

**Palladium(II) complexes bearing a salicylaldiminato ligand with a hydroxyl group:
synthesis, structures, deprotonation, and catalysis.**

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Abstract

Palladium complexes with a salicylaldiminato ligand bearing a hydroxyl group (**1a** and **1b**) have been synthesized and characterized. The structures of these complexes were confirmed by X-ray crystallography. A reversible deprotonation/protonation of the hydroxyl moiety on **1b** was observed, while such behaviour was impossible with a related palladium complex (**1c**) bearing a methoxyl group in place of the hydroxyl group. The deprotonation affected its catalytic behaviour: the activity for polymerization of methyl acrylate catalyzed by **1b** considerably decreased in the presence of 1 equiv of ^tBuOK.

Key Word

palladium, salicylaldiminato ligand, acid-base behaviour, crystal structures, polymerization

1. Introduction

Much attention has been paid to transition-metal-catalyzed polymerization catalysts bearing salicylaldiminato ligands since both electronic and steric parameters of the ligands can be systematically tunable by introducing various substituents on the aromatic ring [1]. Among them, palladium complexes bearing the salicylaldiminato ligands were investigated as catalysts for polymerization of methyl acrylate, acrylonitrile, and norbornene [1n, 2]. Meanwhile, introduction of a hydroxyl group onto the aromatic ring is promising because electronic nature might be regulated by simple deprotonation/protonation procedures. Actually, catalytic activity can be controlled in the presence/absence of protons on ligands [3].

We anticipated that a salicylaldiminato ligand bearing a hydroxyl group would control the catalytic activity in the presence/absence of the proton near a metal center. In the present study, we designed and synthesized palladium complexes with a salicylaldiminato ligand having a hydroxyl functionality. The structures of these complexes were unambiguously determined by X-ray crystallography. Deprotonation of the hydroxyl group affected the electronic nature of the complex as well as catalytic activity for polymerization of methyl acrylate.

2. Experimental

2.1 General procedure

All manipulations were performed under an argon atmosphere using standard Schlenk-type glasswares on a dual-manifold Schlenk line. Unless otherwise noted, materials obtained from commercial suppliers were used without further purification. THF, CH_2Cl_2 and methyl acrylate were dried and purified before use by usual methods [4]. ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^1H NMR chemical shifts are reported relative to tetramethylsilane (TMS, 0.00 ppm). The ^{13}C NMR chemical shifts are reported relative to CDCl_3 (77.0 ppm). The ^{31}P NMR chemical shifts are reported relative to 85% H_3PO_4 (0.00 ppm) as an external standard. Analytical size-exclusion chromatography (SEC) was performed using CHCl_3 as the eluent at a flow rate of 1.0 mL/min on an HPLC (Shimadzu) equipped with a LC-10AT HPLC pump, a RID-10A RI detector through a column set consisting of Shodex -K-601L (0.8 × 30 cm × 2). Average molecular weights (M_n) and the polydisperse index (PDI) of poly(methyl acrylate) were determined by using polystyrene standards. Electron spray ionization time-of-flight mass spectrometry (ESI-TOF mass) was carried out on a waters LCT-Premier instrument. The sprayer was held at a potential of +2.6 kV in the positive detection mode or -2.8 kV in the negative detection mode. The orifice potential was maintained at 50V in each detection modes. Elemental

analysis was carried out at Center for Organic Elemental Microanalysis, Graduate School of Pharmaceutical Science, Kyoto University. TLC analyses were performed on commercial glass plates bearing a 0.25-mm layer of Merck Silica gel 60F254. *N*-(2,6-Diisopropylphenyl)-3-hydroxysalicylaldehyde (HL^{OH}) [1e], *N*-(2,6-diisopropylphenyl)-3-methoxysalicylaldehyde (HL^{OMe}) [1e], *cis*-(1,5-cyclooctadiene)dichloropalladium [PdCl₂(cod)] [5], and *cis*-(1,5-cyclooctadiene)chloromethylpalladium [PdClMe(cod)] [6] were also prepared according to literature procedures.

2.2 Synthesis of palladium complexes

2.2.1. Synthesis of PdCl(PPh₃)(L^{OH}) (**1a**)

To a solution of *N*-(2,6-diisopropylphenyl)-3-hydroxysalicylaldehyde (HL^{OH}, 0.40 g, 1.4 mmol) in THF (5.0 mL) was added a solution of ^tBuOK (1.0 M in THF, 2.8 mL, 2.8 mmol) at room temperature. After stirring for 30 min, all volatiles were removed in vacuo. The resulting solid residue was dissolved in dichloromethane (5.0 mL) and then PdCl₂(cod) (0.38 g, 1.33 mmol) and PPh₃ (0.35 g, 1.3 mmol) were added to the solution. After stirring at room temperature overnight, triethylammonium hydrogen chloride (0.20 g, 1.5 mmol) was added. The reaction mixture was stirred for additional 30 min and then filtered. Removal of all volatiles in vacuo gave crude products as yellow solids. Recrystallization from dichloromethane/hexane afforded **1a** as yellow crystals. Yield 0.63 g (68%). ¹H NMR (CDCl₃): δ 7.86 (d, ⁴J_{PH} = 13.4 Hz, 1H, ArN=CH), 7.8-7.7 (m, 6H, Ar(phosphine)), 7.6-7.5 (m, 3H, Ar(phosphine)), 7.5-7.4 (m, 6H, Ar(phosphine)), 7.2-7.1 (m, 3H, N-Ar), 6.80 (dd, ³J_{HH}=7.44 Hz, ⁴J_{HH}=1.49 Hz, 1H, Ar), 6.74 (dd, ³J_{HH}=7.93 Hz, ⁴J_{HH}=1.49 Hz, 1H, Ar), 6.50 (t, ³J_{HH} = 7.93 Hz, 1H, Ar), 4.99 (s, 1H, OH), 3.45 (sep, ³J_{HH} = 6.94 Hz, 2H, CH(CH₃)₂), 1.40 (d, ³J_{HH} = 6.94 Hz, 6H, CH(CH₃)₂), 1.15 (d, ³J_{HH} = 6.94 Hz, 6H, CH(CH₃)₂). ¹³C{¹H} NMR (CDCl₃): δ 163.3, 152.5, 147.7, 146.9, 141.3, 135.0, 134.8, 131.2, 131.1, 129.0, 128.6, 128.4, 128.3, 126.7, 125.1, 122.9, 118.0, 116.0, 115.6, 28.7, 24.6, 22.9. ³¹P{¹H} NMR (CDCl₃): δ 30.5. ESI-TOF mass (in the negative mode, MeOH), *m/z* 698.2 ([**1a** - H]⁻; *I* = 100% in the range of *m/z* 100-2000). *Anal.* Calcd for C₃₇H₃₇ClNO₂PPd: C 63.44, H 5.32, N 2.00. Found: C 63.37, H 5.43, N 1.91%.

2.2.2. Synthesis of PdMe(PPh₃)(L^{OH}) (**1b**)

The complex was synthesized with PdClMe(cod) (0.35 g, 1.3 mmol) instead of PdCl₂(cod) by the method similar to that used for **1a**. Yield 0.82 g (91%). ¹H NMR (CDCl₃): δ 7.99 (d, ⁴J_{PH} =

11.4 Hz, 1H, ArN=CH), 7.7-7.5 (m, 6H, Ar(phosphine)), 7.5-7.3 (m, 9H, Ar(phosphine)), 7.2 (m, 3H, N-Ar), 6.78 (dd, $^3J_{\text{HH}}=7.44$ Hz, $^4J_{\text{HH}}=1.49$ Hz, 1H, Ar), 6.64 (dd, $^3J_{\text{HH}}=8.43$ Hz, $^4J_{\text{HH}}=1.49$ Hz, 1H, Ar), 6.34 (dd, $^3J_{\text{HH}}=7.44$ Hz, $^3J_{\text{HH}}=8.43$ Hz, 1H, Ar), 5.76 (s, 1H, OH), 3.46 (sep, $^3J_{\text{HH}}=6.94$ Hz, 2H, CH(CH₃)₂), 1.34 (d, $^3J_{\text{HH}}=6.94$ Hz, 6H, CH(CH₃)₂), 1.13 (d, $^3J_{\text{HH}}=6.94$ Hz, 6H, CH(CH₃)₂), -0.35 (d, $^3J_{\text{PH}}=2.98$ Hz, 3H, Pd-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 165.8, 156.9, 149.1, 147.3, 140.9, 134.7, 134.5, 131.0, 130.6, 130.9, 130.3, 128.4, 128.3, 126.2, 125.2, 123.3, 117.0, 113.8, 113.1, 28.0, 25.1, 22.5, 0.19 (d, $^2J_{\text{cp}}=11.2$ Hz, Pd-CH₃). ³¹P{¹H} NMR (CDCl₃): δ 43.32. ESI-TOF mass (in the negative mode, MeOH), m/z 678.2 ([**1b** - H]⁻; $I=100\%$ in the range of m/z 100-2000). *Anal.* Calcd for C₃₈H₄₀NO₂PPd: C 67.11, H 5.93, N 2.06. Found: C 67.05, H 5.97, N 2.09%.

2.2.3. Synthesis of PdMe(PPh₃)(L^{OMe}) (**1c**)

To a solution of *N*-(2,6-diisopropylphenyl)-3-methoxysalicylaldehyde (HL^{OMe}, 0.42 g, 1.4 mmol) in THF (5.0 mL) was added a solution of ^tBuOK (1.0 M in THF, 1.4 mL, 1.4 mmol) at room temperature. After stirring for 30 min, all volatiles were removed in vacuo. The resulting solid residue was dissolved in dichloromethane (5.0 mL), and then PdClMe(cod) (0.35 g, 1.3 mmol) and PPh₃ (0.35 g, 1.3 mmol) were added to the solution. After stirring at room temperature overnight, all volatiles were removed in vacuo. The resulting crude products were purified by recrystallization from dichloromethane/hexane afforded **1c** as yellow crystals. Yield 0.79 g (86%). ¹H NMR(CDCl₃): δ 7.97 (d, $^4J_{\text{PH}}=11.4$ Hz, 1H, ArN=CH), 7.7-7.6 (m, 6H, Ar(phosphine)), 7.5-7.3 (m, 9H, Ar(phosphine)), 7.2 (m, 3H, N-Ar), 6.73 (d, $^3J_{\text{HH}}=7.44$ Hz, 1H, Ar), 6.72 (d, $^3J_{\text{HH}}=8.43$ Hz, 1H, Ar), 6.36 (t, $^3J_{\text{HH}}=7.93$ Hz, 1H, Ar), 3.67 (s, 3H, OCH₃), 3.52 (sep, $^3J_{\text{HH}}=6.94$ Hz, 2H, CH(CH₃)₂), 1.29 (d, $^3J_{\text{HH}}=6.94$ Hz, 6H, CH(CH₃)₂), 1.11 (d, $^3J_{\text{HH}}=6.94$ Hz, 6H, CH(CH₃)₂), -0.45 (d, $^3J_{\text{PH}}=2.53$ Hz, 3H, Pd-CH₃). ¹³C{¹H} NMR (CDCl₃): δ 165.6, 160.5, 152.9, 147.7, 141.1, 135.0, 134.9, 131.9, 131.2, 130.1, 130.0, 128.1, 128.0, 127.2, 126.0, 123.2, 118.7, 113.2, 111.7, 55.4, 27.9, 25.0, 22.5, 1.79 (d, $^2J_{\text{cp}}=11.2$ Hz, Pd-CH₃). ³¹P{¹H} NMR (CDCl₃): δ 35.9. ESI-TOF mass (in the positive mode, MeOH), m/z 716.2 ([**1c** + Na]⁺; $I=100\%$ in the range of m/z 100-2000). *Anal.* Calcd for C₃₉H₄₂NO₂PPd·0.5H₂O: C 66.62, H 6.16, N 1.99. Found: C 66.63, H 6.18, N 1.93%.

2.3 General procedure for polymerization

In a glove box under a nitrogen atmosphere, a 20 mL Schlenk flask was charged with **1** (0.011 mmol), THF (0.30 mL) and dichloromethane (3.6 mL). In the case of the addition of ^tBuOK

(1.0 M in THF, 11 μ L, 0.011 mmol), the base was added before charging dichloromethane. After methyl acrylate (1.0 mL, 12 mmol) was introduced to the flask, the reaction mixture was stirred at the ambient temperature for 24 h. The reaction mixture was poured into 50 mL of methanol and precipitated polymers were collected by filtration and dried under vacuum at 60 $^{\circ}$ C for 24 h. Average molecular weights (M_n) and the polydisperse index (PDI) of poly(methyl acrylate) were determined using polystyrene standards.

2.4 X-ray crystallography

A summary of crystal structure refinements of **1a–1c** was given in Table 1. Data were collected on a Rigaku/Saturn70 CCD diffractometer using graphite-monochromated Mo $K\alpha$ radiation (λ = 0.71070 $\text{\AA}$) at 153 K, and processed using CrystalClear (Rigaku) [7]. The structures were solved by a direct method and refined by full-matrix least-square refinement on F^2 . The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located on the calculated positions and not refined. All calculations were performed using the CrystalStructure software package [8].

3. Results and Discussion

3.1. Synthesis and structure of palladium complexes

A ligand precursor (HL^{OH}) was readily prepared by the reaction of 2,3-dihydroxybenzaldehyde with 2,6-diisopropylaniline in methanol [1e]. Palladium complexes with a salicylaldiminato ligand bearing a hydroxyl group (L^{OH}) were synthesized as shown in Scheme 1. First, the reaction of the ligand precursor with 2 equiv of $t\text{BuOK}$ afforded a dianionic intermediate in situ. Then, addition of $\text{PdCl}(\text{X})(\text{cod})$ ($\text{X} = \text{Cl}$ or $= \text{Me}$) and PPh_3 in CH_2Cl_2 followed by the treatment of $\text{Et}_3\text{N}\cdot\text{HCl}$ afforded $\text{PdX}(\text{PPh}_3)(\text{L}^{\text{OH}})$ ($\text{X} = \text{Cl}$ (**1a**) or $= \text{Me}$ (**1b**)) in good yields. For comparison, a related palladium complex with a salicylaldiminato ligand bearing a methoxyl group (L^{OMe}), $\text{PdMe}(\text{PPh}_3)(\text{L}^{\text{OMe}})$ (**1c**), in place of the hydroxyl group was also synthesized by the reaction of the corresponding salicylaldimine with $t\text{BuOK}$ followed by adding $\text{PdClMe}(\text{cod})$ and PPh_3 (Scheme 2). All complexes were fully characterized by elemental analysis and NMR measurements.

The molecular structures of **1a–1c** have been successfully determined by X-ray crystallography. Suitable single crystals of **1a–1c** were obtained by crystallization from hot heptane solution. For **1a**, there are two independent molecules in a unit cell (see Table 1). Fig. 1a shows the ORTEP drawing for **1a**. The palladium atom has a square-planar coordination geometry. The chlorine atom attached to the Pd atom lies *trans* to the oxygen atom.

Triphenylphosphine ligand occupies the position *trans* to the nitrogen due to a steric hindrance between PPh₃ ligand and the 2,6-diisopropylphenyl group. Selected bond lengths and bond angles were summarized in Table 2. These bond lengths and bond angles around the palladium atom were comparable to those of analogous palladium complexes [1n, 2b-d]. In the structures of **1b** and **1c** shown in Figs. 1b–1c, each palladium atom has also a square-planar coordination geometry. The CH₃ group coordinating to the Pd atom lies *trans* to the oxygen atom. PPh₃ ligand occupies the position *trans* to the nitrogen bearing the bulky 2,6-diisopropyl group. Selected bond lengths and bond angles were summarized in Table 3. The Pd–C bond length of **1b** (2.064(4) Å) was similar to that of **1c** (2.059(5) Å) and other Pd–C(CH₃) bond lengths of the complexes bearing salicylaldiminato ligands are in the range between 2.001 Å and 2.046 Å [1n, 2a-c].

The ¹H NMR spectra of **1a–1c** in CDCl₃ displayed characteristic resonances. Signals corresponding to the methyl protons of the isopropyl moieties on the salicylaldiminato ligand were split into two doublets indicating rotations between the nitrogen and the ipso carbon of **1a–1c** were restricted. The ketimine (HC=N) proton resonances of **1a–1c** were displayed as doublets near 8.0 ppm with a phosphorus coupling (⁴J_{PH} = ca. 12 Hz). These chemical shifts and coupling constants were similar to those observed for analogous complexes [1n, 2b]. As for **1a** and **1b**, proton resonances of the hydroxyl moiety were observed at 4.99 ppm (**1a**) and 5.76 ppm (**1b**), suggesting an existence of intramolecular hydrogen bond with the oxygen atom coordinating to the palladium [9]. Resonances of the methyl group on the palladium appeared as a doublet at –0.36 ppm (³J_{PH} = 2.98 Hz) for **1b** and –0.45 ppm (³J_{PH} = 2.53 Hz) for **1c**, respectively. In ¹³C NMR, a resonance of the methyl group was observed as a doublet at 0.19 ppm (²J_{PC} = 11.2 Hz) for **1b** and 1.79 ppm (²J_{PC} = 11.2 Hz) for **1c**. These resonances are similar to other methylpalladium complexes bearing salicylaldiminato ligands [1n]. ³¹P resonances of **1a–1c** in CDCl₃ appeared at 30.54 ppm, 43.51 ppm and 35.92 ppm, respectively.

3.2. Deprotonation of **1b**

The complex **1b** has the hydroxyl moiety in the close proximity of the palladium center and the hydroxyl functionality can be deprotonated by the addition of a base. In ¹H NMR spectrum of **1b** in THF-*d*₈, a signal at 5.76 ppm attributed to the hydroxyl proton (signal *b* in Fig. 2a) disappeared on adding 1 equiv of ^tBuOK in THF (Fig. 2b). In addition, the signal *a* assigned to the imino proton (8.08 ppm, ⁴J_{PH} = 10.7 Hz) showed down-field shift to 8.64 ppm. The methyl proton resonance of **1b** observed as a doublet peak at –0.36 ppm (signals *c* in Fig. 2a) was shifted to 0.12 ppm (²J_{PH} = 3.17 Hz) on the deprotonation (Fig. 2b). Other resonances of the

salicylaldiminato ligand also moved as shown in Fig. 2b. In addition, a ^{31}P resonance of **1b** at 43.51 ppm was shifted to 36.38 ppm after the addition of $t\text{BuOK}$. Here, no free PPh_3 resonance (-4.54 ppm in $\text{THF-}d_8$) [10] was observed. These clear spectral changes caused with adding $t\text{BuOK}$ was not observed with **1c** bearing the methoxyl moiety in place of the hydroxyl group. Notably, **1b** was restored by adding 1 equiv HCl in Et_2O to the deprotonated **1b** (from Fig. 2b to Fig. 2c), indicating the reversible change observed with **1b** (Figs. 2a–b) must be due to the deprotonation/protonation of the hydroxyl group on the salicylaldiminato ligand.

3.3 Polymerization of methyl acrylate

The polymerization of methyl acrylate was carried out in a mixture of THF and CH_2Cl_2 in the presence of a catalytic amount of **1b** or **1c** ($\text{S/C} = 1000$) at room temperature (Table 3). Employing **1b** as a catalyst, poly(methyl acrylate) was obtained in 79% yield with a moderate polydispersity (entry 1) [11]. According to ^1H and ^{13}C NMR spectra, the polymer thus obtained had atactic microstructures [12]. As a catalyst, **1c** showed the comparable result (entry 2). However, effect of the addition of $t\text{BuOK}$ was quite different between **1b** and **1c**. The catalytic activity of **1b** in the presence of 1 equiv $t\text{BuOK}$ drastically decreased, giving the corresponding polymer in 19% yield (entry 4). On the other hand, in the case of **1c** as the catalyst, the reaction was not suppressed by the added $t\text{BuOK}$ (entry 5). These results clearly indicate that the presence of potassium cation close proximity to the palladium center affects the catalytic activity considerably.

4. Conclusion

New palladium complexes with salicylaldiminato ligands (**1a–1c**) were synthesized and their structures were confirmed by X-ray crystallography. A reversible deprotonated/protonation of the hydroxyl group of **1b** was observed. Notably, the introduction of potassium cation in close proximity to the palladium affected the catalytic activity considerably in the polymerization of methyl acrylate.

Appendix A. Supplementary data

Crystallographic data for complexes **1a–1c** have been deposited with the Cambridge Crystallographic Data Centre, CCDC Nos. 786886, 786887, and 786888, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Table 1Crystallographic data of **1a** – **1c**

	1a	1b	1c
empirical formula	C ₃₇ H ₃₆ NO ₂ ClPdP	C ₃₈ H ₃₉ NO ₂ PdP	C ₃₉ H ₄₂ NO ₂ PdP
formula weight	699.52	679.11	682.05
temp / K	153	153	153
crystal system	monoclinic	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ /c (#14)	<i>P</i> 2 ₁ /c (#14)	<i>P</i> 2 ₁ /n (#14)
<i>a</i> / Å	20.286(5)	14.422(3)	11.423(4)
<i>b</i> / Å	11.491(2)	11.035(2)	24.228(7)
<i>c</i> / Å	29.737(7)	21.495(5)	12.344(4)
β / deg	107.427(3)	105.888(3)	100.144(5)
<i>V</i> / Å ³	6613(3)	3290(1)	3363(1)
<i>Z</i>	8	4	4
$\rho_{\text{calc}}/\text{g cm}^{-3}$	1.405	1.371	1.371
unique reflections	14825 (<i>R</i> _{int} = 0.092)	7224 (<i>R</i> _{int} = 0.064)	7444 (<i>R</i> _{int} = 0.085)
observed reflections	14825 (all data)	7224 (all data)	7444 (all data)
GOF	1.025	1.010	1.047
<i>R</i> 1 (<i>I</i> > 2 σ (<i>I</i>)) ^a	0.055, 0.141 ^b	0.047, 0.095 ^c	0.059, 0.131 ^d
<i>wR</i> 2 (all data) ^a			

^a $R1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $wR2 = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma w(F_o^2)^2]^{1/2}$, ^b $w = 1/[0.7\sigma(F_o^2)]/(4F_o^2)$. ^c $w = 1/[0.9\sigma(F_o^2)]/(4F_o^2)$. ^d $w = 1/[0.7\sigma(F_o^2)]/(4F_o^2)$.

Table 2Selected bond lengths (Å) and angles (deg) for **1a**

	1a (complex A)	1a (complex B)
Pd-Cl	2.2671(11)	2.2817(14)
Pd-N	2.074(4)	2.2454(14)
Pd-P	2.2513(14)	2.073(4)
Pd-O	2.005(3)	2.001(3)
Cl-Pd-N	91.53(11)	93.49(12)
Cl-Pd-O	175.01(10)	175.33(10)
Cl-Pd-P	85.87(4)	84.32(4)
N-Pd-O	91.64(14)	91.01(15)
N-Pd-P	174.03(12)	177.80(12)
O-Pd-P	91.33(10)	91.18(10)

Table 3Selected bond lengths (Å) and angles (deg) for **1b** and **1c**

	1b	1c
Pd-C(1)	2.064(4)	2.059(5)
Pd-N(1)	2.095(2)	2.096(4)
Pd-P(1)	2.2265(8)	2.2620(16)
Pd-O(1)	2.099(2)	2.100(3)
C(1)-Pd(1)-N(1)	92.03(13)	90.99(19)
C(1)-Pd(1)-O(1)	173.72(11)	176.50(19)
C(1)-Pd(1)-P(1)	84.08(10)	83.58(16)
N(1)-Pd(1)-O(1)	89.27(11)	88.45(16)
N(1)-Pd(1)-P(1)	175.48(9)	174.18(12)
O(1)-Pd(1)-P(1)	94.84(7)	97.09(11)

Table 3Palladium-catalyzed polymerization of methyl acrylate^a

entry	catalyst	additive	Yield (%)	$M_n(\times 10^{-3})^b$	PDI ^b
1	1b	none	79	116	2.30
2	1c	none	70	114	2.13
3	1b	^t BuOK ^c	19	129	1.84
4	1c	^t BuOK ^c	70	135	1.94

^a Conditions: methyl acrylate (1.0 mL, 12 mmol), **1** (0.011 mmol, S/C = 1000), THF/CH₂Cl₂ = 0.3 mL/3.6 mL, RT, 24 h. ^b Determined by analytical SEC using polystyrenes as a standard. ^c ^tBuOK (1.0 M solution in THF, 0.011 mmol) was used.

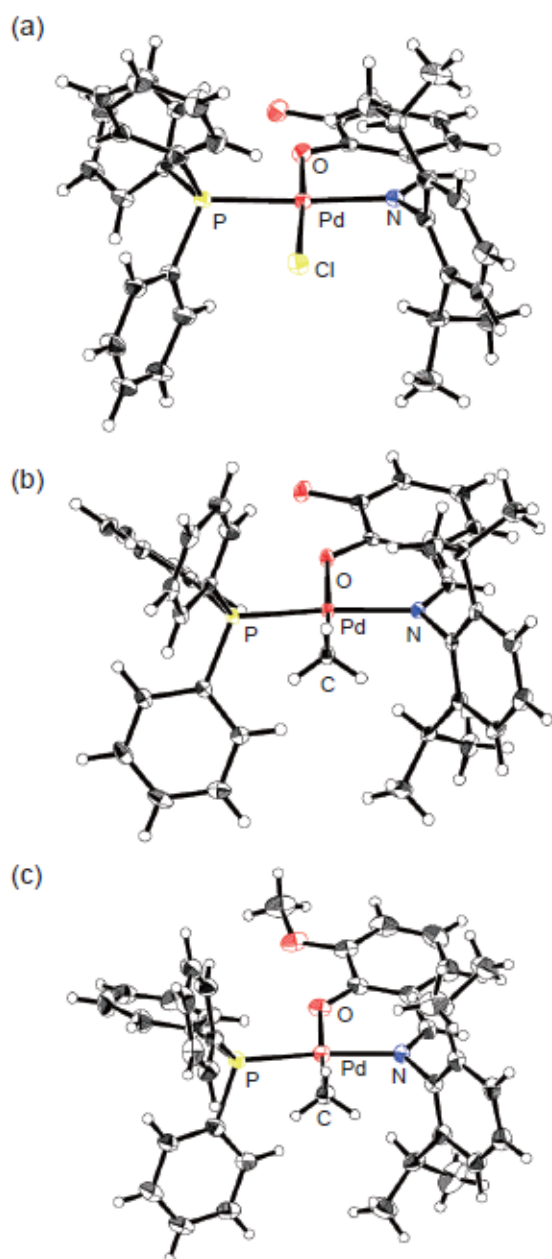


Fig. 1. ORTEP drawings of (a) **1a**, (b) **1b** and (c) **1c** with thermal ellipsoids at 30% probability levels.

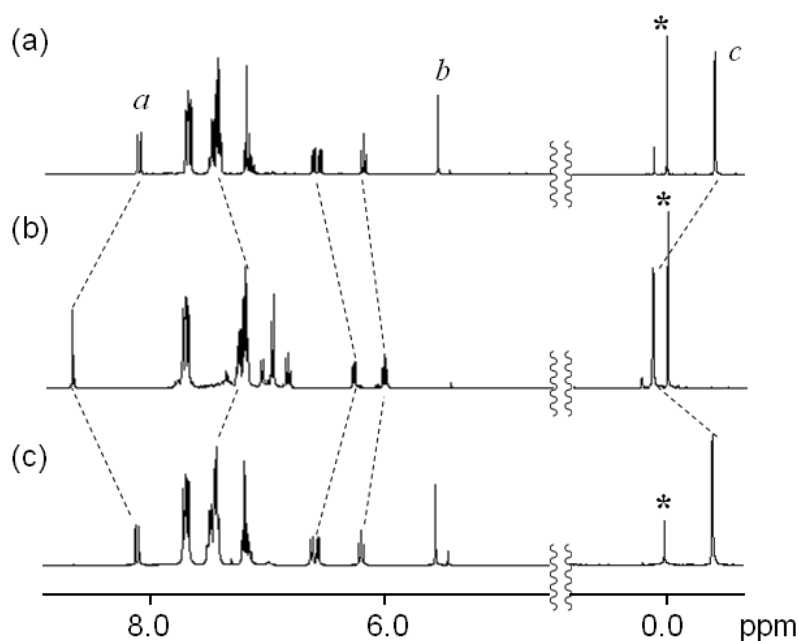
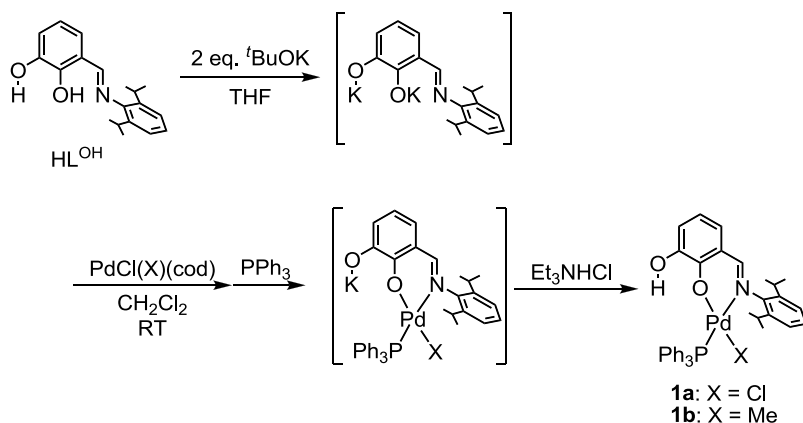
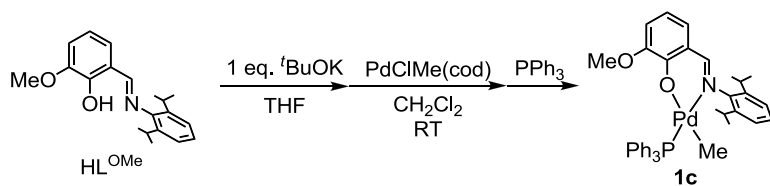


Fig. 2. ^1H NMR spectra of (a) **1b** in $\text{THF-}d_8$, (b) after the addition of 1 equiv $t\text{BuOK}$ in THF, and (c) after further addition of 1 equiv HCl in Et_2O . * indicates TMS.



Scheme 1

Synthesis of palladium complexes **1a** and **1b**.



Scheme 2

Synthesis of a palladium complex **1c**.