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 'BuOK.

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 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$_2$Cl$_2$ 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$_3$PO$_4$ (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 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-hydroxysalicylaldimine (HL\textsuperscript{OH}) [1e], N-(2,6-diisopropylphenyl)-3-methoxysalicylaldimine (HL\textsuperscript{OMe}) [1e], cis-(1,5-cyclooctadiene)dichloropalladium [PdCl\textsubscript{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\textsubscript{3})(L\textsuperscript{OH}) (1a)

To a solution of N-(2,6-diisopropylphenyl)-3-hydroxysalicylaldimine (HL\textsuperscript{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 PdCl\textsubscript{2}(cod) (0.38 g, 1.33 mmol) and PPh\textsubscript{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%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 7.86 (d, J_{PH} = 13.4 \text{ Hz}, 1H, \text{ArN}=\text{CH})\), 7.8-7.7 (m, 6H, Ar(phenyl)), 7.6-7.5 (m, 3H, Ar(phenyl)), 7.5-7.4 (m, 6H, Ar(phenyl)), 7.2-7.1 (m, 3H, N-Ar), 6.80 (dd, \(J_{HH} = 7.44 \text{ Hz}, J_{HH} = 1.49 \text{ Hz}, 1H, \text{Ar}\)), 6.74 (dd, \(J_{HH} = 7.93 \text{ Hz}, J_{HH} = 1.49 \text{ Hz}, \text{Ar}\)), 6.50 (t, \(J_{HH} = 7.93 \text{ Hz}, 1H, \text{Ar}\)), 4.99 (s, 1H, OH), 3.45 (sep, \(J_{HH} = 6.94 \text{ Hz}, 2H, \text{CH(CH\textsubscript{3})\textsubscript{2}}\)), 1.40 (d, \(J_{HH} = 6.94 \text{ Hz}, 6H, \text{CH(CH\textsubscript{3})\textsubscript{2}}\)), 1.15 (d, \(J_{HH} = 6.94 \text{ Hz}, 6H, \text{CH(CH\textsubscript{3})\textsubscript{2}}\)). \textsuperscript{31}P{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}): \(\delta 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. \textsuperscript{31}P{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}): \(\delta 30.5.\) ES-TOF mass (in the negative mode, MeOH), \textit{m/z} 698.2 ([1a - H]\textsuperscript{-}; \textit{I} = 100% in the range of \textit{m/z} 100-2000). Anal. Calcd for C\textsubscript{37}H\textsubscript{37}ClNO\textsubscript{2}Pd: 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\textsubscript{3})(L\textsuperscript{OH}) (1b)

The complex was synthesized with PdClMe(cod) (0.35 g, 1.3 mmol) instead of PdCl\textsubscript{2}(cod) by the method similar to that used for 1a. Yield 0.82 g (91%). \textsuperscript{1}H NMR (CDCl\textsubscript{3}): \(\delta 7.99 (d, J_{PH} = 13.4 \text{ Hz}, 1H, \text{ArN}=\text{CH})\), 7.8-7.7 (m, 6H, Ar(phenyl)), 7.6-7.5 (m, 3H, Ar(phenyl)), 7.5-7.4 (m, 6H, Ar(phenyl)), 7.2-7.1 (m, 3H, N-Ar), 6.80 (dd, \(J_{HH} = 7.44 \text{ Hz}, J_{HH} = 1.49 \text{ Hz}, 1H, \text{Ar}\)), 6.74 (dd, \(J_{HH} = 7.93 \text{ Hz}, J_{HH} = 1.49 \text{ Hz}, \text{Ar}\)), 6.50 (t, \(J_{HH} = 7.93 \text{ Hz}, 1H, \text{Ar}\)), 4.99 (s, 1H, OH), 3.45 (sep, \(J_{HH} = 6.94 \text{ Hz}, 2H, \text{CH(CH\textsubscript{3})\textsubscript{2}}\)), 1.40 (d, \(J_{HH} = 6.94 \text{ Hz}, 6H, \text{CH(CH\textsubscript{3})\textsubscript{2}}\)), 1.15 (d, \(J_{HH} = 6.94 \text{ Hz}, 6H, \text{CH(CH\textsubscript{3})\textsubscript{2}}\)). \textsuperscript{31}P{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}): \(\delta 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. \textsuperscript{31}P{\textsuperscript{1}H} NMR (CDCl\textsubscript{3}): \(\delta 30.5.\) ES-TOF mass (in the negative mode, MeOH), \textit{m/z} 698.2 ([1b - H]\textsuperscript{-}; \textit{I} = 100% in the range of \textit{m/z} 100-2000). Anal. Calcd for C\textsubscript{37}H\textsubscript{37}ClNO\textsubscript{2}Pd: C 63.44, H 5.32, N 2.00. Found: C 63.37, H 5.43, N 1.91%.
2.2.3. Synthesis of PdMe(PPh₃)(L²OMe) (1c)

To a solution of N-(2,6-diisopropylphenyl)-3-methoxysalicylaldimine (HL²OMe, 0.42 g, 1.4 mmol) in THF (5.0 mL) was added a solution of '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 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, ³JₚH = 11.4 Hz, 1H, ArN=CH), 7.7-7.6 (m, 6H, Ar(phenphosphate)), 7.5-7.3 (m, 9H, Ar(phenphosphate)), 7.2 (m, 3H, N-Ar), 6.73 (d, ³JₚH =7.44 Hz, 1H, Ar), 6.72 (d, ³JₚH =8.43 Hz, 1H, Ar), 6.36 (t, ³JₚH = 7.93 Hz, 1H, Ar), 3.67 (s, 3H, OCH₃), 3.52 (sep, ³JₚH =6.94 Hz, 2H, CH(CH₃)₂), 1.29 (d, ³JₚH=6.94 Hz, 6H, CH(CH₃)₂), 1.11 (d, ³JₚH=6.94 Hz, 6H, CH(CH₃)₂), 0.45 (d, ³JₚH = 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, ²JₚH = 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 '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 [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 tBuOK afforded a dianionic intermediate in situ. Then, addition of PdCl(X)(cod) (X = Cl or = Me) and PPh$_3$ in CH$_2$Cl$_2$ followed by the treatment of Et$_3$N·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 methoxy group ($L^{O\text{Me}}$), PdMe(PPh$_3$)($L^{O\text{Me}}$) (1c), in place of the hydroxyl group was also synthesized by the reaction of the corresponding salicylaldimine with tBuOK 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 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\textsubscript{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 [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 CH\textsubscript{3} group coordinating to the Pd atom lies trans to the oxygen atom. PPh\textsubscript{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 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\textsubscript{3}) bond lengths of the complexes bearing salicylaldiminato ligands are in the range between 2.001 Å and 2.046 Å [1n, 2a-c].

The \textsuperscript{1}H NMR spectra of 1a–1c in CDCl\textsubscript{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 (HC=\textsuperscript{15}N) proton resonances of 1a–1c were displayed as doublets near 8.0 ppm with a phosphorus coupling (\(^4\)J\textsubscript{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 (\(^3\)J\textsubscript{PH} = 2.98 Hz) for 1b and –0.45 ppm (\(^3\)J\textsubscript{PH} = 2.53 Hz) for 1c, respectively. In \textsuperscript{13}C NMR, a resonance of the methyl group was observed as a doublet at 0.19 ppm (\(^2\)J\textsubscript{PC} = 11.2 Hz) for 1b and 1.79 ppm (\(^2\)J\textsubscript{PC} = 11.2 Hz) for 1c. These resonances are similar to other methylpalladium complexes bearing salicylaldiminato ligands [1n]. \textsuperscript{31}P resonances of 1a–1c in CDCl\textsubscript{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 \textsuperscript{1}H NMR spectrum of 1b in THF-\textit{d}_8, a signal at 5.76 ppm attributed to the hydroxyl proton (signal \textit{b} in Fig. 2a) disappeared on adding 1 equiv of \textsuperscript{t}BuOK in THF (Fig. 2b). In addition, the signal \textit{a} assigned to the imino proton (8.08 ppm, \(^4\)J\textsubscript{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 \textit{c} in Fig. 2a) was shifted to 0.12 ppm (\(^2\)J\textsubscript{PH} = 3.17 Hz) on the deprotonation (Fig. 2b). Other resonances of the
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 tBuOK. Here, no free PPh$_3$ resonance (–4.54 ppm in THF-$d_8$) [10] was observed. These clear spectral changes caused with adding tBuOK 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$_2$O to the deprotonated 1b (from Fig. 2b to Fig. 2c), indicating the reversibility 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$_2$Cl$_2$ in the presence of a catalytic amount of 1b or 1c (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 $^1$H 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 tBuOK was quite different between 1b and 1c. The catalytic activity of 1b in the presence of 1 equiv tBuOK 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 tBuOK (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.
References


[11] The polymerization reaction of entry 1 in Table 3 was completely halted upon the addition of galvinoxyl, suggesting the reaction would proceed via some radical pathway [2a].

Table 1
Crystallographic data of 1a – 1c

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

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

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Table 3

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

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<td>Pd-P(1)</td>
<td>2.2265(8)</td>
<td>2.2620(16)</td>
</tr>
<tr>
<td>Pd-O(1)</td>
<td>2.099(2)</td>
<td>2.100(3)</td>
</tr>
<tr>
<td>C(1)-Pd(1)-N(1)</td>
<td>92.03(13)</td>
<td>90.99(19)</td>
</tr>
<tr>
<td>C(1)-Pd(1)-O(1)</td>
<td>173.72(11)</td>
<td>176.50(19)</td>
</tr>
<tr>
<td>C(1)-Pd(1)-P(1)</td>
<td>84.08(10)</td>
<td>83.58(16)</td>
</tr>
<tr>
<td>N(1)-Pd(1)-O(1)</td>
<td>89.27(11)</td>
<td>88.45(16)</td>
</tr>
<tr>
<td>N(1)-Pd(1)-P(1)</td>
<td>175.48(9)</td>
<td>174.18(12)</td>
</tr>
<tr>
<td>O(1)-Pd(1)-P(1)</td>
<td>94.84(7)</td>
<td>97.09(11)</td>
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Table 3
Palladium-catalyzed polymerization of methyl acrylate

<table>
<thead>
<tr>
<th>entry</th>
<th>catalyst</th>
<th>additive</th>
<th>Yield (%)</th>
<th>$M_n \times 10^3$</th>
<th>PDI</th>
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<tr>
<td>1</td>
<td>1b</td>
<td>none</td>
<td>79</td>
<td>116</td>
<td>2.30</td>
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<tr>
<td>2</td>
<td>1c</td>
<td>none</td>
<td>70</td>
<td>114</td>
<td>2.13</td>
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<tr>
<td>3</td>
<td>1b</td>
<td>tBuOK(^c)</td>
<td>19</td>
<td>129</td>
<td>1.84</td>
</tr>
<tr>
<td>4</td>
<td>1c</td>
<td>tBuOK(^c)</td>
<td>70</td>
<td>135</td>
<td>1.94</td>
</tr>
</tbody>
</table>

\(^a\) Conditions: methyl acrylate (1.0 mL, 12 mmol), 1 (0.011 mmol, S/C = 1000), THF/CH\(_2\)Cl\(_2\) = 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. $^1$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$_2$O. * indicates TMS.

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

Scheme 2
Synthesis of a palladium complex 1c.