

# Early–late heterobimetallic complexes as initiator for ethylene polymerization. Cooperative effect of two metal centers to afford highly branched polyethylene†

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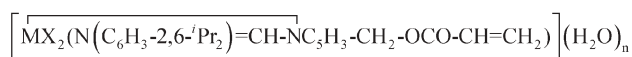
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Ethylene polymerization initiated by early–late transition-metal complexes afforded a polymer with different branched structures and properties depending on the type of late transition-metal.

Soluble transition-metal complexes catalyze ethylene polymerization to yield hydrocarbon polymers with different molecular weights and degree of branching from a single monomer source, depending on the kinds of metal center and ligand of the catalyst.<sup>1</sup> Although binary catalysts composed of two transition-metal components are effective for the synthetic organic reactions,<sup>2</sup> olefin polymerization using these catalysts, however, have attracted little attention until recently. Marks and coworkers designed Ti–Zr dinuclear CGC (constrained geometry catalysts), and observed ethylene polymerization catalyzed by the complex in the presence of diborate anions to form polymers with long branches (number of carbons > 6).<sup>3</sup> Such branches are generated by ethylene oligomerization at the Zr center and the incorporation of an oligomer into a long polymer chain that grows at the Ti center. Bazan<sup>4</sup> and coworkers employed a mixture of Ni and Ti complexes, that promotes ethylene oligomerization<sup>5,6</sup> and the copolymerization of ethylene and  $\alpha$ -olefin,<sup>7</sup> respectively, as the catalyst, and obtained a branched polyethylene as the product.<sup>8</sup> Although early–late heterobimetallic complexes are also expected to catalyze the conversion of ethylene into a branched polymer *via* a smooth intramolecular transfer of an ethylene oligomer from a late transition-metal to an early transition-metal, most bimetallic complexes reported thus far produce a linear polyethylene rather than a highly branched one.<sup>9</sup> Here, we report on molecular tandem catalysts composed of bimetallic Zr and late transition-metal complexes, and their use in ethylene polymerization.

The selective cross-metathesis<sup>10</sup> of a Zr complex with the allyl substituent ( $\eta^5, \eta^5$ -C<sub>5</sub>Me<sub>4</sub>SiMe<sub>2</sub>C<sub>5</sub>H<sub>3</sub>CH<sub>2</sub>CH=CH<sub>2</sub>)ZrCl<sub>2</sub> (**1**) and Pd, Co, and Ni complexes having the acylate pendant



(**2**: Pd, X = Cl,  $n = 0$ ; **3**: Co, X = Cl,  $n = 0$ ; **4**: Ni, X = Br,  $n = 1$ ) affords the corresponding early–late heterobimetallic complexes

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**5–7**, as shown in eqn (1).<sup>11</sup> The <sup>1</sup>H NMR spectrum of the Zr–Pd complex **5** exhibits signals of vinylene hydrogens (7.25 and 5.96 ppm) and CH<sub>2</sub>O hydrogens as a pair of doublets (6.14 and 6.05 ppm). The splitting of the latter signals is consistent with the proposed heterobimetallic structure having a planar chirality within the zirconocenyl group. The Zr–Co complex **6** and Zr–Ni complex **7** were paramagnetic, and were characterized by IR spectroscopy and elemental analysis. Fig. 1 shows molecular structure of **6** determined by X-ray crystallography.‡ Zr and Co atoms are at a distance of *ca.* 9.1 Å.

Table 1 summarizes the results of polymerizations initiated by dinuclear complexes and a mixture of mononuclear complexes. Ethylene polymerization initiated by **5** in the presence of MMAO for 15 min at 50 °C affords a linear polyethylene (entry 1). The polymer obtained from the reaction initiated by **6** contains an ethyl branch (entries 2 and 3). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum of the former polymer (Fig. 2a) does not contain the signal due to the branch of the polymer chain, whereas that of the latter polymer exhibits such a signal at 11.2 and 26.8 ppm (Fig. 2b), which correspond to an ethyl branch.<sup>12</sup> The monometallic Pd complex with the iminopyridine ligand **2** promotes neither the oligomerization nor polymerization of ethylene. Consequently, polymerization initiated by **5** occurs exclusively at the Zr center, giving a linear polyethylene. The ethylene oligomerization initiated by the Co complex **3** produces a mixture of 1- and 2-butenes. Copolymerization of ethylene and 1-butene (1/1 (v/v)) by using **1** as the initiator produced a polymer having an ethyl branch (131 Et branches per 1000 carbons). The reaction initiated by **6** probably involves the dimerization of ethylene at the Co center and the copolymerization of ethylene and 1-butene at the Zr center, yielding a polymer with an ethyl branch.

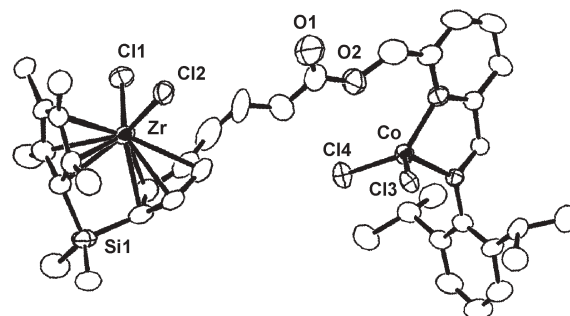
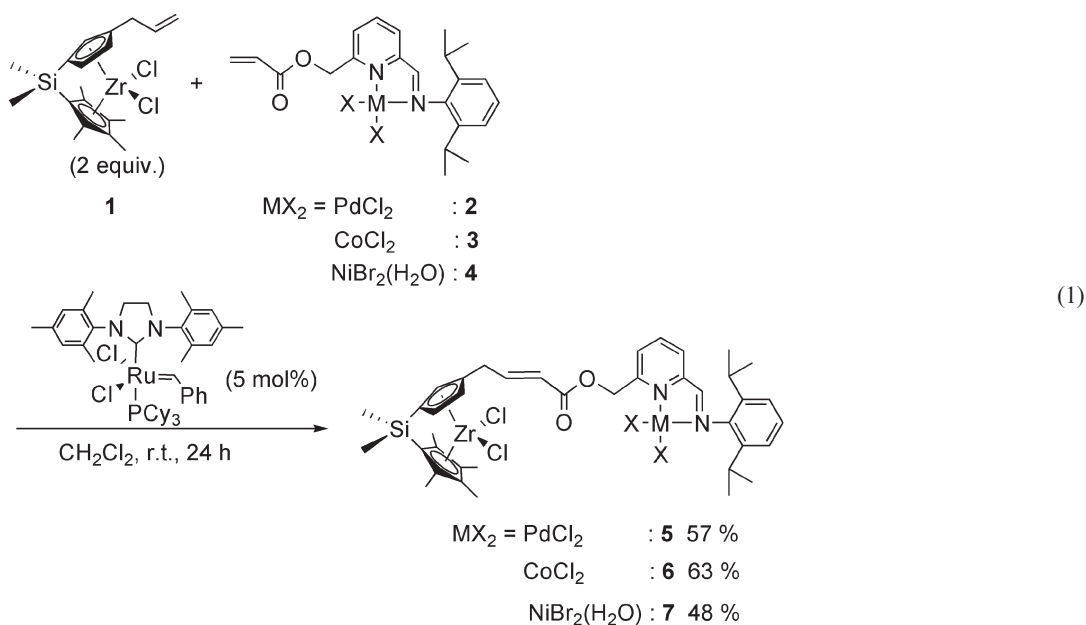


Fig. 1 ORTEP drawing of **6** at 30% ellipsoidal level. C14 shows one of the disordered positions.



**Table 1** Ethylene polymerization initiated by mono- and bimetallic complexes<sup>a</sup>

Entry	Cat.	Temp/°C	Time/min	Activity/ g (mmol Zr) <sup>-1</sup> h <sup>-1</sup>	Branches <sup>b</sup>			<i>M<sub>n</sub></i> <sup>d</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>d</sup>	<i>M<sub>p</sub></i>
					Me	Et	Alkyl <sup>c</sup>			
1	<b>5</b>	50	15	160	0	0	No	13800	2.9	132.4
2	<b>6</b>	50	15	188	0	2.1	No	9400	2.5	130.3
3	<b>6</b>	0	15	218	0	5.6	No	46900	2.9	129.1
4	<b>1 + 3</b>	0	15	121	0	4.6	No	40000	2.7	130.6
5	<b>7</b>	50	15	217	1.5	2.2	Yes	6900	3.0	127.1
6	<b>7</b>	50	30	213	2.1	1.7	Yes	6800	3.4	127.2
7	<b>1 + 4</b>	50	15	259	0	0	No	4500	4.0	130.3
8	<b>1 + 4</b>	50	30	208	0.7	0	Yes	4300	3.6	128.7
9	<b>1</b>	50	15	275	0	0	No	10600	3.4	131.8

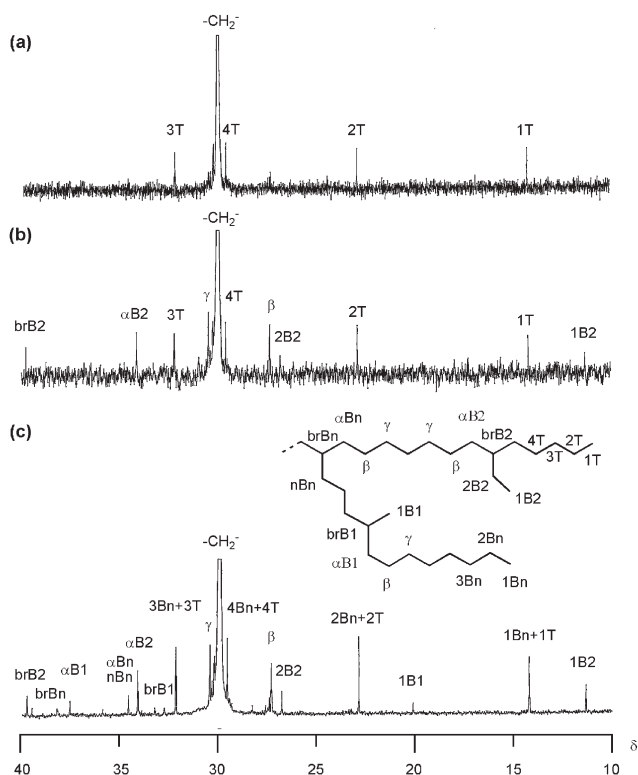
<sup>a</sup> Conditions: Zr = 143 μM, 1 atm ethylene, [Al]/[Zr] = 1000, 30 mL of toluene solvent. <sup>b</sup> Number of branches per 1000 carbons. <sup>c</sup> Existence of long branches in the polymers was confirmed from the <sup>13</sup>C{<sup>1</sup>H} NMR signal due to methin carbon (37.4 ppm). The number of end carbons of long branches (C > 6) was not estimated because of the overlap of the terminal carbon of the polymer. <sup>d</sup> Determined by GPC detected by differential refractometer and calibrated based on polystyrene standards (eluent: using orthodichlorobenzene (152 °C)).

A mixture of **1** and **3** also produces a polymer with an ethyl branch at 0 °C (entry 4). Polymerization initiated by the Zr–Ni dinuclear complex **7** affords a polymer with a branched structure (entries 5 and 6). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum in Fig. 2c contains the carbon signal of an ethyl (11.2 and 26.8 ppm) branch and a methyl branch (20.1 ppm).<sup>12</sup> The signal at 37.4 ppm is assigned to the CH carbon of a long alkyl branch (brBn), although the signal of the terminal carbon of long alkyl branch (lBn) overlaps with that of the terminal carbon of the polymer chain. Branched α-olefins formed at a Ni center undergo copolymerization with ethylene at a Zr center. **4** catalyzes the conversion of ethylene into an oligomer (*M<sub>n</sub>* = 430) with methyl branches, similarly to Ni-dimine complexes.<sup>13</sup> In contrast, ethylene polymerization initiated by a mixture of **1** and **4** produces a polyethylene having almost no methyl and ethyl branches (entries 7 and 8). The <sup>13</sup>C{<sup>1</sup>H} NMR spectrum after polymerization for 15 min exhibits no CH carbon signals, suggesting that the incorporation of the oligomer formed at the Ni center into the polymer in the reaction initiated by the mixture of **1** and **4** is slower than that in the reaction initiated by **7**. All the polymers listed in Table 1 showed GPC traces with unimodal distribution. Polyethylenes formed by dinuclear and

mononuclear initiators change their properties depending on the degree of branching; the melting points of the polymer formed by **7** (127.1 and 127.2 °C) are lower than those formed by a mixture of **1** and **4** (128.7 and 130.3 °C) and by **1** (131.8 °C).

Dinuclear complex **7** initiated the copolymerization of ethylene with 1-hexene and with 8-(trimethylsilyl)-1-octene to form polymers with a C4 branch (15.5 branches per 1000 carbons) or a Si-containing branch (12.4 branches per 1000 carbons). The degree of branching induced by the added olefin is smaller than that for the copolymers formed as initiated by a mixture of **1** and **4** (a C4 branch with 22.4 branches per 1000 carbons for the former polymer and a Si-containing branch with 23.1 branches per 1000 carbons for the latter). Thus, a proximity effect of Zr and Ni in **7** enables the efficient incorporation of the branched oligomer into the polymer, although the enchainment of the linear oligomer in the copolymerization is promoted both by the bimetallic complex and by a mixture of Zr and Ni mononuclear complexes.<sup>14</sup>

In summary, a selective cross-metathesis reaction of two monometallic complexes provides novel early–late transition-metal complexes. Ethylene polymerization initiated by such complexes affords a polymer with different structures and properties



**Fig. 2**  $^{13}\text{C}\{^1\text{H}\}$  NMR spectra ( $\text{C}_2\text{D}_2\text{Cl}_4$ ,  $130\text{ }^\circ\text{C}$ ) of polyethylene produced by (a) **5** (Table 1, entry 1), (b) **6** (entry 2) and (c) **7** (entry 5).

depending on the type of late transition-metal. The dinuclear Zr–Ni complex enables the efficient enchainment of a branched oligomer formed at the Ni center to the polymer grown at the Zr center.

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## Notes and references

† Crystal data for **6**:  $\text{C}_{39}\text{H}_{48}\text{Cl}_4\text{N}_2\text{CoO}_2\text{SiZr}\cdot(\text{C}_6\text{H}_6)_{1.667}\cdot(\text{CH}_2\text{Cl}_2)_{0.5}$ ; Crystal size  $0.28 \times 0.20 \times 0.18$  mm;  $M_r$ , 1144.23; trigonal; space group R-3 (No. 148);  $a$  35.456(5),  $c$  23.121(3) Å;  $V$  25172(6) Å<sup>3</sup>;  $Z$  18;  $\mu(\text{Mo-K}\alpha)$  7.784 cm<sup>-1</sup>;  $F(000)$  9936;  $D_{\text{calcd}}$  1.270 g cm<sup>-3</sup>; unique reflections ( $2\theta < 55^\circ$ ) 10214; used reflections ( $F^2 > 2\sigma(F^2)$ ) 7994; number of variables 605;  $R(F_o)$  0.117;  $R_w(F_o)$  0.364, GOF 1.419. CCDC 610658. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b605800k

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