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Novel syntheses of linked cyclopentadienyl–amide complexes

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The reaction of $C_5H_5CH_2CH_2CH_2NHMe$ with $[W(NBu^t)_2(NHBu^t)_2]$ proceeded in a two-step fashion to give the formally 22-electron complex $[W(NBu^t)_2(\eta^5,\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)]$; the reaction of $Li_2[C_5H_4CH_2CH_2CH_2NMe]$ with $[Mo(NBu^t)_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane) or $[Zr(\eta\text{-}C_5H_5)_2Cl_2]$ gave $[Mo(NBu^t)_2(\eta^5,\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)]$ or $[Zr(\eta\text{-}C_5H_5)Cl(\eta^5:\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)]$ respectively.

The chemistry of bifunctional ligands containing cyclopentadiene and amine functions and their complexes with transition- and main-group metals has been an area of recent interest.[1] Complexes of titanium and zirconium with the $[(C_5Me_4)SiMe_2NR]^{2-}$ (R = Pr^i or Bu^t) ligand and its derivatives have been shown to be precursors to highly active ethylene polymerisation catalysts.[2] In common with standard practice in organometallic chemistry, the main method used to co-ordinate such ligands to metals has been the reaction of alkali-metal salts of the ligand with metal halides, the reaction thermodynamics being driven by the lattice energy of the resulting alkali-metal halides. An alternative approach to the metallation of cyclopentadienes, by reaction with homoleptic metal amides $[M(NR_2)_x]$, was first reported by Chandra and Lappert[3] and applied by one of us to the synthesis of zirconium and hafnium complexes of the trimethylene linked ligand $C_5H_5CH_2CH_2CH_2NHMe$ **I**.[4] The reaction of $Zr(NMe_2)_4$, and other homoleptic amides and metal alkyls of Group 3, 4 and 6 metals, with a range of cyclopentadienes and cyclopentadiene analogues is a useful synthetic method,[5] giving access to good yields of thermodynamic products,[6] or complexes of ligands whose alkali-metal salts are unstable.[7] In seeking to further explore the range of metal complexes which can be prepared from the amine-functionalised cyclopentadiene **I** we have been exploring the reactivity of both the neutral ligand and the dilithium salt of its dianion, $Li_2[C_5H_4CH_2CH_2CH_2NMe]$ **1** with a range of transition-metal complexes. Here we wish to report the aminolysis reaction of **I** with an imido amide complex and an example of cyclopentadienide behaving as a leaving group.

A toluene solution of the trimethylene linked neutral cyclopentadiene amine **I** reacts with 1 equivalent of $[W(NBu^t)_2(NHBu^t)_2]$[8] at 55 °C over 3 d to give approximately 50% conversion to $[W(NBu^t)_2(\eta^5,\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)]$ **2**. Continued heating of the toluene solution, up to 100 °C, with occasional removal of the volatiles (*i.e.* NH_2Bu^t) does not cause the reaction to go to completion. Analysis of the ^1H NMR spectrum of an aliquot of the mixture, in $CDCl_3$, indicates the presence of **2** together with a species proposed to be $[W(NBu^t)_2(NHBu^t)(NMeCH_2CH_2CH_2C_5H_5)]$ **3**,‡ and the starting material $[W(NBu^t)_2(NHBu^t)_2]$; any excess of **I** would be removed in preparing the sample. However, after standing the $CDCl_3$ solution for 10–14 d, the mixture of products converts in high yield to **2**.§ As shown in Scheme 1, the overall reaction involves substitution of two *tert*-butyl amide ligands by one cyclopentadienyl and one dialkyl amide ligand, with the evolution of NH_2Bu^t. The two-stage nature of this reaction is reproducible, and the second stage proceeds in $CHCl_3$, and it has proved possible to isolate moderate quantities of **2** (up to 90% pure by NMR spectroscopy). The direct reaction of **I** with $[W(NBu^t)_2(NHBu^t)_2]$ in $CHCl_3$ gives an inseparable mixture of products.

The neutral ligand **I** contains two acidic centres, at the cyclopentadiene ($pK_a \approx 16$) and the secondary amine ($pK_a \approx 35$–40). Reaction of **I** with 1 equivalent of LiBu in thf gives the thermodynamic product by deprotonation at the cyclopentadiene,[9] the reaction of **I** with 2 equivalents of LiBu generates the dianion of **1**. The observation of complex **3** as an intermediate in the reaction of **I** with $[W(NBu^t)_2(NHBu^t)_2]$ suggests that **3** is the product of a kinetic deprotonation, *i.e.* that a tungsten amide ligand undergoes an amide exchange with a free amine more quickly than the reaction with a cyclopentadiene. The ^1H NMR spectrum of **3** shows the presence of free cyclopentadiene (as a mixture of isomers), together with a tungsten co-ordinated amide as shown by the chemical shift of the N–Me protons (δ 3.41), characteristically shifted with respect to the free ligand NH*Me* group (δ 2.43).

The molybdenum complex $[Mo(NBu^t)_2(\eta^5,\sigma\text{-}C_5H_4CH_2CH_2CH_2NMe)]$ **4** can be prepared by the reaction of $[Mo(NBu^t)_2Cl_2(dme)]$ (dme = 1,2-dimethoxyethane)[10] with the dianion of **1**. Complex **4** is a light yellow oil which can be isolated as crude material in up to 95% yield, an analytically pure sample was obtained by distillation.¶ Complexes **2** and **4** each have a molecular mirror plane, as indicated by the solution NMR spectra. The ^1H NMR spectrum of **2** shows two resonances for the $\eta\text{-}C_5H_4$ protons, and three simple multiplets for the trimethylene backbone; in the molybdenum complex **4** there is some accidental overlap of signals and only one resonance is seen for the $\eta\text{-}C_5H_4$ protons and the NMe singlet coincides with the $N\text{–}CH_2$ triplet. The ^{13}C NMR spectra confirm the molecular mirror plane with two CH resonances observed for the $\eta\text{-}C_5H_4$ ring in both **2** and **4**.

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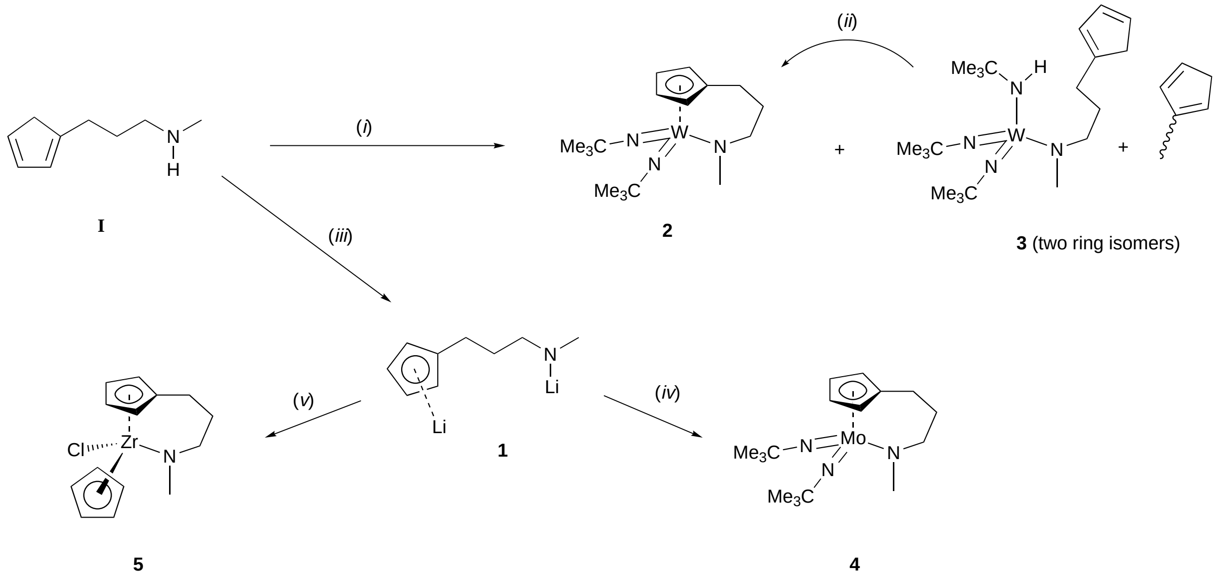
‡ Selected data for complex **3**. Characterised as a mixture with **2** and $[W(NBu^t)_2(NHBu^t)_2]$. δ_H(250 MHz, $CDCl_3$) 6.48–6.18 (3 H, br m, 3 CH in C_5H_5), 5.03 (1 H, br s, N*H*CMe$_3$), 3.63 (2 H, 8 lines, NCH_2), 3.41 (3 H, s, NMe), 2.94 (2 H, dq, CH_2 in C_5H_5), 2.43 (2 H, m, CH_2), 1.78 (obscured by **2**, CH_2), 1.30 (heavily obscured, $NCMe_3$). Electron impact (EI) mass spectrum: *m*/*z* envelope centred at 533 [M^+] with correct isotope pattern.

§ Selected data for complex **2**. A toluene solution of **I** (0.41 g, 3 mmol) and $[W(NBu^t)_2(NHBu^t)_2]$ (1.41 g, 3 mmol) was heated under reduced pressure at 55 °C for 3 d, after which the volatiles were removed under reduced pressure. Chloroform (10 cm^3) was added and the solution stood in a Young's ampoule (20 cm^3) at 20 °C for 10 d. The volatiles were removed under reduced pressure, and a portion of the resulting oil distilled (40 °C, 0.001 mmHg, 1 mmHg = 133.322 Pa) to a probe at −196 °C. Distilled yield 0.14 g, 10%. δ_H(250 MHz, $CDCl_3$) 6.09 (2 H, t, C_5H_4), 6.02 (2 H, t, C_5H_4), 3.25 (2 H, m, NCH_2), 3.23 (3 H, s, NMe), 2.71 (2 H, m, $C_5H_4CH_2$), 1.78 (2 H, qnt, CH_2), 1.23 (18 H, s, CMe_3). δ_C(62.5 MHz, $CDCl_3$) 117.4 (C_5H_4 *ipso*), 107.4 (C_5H_4), 101.7 (C_5H_4), 66.6 (*C*Me$_3$), 62.4 (NCH_2), 56.9 (NMe), 33.4 (C*Me*$_3$), 28.8 (C_5H_4*C*H$_2$), 23.4 (CH_2). The small scale distillation of **2** has not allowed us to obtain satisfactory microanalysis. EI mass spectrum: *m*/*z* envelope centred at 463 [M^+] with correct isotope distribution.



Scheme 1 Summary of the reactions described. (*i*) [W(NBu^t)$_2$(NHBu^t)$_2$], toluene, 55 °C, 3 d; (*ii*) CHCl$_3$, 10 d; (*iii*) LiBu (2 equivalents), 0 °C; (*iv*) [Mo(NBu^t)$_2$Cl$_2$(dme)], tetrahydrofuran (thf) 24 h; (*v*) [Zr(η-C$_5$H$_5$)$_2$Cl$_2$], thf, 24 h

In the absence of structural data, if we assume that both the imide ligands are linear, the amide ligand is planar, and the cyclopentadienyl is co-ordinated in an η^5 fashion, so that they potentially donate all available electrons to the metal, complexes **2** and **4** are formally 22-valence-electron species. It is now well established that in complexes containing multiple π-donor ligands, there are only a limited number of linear combinations of ligand-based π orbitals which have symmetry matches with the metal s, p and d orbitals.[11] Both the imide and cyclopentadienyl ligands are σ^2,π^4 ligands, and the amide ligand is a σ^2,π^2 ligand. Comparison of complexes **2** and **4** with the examples studied by Lin and Hall[11] suggests that there will be two combinations of ligand-based π orbitals which do not have symmetry matches with metal-based orbitals, and these complexes can thus be classed as 18-valence-electron complexes with four electrons occupying ligand-based orbitals.Structural determination by X-ray diffraction may demonstrate that the electron-loading of **2** and **4** is relieved by bent imido ligands, cyclopentadienyl ring slippage or pyramidalisation of the amide nitrogen.

The isolobal 22-electron tris(imido) amide complexes of Group 7, [M(NBu^t)$_3$(NHBu^t)] (M = Mn or Re) are known, and an analogue of **4**, containing unlinked cyclopentadienyl and amide ligands, [Mo(NR)$_2$(NHR)(η-C$_5$H$_5$)] (R = 2,6-diisopropylphenyl),[12] has been reported, although **2** appears to be the first cyclopentadienyl bis(imido) amide complex of tungsten.

The isolobal relationship of the imido ligand and the cyclopentadienyl ligand has been widely exploited in recent studies of early transition-metal organometallic and co-ordination chemistry,[13] and we sought to investigate the relationship between complexes **2** and **4** and complexes where the imido ligands (NR^{2-}) are replaced by cyclopentadienyl ligands (η-C$_5$H$_5$), and moving one metal to the left in the Periodic Table for each such replacement in order to maintain electron count. Thus, in direct analogy to the synthesis of **4**, we investigated the reaction of [Zr(η-C$_5$H$_5$)$_2$Cl$_2$] with the dianion of **1** in thf.[||] The reaction gives a mixture of products, as indicated by the ^{1}H NMR spectrum of the crude material, from which a bright yellow oil (m.p. *ca.* −20 °C) may be isolated in *ca.* 30% yield by careful distillation (100–120 °C, 0.01 mmHg). The spectroscopic data indicate that this is not the analogue of replacing the Mo(NBu^t)$_2$ fragment in **4** by a Zr(η-C$_5$H$_5$)$_2$ fragment, since the ^{1}H and ^{13}C NMR data show that the molecule does not possess a molecular mirror plane, with four ^{1}H and ^{13}C resonances for the η-C$_5$H$_4$ moiety, and the ^{1}H integration indicates only one η-C$_5$H$_5$ per (η^5,σ-C$_5$H$_4$CH$_2$CH$_2$CH$_2$NMe) ligand. The combination of NMR data [including two-dimensional hetero- and homo-nuclear correlation spectroscopy] (HETCOR and COSY respectively) together with mass spectroscopic and microanalytical data identify this oil as [Zr(η-C$_5$H$_5$)(η^5,σ-C$_5$H$_4$CH$_2$CH$_2$CH$_2$NMe)Cl] **5** the product of replacing one chloride and one cyclopentadienyl ligand in [Zr(η-C$_5$H$_5$)$_2$Cl$_2$] by the (η^5,σ-C$_5$H$_4$CH$_2$CH$_2$CH$_2$NMe) ligand. The reaction of [Ti(η-C$_5$H$_5$)$_2$Cl$_2$] with the dianion of **1** appears to give the titanium analogue of **5**, but the reaction seems to be accompanied by some reduction to Ti^{III}; distillation or sublimation of the product is accompanied by significant decomposition. In the synthesis of **3** the choice of leaving groups is between chloride and the *tert*-butyl imide dianion, NBu^{t2-},[14] the loss of chloride being observed. In contrast, during the preparation of **5** there is an opportunity for the stable cyclopentadienide (C$_5$H$_5$$^-$) anion to be a leaving group, and the loss of this ligand removes more electrons from the complex than does a Cl$^-$ leaving group. In the synthesis of **5**, the reaction step in which C$_5$H$_5$$^-$ is displaced by either the amide or cyclopentadienide end of the dianion of **1** is presumably favoured by the chelate effect.

[¶] Selected data for complex **4**. A thf suspension of the dianion of **1** was prepared by reacting **I** (0.82 g, 6 mmol) with LiBu (7.5 cm^3 of 1.6 M in hexanes, 12 mmol) at 0 °C. This suspension was added to [Mo(NBu^t)$_2$Cl$_2$(dme)] (2.30 g, 6 mmol) in thf (40 cm^3) and the mixture stirred at 20 °C for 24 h. The volatiles were removed under reduced pressure, to give a yellow oil which was extracted with hexanes (2 × 40 cm^3). The solvent was removed from the combined extracts and the resulting oil distilled (40 °C, 0.001 mmHg) to a probe at −196 °C. Distilled yield 1.23 g, 55%. δ$_H$(250 MHz, C$_6$D$_6$) 5.90 (4 H, s, C$_5$H$_4$), 3.29 (3 H, s, NMe), 3.27 (2 H, m, NCH$_2$), 2.60 (2 H, m, C$_5$H$_4$C*H*$_2$), 1.62 (2 H, qnt, CH$_2$), 1.29 (18 H, s, CMe$_3$). δ$_C$(62.5 MHz, C$_6$D$_6$) 118.5 (C$_5$H$_4$ *ipso*), 107.3 (C$_5$H$_4$), 102.2 (C$_5$H$_4$), 66.3 (*C*Me$_3$), 63.0 (NCH$_2$), 57.7 (NMe), 32.3 (C*Me*$_3$), 28.8 (C$_5$H$_4$*C*H$_2$), 23.4 (CH$_2$) (Found: C, 55.1; H, 8.2; N, 10.9. C$_{17}$H$_{31}$MoN$_3$ requires C, 54.7; H, 8.3; N, 11.3%). EI mass spectrum: *m*/*z* envelope centred at 375 [*M*$^+$] with correct isotope distribution.

[||] Selected data for complex **5**. Method same as for **4**, except using [Zr(η-C$_5$H$_5$)$_2$Cl$_2$] (1.00 g, 3.4 mmol), extraction was with toluene, and the product was distilled at 100 °C, 0.001 mmHg. Yield 0.34 g, 30%. δ$_H$(250 MHz, C$_6$D$_6$) 6.08 (1 H, q, C$_5$H$_4$), 6.02 (1 H, q, C$_5$H$_4$), 5.92 (5 H, s, C$_5$H$_5$), 5.44 (1 H, q, C$_5$H$_4$), 5.12 (1 H, q, C$_5$H$_4$), 2.91 (1 H, m, NCH*H*), 2.85 (3 H, s, NMe), 2.56 (1 H, m, NC*H*H), 2.21 (2 H, 2m, C$_5$H$_4$C*H*$_2$), 1.66 (1 H, m, CH*H*), 1.20 (1 H, m, C*H*H). δ$_C$(62.5 MHz, C$_6$D$_6$) 120.3 (C$_5$H$_4$ *ipso*), 116.7 (C$_5$H$_4$), 116.0 (C$_5$H$_4$), 112.1 (C$_5$H$_5$), 108.7 (C$_5$H$_4$), 103.9 (C$_5$H$_4$), 60.0 (NCH$_2$), 48.6 (NMe), 33.1 (C$_5$H$_4$*C*H$_2$), 28.0 (CH$_2$) (Found: C, 51.6; H, 5.8; N, 4.1. C$_{14}$H$_{18}$ClNZr requires C, 51.4; H, 5.5; N, 4.3%). EI mass spectrum: *m*/*z* envelope centred at 326 [*M*$^+$] with correct isotope distribution.

Green *et al.*[15] have observed the displacement of $C_5H_5^-$ by substituted cyclopentadienide and indenide anions in the synthesis of $[Mo(NR')(\eta\text{-}C_5H_4R)_2]$, and a recent patent has described the reaction of $[(C_5Me_4)SiMe_2NBu^t]^{2-}$ with cyclopentadienyl complexes of titanium, leading to the displacement of $C_5H_5^-$.[16]

Both complexes **4** and **5** can be prepared in reasonable yields on multigram scales, the synthesis of **2** is more involved. Crude samples of these complexes are oils, and analytically pure samples obtained by distillation solidify on cooling to −30 °C but melt below room temperature. Compounds **2**, **4** and **5** are thermally stable to at least 100 °C but are air-sensitive, reacting with moisture/water, other protic reagents and alkyl halides to cleave the metal–NR_2 bond. Studies are in progress to investigate the chemistry of these complexes, and to prepare derivatives which are crystalline solids suitable for crystallographic studies. We have isolated a few crystals, and obtained a crystal structure of a Ti^{III} reduction product, $[Ti(\eta\text{-}C_5H_5)(\eta^5,\sigma\text{-}C_5H_4CH_2CH_2CH_2NHMe)Cl]$, although we have no analytical or spectroscopic data. The structure determination shows a geometry similar to that depicted for compound **5**, containing Ti^{III} and protonated at nitrogen.[17]

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