Chapter 5

Experimental Details

5.1 General Details

5.1.1 Techniques

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.[1] 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.

5.1.2 Solvents

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. Solvents were thoroughly degassed by the pump-fill technique followed by re-admission of dinitrogen or by purging with dinitrogen for approximately 15 min. prior to use. 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. D_2O was degassed by purging with dinitrogen for approximately 15 min. prior to use. $CDFCl_2$ was prepared by the literature method.[2]

5.1.3 General Materials

WCl_6 (99 %), $NbCl_5$, $LiAlH_4$ (95 %), $LiAlD_4$ (96 %), $LiBH_4$, $NaBH_4$, $NaBD_4$, 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 ºC)), $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ (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.

5.1.4 Preparation of Starting Materials

$NbCl_4.2THF$,[3] $[Li_2\{(C_5H_4)SiMe_2(C_5H_4)\}]$,[4] $[(MgCl)_2\{(C_5H_4)C_2Me_4(C_5H_4)\}.4THF]$,[5] $[(MgCl)_2\{(C_5H_3\text{-}^tBu)C_2Me_4(C_5H_3\text{-}^tBu)\}.4THF]$,[6] $[Nb\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}Cl_2]$,[7] $[Nb\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}(\eta^2\text{–}BH_4)]$,[7] $[Li_2\{(C_5H_4)C(C_5H_{10})(C_5H_4)\}]$,[8] $[K_2\{(C_5H_4)CMe_2(C_5H_4)\}]$,[7] $[V\{(\eta\text{–}C_5H_4)C_2Me_4(\eta\text{–}C_5H_4)\}Cl_2]$,[9] $WCl_4.DME$,[10] $[W\{(\eta\text{–}C_5H_4)CMe_2(\eta\text{–}C_5H_4)\}Cl_2]$,[8] $[W\{(\eta\text{–}C_5H_4)C_2Me_4(\eta\text{–}C_5H_4)\}Cl_2]$,[11] $[Li\{AlD_2(OCH_2CH_2OCH_3)_2\}]$,[12] d^5-iodoethane[13] and $ReCl_5$[14] were prepared using standard literature methods. $[Li_2\{(C_5H_4)CEt_2(C_5H_4)\}]$ was prepared by the reaction between 6,6-diethylfulvene and freshly distilled cyclopentadiene followed by deprotonation with ^{n}BuLi in a procedure analogous to that used to prepare $[Li_2\{(C_5H_4)CMe_2(C_5H_4)\}]$.[15]

5.1.5 Instrumentation

NMR spectra were recorded out on a Varian Unity*Plus* 500 spectrometer (^{1}H, ^{2}H, ^{13}C and ^{11}B spectra were recorded at 499.868, 76.750, 125.703 and 160.380 MHz respectively). The spectra were referenced internally relative to the residual protio-solvent (^{1}H), residual deutero-solvent (^{2}H) and solvent (^{13}C) resonances relative to tetramethylsilane (^{1}H, ^{2}H, ^{13}C; δ = 0 ppm) or externally to $BF_3.Et_2O$ (^{11}B; δ = 0 ppm). Chemical shifts (δ) are expressed in ppm and coupling constants (J) in Hz.

NMR simulations were performed using the program gNMR.[16]

ESR spectra were recorded in dichloromethane on a Varian E 109 instrument and referenced to DPPH.

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

5.2 Experimental Details for Chapter 2

5.2.1 Preparation of [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}Cl_2] (1)

The two solids $NbCl_4$.2THF (4.0 g, 12.7 mmol) and [$(MgCl)_2${(C_5H_4)C_2Me_4(C_5H_4)}.4THF] (2.86 g, 12.7 mmol) were stirred together in the absence of solvent to give a good admixture. Diethyl ether (80 cm^3) was added and the resulting brown suspension stirred for three days. Volatiles were removed under reduced pressure and the resulting pale brown solid was Soxhlet extracted into dichloromethane over 5 h to yield a deep red/brown solution. Removal of volatiles under reduced pressure followed by washing with pentane (2 × 100 cm^3) afforded the compound [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}Cl_2] **(1)** as a pale brown solid.

Yield of the compound **1** = 3.33 g, 70 %.

5.2.2 Preparation of [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BH_4)] (2)

A mixture of the compound **1** (0.20 g, 0.53 mmol) and $LiBH_4$ (0.05 g, 2.9 mmol) was suspended in DME (30 cm^3) at room temperature. Effervescence was observed on addition of the solvent. The brown reaction mixture was stirred overnight and then volatiles were removed under reduced pressure. The resulting brown solid was extracted into petroleum ether (b. p. 100-120 °C) (2 × 30 cm^3). This dark green solution was concentrated to 25 cm^3 and then cooled to -80 °C, affording the compound [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BH_4)] **(2)** as dark green crystals.

Yield of the compound **2** = 0.12 g, 71 %.

5.2.3 Preparation of [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BD_4)] (3)

A mixture of the compound **1** (0.3 g, 0.79 mmol) and $NaBD_4$ (0.16 g, 3.9 mmol) was suspended in DME (40 cm^3) at room temperature. Effervescence was observed on addition of the solvent. The brown reaction mixture was stirred overnight and then volatiles were removed under reduced pressure. The resulting brown solid was extracted

into petroleum ether (b. p. 100-120 °C) (2 × 40 cm^3). This dark green solution was concentrated to 20 cm^3 and then cooled to -80 °C, affording the compound $[Nb\{(\eta-C_5H_4)C_2Me_4(\eta-C_5H_4)\}(\eta^2-BD_4)]$ **(3)** as dark green crystals.

Yield of the compound **3** = 0.14 g, 55%.

5.2.4 Preparation of $[Nb\{(\eta-C_5H_3\text{-}^tBu)C_2Me_4(\eta-C_5H_3\text{-}^tBu)\}Cl_2]$ (4)

The compound $[Nb\{(\eta-C_5H_3\text{-}^tBu)C_2Me_4(\eta-C_5H_3\text{-}^tBu)\}Cl_2]$ **(4)** was prepared by the reaction between $NbCl_4.2THF$ (2.00 g, 6.4 mmol) and $[(MgCl)_2\{(C_5H_3\text{-}^tBu)C_2Me_4(C_5H_3\text{-}^tBu)\}.4THF]$ (4.67 g, 6.4 mmol) in an analogous procedure to that used to prepare the compound **1** and was obtained as a brown solid.

Yield of the crude product **4** = 2.30 g, 74%.

An analytically pure sample of the compound **4** was obtained by sublimation at 160 °C (10^{-1} mm Hg).

5.2.5 Preparation of $[Nb\{(\eta-C_5H_3\text{-}^tBu)C_2Me_4(\eta-C_5H_3\text{-}^tBu)\}(\eta^2-BH_4)]$] (5)

The compound $[Nb\{(\eta-C_5H_3\text{-}^tBu)C_2Me_4(\eta-C_5H_3\text{-}^tBu)\}(\eta^2-BH_4)]$ **(5)** was prepared by the reaction between the compound **4** (0.17 g, 0.34 mmol) and $LiBH_4$ (0.25 g, 1.3 mmol) in an analogous procedure to that used to prepare the compound **2** and was obtained as a green crystalline solid.

Yield of the compound **5** = 0.09 g, 61%.

5.2.6 Preparation of $[Nb\{(\eta-C_5H_4)SiMe_2(\eta-C_5H_4)\}Cl_2]$

The compound $[Nb\{(\eta-C_5H_4)SiMe_2(\eta-C_5H_4)\}Cl_2]$ was prepared by the reaction between $NbCl_4.2THF$ (2.0 g, 0.64 mmol) and $[Li_2\{(C_5H_4)SiMe_2(C_5H_4)\}]$ (1.23 g, 0.64 mmol) in an analogous procedure to that used to prepare the compound **1** and was obtained as brown solid.

Yield of $[Nb\{(\eta-C_5H_4)SiMe_2(\eta-C_5H_4)\}Cl_2]$ = 0.80 g, 36%.

5.2.7 Preparation of [Nb{(η–C_5H_4)$SiMe_2$(η–C_5H_4)}(η^2–BH_4)] (6)

The compound [Nb{(η–C_5H_4)$SiMe_2$(η–C_5H_4)}(η^2–BH_4)] **(6)** was prepared by the reaction between the compound [Nb{(η–C_5H_4)$SiMe_2$(η–C_5H_4)}Cl_2] (0.3 g, 0.86 mmol) and $LiBH_4$ (0.06 g, 2.75 mmol) in an analogous procedure to that used to prepare the compound **2** and was obtained as a green crystalline solid.

Yield of the compound **6** = 0.17 g, 66%.

5.2.8 Preparation of [Nb{(η–C_5H_4)CEt_2(η–C_5H_4)}Cl_2] (7)

To a stirred suspension of $NbCl_4$.2THF (2.59 g, 6.83 mmol) in THF (50 cm^3) was added a suspension of [Li_2{(C_5H_4)CEt_2(C_5H_4)}] (1.45 g , 6.83 mmol) in THF (80 cm^3) over 1 h at room temperature. The resulting purple suspension was stirred overnight. Volatiles were removed under reduced pressure and the resulting oily brown solid was extracted into toluene (3 × 50 cm^3). Toluene was removed under reduced pressure to afford crude [Nb{(η–C_5H_4)CEt_2(η–C_5H_4)}Cl_2] **(7)** as a dark brown solid.

Yield of the crude product **7** = 0.9 g, 37%.

An analytically pure sample of the compound **7** was obtained by sublimation at 165 °C (10^{-1} mm Hg).

5.2.9 Preparation of [Nb{(η–C_5H_4)CEt_2(η–C_5H_4)}(η^2–BH_4)] (8)

The compound [Nb{(η–C_5H_4)CEt_2(η–C_5H_4)}(η^2–BH_4)] **(8)** was prepared by the reaction between the compound **7** (0.25 g, 0.69 mmol) and $LiBH_4$ (0.171 g, 7.9 mmol) in an analogous procedure to that used to prepare the compound **2** and was obtained as a green crystalline solid.

Yield of the compound **8** = 0.13 g, 62%.

5.2.10 Preparation of [Nb{(η–C_5H_4)CMe_2(η–C_5H_4)}(η^2–BD_4)] (9)

The compound [Nb{(η–C_5H_4)CMe_2(η–C_5H_4)}(η^2–BD_4)] **(9)** was prepared by the reaction between [Nb{(η-C_5H_4)CMe_2(η-C_5H_4)}Cl_2] (0.09 g, 0.26 mmol) and $NaBD_4$

(0.10 g, 2.4 mmol) in an analogous procedure to that used to prepare the compound **3** and was obtained as a green crystalline solid.

Yield of the compound **9** = 0.03 g, 41%.

5.2.11 Preparation of [Nb{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}Cl_2] (10)

The compound [Nb{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}Cl_2] **(10)** was prepared by the reaction between $NbCl_4$.2THF (4.0 g, 12.7 mmol) and [Li_2{(C_5H_4)C(C_5H_{10})(C_5H_4)}] (2.86 g, 12.7 mmol) in an analogous procedure to that used to prepare the compound **1** and was obtained as a brown solid.

Yield of the crude product **10** = 3.33 g, 70%.

An analytically pure sample of the compound **10** was obtained by sublimation at 160 °C (10^{-1} mm Hg).

5.2.12 Preparation of [Nb{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}(η^2–BH_4)] (11)

The compound [Nb{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}(η^2–BH_4)] **(11)** was prepared by the reaction between the compound **10** (0.50 g, 1.3 mmol) and $LiBH_4$ (0.15 g, 6.7 mmol) in an analogous procedure to that used to prepare the compound **2** and was obtained as a green crystalline solid.

Yield of the compound **11** = 0.17 g, 41%.

5.2.13 Preparation of [V{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BH_4)] (12)

A green suspension of [V{(η–C_5H_4)C_2Me_4(η–C_5H_4)Cl_2}] (0.15g, 0.45 mmol) in DME (100 cm^3) was added to a flask charged with $NaBH_4$ (0.1g, 2.6 mmol) at -30 °C. The resulting violet suspension was stirred for 5 h whilst the temperature was maintained below -10 °C. The reaction mixture was allowed to warm to room temperature and then filtered to give a violet solution. Removal of volatiles under reduced pressure yielded a pale violet solid which was extracted into petroleum ether (b.p. 100-120 °C) (30 cm^3). The dark violet solution was cooled to -80 °C affording the compound [V{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BH_4)] **(12)** as a dark violet crystalline solid.

Yield of the compound **12** = 0.09g, 74%.

5.2.14 Preparation of [$(C_5H_4Me)SiMe_2Cl$] (13)

To a solution of Me_2SiCl_2 (6.4 ml, 6.79 g, 52.6 mmol) in diethyl ether (300 cm^3) was added a solution of [$Li(C_5H_4Me)$] (4.5 g, 52.2 mmol) in THF (20 cm^3) over 0.5 h at room temperature. The resulting pale yellow suspension was stirrred for 2 h and a yellow solution was isolated by filtration. Careful removal of volatiles at 0 °C under reduced pressure yielded a dark yellow liquid. Residual solvent was removed by distillation at 60 °C (10^{-1} mmHg). The compound [$(C_5H_4Me)SiMe_2Cl$] **(13)** was collected as a pale yellow moisture sensitive oil following distillation at 125 °C (10^{-1} mmHg).

Yield of the compound **13** (based on [$Li(C_5H_4Me)$]) = 4.05 g, 45 %.

5.2.15 Preparation of [$(C_5H_4Me)SiMe_2(C_5H_5)$] (14)

[$Na(C_5H_5)$] (1.4 g, 15.8 mmol) was added to a solution of the compound [$(C_5H_4Me)SiMe_2Cl$] **(13)** (1.8 g, 10.4 mmol) in diethyl ether (100 cm^3) and TMEDA (10 cm^3). The resulting orange suspension was stirred at room temperature for 4 h. A saturated aqueous solution of NH_4Cl (100 cm^3) was added and the organic layer separated and then washed with H_2O (2 × 50 cm^3). The yellow solution was dried over anhydrous $MgSO_4$ and isolated by filtration. Volatiles were removed under reduced pressure to yield the compound [$(C_5H_4Me)SiMe_2(C_5H_5)$] **(14)** as an orange oil.

Yield of the compound **14** (based on the compound **13**) = 0.94 g, 44%.

5.2.16 Preparation of [$Li_2\{(C_5H_3Me)SiMe_2(C_5H_4)\}$]

A solution of ^tBuLi (5.8 cm^3, 1.7 M, 9.9 mmol) in pentane was added dropwise to a solution of [$(C_5H_4Me)SiMe_2(C_5H_5)$] **(14)** (0.94 g, 4.6 mmol) in light petroleum ether (b.p. 40 – 60 ºC) (100 cm^3) at -78 ºC. The reaction mixture was allowed to warm to room temperature and then stirred overnight to yield a yellow suspension. A yellow solid was isolated by filtration and washed with light petroleum ether (b.p. 40 – 60 ºC) (2 × 30 cm^3). Drying under reduced pressure gave the compound [$Li_2\{(C_5H_3Me)SiMe_2(C_5H_4)\}$] as a pale yellow solid.

Yield of the compound [$Li_2\{(C_5H_3Me)SiMe_2(C_5H_4)\}$] = 0.72 g, 72 %.

5.2.17 Preparation of [Nb{(η–C_5H_3Me)$SiMe_2$(η–C_5H_4)}Cl_2] (15)

The compound [Nb{(η–C_5H_3Me)$SiMe_2$(η–C_5H_4)}Cl_2] **(15)** was prepared by the reaction between $NbCl_4$.2THF (1.7 g, 4.5 mmol) and [Li_2{(C_5H_3Me)$SiMe_2$(C_5H_4)}] (0.9 g, 4.5 mmol) in an analogous procedure to that used to prepare the compound **1** and was obtained as a brown solid.

Yield of the compound **15** = 0.82 g, 50 %.

5.2.18 Preparation of [Nb{(η–C_5H_3Me)$SiMe_2$(η–C_5H_4)}(η^2–BH_4)] (16)

A mixture of the compound **15** (0.17 g, 0.47 mmol) and $LiBH_4$ (0.05 g, 2.3 mmol) was suspended in DME (30 cm^3) at room temperature. Effervescence was observed on addition of the solvent. The brown reaction mixture was stirred overnight and then volatiles were removed under reduced pressure. The resulting solid was extracted into petroleum ether (b. p. 100-120 °C) (2 × 20 cm^3). Removal of volatiles under reduced pressure yielded a dark green oily solid. An analytically pure sample of the compound [Nb{(η–C_5H_3Me)$SiMe_2$(η–C_5H_4)}(η^2–BH_4)] **(16)** was obtained by sublimation at 70 °C (10^{-1} mmHg).

Yield of the compound **16** = 0.04 g, 28 %.

5.2.19 Preparation of [Nb{(η–C_5H_3Me)$SiMe_2$(η–C_5H_4)}(η^2–BD_4)] (17)

The compound [Nb{(η–C_5H_3Me)$SiMe_2$(η–C_5H_4)}(η^2–BD_4)] **(17)** was prepared by the reaction between the compound **15** (0.10 g, 0.27 mmol) and $NaBD_4$ (0.030 g, 0.73 mmol) in an analogous procedure to that used to prepare the compound **16**. An analytically pure sample of the compound **17** was obtained by sublimation at 70 °C (10^{-1} mmHg).

Yield of the compound **17** = 0.032 g, 38 %.

5.3 Experimental Details for Chapter 3

5.3.1 Preparation of [Zn{$(CH_2)_nCH_3$}$_2$]

1-Chloro-n-propane (19.9 g, 250 mmol) was added dropwise to a suspension 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.

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

To a suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ (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 ºC. 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 ºC to afford $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}_2]$ **(18)** as a yellow solid.

Yield of the compound **18** = 0.23 g, 44%.

5.3.3 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_3CH_3\}_2]$ (19) and $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_3CH_3\}Cl]$ (20)

To a suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ (0.3 g, 0.6 mmol) in toluene (40 cm^3) a solution of $[Zn\{(CH_2)_3CH_3\}_2]$ (3.0 cm^3, 1.5 M, 4.5 mmol) in toluene was added slowly at -78 ºC. 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 $[Zn_2\{(CH_2)_3CH_3\}]$. 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 ºC afforded the compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_3CH_3\}_2]$ **(19)** as a yellow solid.

Yield of the compound **19** = 0.045 g, 16 %.

Cooling of the toluene/pentane solution to -80 ºC afforded the compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_3CH_3\}Cl]$ **(20)** as a yellow solid.

Yield of the compound **20** = 0.11 g, 41 %.

5.3.4 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_4CH_3\}Cl]$ (21)

To a suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ (1.0 g, 2.34 mmol) in toluene (40 cm^3) a solution of $[Zn\{(CH_2)_4CH_3\}_2]$ (7.0 cm^3, 1.86 M, 13.0 mmol) in toluene was added slowly at -78 ºC. 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 $[Zn\{(CH_2)_4CH_3\}_2]$. 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 $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_4CH_3\}Cl]$ **(21)** as a pale red solid.

Yield of the compound **21** = 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 ºC afforded a yellow solid in low yield (*ca.* 0.010 g, 1 %) which was characterised by ^1H NMR spectroscopy as $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_4CH_3\}_2]$.

5.3.5 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_5CH_3\}_2]$ (22)

To a suspension of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}Cl_2]$ (0.33 g, 0.6 mmol) in toluene (40 cm^3) a solution of $[Zn\{(CH_2)_5CH_3\}_2]$ (2.0 cm^3, 5.3 M, 10.6 mmol) in toluene was added dropwise at -78 ºC. The reaction mixture was allowed to warm to room temperature and stirred overnight. Excess $[Zn\{(CH_2)_5CH_3\}_2]$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 ºC afforded the compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_5CH_3\}_2]$ **(22)** as a yellow solid.

Yield of the compound **22** = 0.095 g, 18 %.

Cooling of the toluene/penatne solution to -78 ºC afforded a small amount (*ca.* 0.025 g, 9 %) of a pale red solid characterised by ^1H NMR spectroscopy as $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_5CH_3\}Cl]$.

5.3.6 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}I]$ (23)

A mixture of the compound **18** (0.06 g, 0.13 mmol) and NH_4I (0.05 g, 0.34 mmol) in THF (25 cm^3) was heated at 65 ºC 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 **18** prior to extraction into a 1:4 mixture of toluene/pentane. Cooling of the red-orange solution to -80 ºC afforded the compound $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}I]$ **(23)** as a pale red solid.

Yield of the compound **23** = 0.032 g, 47 %.

5.3.7 Preparation of $[W\{(\eta-C_5H_4)CMe_2(\eta-C_5H_4)\}\{(CH_2)_2CH_3\}H]$ (24)

To a solution of the compound **23** (0.03g, 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 ºC. 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 ºC. The compound

[W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_2CH_3$}H] **(24)** was obtained as a yellow crystalline solid.

Yield of the compound **24** = 0.012 g, 50 %.

5.3.8 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}H] (25)

The compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_3CH_3$}H] **(25)** was prepared by the reaction between the compound **20** (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 **24** and was obtained as a yellow solid.

Yield of the compound **25** = 0.038 g, 42 %.

5.3.9 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_4CH_3$}H] (26)

The compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{$(CH_2)_4CH_3$}H] **(26)** was prepared by the reaction between the compound **21** (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 **24** and was obtained as a yellow solid.

Yield of the compound **26** = 0.023 g, 49 %.

5.3.10 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 1h. 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 = 46.1g, 94 % D, 40 %.

5.3.11 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 (27g, 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 %.

5.3.12 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 in **Section 5.3.10**, 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 %.

5.3.13 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 ºC) 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 ºC) (100 cm^3) at -78 ºC. 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 ºC) (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 %.

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

The two solids WCl_4.DME (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 $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}Cl_2]$ **(27)** as a purple solid.

Yield of the compound **27** = 1.25 g, 95 % D, 11.3 %.

5.3.15 Preparation of $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}_2]$ (28)

To a suspension of the compound **27** (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 ºC. 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 ºC. 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 ºC afforded the compound $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}_2]$ **(28)** as a yellow crystalline solid.

Yield of the compound **28** = 0.042 g, 46 %.

5.3.16 Preparation of $[W\{(\eta-C_5D_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}I]$ (29)

The compound $[W\{(\eta-C_5H_4)C(CD_3)_2(\eta-C_5D_4)\}\{CH_2CH_3\}I]$ **29** was prepared by the reaction between the compound **28** (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 **23** and was obtained as a pale red solid.

Yield of the compound **29** = 0.037 g, 67 %.

5.3.17 Preparation of [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{CH_2CH_3}D] (30)

To a solution of the compound **29** (0.03g, 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 ºC. 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 ºC. The compound [W{(η–C_5H_4)$C(CD_3)_2$(η–C_5D_4)}{CH_2CH_3}D] **(30)** 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 the compound **30** was not determined.

5.3.18 Preparation of [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}$_2$] (18a)

The compound [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}$_2$] **(18a)** was prepared by the reaction between the compound **27** (0.44 g, 1.0 mmol) and a solution of [Zn{$(CH_2)_2CH_3$}$_2$] (1 cm^3, 1.1 M, 1.10 mmol) in toluene in a procedure analogous to that used to prepare the compound **18**. The compound **18a** was obtained as a yellow solid.

Yield of the compound **18a** = 0. 11 g, 23 %.

5.3.19 Preparation of [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}I] (23a)

The compound [W{(η–C_5H_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}I] **(23a)** was prepared by the reaction between the compound **18a** (0.11 g, 0.24 mmol) and NH_4I (0.07g, 0.48 mmol) in a procedure analogous to that employed to prepare the compound **23** and was obtained as a pale red solid.

Yield of the compound **23a** = 0.057 g, 44 %.

5.3.20 Preparation of [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}D] (24a)

The compound [W{(η–C_5D_4)$C(CD_3)_2$(η–C_5D_4)}{$(CH_2)_2CH_3$}D] **(24a)** was prepared by the reaction between the compound **23a** (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 **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 of the compound **24a** was not calculated.

5.3.21 Preparation of [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_3CH_3$}Cl] (20a)

The compound [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_3CH_3$}Cl] **(20a)** was prepared by the reaction between the compound **27** (0.24 g, 0.55 mmol) and a solution of [Zn{$(CH_2)_3CH_3$}$_2$] (4 cm^3, 1.5 M , 6 mmol) in toluene in a procedure analogous to that used to prepare the compound **20** and was obtained as an yellow solid.

Yield of the compound **20a** = 0.099 g, 39 %.

5.3.22 Preparation of [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_3CH_3$}D] (25a)

The compound [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_3CH_3$}D] **(25a)** was prepared by the reaction between the compound **20a** (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 **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 of the compound **25a** was not calculated.

5.3.23 Preparation of [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_4CH_3$}$_2$] (21a)

To a suspension of the compound **27** (0.27 g, 95 % D, 0.58 mmol) in toluene (50 cm^3) a solution of [Zn{$(CH_2)_4CH_3$}$_2$] (3.0 cm^3, 1.5 M, 4.5 mmol) in toluene was added dropwise at -78 ºC. The reaction mixture was allowed to warm to room temperature and stirred overnight. Excess [Zn{$(CH_2)_4CH_3$}$_2$] 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 ºC afforded the compound [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_4CH_3$}$_2$] **(21a)** as a yellow crystalline solid.

Yield of the compound **21a** = 0.098 g, 33 %.

5.3.24 Preparation of [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_4CH_3$}I] (21b)

The compound [W{(η–C_5H_4)C(CD_3)$_2$(η–C_5D_4)}{$CH_2)_4CH_3$}I] **(21b)** was prepared by the reaction between the compound **21a** (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 **23** and was obtained as a pale red solid.

Yield of the compound **21b** = 0.026 g, 47 %.

5.3.25 Preparation of [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$(CH_2)_4CH_3$}D] (26a)

The compound [W{(η–C_5D_4)C(CD_3)$_2$(η–C_5D_4)}{$CH_2)_4CH_3$}D] **(26a)** was prepared by the reaction between the compound **21b** (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 of the compound **26a** was not calculated.

5.3.26 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_2CD_3}$_2$] = 0.55 g, 9 %.

5.3.27 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}$_2$] (31)

The compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}$_2$] **(31)** was prepared by the reaction between the compound [W{(η–C_5H_4)CMe_2(η–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 **18** and was obtained as a yellow solid.

Yield of the compound **31** = 0.24 g, 52 %.

5.3.28 Preparation of [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}I] (32)

The compound [W{(η–C_5H_4)CMe_2(η–C_5H_4)}{CD_2CD_3}I] **(32)** was prepared by the reaction between the compound **31** (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 **23** and was obtained as a pale red solid.

Yield of the compound **32** = 0.032 g, 69 %.

5.3.29 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}H] **(33)** was prepared by the reaction between the compound **32** (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 **24**. The compound **33** was obtained as a yellow solid.

Yield of the compound **33** = 0.012 g, 62 %.

5.4 Experimental Details for Chapter 4

5.4.1 Preparation of [W{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}Cl_2] (34)

The two solids WCl_4.DME (4.05 g, 9.8 mmol) and [Li_2{(C_5H_4)C(C_5Me_{10})(C_5H_4)}] (2.19 g, 12.8 mmol) were stirred together in the absence of solvent to give a good admixture. Diethyl ether (80 cm^3) was added and the resulting brown suspension stirred for three days. The liquid phase was removed by filtration and DME (25 cm^3) was added to the remaining solid. The dark brown suspension was stirred for 1 h and a brown solid isolated by filtration. The residue was washed with ethanol (40 cm^3) and then diethyl ether (3 × 50 cm^3) until the washings were colourless. After drying under reduced pressure, the resulting pale brown solid was extracted into dichloromethane (2 × 100 cm^3) to give a deep red/brown solution. Removal of volatiles under reduced pressure afforded the compound [W{(η–C_5H_4)C($C_{10}H_{10}$)(η–C_5H_4)}Cl_2] **(34)** as a pale brown solid.

Yield of the compound **34** = 1.25 g, 28 %.

5.4.2 Preparation of [W{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}Me_2] (35)

To a suspension of the compound **34** (0.1 g, 0.21 mmol) in toluene (20 cm^3) at -78 °C, a solution of dimethylzinc (5 cm^3, 1.8 M, 9 mmol) was added dropwise and the resulting mixture allowed to slowly warm to room temperature. After stirring overnight the brown/red suspension was cooled to 0 °C and excess dimethylzinc hydrolysed by the cautious addition of H_2O (1.5 cm^3). After stirring for 1.5 h at room temperature, the reaction mixture was filtered and the residual solid extracted into toluene (10 cm^3). The filtrate and toluene extraction were combined and the solvent was removed under reduced pressure to give a pale orange oily solid. The residue was extracted into pentane (10 cm^3) and the resulting yellow solution was slowly cooled to -80 °C to yield the compound [W{(η–C_5H_4)C($C_{10}H_{10}$)(η–C_5H_4)}Me_2] **(35)** as an orange crystalline solid.

Yield of the compound **35** = 0.028 g, 31 %.

5.4.3 Preparation of [W{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}H_2] (36)

To a suspension of the compound **34** (0.1 g, 0.21 mmol) in diethyl ether (40 cm^3) at -78 °C, a solution of $LiBEt_3H$ (2 cm^3, 1.0 M, 2 mmol) was added dropwise. The reaction mixture was allowed to slowly warm to room temperature and stirred overnight. Unreacted $LiBEt_3H$ was hydrolysed by cautious addition of H_2O (1 cm^3). A yellow solution was separated by filtration and freed from volatiles under reduced pressure to leave a brown/orange solid. The residue was extracted into pentane (2 × 20 cm^3) and the resulting yellow solution concentrated to 15 cm^3, prior to cooling to -80 °C. The compound [W{(η–C_5H_4)C($C_{10}H_{10}$)(η–C_5H_4)}H_2] **(36)** was isolated as a yellow solid by filtration and dried under reduced pressure.

Yield of the compound **36** = 0.035 g, 42 %.

5.4.4 Preparation of [W{(η–C_5H_4)C(C_5H_{10})(η–C_5H_4)}H_3][BF_4] (37)

To a yellow solution of the compound **36** (0.015 g, 0.04 mmol) in diethyl ether (20 cm^3) at -78 °C, a solution of HBF_4 (2 cm^3, 1.0 M, 2mmol) was added. A white solid was immediately precipitated and the reaction mixture stirred at low temperature (< -40 °C) for 0.5 h. The solid was isolated by filtration, washed with diethyl ether

(10 cm^3) and dried under reduced pressure to yield the compound $[W\{(\eta-C_5H_4)C(C_5H_{10})(\eta-C_5H_4)\}H_3][BF_4]$ **(37)** as a white solid.

Yield of the compound **37** = 0.016 g, 83 %.

5.4.5 Preparation of $[W\{(\eta-C_5H_4)C_2Me_4(\eta-C_5H_4)\}Me_2]$ (38)

To a suspension of $[W\{(\eta-C_5H_4)C_2Me_4(\eta-C_5H_4)\}Cl_2]$ (0.6 g, 1.28 mmol) in toluene (60 cm^3) at -78 °C, a solution of dimethylzinc (3 cm^3, 2.0 M, 6 mmol) was added dropwise and the resulting mixture allowed to slowly warm to room temperature. After stirring overnight the brown/red suspension was cooled to 0 °C and excess dimethylzinc hydrolysed by the cautious addition of H_2O (2 cm^3). After stirring for 1.5 h at room temperature, the reaction mixture was filtered and the residual solid extracted into toluene (30 cm^3). The filtrate and toluene extraction were combined and the solvent was removed under reduced pressure to give a pale orange oily solid. The residue was extracted into pentane (10 cm^3) and the resulting orange-yellow solution was slowly cooled to -78 °C to yield crude $[W\{(\eta-C_5H_4)C_2Me_4(\eta-C_5H_4)\}Me_2]$ **(38)** as an orange powder.

Yield of the crude product **38** = 0.12 g.

A solution of the crude product **38** (0.05 g) in pentane (10 cm^3) was transferred onto a chromotography column containing activated alumina. The compound **38** was passed down the column by elution with a 1:1 mixture of toluene/pentane and collected as a yellow solution. Volatiles were removed under reduced pressure to leave a yellow/orange solid. Dissolution of this solid in pentane (10 cm^3) followed by slow cooling to -80 °C afforded crystals of **38** suitable for X-ray diffraction.

5.4.6 Reaction between $[Nb\{(\eta-C_5H_4)SiMe_2(\eta-C_5H_4)\}Cl_2]$ and $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$

To a suspension of the compound $[Nb\{(\eta-C_5H_4)SiMe_2(\eta-C_5H_4)\}Cl_2]$ (0.04 g, 0.11 mmol) in toluene (20 cm^3) at -78 °C, a solution of $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ (1 cm^3, 1.5 M, 1.5 mmol) in toluene was added. The reaction mixture was allowed to warm to room temperature and the resulting red solution was stirred for 0.75 h. Excess $[Na\{AlH_2(OCH_2CH_2OCH_3)_2\}]$ was hydrolysed by the cautious addition of H_2O (0.3 cm^3) and a pale brown solution was isolated by filtration. Volatiles were removed under reduced pressure and the residue washed with ethanol (5 cm^3) to yield a pale brown solid

(*ca.* 0.005 g) which was characterised as [Nb{(η–C_5H_4)$SiMe_2$(η–C_5H_4)}H_3] by ^{1}H NMR spectroscopy. The extremely low yield of the compound [Nb{(η–C_5H_4)$SiMe_2$(η–C_5H_4)}H_3] precluded characterisation by other means. No further product was isolated on cooling the ethanol washings to -20 °C.

^{1}H NMR (500 MHz, 298 K, $C_6D_5CD_3$): δ 4.96 (m., 4H, C_5H_4), 4.88 (m., 4H, C_5H_4), 0.38 (s., 6H, $SiMe_2$), -2.95 (t., 1H, NbH_A), -3.92 (d., 2H, NbH_B)

5.4.7 Reaction between [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}Cl_2] (1) and [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}]

The reaction between the compound **1** (0.41g, 1.09 mmol) and a solution of [Na{$AlH_2(OCH_2CH_2OCH_3)_2$}] (1 cm^3, 1.5 M, 1.5 mmol) in toluene was carried out *via* an analogous procedure to that in described in **Section 5.4.6.** Following washing with ethanol, a pale blue solid (*ca.* 0.01 g) was isolated and characterised as [Nb{(η –C_5H_4)C_2Me_4(η–C_5H_4)}H_3] by ^{1}H NMR spectroscopy.

^{1}H NMR (500 MHz, 298 K, $C_6D_5CD_3$): δ 5.24 (m., 4H, C_5H_4), 4.97 (m., 4H, C_5H_4), 0.83 (s., 6H, $SiMe_2$), -1.22 (br., 1H, NbH_A), -1.58 (br., 2H, NbH_B)

5.4.8 Preparation of [Re{(η–C_5H_4)CMe_2(η–C_5H_4)}Cl] (39)

A suspension of [K_2{(C_5H_4)CMe_2(C_5H_4)}] (3.36 g, 13.52 mmol) in DME (30 cm^3) at -78 °C was added to a stirred suspension of $ReCl_5$ (1.64g, 4.51 mmol) at -78 °C in DME (50 cm^3). The dark red reaction mixture was allowed to slowly warm to room temperature and stirred overnight. The reaction mixture was filtered and volatiles removed under reduced pressure. The resulting dark brown oily solid was extracted into THF (2 × 30 cm^3) to give a dark brown solution. The solvent was removed under reduced pressure and the resulting solid was extracted into dichloromethane (30 cm^3) to give a dark red solution. Removal of volatiles under reduced pressure afforded crude [Re{(η–C_5H_4)CMe_2(η–C_5H_4)}Cl] **(39)** as a red-brown solid.

Yield of the crude product **39** (based on $ReCl_5$) = 0.17g, 9.6%.

An analytically pure sample of the compound **39** was obtained as a red/orange crystalline solid by recrystallisation from a dichloromethane solution at -80 °C.

Yield of the compound **39 =** 0.06 g, 3.4%.

5.5 X-ray Crystal Structure Determinations

5.5.1 General Crystallographic Details

Crystal data, data collection and processing parameters are given in the **Appendices.**

Data were collected on an Enraf-Nonius DIP2000 image plate diffractometer with graphite monochromated Mo-Kα radiation (λ = 0.71069 Å). The images were processed with the DENZO[17] and SCALEPACK[18] programs. Corrections for Lorentz and polarisation effects were performed. All solution, refinement, and graphical calculations were performed using the CRYSTALS[19] and CAMERON[20] software packages.

Crystallographic work was carried out at the Chemical Crystallography Laboratory, 9 Parks Road, Oxford OX1 3PD.

5.5.2 Crystal Structure Determinations for [Nb{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BH_4)] (2), [Nb{(η–C_5H_3-^{t}Bu)C_2Me_4(η–C_5H_3-^{t}Bu)}(η^2–BH_4)] (5), [Nb{(η–C_5H_4)$SiMe_2$(η–C_5H_4)}(η^2–BH_4)] (6), [Nb{(η–C_5H_4)CEt_2(η–C_5H_4)}(η^2–BH_4)] (8) and [V{(η–C_5H_4)C_2Me_4(η–C_5H_4)}(η^2–BH_4)] (12)

The data were collected and the crystal structures solved by Dr. M. A. Leech (**2**) and Dr. L. H. Doerrer (**5**, **6**, **8** and **12**). The structures were solved by direct methods using the SIR92 program[21] and were refined by a full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. Hydrogen atoms bound to boron were located in the final difference map and their positions refined. A three-term Chebychev weighting scheme[22] with the parameters 1.45, 0.293 and 0.737 **(2)**, 1.84, -0.409 and 0.930 **(8)**, 1.94, 0.472 and 1.35 **(12)** or a statistical weighting scheme ((**5**) and (**6**)) was applied.

5.5.3 Crystal Structure Determination for [W{(η–C_5H_4)$C(C_5H_{10})$(η–C_5H_4)}Me_2] (35)

The data was collected and the crystal structure solved by Dr. L. H. Rees. The structure was solved using the program SHELXS-97[23] and refined using full-matrix least-squares on all F_0^2 data.[24] All non-hydrogen atoms were refined anisotropically and

hydrogen atoms were included in calculated positions with isotropic thermal parameters *ca.* 1.2 x (aromatic CH) or 1.5 x (Me) the equivalent isotropic thermal parameters of their parent carbon atoms.

5.5.4 Crystal Structure Determination for [W{(η–C_5H_4)C_2Me_4(η–C_5H_4)}Me_2] (38)

The data were collected and the crystal structure solved by Dr. L. H. Doerrer. The structure was solved by direct methods using the SIR92 program[21] and was refined by full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. A Chebychev weighting scheme[22] with the parameters 2.32, 0.530, and 1.82 was applied, as well as an empirical absorption correction.[25]

5.5.5 Crystal Structure Determination for [Re{(η–C_5H_4)CMe_2(η–C_5H_4)}Cl] (39)

The data were collected and the crystal structure solved by Dr. L. H. Doerrer. The structure was solved by direct methods using the SIR92 program[21] and was refined by full-matrix least squares procedure on F. All non-hydrogen atoms were refined with anisotropic displacement parameters. All carbon-bound hydrogen atoms were generated and allowed to ride on their corresponding carbon atoms with fixed thermal parameters. A Chebychev weighting scheme[22] with the parameters 1.59, 0.554, and 1.16 was applied as well as an empirical absorption correction.[25]

5.6 Density Functional Calculations

5.6.1 Density Functional Calculations on [Nb{(η–C_5H_4)CH_2(η–C_5H_4)}(η^2–BH_4)], [Nb{(η–C_5H_4)SiH_2(η–C_5H_4)}(η^2–BH_4)] and [Nb(η–C_5H_5)$_2$(η^2–BH_4)]

Calculations were performed by Professor J. C. Green and N. Ashworth using density functional methods of the Amsterdam Density Function package (Version 2.3 and 1999.02).[26, 27] Triple IV basis sets used triple-ζ accuracy sets of Slater-type orbitals, with a single polarisation functional added; 2p on hydrogen and 3d on boron and carbon. The cores of the atoms were frozen, carbon up to the 1s, boron up to the 1s, and niobium to the 3d. First order relativistic corrections were made to the cores. The generalised gradient approximation (GCA non-local) method was used, using Vosko, Wilk and Nusair's local exchange correlation,[28] with non-local-exchange corrections by Becke,[29] and non-local correlation corrections by Perdew.[30] Frequency calculations were carried out to test that the optimised structures were local minima and that the proposed transition states were characterised by one imiginary frequency.

Reaction pathways were modelled by stepping a reaction coordinate through a sequence of fixed values and allowing the other structural parameters to optimise.

Fragment analysis was carried out on the compounds. The molecular orbitals were first calculated for the metallocene cation and the tetrahydroborate anion as fragments. In all cases the structure of the fragment taken was that in the optimised structure of the complex. The orbitals of the tetrahydroborate metallocene molecule were then calculated using the fragment orbitals as the basis set. This enabled ready comparison of electronic structure within the series of compounds and the results were used for the construction of MO diagrams.

5.6.2 Density Functional Calculations on [Re{(η–C_5H_4)CH_2(η–C_5H_4)}Cl] and [Re{(η–C_5H_5)$_2$Cl]

Calculations were performed by Professor J. C. Green and A. Scottow using density functional methods of the Amsterdam Density Function package (Version 2.3).[26] The electronic configurations were described by an uncontracted triple-ζ basis set of Slater type orbitals, with a single polarisation functional added; 2p on hydrogen, 3d on carbon and 4d on chlorine atoms. The cores of the atoms were frozen, carbon up to the 1s,

chlorine to the 2p, and rhenium to the 5p. First order relativistic corrections were made to the cores of all atoms using the Pauli formalism. Energies were calculated using Vosko, Wilk and Nusair's local exchange correlation,[28] with non-local-exchange corrections by Becke,[29] and non-local correlation corrections by Perdew.[30] In general the non-local correction terms were not utilised in calculating gradients during geometry optimisations. In the case of [Re{(η−C_5H_4)CH_2(η−C_5H_4)}Cl] optimisation was also carried out including the non-local corrections throughout the calculation.[31]

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