Structural Characterization of Zirconium Cations Derived from a Living Ziegler−Natta Polymerization System: New Insights Regarding Propagation and Termination Pathways for Homogeneous Catalysts

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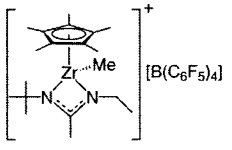
Critical to the continued evolution of highly active and stereoselective catalysts for the homogeneous Ziegler−Natta polymerization of α-olefins is the formulation of comprehensive rate laws that accurately describe the mechanism(s) by which these polymerizations can occur via electron-deficient metallocene and nonmetallocene alkyl cations of group 4 metals.[1] Of particular significance to this objective is the work of Mülhaupt[2] and Brintzinger,[3] which places dimers of ion pairs of the propagating species in the spotlight of potentially playing crucial roles in Ziegler−Natta polymerization. In the absence of concrete structural information that reveals the exact nature of these proposed species, however, it is not possible to visualize the full repertoire of parts that can be played by them, which might run the gamut from activation to stabilization to termination of the system. Herein, we present the structural characterization of several cationic zirconium complexes derived from the zirconium amidinate initiator, $Cp^*ZrMe[N(^tBu)C(Me)N(Et)][B(C_6F_5)_4]$ ($Cp^* = \eta^5\text{-}C_5Me_5$) (**1**), that is known to effect the stereospecific living polymerization of α-olefins and the living cyclopolymerization of α,ω-nonconjugated dienes.[4] Included in this study are the crystal structures of (1) a base-stabilized adduct of **1** itself, (2) the μ-CH_3, μ-CH_3 binuclear dication **2** that possesses unprecedented bridging α-agostic hydrogen interactions, and (3) the μ-CH_2, μ-CH_3 binuclear monocation **3**. In addition to shedding possible light on the origin of stereospecificity found in the present system, these data provide new insights regarding the ramifications that dimerization of cationic propagating species might have for Ziegler−Natta polymerization.



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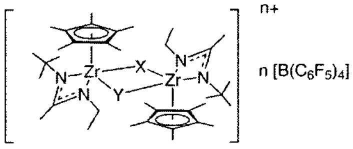

2: X = Y = CH_3, n = 2
3: X = CH_2, Y = CH_3, n = 1

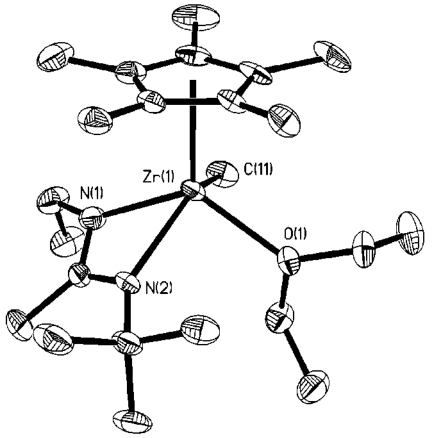

Figure 1. Molecular structure of $\mathbf{1}\cdot[OEt_2]$ (30% thermal ellipsoids). The $[B(C_6F_5)_4]$ and hydrogen atoms have been removed for the sake of clarity.

Table 1. Selected Bond Lengths (Å) for Compounds **1**−**4**[6]

	1	**2**	**3**	**4**
Zr(1)−N(1)	2.171(3)	2.135(4)	2.226(3)	2.251(3)
Zr(1)−N(2)	2.258(3)	2.199(3)	2.252(3)	2.265(2)
Zr(1)−X	2.255(4)	2.441(5)	2.302(3)	2.273(3)
[X]	[C(11)]	[C(11)]	[C(11)]	[C(14)]
Zr(1)−Y	2.233(2)	2.453(4)	2.302(4)	2.272(3)
[Y]	[O(1)]	[C(11A)]	[C(11A)]	[C(15)

Figure 1 and Table 1 provide the molecular structure and selected bond lengths for the bright yellow diethyl ether (OEt_2) complex of **1** obtained by adding a trace amount of this Lewis base to the crystallization medium.[5,6] As a standard feature of all the structures obtained in the present work no close intermolecular halide interactions between the cationic zirconium center with either the borate anion or the crystallographically included chlorobenzene molecules were observed. As can be seen in the table, the electron-deficient metal atom in **1** does have a pronounced shortening effect on the Zr−N bonds when compared to the corresponding values obtained for the neutral precatalyst **4**.[5,6] Thus, the apparent contradiction that propagation from **1** is stereospecific for α-olefin polymerization, while **4** has very low configurational stability, can be attributed, in part, to an increase in metal−amidinate bonding for the former that raises the barrier to racemization.[7] With respect to the possible origin of stereospecificity, it is interesting to note that coordination of the Lewis base to **1** occurs on the more sterically encumbered side of the amidinate ligand. Although there is no guarantee that this translates to being the preferred site for olefin complexation in solution, simple molecular modeling using the positional coordinates provided by the structure of **1** (minus OEt_2) does indicate that this site can, in fact, be highly stereodifferentiating with respect to α-olefin face selectivity.

In the absence of a Lewis base, tan-colored crystals of **2** can be obtained after several days at −10 °C and Figure 2 and Table 1 provide the molecular structure and selected bond lengths of this complex.[6] Of immediate interest is the planar Zr−C−Zr−C four-membered ring that is formed by two bridging methyl groups,

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[1] (a) Brintzinger, H. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143−1170. (b) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed.* **1999**, *38*, 428−447. (c) Gladysz, J. A., Ed. *Chem. Rev.* **2000**, *100*, special issue devoted to Frontiers in Metal-Catalyzed Polymerization.

[2] (a) Fischer D.; Mülhaupt, R. *J. Organomet. Chem.* **1991**, *417*, C7−C11. (b) Fischer, D.; Jüngling, S.; Mülhaupt, R. *Makromol. Chem., Macromol. Symp.* **1993**, *66*, 191−202.

[3] Beck, S.; Geyer; A.; Brintzinger, H. H. *J. Chem. Soc., Chem. Commun.* **1999**, 2477−2478.

[4] (a) Jayaratne, K. C.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 958−959. (b) Jayaratne, K. C.; Keaton, R. J.; Henningsen, D. A.; Sita, L. R. *J. Am. Chem. Soc.* **2000**, *122*, 10490−10491.

[5] Successful crystallizations using the $[B(C_6F_5)_4]$ counterion could only be achieved by severely curtailing the amount of material employed. While this limitation has hampered acquisition of chemical analyses for the new compounds, the ability to obtain single crystals by the following method was found to be reproducible. Typically, within a 5 mm NMR tube, 5 mg of $Cp^*ZrMe_2[N(^tBu)C(Me)N(Et)]$ (**4**)[4a] was demethylated with 1 equiv of $[PhNMe_2H][B(C_6F_5)_4]$ in 0.5 mL of chlorobenzene at −10 °C, to which an equal amount of pentane was then layered on top of the bright yellow solution.

[6] Details are provided in the Supporting Information.

[7] Racemization of **4** occurs through a facile amidinate "ring-flipping" process. By variable-temperature ^1H NMR (500 MHz), $\Delta G_c^\ddagger = 10.9$ kcal mol^{-1} and $T_c = 223$ K for dynamic exchange of diastereotopic methyl group resonances.

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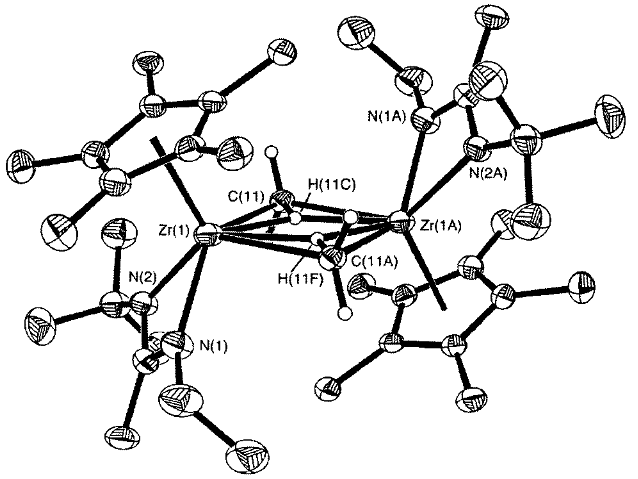


Figure 2. Molecular structure of **2** (30% thermal ellipsoids). The two $[B(C_6F_5)_4]$ anions and all but the bridging methyl hydrogen atoms, represented by spheres of arbitrary size, have been omitted for the sake of clarity. For each bridging methyl group, only the labeled hydrogen atom has been crystallographically located with the other two being placed in logical positions.

within which resides two crystallographically located hydrogen atoms, H(11C) and H(11F), that are engaged in bridging agostic interactions with both of the zirconium centers, Zr(1)−H(11C) 1.899(19) Å and Zr(1)−H(11F) 1.95(2) Å. From Table 1, it can be seen that dimerization of **1** to provide **2** serves to considerably shorten Zr−N bond lengths even further relative to both **1** and **4**. In contrast, the $Zr-C_{Me}$ bond length is remarkably elongated, suggesting a weaker zirconium−carbon bonding interaction that is apparently compensated for by the α-agostic hydrogen interactions. Accordingly, by analogy to the proposal that *intramolecular* α-agostic hydrogen interactions within a mononuclear complex can provide a mechanism for lowering the barrier height for migratory insertion during Ziegler−Natta polymerization,[8] the suggestion is made here that *bridging* α-agostic interactions in dimeric dications, such as **2**, might play a similar role, at least in the present system. Unfortunately, compound **2** is insoluble in all solvents so far tried thus frustrating attempts to obtain evidence for retention of its dimeric structure, and of these α-agostic interactions, in solution.

In contrast to the low-temperature crystallization results obtained above, bringing the initially formed solution of **1** to 25 °C provided orange-red crystals of the μ-CH_2, μ-CH_3 binuclear monocation **3** instead of **2**.[9] Figure 3 and Table 1 provide the molecular structure and selected bond lengths for this compound.[6] As Table 1 reveals, the reduction in charge on the two zirconium centers in **3**, relative to **2**, has the expected effect of lengthening the Zr−N bond lengths back toward the values obtained for **4**, but still somewhat longer than those found in the $\mathbf{1}\cdot OEt_2$ complex. The bridging Zr−C bond lengths (which represent the average of those for the positionally disordered μ-CH_2 and μ-CH_3 groups) are also shorter than those observed in **2**, and as no hydrogen atoms for the bridging methyl groups can be crystallographically located within this structure, we believe that any α-agostic interactions have been "turned off" due to the reduction in the electrophilicity of the zirconium centers. Regarding the uniqueness of **3**, Bochmann and co-workers[10] have previously provided spectroscopic evidence for a similar type of dizirconium μ-CH_2, μ-CH_3 monocation; however, the proposed methane elimination route to their complex can be viewed as being unique to their system. In the present case, we speculate that an increase in the acidity of the bridging methyl groups that occurs upon formation of **2** might provide a pathway to **3** through deprotonation by the dimethylaniline that remains after demethylation of the precatalyst **4**. Naturally, similar deprotonations of dimers formed from propagating species could represent a terminating event during polymerization.

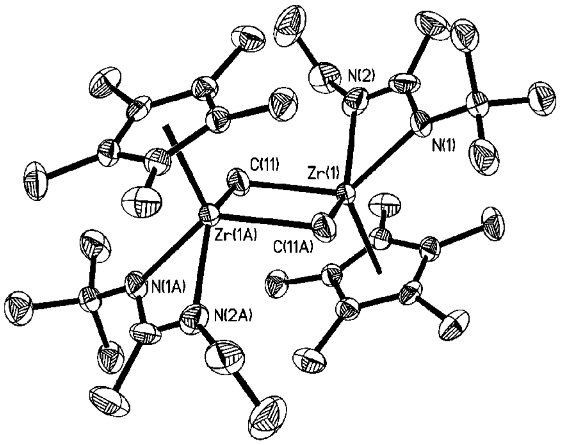
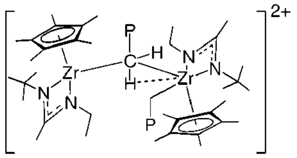


Figure 3. Molecular structure of **3** (30% thermal ellipsoids). The $[B(C_6F_5)_4]$ anion and all the hydrogen atoms have been removed for the sake of clarity.

In summary, the mere existence of **2** in the solid state requires consideration of the possible roles that similar dimers of propagating species might play in both metallocene and nonmetallocene systems. The formation of such species with bridging agostic interactions is certainly more likely to occur when weakly coordinating counteranions are employed. As postulated, these "activating" interactions may serve to lower the barriers to steps involved in both propagation and termination. As originally proposed by Mülhaupt,[2] dimers of propagating species might also serve as dormant, stable, resting states of the system. Indeed, it may be the ability to form dimers that is responsible for the living character of polymerizations employing **1**. Finally, we speculate that an "open"-form of a dimer (structure **A**), formed through a single bridging methyl group, might have a higher associated rate of propagation than the corresponding mononuclear monocation due to an enhancement of metal electrophilicity at one of the metal centers. Possible answers to these questions may become available through extensive kinetic studies now in progress.



A

Supporting Information Available: Details of the crystallographic analyses of compounds **1**−**4** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(8) (a) Brookhart, M.; Green, M. L. H.; Wong, L. L. *Prog. Inorg. Chem.* **1988**, *36*, 1−124. Grubbs, R. H; Coates, G. W. *Acc. Chem. Res.* **1996**, *29*, 85−93.

(9) Formulation of **3** as a Zr(IV)−Zr(IV) dimer is based on the observed Zr/B ratio in the solid state.

(10) Bochmann, M.; Cuenca, T.; Hardy, D. T. *J. Organomet. Chem.* **1994**, *484*, C10−C12.