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Zirconium bent sandwich complex with a dicarbahexaborate ligand: $[Li(THF)_3]\{[\eta^5-C_2B_4H_4(SiMe_3)_2](\eta^5-C_5Me_5)ZrCl_2\}$

Shane S.H. Mao [a], T. Don Tilley [a,*], Arnold L. Rheingold [b], Narayan S. Hosmane [c]

[a] *Department of Chemistry, University of California at Berkeley, Berkeley, CA 94720-1460, USA*
[b] *Department of Chemistry and Biochemistry, University of Delaware, Newark, DE 19716-2522, USA*
[c] *Department of Chemistry, Southern Methodist University, Dallas, TX 75275, USA*

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Abstract

The complex $[Li(THF)_3]\{[\eta^5-C_2B_4H_4(SiMe_3)_2](\eta^5-C_5Me_5)ZrCl_2\}$ was synthesized via reaction of $(C_5Me_5)ZrCl_3$ with the dicarbahexaborate dianion $[C_2B_4H_4(SiMe_3)_2]^{2-}$. This new metallocene derivative may be described as an anionic, bent sandwich complex associated with an $[Li(THF)_3]^+$ cation via interaction with a boron atom of the $[C_2B_4H_4(SiMe_3)_2]^{2-}$ cage. The dicarbahexaborate and pentamethylcyclopentadienide ligands are coordinated to the zirconium in an η^5 fashion, and the coordination geometry about the Zr atom is that of a distorted tetrahedron defined by the two chlorides and the centroids of the pentamethylcyclopentadienyl and dicarbahexaborate ligands. The Cl–Zr–Cl angle is 94.6(1)° and the (C_2B_3 centroid)–Zr–(C_5Me_5 centroid) angle is 131.3°. Attempts to synthesize zirconium silyl and alkyl complexes incorporating this carborane ligand have so far failed.

Keywords: Zirconium; Boron; Lithium; Cyclopentadienyls; Carboranes

1. Introduction

Since the discovery of Ziegler–Natta catalysis, olefin polymerization has become a very important industry [1]. Thus, much interest has focused on the development of new olefin polymerization technologies [2,3]. In recent years, polymerizations with so-called 'second generation' catalysts, which are based on 14-electron, d^0, bent-zirconocene alkyl complexes of the type $[(\eta^5-C_5R_5)_2ZrR']^+$, have been the subject of many investigations [3,4]. Our interest in catalysts of this type stems largely from their ability to also mediate the dehydropolymerization of hydrosilanes to polysilanes [5–7]. We have proposed a σ-bond metathesis mechanism for this polymerization, which is related to the widely-accepted mechanism for olefin polymerization in that it involves 2 + 2 cycloaddition steps with M–R σ-bonds [7]. For dehydropolymerization, metal–hydrogen (rather than metal–carbon) bonds participate in the four-center transition states.

Studies on the influence of catalyst structure on dehydropolymerization suggest that steric properties for the cyclopentadienyl ligands play an important role in determining catalyst activity, the molecular weight for the resulting polymer, and the ratio of linear polymer to cyclic oligomers [6]. Sterically hindered ligands such as pentamethylcyclopentadienyl (Cp*) increase the stability of the catalytically active monomeric hydride species, but decrease the accessibility of the metal center. The sterically less demanding cyclopentadienyl ligand provides a more accessible metal center but a less stable catalyst. Thus the intermediate, 'mixed-ring' CpCp*Zr ligand set provides optimum conditions for maximization of catalytic activity with respect to polymer chain elongation [7]. In general, it appears that the most active catalysts in polymerization are hydride complexes that are sterically protected against formation of μ-hydride dimers, while possessing metal centers that are sufficiently exposed to allow facile coordination of the monomer's Si–H bond [7].

Clearly, a major goal in catalyst design for both olefin and silane polymerization is the synthesis of stable but coordinatively unsaturated species [3,4,7]. One strategy for synthesizing zirconocene derivatives

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[*] Corresponding author.

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with a lower coordination number involves replacement of a cyclopentadienyl ligand in a metallocene complex with an isolobal, dinegative ligand such as a dicarbollide or borollide [8]. This substitution should result in neutral, 14-electron complexes that are isoelectronic with cationic $[(\eta^5\text{-}C_5R_5)_2ZrR']^+$ species. In 1991, the synthesis and high polymerization activity of $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})ZrMe]_n$, which is associated in solution, was reported by Jordan and coworkers [9]. Our interest in metal-catalyzed polymerizations [5–7] led us to attempt development of more hindered (and therefore monomeric) catalysts based on the sterically demanding carborane ligand $[C_2B_4H_4(SiMe_3)_2]^{2-}$ [10,11]. In related studies, Grimes and coworkers have synthesized bent sandwich complexes of Ti, Zr, Hf, Nb, and Ta containing C_2B_3 and C_2B_4 carborane ligands. The complexes $(\eta^5\text{-}C_5R_5)(\eta^5\text{-}C_2B_4H_4Et_2)ZrCl(THF)$ (R = H, Me), and the structures of various related Nb and Ta derivatives were reported [12]. Recently, this group also described the polymerization of ethylene with $(\eta^5\text{-}C_2B_4H_4Et_2)TiCl_2(PMe_3)_2$ as a catalyst component [13,14].

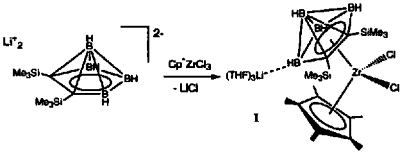
2. Results and discussion

An attempted synthesis of $(\eta^5\text{-}C_5Me_5)[\eta^5\text{-}C_2B_4H_4(SiMe_3)_2]ZrMe$ was based on the reported method for $[(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_2B_9H_{11})ZrMe]_n$, via reaction of the carborane $C_2B_9H_{13}$ with Cp^*ZrMe_3 ($Cp^* = C_5Me_5^-$) [9]. Unfortunately, reaction of the free ligand $(Me_3Si)_2C_2B_4H_6$ with Cp^*ZrMe_3 in THF or benzene gave a complex mixture of products, as indicated by numerous peaks in the C_5Me_5 region of the ^1H NMR spectrum. Monitoring this reaction at low temperature (−78 °C) by ^1H NMR spectroscopy revealed the generation of methane (0.26 ppm) and initial formation of a new species with a Cp^* resonance at 2.1 ppm. The decomposition of this transient species occurred rapidly even at low temperature, indicating that the expected product, $(\eta^5\text{-}C_5Me_5)[\eta^5\text{-}C_2B_4H_4(SiMe_3)_2]ZrMe$, may be unstable.

A second synthetic strategy was based on the intermediate metal chloride complex $(\eta^5\text{-}C_5Me_5)[\eta^5\text{-}C_2B_4H_4(SiMe_3)_2]ZrCl$, which could potentially serve as a precursor to metal alkyl and hydride derivatives. Owing to the ability of Cl to act as a four-electron donor, we expected this species to be more stable than its alkyl analogue. The in situ deprotonation of $(Me_3Si)_2C_2B_4H_6$ by 2 equiv. of ^nBuLi at 0 °C generated the dianion $[C_2B_4H_4(SiMe_3)_2]^{2-}$ in THF [10]. Addition of Cp^*ZrCl_3 to this dianion solution afforded compound **1** in ca. 70% yield (by NMR, Eq. (1)). Recrystallization of this compound from pentane containing a trace amount of THF afforded yellow crystals in about 50% yield. The ^1H NMR spectrum of compound **1** contains a singlet for the C_5Me_5 ligand, a singlet for the trimethylsilyl groups, and peaks for 3 equiv. of tetrahydrofuran.

NMR spectroscopic data for **1**. ^1H NMR (benzene-d_6, 300 MHz): δ 3.49 (t, $J = 8.1$, 12 H, C_4H_8O), 2.17 (s, 15 H, C_5Me_5), 1.38 (t, $J = 8.1$, 12 H, C_4H_8O), 0.74 (s, 18 H, $SiMe_3$). $^{13}C\{^1H\}$ NMR (benzene-d_6, 100.6 MHz): δ 123.34 (C_5Me_5), 68.55 (C_4H_8O), 25.42 (C_5Me_5), 13.23 (C_4H_8), 3.55 ($SiMe_3$). ^{11}B NMR (benzene-d_6, 96 MHz): δ 29.0 (br, 2 B), 20.1 (br, 1 B), −18.9 (d, 1 B, $J_{B-H} = 149$ Hz).

Note that the trimethylsilyl resonance is at low field (0.76 ppm, compared to the resonance of 0.26 ppm for the free carborane). This significant downfield shift may be attributed to aromatization to the six-electron, five-membered carborane ring.



(1)

The $^{11}B\{^1H\}$ NMR spectrum of compound **1** (benzene-d_6) contains a resonance at δ −18.9 attributed to the apical boron atom, and resonances at 21.5 and 29.4 (1:2 ratio) which are assigned to the remaining boron atoms in the C_2B_3 ring. Compared to the ^{11}B resonances for the free carborane, the resonances in compound **1** are shifted upfield by ca. 30 ppm, which may also be attributed to aromatization. Finally, a positive flame test for lithium and the combustion analysis suggested the presence of one equivalent of LiCl in the molecule.

Anal. Found: C, 49.10; H, 8.54. $C_{30}H_{61}B_4Cl_2LiO_3Si_2Zr$ Calc.: C, 48.81; H, 8.33%.

Crystals of **1** suitable for X-ray diffraction were obtained by slow cooling (−10 °C) of a saturated pentane solution containing a trace amount of THF.

Crystal data for **1**. $C_{30}H_{60}B_4Cl_2LiO_3Si_2Zr$, monoclinic, $P2_1/n$, $a = 12.033(3)$, $b = 17.483(3)$, $c = 19.296(5)$ Å, $\beta = 90.16(2)°$, $V = 4059.5(17)$, $Z = 4$, $T(\max)/T(\min) = 1.11$, $D_x = 1.206\ g\ cm^{-3}$, $T = 241$ K, $\mu(Mo\ K\alpha) = 4.88\ cm^{-1}$. Of 7370 data collected ($2\theta_{\max} = 50°$, Siemens P4 diffractometer), 7146 were independent and 3417 were observed at $5\sigma(F)$. All non-hydrogen atoms were refined with anisotropic thermal parameters and hydrogen atoms were treated as idealized contributions. At convergence, $R(F) = 6.16\%$ and $R(wF) = 8.18\%$.

A view of the molecular structure is given in Fig. 1, along with selected bond distances and angles. The

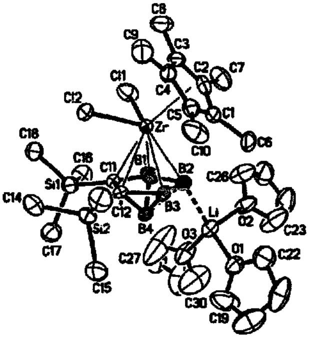


Fig. 1. ORTEP view of compound 1. Important bond distances (Å) and angles (deg): Zr–Cl(1) 2.447(3), Zr–Cl(2) 2.462(2), Zr–Cp 2.244, Zr–B(1) 2.549(11), Zr–B(2) 2.554(8), Zr–B(3) 2.507(10), Zr–Carb 2.151, Li–B(2) 2.501(13), Cl(1)–Zr–Cl(2) 94.6(1), Cp–Zr–Carb 131.3, Li–B(2)–Zr 162.1(5) (Cp and Carb refer to the centroids of the pentamethylcyclopentadienyl ligand and the carborane ligand respectively).

molecule may be described as a 'zwitterion', consisting of an anionic $\{(\eta^5\text{-}C_5Me_5)[\eta^5\text{-}C_2B_4H_4\text{-}(SiMe_3)_2]ZrCl_2\}^-$ bent sandwich fragment that is complexed by an *exo*-polyhedral $[Li(THF)_3]^+$ cation. The $[Li(THF)_3]^+$ cation is associated with the anion via interaction with a boron atom of the $[C_2B_4H_4(SiMe_3)_2]^{2-}$ cage, resulting in an Li ··· B distance of 2.527(17) Å. The dicarbahexaborate and pentamethylcyclopentadienyl ligands are both coordinated to the zirconium in an η^5 fashion. The coordination geometry about the Zr atom is that of a distorted tetrahedron defined by the two chlorides and the centroids of the C_5Me_5 and C_2B_3 rings. The Zr–Cl bond lengths are 2.447(3) and 2.462(2) Å, and the Zr–C_5Me_5 centroid and Zr–C_2B_3 ring centroid distances are 2.244 and 2.151 Å respectively. The Cl–Zr–Cl angle is 94.6(1)° and the (C_2B_3 centroid)–Zr–(C_5Me_5 centroid) angle is 131.3°. In the zirconium analog $[Li(THF)_2]\{[\eta^5\text{-}(Me_3Si)_2C_2B_4H_4]_2ZrCl(THF)\}$, the Zr–Cl bond length is 2.461(1) Å, and the average Zr–C_2B_3 ring centroid distance is 2.17 Å. In the latter complex, the Cl–Zr–O angle is 90.5(1)° and the (C_2B_3 centroid)–Zr–(C_2B_3 centroid) angle is 130.4° [10,11].

Compound 1 does not react with sterically hindered reagents such as $LiSi(SiMe_3)_3$, even at elevated temperature (benzene-d_6, 70 °C for 2 h). Reactions of 1 with MeLi and MeMgBr afforded many products, as determined by ^1H NMR spectroscopy. The reactivity of compound 1 with other reagents is currently under investigation.

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References

[1] K. Ziegler, E. Holzkamp, H. Breil and H. Martin, *Angew. Chem.*, *67* (1955) 541; G. Natta, *Angew. Chem.*, *68* (1956) 393; G. Fink, R. Mulhaupt and H.H. Brintzinger, *Ziegler catalysts: recent scientific innovations and technological improvements*, Springer, Berlin, 1995.

[2] W. Kaminsky, *Catalysis Today*, *20* (1994) 257.

[3] H.H. Brintzinger, D. Fischer, R. Mulhaupt, B. Rieger and R. Waymouth, *Angew. Chem., Int. Ed. Engl.*, *34* (1995) 1143.

[4] R.F. Jordan, C.S. Bajgur, R. Willet and B.J. Scott, *J. Am. Chem. Soc.*, *108* (1986) 7410.

[5] H.G. Woo, R.H. Heyn and T.D. Tilley, *J. Am. Chem. Soc.*, *114* (1992) 5698.

[6] H.G. Woo, J.F. Walzer and T.D. Tilley, *J. Am. Chem. Soc.*, *114* (1992) 7047.

[7] T.D. Tilley, *Acc. Chem. Res.*, *26* (1993) 22.

[8] G.C. Bazan, W.P. Schaefer and J.E. Bercaw, *Organometallics*, *12* (1993) 2126; R.W. Quan, G.C. Bazan, A.F. Kiely, W.P. Schaefer and J.E. Bercaw, *J. Am. Chem. Soc.*, *116* (1994) 4489; G.C. Bazan, S.J. Donnelly and G. Rodriguez, *J. Am. Chem. Soc.*, *117* (1995) 2671.

[9] D.J. Crowther, N.C. Baenziger and R.F. Jordan, *J. Am. Chem. Soc.*, *113* (1991) 1455.

[10] N.S. Hosmane, Y. Wang, H. Zhang, J.A. Maguire, E. Waldhor, W. Kaim, H. Binder and R.K. Kremer, *Organometallics*, *13* (1994) 4156.

[11] C.J. Thomas, L. Jia, H. Zhang, U. Siriwardane, J.A. Maguire, Y. Wang, K.L. Brooks, V.P. Weiss and N.S. Hosmane, *Organometallics*, *14* (1995) 1365.

[12] K.E. Stockman, K.L. Houseknecht, E.A. Boring, M. Sabat, M.G. Finn and R.N. Grimes, *Organometallics*, *14* (1995) 3014. K.L. Houseknecht, K.E. Stockman, M. Sabat, M.G. Finn and R.N. Grimes, *J. Am. Chem. Soc.*, *117* (1995) 1163.

[13] M.A. Curtis, M.G. Finn and R.N. Grimes, paper presented at the *BUSA-V-MEX Workshop, Guanajuato, Mexico, May 1996*, Abstr. No. 7.

[14] R. Uhrhammer, D.J. Crowther, J.D. Olson, D.C. Swenson and R.F. Jordan, *Organometallics*, *11* (1992) 3098; R.F. Jordan, *Makromol. Chem., Makromol. Symp.*, *66* (1993) 121; D.E. Bowen, R.F. Jordan and R.D. Rogers, *Organometallics*, *14* (1995) 3630; C. Kreuder, R.F. Jordan and H. Zhang, *Organometallics*, *14* (1995) 2993.