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Synthesis, structure and norbornene polymerization behavior of neutral palladium complexes ☆

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Abstract

A series of neutral palladium(II) complexes bearing non-symmetric bidentate pyrrole-iminato or salicylaldiminato chelate ligands have been synthesized, and the structure of representative complexes (**3a, 4a**, and **5a**) have been confirmed by X-ray crystallographic analysis. These palladium complexes have been investigated as catalysts for the polymerization of norbornene. Using modified methylaluminoxane (MMAO) as a cocatalyst, these complexes display high activities and produce vinyl-addition polynorborenes. Catalytic activity of up to 8.52×10^3 kg/mol$_{\text{Pd}}$ h has been observed. Wide-angle X-ray diffraction (WAXD) has been used to investigate the polymer microstructure and it has been found that they are non-crystalline.

Keywords: Neutral palladium(II) complex; X-ray crystallography; Catalyst; Methylaluminoxane; Norbornene; Vinylic polymerizaition

1. Introduction

With the boom in transition metal catalysis, there is a rapid development of a wide range of polyolefinic materials. A polymer with a certain microstructure can be easily obtained by employing a certain catalyst. Norbornene is a representative cycloolefin monomer which can be polymerized through ring-opening metathesis polymerization (ROMP), cationic (or radical) and vinylic addition polymerization mechanisms. ROMP yields poly(1,3-cyclopentylenevinylene) which retains one double bond in each polymeric repeat unit [1–3]. Cationic polymerization involves the rearrangement of the norbornene framework and generally produces moderate yields of poly (2,7-bicyclo [2,2,1] hept-2-ene) oligomers [4–7]. Free-radical processes also produce low molecular weight products [3]. In vinylic polymerization, the bicyclic structural unit remains intact and only the double bond is opened. As the vinyl-poly(norbornene) has many unique physical characteristics such as good mechanical strength, heat resistivity, optical transparency and low birefringence [8,9], many interests are focused on this kind of polymerization. The selection of catalysts is the key. Catalysts containing the metals nickel [8–16], chromium [17], titanium [18], zirconium [19–22], cobalt [23,24] and palladium [25–35] are reported in various literatures for the vinyl-type polymerization of nornornene. Nickel and palladium complexes display extremely high catalytic activity and produce high molecular weight polymers with excellent performance. Hence, our interest is keen on the well-defined complexes of nickel and palladium (see Scheme 1).

We found that neutral nickel complexes activated with methylaluminoxane display extremely high activity for the vinylic polymerization of norbornene [14,15], and Novak and co-workers [36] reported that neutral palladium complexes as catalysts for olefin and vinyl monomer polymerizations display excellent activity. This urges us to investigate if neutral palladium(II) complexes have high catalytic activity. Here, we would like to report on the synthesis of novel neutral palladium(II) complexes bearing pyrrole-iminato or

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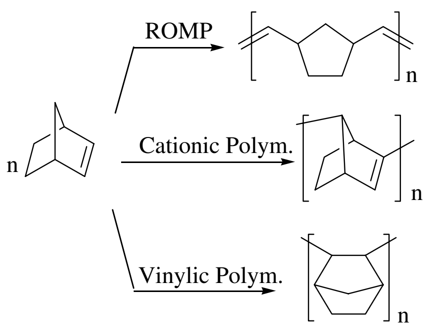


Scheme 1.

salicylaldiminato ligands and the catalysis properties for the vinylic polymerization of norbornene.

2. Experimental

2.1. General procedures and materials

All work involving air and moisture sensitive compounds was carried out using standard Schlenk techniques. NMR data of the ligands and the complexes were obtained on a Varian Unity 300 MHz spectrometer at ambient temperature, with $CDCl_3$ (ligands) or C_6D_6 (complexes) as solvent. IR spectra were recorded on a Bio-Rad FTS-135 spectrophotometer. Single-crystal X-ray diffraction data were received by P4 X-ray crystallography. The wide-angle X-ray diffraction (WAXD) spectrum was measured on a Rigaku D/Max 2500V PC with Cu Kα radiation and a wavelength of 1.54 Å.

Tetrahydrofuran (THF), benzene and diethyl ether were dried over sodium with dibenzophenone as indicator. Chlorobenzene and dichloromethane were refluxed over calcium hydride for two weeks before use. Aniline derivatives were obtained from Acros and purified by distillation before use. Triphenyphosphine, pyrrole-2-carboxaldehyde, sodium tetrachlopalladate-(II) and tetramethyltin were obtained from Aldrich and used without further purification. Pyridine was dried over sodium hydroxide and obtained by reduced distillation. Norbornene from Aldrich was refluxed with sodium, purified by reduced distillation and used as a solution in toluene. Modified methylaluminoxane (MMAO, 7% aluminum in heptane solution) was purchased from Akzo Nobel Chemical Inc. (COD)PdMeCl was prepared by the reaction of $(COD)PdCl_2$ and $SnMe_4$ according to a procedure given by Richard and co-workers [37,38]. Salicylaldehyde derivatives were prepared according to the method of Casiraghi et al. [39], and the salicylaldimines **6a–c** were prepared according to the procedure described by Grubbs and co-workers [40]. The pyrrole-imines **1a–d** were prepared according to the procedure described previously [15].

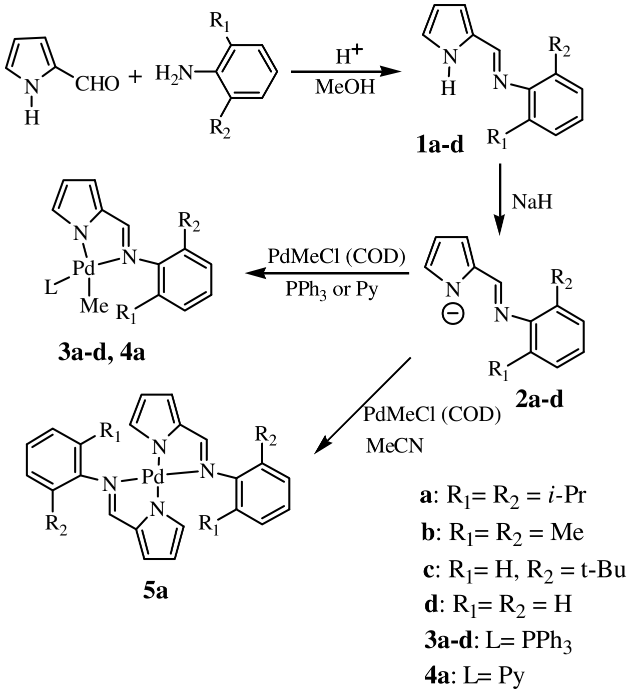
2.2. Synthesis of neutral Pd(II) complexes *3a–d, 4a, 5a* and *8a–c*

A solution of ligand **1a** (0.45 g, 1.76 mmol) in THF (20ml) was added to NaH (0.12 g, 2.5 mmol). The resulting mixture was stirred at room temperature for 3 h, then filtered and the filtrate was evaporated. The solid residue was dried in vacuum. The sodium salt and (COD)PdMeCl (0.32 g, 1.2 mmol) with PPh_3 (0.32 g, 1.2 mmol) were dissolved in benzene (20 ml) in a 100 ml Schlenk flask and stirred at room temperature for 18 h. The resulting mixture was filtered by cannula filtration. The filtrate should be concentrated in a vacuum to ca. 5 ml, and then pentane (ca. 20 ml) was added. After 24 h, some yellow crystals were obtained from the solution and isolated by cannula filtration to yield 0.55 g (71.9%) of **3a**. The other complexes were prepared by the same procedure with similar yields.

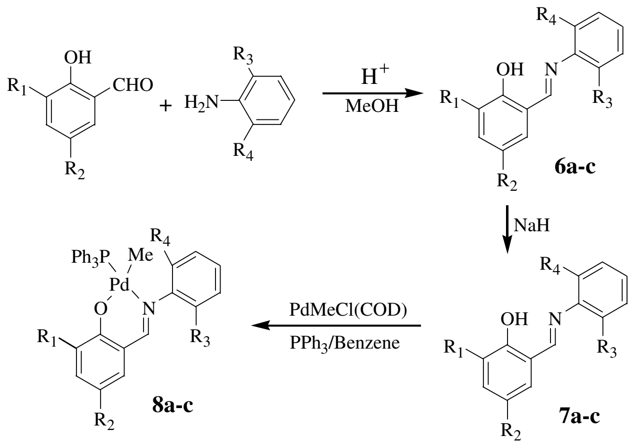
3a: ^{1}H NMR ($CDCl_3$): δ 7.74–7.44 (m, 15 H, PPh–*H*), 7.42 (s,1 H, N=C–*H*), 7.07–6.98 (m, 6 H, Pyrrole-*H* + Ph–*H*), 3.42–3.37 (m, 2 H, C–*H*),1.28–1.19 (m,15 H, *i*-Pr–CH_3 + Pd–CH_3). ^{13}C NMR ($CDCl_3$): δ 4.8, 23.0, 25.0, 28.9, 111.6, 118.0, 123.3, 128.6, 128.7, 130.8, 135.1, 135.5, 142.8, 145.0, 161.6.

3b (73.2%): ^{1}H NMR ($CDCl_3$): δ 7.69 (m, 15 H, PPh–*H*), 7.64 (s, 1 H, N=C–*H*), 7.03–7.01 (s, 3 H, Ph–*H*), 6.65–6.45 (s, 3*H,* Pyrrole-*H*), 2.77 (s, 6 H, Ph–CH_3), 1.07 (s, 3 H, Pd–CH_3). ^{13}C NMR ($CDCl_3$): δ 15.0, 25.2, 25.5, 111.0, 111.6, 118.2, 126.7, 128.8, 131.6, 132.4, 137.9, 161.5, 161.9.

3c (69.4%): ^{1}H NMR ($CDCl_3$): δ 7.75 (s, 1 H, N=C–*H*), 7.71 (m, 15 H, PPh–*H*), 7.13 (s, 5 H, Ph–*H*), 6.75–



Scheme 2.



a: $R_1 = R_2 =$ *t*-Bu, $R_3 = R_4 =$ Me
b: $R_1 = R_2 =$ *t*-Bu, $R_3 = R_4 =$ *i*-Pr
c: $R_1 = R_2 = NO_2$, $R_3 = R_4 =$ *i*-Pr

Scheme 3.

6.70 (s, 3*H*, pyrrole-*H*), 0.80 (s, 3 *H*, Pd–C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 5.9, 6.0, 118.7, 118.9, 124.6, 128.6, 130.9, 135.6, 135.3, 137.9, 138.5, 160.8, 161.1.

3d (67.8%): ^{1}H NMR (CDCl$_3$): δ 7.70–7.65 (m, 15 H, PPh-*H*), 7.65 (s, 1 H, N=C–*H*), 7.29–7.18 (s, 4 H, Ph–*H*), 6.76 (s, 3 H, Pyrrole-*H*), 1.34–1.26 (m, 12 H, *t*-Bu-C*H*$_3$ + Pd–C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 161.6, 149.9, 143.3, 140.5, 138.3, 135.5, 131.6, 130.2, 127.7, 127.4, 126.5, 125.7, 118.0, 111.5, 36.6, 33.1, 32.3, 31.0, 6.3.

4a (73.0%): ^{1}H NMR (CDCl$_3$): δ 8.16 (d, 2 H, Pydine-*H*), 7.60 (s, 1 H, Pydine-*H*), 7.50 (s, 1 H, C*H*=N), 7.18–6.90 (m, 4 H, Ph–H + Pydine-H), 6.74 (d, 2 H), 6.25 (s, 1 H), 3.34 (m, 2 H), 0.99 (m, 12 H), 0.85 (s, 1 H). ^{13}C NMR (CDCl$_3$): δ 158.7, 151.9, 145.2, 141.4, 125.0, 124.4, 123.3, 117.4, 110.7, 27.9, 24.9, 22.2.

5a (66.3%): ^{1}H NMR (CDCl$_3$): δ 7.38 (s, 2 H, N=C–*H*), 7.17–6.80 (s, 10 H, Ph–*H* + Pyrrole-*H*), 6.36 (s, 2H, Pyrrole-*H*), 3.33 (m, 4H, *i*-Pr–C*H*), 0.95 (t, 24 H, 8C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 164.6, 161.1, 146.9, 143.5, 142.7, 139.6, 137.4, 136.3, 127.5, 126.9, 118.5, 118.0, 28.1, 28.0, 25.7, 24.4, 22.7, 22.3.

8a (71.5%): ^{1}H NMR (CDCl$_3$): δ 7.96 (s, 1 H, N=C–*H*), 7.75 (m, 15 H, PPh–*H*), 7.39 (m, 5 H, Ph–*H*), 2.50 (s, 6H, Ph–C*H*$_3$), 1.35–1.25 (s, 21 H, *t*-Bu–C*H*$_3$ + Pd–C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 172.9, 172.7, 156.7, 140.8, 140.6, 137.4, 136.6, 133.6, 133.5, 130.6, 130.0, 124.6, 36.9, 35.2, 24.8, 24.3, 7.57, 7.43.

8b (74.0%): ^{1}H NMR (CDCl$_3$): δ 8.22 (s, 1 H, N=C–*H*), 7.98 (m, 15 H, PPh–*H*), 7.2–6.95 (m, 5 H, Ph–*H*), 3.51–3.47 (m, 2 H, C–*H*), 1.27 (s, 12 H, *i*-Pr–C*H*$_3$), 1.14 (s, 18 H, *t*-Bu–C*H*$_3$), 1.1 (s, 3 H, Pd–C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 167.3, 148.9, 141.8, 135.1, 132.0, 130.9, 130.6, 127.1, 126.3, 125.6, 123.3, 118.4, 35.3, 34.1, 31.9, 29.9, 29.0, 28.2, 25.4, 23.9, 23.3, 3.9.

8c (77.2%): ^{1}H NMR (CDCl$_3$): δ 8.31–8.12 (s, 2 H, Ph–*H*), 7.44 (s, 15 H, PPh$_3$–*H*), 7.16 (s, 3 H, Ph–*H*), 3.36 (m, 2 H, C–*H*), 1.41–1.01 (m, 15 H, C–C*H*$_3$ + Pd–C*H*$_3$). ^{13}C NMR (CDCl$_3$): δ 165.2, 162.4, 146.3, 140.5, 140.1, 135.9, 134.9, 134.0, 131.4, 128.1, 124.4, 122.6, 122.4, 29.0, 28.9, 28.2, 24.7, 24.3, 23.0.

2.3. Typical polymerization procedure

1.0 ml of a fresh catalyst solution (chlorobenzene, 0.5 μmol catalyst), 3.0 ml of a solution of norbornene (26.0 mmol, 2.45 g) in chlorobenzene, and 6.5 ml of

Table 1
Crystal data and structure refinements of **3a**, **4a** and **5a**

	3a	**4a**	**5a**
Empirical formula	$C_{36}H_{39}N_2PPd$	$C_{23}H_{29}N_3Pd$	$C_{34}H_{42}N_4Pd$
Formula weight	637.06	453.89	613.12
Crystal system	orthorhombic	monoclinic	monoclinic
Space group	$Pna2_1$	$P2_1/n$	$P2_1/n$
a (Å)	19.017(8)	8.7190(18)	17.392(3)
b (Å)	12.375(5)	20.457(3)	10.5998(18)
c (Å)	13.986(5)	12.4825(12)	17.800(4)
α (°)	90	90	90
β (°)	90	94.977(13)	108.351(15)
γ (°)	90	90	90
Volume (Å^3)	3291(2)	2218.1(6)	3114.5(9)
ρ_{calc} (Mg m^{-3})	1.286	1.359	1.308
Wavelength (Å)	0.71073	0.71073	0.71703
$F(000)$	1320	936	1280
θ Range (°)	1.96–26.01	1.92–25.99	1.98–26.00
Independent reflections	3648 ($R_{int} = 0.0192$)	4363 ($R_{int} = 0.0229$)	6113 ($R_{int} = 0.0242$)
Absorption correction	ψ-scan	ψ-scan	ψ-scan
Maximum and minimum transmission	0.4728 and 0.4239	0.4895 and 0.4186	0.5681 and 0.5130
Parameters	366	249	360
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0288$, $wR_2 = 0.0561$	$R_1 = 0.0286$, $wR_2 = 0.0669$	$R_1 = 0.0392$, $wR_2 = 0.0519$
Goodness-of-fit on F^2	1.026	1.045	0.860
Largest differential peak and hole (e Å^{-3})	0.354 and −0.375	0.209 and −0.629	0.353 and −0.408

chlorobenzene were added under inert gas atmosphere into a Schlenk flask with a mechanical stirrer. The reaction was started by the addition of 0.5 ml of a MMAO solution (1.0 mmol in heptane) at 30 °C. After 10 min, the reaction mixture was poured into 200 ml of acidic ethanol (ethanol/$\text{HCl}_{\text{conc.}} = 50/1$). The polymer was isolated by filtration, washed with methanol, and dried under vacuum at 80 °C for 24 h. Total reaction volume was 11 ml, unless otherwise stated. This was achieved by variation of the amount of chlorobenzene if necessary.

3. Results and discussion

3.1. Synthesis and characterization of neutral palladium complexes

Ligands **1a–d** were prepared by the condensation of the corresponding aniline derivatives according to the procedure described previously [15], they were deprotonated using sodium hydride and the anions allowed to react with (COD)PdMeCl in the presence of neutral, two-electron donor ligands to give palladium complexes **3a–d**, and **4a**. The neutral donors ligands are necessary to stabilize the complexes. Different ligands have been used to study their effects on metal catalytic activity. Interestingly, attempts to prepare palladium complex with the acetonitrile ligand have failed and complex **5a** was obtained instead. This shows that the binding strength of the CH_3CN ligand with palladium atom is poorer than that of triphenylphosphine or pyridine, which is in accordance with the results of Novak and coworkers [36]. The general synthetic route for the kind of neutral palladium complex in this study is shown in Scheme 2. Meanwhile we have synthesized neutral palladium complexes **8a–c** bearing salicylaldiminato ligands with a similar method, which is shown in Scheme 3.

Table 2
Selected bond lenths (Å) and angles (°) of **3a**, **4a** and **5a**

3a					
Bond lengths					
Pd–C(1)	2.022(7)	N(1)–C(2)	1.336(8)	P–C(25)	1.819(4)
Pd–N(1)	2.123(6)	N(1)–C(5)	1.354(7)	P–C(19)	1.818(5)
Pd–N(2)	2.121(3)	N(2)–C(6)	1.304(6)	P–C(31)	1.834(5)
Pd–P	2.2279(14)	N(2)–C(7)	1.430(5)		
Bond angles					
C(1)–Pd–N(1)	171.8(2)	C(1)–Pd–P	90.5(2)	C(25)–P–C(19)	106.3(2)
C(1)–Pd–N(2)	93.8(2)	N(1)–Pd–P	96.80(15)	C(25)–P–C(31)	102.3(2)
N(1)–Pd–N(2)	79.12(17)	N(2)–Pd–P	175.23(11)	C(19)–P–C(31)	104.8(2)
C(25)–P–Pd	112.16(15)	C(19)–P–Pd	108.00(15)	C(31)–P–Pd	122.10(16)
4a					
Bond lengths					
Pd–C(1)	2.018(3)	Pd–N(2)	2.004(2)	Pd–N(3)	2.168(2)
N(1)–C(6)	1.325(4)	N(2)–C(10)	1.369(3)	N(3)–C(11)	1.288(3)
N(3)–C(12)	1.436(3)				
Bond angles					
N(2)–Pd–C(1)	94.05(11)	N(2)–Pd–N(1)	174.50(9)	C(1)–Pd–N(1)	90.08(11)
N(2)–Pd–N(3)	79.39(8)	C(1)–Pd–N(3)	172.86(10)	N(1)–Pd–N(3)	96.65(8)
C(6)–N(1)–C(2)	116.9(2)	C(6)–N(1)–Pd	118.7(2)	C(2)–N(1)–Pd	124.4(2)
C(10)–N(2)–Pd	118.7(2)	C(7)–N(2)–C(10)	105.9(2)	C(7)–N(2)–Pd	140.0(2)
C(11)–N(3)–C(12)	121.0(2)	C(11)–N(3)–Pd	110.32(16)	C(12)–N(3)–Pd	128.62(15)
5a					
Bond lengths					
Pd–N(1)	2.026(3)	Pd–N(2)	2.052(3)	Pd–N(3)	2.030(3)
Pd–N(4)	2.052(3)	N(1)–C(1)	1.337(4)	N(1)–C(4)	1.383(4)
N(2)–C(5)	1.298(4)	N(2)–C(6)	1.437(4)	N(3)–C(18)	1.342(4)
N(3)–C(21)	1.384(4)	N(4)–C(22)	1.305(4)	N(4)–C(23)	1.442(4)
Bond angles					
N(1)–Pd–N(3)	179.75(13)	N(1)–Pd–N(2)	80.37(11)	N(2)–Pd–N(3)	99.50(11)
N(1)–Pd–N(4)	99.84(11)	N(3)–Pd–N(4)	80.29(12)	N(2)–Pd–N(4)	179.16(13)
C(1)–N(1)–C(4)	105.8(3)	C(1)–N(1)–Pd	142.0(2)	C(4)–N(1)–Pd	112.3(2)
C(5)–N(2)–C(6)	120.9(3)	C(5)–N(2)–Pd	112.4(2)	C(46)–N(2)–Pd	126.6(2)
C(18)–N(3)–C(21)	106.5(3)	C(18)–N(3)–Pd	141.0(2)	C(21)–N(3)–Pd	112.5(2)
C(22)–N(4)–C(23)	120.7(3)	C(22)–N(4)–Pd	112.3(2)	C(23)–N(4)–Pd	126.9(2)

3.2. Crystal structures of complexes 3a, 4a and 5a

Crystals of **3a**, **4a** and **5a** suitable for X-ray structure determination were grown from a benzene–pentane (volume ratio = 1:2) solution. The data collection and refinement data of the analysis are summarized in Table 1, the selected bond lengths and bond angles are summarized in Table 2, and the molecule structures of **3a**, **4a** and **5a** are shown in Figs. 1–3, respectively.

The Pd atom is at the center of an approximately square-planar arrangement, which is applied to all these three complexes. For **3a**, the bulky 2,6-diisopropylbenzimine filled the position *trans* to the triphenylphosphine ligand with a P–Pd–N2 angle of 175.23(11)°;

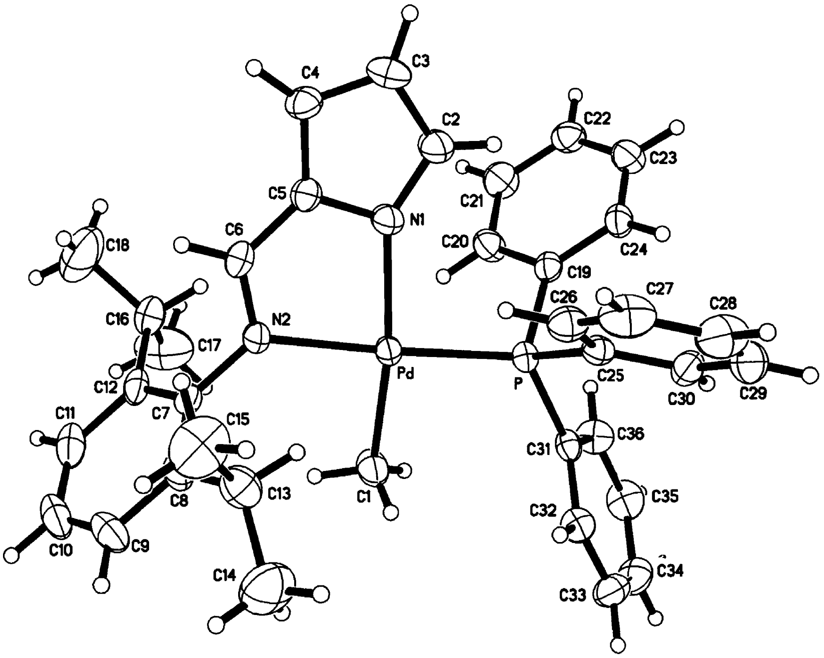


Fig. 1. ORTEP plot of the molecular structure of complex **3a**. Displacement ellipsoids are drawn at the 50% probability level.

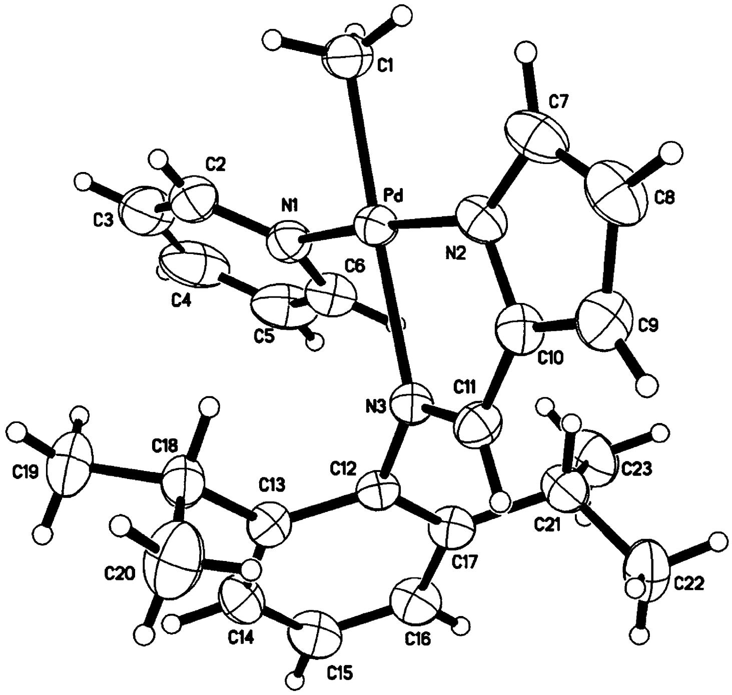


Fig. 2. ORTEP plot of the molecular structure of complex **4a**. Displacement ellipsoids are drawn at the 50% probability level.

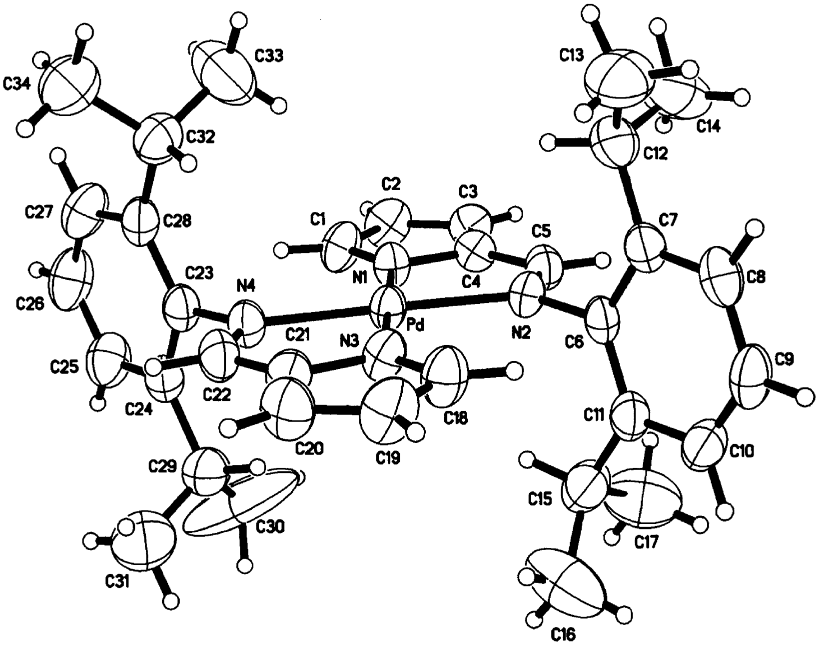


Fig. 3. ORTEP plot of the molecular structure of complex **5a**. Displacement ellipsoids are drawn at the 50% probability level.

the pyrrole group attached to Pd is in the position *trans* to the methyl ligand with a N1–Pd–C1 angle of 171.8(2)°, as shown in Fig. 1. While for **4a**, the 2,6-diisopropylbenzimine is at the position opposite to the methyl ligand with a N3–Pd–C1 angle of 172.86(10)°. The pyridine ligand lies *trans* to the pyrrole ligand through Pd with a N1–Pd–N2 angle of 174.50(9)°, as shown in Fig. 2. For **5a**, the two 2,6-diisopropylbenzimine ligands are *trans* to each other through Pd with a N4–Pd–N2 angle of 179.16(13)°, so are the two pyrrole ligands with a N1–Pd–N3 angle of 179.75(13)°, as shown in Fig. 3. From X-ray structural data by comparison of **3a** and **4a**, the Pd–C1 is sensitive to the nature of the *trans* ligand. The Pd–C1 length of **3a** is 2.022(7) Å and the Pd–C1 length of **4a** is shorter than that of **3a**, being 2.018(3) Å. This shows the ligand 2,6-diisopropylbenzimine has a stronger influence than the pyrrole ligand, according to Abu-Surrah et al. [31].

3.3. Polymerization of norbornene

Our main interest in the study of these complexes is their possible application as catalysts for the polymerization of norbornene and its derivatives. Preliminary experiments indicated that the single-component palladium complexes in the study, like single-component nickel complexes [14,15], are not able to catalyze norbornene polymerization, and MMAO alone is not able to catalyze norbornene polymerization too. From experiments, however, we found that these new neutral palladium complexes display high activities for norbornene polymerization when MMAO is used as a co-catalyst. Yet these catalysts do not work for polymerization of norbornene derivatives, which was not listed in this article.

Catalyst activities and polymer yields depended significantly on the reaction parameters applied to the polymerization of norbornene, as shown in Figs. 4–7. The concentration of norbornene should meet some requirements for good polymerization. In this system when the catalyst concentration reached 0.025 μmol/ml it did well, as shown in Fig. 4. Variation of molar ratio of MMAO to the catalyst **3c**, which is expressed here as the Al/Pd molar ratio, showed considerable effect on the polymerization reaction. When the mole ratio of Al/Pd

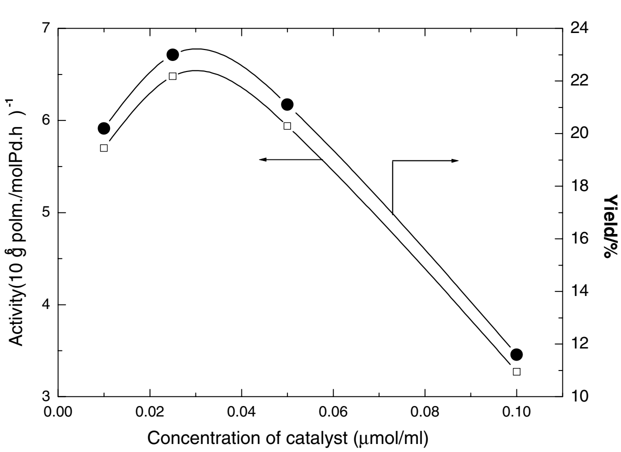


Fig. 4. Plot of polymer yield and catalytic activity versus catalyst concentration. **3a** as catalyst. $V_{\text{total}} = 20$ ml, polymerization reaction at 30 °C for 10 min.

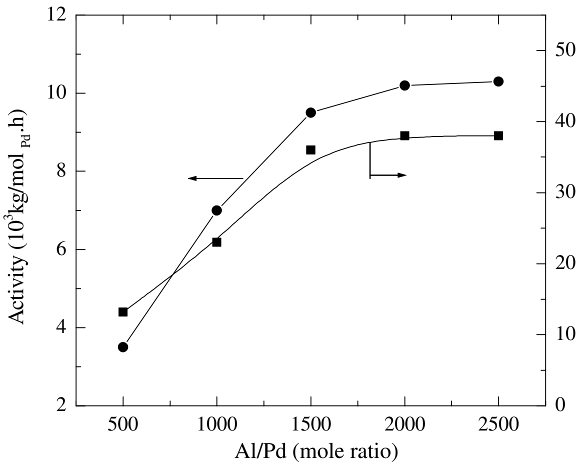


Fig. 5. Plot of polymer yield and catalytic activity versus Al/Pd molar ratio. $V_{total} = 20$ ml, polynorbornene/Pd = 50 000, catalyst (**3a**) = 0.5 μmol, polymerization reaction at 30 °C for 10 min.

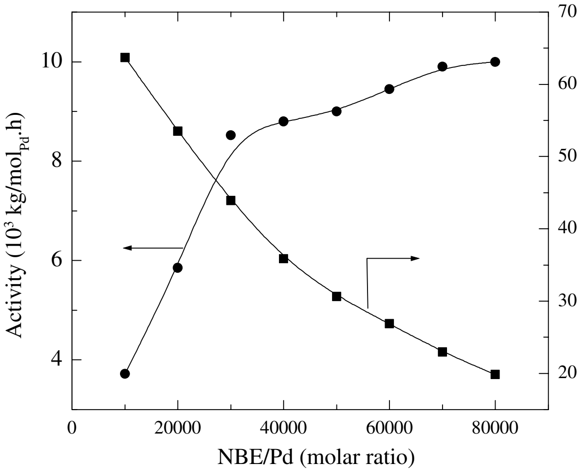


Fig. 6. Plot of polymer yield and catalytic activity versus norbornene/Pd molar ratio. $V_{total} = 20$ ml, catalyst (**3a**) = 0.5 μmol, Al/Pd = 1500, polymerization reaction at 30 °C for 10 min.

was 1500/1, the catalyst activity reached 1.01×10^7 g polym/mol$_{Pd}$ h, as shown in Fig. 5. On increasing the mole ratio of norbornene/Pd, while other conditions were kept constant, the catalyst activity of the catalyst **3c** grew, reaching 1.0×10^7 g polym/mol$_{Pd}$ h when the mole ratio of norbornene/Pd equalled 70 000, as shown in Fig. 6.

Meanwhile, the catalyst activity of the catalyst **8a** has been examined by varying the polymerization temperature, which is shown in Fig. 7. The catalyst activity first reached a peak and then gradually decreased with the increase of temperature, which means that to get high catalytic activity, polymerization reaction should be at the proper temperature.

The polymerization results using complexes **3a–d**, **4a**, **5a** and **8a–c** activated with MMAO are summarized in Table 3. From the results, we can see that the neutral palladium complexes bearing salicylaldiminato ligands displayed higher catalytic activities than those bearing pyrrole-imine chelate ligands. According to entries 1–4, with increasing the bulk in the *ortho* position of nitrogen atom of aniline, the polymerization activities decline, which means the bulkier the volumes of the substituents, the harder the insertion of norbornene. This is similar to some neutral nickel complexes [15].

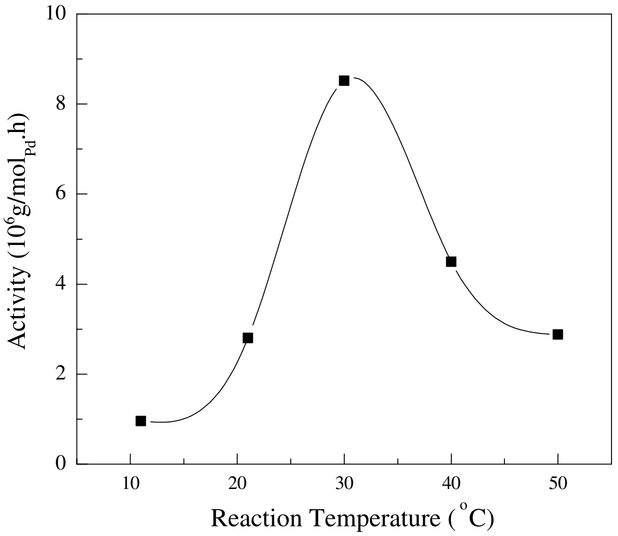


Fig. 7. Plot of polymer yield and catalytic activity versus reaction temperature (°C). $V_{total} = 11$ ml, catalyst (**8a**) = 0.5 μmol, Al/Pd = 2000, norbornene/Pd = 51 900, polymerization reaction at 30 °C for 10 min.

Table 3
Norbornene polymerizations catalysted with different neutral palladium complexes[a]

Entry	Catalyst	Al/Pd (molar ratio)	Yield (g)	Activity (10^6 g/mol$_{Pd}$ h)
1	**3a**	2000	0.14	1.68
2	**3b**	2000	0.23	2.76
3	**3c**	2000	0.22	3.00
4	**3d**	2000	0.25	2.64
5	**4a**	2000	0.32	3.84
6	**5a**	2000	0.13	1.56
7	**8a**	2000	0.71	8.52
8	**8b**	2000	0.47	5.64
9	**8c**	2000	0.26	3.12

[a] 0.5 μmol catalyst, 2.443 g norbornene, $V_{total} = 11$ ml, polymerization reaction for 10 min at 30 °C.

The poly(norbornene)s obtained are insoluble in choloform, benzene, chlorobenzene, 1,2-dichlorobenzene, *N*,*N*-dimethylformamide and *N*,*N*-dimethylacetamide, which is different from polymers got with neutral nickel catalysts [14,15]. The molecular weights of the polymers obtained could not be determined because of their insolubility, which is similar to the result reported by Hu and co-workers [16]. FTIR analyses of the poly(norbornene)s were performed. In the range of 1600–1670 cm^{-1} no absorption is observed which means the catalytic polymerization is via vinyl addition

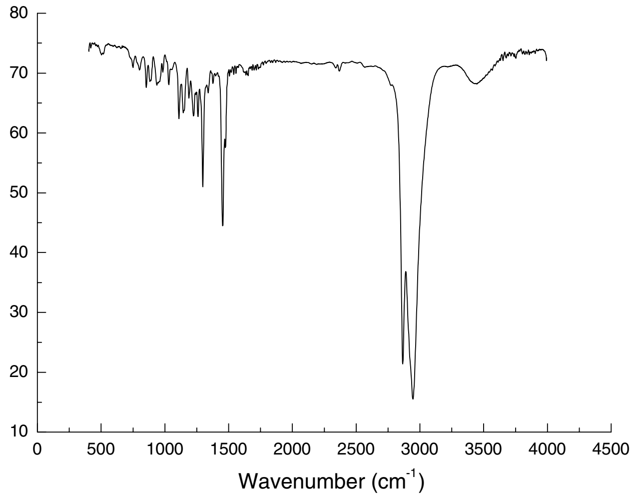


Fig. 8. FTIR spectrum of polynorbornene catalyzed by complex **3d**.

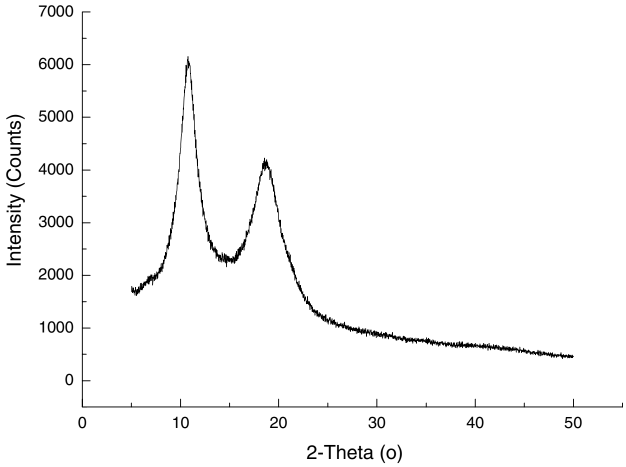


Fig. 9. WAXD plot of polynorbornene catalyzed by the catalyst **3d**.

polymerization, as shown in Fig. 8. WAXD has been employed to get information on the conformation of the polymer obtained. As shown in Fig. 9, we can see two peaks in the figure, 2θ equals 10.759 at peak 1, while 18.899 at peak 2. Haselwender et al. [41] and Zhao et al. [42] reported similar results which mean peak 1 is the reflection of the interchain or intersegment distance of the polymer, while peak 2 is the reflection of the intrachain distance. No traces of Bragg reflection, which is characteristic of a crystalline region were detected. Therefore, the polymer is non-crystalline.

4. Conclusions

In this article, several novel neutral palladium(II) complexes have been synthesized. The crystal structures of some of these complexes have been confirmed by X-ray analysis. High catalytic activities can be reached using these complexes activated with MMAO for vinyl-polymerization of norbornene. The complexes bearing salicylaldiminato ligands have more excellent activity than those bearing pyrrole-imine ligands for norbornene polymerization. IR analysis of the polymers identifies the polymerization is via vinyl addition mechanism. WAXD measurement implies the polymers are non-crystalline.

5. Supplementary material

Crystallographic data for the structures reported in this paper have been deposited at the Cambridge Crystallographic Data Center as supplementary publication numbers CCDC-219639, CCDC-219640 and CCDC-219641. Copies of the data can be obtained on application to: The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336-033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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