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Synthesis of *ansa*-Zirconocene/Rhodium Heterobimetallic Complexes: Enhanced Catalytic Activity in Stereospecific Polymerization of α-Olefins

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Novel heterobimetallic complexes that consist of zirconium and rhodium, LRh(η^2-$CH_2{=}CH)_2Si(\eta^5$-C_5H_2-2,4-$Me_2)_2ZrCl_2$ (**3a** L = η^5-C_9H_7, **3b** η^5-C_5H_5, **3c** η^5-C_5Me_5), were synthesized, and **3b** was structurally characterized. The complexes have a "C_2-symmetric" *ansa*-zirconocene part and the rhodium metal on the bridge part. The complexes **3a**−**c** in combination with methylaluminoxane catalyzed highly isospecific polymerization of α-olefins. Their catalytic activities were higher than that of the parent zirconocene complex, and the obtained polymer had a larger molecular weight.

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Introduction

Early−late heterobimetallic complexes have been extensively investigated in the past few decades.[1−3] Group 4 metallocenes are attractive components of these complexes because of their high reactivity as olefin polymerization catalysts.[4] Although a number of such heterobimetallic complexes have been prepared,[3] surprisingly few cases report their utilization as polymerization catalysts.[5] It is, in many cases, probably because the reactive sites of metallocenes are used to construct the bimetallic structures and the olefins may not be allowed to interact with the metal center. Although such complexes show catalytic activity in a few cases, it is simply because they dissociate into monometallic components in catalytic systems.[5a,b] In view of catalysis, a bimetallic structure should be designed so that late transition metals do not block the reaction sites of the group 4 metallocenes. There have been two examples of olefin polymerization catalyzed by heterobimetallic complexes which have late transition metal units as substituents on the Cp rings of metallocenes. Mitani et al. reported that dimethyl(ferrocenyl)silyl-substituted

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(1) For review, see: (a) *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 10. (b) Barlow, S.; O'Hare, D. *Chem. Rev.* **1997**, *97*, 637. (c) Hey-Hawkins, E. *Chem. Rev.* **1994**, *94*, 1661. (d) Stephan, D. W. *Coord. Chem. Rev.* **1989**, *95*, 41. (e) Bullock, R. M.; Casey, C. P. *Acc. Chem. Res.* **1987**, *20*, 167, and references therein.

(2) For recent examples, see: (a) Murata, T.; Gao, H.; Mizobe, Y.; Nakano, F.; Motomura, S.; Tanase, T.; Yano, S.; Hidai, M. *J. Am. Chem. Soc.* **1992**, *114*, 8287. (b) Hostetler, M. J.; Butts, M. D.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 2743. (c) Brown, D. S.; Delville, M.-H.; Vollhardt, K. P. C.; Astruc, D. *Organometallics* **1996**, *15*, 2360. (d) Aubart, M. A.; Bergman, R. G. *J. Am. Chem. Soc.* **1996**, *118*, 1793. (e) Orth, S. D.; Terry, M. R.; Abboud, K. A.; Dodson, B.; McElwee-White, L. *Inorg. Chem.* **1996**, *35*, 916. (f) Chetcuti, M. J.; Grant, B. E.; Fanwick, P. E. *Organometallics*, **1996**, *15*, 4389. (g) Wadepohl, H.; Galm, W.; Pritzkow, H. *Organometallics* **1996**, *15*, 570. (h) Lang, J.-P.; Kawaguchi, H.; Tatsumi, K. *Inorg. Chem.* **1997**, *36*, 6447. (i) Nakajima, T.; Mise, T.; Shimizu, I.; Wakatsuki, Y. *Organometallics* **1995**, *14*, 5598. (j) Nakajima, T.; Shimizu, I.; Koshino, H.; Kobayashi, K.; Wakatsuki, Y. *Inorg. Chem.* **1997**, *36*, 6440. (k) Nakajima, T.; Shimizu, I.; Kobayashi, K.; Wakatsuki, Y. *Organometallics* **1998**, *17*, 262. (l) Spannenberg, A.; Oberthür, M.; Noss, H.; Tillack, A.; Arndt, P.; Kempe, R. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2079. (m) Yuki, M.; Okazaki, M.; Inomata, S.; Ogino, H. *Angew. Chem., Int. Ed. Engl.* **1998**, *37*, 2126. (n) Schneider, A.; Gade, L. H.; Breuning, M.; Bringmann, G.; Scowen, I. J.; McPartlin, M. *Organometallics* **1998**, *17*, 1643. (o) Cecchetto, P.; Ceccon, A.; Gambaro, A.; Santi, S.; Ganis, P.; Gobetto, R.; Valle, G.; Venzo, A. *Organometallics* **1998**, *17*, 752. (p) Hsiao, S.-M.; Shyu, S.-G. *Organometallics* **1998**, *17*, 1151. (q) Jansen, G.; Schubart, M.; Findeis, B.; Gade, L. H.; Scowen, I. J.; McPartlin, M. *J. Am. Chem. Soc.* **1998**, *120*, 7239. (r) Odon, A. L.; Arnold, P. L.; Cummins, C. C. *J. Am. Chem. Soc.* **1998**, *120*, 5836. (s) Sanada, T.; Suzuki, T.; Yoshida, T.; Kaizaki, S. *Inorg. Chem.* **1998**, *37*, 4712. (t) Nishibayashi, Y.; Iwai, S.; Hidai, M. *Science* **1998**, *279*, 540.

(3) For examples containing group 4 metallocenes, see: (a) Chetcuti, M. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W., Stone, F. G. A., Wilkinson, G., Eds.; Pergamon: Oxford, 1995; Vol. 10, Chapter 2, p 23. (b) Casey, C. P. *J. Organomet. Chem.* **1990**, *400*, 205, and references therein. (c) Glassman, T. E.; Liu, A. H.; Schrock, R. R. *Inorg. Chem.* **1991**, *30*, 4723. (d) Baranger, A. M.; Hollander, F. J.; Bergman, R. G. *J. Am. Chem. Soc.* **1993**, *115*, 7890. (e) Baranger, A. M.; Bergman, R. G. *J. Am. Chem. Soc.* **1994**, *116*, 3822. (f) Dick, D. G.; Hou, Z.; Stephan, D. W. *Organometallics* **1992**, *11*, 2378. (g) Lang, H.; Wu, I.-Y.; Weinmann, S.; Weber, C.; Nuber, B. *J. Organomet. Chem.* **1997**, *541*, 157. (h) Fujita, K.; Ikeda, M.; Kondo, T.; Mitsudo, T. *Chem. Lett.* **1997**, 57. (i) Lang, H.; Wu, I.-Y.; Weinmann, S.; Weber, C.; Nuber, B. *J. Organomet. Chem.* **1997**, *541*, 157. (j) Qian, C.; Guo, J.; Sun, J.; Chen, J.; Zheng, P. *Inorg. Chem.* **1997**, *36*, 1286. (k) Bakhmutov, V. I.; Visseaux, M.; Baudry, D.; Dormond, A.; Richard, P. *Inorg. Chem.* **1996**, *35*, 7316. (l) Desmurs, P.; Visseaux, M.; Baudry, D.; Dormond, A.; Nief, F.; Ricard, L. *Organometallics* **1996**, *15*, 4178. (m) Hayashi, Y.; Osawa, M.; Kobayashi, K.; Sato, T.; Sato, M.; Wakatsuki, Y. *J. Organomet. Chem.* **1997**, *542*, 241. (n) Hayashi, Y.; Osawa, M.; Kobayashi, K.; Sato, T.; Sato, M.; Wakatsuki, Y. *J. Organomet. Chem.* **1998**, *569*, 169. (o) Schwink, L.; Knochel, P.; Eberle, T.; Okuda, J. *Organometallics* **1998**, *17*, 7. (p) Zhang, D.; McConville, D. B.; Hrabusa, J. M., III; Tessier, C. A.; Youngs, W. J. *J. Am. Chem. Soc.* **1998**, *120*, 3506. (q) Zippel, T.; Arndt, P.; Ohff, A.; Spannenberg, A.; Kempe, R.; Rosenthal, U. *Organometallics* **1998**, *17*, 4429. (r) Danjoy, C.; Zhao, J.; Donnadieu, B.; Legros, J.-P.; Valade, L.; Choukroun, R.; Zwick, A.; Cassoux, P. *Chem. Eur. J.* **1998**, *4*, 1100.

(4) For recent reviews, see: (a) Brintzinger, H.-H.; Fischer, D.; Mülhaupt R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Kaminsky, W. *J. Chem. Soc., Dalton Trans.* **1998**, 1413. (c) Soga, K.; Shiono, T. *Prog. Polym. Sci.* **1997**, *22*, 1503. (d) Chien, J. C. W.; Rieger, B.; Sugimoto, R.; Mallin, D. T.; Rausch, M. D. *Catalytic Olefin Polymerization*; Kodansha: Tokyo, 1989. (e) Soga, K., Terano, M., Eds. *Catalyst Design for Tailor-Made Polyolefins*; Kodansha: Tokyo, 1994. (f) Fink, G., Mülhaupt, R., Brintzinger, H.-H., Eds. *Ziegler Catalyst*; Springer-Verlag: Berlin, 1995.

(5) (a) Lindenberg, F.; Shribman, T.; Sieler, J.; Hey-Hawkins, E.; Eisen, M. S. *J. Organomet. Chem.* **1996**, *515*, 19. (b) Shribman, T.; Kurz, S.; Senff, U.; Lindberg, F.; Hey-Hawkins, E.; Eisen, M. S. *J. Mol. Catal. A: Chem.* **1998**, *129*, 191. (c) Mitani, M.; Oouchi, K.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Macromol. Chem. Phys.* **1996**, *197*, 1815. (d) Mitani, M.; Hayakawa, M.; Yamada, T.; Mukaiyama, T. *Bull. Chem. Soc. Jpn.* **1996**, *69*, 2967. (e) Yan, X.; Chernega, A.; Green, M. L. H.; Sanders, J.; Souter, J.; Ushioda, T. *J. Mol. Catal. A: Chem.* **1998**, *128*, 119.

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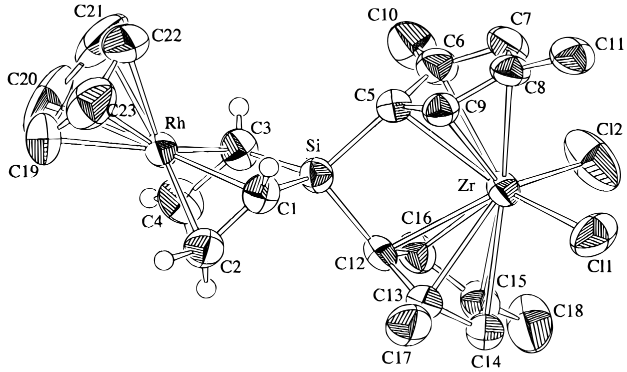


Figure 1. ORTEP drawing of **3b**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted in part for clarity.

zirconocene dichloride has enhanced catalytic activity, although comparison with the trimethylsilyl-substituted zirconocene has not been made.[5c,d] Green et al. reported zirconocene and hafnocene complexes with (diene)RhCp-substituted cyclopentadienyl rings and methylaluminoxane(MAO)-activated polymerization of ethylene or propylene.[5e] However, the complexes have much lower activities than the parent unsubstituted zirconocene dichloride probably due to steric hindrance of the Rh moiety bound to Cp rings. Since their metallocenes have no chirality, the polypropylene produced by these bimetallic catalysts were atactic. We reasoned that attachment of a late transition metal moiety to the bridge part of the *ansa*-metallocene, instead of Cp rings, would be one effective strategy for the synthesis of chiral bimetallic catalysts. To the best of our knowledge, isospecific polymerization using heterobimetallic complexes has not appeared in the literature. Herein we report the synthesis and structural characterization of early−late (Zr−Rh) heterobimetallic complexes that have a C_2-symmetric *ansa*-zirconocene moiety. We also describe isospecific olefin polymerization using the complexes as catalyst precursors and the enhancement of the catalytic activity due to the presence of late transition metals.

Results and Discussion

We recently reported the "C_2-symmetric" *ansa*-zirconocene complex **1** with a divinylsilylene bridge.[6] When **1** was treated with bis(ethylene)rhodium complexes **2a**−**c** (**a** L = η^5-C_9H_7,[7] **b** η^5-C_5H_5,[8] **c** η^5-C_5Me_5[9]) in THF or DME under refluxing conditions, olefin exchange cleanly took place to give the zirconium−rhodium dinuclear complexes **3a**−**c** in moderate to good isolated yields (eq 1). ^{1}H NMR spectroscopy of **3a**−**c** showed upfield shifts of the vinyl protons (1.4−3.5 ppm), indicating their coordination to rhodium. Coupling of the vinyl carbons to rhodium metal was observed in the ^{13}C NMR spectra (J_{Rh-C} = 9−14 Hz). The four methyl groups on the cyclopentadienyl rings, which appeared as two signals in **1**, were observed as four singlets in **3**. This inequivalence of the two Cp rings implies that the vinyl groups are fixed due to their coordination to rhodium.

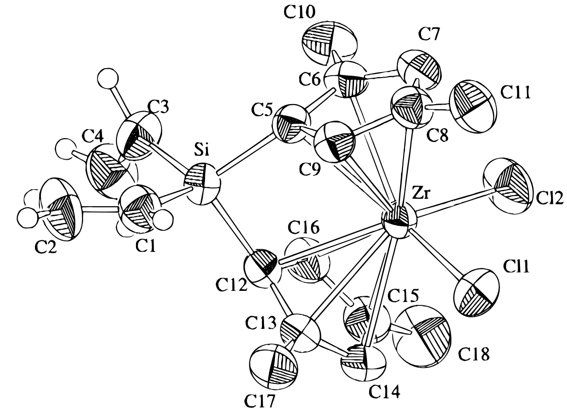
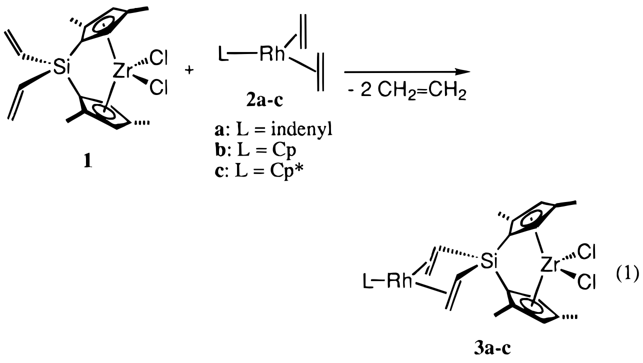


Figure 2. ORTEP drawing of **1**. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms are omitted in part for clarity.



The crystal structure of **3b** was determined by X-ray diffraction analysis (Figure 1). The bond lengths of the vinyl carbons (C1−C2 1.407(4) Å, C3−C4 1.402(4) Å) were longer than those observed in **1** (C1−C2 1.307(4) Å, C3−C4 1.284(4) Å; Figure 2) and similar to those reported in other rhodium−olefin complexes.[10] The angle of C1−Si−C3 (99.0(1)°) in **3b** is smaller than the one observed in **1** (109.8(1)°) due to coordination to rhodium. The bond distances and angles around the zirconocene part of **3b** are similar to those of **1** (Table 1). Thus the "C_2-symmetric" environment of the metallocene moiety is virtually identical to that of the parent complex **1**.

The zirconocene part of **3** can be considered structurally equivalent to *rac*-$Me_2Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrCl_2$ (**5**), which is known to be an isospecific catalyst for olefin polymerization.[11] The results of the polymerization of 1-hexene using **3**/methylaluminoxane (MAO) are shown in Table 2. Interestingly, the catalytic activity of the rhodium-ligated complexes **3a**−**c** was found to be significantly higher than the parent zirconocene complex

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[6] Huhn, T.; Suzuki, N.; Yamaguchi, Y.; Mise, T.; Chihara, T.; Wakatsuki, Y. *Chem. Lett.* **1997**, 1201.

[7] Caddy, P.; Green, M.; O'Brien, E.; Smart, L. E.; Woodward, P. *J. Chem. Soc., Dalton Trans.* **1980**, 962.

[8] Moseley, K.; Kang, J. W.; Maitlis, P. M. *J. Chem. Soc.* **1970A**, 2875.

[9] King, R. B. *Inorg. Chem.* **1963**, *2*, 528.

[10] For example, see: (a) Brown, S. S. D.; Heaton, S. N.; Moore, M. H.; Perutz, R. N.; Wilson, G. *Organometallics* **1996**, *15*, 1392. (b) Arthurs, M.; Piper, C.; Morton-Blake, D. A.; Drew, M. G. B. *J. Organomet. Chem.* **1992**, *429*, 257. (c) Mlekuz, M.; Bougeard, P.; Sayer, B. G.; McGlinchey, M. J.; Rodger, C. A.; Churchill, M. R.; Ziller, J. W.; Kang, S.-K.; Albright, T. A. *Organometallics* **1986**, *5*, 1656. (d) Marder, T. B.; Calabrese, J. C.; Roe, D. C.; Tulip, T. H. *Organometallics* **1987**, *6*, 2012.

[11] (a) Mise, T.; Miya, S.; Yamazaki, H. *Chem. Lett.* **1989**, 1853. (b) Wiesenfeldt, H.; Reinmuth, A.; Barsties, E.; Evertz, K.; Brintzinger, H.-H. *J. Organomet. Chem.* **1989**, *369*, 359.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 1 and 3b

	Complex **1**		
Zr–Cl1	2.4303(7)	Zr–Cp1(c)	2.223
Zr–Cl2	2.4357(7)	Zr–Cp2(c)	2.212
Si–C1	1.848(3)		
Si–C3	1.845(3)	Zr ⊥ Cp1	2.219
C1–C2	1.307(4)	Zr ⊥ Cp2	2.208
C3–C4	1.284(4)		
Cl1–Zr–Cl2	99.49(3)		
C1–Si–C3	109.8(1)	Cp1(c)–Zr–Cp2(c)	126.5
C5–Si–C12	94.98(9)	∠Cp1–Cp2	119.6
Si–C1–C2	123.2(3)		
Si–C3–C4	124.6(2)		
	Complex **3b**		
Rh–C1	2.161(4)	Zr–Cp1(c)	2.224
Rh–C2	2.134(4)	Zr–Cp2(c)	2.206
Rh–C3	2.172(4)	Rh–Cp3(c)	1.882
Rh–C4	2.149(5)	Zr ⊥ Cp1	2.221
Zr–Cl1	2.425(1)	Zr ⊥ Cp2	2.202
Zr–Cl2	2.415(1)	Rh ⊥ Cp3	1.882
Si–C1	1.840(4)		
Si–C3	1.832(4)	(Rh···Si	2.837(1))
C1–C2	1.401(6)	(Rh···Zr	6.1296(6))
C3–C4	1.401(6)		
C1–Rh–C2	38.1(2)	Rh–C3–Si	89.8(2)
C1–Rh–C3	80.2(1)	Si–C1–C2	120.3(3)
C2–Rh–C4	89.7(2)	Si–C3–C4	119.5(3)
C3–Rh–C4	37.8(2)		
Cl1–Zr–Cl2	98.47(6)	Cp1(c)–Zr–Cp2(c)	127.3
C1–Si–C3	98.9(2)	∠Cp1–Cp2	120.2
C5–Si–C12	95.6(1)		
Rh–C1–Si	89.9(1)		

[a] Cp1: C5–C9. Cp2: C12–C16. Cp3: C19–C23. Cp*n*(c): centroid of Cp*n*. Estimated standard deviations in the least significant figure are given in parentheses.

Table 2. Polymerization of 1-Hexene Catalyzed by 3a–c[a]

catalyst	yield/g	rate[b]	M_w	M_w/M_n	[*mmmm*]
1	0.62	24.7	390 000	2.25	98.8
3a	1.08	43.2	750 000	2.35	96.2
3b	1.17	46.9	641 000	2.41	98.5
3c	1.07	42.6	623 000	2.27	97.8
5	0.73	29.2	446 000	2.25	94.0
1+**2c**	0.50	20.0	373 000	2.06	94.5

[a] Zr, 0.05 μmol, Al/Zr = 10 000, 1-hexene = 25 mL, 30 °C, 0.5 h. [b] $\times 10^6$ g polyhexene/(mol Zr h).

1 or its anologue, **5**. Furthermore, the molecular weight of the polyhexene obtained with **3a**–**c** was larger than those produced by **1** and **5**. We carefully repeated the reactions at least five times for each catalysts to confirm the reproductivities of the activity and of the molecular weight values. The molecular weight distributions, M_w/M_n, were nearly 2.0, indicating that a single catalytic species was responsible for the polymerization. The isotacticity of the polymers obtained with **3** was excellent. When a mixture of **1** and the bis(ethylene)rhodium complex **2c** was used as a catalyst system instead of **3c**, it showed activity similar to **1**, implying that the active species derived from **3c** maintained its bimetallic structure during the polymerization even in the presence of large excess of 1-hexene. In fact, when **3c** was dissolved in a 1-hexene/toluene-d_8 (3:1) solution, ^{1}H NMR monitoring showed that 87% of **3c** remained intact after 1 h at 30 °C in the presence of 100-fold excess of 1-hexene.[12]

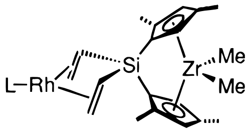
Table 3. Polymerization of Propylene Catalyzed by 3a–c[a]

catalyst	yield/g	rate[b]	M_w	M_w/M_n	[*mmmm*]	mp (°C)
1	1.32	4.38	136 000	1.94	96.6	161.9
3a	2.25	7.52	150 000	2.10	97.4	162.0
3b	1.85	6.18	161 000	1.94	96.8	162.1
3c	2.26	7.53	166 000	2.03	97.1	161.4

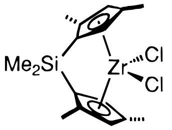
[a] Zr, 0.1 μmol, Al/Zr = 10 000, propylene = 3 atm, toluene = 30 mL, 23 °C, 1 h. [b] $\times 10^6$ g polypropylene/(mol Zr h atm).

Polymerization of propylene using **3a**–**c** gave results similar to those observed in the 1-hexene polymerization (Table 3). Compared to **1**, the heterobimetallic complexes showed higher catalytic activity and gave polymers with larger molecular weight. Isotacticity of the obtained polypropylene was again excellent.

It is noteworthy that coordination of rhodium at the backside of the *ansa*-zirconocenes gave rise to enhanced catalytic activity of the zirconium center although the Zr and Rh centers are far remoted from each other (6.1296(6) Å).[13] To obtain some information on the effect of rhodium, dimethyl derivatives of **3** were prepared and their ^{1}H and ^{13}C NMR were examined.



4a-c
a: L = indenyl
b: L = Cp
c: L = Cp*



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Treatment of **3a**–**c** with 2 equiv of methylmagnesium bromide in THF at 50 °C for 1 h cleanly gave the dimethyl compounds $LRh(\eta^2\text{-}CH_2{=}CH)_2Si(C_5H_2\text{-}2,4\text{-}Me_2)_2ZrMe_2$ (**4a**–**c**). The methyl groups on zirconium appeared upfield (−0.65 to −0.69 ppm) of the corresponding signal of the dimethyl derivative of **1** (−0.62 ppm) in the ^{1}H NMR spectra. The ^{13}C NMR resonances also shifted upfield (30.90–31.21 ppm in **4a**–**c**, while 31.75 ppm in dimethylated **1**). These shifts would indicate the influence of an electron-donating character of the Rh unit in the complexes. Mulliken population analysis, based on ab initio MO calculation of the cationic zirconium hydride species (Zr^+–H) derived from **3b** and **1**, showed that the Zr center of the Rh–Zr complex (**3b**$^+$) had a smaller positive charge ($\Delta = -0.0179$) than the mononuclear complex (**1**$^+$): (+0.4998 for **3b**$^+$ and +0.5177 for **1**$^+$, Figure 3). This result is consistent with the NMR observation.[14]

In conclusion, it was found that a late transition metal located far away (>6 Å) from the early transition metal still could influence the catalytic activity of the latter. This should allow us various ways of designing effective heterobimetallic catalysts. Further investigation in this area is now in progress in our laboratory.

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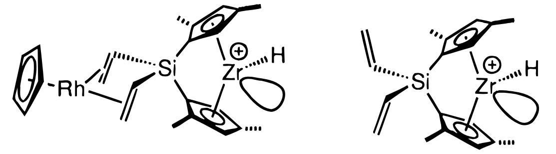
(12) Although 13% of **3c** disappeared, the formation of **1** was not observed by ^{1}H NMR spectroscopy. It seemed that **3c** decomposed to some other species.

(13) A few examples of "metal ligand effect" in heteromultimetallic complexes were reported recently. (a) Dias, E. L.; Grubbs, R. H. *Organometallics* **1998**, *17*, 2758. (b) Adams, R. D.; Barnard, T. S. *Organometallics* **1998**, *17*, 2885.

(14) The possibility that the rigid structure of the bridging part due to the coordination to rhodium caused the increase of the catalytic activity cannot be ruled out. However, the reported C_2-symmetric complexes with the sila-cylcopentyl bridge did not show significant improvement in their ability as polymerization catalysts compared to that with a dimethylsilylene bridge. Tsai, W.-M.; Chien, J. C. W. *J. Polym. Sci.: Part A: Polym. Chem.* **1994**, *32*, 149.



3b$^+$ **1**$^+$

Δ (positive charge) = **-0.0179**
= {+0.4998 (**3b**$^+$) }- {+0.5177(**1**$^+$)}

Figure 3. Comparison of Mulliken population on the Zr center.

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Experimental Section

General Comments. All manipulation was carried out under an atmosphere of dry argon by using standard Schlenk techniques. Tetrahydrofuran, dimethoxyethane, and toluene were distilled from sodium benzophenone ketyl prior to use. Zirconium tetrachloride was purchased from Aldrich Chemical Co., Inc. Divinyldichlorosilane was purchased from Chisso Corporation. *n*-Butyllithium (as hexane solution) was purchased from Kanto Chemical Co., Inc. The bis(ethylene)rhodium complexes **2a**–**c** (**a** L = η^5-C_9H_7,[7] **b** η^5-C_5H_5,[8] **c** η^5-C_5Me_5[9]) were prepared according to the literature. 1-Hexene was distilled from sodium and kept over potassium–sodium alloy. Propylene (research grade) was purchased from Takachiho Chemical Industry Co., Ltd., and used without further purification. Methylaluminoxane was purchased as a toluene solution (MMAO-3A, 5.98 wt %) from Tosoh-Akzo corporation. ^{13}C NMR of isotactic polyolefins was measured at 120 °C in 1,2-dichlorobenzene-d_4. The molecular weight of polyolefins was determined by gel permeation chromatography (GPC). The GPC for poly-1-hexene was recorded on SHODEX GPC-System 11 eluted with THF at 40 °C using monodispersed polystyrene as standards. The GPC for polypropylene was recorded on SSC-7100 high-temperature GPC (Senshu Scientific Co., Ltd.) at 135 °C using 1,2-dichlorobenzene as an eluent and monodispersed polystyrene as standards. NMR was performed on JEOL GX500 and AL-300 spectrometers; DSC, on Rigaku DSC8230.

Preparation of *rac*-(CH_2=CH)$_2$Si(η^5-C_5H_2-2,4-Me_2)$_2$ZrCl$_2$ (1). To a solution of divinylbis(2,4-dimethylcyclopentadien-1-yl)silane (4.67 g, 17.4 mmol) in dimethoxyethane (100 mL) was added *n*-butyllithium (1.69 M hexane solution, 35 mmol) dropwise at −78 °C. The mixture was stirred at room temperature overnight. This mixture was added dropwise to a DME solution of zirconium tetrachloride (4.04 g, 17.3 mmol) at −78 °C and then heated at 80 °C for 68 h. The solvent was removed in vacuo, and the residue was dissolved in toluene. Filtration to remove Li salts and cooling the filtrate at −30 °C gave the crystals of the title compound. The crystals were repeatedly recrystallized from toluene or hexane, yielding finally a total of 1.13 g (15% yield) of the *rac*-isomer of **1**. ^{1}H NMR ($CDCl_3$, Me_4Si): δ 2.04 (s, 6H), 2.29 (s, 6H), 5.34 (d, J = 2.3 Hz, 2H), 6.27 (dd, J = 19.5, 4.1 Hz, 2H), 6.43 (dd, J = 14.7, 4.1 Hz, 2H), 6.45 (d, J = 2.3 Hz, 2H), 6.57 (dd, J = 19.5, 14.7 Hz, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ 15.68, 16.97, 101.00, 113.21, 129.15, 129.60, 131.22, 138.05, 138.13. Anal. Calcd for $C_{18}H_{22}Cl_2SiZr$: C, 50.44; H, 5.17. Found: C, 50.62; H, 5.21.

Preparation of *rac*-(η^5-C_9H_7)Rh(η^2-CH_2=CH)$_2$Si(η^5-C_5H_2-2,4-Me_2)$_2$ZrCl$_2$ (3a). To a solution of (η^5-C_9H_7)Rh(η^2-CH_2=CH_2)$_2$ (**2a**) (31 mg, 0.11 mmol) in THF (50 mL) was added **1** (46 mg, 0.11 mmol). The mixture was refluxed with stirring for 60 h. After the volatile was removed in vacuo, the residue was dissolved in toluene (20 mL) and filtered. The filtrate was concentrated and recrystallized from toluene/hexane at −30 °C. Yellow crystals of the title compound were obtained in 81% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 1.83 (dd, J = 14.7, 1.4 Hz, 1H), 1.87 (dd, J = 14.7, 1.4 Hz, 1H), 1.95 (s, 3H), 2.06 (s, 3H), 2.19 (s, 3H), 2.32 (s, 3H), 2.42 (dd, J = 14.7, 11.9 Hz, 1H), 2.51 (dd, J = 14.7, 11.9 Hz, 1H), 3.48 (dd, J = 11.9, 1.4 Hz, 1H), 3.51 (dd, J = 11.9, 1.4 Hz, 1H), 5.03 (d, J = 2.0 Hz, 1H), 5.27 (d, J = 2.0 Hz, 1H), 5.31 (d, J = 3.0 Hz, 2H), 6.16 (q, J = 2.6 Hz, 1H), 6.29 (d, J = 2.0 Hz, 1H), 6.44 (d, J = 2.0 Hz, 1H), 7.03 (m, 2H), 7.30 (m, 2H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 15.53, 15.66, 16.01, 17.50, 29.76 (d, J_{Rh-C} = 9.0 Hz), 30.47 (d, J_{Rh-C} = 9.0 Hz), 52.47 (d, J_{Rh-C} = 14.0 Hz), 53.08 (d, J_{Rh-C} = 14.0 Hz), 77.25 (d, J_{Rh-C} = 5.0 Hz), 77.34 (d, J_{Rh-C} = 5.0 Hz), 88.98 (d, J_{Rh-C} = 6.2 Hz), 101.85, 109.60 (d, J_{Rh-C} = 3.4 Hz), 109.70 (d, J_{Rh-C} = 3.4 Hz), 110.18, 110.44, 112.25, 119.06, 119.42, 124.51, 124.54, 129.01, 129.01, 127.92, 128.31, 137.03, 137.58. Anal. Calcd for $C_{27}H_{29}Cl_2RhSiZr$: C, 50.15; H, 4.52. Found: C, 50.42; H, 4.57.

Preparation of *rac*-(η^5-C_5H_5)Rh(η^2-CH_2=CH)$_2$Si(η^5-C_5H_2-2,4-Me_2)$_2$ZrCl$_2$ (3b). (η^5-C_5H_5)Rh(η^2-CH_2=CH_2)$_2$ (**2b**) (31 mg, 0.138 mmol) and **1** (56.9 mg, 0.133 mmol) were dissolved in 1,2-dimethoxyethane (50 mL), and the reaction mixture was refluxed for 12 days. ^{1}H NMR of the reaction mixture indicated the formation of **3b** in good yield (>80%). After the volatile was removed in vacuo, the residue was dissolved in toluene and filtered. The filtrate was concentrated and recrystallized from toluene/hexane at −30 °C. Orange crystals of the title compound were obtained in 55% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 1.74 (dd, J = 13.8, 1.8 Hz, 1H), 1.77 (dd, J = 13.8, 1.8 Hz, 1H), 2.03 (s, 3H), 2.20 (s, 3H), 2.23 (s, 3H), 2.35 (s, 3H), 2.49 (dd, J = 13.8, 10.1 Hz, 1H), 2.54 (dd, J = 13.8, 10.1 Hz, 1H), 3.21 (dd, J = 10.1, 1.8 Hz, 1H), 3.25 (dd, J = 10.1, 1.8 Hz, 1H), 5.13 (d, J = 1.8 Hz, 1H), 5.31 (d, J_{Rh-H} = 0.8 Hz, 5H), 5.48 (d, J = 1.8 Hz, 1H), 6.34 (d, J = 1.8 Hz, 1H), 6.52 (d, J = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 15.62, 15.66, 16.13, 17.16, 18.86 (d, J_{Rh-C} = 9.0 Hz), 19.80 (d, J_{Rh-C} = 9.0 Hz), 44.75 (d, J_{Rh-C} = 14.0 Hz), 45.27 (d, J_{Rh-C} = 14.0 Hz), 85.65 (d, J_{Rh-C} = 5.0 Hz), 103.08, 111.00, 110.61, 112.26, 127.95, 128.93, 129.01, 129.38, 137.25, 137.93. Anal. Calcd for $C_{23}H_{27}Cl_2RhSiZr$: C, 46.31; H, 4.56. Found: C, 46.77; H, 4.63.

Preparation of *rac*-(η^5-C_5Me_5)Rh(η^2-CH_2=CH)$_2$Si(η^5-C_5H_2-2,4-Me_2)$_2$ZrCl$_2$ (3c). The title compound was prepared in a manner similar to **3b** using (η^5-C_5Me_5)Rh(η^2-CH_2=CH_2)$_2$ (**2c**) (39.5 mg, 0.134 mmol) and **1** (56.4 mg, 0.132 mmol). The reaction mixture was refluxed for 40 h. Recrystallization from hexane at −30 °C gave yellow crystals of **3c** in 49% yield. ^{1}H NMR ($CDCl_3$, Me_4Si): δ = 1.42 (dd, J = 13.3, 11.0 Hz, 1H), 1.52 (dd, J = 13.3, 11.0 Hz, 1H), 1.82 (s, 15H), 1.85 (dd, J = 13.3, 1.8 Hz, 1H), 1.89 (dd, J = 13.3, 1.8 Hz, 1H), 2.03 (s, 3H), 2.18 (s, 3H), 2.23 (s, 3H), 2.28 (dd, J = 11.0, 1.8 Hz, 1H), 2.33 (dd, J = 11.0, 1.8 Hz, 1H), 2.34 (s, 3H), 5.11 (d, J = 1.8 Hz, 1H), 5.45 (d, J = 1.8 Hz, 1H), 6.33 (d, J = 1.8 Hz, 1H), 6.49 (d, J = 1.8 Hz, 1H). ^{13}C NMR ($CDCl_3$, Me_4Si): δ = 9.71, 15.59, 15.72, 15.92, 17.57, 27.39 (d, J_{Rh-C} = 8.6 Hz), 28.78 (d, J_{Rh-C} = 8.6 Hz), 52.20 (d, J_{Rh-C} = 14.3 Hz), 52.52 (d, J_{Rh-C} = 14.3 Hz), 96.93 (d, J_{Rh-C} = 4.8 Hz), 103.76, 110.46, 112.47, 113.09, 127.76, 128.74, 128.88, 129.16, 136.83, 137.56. Anal. Calcd for $C_{28}H_{37}Cl_2RhSiZr$: C, 50.44; H, 5.59. Found: C, 50.86; H, 5.76.

X-ray Crystallographic Analysis of 1. Crystals of **1** suitable for X-ray analysis were obtained by recrystalization from a hexane solution. A pale yellow crystal of dimensions 0.5 × 0.3 × 0.2 mm was used. Data were collected on an Enraf-Nonius CAD4 diffractometer at 296 K with a graphite monochromator using Mo Kα radiation. A total of 4389 unique reflections were measured in the $\omega-2\theta$ scan mode (5.0° < 2θ < 55°). The structure was solved by direct methods[15] and expanded using Fourier techniques.[16] Hydrogen atoms were located from difference Fourier syntheses and refined isotropically. The final cycle of full-matrix least-squares refinement was based on 3678 observed reflections ($F > 3\sigma(F)$) with 288

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[15] SIR92: Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, M.; Giacovazzo, C.; Guagliardi, A.; Polidori, G. *J. Appl. Crystallogr.* **1994**, *27*, 435.

[16] PATTY: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; Garcia-Granda, S.; Gould, R. O.; Smits, J. M. M.; Smykalla, C. *The DIRDIF program sytstem*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

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Table 4. Crystallographic Data for 1 and 3b

	1	**3b**
formula	$C_{18}H_{22}Cl_2SiZr$	$C_{23}H_{27}Cl_2RhSiZr$
fw	428.59	596.58
color, habit	pale yellow, cubic	orange, cubic
cryst size, mm	0.5 × 0.3 × 0.2	0.14 × 0.43 × 0.41
cryst syst	triclinic	monoclinic
space group	$P\bar{1}$ (No.2)	$P2_1/n$ (No. 14)
a, Å	8.9406(5)	12.828(1)
b, Å	8.9635(4)	11.1354(8)
c, Å	12.6915(7)	16.6926(8)
α, deg	86.759(5)	
β, deg	86.512(4)	100.052(5)
γ, deg	70.169(4)	
V, Å^3	954.30(9)	2347.8(3)
Z	2	4
temp, °C	23	23
linear abs coeff, cm^{-1}	9.12	14.3
F(000), e	436	1192
density calcd, g/cm^3	1.49	1.688
collection region	$-10 < h < 11$ $0 < k < 11$ $-16 < l < 16$	$0 \le h \le 16$ $0 \le k \le 14$ $-21 \le l \le 21$
2 θ range, deg	$5 < 2\theta < 55$	$5 < 2\theta < 55$
no. of measured reflns	4668	5905
no. of unique reflns	4389	5662
final cycle	3678	4079
parameter, data/param.	288	272
criteria for observed, F	$F > 3\sigma(F)$	$F > 3\sigma(F)$
R	0.034	0.036
R_w[a]	0.050	0.054
residuals: R1	0.034	0.030
S, goodness of fit	1.24	1.18
max shift/esd max. (final cycle)	0.61	0.42
final residual electron density (e/Å^3)	0.50, −0.64	0.51, −0.66

[a] $w = 1/\sigma^2(F_o) = [\sigma_c^2(F_o) + (p^2/4)F_o^2]^{-1}$ (**1**, $p = 0.0695$; **3b**, $p = 0.0770$).

variable parameters and converged with unweighted and weighted agreement factors of $R = 0.034$, $R_w = 0.050$ ($w = 1/\sigma^2(F_o)$). Goodness of fit indicator was 1.24. All calculations were performed using the teXsan[17] crystallographic software of Molecular Structure Corporation. The data were deposited in the Cambridge Crystallographic Database Center (CCDC-103224). Crystallographic data are summarized in Table 4.

X-ray Crystallographic Analysis of 3b. Crystals of **3b** suitable for X-ray analysis were obtained by recrystalization from a toluene solution. A yellow crystal of dimensions 0.14 × 0.43 × 0.41 mm was used. Data were collected on an Enraf-Nonius CAD4 diffractometer at 296 K with a graphite monochromator using Mo Kα radiation. A total of 5662 unique reflections were measured in the $\omega-2\theta$ scan mode ($5.0° < 2\theta < 55°$). The structure was solved by heavy-atom Patterson methods[16] and expanded using Fourier techniques.[17] Hydrogens on the vinyl groups (hydrogens on C1−C4) were located with difference Fourier synthesis and refined isotropically. Other hydrogens were put in the ideal position with calculation and not refined. The final cycle of full-matrix least-squares refinement was based on 4079 observed reflections ($F > 3\sigma(F)$) with 272 variable parameters and converged with unweighted and weighted agreement factors of $R = 0.036$, $R_w = 0.054$ ($w = 1/\sigma^2(F_o)$). Goodness of fit indicator was 1.18. All calculations were performed using the teXsan[18] crystallographic software of Molecular Structure Corporation. The data were deposited in the Cambridge Crystallographic Database Center (CCDC-103225). Crystallographic data are summarized in Table 4.

Preparation of *rac*-$LRh(\eta^2\text{-}CH_2{=}CH_2)_2Si(\eta^5\text{-}C_5H_2\text{-}2,4\text{-}Me_2)_2ZrMe_2$ (4a−c). Typically, to a THF (0.5 mL) solution of **3a** (28.5 mg, 0.044 mmol) was added methylmagnesium bromide (0.092 mmol, 0.1 mL of THF solution) at −78 °C. The mixture was warmed to room temperature and was stirred at 50 °C for 1 h. The volatiles were removed in vacuo and the residue was dissolved in THF-d_8. The quantitative formation of **4a** (L = indenyl, η^5-C_9H_7) was observed in ^{1}H and ^{13}C NMR. **4b** and **4c** were prepared similarly.

4a (L = η^5-C_9H_7): ^{1}H NMR (THF-d_8): $\delta = -0.69$ (s, 6H), 1.61 (dd, $J = 14, 2$ Hz, 1H), 1.65 (dd, $J = 14, 2$ Hz, 1H), 1.7 (s, 3H), 1.84 (s, 3H), 2.04 (s, 3H), 2.16 (s, 3H), 2.35 (dd, $J = 14, 12$ Hz, 1H), 2.43 (dd, $J = 14, 12$ Hz, 1H), 3.26 (dd, $J = 12, 2$ Hz, 1H), 3.30 (dd, $J = 12, 2$ Hz), 4.76 (d, $J = 1.8$ Hz, 1H), 5.09 (d, $J = 1.8$ Hz, 1H), 5.23 (d, $J = 2.3$ Hz, 2H), 6.08 (t, 2.3 Hz, 2H), 6.10 (d, $J = 1.8$ Hz, 1H), 6.27 (d, $J = 1.8$ Hz, 1H), 6.95 (m, 2H), 7.24 (m, 2H). ^{13}C NMR (THF-d_8): $\delta = 14.94$, 15.09, 15.64, 16.91, 30.63 (d, $^1J_{Rh-C} = 9.0$ Hz), 31.10, 31.18, 31.20 (d, $^1J_{Rh-C} = 9.0$ Hz), 52.24 (d, $^1J_{Rh-C} = 14.0$ Hz), 52.93 (d, $^1J_{Rh-C} = 14.0$ Hz), 77.75 (d, $^1J_{Rh-C} = 5.0$ Hz), 77.85 (d, $^1J_{Rh-C} = 5.0$ Hz), 89.70 (d, $^1J_{Rh-C} = 5.6$ Hz), 95.76, 103.23, 110.26, 110.75 (d, $^1J_{Rh-C} = 2.8$ Hz), 110.78 (d, $^1J_{Rh-C} = 2.8$ Hz), 111.90, 119.69, 119.91, 123.14, 123.20, 124.74, 125.97, 126.02, 128.44, 128.57.

4b (L = η^5-C_5H_5): ^{1}H NMR (THF-d_8): $\delta = -0.65$ (s, 6H), 1.53 (dd, $J = 13.7, 2.0$ Hz, 1H), 1.56 (dd, $J = 13.7, 2.0$ Hz, 1H), 1.77 (s, 3H), 1.94 (s, 3H), 2.08 (s, 3H), 2.20 (s, 3H) 2.31 (m, 2H), 3.04 (dd, $J = 11, 2$ Hz, 1H), 3.08 (dd, $J = 11, 2$ Hz, 1H), 4.85 (d, $J = 2$ Hz, 1H), 5.22 (d, $J_{Rh-H} = 0.5$ Hz, 5H), 5.25 (d, $J = 1.8$ Hz, 1H), 6.15 (d, $J = 2$ Hz, 1H), 6.33 (d, $J = 1.8$ Hz, 1H). ^{13}C NMR (THF-d_8): $\delta = 15.01$, 15.11, 15.71, 16.64, 19.95 (d, $^1J_{Rh-C} = 9.0$ Hz), 20.76 (d, $^1J_{Rh-C} = 9.0$ Hz), 31.18, 31.21, 44.74 (d, $^1J_{Rh-C} = 14.0$ Hz), 45.34 (d, $^1J_{Rh-C} = 14.0$ Hz), 86.20 (d, $^1J_{Rh-C} = 4.5$ Hz), 96.93, 104.28, 110.29, 111.93, 123.16, 123.33, 125.98, 126.36, 128.64, 128.73.

4c (L = η^5-C_5Me_5): ^{1}H NMR (THF-d_8): $\delta = -0.66$ (s, 6H), 1.29 (m, 2H), 1.67 (m, 2H), 1.74 (s, 15H), 1.78 (s, 3H), 1.94 (s, 3H), 2.07 (s, 3H), 2.15 (m, 2H), 2.19 (s, 3H), 4.82 (d, $J = 2$ Hz, 1H), 5.26 (d, $J = 2$ Hz, 1H), 6.12 (d, $J = 2$ Hz, 1H), 6.31 (d, $J = 2$ Hz, 1H). ^{13}C NMR (THF-d_8): $\delta = 9.66$, 15.02, 15.17, 15.54, 17.14, 28.79 (d, $^1J_{Rh-C} = 9.0$ Hz), 29.85 (d, $^1J_{Rh-C} = 9.0$ Hz), 30.90, 30.97, 52.32 (d, $^1J_{Rh-C} = 14.6$ Hz), 52.85 (d, $^1J_{Rh-C} = 14.6$ Hz), 97.15 (d, $^1J_{Rh-C} = 5.0$ Hz), 97.33, 105.85, 110.12, 112.13, 122.99, 123.29, 125.86, 126.19, 128.21, 128.40.

Preparation of *rac*-$(CH_2{=}CH_2)_2Si(C_5\text{-}2,4\text{-}Me_2)_2ZrMe_2$. The dimethyl derivative of **1** was prepared similarly to **4**. ^{1}H NMR (THF-d_8): $\delta = -0.62$ (s, 6H), 1.78 (s, 6H), 2.14 (s, 6H), 5.14 (d, $J = 2$ Hz, 2H), 6.03 (dd, $J = 20, 4$ Hz, 2H), 6.19 (dd, $J = 20, 4$ Hz, 2H), 6.29 (d, $J = 2$ Hz, 2H), 6.39 (dd, $J = 20, 15$ Hz, 2H). ^{13}C NMR (THF-d_8): $\delta = 14.99$, 16.47, 31.75, 94.52, 112.87, 123.75, 126.85, 129.20, 134.02, 136.42.

Polymerization of 1-Hexene. Typically, in a 50 mL Schlenk tube, to a toluene solution of methylaluminoxane (0.5 mmol, 0.25 mL) was added **3a** (0.05 μmol) in toluene (100 μL) at room temperature. After 10 min, 1-hexene (0.2 mol, 25 mL) was added and the mixture was stirred at 30 °C for 0.5 h. MeOH and 1 N HCl were added to quench the reaction, and the polymer was extracted into hexane. Removal of volatiles from the organic layer left rubberlike polyhexene. Since the values of the polymerization rates were obtained with some experimental variance, the reactions were repeatedly examined to confirm their activity (see the Supporting Information).

Polymerization of Propylene. A typical procedure for propylene polymerization was as follows. To a toluene solution (30 mL) of methylaluminoxane (1.0 mmol) was added **3a** (0.1 μmol) in toluene (200 μL) at room temperature in a 100 mL autoclave. The mixture was stirred at room temperature for 10 min. Then propylene was charged, and the mixture was stirred at 23 °C for 1 h. The pressure was kept at 3 atm during

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(17) DIRDIF94: Beurskens, P. T.; Admiraal, G.; Beurskens, G.; Bosman, W. P.; de Gelder, R.; Israel, R.; Smits, J. M. M. *The DIRDIF-94 program sytstem*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1994.

(18) *teXsan*: Crystal Structure Analysis Package; Molecular Structure Corporation: The Woodlands, TX, 1985 & 1992.

the reaction. The mixture was poured into acidic methanol and filtered to collect the polymer. Isotacticity was determined by ^{13}C NMR. Molecular weight was determined by a high-temperature GPC system. The reactions were repeatedly examined to confirm their reproducibility (see the Supporting Information).

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Supporting Information Available: Experimental details of the polymerization reactions and tables of crystallographic data, atomic coordinates, thermal parameters, bond lengths, and bond angles for **1** and **3b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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