

Synthesis and properties of Zr–Co heterodinuclear complexes with a bridging bis(cyclopentadienyl) ligand

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Abstract

$[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\text{C}_5\text{H}_5)]$ reacted with $\text{Co}_2(\text{CO})_8$ to produce a heterodinuclear Zr(IV)–Co(I) complex $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{CO})_2]$ (**3**). Complex **3** underwent oxidative addition of I_2 to give $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{CO})]$ (**4**) having Zr(IV) and Co(III) centers. The carbonyl ligand of **4** was easily replaced with $\text{P}(\text{OMe})_3$ and PPh_3 to afford $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{L})]$ (**5**: $\text{L} = \text{P}(\text{OMe})_3$, **6**: $\text{L} = \text{PPh}_3$). Structures of **5** and **6** were determined by X-ray crystallography. These Zr–Co heterodinuclear complexes catalyzed polymerization of ethylene and propylene.

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1. Introduction

Recent studies on single site catalysts of olefin polymerization revealed that polymerization of ethylene and propylene were catalyzed not only by Ti and Zr complexes [1] but also by the complexes of late transition metals such as Ni, Fe, and Co [2]. The catalysts that contain two transition metal centers were also reported to show unique properties in the polymerization. Ethylene polymerization by tandem catalysts, prepared by mixing the Ti and Ni complexes, afforded branched polymer formed via chain transfer reaction of the ethylene oligomer from Ni complex to Ti complex [3]. Gibson and co-workers [4] reported reversible chain transfer of the growing polyethylene between Fe, Ni and Zn in the reaction using these metal complexes as the catalyst. Marks and co-workers [5] designed the Ti–Zr catalyst in

which Ti and Zr complexes exhibit different roles in the ethylene polymerization. Erker and co-workers [6] reported preparation of dinuclear Zr complexes by using olefin metathesis reaction and the catalytic activity as the catalyst for ethylene and propylene polymerization. Early–late heterodinuclear complexes [7] also polymerize ethylene and propylene. These reactions using the early and late heterodinuclear complexes as the catalyst, however, were actually catalyzed only by the early transition metal center of the dinuclear complexes [8–11]. More extensive studies of the heterodinuclear catalysts for olefin polymerization would provide new catalytic system which involves the cooperative effect of the two metal centers in the polymer growth or chain transfer of the growing polymer between the different active sites of the catalyst.

In this study, we conducted preparation of Zr–Co heterobimetallic complexes with Cp–Co unit. Cyclopentadienyl Co(III) complexes show catalytic activity for polymerization of olefin and polar vinyl monomer. [12]. Herein, we report synthesis of novel Zr(IV)–Co(I)

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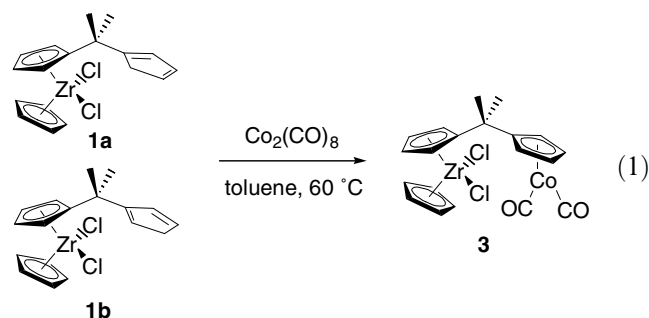
and Zr(IV)–Co(III) heterodinuclear complexes and their catalytic behavior for olefin polymerization.

2. Results and discussion

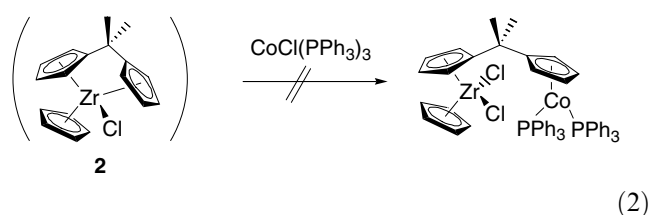
2.1. Synthesis and characterization of Zr–Co heterodinuclear complexes

2,2-Bis(cyclopentadienyl) propane can be used as a bridging ligand to form the thermodynamically stable heterodinuclear complexes [13–16]. The reaction of $\text{Li}_2[\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2]$ and $\text{CpZrCl}_3(\text{dme})$ ($\text{dme} = 1,2$ -dimethoxyethane) and subsequent treatment with HCl produce a $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\text{C}_5\text{H}_5)]$ (**1**). The ^1H NMR spectrum contains six signals due to olefinic hydrogens of uncoordinated cyclopentadienyl group (δ 6.38, 6.33, 6.21, 6.13, 5.97 and 5.76), indicating the presence of equimolar isomers in the product (Scheme 1). The isomers correspond to **1a** and **1b** in Scheme 1 but the assignment of the structure was not feasible. **1** remaining cyclopentadiene moiety was used as a building block of heterodinuclear complex. The reaction mixture before treatment with HCl contains $[\text{Zr}\{\text{Me}_2\text{C}(\text{C}_5\text{H}_4)_2\}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}]$ (**2**), as reported by Green and co-workers [17].

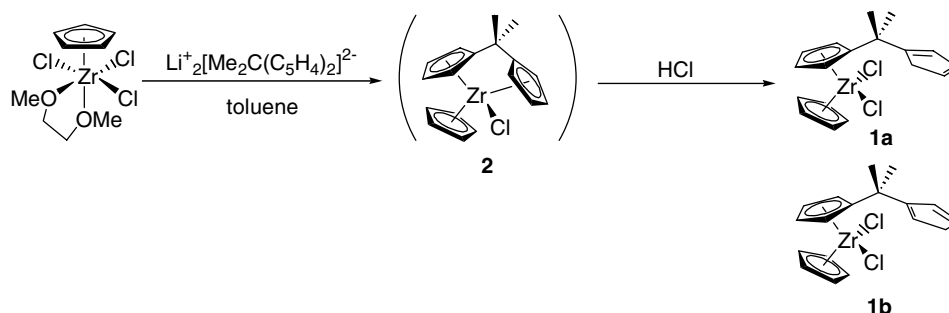
The reaction of **1** with $\text{Co}_2(\text{CO})_8$ gave $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{CO})_2]$ (**3**) containing Zr(IV) and Co(I) centers in 70% yield (Eq. (1)) [18]. ^1H NMR spectrum of **3** shows four signals of the bridging cyclopentadienyl protons at δ 6.05, 5.70, 4.36 and 4.34. The former two signals were assigned to protons bound to Zr center, while the latter two signals are due to those bonded to Co center based on the comparison of the chemical shift with those of homodinuclear complexes, $[(\text{C}_4\text{H}_8)\text{C}(\eta^5\text{-C}_5\text{H}_4)_2][\text{Zr}(\eta^5\text{-C}_5\text{H}_5)\text{Cl}_2]$ [8c] and $[\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2][\text{Co}(\text{CO})_2]_2$ [19]. The IR spectrum of **3** shows strong absorption at 2006 and 1956 cm^{-1} due to $\eta(\text{CO})$ stretching. The peak positions are similar to those of $[\text{CH}_2(\eta^5\text{-C}_5\text{H}_4)_2][\text{Co}(\text{CO})_2]_2$ (2017 and 1952 cm^{-1}).



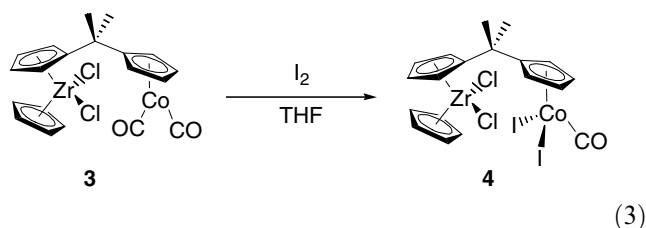
An attempt to prepare a Zr–Co heterodinuclear complex by the reaction of **2**, generated in situ, and $\text{CoCl}(\text{PPh}_3)_3$ gave a mixture of the products composed of paramagnetic Co species, and did not lead to the desired complexes.



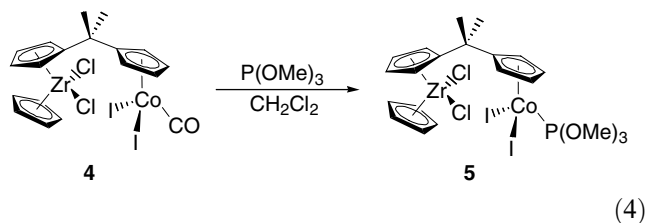
Addition of I_2 to a solution of **3** causes oxidative addition to Co center to give **4** [20]. During the reaction, gas evolution and color change from red to dark purple were observed similarly to the reaction of $\text{CpCo}(\text{CO})_2$. Recrystallization of the product from THF/hexane gave $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{CO})]$ (**4**) as deep purple crystals in 93% yield (Eq. (3)). IR spectrum of **4** shows strong absorption at 2056 cm^{-1} . The lower frequency of the CO stretching vibration than that of **3** is ascribed to more significant electron deficient character of Co(III) center than Co(I) center. ^1H NMR signals of cyclopentadienyl group bound to Co of **4** appeared at downfield (δ 5.82 and 4.48) in comparison with those of **3** (δ 4.36 and 4.34). Signal of unsubstituted Cp ligand of **4** were also observed downfield (δ 6.46) from that of **3** (δ 5.88).



Scheme 1.



Lewis basic $\text{P}(\text{OMe})_3$ easily substitutes CO ligand on the electron deficient Co center of **4** to give complex $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{P}(\text{OMe})_3)]$ (**5**) in 82% yield (Eq. (4)). The IR spectrum of **5** shows absence of the CO ligand.



Addition of excess PPh_3 to CDCl_3 solution of **4** gave $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{PPh}_3)]$ (**6**) quantitatively. Complex **6** could be also synthesized from the direct reaction of I_2 with **3** in the presence of PPh_3 (Scheme 2). The reaction using $\text{P}(\text{OMe})_3$ instead of PPh_3 , however, did not give **5** but a complex mixture. The ^1H NMR spectrum of **6** shows the signal of cyclopentadienyl group bound to Co center at δ 3.65 and 5.54. The much higher magnetic field position of the former peak to the latter can be ascribed to a shielding effect of a phenyl ring of the PPh_3 ligand. Close contact of the Cp hydrogens and a phenyl plane is observed also in the crystal structure.

Fig. 1 shows molecular structures of **5** and **6** determined by X-ray crystallography. Both complexes have Zr and Co centers bound to cyclopentadienyl ligand with η^5 fashion. The metal–ligand distances are similar to each other except for the Co–P distance, which differs between **6** (2.284(7) Å) and **5** (2.167(2) Å) because of large cone angle of PPh_3 . The conformation of the com-

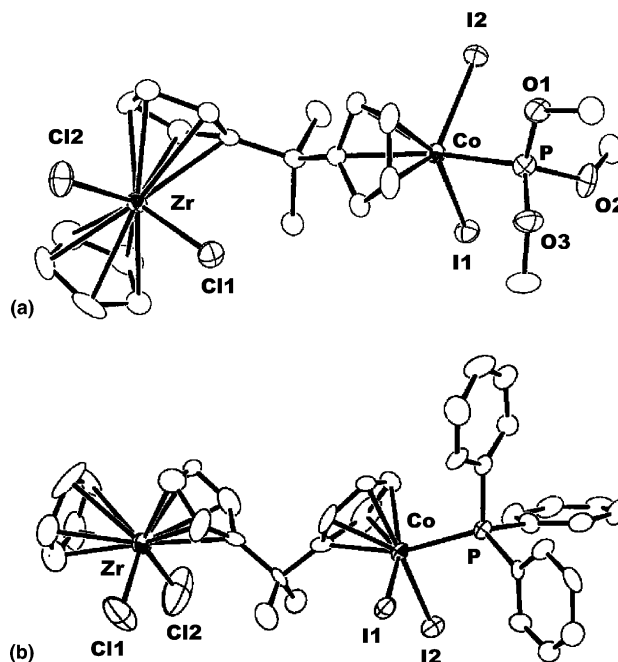
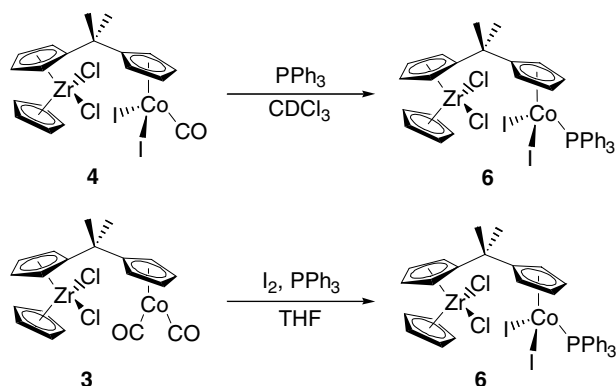


Fig. 1. (a) ORTEP drawing of **5** at the 30% ellipsoidal level. The hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles ($^\circ$): Zr–Cl1, 2.425(2); Zr–Cl2, 2.459(2); Co–I1, 2.586(1); Co–I2, 2.584(1); Co–P, 2.167(2); Cl1–Zr1–Cl2, 96.01(9); I1–Co–I2, 97.22(4); I1–Co–P1, 90.81(7); I2–Co–P, 91.11(7). (b) ORTEP drawing of **6** at the 30% ellipsoidal level. The hydrogen atoms are omitted for simplicity. Selected bond distances (Å) and angles ($^\circ$): Zr–Cl1, 2.43(1); Zr–Cl2, 2.40(1); Co–I1, 2.583(4); Co–I2, 2.588(4); Co–P, 2.284(7); Cl1–Zr1–Cl2, 100.7(6); I1–Co–I2, 95.6(1); I1–Co–P1, 94.0(2); I2–Co–P, 92.2(2).

plexes are different caused by the bulkiness of phosphorous ligand; each dihedral angle of Zr–C–C–C and Co–C–C–C including bridging carbon of **6** is almost 180° , while that of Zr–C–C–C of **5** is closed to 90° . The molecular structure of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{Rh}(\text{cod})]$ (cod = cyclooctadiene), which has bulky bidentate cod ligand, shows similar conformation of **6**, and the dihedral angles Zr–C–C–C and Rh–C–C–C are closed to 180° . Although heterodinuclear complexes which contain group 4 metal and Rh [8,15c,16b] or Ir [16a] were known, $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_9\text{H}_6)\text{Co}(\text{C}_5\text{Me}_5)]$ is the sole known Zr–Co(II) heterodinuclear complex with bridged cyclopentadienyl ligands [8c].

2.2. Olefin polymerization

Zr–Co heterodinuclear complexes (**3–6**) promote the polymerization of ethylene (1 atm) in the presence of 1000-fold amount of MAO at room temperature to give polyethylene. **3** has moderate catalytic activity but, **4–6** show low catalytic activity. These heterodinuclear complexes show the lower catalytic activity than that of Cp_2ZrCl_2 (Table 1). It has been reported that Zr–Rh

Table 1
Ethylene polymerization catalyzed by Zr–Co heterodinuclear complexes^a

Run	Complex	Activity (g mmol ⁻¹ h ⁻¹)	<i>M</i> _n	<i>M</i> _w / <i>M</i> _n
1	3	296	429000	2.8
2	4	142	251000	3.1
3	5	34	256000	3.5
4	6	82	285000	4.9
5	Cp ₂ ZrCl ₂	872	370000	3.1

^a Reactions were carried out by stirring the solution of catalyst under atmospheric pressure of ethylene for 1 h. [Al]/[cat.] = 1000, [cat.] = 16.7 μM in toluene.

heterodinuclear complexes having C1-bridged cyclopentadienyl ligand also show low catalytic activity [8–11]. Molecular weights of obtained polymers are 251000–428000. The highest molecular weight polyethylene was obtained by using **3** as catalyst (run 1). Co moieties of heterobimetallic complexes are considered to have very low or no catalytic activity in this polymerization. Molecular weight distribution was broadened as the bulkiness of ligand bound Co center increases (**6** > **5** > **4** > **3**). ¹³C NMR spectra of the obtained polyethylene show linear structure.

Propylene polymerization catalyzed by the heterobimetallic complexes combined with MAO produces the polymer with broader molecular weight distribution than that prepared by the reaction catalyzed by Cp₂ZrCl₂ (Table 2). ¹³C NMR spectra of the polypropylene show atactic structure. Zr–Co(I) heterobimetallic complex **3** was found to be more active than Cp₂ZrCl₂. It was reported by Mukaiyama and co-workers [10] that ferrocenyl substituted zirconocene catalyst has higher activity than Cp₂ZrCl₂ at around room temperature. This is accounted for by intramolecular electron-donation from ferrocenyl group to Zr center. Co(CO)₂ moiety of **3** also enhances the polymer growth by the stabilizing the Zr⁺ species during the reaction. The catalyst prepared by mixing equimolar amounts of CpCo(CO)₂ and Cp₂ZrCl₂ also promote the polymer growth in enhanced rate and produces the polymer with narrow molecular weight distribution (*M*_w/*M*_n = 1.8) (run 5).

Table 2
Propylene polymerization catalyzed by Zr–Co heterodinuclear complexes^a

Run	Complex	Activity (g mmol ⁻¹ h ⁻¹)	<i>M</i> _n	<i>M</i> _w / <i>M</i> _n
1	3	40	1900	4.8
2	4	6	1270	4.8
3	5	12	1690	4.0
4	6	13	1880	5.2
5	Cp ₂ ZrCl ₂ :CpCo(CO) ₂ = 1:1	52	1740	1.8
6	Cp ₂ ZrCl ₂ :CpCo(CO) ₂ = 1:10	20	900	1.5
7	Cp ₂ ZrCl ₂	20	1250	2.3

^a Reactions were carried out by stirring the solution of catalyst under atmospheric pressure of propylene for 5 h. [Al]/[cat.] = 1000, [cat.] = 167 μM in toluene.

Addition of a larger amount of CpCo(CO)₂ to Cp₂ZrCl₂ did not increase the catalytic activity (run 6). CpCo(CO)₂ may scavenge oxygen that is contained in a small amount in the solution and retards the reaction catalyzed by the Zr complex in these cases. Further studies of the early–late heterobimetallic complexes in which the two metal centers are linked by a long tether would form a new catalysis containing two metal centers function cooperatively.

3. Experimental

3.1. General

All manipulations of the complexes were carried out using standard Schlenk techniques under argon or nitrogen atmosphere. Toluene, THF and hexane were distilled from sodium benzophenone ketyl prior to use. CpZrCl₃(dme) [21], Li₂[Me₂C(C₅H₄)₂] [17], and CpCo(CO)₂ [18] were synthesized according to the reported procedure. MAO was purchased from TOSOH-FINE-CHEM and stored under argon. Cp₂ZrCl₂, Co₂(CO)₈, and other chemicals were used as received from commercial suppliers. NMR spectra (¹H, ¹³C{¹H}) were recorded on JEOL JNM LA-500 or Varian Mercury 300 spectrometers. IR spectra were recorded on Shimadzu FTIR-8100A. Elemental analyses were carried out with a Yanaco MT-5 CHN autocorder. Gel permeation chromatography (GPC) was performed on a TOSOH HPLC-8121GPC/HT using orthodichlorobenzene (152 °C) as eluent for polyethylene, and a TOSOH HLC-8020 high-speed liquid chromatograph using THF as eluent for polypropylene.

3.1.1. Preparation of [(η⁵-C₅H₅)ZrCl₂(η⁵-C₅H₄)CMe₂(C₅H₅)] (**1**)

Li₂[Me₂C(C₅H₄)₂] (499 mg, 2.7 mmol) and CpZrCl₃(dme) (956 mg, 2.7 mmol) were stirred in toluene (20 mL) for 60 h at room temperature. HCl in Et₂O (1 M, 1.90 mL, 1.9 mmol) was slowly added to the suspension at room temperature, and the mixture was stirred for 5 min. After filtration, the yellow solution was concentrated. The hexane was added to the solution to cause separation of solid. The resulting solid was washed with hexane and dried under reduced pressure to give **1** as white solid (712 mg, 66%, mixture of isomers). ¹H NMR (300 MHz, C₆D₆): δ 6.38 (dq, 1H, *J* = 5 Hz, 2 Hz, olefinic), 6.33 (dq, 1H, *J* = 5 Hz, 2 Hz, olefinic), 6.33 (dq, 1H, *J* = 5 Hz, olefinic) 6.13 (m, 1H, olefinic), 6.11 (t, 2H, *J* = 3 Hz, H_a or b), 6.02 (t, 2H, *J* = 3 Hz, H_a or b), 5.97(m, 1H, olefinic), 5.93 (s, 5H, H_c), 5.92 (s, 5H, H_c), 5.77 (t, 2H, H_a or b), 5.76 (m, 1H, olefinic), 5.73 (t, 2H, *J* = 3 Hz, H_a or b), 2.67 (q, 2H, *J* = 2 Hz, H_c), 2.52 (q, 2H, *J* = 2 Hz, H_c), 1.74 (s, 6H, H_d), 1.58 (s, 6H, H_d). (see Chart 1).

3.1.2. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{Co}(\text{CO})_2]$ (**3**)

A toluene solution (50 mL) of **1** (853 mg, 2.1 mmol) and Co_2CO_8 (803 mg, 2.4 mmol) was stirred for 10 h at 60 °C. The volatiles were evaporated to dryness. The residue was washed with hexane and extracted with toluene. Evaporation of the solvent formed **3** as a red solid (860 mg, 70%). Anal. Calc. for $\text{C}_{20}\text{H}_{19}\text{O}_2\text{Cl}_2\text{CoZr}$: C, 46.78; H, 3.74. Found: C, 46.88; H, 3.95%. ^1H NMR (300 MHz, C_6D_6): δ 6.05 (t, 2H, $J = 3$ Hz, H_f or g), 5.88 (s, 5H, H_h), 5.70 (t, 2H, $J = 3$ Hz, H_f or g), 4.36 (d, 2H, $J = 2$ Hz, H_a or b), 4.34 (d, 2H, $J = 2$ Hz, H_a or b), 1.55 (s, 6H, H_i). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, C_6D_6): δ 202.6 (br, $\text{C}_{(\text{CO})}$), 140.5 (s, C_e), 120.6 (s, C_c), 116.0 (s, C_h), 115.8 (s, C_f or g), 113.0 (s, C_f or g), 83.2 (s, C_a or b), 83.0 (s, C_a or b), 36.2 (s, C_d), 30.5 (s, C_i). IR: 2006, 1956 cm^{-1} (CO).

3.1.3. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{CO})]$ (**4**)

To a solution of **3** (204.1 mg, 0.40 mmol) in THF (2 mL) was added a THF solution (5 mL) of I_2 (101.9 mg, 0.40 mmol). The reaction mixture was stirred for 30 min at room temperature. Hexane was added to the solution to cause separation of purple crystals of **4**. The product was collected by filtration and washed with hexane to give **4**. (242.2 mg, 93%). Anal. Calc. for $\text{C}_{20}\text{H}_{19}\text{Cl}_2\text{CoO}_2\text{Zr}$: C, 30.91; H, 2.59. Found: C, 30.57; H, 2.81%. ^1H NMR (300 MHz, CDCl_3): δ 6.47 (s, 5H, H_h), 6.46 (t, 2H, $J = 3$ Hz, H_f or g), 6.35 (t, 2H, $J = 3$ Hz, H_f or g), 5.82 (t, 2H, $J = 2$ Hz, H_a or b), 4.48 (t, 2H, $J = 2$ Hz, H_a or b), 1.92 (s, 6H, H_i). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 137.7 (s, C_e), 118.1 (s, C_f or g), 116.4 (s, C_c), 116.3 (s, C_h), 110.3 (s, C_f or g), 89.5 (s, C_a or b), 88.0 (s, C_a or b), 36.7 (s, C_d), 29.5 (s, C_i). IR: 2056.4 cm^{-1} (CO).

3.1.4. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{P}(\text{OMe})_3)]$ (**5**)

To a solution of **4** (104.5 mg, 0.14 mmol) in CH_2Cl_2 (5 mL) was added a CH_2Cl_2 solution (5 mL) of $\text{P}(\text{OMe})_3$ (16.7 μL , 0.14 mmol) dropwise at 0 °C. After

it was stirred for 5 h, the reaction mixture was concentrated. Hexane was added to the solution to cause separation of the crystals. The formed purple crystals were collected by filtration and washed with hexane (96.8 mg, 82%). Anal. Calc. for $\text{C}_{21}\text{H}_{28}\text{Cl}_2\text{CoI}_2\text{O}_3\text{PZr}$: C, 30.23; H, 3.38. Found: C, 30.50; H, 3.60%. ^1H NMR (300 MHz, CDCl_3): δ 6.74 (t, 2H, $J = 3$ Hz, H_f or g), 6.47 (s, 5H, H_h), 6.38 (t, 2H, $J = 3$ Hz, H_f or g), 5.28 (br, 2H, H_a or b), 4.48 (br, 2H, H_a or b), 3.87 (d, 9H, $J_{\text{P-H}} = 10$ Hz, $\text{P}(\text{OMe})_3$), 2.15 (s, 6H, H_i). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 137.7 (d, C_e , $J_{\text{P-C}} = 7$ Hz), 118.1 (d, C_c , $J_{\text{P-C}} = 16$ Hz), 116.7 (s, C_f or g), 116.2 (s, C_h), 113.0 (s, C_f or g), 92.0 (s, C_a or b), 76.0 (s, C_a or b), 56.8 (d, $\text{P}(\text{OMe})_3$, $J_{\text{P-C}} = 8$ Hz), 38.1 (d, C_d , $J_{\text{P-C}} = 3$ Hz), 29.6 (s, C_i).

3.1.5. Preparation of $[(\eta^5\text{-C}_5\text{H}_5)\text{ZrCl}_2(\eta^5\text{-C}_5\text{H}_4)\text{CMe}_2(\eta^5\text{-C}_5\text{H}_4)\text{CoI}_2(\text{PPh}_3)]$ (**6**)

To a solution of **3** (111 mg, 0.22 mmol) and PPh_3 (56.9, 0.27 mmol) in CH_2Cl_2 (1 mL) was added a THF solution (1.5 mL) of I_2 (55.1, 0.22 mmol). After 20-min stirring, the reaction mixture was concentrated and allowed to stand overnight. Formed purple crystals were collected by filtration and washed with hexane (100 mg, 53%). Anal. Calc. for $\text{C}_{36}\text{H}_{34}\text{Cl}_2\text{CoI}_2\text{PZr}$: C, 44.46; H, 3.52. Found: C, 44.09; H, 3.56%. ^1H NMR (300 MHz, CDCl_3): δ 7.9–7.2 (br, 15H, PPh_3), 6.68 (t, 2H, $J = 3$ Hz, H_f or g), 6.45 (s, 5H, H_h), 6.35 (t, 2H, $J = 3$ Hz, H_f or g), 5.54 (br, 2H, H_a or b), 3.65 (br, 2H, H_a or b), 2.26 (s, 6H, H_i). $^{13}\text{C}\{^1\text{H}\}$ NMR (75 MHz, CDCl_3): δ 140.2 (s, C_e), 134.7–127.2 (m, C_{Ph}), 116.7 (s, C_f or g), 116.1 (s, C_h), 113.2 (s, C_f or g), 91.9 (s, C_a or b), 76.4 (s, C_a or b), 38.3 (s, C_d), 29.7 (s, C_i), $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz, CDCl_3): δ 30.2.

3.2. Olefin polymerization

A mixture of complex (0.50 μmol) and MAO (0.50 mmol Al) in toluene (30 mL) was stirred at room temperature for 15 min. After freeze–pump–thaw cycles, ethylene or propylene (1 atm) was introduced to the flask at room temperature. After stirring for specified time at room temperature, MeOH and 5 M HCl–MeOH were subsequently added. Separated polyethylene solid was filtered, washed with MeOH, H_2O and hexane, and dried in vacuo. Polypropylene was extracted with toluene and washed with H_2O and dried in vacuo.

3.3. Crystal structure determination

Crystals of **5** and **6** were mounted in glass capillary tubes under Ar. Intensities were collected for Lorentz and polarization effects on a Rigaku AFC-7R automated four-cycle diffractometer by using Mo $\text{K}\alpha$ radiation ($\lambda = 0.71069$ Å) and $\omega - 2\theta$ scan method, and

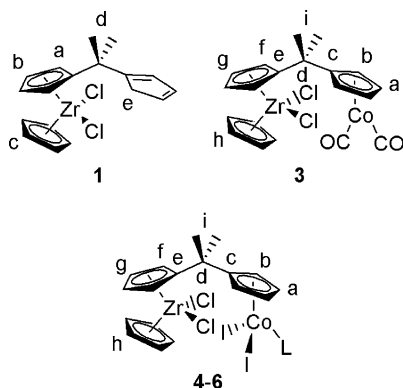


Chart 1.

Table 3
Crystal data and details of structure refinement of complexes of **5** and **6**

	5	6
Empirical formula	C ₂₁ H ₂₈ Cl ₂ CoI ₂ O ₃ PZr	C ₃₆ H ₃₄ CoCl ₂ I ₂ PZr
Formula weight	834.29	972.51
Crystal system	Triclinic	Orthorhombic
Space group	<i>P</i> $\bar{1}$ (No. 2)	<i>Pbca</i> (No. 61)
Unit cell dimensions		
<i>a</i> (Å)	14.671(4)	25.84(1)
<i>b</i> (Å)	14.787(4)	26.454(9)
<i>c</i> (Å)	7.0114(8)	10.493(4)
α (°)	93.89(2)	
β (°)	99.954(1)	
γ (°)	62.493(1)	
<i>V</i> (Å ³)	1328.6(4)	7172(4)
<i>Z</i>	2	8
μ (cm ⁻¹)	36.33	26.93
<i>F</i> (000)	800	3776
<i>D</i> _{calc} (g cm ⁻³)	2.085	1.801
Crystal size (mm)	0.50 × 0.20 × 0.15	0.50 × 0.30 × 0.20
2 θ Range (°)	5–55.0	5–55.0
Scan rate (deg min ⁻¹)	8.0	8.0–4.0
No. of unique reflections	6098	8535
No. of used reflections (<i>I</i> > 3 σ (<i>I</i>))	4477	3423
No. of variables	280	388
<i>R</i> (<i>F</i> _o)	0.040	0.090
<i>R</i> _w (<i>F</i> _o)	0.039	0.099
Goodness-of-fit	2.40	3.40

an empirical absorption correction (Φ scan) was applied. Calculations were carried out with a 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 [22]. Crystallographic data and details of refinement of the complexes are summarized in Table 3. Crystallographic data (excluding structural factors) have been deposited with the Cambridge Crystallographic Data Center as Supplemental Publication Nos. CCDC 233764–233765. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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Appendix A. Supporting information available

Crystallographic data of **5** and **6**. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorgchem.2004.09.027.

References

- [1] (a) H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1143; (b) L. Resconi, L. Cavallo, A. Fait, F. Piemontesi, *Chem. Rev.* 100 (2000) 1253; (c) V.C. Gibson, S.K. Spitzmesser, *Chem. Rev.* 103 (2003) 283.
- [2] S.D. Ittel, L.K. Johnson, M. Brookhart, *Chem. Rev.* 100 (2000) 1169.
- [3] (a) Z.J.A. Komon, X. Bu, G.C. Bazan, *J. Am. Chem. Soc.* 122 (2000) 1830; (b) R. Quijada, R. Rojas, G. Bazan, Z.J.A. Komon, R.S. Mauler, G.B. Galland, *Macromolecules* 34 (2001) 2411; (c) Z.J.A. Komon, G.M. Diamond, M.K. Leclerc, V. Murphy, M. Okazaki, G.C. Bazan, *J. Am. Chem. Soc.* 124 (2002) 15280.
- [4] (a) G.J.P. Britovsek, S.A. Cohen, V.C. Gibson, P.J. Maddox, M. van Meurs, *Angew. Chem., Int. Ed.* 41 (2002) 489; (b) V.C. Gibson, Abstract of the 15th Int. Symp. on Olefin Metathesis and Related Chemistry, Kyoto, 28 July–1 August, 2003, 28.
- [5] (a) L. Li, M.V. Metz, H. Li, M.-C. Chen, T.J. Marks, L. Liable-Sands, A.L. Rheingold, *J. Am. Chem. Soc.* 124 (2002) 12725; (b) G.P. Abramo, L. Li, T.J. Marks, *J. Am. Chem. Soc.* 124 (2002) 13966.
- [6] J.C. Sierra, D. Hüländer, M. Hill, G. Kehr, G. Erker, R. Frölich, *Chem. Eur. J.* 9 (2003) 3618.
- [7] For the reviews on early–late heterodinuclear complexes: (a) D.W. Stephan, *Coord. Chem. Rev.* 95 (1989) 41; (b) M.J. Chetcuti, in: E.W. Abel, F.G.A. Stone, G.W. Wilkinson (Eds.), *Comprehensive Coordination Chemistry II*, vol. 10, Pergamon, New York, 1994, pp. 23–84; (c) N. Wheatley, P. Kalck, *Chem. Rev.* 99 (1999) 3379; (d) L.H. Gade, *Angew. Chem., Int. Ed.* 39 (2000) 2658.
- [8] (a) G.M. Diamond, M.L.H. Green, N.A. Popham, A.N. Chernega, *J. Chem. Soc., Chem. Commun.* (1994) 727; (b) G.M. Diamond, A.N. Chernega, P. Mountford, M.L.H. Green, *J. Chem. Soc., Dalton Trans.* (1996) 921; (c) X. Yan, A. Chernega, M.L.H. Green, J. Sanders, J. Souter, T. Ushioda, *J. Mol. Catal. A.* 128 (1998) 119; (d) M.L.H. Green, N.H. Popham, *J. Chem. Soc., Dalton Trans.* (1999) 1049.
- [9] D. Takeuchi, J. Kuwabara, K. Osakada, *Organometallics* 22 (2003) 2305.
- [10] (a) M. Mitani, K. Oouchi, M. Hayakawa, T. Yamada, T. Mukaiyama, *Chem. Lett.* (1995) 905; (b) M. Mitani, K. Oouchi, M. Hayakawa, T. Yamada, T. Mukaiyama, *Macromol. Chem. Phys.* 197 (1996) 1815; (c) M. Mitani, M. Hayakawa, T. Yamada, T. Mukaiyama, *Bull. Chem. Soc. Jpn.* 69 (1996) 2967.
- [11] Y. Yamaguchi, N. Suzuki, T. Mise, Y. Wakatsuki, *Organometallics* 18 (1999) 996.
- [12] (a) G.F. Schmidt, M. Brookhart, *J. Am. Chem. Soc.* 107 (1985) 1443; (b) M. Brookhart, J.M. DeSimone, B.E. Grant, M.J. Tanner, *Macromolecules* 28 (1995) 5378; (c) K. Tsuchihara, Y. Suzuki, M. Asai, K. Soga, *Polym. J.* 32 (2000) 700;

- (d) M. Enders, G. Ludwig, H. Pritzkow, *Organometallics* 20 (2001) 827.
- [13] (a) U.T. Mueller-Westerhoff, A. Nazzal, M. Tanner, *J. Organomet. Chem.* 236 (1982) C41;
(b) U.T. Mueller-Westerhoff, *Angew. Chem., Int. Ed. Engl.* 25 (1986) 702;
(c) D. Schneider, H. Werner, *Organometallics* 12 (1993) 4420;
(d) B. Stempfle, S. Schmidt, J. Sundermeyer, H. Werner, *Chem. Ber.* 128 (1995) 877;
(e) H. Komatsu, H. Yamazaki, *J. Organomet. Chem.* 634 (2001) 109.
- [14] (a) J.F. Buzinkai, R.R. Schrock, *Organometallics* 6 (1987) 1447;
(b) J.F. Buzinkai, R.R. Schrock, *Inorg. Chem.* 28 (1989) 2837;
(c) J. Heck, J. Körnich, *J. Organomet. Chem.* 543 (1997) 153;
(d) J. Körnich, S. Haubold, J. He, O. Reimelt, J. Heck, *J. Organomet. Chem.* 584 (1999) 329.
- [15] (a) P. Härter, G. Boguth, E. Herdweck, J. Riede, *Angew. Chem., Int. Ed. Engl.* 28 (1989) 1008;
(b) P.A. McGovern, K.P.C. Vollhardt, *Synlett* (1990) 493;
- (c) I.E. Nifant'ev, M.V. Borzov, A.V. Churakov, *Organometallics* 11 (1992) 3942.
- [16] (a) H. Werner, D. Schneider, M. Schulz, *Chem. Ber.* 125 (1992) 1017;
(b) B. Stempfle, O. Gevert, H. Werner, *J. Organomet. Chem.* 681 (2003) 70.
- [17] G.M. Diamond, M.L.H. Green, N.A. Popham, A.N. Chernega, *J. Chem. Soc., Dalton Trans.* (1993) 2535.
- [18] T.S. Piper, F.A. Cotton, G. Wilkinson, *J. Inorg. Nucl. Chem.* 1 (1955) 165.
- [19] N.E. Schore, C.S. Ilenda, M.A. White, H.E. Bryndza, M.G. Matturro, R.G. Bergman, *J. Am. Chem. Soc.* 106 (1984) 7451.
- [20] (a) R.B. King, *Inorg. Chem.* 5 (1966) 82;
(b) H. Yamazaki, N. Hagihara, *J. Organomet. Chem.* 21 (1970) 431.
- [21] E.C. Lund, T. Livinghouse, *Organometallics* 9 (1990) 2426.
- [22] *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974, Vol. 4.