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# Synthesis of zirconium(III) complex by reduction of O[SiMe$_2$($\eta^5$-C$_5$H$_4$)]$_2$ZrCl$_2$ and its selectivity in catalytic dimerization of hex-1-ene

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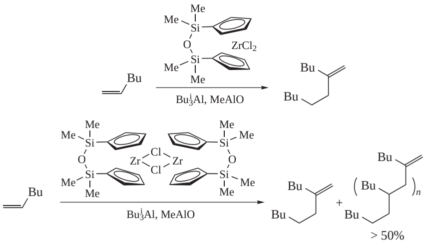
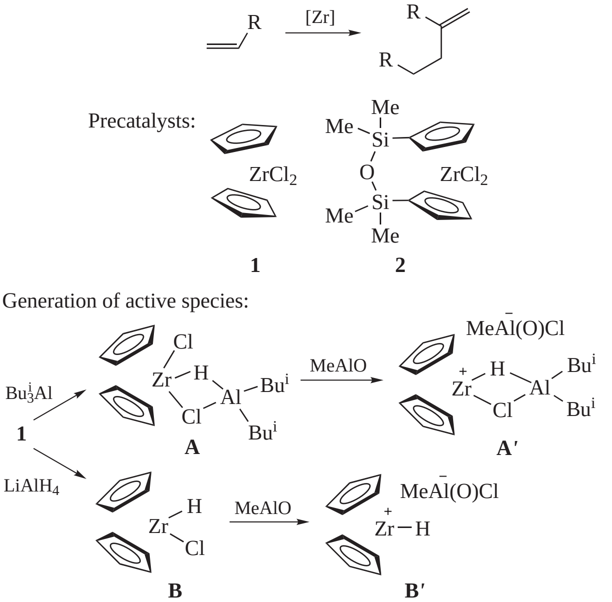
***ansa*-Complex O[SiMe$_2$($\eta^5$-C$_5$H$_4$)]$_2$ZrCl$_2$ upon reduction with LiAlH$_4$ in contrast to zirconocene dichloride forms a diamagnetic Zr$^{III}$ complex with the dimeric molecular structure proved by X-ray analysis. This complex after activation by MeAlO initiates oligomerization of $\alpha$-olefins.**



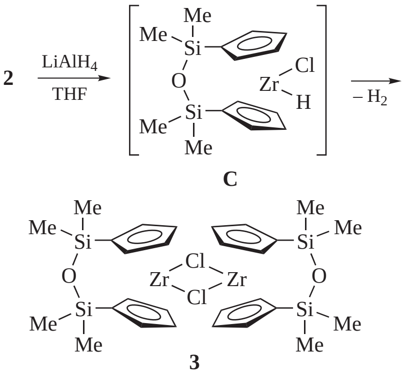
Selective dimerization of $\alpha$-olefins catalyzed by zirconocene dichloride Cp$_2$ZrCl$_2$ **1** in the presence of methylaluminoxane (MeAlO) allows one to synthesize unique hydrocarbons, 1,1-disubstituted olefins (Scheme 1) in high yields.[1–3] In the search for more effective zirconocene dimerization catalyst,[4] we developed an effective two-step activation procedure for the precatalyst LZrCl$_2$, based on the interaction of LZrCl$_2$ with 10–20 equiv. triisobutylaluminium (TIBA) to form soluble hydride chloride complexes of the proposed structure **A** with their subsequent reaction with a minimal amount of MeAlO (Scheme 1).[5,6] As a result of the studies, we found that the *ansa*-zirconocene O[SiMe$_2$($\eta^5$-C$_5$H$_4$)]$_2$ZrCl$_2$ **2** significantly exceeds complex **1** in performance and selectivity being activated by 20 equiv. TIBA and 10 equiv. MeAlO. We also revealed that the selectivity of the formation of dimers in catalysis by complex **2** significantly increased when minimal amounts of R$_2$AlCl were introduced into the reaction mixture, which indirectly confirms the structure of the catalytic particle **A′** in selective dimerization (see Scheme 1).[5]



**Scheme 1**

An alternative method for generating the dimerization catalyst, which was proposed earlier by Bergman,[2] is based on the activation of zirconocene chloride hydride ($\eta^5$-C$_5$H$_5$)$_2$ZrHCl **B** (see Scheme 1) with a minimum amount of MeAlO. It is assumed that during this activation cationic catalytic particles of the **B′** type are formed.

In order to estimate the effectiveness of the Bergman activation in relation to complex **2**, we attempted to synthesize its hydride analogue O[SiMe$_2$($\eta^5$-C$_5$H$_4$)]$_2$ZrHCl similarly to ($\eta^5$-C$_5$H$_5$)$_2$ZrHCl (see Scheme 1).[7,8] Unexpectedly, reduction of complex **2** with LiAlH$_4$ afforded a dimeric diamagnetic complex of trivalent zirconium **3** in a yield of 56% (Scheme 2). Note that the Zr$^{III}$ sandwich complexes containing the Zr–($\mu$-Cl)$_2$–Zr fragment were previously synthesized only by the reaction of LZrCl$_2$ with



**Scheme 2**

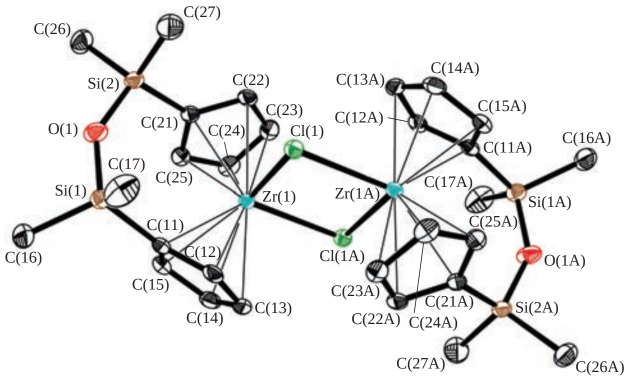
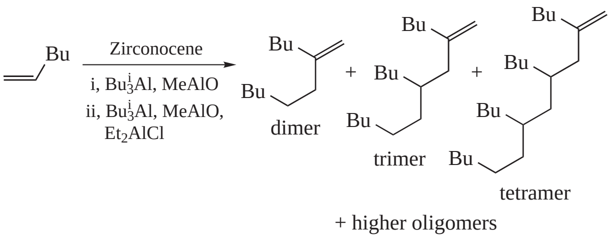


**Figure 1** Molecular structure of complex **3**.

**Table 1** Comparison of the main structural parameters of zirconium complex **3** and previously synthesized dimers **4**–**7**.

| Complex | Average distance/Å | | | Average angle/deg | | |
|---|---|---|---|---|---|---|
| | Zr···Zr | Zr–Cl | Zr–Cp | Cp–Zr–Cp | Cl–Zr–Cl | Zr–Cl–Zr |
| **3** | 3.547 | 2.589 | 2.202 | 131.20 | 93.51 | 86.49 |
| **4** | 3.233 | 2.578 | 2.183 | 135.25 | 100.00 | 77.66 |
| **5** | 3.385 | 2.573 | 2.204 | 127.94 | 97.70 | 82.30 |
| **6** | 3.508 | 2.563 | 2.203 | 130.99 | 93.30 | 86.70 |
| **7** | 3.605 | 2.602 | 2.203 | 130.99 | 82.77 | 97.23 |

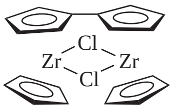


**Scheme 3**

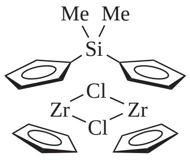
alkali metals. We assume that hydride-chloride intermediate **C** is inferior to ($\eta^5$-$C_5H_5$)$_2$ZrHCl in terms of stability since the electron-donor disilylated *ansa*-ligand facilitates disproportionation of **C** with a formation of dimer **3** and molecular hydrogen (see Scheme 2).

To date, a small number of sandwich zirconium(III) monochlorides has been known. The complex type depends on the nature of the substituents in the cyclopentadienyl rings: diamagnetic complexes **4**,[9] **5**,[10] and **6**,[11] as well as the paramagnetic one **7**[12] have a dimeric structure, while the zirconocene monochloride based on di-*tert*-butylcyclopentadiene **8** is monomer.[13] We have proved the dimeric nature of complex **3** using X-ray analysis (Figure 1).[†] The complex is diamagnetic, the bridged $SiMe_2OSiMe_2$ fragment retains conformational rigidity even in solution, which leads to nonequivalence (Figure S4, Online Supplementary Materials) of the signals in $^1$H and $^{13}$C NMR spectra (see Online Supplementary Materials) of methyl groups and all atoms in each of four equivalent cyclopentadienyl rings;[‡] the molecule of **3** has unique $C_{2h}$ group of symmetry.The main structural parameters of complex **3** and of the previously obtained dimeric zirconocene monochorides **4**–**7** are presented in Table 1. Structural parameters of **3** are close to previously determined for complex **6** containing monosubstituted cyclopentadienyl ligands. Note that compound **3** is characterized by the maximum distance Zr–Zr among the diamagnetic complexes **3**–**6**.

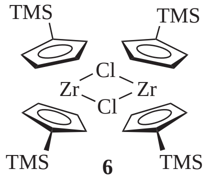
We investigated the kinetics of dimerization of hex-1-ene (Scheme 3) in the presence of zirconocenes **1**, **2** and **3** in a liquid monomer medium using two-step activation with TIBA and MeAlO (Figure 2). With the activation of TIBA (20 equiv.) and MAO (10 equiv.), zirconocene dichlorides **1** and **2** showed comparable selectivity, complex **2** significantly exceeding complex **1** in productivity. At the same time, complex **3**, being activated under the same conditions, catalyzed dimerization and oligomerization of hex-1-ene with comparable rates. The addition of $Et_2AlCl$ to reaction mixtures containing complexes **1** and **2** resulted in an increase in selectivity of dimerization, this effect being most noticeable for complex **2**.



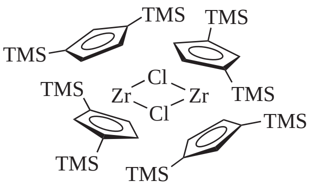
**4**



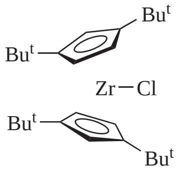
**5**



**6**



**7**



**8**

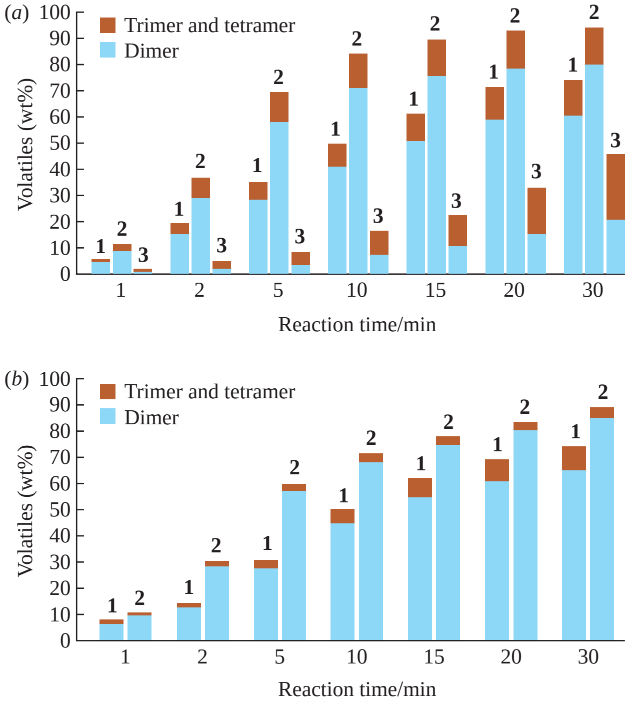


**Figure 2** Oligomerization of hex-1-ene (0.05 mol%, 60 °C in liquid monomer substance, activation with 20 equiv. $Bu^i_3Al$ and 10 equiv. MeAlO) (*a*) catalyzed by zirconocenes **1**–**3** in the absence of $Et_2AlCl$ and (*b*) in the presence of zirconocenes **1** and **2** with 2 equiv. $Et_2AlCl$.

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[†] *Crystal data for* **3**: $C_{28}H_{40}Cl_2O_2Si_4Zr_2$, $M = 774.30$, monoclinic, space group $P2_1/c$, $a = 14.6798(10)$, $b = 7.5088(5)$ and $c = 15.9338(11)$ Å, $\beta = 113.3880(9)°$, $V = 1612.04(19)$ Å$^3$, $Z = 2$, $d_{calc} = 1.595$ g cm$^{-3}$, $F(000) = 788$, $\mu$(MoK$\alpha$) = 0.986 mm$^{-1}$, $T = 150$ K, $\theta_{min} = 2.59°$, $\theta_{max} = 29.00°$, 17201 reflections measured, 4283 independent reflections ($R_{int} = 0.0222$), $R_1 = 0.0299$, $wR_2 = 0.0765$ for 3791 reflections with $I > 2\sigma(I)$; $R_1 = 0.0370$, $wR_2 = 0.0796$ for all data and 179 parameters, GOF = 1.052, $\rho_{max}/\rho_{min} = 0.377/–0.397$ e Å$^{-3}$.

CCDC 1834316 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* http://www.ccdc.cam.ac.uk.

[‡] For **3**: $^1$H NMR (THF-$d_8$, 20 °C) $\delta$: 6.41 (br. s, 2H), 6.15 (br. s, 2H), 5.94 (br. s, 2H), 5.45 (br. s, 2H), 0.31 (s, 6H), 0.24 (s, 6H). $^{13}$C NMR (THF-$d_8$, 20 °C) $\delta$: 114.14, 108.86, 106.93, 105.94, 105.71, 1.60, 0.97.

The results of experiments on the oligomerization of hex-1-ene in the presence of complexes **1–3** activated by organoaluminum compounds suggest that the $Zr^{III}$ complexes play an important role in the catalytic dimerization of olefins. The reduction of $Zr^{IV}$ complexes at the stage of activation of the precatalyst $LZrCl_2$ sharply reduces the selectivity of the reaction, shifting the distribution of the products towards the formation of oligomers. Excess dialkylaluminum chloride promotes the formation of $Zr^{IV}$ complexes responsible for the selective formation of the dimer.

Bercaw and Brintzinger have recently shown[14] that $Zr^{III}$ sandwich complexes play a significant role in the 'classical' zirconocene catalysis of olefin polymerization. The formation of such species is a new catalytic tool in the synthesis of low molecular weight derivatives of olefins such as dimers and lower oligomers with a given molecular structure, the prospects for the practical use of which are being actively studied.[6,15–21]

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*Online Supplementary Materials*

Supplementary data associated with this article (experimental details for the synthesis and X-ray diffraction study of complex **3**, and oligomerization procedures) can be found in the online version at doi: 10.1016/j.mencom.2018.09.004.

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