_3\}_2]$ (**18**)*

The compound **18** was prepared by the reaction between the compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}Cl_2]$ (0.47 g, 1.1 mmol) and a solution of $[Zn\{CD_2CD_3\}_2]$ (5 cm^3, 0.4 M, 2 mmol) in toluene in a procedure analogous to that used to prepare the compound **3** and was obtained as a yellow solid. Yield: 0.24 g, 52%.

*3.27. Preparation of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}\{CD_2CD_3\}I]$ (**19**)*

The compound $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\{CD_2CD_3\}I]$ (**19**) was prepared by the reaction between the compound **18** (0.04 g, 0.09 mmol) and NH_4I (0.025 g, 0.17 mmol) in a procedure analogous to that employed to prepare the compound **9** and was obtained as a pale red solid. Yield: 0.032 g, 69%.

*3.28. Preparation of $[W\{(\eta\text{-}C_5H_4)CMe_2(\eta\text{-}C_5H_4)\}\text{-}\{CD_2CD_3\}H]$ (**20**)*

The compound **20** was prepared by the reaction between the compound **19** (0.027 g, 0.05 mmol) and a solution of $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ (0.5 cm^3, 2.5 M, 1.25 mmol) in toluene in a procedure analogous to that used to prepare the compound **10**. The compound **20** was obtained as a yellow solid. Yield: 0.012 g, 62%.

Acknowledgements

We thank the EPSRC for a studentship (to S.L.J. Conway) and St John's College for a Junior Research Fellowship (to L.H. Doerrer).

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