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Synthesis of a Novel Annulated C_1-Bridged *ansa*-Metallocene System

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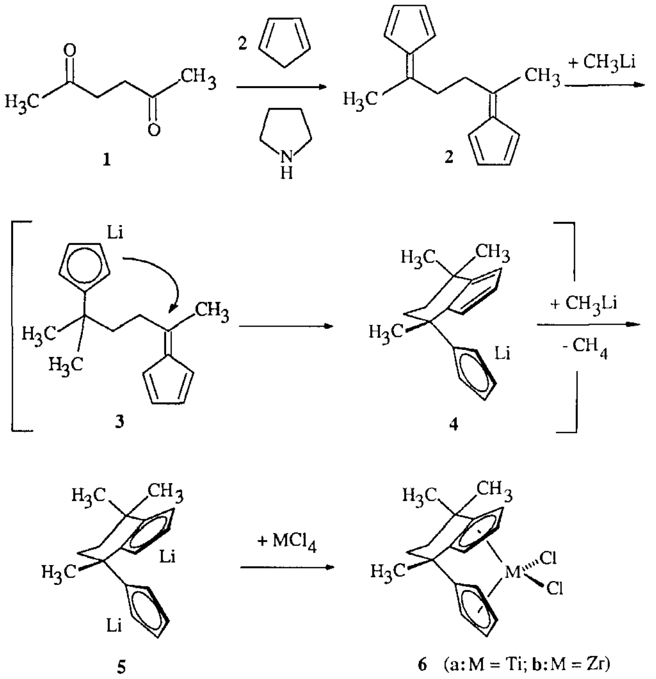
2,5-Hexanedione (**1**) was converted into the bis(fulvene) **2**, which was then treated with 2 molar equiv. of ethereal methyllithium to give the novel annulated C_1-bridged dilithium bis(cyclopentadienide) **5**. Reagent **5** was treated with MCl_4 (M = Ti, Zr) to yield the annulated C_1-bridged ansa-metallocene dichlorides **6a** and **6b**, respectively. The homogeneous **6a**, **6b**/methylalumoxane Ziegler-type systems were employed in propene polymerization reactions.

In the 1970s Sinn and Kaminsky discovered that the activation of group-4 bent metallocene complexes by excess oligomeric methylalumoxane generated extremely active homogeneous Ziegler-type catalysts for the polymerization of ethylene and some α-olefins[1]. Then Brintzinger et al. disclosed their syntheses of chiral -$[CH_2]_n$-bridged *ansa*-metallocenes of titanium and zirconium[2]. The combination of these two discoveries has initiated a revolutionary development in stereoselective olefin polymerization[3]. Since then *ansa*-metallocenes have been employed in some variety for the generation of homogeneous Ziegler-type catalysts, which are mostly derivatives or analogues of the original Brintzinger systems containing one- or two-carbon- or silicon-atom bridges[4]. We have now synthesized a novel type of an *ansa*-metallocene system where the bridging hydrocarbyl moiety contains a fused annulated ring. The examples described below contain a single Cp−Cp bridging unit which constitutes an effective C_1 connection and at the same time is part of a C_4-*ansa* chain. This specific *ansa*-metallocene system, of which we have prepared the titanium and zirconium derivatives, is very rigid.

We have treated the bis(fulvene) **2**[5] with two molar equivalents of methyllithium in ether at 0°C to obtain the dilithiated *ansa* ligand **5**. Presumably, the bis(fulvene) **2** is attacked by methyllithium at C-2 of the hydrocarbon chain[6], thereby generating the substituted Cp anion **3** which then intramolecularly attacks the remaining fulvene functionality[7] to yield product **4** with a six-membered ring. Subsequent deprotonation of **4** by the additional equivalent of methyllithium then leads to **5** which is treated with one molar equivalent of $TiCl_4$ in toluene (−78°C to ambient temp.) to give the metallocene **6a** (isolated in 13% yield after recrystallization from dichloromethane). The corresponding *ansa*-zirconocene dichloride **6b** is prepared analogously by treatment of **5** with zirconium tetrachloride (isolated in 14% yield).



The chiral zirconium complex **6b** (*C_1* symmetry) exhibits seven cyclopentadienyl CH signals [^1H NMR, ($CDCl_3$)] at δ = 6.72, 6.69, 6.50, 6.43, 6.05, 5.86, and 5.72 [^{13}C NMR ($CDCl_3$): δ = 125.9, 123.6, 117.9, 116.0, 110.3, 107.3, 105.8 plus three quaternary Cp signals at δ = 137.7, 121.3, and 113.7] and three methyl singlets (^1H NMR) at δ = 1.83, 1.33, and 1.10 (^{13}C NMR: δ = 35.1, 27.7, 26.5). The titanium complex **6a** has been characterized by X-ray diffraction. In **6a** the titanium center is pseudotetrahedrally coordinated to two chloride ligands [Ti−Cl(1) 2.362(1), Ti−Cl(2) 2.331(1) Å] and two cyclopentadienyl groups. The Cp ligands are both η^5-coordinated. The monosubstituted Cp ligand exhibits a pronounced variation of the metal−carbon bond lengths with short Ti−C(10)/C(11)/C(14) [2.336(2), 2.349(2), 2.351(2) Å] and longer Ti−C(12)/C(13) distances [2.446(3), 2.445(3) Å]. The C(12)−C(13) bond, which is located opposite to the substituted Cp carbon atom C(10), is shorter [1.382(4) Å] than the remaining $C(sp^2)-C(sp^2)$ Cp bonds [1.411(3)−1.423(3) Å]. The disubstituted cyclopentadienyl ligand exhibits two short [Ti−C(1) 2.328(2), Ti−C(2) 2.291(2) Å] and three longer metal−carbon π contacts [Ti−C(3)/C(4)/C(5)

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2.413(2), 2.482(2), 2.436(2) Å]. In this Cp ring the distal $C(sp^2)-C(sp^2)$ linkages [C(3)–C(4) 1.391(3), C(2)–C(3) 1.411(3) Å] are only slightly shorter than the proximal C–C bonds [C(4)–C(5) 1.419(3), C(1)–C(5) 1.417(3) and C(1)–C(2) 1.418(3) Å.

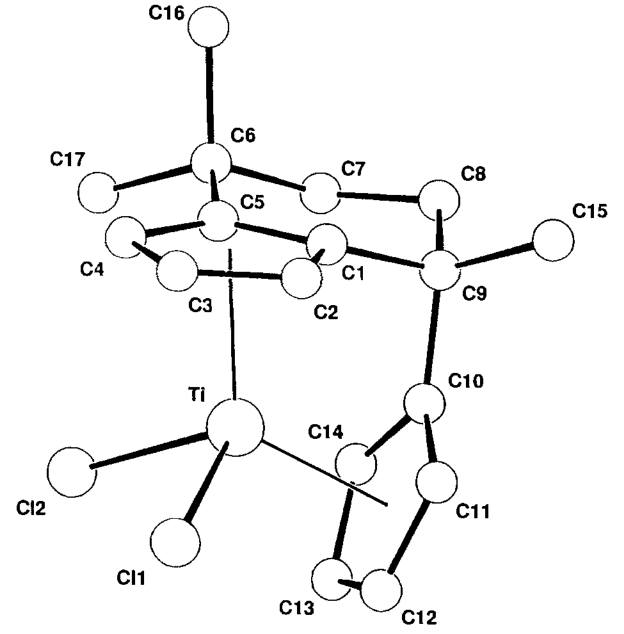

Figure 1. View of the molecular geometry of complex **6a** in the crystal

The annulated six-membered ring adopts a half-chair conformation. The ring carbon atom C(9) serves as the C_1 bridge between the two cyclopentadienyl rings. The C(1)–C(9) and C(10)–C(9) bond lengths [1.522(3), 1.533(3) Å] are in the typical $C(sp^2)-C(sp^3)$ σ-bond range. The C(1)–C(9)–C(10) angle [97.1(2)°] deviates from tetrahedral. This is very typical of C_1-bridged *ansa*-titanocenes as is the out-of-plane bending of the C(1)–C(9)/C(10)–C(9) vectors *toward* the metal center by ca. 16–17°. In complex **6a** the Cp(centroid)–Ti–Cp(centroid) angle is 120.9° which is at the low end of the range of corresponding values (ca. 129°–121°) observed for *ansa*-titanocenes[8]. The Cl(1)–Ti–Cl(2) angle in **6a** is 95.3(1)°.

Both complexes **6a** and **6b** have been used to generate active homogeneous Ziegler catalysts for propene polymerization. In a typical experiment the *ansa*-titanocene dichloride **6a** is treated with an excess of methylalumoxane ([Al]:[Ti] molar ratio ca. 550:1) in toluene solution at −50°C in the presence of propene. Partly isotactic high-molecular-weight polypropylene ($\bar{M}_\eta \approx 680000$) is formed (activity: a = 300 g polymer/g [Ti] · h). According to the ^{13}C-NMR methyl pentade analysis[9] only chain-end stereocontrol has taken place (ca. 40% mmmm, $\sigma = 0.78$). With increasing temperature the chiral metallocene backbone also takes part in the overall stereocontrol of the C–C coupling reaction. Similar to other previously described examples a situation is encountered here where both the "enantiomorphic site" and the chiral chain end are contributing simultaneously to the overall observed stereocontrol (double stereodifferentiation)[6b,9b] [−40°C: $\bar{M}_\eta = 290000$, 40% mmmm, $\omega = 0.29$, $\alpha = 0.88$, $\sigma = 0.77$; −30°C: $\bar{M}_\eta = 215000$, $a = 640$, 22% mmmm, $\omega = 0.39$, $\alpha = 0.88$, $\sigma = 0.66$; −20°C: $\bar{M}_\eta = 56000$, 24% mmmm, $\omega = 0.56$, $\alpha = 0.78$, $\sigma = 0.66$; −11°C: $\bar{M}_\eta = 23000$, $a = 1100$, 22% mmmm, $\omega = 0.45$, $\alpha = 0.77$, $\sigma = 0.66$].

Activation of the analogous *ansa*-zirconocene dichloride **6b** with methylalumoxane ([Al]:[Zr] = 310:1) generates a catalyst which produces a polypropylene with a different stereochemical characteristic. At −30°C a polymer is obtained ($a = 330$; $\bar{M}_\eta = 26000$) that is slightly syndiotactic. In the methyl region of the ^{13}C-NMR spectrum (1,2,4-trichlorobenzene, +90°C) the mmmm signal is absent (<2% mmmm, 21% rrrr, 20% mrrr; chain-end control model: $\sigma = 0.32$). At −50°C ($a = 17$; $\bar{M}_\eta = 29000$, 23% rrrr, 20% mrrr, $\sigma = 0.31$) and −5°C ($a = 1500$; $\bar{M}_\eta = 5000$, 18% rrrr, 19% mrrr, $\sigma = 0.35$) similar polypropylenes are formed.

From the structure of the titanium compound it appears that the group-4 metal centers in the new *ansa*-metallocenes **6** and the catalysts derived thereof are rather exposed and easy to approach by incoming ligands. This results in high catalyst activities and a rapid decrease of polymer molecular weights with increasing temperatures. This special feature may provide a very suitable basis for developing novel homogeneous Ziegler-type systems to be employed in catalytic carbon–carbon coupling processes for the synthesis of monomeric organic products. We have begun to prepare derivatives of **6** that can be used as active catalysts in organic synthesis.

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Experimental

All reactions were carried out under Ar using Schlenk-type glassware or in a glovebox. Solvents were dried and distilled under Ar prior to use. For additional general information including a list of spectrometers used see ref.[9b].

Preparation of **6a**: The lithium reagent **5** · 2 Et_2O was prepared by addition of 62.4 ml of a 1.6 M ethereal CH_3Li solution to a solution of 10.0 g (47.5 mmol) of bis(fulvene) **2**[5] in 150 ml of ether; 13.2 g (89%) of **5** was isolated after washing with pentane. Complex **6a** was obtained from the reaction of $TiCl_4$ (3.3 g, 17.5 mmol) with 5.5 g (17.5 mmol) of **5** · 2 Et_2O in 200 ml of toluene (−78°C to room temp.); yield 780 mg (13%), m.p. 260°C (DSC). – ^{1}H NMR ($CDCl_3$): δ = 7.05, 6.92, 6.80, 6.78, 5.86, 5.80, 5.60 (m, each 1H, cyclopentadienyl CH), 2.5–2.2 (m, 2H, CH_2), 1.99–1.82 and 1.75–1.63 (m, 2H, CH_2), 1.86, 1.25, 1.11 (s, each 3H, CH_3). – ^{13}C NMR ($CDCl_3$): δ = 142.3, 114.8, 106.9, 37.0, 33.7 (quat. C), 134.1, 131.6, 126.3, 126.2, 113.6, 112.1, 111.1 (CH), 35.3, 31.5 (CH_2), 35.4, 27.4, 25.5 (CH_3). – $C_{17}H_{20}Cl_2Ti$ (343.15): calcd. C 59.50, H 5.87; found C 59.54, H 5.97. – X-ray crystal structure analysis: monoclinic; space group $P2_1/n$; a = 9.233(2), b = 10.543(1), c = 16.665(1) Å; β = 105.62(1)°; Z = 4; λ = 0.71069 Å; 3889 total, 3565 independent, 2914 observed reflections; 181 refined parameters; R = 0.033, R_w = 0.042[10].

Preparation of **6b**: Complex **6b** was prepared by reaction of 9.6 g (30.7 mmol) of **5** with 7.5 g (32.2 mmol) of $ZrCl_4$ analogously as described above; yield 1.7 g (14%) after extraction with pentane, m.p. 223°C (decomp.; DSC). – $C_{17}H_{20}Cl_2Zr$ (386.47): calcd. C 52.83, H 5.22; found C 52.35, H 5.19. – For spectral data see text.

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