

Reaction of AlMe₃ with Heterobimetallic Zr/Rh Complexes Having a C₅H₄-CMe₂-Ind (or C₅H₄-CMe₂-C₅H₄) Ligand. Formation of Complexes with a Zr–Indenyl (or Zr–Cyclopentadienyl) σ -Bond

Daisuke Takeuchi, Junpei Kuwabara, and Kohtaro Osakada*

Chemical Resources Laboratory, Tokyo Institute of Technology,
4259 Nagatsuta, Midori-ku, Yokohama 226-8503, Japan

Received September 6, 2002

Cp(Cl)₂Zr(C₅H₄-CMe₂-Ind)Rh(cod) (**1**; Ind = η^5 -C₉H₆) reacts with excess AlMe₃ in toluene to form Cp(Cl)Zr(C₅H₄-CMe₂-C-C-CH-C₆H₄)Rh(cod) (**2**), which has a σ -bond between the Zr center and an indenyl carbon. Crystallography of **2** shows the molecular structure with a Cl ligand and Rh on the same side of the indenyl plane. The reaction at 0 °C gives a mixture of the diastereomers of Cp(Cl)(Me)Zr(C₅H₄-CMe₂-Ind)Rh(cod) (**3a** and **3b**). The ratio of the isomers is estimated as 6:1 (or 1:6) from the ¹H NMR peak area ratio of the hydrogen signals of the Me ligand. Addition of AlMe₃ to the mixture changes the ratio to 2:1 within 5 min in toluene, followed by gradual conversion of the equilibrated mixture of **3a** and **3b** into **2**. The reaction of excess AlClMe₂ with **1** does not cause methylation of the complex, whereas addition of AlClMe₂ to a mixture of **1**, **3a**, and **3b** changes the latter two complexes into **1**. Cp(Cl)₂Zr(C₅H₄-CMe₂-C₅H₄)Rh(cod) (**4**) reacts with AlMe₃ to produce Cp(Cl)Zr(C₅H₄-CMe₂-C-C-CH-C₂H₂)Rh(cod) (**5**) at 60 °C. The NMR spectra of the reaction mixture reveal formation of **5** via the intermediate Cp(Cl)(Me)Zr(C₅H₄-CMe₂-C₅H₄)Rh(cod) (**6**).

Introduction

The hydrocarbon ligands, which have two cyclopentadienyl groups or a cyclopentadienyl and indenyl groups connected with an alkylene, dialkylsilylene, or phenylene group, form dinuclear transition metal complexes with the metal centers bridged by the ligand.^{1–3} These bridging ligands were used also to stabilize the dinuclear complexes having one or two Zr centers.^{4–7} These complexes bring about Zr-catalyzed olefin polymerization in the presence of organoaluminum co-catalyst.^{5–8} Alkylation of the dichlorozirconocene part

of the above dinuclear complexes by the organoaluminum reagent plays an important role in the initiation step of the polymerization, although details of the reaction of organoaluminum compounds with the above dinuclear complexes have not been studied. In this paper, we report the reaction of AlMe₃ with Zr/Rh complexes having cyclopentadienyl-indenyl or bis-cyclopentadienyl ligand to produce new heterobimetallic complexes.

Results and Discussion

Methylation and Ligand Metalation of Cp(Cl)₂Zr(C₅H₄CMe₂L)Rh(cod) (L = C₅H₄, Ind). Cp(Cl)₂Zr(C₅H₄-CMe₂-Ind)Rh(cod) (**1**) was obtained from the reaction of CpZrCl₃(dme) (dme = 1,2-dimethoxyethane)

(1) Recent papers of late transition metal complexes with C₅H₄-X-C₅H₄ type ligands. (a) Werner, H. *Inorg. Chim. Acta* **1992**, *198–200*, 715. (b) Werner, H.; Schneider, D.; Schulz, M. *Chem. Ber.* **1992**, *125*, 1017. (c) Schneider, D.; Werner, H. *Organometallics* **1993**, *12*, 4420. (d) Amor, F.; Gómez-Sal, P.; de Jeseús, E.; Martín, A.; Pérez, A. I.; Royo, P.; Vazquez de Miguel, A. *Organometallics* **1996**, *15*, 2103. (e) van der Berg, W.; Crowsigt, J. A. M. T. C.; Bosman, W. P.; Smits, J. M. M.; de Gelder, R.; Gal, A. W.; Heck, J. *J. Organomet. Chem.* **1996**, *524*, 281. (f) Heck, J.; Körnich, J. *J. Organomet. Chem.* **1997**, *543*, 153. (g) Körnich, J.; Hanbold, S.; He, J.; Reimelt, O.; Heck, J. *J. Organomet. Chem.* **1999**, *584*, 329. (h) Fröhlich, R.; Gimeno, J.; González-Cueva, M.; Lastra, E.; Borge, J. García-Granada, S. *Organometallics* **1999**, *18*, 3008. (i) Komatsu, H.; Yamazaki, H. *J. Organomet. Chem.* **2001**, *634*, 109.

(2) Stern, D.; Sabat, M.; Marks, T. J. *J. Am. Chem. Soc.* **1990**, *112*, 9558.

(3) Reviews of heterobimetallic transition metal complexes. (a) Wheatley, N.; Kalck, P. *Chem. Rev.* **1999**, *99*, 3379. (b) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167. (c) Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205. (d) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41.

(4) (a) Reddy, K. P.; Petersen, J. L. *Organometallics* **1989**, *8*, 547. (b) Nifant'ev, I. E.; Borzov, M. V.; Churakov, A. V.; Mkoyan, S. G.; Atovmyun, L. O. *Organometallics* **1992**, *11*, 3942.

(5) (a) Diamond, G. M.; Green, M. L. H.; Popham, N. A.; Chernega, A. M. *J. Chem. Soc., Chem. Commun.* **1994**, 727. (b) Diamond, G. M.; Chernega, A. N.; Mountford, P.; Green, M. L. H. *J. Chem. Soc., Dalton Trans.* **1996**, 921. (c) Yan, X.; Chernega, A.; Green, M. L. H.; Sanders, J.; Souter, J.; Ushioda, T. *J. Mol. Catal. A: Chem.* **1998**, *128*, 119. (d) Green, M. L. H.; Popham, N. H. *J. Chem. Soc., Dalton Trans.* **1999**, 1049.

(6) Jüngling, S.; Mülhaupt, R.; Plenio, H. *J. Organomet. Chem.* **1993**, *460*, 191.

(7) (a) Mitani, M.; Oouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Polym. Bull.* **1995**, *35*, 677. (b) Mitani, M.; Oouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Macromol. Chem. Phys.* **1996**, *197*, 1815.

(8) Heterobimetallic complexes closely related to olefin polymerization. (a) Bosch, B. E.; Brümmer, I.; Kunz, K.; Erker, G.; Fröhlich, R.; Kotila, S. *Organometallics* **2000**, *19*, 1255. (b) Yamaguchi, Y.; Suzuki, N.; Mise, T.; Wakatsuki, Y. *Organometallics* **1999**, *18*, 996.

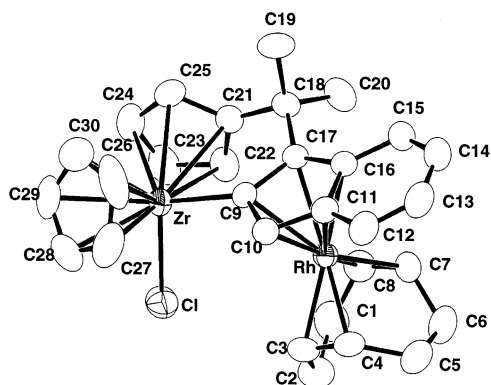
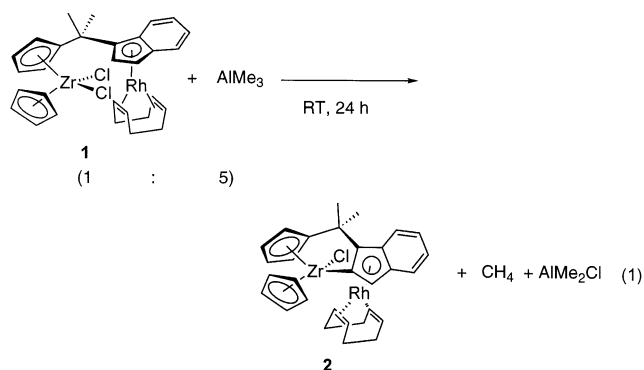


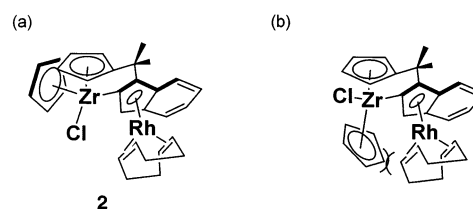
Figure 1. ORTEP drawing of **2** at the 50% probability level. Selected bond distances (Å) and angles (deg): Zr–C9 2.254(4), Zr–Cl 2.461(1), C9–C10 1.432(5), C10–C11 1.451(5), C11–C16 1.424(5), C16–C17 1.458(5), C9–C17 1.444(5), C17–C18 1.512(5), C18–C21 1.516(6), C18–C19 1.545(6), C18–C20 1.538(6), Zr–C21 2.532(4), Rh–C9 2.274(4), Rh–C10 2.171(4), Rh–C11 2.322(4), Rh–C16 2.369(4), Rh–C17 2.269(4), Rh–C3 2.142(4), Rh–C4 2.123(4), Rh–C7 2.129(4), Rh–C8 2.155(4), C9–Zr–C21 69.2(1), Zr–C9–C10 131.2(3), Zr–C9–C17 122.7(3), C9–C17–C18 119.7(4), C17–C18–C21 107.2(3), C17–C18–C19 107.7(4), C17–C18–C20 114.1(4), Zr–C21–C18 117.6(3), C19–C18–C21 110.5(4), C20–C18–C21 109.1(4), C19–C18–C20 108.2(4).

with $\text{Li}_2[\text{CMe}_2(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)]$ followed by addition of $[\text{RhCl}(\text{cod})_2]$, according to the method of preparation of $\text{Cp}(\text{Cl})_2\text{Zr}\{\text{C}_5\text{H}_4\text{-C}(\text{CH}_2)_4\text{-C}_5\text{H}_4\}\text{Rh}(\text{cod})$ by Green et al.⁵ Complex **1** reacts with excess AlMe_3 ($1:\text{AlMe}_3 = 1:5$) at room temperature to form Zr/Rh heterobimetallic complexes. Recrystallization of the products after the reaction for 24 h gives $\text{Cp}(\text{Cl})\text{Zr}(\text{C}_5\text{H}_4\text{-CMe}_2\text{-C-C-CH-C}_6\text{H}_4)\text{-Rh}(\text{cod})$ (**2**) as red crystals (eq 1).



Addition of a large excess of THF to the solvent inhibited the reaction. Figure 1 depicts molecular structure of **2** determined by X-ray crystallography. The cyclopentadienyl groups of the Cp and $\text{C}_5\text{H}_4\text{CMe}_2\text{Ind}$ ligands coordinate to Zr in a η^5 -manner, while the indenyl carbon adjacent to that bonded to the bridging CMe_2 group is σ -bonded to the metal (Zr–C = 2.254(4) Å). The indenyl group coordinates to the Rh center as the η^5 -ligand. The cyclopentadienyl and indenyl planes of the bridging ligand are almost perpendicular to each other. The Cl ligand attached to the Zr and the Rh(cod) moiety are positioned on the same side of the indenyl plane as shown in Chart 1a. Another possible isomer of **2** shown in Chart 1b is not formed by the reaction

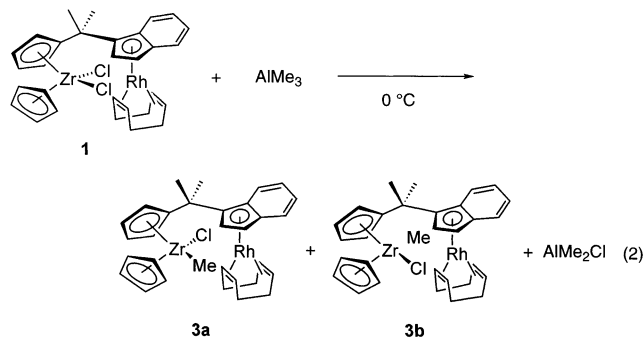
Chart 1



because it is less stable than **2** due to severe steric repulsion between the Cp ligand bonded to Zr and cod ligand bonded to Rh.

The ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **2** contain peaks due to two inequivalent methyl groups of the bridging ligand (δ_{H} : 1.59 and 1.35, δ_{C} : 29.7 and 26.7). The $^{13}\text{C}\{^1\text{H}\}$ NMR signals at δ 150.2, 131.1, and 79.6 are split by Rh–C coupling (4–5 Hz). The former two carbons, which are not bonded to a hydrogen, are assigned to the indenyl carbon attached to Zr and that bonded to the CMe_2 group. The third signal at higher field than the others is due to the CH carbon of the five-membered ring of the indenyl group.

The reaction of AlMe_3 with **1** at 0 °C followed by addition of Et_2O to the reaction mixture forms a mixture of complexes **3a** and **3b** as shown in eq 2. The products



are a pair of diastereomers, having chiral centers at the Zr and the chiral indenyl plane. Formation of **2** is almost negligible under these conditions. Four repeated cycles of addition of AlMe_3 to the reaction products and removal of Al-containing products such as AlClMe_2 by washing them with hexane afford a mixture of the two isomeric complexes in 6:1 molar ratio. The products contain a small amount of unreacted **1** (<3%), which could not be removed by the above purification procedure and recrystallization. The major and minor products of the reaction, observed in the reaction mixture, are named **3major** and **3minor**, respectively. Complexes **3major** and **3minor** correspond to the isomers **3a** and **3b** in eq 2, although assignment of each for the structures is not possible (vide infra). The ^1H NMR signals of the mixture at δ 0.53 and 0.52 in a 6:1 peak area ratio are due to the hydrogens of the methyl ligand bonded to Zr. The crystal structure of $\text{Cp}(\text{Cl})_2\text{Zr}\{\text{C}_5\text{H}_4\text{C}(\text{CH}_2)_4\text{C}_5\text{H}_4\}\text{-Rh}(\text{cod})$ shows that the two Cl ligands bonded to Zr have different distances from the Cp group attached to Rh.^{5c} The ^1H NMR spectrum of a mixture of **3a** and **3b**, however, did not provide different NOEs between the hydrogens of the Me ligand of the isomers and the C_9H_5 group bonded to Rh. The two CH_3 groups' hydrogens of the bridging ligand of **3major** and **3minor** are observed at δ 1.88 and 1.66 and δ 1.83 and 1.72, respectively. The

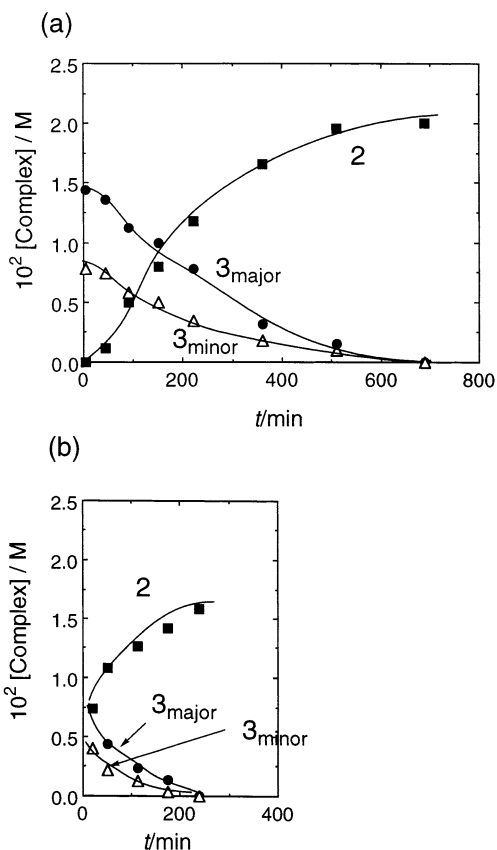


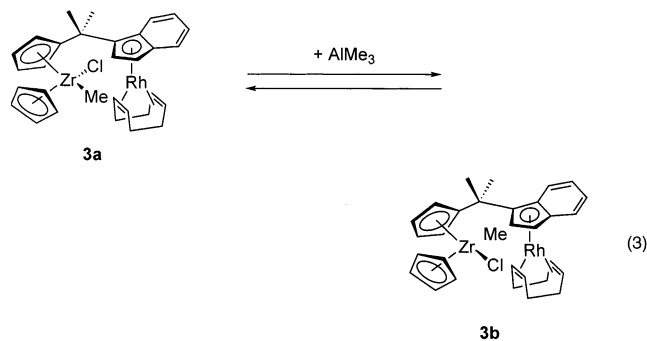
Figure 2. Time profile of the reaction of AlMe₃ with a mixture of **3**_{major} and **3**_{minor} (6:1 before addition of AlMe₃) in (a) C₆D₆ and (b) CD₂Cl₂. [Al]₀/[**3**]₀ = 5. Complex **1** in a small amount (<3%) is contained in the complex used. The reaction was monitored by ¹H NMR peak area ratios by using anthracene as an internal standard.

other NMR signals are reasonably assigned to the hydrogens of **3**_{major} and **3**_{minor}.

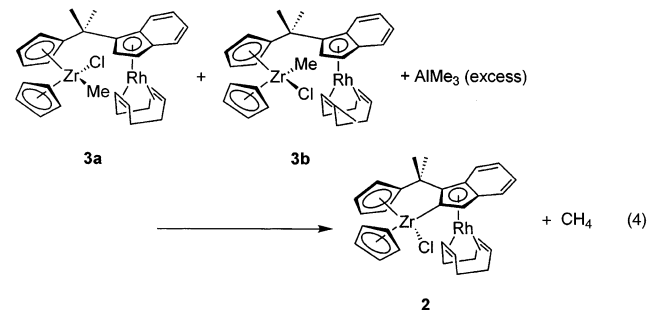
The molar ratio of **3**_{major} and **3**_{minor} in solution does not change at room temperature. Addition of AlMe₃ to a benzene or CH₂Cl₂ solution of the mixture causes mutual isomerization of **3**_{major} and **3**_{minor} and conversion of the complexes into **2**. Figure 2 plots the change of the molar ratio of the complexes in C₆D₆ and in CD₂Cl₂. After 10 min of addition of AlMe₃ to **3**_{major} and **3**_{minor} (5:1 molar ratio), the isomer ratio changed to 2:1 in both solvents soon. It is followed by formation of **2** and decrease of **3**. The ratio between **3**_{major} and **3**_{minor} is constant during conversion of the complexes into **2**, suggesting the existence of rapid equilibrium between the isomers in the presence of organoaluminum reagent. Formation of **2** in C₆D₆ (Figure 2a) is slower than that in CD₂Cl₂ (Figure 2b); complete conversion of a mixture of **3**_{major} and **3**_{minor} requires 11 h in C₆D₆ and 4 h in CD₂Cl₂. A similar reaction with equimolar AlMe₃ to **3** (Al:Zr = 1:1) produces **2** in 3% yield after 12 h, while the isomerization of complex **3** is completed within 5 min. The reaction of AlMe₃ with **3**_{major} and **3**_{minor} in toluene with addition of THF (20 molar equiv to the complexes) and Et₂O (excess) does not change the ratio between the complexes nor form **2**.

The above results indicate clearly that **3a** and **3b** isomerize rapidly promoted by equimolar AlMe₃ in

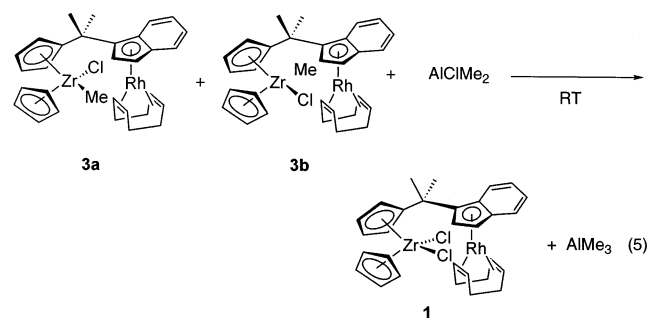
benzene or CH₂Cl₂ (eq 3). The isomerization takes place smoothly even in the presence of a catalytic amount of



AlMe₃ but does not occur in the absence of AlMe₃. An excess amount of AlMe₃ promotes not only the isomerization but also transformation of **3a** and **3b** into **2** via formation of the σ -bond between an indenyl carbon and the Zr center (eq 4). The reaction of AlClMe₂ with **1** in



toluene does not form **2** nor **3a** and **3b** at room temperature. Addition of AlClMe₂ to a mixture of **1**, **3**_{major}, and **3**_{minor} (63:32:5) converts the latter two complexes into **1**, as shown in eq 5. Intermolecular

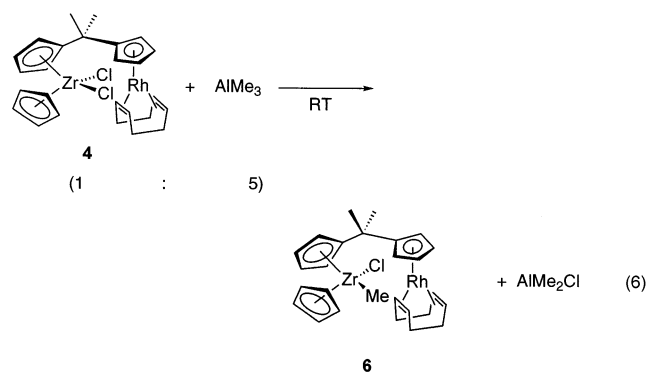


exchange between the Cl ligand attached to Al and the Me ligand bonded to Zr occurs during the reaction. Since the reactions in eqs 1 and 2 give AlClMe₂, AlCl₂Me, and Al₂Cl₃Me₃ as the Al-containing product, substitution of the Me ligand of the once formed **3a** and **3b** by the Cl ligand attached to Al also takes place to regenerate **1** and AlMe₃ during the reaction. This facile ligand exchange among Zr and Al renders the above reactions reversible. Negishi et al. investigated the reaction of AlMe₃ with Cp₂ZrCl₂ and revealed that Cp₂ZrCl₂ and Cp₂Zr(Cl)Me are equilibrated in the presence of AlMe₃ through reversible methylation of Cp₂ZrCl₂ by AlMe₃ and chlorination of Cp₂ZrCl(Me) by AlClMe₂.⁹ Equilib-

(9) Negishi, E.; van Horn, D. E.; Yoshida, T. *J. Am. Chem. Soc.* **1985**, *107*, 6639.

rium of the reversible transmetalation reactions between the Zr/Rh complexes is shifted by addition of methylaluminum reagents such as AlMe_3 and AlClMe_2 to the reaction mixture or by irreversible transformation of complexes **3a** and **3b** into **2**. The ligand transfer is considered to involve associative intermediates containing Zr and Al centers bridged by Cl and/or Me ligands, similarly to other transmetalation between non-transition and transition metal compounds.

The reaction of AlMe_3 with $\text{Cp}(\text{Cl})_2\text{Zr}(\text{C}_5\text{H}_4\text{-CMe}_2\text{-C}_5\text{H}_4)\text{Rh}(\text{cod})$ (**4**) produces $\text{Cp}(\text{Cl})\text{Zr}(\text{C}_5\text{H}_4\text{-CMe}_2\text{-C-C-CH-C}_2\text{H}_2)\text{Rh}(\text{cod})$ (**5**) and $\text{Cp}(\text{Cl})(\text{Me})\text{Zr}(\text{C}_5\text{H}_4\text{-CMe}_2\text{-C}_5\text{H}_4)\text{Rh}(\text{cod})$ (**6**) via metalation of a C_5H_4 group of **4** and substitution of the Cl ligand of **4** by a Me group, respectively. Complex **4** reacts with excess AlMe_3 at room temperature to produce a mixture of **6** and unreacted **4** (5:3 by ^1H NMR) within 10 min (eq 6). The



^1H NMR spectrum shows the signals of **6** at δ 0.56 (Zr- CH_3) and at δ 1.60 and 1.81 ($\text{C}(\text{CH}_3)_2$), although isolation of **6** from the mixture was unsuccessful. Complex **6** does not undergo metalation of the C_5H_4 group even in the presence of AlMe_3 at room temperature. At 60°C , complex **4** reacts with AlMe_3 to produce **5** (eq 7).

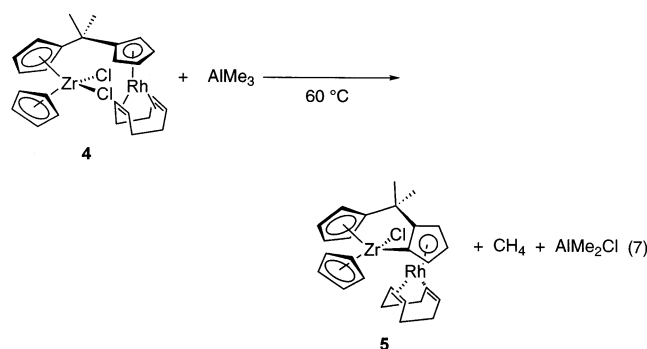


Figure 3 plots a profile of the reaction that gives **5** from **4** via intermediate complex **6**. Thus, complex **4** undergoes substitution of a Cl ligand by AlMe_3 at room temperature to form **6** and metalation of the C_5H_4 ring at 60°C to afford **5**.

Ethylene Polymerization. Complexes **1**, **2**, **4**, and **5** catalyze polymerization of ethylene in the presence of MAO cocatalyst. Table 1 summarizes the results at ambient pressure of the monomer. Catalytic activities of **1** and **4** (172 and 262 $\text{g}(\text{mmol cat})^{-1}\text{h}^{-1}$) are lower than that of Cp_2ZrCl_2 measured under the same conditions (862 $\text{g}(\text{mmol cat})^{-1}\text{h}^{-1}$). It is partly due to the

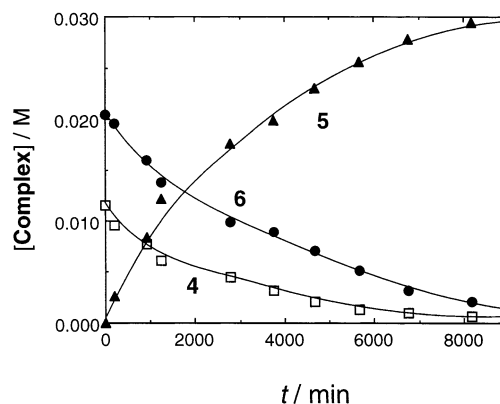


Figure 3. Time profile of the reaction of AlMe_3 with **4** in C_6D_6 at 60°C . The concentration of the substrates is as follows: $[\mathbf{4}]_0 = 0.032\text{ M}$ and $[\text{AlMe}_3]_0 = 0.16\text{ M}$. The reaction was monitored by relative ^1H NMR peak area ratios.

Table 1. Ethylene Polymerization Catalyzed by Zr/Rh Heterobimetallic Complexes^a

complex	yield (mg)	activity ($\text{g}(\text{mmol cat})^{-1}\text{h}^{-1}$)	M_n	M_w/M_n
1	86	172	26 400	3.73
2	20	40	25 100	3.35
4	131	262	25 300	3.76
5	20	40	18 600	3.94
Cp_2ZrCl_2	436	872	24 500	3.18

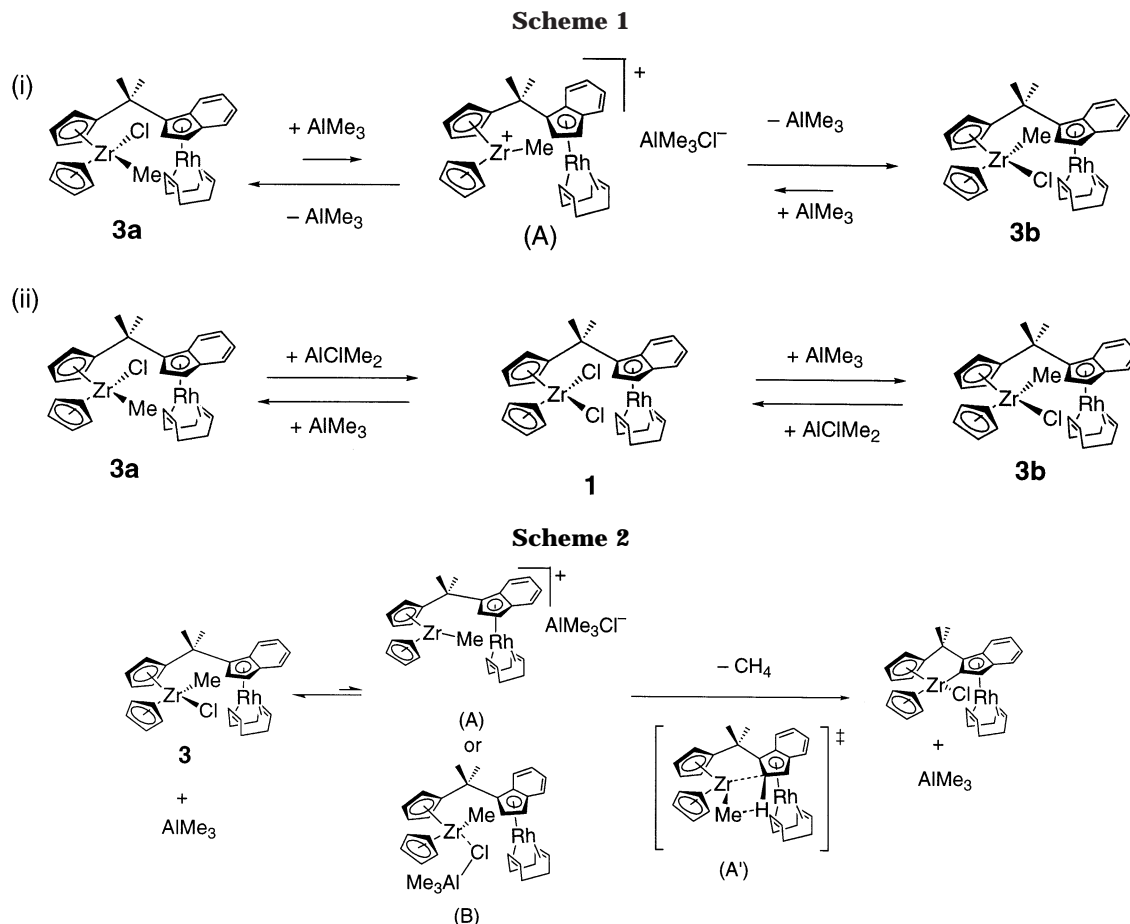
^a Reactions were carried out by stirring the solution of catalyst under atmospheric pressure of ethylene for 1 h. $[\text{Al}]/[\text{cat.}] = 1000$, $[\text{cat.}] = 16.7\ \mu\text{M}$ in toluene.

Rh(cod) part, whose steric hindrance retards the polymerization of ethylene at the Zr site. Complexes **2** and **5** show even lower catalytic activity than **1** and **4**. Mononuclear Zr complexes were also reported to undergo intramolecular C-H bond activation of the hydrocarbon ligand by Zr. Dimethylzirconocene with the cyclopentadienyl ligand having a *t*-Bu substituent reacts with $\text{B}(\text{C}_6\text{F}_5)_3$ to produce a cationic Zr complex in which a carbon of the *t*-Bu substituent is bonded to the metal center.¹⁰ A cationic Zr complex with a tridentate amine ligand with a 2,4,6-trimethylphenyl substituent at the nitrogen also undergoes metalation of the methyl group of the ligand.¹¹ Since the produced complex shows a much lower catalytic activity for alkene polymerization than the original complex, the intramolecular metalation of the ligand deactivates the catalyst of alkene polymerization.

Reaction Mechanism. The reactions of AlMe_3 with **1** and with **4** in this paper involve formation of several Zr/Rh complexes. Complexes **1** and **4** are methylated to form complexes with a methyl ligand bonded to the Zr center, **3a** (and **3b**) and **6**, respectively. These methyl complexes undergo metalation of the ligand to afford **2** and **5**. The latter reactions, which occur at higher temperature than the former, are much slower than the methylation of the starting complexes. A plausible mechanism for the isomerization of **3a** and **3b** involves AlMe_3 -assisted dissociation of the Cl ligand, giving an intermediate **A**, followed by nucleophilic attack of the Cl ligand of the AlClMe_3 anion to the cationic Zr center

(10) Yang, X.; Stern, C. L.; Marks, T. J. *J. Am. Chem. Soc.* **1994**, *116*, 10015.

(11) Schrock, R. R.; Bonitatebus, P. J., Jr.; Schrodi, Y. *Organometallics* **2001**, *20*, 1056.



(Scheme 1(i)). Reaction of AlCl₃ with Cp₂TiCl(Me) was reported to produce [Cp₂TiMe]⁺AlCl₄⁻ via abstraction of the Cl ligand bonded to Ti by Lewis acidic AlCl₃.¹² In the present study, there is another possible reaction pathway involving intermediate **1** (Scheme 1(ii)) because the mixture of **3a** and **3b** used in the experiments contains a small amount of **1** (3%). The reaction of AlMe₃ with **1** to give a mixture of **3a** and **3b** and their conversion into **1** promoted by AlClMe₂ take place rapidly. The pathway in Scheme 1(ii) would contribute to the equilibrium between **3a** and **3b** in the presence of the Al-containing reagents, if it might occur faster than that in Scheme 1(i).

Addition of Al(*i*-Bu)₃, instead of AlMe₃, to a mixture of **3a** and **3b** (6:1 or 1:6) containing a small amount (3%) of **1** in C₆D₆ was conducted in order to retard the isomerization and to decide which mechanism is operative in the isomerization. Since the reaction did not give **3a** nor **3b** but contained **2** in 13% and other uncharacterized dinuclear complexes, it did not provide a clue to choose either of the mechanisms in Scheme 1.

Scheme 2 depicts a possible pathway for formation of **2** from **3a** and **3b** promoted by AlMe₃. The reaction contains activation of the C–H bond of the indenyl group to form the new Zr–C bond accompanied by extrusion of methane, which belongs to intramolecular σ -bond metathesis. The cationic intermediate **A**, proposed also for the isomerization in Scheme 1(i), has a Zr center with high Lewis acid character and vacant coordination site. The cationic Zr center of **A** is more

ready to cause the σ -bond metathesis of the indenyl group of the ligand than that of **3a** and **3b**. σ -Bond metathesis of organotransition metal complexes proceeds via an intermediate with an M–C–H–C (M: early transition metal) four-membered ring. Green et al. found mononuclear Zr and Hf complexes with the composition CpMCl(L) (M = Zr, Hf; L = C₅H₄-CRR'-Ind), in which two carbons of the five-membered ring of the indenyl group are bonded to the metal center in a σ, π -type η^2 -fashion.^{5b,13} Approach of the five-membered ring of the indenyl group of **3a** and/or **3b** would form the intermediate that is suited for σ -bond metathesis of the C–H bond of the indenyl group and the Zr–Me bond.

Experimental Section

General Methods. All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. Toluene and hexane were distilled from sodium benzophenone ketyl prior to use. CpZrCl₃(dme) (dme = 1,2-dimethoxyethane)¹⁴ and Li₂[Me₂C(C₅H₄)-(C₉H₆)]·0.6Et₂O^{5b} were prepared according to the literature method. [RhCl(cod)]₂ was synthesized according to the reported procedure.¹⁵ Zirconium tetrachloride was purchased from Aldrich Chemical Co. Inc. AlMe₃ and MAO were purchased from TOSOH-FINECHEM and stored under argon. NMR spectra (¹H, ¹³C{¹H}) were recorded on JEOL JNM LA-500 and

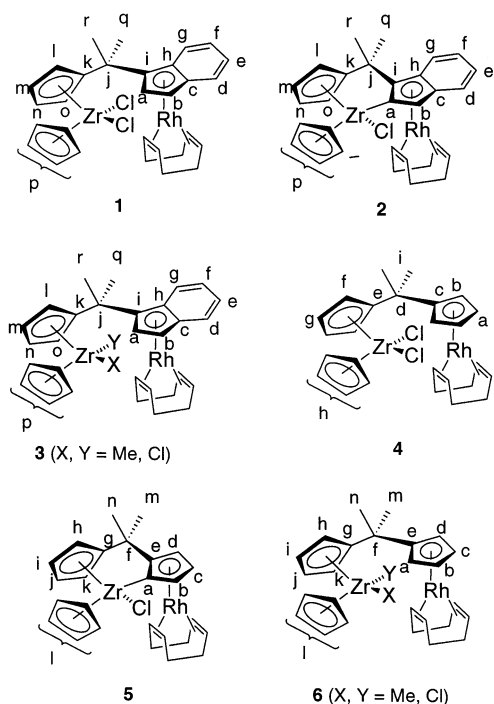
(12) Eisch, J. J.; Pombrik, S. I.; Zheng, G. X. *Organometallics* **1993**, *12*, 3856.

(13) Diamond, G. M.; Green, M. L. H.; Mountford, P.; Popham, N. A.; Chernega, A. N. *J. Chem. Soc., Chem. Commun.* **1994**, 103. See also: Lucas, C. R.; Green, M. L. H.; Forster, R. A.; Prout, K. *J. Chem. Soc., Chem. Commun.* **1973**, 97.

(14) (a) Stone, K. J.; Little, R. D. *J. Org. Chem.* **1984**, *49*, 1849. (b) Lund, E. C.; Livinghouse, T. *Organometallics* **1990**, *9*, 2426.

(15) Giordano, G.; Crabtree, R. H. *Inorg. Synth.* **1979**, *19*, 218.

Chart 2



Varian Mercury 300 spectrometers. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder.

Preparation of 1. $\text{Li}_2[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)(\text{C}_9\text{H}_6)] \cdot 0.6\text{Et}_2\text{O}$ (1.90 g, 6.8 mmol) and $\text{CpZrCl}_3(\text{dme})$ (2.30 g, 6.5 mmol) were stirred in toluene (150 mL) at -78°C and were allowed to warm to room temperature over 1 h. The resulting deep red reaction mixture was stirred for an additional 20 h. $[\text{RhCl}(\text{cod})]_2$ (1.60 g, 3.2 mmol) was then added to the suspension at room temperature and the mixture was stirred for 20 h. After filtration, the yellow solution was concentrated to 30 mL and decanted. The yellow residue was washed with hexane (20 mL \times 3) and dried under reduced pressure (3.50 g, 82%). Anal. Calcd for $\text{C}_{30}\text{H}_{33}\text{Cl}_2\text{RhZr}$: C, 54.71; H, 5.05; Cl, 10.77. Found: C, 54.69; H, 5.11; Cl, 10.76. ^1H NMR (300 MHz, C_6D_6): δ 7.41 (m, 1H, H_d), 7.00–7.09 (m, 3H, H_{e-g}), 6.33 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or o), 6.16 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or o), 5.88–5.91 (1H, H_m or n), 5.87–5.90 (1H, H_a), 5.82 (s, 5H, H_p), 5.41 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_m or n), 4.46 (dd, 1H, $^3J = 3$ Hz, $^4J = 1$ Hz, H_b), 4.04 (m, 2H, cod), 3.97 (m, 2H, cod), 1.98 (s, 3H, H_q or r), 1.51–1.96 (m, 8H, cod), 1.74 (s, 3H, H_q or r). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 142.2 (s, C_k), 123.0 (s, C_{e-g}), 122.4 (s, C_{e-g}), 120.7 (s, C_{e-g}), 120.0 (s, C_d), 116.5 (s, C_l or o), 116.5 (s, C_l or o), 115.8 (s, C_p), 115.3 (s, C_m or n), 113.7 (s, C_c or h), 112.5 (s, C_c or h), 109.7 (s, C_m or n), 107.0 (d, $J_{\text{Rh}-\text{C}} = 3$ Hz, C_j), 93.3 (d, $J_{\text{Rh}-\text{C}} = 3$ Hz, C_a), 73.0 (d, $J_{\text{Rh}-\text{C}} = 3$ Hz, C_b), 69.0 (d, $J_{\text{Rh}-\text{C}} = 8$ Hz, cod), 68.8 (d, $J_{\text{Rh}-\text{C}} = 8$ Hz, cod), 38.7 (s, C_j), 32.1 (s, cod), 31.1 (s, cod), 29.2 (s, C_q or r), 28.5 (s, C_q or r). Assignment of the carbon and hydrogen is shown in Chart 2.

Preparation of 2. To a solution of **1** (85.1 mg, 0.14 mmol) in toluene (10 mL) was added a toluene solution of AlMe_3 (2.0 M, 0.4 mL, 0.7 mmol) dropwise at room temperature. Stirring the solution at room temperature for 24 h changed the color of the solution from yellow to red. The solvent was removed at reduced pressure. The resultant residue was washed with hexane (3 mL \times 2). The product yield at this stage is approximately 80%, but it contains a small amount of Al-containing impurities. Further purification by recrystallization of the product from toluene/hexane at -40°C afforded Al-free complex **2** (37.8 mg, 38%). Anal. Calcd for $\text{C}_{30}\text{H}_{32}\text{ClRhZr}$: C, 57.91; H, 5.18; Cl, 5.70. Found: C, 57.69; H, 5.15; Cl, 5.60. ^1H NMR (300 MHz, C_6D_6): δ 7.22–7.26 (m, 2H, H_{d-g}), 7.10 (1H, H_i or o), 7.09–7.16 (m, 2H, H_{d-g}), 6.31 (dt, 1H, $^3J = 3$ Hz, $^4J =$

2 Hz, H_m or n), 5.86 (s, 5H, H_p), 5.35 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_m or n), 5.17 (pseudo q, 1H, $J = 3$ Hz, H_l or o), 4.38 (d, 1H, $^4J = 1$ Hz, H_b), 4.27 (m, 2H, cod), 4.06 (m, 2H, cod), 2.09 (m, 4H, cod), 1.72 (m, 4H, cod), 1.59 (s, 3H, H_q or r), 1.35 (s, 3H, H_q or r). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 152.5 (s, C_k), 150.2 (d, $J_{\text{Rh}-\text{C}} = 4$ Hz, C_a or i), 131.1 (d, $J_{\text{Rh}-\text{C}} = 5$ Hz, C_a or i), 123.5 (s, C_{d-g}), 123.1 (s, C_{d-g}), 121.4 (s, C_{d-g}), 118.5 (s, C_{d-g}), 115.4 (s, C_m or n), 114.4 (s, C_c or h), 113.5 (d, $J_{\text{Rh}-\text{C}} = 3$ Hz, C_c or h), 112.7 (s, C_l or o), 111.4 (s, C_p), 104.4 (s, C_l or o), 101.4 (s, C_m or n), 79.6 (d, $J_{\text{Rh}-\text{C}} = 5$ Hz, C_b), 71.8 (d, $J_{\text{Rh}-\text{C}} = 13$ Hz, cod), 70.3 (d, $J_{\text{Rh}-\text{C}} = 13$ Hz, cod), 39.8 (s, C_j), 31.0 (s, cod), 30.8 (s, cod), 29.7 (s, C_q or r), 26.7 (s, C_q or r).

Preparation of 3. To a solution of **1** (90 mg, 0.14 mmol) in toluene (10 mL) was added a toluene solution of AlMe_3 (2.0 M, 0.34 mL, 0.68 mmol) dropwise at 0°C , and the mixture was stirred. After addition of Et_2O (1 mL), volatiles were removed at reduced pressure, and the residue was washed with hexane (10 mL \times 3) and dried under reduced pressure. Repetition of the above procedure (four times) gives a pale yellow solid, which consists of a mixture of isomers (**3**_{major}:**3**_{minor} = 6:1) as well as a small amount of **1** (<3%) (60.9 mg, 79%).

^1H NMR data obtained as the mixtures of 6:1 and 2:1 molar ratios. **3**_{major} (300 MHz, C_6D_6): δ 7.52 (m, 1H, H_d), 7.00–7.14 (m, 3H, H_{e-g}), 6.39 (dt, 1H, $J_3 = 3$ Hz, $J_4 = 2$ Hz, H_i or o), 6.36 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_m or n), 6.01 (dd, 1H, $J = 3$ Hz, $J_{\text{Rh}-\text{H}} = 2$ Hz, H_a), 5.61 (s, 5H, H_p), 5.59 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or o), 4.74 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_m or n), 4.46 (d, 1H, $J = 3$ Hz, H_b), 4.04 (m, 2H, cod), 3.97 (m, 2H, cod), 1.56–1.96 (m, 8H, cod), 1.88 (s, 3H, H_q or r), 1.66 (s, 3H, H_q or r), 0.53 (s, 3H, $\text{Zr}-\text{CH}_3$). ^1H NMR of **3**_{minor} (300 MHz, C_6D_6): δ 7.48 (m, 1H, H_d), 7.00–7.14 (m, 3H, H_{e-g}), 6.27 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or o), 6.03 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_m or n), 5.86 (dd, 1H, $J = 3$ Hz, $J_{\text{Rh}-\text{H}} = 2$ Hz, H_a), 5.68 (s, 5H, H_p), 5.63 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or o), 4.94 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_m or n), 4.51 (d, 1H, $J = 3$ Hz, H_b), 4.04 (m, 2H, cod), 3.97 (m, 2H, cod), 1.56–1.96 (m, 8H, cod), 1.83 (s, 3H, H_q or r), 1.72 (s, 3H, H_q or r), 0.52 (s, 3H, $\text{Zr}-\text{CH}_3$).

Preparation of 4. $\text{Li}_2[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2]$ (469 mg, 2.5 mmol) and $\text{CpZrCl}_3(\text{dme})$ (898 mg, 2.5 mmol) were stirred in toluene (50 mL) for 60 h at room temperature. $[\text{RhCl}(\text{cod})]_2$ (502 mg, 1.0 mmol) was added to the suspension at room temperature, and the mixture was stirred at 80°C for 20 h. After filtration, the yellow solution was evaporated to dryness. The resulting solid was washed with hexane and dried under reduced pressure (860 mg, 70%). Anal. Calcd for $\text{C}_{26}\text{H}_{31}\text{Cl}_2\text{RhZr}$: C, 51.31; H, 5.13; Cl, 11.65. Found: C, 51.30; H, 4.76; Cl, 11.81. ^1H NMR (300 MHz, C_6D_6): δ 6.15 (t, 1H, $J = 3$ Hz, H_f or g), 5.93 (s, 5H, H_h), 5.86 (t, 1H, $J = 3$ Hz, H_f or g), 4.93 (t, 1H, $J = 2$ Hz, H_a or b), 4.56 (t, 1H, $J = 2$ Hz, H_a or b), 3.93 (m, 4H, cod), 2.23 (m, 4H, cod), 1.95 (m, 4H, cod), 1.71 (s, 6H, H_i). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 142.4 (s, C_e), 119.3 (d, $J_{\text{Rh}-\text{C}} = 2$ Hz, C_j), 116.1 (s, C_h), 114.9 (s, C_f or g), 114.3 (s, C_f or g), 86.3 (d, $J_{\text{Rh}-\text{C}} = 3$ Hz, C_a or b), 85.0 (d, $J_{\text{Rh}-\text{C}} = 2$ Hz, C_a or b), 63.6 (d, $J_{\text{Rh}-\text{C}} = 8$ Hz, cod), 37.0 (s, C_d), 32.7 (s, cod), 31.0 (s, C_i).

Preparation of 5. To a solution of **4** (124 mg, 0.20 mmol) in toluene (5 mL) was added a toluene solution of AlMe_3 (2.0 M, 0.5 mL, 1.0 mmol) dropwise at room temperature. After stirring the solution at 60°C for 60 h, the solvent was removed at reduced pressure, and the residue was extracted with hexane (5 mL). The extracts were concentrated and cooled to -40°C , giving **5** as an orange powder (51.3 mg, 44%). Anal. Calcd for $\text{C}_{26}\text{H}_{30}\text{ClRhZr}$: C, 54.59; H, 5.29; Cl, 6.20. Found: C, 54.39; H, 5.29; Cl, 6.37. ^1H NMR (300 MHz, C_6D_6): δ 7.20 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_h or k), 6.31 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or j), 5.84 (s, 5H, H_l), 5.35 (dt, 1H, $^3J = 3$ Hz, $^4J = 2$ Hz, H_i or j), 5.30 (dt, 1H, $J = 2$ Hz, $J_{\text{Rh}-\text{H}} = 1$ Hz, H_c), 5.16 (pseudo q, 1H, $J = 2$ Hz, H_h or k), 4.82 (dd, 1H, $J = 3$ Hz, $J_{\text{Rh}-\text{H}} = 2$ Hz, H_b or d), 4.13 (m, 4H, cod), 3.93 (dd, 1H, $J = 2$ Hz, $J_{\text{Rh}-\text{H}} = 1$ Hz, H_b or d), 2.48 (m, 4H, cod), 2.05 (m, 4H, cod), 1.25 (s,

3H, H_m or n), 1.17 (s, 3H, H_m or n). ¹³C{¹H} NMR (75 MHz, C₆D₆): δ 151.5 (s, C_g), 145.4 (d, J_{Rh-C} = 3 Hz, C_a or e), 143.3 (d, J_{Rh-C} = 2 Hz, C_a or e), 115.8 (s, C_i or j), 112.6 (s, C_h or k), 111.2 (s, C_i), 104.6 (s, C_h or k), 101.1 (s, C_i or j), 88.9 (d, J_{Rh-C} = 3 Hz, C_b or d), 86.9 (d, J_{Rh-C} = 2 Hz, C_b or d), 85.5 (d, J_{Rh-C} = 2 Hz, C_c), 67.3 (d, J_{Rh-C} = 8 Hz, cod), 65.6 (d, J_{Rh-C} = 8 Hz, cod), 38.1 (s, C_f), 32.6 (s, C_m or n), 32.5 (s, cod), 32.1 (s, cod), 27.8 (s, C_m or n).

Preparation of 6. To a solution of **4** (56 mg, 0.092 mmol) in toluene was added a toluene solution of AlMe₃ (2.0 M, 0.23 mL, 0.46 mmol Al) at 0 °C. After stirring the solution at room temperature for 5 min, the ¹H NMR spectrum indicates the presence of **6** and unreacted **4** in a molar ratio of 5:3. Solvents and Al compounds were removed at reduced pressure at 0 °C. The ¹H NMR spectrum indicates the formation of a mixture of **4** and **6** (1:1). Data of **6** obtained from the mixture with **4** are as follows. ¹H NMR (300 MHz, C₆D₆): δ 6.37 (q, 1H, J = 3 Hz, H_i or j), 6.31 (dt, 1H, ³J = 3 Hz, ⁴J = 2 Hz, H_h or k), 5.77 (s, 5H, H_i), 5.44 (q, 1H, J = 3 Hz, H_i or j), 4.99 (m, 1H, H_{a-d}), 4.90–4.93 (1H, H_h or k), 4.90–4.93 (1H, H_{a-d}), 4.74 (q, 1H, J = 2 Hz, H_{a-d}), 4.58 (q, 1H, J = 2 Hz, H_{a-d}), 3.95 (m, 4H, cod), 2.22 (m, 4H, cod), 1.93 (m, 4H, cod), 1.81 (s, 3H, H_m or n), 1.60 (s, 3H, H_m or n), 0.56 (s, 3H, Zr–CH₃).

Reaction of AlMe₃ with 3 (5 equiv). To a solution of a mixture of **3**_{major}, **3**_{minor} (6:1), and **1** (<3%) (6.4 mg, 0.01 mmol) and anthracene (3.6 mg, 0.02 mmol, internal standard) in C₆D₆ (0.4 mL) was added a C₆D₆ solution of AlMe₃ (0.5 M, 0.1 mL, 0.05 mmol) at room temperature. The reaction profile was examined by ¹H NMR measurement.

Reaction of AlClMe₂ with 3. A mixture of **1**, **3**_{major}, and **3**_{minor} (13:6.5:1) (6.4 mg, approximately 0.011 mmol) was obtained from the reaction of **1** with AlMe₃ (**1**:AlMe₃ = 1:5) for 16 h at room temperature and removal of the produced **2** by filtration. To a C₆D₆ (0.5 mL) solution of the mixture was added a hexane solution of AlMe₂Cl (1.0 M, 0.055 mL, 0.055 mmol) at room temperature. The ¹H NMR spectrum of the solution after 10 min showed complete conversion of **3**_{major} and **3**_{minor} into **1**.

Reaction of Al(*i*-Bu)₃ with 3. To a mixture of **3a**, **3b** (6:1), and **1** (<3%) (6.4 mg, 0.01 mmol) and anthracene (3.6 mg, 0.02 mmol, internal standard) in C₆D₆ (0.4 mL) was added a C₆D₆ solution of Al(*i*-Bu)₃ (0.5 M, 0.1 mL, 0.05 mmol) at room temperature. After 3 min, the ¹H NMR spectrum of the solution indicated complete conversion of **3**_{major} and **3**_{minor} into **2** (13%) and other uncharacterized complexes.

Crystal Structure Determination. A crystal of **2** was mounted in a glass capillary tube under Ar. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-7R automated four-cycle diffractometer by using Mo Kα radiation (λ = 0.71069 Å) and the ω–2θ scan method, and an empirical absorption correction (Ψ scan) was applied. Calculations were carried out with the program package teXsan for Windows. Atomic scattering factors were obtained from the literature. A full matrix least-squares refinement was used for non-hydrogen atoms with anisotropic thermal parameters. Hydrogen atoms were located by assuming the ideal geometry and included in the structure calculation without further refinement of the parameters.¹⁶ Crystal data for **2**: C₃₀H₃₂ClRhZr, 622.16, red, 0.40 × 0.30 × 0.13 mm; monoclinic, space group P2₁/a (No. 14); a = 9.469(2) Å, b = 25.864(5) Å, c = 10.687(3) Å, β = 105.58(2)°, V = 2521(2) Å³, Z = 4, D_{calcd} = 1.639 g cm⁻³, μ = 1.189 mm⁻¹; 293 K; 2θ range 5–55°; number of independent reflections (I > 3.00σ(I)) 3983 (R_{int} = 0.057); 298 variable parameters: R = 0.036 and R_w = 0.037; GOF = 1.55.

Polymerization of Ethylene. A typical experimental procedure is as follows. A mixture of complex **1** (0.50 μmol) and MAO (0.50 mmol) in toluene (30 mL) was stirred at room temperature for 15 min. After freeze–pump–thaw cycles, ethylene (1 atm) was introduced to the flask at room temperature. The mixture was stirred for 1 h at room temperature and quenched by MeOH and then by 5 M HCl/MeOH. Separated polymer solid was filtered, washed with MeOH, H₂O, and then hexane, and dried in vacuo. The results are summarized in Table 1.

Acknowledgment. This work was supported by a Grant-in-Aid for Scientific Research from the Ministry of Education, Science, Sports, and Culture, Japan.

Supporting Information Available: Crystallographic data of **2**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM0207360

(16) *International Tables for X-ray Crystallography*, Kynoch: Birmingham, England, 1974; Vol. 4.