Facile α-C–H activation in 14-electron zirconium half-sandwich compounds: evidence for a new catalyst deactivation pathway

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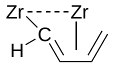
The electron-deficient zirconium diene complex [Zr(Cp″)Me($C_4H_4Me_2$-2,3)] [Cp″ = $C_5H_3(SiMe_3)_2$-1,3] cleanly eliminates methane to give an unusual dinuclear dienyl complex [Zr(Cp″)(μ-η^1 : η^4-$C_4H_3Me_2$-2,3)]$_2$, characterised by a new type of μ-η^1 : η^4-butadienyl coordination mode; the complex and its zwitterionic reaction product with $B(C_6F_5)_3$ provide support for catalyst deactivation processes involving alkane elimination reactions.

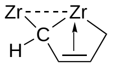
Electron deficient group 4 metallocene and half-sandwich complexes are known to give rise to extremely active alkene polymerisation catalysts.[1] The activity profile of these catalysts typically shows a very high initial activity, followed by an exponential decay to a lower steady-state level after some time. Little is known however about the nature of the deactivation processes involved. The kinetics of propene polymerisation with [Zr(η-C_5H_5)$_2$$Cl_2$]–methylaluminoxane catalysts suggest a catalyst deactivation process which is second order in [Zr].[2] We have previously shown two types of C–H activation processes which may be relevant in this context: α-C–H activation leading to dinuclear cationic μ-CH_2 zirconium fulvalene complexes,[3] and the formation of μ-C_2H_4-bridged species by a β-elimination process.[4] We report here the facile decomposition of a neutral catalyst precursor *via* an α-C–H activation process, to give a dinuclear dienyl complex exhibiting a novel μ-η^1 : η^4-butadienyl coordination mode.

The reaction of [Zr(Cp″)Cl(η^4-2,3-dimethylbutadiene)] [Cp″ = $C_5H_3(SiMe_3)_2$-1,3] with methyllithium in diethyl ether affords the methyl complex [Zr(Cp″)Me(η^4-2,3-dimethylbutadiene)] **1a** which can be isolated at room temperature as a red solid in > 80% yield. The analogous hafnium complex **1b** is similarly obtained as a spectroscopically pure yellow oil.† These isolated compounds are thermally more stable than related C_5Me_5 derivatives which have to be kept below 0 °C.[5] However, monitoring the behaviour of **1a** by NMR spectroscopy over a period of time revealed a slow clean transformation to a new product at room temperature, with elimination of methane. Attempts to recrystallise **1a** from light petroleum at −16 °C led to the isolation of deep red crystals of [Zr(Cp″)(μ$_2$-η^1 : η^4-$C_4H_3Me_2$-2,3)]$_2$ **2** in *ca.* 40% yield, evidently formed by abstraction of a methylene hydrogen from the diene ligand (Scheme 1).

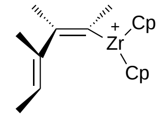
Compound **2** was identified spectroscopically† and shows a characteristic ^{13}C NMR resonance at δ 175 for the μ-CHR carbon. Single-crystal X-ray diffraction‡ confirmed the dinuclear structure of **2** and revealed the novel coordination mode of the butadienyl ligand (Fig. 1). Each half of the molecule forms a (cyclopentadienyl)zirconium(butadienyl) sandwich with an almost symmetrical μ-CHR bridge [Zr(1)–C(6) 2.216(2), Zr(1)–C(6′) 2.191(2) Å]. The four sp^2-hydridised carbon atoms of the butadienyl moiety are coplanar and η^4-coordinated. As in mononuclear diene complexes[6] the bonding in the dienyl moiety may be described by two resonance structures **A** and **B**, with a significant contribution of a zirconacyclopentene resonance structure **B** to account for the bond length distribution within the C_4 unit. The [Zr(dienyl)]$_2$ moiety in **2** closely resembles the ‘envelope’ structure of a Zr(diene) complex in which one diene α-hydrogen is replaced by a zirconium atom. The geometry of the butadienyl ligand in **2** contrasts sharply with that in the zwitterionic 16-electron metallocene complex [{$(C_6F_5)_3BC_5H_4$}(η-C_5H_5)Zr(C_4HMe_4-1,2,3,4)] where the dienyl ligand is η^1-bonded, with a long C(2)–C(3) single and short C(1)–C(2) and C(3)–C(4) double bonds (**C**), and where coordination of an *o*-F atom of a C_6F_5 unit is favoured over the interaction of the diene with the metal centre.[7] The Zr–Zr distance of 3.1516(5) Å in **2**, with a formal electron count of 14 per Zr centre, is short compared to the metal–metal distance in 16 electron metallocene dimers such as [(C_5H_4Me)$_2$ZrH(μ-H)]$_2$ (3.46 Å);[8] to our knowledge there are



A



B



C

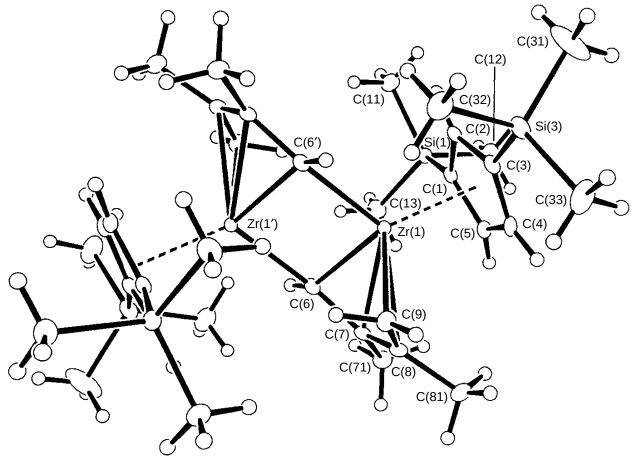
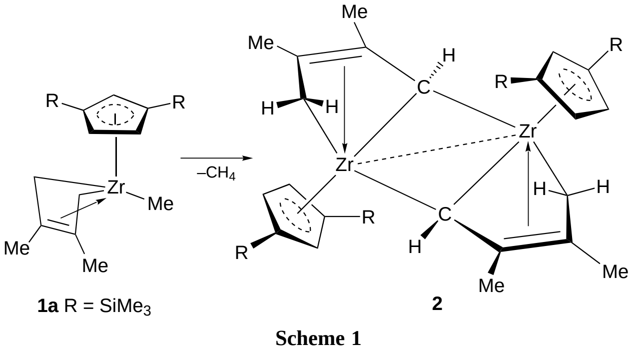
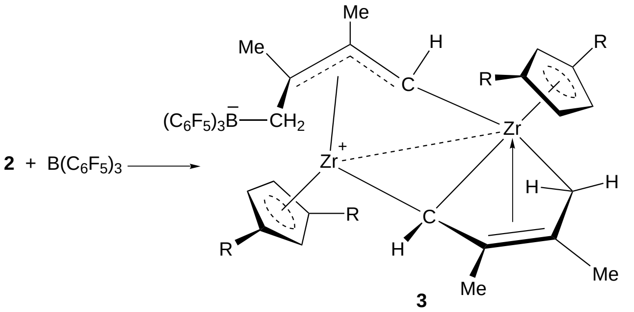


Fig. 1 Crystal structure of **2** (H atoms omitted for clarity). Selected bond lengths (Å) and angles (°): Zr(1)–Zr(1′) 3.1516(5), Zr(1)–C(1) 2.497(2), Zr(1)–C(2) 2.501(2), Zr(1)–C(3) 2.556(2), Zr(1)–C(4) 2.558(2), Zr(1)–C(5) 2.520(2), Zr(1)–C(6′) 2.191(2), Zr(1)–C(6) 2.216(2), Zr(1)–C(7) 2.470(2), Zr(1)–C(8) 2.480(2), Zr(1)–C(9) 2.289(2), C(6)–C(7) 1.435(3), C(7)–C(8) 1.409(3), C(8)–C(9) 1.443(3) Å; C(6)–Zr(1)–C(6′) 88.69(8), Zr(1)–C(6)–Zr(1′) 91.31(4°), H(6)–C(6)–C(7) 115(2)°, C(6)–C(7)–C(8) 122.1(2)°, C(7)–C(8)–C(9) 123.7(2)°.



Scheme 1



3

Scheme 2 R = $SiMe_3$

only two previous examples of dinuclear 14-electron complexes with comparable Zr–Zr bond lengths.[9] Evidently electron deficiency significantly favours metal–metal interactions. The hafnium compound **1b** decomposes less cleanly than **1a**, to give a mixture of products which could not be separated. There was, however, no evidence for the formation of a dinuclear hafnium analogue of **2**.

Treatment of **2** with $B(C_6F_5)_3$ leads to the zwitterionic complex **3** (Scheme 2). Only one of the two butadienyl ligands is attacked by the borane, even in the presence of an excess of $B(C_6F_5)_3$. At −50 °C the ^{19}F NMR spectrum shows six signals for the *o*-F atoms of three different C_6F_5 substituents, indicative of hindered rotation; there is however no evidence for an *ortho*-F···Zr coordination, unlike in the structurally related zwitterionic allyl complex $[Zr(\eta\text{-}C_5H_5)_2(\eta^3\text{-}CH_2CHCHCH_2\text{-}B(C_6F_5)_3]$.[10]

Toluene solutions of **1a** do not react with ethene (1 bar) at 0 °C§ but on addition of 1 equiv. of $B(C_6F_5)_3$ catalyse the polymerisation of ethene with a productivity of 3×10^4 g PE (mol Zr)$^{-1}$h^{-1}. Related allyl complexes $[Zr(Cp'')(\eta^3\text{-allyl})\text{-}(diene)]$ are similarly active.[11] By contrast, complex **3** is inactive under identical conditions, though some polymerisation takes place on warming to 64 °C. These findings support the notion that, apart from hydrolysis reactions and the intervention of nucleophilic impurities, deactivation of metallocene-type polymerisation catalysts is linked to the formation of dinuclear products as a result of a number of C–H activation pathways.

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Footnotes

† *NMR spectroscopic data*: **1a**; ^1H (C_6D_6, 300 MHz, 25 °C) δ −0.30 (br s, 3 H, ZrMe), 0.27 (s, 18 H, SiMe), 0.45 (d, 2 H, *J* 9.6 Hz, $=CH_2$ *anti*); 2.00 (s, 6 H, diene-Me), 2.34 (d, 2 H, *J* 9.6 Hz, $=CH_2$ *syn*), 6.04 (br s, 2 H,, 4,5-C_5H_3) 7.10 (br s, 1 H, 2-C_5H_3). ^{13}C (C_6D_6, 75.4 MHz, 25 °C) δ 0.11 (q, *J* 119.0 Hz, SiMe), 23.3 (q, *J* 126.1 Hz, diene-Me), 45.2 (br q, *J* 113.2 Hz, ZrMe), 63.2 (t, *J* 142.3 Hz, $=CH_2$), 117.4 (d, *J* 169.8 Hz, 4,5-C_5H_3), 122.6 (d, *J* 167.5 Hz, 2-C_5H_3), 123.4 (m, =*C*Me) 119.84 (m, 1,3-C_5H_3). **1b**; ^1H (C_6D_6, 300 MHz, 25 °C) δ −0.65 (s, 3 H, HfMe), −0.21 (d, 2 H, *J* 11.4 Hz, $=CH_2$ *anti*), 0.25 (s, 18 H, SiMe), 2.11 (s, 6 H, diene-Me), 2.33 (d, 2 H, *J* 11.4 Hz, $=CH_2$ *syn*), 6.0 (d, 2 H, *J* 1.8 Hz, 4,5-C_5H_3), 6.91 (t, 1 H, *J* 1.8 Hz, 2-C_5H_3). ^{13}C (C_6D_6, 25 °C) δ 0.7 (q, *J* 119.1 Hz, SiMe), 23.2 (q, *J* 126.1 Hz diene-Me), 53.4 (q, *J* 111.4 Hz, HfMe), 68.0 (t, *J* 139.5 Hz, $=CH_2$), 117.2 (d, *J* 169.0 Hz, 4,5-C_5H_3), 122.4 (d, *J* 168.3 Hz, 2-C_5H_3), 123.7 (m, =*C*Me), 126.8 (m, 1,3-C_5H_3). **2**; ^1H (C_6D_6, 300 MHz, 25 °C) δ 0.06, 0.52 (s, 9 H, SiMe), 1.50 (s, 1 H, ZrCHZr), 1.80, 1.85 (s, 3 H, diene-Me), 2.03, 3.78 (d, 1 H, *J* 5.7 Hz, $=CH_2$), 4.58, 6.20 (dd, 1 H, *J* 2.9, 1.9 Hz, 4,5-C_4H_3), 6.60 (t, 1 H, *J* 1.9 Hz, 2-C_5H_3). ^{13}C (C_6D_6, 25 °C) δ 0.7, 0.8 (q, *J* 119.0 Hz, SiMe), 24.0 (q, *J* 126.0 Hz, diene-Me), 25.4 (q, *J* 126.2 Hz, diene-Me), 65.6 (t, *J* 144.5 Hz, $=CH_2$), 116.0, 116.7 (d, *J* 168.3 Hz, 4,5-C_5H_3), 116.9 (d, *J* 169.0 Hz, 2-C_5H_3), 111.8, 115.2, 118.6, 127.5 (m, 1,3-C_5H_3 and =*C*Me), 174.9 (d, *J* 111 Hz, ZrCHZr); **3**; ^1H (CD_2Cl_2, 300 MHz, −20 °C) δ 0.31, −0.08, 0.16, 0.48 (s, 9 H, SiMe), 0.58, 2.78 (s, 1 H, ZrCHZr), 1.23, 3.17 (d, 1 H, *J* 6.3 Hz, $=CH_2$), 1.66, 1.81, 1.97 (s, 6 H, 3 H, 3H diene-Me), 1.69 and 1.98 (two s, 1 H each, CH_2B. These signals overlap with those for diene-Me and were identified from difference spectra), 5.29, 5.63, 6.48, 6.55 (m, 1 H each, Cp″), 6.61 (m, 2 H, Cp″). $^{13}C\{^1H\}$ (CD_2Cl_2, 75.4 MHz, −50 °C) δ −0.9, −0.6, −0.3, 0.2 (SiMe), 18.9, 23.4, 24.7, 27.0 (diene-Me), 29.8 (br, BCH_2), 67.6 (br, $=CH_2$), 106.8, 112.4, 115.7, 119.7, 119.9, 122.7, 123.0, 123.9, 124.5, 131.1, 133.7, 146.6, 149.9, (Cp″, =*C*Me), 180.4, 179.2 (ZrCHZr). $^{11}B\{^1H\}$ (CD_2Cl_2, 96.25 MHz, −70 °C) δ −12.0. ^{19}F (CD_2Cl_2, 2.82 MHz, −50 °C) δ −129.0, −129.3, −130.7, −132.8, −133.08, −135.0 (*o*-F of C_6F_5), −160.9 (2 F, *p*-F of C_6F_5), −161.54 (1 F, *p*-F of C_6F_5), −165.0, −165.35, −165.7 (2 F each, *m*-F of C_6H_5).

‡ *Crystal data* for **2**: $C_{34}H_{60}Si_4Zr_2$, M = 763.62, crystal size 0.38 × 0.26 × 0.19 mm, triclinic, space group $P\bar{1}$, a = 8.957(2), b = 10.105(2), c = 12.1262(14) Å, α = 86.249(12), β = 76.699(12), γ = 66.353(14)°, U = 978.0(3) Å^3, Z = 1, D_c = 1.297 Mg m^{-3}, $F(000)$ = 400, μ = 0.676 mm^{-1}, T = 160 K. 3434 reflections were collected on a Stoe STADI4 4-circle diffractometer using graphite monochromated Mo-Kα radiation (λ = 0.710 73 Å) and ω–θ scans. Data were corrected for absorption empirically using azimuthal ψ-scans. The structure was solved by heavy-atom methods[12] and was refined by full-matrix least-squares analysis on F^2 using all 3434 reflections.[13] $R_w = \{\Sigma[w(F_o^2 - F_c^2)^2/\Sigma\{w(F_o^2)^2]\}^{1/2} = 0.0608$ for all data, conventional R [on F values of 3173 reflections with $R_o^2 > 2\sigma(F_o^2)$] = 0.0232, goodness of fit S 1.141 on all F^2 for 201 parameters. All non-hydrogen atoms were refined with anisotropic displacement parameters. All hydrogen atoms were constrained to idealised positions with fixed isotropic displacement parameters of nU_{eq} (where n was 1.5 for methyl and 1.2 for all others) except those on atoms C(6) and C(9) which were located on a Fourier difference synthesis and were freely refined with individual isotropic displacement parameters. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 182/381.

§ After the submission of this article the oligomerisation of ethene by the related complex $[Zr(\eta\text{-}C_5Me_5(C_6H_{10})Bu^n]$ in the absence of $B(C_6F_5)_3$ has been reported: B. Hessen and H. van der Heijden, *J. Am. Chem. Soc.*, 1996, **118**, 11670.

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