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Preparation and Characterization of a Zwitterionic (Iminopyrrolyl)zirconium Complex with Benzylaluminate Anion and Its Catalytic Performance for 1-Hexene Polymerization

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*Summary: An alkyl abstraction from (DIP-pyr)Zr(CH_2Ph)$_3$ (DIP-pyr = 2-{N-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl) using Al(C_6F_5)$_3$ affords a zwitterionic dibenzyl complex, [(DIP-pyr)Zr(CH_2Ph)$_2$][η^6-PhCH$_2$Al(C_6F_5)$_3$] (**2**), which becomes an active catalyst for 1-hexene polymerization. The similar reaction by using B(C_6F_5)$_3$ affords a less stable adduct. The more stable character of **2** is ascribed to the tight ion-pair formation between the zirconium cation and the benzyl aluminate anion.*

The weakly coordinating anions of α-olefin polymerization catalysts have an important role as counterparts of the cationic early transition metal alkyl complexes, and the anions affect the molecular weight, branching, and microstructure of the resulting polyolefins.[1] The use of perfluoroaryl borate counteranions in metallocene catalysts enhances not only the thermal stability but also the catalytic activity of cationic alkyl species.[2] Moreover, the interaction between metallocene precursors and Lewis acidic organoboranes was elucidated by several research groups.[3] In sharp contrast, the interaction between organoalane, Al(C_6F_5)$_3$,[4] and alkyl complexes of metallocene and nonmetallocene catalyst precursors has attracted less attention.[5] Bochmann et al. reported that the mixture of Cp_2ZrMe_2 and Al(C_6F_5)$_3$ produced a less stable zwitterionic adduct than that of Cp_2ZrMe_2 and B(C_6F_5)$_3$, due to the facile decomposition by the C_6F_5 group transfer from aluminum to zirconium.[6] Another feature of the reaction between Al(C_6F_5)$_3$ and dimethyl zirconocene is that the alane adduct forms a more tightly bound ion pair. Landis and his co-workers revealed by the X-ray analyses of (C_5Me_4H)$_2$ZrCH$_3${μ-CH$_3$M(C_6F_5)$_3$} (M = B, Al) that the bond distance of Zr−(CH$_3$)$_{\text{bridge}}$ was shorter for the alane adduct (2.51 Å) than for the borane adduct (Zr−(CH$_3$)$_{\text{bridge}}$: 2.60 Å), indicating tight ion-pair formation for the Al(C_6F_5)$_3$ adduct.[7] Marks et al. also reported a similar trend by the structural and thermochemical analyses of B(C_6F_5)$_3$- and Al(C_6F_5)$_3$-derived metallocenium ion pairs.[5o]

Bochmann, Fujita, Okuda, and our group independently reported the preparation and α-olefin polymerization activities of group 4 metal iminopyrrolyl complexes.[8] Our continuing efforts to synthesize iminopyrrolyl complexes of group 4 metals

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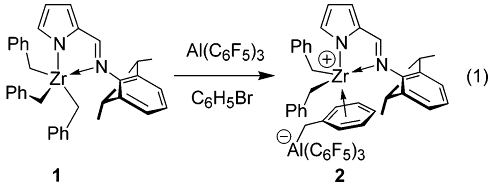
have been extended to isolate the cationic alkyl complexes applicable to the α-olefin polymerization reaction. During the course of our studies, we found that the $Al(C_6F_5)_3$-derived anion $[PhCH_2Al(C_6F_5)_3]^-$ was suitable for stabilizing a coordinatively unsaturated metal center, while the corresponding $B(C_6F_5)_3$-derived adduct was too unstable to be isolated. Herein, we describe the synthesis of zwitterionic dibenzyl complexes $[(DIP\text{-}pyr)Zr(CH_2Ph)_2][\eta^6\text{-}PhCH_2Al(C_6F_5)_3]$ (**2**) and revealed the molecular structure by an X-ray diffraction study. This is the first example of a zwitterionic complex with an η^6-benzylaluminate anion. The 1-hexene polymerization behavior of **2** and the product between $(DIP\text{-}pyr)Zr(CH_2Ph)_3$ (**1**) and $B(C_6F_5)_3$ is also disclosed.

Treatment of $(DIP\text{-}pyr)Zr(CH_2Ph)_3$ (**1**) (DIP-pyr = 2-{*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl)[8i] with an equimolar amount of tris(pentafluorophenyl)alane in bromobenzene afforded the corresponding zwitterionic complex, $[(DIP\text{-}pyr)Zr(CH_2Ph)_2][\eta^6\text{-}PhCH_2Al(C_6F_5)_3]$ (**2**) (eq 1), which was sparingly soluble in aromatic solvents.[9] The $Al(C_6F_5)_3$ adduct **2** was stable at room temperature for several hours. The ^1H NMR spectrum displayed the benzylic proton resonance bound to aluminum at δ 3.08. The notable feature in the ^1H NMR spectrum was the upfield shift of $[\mathit{Ph}CH_2Al(C_6F_5)_3]^-$ that was observed as broad resonances at δ_H 7.20, 6.58, and 5.79, assignable to *ortho*, *meta*, and *para* protons, respectively. The upfield shift of the aromatic resonances of $[\mathit{Ph}CH_2Al(C_6F_5)_3]^-$ suggested the presence of a cation−anion interaction through the η^6-coordination of $[\eta^6\text{-}\mathit{Ph}CH_2Al(C_6F_5)_3]^-$ to the cationic zirconium atom.[10] In the ^{19}F NMR spectrum, three sharp resonances, corresponding to the *ortho*, *para*, and *meta* fluorine atoms, were observed at δ_F −122.1, −155.8, and −162.7. The reaction of **1** with 1 equiv of $B(C_6F_5)_3$ in bromobenzene, followed by recrystallization at −30 °C, gave orange microcrystals of $[(DIP\text{-}pyr)Zr(CH_2Ph)_2][PhCH_2B(C_6F_5)_3]$ (**3**) in 86% yield, whose full characterization by NMR spectroscopy resulted in failure due to the poor solubility and the thermal instability in solution. The stability of **2** compared to **3** may reflect the tight ion-pair formation of the $Al(C_6F_5)_3$ adduct, and the stronger interaction between the benzylaluminate anion and the zirconium atom is in accordance with the trend of cation−anion interactions in $B(C_6F_5)_3$- and $Al(C_6F_5)_3$-derived metallocenium ion pairs.[5o,7]



1 **2** (1)

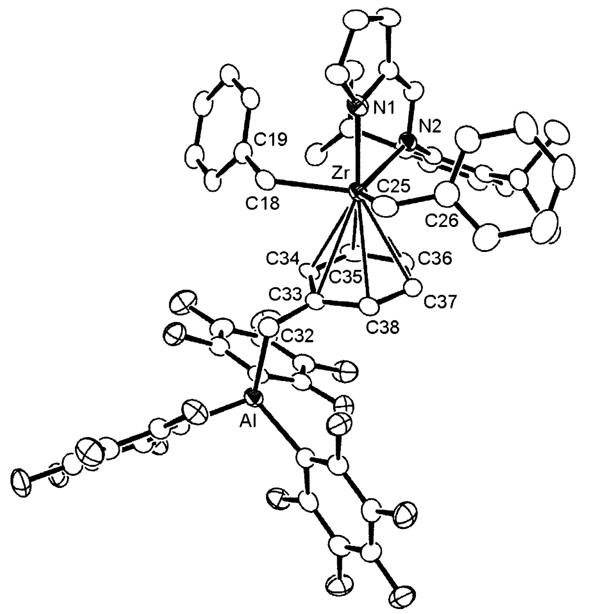


Figure 1. Molecular structure of **2**. All hydrogen atoms and toluene are omitted for clarity.

Table 1. Selected Bond Distances (Å) and Angles (deg) of 2

Zr−N1	2.203(4)	Zr −N2	2.361(4)
Zr−C18	2.290(5)	Zr−C25	2.257(5)
Zr−C33	2.898(4)	Zr−C34	2.697(4)
Zr−C35	2.593(4)	Zr−C36	2.656(4)
Zr−C37	2.760(5)	Zr−C38	2.844(5)
Al−C32	2.033(5)		
N1−Zr−N2	71.9(1)	N1−Zr−C18	81.3(2)
N1−Zr−C25	82.0(2)	N2−Zr−C18	121.3(2)
N2−Zr−C25	123.4(2)	C18−Zr−C25	102.2(2)
Zr−C18−C19	112.7(3)	Zr−C25−C26	105.8(3)
Al−C32−C33	109.0(3)		

Single crystals of **2** suitable for X-ray diffraction were obtained by cooling a toluene/hexane solution of **2** to −30 °C. The molecular structure is shown in Figure 1, and selected bond distances and angles are listed in Table 1.[11] Complex **2** is the first example of a zwitterionic complex with an η^6-benzylaluminate anion, although several structurally characterized group 4 metal zwitterionic complexes with η^6-benzylborate[3i,10,12] and μ-methylaluminate[5a,c,o,7] anions have been reported. Complex **2** has pseudo-trigonal bipyramidal geometry around the zirconium atom, where the pyrrolyl nitrogen atom and the centroid of the η^6-phenyl ring occupy the apical position. Two benzyl groups are bound to the zirconium atom in an η^1-fashion, based on the large bond angles of Zr−C(18)−C(19) [112.7(3)°] and Zr−C25−C26 [105.8(3)°].[3i,13] The distances between the zirconium atom and carbon atoms of the η^6-arene ring are 2.593(4)−2.898(4) Å, in the range typically observed for an η^6-

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[9] $[(DIP\text{-}pyr)Zr(CH_2Ph)_2][\eta^6\text{-}PhCH_2Al(C_6F_5)_3]$ (**2**): In a glovebox, $(DIP\text{-}pyr)Zr(CH_2Ph)_3$ (62 mg, 0.10 mmol) and $Al(C_6F_5)_3toluene_{0.5}$ (58 mg, 0.10 mmol) were placed in a Schlenk vessel. Cold bromobenzene (−30 °C) was added to the solid mixture, and the reaction mixture was shaken until each component was dissolved. The solution was stored at −30 °C overnight, and then orange microcrystals were formed. Hexane (ca. 5 mL) was added to the reaction mixture, and the supernatant was separated. The orange microcrystals were washed with hexane (1 mL) and dried in vacuo to give orange microcrystals (94.2 mg, 82% yield), mp 99−105 °C (dec.). ^1H NMR (300 MHz, C_6D_5Br, 298 K): δ 7.44 (s, 1H, N═CH), 7.20 (br d, $^3J_{H-H}$ = 5.7 Hz, 2H, *o*-Ph of η^6-$AlCH_2\mathit{Ph}$), 7.05−6.95 (aromatic protons), 6.87 (d, $^3J_{H-H}$ = 6.3 Hz, 2H, *m*-Ar of 2,6-$^iPr_2C_6\mathit{H}_3$), 6.80 (m, 3H, *p*-Ph of $ZrCH_2Ph$ and pyrrolyl ring), 6.58 (br, 2H, *m*-Ph of η^6-$AlCH_2\mathit{Ph}$), 6.40 (br, 1H, pyrrolyl ring), 6.30 (d, $^3J_{H-H}$ = 6.9 Hz, 4H, *o*-Ph of $ZrCH_2\mathit{Ph}$), 5.79 (br, 1H, *p*-Ph of η^6-$AlCH_2\mathit{Ph}$), 3.06 (br, 2H, $AlC\mathit{H}_2Ph$), 2.76 (br, 4H, $ZrC\mathit{H}_2Ph$), 1.55 (br, 2H, $C\mathit{H}Me_2$), 0.78 (d, $^3J_{H-H}$ = 6.0 Hz, 6H, $CH\mathit{Me}_2$), 0.65 (d, $^3J_{H-H}$ = 6.0 Hz, 6H, $CH\mathit{Me}_2$). ^{19}F NMR (282 MHz, C_6D_5Br, 298 K): δ −122.1 (d, $^3J_{F-F}$ = 20 Hz, 6F, *ortho*), −155.8 (t, $^3J_{F-F}$ = 19 Hz, 3F, *para*), −162.7 (m, 6F, *meta*).

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[11] Crystal data for complex **2** ($(C_{56}H_{42}N_2F_{15}AlZr)(C_7H_8)$, 120(1) K): monoclinic, $P2_1/n$ (No. 14), a = 11.4095(15) Å, b = 21.711(4) Å, c = 22.396(4) Å, V = 5547.1(16) Å^3, Z = 4, D_{calcd} = 1.483 g cm^{-3}, μ = 3.07 cm^{-1}, R_1 = 0.1336 and wR_2 = 0.1891 (all data), GOF = 1.021.

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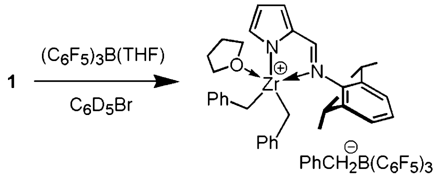
coordinating arene ring. Two adjacent Zr−C(arene) distances, Zr−C(33) [2.898(4) Å] and Zr−C(38) [2.844(5) Å], are longer than the distances between zirconium and other carbon atoms, deforming from the ideal η^6-coordination, due to the steric repulsion between the η^6-coordinating arene ring and the bulky {*N*-(2,6-diisopropylphenyl)iminomethyl}pyrrolyl ligand. It is notable that zwitterionic zirconium complexes [$(PhCH_2)_3Zr(\eta^6\text{-}PhCH_2B(C_6F_5)_3)$],[10c] [$CpZr(CH_2Ph)_2(\eta^6\text{-}PhCH_2B(C_6F_5)_3)$],[10e] [(2,6-$Ph_2$-3,5-$Me_2C_6HO)_2Zr(CH_2Ph)(\eta^6\text{-}PhCH_2B(C_6F_5)_3)$],[12a] and [(1,1′-Fc-$(NSiMe_3)_2)Zr(CH_2Ph)(\eta^6\text{-}PhCH_2B(C_6F_5)_3)$][12b] had similar asymmetry in the bonding of the benzyl borate anion to the zirconium atom.

The reactions of **1** with Lewis acid−base adducts $(C_6F_5)_3Al(THF)$ and $(C_6F_5)_3B(THF)$ were examined in order to stabilize the cationic zirconium center by the coordination of the Lewis base. The benzyl abstraction did not proceed by adding $(C_6F_5)_3Al(THF)$ to **1** because of the lower affinity of $Al(C_6F_5)_3$ to the benzyl anion compared to THF. This behavior was the same toward other group 4 metal dimethyl complexes in the presence of THF.[5g,m] On the other hand, mixing of **1** and 1 equiv of $(C_6F_5)_3B(THF)$ in C_6D_5Br cleanly afforded an ionic species, [(DIP-pyr)$Zr(CH_2Ph)_2(THF)$][$(PhCH_2)B(C_6F_5)_3$] (**4**) (eq 2), which was stable at room temperature.[14] The resonances of the coordinating THF molecule were observed at δ 3.24 and 1.22 in the ^{1}H NMR spectrum. In the ^{19}F NMR, the $\Delta\delta(m,p\text{-F})$ was 2.8 ppm, indicating that the [$PhCH_2B(C_6F_5)_3$]$^-$ anion was separated from the metal center.[15] The quantitative formation of **4** from **1** and $(C_6F_5)_3B(THF)$ suggests that $B(C_6F_5)_3$ may abstract a benzyl anion from the zirconium center to give **3** as an ionic pair.



4 (2)

Polymerization of 1-hexene was conducted by $Al(C_6F_5)_3$ adduct **2** in chlorobenzene, and the results are summarized in Table 2. The resulting polymers had narrow molecular weight distributions ($M_w/M_n < 2$), indicating that polymerization using **2** has a single-site character. The time dependency for the 1-hexene polymerization was also investigated (runs 2−4), and the values of M_n and M_w were almost the same among all runs, suggesting that the catalytically active species does not have living polymerization behavior. In the ^{1}H NMR spectra of the resulting polymers, the signal characteristic of the internal olefin (δ 5.3−5.4) was observed,[16] confirming that the termination was a β-hydrogen elimination from the growing polymer chain. We also examined the $B(C_6F_5)_3$-derived complexes **3** and **4** for 1-hexene polymerization. In sharp contrast to the *atactic* poly(1-hexene)s obtained by **2**, complex **3** afforded an *isotactic*-rich poly(1-hexene) ([*mmmm*] up to 85%). The Lewis base-stabilized adduct **4**, which was generated in situ before adding an excess amount of 1-hexene monomer, was inactive for the 1-hexene polymerization. Our preliminary study indicated that **3** showed low efficiency and broad molecular weight distribution,[17] which might be associated with the rapid decomposition of the active species. The ligand activation might be expected to construct the active species for higher isotacticity,[18] but the details of the process are not clear yet.

Table 2. 1-Hexene Polymerization Catalyzed by [(DIP-pyr)$Zr(CH_2Ph)_2$][η^6-$PhCH_2Al(C_6F_5)_3$] (2)[a]

run	temp (°C)	time (h)	yield (%)	activity[b]	M_n	M_w	M_w/M_n
1	0	6	49	3.5	7.2×10^4	1.3×10^5	1.8
2	rt	1	23	9.7	4.6×10^4	8.4×10^4	1.8
3	rt	3	77	11.0	4.6×10^4	8.6×10^4	1.9
4	rt	6	92	6.6	4.0×10^4	7.3×10^4	1.8
5	50	6	83	5.9	2.1×10^4	4.0×10^4	1.9

[a] Conditions: [cat.] = 5 mM (5 μmol catalyst) in a C_6H_5Cl (0.70 mL) and 1-hexene (0.32 mL, 500 equiv) mixture. [b]Activity [kg polymer/mol cat•h].

In summary, we demonstrated the preparation of an $Al(C_6F_5)_3$-derived zwitterionic complex, [(DIP-pyr)$Zr(CH_2Ph)_2$][η^6-$PhCH_2Al(C_6F_5)_3$] (**2**), and the molecular structure of the $Al(C_6F_5)_3$ adduct **2** was revealed by X-ray analysis. The complex **3**, prepared by mixing of **1** and $B(C_6F_5)_3$, was too thermally unstable to characterize. The difference in the stability of **2** and **3** may depend on the strength of the cation−anion interaction. The $Al(C_6F_5)_3$ adduct **2** was found to become an active catalyst for 1-hexene polymerization with single-site character (M_w/M_n < 2).

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Supporting Information Available: Text giving experimental details for the syntheses of all compounds, ^{1}H and ^{19}F NMR spectra of **2** and **4**, 1-hexene polymerization procedures, and CIF files giving crystallographic data for **2**. These materials are available free of charge via the Internet at http://pubs.acs.org.

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(14) [(DIP-pyr)$Zr(CH_2Ph)_2(THF)$][$PhCH_2B(C_6F_5)_3$] (**4**): ^{1}H NMR (300 MHz, C_6D_5Br, 298 K): δ 7.81 (s, 1H, N=CH), 7.2−6.8 (aromatic protons), 6.87 (d, 1H, $^3J_{H-H}$ = 3.6 Hz, pyrrolyl ring), 6.27 (m, 1H, pyrrolyl ring), 6.17 (br d, $^3J_{H-H}$ = 7.4 Hz, 4H, *o*-Ph of $ZrCH_2$*Ph*), 3.34 (br, 2H, BCH_2-Ph), 3.24 (br, 4H, THF), 2.42 (br, 2H, C*H*Me$_2$), 2.17 (br d, $^2J_{H-H}$ = 11.3 Hz, 2H, ZrC*H*HPh), 1.93 (br, 2H, ZrCH*H*Ph), 1.22 (br, 4H, THF), 1.02 (br, 6H, CH*Me*$_2$), 0.86 (br d, $^3J_{H-H}$ = 5.8 Hz, 6H, CH*Me*$_2$). ^{13}C NMR (75 MHz, C_6D_5Br, 308 K): δ 164.2 (d, $^1J_{C-H}$ = 170 Hz, N=CH), 148.3, 148.1 (d, $^1J_{C-F}$ = 244 Hz, *o*-C_6F_5), 141.1, 140.9 (d, $^1J_{C-F}$ = 314 Hz, *p*-C_6F_5), 136.1 (d, $^1J_{C-F}$ = 269 Hz, *m*-C_6F_5), 135.9, 131.3, 130.1, 129.2, 129.1, 128.5, 127.2, 126.6, 126.2, 124.0, 122.2, 116.2, 80 (br, $ZrCH_2$), 75.7 (t, $^1J_{C-H}$ = 157 Hz, THF), 28.6 (d, $^1J_{C-H}$ = 125 Hz, *C*HMe$_2$), 25.6 (q, $^1J_{C-H}$ = 127 Hz, CH*Me*$_2$), 24.5 (t, $^1J_{C-H}$ = 129 Hz, THF), 21.7 (q, $^1J_{C-H}$ = 127 Hz, CH*Me*$_2$), some carbon signals were overlapped with C_6D_5Br resonances. ^{19}F NMR (282 MHz, C_6D_5Br, 298 K): δ −131.5 (d, $^3J_{F-F}$ = 22 Hz, 6F, *ortho*), −164.7 (t, $^3J_{F-F}$ = 21 Hz, 3F, *para*), −167.5 (t, $^3J_{F-F}$ = 20 Hz, 6F, *meta*).

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