Electronic effects in homogeneous Ziegler–Natta catalysts: Zr–Rh early–late heterobimetallic complexes†

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The correlation between electron density at zirconium and catalytic activity in olefin polymerization was investigated with exclusion of any steric factors. Two novel Zr–Rh heterobimetallic complexes, *meso*-(η^5-C_9H_7)-Rh$\{(\eta^2$-$CH_2=CH)_2Si(\eta^5$-$C_5H_2Me_2)_2\}ZrCl_2$ **1m** and (η^5-C_9H_7)Rh$\{(\eta^2$-$CH_2=CH)_2Si(\eta^5$-$C_5Me_4)_2\}ZrCl_2$ **2** (C_9H_7 = indenyl), were synthesized and **2** was structurally characterized. These complexes and the racemic isomer of **1** (**1r**) were investigated in terms of effects of the rhodium units on the electron density of the zirconium. The redox behavior examined by cyclic voltammetry and NMR study of the dimethylated complexes indicated the electron-rich character of zirconium in the bimetallic complexes **1r**, **1m** and **2**. The catalytic activity of **1r** and **1m** for hexene polymerization was found to be significantly higher than for the corresponding monometallic complexes, and they formed polyhexene of higher molecular weight, while **2** did not show significant differences in its catalytic performance compared to those of the monometallic ones. The results implied that the electron-donating rhodium units give rise to higher catalytic activity in olefin polymerization unless they have sterically hindered structures.

Introduction

Since the discovery of Group 4 metallocene catalysts for olefin polymerization much effort has been made in modification of ligands, such as cyclopentadienyl and indenyl, to improve their catalytic performance.[2] The effects of substituents of these ligands on catalytic activity, polymer molecular weight and stereoregularity are often discussed in terms of electronic and steric effects.[3] It is proposed that electron-donating substituents, such as methyl groups, increase the activity, and *vice versa*. However, it is difficult to separate electronic and steric factors because most substituents of ligands must change both. For example, permethylated zirconocenes show lower activity due to their steric hindrance.[4] It is very important to clarify the correlation of electron density at the active center and catalytic activity for understanding the nature of metallocene catalysts.

Studies on electronic effects of substituents using 5,6- or 4,7-substituted indenyl ligands have been reported by Pino[5a] and Collins[5b] and their co-workers. They designed indenyl ligands to minimize steric differences in bis(indenyl)zirconocene complexes. Their attempts were successful to some extent and it was proposed that electron deficient substituents decrease the activity. However, complexes of 4,7-substituted indenyl ligands showed lower activity probably due to their steric hindrance.[5b] It seems that ideal complexes for this kind of study must have the same (not *similar*) steric environments around the active center and different electron density at the central metal.

Recently we reported the first example of Zr–Rh heterobimetallic complexes that catalyse isospecific olefin polymerization (Fig. 1).[1,6] These heterobimetallic complexes have a rhodium unit on the rear side of *ansa*-zirconocene moieties, and their catalytic activity was higher than that of corresponding monometallic *ansa*-zirconocenes, as was the molecular weight of the polymer obtained. The structure of *rac*-CpRh$\{\eta^2$-$CH_2=CH)_2$-Si$(\eta^5$-$C_5H_2Me_2$-2,4)_2\}ZrCl_2$ was determined, and its zirconocene part has the same structure as that of the parent monometallic zirconocene *rac*-ZrCl_2$\{(CH_2=CH)_2Si(\eta^5$-C_5H_2-Me_2$-2,4)_2\}$. These results prompted us to study further these
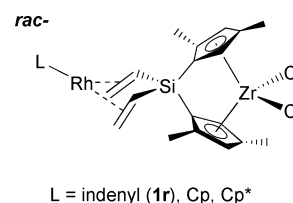

Fig. 1 Heterobimetallic complexes for isospecific olefin polymerization.

series of complexes in the context of the electron density at zirconium, since they are suitable to examine the correlation of catalytic activity and electron density if the rhodium units have significant electronic effects on the zirconium centers. It is also of interest to examine the "bimetallic effect" in these complexes.

Herein we report the synthesis of a few novel heterobimetallic complexes, studies on the electron density of the zirconium centers by electrochemical analysis and NMR, and the catalytic activity for olefin polymerization. The electronic effect of rhodium units on the catalytic performance of the zirconocene moieties is discussed.

Results and discussion
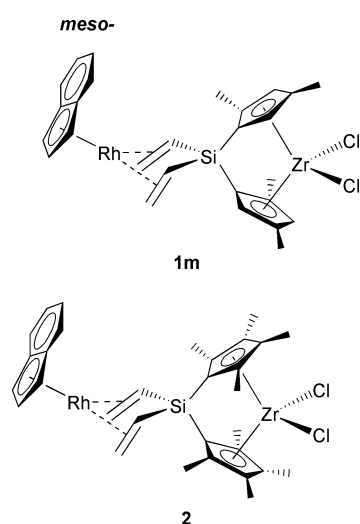
Synthesis and structure of bimetallic complexes

The Zr–Rh bimetallic complexes **1** and **2** were used for the present study (Fig. 2). Monometallic zirconocenes *rac*- and *meso*-ZrCl_2$\{(CH_2=CH)_2Si(\eta^5$-$C_5H_2Me_2$-2,4)_2\}$ **3r**, **3m**, ZrCl_2-$\{(CH_2=CH)_2Si(\eta^5C_5Me_4)_2\}$ **4** and ZrCl_2$\{Me_2Si(\eta^5$-$C_5Me_4)_2\}$ **5** were examined for comparison. Novel complexes **1m** and **2** were prepared similarly to the previously reported method, and **2** was structurally characterized by X-ray diffraction analysis as well as **4** (Fig. 3). Bond lengths and angles are similar to those of the *racemic* complex, *rac*-(η^5-C_5H_5)-Rh$(\eta^2$-$CH_2=CH)_2Si(\eta^5$-$C_5H_2Me_2$-2,4)_2ZrCl_2$, that was previously reported (Table 1). The structure of the metallocene moiety of **2** is very close to that of the corresponding monometallic complex **4**.[7]

DOI: 10.1039/b008491n

Table 1 Selected bond lengths (Å) and angles (°) for complexes **2** and **4**

Complex 2

Rh–C1	2.193(8)	Zr–C16	2.591(5)
Rh–C2	2.161(9)	Zr–C17	2.611(4)
Rh–C3	2.168(8)	Zr–C18	2.501(6)
Rh–C4	2.162(10)	Si–C1	1.856(8)
Zr–Cl1	2.438(3)	Si–C3	1.863(8)
Zr–Cl2	2.443(3)	C1–C2	1.398(12)
Zr–C5	2.473(4)	C3–C4	1.413(13)
Zr–C6	2.525(3)		
Zr–C7	2.622(3)	Zr–Cp1(c)	2.240
Zr–C8	2.607(4)	Zr–Cp2(c)	2.239
Zr–C9	2.500(3)	Zr⊥Cp1	2.231
Zr–C14	2.474(3)	Zr⊥Cp2	2.232
Zr–C15	2.528(4)		
C1–Rh–C2	37.5(4)	Rh–C1–Si	90.7(4)
C1–Rh–C3	79.7(3)	Rh–C3–Si	91.3(4)
C2–Rh–C4	88.7(4)	Si–C1–C2	120.5(6)
C3–Rh–C4	38.1(4)	Si–C3–C4	118.0(7)
Cl1–Zr–Cl2	100.3(1)		
C1–Si–C3	97.4(4)	Cp1(c)–Zr–Cp2(c)	129.0
C5–Si–C14	96.7(3)	Cp1–Cp2	119.5

Complex 4

Zr–Cl1	2.4342(6)	Si–C1	1.856(3)
Zr–Cl2	2.4323(5)	Si–C3	1.871(3)
Zr–C5	2.466(2)	Si–C5	1.873(2)
Zr–C6	2.508(2)	Si–C14	1.889(2)
Zr–C7	2.615(2)	C1–C2	1.278(4)
Zr–C8	2.615(2)	C3–C4	1.246(4)
Zr–C9	2.514(2)		
Zr–C14	2.472(2)	Zr–Cp1(c)	2.237
Zr–C15	2.523(2)	Zr–Cp2(c)	2.233
Zr–C16	2.604(2)	Zr⊥Cp1	2.230
Zr–C17	2.598(2)	Zr⊥Cp2	2.227
Zr–C18	2.499(2)		
Cl1–Zr–Cl2	99.24(3)		
C1–Si–C3	105.5(1)	Cp1(c)–Zr–Cp2(c)	128.7
C5–Si–C14	96.3(1)	Cp1–Cp2	119.7
Si–C1–C2	128.7(3)		
Si–C3–C4	128.0(3)		

Cp1: C5–C9. Cp2: C14–C18. Cpn(c) = centroid of Cpn. Zr⊥Cpn represents the perpendicular distance from the Zr atom to the Cpn plane. Estimated standard deviations in the least significant figure are given in parentheses.
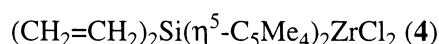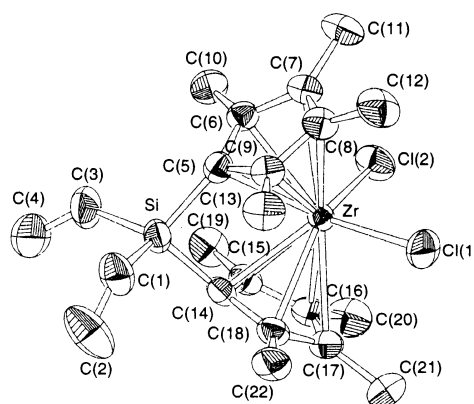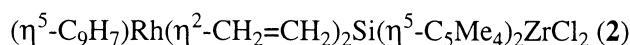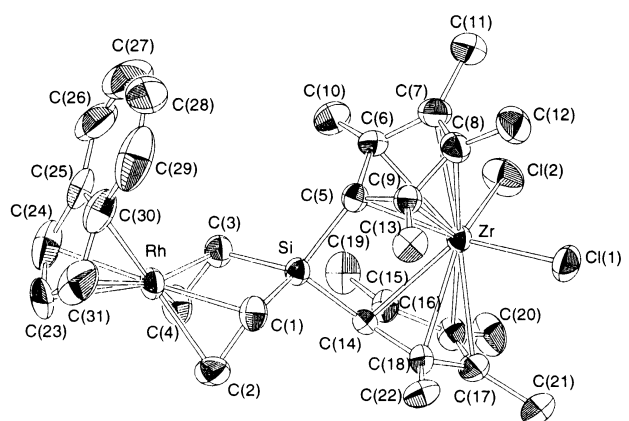
Table 2 Reduction potentials of the zirconocenes

Bimetallic complex	Reduction $E_{1/2}$/ V vs. Fc–Fc$^+$	Monometallic complex	Reduction $E_{1/2}$/ V vs. Fc–Fc$^+$
1m	−2.35	**3m**	−2.30
1r	−2.35	**3r**	−2.30
2	−2.49	**4**	−2.44

$(\eta^5\text{-}C_9H_7)Rh(\eta^2\text{-}CH_2\text{=}CH_2)_2Si(\eta^5\text{-}C_5Me_4)_2ZrCl_2$ (**2**)

$(CH_2\text{=}CH_2)_2Si(\eta^5\text{-}C_5Me_4)_2ZrCl_2$ (**4**)

Fig. 3 Molecular structures of compounds **2** and **4** drawn with 50% probability ellipsoids. Hydrogens are omitted for clarity.

meso-

1m

2

Fig. 2 Achiral heterobimetallic complexes.
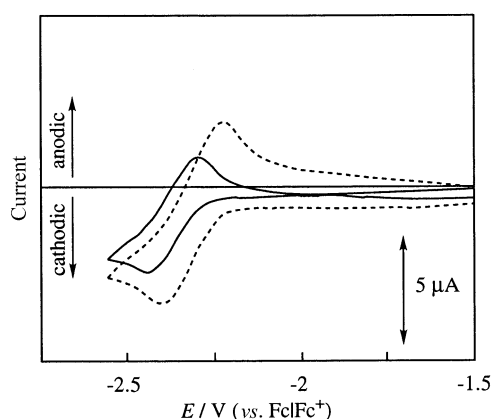
Fig. 4 Cyclic voltammograms of complexes **1m** (full) and **3m** (broken) (1 mM) in 0.1 M NBu$_4$ClO$_4$–THF, scan rate 100 mV s^{-1}.

Electrochemistry of the heterobimetallic complexes

In order to get information on the electron density at the zirconium center, cyclic voltammetry (CV) of complexes **1**–**4** was examined in THF solutions.[8] Table 2 summarizes the reduction

potentials. All the complexes exhibited well defined reversible or quasi-reversible one-electron reduction waves. The voltammograms for **1m** and **3m** are shown in Fig. 4. The one-electron reduction waves are ascribed to reduction of the zirconium atom, and it can be thought that the half-wave potentials ($E_{1/2}$)

J. Chem. Soc., Dalton Trans., 2001, 948–953　**949**

Table 3 Chemical shifts for Zr–CH$_3$ groups^a

| | | δ | |
	Dimethyl complex	^{1}H	^{13}C
1m′	meso-(C$_9$H$_7$)Rh{(CH$_2$CH)$_2$Si(C$_5$H$_2$Me$_2$)$_2$}ZrMe$_2$	−0.75, −0.52	30.70, 38.80
3m′	meso-ZrMe$_2${(CH$_2$CH)$_2$Si(C$_5$H$_2$Me$_2$)$_2$}	−0.66, −0.43	31.46, 39.43
2′	(C$_9$H$_7$)Rh{(CH$_2$CH)$_2$Si(C$_5$Me$_4$)$_2$}ZrMe$_2$	−1.00	34.16
4′	ZrMe$_2${(CH$_2$CH)$_2$Si(C$_5$Me$_4$)$_2$}	−0.91	34.77
1r′	rac-(C$_9$H$_7$)Rh{(CH$_2$CH)$_2$Si(C$_5$H$_2$Me$_2$-2,4)$_2$}ZrMe$_2$ ^{b}	−0.69 (×2)	31.10, 31.18
3r′	rac-ZrMe$_2${(CH$_2$CH)$_2$Si(C$_5$H$_2$Me$_2$-2,4)$_2$} ^{b}	−0.62	31.75

^{a} In THF-d$_8$, reference Me$_4$Si. ^{b} Ref. 1.

Table 4 Polymerization of 1-hexene: monometallic metallocenes and heterobimetallic complexes^a

Run	Catalyst	Amount/μmol	T/°C	t/h	Yield/g	Rate^b	M_w	M_n	M_w/M_n
1	**1m**	0.2	30	0.5	0.619	6.19	162000	92000	1.76
2		0.1	60	0.5	0.742	14.8	63200	33600	1.88
3	**3m**	0.2	30	0.5	0.403	4.03	98300	59200	1.66
4		0.2	60	0.5	1.038	10.4	44000	23400	1.88
5^c	**1r**	0.05	30	0.5	1.08	43.2	750000	319000	2.35
6^c	**3r**	0.05	30	0.5	0.62	24.7	390000	173000	2.25
7	**2**	0.2	24	1	0.243	1.22	118000	75200	1.57
8	**4**	0.2	24	2	0.508	1.27	118000	74200	1.59
9	**5**	0.2	24	1	0.318	1.59	106000	71100	1.49

^{a} Conditions: Al/Zr = 10000, 1-hexene = 20–25 mL. ^{b} ×10^6 g polymer (mol Zr)$^{-1}$ h^{-1}. ^{c} From ref. 1, isotactic polyhexene was formed.

reflect the electron densities of the central metal (Zr). These values were in the same range as those reported for monometallic zirconocene complexes.[9] The half-wave potentials of reduction of the bimetallic complexes are more negative than those of the corresponding monometallic ones. These results suggest higher electron density at zirconium in the bimetallic complexes compared to that in the corresponding monometallic zirconocenes. Complex **2** exhibited a more negative reduction potential than those of **1r** and **1m**, indicating its higher electron density due to the presence of more methyl groups on the Cp rings. Similar trends were also observed in the monometallic complexes, **3r**, **3m** and **4**.

In the oxidation the bimetallic complexes **1** and **2** showed irreversible oxidation waves due to the rhodium atoms, as for Rh(η^5-C$_9$H$_7$)(CH$_2$=CH$_2$)$_2$ **6**. The monometallic zirconocene complexes **3** and **4** showed no oxidation waves. The half-wave potentials of oxidation of **1** and **2** were more positive (+0.25 and +0.24 V, respectively) than that of **6** (+0.03 V). These results seem consistent with the relatively high electron density of zirconium in the bimetallic complexes.

NMR studies on dimethyl derivatives of the heterobimetallic complexes

We previously reported for *racemic* bimetallic complexes that methyl groups (Zr–CH$_3$) of dimethyl derivatives appeared upfield in NMR spectroscopy compared to the corresponding monometallic metallocenes. In this study we prepared dimethyl derivatives **1m′**–**4′** of the *achiral* complexes **1m**–**4** similarly. Table 3 summarizes the chemical shifts of methyl groups adjacent to zirconium for **1m′**–**4′** observed in ^{1}H and ^{13}C NMR. The upfield shifts of the Zr–CH$_3$ groups were also observed for achiral bimetallic complexes, which implies electron-rich character of the zirconium atoms due to bimetallic structures. These results are consistent with the electrochemical studies.

Olefin polymerization with mono- and bi-metallic complexes

In our previous report on isospecific polymerization we reported higher activity of complex **1r** compared to **3r**, and a higher molecular weight of the isotactic polyhexene obtained.[1] In that study differences were observed more clearly in hexene

polymerization than in propylene polymerization. Thus we first studied hexene as a monomer. Polymerization of 1-hexene using **1**–**5** in combination with methylaluminoxane (MAO) was investigated (Table 4).‡ The bimetallic complex **1m** showed significantly higher catalytic activity than monometallic **3m**. The molecular weight of the polymer obtained with **1m** was higher than that with **3m**. It is noteworthy that the "bimetallic effect" was observed in aspecific catalysts also, although the *meso* complex **1m** was less active than its *racemic* isomer **1r**. Permethylated zirconocenes **2**, **4** and **5** exhibited lower catalytic activity. Interestingly, the heterobimetallic zirconocene **2** exhibited no significant difference in activities and molecular weight compared to those of the corresponding monometallic metallocenes **4** and **5**.

An increase of the polymer yield can be due to an increase of active species and/or acceleration of propagation. If the concentration of active species increases and the propagation is *not* accelerated the molecular weight will not increase. It should be noted that the enhanced ratios in the catalytic activity of **1r** and **1m** are in accord with those of the molecular weight. The activity of **1m** at 30 °C was 1.54 times larger than that of **3m** (6.19/4.03; runs 1 and 3), and the number-average molecular weight (M_n) of polyhexene produced by **1m** was 1.55 times higher than that by **3m** (92,000/59,200). This trend is also observed at 60 °C (×1.42 and ×1.44, respectively; runs 2 and 4), and for **1r**/**3r** at 30 °C as well (×1.75 in rates and ×1.84 in M_n; runs 5 and 6). This suggests that the propagation was accelerated due to electronic effects, whereas the concentration of the active species was apparently little affected. The possibility of both an increase in active species and a retardation of chain-transfer reactions due to the bimetallic structure can not be ruled out.

Table 5 illustrates the results of ethylene polymerization. In contrast to the results for hexene, the bimetallic complexes exhibited similar polymerization rates to those of the monometallic ones. Although some bimetallic complexes exhibited slightly higher (**2**, run 16) or lower (**1m**, run 10) activity than the corresponding monometallic ones, the molecular weights of the

‡ A part of the polymerization results was presented at the Organometallic Catalysts and Olefin Polymerization International Conference, Oslo, June 2000.

Table 5 Polymerization of ethylene catalysed by monometallic and heterobimetallic metallocenes ^{a}

Run	Catalyst	Amount/μmol	Ethylene/kg cm^{-2}	T/°C	t/h	Yield/g	Rate ^{b}	M_w	M_w/M_n
10	**1m**	0.02	1	30	1	0.268	6.76	343000	1.67
11		0.04	10	0	0.5	0.226	1.13	402000	1.58
12	**3m**	0.02	1	30	1	0.208	8.91	370000	1.61
13		0.05	10	0	0.5	0.288	1.15	408000	1.65
14	**1r**	0.02	10	0	0.5	0.332	3.32	549000	1.68
15	**3r**	0.025	10	0	0.5	0.487	3.90	496000	1.84
16	**2**	0.02	1	30	1	0.313	15.7	440000	1.61
17	**5**	0.02	1	30	1	0.248	12.4	454000	1.45

^{a} Conditions: Al/Zr = 10000, toluene = 30 mL. ^{b} ×10^6 g polymer (mol Zr)$^{-1}$ h^{-1} atm^{-1}.

polymers were similar. These results were observed both in diluted and concentrated solutions.

Taking into account our previous results on propylene,[1] the "bimetallic effect" was observed to be more pronounced in the order: hexene > propylene > ethylene. Although the reason for the different effects of the bimetallic complexes among these monomers is not clear yet, a possible explanation is as follows.§ As generally accepted, there are two steps in the propagation, (a) coordination of the olefin to Zr, (b) insertion of the olefin into a Zr–C bond. A higher electron density on Zr is expected to facilitate step (b) whereas it might have little effect on (a). The "bimetallic effects" will be observed as an increase of rates and molecular weight when step (b) is rate-determining and might not appear clearly when (a) is a rate-limiting step. Theoretical studies propose that the barrier to insertion (step b) for ethylene is much smaller than that of step (a),[10] while the barrier for (b) is considerably higher for higher α-olefins.[11] Thus the bimetallic complexes are more effective in the polymerization of higher olefins.

Electronic effects of rhodium on the catalytic performance

The results of CV and NMR spectroscopy indicated that rhodium units have significant electron-donating effects on the catalytic center. Steric factors can be ignored in this study since structural characterization showed that the metallocene moieties of the heterobimetallic compounds are very close to those of the monometallic ones. The proposed electron-rich character of zirconium in the bimetallic complexes would be responsible for the higher catalytic activity in the olefin polymerization and higher molecular weight of the polymers produced. This conclusion is consistent with some previous studies.[3,5] The electronic effects on metallocene catalysts were successfully extracted using the heterobimetallic metallocene complexes.

The permethylated bimetallic complex **2**, on the other hand, did not show enhanced activity despite the electron-rich character of the central metal. Both bimetallic and monometallic complexes showed low activity for hexene polymerization. It might be because their steric hindrance suppressed the appearance of electronic effects in the catalytic activity. The slightly smaller enhanced ratio of *meso* complexes (**1m/3m**) compared to their racemic isomers may be also due to the steric environment of the *meso* isomers, where two methyl groups on the Cp rings are located on the same side of the polymerization site.

Conclusion

It can be concluded that the rhodium units in the heterobimetallic complexes have significant electron-donating effects on the active center. The bimetallic complexes exhibited higher catalytic activity for olefin polymerization probably due to their

electron-rich character, in both isospecific and aspecific polymerizations, unless they have sterically hindered structures. Highly congested structures may prevent the appearance of electronic effects in the polymerization reactions.

Experimental

General comments

All manipulations were carried out under an atmosphere of dry argon or nitrogen by using standard Schlenk techniques. Tetrahydrofuran and toluene were distilled from sodium–benzophenone prior to use. Rh(η^5-C$_9$H$_7$)(η^2-CH$_2$=CH$_2$)$_2$[12] and the zirconocene complex **5**[13] were prepared according to the literature. 1-Hexene was distilled from sodium and stored over sodium–potassium alloy. Methylaluminoxane was purchased as a toluene solution (MMAO-3A, 5.6 wt%) from Tosoh Finechem Corporation. The GPC for polyhexene was performed on Shodex GPC-System 11 with THF at 40 °C, and for polyethylene on a SSC-7100 high temperature instrument (Senshu Scientific Co., Ltd.) at 135 °C using 1,2-dichlorobenzene as an eluent and monodispersed polystyrene as standards. NMR was carried out on a JEOL AL-300 spectrometer.

Preparation of heterobimetallic complexes

***meso*-(η^5-C$_9$H$_7$)Rh{(η^2-CH$_2$=CH)$_2$Si(η^5-C$_5$H$_2$Me$_2$)$_2$}ZrCl$_2$ 1m.** To a solution of *meso*-ZrCl$_2${(η^2-CH$_2$=CH)$_2$Si(η^5-C$_5$H$_2$Me$_2$)$_2$} (53.4 mg, 0.125 mmol) in THF (50 mL) was added Rh(η^5-C$_9$H$_7$)(η^2-CH$_2$=CH$_2$)$_2$ (35.7 mg, 0.13 mmol). The mixture was refluxed with stirring for 85 h. After the volatiles were removed *in vacuo* the residual solid was dissolved in toluene–hexane and recrystallized at −30 °C. Yellow crystals were obtained in 55% yield. ^{1}H NMR (THF-d$_8$, Me$_4$Si): δ 1.81 (dd, J = 14.5, 2.0, 1H), 1.85 (dd, J = 14.5, 2.0, 1H), 2.05 (s, 3H), 2.07 (s, 3H), 2.18 (s, 3H), 2.19 (s, 3H), 2.42 (dd, J = 11.7, 14.5, 1H), 2.69 (dd, J = 11.7, 14.5, 1H), 3.49 (dd, J = 11.7, 2.0, 1H), 3.51 (dd, J = 11.7, 2.0, 1H), 5.05 (d, J = 2.1, 1H), 5.39 (d, J = 2.3, 1H), 5.39 (d, J = 2.3, 2H), 5.99 (d, J = 2.1, 1H), 6.14 (d, J = 2.3, 1H), 6.18 (dd, J = 2.3, 2.5 Hz, 1H), 7.00 (m, 2H) and 7.33 (m, 2H). ^{13}C NMR (THF-d$_8$, Me$_4$Si): δ 16.14, 16.29, 17.14, 18.63, 30.68 (d, J_{Rh-C} = 8.4), 30.88 (d, J_{Rh-C} = 8.4), 52.82 (d, J_{Rh-C} = 14.0), 53.52 (d, J_{Rh-C} = 14.0), 78.35 (d, J_{Rh-C} = 5.0), 78.48 (d, J_{Rh-C} = 5.0), 89.69 (d, J_{Rh-C} = 6.2), 101.25, 108.74, 109.69, 110.85, 110.91, 110.95 (d, J_{Rh-C} = 2.8 Hz), 119.98, 120.23, 125.14, 125.21, 125.46, 125.82, 134.81, 134.81, 141.07 and 141.26. Calc. for C$_{27}$H$_{29}$Cl$_2$RhSiZr: C, 50.15; H, 4.52. Found: C, 49.80; H, 4.59%.

***meso*-ZrCl$_2${(η^2-CH$_2$=CH)$_2$Si(η^5-C$_5$H$_2$Me$_2$)$_2$} 3m.** A mixture of *rac*/*meso* isomers of ZrCl$_2${(η^2-CH$_2$=CH)$_2$Si(η^5-C$_5$H$_2$Me$_2$)$_2$} were prepared by the published method.[1] The *meso* isomer was isolated by recrystallization from toluene solution. Yield 5.1%. ^{1}H NMR (CDCl$_3$, Me$_4$Si): δ 2.20 (s, 6H), 2.23 (s, 6H), 5.31 (d, J = 2.4, 2H), 6.27 (d, J = 2.4, 2H), 6.21–6.32 (m, 2H), 6.42–6.51 (m, 3H) and 6.72 (dd, J = 20.2, 14.9 Hz, 1H). ^{13}C NMR (CDCl$_3$,

§ We acknowledge the referees for valuable suggestions on the explanation for the results of ethylene polymerization reactions.

Me₄Si): δ 16.06, 18.07, 99.40, 110.90, 125.91, 130.94, 131.26, 134.98, 138.25, 139.19, 141.77.

(η⁵-C₉H₇)Rh{(η²-CH₂=CH)₂Si(η⁵-C₅Me₄)}₂ZrCl₂ 2. To a solution of Rh(η⁵-C₉H₇)(η²-CH₂=CH₂)₂ (60.8 mg, 0.22 mmol) in THF (50 mL) was added ZrCl₂{(CH₂CH)₂Si(η⁵-C₅Me₄)₂} (106 mg, 0.22 mmol). The mixture was refluxed with stirring overnight. After the volatiles were removed *in vacuo* the residue was dissolved in toluene and filtered (crude yield 81%). The filtrate was concentrated and recrystallized from toluene at −30 °C. Yellow crystals were obtained in 52% yield. ¹H NMR (CDCl₃, Me₄Si): δ 1.88 (dd, *J* = 14.5, 2.0, 2H), 1.83 (s, 6H), 1.93 (s, 6H), 1.95 (s, 6H), 2.06 (s, 6H), 2.76 (dd, *J* = 11.5, 14.5, 2H), 3.41 (dd, *J* = 11.5, 2.0, 2H), 5.28 (d, *J* = 2.6, 2H), 6.21 (m, 1H), 7.11 (dd, *J* = 6.3, 2H) and 7.34 (dd, *J* = 6.3 Hz, 2H). ¹³C NMR (CDCl₃, Me₄Si): δ 12.02, 12.39, 14.56, 15.56, 29.06 (d, J_{Rh-C} = 9.5), 51.13 (d, J_{Rh-C} = 14.3), 77.12 (d, J_{Rh-C} = 4.8 Hz), 89.52 (br), 97.97, 109.89, 119.31, 124.36, 124.70, 124.83, 135.55 and 135.93. Calc. for C₃₁H₃₇Cl₂RhSiZr: C, 52.98; H, 5.31. Found: C, 53.06; H, 5.23%.

ZrCl₂{(CH₂=CH)₂Si(η⁵-C₅Me₄)₂} 4. This compound was prepared similarly to the previously reported method.[7] Yield 38% ¹H NMR (CDCl₃, Me₄Si): δ 1.93 (s, 12H), 2.06 (s, 12H), 6.20 (dd, *J* = 20.6, 3.2, 2H), 6.40 (dd, *J* = 14.7, 3.2, 2H) and 6.83 (dd, *J* = 20.6, 14.7 Hz, 2H). ¹³C NMR (CDCl₃, Me₄Si): δ 12.45, 15.59, 91.62, 125.22, 134.96, 136.31 and 136.74. Calc. for C₂₂H₃₀Cl₂SiZr: C, 54.52; H, 6.24. Found: C, 54.61; H, 6.30%.

Preparation of dimethyl derivatives of zirconocene complexes

Typically, to a THF (2.0 mL) solution of complex **1m** (64.6 mg, 0.1 mmol) was added methylmagnesium bromide (0.092 mmol, 0.1 mL of THF solution) at 0 °C. The mixture was warmed to room temperature and stirred at 50 °C for 1 h. The volatiles were removed *in vacuo* and the residue was dissolved in THF-d₈. The quantitative formation of the dimethyl derivative was observed by ¹H and ¹³C NMR.

meso-(η⁵-C₉H₇)Rh{(η²-CH₂=CH)₂Si(η⁵-C₅H₂Me₂)₂}ZrMe₂ 1m′. ¹H NMR (THF-d₈, Me₄Si): δ −0.75 (s, 3H, Zr-CH₃), −0.52 (s, 3H, Zr-CH₃), 1.89 (s, 3H), 2.02 (s, 3H), 2.04 (s, 3H), 2.13 (s, 3H), 1.68 (dd, *J* = 14, 2, 1H), 1.72 (dd, *J* = 14, 2, 1H, partly overlapped with the solvent peak), 2.29 (dd, *J* = 14, 11, 1H), 2.60 (dd, *J* = 14, 11, 1H), 3.36 (dd, *J* = 11, 2, 1H), 3.37 (dd, *J* = 11, 2, 1H), 4.72 (d, *J* = 2, 1H), 5.06 (d, *J* = 2, 1H), 5.31 (d, 2.8, 2H), 6.06 (d, *J* = 2, 1H), 6.14 (dd, *J* = 2.8, J_{H-Rh} = 2.3, 1H), 6.21 (d, *J* = 2 Hz, 1H), 6.96–7.07 (m, 2H) and 7.28–7.34 (m, 2H). ¹³C (THF-d₈, Me₄Si): δ 15.07, 15.20, 16.36, 17.62, 30.63 (d, J_{Rh-C} = 9), 30.697 (Zr-CH₃), 30.99 (d, J_{Rh-C} = 9 Hz), 38.801 (Zr-CH₃), 52.20 (d, J_{Rh-C} = 14), 52.98 (d, J_{Rh-C} = 14), 77.62 (d, J_{Rh-C} = 5), 77.79 (d, J_{Rh-C} = 5), 89.53 (d, J_{Rh-C} = 6), 94.56, 102.09, 107.57, 109.55, 110.58 (d, J_{Rh-C} = 2.8), 110.62 (d, J_{Rh-C} = 2.8 Hz), 119.50, 119.74, 121.11, 121.31, 124.49, 124.56, 129.32, 129.40, 130.00 and 130.09.

meso-ZrMe₂{(CH₂CH)₂Si(η⁵-C₅H₂Me₂)₂} 3m′. ¹H (THF-d₈, Me₄Si): δ −0.66 (s, 3H, Zr-CH₃), −0.43 (s, 3H, Zr-CH₃), 2.03 (s, 6H), 2.12 (s, 6H), 5.09 (d, *J* = 2.0, 2H), 6.26 (d, *J* = 2.0, 2H), 6.01–6.16 (m, 2H), 6.20–6.41 (m, 3H) and 6.62 (dd, *J* = 20.3, 14.8 Hz, 1H). ¹³C (THF-d₈, Me₄Si): δ 15.13, 17.52, 31.46 (Zr-CH₃), 39.43 (Zr-CH₃), 93.65, 110.72, 122.09, 129.92, 130.90, 133.71, 133.75, 136.31 and 137.41.

(η⁵-C₉H₇)Rh{(η²-CH₂=CH)₂Si(η⁵-C₅Me₄)₂}ZrMe₂ 2′. ¹H NMR (THF-d₈, Me₄Si): δ −1.00 (s, 3H, Zr-CH₃), 1.68 (s, 3H), 1.75 (partly overlapped with solvent, 2H), 1.82 (s, 3H), 1.88 (s, 3H), 2.01 (s, 3H), 2.68 (dd, *J* = 11.4, 14.0, 2H), 3.31 (dd, *J* = 11.4, 2.0, 2H), 5.29 (d, *J* = 2.6, 2H), 6.17–6.20 (m, 1H),

Table 6 Crystallographic data for complexes **2** and **4**

	2	4
Formula	C₃₁H₃₇Cl₂RhSiZr	C₂₂H₃₀Cl₂SiZr
M	702.8	484.7
Crystal system	Triclinic	Triclinic
Space group	P1̄ (no. 2)	P1̄ (no. 2)
a/Å	9.363(2)	9.7793(8)
b/Å	10.570(2)	10.2885(5)
c/Å	16.030(3)	12.913(1)
α/°	76.17(1)	73.448(5)
β/°	74.56(1)	89.832(7)
γ/°	79.08(1)	63.875(5)
V/Å³	1471.4(5)	1106.8(1)
Z	2	2
μ/mm⁻¹	1.145	0.796
Reflections collected	7387	5366
Independent reflections	5806	5071
R_{int}	0.048	0.041
Final *R*1, *wR*2	0.0407, 0.0694	0.0291, 0.0475
	[*I* > 3σ(*I*)]	[*I* > 2σ(*I*)]
(all data)	0.0824, 0.0953	0.0352, 0.0495

7.04 (dd, *J* = 6.3, 3.0, 2H) and 7.33 (dd, *J* = 6.3, 3.0, 2H). ¹³C NMR (THF-d₈, Me₄Si): δ 11.57, 11.93, 14.28, 15.15, 30.34 (d, J_{Rh-C} = 8.7), 34.16 (Zr-CH₃), 51.28 (d, J_{Rh-C} = 14.3), 77.84 (d, J_{Rh-C} = 4.4), 88.05, 90.13 (d, J_{Rh-C} = 5.6), 93.19, 111.0 (d, J_{Rh-C} = 3.1 Hz), 119.94, 122.45, 122.56, 124.64, 127.50 and 127.75.

ZrMe₂{(CH₂=CH)₂Si(η⁵-C₅Me₄)₂} 4′. ¹H NMR (THF-d₈, Me₄Si): δ −0.91 (s, 6H, Zr-CH₃), 1.79 (s, 12H), 2.01 (s, 12H), 6.03 (dd, *J* = 20.2, 3.3, 2H), 6.23 (dd, *J* = 14.7, 3.3, 2H) and 6.70 (dd, *J* = 20.3, 14.7 Hz, 2H). ¹³C NMR (THF-d₈, Me₄Si): δ 12.00, 15.31, 34.77 (Zr-CH₃), 87.09, 123.02, 128.36, 135.51 and 137.74.

CV measurement

All the electrochemical measurements were done in 1 mmol dm⁻³ THF solutions containing 0.1 mol dm⁻³ tetrabutyl-ammonium perchlorate at 25 °C. A stationary platinum disk (1.6 mm in diameter) was used as a working electrode, a coiled platinum wire as a counter electrode, with the reference electrode Ag–AgCl corrected for junction potentials by being referenced internally to the ferrocene–ferrocenium (Fc–Fc⁺) couple.

X-Ray crystallographic analysis of complexes 2 and 4

Crystals of complex **2** suitable for X-ray analysis were obtained by recrystallization from a toluene–hexane solution. A yellow crystal was used. Data were collected on a MAC Science MXC3K diffractometer at 296 K with a graphite monochromator using Mo-Kα radiation. A total of 5806 unique reflections was measured in the ω–2θ scan mode. The structure was solved by direct methods using SIR 92[14] in the CRYSTAN-GM software package. Hydrogens were placed at calculated positions and not refined. Crystallographic data are summarized in Table 6.

Crystals of compound **4** were obtained by recrystallization from a toluene solution. A colorless crystal 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 5071 unique reflections was measured in the ω–2θ scan mode. The structure was solved by direct methods and expanded using Fourier techniques.[15] Hydrogen atoms were placed at calculated positions but not refined. All calculations were performed using the TEXSAN crystallographic software.[16]

CCDC reference numbers 149756 and 149757.

See http://www.rsc.org/suppdata/dt/b0/b008491n/ for crystallographic data in CIF or other electronic format.

Polymerization of 1-hexene

Typically, in a 50 mL of Schlenk tube, to a toluene solution of methylaluminoxane (2.0 mmol, 1.1 mL) was added complex **1m** (0.2 μmol) in toluene (100 μL) at room temperature. After 10 min, 1-hexene (0.2 mol, 25 mL) was added and the mixture stirred at 30 °C for 0.5 h. MeOH and 1 M HCl were added to quench the reaction and the polymer was extracted into hexane. Removal of volatiles from the organic layer left rubber-like polyhexene.

Polymerization of ethylene

Typically, to a toluene solution (2.2 mL) of methylaluminoxane (0.4 mmol) was added complex **1m** (0.04 μmol) in toluene (100 μL) at r.t. in a 100 mL glass autoclave. After 10 min, toluene (28 mL) was added, ethylene gas charged and the mixture stirred at 0 °C for 30 min. The pressure was kept at 10 atm during the reaction. The mixture was poured into acidic methanol and filtered to collect the polymer. The reactions were repeatedly examined to confirm their reproducibility.

Acknowledgements

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