

# Insight into the Mechanism of Carbonyl Hydrosilylation Catalyzed by Brookhart's Cationic Iridium(III) Pincer Complex

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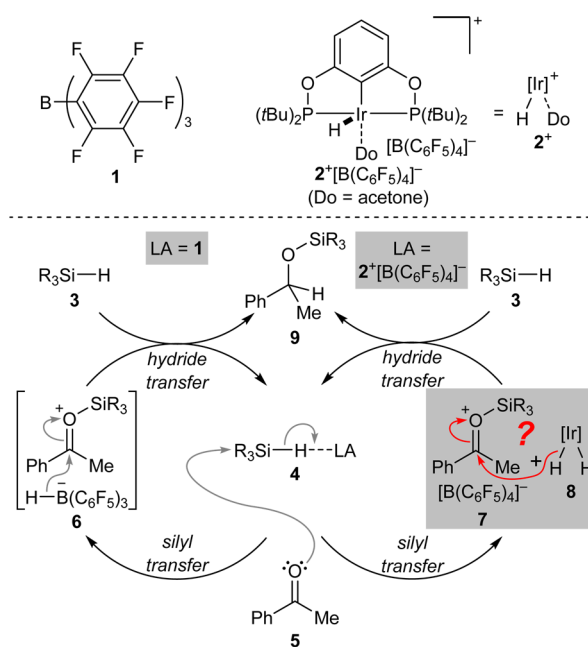
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**S** Supporting Information

**ABSTRACT:** New experimental findings suggest partial revision of the currently accepted mechanism of the carbonyl hydrosilylation catalyzed by the iridium(III) pincer complex introduced by Brookhart. Employing silicon-stereogenic silanes as a stereochemical probe results in racemization rather than inversion of the configuration at the silicon atom. The degree of the racemization is, however, affected by the silane/carbonyl compound ratio, and inversion is seen with excess silane. Independently preparing the silylcarboxonium ion intermediate and testing its reactivity then helped to rationalize that effect. The stereochemical analysis together with these control experiments, rigorous multinuclear NMR analysis, and quantum-chemical calculations clearly prove that another silane molecule participates in the hydride transfer. The activating role of the silane is unexpected but, in fact, vital for the catalytic cycle to close.

Activation of Si–H bonds with Lewis acids is the initiation step of a number of catalytic processes.<sup>1</sup> The mechanisms of these reactions are, however, often not thoroughly understood. In a recent highlight article,<sup>2</sup> we discussed the similarities of two widely used catalysts known to activate the Si–H bond,  $B(C_6F_5)_3$  (**1**)<sup>3</sup> and cationic iridium(III) pincer complex  $2^+[B(C_6F_5)_4]^-$  (Scheme 1, top). Si–H bond activation with either **1** or  $2^+$  is believed to commence with  $\eta^1$ - $\sigma$  coordination of the Si–H bond of **3** to the Lewis acidic center (**3**  $\rightarrow$  **4**, Scheme 1, bottom),<sup>5,6</sup> followed by nucleophilic attack of a Lewis base at the silicon atom. For carbonyl hydrosilylation (**5**  $\rightarrow$  **9**), it is the oxygen atom of **5** that acts as the nucleophile, and the net reaction is a formal transfer of a silicenium ion onto the carbonyl group (**4**  $\rightarrow$  **6** with **1**, left cycle and **4**  $\rightarrow$  **7** + **8** with  $2^+$ , right cycle).<sup>3b,4,6,7</sup> The nature of the hydride “complex” generated in the silyl transfer step critically depends on the Lewis acid catalyst used. With neutral **1**, an ate complex,  $[HB(C_6F_5)_3]^-$ , is released that forms an ion pair with the silylcarboxonium ion (**6**, left cycle). Conversely, cationic  $2^+$  transforms into the neutral iridium(III) dihydride **8**, likely to be separated from silylcarboxonium ion **7** (**7** + **8**, right cycle).<sup>6</sup> For the catalysis with  $B(C_6F_5)_3$  (**1**), it was shown both experimentally<sup>3b,7</sup> and computationally<sup>8</sup> that ion pair **6** undergoes rapid hydride transfer to produce **9** and regenerate catalyst **1**. However, such in-depth analysis of the fate of the corresponding intermediates **7** + **8** remains to be conducted.<sup>9</sup> Kinetic measurements by Brookhart and co-workers<sup>4</sup> indicated that the carbonyl hydrosilylation catalyzed by  $2^+$  is first order in silane **3** and zero order in carbonyl compound **5**. These findings

**Scheme 1. Carbonyl Hydrosilylation Catalyzed by Lewis Acids (LAs)  $B(C_6F_5)_3$  (**1**) or Pincer Complex  $2^+$**



were inconclusive, though, as to whether the silyl or the hydride transfer is the rate-determining step. Also, the involvement of silicon cation intermediates cannot be excluded on the basis of these results.

Our laboratory elucidated the mechanism of  $B(C_6F_5)_3$ -catalyzed carbonyl hydrosilylation using a silicon-stereogenic silane as a mechanistic probe.<sup>7</sup> The observed inversion of the configuration at the silicon atom unambiguously showed the transfer of the silicon group to obey the  $S_N2$ -Si mechanism, as proposed earlier by Piers and co-workers (**4**  $\rightarrow$  **6**, left).<sup>3b</sup> Moreover, the absence of racemization precluded the release of a silicon cation from complex **4** or ion pair **6** and lent further support for rapid hydride transfer (**6**  $\rightarrow$  **9**, left). We envisioned that a related analysis of the catalysis with the iridium(III) POCOP complex  $2^+[B(C_6F_5)_4]^-$  would provide similar insight [POCOP = 2,6-bis(di-*tert*-butylphosphinito)phenyl].

We knew from the  $B(C_6F_5)_3$ -mediated Si–H bond activation that the steric situation around the silicon atom is crucial (*t*-Bu group not tolerated),<sup>7</sup> and we therefore chose cyclic *i*-Pr-substituted silane (<sup>Si</sup>S)-**3a**<sup>10a</sup> (e.r. = 97:3). We were then

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delighted to find that catalyst  $2^+$  promoted the reaction of rigid ( $^{Si}S$ )-**3a** and an equimolar amount of acetophenone (**5**), affording ether **9a** with poor diastereocontrol (*cyclic* scenario, Table 1, columns 2 and 3). The reaction was slow, requiring 20 h

**Table 1. Two-Step Stereochemical Analysis with Silicon-Stereogenic Silanes ( $^{Si}S$ )-**3a** and ( $^{Si}S$ )-**3b**<sup>a,b</sup>**

scenario	( $^{Si}S$ )- <b>3</b> (1 equiv) <sup>c</sup>		( $^{Si}S$ )- <b>3</b> (4 equiv) <sup>d</sup>	
	e.r. <sup>e</sup>	yield (%)	e.r. <sup>e</sup>	yield (%)
<i>cyclic</i> with ( $^{Si}S$ )- <b>3a</b>				
<b>9a</b>	55:45 <sup>f</sup>	86	55:45 <sup>f</sup>	86
recovered <b>3a</b>	—	0	94:6	95
reformed <b>3a</b>	49:51	79	48:52	99
<b>10</b>	51:49	69	51:49	86
<i>acyclic</i> with ( $^{Si}S$ )- <b>3b</b>				
<b>9b</b>	59:41 <sup>f</sup>	90	62:38 <sup>f</sup>	89
recovered <b>3b</b>	—	0	74:26	85
reformed <b>3b</b>	48:52	85	36:64	86
<b>10</b>	49:51	99	46:54	93

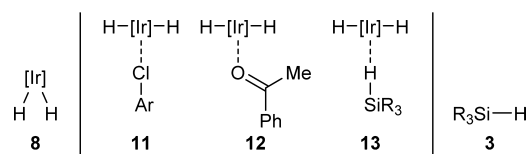
<sup>a</sup>Hydrosilylation according to General Procedure 1. <sup>b</sup>Reductive cleavage according to General Procedure 2. <sup>c</sup>Reaction time 20 h. <sup>d</sup>Reaction time 30 min. <sup>e</sup>Enantiomeric ratios determined by HPLC analysis using chiral stationary phases; e.r. = *S*/*R*. <sup>f</sup>Diastereomeric ratio determined by GLC analysis.

for completion. Using excess ( $^{Si}S$ )-**3a** dramatically accelerated the reaction, producing the same result in minutes rather than hours; unconsumed ( $^{Si}S$ )-**3a** was recovered without any racemization (*cyclic* scenario, Table 1, columns 4 and 5). To our surprise, the reductive cleavage of the Si–O bond with DIBAL–H (proceeding with retention at the silicon atom<sup>11</sup>) yielded both reformed **3a** and alcohol **10** essentially in racemic form within the experimental error.

This outcome stands in stark contrast to the catalysis with  $B(C_6F_5)_3$  (**1**),<sup>7</sup> and it was, at least at this stage, not meaningful. To rule out any detrimental effect of the rigid cyclic structure of ( $^{Si}S$ )-**3a**, we repeated the same set of experiments with acyclic *i*-Pr-substituted silane ( $^{Si}S$ )-**3b**<sup>10b</sup> (e.r. = 97:3). Again, the reaction time was dependent on the amount of ( $^{Si}S$ )-**3b** used relative to **5**, and results were discouraging with an equimolar ratio (*acyclic* scenario, Table 1, columns 2 and 3). The setup with excess ( $^{Si}S$ )-**3b** was, however, markedly different from the previous ones (*acyclic* scenario, Table 1, columns 4 and 5). Recovered ( $^{Si}S$ )-**3b** was now partially racemized, indicating that unconsumed ( $^{Si}S$ )-**3b** (e.r. = 74:26) had been involved in the catalysis. It must be noted here that neither cationic  $2^+$  (iridium monohydride) nor neutral **8** (iridium dihydride) racemizes ( $^{Si}S$ )-**3b**, while  $^1H/^2H$  scrambling of deuterium-labeled  $Me_2PhSiD$  (**3c-d**<sub>1</sub>) is fast with  $2^+$  and slow with **8** (see the Supporting Information (SI) for details). More importantly, the reductive cleavage of the Si–O

bond in ( $^{Si}S,RS$ )-**9b** furnished ( $^{Si}R$ )-**3b** (e.r. = 36:64) with opposite absolute configuration. While the degree of racemization is certainly substantial, the remaining enantioenrichment of ( $^{Si}R$ )-**3b** is evidence of the rate of racemization being dependent on the silane/carbonyl compound ratio. Partial racemization of the recovered silane ( $^{Si}S$ )-**3b** confirms the reversibility of the silane coordination as well as the silyl transfer.

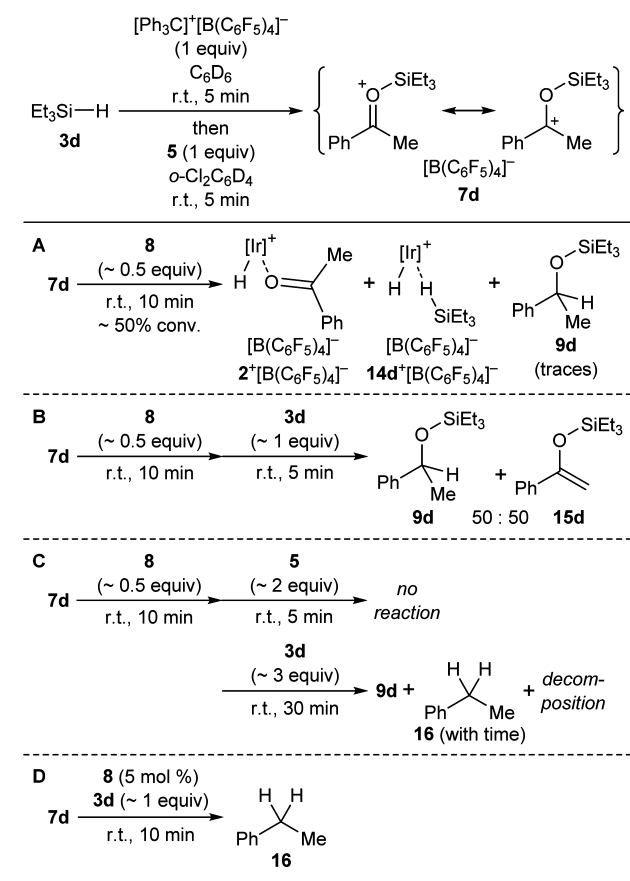
The experiments with the silicon-stereogenic silanes provide valuable information but do not explain the entirely different behavior of ( $^{Si}S$ )-**3a** and ( $^{Si}S$ )-**3b**. These seemingly inconclusive results again made us compare the catalytic cycles with **1** and  $2^+$  as catalysts (cf. Scheme 1, bottom). It is the nature of the silylcarboxonium intermediates that distinguishes these processes, with the  $B(C_6F_5)_3$  catalysis passing through an ion pair known to immediately react (**6** → **9**, left). Less information is available on the hydride transfer from the iridium dihydride **8** (**7** + **8** → **9**, right). Brookhart proposed that either neutral **8** would directly donate a hydride, forming cationic  $2^+$  (without Do molecule) or, alternatively, the hydride transfer would be assisted by solvent coordination (**11** with ArCl =  $C_6H_5Cl$  or  $o\text{-}Cl_2C_6D_4$ , Figure 1).<sup>4,12</sup> In addition to the solvent, both reactants, silanes **3** and carbonyl compound **5**, are likely to coordinate to the iridium center (**12** and **13**, Figure 1).



**Figure 1.** Conceivable hydride donors for the reduction of the silylcarboxonium ion intermediate.

To identify the hydride source, we independently synthesized intermediates **7** and **8** (cf. Scheme 1, right). The silylcarboxonium ion  $7d^{13}$  was generated from benzene-stabilized silicenium ion  $[Et_3Si(C_6D_6)]^+[B(C_6F_5)_4]^-$ <sup>14</sup> (derived from the corresponding silane **3d**) and acetophenone (**5**, 1 equiv) in  $o\text{-}Cl_2C_6D_4$  (Scheme 2, top). We then conducted a series of control experiments (Schemes 2A–D, bottom), and clean formation of freshly prepared **7d** was confirmed by  $^1H$  NMR spectroscopy prior to each run. Treatment of **7d** with dihydride **8** produced a remarkable result: **8** that was originally assumed to be the hydride source<sup>4,9</sup> is reluctant to transfer a hydride onto the carbon atom of **7d**! Instead, immediate hydride transfer onto the silicon atom of **7d** occurred, as indicated by formation of  $2^+[B(C_6F_5)_4]^-$  and  $14d^+[B(C_6F_5)_4]^-$  (Scheme 2A). The backward reaction is thus favored over closing the catalytic cycle at short reaction times, despite the fact that the forward reaction, i.e., the reduction (**7d** → **9d**), is more exoenergetic by about 64 kJ/mol (see Figure S1 in the SI for free energies calculated at the B3LYP-D3(BJ)/ECP/6-31++G(d,p) level using an SMD solvation model). That hints at a somewhat higher reaction barrier for the reduction as compared to the backward reaction associated with the cleavage of the Si–O bond in **7d**. Attempts to find the transition states on the electronic energy surface for the hydride transfer from **8** to the carbon or silicon atom of **7d** were not successful, suggesting a process without a potential energy barrier for both the forward and backward reactions. The experimental observation could hence be related to a higher entropy barrier for the reduction, connected also with ion pair dissociation (not taken into account in our DFT simulations). Then, addition of silane **3d** (1 equiv) resulted in instantaneous consumption of **7d** as well as any

Scheme 2. Identification of the Hydride Source in the Reduction of Silylcarboxonium Ion 7

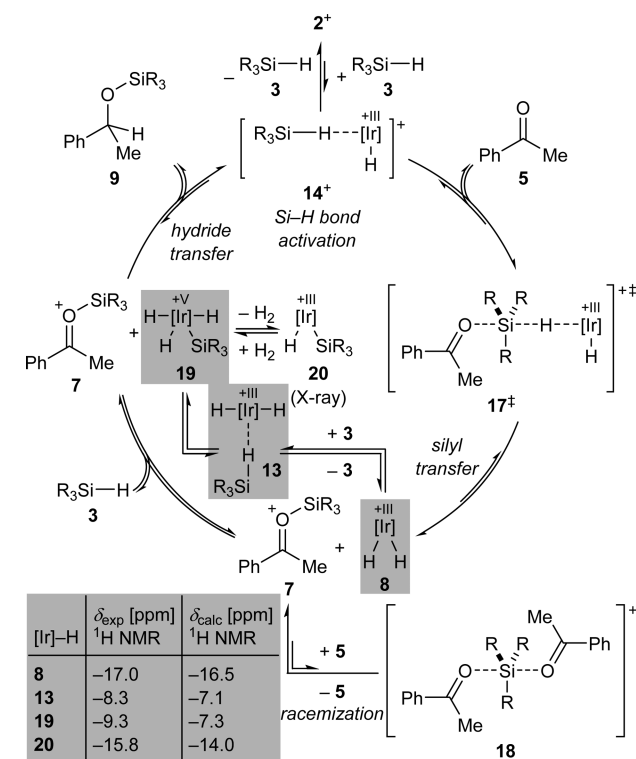


acetophenone (5) released earlier (Scheme 2B). The expected silyl ether 9d formed along with the corresponding silyl enol ether 15d.<sup>4,15</sup>

To probe the reactivity of the proposed acetophenone adduct 12 (Figure 1), we treated the coexisting mixture of silylcarboxonium ion 7d and dihydride 8 with excess acetophenone (5, 2 equiv), yet no reaction was observed. The crucial role of the silane was again demonstrated by the addition of excess 3d (3 equiv). As expected, reduction proceeded immediately (7d  $\rightarrow$  9d), but the silyl ether reacted further to finally yield ethylbenzene (9d  $\rightarrow$  16, Scheme 2C). Not surprisingly, addition of 8 (5 mol %) and 3d (1 equiv) to freshly prepared 7d afforded solely 16 (Scheme 2D). Hence, the reduction does not stop at the alcohol oxidation level when silanes 3 act as reductants.<sup>16</sup> We must conclude from this that, despite being the most available hydride source, free silanes 3 cannot fulfill the role of the hydride donor in the real catalytic process using  $2^+[\text{B}(\text{C}_6\text{F}_5)_4]^-$ , since only traces of deoxygenation are observed. The difference between the experiments shown in Scheme 2C,D and the catalytic setup is that the equimolar ratio of 7d and 8 is out of balance, and with excess 7d relative to 8, reduction by 3 becomes kinetically competent. It is also clear from the reaction between 7d and 8 that the neutral dihydride 8 alone cannot donate that hydride (Scheme 2A), and coordination of neither solvent (as in 11) nor carbonyl compound (as in 12) to 8 is able to mediate the hydride transfer (Scheme 2C).

The key actor in the hydride transfer is silane 3 that is required to boost the hydride donor strength of iridium(III) dihydride 8. NMR experiments on a mixture of 8 and 3 show that these are in

fast equilibrium with the originally proposed silane adduct 13, iridium(V) silyl trihydride 19<sup>17</sup> after oxidative addition of the Si–H bond to the iridium(III) center of 13, and iridium(III) monohydride 20<sup>12</sup> after reductive elimination of dihydrogen (Scheme 3; see the SI for NMR measurements, crystallographic

Scheme 3. Revised Catalytic Cycle, a Two-Silicon Cycle ( $[\text{B}(\text{C}_6\text{F}_5)_4]^-$  as Counteranion Omitted for Clarity)

characterization of 20c and 20d, and detailed bonding analysis). The assignment of the resonance signals (cf. Scheme 3) was guided by our state-of-the-art relativistic four-component DFT calculations of NMR shifts<sup>18</sup> (Tables S4 and S5 in the SI) and by the elegant work of Heinekey and co-workers on related borane complexes.<sup>19</sup> Based on our control experiments (cf. Scheme 2) and computed hydricities of iridium POCOP complexes present in the reaction mixture with excess 3 (cf. Figure 1 and Table S6 in the SI), either 13 or 19, with more ionic metal–hydrogen bond character and hydricity as compared to 8, is *de facto* the active hydride donor. We cannot decide either experimentally or computationally whether 13 or 19 ultimately acts as the hydride source, but the elusive iridium(V) complex 19 appears somewhat more likely because adduct formation alone, as in 11 and 12, is not sufficient. The reaction could be classified as a silane-mediated hydride transfer. The final hydride shift step is also reversible, as 14<sup>+</sup> slowly racemizes enantioenriched 9d (see the SI for racemization experiments).

On the basis of these findings, we propose a revised catalytic cycle (Scheme 3) where the initial Si–H bond activation is in agreement with the previously proposed mechanism.<sup>4,6</sup> The silane 3 is reversibly coordinated by cationic monohydride 2<sup>+</sup> (concomitant with liberation of the donor) to form the  $\eta^1-\sigma$  complex 14<sup>+</sup>. Nucleophilic substitution with the carbonyl oxygen atom of 5 through transition state 17<sup>‡</sup> yields the silylcarboxonium ion 7 with inversion at the silicon atom along with neutral dihydride 8. Racemization then occurs at this stage by reversible

formation of siliconium ion **18** that emerges from coordination of another molecule of **5** to **7**. The net result is exchange of the siliconium ion fragment between two molecules of **5**. A related transfer process was recently considered by Oro and co-workers in a hydrosilylation of C–C triple bonds,<sup>20</sup> and a similar mechanism was reported by Brookhart and co-workers in the ether cleavage with silanes.<sup>12</sup>

The revised catalytic cycle also explains the results obtained with the silicon-stereogenic silanes (<sup>Si</sup>S)-**3a** and (<sup>Si</sup>S)-**3b** (Table 1). At low silane concentration, i.e., using equimolar amounts of **3** (both scenarios, Table 1, columns 2 and 3), the hydride transfer is much slower than racemization through siliconium ion **18**. Conversely, excess (<sup>Si</sup>S)-**3b** greatly enhances the hydride transfer, and its increased rate is reflected in the inversion at the silicon atom of reformed (<sup>Si</sup>R)-**3b** (*acyclic* scenario, Table 1, columns 4 and 5). Recovered (<sup>Si</sup>S)-**3b** is partially racemized, and that is a clear indication of the reversibility of the silyl transfer and the Si–H bond activation (**7b** → **17b**<sup>‡</sup> → **14b**<sup>+</sup> → (<sup>Si</sup>S)-**3b**). The situation is different in the *cyclic* scenario with (<sup>Si</sup>S)-**3a** (Table 1, columns 4 and 5). Neither inversion of reformed *rac*-**3a** nor partial racemization of recovered (<sup>Si</sup>S)-**3a** is detected. We reason that both hydride transfers, onto the carbon atom of **7a** (forward) or onto the silicon atom of **7a** (backward), are hampered by the steric bulk of rigidified (<sup>Si</sup>S)-**3a**. Consequently, **7a** → **9a** is again outcompeted by formation of **18**, and **7a** → **17a**<sup>‡</sup> → **14a**<sup>+</sup> is even slower.

The fact that B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> (**1**) and iridium complex 2<sup>+</sup>[B(C<sub>6</sub>F<sub>5</sub>)<sub>4</sub>]<sup>−</sup> catalyze the same set of transformations<sup>2</sup> had prompted us to compare the individual mechanisms of action of these fundamentally different Lewis acids. Carbonyl hydrosilylation was chosen as a model reaction, and the basic steps of the catalysis with **1** were fully understood at the outset of the present investigation.<sup>3b,7,8</sup> Conversely, hydride transfer in the catalysis by 2<sup>+</sup> had been unclear, and we demonstrated here that the originally assumed hydride source<sup>4,9</sup> is not the active reductant. The hydride donor strength of that iridium(III) dihydride is greatly enhanced by η<sup>1</sup>-σ coordination or even oxidative addition of another molecule of the silane. The overall transformation is a two-silicon rather than a one-silicon cycle. These findings are likely to have implications for related processes.<sup>2</sup>

## ■ ASSOCIATED CONTENT

### 📄 Supporting Information

Experimental details; characterization, crystallographic, and quantum-chemical calculation data; <sup>1</sup>H, <sup>13</sup>C, and <sup>29</sup>Si NMR spectra. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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### Notes

The authors declare no competing financial interest.

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