Direct Observation of β-Methyl Elimination in Cationic Neopentyl Complexes: Ligand Effects on the Reversible Elimination of Isobutene

Andrew D. Horton

Shell Research and Technology Centre, Amsterdam, Postbus 38000, 1030 BN Amsterdam, The Netherlands

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Summary: β-Me elimination from cationic neopentyl complexes, $[Cp'_2Zr(CH_2CMe_3)]^+$, has been demonstrated. The more crowded complex ($Cp' = C_5Me_5$) eliminates isobutene instantaneously at −75 °C, whereas the less crowded analogue ($Cp' = C_5H_5$) is stable in solution at 0 °C but undegoes reversible β-Me elimination at 25 °C; strong anion or Lewis base coordination suppresses β-Me elimination, consistent with involvement of a 14-electron species.

β-Alkyl elimination, although much less common than β-hydrogen elimination/transfer in alkene polymerization catalysis, has recently been implicated in several processes using $[(C_5Me_5)_2ZrR]^+$ catalysts, including the formation of propene oligomers with vinyl end groups ($CH_2{=}CHCH_2-$)[1] and the cyclopolymerization of 2-methyl-1,5-hexadiene.[2] The propagation step in the ring-opening polymerization of methylenecyclobutane involves a β-alkyl shift.[3] *Direct observation* of β-Me elimination in d^0 complexes is, however, rare and limited to *in situ* generated isobutyl (and related) complexes which also undergo competing β-hydrogen elimination.[4] Although widely used neopentyl ligands are known to decompose by α- or γ-hydrogen activation,[5] we postulated that complexes of the form $[Cp'_2Zr(CH_2CMe_3)]^+$ would undergo β-Me elimination.[6,7] Here we report the first direct observations of β-Me elimination at a base-free d^0 metallocene, which also represent the first cases of neopentyl ligand decay by this process.[8−10] Irreversible allylic activation of the isobutene elimination product has been found to compete with the reversible insertion of isobutene in the Zr−Me bond.[10]

The proposed route to cationic metallocene neopentyl complexes relied on the hypothesis that the mixed complexes $Cp'_2ZrMe(CH_2CMe_3)$ ($Cp' = C_5Me_5$, **1**; $Cp' = C_5H_5$, **2**)[11−13] would undergo selective abstraction of the sterically more accessible methyl ligand.[14] This route was chosen due to the difficulty in synthesizing bis(neopentyl) adducts of crowded metallocenes and the expected inertness of such crowded dialkyls toward alkyl abstraction (using Brönstead or, particularly, Lewis acids).[8]

Reaction of **1** with $B(C_6F_5)_3$ in C_6D_5Br or C_7D_8 solution at 25 °C cleanly generates $(C_5Me_5)_2ZrMe\{MeB(C_6F_5)_3\}$ (**3**), identified by ^1H and ^{19}F NMR spectroscopy and comparison to literature data,[15] together with 1 equiv of isobutene (Scheme 1). The putative neopentyl intermediate, $(C_5Me_5)_2Zr(CH_2CMe_3)\{MeB(C_6F_5)_3\}$, is not observed, even when the reaction is carried out at −75 °C in an NMR tube. Similarly, $[PhMe_2NH][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ cleanly and instantly afford $[(C_5Me_5)_2ZrMe][B(C_6F_5)_4]$ and isobutene.

Although the neopentyl cation is too unstable to be observed, even at low temperatures, preliminary results indicate that it may be trapped as Lewis base adducts, $[(C_5Me_5)_2Zr(CH_2CMe_3)(L)]^+$ (**4a**−**c**). Whereas the labile THF adduct **4a** (formed with 1.2 equiv of THF) undergoes β-Me elimination with a $t_{1/2}$ of about 5 min at 25 °C, the adducts formed with a 1.5-fold excess of RCN (R = Me, Me_3C) are stable in solution for several hours (Scheme 1) and isobutene formation may not be ob-

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(7) Evidence for β-Me elimination from the (unobserved) neopentyl cation, $[(C_5H_5)_2Zr(CH_2CMe_3)]^+$, has been obtained from gas-phase studies: Christ, C. S., Jr.; Eyler, J. R.; Richardson, D. E. *J. Am. Chem. Soc.* **1990**, *112*, 596.

(8) Protonolysis of the Schiff-base complex $(R_6\text{-acen})Zr(CH_2CMe_3)_2$ gives cationic neopentyl complexes, which appear not to undergo β-Me elimination: Tjaden, E. B.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1995**, *14*, 371.

(9) Evidence for reversible β-Me elimination involving a $Pd{-}CH_2SiMe_3$ fragment has been obtained: Ankianiec, B. C.; Christou, V.; Hardy, D. T.; Thompson, S. K.; Young, G. B. *J. Am. Chem. Soc.* **1994**, *116*, 9963.

(10) The first direct observation of reversible β-Me elimination/migratory insertion (in a 3,3-dimethylruthenacyclobutane) was very recently reported: McNeill, K.; Andersen, R. A.; Bergman, R. *J. Am. Chem. Soc.* **1995**, *117*, 3625.

(11) Complexes **1** and **2** were synthesized by reaction of $[Cp'_2ZrMe(THF)]^+[B(4\text{-}C_6H_4F)_4]^-$ ($Cp' = C_5Me_5$ or C_5H_5)[12] with $LiCH_2CMe_3$ in THF/Et_2O, followed by crystallization from hexane/toluene.

(12) Horton, A. D.; Orpen, A. G. *Organometallics* **1991**, *10*, 3910.

(13) Selected NMR data (^1H NMR, C_6D_5Br, 25 °C, unless otherwise stated). **1**: δ 1.80 (C_5Me_5), 0.95 (CMe_3), −0.10 ($ZrCH_2$), −0.57 ($ZrMe$). **2**: δ 5.92 (C_5H_5), 0.98 (CMe_3), 0.42 ($ZrCH_2$), 0.17 ($ZrMe$). **4a**: δ 3.31 (br, THF, averaged), 1.65 (C_5Me_5 and THF), 1.07 ($ZrCH_2CMe_3$), 0.75 ($ZrCH_2$). **4c**: δ 1.64 (C_5Me_5), 1.06 (Me_3CN averaged), 0.84 ($ZrCHCMe_3$), 0.44 ($ZrCH_2$). **5a**: ^1H NMR (C_7D_8, 25 °C) δ 5.63 (C_5H_5), 1.13 ($ZrCH_2$), 0.79 (CMe_3), 0.16 (br, BMe); ^{13}C NMR (C_7D_8, −25 °C) δ 101.8 (t, $^1J_{CH}$ = 109 Hz, $ZrCH_2$), 42.1 (CMe_3), 33.9 (CMe_3); ^{19}F NMR (C_7D_8, −50 °C) δ −135.12 (d), −159.76 (t), −165.16 (m). **5b**: δ 5.92 (C_5H_5), 1.12 ($ZrCH_2$), 0.85 (CMe_3). **7a**: δ 5.97 (C_5H_5), 3.19 (THF), 1.47 (THF), 1.17 ($ZrCH_2$), 0.92 (CMe_3). **8**: ^1H NMR (1:1 C_7D_8:C_6D_5Br, −60 °C) δ 5.16, 5.08 (C_5H_5), 2.79, 2.32 (allyl CH_2), 1.52 (allyl Me), 1.37 (BMe); ^{13}C NMR ($C_2D_2Cl_4$, −30 °C) δ 158.8 (allyl C), 67.5 (allyl CH_2), 29.7 (allyl Me). **9**: ^1H NMR ($C_2D_2Cl_4$, −35 °C) δ 6.10, 5.87 (C_5H_5), 4.90 (1H, allyl CH), 3.10, 2.71 (1H, allyl CH_2), 2.63 (2H, CH_2), 2.16, 1.92, 1.68, 1.22 (1H, CH_2), 0.20 (BMe); ^{13}C NMR ($C_2D_2Cl_4$, −10 °C) δ 152.4 (allyl C), 104.4 (allyl CH), 48.6 (allyl CH_2).

(14) Temme, B.; Erker, G. *J. Organomet. Chem.* **1995**, *488*, 177.

(15) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

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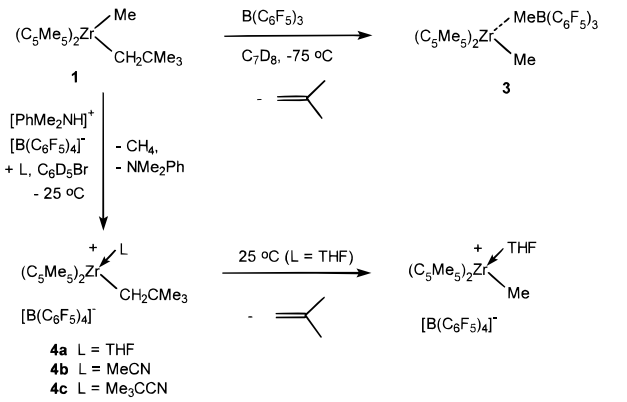
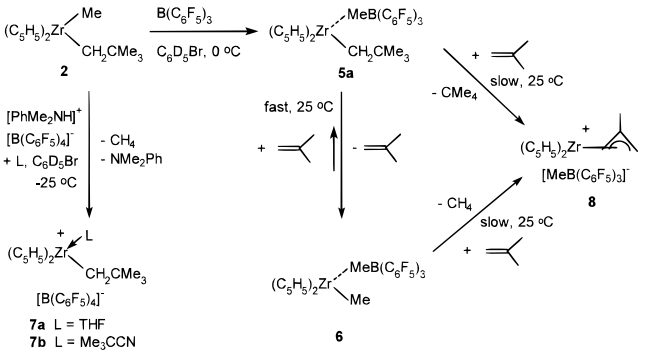
Scheme 1



Scheme 2

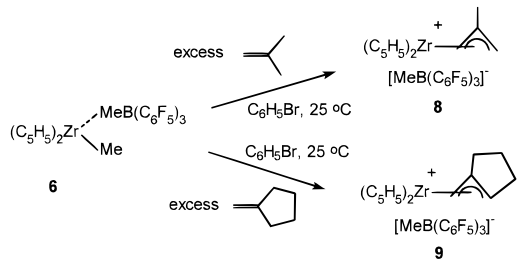


served. In the case of **4c**, slow decomposition to unidentified organometallic species occurs over 24 h, with formation of CMe_4. These results are consistent with β-Me elimination proceeding via a cationic 14-electron species, formed by Lewis base or anion ($[MeB(C_6F_5)_3]^-$) dissociation. Strong nitrile coordination to zirconium therefore totally suppresses β-elimination.

A significant increase in stability of cationic neopentyl complexes is observed for the cyclopentadienyl system. Selective methyl abstraction from **2** with $B(C_6F_5)_3$ rapidly generates $(C_5H_5)_2Zr(CH_2CMe_3)\{MeB(C_6F_5)_3\}$ (**5a**), which is stable in C_7D_8 solution at 0 °C (Scheme 2). The upfield location of the B−*Me* ^{1}H NMR resonance (C_7D_8, −25 °C) at δ 0.16 ppm (free anion: δ 1.1 ppm)[14] and the characteristic large difference (5.4 ppm) in the chemical shifts of the *meta*- and *para*-fluorines of the anion (free anion: $\Delta\delta(m,p\text{-F}) = 2.7$ ppm)[16] are consistent with anion coordination to zirconium. Neither **5a** (^{1}H NMR in range −50 to 25 °C; ^{13}C NMR, −25 °C) nor the more electrophilic analogue $[(C_5H_5)_2Zr(CH_2CMe_3)][B(C_6F_5)_4]$ (**5b**) (^{1}H NMR, −25 °C),[17] obtained using the trityl reagent, show evidence for β-C−Me···Zr agostic stabilization of the zirconium center.[18]

On warming solutions of **5a** to 25 °C (C_6D_5Br, 0.03 M), resonances appear for isobutene and the methylzirconocene complex $(C_5H_5)_2ZrMe\{MeB(C_6F_5)_3\}$ (**6**).[13] In contrast to the pentamethylcyclopentadienyl analogue, β-Me elimination appears to be reversible,[9] as shown

Scheme 3



by the observation of a constant 1:3 molar ratio of **5a** and **6** after 20 min (Scheme 2). Indeed, exposure of a solution of **6** (C_6D_5Br, 0.02 M) to 20 equiv of isobutene affords a 4:1 mixture of **5a** and **6** at equilibrium. Lewis base coordination to the neopentyl cation again suppresses β-Me elimination: THF adduct **7a** (formed *in situ* by protonolysis using 1.2 equiv of Lewis base) and Me_3CCN adduct **7b** (1.5 equiv base) are stable in solution for 24 h. The greater stability of **7a**, compared to C_5Me_5 analogue **4a**, reflects the lower tendency toward THF dissociation in the less crowded system (distinct resonances for coordinated and free THF in **7a**; ^{1}H NMR, 25 °C).

The isobutene product of β-Me elimination from **5a** is partially consumed over several hours, giving the η^3-(2-methylallyl) complex, **8**,[1b,19,20] together with minor decomposition products (C_6D_5Br).[21] The release of *both* methane and neopentane, in amounts related to the relative concentrations of the two complexes, suggests that allylic activation (via σ-bond metathesis)[20a] involves both Zr−methyl and Zr−neopentyl complexes (Scheme 2). The more electon-deficient neopentyl cation, **5b**, also undegoes β-Me elimination, followed by isobutene activation, but more rapidly than the $[MeB(C_6F_5)_3]^-$ adduct. In one experiment the ratio of the neopentyl, methyl, and the 2-methylallyl complexes after 35 min was 1:8:11 (C_6D_5Br, 25 °C). Allyl formation is faster and cleaner in the presence of excess isobutene, and **8** may be isolated by treatment of **6** with a large excess of the alkene (Scheme 3).[22]

Preliminary investigations of other 1,1-disubstituted alkenes, CH_2=C(Me)(Et), CH_2=C(Me)(*n*-Pr), and CH_2=CEt_2, have shown that reversible insertion in the Zr−Me bond of **6** and (slower) irreversible allylic activation form a general reactivity pattern. Formation of a mixture of **6** and insertion product $(C_5H_5)_2Zr\{CH_2CMe(R^1)(R^2)\}\{MeB(C_6F_5)_3\}$ (ratio dependent on the alkene and the excess used) is followed by conversion to η^3-allyl complexes.[1b,19,20] Methylenecyclopentane, in con-

(16) The value of $\Delta\delta(m,p\text{-F})$ (^{19}F NMR) is a good probe of coordination of $[RB(C_6F_5)_3]^-$ (R = Me, CH_2Ph), to cationic d^0 metals (values 3−6 ppm indicate coordination; <3 ppm indicates noncoordination): Horton, A. D. Unpublished results.

(17) The complex reaction of **2** with $[PhMe_2NH][B(C_6F_5)_4]$, involving C−H activation of the Lewis base, will be published elsewhere.

(18) (a) Gleiter, R.; Hyla-Kryspin, I.; Niu, S.; Erker, G. *Organometallics* **1993,** *12*, 3828. (b) Koga, N.; Kawamura-Kuribayashi, H. *J. Am. Chem. Soc.* **1988**, *110*, 108.

(19) For examples of electrophilic allyl complexes of d^0 metallocenes see ref 20 and the following: (a) Tjaden, E. B.; Casty, G. L.; Stryker, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 9814. (b) Horton, A. D. *Organometallics* **1992**, *11*, 3271. (c) Jordan, R. F.; LaPointe, R. E.; Bradley, P. K.; Baenziger, N. *Organometallics* **1989**, *8*, 2892.

(20) For well-defined cases of η^3-allyl formation on activation of 1-alkenes by d^0 metallocenes see the following: (a) Thompson, M. E.; Baxter, S. M.; Bulls, A. R.; Burger, B. J.; Nolan, M. C.; Santarsiero, B. D.; Schaefer, W. P.; Bercaw, J. E. *J. Am. Chem. Soc.* **1987**, *109*, 203. (b) Jeske, G.; Lauke, H.; Mauermann, H.; Schumann, H.; Marks, T. J. *J. Am. Chem. Soc.* **1985**, *107*, 8091.

(21) Solvent effects were significant. In less polar C_7D_8 (0.03 M), β-Me elimination is slower than in C_6D_5Br (1:4 ratio of **5a** and **6** after 3 h). Over longer periods unidentified decomposition products were observed, but η^3-allyl formation was insignificant.

(22) Preparation of **8** and **9**: A large excess of isobutene (or 2.5 mmol of methylenecyclopentane) was added to a bromobenzene (4−7 mL) solution of **6** (0.60 mmol) at 25 °C. After 5−15 min, hexane addition afforded a yellow oil, which was washed with hexane; the resulting solid was dried *in vacuo* (NMR: **8**, 85% pure; **9**, >90% pure).

trast, undergoes virtually instantaneous and clean C−H bond activation (C_6D_5Br, 25 °C, <5 min, >90% selectivity), giving isolable η^3-allyl product **9** (Scheme 3).[22] The sterically accessible nature of the allylic hydrogens may facilitate this reaction, which contrasts to the ring-opening polymerization reported for more strained methylenecyclobutane.[3] Complexes **8** and **9** exhibit characteristic ^1H and ^{13}C NMR resonances for the η^3-allyl ligand, and each undergoes a fluxional process involving η^3,η^1-allyl interconversion.[23]

Given the wide use of neopentyl ligands, the demonstration of ligand degradation by β-Me elimination is of importance. The neopentyl cations undergo β-Me elimination without the competing β-hydrogen elimination, which has complicated previous studies of this process. The facility of β-Me elimination is strongly dependent on the ligand and anion environment, consistent with involvement of a coordinatively unsaturated 14-electron species. The rapid β-Me elimination observed for the more crowded metallocene presumably reflects labile anion/base/solvent coordination and is consistent with β-Me elimination as the major chain transfer step in propene oligomerization using $[(C_5Me_5)_2ZrR]^+$. The discovery that 1,1-disubstituted alkenes undergo allylic activation (in one case rapidly) provides support for allyl formation as a potential catalyst deactivation mechanism.[1b,20]

(23) The following approximate values of $\Delta G^{\ddagger}$ for the fluxional process involving η^3,η^1-allyl interconversion were determined. Complex **8**: 13.7 kcal mol^{-1} (C_5H_5 coalescence, T_c = 0 °C) and 14.2 kcal mol^{-1} (allyl syn/anti-hydrogen coalescence, T_c = 10 °C); the two values are effectively identical. Complex **9**: 11.7 kcal mol^{-1} (C_5H_5 coalescence, T_c = −30 °C).

Supporting Information Available: Text describing full details of the preparation and characterization of the compounds (11 pages). Ordering information is given on any current masthead page.

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