

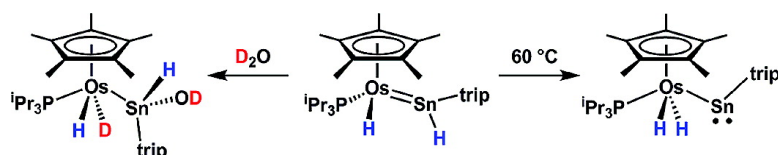
Communication

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# A Hydrogen-Substituted Osmium Stannylyene Complex: Isomerization to a Metallostannylyene Complex via an Unusual $\alpha$ -Hydrogen Migration from Tin to Osmium

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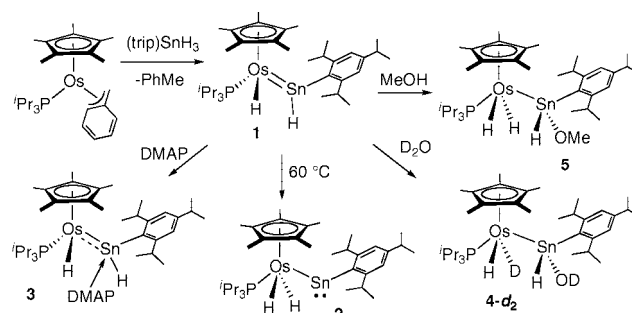
The fundamental step of  $\alpha$ -hydrogen migration is well-documented for transition-metal hydrocarbyl systems; however, much less is known about the  $\alpha$ -migration chemistry of heavier group 14 elements.<sup>1</sup> It has long been speculated that  $\alpha$ -migration processes, usually accompanied by formation of a metal–element multiple bond, may be key to catalytic processes for the heavier group 14 elements, including silane redistribution and oligomerization,<sup>2</sup> Ni-catalyzed hydrogenation of germynes,<sup>3</sup> and demethanative polymerization of HGeMe<sub>3</sub> to (GeMe<sub>2</sub>)<sub>n</sub> polygermanes.<sup>4</sup>

Recent studies support the significance of  $\alpha$ -migration steps in the chemistry of heavier group 14 elements.<sup>2,5,6</sup> For example, the silylene complex [Cp\*(iPr<sub>3</sub>P)(H)Ru=SiH(Ph)Et<sub>2</sub>O][B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>] catalyzes the hydrosilylation of olefins by a novel mechanism that appears to involve direct insertion of the olefin into the Si–H bond of the silylene ligand eventually followed by  $\alpha$ -hydrogen migration to regenerate the silylene catalyst.<sup>5</sup> A related  $\alpha$ -elimination process involving migration of hydrogen from tin to a metal center with concomitant elimination of a stannylyene species has been implicated in the dehydropolymerization of stannanes to polystannanes as catalyzed by group 4 metallocenes.<sup>7</sup> On the basis of these results, it seemed that  $\alpha$ -hydrogen migration from a stannyl ligand to a metal center without release of the stannylyene fragment could result in the formation of a terminal stannylyene ligand. Current synthetic methodologies for introduction of stannylyene ligands are largely limited to coordination of stable, free stannylenes to metal centers or salt metathesis involving the reaction of an anionic complex with R<sub>2</sub>SnCl<sub>2</sub>.<sup>8</sup> Herein, we report the synthesis of the first hydrogen-substituted stannylyene complex, Cp\*(iPr<sub>3</sub>P)(H)Os=SnH(trip) (**1**) (trip = 2,4,6-triisopropylphenyl), through direct activation of the stannane (trip)SnH<sub>3</sub> as well as the surprising isomerization of **1** under mild conditions to form the metallostannylyene Cp\*(iPr<sub>3</sub>P)(H)<sub>2</sub>OsSn(trip) (**2**).

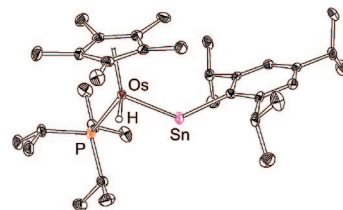
The benzyl complex Cp\*(iPr<sub>3</sub>P)OsCH<sub>2</sub>Ph<sup>9</sup> reacted with 1 equiv of (trip)SnH<sub>3</sub> in benzene to eliminate toluene and afford the stannylyene complex **1** as analytically pure dark-red crystals in 69% yield (Scheme 1). Complex **1** exhibits a significantly downfield-shifted <sup>119</sup>Sn resonance at  $\delta$  786 and <sup>1</sup>H NMR signals at  $\delta$  19.4 (<sup>1</sup>J<sub>H<sub>Sn</sub></sub> = 775 Hz) and –15.6, attributed to Sn–H and Os–H, respectively. Efforts to better address the location of the metal hydride ligand by determination of the <sup>2</sup>J<sub>SnH</sub> value were unsuccessful despite repeated attempts using a variety of direct and indirect one- and two-dimensional NMR techniques. The downfield Sn–H resonance at  $\delta$  19.4 is consistent with the observed trend for hydrogen-substituted carbene and silylene complexes, which display characteristically low-field C–H and Si–H resonances.<sup>2g,5,6,10</sup>

X-ray-quality single crystals of complex **1** were grown from a concentrated solution of hexane at –30 °C. The most outstanding

## Scheme 1



feature of the solid-state structure (Figure 1) is the short Os–Sn bond length of 2.4938(6) Å, which to the best of our knowledge is



**Figure 1.** Molecular structure of complex **1**, with thermal ellipsoids shown at the 30% probability level. Carbon-bound hydrogen atoms have been omitted for clarity.

the shortest yet reported. The stannylyene hydrogen was not located, but the Os–Sn–C<sub>ipso</sub> angle of 131.4(2)° is consistent with sp<sup>2</sup> hybridization at Sn. The Os–Sn multiple-bond character in **1** is also supported by the fact that **1** is essentially isostructural with the analogous silylene complex Cp\*(iPr<sub>3</sub>P)(H)Os=SiH(trip).<sup>9</sup>

Reaction of stannylyene complex **1** with an equimolar amount of *N,N*-*p*-dimethylaminopyridine (DMAP) resulted in formation of the corresponding base-stabilized stannylyene complex Cp\*(iPr<sub>3</sub>P)(H)Os=SiH(trip)(DMAP) (**3**), which was obtained as an orange powder in 80% yield. The <sup>1</sup>H NMR resonance of **3** at  $\delta$  15.6, attributed to the Sn hydrogen, is upfield-shifted by only  $\delta$  3.8 from that observed for stannylyene **1**. This would seem to indicate the presence of residual Os–Sn double-bond character in **3**. Stannylyene complex **1** also reacts with the O–H bonds of water and simple alcohols. Addition of 1 equiv of dry, deoxygenated water or methanol to benzene-*d*<sub>6</sub> solutions of **1** at ambient temperature rapidly resulted in the formation of the corresponding stannyl complexes Cp\*(iPr<sub>3</sub>P)(H)<sub>2</sub>OsSnH(OR)(trip) [R = OH (**4**), OMe (**5**)]. As expected, the <sup>1</sup>H NMR spectra of **4** and **5** display Sn–H resonances at  $\delta$  8.50 and 8.65, respectively, that are dramatically upfield-shifted with respect to that for **1**. The O–H addition reactions of water and methanol to transition-metal stannylyene complexes was first reported for (R'<sub>2</sub>PCH<sub>2</sub>CH<sub>2</sub>PR'<sub>2</sub>)Pd=SnR<sub>2</sub> [R' = <sup>i</sup>Pr, <sup>t</sup>Bu; R =

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CH(SiMe<sub>3</sub>)<sub>2</sub>].<sup>11</sup> Reaction of **1** with D<sub>2</sub>O exclusively formed Cp\*(<sup>i</sup>Pr<sub>3</sub>P)(H)(D)OsSnH(OD)(trip) (**4-d<sub>2</sub>**) (>95% by <sup>1</sup>H and <sup>2</sup>H NMR spectroscopy).

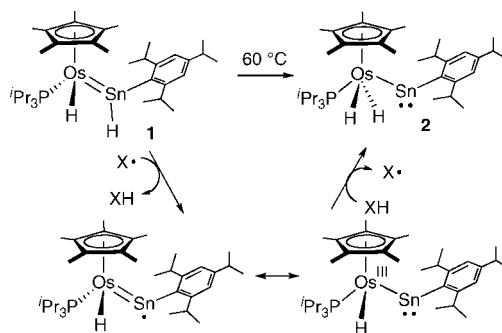
Heating benzene solutions of **1** to 60 °C resulted in the formation of the new Os-containing product **2**. This product, an isomer of **1**, was also obtained by exposure of benzene-*d*<sub>6</sub> solutions of **1** to ambient light for 8 h. The transformation of **1** to **2** is accompanied by the disappearance of the Sn–H and Os–H <sup>1</sup>H NMR signals for **1** and the appearance of a new OsH resonance at δ –14.01 (2H, <sup>2</sup>J<sub>HP</sub> = 30.4 Hz) assigned to the metallostannylene complex **2**. Unfortunately, attempts to observe the <sup>119</sup>Sn resonance of metallostannylene **2** by liquid- and solid-state NMR experiments were unsuccessful.<sup>12</sup> Addition of AlMe<sub>3</sub> to a benzene-*d*<sub>6</sub> solution of **2** resulted in the formation of the adduct Cp\*(<sup>i</sup>Pr<sub>3</sub>P)(H)<sub>2</sub>OsSn(AlMe<sub>3</sub>)(trip) (**6**), which is consistent with the presence of a lone pair of electrons at tin. Isolation of **6** was precluded by its thermal sensitivity, but the formation of **6** was established by solution NMR spectroscopy. The hydride resonance in the <sup>1</sup>H NMR spectrum of **6** is upfield-shifted from that of **2** (δ –14.0) to δ –16.7, and a resonance for the methyl group of the coordinated AlMe<sub>3</sub> is observed at δ –0.2. Divalent tin complexes are well-known, yet those with a transition-metal substituent are quite rare. Power and co-workers<sup>13</sup> have reported several examples of metallostannylenes of the type Cp(CO)<sub>3</sub>M–Sn–Ar', (M = Cr, Mo, W; Ar' = terphenyl) obtained by reaction of an arylytin(II) halide with [CpM(CO)<sub>3</sub>]<sup>–</sup>, and related stannylyne complexes of the type *trans*-Cl(Me<sub>3</sub>P)<sub>4</sub>W≡Sn(terphenyl) have been reported by the Filippou group.<sup>14</sup>

The conversion of **1** to **2** is somewhat surprising in that it involves an α-migration unlike those previously described for a variety of metal complexes.<sup>1</sup> In particular, the absence of an empty osmium orbital in **1** would seem to make a direct Sn-to-Os migration unlikely. Kinetic plots of the concentration of **2** versus time (see the Supporting Information) were linear over 4 half-lives, indicating a zero-order dependence on the starting material, although variations in the concentration of **1** resulted in fluctuations in the reaction rate. This indicates that the reaction is not rigorously zero-order. The rate of conversion of **1** to **2** fluctuated erratically across separate batches of complex **1** but was consistent within a given batch. Thus, it was possible to determine that the rate of isomerization is unaffected by the presence of excess P<sup>i</sup>Pr<sub>3</sub> (20 equiv). This appears to rule out a mechanism involving phosphine dissociation followed by direct α-migration.

These observations suggest that the conversion of **1** to **2** does not involve a concerted, direct migration but instead is catalyzed by an impurity in samples of **1**, giving a rate law of the form rate = *k*<sub>obs</sub>[**1**]<sup>0</sup>, where *k*<sub>obs</sub> = *k*[catalyst]<sup>*n*</sup>. Because the reaction rate is unaffected by 1 equiv of added proton sponge, it is unlikely that the catalyst/impurity is adventitious acid. It seems more likely that the catalyst is a radical species, and this is supported by the fact that **1** is greatly stabilized by the addition of 0.2 equiv of HSnBu<sub>3</sub> and by 10 equiv of 9,10-dihydroanthracene. The latter result suggests a mechanism involving abstraction of H from the tin atom of **1** by an adventitious radical (X) to give the Os- and/or Sn-centered radical species Cp\*(<sup>i</sup>Pr<sub>3</sub>P)(H)OsSn(trip) and XH. The two latter species would then react via H-atom transfer to form **2** and regenerate the radical (Scheme 2).

In conclusion, the first example of a hydrogen-substituted stannylyne complex, Cp\*(<sup>i</sup>Pr<sub>3</sub>P)(H)Os≡SnH(trip) (**1**), has been prepared and structurally characterized. This hydrogen-substituted stannylyne complex undergoes an unusual α-migration reaction to provide a new type of metallostannylene complex (**2**). Preliminary mechanistic studies point to a catalytic isomerization involving a radical-mediated transfer of H• from the coordinated Sn atom to Os. Such abstraction/migration processes may be more common

## Scheme 2



and could represent a general synthetic pathway to unsaturated metal–main-group complexes. Future investigations are designed to address such possibilities.

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**Supporting Information Available:** Experimental details for the syntheses of new compounds, kinetic data, and crystallographic information for **1** (CIF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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