Vinylic and Ring-Opening Metathesis Polymerization of Norbornene with Novel Half-sandwich Iridium (III) Complexes Bearing Hydroxyindanimine Ligands

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(Supporting Information)

General Procedures.

All manipulations of air- and/or water-sensitive compounds were carried out under nitrogen using standard Schlenk techniques. Solvents were dried by refluxing with appropriate drying agents and distilled under nitrogen prior to use. All chemicals commercially available were used as received without further purification. The starting material $[Cp^*IrCl(\mu\text{-}Cl)]_2$ was prepared according to literature methods. Methylaluminoxane (MAO) was purchased from Aldrich as 10% weight of a toluene solution and used without further purification. ^{1}H NMR spectra were recorded with a Varian Unity-400 pectrometer. Elemental analyses were performed on an Elementarvario EL III Analyzer. FT-IR analyses were detected with a Nicolet-FT-IR-50X spectrometer.

Synthesis of complex 1:

A solution of *n*-BuLi (1.6M, 0.28 mL, 0.45 mmol) in hexane was added dropwise to a stirred solution of ligand $\mathbf{L_1}$ (0.11g, 0.41mmol) in THF (10 mL) at -78 °C. The mixture was slowly warmed to room temperature and stirred for 3 h before it was channeled into a suspension of $(Cp^*IrCl_2)_2$ (0.16g, 0.2 mmol) in THF (10 mL) and continuously stirred overnight to get an orange solution. The solvent was removed under vacuum and the residual solid was solved in toluene and filtered to remove LiCl. The red solution was concentrated to about 5 mL, and cooled to -30 °C to give red solid. Red crystals were obtained through recrystallization from hexane/toluene solution at -30 °C. (0.20g, 80%). Anal. Calcd for $C_{27}H_{31}ClIrNO$ (613.2): C, 52.88; H, 5.10; N, 2.28. Found: C, 52.55; H, 5.01; N, 2.09. ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.40 -7.09 (m, 6H, Ph-H), 6.73 (d, 1H, Ph-H), 3.15 (s, 1H, CH), 2.55 (br, 1H, CH_2), 2.14 (s, 3H, Ph-CH_3), 1.66 (br, 1H, CH_2), 1.27 (s, 15H, Cp*-5CH_3) 1.18 (d, 3H, CH_3) ppm.

Synthesis of complex 2:

A solution of *n*-BuLi (1.6M, 0.28 mL, 0.45 mmol) in hexane was added dropwise to a stirred solution of ligand **L2** (0.144g, 0.41mmol) in THF (10 mL) at -78 °C. The mixture was slowly warmed to room temperature and stirred for 3 h. The solution was channeled to a suspension of $(Cp^*IrCl_2)_2$ (0.16g, 0.2 mmol) in THF (10 mL) and continuously stirred overnight at room temperature. An orange solution was obtained and the solvent was removed under vacuum. After the residual solid was solved in toluene and filtered to remove LiCl, a red solution was concentrated to about 5 mL, and cooled to -30 °C to give red solid. Red crystals were obtained through recrystallization from hexane/toluene solution at -30 °C. (0.25g, 87%). Anal. Calcd for $C_{33}H_{43}ClIrNO$ (697.3): C, 56.84; H, 6.21; N, 2.01. Found: C, 57.08; H, 6.71; N, 1.97. ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.26 -7.02 (m, 4H, Ph-H), 6.61 (d, 1H, Ph-H), 3.10 (m, 1H, CH), 2.47 (m, 1H, CH_2), 2.96 (m, 1H, C*H*(iso-Pro.)$_2$), 2.89 (m, 1H, C*H*(iso-Pro.)$_2$), 2.09(s, 3H, Ph-CH_3), 1.87(d, 1H, CH_2), 1.29-1.10(m, 15H, Cp*-5CH_3, 12H, *iso*-Pro.), 1.00(d, 3H, CH_3) ppm.

Synthesis of complex 3:

A solution of *n*-BuLi (1.6M, 0.28 mL, 0.45 mmol) in hexane was added dropwise to a stirred solution of ligand **L3** (0.132g, 0.41mmol) in THF (10 mL) at -78 °C. The mixture was slowly warmed to room temperature and stirred for 3 h. The solution was channeled to a suspension of $(Cp^{*}IrCl_2)_2$ (0.16g, 0.2 mmol) in THF (10 mL) and continuously stirred overnight at room temperature. A red solution was obtained and the solvent was removed under vacuum. After the residual solid was solved in toluene and filtered to remove LiCl, a red solution was concentrated to about 5 mL, and cooled to -30 °C to give red solid. Red crystals were obtained through recrystallization from hexane/toluene solution at -30 °C. (0.23g, 81%). Anal. Calcd for $C_{31}H_{39}ClIrNO$ (669.3): C, 55.63; H, 5.87; N, 2.09. Found: C, 55.45; H, 6.06; N, 1.89. ^1H NMR (400 MHz, $CDCl_3$, 293 K): δ 7.41 -7.09 (m, 6H, Ph-H), 3.05 (s, 1H, CH), 2.57 (d, 1H, CH_2), 2.12 (s, 3H, Ph-CH_3), 1.91 (d, 1H, CH_2), 1.47 (s, 9H, $C(CH_3)_3$), 1.32 (s, 15H, Cp^{*}-5CH_3), 1.13 (d, 3H, CH_3) ppm.

X-ray Structure Determinations of complex 1 and 3.

Single crystals of complex **1** and **3** suitable for X-ray structural analysis were obtained from *n*-hexane and toluene. The intensity data of the single crystal were collected on the CCD-Bruker Smart APEX system. All determinations of the unit cell and intensity data were performed with graphite-monochromated Mo*Ka* radiation (λ = 0.71073 Å) at room temperature. These structures were solved by direct methods, using Fourier techniques, and refined on F^2 by full matrix least-squares method. All the non-hydrogen atoms were refined anisotropically, and all the hydrogen atoms were included but not refined. For complex **3**, there are two iridium complex molecules and half a n-hexane solvent molecule in the asymmetric unit.

Density functional theory (DFT) calculations.

The simplified structure of **2** was optimized for the singlet state using the DFT method with B3LYP functional in the gas phase in the GAUSSIAN 03 packages. LANL2DZ basis set was used for Ir, and 6-31G basis set was used for C, N, O, H and Cl atoms.

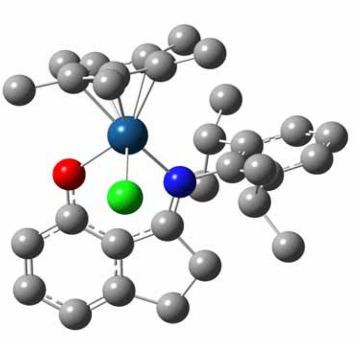

Figure 3 Optimized structure of simplified complex **2**

Norbornene polymerization.

Typical procedure for ROMP: 5.0 μmol of complex **2** in 1.0 mL of chlorobenzene, 1.3 g of norbornene in 2.0 mL of chlorobenzene and 2.0mL of fresh chlorobenzene were added into a polymerization bottle under nitrogen atmosphere at different temperatures. After the mixture was stirred for 15min, certain amount of MAO (0.017-0.17mL, 1.5mmol/mL) was charged into the system and the reaction was initiated. Sometime later, acidic methanol (V_{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 μmol of complex **2** in 1.0 mL of chlorobenzene, 1.3 g of norbornene in 2.0 mL of chlorobenzene and another fresh chlorobenzene were added into a polymerization bottle under nitrogen atmosphere at different temperatures. The total volume of the system is 5 mL. Certain amount of MAO (0.06-2mL, 1.5mmol/mL) was added into the system. One hour later, acidic methanol (V_{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.

Analysis of polynorbornenes.

^{1}H NMR data for PNB were obtained at ambient temperature on Bruker AC 500 spectrometer instrument using *o*-chlorobenzene-d_4 as solvent. ^{13}C NMR spectra were recorded by Varian Unity-400 pectrometer using *o*-chlorobenzene-d_4 for vinyl polymer and $CDCl_3$ for ROMP polymer. FT-IR analyses were detected with a Nicolet-FT-IR-50X spectrometer. Average molecular weight (M_w) and molecular weight distribution (M_w/M_n) values of polynorbornene products were determined using a PL GPC-220 gel permeation chromatograph at 150 °C using a narrow standards calibration and equipped with three PL gel columns (sets of PL gel 10 m MIXED-B LS). Trichlorobenzene was employed as a solvent at a flow rate of 1.00 mL min^{-1}.