# **ORGANOMETALLICS**

# Triangular Triplatinum Complex with Four Bridging Si Ligands: Dynamic Behavior of the Molecule and Catalysis

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# **Supporting Information**



**ABSTRACT:** A triangular triplatinum(0) complex with bridging diphenylsilylene ligands,  $[\{(Pt(PMe_3)\}_3(\mu-SiPh_2)_3]$  (1a), reacts with H<sub>2</sub>SiPh<sub>2</sub> to produce the 1:1 adduct,  $[\{Pt(PMe_3)\}_3(H)_2(\mu-SiPh_2)_4]$  (2a), which was isolated and characterized by X-ray crystallography. Two Pt–Pt bonds of the triangular Pt<sub>3</sub> core are bridged by a diphenylsilylene ligand, while the remaining Pt–Pt bond has two unsymmetrical bridging Si ligands. Dissolution of 1a and H<sub>2</sub>SiPh<sub>2</sub> at a 1:3 molar ratio forms a mixture of complex 2a and unreacted 1a. NMR measurement of the solution at -90 °C revealed the structure of 2a as having two hydride ligands and four bridging silylene ligands. Reversible addition of H<sub>2</sub>SiPh<sub>2</sub> to 1a yielded 2a with  $\Delta G^{\circ} = -8.0$  kJ mol<sup>-1</sup>,  $\Delta H^{\circ} = -51.7$  kJ mol<sup>-1</sup>, and  $\Delta S^{\circ} = -146$  J mol<sup>-1</sup> K<sup>-1</sup>. Addition of bis(4-fluorophenyl)silylene ligands, respectively, also occurs reversibly in the solution, and the diarylsilane with an electron-withdrawing substituent is favored for the formation of Pt<sub>3</sub>Si<sub>4</sub> complexes. Complex 1a catalyzes hydrosilyation of benzaldehyde with H<sub>2</sub>SiPh<sub>2</sub> to produce diphenyl(benzyloxy)silane along with concurrent hydrosilyation and dehydrosilyation of phenyl(methyl)ketone. Dehydrogenative coupling of H<sub>2</sub>SiPh<sub>2</sub> and phenol is also catalyzed to yield diphenyl(phenoxy)silane. The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of the mixtures during the catalytic reaction show 2a as the major Pt-containing species.

# INTRODUCTION

Triangular trinuclear complexes of late transition metals are regarded as minimal metal clusters. These complexes are normally supported by bridging ligands such as CO, CNR, and PR<sub>2</sub>.<sup>1,2</sup> The two former ligands have a  $\pi$ -acceptor characteristic and stabilize a molecule composed of d-electron-rich metal centers. Recently, triplatinum(0) complexes with three bridging diphenylsilylene and diphenylgermylene ligands, formulated as [{Pt(PMe<sub>3</sub>)}<sub>3</sub>( $\mu$ -EPh<sub>2</sub>)<sub>3</sub>] (E = Si (1a) and Ge), have been reported to have high thermal stability in spite of the mismatched combination of electron-releasing ligands and d<sup>10</sup> metal centers (Chart 1).<sup>3,4</sup>

We have investigated structures and electronic states of these complexes and have determined their chemical properties. Reaction of dimethyl acetylenedicarboxylate with the  $Pt_3Si_3$  complex, for example, causes expansion of the  $Pt_3$  ring to produce new complexes. A linear  $Pt_3$  complex having  $\mu_3$ -silylene and phenyl ligands and the complex whose  $Pt_2$  and  $Pt_1$ 

Chart 1. Structures of  $[{Pt(PMe_3)}_3(\mu - EPh_2)_3]$  (E = Si and Ge)



fragments are separated by an acetylene ligand are obtained depending on the aryl group.<sup>3d</sup> In this paper, we report the addition of  $H_2SiPh_2$  to complex **1a** with three bridging silylene ligands to form a new  $Pt_3Si_4$  type complex. The complex undergoes unique fluxional behavior and catalyzes the hydrosilyation of benzaldehydes as well as the dehydrocoupling of diarylsilane with phenol at room temperature.

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# RESULTS AND DISCUSSION

**Triplatinum Complexes with Four Bridging Si Ligands.** A triplatinum(0) complex with three bridging diphenylsilylene ligands,  $[{Pt(PMe_3)}_3(\mu-SiPh_2)_3]$  (1a), reacted with an excess amount of H<sub>2</sub>SiPh<sub>2</sub> to yield the 1:1 adduct,  $[{Pt(PMe_3)}_3-(H_2)_{(\mu-SiPh_2)_4}]$  (2a), as orange crystals (eq 1).



X-ray crystallography of 2a, which was obtained from the solution of 1a and  $H_2SiPh_2$  at a 1:5 molar ratio, clarified the molecular structure as having a triangular Pt<sub>3</sub> framework, as shown in Figure 1. The Pt–Pt bond distances, 2.747(1), 2.795(1), and



Figure 1. (a) Thermal ellipsoids (50% probability) of 2a and (b) selected bond distances (Å). The positions of hydrogen atoms close to Pt2 and Pt3 were not determined. Selected bond angles (deg): Pt2-Pt1-Pt3 58.72(3), Pt1-Pt2-Pt3 60.87(3), Pt1-Pt3-Pt2 60.41(2), P1-Pt1-Pt2 150.4(1), P1-Pt1-Pt3 150.1(1), P2-Pt2-Pt1 155.2(1), P2-Pt2-Pt3 143.9(1), P3-Pt3-Pt1 151.4(1), P3-Pt3-Pt2 143.2(1), Si3-Pt1-Si4 166.4(2), Si1-Pt2-Si2 105.0(2), Si1-Pt2-Si3 116.9(2), Si2-Pt2-Si3 115.3(2), Si1-Pt3-Si2 104.3(2), Si1-Pt3-Si4 113.7(2), Si2-Pt3-Si4 117.7(2).

2.808(1) Å, are longer than those of 1a (2.697(1)-2.716(1) Å). The two latter Pt–Pt bonds of 2a are single-bridged by a SiPh<sub>2</sub> ligand with Pt–Si bonds of 2.371(4)–2.392(4) Å, while the corresponding bonds are shorter for those of 1a (2.337(5)-2.364(5) Å). The other Pt–Pt bond of 2a is bridged by two Si ligands, and the two Pt and two Si atoms form a concave quadrilateral (the dihedral angle of two PtSi<sub>2</sub> planes: 148.9°) composed of four Pt–Si bonds with different lengths: Pt2–Si1, 2.408(5) Å; Pt3–Si1, 2.378(5) Å; Pt3–Si2, 2.449(5) Å; Pt2–Si2, 2.397(5) Å.

Bridging coordination of a secondary silyl group  $(-\text{SiHR}_2)$ in dinuclear transition metal complexes is classified as the  $\mu$ - $\eta^2$ -silyl form (Scheme 1a) or the hydride and  $\mu$ -silylene forms (Scheme 1b), depending on the degree of interaction between

#### Scheme 1



the metal center and the H and Si atoms.<sup>5</sup> Another isomeric form without interaction between the hydride and the coordinating Si atom is also possible (Scheme 1c). Nonclassical interactions among Si, H, and metal atoms were involved in the two former structures, which have been examined on the basis of the geometry of the atoms and spectroscopic results of the complexes reported thus far.<sup>5,6</sup>

Diplatinum(I) complexes having two bridging Si ligands as well as their Pd(I) analogues were reported to have structures that depended on the substituents of the Si ligand and auxiliary phosphine ligands. The common structure has a rectangular Pt<sub>2</sub>Si<sub>2</sub> unit composed of four alternatingly long and short Pt–Si bonds.<sup>7</sup> Two unsymmetrically bridging silyl (e.g.,  $\mu$ - $\eta^2$ -HSiR<sub>2</sub> and  $\mu$ - $\eta^2$ -H<sub>2</sub>SiR) ligands, which are bonded to one metal by  $\sigma$ -bonding and to the other by Si–H–M bonding (Scheme 1a,b), favor coordination in opposite directions. A typical complex, [{Pt(PCy<sub>3</sub>)}<sub>2</sub>( $\mu$ - $\eta^2$ -HSiMe<sub>2</sub>)<sub>2</sub>], has a crystallographic  $C_2$  center of symmetry at the midpoint of the Pt–Pt bond, and its Pt–Si bond distances are 2.420(2) and 2.324(2) Å.<sup>7a</sup>

A mirror-image symmetrical isomer with  $\mu$ -silane and  $\mu$ -silylene ligands (Scheme 2b) has also been reported,



although it is rare.<sup>8</sup> Braddock-Wilking reported on dinuclear Pt complexes having bridging  $\mu$ - $\eta^2$ -SiHAr<sub>2</sub> and  $\mu$ -SiAr<sub>2</sub> ligands in addition to a hydride ligand attached to a Pt center, as shown in Scheme 2c.<sup>4b,9</sup> The hydride and bridging silylene ligands are bonded on the same side of the Pt–Pt bond, while the  $\mu$ -silyl ligand bridges the other side. The Pt–Si bond lengths of the Pt<sub>2</sub>Si<sub>2</sub> unit of [{PtH(PPh<sub>3</sub>)<sub>2</sub>}{Pt(PPh<sub>3</sub>)}( $\mu$ -SiAr<sub>2</sub>)( $\mu$ - $\eta^2$ -SiHAr<sub>2</sub>)] (Ar<sub>2</sub> = C<sub>13</sub>H<sub>9</sub>Br<sub>2</sub>N) are 2.393(1), 2.341(1), 2.498(1), and 2.315(1) Å,<sup>4b</sup> and the relationship with their magnitudes is similar to that in **2a** (2.408(5), 2.378(5), 2.449(5), and 2.397(5) Å). Thus, the Pt<sub>2</sub>Si<sub>2</sub> unit of **2a** resembles that of the unsymmetrical Pt<sub>2</sub> complex with bridging silylene and silyl ligands. X-ray crystallographic results, however, did not provide the positions of the hydrogens of the complex in the solid state.

In Scheme 3, possible structures of 2a are summarized on the basis of X-ray crystallographic results. Scheme 3a is composed of two Pt atoms double-bridged by two SiHPh<sub>2</sub> ligands, similar

# Scheme 3



DOI: 10.1021/acs.organomet.7b00048 Organometallics XXXX, XXX, XXX–XXX to the dinuclear complex having  $C_2$  symmetry in Scheme 2a. Scheme 3b contains bridging silylene and silyl ligands as well as a hydride bonded to a Pt atom. Scheme 3c has two bridging silylene ligands between the Pt centers and two hydride ligands bonded to each of the Pt centers. Unsymmetrical coordination of the silylene ligands that bridges a Pt–Pt bond is explained by interaction of Si atom and the hydride ligand.

DFT calculations were applied to **2a** with Gaussian 09 quantum chemistry program package. The optimized structure of the complex contains two hydrogen atoms positions close to the elongated Pt–Si bond, and the Si–H and Pt–H distances are 1.776 and 1.757 Å and 1.738 and 1.769 Å, respectively (Figure S2). The Wiberg bond indices are obtained as 0.382 and 0.432 (Si–H) and 0.429 and 0.404 (Pt–H). These results as well as their comparison with a model diplatinum complex with bridging silyl ligand [{Pt(PMe<sub>3</sub>)}<sub>2</sub>( $\mu$ - $\eta$ <sup>2</sup>-HSiPh<sub>2</sub>)<sub>2</sub>] (Si–H: 0.451 and 0.455, Pt–H: 0.371 and 0.374) suggest that the calculated structure of complex **2a** is similar to that in Scheme 3b.

Thus, both X-ray crystallography and DFT calculations are consistent with the structure shown in Scheme 3b. The NMR results mentioned below, however, indicate that the complex exists with the structure in Scheme 3c in solution. Since change of the coordination bonds between Scheme 1a,b is considered to be facile, isomerization of the molecules among the structures in Scheme 3a-c may occur smoothly in solution.

Dynamic Behavior of Complex in Solution. Dissolution of isolated 2a in toluene- $d_8$  at room temperature resulted in NMR spectra that contain signals corresponding to 1a and H<sub>2</sub>SiPh<sub>2</sub> at a 1:1 ratio, which indicates high reversibility in the formation of 2a from a mixture of 1a and H<sub>2</sub>SiPh<sub>2</sub> in the solution. A solution of 1a and H<sub>2</sub>SiPh<sub>2</sub> at a 1:3 molar ratio shows a new  ${}^{31}P{}^{1}H$  NMR signal at  $\delta$  -22.1 ( $J_{PtP}$  = 3893 Hz,  ${}^{2}J_{PtP}$  = 144 Hz,  ${}^{3}J_{PP}$  = 53 Hz at -8 °C). The signal is assigned to complex 2a, which exists as the major species at this temperature. Warming to room temperature, however, causes a decrease in the intensity of this signal of 2a and an increase in that of the signal of 1a. The spectrum of a mixture of 1a and H<sub>2</sub>SiPh<sub>2</sub> at a 1:10 molar ratio contains 2a as the dominant Pt-containing species even at room temperature. 2a was characterized by multinuclear NMR spectroscopy in solution using the 1:3 mixture of 1a and H<sub>2</sub>SiPh<sub>2</sub> in deuterated toluene and THF. Although the three phosphorus nuclei are magnetically equivalent at -50 °C, cooling the solution to -90 °C causes a doublet at  $\delta$  -20.0 and a triplet at  $\delta$ -22.3 at a 2:1 ratio ( ${}^{3}J_{PP} = 50$  Hz), as shown in Figure 2a. The former signal is ascribed to two PMe<sub>3</sub> ligands bonded to the Pt atoms, each of which is bonded to three Si ligands, while the triplet is due to the ligand bonded to the other Pt center. The <sup>1</sup>H NMR spectrum of complex 2a at -90 °C contains a signal corresponding to two hydrogens at  $\delta$  –6.21, flanked by satellite peaks ( $J_{PtH}$  = 520 Hz, Figure 2b). The corresponding signal is also observed in the <sup>2</sup>H NMR spectrum of the mixture of 1a and excess D<sub>2</sub>SiPh<sub>2</sub> at -10 °C  $(\delta$  -6.06). The signals are assigned to the hydride ligands on the basis of the position of the peak at a high magnetic field, and coupling with <sup>29</sup>Si nuclei suggests interaction between the H and Si atoms (Scheme 1b). ortho-Hydrogen signals appear as four peaks with equal intensity in the range of  $\delta$  7.4–8.1 at -90 °C, suggesting that the phenyl groups bonded to Si atoms are not magnetically equivalent at this temperature. The <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum of **2a** contains two signals at  $\delta$  291.7  $(J_{\text{PtSi}} = 981 \text{ Hz})$  and 253.6  $(J_{\text{PtSi}} = 583 \text{ Hz})$  at -10 °C. Since data of the former are more similar to those of 1a ( $\delta$  279.4,



**Figure 2.** (a) <sup>31</sup>P{<sup>1</sup>H} NMR (r.t. and  $-90 \, ^{\circ}$ C) and (b) <sup>1</sup>H NMR (-30 and  $-90 \, ^{\circ}$ C) spectra of **2a** in toluene-*d*<sub>8</sub>. Peaks with asterisks in (a) and (b) are due to <sup>195</sup>Pt satellites, while <sup>1</sup>H NMR peaks due to <sup>29</sup>Si-<sup>1</sup>H coupling are shown with arrows in (b). These spectra were obtained by dissolving **1a** and H<sub>2</sub>SiPh<sub>2</sub> at a 1:3 molar ratio.

 $J_{PtSi}$  = 945 Hz) than of the latter, they are assigned to the singly bridged silylene ligands.

Thus, complex 2a shows two magnetically equivalent hydride ligands bonded to each of the two Pt centers, which are doublebridged by the silylene ligands, as shown in Scheme 3c. Raising the temperature to -30 °C gave rise to a single <sup>31</sup>P{<sup>1</sup>H} NMR signal attributable to the coalescence of the doublet and triplet observed at -90 °C. The <sup>1</sup>H NMR spectrum at this temperature shows a single signal for the *ortho*-hydrogen of the SiPh<sub>2</sub> groups and a hydride signal with satellite peaks (apparent coupling constant, 187 Hz). The fluxional behavior that renders three phosphorus nuclei equivalent at this high temperature also renders the apparent coupling constant to be <sup>1</sup>/<sub>3</sub> that of the signal at -90 °C.

The <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra at -90 °C and the <sup>29</sup>Si{<sup>1</sup>H} NMR spectrum at -10 °C contain a minor signal that may be due to uncharacterized products of the reaction, such as an isomer of **2a** or an adduct of the diarylsilane to **1a** with different stoichiometries (<sup>1</sup>H:  $\delta$  -6.4, <sup>31</sup>P{<sup>1</sup>H}:  $\delta$  -15.4, <sup>29</sup>Si{<sup>1</sup>H}: $\delta$  214). Raising temperature caused coalescence or changes in the peaks of the <sup>1</sup>H and <sup>31</sup>P{<sup>1</sup>H} NMR spectra, which rendered the minor signals invisible. The minor species observed at the low temperature are involved in the reversible reaction on the NMR time scale.

The fluxional process of the molecules is considered to involve formation of a silyl ligand from a silylene and hydride ligand, as shown in Scheme 4a. The reaction corresponds to the isomerization of the molecule with structure in Scheme 3c

Scheme 4



DOI: 10.1021/acs.organomet.7b00048 Organometallics XXXX, XXX, XXX–XXX into Scheme 3b. The resultant silyl ligand will cause further change of the structure of the complex.

We reported that Pt–Pd dinuclear complex with bridging Si ligands exists as the molecule having silyl, silylene, and hydride ligands at -60 °C, and is converted to the molecule having two silyl ligands at 25 °C.<sup>10</sup> The reaction involves a change in the coordination mode of Si and H atoms to a Pt center from that with two  $\sigma$ -bonds (Si–Pt and H–Pt) to the bonding between Si, H, and Pt atoms, similar to the structural change of the triplatinum complex shown in Scheme 4b.

Scheme 5 summarizes an intramolecular mechanism for exchange of the Si ligand. The complex with two hydride ligands



is equilibrated to an intermediate, with a bridging SiHAr<sub>2</sub> ligand via formation of a Si–H<sub>a</sub> bond and activation of Pt–Si and Pt–H<sub>a</sub> bonds (A). Rotation of the remaining Pt–Si bond to form a new bond between the Si–H<sub>a</sub> group and the remaining Pt center produces intermediate (A'). The facile and reversible intra- and intermolecular switching of the Pt–Si bonds occurs over all the Si ligands. The NMR spectra of the solution prepared by dissolving Pt<sub>3</sub>Si<sub>3</sub> complex 1a and H<sub>2</sub>SiPh<sub>2</sub> in 1:3 molar ratio suggested that the mixture is composed of Pt<sub>3</sub>Si<sub>4</sub> complex 2a and unreacted H<sub>2</sub>SiPh<sub>2</sub> below –30 °C.

The  ${}^{31}P{}^{1}H}$  and  ${}^{1}H$  NMR spectra of the mixtures of **1a** and excess  $H_2SiPh_2$  in different concentration show similar coalescence behavior at -30 and -90 °C (Figures S10 and S11). This suggests that the pathway in Scheme 5 is operative to the observed dynamic behavior of the NMR signals and that the intermolecular exchange of the Si ligand occurs more slowly. Concentration of the complex and diarylsilane influences both equilibrium between  $Pt_3Si_3$  and  $Pt_3Si_4$  complexes and rate of their mutual conversion, and detailed NMR studies did not provide further information on this issue. Thus, we do not have conclusion on whether the intramolecular process in Scheme 5 is the sole one of the complex on the NMR time scale or not.

The <sup>31</sup>P{<sup>1</sup>H} NMR spectra of mixtures of  $[{Pt(PMe_3)}_3 {\mu-Si(C_6H_4-4-F)_2}_3]$  (**1b**) and  $H_2Si(C_6H_4-4-F)_2$  as well as that of  $[{Pt(PMe_3)}_3{\mu-Si(C_6H_4-4-Me)_2}_3]$  (**1c**) and  $H_2Si(C_6H_4-4-Me)_2$  also contain signals that can be assigned to  $[{Pt-(PMe_3)_3}(H)_2{\mu-Si(C_6H_4-4-F)_2}_4]$  (**2b**,  $\delta - 23.3$ ,  $J_{PtP} = 3883$  Hz,

 ${}^{2}J_{\text{PtP}} = 145 \text{ Hz}, {}^{3}J_{\text{PP}} = 47 \text{ Hz}$  and  $[\{\text{Pt}(\text{PMe}_{3})_{3}\}(\text{H})_{2}\{\mu\text{-Si}(\text{C}_{6}\text{H}_{4}\text{-}4\text{-}\text{Me})_{2}\}_{4}]$  (2c,  $\delta$  -22.8,  $J_{\text{PtP}} = 3998 \text{ Hz}, {}^{2}J_{\text{PtP}} = 150 \text{ Hz}, {}^{3}J_{\text{PP}} = 49 \text{ Hz}$ ). The reaction is summarized in eq 2.

${Pt(PMe_3)}_3(\mu$ -SiAr <sub>2</sub> ) <sub>3</sub> + H <sub>2</sub> SiAr <sub>2</sub>	★ {Pt(PMe <sub>3</sub> )} <sub>3</sub> (H) <sub>2</sub> (μ-SiAr <sub>2</sub> ) <sub>4</sub> (2)
<b>1a</b> : Ar = Ph,	<b>2a</b> : Ar = Ph,
<b>1b</b> : Ar = C <sub>6</sub> H <sub>4</sub> -4-F,	<b>2b</b> : Ar = C <sub>6</sub> H <sub>4</sub> -4-F,
1c: Ar = C <sub>6</sub> H <sub>4</sub> -4-Me.	<b>2c</b> : Ar = $C_6H_4$ -4-Me.

Addition of  $H_2Si(C_6H_4-4-F)_2$  to complex 1a forms a complicated mixture of the Pt complexes, which suggests reversibility of the reactions. Equilibrium constants for the addition of diarylsilanes to the Pt<sub>3</sub>Si<sub>3</sub> complex were determined by comparing of the <sup>1</sup>H NMR signals assigned to *ortho*-hydrogens of 1a-c, diarylsilanes, and 2a-c, which have the three bridging silylene ligands with the same aromatic groups. Figure 3 shows van 't Hoff plots of the reactions.



Figure 3. van 't Hoff plots for the addition of diarylsilanes to complexes (i) 1a, (ii) 1b, and (iii) 1c. Hammett plots of the thermodynamic parameters are shown as an inset.

Thermodynamic parameters are determined as  $\Delta G^{\circ} = -8.0 \text{ kJ mol}^{-1}$ ,  $\Delta H^{\circ} = -51.7 \text{ kJ mol}^{-1}$ , and  $\Delta S^{\circ} = -146 \text{ J mol}^{-1} \text{ K}^{-1}$  for **2a** formation;  $\Delta G^{\circ} = -10.0 \text{ kJ mol}^{-1}$ ,  $\Delta H^{\circ} = -47.5 \text{ kJ mol}^{-1}$ , and  $\Delta S^{\circ} = -126 \text{ J mol}^{-1} \text{ K}^{-1}$  for **2b** formation; and  $\Delta G^{\circ} = -5.9 \text{ kJ mol}^{-1}$ ,  $\Delta H^{\circ} = -48.2 \text{ kJ mol}^{-1}$ , and  $\Delta S^{\circ} = -142 \text{ J mol}^{-1} \text{ K}^{-1}$  for **2c** formation. The reaction enthalpy and entropy are comparable to those of oxidative addition of H<sub>2</sub>SiPh<sub>2</sub> to a mononuclear Ni(0) complex with a diphosphinoborane ligand ( $\Delta H^{\circ} = -50 \text{ kJ mol}^{-1}$ ,  $\Delta S^{\circ} = -113 \text{ J mol}^{-1} \text{ K}^{-1}$ ) and of HSiMe<sub>3</sub> with RuH(SiMe<sub>3</sub>) (PMe<sub>3</sub>)<sub>4</sub> ( $\Delta H^{\circ} = -46.0 \text{ kJ mol}^{-1}$ ,  $\Delta S^{\circ} = -167 \text{ J mol}^{-1} \text{ K}^{-1}$ ).<sup>11</sup> Hammett plots of the equilibrium constants of the reaction versus  $\sigma_{\rm p}$  suggest that the Pt<sub>3</sub>Si<sub>4</sub> adduct is stabilized more significantly by less electron-donating substituents on the aromatic group.

**Catalysis.** Generation of the  $Pt_3Si_4$  complex having hydride ligands from the reaction of  $H_2SiPh_2$  with complex 1a prompted us to conduct the study on the reactions using the triplatinum complex as the catalyst. Hydrosilyation of aldehydes and ketones was reported to be catalyzed by the complexes of transition metals such as Rh,<sup>12</sup> Cu,<sup>13</sup> and Fe.<sup>14</sup> Pt is known as the most common and effective transition metal for catalysts of olefin hydrosilyation.<sup>15</sup> Although molecular Pt complexes and Pt metal formed by reduction of them are often employed as the catalyst, there have been only a few reports on the hydrosilyation of carbonyl compounds using Pt catalyst. H<sub>2</sub>PtCl<sub>6</sub> promotes

hydrosilyation of  $\alpha,\beta$ -unsaturated aldehydes and ketones, accompanied by isomerization, to produce the silyl enol ether.<sup>16</sup>

Complex 1a catalyzes hydrosilyation of benzaldehyde derivatives with  $H_2SiPh_2$  as the substrates. Benzyloxy(diaryl)-silane compounds (3a) were obtained as the product in 98% NMR yield (R = Me), as determined from eq 3.

$$\begin{array}{c} \mathsf{R} \\ H \\ \mathsf{H} \\ \mathsf{H}$$

The reaction rate is affected significantly by the substituent on the aryl group of the diarylsilylene ligand and aldehyde. A similar hydrosilylation with  $H_2Si(C_6H_4-4-F)_2$  catalyzed by **1b** proceeds slowly at room temperature to give the product (**3b**) in a lower yield (32%). 4-(Trifluoromethyl)phenylaldehyde is converted to the corresponding hydrosilylation product (**4**) in 43% yield under the same conditions. The <sup>31</sup>P{<sup>1</sup>H} NMR spectrum of the reaction mixture after 8 h contains the signal of **2** only, but after completion of the reaction (after 24 h), the NMR signals corresponding to complex **1** and other uncharacterized complex ( $\delta$  18.4) were observed.

Complex 1a catalyzes hydrosilyation of methyl(phenyl)ketone and produces a mixture of the hydrosilyation product (5, 20%) and that of dehydrosilyation (6, 45%), as shown in eq 4. A longer reaction time (24 h) produced the hydrosilylated

dimer (7) composed of a mixture of **5** and **6**. The products are similar to those obtained using other metal catalysis.<sup>17</sup> Plausible mechanisms of the hydrosilyation of ketones catalyzed by mononuclear Rh complexes have been examined by several research groups.<sup>18</sup> The reactions mostly involve complexes with silyl ligands as intermediates, although other intermediates having silylene ligands were also proposed to explain the reaction mechanisms.

Recently, dehydrogenative couplings of organosilane with OH-containing compounds using several late transition metal complexes have been reported.<sup>19</sup> This is a thermodynamically favored reaction, supported by formation of Si–O bonds with high bond energy and enhanced by the catalysts that forms silylmetal intermediates. Addition of phenol and H<sub>2</sub>SiPh<sub>2</sub> to a solution of a catalytic amount of **1a** forms diphenyl(phenoxy)-silane (**8**, 79%) in a high yield (eq 5).



# CONCLUSIONS

A triplatinum complex with bridging silylene ligands, [{Pt-(PMe<sub>3</sub>)}<sub>3</sub>( $\mu$ -SiPh<sub>2</sub>)<sub>3</sub>], reacts with H<sub>2</sub>SiPh<sub>2</sub> to produce the complex composed of a trianglular Pt<sub>3</sub>Si<sub>4</sub> core and two hydride and three PMe<sub>3</sub> ligands. The resulting complex has four bridging silvlene ligands in solution at a low temperature. Changes in NMR signals as a function of the temperature are assigned to the inter- and intramolecular switching of the Pt-Si bonds over all the Si ligands. Hydride and silylene ligands are converted to silyl (-SiHAr<sub>2</sub>) ligands easily and reversibly, which contributes to the facilitation of fluxional behavior. The addition of H<sub>2</sub>SiAr<sub>2</sub> to the Pt<sub>3</sub>Si<sub>3</sub> complexes occurs reversibly, and the thermodynamic parameters suggest that electron-withdrawing substituents on the aryl groups favor the Pt<sub>3</sub>Si<sub>4</sub> adduct and thereby favor its formation. [{ $Pt(PMe_3)$ }\_3( $\mu$ -SiPh<sub>2</sub>)\_3] catalyzes hydrosilyation of benzaldehyde and hydrosilyation/dehydrosilyation of methyl-(phenyl)ketone to yield the expected products, although previous reports on the Pt-catalyzed hydrosilyation of a C=O group are quite rare. The complex also promotes dehydrogenative condensation of H2SiPh2 with phenol to form diphenyl-(phenoxy)silane at room temperature. NMR analysis of the reaction mixtures revealed that the catalyst preserves the cyclic triplatinum structure during the reaction.

#### EXPERIMENTAL SECTION

General Procedures. All manipulations were carried out using standard Schlenk line techniques under an atmosphere of argon or nitrogen or in a nitrogen-filled glovebox (Miwa MFG). Hexane, toluene, and tetrahydrofuran (THF) were purified by using a Grubbstype solvent purification system (Glass Contour).<sup>20</sup> The <sup>1</sup>H, <sup>2</sup>H{<sup>1</sup>H},  ${}^{13}C{}^{1}H{}, {}^{29}Si{}^{1}H{}, and {}^{31}P{}^{1}H{} NMR$  spectra were recorded on Bruker Biospin Avance III 400 MHz and Avance III HD 500 MHz NMR spectrometers. The chemical shifts in <sup>1</sup>H and <sup>13</sup>C{<sup>1</sup>H} NMR spectra were referenced to the residual peaks of the solvents used.<sup>21</sup> The peak positions of the  ${}^{29}$ Si{ $^{1}$ H} and  ${}^{31}$ P{ $^{1}$ H} NMR spectra were referenced to external SiMe<sub>4</sub> ( $\delta$  0) and 85% H<sub>3</sub>PO<sub>4</sub> ( $\delta$  0) in deuterated solvents. Elemental analysis was performed using a J-science JM10 or a Yanaco HSU-20 autorecorder. H<sub>2</sub>SiPh<sub>2</sub> (Aldrich), D<sub>2</sub>SiPh<sub>2</sub> (Aldrich), benzaldehyde (TCI), methyl(phenyl)ketone (TCI), and p-cresol (Kanto Chemical) were purchased and used without further purification. Complexes  $[{Pt(PMe_3)}_3(\mu-SiAr_2)_3]$  (1a: Ar = Ph, 1b: Ar = C<sub>6</sub>H<sub>4</sub>-4-F) were prepared according to the literature.<sup>3d</sup> H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-F)<sub>2</sub> was synthesized from LiAlH<sub>4</sub> reduction of HClSi( $C_6H_4$ -4-F)<sub>2</sub>, which was obtained by the coupling of HCl<sub>3</sub>Si (TCI) and the corresponding Grignard reagent in 1:2 ratio. The  $H_2Si(C_6H_4-4-Me)_2$  was obtained via LiAlH<sub>4</sub> reduction of Cl<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub> (Wako Chemical).

**Preparation of [{Pt(PMe<sub>3</sub>)}<sub>3</sub>[μ-Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub>]<sub>3</sub>] (1c).** To a toluene solution (6 mL) of [Pt(PMe<sub>3</sub>)<sub>4</sub>] (406 mg, 0.81 mmol) was added H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub> (190 mg, 0.89 mmol), and the reaction mixture was stirred at 100 °C for 15 h. The solvent was removed under reduced pressure to give a residue, which was washed with hexane (3 mL × 2) and MeCN (2 mL × 3) and dried *in vacuo* to give 1c (212 mg, 54%) as a red powder. The single crystals suitable for X-ray crystallography were obtained by slow diffusion of the hexane/toluene (5:1) solution at 0 °C. <sup>1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): δ 8.22 (d, 12H, C<sub>6</sub>H<sub>4</sub> *ortho*, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 7.14 (d, 12H, C<sub>6</sub>H<sub>4</sub> *meta*, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 2.09 (s, 18H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.24 (br, 27H, PCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (126 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): δ 150.2 (C<sub>6</sub>H<sub>4</sub> *ipso*), 137.7 (C<sub>6</sub>H<sub>4</sub> *para*), 136.6 (C<sub>6</sub>H<sub>4</sub> *ortho*), 129.2 (C<sub>6</sub>H<sub>4</sub> *meta*), 22.0 (m, PCH<sub>3</sub>), 21.7 (C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): δ 26.9 (J<sub>PtP</sub> = 2978 Hz, <sup>2</sup>J<sub>PtP</sub> = 425 Hz, <sup>3</sup>J<sub>PP</sub> = 85 Hz). <sup>29</sup>Si{<sup>1</sup>H} NMR (99 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): δ 280 (J<sub>PtSi</sub> = 938 Hz).

**Preparation of [{Pt(PMe<sub>3</sub>)}<sub>3</sub>(H)<sub>2</sub>(\mu-SiPh<sub>2</sub>)<sub>4</sub>] (2a). To a toluene solution (2 mL) of 1a (102 mg, 75 \mumol) was added excess H<sub>2</sub>SiPh<sub>2</sub> (68 mg, 369 \mumol), and the reaction mixture was stirred at room temperature for 15 h. The solvent was removed under reduced pressure to give a red residue, which was washed with hexane (3 mL × 3) and dried in a** *vacuo* **to give 2a (58 mg, 38 \mumol, 51%). Dissolving isolated 2a in toluene-d<sub>8</sub> at room temperature caused an immediate** 

dissociation of  $H_2SiPh_2$  from the  $Pt_3$  core, resulting in formation of 1a and  $H_2SiPh_2$  in 1:1 ratio. Therefore, recrystallization of 2a was carried out by slow diffusion of hexane into the toluene solution containing excess  $H_2SiPh_2$ , forming the red crystals in a few days at 0 °C. Anal. Calcd for  $C_{70}H_{69}P_3Pt_3Si_4$  + toluene: C, 46.96; H, 4.47. Found: C, 46.79; H, 4.74.

NMR Characterization of 2a with H<sub>2</sub>SiPh<sub>2</sub>. In a J. Young NMR tube to a toluene- $d_8$  solution (0.6 mL) of 1a (5 mg, 4  $\mu$ mol) was added 3-fold  $H_2SiPh_2$  (2 mg, 11  $\mu$ mol). The multinuclear NMR measurements were performed at 293 and 183 K. <sup>1</sup>H NMR (500 MHz, toluene- $d_{8}$ , 265 K):  $\delta$  7.66 (br, 16H, C<sub>6</sub>H<sub>5</sub> ortho), 7.3-6.9 (24H, C<sub>6</sub>H<sub>5</sub> meta and para), 1.22 (br, 27H, PCH<sub>3</sub>), -6.14 (PtH, 2H,  $J_{PtH} = 187$  Hz,  ${}^{2}J_{PH} = 4.5$  Hz).  ${}^{13}C{}^{1}H$  NMR (126 MHz, THF-d<sub>8</sub>, 263 K): δ 151.5 (br, C<sub>6</sub>H<sub>5</sub> ipso), 137.1 (C<sub>6</sub>H<sub>5</sub> ortho), 128.2  $(C_6H_5 \text{ para})$ , 127.5  $(C_6H_5 \text{ meta})$ , 24.3  $(PCH_3)$ .  ${}^{31}P{}^{1}H{}^{1}$  NMR (202 MHz, toluene- $d_8$ , 265 K):  $\delta$  –22.1 ( $J_{PtP}$  = 3893 Hz,  ${}^2J_{PtP}$  = 144 Hz,  ${}^3J_{PP}$  = 53 Hz).  ${}^{29}\text{Si}\{{}^1\text{H}\}$  NMR (99 MHz, THF- $d_8$ , 263 K):  $\delta$ 291.7 ( $J_{PtSi}$  = 981 Hz), 253.6 ( $J_{PtSi}$  = 583 Hz). <sup>1</sup>H NMR (400 MHz, toluene-d<sub>80</sub> 183 K):δ 8.11, 7.87, 7.60, 7.36 (br, 16H, C<sub>6</sub>H<sub>5</sub> ortho), 7.3-6.9 (m, 24H, C<sub>6</sub>H<sub>5</sub> meta and para), 1.3-0.9 (br, 27H, PCH<sub>3</sub>), -6.21 (s, 2H, PtH,  $J_{PtH} = 520 \text{ Hz}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (161 MHz, toluene- $d_8$ , 183 K)  $\delta$  -20.0 (d,  $J_{\text{PtP}}$  = 3707 Hz,  ${}^{3}J_{\text{PP}}$  = 50 Hz), -22.3 (t,  $J_{\text{PtP}}$  = 4159 Hz,  ${}^{3}J_{\rm PP} = 50$  Hz).

NMR Characterization of  $[\{Pt(PMe_3)\}_3(D)_2(\mu-SiPh_2)_4]$  (2a-d<sub>2</sub>). In a J. Young NMR tube to a toluene-d<sub>8</sub> solution (0.6 mL) of 1a (10 mg, 8  $\mu$ mol) was added D<sub>2</sub>SiPh<sub>2</sub> (4 mg, 21  $\mu$ mol) to form the deuterated Pt<sub>3</sub>Si<sub>4</sub> adduct 2a-d<sub>2</sub> in a few minutes. <sup>2</sup>H{<sup>1</sup>H} NMR (77 MHz, toluene, 263 K):  $\delta$  -6.06 (br, PtD).

NMR Characterization of [{Pt(PMe<sub>3</sub>)}<sub>3</sub>(H)<sub>2</sub>(μ-Si(C<sub>6</sub>H<sub>4</sub>-4-F)<sub>2</sub>]<sub>4</sub>] (2b). In a J. Young NMR tube to a toluene- $d_8$  solution (0.6 mL) of 1b (6 mg, 4 μmol) was added H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-F)<sub>2</sub> (3 mg, 14 μmol) at room temperature to form [{Pt(PMe<sub>3</sub>)}<sub>3</sub>(H)<sub>2</sub>{μ-Si(C<sub>6</sub>H<sub>4</sub>-4-F)<sub>2</sub>}<sub>4</sub>] (2b). <sup>1</sup>H NMR (500 MHz, toluene- $d_8$ , 293 K):  $\delta$  7.38 (br, 16H, C<sub>6</sub>H<sub>4</sub> ortho),  $\delta$  7.3–6.9 (16H, C<sub>6</sub>H<sub>4</sub> meta), 1.09 (br, 27H, PCH<sub>3</sub>), -6.51 (PtH, 2H, J<sub>PtH</sub> = 186 Hz, <sup>2</sup>J<sub>PH</sub> = 5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, toluene- $d_8$ , 293 K):  $\delta$  -23.3 (J<sub>PtP</sub> = 3883 Hz, <sup>2</sup>J<sub>PtP</sub> = 145 Hz, <sup>3</sup>J<sub>PP</sub> = 47 Hz).

NMR Characterization of [{Pt(PMe<sub>3</sub>)}<sub>3</sub>(H)<sub>2</sub>{μ-Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub>}<sub>4</sub>] (2c). In a J. Young NMR tube to a toluene- $d_8$  solution (0.6 mL) of 1c (6 mg, 4 μmol) was added H<sub>2</sub>Si(C<sub>6</sub>H<sub>4</sub>-4-Me)<sub>2</sub> (3 mg, 14 μmol). <sup>1</sup>H NMR (500 MHz, toluene- $d_8$ , 293 K):  $\delta$  7.65 (d, 16H, C<sub>6</sub>H<sub>4</sub> ortho), 7.2–6.9 (16H, C<sub>6</sub>H<sub>4</sub> meta), 2.23 (s, 24H, C<sub>6</sub>H<sub>4</sub>CH<sub>3</sub>), 1.32 (br, 27H, PCH<sub>3</sub>), -6.11 (PtH, 2H, J<sub>PtH</sub> = 182 Hz, <sup>2</sup>J<sub>PH</sub> = 5 Hz). <sup>31</sup>P{<sup>1</sup>H} NMR (202 MHz, toluene- $d_8$ , 285 K):  $\delta$  -22.8 (J<sub>PtP</sub> = 3998 Hz, <sup>2</sup>J<sub>PtP</sub> = 150 Hz, <sup>3</sup>J<sub>PP</sub> = 49 Hz).

Hydrosilyation of *p*-Tolualdehyde Catalyzed by 1a. In a NMR tube with a septum cap to a C<sub>6</sub>D<sub>6</sub> solution (0.6 mL) of 1a (10 mg, 7.4 μmol) were added H<sub>2</sub>SiPh<sub>2</sub> (33 mg, 0.18 mmol) and *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO (16 mg, 0.13 mmol). The reaction was performed at room temperature for 24 h to form hydrosilylated products 3a in 98% NMR yield. The <sup>31</sup>P NMR signal of 2a was observed during the catalytic reactions. The <sup>1</sup>H NMR spectroscopic data of the product was consistent with the literature.<sup>14c 1</sup>H NMR (400 MHz, C<sub>6</sub>D<sub>6</sub>, room temperature): δ 7.67 (d, 4H, C<sub>6</sub>H<sub>5</sub>, <sup>3</sup>J<sub>HH</sub> = 7.6 Hz), 7.21 (d, 2H, C<sub>6</sub>H<sub>4</sub>, J<sub>HH</sub> = 7.6 Hz), 5.71 (s, 1H, SiH), 4.75 (s, 2H, CH<sub>2</sub>), 2.08 (s, 3H, CH<sub>3</sub>).

Hydrosilyation of *p*-Tolualdehyde Catalyzed by 1b. In a NMR tube with a septum cap to a  $C_6D_6$  solution (0.6 mL) of 1b (10 mg, 7.1 μmol) were added  $H_2Si(C_6H_4F-4)_2$  (36 mg, 0.16 mmol) and *p*-CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO (16 mg, 0.13 mmol). The reaction was performed at room temperature for 24 h to form hydrosilylated products 3b in 32% NMR yield. <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  7.41 (dd, 4H,  $C_6H_4$ , J = 7.6, 8.4 Hz), 7.14 (app t, 4H,  $C_6H_4$ , J = 7.6 Hz), 6.8–6.7 (m, 4H,  $C_6H_4$ ), 5.55 (s, 1H, SiH), 4.68 (s, 2H, CH<sub>2</sub>), 2.12 (s, 3H, CH<sub>3</sub>).

Hydrosilyation of p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO Catalyzed by 1a. In a NMR tube with a septum cap to a C<sub>6</sub>D<sub>6</sub> solution (0.6 mL) of 1a (10 mg, 7.4  $\mu$ mol) were added H<sub>2</sub>SiPh<sub>2</sub> (33 mg, 0.18 mmol) and p-CF<sub>3</sub>C<sub>6</sub>H<sub>4</sub>CHO (16 mg, 0.13 mmol). The reaction was performed at room temperature for 24 h to form hydrosilylated product 4 in 43% NMR yield. The <sup>31</sup>P NMR signal of 2a was observed during the catalytic reactions.

<sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  7.6 (m, 4H,  $C_6H_4$ ), 7.29 (d, 2H,  $C_6H_4$ , <sup>3</sup> $J_{HH}$  = 8.0 Hz), 7.2–6.9 (m, 8H,  $C_6H_4$ ), 5.64 (s, 1H, SiH), 4.55 (s, 2H,  $CH_2$ ).

Hydrosilyation of Methyl(phenyl)ketone Catalyzed by 1a. In a NMR tube with a septum cap to a  $C_6D_6$  solution (0.6 mL) of 1a (10 mg, 7.4 μmol) were added  $H_2SiPh_2$  (31 mg, 0.17 mmol) and  $CH_3COC_6H_5$  (19 mg, 0.16 mmol). The reaction was performed at 60 °C for 54 h to yield a mixture of hydrosilylated product 5 (20%), dehydrosilylated product 6 (45%), and their coupling dimer, 7 (14%), in NMR yields. The <sup>1</sup>H NMR spectroscopic data of 5–7 were consistent with the literature.<sup>17</sup> Data for 5: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  5.67 (s, 1H, SiH), 4.95 (q, 1H, CH, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz), 1.42 (d, 3H, CH<sub>3</sub>, <sup>3</sup>J<sub>HH</sub> = 6.4 Hz). Data for 6: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  5.89 (s, 1H, SiH), 4.89 (d, 1H, =  $CH_2$ , <sup>2</sup>J<sub>HH</sub> = 2.4 Hz), 4.65 (d, 1H, =  $CH_2$ , <sup>2</sup>J<sub>HH</sub> = 2.4 Hz). Data for 7: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  5.67 (s, 1H, SiH), 4.95 (room temperature):  $\delta$  5.67 (s, 1H, SiH), 4.95 (room temperature):  $\delta$  5.67 (s, 1H, SiH), 4.95 (room temperature):  $\delta$  5.89 (s, 1H, SiH), 4.89 (d, 1H, =  $CH_2$ , <sup>2</sup>J<sub>HH</sub> = 2.4 Hz), 4.65 (d, 1H, =  $CH_2$ , <sup>2</sup>J<sub>HH</sub> = 2.4 Hz). Data for 7: <sup>1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  5.67 (s, 1H, SiH).

**Dehydrocoupling of Phenol and H<sub>2</sub>SiPh<sub>2</sub> Catalyzed by 2a.** In a NMR tube with a septum cap to a  $C_6D_6$  solution (0.6 mL) of **1a** (11 mg, 8.1  $\mu$ mol) were added H<sub>2</sub>SiPh<sub>2</sub> (54 mg, 0.29 mmol) and PhOH (14 mg, 0.15 mmol). The reaction was performed at room temperature for 96 h to yield diphenyl(phenoxy)silane (8) in 79% NMR yield. The <sup>1</sup>H NMR spectroscopic data of **8** were consistent with the literature.<sup>19c 1</sup>H NMR (400 MHz,  $C_6D_6$ , room temperature):  $\delta$  7.65 (m, 4H,  $C_6H_5$ ), 7.2–7.1 (m, 7H,  $C_6H_5$ ), 6.9–6.8 (m, 4H,  $C_6H_5$ ), 5.93 (s, 1H, SiH, J<sub>SiH</sub> = 218 Hz).

X-ray Crystal Structure Analyses. Single crystals of 1c and 2a suitable for X-ray diffraction were mounted on MicroMountsTM (MiTeGen). The crystallographic data were collected on a Bruker SMART APEX II ULTRA/CCD diffractometer equipped with monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å) at 90 K. Calculations were carried out using the program packages APEX II and OLEX2 for Windows. The positional and thermal parameters of non-hydrogen atoms were refined anisotropically on  $F^2$  by the full-matrix least-squares method using SHELXL-2014. Hydrogen atoms were placed at calculated positions and refined with a riding mode on their corresponding carbon atoms. CCDC numbers 1526079 (1c) and 1526710 (2a) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.7b00048.

NMR spectra (1-8), X-ray structures and the data (1c, 2a), and optimized structure (2a) (PDF) Cartesian coordinates of 2a and the model (PDF) Crystallographic data of 1c and 2a (CIF)

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#### Notes

The authors declare no competing financial interest.

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