

Divalent *ansa*-Zirconocenes: Stereoselective Synthesis and High Activity for Propylene Polymerization

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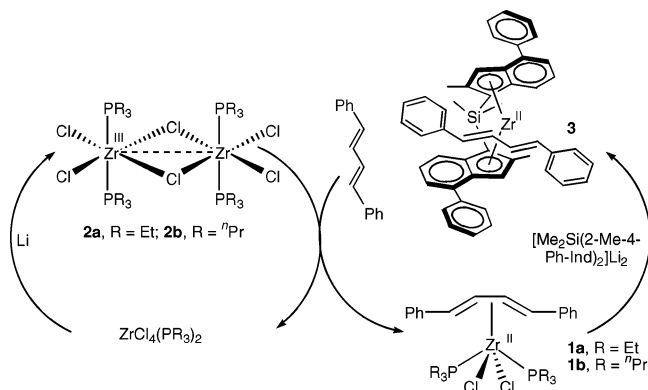
The development of new metalation methodologies/reagents for the stereoselective synthesis of group 4 *ansa*-metallocenes in high racemic purity has been a subject of intense research for the past eight years.¹ This significant interest arises from the critical need to substantially suppress or completely eliminate the achiral *meso*-isomeric coproduct often formed up to 50% during the synthesis of the chiral racemic *ansa*-metallocene catalyst, which is essential for stereoselective olefin polymerization. A success in this regard will require little or no purification of the product and achieve high to quantitative conversion of the expensive *ansa*-ligands to the desired chiral racemic catalyst.

Jordan's seminal amine elimination approach that utilizes the reaction of neutral ligands with $Zr(NR_2)_4$ works well for simple *ansa*-bis(indenyl) ligands. However, this approach is not successful for sterically crowded ligands such as 2,4-substituted and related indenyls;^{1b-c,e-f} the incorporation of such a ligand framework into a propylene-polymerization-catalyst structure is necessary for achieving high polymer isotacticity and molecular weight.² The use of $Zr\{PhN(CH_2)_3NPh\}Cl_2(THF)_2$ ^{1b} solved this problem, but the needed conversion of the zirconocene diamide product to the dichloride precatalyst seems not as straightforward as with the unsubstituted indenyl derivative.^{1b} The Zr biphenolate complexes $Zr(OAr-ArO)Cl_2(THF)_2$ ^{1a} are also found to undergo stereoselective reaction with dianionic salts of various *ansa*-bis(indenyl) ligands; with highly substituted indenyl ligands, the reaction gives an initially kinetically controlled mixture of *rac*- and *meso*-zirconocene biphenolates, which requires subsequent heating to yield the predominant *rac*-product.

We have been interested in the stereoselective synthesis of chiral *divalent* group 4 metallocenes and recognized that, in addition to having a high degree of control over chemo- and diastereoselectivity, it is also important that the synthesis lead directly to the final precatalyst. To this end, we have recently developed a highly efficient, stereoselective synthesis of racemic, divalent *ansa*-zirconocene catalysts using the Zr(II) diene synthon.³ Attractive attributes of this novel synthesis include the formation of *rac*-only Zr(II) complexes in high yield for substituted ligands such as 2-Me-4-Ph-indene⁴ and a one-pot reaction for the generation of the final precatalyst which can be readily activated to the highly active catalyst for propylene polymerization with common activators.

The reduction of $ZrCl_4(PR_3)_2$ in toluene or hexanes with Li powder and in the presence of 1 equiv of *trans*-1,4-diphenyl-1,3-butadiene proceeds cleanly at ambient temperature to yield the Zr(II) diene complexes $Cl_2Zr(1,4-Ph_2C_4H_4)(PR_3)_2$ (R = Et, **1a**; R = ⁿPr, **1b**).⁵ Green et al. first reported⁶ the phosphine-stabilized Zr(II) diene complexes prepared in low yield (18%) from the

Scheme 1



reduction of $ZrCl_4$ using sodium amalgam (Na/Hg) in the presence of PMe_3 . The current approach produces the Zr(II) diene complexes in high isolated yields (90–93%) under mild reaction conditions with the avoidance of Hg. As is demonstrated below, the reaction sequence consists of a rate-limiting step for the reduction of $ZrCl_4(PR_3)_2$ by Li to the chloride-bridged Zr(III) dimer $[ZrCl_3(PR_3)_2]_2$ (**2**)⁷ and a fast diene-driven disproportionation of the Zr(III) dimer to the Zr(II) **1** and $Zr^{IV}Cl_4(PR_3)_2$. The one-half of 1 equiv of $ZrCl_4(PR_3)_2$ generated in the fast disproportionation step re-enters the reduction cycle, and the reaction proceeds until all of the diene is consumed (Scheme 1).

The use of a suitable solvent, reductant, and phosphine ligand is critical for achieving high isolated yields of **1**. In hydrocarbon solvents, Li metal only reduces $ZrCl_4(PR_3)_2$ but not the diene; however, in ethereal solvents Li metal reacts rapidly with the diene to form the dianionic 1,4-diphenyl-2-butene-1,4-diyl species. The reaction of such diyl species with $ZrCl_4(PR_3)_2$ produced **1** in low yield and a significant amount of free diene. Among the reducing agents (Na, Na/naphthalene, Li, Mg, Rieke Mg, K, KC_8 , Na/K, lithium alkyls, and Grignard reagents) investigated, low-sodium Li powder gave the best result. Because of the poor solubility of $ZrCl_4(PMe_3)_2$ in toluene, the reaction does not proceed to completion with this phosphine, but with PEt_3 and $P(^nPr)_3$ the reaction proceeds cleanly to produce green **2** in quantitative yield in the absence of 1,4-diphenyl-1,3-butadiene, or purple **1** in the presence of a stoichiometric amount of the diene. The independent reaction of the Zr(III) dimer **2b** with 1,4-diphenyl-1,3-butadiene is fast, leading to a 1:1 mixture of the Zr(II) **1b** and the Zr(IV) $ZrCl_4(P^nPr)_2$.⁵

The structure of **1a** (Figure 1) reveals a square pyramidal coordination sphere about Zr, with the π -bound diene ligand occupying the apex of the pyramid and adopting an *s-cis* orientation. The Δd^8 parameter for the diene ligand in **1a** is -0.027 \AA , which is consistent with the diene ligand being bound in a π -fashion.⁹

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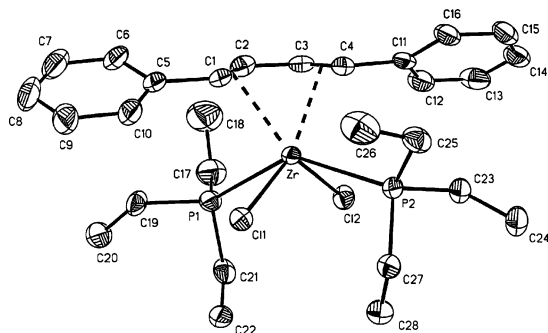


Figure 1. Molecular structure of **1a**. Selected bond lengths (Å): Zr–C1 = 2.438(3), Zr–C2 = 2.488(5), Zr–C3 = 2.424(5), Zr–C4 = 2.421(3), C1–C2 = 1.263(3), C2–C3 = 1.406(5), C3–C4 = 1.267(3).

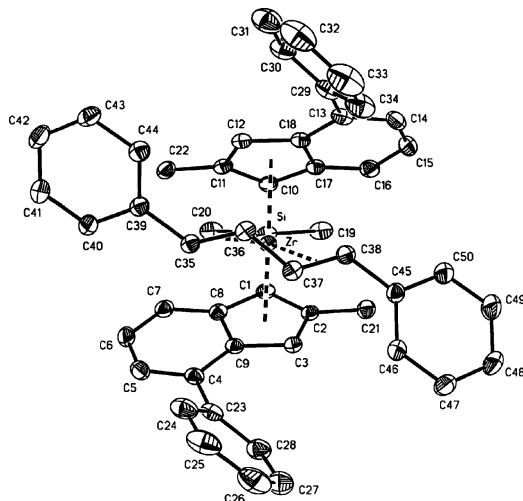


Figure 2. Molecular structure of **3**. Selected bond lengths (Å): Zr–C35 = 2.523(2), Zr–C36 = 2.394(2), Zr–C37 = 2.387(2), Zr–C38 = 2.515(2), C35–C36 = 1.423(3), C36–C37 = 1.412(2), C37–C38 = 1.417(3).

The two phosphine ligands are arranged in a *trans* orientation, as are the two chloride ligands.

The reaction of **1** with $\text{Li}_2\{\text{Me}_2\text{Si}(2\text{-Me-4-Ph-Ind})_2\}$ (Scheme 1) in toluene proceeds cleanly to form the desired racemic *ansa*-zirconocene(II) diene complex **3** in quantitative yield (for an isolation of 8.6 g of **3**, the yield was 98%).⁵ At no time during the reaction is any *meso*-isomer detected by ¹H NMR spectroscopy. The crystal structure of **3** (Figure 2) features the *s-trans*, π -bound diene ligand, consistent with the Zr center being in the formal +2 oxidation state. The average Zr–C bond distance to the diene termini is 0.128 Å longer than those to the internal carbon atoms, which supports the Zr(II) assignment. The indenyl ligands are arranged in the desired *rac*-orientation, and the “lock and key” fit between the 1,4-diphenyl-1,3-butadiene ligand and the two substituted indenyl ligands is readily apparent from the structure, where the two diene phenyl groups are placed into the coordination sphere voids of the *rac*-structure. This “lock and key” arrangement clearly minimizes the steric interactions of the diene phenyl rings with the methyl and phenyl indenyl substituents. A *meso*-indenyl arrangement would dispose at least two phenyl rings (one diene and one indenyl) to very close proximity that clearly would be destabilizing; this is probably why the *meso*-isomer is not observed.

The question arises as to how the diene-bonding mode transforms from a π -bound, *s-cis* coordination in **1** to a π -bound *s-trans*

coordination in **3**. Diene coordination isomerization has previously been reported for bis-Cp zirconium diene complexes, where heat and light interconverted a σ -bound *s-cis* and a π -bound *s-trans* butadiene or alkyl substituted diene ligand.¹⁰ It seems unlikely in the current case that such an interconversion is occurring because an aryl substituted diene ligand is used, which previously have been shown not to interconvert, and **3** has been subjected to temperatures as high as refluxing octane with no change in diene coordination. The most likely scenario is a coordination isomerization during the stepwise metalation reaction. After one-half of the *ansa*-bis(indenyl) ligand coordinates to the zirconium center, the diene ligand isomerizes to the π -bound *s-trans* coordination mode and then directs the second half of the *ansa*-bis(indenyl) ligand to coordinate to Zr in exclusively the *rac*-orientation.

The divalent *ansa*-zirconocene **3** can be readily activated with common activators such as MAO and perfluorophenyl derivatives of neutral or ionic B and Al complexes, generating a highly active propylene polymerization catalyst. For example, upon activation with $\text{B}(\text{C}_6\text{F}_5)_3/\text{iBu}_2\text{Al}(\text{BHT})$, zirconocene **3** produces isotactic polypropylene having $T_m = 157$ °C, $M_w = 1.92 \times 10^5$, PDI = 1.79 at a 70 °C polymerization temperature and with an extremely high efficiency of 1.17×10^8 g PP/g Zr.^{3,5}

In conclusion, this work introduces a novel, highly efficient synthesis of racemic *ansa*-zirconocene(II) catalysts. The proposed configurational interplay between the diene and *ansa*-bis(indenyl) ligands accounts for the high stereoselectivity in this synthesis.

Supporting Information Available: Experimental details (PDF) and complete X-ray crystallographic data for complexes **1a** and **3** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA0381611