

# Vinyl and ring-opening metathesis polymerization of norbornene with novel half-sandwich iridium(III) complexes bearing hydroxyindanimine ligands†

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Half-sandwich iridium complexes bearing hydroxyindanimine ligands were synthesized and employed as catalysts for the ROMP and vinyl-type polymerization of norbornene in the presence of methylaluminoxane (MAO).

Norbornene polymerization has been widely used in industrial productions due to the special optical and mechanical properties of the polymers.<sup>1</sup> It has been established that different methods of polymerization produce polynorbornene with different microstructures. Ring opening metathesis polymerization (ROMP) produces polynorbornene with double bonds remaining in the polymer backbone. Up to now, there are two major types of catalysts used for ROMP of norbornene: one is tungsten, molybdenum, rhenium and ruthenium catalysts as metal halides or metal oxides in combination with alkylating agents, the other is metal-carbene complexes based on tungsten, molybdenum or ruthenium, *etc.* Another type of polymerization is vinyl-type polymerization. It opens the  $\pi$ -component of the double bond in norbornene, keeping the bicyclic unit in the polymer chain. Catalysts containing titanium, zirconium, cobalt, chromium, nickel and palladium have been reported for vinyl-type polymerization of norbornene and copolymerization of norbornene with acyclic olefins.<sup>1</sup> Recently, our group has also developed some high activity late transition metal catalysts for vinyl-type polymerization.<sup>2</sup> Although the catalysts for ROMP and vinyl polymerization have been widely developed, there are only a few iridium complexes involved in this field (Chart 1).<sup>1</sup>

In addition, there are several reports on catalysts which can initiate both ROMP and vinyl-type polymerization, such as titanium<sup>3</sup> and cobalt,<sup>4</sup> depending on the cocatalyst ratio or the type of cocatalyst. However, the polymers obtained by those catalysts are only mixtures of the two types, and cannot be separated effectively.

Herein we report half-sandwich iridium complexes containing hydroxyindanimine ligands, which could be used as norbornene polymerization catalysts, producing pure ROMP and

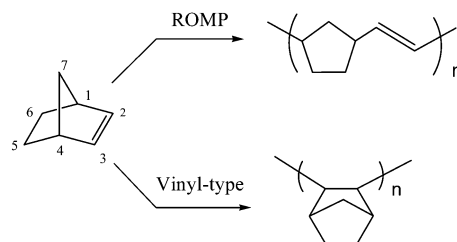


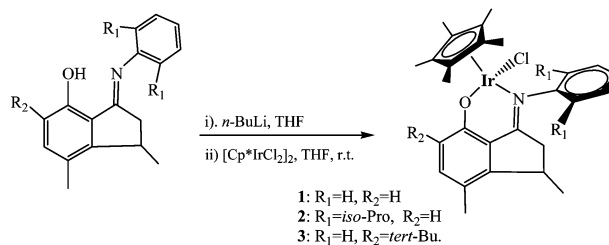
Chart 1 ROMP and vinyl polymerization of norbornene.

vinyl-type polymers under different ratios of cocatalyst (MAO) to iridium.

The half-sandwich iridium complexes **1–3** were synthesized by the reaction of  $[\text{Cp}^*\text{IrCl}(\mu\text{-Cl})_2]$  ( $\text{Cp}^* = \eta^5\text{-pentamethylcyclopentadienyl}$ ) with the corresponding lithium salts of the  $[\text{C}_6\text{H}_3\text{-}i\text{-(R}_1)_2\text{-2,6}]\text{N}=\text{CC}_2\text{H}_3(\text{CH}_3)\text{C}_6\text{H}(\text{CH}_3)(\text{R}_2)\text{OH}$  ligands in THF (Scheme 1).<sup>‡</sup> Complexes **1–3** are air stable orange-red solids. Single crystals of complex **1** and **3** were obtained by recrystallization from hexane-toluene solution at low temperature. The <sup>1</sup>H NMR resonance of complexes **1–3** is well consistent with the expected hydroxyindanimine structure. A sharp single resonance of  $\text{Cp}^*$  appears at about 1.32–1.28 ppm.

X-Ray crystallographic analysis shows that complexes **1** and **3** have similar configurations (Fig. 1(a, b)). Both of them adopt three-legged piano stool geometry, containing a hydroxyindanimine ligand, a  $\text{Cp}^*$  ligand and chloride. The six-membered chelating rings  $\text{Ir}(1)\text{-O}(1)\text{-C}(1)\text{-C}(6)\text{-C}(7)\text{-N}(1)$  locate in the same plane. Although well-refined crystallographic analysis data for complex **2** were not achieved, the DFT optimised molecular structure based on complex **1** and **3** proved to have a similar configuration and bonding character.

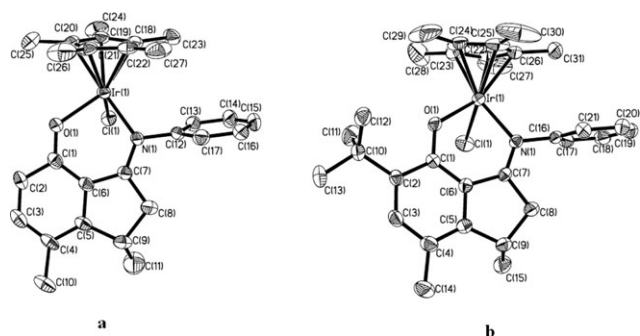
On the basis of our previous experience, iridium complexes can probably initiate olefin polymerization in an efficient way.<sup>5</sup> As a trial, norbornene polymerization tests were carried out. The first attempt consisted of activating complex **1**, **2** and **3** with 1000 eq. methylaluminoxane (MAO) to form an active



Scheme 1 Synthesis of complexes **1**, **2**, **3**.

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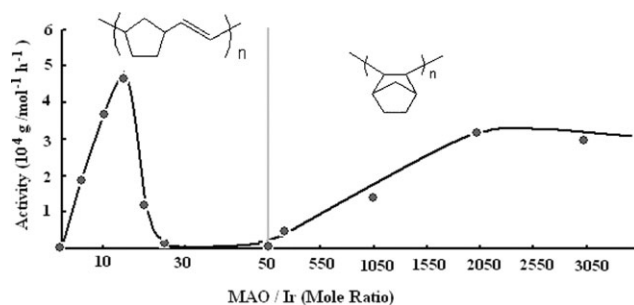


**Fig. 1** Thermal ellipsoid plot of **1** (a) and **3** (b) (30% probability thermal ellipsoids). Selected bond lengths [Å] and angles [°]: **1**, Ir(1)–O(1) = 2.081(6), Ir(1)–N(1) = 2.091(6), Ir(1)–Cl(1) = 2.419(3), O(1)–Ir(1)–N(1) = 90.0(2), O(1)–Ir(1)–Cl(1) = 84.75(19), N(1)–Ir(1)–Cl(1) = 82.67(19). **3**, Ir(1)–O(1) = 2.080(3), Ir(1)–N(1) = 2.101(4), Ir(1)–Cl(1) = 2.4201(17), O(1)–Ir(1)–N(1) = 88.38(13), O(1)–Ir(1)–Cl(1) = 86.57(10), N(1)–Ir(1)–Cl(1) = 83.30(11).

species and employing them in norbornene polymerization. Successively, white precipitate of polymer product was obtained after the system was stirred for 1 hour and terminated with acidic methanol. Besides, a notable color change during polymerization was observed. Especially for complex **2**, when MAO was added into the catalyst (in chlorobenzene) drop by drop, the color of the mixture would change from light orange to dark red gradually. This color would suddenly diminish to light yellow if more MAO was charged. The remarkable color change suggested that some stable intermediate<sup>¶</sup> might be formed by employing a little amount of cocatalyst but easily destroyed when an excessive amount of MAO was added.

Exploration of this intermediate and its catalytic behavior was carried out by adding a small amount of MAO (about 10 eq.) into the precatalyst (complex **2**) so that the mixture maintained the dark red color. Interestingly, white polynorbornene product could also be obtained. If the temperatures rose up to 60 °C within 15 minutes, the viscosity of the solution increased distinctively and made it hard for magnetic stirring, indicating a high activity of this low-MAO system. Due to a more distinct color change than complex **1** and **3**, complex **2** was chosen as precatalyst for the study of the polymerization in detail.

In order to get a full image of the catalytic behavior of this low- (10 eq.) and high- (1000 eq.) MAO/iridium complex system, a series of experiments was carefully performed: a determined amount of MAO (range from 5 eq. to 3000 eq.) was charged into the catalyst–norbornene chlorobenzene solution at 60 °C, and stirred for certain time. The polymer was precipitated from acidic methanol, washed with a great amount of methanol and dried under vacuum. The activities were measured and are shown in Fig. 2. As it demonstrates, the highest activity appears at 15 eq. of MAO which is  $4.8 \times 10^4$  g PNB mol<sup>-1</sup> h<sup>-1</sup>. When more MAO is added, the activity decreases distinctively and 30 eq. of MAO makes this system inactive for norbornene polymerization. After this point, the activity increases gradually with the increase of MAO, and the highest point is observed at 2000 eq. of MAO which is  $2.8 \times 10^4$  g PNB mol<sup>-1</sup> h<sup>-1</sup>. It is important to mention that the zero point of activity coincides with the changing point of color,



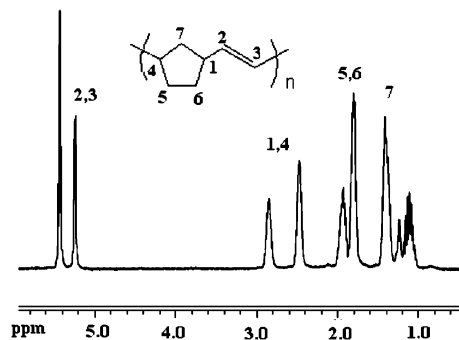
**Fig. 2** Catalytic behaviour of complex **2**.

suggesting two different mechanisms might occur with the increase in amount of cocatalyst (MAO).

Surprisingly, IR, <sup>1</sup>H NMR and <sup>13</sup>C NMR studies of the polymers indicate that: low-MAO catalyst produces the ROMP polymer, while the high-MAO catalyst initiates vinyl-type polymerization. In FT-IR spectra, the low-MAO polymer shows broad bands at 2900 cm<sup>-1</sup> (C–H stretch), 1680 cm<sup>-1</sup> (C=C stretch), and several bands in the fingerprint region especially at 966 cm<sup>-1</sup> and 733 cm<sup>-1</sup> (*trans* and *cis* form of C=C bonds).<sup>6</sup> On the contrary, high-MAO polymer shows no absorption at 1600–1700 cm<sup>-1</sup>, 966 cm<sup>-1</sup> and 733 cm<sup>-1</sup>. But a peak appears at about 942 cm<sup>-1</sup> assigned to the ring system of bicycle [2.2.1] heptane suggesting vinyl-type polymerization.<sup>7</sup>

The <sup>1</sup>H NMR spectra could also prove that low-MAO polymer (Fig. 3) is a pure ROMP product. The =CH resonances appear at 5.22 ppm (*trans*) and 5.04 ppm (*cis*), and the α-H at 2.65 ppm (*cis*) and 2.27 ppm (*trans*). The ratio of *cis/trans* is 0.7. The <sup>13</sup>C NMR shows resonance at 134.0–133.1 ppm (C<sub>2</sub>, C<sub>3</sub>), 43.0–42.0 ppm (C<sub>1</sub>, C<sub>4</sub>), 38.8 ppm (C<sub>7</sub>), 32.7 ppm (C<sub>5</sub>, C<sub>6</sub>), consistent with the previous data reported for polymers of NBE prepared *via* ROMP.<sup>8</sup> In <sup>1</sup>H NMR spectra of the high-MAO polymer (Fig. 4), several broad resonances show at 2.19–2.16 ppm, 2.11–2.07 ppm, 1.64–1.61 ppm, 1.35 ppm, 1.07–0.66 ppm.<sup>9</sup> And resonances at 52–45 ppm (C<sub>2</sub>, C<sub>3</sub>), 39–38 ppm (C<sub>1</sub>, C<sub>4</sub>), 36 ppm (C<sub>7</sub>), 30 ppm (C<sub>5</sub>, C<sub>6</sub>) in <sup>13</sup>C NMR are all in good agreement with the reported vinyl type polymer.<sup>9</sup>

Temperature greatly affects the activity of ROMP in the low-MAO system. At 30 °C, the yield of ROMP polymer was only 1.4% (norbornene : catalyst = 1000 : 1) after 6 hours, but it rose up to 30% at 60 °C. However, for the high-MAO system, the temperature effect is negligible.



**Fig. 3** <sup>1</sup>H NMR of the low-MAO polymer initiated with complex **2**.

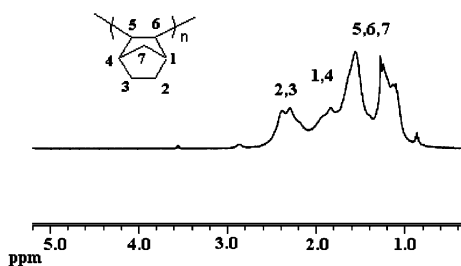


Fig. 4  $^1\text{H}$  NMR of the high-MAO polymer initiated with complex 2.

Attempts to isolate the dark red intermediate were unsuccessful because the addition of MAO brought great complexity and sensitivity to the system. Neither the single component of MAO nor complexes 1–3 in the absence of MAO show any activity for ROMP or vinyl-type polymerization of norbornene. GPC analysis revealed that the molecular weight distributions ( $M_w/M_n$ ) of typical low-MAO (complex 2, 15 eq. of MAO, 60 °C) and high-MAO (complex 2, 1000 eq. of MAO, 60 °C) polymers are 2.63 ( $M_w = 2.90 \times 10^4$ ) and 3.49 ( $M_w = 3.35 \times 10^6$ ), respectively, suggesting a single-site Ir species exists in polymerization. According to the literature, we infer that the catalytically active intermediate might be an iridium carbene complex generated from the alkalization of MAO and subsequent  $\alpha$ -hydrogen abstraction.<sup>10</sup> With the increase of cocatalyst, this carbene complex decomposed, so the activity decreased to zero. After that, another active species formed with greater amount of MAO and the system exhibited vinyl-type polymerization. The mechanism of this catalytic process is still under investigation.

In summary, novel half-sandwich iridium complexes 1–3 were synthesized and employed for norbornene polymerization. Pure ROMP polymer and vinyl-type polymer were obtained depending on the amount of MAO (0–30 eq. for ROMP and >30 eq. for vinyl-type polymerization). This interesting behavior not only provides a promising iridium catalyst for ROMP and vinyl polymerization of norbornene for the first time, but also shed light on copolymerization of norbornene by ROMP and vinyl-type polymerization by changing the cocatalyst ratio.

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## Notes and references

† General procedures for the synthesis of complexes 1, 2 and 3: a solution of *n*-BuLi (1.6 M, 0.28 mL, 0.45 mmol) in hexane was added dropwise to a stirred solution of ligand L<sub>1</sub>–L<sub>3</sub> (0.41 mmol) in THF (10 mL) at –78 °C. The mixture was slowly warmed to room temperature and stirred for 3 h, then channeled to a suspension of [Cp\*IrCl<sub>2</sub>]<sub>2</sub> (0.16 g, 0.2 mmol) in THF (10 mL) and continuously stirred overnight. The solvent was removed under vacuum and the residual solid was extracted with toluene and filtered to remove LiCl. The red solution was concentrated to about 5 mL, and cooled to

–30 °C to give a red solid. Red crystals were obtained through recrystallization from hexane–toluene solution at –30 °C. Crystal data: for complex 1: C<sub>27</sub>H<sub>31</sub>ClIrNO,  $M = 613.18$ , triclinic, space group *P*-1,  $a = 8.659(5)$ ,  $b = 9.353(8)$ ,  $c = 16.720(10)$  Å,  $\alpha = 84.110(12)^\circ$ ,  $\beta = 85.694(9)^\circ$ ,  $\gamma = 63.243(7)^\circ$ ,  $V = 1202.2(14)$  Å<sup>3</sup>,  $D_c = 1.694$  g cm<sup>-3</sup> ( $Z = 2$ ) at 20 °C,  $R_1 = 0.0585$  (all data),  $R_w = 0.1228$  (all data), reflections collected/unique = 5039/4150,  $R_{int} = 0.0347$ . For complex 3: C<sub>32.5</sub>H<sub>42.5</sub>ClIrNO,  $M = 690.83$ , monoclinic, space group *P*2(1)/*c*,  $a = 18.612(14)$ ,  $b = 23.534(12)$ ,  $c = 14.195(9)$  Å,  $\alpha = 90^\circ$ ,  $\beta = 103.526(8)^\circ$ ,  $\gamma = 90^\circ$ ,  $V = 6045(6)$  Å<sup>3</sup>,  $D_c = 1.518$  g cm<sup>-3</sup> ( $Z = 8$ ) at 20 °C,  $R_1 = 0.0531$  (all data),  $R_w = 0.0943$  (all data), reflections collected/unique = 29594/13144,  $R_{int} = 0.0281$ . CCDC 679281 and 679282.

§ Typical procedure for ROMP: 5.0  $\mu\text{mol}$  of complex 2 in 1.0 mL of chlorobenzene, 1.3 g of norbornene in 2.0 mL of chlorobenzene and 2.0 mL of chlorobenzene were added into a polymerization bottle under nitrogen atmosphere at different temperatures. Certain amount of MAO (0.017–0.17 mL, 1.5 mmol mL<sup>-1</sup>) was charged into the system to initiate polymerization. Sometime later, acidic methanol ( $V_{\text{methanol}} : V_{\text{concd.HCl}} = 20 : 1$ ) was added to terminate the reaction. The polymer was isolated by filtration, washed with a large amount of methanol and dried under vacuum for 48 h. Typical procedure for vinyl polymerization: 1.0  $\mu\text{mol}$  of complex 2 in 1.0 mL of chlorobenzene, 1.3 g of norbornene in 2.0 mL of chlorobenzene and 2.0 mL of chlorobenzene were added into a polymerization bottle under nitrogen atmosphere at different temperatures. The total volume of the system was 5 mL. Certain amount of MAO (0.06–2 mL, 1.5 mmol mL<sup>-1</sup>) was added into the system. One hour later, acidic methanol ( $V_{\text{methanol}} : V_{\text{concd.HCl}} = 20 : 1$ ) was added to terminate the reaction. The polymer was isolated by filtration, washed with methanol and dried at 80 °C under vacuum for 48 h.

¶ The intermediate is stable enough to keep in the Schlenk tube in the absence of air and water for a long time (more than 3 days).

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