Chapter 3

Hydrogen Scrambling in Group 6 *ansa*-Metallocene Alkyl Hydrides

3.1 Introduction to Chapter 3

Since the discovery that strong C-H bonds in alkanes undergo oxidative addition to certain transition metal complexes, the mechanism of this so-called C-H bond activation has been the subject of much research and debate.[1-4] The importance of C-H bond activation in many homogeneous catalytic processes has further focussed efforts towards the understanding of this phenomenon. Like unsaturated hydrocarbons, alkanes are highly attractive feedstocks for large-scale processes due to their plentiful availability; they are major constituents of natural gas and petroleum. However the inertness of alkanes to all but a few of the most reactive transition metal complexes has restricted their use as organic feedstocks.

The oxidative addition of a C-H bond of an alkane RH to a transition metal centre M results in the formation of an alkyl hydride species M(R)H. Thermodynamic evidence shows that there is often little energy difference between resulting alkyl hydride and the combination of alkane and lower valent metal, even for third row transition metals.[5] Thus alkyl hydride species are in general highly labile, readily undergoing reductive elimination of alkane. This transformation generates an electron deficient intermediate that is itself highly reactive towards other C-H bonds. Further understanding of C-H bond activation can thus be gleaned by the study of transition metal alkyl hydride complexes. The preparation of alkyl hydride species that display increased stability with respect to reductive elimination of alkane is fundamental to such a study.

This chapter describes the synthesis of 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 = 2-4) (**Section 3.6**). The isotopically labelled compounds $[W\{(\eta\text{–}C_5D_4)C(CD_3)_2(\eta\text{–}C_5D_4)\}(R)D]$ ($R = \{(CH_2)_nCH_3\}$ n = 1-4) and $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{CD_2CD_3\}H]$ have been prepared (**Section 3.7-3.8**) and the hydrogen exchange processes under thermal conditions in these compounds investigated (**Section 3.8**). Evidence for the intermediacy of an alkane σ-complex in the exchange pathway is presented.

3.2 C-H Bond Activation by Group 6 Metallocenes

The electronically unsaturated, highly reactive 16 electron tungstenocene species $[W(\eta\text{–}C_5H_5)_2]$ has long been known to undergo intermolecular insertion into sp^2 and sp^3 C-H bonds.[6] Green and co-wokers have reported that thermoylsis or photolysis of the

dihydride complex $[W(\eta\text{–}C_5H_5)_2H_2]$, or the methyl hydride complex $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$, affords $[W(\eta\text{–}C_5H_5)_2]$ which is reactive towards aliphatic or aromatic C-H bonds (**Figure 3.1**). [7-9]

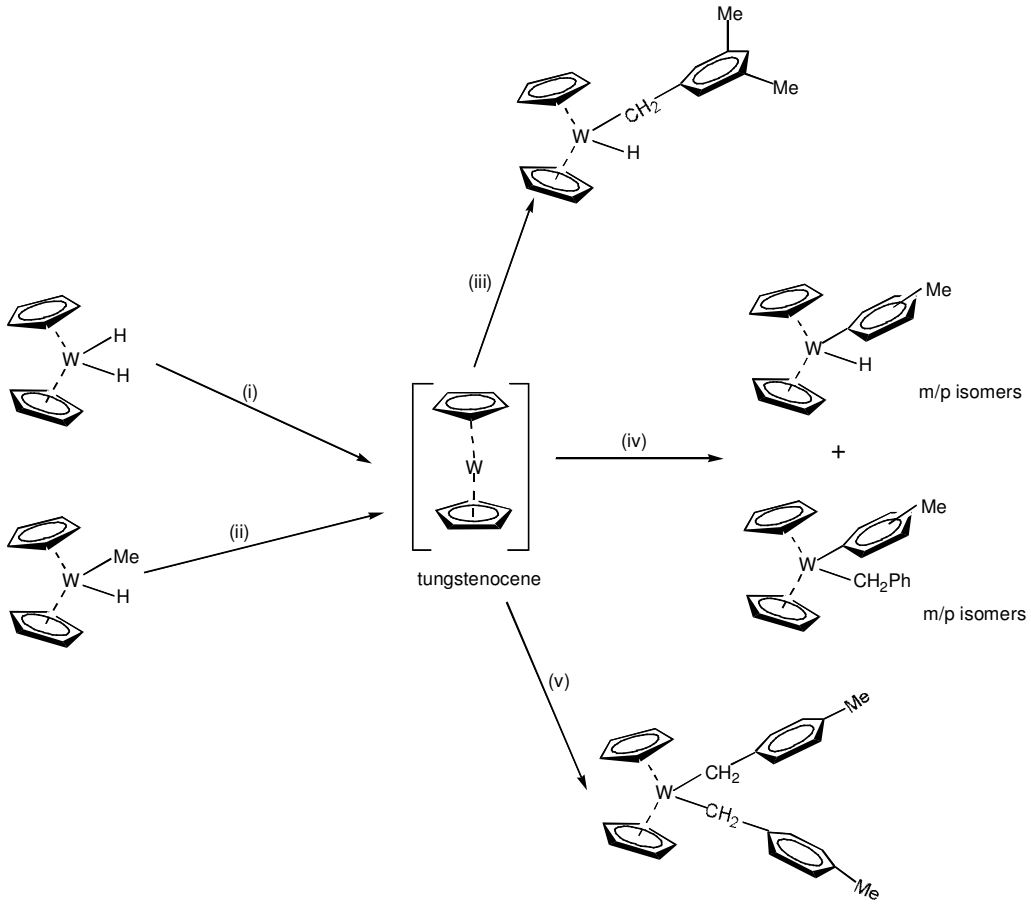


Figure 3.1 (i) Photolysis. (ii) Thermolysis. (iii) Thermolysis in mesitylene. (iv) Photolysis in toluene. (v) Photolysis in p-xylene.

3.3 Investigations into the Molecularity of Methane Elimination from $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$

A thorough and elegant study of the elimination of methane from $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$ has been carried out by Norton.[10] Thermolysis studies were performed in an acetonitrile/toluene solvent mixture, with acetonitrile acting as a trap for the highly reactive tungstenocene complex $[W(\eta\text{–}C_5H_5)_2]$. Previous work by Green had shown that in the presence of unreactive substrates, such as cyclohexane, the tungstenocene intermediate $[W(\eta\text{–}C_5H_5)_2]$, formed by elimination of methane reacts with

the C-H bonds of the cyclopentadienyl rings of $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$ to give the dinuclear products shown in **Figure 3.2**.[11]

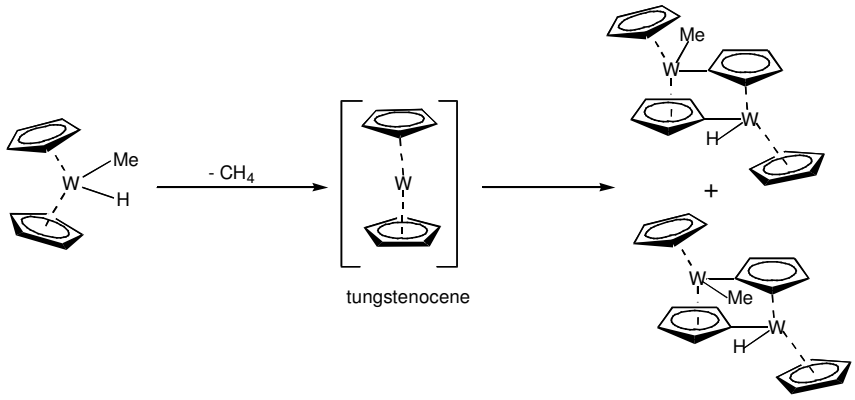


Figure 3.2 Thermolysis of $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$ in cyclohexane

Heating of a dilute equimolar solution of $[W(\eta\text{–}C_5H_5)_2(CH_3)D]$ and $[W(\eta\text{–}C_5H_5)_2(CD_3)H]$ in acetonitrile/toluene at 82 ºC resulted in reductive elimination of methane. The liberated methane was shown by mass spectrometry to be predominately a mixture of CH_3D and CD_3H indicating an intramolecular elimination process (**Figure 3.3**).

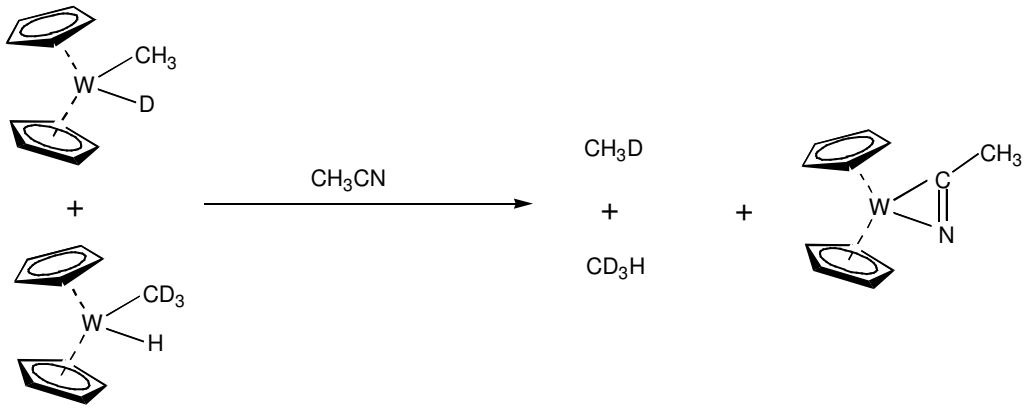


Figure 3.3 Thermolysis of $[W(\eta\text{–}C_5H_5)_2(CH_3)D]$ and $[W(\eta\text{–}C_5H_5)_2(CD_3)H]$ in the presence of acetonitrile

At 48 ºC and in dilute solution $[W(\eta\text{–}C_5H_5)_2(CH_3)D]$ showed hydride exchange between the hydride and alkyl ligand sites as shown in **Figure 3.4.** This exchange was

monitored by ^{1}H NMR spectroscopy, showing a decrease in the intensity of the methyl proton resonance and a concomitant increase in the intensity of hydride resonance. Thus the rate of methane elimination in $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$ is slower than the rate of hydrogen exchange. The equilibrium constant for exchange in $[W(\eta\text{–}C_5H_5)_2(CD_3)H]$ was found to be 1.4 rather than the statistical value of 3. This can be attributed to the fact that the difference between C-H and C-D zero point energies is greater than the difference between the W-H and W-D zero-point energies.[10]

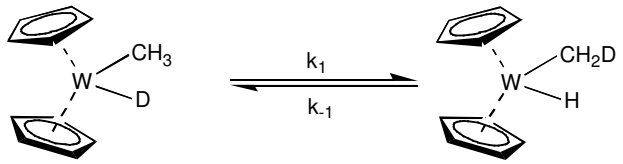


Figure 3.4 Intramolecular hydrogen exchange in $[W(\eta\text{–}C_5H_5)_2(CH_3)D]$

At concentrations greater than 0.01 M isotopically labelled derivatives of $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$ undergo hydrogen scrambling by an intermolecular process prior to methane elimination. A double labelling experiment confirms this deduction. When a concentrated solution of $[W(\eta\text{–}C_5H_5)_2(CD_3)H]$ and $[W(\eta\text{–}C_5H_5)_2(^{13}CH_3)H]$ was heated to facilitate methane elimination, mass spectrometry of the resulting methane showed various isotopomers including methane containing both labelled nuclei, i.e. $^{13}CH_3D$. A four centred-associative mechanism was proposed for this intermolecular hydrogen exchange. A similar associative mechanism is believed to account for the intermolecular alkane elimination from $[cis\text{-}Os(CO)_4(CH_3)H]$.[12]

Intermolecular hydrogen exchange *via* an associative four-centred intermediate would be expected to be inhibited by steric crowding. Indeed Bercaw has shown that in isotopically labelled $[W(\eta\text{–}C_5Me_5)_2(CH_3)H]$ compounds scrambling between hydride and alkyl ligand sites occurs by an intramolecular process only, even at high concentrations.[13] However in this case the rate of reductive elimination of methane is faster than the rate for hydrogen exchange.

3.4 Hydrogen Scrambling Facilitated by an Alkane σ-Complex

The observation of intramolecular hydrogen exchange in $[W(\eta\text{–}C_5R_5)_2(CH_3)D]$ (R = H, Me) led to the proposal of an exchange pathway involving an alkane σ-complex (η^1- or η^2-CH_4) as a transition state, or more likely an intermediate.[13] This intermediate has an intact C-H σ-bond of the alkane coordinated to the metal centre, similar to the bonding in alkyl derivatives having agostic M-H-C ligands.[14] **Figure 3.5** shows methane elimination and hydrogen exchange for $[W(\eta\text{–}C_5Me_5)_2(CH_3)D]$ *via* η^1-H and η^2-H,H σ-complexes. Further evidence for the existence of σ-complexes as intermediates on the elimination/exchange pathway is provided by the inverse primary kinetic isotope effect for elimination of CH_3D from $[W(\eta\text{–}C_5R_5)_2(CH_3)D]$ (R = H, Me).[13]

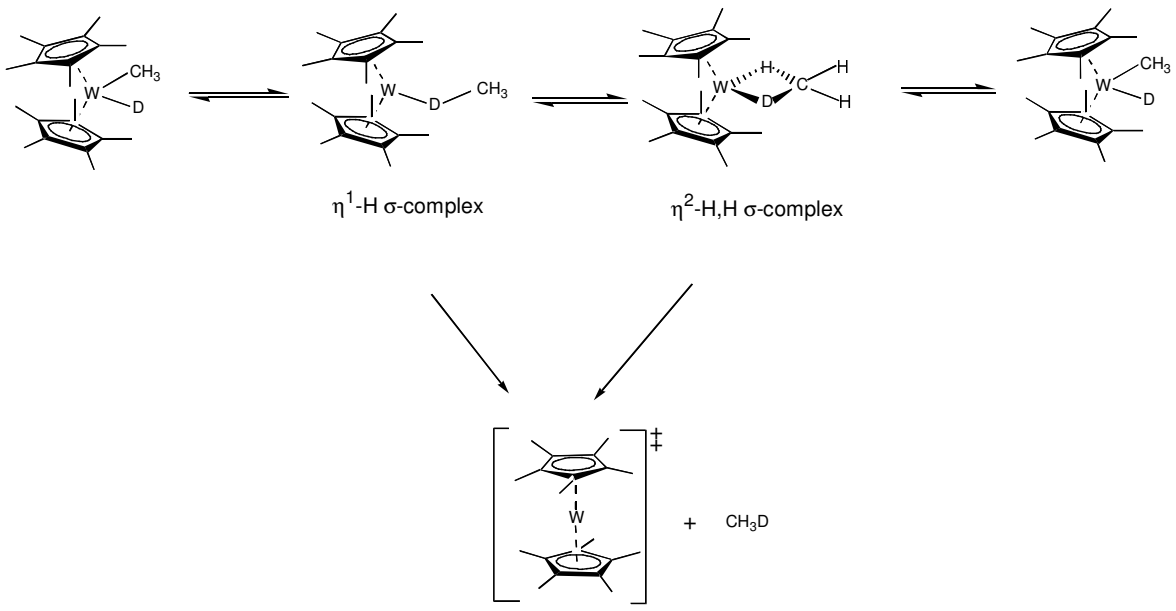


Figure 3.5 Proposed mechanism for intramolecular scrambling and methane elimination *via* η^1-H and η^2-H,H alkane σ-complexes in $[W(\eta\text{–}C_5Me_5)_2(CH_3)D]$

Bergman has undertaken a rigorous study of the elimination and exchange processes in transition metal hydride complexes. An inverse primary isotope effect for alkane elimination in $[Ir(\eta\text{–}C_5Me_5)PMe_3(Cy)X]$ (Cy = cyclohexyl, X = H, D) has been observed, along with competitive deuterium scrambling between hydride and

α-cyclohexyl positions.[15] (Note: in this thesis the carbons of the alkyl group of a transition metal alkyl compound are denoted α, β, γ… where the α-position is the carbon closest to the metal.) The intermediacy of a cyclohexane/[Ir(η–C_5Me_5)PMe_3] σ-complex was proposed. A mechanism involving simple reductive elimination and subsequent oxidative addition of $C_6H_{11}D$ was ruled out since in this case deuterium should appear in all positions of the cycloalkane, rather than just in the α-position.

An investigation of intramolecular scrambling in [Rh(η–C_5Me_5)PMe_3($^{13}CH_2CH_3$)D] has provided further evidence in favour of the intermediacy of σ-complexes in exchange and elimination processes.[16] Scrambling of deuterium into the α-position of the ethyl group occurred rapidly at -80 ^oC with migration to the β-position only observed when the temperature is raised. A significant observation was that deuterium remained attached to the labelled carbon atom following the exchange processes. Furthermore the analogous (1-methylcyclopropyl)methyl hydrido rhodium compound undergoes rapid γ-rearrangement at -45 ^oC to give two diastereomers of a 2, 2-dimethylcyclopropyl hydrido rhodium compound in a 1:1 ratio (**Figure 3.6**).

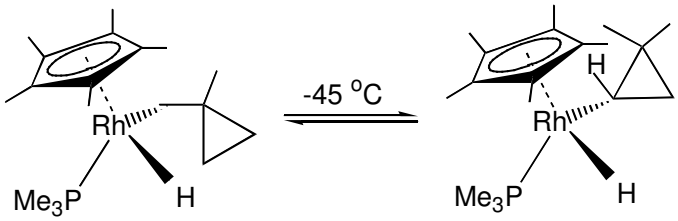


Figure 3.6 Intramolecular γ-rearrangement in a (1-methylcyclopropyl)methyl hydrido rhodium compound

Several mechanisms can be proposed to explain the scrambling and isomerisation processes in the ^{13}C labelled ethyl deuteride [Rh(η–C_5Me_5)PMe_3($^{13}CH_2CH_3$)D] and are shown in **Figure 3.7** as mechanisms A, B, C and D. Mechanism A involves reductive elimination and subsequent oxidative addition. This can be ruled out since deuterium is observed to remain attached to the labelled carbon as rearrangement occurs. Mechanism B involves reversible dissociation of PMe_3 followed by reversible α- and β-eliminations to produce intermediate dihydrocarbene or olefin species, respectively. However addition of

PMe_3 was found not to inhibit the rate of isomerisation thus disfavouring such a mechanism.

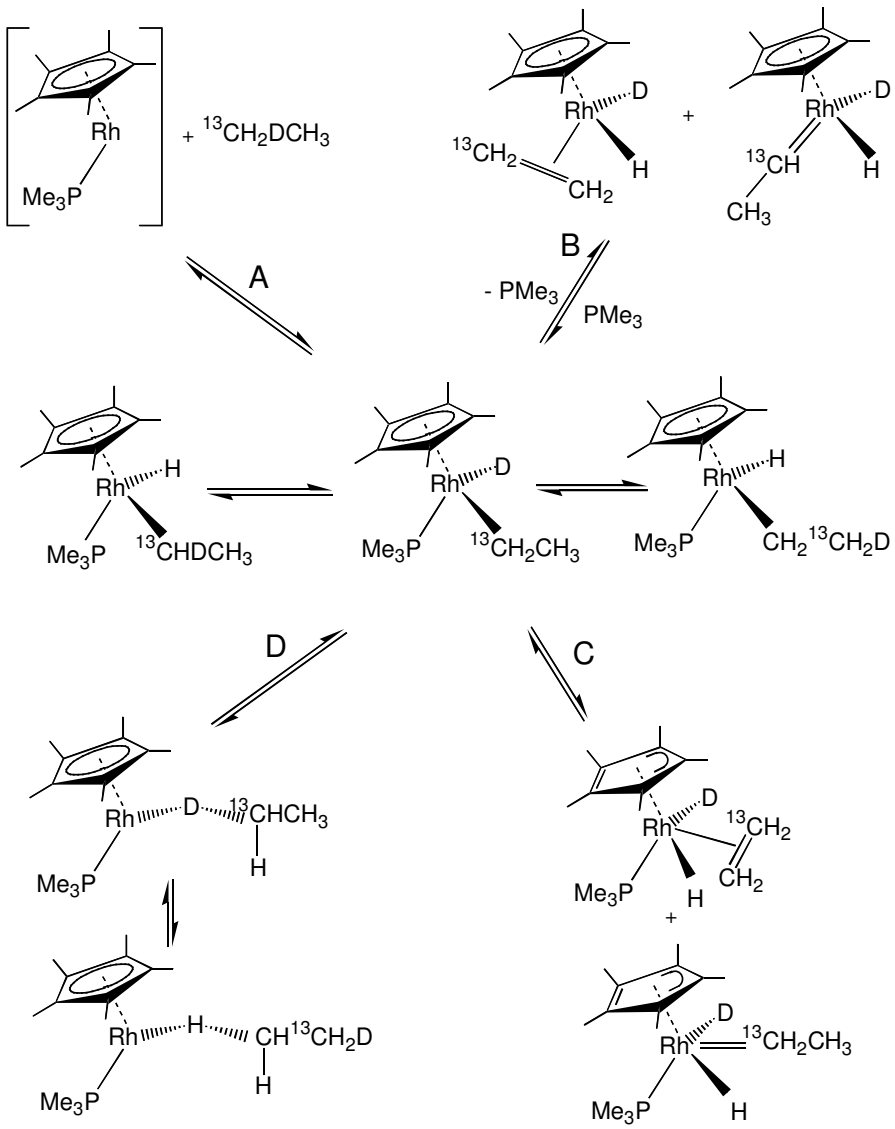


Figure 3.7 Possible mechanisms for H/D scrambling in the compound $[Rh(\eta\text{–}C_5Me_5)PMe_3(^{13}CH_2CH_3)D]$

In mechanism C α- and β-eliminations again lead to carbene and olefin complexes respectively, giving a high energy 20-electron species unless η^5-η^3 ring slippage of the C_5Me_5 ring occurs. To maintain the connectivity between D and ^{13}C in the ethyl ligand, rotation of the coordinated olefin must not occur. This combination of restrictions disfavour such a mechanism. The experimental observations can be rationalised more

convincingly by considering a mechanism involving a σ-complex (Mechanism D). Hydrogen exchange can occur readily at the α-position, while migration of the fragment [Rh(η−C_5Me_5)PMe_3] to the β-carbon accounts for the presence of deuterium in this position. This migration process would be expected to be less facile than the scrambling at the α-position *via* an alkane σ-complex. Indeed, scrambling into the β position is only seen when the temperature is raised. This mechanism is also favoured by the observation that isomerisations can occur past carbons which do not possess β-C-H bonds, as in the isomerisation of the (1-methylcyclopropyl)methyl hydrido rhodium compound (**Figure 3.6**).

Several other studies support the presence of alkane σ-complexes as intermediates in the reductive elimination pathway.[17] Heinekey has described evidence for an intermediate methane σ-complex in the hydrogen scrambling process between hydride and alkyl ligand sites observed in [Re(η−C_5H_5)$_2$(CD_3)H]$^+$ prior to methane elimination.[18] Girolami reported that for the compound [Os(η−C_5Me_5)(dmpm)(CH_3)H]$^+$ the hydrogen atoms in the methyl and hydride sites exchange at a rate observable on the NMR time scale.[19] Density functional calculations on this compound found bound methane σ-complexes on the exchange pathway at *ca.* 25 kJ mol^{-1} above the parent methyl hydride complex.[20]

Complexes of the type $W(CO)_5$(alkane) have been characterised by infrared spectroscopy in matrix isolated, solution and gas phases.[21-23] The first structurally characterised transition metal complex containing a simple alkane as a ligand, [Fe(DAP)(n-heptane)] (DAP = a double A-frame porphyrin), has been reported, although hydrogen atoms of the bound heptane moiety were not located.[24] The inherent weakness of the interaction of an sp^3 saturated C-H bond with a metal centre is compensated for by a host/guest effect. Recently Ball has described the direct observation of a transition metal alkane complex, [Re(η−C_5H_5)$(CO)_2$(cyclopentane)], using NMR spectroscopy.[25] Continuous UV irradiation of the parent tricarbonyl [Re(η−C_5H_5)$(CO)_3$] in cyclopentane, whilst in the NMR spectrometer, gave a species consistent with a metal alkane complex with a lifetime of *ca.* 1h, thus allowing time to undertake various NMR experiments.

3.5 Hydrogen Exchange in [W{(η–C_5H_4)CMe_2(η–C_5H_4)}(CH_3)H]

As described in **Section 1.5.2** the *ansa*-metallocene methyl hydride compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}(CH_3)H] was found to be stable towards reductive elimination of methane under both thermal and photochemical conditions,[26] whereas the nonbridged analogue undergoes reductive elimination of methane at 48 °C.[9] Previous work in this laboratory has shown that hydrogen scrambling in [W{(η–C_5H_4)CMe_2(η–C_5H_4)}(CH_3)D] occurs *via* an intramolecular mechanism in both concentrated and dilute solution.[27] A density functional study by Green and Jardine of hydrogen exchange and methane elimination from [W(η–C_5H_5)$_2$(CH_3)H] and [W{(η–C_5H_4)CMe_2(η–C_5H_4)}(CH_3)H] has examined the reaction pathway for both processes.[28] It is postulated that both exchange and elimination occur *via* the same pathway on which is found both singly agostic η^1-H and doubly agostic η^2-H,H methane σ-complexes. The stability of the *ansa*-bridged compound towards reductive elimination of methane can be attributed to the high energy of the resulting 16 electron triplet tungstenocene intermediate, where the constraining CMe_2 bridge prevents adoption of a parallel ring configuration. In contrast there is considerable energy gain as the nonbridged tungstenocene undergoes geometric relaxation to a parallel ring structure.

3.6 Preparation of n-Alkyl *ansa*-Metallocene Derivatives

3.6.1 Introduction

The kinetic lability of n-alkyl derivatives with respect to β-hydrogen elimination is reflected in the relative paucity of organometallic compounds bearing ligands with hydrogen atoms in the β-position relative to the metal. The first such Group 6 metallocene di-n-alkyl compounds were reported in 1991 with the synthesis of the diethyl and di-n-butyl molybdocene derivatives [Mo(η–C_5H_5)$_2$$R_2$] (R = {$CH_2CH_3$}, {$(CH_2)_3CH_3$}) by the reaction between [Mo(η–C_5H_5)$_2$$I_2$] and the appropriate alkyl lithium reagent RLi.[29]

The increased stability with respect to elimination processes afforded by the presence of a sterically constraining one carbon *ansa*-bridge suggests potential for the successful synthesis of higher n-alkyl metallocene derivatives. Souter has reported the synthesis of the thermally stable *ansa*-metallocene ethyl complexes [W{(η–C_5H_4)CMe_2(η–C_5H_4)}(CH_2CH_3)$_2$] and [W{(η–C_5H_4)CMe_2(η–C_5H_4)}

$(CH_2CH_3)X]$ (X = I, H, D).[27]

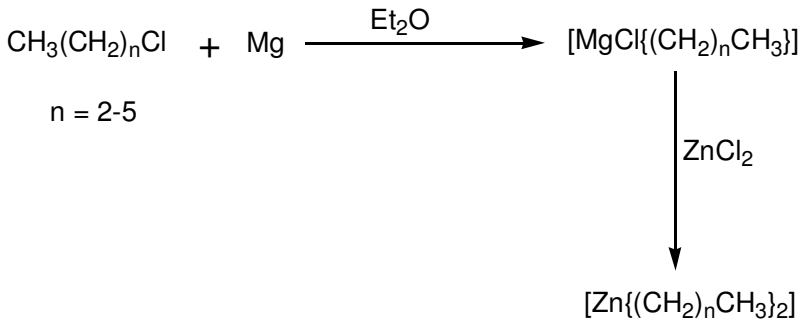
Heating of the ethyl deuteride compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CH_2CH_3)D]$ at 65 ºC showed the appearance of a new peak in the ^2H NMR spectrum at δ 0.98 ppm, concomitant with a decrease in intensity of the peak corresponding to the metal deuteride. After heating for 125 h, a second resonance appeared in the ^2H NMR spectrum at δ 0.81 ppm. After *ca.* 500 h, the relative intensity of the resonances at δ 0.98 and 0.81 ppm was found to be *ca.* 3:2 and on this basis were assigned to deuterium bound in the β- and α-positions of the ethyl ligand respectively. It should be noted however that the chemical shifts of the new peaks reported in the ^2H NMR spectrum are significantly different to the peaks due to the β-methyl and α-methylene protons in the ^1H NMR spectrum of the compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CH_2CH_3)D]$, which are found at δ 1.58 ppm and 1.12 ppm respectively. These assignments, which must be treated with caution, imply that deuterium scrambles faster into the β-position than the α-position. Such a situation is unexpected in the light of the scrambling processes studied in the related compounds described above, where the intermediacy of an alkane σ-complex is proposed. In particular the conclusions were in contrast to scrambling in the compound $[Rh(\eta-C_5Me_5)PMe_3(^{13}CH_2CH_3)D]$ where deuterium is incorporated into the α-position faster than into the β-position (**Section 3.4**). A tentative mechanism for hydrogen scrambling in $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CH_2CH_3)D]$ involving the alkene complex intermediate $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}H(D)(CH_2CH_2)]$ has been proposed.[27]

The aims of this chapter were two-fold. The primary aim was to exploit the *ansa*-effect with regard to the increased stability imparted on tungstenocene alkyl hydride compounds towards reductive alkane elimination and prepare and isolate the first examples of stable, long chain n-alkyl hydride compounds $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}H]$ (n > 2). A second aim was to prepare isotopically labelled derivatives of these compounds in order to investigate hydrogen scrambling processes between alkyl ligand and hydride sites in these compounds. This area is of particular interest given the unexpected observations detailed above for the compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CH_2CH_3)D]$.

3.6.2 Preparation of Group 6 *ansa*-Metallocene di-n-Alkyl and n-Alkyl Halide Compounds

3.6.2.1 Preparation of $[Zn\{(CH_2)_nCH_3\}_2]$ (n = 1-4)

The *ansa*-metallocene di-alkyl $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}_2]$ (n = 0, 1) compounds are prepared by the reaction between $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ and $[Zn\{(CH_2)_nCH_3\}_2]$ (n = 0, 1).[26, 27] The di-n-propyl zinc reagent $[Zn\{(CH_2)_2CH_3\}_2]$ was prepared in a two step procedure (**Scheme 3.1**). Addition of 1-chloro-n-propane to activated magnesium turnings in diethyl ether gives the n-propyl Grignard reagent $[MgCl\{(CH_2)_2CH_3\}]$ in a vigorous reaction. Subsequent addition of anhydrous zinc chloride prior to removal of volatiles affords $[Zn\{(CH_2)_2CH_3\}_2]$ as a pyrophoric colourless liquid in 28 % yield.

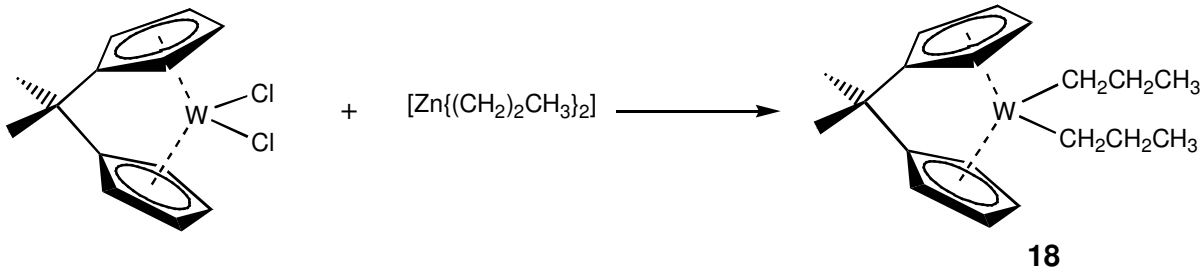


Scheme 3.1 Synthesis of $[Zn\{(CH_2)_nCH_3\}_2]$ (n = 2-5)

The corresponding n-butyl, n-pentyl and n-hexyl reagents were prepared in an analogous procedure to give $[Zn\{(CH_2)_3CH_3\}_2]$, $[Zn\{(CH_2)_4CH_3\}_2]$ and $[Zn\{(CH_2)_5CH_3\}_2]$ in 42 %, 61 % and 85 % yield respectively. The increased yields as the alkyl chain is lengthened can be attributed to the synthetic procedure employed for these compounds, where the compounds $[Zn\{(CH_2)_nCH_3\}_2]$ were freed from volatiles under reduced pressure.

3.6.2.2 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}_2]$ (18)

The n-propyl di-alkyl complex $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}_2]$ **(18)** was prepared by the reaction between $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$[26] and $[Zn\{(CH_2)_2CH_3\}_2]$ in toluene at low temperature (**Scheme 3.2**). After stirring overnight at room temperature unreacted $[Zn\{(CH_2)_2CH_3\}_2]$ was cautiously hydrolysed by the addition of H_2O, prior to passing down an alumina column with toluene. The compound **18** was extracted into pentane and isolated as a yellow crystalline solid in 44 % yield on cooling to -80 ºC.



18

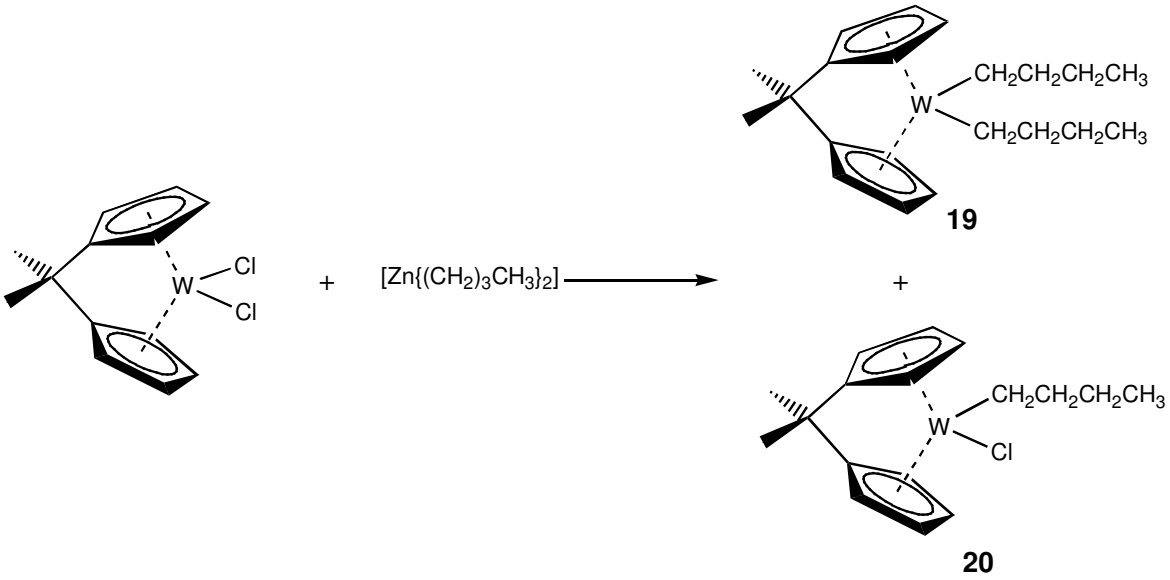
Scheme 3.2 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}_2]$ **(18)**

The compound **18** was characterised by elemental analyis, FAB mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The FAB mass spectrum of the compound **18** shows peaks due to the molecular ion and a fragment peak corresponding to the loss of the n-propyl ligands.

The ^1H NMR spectrum of the compound **18** consists of the expected pair of partial triplets at δ 4.28 and 4.19 ppm corresponding to the two sets of protons of the cyclopentadienyl ring. Three peaks due to the protons of the n-propyl ligands are present. A multiplet at δ 1.45 ppm, a triplet at δ 1.21 ppm and a triplet at δ 0.55 ppm corresponding to the methylene protons of the β-carbon, the methyl protons of the γ-carbon and the methylene protons of the α-carbon respectively. Assignments were confirmed by a ^1H-^1H NMR COSY experiment. As expected the protons of the carbon nearest the metal are found at high field relative to the other protons of the alkyl ligand. The protons of the CMe_2 bridge occur as a singlet at δ 0.43 ppm. The $^{13}C\{^1H\}$ NMR spectrum is straightforward and not discussed here.

3.6.2.3 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}$_2$] (19) and [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}Cl] (20)

Treatment of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}Cl_2] with [Zn{$(CH_2)_3CH_3$}$_2$] in toluene at low temperature affords a mixture of the compounds [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}$_2$] **(19)** and [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}Cl] **(20)** (**Scheme 3.3**). The yellow di-n-butyl compound **19** and the corresponding pale red n-butyl chloride compound **20** can be conveniently separated by fractional recrystallisation from a 1:1 toluene/pentane solution in 16 and 41 % yield respectively.



Scheme 3.3 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}$_2$] **(19)** and [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}Cl] **(20)**

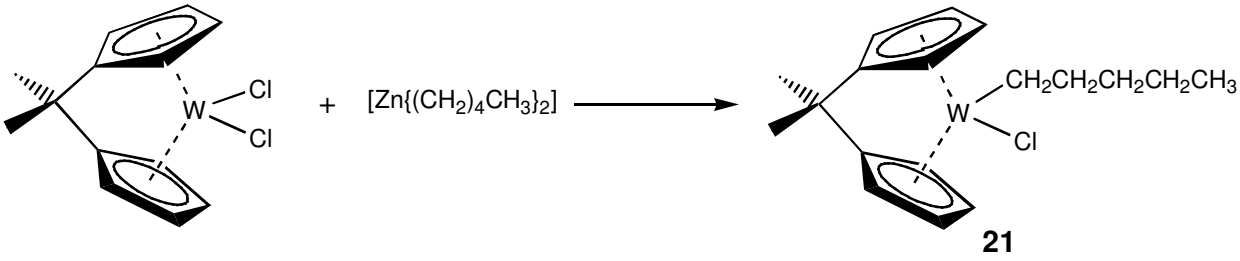
The compound **19** was characterised by elemental analysis, FAB mass spectrometry and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The FAB mass spectrum of the compound **19** shows peaks due to the molecular ion and fragmentation products arising from the consecutive loss of the two n-butyl groups. Of particular note in the ^{1}H NMR spectrum are the peaks due to the protons of the n-butyl group. A broad resonance at δ 1.52 ppm corresponds to the methylene protons in the β- and γ-positions relative to the metal. A triplet at δ 1.16 ppm and a distorted triplet at δ 0.56 ppm correspond to the methyl protons in the δ-position and the α-methylene protons respectively. Assignments were confirmed by a ^{1}H-^{1}H NMR COSY experiment.

The compound **20** was also fully characterised. Elemental analyses were consistent with the proposed empirical formulae. The FAB mass spectrum of the compound **20** show peaks due to the molecular ion and fragmentation products arising from the loss of chloride and n-butyl ligands.

Two different ligands bound to the metallocene render the four protons of the cyclopentadienyl rings inequivalent. Four peaks in the ^{1}H NMR spectrum of the compound **20** at δ 5.20, 4.71, 4.68 and 3.96 ppm are assigned to the ring protons. A pair of multiplets at δ 1.55 and 1.37 ppm correspond to protons in the γ- and β-positions respectively, while a distorted triplet at δ 1.31 ppm is assigned to the protons in the α-position. Distortion of the triplet is due to coupling to ^{183}W (I = ½). The methyl protons in the δ position occur as a triplet at δ 1.15 ppm. Assignments were confirmed by a ^{1}H-^{1}H NMR COSY experiment. Unexpectedly the peak due to the protons in the α-position relative to the metal is not the highest field resonance of the peaks due to the n-butyl ligand. In the analogous compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}$(CH_2CH_3$}I] the peak due to the α-methylene protons is also found at low field relative to the β-methyl protons.[27]

3.6.2.4 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_4CH_3$}Cl] (21)

The n-pentyl chloride compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_4CH_3$}Cl] **(21)** was prepared by the reaction between [W{(η–C_5H_4)CMe_2(η–C_5H_4)}Cl_2] and [Zn{$(CH_2)_4CH_3$}$_2$] in an analogous procedure to that employed to prepare the compounds **18-20** (**Scheme 3.4**). The compound **21** is obtained as a pale orange/red solid in 29 % yield following passage in diethyl ether down a column packed with activated alumina. The corresponding di-n-pentyl compound [W{(η–C_5H_4)CMe_2(ηC_5H_4)}{$(CH_2)_4CH_3$}$_2$] was isolated as a minor product (*ca.* 1 %) from the reaction mixture *via* extraction into pentane and cooling to -80 ºC. The compound [W{(η–C_5H_4)CMe_2(ηC_5H_4)}{$(CH_2)_4CH_3$}$_2$] was characterised by ^{1}H NMR spectroscopy only.



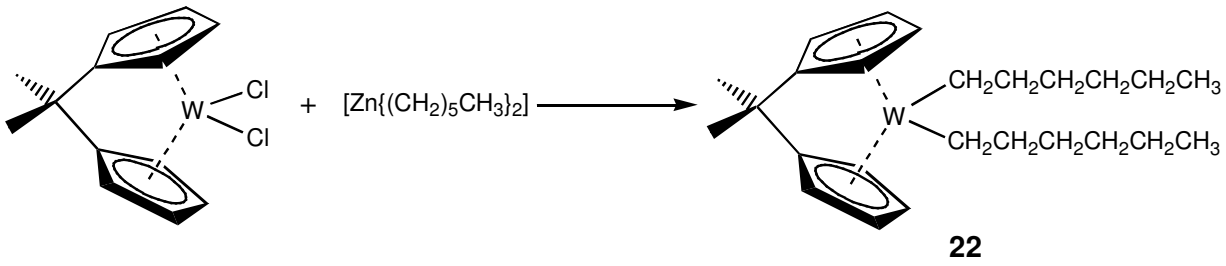
21

Scheme 3.4 Preparation [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_4CH_3$}Cl] **(21)**

The compound **21** was characterised by elemental analysis, FAB mass spectrometry and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The FAB mass spectrum of the compound **21** shows peaks due to the molecular ion and a fragmentation product arising from the loss of the n-pentyl ligand. A ^1H-^1H NMR COSY experiment allows the assignation of five peaks in the region δ 1.55 - 1.11 ppm to the hydrogens in the five positions of the n-pentyl group relative to the metal. As observed for the compound **20**, the resonance due to the protons in the α-position (δ 1.29 ppm) is found at low field relative to the resonance due to protons in the terminal methyl position (δ 1.11 ppm) .

3.6.2.5 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_5CH_3$}$_2$] (22)

The di-n-hexyl compound [W{(η–C_5H_4)CMe_2(ηC_5H_4)}{$(CH_2)_5CH_3$}$_2$] **(22)** was prepared by the reaction between [W{(η–C_5H_4)CMe_2(η–C_5H_4)}Cl_2] and [Zn{$(CH_2)_5CH_3$}$_2$] in an analogous procedure to that employed to prepare the compounds **18-21** (**Scheme 3.5**). The compound **22** was obtained as a yellow solid in 29 % yield following passage in toluene down a column packed with activated alumina prior to recrystallisation from a pentane solution.



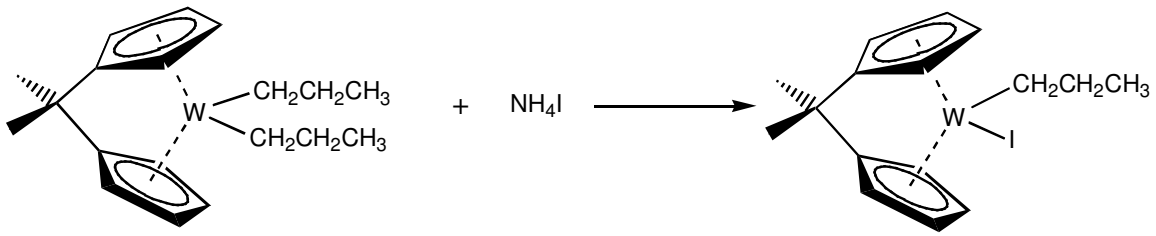
22

Scheme 3.5 Preparation [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_5CH_3$}$_2$] **(22)**

The compound **22** was characterised by elemental analysis, FAB mass spectrometry and ^{1}H and ^{13}C{^{1}H} NMR spectroscopy. The FAB mass spectrum of the compound **22** shows peaks due to the molecular ion and a fragmentation product arising from the consecutive loss of the n-hexyl ligands. A broad multiplet resonance centred at δ 1.52 ppm is assigned to the protons in the β–ε positions. A triplet at δ 1.06 ppm and a distorted triplet at δ 0.58 ppm correspond to the terminal methyl protons and the methylene protons in the α-position respectively. Again assignments were confirmed by a ^{1}H-^{1}H NMR COSY experiment.

3.6.2.6 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_2CH_3$}I] (23)

Reaction of the compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_2CH_3$}$_2$] **(18)** with NH_4I in THF at 65 ºC affords the compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_2CH_3$}I] **(23)** as a pale red solid in 47 % yield (**Scheme 3.6**).



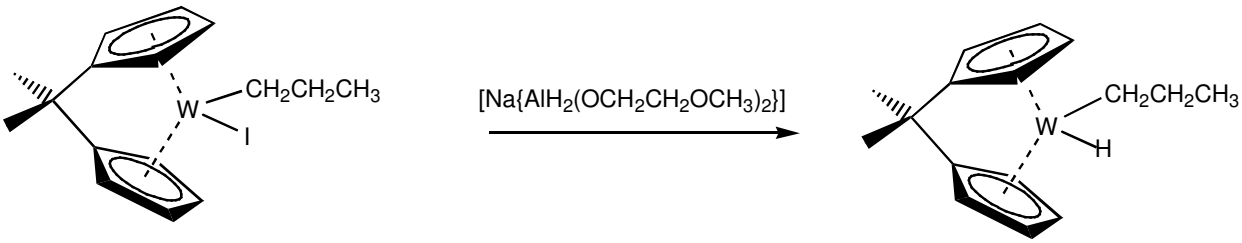
18 **23**

Scheme 3.6 Preparation [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_2CH_3$}I] **(23)**

Elemental analyses and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectra were fully consistent with the product $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_2CH_3\}I]$ **(23)**. The FAB mass spectrum of the compound **23** shows a peak due to the molecular ion and a fragmentation product corresponding to the loss of the n-propyl ligand.

3.6.3 Preparation of $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ (n = 2 (24), 3 (25), 4 (26))

The reduction of metal halides by sodium *bis*(2-methoxyethoxy)aluminium hydride, $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$, to give the corresponding metal hydride compound was reported in 1979 when $[W(\eta\text{–}C_5H_5)_2(CH_3)I]$ was treated with $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ to give $[W(\eta\text{–}C_5H_5)_2(CH_3)H]$.[9] The *ansa*-metallocene alkyl hydride species $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ (n = 0, 1) were similarly prepared from the corresponding alkyl iodide compounds.[26, 27] In an analogous procedure the compound $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_2CH_3\}I]$ **(23)** was treated 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 $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_2CH_3\}H]$ **(24)** as a yellow crystalline solid in 50 % yield (**Scheme 3.7**).

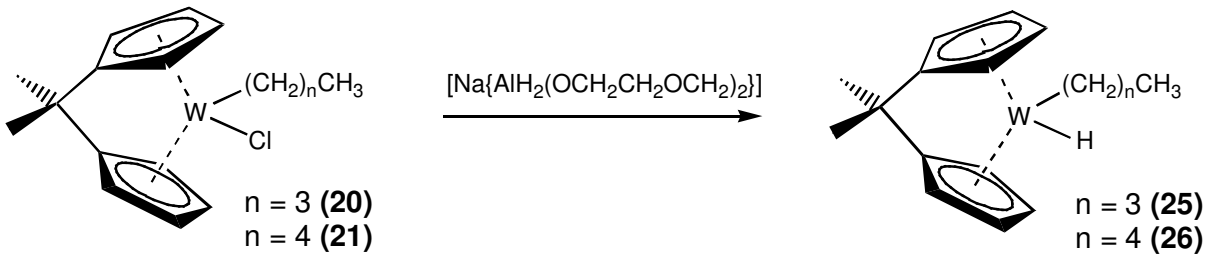


23 **24**

Scheme 3.7 Preparation $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_2CH_3\}H]$ **(24)**

The compound **24** was characterised by elemental analysis and ^{1}H and $^{13}C\{^{1}H\}$ NMR spectroscopy. A multiplet at δ 1.36 ppm, a triplet at δ 1.13 ppm and a distorted triplet at δ 1.04 ppm are assigned to the β-methylene protons, the γ-methyl protons and the α-methylene protons of the n-propyl ligand respectively, as confirmed by a ^{1}H-^{1}H NMR COSY experiment. A singlet at δ -6.47 ppm is assigned to the hydride ligand. Associated with this singlet are characteristic ^{183}W (I = ½) satellites ($^{1}J_{WH}$ = 50 Hz).

The analogous n-butyl 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 **(25),** 4 **(26)**) were prepared in an analogous procedure by the reaction between the corresponding n-alkyl halide compounds $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_nCH_3\}Cl]$ (n = 3 **(20),** 4 **(21)**) and $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ (**Scheme 3.8**). The compounds **25** and **26** were isolated as yellow crystalline solids in 42 and 49 % respectively.



Scheme 3.8 Preparation $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_nCH_3\}H]$ (n = 3 **(25)**, 4 **(26)**)

The compounds **25** and **26** were characterised by elemental analysis and ^1H and $^{13}C\{^1H\}$ NMR spectroscopy. The n-pentyl hydride compound **26** was further characterised by FAB mass spectrometry. ^1H-^1H NMR COSY spectroscopy allowed assignation of the peaks due to the protons of the n-alkyl ligands. In the n-butyl hydride compound **25** two multiplet resonances at δ 1.45 and 1.36 ppm correspond to the methylene protons in the γ- and β-positions respectively. A triplet at δ 1.11 ppm is assigned to the methyl protons in the terminal δ-position, while a distorted triplet at δ 1.02 ppm corresponds to the methylene protons in the α-position.

The isolation and 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 **(24)**, 3 **(25)**, 4 **(26)**) in both the solid state and in solution reflect the increased stability of Group 6 metallocenes with respect to reductive alkane elimination upon the introduction of a single carbon *ansa*-bridge.

3.6.4 Reaction between $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{(CH_2)_nCH_3\}X]$ (X = I, n = 2 (23); X = Cl, n = 3 (20), 4 (21),) and $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$

In order to study hydrogen exchange process between alkyl and hydride ligands in n-alkyl hydride species it was necessary to prepare appropriately isotopically labelled

compounds, namely $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}D]$. Souter reported that the reaction between $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CH_2CH_3\}I]$ and $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ gave a mixture of the desired ethyl deuteride species $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CH_2CH_3\}D]$ and the partially ring-deuterated alkyl hydride species $[W\{(\eta-C_5H_{4-x}D_x)CMe_2(\eta-C_5H_{4-x}D_x)\}\{CH_2CH_3\}H]$.[27] In addition to a mechanism involving direct attack of deuteride at the metal centre to give the ethyl deuteride compound a competing reaction is taking place. A possible mechanism for ring deuteration has been proposed by Norton and is presented in **Figure 3.8**.[10] The alkyl halide species is in equilibrium with an ion pair. The cationic metallocene species is susceptible to *exo* attack of deuteride at the cyclopentadienyl rings followed by *endo* transfer of hydride onto the metal.

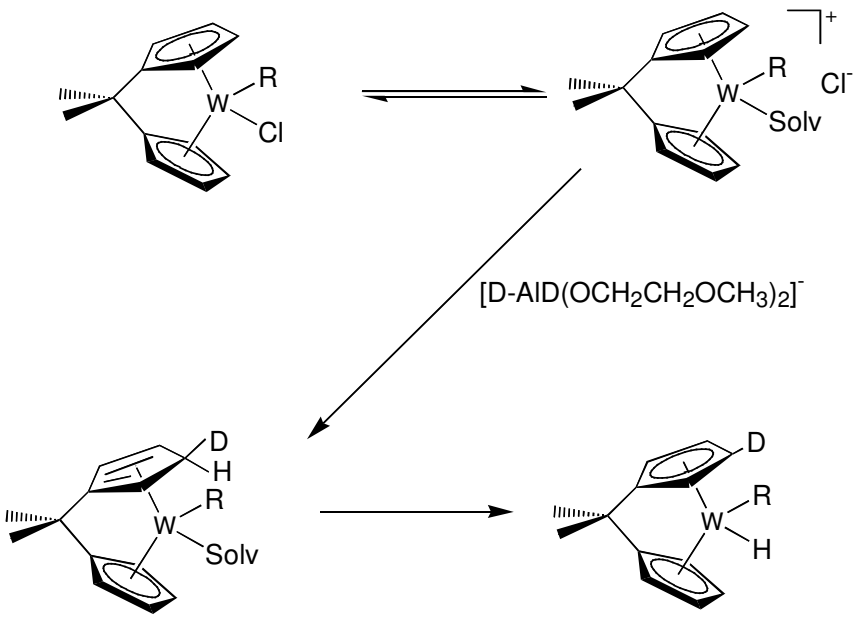


Figure 3.8 Possible mechanism for ring deuteration in $[W\{(\eta-C_5H_{4-x}D_x)CMe_2(\eta-C_5H_{4-x}D_x)\}(R)H]$

Reaction between the n-alkyl halides species $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}X]$ (X = I, n = 2 (**23**); X = Cl, n = 3 (**20**), 4 (**21**)) and $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ results in the formation of ring-deuterated n-alkyl

hydride species $[W\{(\eta-C_5H_{4-x}D_x)CMe_2(\eta-C_5H_{4-x}D_x)\}\{(CH_2)_nCH_3\}H]$ only, as confirmed by ^1H and ^2H NMR spectroscopy. None of the desired alkyl deuteride species $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}D]$ were observed, implying that as the length of the n-alkyl chain is increased from ethyl to n-propyl and longer, direct attack of deuteride at the metal centre is disfavoured compared to *exo* attack at one of the cyclopentadienyl rings.

Various alternative routes to the desired compounds $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}H]$ were investigated although none were successful. For example, deprotonation of the compounds $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_nCH_3\}H]$ with KH in the presence of 18-crown-6, followed by quenching with D_2O, failed to give a tractable product. Alternative deuteride reagents such as $NaBD_4$ or $LiBEt_3D$ gave only ring deuterated n-alkyl hydride species. Experimental difficulties were exacerbated by the availability of the alkyl hydride compounds in small, typically 20-40 mg, quantities.

3.7 Preparation of Perdeuterated *ansa*-Metallocenes

3.7.1 Introduction

The problem of the ring-deuteration reaction leading to the formation of alkyl hydride rather than the desired alkyl deuteride species can be overcome if the cyclopentadienyl rings are deuterated. Then *endo* migration from the rings to the metal centre will result in the formation of alkyl deuteride species. It was therefore decided to prepare perdeuterated *ansa*-metallocene alkyl halides $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}X]$ (n = 1-4; X = Cl, I) with a view to synthesising the corresponding alkyl deuteride compounds, thus facilitating an investigation of intramolecular H/D scrambling.

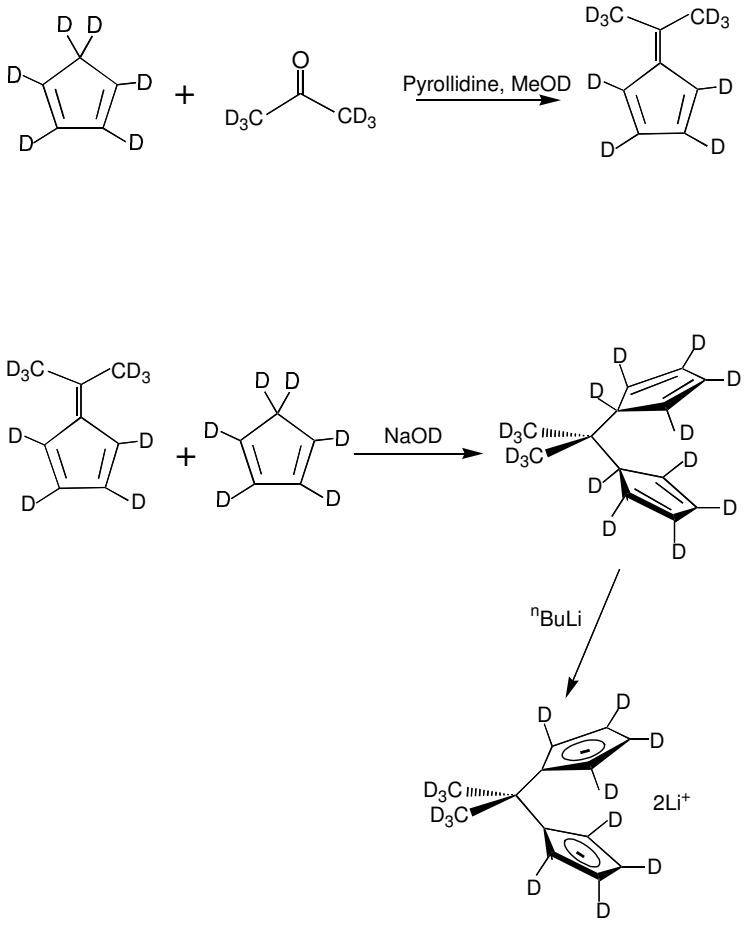
3.7.2 Preparation of d^6-Cyclopentadiene

Perdeuterated cyclopentadiene is prepared by the reaction of freshly distilled cyclopentadiene monomer with NaOD in a mixture of D_2O/DMSO at 0 ºC. After 1 h the cyclopentadiene monomer is removed from the reaction mixture and transferred into a

flask containing fresh NaOD in D_2O/DMSO. After 5 exchanges the extent of deuteration was determined to be 94 %, with a 40 % yield of d^6-cyclopentadiene.

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

The perdeuterated *ansa*-ligand $[Li_2\{(C_5D_4)C(CD_3)_2(C_5D_4)\}]$ was prepared by a modified procedure to that used to prepare the analogous protio *ansa*-ligand $[Li_2\{(C_5H_4)CMe_2(C_5H_4)\}]$ (**Scheme 3.9**).[30]



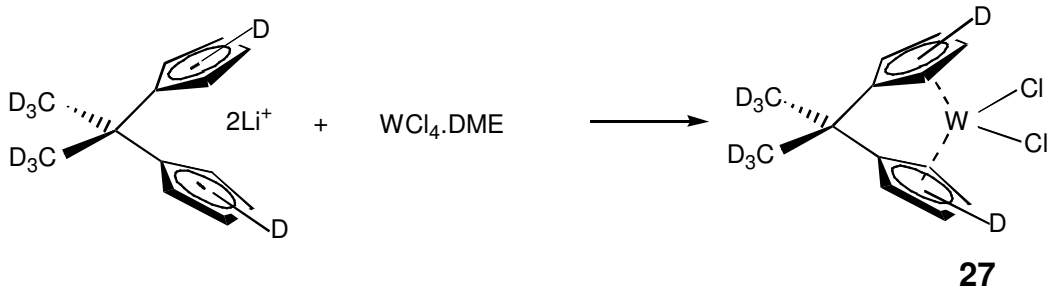
Scheme 3.9 Preparation of $[Li_2\{(C_5D_4)C(CD_3)_2(C_5D_4)\}]$

Reaction between d^6-cyclopentadiene monomer and d^6-acetone in d^1-methanol, in the presence of pyrollidine, gives d^{12}-6, 6-dimethylfulvene as an orange liquid (95 % D). Deprotonation of d^6-cyclopentadiene monomer with NaOD in THF affords sodium d^5-cyclopentadienide as a pale pink suspension. To this suspension is added d^{12}-6, 6-dimethylfulvene which, following work up, gives $[(C_5D_5)C(CD_3)_2(C_5D_5)]$ (93 % D) as a

pale yellow oil. Addition of a solution of ^{n}BuLi in light petroleum ether (b.p. 40 – 60 ºC) at low temperature affords the ligand $[Li_2\{(C_5D_4)C(CD_3)_2(C_5D_4)\}]$ (95 % D) as a flocculent white solid.

3.7.4 Preparation of $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}Cl_2]$ (27)

The perdeuterated *ansa*-metallocene dichloride compound $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}Cl_2]$ **(27)** is prepared by the reaction between WCl_4.DME and $[Li_2\{(C_5D_4)C(CD_3)_2(C_5D_4)\}]$ in diethyl ether in an analogous procedure to that used to prepare the protio compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ (**Scheme 3.10**). The compound **27** was characterised by ^{2}H NMR spectroscopy and by its subsequent reactions. From subsequent reactions of the compound **27** the extent of deuteration of the metallocene fragment was determined to be 95 %.

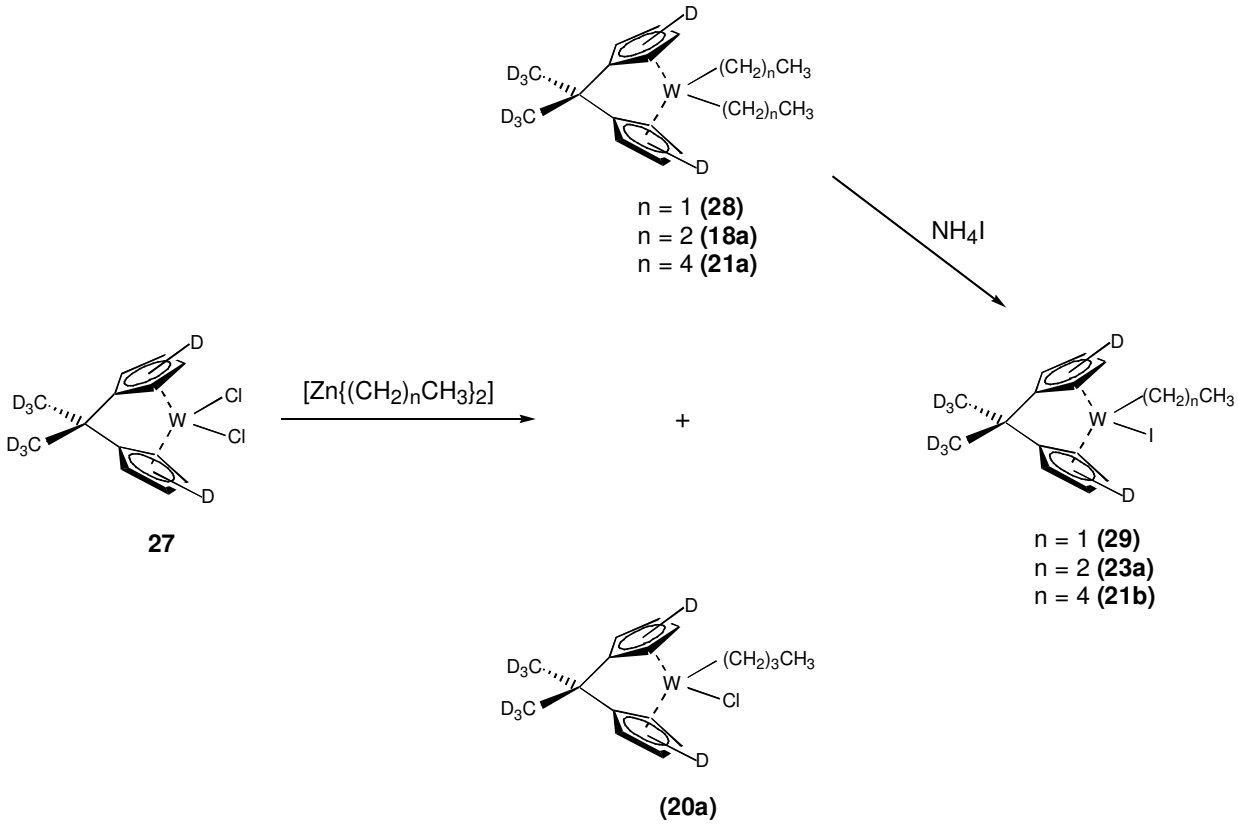


Scheme 3.10 Preparation of $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}Cl_2]$ **(27)**

3.7.5 Preparation of Perdeuterated *ansa*-Metallocene n-Alkyl Compounds

The preparation of the perdeuterated di-n-alkyl compounds $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}_2]$ (n = 1 **(28)**, 2 **(18a)**, 4 **(21a)**) and the n-alkyl halide compounds $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}X]$ (X = I, n = 1 **(29)**, n = 2 **(23a)**, n = 4 **(21b)**; X = Cl, n = 3 **(20a)**) is summarised in **Scheme 3.11**. The ethyl compounds **28** and **29** were prepared by an analogous procedure to that used for the protio-compounds $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CH_2CH_3\}_2]$ and $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CH_2CH_3\}I]$.[27] The higher n-alkyl compounds **18a**, **20a**,

21a, **21b** and **23a** were prepared by analogous procedures to those described for the preparation of the corresponding protio-compounds in **Section 3.6.2**. Due to the small amount of compounds prepared and the fact that all corresponding protio-compounds have been fully characterised, the perdeuterated *ansa*-metallocenes described in this chapter have been characterised by ^{1}H and ^{2}H NMR spectroscopy only. The extent of deuteration of the metallocene fragment in all compounds was 95 %.

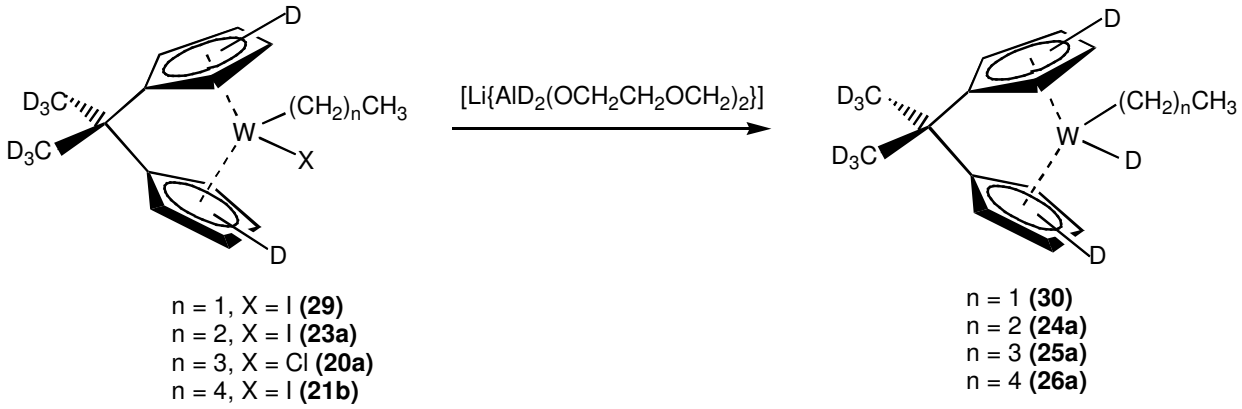


Scheme 3.11 Preparation of $[W\{(\eta\text{–}C_5D_4)C(CD_3)_2(\eta\text{–}C_5D_4)\}\{(CH_2)_nCH_3\}_2]$ (n = 1 **(28)**, 2 **(18a)**, 4 **(21a)**) and $[W\{(\eta\text{–}C_5D_4)C(CD_3)_2(\eta\text{–}C_5D_4)\}\{(CH_2)_nCH_3\}X]$ (X = I, n = 1 **(29)**, 2 **(23a)**, 4 **(21b)**; X = Cl, n = 3 **(20a)**)

3.7.6 Preparation of $[W\{(\eta\text{–}C_5D_4)C(CD_3)_2(\eta\text{–}C_5D_4)\}\{(CH_2)_nCH_3\}D]$ (n = 1 (30), 2 (24a), 3 (25a), 4 (26a))

Addition of $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$ to a solution of $[W\{(\eta\text{–}C_5D_4)C(CD_3)_2(\eta\text{–}C_5D_4)\}\{CH_2CH_3\}I]$ **(29)** in toluene at low temperature affords a pale yellow solution. Hydrolysis with D_2O prior to extraction into pentane yields the ethyl

deuteride compound $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}D]$ **(30)** as a yellow crystalline solid (**Scheme 3.12**).



Scheme 3.12 Preparation of $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}D]$ (n = 1 **(30)**, 2 **(24a)**, 3 **(25a)**, 4 **(26a)**)

The compound **30** was characterised by ^1H and ^2H NMR spectroscopy. The ^1H NMR spectrum of the compound **30** consists of a triplet and a quartet at δ 1.58 and 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 **30** in C_6H_6 is shown in **Figure 3.9**. The four deuteriums 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 deuteriums 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 alkyl hydride compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CH_2CH_3\}H]$ the hydride resonance is found at δ -6.46 ppm.[27]

The higher n-alkyl deuteride compounds $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}D]$ (n = 2 **(24a)**, 3 **(25a)**, 4 **(26a)**) were prepared by the reaction between $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}X]$ (X = I, n = 2 **(23a),** 4 **(21b)**; X = Cl, n = 3 **(20a)**) and $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$. Again all compounds were obtained as pale yellow solids and characterised by ^1H and ^2H NMR spectroscopy. It is noted that for all the n-alkyl deuterides there is no evidence of

intramolecular hydrogen scrambling between alkyl and hydride positions at room temperature.

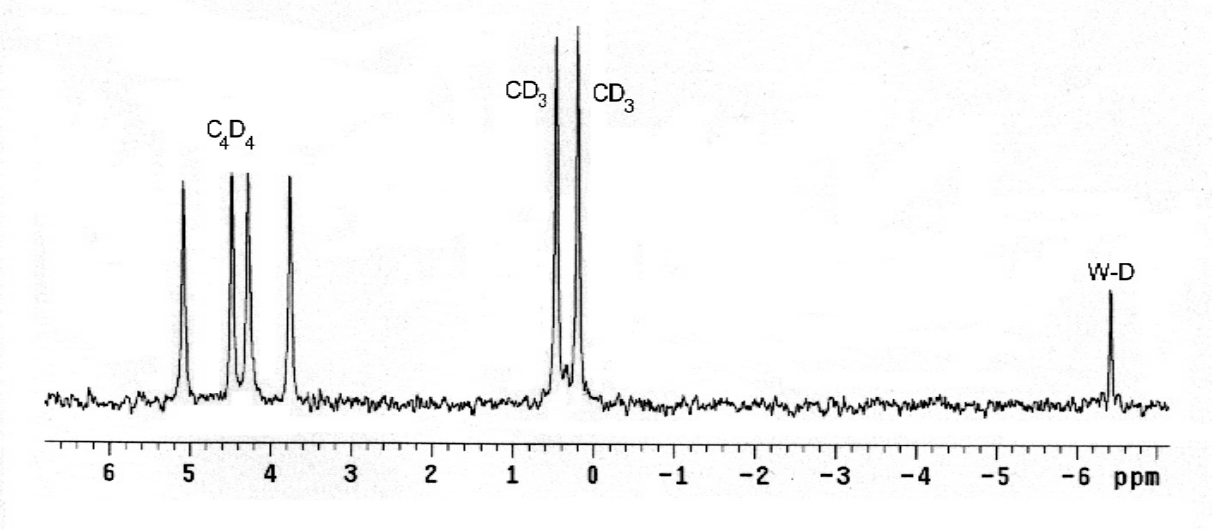


Figure 3.9 ^{2}H NMR spectrum of the compound $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}D]$ **(30)** in C_6H_6

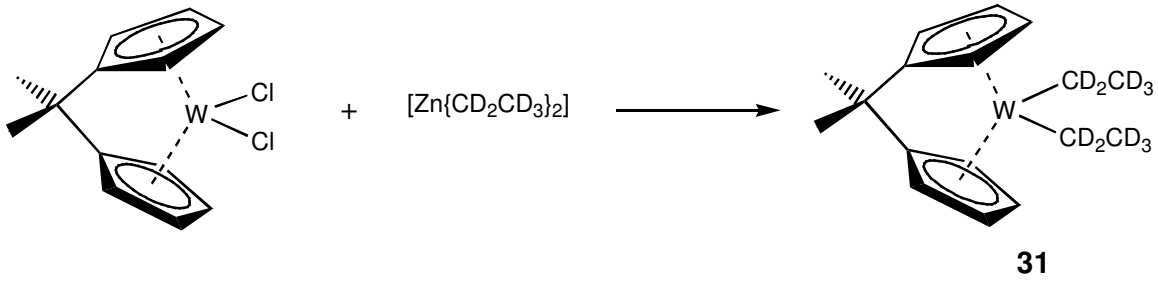
3.8 Preparation of *ansa*-Tungstenocene Perdeutero-n-Alkyl Hydrides

3.8.1 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CD_2CD_3\}_2]$ (31)

An alternative approach by which to study hydrogen scrambling in *ansa*-metallocene n-alkyl hydride compounds is to prepare species in which the n-alkyl group is isotopically substituted i.e. $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CD_2)_nCD_3\}H]$. Souter has studied the hydrogen scrambling process in $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CD_3)H]$ and shown that hydrogen scrambles from the hydride position into the methyl ligand.[27] The problem of competing ring substitution reactions in the synthesis of the alkyl hydride compound is also avoided in this case.

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 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ with a 0.4 M solution of $[Zn\{CD_2CD_3\}_2]$ in toluene gave a dark red suspension from

which the compound $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{CD_2CD_3\}_2]$ **(31)** was isolated (**Scheme 3.13**).



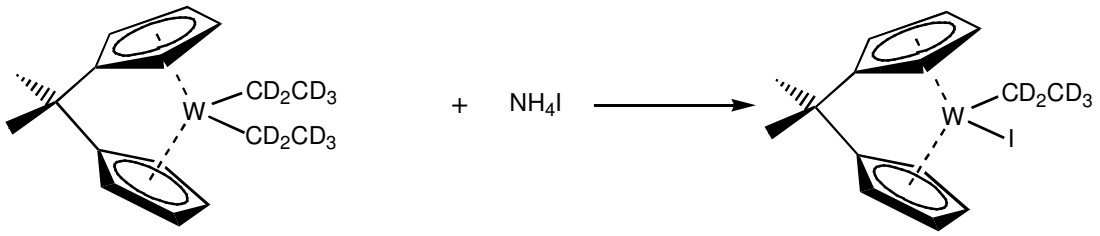
31

Scheme 3.13 Preparation of $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{CD_2CD_3\}_2]$ **(31)**

The compound **31** was characterised by ^1H and ^2H NMR spectroscopy. The ^2H NMR spectrum shows two peaks at δ 1.60 and 0.62 ppm corresponding to the β-methyl and α-methylene protons of the ethyl ligands respectively.

3.8.2 Preparation of [W{(η–C5H4)CMe2(η–C5H4)}{CD2CD3}I] (32)

Reaction of the compound $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{CD_2CD_3\}_2]$ **(31)** with NH_4I in THF at 65 ºC gives the compound $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{CD_2CD_3\}I]$ **(32)** as a pale red solid in 47 % yield (**Scheme 3.14**). ^1H and ^2H NMR spectra are fully consistent with the proposed product

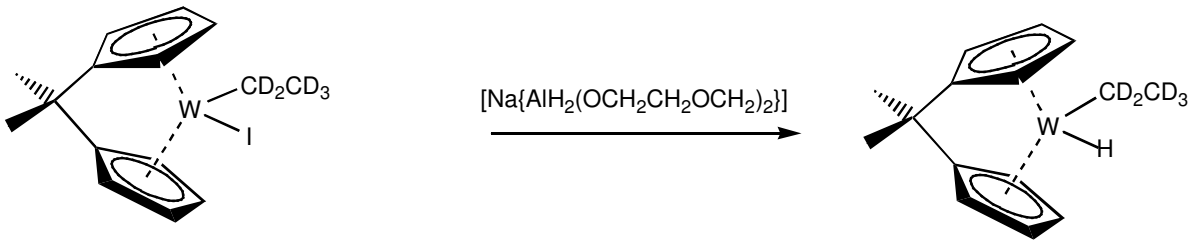


31 **32**

Scheme 3.14 Preparation $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}\{CD_2CD_3\}I]$ **(32)**

3.8.3 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}H] (33)

The compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}I] **(32)** 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] **(33)** as a yellow crystalline solid (**Scheme 3.15**).



32 **33**

Scheme 3.15 Preparation [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}H] **(33)**

The compound **33** was characterised by ^{1}H and ^{2}H NMR spectroscopy. In the ^{1}H NMR spectrum, in addition to four singlets at δ 5.11, 4.48, 4.29 and 3.77 ppm corresponding to the protons 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, a 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 **33** shows two peaks at δ 1.58 and 1.13 ppm corresponding to the methyl and methylene protons of the ethyl group respectively. The spectroscopic data for the compound **33** are in agreement with that reported for the nonsubstituted compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CH_2CH_3}H].[27]

3.9 Thermolysis Studies

3.9.1 Thermolysis of [W{(η−C_5D_4)$C(CD_3)_2$(η−C_5D_4)}{CH_2CH_3}D] (30)

The thermolysis of the ethyl deuteride compound [W{(η−C_5H_4)CMe_2(η−C_5H_4)}{CH_2CH_3}D] has been previously reported and is discussed in **Section 3.6.1**.[27] In this case the compound could not be prepared free of the partially ring deuterated product [W{(η−$C_5H_{4-x}D_x$)CMe_2(η−$C_5H_{4-x}D_x$)}{CH_2CH_3}H] and therefore quantitative kinetic data for the intramolecular hydrogen scrambling processes could not be obtained. The development of the synthesis of perdeutero ansa-metallocenes described in **Section 3.7** has allowed the preparation of n-alkyl deuteride compounds free from such undesired side products. Therefore the behaviour of the ansa-tungstenocene ethyl deuteride compound under thermal conditions has been reinvestigated in a study of the compound [W{(η−C_5D_4)$C(CD_3)_2$(η−C_5D_4)}{CH_2CH_3}D] **(30)**.

A 8 mM solution of the compound **30** in C_6H_6 and a 6 mM solution of the compound **30** in C_6D_6 were prepared and sealed in separate NMR tubes. ^{1}H and ^{2}H NMR spectroscopy shows that at room temperature there is no observable scrambling between alkyl and hydride sites. The samples were heated at 65 °C and ^{1}H and ^{2}H NMR spectra recorded periodically. In the ^{2}H NMR spectrum after *ca.* 8 h, a peak at δ 1.10 ppm appears and grows in over time (**Figure 3.10**). The intensity of the peak due to the tungsten deuteride at δ -6.44 ppm decreases. Inspection of the ^{1}H NMR spectrum shows a decrease in intensity of the quartet at δ 1.12 ppm due to the α-methylene protons compared to the triplet at δ 1.58 ppm corresponding to the β-methyl protons of the ethyl ligand and the internal residual solvent standard. Additionally a peak at δ -6.45 ppm corresponding to a tungsten hydride appears and grows in intensity over time. The spectroscopic data are consistent with scrambling of deuterium between the metal and the α-position of the alkyl group. This is in contrast to that previously reported for [W{(η−C_5H_4)CMe_2(η−C_5H_4)}{CH_2CH_3}D] where scrambling into the β-position is suggested to occur faster than into the α-position.[27]

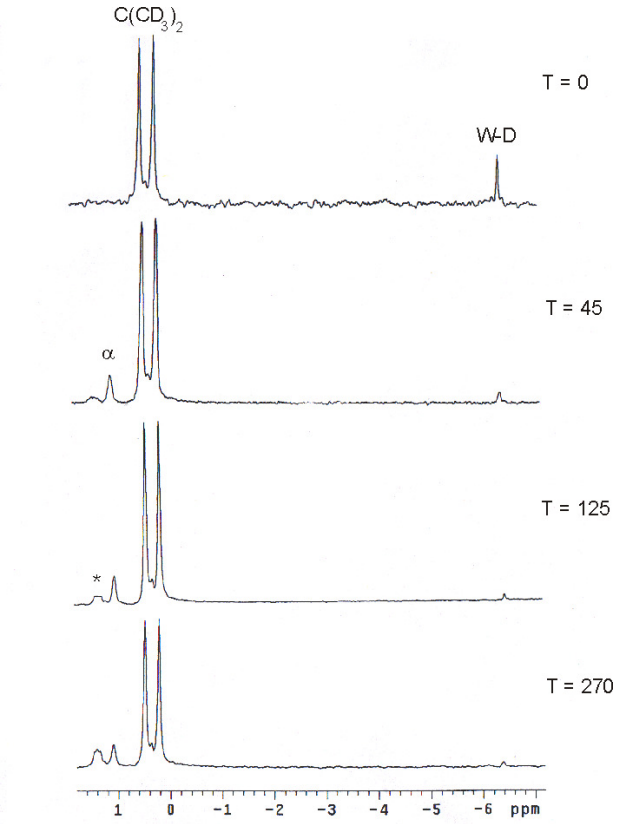


Figure 3.10 Partial ^{2}H NMR spectra of the compound $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}D]$ **(30)** in C_6H_6 at 65 °C (T in h). The peak marked α corresponds to deuterium in the α-methylene position of the ethyl ligand. The peak marked * is due to a decomposition product.

After 45 h there is evidence of decomposition of the compound **30** to one or more other compounds. Firstly in the ^{2}H NMR spectra a number of peaks in the cyclopentadienyl region δ 6.65 – 5.32 ppm and broad peaks at δ 2.71 and 1.38 ppm appear. The peak at δ 1.38 ppm can be seen in **Figure 3.10**. These new peaks grow in intensity over time while the intensity of the peaks due to the compound **30** decrease. A possible decomposition route involves reductive elimination of alkane generating the tungstenocene intermediate $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}]$, similar to that observed in the thermolysis of the analogous nonbridged compounds $[W(\eta\text{-}C_5R_5)_2(CH_3)H]$ (R = H, Me). However, this was ruled out for a number of reasons. Firstly the ^{1}H NMR spectrum of the compound **30** in C_6D_6 showed no evidence of the generation of ethane. Furthermore the tungstenocene intermediate $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}]$ is predicted by theoretical calculations to be highly reactive[28] and thus would be expected to

activate C-H/D bonds of the solvent or C-D bonds of the *ansa*-metallocene fragment of the compound **30**. However there is no evidence in either the ^{1}H or ^{2}H NMR spectra of the compound **30** of the formation of new W-D or W-H containing species. Attempts to identify the nature the new compounds were not successful with efforts hampered by the small quantity of alkyl hydride and deuteride species synthetically available.

No evidence for scrambling of deuterium into the β-position of the ethyl group of the compound **30** was observed. Scrambling of deuterium into this position should be evidenced in the ^{2}H NMR spectrum by a peak growing in at, or close to, δ 1.58 ppm by analogy to the ^{1}H NMR spectrum of the compound **30**. A peak in this region (δ ± 0.15 ppm) was not observed. Kinetic data for the scrambling of deuterium from the metal to the α-position of the ethyl group in the compound **30** compared to related alkyl deuteride species may be instructive. However due to the presence of one or more competing reactions quantitative analysis is not possible.

3.9.2 Thermolysis of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}H] (33)

Thermolysis of the d^5-ethyl hydride compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}H] **(33)** confirms intramolecular hydrogen scrambling between the metal hydride and the α-position of the ethyl ligand and that no scrambling into the β-position is observed. A 10 mM solution of the compound **33** in C_6D_6 was sealed in a NMR tube and heated at 65 °C over a prolonged period with ^{1}H NMR spectra recorded periodically. After 8 h a peak at δ 1.11 ppm appears corresponding to hydrogen in the α-position of the alkyl group. Concomitant with an increase in the intensity of this resonance is a decrease in the intensity of the singlet at δ -6.47 ppm corresponding to the metal hydride.

After heating at 65 °C for 77 h a number of peaks in the cyclopentadienyl region of the spectrum and complex peaks in the region δ 2.65 – 1.35 ppm, presumably corresponding to one or more decomposition products, appear and grow in intensity over time. No peak at, or close to, δ 1.58 ppm is observed implying that scrambling of hydrogen into the β-position of the d^5-ethyl ligand does not occur.

3.9.3 Thermolysis of [W{(η−C_5D_4)$C(CD_3)_2$(η−C_5D_4)}{$(CH_2)_2CH_3$}D] (24a)

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] **(24a)** in C_6H_6 and a 3 mM solution of the compound **24a** in C_6D_6 were prepared and sealed in separate NMR tubes. ^1H and ^2H NMR spectroscopy shows that at room temperature there is no observable scrambling between alkyl and hydride sites. The samples were heated at 65 °C and ^1H and ^2H NMR spectra recorded periodically. In the ^2H NMR spectrum after *ca.* 12 h a peak at δ 1.02 ppm starts to appear as shown in **Figure 3.11** (In the ^1H NMR spectrum of the compound **24a** the peak due to the α-methylene protons is located at δ 1.04 ppm.) This peak grows in intensity over time and the peak due to the intensity of the tungsten deuteride at δ -6.44 ppm decreases. The relative intensity of the peak due to the α-methylene protons in the ^1H NMR spectrum of the compound **24a** decreases compared to the resonance due to the β-methylene and γ-methylene protons of the n-propyl ligand and the internal residual solvent standard. Additionally a peak at δ -6.47 ppm corresponding to a tungsten hydride species grows in intensity. The spectroscopic data are consistent with scrambling of deuterium between the metal and the α-position of the n-propyl group.

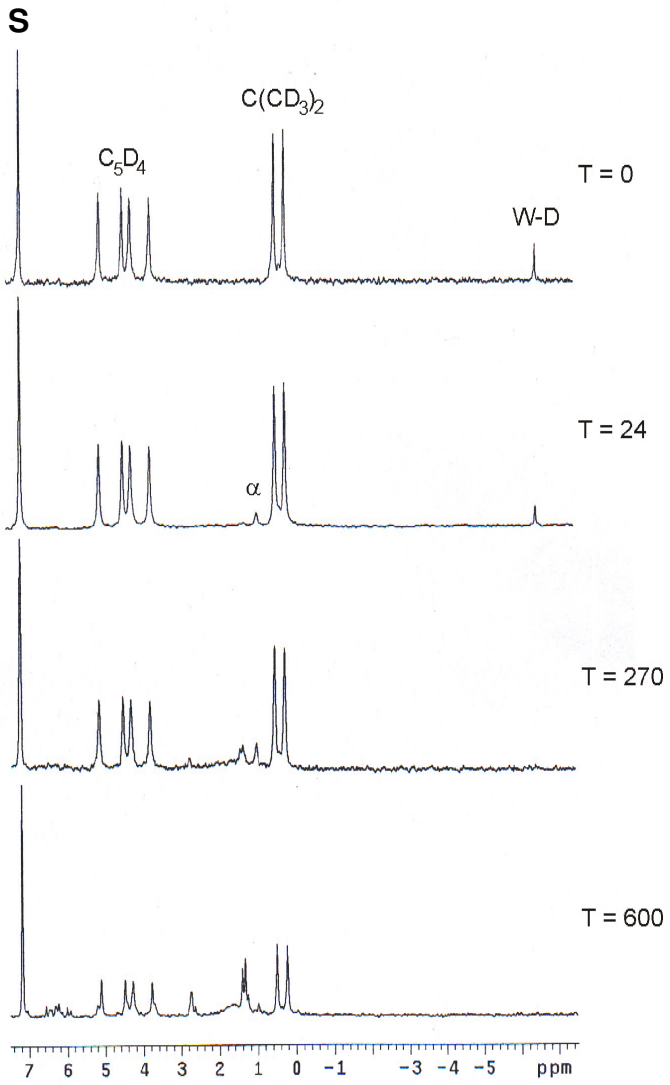


Figure 3.11 ^{2}H NMR spectrum of the compound [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}D] **(24a)** in C_6H_6 at 65 °C (T in h). The peak marked α corresponds to deuterium in the α-methylene position of the n-propyl ligand. S denotes the residual solvent peak.

As for the ethyl deuteride compound **30** one or more new compounds are formed in addition to the α-isomerisation process. Attempts to characterise these compounds were unsuccessful. The rate of scrambling into the α–position is faster than the rate of formation of decomposition products. Again the intensity of peaks due to the parent compound **24a** decreases while new peaks in the cyclopentadienyl region and two broad peaks at δ 2.71 and 1.39 ppm appear (**Figure 3.11**). The broad peak at δ 1.39 ppm obscures the region where a peak due to deuterium in the β–position would be expected

(*ca.* δ 1.37 ppm). However inspection of the relative intensities of the peaks due to the n-propyl ligand of the compound **24a** in the ^{1}H NMR spectrum shows no change in that due to the β-methylene and γ-methyl protons. Attempts to observe C-D coupling in $^{13}C\{^{1}H\}$ NMR spectrum of the compound **24a** were thwarted due to the small quantity of compound synthetically available and thus an inability to obtain spectra with a sufficiently high signal to noise ratio. No new peak is observed in the ^{2}H NMR spectra at, or close to, δ 1.16 ppm suggesting that there is no scrambling into the γ-position of the n-propyl group.

3.9.4 Thermolysis of [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_3CH_3$}D] (25a) and [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_4CH_3$}D] (26a)

As for the analogous ethyl and n-propyl compounds, thermolysis of the n-butyl deuteride compound [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_3CH_3$}D] **(25a)** facilitated scrambling of deuterium into the α-position of the n-butyl group. An 8 mM solution of the compound **25a** in C_6H_6 and a 5 mM solution of the compound **25a** in C_6D_6 were prepared, sealed in separate NMR tubes and heated at 65 °C. In the ^{2}H NMR spectra the resonance due to the tungsten deuteride 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 protons in the α-position 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-scrambling process is faster than the decomposition reaction which gives rise to one of more new compounds, the nature of which could not be determined. No evidence of scrambling into other positions of the n-butyl group is 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] **(26a)** 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 separate sealed NMR tubes. A peak at δ 1.04 ppm appears in the ^{2}H NMR spectra along with a decrease in the resonance due to the tungsten deuteride (δ -6.49 ppm). This scrambling process is accompanied by the formation of one or more decomposition products as for the analogous n-alkyl deuteride compounds described above. No evidence for scrambling into other positions of the n-pentyl chain is observed by ^{1}H and ^{2}H NMR spectroscopy.

3.9.5 Comments

Intramolecular hydrogen scrambling between the metal hydride and α-methylene position of the alkyl ligand in the n-alkyl deuteride compounds $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3)_2D]$ (n = 1-4) and the perdeutero-ethyl hydride compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{CD_2CD_3)_2H]$ has been observed by NMR spectroscopy. Such scrambling has been previously reported for the related compounds $[W(\eta-C_5R_5)_2(CH_3)D]$ (R = H, Me) and $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CH_3)D]$. The results described in this chapter are consistent with a mechanism for intramolecular hydrogen exchange involving an alkane σ-complex intermediate as shown in **Figure 3.12**. Whereas the methyl deuteride compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}(CH_3)D]$ is stable at 120 ºC, the higher n-alkyl deuteride compounds $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3)_2D]$ (n = 1-4) slowly decompose at 65 ºC.

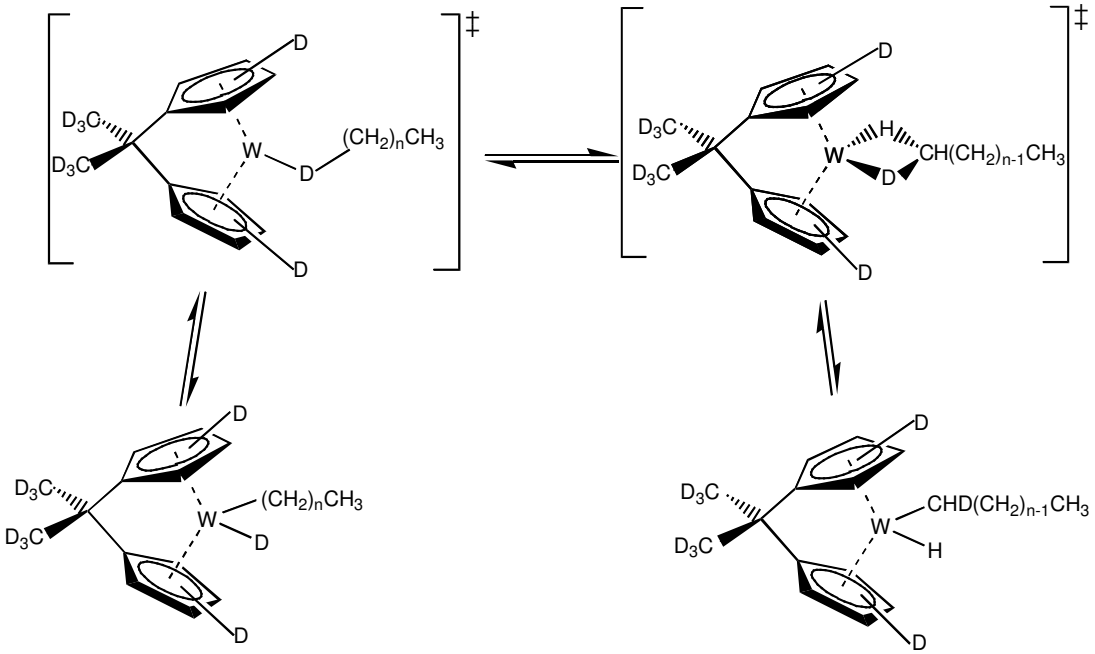


Figure 3.12 Intramolecular hydrogen scrambling in the compounds $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{(CH_2)_nCH_3\}D]$ (n = 1-4) *via* η^1-H and η^2-H,H-σ-complexes

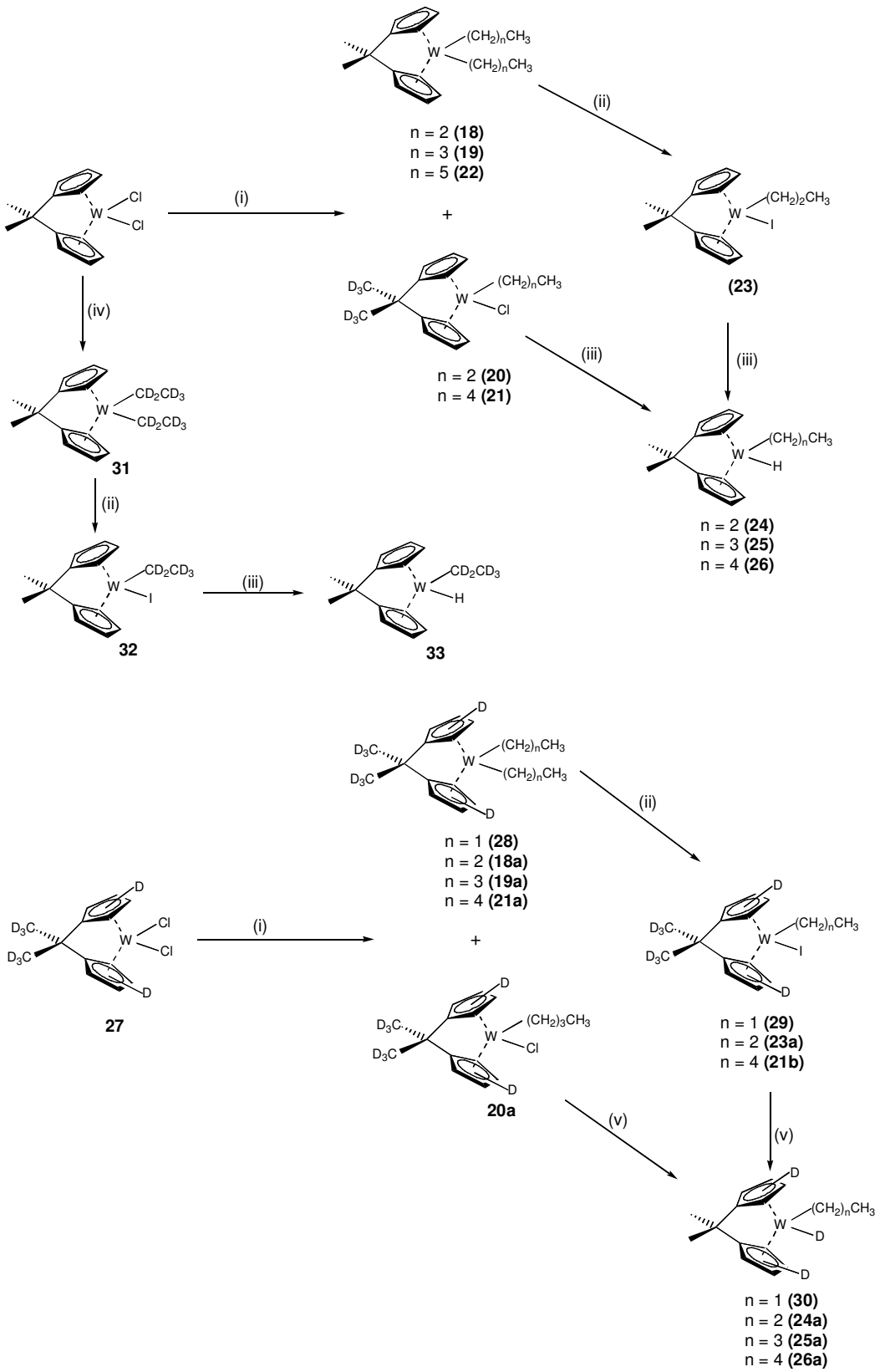
3.10 Summary

This chapter describes the synthesis of new *ansa*-metallocene n-alkyl compounds. The increased stability towards reductive alkane elimination imparted by a constraining single carbon *ansa*-bridge allows the synthesis and isolation of the higher n-alkyl hydride compounds [W{(η−C_5H_4)CMe_2(η−C_5H_4)}{$(CH_2)_nCH_3)_2$H] (n = 2-4).

Attempts to prepare the isotopically labelled n-alkyl deuteride compounds [W{(η−C_5H_4)CMe_2(η−C_5H_4)}{$(CH_2)_nCH_3)_2$D] (n = 1-4) *via* the reaction between the corresponding n-alkyl halide compounds and deuteride reagents such as [Li{$AlD_2(OCH_2CH_2OCH_3)_2$}] yield only the partially ring deuterated species compounds [W{(η−$C_5H_{4-x}D_x$)CMe_2(η−$C_5H_{4-x}D_x$)}{$(CH_2)_nCH_3)_2$H] and none of the desired n-alkyl deuteride compound [W{(η−C_5H_4)CMe_2(η−C_5H_4)}{$(CH_2)_nCH_3)_2$D]. Therefore a synthesis of the perdeuterated *ansa*-metallocene precursor [W{(η−C_5D_4)$C(CD_3)_2$(η−C_5D_4)}Cl_2] has been developed. From this dichloride compound the n-alkyl deuteride compounds [W{(η−C_5D_4)$C(CD_3)_2$(η−C_5D_4)}{$(CH_2)_nCH_3)_2$D] (n = 1-4) have been prepared.

Thermolysis of the n-alkyl deuteride compounds [W{(η−C_5D_4)$C(CD_3)_2$(η−C_5D_4)}{$(CH_2)_nCH_3)_2$D] (n = 1-4) and [W{(η−C_5H_4)CMe_2 (η−C_5H_4)}{$CD_2CD_3)_2$H] shows intramolecular hydrogen exchange between the α-position of the n-alkyl ligand and the metal hydride sites. An exchange process facilitated by an alkane σ-complex is proposed. Exchange into other positions of the n-alkyl ligand is not observed for any of the compounds studied. In contrast to the methyl deuteride compound [W{(η−C_5H_4)CMe_2(η−C_5H_4)}(CH_3)D] which is stable at 120 °C, thermolysis of the higher n-alkyl deuterides at 65 ºC results in slow decomposition. The nature of the decomposition products could not be determined.

The new chemistry described in this chapter is summarised in **Scheme 3.16**.



Conditions (i) $[Zn\{(CH_2)_nCH_3\}_2]$ in toluene. (ii) NH_4I in THF, 65 ºC.
(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.

Scheme 3.16 New chemistry presented in Chapter 3

3.11 References

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