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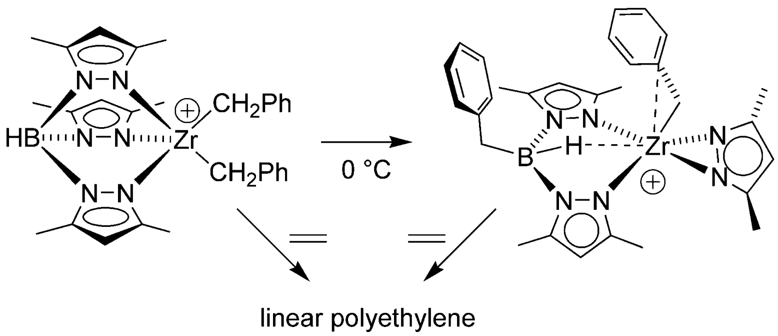

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Unusual Reactivity of Tris(pyrazolyl)borate Zirconium Benzyl Complexes

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MAO activation of group 4 Tp′MCl$_3$ complexes that contain sterically bulky tris(pyrazolyl)borate ligands (Tp′) generates highly active ethylene polymerization catalysts with interesting properties, including the production of ultrahigh molecular weight polyethylene (PE) and high 1-hexene incorporation in ethylene/hexene copolymerization.[1] These systems differ from metallocene catalysts in several ways. First, Tp′M complexes can undergo a variety of rearrangements, suggesting that Tp′ ligands may not be innocent in olefin polymerization.[1a,c,2,3] In contrast, the Cp$_2$M units in metallocene catalysts are very robust. Second, Tp′MR$_2^+$ cations, which are potential active species in Tp′MCl$_3$/MAO catalysts, contain two alkyl groups capable of undergoing olefin insertion, whereas monoalkyl Cp$_2$MR$^+$ species are active in metallocene catalysts. However, the active species in Tp′MCl$_3$/MAO catalysts are unknown, and the chemistry of Tp′MR$_3$ and Tp′MR$_2^+$ complexes is unexplored. Group 4 Tp′M alkyl complexes are limited to Tp*ZrR$_2$(O^{t}Bu) (Tp* = HB(3,5-Me$_2$pz)$_3$; R = Me, CH$_2$Ph; pz = pyrazolyl) and Tp*TiMe$_2$OR′ (R′ = Me, ^{i}Pr, ^{t}Bu).[4] Here, we describe the synthesis of Tp*Zr(CH$_2$Ph)$_3$ (**1**) and the generation and unusual reactivity of the cationic complex [Tp*Zr(CH$_2$Ph)$_2$][B(C$_6$F$_5$)$_4$] (**2**).

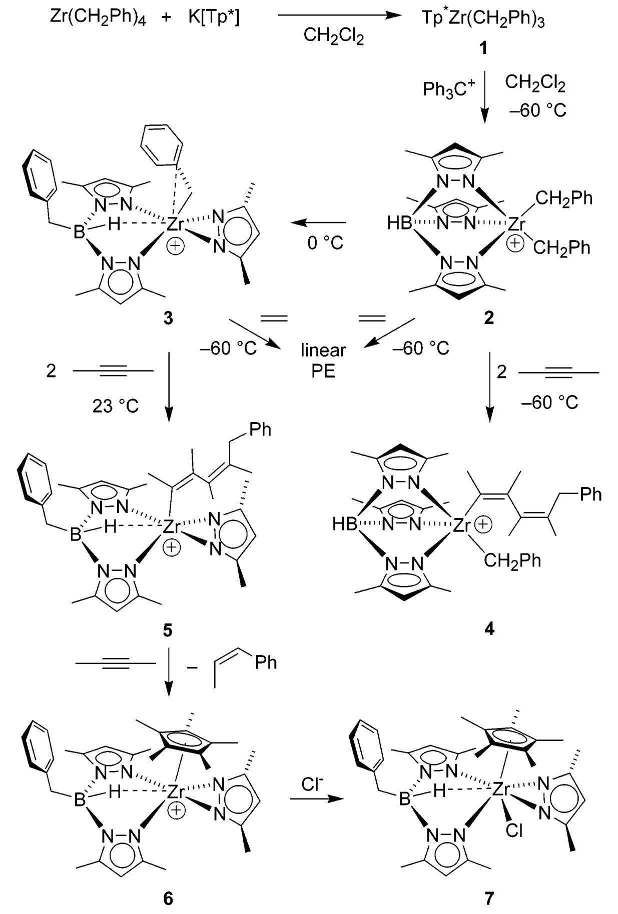
The reaction of Zr(CH$_2$Ph)$_4$ with K[Tp*] in CH$_2$Cl$_2$ affords **1** in 68% isolated yield, as shown in Scheme 1. This unusual reaction is based on Parkin's syntheses of (κ^3-Tp*)AlMe$_2$ and {κ^2-HB(3-^{t}Bupz)$_3$}AlMe$_2$ by reaction of AlMe$_3$ with K[Tp*] or Tl{HB(3-^{t}Bupz)$_3$}.[5] NMR data show that **1** has C_{3v} symmetry in CD$_2$Cl$_2$. The $^1J_{CH}$ value for the Zr*CH*$_2$Ph unit (113 Hz) shows that the benzyl ligands are η^1-coordinated. The structure of **1** was confirmed by X-ray crystallography (Figure 1).

Cationic complex **2** was generated quantitatively by the reaction of **1** with [Ph$_3$C][B(C$_6$F$_5$)$_4$] in CD$_2$Cl$_2$ at −60 °C. The ^{1}H and ^{13}C NMR spectra of **2** each contain a single set of pyrazolyl resonances and a single set of benzyl resonances. The $^1J_{CH}$ value for the Zr*CH*$_2$Ph groups (127 Hz) is intermediate between the values expected for η^1 (ca. 115 Hz) and η^2 (ca. 145 Hz) coordination,[6] which suggests that **2** contains one η^1-benzyl and one η^2-benzyl that exchange rapidly in solution.[7] ^{1}H NMR spectra do not show splitting or broadening of the benzyl resonances down to −95 °C, implying that the barrier for this process is low.

2 cleanly rearranges to [{(PhCH$_2$)(H)B(μ-Me$_2$pz)$_2$}Zr(η^2-Me$_2$pz)(CH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**3**) by net exchange of Zr−CH$_2$Ph and B−pz ligands within 10 min at 0 °C in CD$_2$Cl$_2$. X-ray analysis shows that **3** contains an η^2-Me$_2$pz ligand and a bis(pyrazolyl)borate ligand that is coordinated through two nitrogens and by a B−H−Zr agostic interaction (Zr−B 2.870 Å, Zr−H ca. 2.03 Å; Figure 1). Reger reported a similar but apparently weaker interaction in [H(μ-H)B(pz)$_2$]CpZrCl$_2$ (Zr−B 2.957 Å, Zr−H ca. 2.27 Å), a neutral, less coordinatively unsaturated analogue of **3**.[8] The Zr−benzyl ligand of **3** is η^2-coordinated in CD$_2$Cl$_2$ solution ($^1J_{CH}$ = 144 Hz) and in the solid state (Zr−C$_{ipso}$ 2.542 Å; Zr−C−C$_{ipso}$ = 84.0°). An HMQC NMR spectrum of **3** (−20 °C) shows that an extremely broad ^{13}C resonance at δ 24.6 correlates with a broad ^{1}H resonance at δ 2.95. These resonances are assigned to the B-*CH*$_2$-Ph unit, consistent with data for Ph*C*H$_2$(CF$_3$)$_2$B•NMe$_3$ (δ ^{13}C 23.9).[9] The identity of **3** was confirmed by conversion to the PMe$_3$ complex **3**•PMe$_3$ (Figure 1). Takats reported a similar rearrangement of Tp*$_2$-Sm(C≡CPh) to (Tp*){H(PhC≡C)B(μ-Me$_2$pz)$_2$}Sm(η^2-Me$_2$pz) by exchange of Sm−C≡CPh and B−pz ligands.[3] **3** exhibits C_s symmetry by ^{1}H and ^{13}C NMR above −40 °C, indicative of a dynamic structure under these conditions. However, the ^{1}H NMR spectrum exhibits selective broadening of the bis(pyrazolyl)borate 3-Me resonance and the Zr−benzyl resonances at −60 °C.[10] The 3-*Me*-pz and *o*-Ph resonances each split into two resonances, and the other benzyl resonances broaden more at −94 °C, while the remaining resonances of **3** remain sharp. These results are consistent with net rotation around the Zr−CH$_2$Ph bond, by either simple rotation or slippage to η^1-coordination.[6]

Both **2** and **3** react with ethylene at −60 °C to produce linear PE, which demonstrates that both are, or are precursors to, active ethylene polymerization catalysts under very mild conditions. Detailed studies of these polymerizations to probe the possible role

Scheme 1. Anion = B(C$_6$F$_5$)$_4^-$



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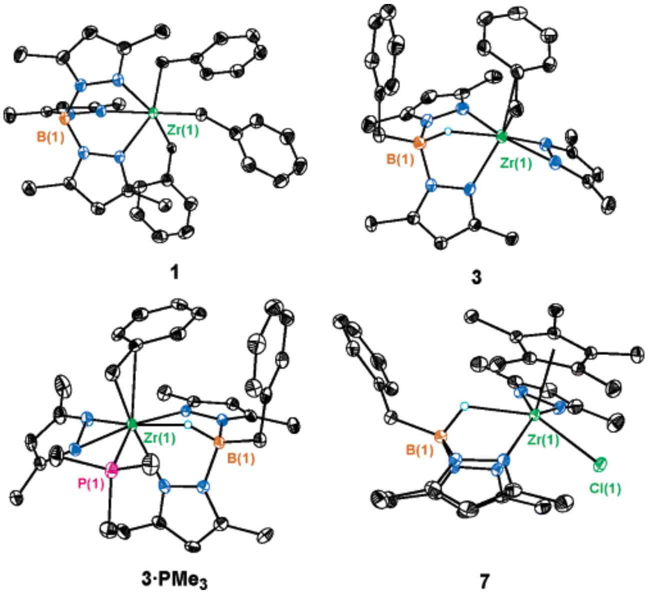


1 **3** **3·PMe$_3$** **7**

Figure 1. ORTEP views of **1**, the cations of **3** and **3**·PMe$_3$, and **7**. Hydrogen atoms are omitted, except for the B−*H*−Zr hydrogens.

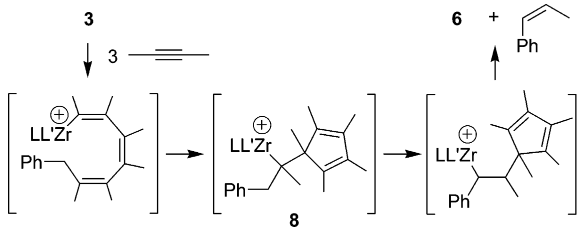
of Tp′ZrR$_2^+$ and {RHB(μ-pz)$_2$}ZrXR$^+$ species in Tp′ZrCl$_3$/MAO systems are in progress.

The reactions of **2** and **3** with 2-butyne were explored to compare the insertion reactivity of these species. **2** reacts with 2 equiv of 2-butyne within minutes at −60 °C in CD_2Cl_2 to form [Tp*Zr(CH$_2$-Ph)(CMe═CMeCMe═CMeCH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**4**) quantitatively by double insertion into a Zr−CH$_2$Ph bond.[11] Hydrolysis of **4** gives toluene and (*Z*,*E*)-2,3,4-trimethyl-1-phenyl-2,4-hexadiene, while deuteriolysis gives (*Z*,*E*)-5-deutero-2,3,4-trimethyl-1-phenyl-2,4-hexadiene, confirming the double insertion. No further reaction of **4** with 2-butyne is observed at −60 °C. NMR studies at −60 °C show that **4** has C_1 symmetry, and that the −CMe═CMeC*H*$_2$Ph hydrogens are diastereotopic. These results suggest that the terminal double bond or phenyl group of the −CMe═CMeCH$_2$Ph unit coordinates to Zr, which may inhibit further reaction with 2-butyne.[11b] The exclusive formation of **4** shows that insertion into the Zr−alkenyl bond is faster than insertion into the Zr−benzyl bond of the presumed monoinsertion intermediate Tp*Zr(CH$_2$Ph)(CMe═CMeCH$_2$Ph)$^+$.

3 also reacts with 2 equiv of 2-butyne (CD_2Cl_2, 23 °C) to form the double insertion product [{(PhCH$_2$)(H)B(μ-Me$_2$pz)$_2$}Zr(η^2-Me$_2$-pz)(CMe═CMeCMe═CMeCH$_2$Ph)][B(C$_6$F$_5$)$_4$] (**5**), which was identified by NMR. Deuteriolysis experiments confirm that **5** possesses a −CMe═CMeCMe═CMeCH$_2$Ph ligand. However, unlike **4**, **5** readily reacts with an additional 1 equiv of 2-butyne to yield the Cp* complex [{(PhCH$_2$)(H)B(μ-Me$_2$pz)$_2$}Zr(Cp*)(η^2-Me$_2$pz)]-[B(C$_6$F$_5$)$_4$] (**6**; Cp* = C$_5$Me$_5$) and *cis*-β-methylstyrene. **6** was synthesized independently by the reaction of **3** with 1,2,3,4,5-pentamethylcyclopentadiene. The reaction of **3** with 3 equiv of 2-butyne also gives **6** and *cis*-β-methylstyrene. The structure of **6** was confirmed by derivatization to {(PhCH$_2$)(H)B(μ-Me$_2$pz)$_2$}Zr-(Cp*)(η^2-Me$_2$pz)Cl (**7**, Figure 1) by reaction with [^{n}Bu$_3$(PhCH$_2$)N]-Cl.

A plausible mechanism for the conversion of **3** to **6** is shown in Scheme 2. Three successive 2-butyne insertions followed by intramolecular insertion/cyclization yields intermediate **8**. Chain walking of **8** (i.e., β-H elimination, olefin rotation, and reinsertion) followed by β-Cp* elimination produces **6**. Related alkyne insertion/cyclization sequences to form cyclopentadienyl−alkyl ligands have been observed in Hf carborane and Pd systems.[12] The viability of β-Cp* elimination was established by the reaction of **3** with allylpentamethylcyclopentadiene, which produced **6** in 25% NMR yield. β-Alkyl and β-allyl eliminations are known.[13]

Scheme 2. L = (PhCH$_2$)(H)B(Me$_2$pz)$_2$, L′ = η^2-Me$_2$pz



These studies show that Tp*Zr(CH$_2$Ph)$_2^+$ (**2**) can be generated at low temperature and rearranges rapidly at 0 °C to the bis-(pyrazolyl)borate complex **3**. Both **2** and **3** are highly reactive for ethylene and alkyne insertions. Similar rearrangements can be anticipated for other group 4 Tp′MR$_2^+$ species, and both Tp′ZrR$_2^+$ and {RHB(μ-pz)$_2$}ZrXR$^+$ species may be important in Tp′ZrCl$_3$/MAO catalysts. The unexpected formation of **6** by the reaction of **3** with 2-butyne suggests that other interesting insertion/cyclization chemistry may be possible with this system.

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Supporting Information Available: Experimental procedures and characterization data (PDF). Crystallographic data for **1**, **3**, **3**·PMe$_3$, and **7** (CIF). This material is available free of charge via the Internet at http://pubs.acs.org.

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