Synthesis and Characterization of Bis(iminopyrrolyl)zirconium Complexes

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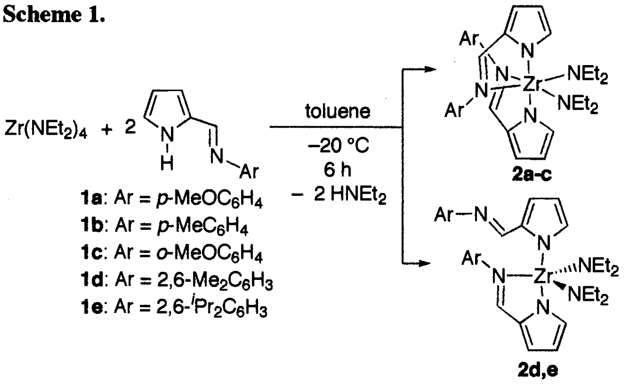
Diamido and dichloro zirconium complexes having two iminopyrrolyl ligands, $Zr(NEt_2)_2(pyr)_2$ (**2a–e**) (pyr = 2-(*N*-aryliminomethyl)pyrrolyl) and $ZrCl_2(pyr)_2$ (**3a–e**), were prepared. The *cis*-configuration of diamido and dichloro moieties was elucidated on the basis of NMR spectroscopy as well as by a crystallographic study for complex **3a**. We demonstrated that these zirconium complexes became catalyst precursors for the polymerization of ethylene in the presence of excess amounts of methylaluminoxane.

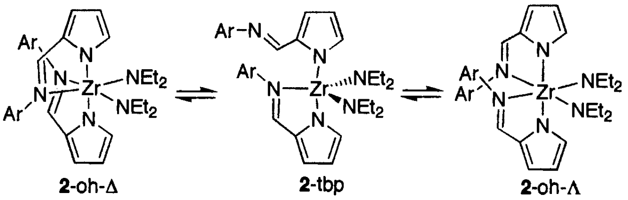
In recent years there has been increasing interest in the development of polymerization of α-olefins using well-defined transition metal complexes (single site catalysts).[1–9] Some zirconium complexes having *N*,*O*-chelate ligands were recently reported to be highly active ethylene polymerization catalysts.[10–12] As it is obviously noted that the combination of an anionic non-Cp ligand and Group 4 metal has a capability to be a catalyst precursor for polymerization and that the *N*,*O*- and *N*,*N*-bidentate ligands have remarkable flexibility in design,[13–15] we have synthesized zirconium complexes bearing five-membered *N*,*N*-chelating iminopyrrolyl ligands as ethylene polymerization catalyst precursors.

Bis(iminopyrrolyl)zirconium complexes, $Zr(NEt_2)_2(pyr)_2$ (**2a–e**) (pyr = 2-(*N*-aryliminomethyl)pyrrolyl) were prepared by the treatment of $Zr(NEt_2)_4$ with the corresponding iminopyrroles **1a–e**[16] in toluene to release two moles of diethylamine (Scheme 1).[17] In sharp contrast to the synthetic route starting from $Zr(NEt_2)_4$, the reaction of $ZrCl_4$ with the lithium salt of **1a** resulted in a complex mixture. In the case of the reactions of $Zr(NEt_2)_4$ with bulky ligands **1d,e**, five coordinated complexes **2d,e** predominantly formed, while the reactions with less bulky ligands **1a–c** selectively afforded six coordinated complexes **2a–c**. The ^1H NMR spectra of the complexes **2d,e** exhibited one set of signals assignable to a trigonal bipyramidal geometry, where apical positions were occupied by two pyrrolyl nitrogen atoms and three equatorial positions by one imino nitrogen atom and two amido nitrogen atoms. On the other hand, the ^1H NMR spectra of the complexes **2a–c** at room temperature showed signals assignable to two geometric isomers **2a–c**-tbp and **2a–c**-oh and then at 70 °C two signals coalesced presumably due to the rapid interconversion between Δ- and Λ-complexation through a similar trigonal bipyramidal species as observed for **2d,e** (Scheme 2), suggesting *cis*-amido-configuration for **2a–c**. The same argument has already been reported for the fluxional behavior of pyridine–alkoxide complexes of Group 4 metals.[13–15] The coalescence of the NCH_2CH_3 resonances in the ^1H NMR spectra allowed to estimate the energy parameters for the interconversion process to be $\Delta G^{\ddagger} = 13.9$ kcal/mol (**2a**), 13.7 kcal/mol (**2b**), and 16.5 kcal/mol (**2c**); these value are unexceptionably comparable to those found for the pyridine–alkoxide complexes ($\Delta G^{\ddagger} = 12.2–14.0$ kcal/mol).[15]

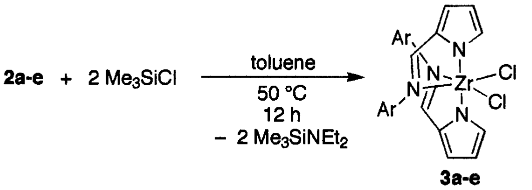
Scheme 1.



Scheme 2.



The *cis*-$(NEt_2)_2$ moieties of **2a–e** can be replaced by two chloro anions with retaining the *cis*-geometry. Treatment of the complexes **2a–e** with trimethylsilyl chloride in toluene for 12 h at 50 °C resulted in the quantitative formation of the corresponding dichloro complexes **3a–e** (eq 1).[18] The ^1H NMR spectra of all dichloro complexes **3a–e** exhibited sharp signals due to the octahedral structure. The structure was revealed by a crystallographic study for complex **3a** (Figure 1).[19] Complex **3a** adopts a distorted octahedral structure where two pyrrolyl nitrogen atoms, N1 and N1*, are arranged in a *trans*-fashion, while the two imino nitrogen atoms, N2 and N2*, and the two chlorine atoms are coordinated in a *cis*-fashion.



(1)

The diamido or dichloro moieties of zirconium complexes **2a–e** and **3a–e** evidently have the *cis*-configuration, which is a requirement to exhibit polymerization activity. These complexes on activation by excess amounts of methylaluminoxane became active catalysts for ethylene polymerization. The activities of these catalysts are lower than the recently developed zirconium complexes bearing salicylaldimine ligands,[10–12] but these are comparable to the activities of pyridine–alkoxide complexes of Group 4 metals.[15] The catalytic activities of **2a–e**

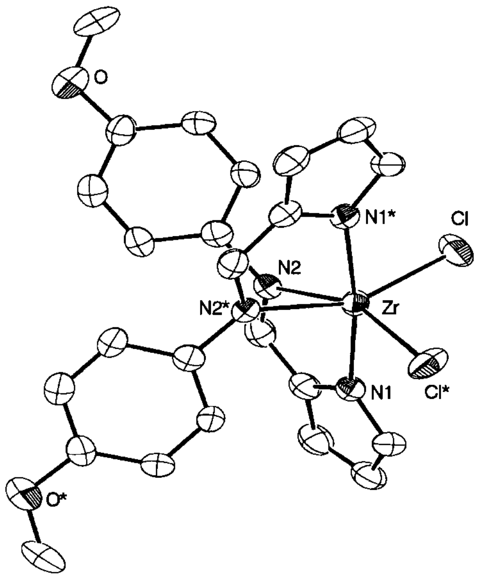


Figure 1. The molecular structure of **3a**. Selected bond distances (Å) and angles (deg); Zr—Cl = 2.405(2), Zr—N1 = 2.191(5), Zr—N2 = 2.280(4), Cl—Zr—Cl* = 101.47(9), N1—Zr—N2 = 72.8(2), N1—Zr—N1* = 172.8(2), N2—Zr—N2* = 79.1(2).

(17 (**2a**), 20 (**2b**), 18 (**2c**), 32 (**2d**), 18 (**2e**) kg-PE/mol-cat·h) were found to be almost the same as those found for **3a–e** (12 (**3a**), 31 (**3b**), 33 (**3c**), 38 (**3d**), 46 (**3e**) kg-PE/mol-cat·h)[20], indicating the *cis*-arranged diamido and dichloro complexes were converted to the same catalytically active species.

In summary, we have prepared bis(iminopyrrolyl)zirconium diamido/dichloro complexes and preliminarily demonstrated that these zirconium complexes became catalyst precursors for the polymerization of ethylene in the presence of excess amounts of methylaluminoxane. The substituent effects on the pyrrolyl skeleton are our current interest.

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17 **2a**: 78% yield, mp 220–222 °C. **2b**: 91% yield, mp 105–106 °C. **2c**: 93% yield, mp 98–102 °C. **2d**: 99% yield, mp 120–121 °C. **2e**: 98% yield, mp 226–228 °C. Selected data for typical complex **2c**, ^{1}H NMR (400 MHz, C_6D_6, 70 °C): δ 0.84 (br s, 12H, $N(CH_2CH_3)_2$), 1.90 (br s, 6H, Ar–CH_3), 3.40 (br s, 8H, $N(CH_2CH_3)_2$), 6.4–7.2 (br m, 14H, pyrrolyl and aromatic protons), 7.33 (br s, 2H, N=C*H*). Anal. Calcd for $C_{32}H_{42}N_6Zr$: C, 63.85; H, 7.03; N, 13.96%. Found: C, 63.94; H, 7.03; N, 13.74%. Selected data for typical complex **2d**, ^{1}H NMR (300 MHz, toluene-d_8, 35 °C): δ 0.37 (t, 6H, $N(CH_2CH_3)_2$), 0.83 (t, 3H, $N(CH_2CH_3)_2$), 1.17 (t, 3H, $N(CH_2CH_3)_2$), 1.96 (s, 3H, Me), 1.97 (s, 6H, Me), 2.09 (s, 3H, Me), 2.78 (m, 2H, $N(CH_2CH_3)_2$), 3.14 (m, 2H, $N(CH_2CH_3)_2$), 3.29 (m, 2H, $N(CH_2CH_3)_2$), 3.92 (m, 2H, $N(CH_2CH_3)_2$), 6.03 (dd, 1H, 4-pyr (*N* coordinated)), 6.40 (br s, 1H, 5-pyr (*N* coordinated)), 6.40 (dd, 1H, 4-pyr (*N*,*N* coordinated)), 6.44 (d, 1H, 3-pyr (*N* coordinated)), 6.58 (d, 1H, 3-pyr (*N*,*N* coordinated)), 6.92 (s, 1H, N=C*H*), 7.0–7.2 (m, 6H, C_6H_3), 7.09 (s, 1H, N=C*H*), 7.42 (br s, 1H, 5-pyr (*N*,*N* coordinated)). Anal. Calcd for $C_{34}H_{46}N_6Zr$: C, 64.82; H, 7.36; N, 13.34%. Found: C, 64.88; H, 7.19; N, 13.00%.
18 **3a**: 88% yield, mp 102–104 °C; **3b**: 73% yield, mp 105–107 °C; **3c**: 76% yield, mp 98–101 °C; **3d**: 47% yield, mp 76–79 °C; **3e**: 88% yield, mp 130–131 °C. Selected data for typical complex **3b**: ^{1}H NMR (400 MHz, $CDCl_3$, 35 °C): δ 2.29 (s, 6H, CH_3), 6.21 (dd, 2H, 4-pyr), 6.68 (d, 2H, 3-pyr), 6.81 (m, 4H, *o*-C_6H_4), 6.98 (m, 4H, *m*-C_6H_4), 7.46 (d, 2H, 5-pyr), 7.82 (s, 2H, N=C*H*). Anal. Calcd for $C_{24}H_{22}Cl_2N_4Zr$: C, 54.53; H, 4.20; N, 10.60%. Found: C, 54.37; H, 4.65; N, 10.36%.
19 Crystal data for **3a**: orthorhombic, space group *P*ccn (No. 56), $a = 9.322(8)$, $b = 14.125(6)$, $c = 18.39(2)$ Å, $V = 2421(2)$ Å^3, $Z = 4$, Mo Kα radiation ($\lambda = 0.71069$ Å), μ(Mo Kα) = 7.03 mm^{-1}, $F(000) = 1136.00$. Data were collected in the range of $5.0 < 2\theta < 55.0$ (ω–2θ scan), $T = 296(1)$ K. The structure was solved using the direct method (SHELXS 86) and refined by full-matrix least-squares on F^2 to give $R1 = 0.159$ and wR2 = 0.088 (all data); $R = 0.040$ and $R_w = 0.038$ [$I > 3.0\,\sigma(I)$].
20 General conditions: ethylene 1 atm, at 20 °C, in toluene ([Zr] = 1.0 mM), in the presence of 1000 equiv of MMAO.