This is an *Accepted Manuscript*, which has been through the Royal Society of Chemistry peer review process and has been accepted for publication.

Accepted Manuscripts are published online shortly after acceptance, before technical editing, formatting and proof reading. Using this free service, authors can make their results available to the community, in citable form, before we publish the edited article. We will replace this *Accepted Manuscript* with the edited and formatted *Advance Article* as soon as it is available.

You can find more information about *Accepted Manuscripts* in the **Information for Authors**.

Journal Name

ARTICLE

Synthesis, Structures, and Norbornene Polymerization Behavior of C(sp^3), N-Chelated Palladacycles Bearing *o*-Aryloxide-N-Heterocyclic Carbene Ligands†

Liang Dang,[a] Jing Guo,[b] Haibin Song,[a] Binyuan Liu[b] and Baiquan Wang[*a,c]

Treatment of the *o*-hydroxyaryl imidazolium pro-ligands (2-OH-3,5-*t*Bu$_2$C$_6$H$_2$)(R)(C$_3$H$_3$N$_2$)$^+$Br$^-$ [R = Mes (**1a**), Ph (**1b**), iPr (**1c**), Me (**1d**)] with Ag$_2$O afforded the corresponding silver complexes **2a–d**. Subsequent metal-exchange reactions of **2a–d** with [Pd(OAc)(8-Me-quin-H)]$_2$ (**3**) yielded the desired C(sp^3), N-chelated and *o*-aryloxide-NHC-ligated palladacycle complexes **4a–d** in 60–80% yields. When the *N*-tert-butyl substituted *o*-hydroxyaryl imidazolium pro-ligand **1e** reacted with **3** in the presence of K$_2$CO$_3$ in dioxane, the palladacycle complex **4e**, in which the NHC adopted an abnormal binding (C$_4$-bonding), was obtained in 20% yield. All these complexes were fully characterized by ^{1}H and ^{13}C NMR spectra, high-resolution mass spectrometry (HRMS), and elemental analysis. Single-crystal X-ray diffraction analysis results further confirmed the molecular structures of **4a–c** and the abnormal binding of NHC in **4e**. With methylaluminoxane (MAO) as cocatalyst these palladacycles showed excellent catalytic activities up to 10^7 g of PNB (mol of Pd)$^{-1}$ h^{-1} in the addition polymerization of norbornene.

Introduction

In recent years, as a kind of important late transition metal catalysts, palladium complexes have been extensively studied and applied for polymerization.[1] Palladacycles are one of the most important classes of organopalladium complexes because of their versatile frameworks, remarkable catalytic activity, synthetically easy accessibility, extra stability toward air and moisture, and relatively low toxicity.[2] However, only a few palladacycles have been applied for the homo- and copolymerization of vinyl monomers.[3,4]

Since the isolation and structural characterization of the free N-heterocyclic carbenes (NHC) by Arduengo,[5] N-heterocyclic carbenes have become a well established class of new ligands in organometallic chemistry and catalysis.[6] Recently, we succeeded in developing of a series of *o*-hydroxyaryl-substituted unsaturated NHC pro-ligands and their transition metal complexes.[4,7] The *o*-aryloxide-NHC ligands possess an analogue of the salicylaldimine framework, a common motif in organometallic chemistry and extensively employed in catalytic organic reactions and olefin polymerization.[8] As expected, this kind of salicylaldimine-like NHC metal complexes showed excellent catalytic properties in the addition polymerization or ROMP of norbornene. Following these works, in this paper we further synthesized a series of C(sp^3), N-chelated and *o*-aryloxide-NHC-ligated palladacycle complexes. This kind of complexes combines the reactivity of the C(sp^3)–Pd bonds and stability of the palladacycle complexes, and may be potential polymerization catalysts. In order to examine the influence of the C(sp^3), N-chelated palladacycle structure on the catalytic properties, the addition polymerization of norbornene with these complexes is also investigated in the presence of methylaluminoxane (MAO).

Results and discussion

Synthesis of Palladium Complexes

Following the synthetic route reported previously by our group,[7a,b] a series of *o*-hydroxyaryl imidazolium pro-ligands can be easily synthesized by the reactions of 4-bromo-2,4,6-tri-*tert*-butyl-2,5-cyclohexadien-1-one with different N-substituted imidazoles. Treatment of *o*-hydroxyaryl imidazolium pro-ligands **1a–d** with Ag$_2$O afforded the corresponding silver complexes **2a–d**. Subsequent metal-exchange reactions of **2a–d** with [Pd(OAc)(8-Me-quin-H)]$_2$ (**3**) yielded the desired C(sp^3), N-chelated *o*-aryloxide-NHC-ligated palladacycle complexes **4a–d** (Scheme 1). However, treatment of the *N*-tert-butyl substituted *o*-hydroxyaryl imidazolium pro-ligand **1e** with Ag$_2$O and **3** cannot afford the desired C(sp^3), N-chelated *o*-aryloxide-NHC-ligated palladacycle complex, due to the steric effect of the bulky *tert*-butyl group at the NHC. Instead, by the reaction of **1e**, K$_2$CO$_3$, and **3** in dioxane at 20 °C, an abnormal NHC palladium complex **4e** was obtained in 20% yield.
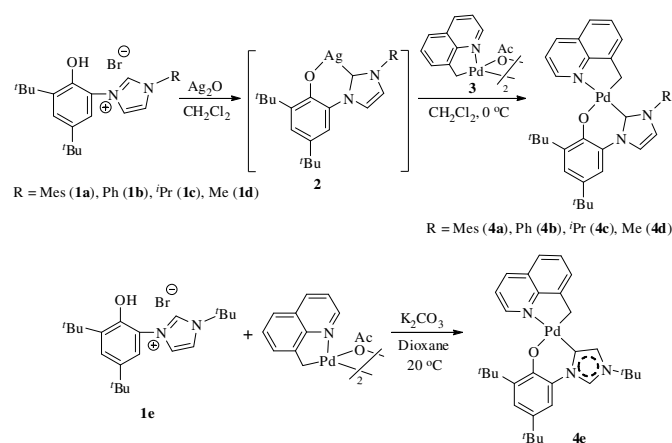
Scheme 1 Synthesis of Palladium Complexes **4a–d** and **4e**.

Complexes **4a–e** are soluble in CH_2Cl_2, THF, dioxane, acetone, toluene, diethyl ether, and even hydrocarbon solvents like pentane. Complexes **4a** and **4b** are air and moisture stable, while complexes **4c–e** are air and moisture sensitive and decompose slowly even under −20 °C in solution and solid state. This is different from the corresponding $C(sp^2)$, N-chelated and *o*-aryloxide-NHC-ligated palladacycle complexes, which are all air and moisture stable.[4]

In the ^{1}H NMR spectra of **4a–d** the signals of the imidazole and phenol protons for the pro-ligands disappeared completely. The signals of CH_2-Pd are all sharp singlet for **4a–d**. The characteristic signals of carbene carbons in their ^{13}C NMR spectra (168.8 ppm for **4a**, 168.1 ppm for **4b**, 166.6 ppm for **4c**, 167.7 ppm for **4d**) indicated that the structures of complexes **4a–d** are close to those of other *o*-aryloxide-NHC palladium complexes.[4,7a,b] The presence of the signals at 8.18 and 6.86 ppm in the ^{1}H NMR spectrum of **4e** for the imidazole ring C(2) and C(5) protons and the much larger chemical shift difference (1.32 ppm) between them than those in complexes **4b** (0.28 ppm), **4c** (0.14 ppm), and **4d** (0.15 ppm) supported the abnormal binding (C4-bonding) of the NHC ligand in **4e**.[4,7b,9] In addition, there were two peaks at 158.3 and 152.0 ppm for the imidazole carbons and no the characteristic peak of the carbene carbon appeared at about 167 ppm in the ^{13}C NMR spectrum of **4e**. High-resolution mass spectrometry (HRMS) analysis further confirmed all the assignments of **4a–e** by showing their molecular ion peaks.

In order to evaluate the difference in the structural parameters between the $C(sp^3)$, N-chelated *o*-aryloxide-NHC-ligated palladacycle complexes and the corresponding $C(sp^2)$,N-palladacycle analogues, the molecular structures of **4a–c** and **4e** were determined by single-crystal X-ray diffraction analysis as shown in Figs 1–4. All three of the normal NHC complexes **4a–c** show slightly distorted square planar structures with dihedral angles of 7.0°, 2.3°, and 6.2(3.8)°, respectively. The N atom of quinoline unit is trans to the carbene carbon, in agreement with the corresponding $C(sp^2)$,N-palladacycle complexes. From Table 1 it can be seen that the Pd–C(NHC) (1.971(2)–1.979(4) Å) bond lengths are

comparable to those observed in the corresponding $C(sp^2)$,N-palladacycle analogues (1.959(4)–1.973(3), while the Pd–$C(CH_2)$ (2.033(5)–2.052(5) Å) bond lengths are much longer than the Pd–C(Ph) (1.985(2)–1.999(2) Å) bond lengths observed in the corresponding $C(sp^2)$,N-palladacycle analogues.[4]

Fig. 1 ORTEP view of **4a** showing 30% ellipsoids. Hydrogen atoms have been omitted for clarity.

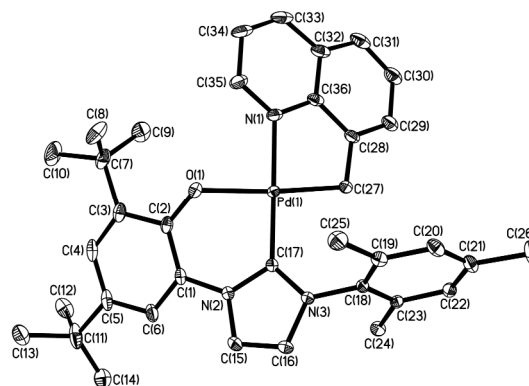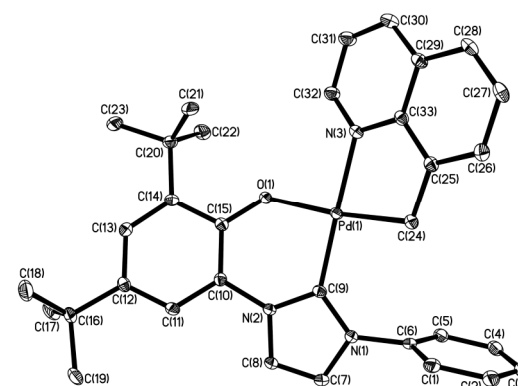**Fig. 2** ORTEP view of **4b** showing 30% ellipsoids. Hydrogen atoms have been omitted for clarity.

Fig. 3 ORTEP view of **4c** showing 30% ellipsoids (showing one of two independent molecules in the unit cell). Hydrogen atoms have been omitted for clarity.

The molecular structure of **4e** (Fig. 4) shows that the NHC is bonded through an abnormal binding mode (C4 bonding),

which is similar to previous reports.[4,7b,9] The N atom of quinoline unit is also trans to the carbene carbon. The Pd-C(NHC) [1.964(3), 1.962(3) Å] and Pd-C(CH$_2$) [2.028(3), 2.029(3) Å] bond lengths are comparable or slightly shorter than those of the normal binging complexes **4a-c**. The five-membered palladacycle moiety is also puckered. Similar to other *o*-aryloxide-NHC palladium complexes,[4,7b] the abnormal binding in **4e** may be also due to the steric effect of the *tert*-butyl group at the NHC.
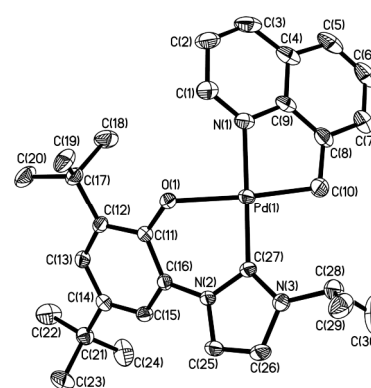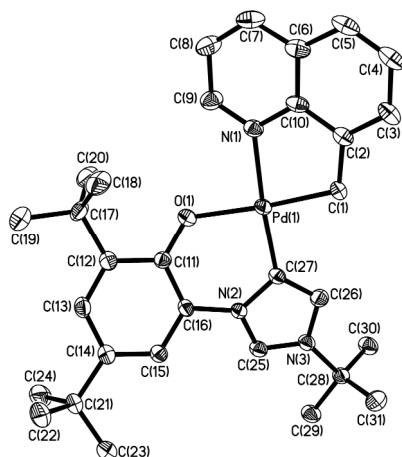

Fig. 4 ORTEP view of **4e** showing 60% ellipsoids (showing one of two independent molecules in the unit cell). Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for **4a–c** and **4e**.

Parameter	4a	4b	4c	4e
C(NHC)–Pd	1.973(5)	1.971(2)	1.979(4) 1.974(4)	1.964(3) 1.962(3)[a]
C(CH$_2$)–Pd	2.033(5)	2.042(2)	2.052(5) 2.051(4)	2.028(3) 2.029(3)
N–Pd	2.059(4)	2.0776(18)	2.072(3) 2.082(3)	2.075(3) 2.077(3)
O–Pd	2.073(3)	2.0950(16)	2.118(3) 2.115(3)	2.078(2) 2.079(2)
C(NHC)–Pd–C(CH$_2$)	98.70(19)	97.14(9)	98.53(17) 98.80(16)	93.89(12) 93.77(13)
C(NHC)–Pd–N	175.48(17)	178.14(8)	177.75(15) 179.46(14)	174.34(11) 174.85(12)[a]
C(NHC)–Pd–O	86.94(17)	88.51(8)	86.60(13) 85.82(13)	89.78(11) 89.68(11)[a]
N–Pd–C(CH$_2$)	83.09(19)	82.54(8)	82.54(17) 81.14(15)	82.49(12) 82.68(12)
O–Pd–C(CH$_2$)	172.50(16)	174.25(7)	172.47(17) 174.09(14)	176.01(11) 176.29(11)
O–Pd–N	91.65(16)	91.85(7)	92.53(13) 94.26(12)	93.72(10) 93.78(10)

[a] For the abnormal NHC ligand

Norbornene Polymerization.

Vinyl polynorbornene has received considerable attention owing to its dielectric and mechanical properties for technical application as an interlevel dielectric in microelectronics applications.[10] Recently, some N-heterocyclic carbene nickel

and palladium complexes have been utilized in the addition polymerization of norbornene with excellent activities.[11] The nickel and palladium complexes with a salicylaldiminato ligand have been extensively applied in catalytic olefin polymerization.[8a,10,12] By introduction of a NHC ligand instead of the imine unit in the salicylaldiminato framework, we have designed and synthesized a series of *o*-aryloxide-NHC palladium, nickel, and ruthenium complexes.[4,7] As expected, this kind of salicylaldimine-like NHC metal complexes showed excellent catalytic properties in the addition polymerization or ROMP of norbornene. Following these works, we further studied the addition polymerization of norbornene with C(sp^3), N-chelated and *o*-aryloxide-NHC-ligated palladacycle complexes **4a–d** in the presence of MAO. The results are listed in Table 2.

Complex **4a** was chosen as the precatalyst for the study of the polymerization in detail. The preliminary experiments indicated that the C(sp^3),N-palladacycles can also be activated by treatment with MAO to polymerization norbornene, where the catalytic activities lie in the range of 10^7 g PNB mol^{-1} Pd h^{-1}. The activity of **4a** increased with the polymerization temperature rising from 20 °C to 40 °C (entries 1, 2), possibly due to the increasing concentration of metal centers activated by MAO. The activity decreased with increasing temperature from 40 °C to 80 °C (entries 2–4). The colour of the polynorbornene obtained at 80 °C is slightly black, indicating that the active species is unstable at high temperature and decomposes. The activity increased with increasing the Al/Pd ratio (entries 5–8). We chose the temperature of 40 °C and with an Al/Pd molar ratio of 5000 as the optimal polymerization conditions for the catalytic system (entry 7). Similarly, complexes **4b–e** also exhibited excellent catalytic activities (10^7 g PE mol^{-1} Pd h^{-1}) (entries 9–12). For the different substituted group, the steric effect resulted in different activities for the precatalysts (**4a** > **4b** > **4d** ~ **4e** > **4c**). The abnormal coordination of the NHC in complex **4e** seems have little effect on the activity, which is similar to that of **4d**. A C(sp^2),N-palladacycle complex **5** was also exploited at the present polymerization conditions (with same MAO) for comparison. The catalytic activity of **5** (2.644×10^7 g PE mol^{-1} Pd h^{-1}, entry 13) is slightly lower than that of the corresponding C(sp^3), N-chelated analogue (entry 7), possibly due to the higher reactivity of C(sp^3)–Pd bond than that of C(sp^2)–Pd bond.

The polymers obtained are insoluble in most organic solvents, such as cyclohexane, chloroform, benzene, chlorobenzene, acetone, dioxane, methanol, 1,2,4-trichlorobenzene, and tetrachloroethane. Therefore, we cannot measure the molecular weights of the polymers. The missing absorption of a double bond at 1600–1700 cm^{-1} in the IR spectra of the polymers (see the Supporting Information) indicates that the polymerization initiated by the palladacycles/MAO system adopts a vinyl-type addition manner. DSC analysis shows multiple transitions of the PNB derived from the palladacycles, and it is impossible to determine the glass transition temperatures. The difficulty of determining the glass transition temperature of vinyl

polynorbornene has been attributed to the fact that it is located close to the temperature range where decomposition tends to set in.[13] According to the TGA study (see the Supporting Information), the polymers are thermally stable up to 400 °C.

Table 2. Addition polymerization of norbornene with palladacycles activated with MAO[a]

Entry	Catalyst	[Cat] (μmol)	MAO (Al/Pd)	T (°C)	PNB (g)	Activity[b]
1	**4a**	0.4	4000	20	0.5486	27.47
2	**4a**	0.4	4000	40	0.6896	34.48
3	**4a**	0.4	4000	60	0.5176	25.88
4	**4a**	0.4	4000	80	0.2582	12.91
5	**4a**	0.4	2000	40	0.1560	7.80
6	**4a**	0.4	3000	40	0.4750	23.75
7	**4a**	0.4	5000	40	0.9755	48.78
8	**4a**	0.4	6000	40	0.9900	49.50
9	**4b**	0.4	5000	40	0.6381	31.91
10	**4c**	0.4	5000	40	0.2845	14.22
11	**4d**	0.4	5000	40	0.4644	23.22
12	**4e**	0.4	5000	40	0.5445	27.23
13	**5**	0.4	5000	40	0.5287	26.44

[a]Polymerization conditions: in 15 mL of toluene; norbornene 1.0 g; reaction time 3 min; MAO (1.0 N) in toluene. [b]In units of $(10^6$ g of PNB) (mol of Pd)$^{-1}$h^{-1}.
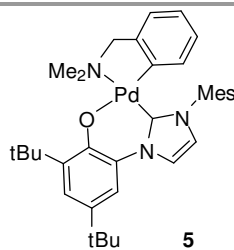

Chart 1

Conclusions

In summary, we have successfully synthesized a series of C(sp³), N-chelated o-aryloxide-NHC-ligated palladacycle complexes. The NHC adopts an abnormal binding (C4-bonding) when the N-functional group on the NHC is changed to *tert*-butyl. By treatment with MAO, all the C(sp³), N-chelated o-aryloxide-NHC-ligated palladacycles showed excellent catalytic activities [10^7 g of PNB (mol of Pd)$^{-1}$ h^{-1}] in the addition polymerization of norbornene. In comparison with the corresponding C(sp²), N-chelated o-aryloxide-NHC-ligated palladacycle analogues, the C(sp³), N-chelated o-aryloxide-NHC-ligated palladacycles showed slightly higher activities for the addition polymerization of norbornene, but with lower stability both in solution and solid.

Experimental section

General Considerations. All manipulations were carried out under an atmosphere of dry argon using standard Schlenk techniques, unless stated otherwise. All solvents were purified and dried according to standard procedures. MAO (1.0 N in toluene) was purchased from Arbemarle Co. ^{1}H and ^{13}C NMR spectra were recorded in CDCl₃ on a Bruker A V 400 spectrometer. HRMS were done on a Varian 7.0 T FTICR-mass spectrometer. Elemental analyses were performed on a Perkin-Elmer 240C analyzer. The o-hydroxyaryl imidazolium pro-ligands **1a–e**,[7a,b] complex **5**,[4] and [Pd(OAc)(8-Me-quin-H)]₂ (**3**)[14] were prepared according to the literature procedures.

General Procedure for Preparation of Complexes 4a–d. A mixture of o-hydroxyaryl-substituted imidazolium salt **1a** (1 mmol), Ag₂O (3 mmol) and CH₂Cl₂ (20 mL) was stirred for overnight in dark. The reaction mixture was then filtered through a pad of Celite and washed with CH₂Cl₂ (3×10 mL). Then the filtrate was dropwise to a stirred suspension of **3** (0.5 mmol) in CH₂Cl₂ (20 mL) by a dropping funnel for approximately 3 h at 0 °C. The color of the solution became pale yellow and the reaction mixture was maintained at 0 °C for additional 1 h. After removal of the solvent under vacuum, the residue was chromatographed on silica gel and eluted with petroleum ether/ethyl acetate to give **4a** as a yellow solid.

Compound 4a *(R = Mes)*. Yield 80%, mp 284–286 °C. Anal. Calcd for C₃₆H₄₁N₃OPd: C, 67.76; H, 6.48; N, 6.58. Found: C, 67.42; H, 6.84; N, 6.78. ^{1}H NMR (CDCl₃): δ 9.43 (d, J = 4.5 Hz 1H, Ar-H), 8.18 (d, J = 8.3 Hz, 1H, Ar-H), 7.58 (s, 1H, Ar-H), 7.46–7.40 (m, 2H, Ar-H, im-H), 7.29 (t, J = 7.5 Hz, 1H, Ar-H), 7.22 (s, 1H, Ar-H), 7.17 (d, J = 7.0 Hz, 1H, im-H), 7.13 (s, 1H, Ar-H), 6.99 (s, 2H, Ar-H), 6.92 (s, 1H, Ar-H), 2.36 (s, 3H, Ar-CH_3), 2.28 (s, 6H, Ar-CH_3), 2.12 (s, 2H, Ar-CH_2), 1.56 (s, 9H, C(CH_3)₃), 1.33 (s, 9H, C(CH_3)₃). ^{13}C NMR (100 MHz ,CDCl₃): δ 168.8, 157.7, 151.7, 151.4, 149.2, 139.7, 138.8, 137.2, 136.7, 135.9, 133.5, 129.1, 128.7, 128.7, 128.4, 127.3, 122.2, 122.1, 120.4, 120.2, 116.9, 35.8, 34.0, 31.8, 30.2, 21.1, 18.4, 13.4. HRMS (ESI, m/z): calcd for C₃₆H₄₁N₃OPd (M+H): 638.2363, found 638.2370.

Compound 4b *(R = Ph)*. Yield 72%, mp 281–283 °C. Anal. Calcd for C₃₃H₃₅N₃OPd: C, 66.49; H, 5.92; N, 7.05. Found: C, 66.38; H, 5.57; N, 6.95. ^{1}H NMR (CDCl₃): δ 9.35 (dd, J = 4.8, 1.4 Hz, 1H, Ar-H), 8.18 (dd, J = 8.3, 1.4 Hz, 1H, Ar-H), 7.87–7.82 (m, 2H, Ar-H), 7.49 (d, J = 2.0 Hz, 1H, im-H), 7.48–7.41 (m, 5H, Ar-H), 7.27 (t, J = 7.6 Hz, 1H, Ar-H), 7.24 (d, J = 2.6 Hz, 1H, Ar-H), 7.21 (d, J = 2.0 Hz, 1H, im-H), 7.15-7.11 (m, 2H, Ar-H), 2.20 (s, 2H, Ar-CH_2), 1.57 (s, 9H, C(CH_3)₃), 1.33 (s, 9H, C(CH_3)₃). ^{13}C NMR(100 MHz ,CDCl₃): δ 168.1, 157.8, 151.4, 149.1, 140.5, 140.1, 137.3, 133.7, 129.4, 128.8, 128.6, 128.4, 128.3, 127.5, 127.1, 122.8, 122.5, 122.3, 120.6, 120.3, 116.6, 35.8, 34.0, 31.8, 30.4, 16.1. HRMS (MALDI, m/z): calcd for C₃₃H₃₅N₃OPd (M+H): 596.1893, found 596.1895.

Compound 4c *(R = ^{i}Pr)*. Yield 60%, mp 225–227 °C. Anal. Calcd for C₃₀H₃₇N₃OPd: C, 64.11; H, 6.64; N, 7.48. Found: C, 64.30; H, 6.95; N, 7.50. ^{1}H NMR (CDCl₃): δ 9.34 (dd, J = 4.7, 1.1 Hz, 1H, Ar-H), 8.23 (dd, J = 8.3, 1.4 Hz, 1H, Ar-H), 7.53 (t, J = 7.2 Hz, 2H, Ar-H), 7.47 (dd, J = 8.3, 4.8 Hz,

1H, Ar-*H*), 7.41 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.35 (d, *J* = 2.0 Hz, 1H, Ar-*H*), 7.19 (d, *J* = 2.6 Hz, 1H, im-*H*), 7.10 (d, *J* = 2.1 Hz, 1H, Ar-*H*), 7.05 (d, *J* = 2.6 Hz, 1H, im-*H*), 5.12 (m, 1H, C*H*(CH$_3$)$_2$), 3.21 (s 2H, Ar-C*H*$_2$), 1.55 (d, *J* = 6.8 Hz, 6H, CH(C*H*$_3$)$_2$), 1.52 (s, 9H, C(C*H*$_3$)$_3$), 1.30 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (100MHz ,CDCl$_3$): δ 166.6, 157.7, 151.4, 151.0, 149.4, 139.6, 137.3, 133.6, 129.9, 128.6, 128.5, 127.7, 122.7, 122.2, 120.8, 120.6, 116.6, 116.6, 51.1, 35.6, 33.9, 31.7, 30.4, 24.0, 22.3, 14.6, 14.1. HRMS (MALDI, m/z): calcd for C$_{30}$H$_{37}$N$_3$OPd (M+H): 562.2049, found 562.2047.

Compound 4d *(R = Me)*. Yield 65%, mp 193–195 °C. Anal. Calcd for C$_{28}$H$_{33}$N$_3$OPd: C, 62.98; H, 6.23; N, 7.87. Found: C, 63.40; H, 6.54; N, 7.55. ^{1}H NMR (CDCl$_3$): δ 9.34 (dd, *J* = 4.7, 1.3 Hz, 1H, Ar-*H*), 8.23 (dd, *J* = 8.3, 1.2 Hz, m, 1H, Ar-*H*), 7.52 (t, *J* = 7.3 Hz, 2H, Ar-*H*), 7.47 (dd, *J* = 8.3, 4.8 Hz, 1H, Ar-*H*), 7.40 (t, *J* = 7.5 Hz, 1H, Ar-*H*), 7.32 (d, *J* = 1.9 Hz, 1H, Ar-*H*), 7.21 (d, *J* = 2.5 Hz, 1H, im-*H*), 7.06 (d, *J* = 2.5 Hz, 1H, im-*H*), 6.99 (d, *J* = 1.8 Hz, 1H, Ar-*H*), 3.87 (s, 3H, N(C*H*$_3$)), 3.22 (s, 2H, Ar-C*H*$_2$), 1.54 (s, 9H, C(C*H*$_3$)$_3$), 1.31 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (100MHz ,CDCl$_3$): δ 167.7, 157.6, 151.4, 151.1, 149.3, 139.8, 137.4, 133.6, 129.7, 128.6, 128.5, 127.7, 122.7, 122.4, 122.3, 120.7, 120.1, 116.3, 38.0, 35.7, 34.0, 31.8, 30.3, 15.4. HRMS (MALDI, m/z): calcd for C$_{28}$H$_{33}$N$_3$OPd (M+H): 534.1737, found 534.1739.

Synthesis of Complex 4e. A mixture of **1e** (0.407 mg, 1 mmol), K$_2$CO$_3$ (0.400 mg, 3 mmol), **3** (0.308 mg, 0.5 mmol), and dioxane (20 mL) was stirred at 20 °C for 48 h to give a pale yellow solution. After removal of the solvent under vacuum, the residue was chromatographed on silica gel and eluted with petroleum ether/ethyl acetate to give 118 mg (20%) of **4e** as a yellow green solid. Mp 262–264 °C. Anal. Calcd for C$_{31}$H$_{39}$N$_3$OPd: C, 64.63; H, 6.82; N, 7.29. Found: C, 64.40; H, 7.11; N, 7.32. ^{1}H NMR (CDCl$_3$): δ 9.39 (d, *J* = 3.7 Hz, 1H, Ar-*H*), 8.21 (s, 1H, Ar-*H*), 8.18 (s, 1H, N(C*H*)N), 7.62 (d, *J* = 6.6 Hz, 1H, Ar-*H*), 7.49 (d, *J* = 7.7 Hz, 1H, Ar-*H*), 7.44-7.36 (m, 2H, Ar-*H*), 6.95 (s, 1H, Ar-*H*), 6.86 (s, 1H, im-*H*), 3.12 (s, 2H, Ar-C*H*$_2$), 1.64 (s, 9H, C(C*H*$_3$)$_3$), 1.61 (s, 9H, C(C*H*$_3$)$_3$), 1.33 (s, 9H, C(C*H*$_3$)$_3$). ^{13}C NMR (100MHz ,CDCl$_3$): δ 158.3, 151.9, 151.6, 148.3, 148.0, 140.7, 136.8, 132.7, 129.3, 128.7, 127.3, 127.2, 126.0, 122.6, 122.5, 120.5, 119.5, 115.6, 56.9, 35.8, 33.8, 31.7, 30.0, 29.9, 14.7. HRMS (ESI, m/z): calcd for C$_{31}$H$_{39}$N$_3$OPd (M+H): 576.2206, found 576.2213.

Crystallographic Studies. Single crystals for X-ray diffraction were from CH$_2$Cl$_2$/hexane for **4a–c** and **4e**. Date collections were performed on a Rigaku Saturn 724 CCD (for **4a** and **4b**) or a Rigaku Saturn 70 (for **4c** and **4e**) diffractometer equipped with a rotating anode system at 113(2) K (for **4a**, **4b**, and **4e**) or 293(2) K (for **4c**) by using graphite-monochromated Mo Kα radiation (ω-2θ scans, λ = 0.71073 Å). Semiempirical absorption corrections were applied for all complexes. The structures were solved by direct methods and refined by full-matrix least-squares. All calculations were performed by using the SHELXL-97 program system. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were assigned ideally positions and were included in structure factor

calculations. Selected bond lengths and angles are listed in Table 1.

Norbornene Polymerization. In a typical procedure, 1.00 g of norbornene in 10 mL of toluene and 1.6 mL of MAO (1.0 M) were added into a flask (100 mL) with stirring under Ar atmosphere .After the mixture was kept at the desired temperature for 2 min, 0.4 μmol of the palladium complex in 2 mL of toluene was injected into the flask via syringe, and the reaction was started. Three minutes later, the polymerization was terminated by addition of 10% HCl in ethanol. The precipitated polymer was washed with ethanol and water and dried at 60 °C in vacuo to a constant weight. For all the polymerization procedures, the total reaction volume was 15 mL, which can be achieved by variation of the added toluene when necessary.

Acknowledgements

Notes and references

^{a}State Key Laboratory of Elemento-Organic Chemistry, College of Chemistry, Nankai University, Tianjin 300071, China. E-mail: bqwang@nankai.edu.cn

^{b}Institute of Polymer Science and Engineering, Hebei University of Technology, Tianjin 300130, China

^{c} Collaborative Innovation Center of Chemical Science and Engineering (Tianjin), Tianjin 300072, China.

†Electronic Supplementary Information (ESI) available. CCDC 1015090 (**4a**), 1015091 (**4b**), 1015092 (**4c**), and 1015093 (**4e**). See DOI: 10.1039/b000000x/

1   For recent reviews see: (*a*) T. M. J. Anselment, S. I. Vagin, B. Rieger, *Dalton Trans.*, 2008, 4537; (*b*) A. Nakamura, S. Ito, K. Nozaki, *Chem. Rev.*, 2009, **109**, 5215; (*c*) D. H. Camachoa, Z. Guan, *Chem. Commun.*, 2010, **46**, 7879; (*d*) S. Ito, K. Nozaki, *Chem. Rec.*, 2010, **10**, 315; (*e*) A. Nakamura, T. M. J. Anselment, J. Claverie, B. Goodall, R. F. Jordan, S. Mecking, B. Rieger, A. Sen, P. W. N. M. Van Leeuwen, K. Nozaki, *Acc. Chem. Res.*, 2013, **46**, 1438.

2   Selected reviews for palladacycles: (*a*) W. A. Herrmann, V. P. W. Böhm, C.-P. Reisinger, *J. Organomet. Chem.*, 1999, **576**, 23; (*b*) J. Dupont, M. Pfeffer, J. Spencer, *Eur. J. Inorg. Chem.*, 2001, 1917; (*c*) R. B. Bedford, *Chem. Commun.*, 2003, 1787; (*d*) V. Farina, *Adv. Synth. Catal.*, 2004, **346**, 1553; (*e*) I. P. Beletskaya, A. V. Cheprakov, *J. Organomet. Chem.*, 2004, **689**, 4055; (*f*) J. Dupont, C. S. Consorti, J. Spencer, *Chem. Rev.*, 2005, **105**, 2527; (*g*) N. T. S. Phan, M. Van Der Sluys, C. W. Jones, *Adv. Synth. Catal.*, 2006, **348**, 609; (*h*) N. Marion, S. P. Nolan, *Acc. Chem. Res.*, 2008, **41**, 1440; (*i*) H. Nomura, C. Richards, *J. Chem. Asian J.,* 2010, **5**, 1726; (*j*) D. A. Alonso, C. Nájera, *Chem. Soc. Rev.*, 2010, **39**, 2891; (*k*) Y. J. Wu, F. Yang, J. L. Zhang, X. L. Cui, J. F. Gong, M. P. Song, T. S. Li, *Chin. Sci. Bull.*, 2010, **55**, 2784.

3   (*a*) J. Schwarz, E. Herdtweck, W. A. Herrmann, M. G. Gardiner, *Organometallics*, 2000, **19**, 3154; (*b*) M. A. Pérez, R. Quijada, F. Ortega-Jiménez, C. Alvarez-Toledano, *J. Mol. Catal. A. Chem.*, 2005, **226**, 291; (*c*) C. Zuccaccia, G. Bellachioma, G. Cardacia, A. Macchioni, B. Binotti, C. Carfagna, *Helv. Chim. Acta*, 2006, **89**, 1524; (*d*) J. Hurtado, M. Portaluppi, R. Quijada, R. Rojas, M. Valderrama, *J. Coord. Chem.*, 2009, **62**, 2772; (*e*) J. Hurtado, A. Ibañez, R. Rojas, M. Valderrama, *Inorg. Chem. Commun.*, 2010, **13**, 1025.

4   Y. Kong, L. Wen, H. Song, S. Xu, M. Yang, B. Liu, B. Wang *Organometallics*, 2011, **30**, 153.

5   (*a*) A. J. Arduengo, R. L. Harlow, M. Kline, *J. Am. Chem. Soc.*, 1991, **113**, 361; (*b*) A. Arduengo, J. *Acc. Chem. Res.*, 1999, **32**, 913;

6   For recent reviews see: (*a*) *Topics in Organometallic Chemistry, N-Heterocyclic Carbenes in Transition Metal Catalysis*; F. Glorius Ed.; Springer: Berlin, 2007; Vol. **21**; (*b*) E. A. B. Kantchev, C. J. O'Brien, M. G. Organ, *Angew. Chem., Int. Ed.*, 2007, **46**, 2768; (*c*) S. T. Liddle, I. S. Edworthy, P. L. Arnold, *Chem. Soc. Rev.*, 2007, **36**, 1732; (*d*) F. E. Hahn, M. C. Jahnke, *Angew. Chem., Int. Ed.*, 2008, **47**, 3122; (*e*) S. Díez-González, N. Marion, S. P. Nolan, *Chem. Rev.*, 2009, **109**, 3612; (*f*) H. Jacobsen, A. Correa, A. Poater, C. Costabile, L. Cavallo, *Coord. Chem. Rev.*, 2009, **253**, 687; (*g*) de P. Frémont, N. Marion, S. P. Nolan, *Coord. Chem. Rev.*, 2009, **253**, 862; (*h*) O. Kühl, *Coord. Chem. Rev.*, 2009, **253**, 2481; (*i*) A. John, P. Ghosh, *Dalton Trans.*, 2010, **39**, 7183; (*j*) W. Levason, G. Reid, W. Zhang. *Coord. Chem. Rev.*, 2011, **255**, 1319; (*k*) F. Wang, L.-J. Liu, W. Wang, S. Li, M. Shi, *Coord. Chem. Rev.*, 2012, **256,** 804; (*l*) S. Budagumpi, R. A. Haque, A. W. Salman, *Coord. Chem. Rev.*, 2012, **256**, 1787; (*m*) L.-A. Schaper, S. J. Hock, W. A. Herrmannn, F. E. Kühn, *Angew. Chem., Int. Ed*., 2013, **52**, 270.

7   (*a*) H. Ren, P. Yao, S. Xu, H. Song, B. Wang, *J. Organomet. Chem.*, 2007, **692**, 2092; (*b*) Y. Kong, H. Ren, S. Xu, H. Song, B. Liu, B. Wang, *Organometallics*, 2009, **28**, 5934; (*c*) Y. Kong, M. Cheng, H. Ren, S. Xu, H. Song, M. Yang, B. Liu, B. Wang, *Organometallics*, 2011, **30**, 1677; (*d*) Y. Kong, S. Xu, H. Song, B. Wang, *Organometallics*, 2012, **31**, 5527; (*e*) Y. Kong, Y. Tang, Z. Wang, S. Xu, H. Song, B. Wang, *Macromol. Chem. Phys.*, 2013, **214**, 492.

8   (*a*) T. R. Younkin, E. F. Connor, J. I. Henderson, S. K. Friedrich, R. H. Grubbs, D. A. Bansleben, *Science*, 2000, **287**, 460; (*b*) K. C. Gupta, A. K. Sutar, *Coord. Chem. Rev.*, 2008, **252**, 1420; (*c*) H. Makio, T. Fujita, *Acc. Chem. Res.*, 2009, **42**, 1532; (*d*) H. Makio, H. Terao, A. Iwashita, T. Fujita, *Chem. Rev.*, 2011, **111**, 2363; (*e*) C. Redshaw, Y. Tang, *Chem. Soc. Rev.*, 2012, **41**, 4484.

9   (*a*) P. L. Arnold, S. Pearson, *Coord. Chem. Rev.*, 2007, **251**, 596; (*b*) M. Albrecht, *Chem. Commun.*, 2008, 3601; (*c*) O. Schuster, L. Yang, H. G. Raubenheimer, M. Albrecht, *Chem. Rev.*, 2009, **109***,* 3445; (*d*) R. H. Crabtree, *Coord. Chem. Rev.*, 2013, **257**, 755.

10 (*a*) C. Janiak, P. G. Lassahn, *J. Mol. Catal. A Chem.*, 2001, **166**, 193; (*b*) F. Blank, C. Janiak, *Coord. Chem. Rev.*, 2009, **253**, 827.

11 (*a*) X. Wang, S. Liu, G.-X. Jin, *Organometallics*, 2004, **23**, 6002; (*b*) X. Wang, S. Liu, L.-H. Weng, G.-X. Jin, *Organometallics*, 2006, **25***,* 3565; (*c*) I. G. Jung, J. Seo, Y. K. Chung, D. M. Shin, S. H. Chun, S. U. Son, *J. Polym. Sci. A: Polym. Chem.*, 2007, **45**, 3042; (*d*) D. Crosbie, J. Stubbs, D. Sundberg, *Macromolecules*, 2007, **40***,* 5743; (*e*) D. Crosbie, J. Stubbs, D. Sundberg, *Macromolecules*, 2007, **40***,* 8947; (*f*) S. Sujith, E. K. Noh, B. Y. Lee, J. W. Han, *J. Organomet.* *Chem.*, 2008, **693**, 2171; (*g*) D. Crosbie, J. Stubbs, D. Sundberg, *Macromolecules*, 2008, **41**, 2445; (*h*) I. G. Jung, Y. T. Lee, S. Y. Choi, D. S. Choi, Y. K. Kang, Y. K. Chung, *J. Organomet. Chem.*, 2009, **694**, 297; (*i*) J. H. Park, C. Yun, M. H. Park, Y. Do, S. Yoo, M. H. Lee, *Macromolecules*, 2009, **42**, 6840; (*j*) M. H. Park, C. Yun, J. O. Huh, Y. Do, S. Yoo, M. H. Lee, *Synth. Met.*, 2010, **160**, 2000; (*k*) J. Berding, M. Lutz, A. L. Spek, E. Bouwman, *Appl. Organometal. Chem.*, 2011, **25**, 76; (*l*) J. H. Park, C. Yun, T.-W. Koh, Y. Do, S. Yoo, M. H. Lee, *J. Mater. Chem.*, 2011, **21**, 5422; (*m*) T.-X. Zhang, M.-R. Xia, Z. Li, B.-Q. Mao, *Comput. Theor. Chem.*, 2012, **997**, 110; (*n*) M. Eo, S. Lee, M. H. Park, M. H. Lee, S. Yoo, Y. Do, *Macromol. Rapid Commun.*, 2012, **33**, 1119; (*o*) W. Y. Sung, M. H. Park, J. H. Park, M. Eo, M.-S. Yu, Y. Do, M. H. Lee, *Polymer*, 2012, **53**, 1857; (*p*) D. Zhang, S. Zhou, Z. Li, Q. Wang, L. Weng, *Dalton Trans.,* 2013, **42**, 12020; (*q*) H. Song, D. Fan, Y. Liu, G. Hou, G. Zi, *J. Organomet. Chem.*, 2013, **729**, 40; (*r*) J. Deng, H. Gao, F. Zhu, Q. Wu, *Organometallics*, 2013, **32**, 4507. (*s*) S. Budagumpi, R. A. Haque, A. W. Salman, *Coord. Chem. Rev.*, 2012, **256**, 1787.

12 For selected examples see: (*a*) W. Sun, H. Yang, Z. Li, Y. Li, *Organometallics*, 2003, **22**, 3678; (*b*) D. Zhang, G. Jin, L. Weng, F. Wang, *Organometallics*, 2004, **23**, 3270; (*c*) A. W. Waltman, T. R. Younkin, R. H. Grubbs, *Organometallics*, 2004, **23**, 5121; (*d*) L. F. Groux, T. Weiss, D. N. Reddy, P. A. Chase, W. E. Piers, T. Ziegler, M. Parvez, J. Benet-Buchholz, *J. Am. Chem. Soc.*, 2005, **127**, 1854; (*e*) M. Kang, A. Sen, *Organometallics*, 2005, **24**, 3508; (*f*) W. Li, H. Sun, M. Chen, Z. Wang, D. Hu, Q. Shen, Y. Zhang, *Organometallics*, 2005, **24**, 5925; (*g*) I. Göttker-Schnetmann, B. Korthals, S. Mecking, *J. Am. Chem. Soc.*, 2006, **128**, 7708; (*h*) I. Göttker-Schnetmann, P. Wehrmann, C. Röhr, S. Mecking, *Organometallics*, 2007, **26**, 2348; (*i*) T. Hu, Y.-G. Li, J.-Y. Liu, Y.-S. Li, *Organometallics*, 2007, **26**, 2609; (*j*) P. Wehrmann, S. Mecking, *Organometallics*, 2008, **27**, 1399; (*k*) B. A. Rodriguez, M. Delferro, T. J. Marks, *Organometallics,* 2008, **27**, 2166; (*l*) D.-P. Song, J.-Q. Wu, W.-P. Ye, H.-L. Mu, Y.-S. Li, *Organometallics*, 2010, **29**, 2306; (*m*) Y. Chen, S. Mandal, A. Sen, *Organometallics*, 2010, **29**, 3160; (*n*) M. Delferro, J. P. McInnis, T. J. Marks, *Organometallics*, 2010, **29**, 5040; (*o*) H.-L. Mu, W.-P. Ye, D.-P. Song, Y.-S. Li, *Organometallics*, 2010, **29**, 6282; (*p*) D.-P. Song, Y.-X. Wang, H.-L. Mu, B.-X. Li, Y.-S. Li, *Organometallics*, 2011, **30**, 925; (*q*) Jr. M. P. Weberski, C. Chen, M. Delferro, C. Zuccaccia, A. Macchioni, T. J. Marks, *Organometallics*, 2012, **31**, 3773; (*r*) A. Osichow, I. Göttker-Schnetmann, S. Mecking, *Organometallics*, 2013, **32**, 5239; (*s*) T. Wiedemann, G. Voit, A. Tchernook, P. Roesle, I. Göttker-Schnetmann, S. Mecking, *J. Am. Chem. Soc.*, 2014, **136**, 2078.

13 T. F. A. Haselwander, W. Heitz, S. A. Krügel, J. H. Wendorff, *Macromol. Chem. Phys.*, 1996, **197**, 3435.

14 A. J. Deeming L. P. Rothwell, *J. Organomet. Chem.*, 1981, **205**, 117.

Table of contents entry

A series of $C(sp^3)$, N-chelated *o*-aryloxide-NHC-ligated palladacycles were synthesized and applied to catalyze the addition polymerization of norbornene.