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Note

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 ^{t}BuOK.

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 [1b,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 salicylaldimiato 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]. ^{1}H, ^{13}C{^{1}H} and ^{31}P{^{1}H} NMR spectra were measured with a JEOL ECX-400P spectrometer. The ^{1}H 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 (*Mn*) 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 50 V 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

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Merck Silica gel 60F254. *N*-(2,6-Diisopropylphenyl)-3-hydroxysalicylaldimine (HL^{OH}) [1a], *N*-(2,6-diisopropylphenyl)-3-methoxysalicylaldimine (HL^{OMe}) [1a], *cis*- (1,5-cyclooctadiene)dichloropalladium [$PdCl_2$(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 $PdCl(PPh_3)(L^{OH})$ (**1a**)

To a solution of *N*-(2,6-diisopropylphenyl)-3-hydroxysalicylaldimine (HL^{OH}, 0.40 g, 1.4 mmol) in THF (5.0 mL) was added a solution of ^{t}BuOK (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 $PdCl_2$(cod) (0.38 g, 1.33 mmol) and PPh_3 (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%). ^{1}H NMR ($CDCl_3$): δ 7.86 (d, $^4J_{PH}$ = 13.4 Hz, 1H, ArN=C*H*), 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, O*H*), 3.45 (sep, $^3J_{HH}$ = 6.94 Hz, 2H, C*H*(CH_3)$_2$), 1.40 (d, $^3J_{HH}$ = 6.94 Hz, 6H, CH(C*H*$_3$)$_2$), 1.15 (d, $^3J_{HH}$ = 6.94 Hz, 6H, CH(C*H*$_3$)$_2$). ^{13}C{^{1}H} NMR ($CDCl_3$): 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. ^{31}P{^{1}H} NMR ($CDCl_3$): 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.* Calc. for $C_{37}H_{37}ClNO_2PPd$: C, 63.44; H, 5.32; N, 2.00. Found: C, 63.37; H, 5.43; N, 1.91%.

2.2.2. Synthesis of $PdMe(PPh_3)(L^{OH})$ (**1b**)

The complex was synthesized with PdClMe(cod) (0.35 g, 1.3 mmol) instead of $PdCl_2$(cod) by the method similar to that used for **1a**. Yield 0.82 g (91%). ^{1}H NMR ($CDCl_3$): δ 7.99 (d, $^4J_{PH}$ = 11.4 Hz, 1H, ArN=C*H*), 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, $^3J_{HH}$ = 7.44 Hz, $^4J_{HH}$ = 1.49 Hz, 1H, Ar), 6.64 (dd, $^3J_{HH}$ = 8.43 Hz, $^4J_{HH}$ = 1.49 Hz, 1H, Ar), 6.34 (dd, $^3J_{HH}$ = 7.44 Hz, $^3J_{HH}$ = 8.43 Hz, 1H, Ar), 5.76 (s, 1H, O*H*), 3.46 (sep, $^3J_{HH}$ = 6.94 Hz, 2H, C*H*(CH_3)$_2$), 1.34 (d, $^3J_{HH}$ = 6.94 Hz, 6H, CH(C*H*$_3$)$_2$), 1.13 (d, $^3J_{HH}$ = 6.94 Hz, 6H, CH(C*H*$_3$)$_2$), −0.35 (d, $^3J_{PH}$ = 2.98 Hz, 3H, Pd–C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 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, $^2J_{cp}$ = 11.2 Hz, Pd–C*H*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): 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.* Calc. for $C_{38}H_{40}NO_2PPd$: C, 67.11; H, 5.93; N, 2.06. Found: C, 67.05; H, 5.97; N, 2.09%.

2.2.3. Synthesis of $PdMe(PPh_3)(L^{OMe})$ (**1c**)

To a solution of *N*-(2,6-diisopropylphenyl)-3-methoxysalicylaldimine (HL^{OMe}, 0.42 g, 1.4 mmol) in THF (5.0 mL) was added a solution of ^{t}BuOK (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 PPh_3 (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%). ^{1}H NMR($CDCl_3$): δ 7.97 (d, $^4J_{PH}$ = 11.4 Hz, 1H, ArN=C*H*), 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, $^3J_{HH}$ = 7.44 Hz, 1H, Ar), 6.72 (d, $^3J_{HH}$ = 8.43 Hz, 1H, Ar), 6.36 (t, $^3J_{HH}$ = 7.93 Hz, 1H, Ar), 3.67 (s, 3H, OC*H*$_3$), 3.52 (sep, $^3J_{HH}$ = 6.94 Hz, 2H, C*H*(CH_3)$_2$), 1.29 (d, $^3J_{HH}$ = 6.94 Hz, 6H, CH(C*H*$_3$)$_2$), 1.11 (d, $^3J_{HH}$ = 6.94 Hz, 6H, CH(C*H*$_3$)$_2$), −0.45 (d, $^3J_{PH}$ = 2.53 Hz, 3H, Pd–C*H*$_3$). ^{13}C{^{1}H} NMR ($CDCl_3$): 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, $^2J_{cp}$ = 11.2 Hz, Pd–C*H*$_3$). ^{31}P{^{1}H} NMR ($CDCl_3$): 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.* Calc. for $C_{39}H_{42}NO_2PPd{\cdot}0.5H_2O$: 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 ^{t}BuOK (1.0 M in THF, 11 μL, 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 °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 Kα radiation (λ = 0.71070 Å) 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

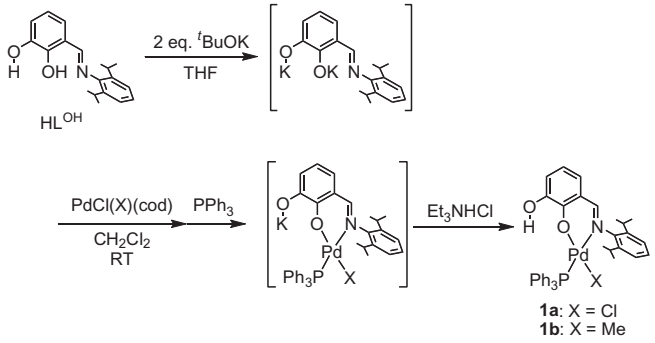
A ligand precursor (HL^{OH}) was readily prepared by the reaction of 2,3-dihydroxybenzaldehyde with 2,6-diisopropylaniline in methanol [1a]. Palladium complexes with a salicylaldiminato ligand bearing a hydroxyl group (L^{OH}) were synthesized as shown in Scheme 1. First, the reaction of the ligand precursor with 2 equiv. of ^{t}BuOK afforded a dianionic intermediate in situ. Then, addition of PdCl(X)(cod) (X = Cl or = Me) and PPh_3 in CH_2Cl_2 followed by the treatment of $Et_3N{\cdot}HCl$ afforded $PdX(PPh_3)(L^{OH})$ (X = Cl (**1a**) or = Me (**1b**)) in good yields. For comparison, a related palladium complex with a salicylaldiminato ligand bearing a methoxyl group (L^{OMe}), $PdMe(PPh_3)(L^{OMe})$ (**1c**), in place of the hydroxyl group was also synthesized by the reaction of the corresponding salicylaldimine with ^{t}BuOK followed by adding PdClMe(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

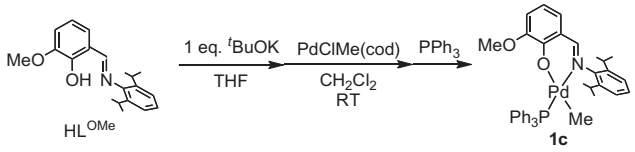
Table 1
Crystallographic data of **1a**–**1c**.

	1a	1b	1c
Empirical formula	$C_{37}H_{36}NO_2ClPdP$	$C_{38}H_{39}NO_2PdP$	$C_{39}H_{42}NO_2PdP$
Formula weight	699.52	679.11	682.05
T (K)	153	153	153
Crystal system	monoclinic	monoclinic	monoclinic
Space group	$P2_1/c$ (#14)	$P2_1/c$ (#14)	$P2_1/n$ (#14)
a (Å)	20.286(5)	14.422(3)	11.423(4)
b (Å)	11.491(2)	11.035(2)	24.228(7)
c (Å)	29.737(7)	21.495(5)	12.344(4)
β (°)	107.427(3)	105.888(3)	100.144(5)
V (Å^3)	6613(3)	3290(1)	3363(1)
Z	8	4	4
ρ_{cacd} (g cm^{-3})	1.405	1.371	1.371
Unique reflections	14825 (R_{int} = 0.092)	7224 (R_{int}= 0.064)	7444 (R_{int} = 0.085)
Observed reflections	14825 (all data)	7224 (all data)	7444 (all data)
Goodness-of-fit (GOF)	1.025	1.010	1.047
R_1 ($I > 2\sigma(I)$)[a] $wR2$ (all data)[a]	0.055, 0.141[b]	0.047, 0.095[c]	0.059, 0.131[d]

[a] $R_1 = \Sigma[|F_o| - |F_c|]/\Sigma|F_o|$, $wR_2 = [\Sigma(w(F_o^2 - F_c^2)^2)/\Sigma w(F_o^2)^2]^{1/2}$.
[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] $w = 1/[0.7\sigma(F_o^2)]/(4F_o^2)$.



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



Scheme 2. Synthesis of a palladium complex **1c**.

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 PPh_3 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 [1b,2b–d]. In the structures of **1b** and **1c** shown in Fig. 1b and c, each palladium atom has also a square-planar coordination geometry. The CH_3 group coordinating to the Pd atom lies *trans* to the oxygen atom. PPh_3 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

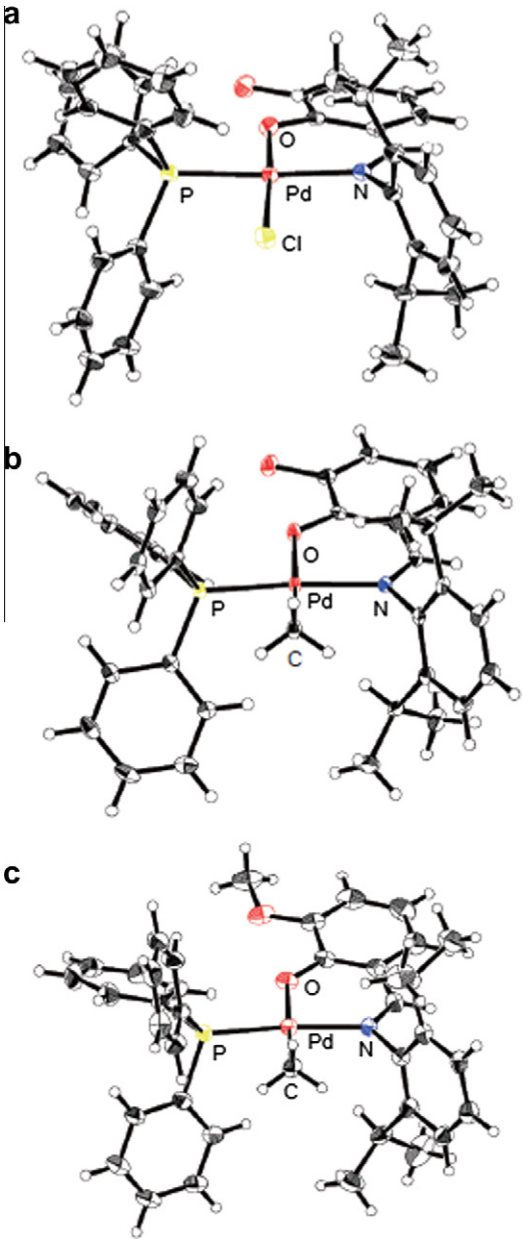


Fig. 1. ORTEP drawings of (a) **1a**, (b) **1b** and (c) **1c** with thermal ellipsoids at 30% probability levels.

Table 2
Selected bond lengths (Å) and angles (°) 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)

Pd–C bond length of **1b** (2.064(4) Å) was similar to that of **1c** (2.059(5) Å) and other Pd–C(CH_3) bond lengths of the complexes

Table 3
Selected bond lengths (Å) and angles (°) 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)

bearing salicylaldiminato ligands are in the range between 2.001 and 2.046 Å [1b,2a–c].

The ^{1}H NMR spectra of **1a**–**1c** in $CDCl_3$ 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 (*H*C=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 [1b,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 ^{13}C 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 [1b]. ^{31}P resonances of **1a**–**1c** in $CDCl_3$ 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 ^{1}H 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 ^{t}BuOK 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}BuOK. Here, no free PPh_3 resonance (−4.54 ppm in THF-d_8) [10] was observed. These clear spectral changes caused with adding ^{t}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 c), indicating the reversible change observed with **1b** (Fig. 2a and 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** (S/C = 1000) at room temperature (Table 4). Employing **1b** as a catalyst, poly(methyl acrylate) was obtained in 79% yield with a moderate polydispancy (entry 1).[1] According to ^{1}H and ^{13}C NMR spectra, the polymer thus obtained had atactic microstructures [11]. As a catalyst, **1c** showed the comparable result (entry 2). However, effect of the addition of ^{t}BuOK was quite different between **1b** and **1c**. The catalytic activity of **1b** in the presence of 1 equiv. ^{t}BuOK drastically decreased, giving the corresponding polymer in 19% yield (entry 3). On the other hand, in the case of **1c** as the catalyst, the reaction was not suppressed by the added ^{t}BuOK (entry 4). These results clearly indicate that the presence of potassium cation close proximity to the palladium center affects the catalytic activity considerably.

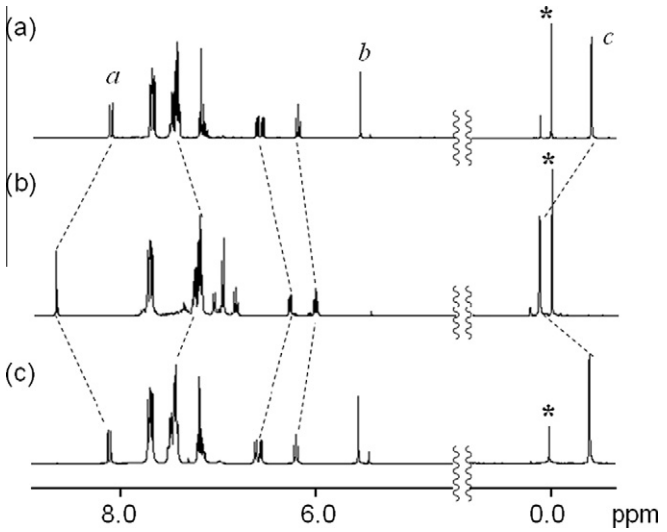


Fig. 2. ^{1}H NMR spectra of (a) **1b** in THF-d_8, (b) after the addition of 1 equiv. ^{t}BuOK in THF, and (c) after further addition of 1 equiv. HCl in Et_2O. *Indicates TMS.

Table 4
Palladium-catalyzed polymerization of methyl acrylate.[a]

Entry	Catalyst	Additive	Yield (%)	$Mn(\times 10^{-3})$ [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 acylate (1.0 mL, 12 mmol), **1** (0.011 mmol, S/C = 1000), THF/CH_2Cl_2 = 0.3 mL/3.6 mL, RT, 24 h.
[b] Determined by analytical SEC using polystyrenes as a standard.
[c] ^{t}BuOK (1.0 M solution in THF, 0.011 mmol) was used.

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 material

CCDC 786886, 786887, and 786888; contain the supplementary crystallographic data for complexes **1a**–**c**. These data can be

[1] The polymerization reaction of entry 1 in Table 4 was completely halted upon the addition of galvinoxyl, suggesting the reaction would proceed via some radical pathway [2a].

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.ica.2010.12.036.

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