

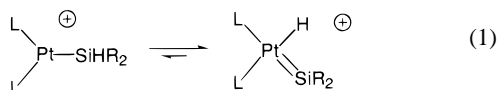
## Communications to the Editor

Silylene Extrusion from a Silane: Direct Conversion of  $\text{Mes}_2\text{SiH}_2$  to an Iridium Silylene DihydrideJonas C. Peters,<sup>†</sup> Jay D. Feldman, and T. Don Tilley\*

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The activation of silanes by transition metals is a key component of many catalytic reactions. These activations are generally viewed as involving the oxidative addition of H–SiR<sub>3</sub> bonds to a metal center, but it is often unclear to what extent further rearrangements of the resulting metal silyl derivative may contribute to observed transformations.<sup>1</sup> Considerable speculation has focused on the possibility of 1,2-migrations between the metal center and silicon, which could produce reactive transition metal silylene derivatives of the type  $\text{L}_m\text{M}=\text{SiR}_2$ .<sup>1,2</sup> To better understand the potential role of silylene complexes in catalytic processes, we have developed syntheses of such species<sup>3</sup> and have recently reported the first direct observations of 1,2-shifts that convert a metal silyl derivative  $\text{M}-\text{SiHR}_2$  to silylene hydrides  $(\text{H})\text{M}=\text{SiR}_2$ . These processes were found to occur in cationic, 3-coordinate platinum silyl complexes for which the 1,2-migration leads to the formation of a more stable, square planar complex (eq 1).<sup>4</sup> In



an attempt to extend this concept to the highly common case involving octahedral coordination, we have targeted generation of a 5-coordinate Ir–SiHR<sub>2</sub> complex, which might be expected to spontaneously rearrange to a d<sup>6</sup> octahedral (H)Ir=SiR<sub>2</sub> silylene

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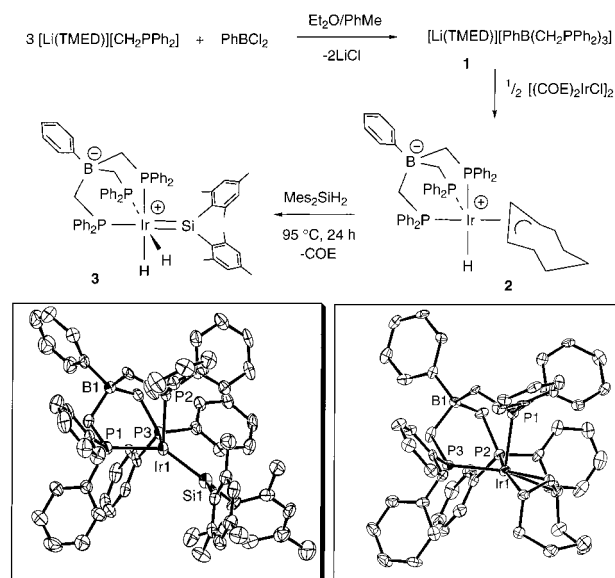
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(5) See Supporting Information for experimental details. This method is analogous to that reported by Riordan for the synthesis of related  $[\text{PhB}(\text{CH}_2\text{SR})_3]^-$  reagents. See, for example: Schebler, P. J.; Riordan, C. G.; Guzei, I. A.; Rheingold, A. L. *Inorg. Chem.* **1998**, *37*, 4754. Also, the  $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]^-$  ligand has recently been employed by D. Nocera and co-workers (personal communication).

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## Scheme 1



complex. Herein we introduce a new, anionic, tripodal phosphine ligand,  $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]^-$ , and demonstrate its utility in the facile preparation of a neutral iridium silylene complex,  $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3](\text{H})_2\text{Ir}=\text{SiMes}_2$  (**3**), directly from dimethylsilane ( $\text{H}_2\text{SiMes}_2$ ; Mes = 2,4,6- $\text{Me}_3\text{C}_6\text{H}_2$ ). The formation of a related cationic species,  $[(\text{PMe}_3)_3(\text{H})_2\text{Ir}=\text{SiMes}_2][\text{MeB}(\text{C}_6\text{F}_5)_3]$  (**5**), provides insight into the mechanism of this silane activation.

The key starting iridium complex was obtained by reaction of  $[\text{Li}(\text{TMED})][\text{PhB}(\text{CH}_2\text{PPh}_2)_3]$  (**1**), readily prepared by addition of 3 equiv of  $[\text{Li}(\text{TMED})][\text{CH}_2\text{PPh}_2]$  to dichlorophenylborane,<sup>5</sup> with  $[(\text{COE})_2\text{IrCl}]_2$ .<sup>6</sup> As shown in Scheme 1 this reaction gave  $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3]\text{Ir}(\text{H})(\eta^3\text{-C}_8\text{H}_{13})$  (**2**), the product of C–H activation in a cyclooctene ligand, obtained as white crystals in 65% yield. A related process has been observed in the reaction of  $[(\text{COE})_2\text{IrCl}]_2$  with KTp (Tp = tris(pyrazolyl)hydroborate) to give the vinyl hydride  $\text{TpIr}(\text{H})(\text{COE})(\text{C}_8\text{H}_{13})$ , which on warming converts to  $\text{TpIr}(\text{H})(\eta^3\text{-C}_8\text{H}_{13})$  with loss of cyclooctene.<sup>7</sup> The  $\eta^3$ -binding mode of the cyclooctenyl ligand of **2** was confirmed by X-ray crystallography (Scheme 1). The hydride ligand was not located by X-ray diffraction; however its presence is confirmed by its <sup>1</sup>H NMR resonance appearing at –12.6 ppm (dt, <sup>2</sup>J<sub>HPtrans</sub> = 150 Hz; <sup>2</sup>J<sub>HPcis</sub> = 14.3 Hz). Notably, **2** exhibits an elongated Ir–P bond (2.408(2) Å for Ir–P(1); compare 2.304(2) and 2.311(2) Å for Ir–P(2) and Ir–P(3), respectively), presumably due to the trans influence of the hydride ligand.

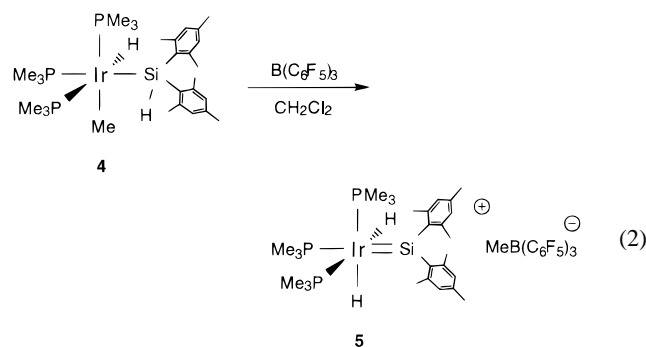
Addition of  $\text{H}_2\text{SiMes}_2$  to **2** in benzene afforded a clear, colorless solution at ambient temperature, which turned bright yellow on warming to 95 °C. Within 24 h, quantitative conversion to the silylene complex  $[\text{PhB}(\text{CH}_2\text{PPh}_2)_3](\text{H})_2\text{Ir}=\text{SiMes}_2$  (**3**) was observed (by NMR spectroscopy in benzene-*d*<sub>6</sub>). The <sup>1</sup>H NMR spectrum of **3** exhibits two distinct methylene resonances in a 2:1 ratio, a single set of resonances corresponding to the mesityl groups, and a hydride signal at  $\delta$  –9.47 ( $J_{\text{HPtrans}} = 70$  Hz).

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Consistent with the structure shown in Scheme 1, the  $^{31}\text{P}$  NMR spectrum exhibits a doublet and a triplet in a 2:1 ratio ( $J_{\text{PP}} = 18$  Hz). The silylene ligand gives rise to a doublet of triplets in the  $^{29}\text{Si}$  NMR spectrum ( $\delta = 241.2$ ), presumably resulting from strong coupling to a trans phosphine group (172.4 Hz) and weaker coupling to the cis phosphines (4 Hz).

The P–Ir–P angles in **3** are close to  $90^\circ$  ( $86^\circ$ – $91^\circ$ ), and although the hydride ligands were not located during refinement, their positions are indicated by the inequivalent P–Ir–Si angles which vary from  $112.3^\circ$  to  $141.5^\circ$ . Thus, it seems that the molecular structure is best described as a highly distorted octahedron, as might be expected for a complex with ligands of vastly different steric properties. The markedly short Ir(1)–Si(1) bond length of 2.260(3) Å suggests multiple bond character, as most structurally characterized iridium silyl complexes exhibit longer Ir–Si bonds.<sup>16</sup> For example, a highly related silyl complex with an  $\text{sp}^3$  silicon center, *fac*-( $\text{Me}_3\text{P}$ )<sub>3</sub>(H)<sub>2</sub>IrSiHPh<sub>2</sub>, possesses an Ir–Si bond length of 2.361(3) Å.<sup>8</sup> The  $\text{sp}^2$  Si center sits in a plane containing its substituent Ir and carbon atoms, and the sum of the angles about Si is  $359^\circ$  (these angles vary considerably: C–Si–C  $103.5(4)^\circ$ ; Ir–Si–C  $122.5(3)$ ,  $133.0(3)^\circ$ ).

Although the detailed mechanism of the conversion of **2** to **3** is yet to be established, we assume that  $\text{H}_2\text{SiMes}_2$  oxidatively adds to iridium to produce a transient Ir–SiHMe<sub>2</sub> species that rapidly undergoes a 1,2-hydrogen migration to give the final silylene product. Results that are consistent with this hypothesis were found in a related iridium system. Addition of  $\text{H}_2\text{SiMes}_2$  to ( $\text{Me}_3\text{P}$ )<sub>4</sub>IrMe<sup>9</sup> afforded the neutral iridium(III) complex *fac*-( $\text{Me}_3\text{P}$ )<sub>3</sub>Ir(Me)(H)(SiHMe<sub>2</sub>) (**4**). An attempt to generate the cationic 5-coordinate complex [( $\text{Me}_3\text{P}$ )<sub>3</sub>Ir(H)(SiHMe<sub>2</sub>)]<sup>+</sup>, by abstraction of the methyl ligand of **4** by  $\text{B}(\text{C}_6\text{F}_5)_3$ , led directly to the silylene complex [( $\text{Me}_3\text{P}$ )<sub>3</sub>(H)<sub>2</sub>Ir=SiMes<sub>2</sub>][ $\text{MeB}(\text{C}_6\text{F}_5)_3$ ] (**5**), isolated as a yellow solid (eq 2). By  $^1\text{H}$  and  $^{31}\text{P}$  NMR



spectroscopy, this reaction is quantitative. The  $^{29}\text{Si}$  NMR resonance of  $\delta$  254.1 ( $J_{\text{SiPtrans}} = 168$  Hz; unresolved *cis*-phosphine coupling) is in the region expected for a silylene ligand<sup>3,4</sup> and is 300.1 ppm downfield from the shift for the silyl precursor **4** ( $\delta$  –46.7 ppm). The similarity between the  $^{29}\text{Si}$  NMR chemical shifts for **5** and **3** lends considerable support to the formulation of **5** as a discrete salt, rather than an ion-paired, donor-stabilized silylene complex.

In conclusion, the activation of both Si–H bonds in a secondary silane has provided the first synthetic pathway to iridium silylene complexes.<sup>10</sup> This process is related to the conversion of a saturated carbon center to a carbene ligand in the activation of  $\text{tBu}_2\text{P}(\text{CH}_2)_3\text{P}^t\text{Bu}_2$  by iridium.<sup>11</sup> Also, Banaszak-Holl has reported the reaction of  $\text{H}_2\text{Ge}[\text{N}(\text{SiMe}_3)_2]_2$  with a Pt(0) complex, which proceeds via  $\text{H}_2$  elimination to give a germylene complex.<sup>12</sup> The process reported here, by which a silane directly delivers a silylene fragment to a transition metal center, is particularly relevant to postulated mechanisms for the metal-catalyzed dehydrogenative coupling of silanes to polysilanes.<sup>1c</sup> Observation of this chemistry was facilitated by the use of a novel, tris(phosphino)borate ligand, which was used to obtain a neutral silylene complex. The zwitterionic nature of **3** allows the study of an  $\text{L}_3\text{H}_2\text{Ir}=\text{SiR}_2^+$  fragment as a neutral species, soluble in a wide range of hydrocarbons and therefore amenable to mechanistic investigations. Preliminary results indicate that **3** extrudes silylene fragments from a variety of silanes, and this chemistry is currently under investigation.

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**Supporting Information Available:** Detailed experimental procedures for the preparation and spectroscopic characterization of complexes **1**–**5**, tables of crystal, data collection, refinement parameters, atomic coordinates, bond distances, bond angles, and anisotropic displacement parameters for **2** and **3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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