# Highly Efficient Ethylene/Cyclopentene Copolymerization with Exclusive 1,2-Cyclopentene Incorporation by (Cyclopentadienyl)-(ketimide)titanium(IV) Complex–MAO Catalysts

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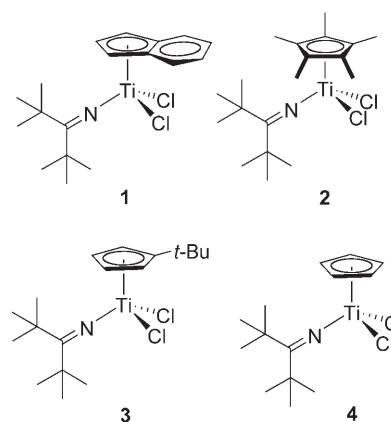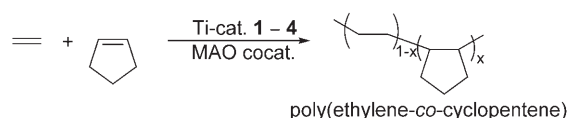Supporting information for this article is available on the WWW under http://asc.wiley-vch.de/home/.

**Abstract:** The (cyclopentadienyl)-(ketimide)titanium(IV) complex $(t\text{-BuC}_5\text{H}_4)\text{TiCl}_2[\text{N}=\text{C}(t\text{-Bu})_2]$ exhibited remarkable catalytic activities $(1.99–3.16 \times 10^4$ kg polymer/mol Ti·h) with efficient cyclopentene incorporation in ethylene/cyclopentene copolymerization in the presence of methylaluminoxane (MAO). The polymerization took place with exclusive 1,2-cyclopentene incorporation, affording high molecular weight (alternating) copolymers (cyclopentene $< 43.6$ mol %) with uniform distributions. The effect of the cyclopentadienyl fragment (Cp′) in the copolymerization using $\text{Cp}'\text{TiCl}_2[\text{N}=\text{C}(t\text{-Bu})_2]$ [Cp′ = indenyl, $t\text{-BuC}_5\text{H}_4$, $\text{C}_5\text{Me}_5$ (Cp*), $\text{C}_5\text{H}_5$ (Cp)] has been explored in the presence of MAO; the Cp′ plays an important key role in terms of both activity and efficient cyclopentene incorporation.

**Keywords:** copolymerization; cyclopentadienyl ligands; cyclopentene; ethylene; titanium

Certain cyclic olefin copolymers are known to be amorphous materials with a promising combination of high transparency in the UV-Vis region along with humidity- and heat-resistance.[1] Therefore, the transition metal-catalyzed copolymerization of ethylene with cyclic olefins such as norbornene,[2–5] cyclopentene,[4b,6–11] cyclohexene[12] attracts considerable attention. Although many examples were known for the ethylene/norbornene copolymerization using ordinary metallocenes,[2] linked half-titanocenes (so-called constrained geometry type),[3] unbridged half-titanocenes,[4] and other so-called non-metallocenes;[5] however, examples for the ethylene/cyclopentene copolymerization have been limited.[4b,6–11] Moreover, the resultant copolymers prepared by ordinary metallo-

cenes[6] or late metal complexes[11] possessed a mixture of 1,2- and 1,3-cyclopentene inserted units due to the tendency for favored β-hydrogen elimination-reinsertion after insertion. Recently, copolymerization with exclusive 1,2-cyclopentene insertion had been achieved by using half-titanocenes[4b,7] and others,[8–10] however, the activities were low[13] and/or the resultant copolymers possessed low molecular weights.[4b,7a] In this report, we present the unique example that half-titanocenes containing a ketimide ligand of the type, $\text{Cp}'\text{TiCl}_2[\text{N}=\text{C}(t\text{-Bu})_2]$ [Cp′ = indenyl (1) Cp* (2, Cp* = $\text{C}_5\text{Me}_5$), $t\text{-BuC}_5\text{H}_4$ (3), Cp (4, Cp = $\text{C}_5\text{H}_5$)] exhibit remarkably high activities for the ethylene/cyclopentene copolymerization with efficient exclusive 1,2-cyclopentene insertion, affording high molecular weight alternating copolymers with uniform distributions (Scheme 1).



poly(ethylene-co-cyclopentene)

**Scheme 1.**

**Table 1.** Copolymerization of ethylene with cyclopentene, norbornene, or cyclohexene by Cp′TiCl$_2$[N=C(t-Bu)$_2$] [Cp′: indenyl (**1**) Cp* (**2**), t-BuC$_5$H$_4$ (**3**), Cp (**4**)]–MAO catalyst systems.[a]

| Run | Catalyst (μmol) | Cyclic olefin[b] (concentration) | Ethylene [atm] | Yield [mg] | Activity[c] | Cyclic olefin content[d] [mol%] | $M_n$[e] [×10$^{-4}$] | $M_w/M_n$[e] |
|---|---|---|---|---|---|---|---|---|
| 1 | **1** (0.1) | - | 4 | 122 | 7320 | - | 95.6 | 2.80 |
| 2 | **1** (0.1) | cyclopentene (1.0) | 4 | 264 | 15800 | 7.5 | 29.1 | 2.48 |
| 3 | **1** (0.1) | cyclopentene (5.0) | 4 | 480 | 28800 | 19.4 | 27.2 | 2.42 |
| 4[f] | **1** (0.1) | cyclopentene (5.0) | 2 | 438 | 26300 | 32.9 | 24.7 | 2.03 |
| 5 | **2** (0.05) | - | 4 | 88 | 10600 | - | 49.6 | 2.57 |
| 6 | **2** (0.1) | cyclopentene (1.0) | 4 | 144 | 8640 | 1.1 | 43.1 | 2.05 |
| 7 | **2** (1.0) | cyclopentene (5.0) | 4 | 264 | 1580 | 7.4 | 16.4 | 2.19 |
| 8[f] | **2** (1.0) | cyclopentene (5.0) | 2 | 118 | 708 | 13.3 | 10.1 | 2.20 |
| 9 | **3** (0.05) | - | 4 | 182 | 21800 | - | 52.2 | 2.66 |
| 10 | **3** (0.1) | cyclopentene (1.0) | 4 | 455 | 27300 | 18.1 | 31.1 | 3.59 |
| 11 | **3** (0.1) | cyclopentene (5.0) | 4 | 332 | 19900 | 35.1 | 23.4 | 3.29 |
| 12[f] | **3** (0.1) | cyclopentene (1.0) | 2 | 527 | 31600 | 33.5 | 36.9 | 3.59 |
| 13[f] | **3** (0.1) | cyclopentene (5.0) | 2 | 372 | 22600 | 43.6 | 13.4 | 1.69 |
| 14 | **4** (0.04) | cyclopentene (1.0) | 4 | 99 | 14900 | 18.0 | 67.3 | 2.47 |
| 15[f] | **4** (1.0) | cyclopentene (2.5) | 2 | 192 | 1150 | 41.3 | 16.9 | 1.97 |
| 16[f] | **4** (1.0) | cyclopentene (5.0) | 2 | 151 | 906 | 43.1 | 17.6 | 2.01 |
| 17 | **1** (0.1) | norbornene (5.0) | 4 | 166 | 9960 | 45.2 | 24.5 | 1.81 |
| 18[f] | **1** (0.1) | norbornene (5.0) | 2 | 89 | 5340 | 62.1 | 15.2 | 2.26 |
| 19 | **2** (0.05) | norbornene (5.0) | 4 | 63 | 7560 | 37.9 | 17.9 | 2.32 |
| 20[f] | **2** (1.0) | norbornene (5.0) | 2 | 643 | 3860 | 41.4 | 12.7 | 2.13 |
| 21 | **3** (0.01) | norbornene (1.0) | 4 | 114 | 68400 | 38.2 | 62.4 | 2.78 |
| 22 | **3** (0.1) | norbornene (5.0) | 4 | 250 | 15000 | 52.7 | 17.5 | 2.05 |
| 23[f] | **3** (0.1) | norbornene (5.0) | 2 | 83 | 4980 | 64.8 | 14.2 | 1.94 |
| 24 [g] | **4** (0.02) | norbornene (1.0) | 4 | 134 | 40200 | 40.7 | 71.9 | 2.92 |
| 25[f,g] | **4** (0.01) | norbornene (2.5) | 2 | 150 | 90000 | 58.8 | 32.3 | 2.09 |
| 26[f,g] | **4** (0.01) | norbornene (5.0) | 2 | 143 | 85800 | 65.8 | 34.0 | 2.00 |
| 27[f] | **1** (0.5) | cyclohexene (5.0) | 2 | 298 | 3576 | none | 17.4 | 2.80 |
| 28[f] | **2** (0.1) | cyclehexene (5.0) | 2 | 83 | 4980 | none | 12.2 | 1.99 |
| 29[f] | **3** (0.1) | cyclohexene (5.0) | 2 | 95 | 5700 | none | 12.9 | 2.48 |
| 30[f,h] | **4** (1.0) | cyclohexene (5.0) | 2 | 324 | 1944 | 0.3 | **5.0** | 1.83 |

[a] *Conditions:* toluene+norbornene, cyclopentene or cyclohexene total 50 mL, d-MAO (prepared by removing AlMe$_3$ and toluene from PMAO) 3.0 mmol, ethylene 2 or 4 atm, 25 °C, 10 min.

[b] Cyclic olefin concentration charged in mmol mL$^{-1}$.

[c] Activity in kg polymer/mol Ti·h.

[d] Cyclic olefin (norbornene, cyclopentene, cyclohexene) content (mol%) estimated from NMR spectra.

[e] GPC data in *o*-dichlorobenzene *vs.* polystyrene standards.

[f] *Conditions:* toluene+cyclic olefin total 10 mL (instead of 50 mL).

[g] Cited from ref.[4c]

[h] Cited from ref.[12]

Various half-titanocenes containing ketimide ligands of type Cp′TiCl$_2$[N=C(t-Bu)$_2$] [Cp′ = indenyl (**1**) Cp* (**2**), t-BuC$_5$H$_4$ (**3**), Cp (**4**)], have been chosen, not only because **4** was quite effective for the ethylene/norbornene copolymerization,[4c] but also because that efficient catalyst precursors for other ethylene copolymerizations could be modified by the cyclopentadienyl fragments.[14–16] The results for the ethylene/cyclopentene copolymerization in toluene in the presence of MAO cocatalyst are summarized in Table 1.[17,18] Ethylene/norbornene copolymerizations using the same catalyst systems were also explored for comparison, and the results are summarized in Table 1.[17]

The Cp analogue (**4**) showed both notable catalytic activities and efficient norbornene incorporations in ethylene/norbornene copolymerization (runs 24–26), as reported previously,[4c] and the activity did not decrease even under high norbornene concentration (norbornene/ethylene feed) conditions (runs 25 and 26). In contrast, a significant decrease in the activity was observed upon increasing the cyclopentene concentration (initial cyclopentene/ethylene feed molar ratios) in the ethylene/cyclopentene copolymerization by **4** (runs 14–16), although **4** exhibited the notable activity with efficient cyclopentene incorporation under certain conditions (run 14). The activities by

the Cp* analogue (**2**, runs 6–8) in the ethylene/cyclopentene copolymerizations were lower than those by the Cp analogue (**4**, runs 14–16), and the cyclopentene content in the copolymer was low even under high cyclopentene concentration conditions (13.3 mol%, run 8).

Note that both the indenyl analogue (**1**) and the $t$-BuC$_5$H$_4$ analogue (**3**) showed significant catalytic activities in the ethylene/cyclopentene copolymerization (runs 2–4, 10–13), and that significant decreases in the activities by **1** and **3** were not seen even under the high cyclopentene concentration (high initial cyclopentene/ethylene feed molar ratio) conditions (runs 3, 4, 11, 13). The resultant copolymers possessed high molecular weights with unimodal molecular weight distributions, and the $M_n$ values for the copolymers decreased upon increasing the cyclopentene contents. The cyclopentene contents in the copolymers by **3** were higher than those by **1**, and these results thus indicate that the $t$-BuC$_5$H$_4$ analogue (**3**) should be the most suited catalyst precursor for the ethylene/cyclopentene copolymerization in terms of both catalytic activity and cyclopentene incorporation.

In contrast, the activities in the ethylene/norbornene copolymerizations by **1**- and **3**-MAO catalyst systems decreased upon increasing the norbornene concentration (initial norbornene/ethylene feed ratio, runs 17, 18, 21–23). The observed effect of substituents in the cyclopentadienyl group for the copolymerization between norbornene and cyclopentene should be promising because, as demonstrated previously in the ethylene copolymerizations using the Cp′-aryloxo analogues,[14] the results clearly demonstrate that the efficient catalyst precursors for the desired (co)polymerization can be tuned by modification of the cyclopentadienyl fragment. Copolymerizations of ethylene with cyclohexene by **1**–**4**-MAO catalyst systems were also attempted, but the resultant polymers did not contain cyclohexene (or contained trace amounts of cyclohexene); no improvement in the cyclohexene incorporations could be achieved under these conditions (runs 27–30).

Figure 1 shows selected $^{13}$C NMR spectra for the resultant poly(ethylene-$co$-cyclopentene)s prepared by the Cp′-ketimide analogue–MAO catalyst systems.[17] It is clear that cyclopentene was incorporated with the 1,2-insertion mode, and that no or negligible amounts of 1,3-inserted units which are observed in the copolymer using ordinary zirconocene catalysts[6] were seen. This fact clearly suggests that the cyclopentene incorporation took place in a regioselective manner as seen in some titanium complex catalysts,[4b,7–9] and this exclusive selectivity would be attributed to the lower tendency to undergo β-hydrogen elimination than those using zirconocene complex catalysts as proposed previously.[7,8] These microstructures possessed both isolated and alternating cyclo-

pentene sequences, and resonances ascribed to the repeated cyclopentene inserted units were not seen. Although the resultant poly(ethylene-$co$-cyclopentene)s have no stereoregularity (isotactic, syndiotactic etc.) in all cases, these results strongly suggest that efficient synthesis of alternating poly(ethylene-$co$-cyclopentene)s are possible in this catalysis.

We have shown that the $(t$-BuC$_5$H$_4$)TiCl$_2$[N=C($t$-Bu)$_2$] (**3**)–MAO catalyst system exhibited remarkable catalytic activity with notable cyclopentene incorporation in the ethylene/cyclopentene copolymerization and both the activity as well as the cyclopentene incorporation were highly dependent upon the cyclopentadienyl fragment employed. A unique contrast concerning the ligand effect between the ethylene/NBE copolymerization and the ethylene/cyclopentene copolymerization was observed, and we believe that these results should be promising for designing efficient catalyst precursors for the efficient preparation of cyclic olefin copolymers.

## Experimental Section

### General Procedure

All experiments were carried out under a nitrogen atmosphere in a vacuum atmospheres drybox unless otherwise specified. Anhydrous grade toluene (Kanto Kagaku Co. Ltd) was transferred into a bottle containing molecular sieves (mixture of 3 Å and 4 Å 1/16, and 13×) in the drybox, and was used without further purification. Ethylene was of polymerization grade (purity >99.9%, Sumitomo Seika Co. Ltd) and was used as received. Cyclopentene of reagent grade (Aldrich) was stored in a bottle in the drybox in the presence of molecular sieves. Toluene and AlMe$_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at $ca.$ 50 °C for removing toluene, AlMe$_3$, and then heated at >100 °C for 1 h for completion) in the drybox to give white solids. Various half-titanocenes such as (indenyl)TiCl$_2$[N=C($t$-Bu)$_2$] (**1**),[19] Cp*TiCl$_2$[N=C($t$-Bu)$_2$] (**2**),[20] $(t$-BuC$_5$H$_4$)TiCl$_2$[N=C($t$-Bu)$_2$] (**3**),[19] CpTiCl$_2$[N=C($t$-Bu)$_2$] (**4**)[20] were prepared according to the reported procedures.

Molecular weights and molecular weight distributions for polyethylene, poly(ethylene-$co$-norbornene)s, poly(ethylene-$co$-cyclopentene)s were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH$_{HR}$-H HT×2, 30 cm×7.8 mm ID), ranging from <10$^2$ to <2.8×10$^8$ MW) at 140 °C using $o$-dichlorobenzene containing 0.05 wt/v% 2,6-di-$tert$-butyl-$p$-cresol as eluent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

All $^{13}$C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, $^1$H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me$_4$Si. $^{13}$C NMR spectra for poly(eth-
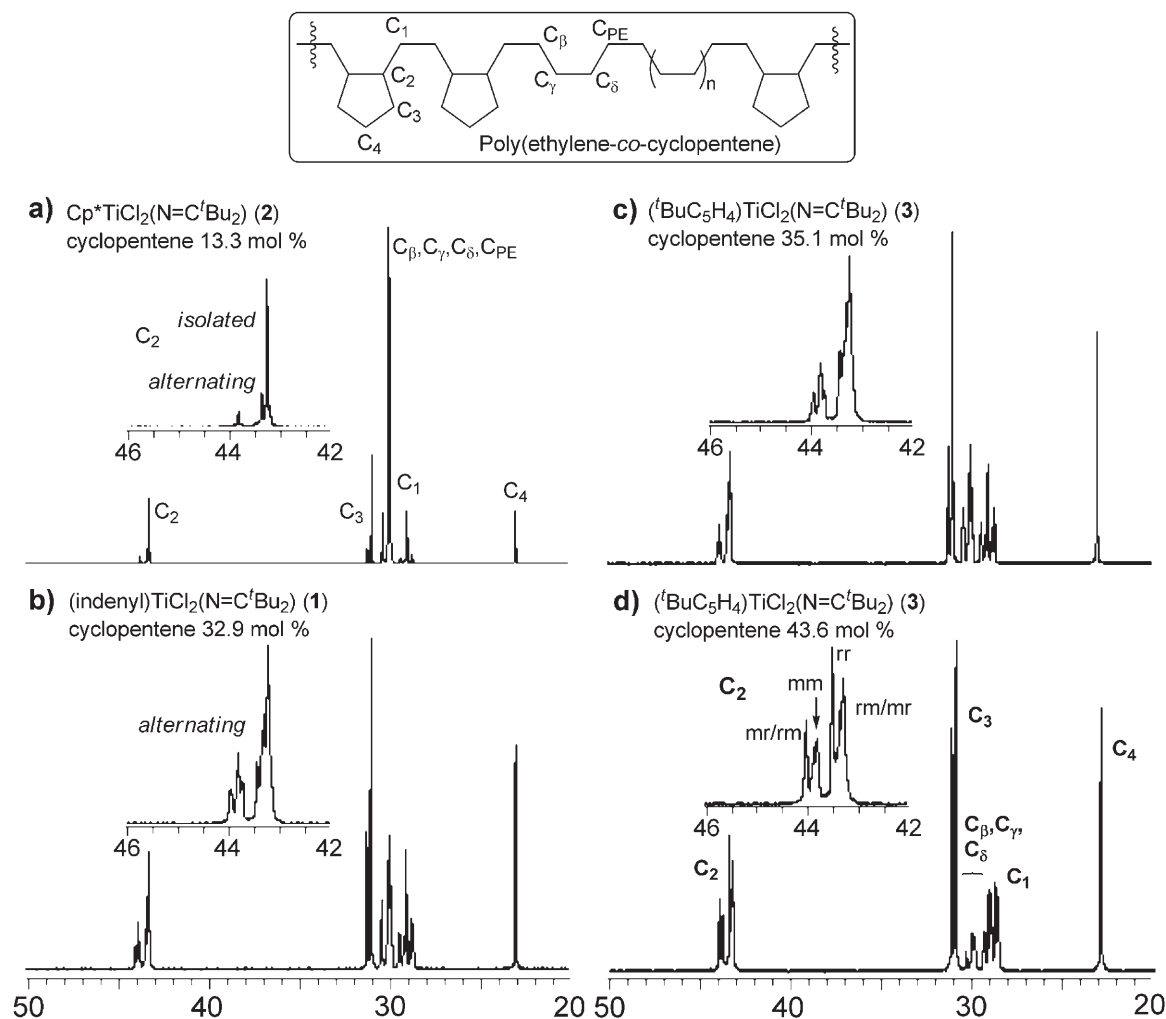
**Figure 1.** $^{13}$C NMR spectra (in benzene-$d_6$/1,2,4-trichlorobenzene at 110 °C) for poly(ethylene-*co*-cyclopentene)s by Cp′TiCl$_2$[N=C(*t*-Bu)$_2$] [Cp′ = indenyl (**1**), Cp* (**2**), and *t*-BuC$_5$H$_4$ (**3**)]–MAO catalyst systems. Poly(ethylene-*co*-cyclopentene)s prepared by (a) **2** (run 8), (b) **1** (run 4), (c) **3** (run 11), (d) **3** (run 13). Detailed polymerization results are shown in Table 1.

ylene-*co*-norbornene)s and poly(ethylene-*co*-cyclopentene)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, $^{13}$C) with proton decoupling. The pulse interval was 5.2 sec, the acquisition time was 0.8 sec, the pulse angle was 90°, and the number of transients accumulated was *ca*. 8000. The analysis samples were prepared by dissolving polymers in a mixed solution of 1,2,4-trichlorobenzene/ benzene-$d_6$ (90/10 wt), and these spectra were measured at 110 °C.

## Copolymerization of Ethylene with Cyclic Olefins (Cyclopentene, Norbornene, Cyclohexene)

A typical procedure (Table 1, run 2) for ethylene/cyclopentene copolymerization was performed as follows: the prescribed amounts of toluene (44.58 mL), cyclopentene (50.0 mmol, 4.42 mL), d-MAO (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale) in the drybox, and the apparatus was then purged with ethylene. The reaction

mixture was then pressurized to 3 atm (total ethylene 4 atm) soon after the addition of a toluene solution (1.0 mL) containing **1** (0.10 μmol). The mixture was magnetically stirred for 10 min, the ethylene remaining was purged after the reaction, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH, and was then dried under vacuum for several hours.

Experimental procedures for (attempted) copolymerization of ethylene with cyclohexene were the same as those for the ethylene/cyclopentene copolymerization except that cyclohexene was used in place of cyclopentene.

Experimental procedures for ethylene/norbornene copolymerization were also the same as those for the ethylene/cyclopentene copolymerization except that toluene (total 50.0 mL) and the prescribed amount of norbornene (50 mmol) were added into the autoclave (100 mL scale).

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[13] For reported examples, the catalytic activities by [Me$_2$Si(C$_5$Me$_4$)(N-t-Bu)]TiCl$_2$, [Me$_2$Si(indenyl)(N-t-Bu)]TiCl$_2$ or the related complexes (modified by Cp, indenyl fragment)–MMAO catalysts were 10–469 kg mol$^{-1}$ Ti·h (ethylene ca. 1 atm, toluene 5 mL, cyclopentene 15 mL)[7]; the activities by bis(phenoxyimine)titanium complex–MAO catalysts were <49 kg mol$^{-1}$ Ti·h (ex. ethylene <1 atm, toluene total 10–15 mL, cyclopentene 13.2 mL).[8] The activities by [(Ph)NC(R$^2$)CHC(R$^1$)O]$_2$TiCl (R$^1$;R$^2$=CF$_3$;CH$_3$, Ph;CF$_3$, t-Bu;CF$_3$)–MMAO catalysts were 38–310 kg-polymer/mol Ti·h (ex. ethylene 1 atm, cyclopentene 5.0 mmol mL$^{-1}$ in toluene).[9] The activities by Ti{3-t-Bu-2-(O)C$_6$H$_3$CH=N(C$_6$F$_5$)}-{2-(C$_6$H$_5$NCH)C$_4$H$_3$N}-Cl$_2$–MAO catalyst were 260–1000 kg polymer/mol Ti·h (ex. ethylene 1 atm, cyclopentene 0.66–4.9 mmol mL$^{-1}$ in toluene);[10] the activity decreased at higher cyclopentene concentration conditions and the molecular weight distributions for the polymers with high cyclopentene contents were broad ($M_w/M_n$=3.6–4.5).

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[16] We did not choose the Cp′-aryloxo analogues, Cp′TiCl$_2$(O-2,6-i-Pr$_2$C$_6$H$_3$), because these complexes–MAO catalyst systems afforded low molecular weight copolymers. Other ketimide analogues, CpTiCl$_2$[N=C(R$^1$)R$^2$] (R$^1$,R$^2$=t-Bu,Ph, Ph,Ph etc.), were not chosen, because these complexes showed low activities to afford polymers with broad molecular weight distributions.[4d]

[17] ¹³C NMR spectra for poly(ethylene-*co*-norbornene)s, poly(ethylene-*co*-cyclopentene)s are shown in the Supporting Information.

[18] In order to control the comonomer (norbornene, cyclopentene) conversion less than 10 mol%, these copolymerizations were terminated for 10 min (at the initial stage). As presented in ref.[4c] no notable decreases in the activities were seen even after 30 min.

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