



Functionalized N-heterocyclic carbene iridium complexes: Synthesis, structure and addition polymerization of norbornene

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ABSTRACT

Picolyl, pyridine, and methyl functionalized N-heterocyclic carbene iridium complexes $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}]\text{Cl}$ (**4**, $\text{C}^{\wedge}\text{N}$ = 3-Methyl-1-picolylimidazol-2-ylidene), $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}][\text{Cp}^*\text{IrCl}_3]$ (**5**), $[\text{Cp}^*\text{Ir}(\text{C}-\text{N})\text{Cl}]\text{Cl}$ (**6**, $\text{C}-\text{N}$ = 3-Methyl-1-pyridylimidazol-2-ylidene) and $[\text{Cp}^*\text{Ir}(\text{L})\text{Cl}_2]$ (**7**, L = 1,3-dimethylimidazol-2-ylidene) have been synthesized by transmetalation from Ag(I) carbene species, and characterized by ^1H NMR, ^{13}C NMR spectra and elemental analyses. The molecular structures of **5–7** have been confirmed by X-ray single-crystal analyses. The iridium carbene complexes **4** and **6** show moderate catalytic activities (3.03×10^5 g PNB ($\text{mol Ir}^{-1} \text{h}^{-1}$) and 1.70×10^6 g PNB ($\text{mol Ir}^{-1} \text{h}^{-1}$)) for the addition polymerization of norbornene in the presence of methylaluminoxane (MAO) as co-catalyst. The produced polynorbornene have been characterized by IR, ^1H NMR and ^{13}C NMR spectra, showing it follows the vinyl-addition-type of polymerization.

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1. Introduction

N-Heterocyclic carbene ligands (NHCs), which were first reported by Öfele [1], Wanzlick [2] and later isolated in the free state by Arduengo et al. [3], have attracted increasing attention as an extremely useful class of ligands in homogeneous catalysis and organometallic chemistry [4]. Among these, some carbene complexes can catalyze ring-opening metathesis polymerization (ROMP) of norbornene [5], but only a few carbene complexes can be used as the catalysts for the addition polymerization of norbornene.

Bidentate or polydentate ligands containing both strong and weak donor groups (hemilabile ligands) have been widely used in homogeneous catalysis [6,7]. The hemilabile arm in such ligands is capable of reversible dissociation from the metal center. Such dynamic behavior will produce vacant coordination sites that allow complexation of substrates during the catalytic cycle; at the same time the strong donor moiety remains connected to the metal center. The possibility of functionalized nitrogen groups in heterocyclic carbenes makes them suitable for the generation of hemilabile ligands. Recently, our group has reported the facile synthesis of nickel, silver and palladium carbene complexes with functionalized carbene ligands and investigated their application in olefin polymerization [6]. The weak coordinated nitrogen ligands in these carbene complexes makes them possible to cleave off the metal center to form empty site and thus create active center, which is essential for the chain propagation of polymerization.

Concomitantly, the strong σ bond between the carbene electron pair and metal remains and stabilizes the metal center. In order to understand the properties of such hemilabile ligands, their versatile coordination to different metal and the polymerization mechanism of such complexes, herein we report the synthesis and characterization of picolyl, pyridine, and methyl functionalized iridium carbene complexes $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}]\text{Cl}$ (**4**, $\text{C}^{\wedge}\text{N}$ = 3-Methyl-1-picolylimidazol-2-ylidene), $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}][\text{Cp}^*\text{IrCl}_3]$ (**5**), $[\text{Cp}^*\text{Ir}(\text{C}-\text{N})\text{Cl}]\text{Cl}$ (**6**, $\text{C}-\text{N}$ = 3-Methyl-1-pyridylimidazol-2-ylidene) and $[\text{Cp}^*\text{Ir}(\text{L})\text{Cl}_2]$ (**7**, L = 1,3-dimethylimidazol-2-ylidene) (Scheme 1), as well as their catalytic activities towards addition polymerization of norbornene.

2. Results and discussion

It is known that metal–carbene complexes can be synthesized directly from the free NHC ligands prepared by deprotonation of the corresponding imidazolium salts with a strong base, or transmetalation from silver–NHC complexes prepared by direct reaction of the imidazolium salts with silver oxide or etc. [8]. Based on our previous report [6], it was found that the silver (I) carbene routes can function effectively as carbene transfer reagents. In this contribution, we report the iridium complexes by transmetalation from the silver carbene derivatives by a two-step process. The first involves deprotonation of the corresponding imidazolium salts (3-methyl-1-picolylimidazolium iodide (**1**), 3-methyl-1-pyridylimidazolium bromide (**2**) and 1,3-dimethylimidazolium iodide (**3**)) with silver oxide to form the silver carbene species. After filtering the reaction mixture through Celite, the silver carbenes are isolated

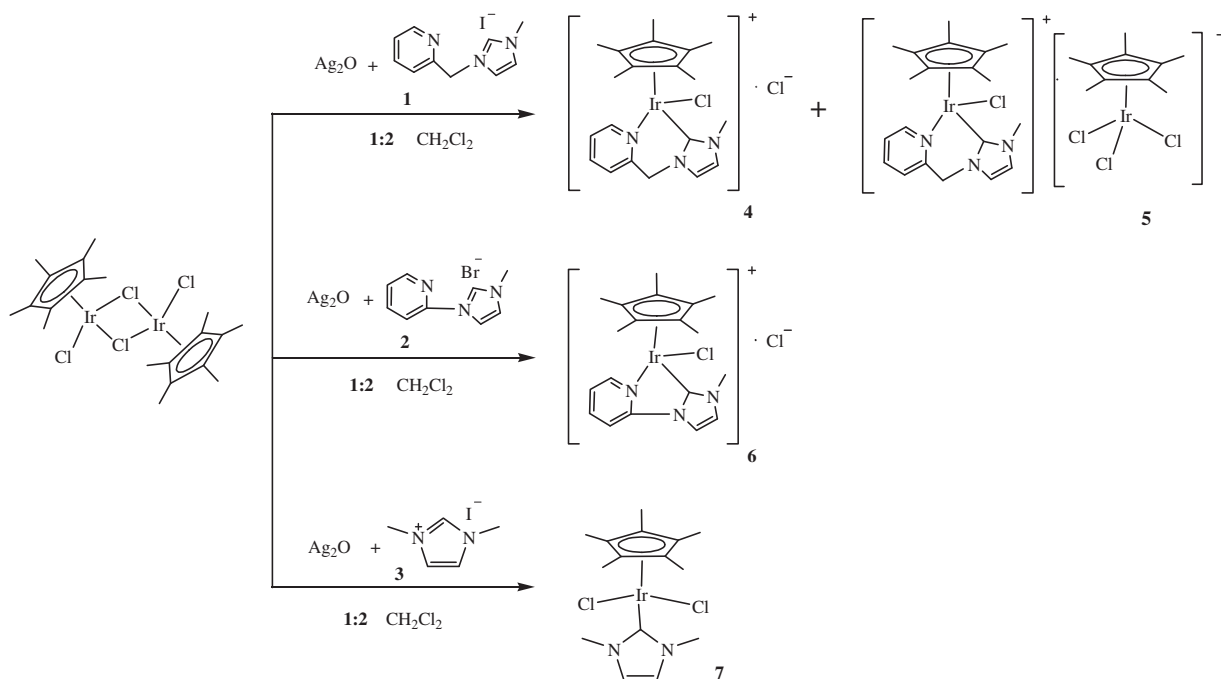
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and used in situ in the second step. The addition of $[\text{Cp}^*\text{IrCl}_2]_2$ to the filtrate afforded the desired complexes, $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}]\text{Cl}$ (**4**), $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}][\text{Cp}^*\text{IrCl}_3]$ (**5**, vide infra), $[\text{Cp}^*\text{Ir}(\text{C}-\text{N})\text{Cl}]\text{Cl}$ (**6**) and $\text{Cp}^*\text{Ir}(\text{L})\text{Cl}_2$ (**7**).

The ^1H NMR spectrum of complex **4** shows a singlet at about 1.6 ppm, characteristic for the Cp^* group. However, the ratio of integrals did not match with stoichiometry, hence column chromatography [9] was applied to purify complex **4**, and complex **5** was also afforded as by-product. Interestingly, the two Cp^* ligands in complex **5** show same chemical shift in NMR spectra (see Supporting information). Differently, complex **6** was isolated as pure product and no by-product was found in ^1H NMR. Considering the ratio of iridium to ligand **1** is 2:1 in complex **5**, we changed the ratio of starting materials $[\text{Cp}^*\text{IrCl}_2]_2$ to ligand **1** to 1:1, and produced com-

plex **5** in a yield of 64%. The ^1H NMR spectra of complexes **4–7** show no signal at δ 9–12 ppm, where the imidazolium $\text{C}_2\text{-H}$ signals of precursors were found (11.66 ppm for **1**, 9.84 ppm for **2** and 10.18 ppm for **3**). The ^{13}C NMR spectroscopic data of **4–7** revealed that metalation of the carbene had occurred, as evidenced by presence of signals at δ = 156.3 ppm (**4**), 156.6 ppm (**5**), 152.8 ppm (**6**) and 158.8 ppm (**7**) in the ^{13}C NMR spectra, which is typical for metal–carbene carbon [10].

Yellow tabular crystals suitable for X-ray diffraction were grown from slow diffusion of toluene to a nearly saturated solution of **5** in dichloromethane. The molecular structure of complex **5** is depicted in Fig. 1 with selected bonds lengths and angles. The molecular structure of the cationic $[\text{Cp}^*\text{Ir}(\text{C}^{\wedge}\text{N})\text{Cl}]^+$ reveals that the metal centre is in a distorted octahedral environment with Cp^* as a



Scheme 1. Synthesis of half-sandwich iridium carbene complexes **4–7**.

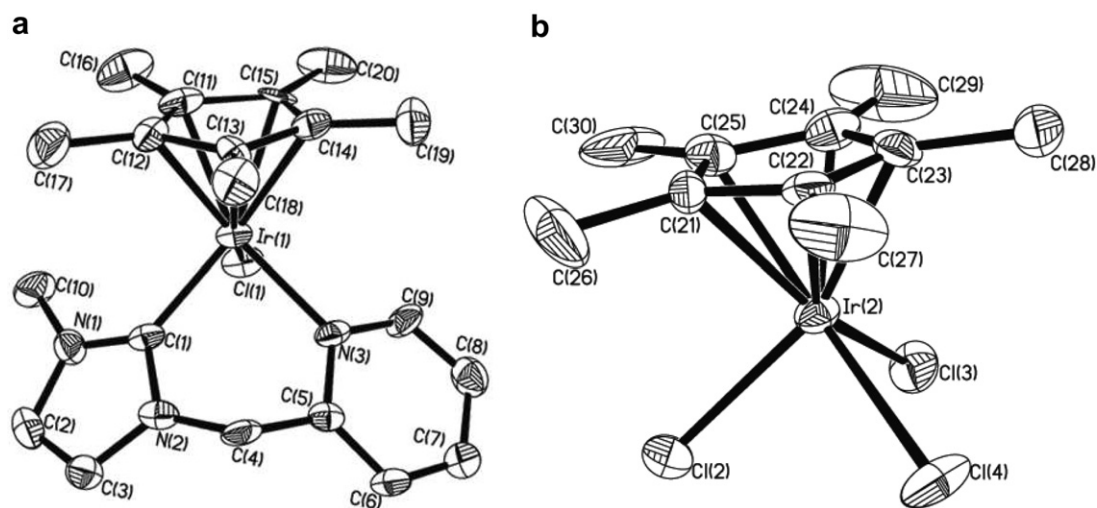


Fig. 1. Molecular structure of complexes **5** (a, cation; b, anion, hydrogen atoms are omitted for clarity), ellipsoids set at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.022(14), Ir(1)–N(3) 2.097(10), Ir(1)–Cl(1) 2.441(3), Ir(2)–Cl(2) 2.423(4), Ir(2)–Cl(3) 2.397(4), Ir(2)–Cl(4) 2.427(4); C(1)–Ir(1)–N(3) 85.4(5), C(1)–Ir(1)–Cl(1) 88.4(4), N(3)–Ir(1)–Cl(1) 84.7(3), Cl(2)–Ir(2)–Cl(3) 88.4(1), Cl(2)–Ir(2)–Cl(4) 88.4(1), Cl(3)–Ir(2)–Cl(4) 86.1(1).

three-coordinated ligand. The Ir–C_{carbene} and Ir–N distances are 2.02 and 2.10 Å, respectively. The Ir–Cl (2.44 Å) and Ir–C_{cent} (1.82 Å) distances lie in the expected range for other known Cp⁺Ir(NHC) complexes [11]. The formation of the six-membered chelate ring of the picolyl-functionalized carbene distorts the coordination geometry of the iridium, with the C–Ir–N bite angle being reduced to 85.4°, similar to 86.6° in our previous picolyl-functionalized nickel carbene complexes [6] and 85.7° in benzyl-functionalized iridium carbene complexes [12]. The dihedral angle of the N-heterocyclic carbene plane with the picolyl plane is 50.0°, which is bigger compared with those in the nickel carbene complexes (44.6°) and the mentioned iridium carbene complex [12] (40.8°). The C–C and C–N bond distances within the imidazol-2-ylidene-based ring systems and the Ir–C bond distances are consistent with both contributions from σ and π donation to the metal center and π stabilization of the carbene onto the adjacent nitrogen atoms. The drawing of the anion shows that the Ir(2) adopts a three-leg stool geometry, with three chlorine symmetrical arranged.

Red prismatic crystals suitable for X-ray diffraction were grown from slow diffusion of hexane to a nearly saturated solution of **6** in dichloromethane. The structure of complex **6** is presented in Fig. 2 with selected bonds lengths and angles. The structure of the cationic [Cp⁺Ir(C–N)Cl]⁺ shows an octahedral iridium centre with Cp⁺ as a three-coordinated ligand. The Ir–C_{carbene} and Ir–N distances are 2.00 and 2.12 Å, respectively. The formation of the five-membered chelate ring of the pyridine-functionalized carbene distorts the coordination geometry of the iridium, with the C–Ir–N bite angle being reduced to 76.0(3)°, comparing to 85.4° in complex **5**. The chelating pyridine is almost in the same plane with the imidazolium ring, with the dihedral angles only 4.85°, which are much smaller compared with 50.0° in complex **5**. The Ir–Cl bond is almost perpendicular to the pyridine and imidazolium ring plane, with an angle of 88.52°.

Light yellow prismatic single-crystals suitable for X-ray crystallography of **7** were also obtained by slow diffusion of hexane into a dichloromethane solution of **7**. The metal center of complex **7** adopts distorted octahedral geometry (Fig. 3). The Ir–C_{carbene} bond length (2.05 Å) are typical for Ir–C σ bonds with very little back-donation. The bond angle C_{cent}–Ir–C_{carbene} (C_{cent} is the central point of the Cp⁺) is 126.9°, thus minimizing the repulsion between the Cp⁺

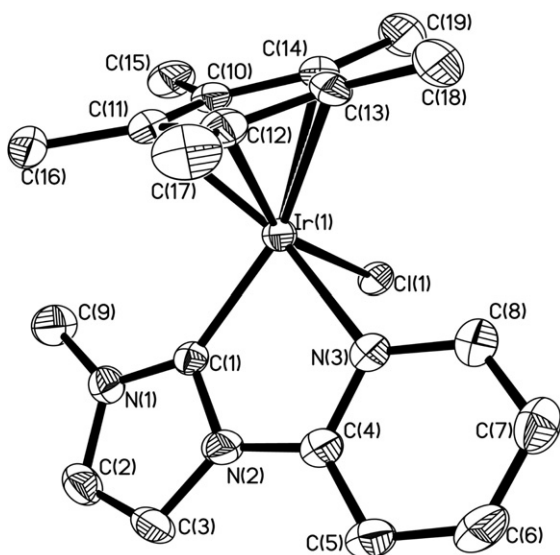


Fig. 2. Molecular structure of complex **6** (cation only, hydrogen atoms are omitted for clarity), ellipsoids set at the 30% probability level. Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.004(7), Ir(1)–N(3) 2.120(6), Ir(1)–Cl(1) 2.441(2); C(1)–Ir(1)–N(3) 76.0(3), C(1)–Ir(1)–Cl(1) 88.53(19), N(3)–Ir(1)–Cl(1) 87.58(17).

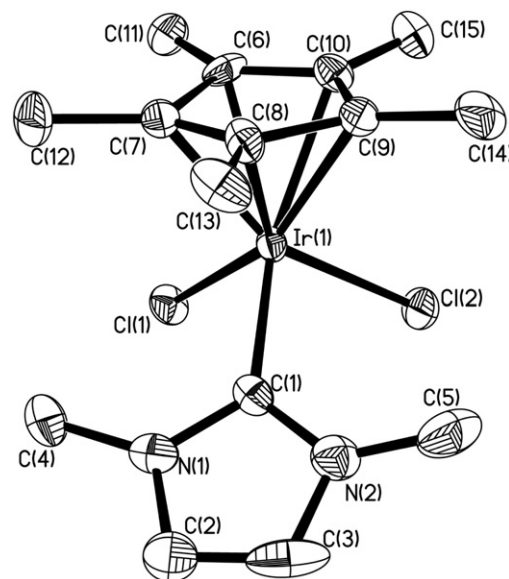


Fig. 3. Molecular structure of **7** (hydrogen atoms are omitted for clarity, ellipsoids set at the 30% probability level). Selected bond lengths [Å] and angles [°]: Ir(1)–C(1) 2.055(13), Ir(1)–Cl(1) 2.440(3), Ir(1)–Cl(2) 2.438(3); C(1)–Ir(1)–Cl(1) 92.7(4), C(1)–Ir(1)–Cl(2) 93.1(4), Cl(1)–Ir(1)–Cl(2) 85.49(13), N(1)–C(1)–N(2) 105.2(12).

and the imidazole ring. The Ir–C_{carbene} bond is almost perpendicular to the Ir–Cl(1)–Cl(2) plane with an angle of 86.0°. The collection data and refinement parameters of **5–7** are summarized in Table 3.

Preliminary experiments indicated that the iridium carbene catalyst **4**, **5** and **6** are active as precatalysts for the addition-type polymerization of norbornene by treatment with MAO. The polymerization results catalyzed by **4–7** in the presence of MAO are summarized in Table 1. No catalytic activity was observed for **4–6** in the absence of MAO. Therefore, the co-catalyst MAO, which can create an empty site for the coordination and insertion of the norbornene, [13] is essential for the norbornene polymerization catalyzed by **4–6**. As seen from the polymerization data in Table 1, complex **6** displays highest catalytic activities than complexes **4**, **5** and **7**. The catalytic activity of complex **5** was tested under the same condition with complexes **4** and **6**, but only trace polymer was obtained. When the polymerization time prolonged to 60 min, complex **5** shows activity about 5.2×10^4 g PNB (mol Ir)^{−1} h^{−1}, which is significantly lower than that of complex **4**. Mechanistically, in the presence of MAO, iridium bonded chlorine group was firstly substituted by a methyl group of MAO and the hemilabile coordinated nitrogen ligand of pyridine dissociate from the Ir center, which generates an empty site essentially for the coordination of norbornene and then insertion of coordinated norbornene to Ir–C bond in the polymerization cycle. At the same time, the strong donor moiety still connects to the iridium, which stabilizes and activates the metal center. This is especially true when an alkyl

Table 1
Polymerization of norbornene with **4–7** activated by methylaluminumoxane (MAO)^a

Entry	Complex	Time	Yield (mg)	Activity ^b
1	4	10	20.2	30.3
2	5	60	20.9	5.2
3	6	10	76.7	115
4	7	60	Trace	–

^a Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; Ir complexes, 0.4 μ mol; norbornene, 20 mmol [norbornene/iridium(molar) = 50000]; Al/Ir = 3500; temperature, 30 °C.

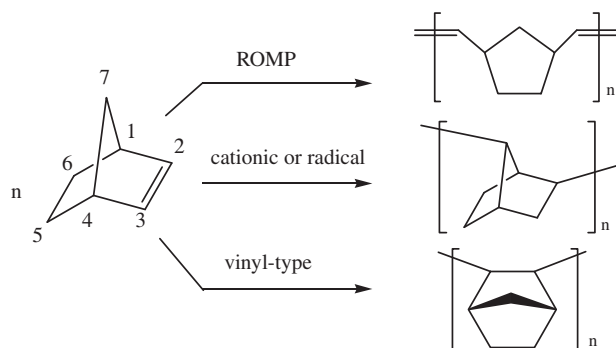
^b In units of 10^4 g PNB (mol Ir)^{−1} h^{−1}.

group coordinates to the iridium center under the activation of MAO, where the alkyl group might accelerate catalysis through olefin insertion into the metal-alkyl bond with subsequent β -H elimination [14]. Considering that the five-member ring (Ir-C_{carbene}-N-C_{py}-N) in complex **6** has a more ring tension than the six-member ring (Ir-C_{carbene}-N-C_{linker}-C_{py}-N) in complexes **4** and **5**, then the five-member ring in the complex **6** is easier to be opened than the six-member ring in complex **4** and **5**, thus the empty site is formed more easily in complex **6** than in complexes **4** and **5** and the catalytic activity of **6** is more higher than that of **4** and **5**. Indeed, the complex **7** shares no hemilabile ligands and shows no catalytic ability towards norbornene polymerization. As for the activities difference of **4** and **5**, we speculate that the chlorine group in anion of **5** consumed many MAO and not enough empty site for the polymerization is created, which make the polynorbornene yield reduced.

To investigate the reaction parameters affecting addition polymerization of norbornene, the catalytic precursor **6** was studied under different reaction conditions. Varying the MAO:**6** ratio (expressed here as Al:Ir ratio) had considerable effects on catalytic activities and molecular weight, as shown in Table 2. When Al:Ir is below 1000, the obtained polymer is negligible. The activities increase first and then decrease with the increase of the Al/Ir ratio under the experimental conditions (entry 1–4, Table 2). The molecular weights of polynorbornene are in the level of 10^5 g mol⁻¹. The effect of Al/Ir ratio on the molecular weight of polymer is not as sensitive as that on the activity. M_v varies irregularly with the increase of Al/Ir ratio.

The influence of the reaction temperature on the catalytic activities and M_v was also studied. When the temperature is below -20 °C or above 70 °C, only negligible polymer can be obtained. With increasing reaction temperature (entry 3, 5–8, Table 2), the catalytic activities first increase and then decrease showing the highest activity (entry 7, Table 2 and 1.70×10^6 g PNB mol⁻¹ Ir h⁻¹) at 10 °C. This is because the concentration of active centers activated by MAO increases as the temperature is increased. At the same time complex **6** usually becomes unstable at high temperature under the presence of MAO. The highest activity at 10 °C is the result of the compromise of two factors. The molecular weights drop first then increase when the polymerization temperature rises from -10 °C to 50 °C. The highest activity of complex **6** is no doubt lower than that of our previous nickel [6a] and palladium [6b] complexes. It can be speculated that the group 10 metal complexes are superior to the group 9 metal complexes when as catalyst of norbornene polymerization reaction.

Norbornene and its derivatives can be polymerized in three different ways: ring-opening metathesis polymerization (ROMP), cationic or free-radical polymerization, and addition polymerization (Scheme 2) [15], each route leading to its own polymer type with



Scheme 2. Schematic representation of the three different types of polymerization for norbornene.

different in structure and properties from the other two. The addition-type polymer shows interesting and unique properties like high glass transition temperature, large refractive index, low dielectric constant, and excellent optical transparency due to the bicyclic structure remains intact and only the π -bond of the cycloolefin is opened [16]. The microstructure of the obtained polymers is characterized by IR, ¹H NMR and ¹³C NMR. All the polymers have similar IR, ¹H NMR and ¹³C NMR spectra and characteristic of addition-type PNB, and revealed no traces of double bonds that are typical for ROMP PNB.

In IR spectra, there are no absorption at 1680–1620 cm⁻¹, especially about 960 cm⁻¹ and 735 cm⁻¹, assigned to the *trans* and *cis* form of double bonds [16], respectively, which are characteristic of the ROMP structure of polynorbornene. On the contrary, these absorption peaks at about 942 cm⁻¹ are observed, which can be

Table 3
Summary of Crystallographic Data for 5–7

	5	6	7
Chemical formula	C ₃₀ H ₄₃ Cl ₄ Ir ₂ N ₃ O	C ₁₉ H ₃₀ Cl ₂ IrN ₃ O ₃	C ₁₅ H ₂₃ Cl ₂ IrN ₂
Formula weight	987.87	611.56	494.45
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	P2 ₁ /n	P1	Cc
a (Å)	7.517(2)	8.157(6)	8.939(4)
b (Å)	29.924(9)	11.395(8)	14.300(4)
c (Å)	14.945(5)	13.383(9)	13.092(4)
α (°)	90	102.469(9)	90
β (°)	92.82	106.914(9)	100.506(6)
γ (°)	90	95.059(9)	90
V (Å ³)	3357.8(18)	1146.8(14)	1645.6(9)
Z	4	2	4
D _{calcd} (mg/m ³)	1.954	1.771	1.996
μ (mm ⁻¹)	8.264	6.078	8.430
F(000)	1896	600	952
θ Limits (°)	1.36–25.01	1.64–27.12	2.72–27.11
Limiting indices	-8, 8; -35, 35; -17, 9	-10, 10; -14, 11; -15, 17	-11, 8; -18, 18; -16, 16
Reflections collected	14032	5700	4040
Independent reflections	5894 (0.0896)	4821 (0.0239)	2551 (0.0578)
[R _{int}]			
Completeness to theta (°)	25.01 (99.8%)	27.12 (94.8%)	27.11 (98.2%)
Maximum and minimum transmission	0.6369 and 0.4920	0.5816 and 0.3761	0.4861 and 0.2834
Goodness-of-fit (GOF) on F ²	1.029	1.035	1.012
Final R indices [I > 2(I)] ^a	R ₁ = 0.0619 wR ₂ = 0.1051	R ₁ = 0.0355 wR ₂ = 0.0955	R ₁ = 0.0401 wR ₂ = 0.0920
R indices (all data)	R ₁ = 0.1097 wR ₂ = 0.1185	R ₁ = 0.0528 wR ₂ = 0.1075	R ₁ = 0.0397 wR ₂ = 0.0937
Largest difference peak and hole (e/Å ³)	2.559 and -0.942	1.593 and -0.848	1.319 and -0.885

$$^a R_1 = \frac{\sum w|F_o| - |F_c|}{\sum w|F_o|}; wR_2 = \left[\frac{\sum w(F_o^2 - |F_c|^2)^2}{\sum w|F_o|^2} \right]^{1/2}$$

Table 2
Influence of MAO amount on the activities of complex **6**^a

Entry	Al/Ir	T (°C)	Yield (mg)	Activity ^b	M_v ^c
1	2000	30	66.4	9.96	5.1
2	3000	30	68.1	10.2	5.0
3	4000	30	84.7	12.7	5.8
4	5000	30	67.8	10.2	4.9
5	4000	-10	98.5	14.8	8.2
6	4000	0	104.4	15.7	3.2
7	4000	10	113	17.0	2.4
8	4000	20	108.7	16.3	2.5

^a Polymerization conditions: solvent, chlorobenzene; total volume, 10 mL; Ir complex **6**, 0.4 μ mol; norbornene, 20 mmol [norbornene/iridium(molar)] = 50000; reaction time, 10 min.

^b In units of 10^5 g of PNB (mol of Ir)⁻¹ h⁻¹.

^c 10^5 g/mol.

assigned to the ring system of bicycle [2.2.1] heptane, as Kennedy noted [17]. ^1H NMR and ^{13}C NMR spectra confirmed the above conclusions. ^1H NMR spectrum shows signals in the 0.7–3.0 ppm range (maxima at 1.22, 1.59, 2.29 ppm). No resonances are displayed at about δ 5.1 and 5.3 ppm, assigned to the *cis* and *trans* form of double bonds, which generally indicates the presence of the ROMP structure. The ^{13}C NMR spectrum shows the main four groups of resonances: δ (50.4, 48.1, 47.2), (39.4, 38.6), (35.8, 35.0), (31.6, 29.3) ppm, attributed to carbons 2 and 3, carbons 1 and 4, carbon 7, carbons 5 and 6, respectively. The ^{13}C NMR spectrum is similar to that reported by Patil et al. [18]. These data indicate that the polynorbornene obtained with the aforementioned catalysts was an addition polymerization (2, 3-linked) product, i.e. no ROMP was observed.

3. Conclusion

Four iridium carbene complexes were synthesized by the transmetalation method. Preliminary study indicates that the new iridium carbene complexes **4** and **6** show moderate activity as catalyst precursor in vinyl-addition polymerization of norbornene in the presence of MAO. To the best of our known, this is the first report that the iridium carbene complexes catalyze vinyl-addition polymerization of norbornene. The mechanism of norbornene polymerization reaction is discussed.

4. Experimental

4.1. General procedures

Manipulation of air-sensitive compounds was performed under a controlled dry argon atmosphere using standard Schlenk techniques or inert-gas gloveboxes. Solvents were purified by standard methods prior to use. Norbornene was dried over Na and then distilled under argon immediately prior to use. Methylaluminoxane (MAO), 1-methylimidazole, 2-bromopyridine and 2-picolychloride hydrochloride were purchased from Witco and Acros, respectively. 3-Methyl-1-picolyimidazolium bromide (**1**), 3-methyl-1-pyridylimidazolium iodide (**2**) [19] and 1,3-dimethylimidazolium iodide (**3**) [20] were prepared according to the literatures reported. Other solvents were used as received as technical grade solvents. ^1H NMR (500 MHz), ^{13}C NMR (125 MHz) spectra were recorded on a Bruker DMX 500 Spectrometer at room temperature in CDCl_3 solutions for ligands and complexes, and *o*-dichlorobenzene- d_4 solutions for polymers using TMS as an internal standard. IR spectra were recorded on the Nicolet AVATAR-360 IR spectrometer. Elemental analyses for C, H and N were carried out on an Elementar III Vario El Analyzer. The intrinsic viscosity $[\eta]$ was measured in chlorobenzene at 25 °C using an Ubbelohde viscometer. Viscosity average molecular weight (M_v) values of polymer were calculated by the following equation [16h]: $[\eta] = 5.97 \times 10^{-4} M_v^{0.56}$.

4.2. Synthesis of **4** and **5**

A mixture of **1** (90 mg, 0.3 mmol) and silver oxide (42 mg, 0.18 mmol) was taken up in 10 mL of CH_2Cl_2 and was stirred for 4 h. The solution was filtered through Celite, and then $[\text{Cp}^*\text{IrCl}_2]_2$ (120 mg, 0.15 mmol) was added; the solution was stirred at room temperature for 10 h and filtered. After evaporating the solvent under reduced pressure, the residue was redissolved in CH_2Cl_2 and purified by column chromatography. Elution with CH_2Cl_2 /acetone (10:1) and then CH_2Cl_2 /acetone (1:1) resulted in the separation of an orange band containing compound **4** and a yellow band containing compound **5**. Yield: 105 mg (61%). ^1H NMR (500 MHz, CDCl_3): δ 8.72 (d, 1H, H_{py}), 8.27 (d, 1H, H_{py}), 7.98 (s, 1H, H_{py}), 7.85

(t, 1H, H_{im}), 7.31 (t, 1H, H_{im}), 6.99 (s, 1H, H_{py}), 6.55 (d, 1H, NCH_2), 4.70 (d, 1H, NCH_2), 3.83 (s, 3H, NCH_3), 1.64 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR (125 MHz, CDCl_3): δ 156.3 ($\text{C}_{\text{carbene-Ir}}$), 155.4 (C_{py}), 153.5 (C_{py}), 140.2 (C_{py}), 127.5 (C_{py}), 125.8 (C_{im}), 124.2 (C_{im}), 122.4 (C_{py}), 90.5 ($\text{C}_5(\text{CH}_3)_5$), 55.0 (NCH_2), 36.8 (NCH_3), 9.4 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calc. for $\text{C}_{20}\text{H}_{26}\text{Cl}_2\text{IrN}_3$ (571.6): C, 42.03; H, 4.58; N, 7.35. Found: C, 41.92; H, 4.60; N, 7.31%. Yellow tabular crystals suitable for X-ray diffraction analysis were grown by diffusion of toluene into a nearly saturated solution of **5** in CH_2Cl_2 at ambient environment and room temperature. Yield: 43 mg (15%, according to the ligand **1**). ^1H NMR (500 MHz, CDCl_3): δ 8.69 (d, 1H, H_{py}), 8.59 (d, 1H, H_{py}), 8.21 (s, 1H, H_{py}), 7.91 (t, 1H, H_{im}), 7.24 (t, 1H, H_{im}), 6.88 (s, 1H, H_{py}), 6.59 (d, 1H, NCH_2), 4.80 (d, 1H, NCH_2), 3.81 (s, 3H, NCH_3), 1.63 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ from the cation), 1.63 (s, 15H, $\text{C}_5(\text{CH}_3)_5$ from the anion). ^{13}C NMR (125 MHz, CDCl_3): δ 156.6 ($\text{C}_{\text{carbene-Ir}}$), 155.1 (C_{py}), 153.0 (C_{py}), 139.9 (C_{py}), 128.0 (C_{py}), 125.6 (C_{im}), 124.6 (C_{im}), 121.9 (C_{py}), 90.4 ($\text{C}_5(\text{CH}_3)_5$ from the cation) 90.4 ($\text{C}_5(\text{CH}_3)_5$), 55.2 (NCH_2), 36.6 (NCH_3), 9.3 ($\text{C}_5(\text{CH}_3)_5$ from the cation), 9.3 ($\text{C}_5(\text{CH}_3)_5$ from the anion). Anal. Calc. for $\text{C}_{30}\text{H}_{41}\text{Cl}_4\text{Ir}_2\text{N}_3 \cdot \text{H}_2\text{O}$ (987.87): C, 36.47; H, 4.39; N, 4.25. Found: C, 36.38; H, 4.37; N, 4.27%.

4.3. Synthesis of **6**

A mixture of **2** (72 mg, 0.3 mmol) and silver oxide (42 mg, 0.18 mmol) was taken up in 10 mL of CH_2Cl_2 and was stirred for 4 h. The solution was filtered through Celite, and then $[\text{Cp}^*\text{IrCl}_2]_2$ (120 mg, 0.15 mmol) was added; the solution was stirred at room temperature for 10 h and filtered. After evaporating the solvent under reduced pressure, the residue was washed with ether and then dried in a vacuum. Yellow crystals suitable for X-ray diffraction analysis were grown by diffusion of hexane into a nearly saturated solution of **6** in CH_2Cl_2 at ambient environment and room temperature. Yield: 137 mg (82%). ^1H NMR (500 MHz, CDCl_3): δ 9.04 (s, 1H, H_{py}), 8.91 (d, 1H, H_{py}), 8.44 (t, 1H, H_{py}), 8.21 (t, 1H, H_{im}), 7.43 (t, 1H, H_{im}), 7.39 (t, 1H, H_{py}), 4.04 (s, 3H, NCH_3), 1.80 (s, 15H, $\text{C}_5(\text{CH}_3)_5$). ^{13}C NMR (125 MHz, CDCl_3): δ 152.8 ($\text{C}_{\text{carbene-Ir}}$), 149.4 (C_{py}), 143.0 (C_{py}), 135.1 (C_{py}), 125.9 (C_{py}), 123.7 (C_{im}), 120.2 (C_{im}), 115.0 (C_{py}), 92.0 ($\text{C}_5(\text{CH}_3)_5$), 37.6 (NCH_3), 9.6 ($\text{C}_5(\text{CH}_3)_5$). Anal. Calc. for $\text{C}_{19}\text{H}_{24}\text{Cl}_2\text{IrN}_3 \cdot 3\text{H}_2\text{O}$ (611.59): C, 37.31; H, 4.94; N, 6.87. Found: C, 37.30; H, 4.98; N, 6.85%.

4.4. Synthesis of **7**

A mixture of **3** (112 mg, 0.5 mmol) and silver oxide (70 mg, 0.3 mmol) was taken up in 10 mL of CH_2Cl_2 and was stirred for 4 h. The solution was filtered through Celite, and then $[\text{Cp}^*\text{IrCl}_2]_2$ (200 mg, 0.25 mmol) was added; the solution was stirred at room temperature for 10 h and filtered. After and evaporating the solvent under reduced pressure, the residue was washed with ether and then dried in a vacuum. Light yellow crystals suitable for X-ray diffraction analysis were grown by diffusion of hexane into a nearly saturated solution of **7** in CH_2Cl_2 at ambient environment and room temperature. Yield: 205 mg (83%). ^1H NMR (500 MHz, CDCl_3): 6.97 (d, 2H, H_{im}), 3.99 (s, 6H, CH_3), 1.65 (s, 15H, $\text{C}_5(\text{CH}_3)_5$) ppm. ^{13}C NMR (125 MHz, CDCl_3): δ 158.8 ($\text{C}_{\text{carbene-Ir}}$), 123.7 (C_{im}), 92.2 ($\text{C}_5(\text{CH}_3)_5$), 37.6 (NCH_3), 9.78 ($\text{C}_5(\text{CH}_3)_5$) ppm. Anal. Calc. for $\text{C}_{15}\text{H}_{23}\text{Cl}_2\text{IrN}_2$ (494.45): C, 36.43; H, 4.69; N, 5.67. Found: C, 36.32; H, 4.65; N, 5.70%.

4.5. Norbornene polymerization

In a typical procedure (entry 5, Table 2), 0.4 μmol of Iridium carbene complex **6** in 0.5 mL of chlorobenzene, 0.02 mol of norbornene in 4.7 mL of chlorobenzene and another 3.7 mL of fresh chlorobenzene were added into a polymerization bottle with strong stirring under an Ar atmosphere. After the mixture was kept at

30 °C for 10 min, 1.1 mL of MAO was charged into the polymerization system via a syringe and the reaction was started. Ten minutes later, the acidic ethanol ($V_{\text{ethanol}}:V_{\text{concd.HCl}} = 20:1$) was added to terminate the reaction. The PNB was isolated by filtration, washed with ethanol and dried. For all polymerization procedures, the total reaction volume was 10 mL, which can be achieved by the variation of the amount of chlorobenzene when necessary. IR, ^1H and ^{13}C NMR spectra of the polymers produced by the different precatalysts and conditions are similar; therefore only one set of data is given. IR (KBr disk): 2947, 2870, 1475, 1452, 1371, 1296, 1259, 1223, 1147, 1107, 943, 893, 806 cm^{-1} . ^1H NMR (500 MHz, *o*-chlorobenzene- d_4): δ 0.7–3.0 (m, maxima at 1.22, 1.59, 2.29 ppm). ^{13}C NMR (125 MHz, *o*-chlorobenzene- d_4): δ (50.4, 48.1, 47.2), (39.4, 38.6), (35.8, 35.0), (31.6, 29.3) ppm.

4.6. X-ray crystallography

Diffraction data of **5**, **6** and **7** were collected on a Bruker SMART APEX CCD diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). All the data were collected at ambient temperature and the structures were solved by Patterson method (**6**) or direct method (**5**, **7**) and subsequently refined on F^2 by using full-matrix least-squares techniques (SHELXL) [21]. The non-hydrogen atoms were refined anisotropically, and hydrogen atoms were located at calculated positions. Details of the data collection and refinement are summarized in Table 3.

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Appendix A. Supplementary material

CCDC 693361, 693362 and 693363 contains the supplementary crystallographic data for **5**, **6** and **7**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2008.08.019.

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