Distorted Trimethylenemethane Complexes of Zirconium

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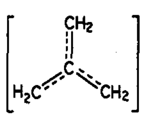
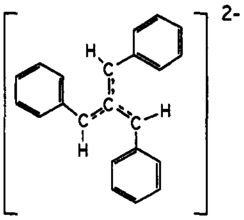
The design and synthesis of catalysts for the polymerization of monosubstituted olefins are difficult but important challenges for organometallic and polymer chemists in both academic and industrial laboratories. The ultimate goal of such an effort is an initiator for the living and potentially stereospecific polymerization of α-olefins. Advances in the field of homogeneous, well-defined, Ziegler–Natta catalysts have relied primarily on the progressive optimization of d^0, *cationic*, bent metallocene systems of general composition $[(C_5R_5)_2ZrR']^+[X]^-$ (R or R′ = H or alkyl group, X = noncoordinating anion),[1] although a notable *neutral* yttrium-based initiator has recently been reported by Bercaw and Coughlin.[2] A relatively new extension to zirconocene-supported polymerization is the substitution of one or two uninegative cyclopentadienyl ligands with an isoelectronic but dianionic analog. As originally pointed out by Jordan,[3] these substitutions should not affect the overall molecular structure or frontier orbitals of a bent metallocene significantly but would enable mechanistic studies aimed at clarifying how charge, metal, and electron count affect olefin insertion chemistry. The series of compounds $[Cp^*(C_2B_9H_{11})Sc]^-[Li(THF)_x]^+$,[4] $Cp^*(C_2B_9H_{11})ZrCH_3$,[3] and $(C_5H_4CH_3)(C_2B_9H_{11})Ta(CH_3)_2$[5] ($Cp^* = C_5Me_5$) exemplifies this strategy using the "dicarbollide" ligand, $(C_2B_9H_{11})^{2-}$. In some instances, these complexes exhibit olefin and alkyne insertion chemistry similar, albeit more attenuated, to their cationic counterparts, but in several cases a deactivation pathway exists whereby a hydridic B–H bond from the dicarbollide cluster coordinates to the metal center, further reducing reactivity.

We are interested in studying how the trimethylenemethane $(TMM)^{2-}$ ligand and its derivatives behave as dianionic mimics of the $[C_5R_5]^-$ ligand in early transition metal chemistry,[6] noting that both ligands contain six electrons of π symmetry. Advantages of these ligands include the absence of basic functionalities as well as ease of preparation. Of the possible TMM derivatives, we have focused on the C_3 symmetric tribenzylidenemethane dianion $[C(CHPh)_3]^{2-}$, $(TBM)^{2-}$,[7] because of its lower reduction potential (relative to TMM) and the anticipated asymmetry of its metal complexes:

Cp
6 π electrons



TMM
6 π electrons



TBM
6 π electrons, C_3 symmetric

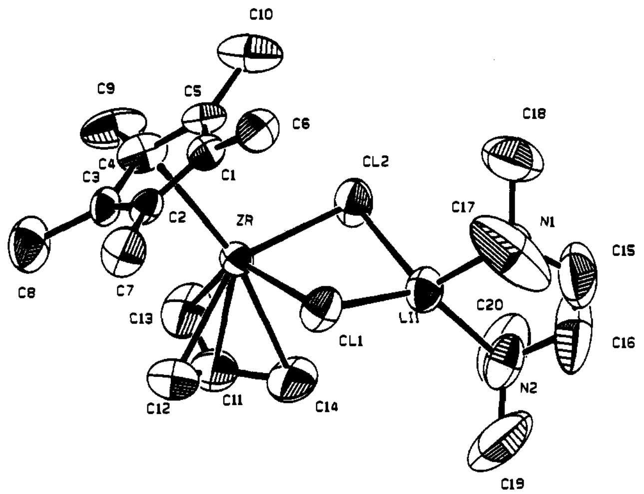
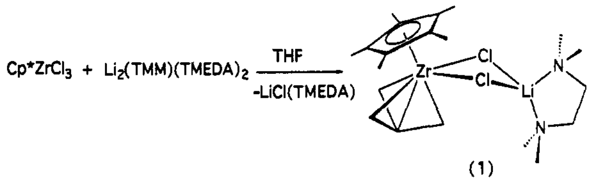


Figure 1. ORTEP diagram of **1**. Important bond distances (Å) and angles (deg): C(11)–C(14) = 1.39(2); C(11)–C(12) = 1.38(2); C(11)–C(13) = 1.40(2); C(12)–C(11)–C(13) = 114(1); C(13)–C(11)–C(14) = 116(1); C(12)–C(11)–C(14) = 118(2). Thermal ellipsoids are drawn at the 50% probability level.

The reaction of equimolar quantities of Cp^*ZrCl_3 ($Cp^* = C_5Me_5$)[8] and $TMM(Li{\cdot}TMEDA)_2$ (TMEDA = tetramethylenediamine) yields $Cp^*(TMM)ZrCl_2Li(TMEDA)$ (**1**) as a yellow, air-sensitive solid (eq 1). An X-ray analysis of **1** (Figure 1)[9] establishes that the overall molecular geometry is analogous to that of bent metallocenes with features similar to those of the structurally characterized, isoelectronic, bis-cyclopentadienyl complex of yttrium.[10] The TMM ligand is bound in a pyramidal,[11] η^4-*syn* fashion with the central carbon (C_{11}) directed away from Zr. The angle defined by C_{11}–Zr–Cp^*_{cent} (129(1)°) is similar to the Cp_{cent}–Zr–Cp_{cent} angle measured in Cp_2ZrMe_2 (132.5°).[12] Distances and angles between Zr, Cp*, and the chloride ligands are normal. The electronic and steric properties of the Cp* ligand are responsible for the more subtle structural features of **1**. For example, the difference in Zr–methylene bond lengths (2.39(1) Å (Zr–C_{12}) and 2.35(1) Å (Zr–C_{13}) vs 2.56(1) Å (Zr–C_{14})) is a clear manifestation of the strong trans effect of Cp*. The Li(TMEDA) group deviates 27° from the Cl–Zr–Cl plane toward the sterically more accommodating TMM ligand. The ^{1}H NMR spectrum of **1** in C_6D_6 at 25 °C exhibits signals typical of a static TMM ligand that coalesce to one resonance upon warming to 90 °C.



(1)

(1)

Slow addition of $Li_2(TBM)(TMEDA)_2$ to Cp^*ZrCl_3 yields LiCl and a red complex, which by elemental analysis and NMR

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[1] For a review, see: Jordan, R. F. *Adv. Organomet. Chem.* **1991,** *32,* 325.

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[9] Crystal data for **1**: space group $Pca2_1$ (No. 29) with $a = 17.33(3)$ Å, $b = 9.074(3)$ Å, $c = 15.59(2)$ Å, $Z = 4$, FW = 474.59, and $\rho = 1.286$ g/cm^3. A total of 2483 reflections (hkl) were collected in the range $4° < 2\theta < 50°$ with the 1477 having $I > 3.00\sigma(I)$ being used in the structural refinement by full-matrix least-squares techniques (234 variables) using the TEXSAN crystallographic package from Molecular Structures Corporation. Final $R_1 = 0.036$, $R_2 = 0.036$.

[10] Marsh, R. E.; Shaefer, W. P.; Coughlin, E. B.; Bercaw, J. E. *Acta Crystallogr.* **1993,** *C48,* 1773.

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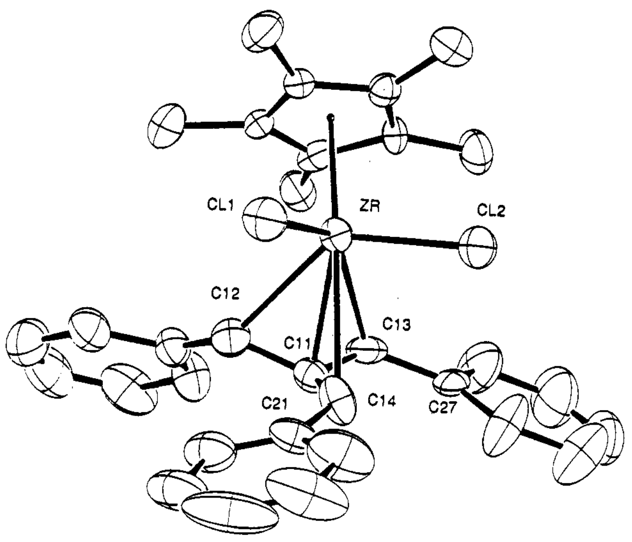
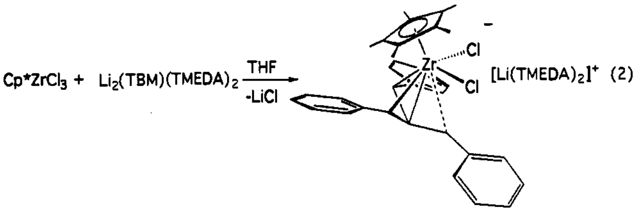


Figure 2. ORTEP diagram of the zirconium containing anion of **2**. Important bond distances (Å) and angles (deg): Zr–C(11) = 2.36(1); Zr–C(12) = 2.48(1); Zr–C(13) = 2.45(1); Zr–C(14) = 2.78(1); C(11)–C(14) = 1.38(1); C(11)–C(12) = 1.47(1); C(11)–C(13) = 1.42(1); C(13)–C(11)–C(14) = 122(1); C(12)–C(11)–C(13) = 113(1); C(12)–C(11)–C(14) = 119(1); C(11)–C(14)–C(21) = 132(1); C(11)–C(13)–C(27) = 130(1). Thermal ellipsoids are drawn at the 50% probability level.

spectroscopy has the composition $Cp^*(TBM)ZrCl_2Li(TMEDA)_2$ (**2**). Two features obtained from solution data make **2** different from the parent **1**. First, the TBM ligand in **2** rotates quickly on the ^1H NMR time scale at temperatures above −35 °C (d_8-THF), a result that suggests weaker bonding to the metal. Second, a pair of TMEDA chelates are present relative to the zirconium core. An X-ray structure study of **2** (Figure 2)[13] revealed that, unlike **1**, the formulation of **2** is best described as a salt consisting of $[Cp^*(TBM)ZrCl_2]^-$ anions with tetrahedral $[Li(TMEDA)_2]^+$ countercations (eq 2).



(2)

The TBM ligand is bound in the electronically favored *syn* geometry.[11] It is likely that coordination of the bulky TBM and Cp* ligands to zirconium prevents a zwitterionic arrangement similar to **1** and therefore the final structure represents a compromise between competing steric and electronic effects. The resulting charge and the additional steric contacts increase the distances between Zr and the carbons on TBM relative to the TMM–Zr distances in **1**. The strong trans effect of Cp* in **2** is demonstrated by the exceptionally long $Zr–C_{14}$ bond length (2.78(1) Å).

In summary, the structural features of **1** support the view of the TMM ligand as an isoelectronic but dianionic mimic of the cyclopentadienyl ligand. Addition of sterically significant substituents on the periphery of the trimethylenemethane skeleton causes the formation of the ion pair observed in **2**. As a consequence of the negative charge the trimethylenemethane framework is not as tightly bound to Zr in **2** as in **1** and hence exhibits significant distortion. Interestingly, high molecular weight polyethylene is obtained when **2** is treated with methylalumoxane (MAO) cocatalyst and ethylene.[14] It is reasonable to postulate that in such a catalytic mixture a neutral (TBM)-Cp*ZrR (R = alkyl) species is generated that initiates and propagates the polymerization. We are currently pursuing the synthesis of well-defined neutral alkyl complexes as well as the study of MAO-activated polymerizations.

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Supplementary Material Available: Experimental procedures for the preparation of **1** and **2**, and tables of crystal data, positional parameters, bond distances, and anisotropic thermal parameters for **1** and **2** (46 pages); listing of observed and calculated structure factors for **1** and **2** (30 pages). This material is contained in many libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see any current masthead page for ordering information.

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(13) Crystal data for **2**: space group $P2_1/n$ (No. 14) with a = 11.941(3) Å, b = 23.438(8) Å, c = 16.931(8) Å, β = 110.43(3)°, Z = 4, FW = 819.09, and ρ = 1.225 g/cm³. A total of 5916 reflections ($h,k,\pm l$) were collected in the range $4° < 2\theta < 50°$ with the 2698 having $I > 3.00\sigma(I)$ being used in the structural refinement by full-matrix least-squares techniques (469 variables) using the TEXSAN crystallographic package from Molecular Structures Corporation. Final R_1 = 0.059, R_2 = 0.060.

(14) Bazan, G. C.; Fisher, R. A. Work in progress.