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Article

The Higher Propensity of Pd-$SiHEt_2^+$ over Pd-$SiMe_2Et^+$ to Transfer Silylium to Silyl Ether Intermediates Explains Divergent Products in Ketone Hydrosilylation Catalysis

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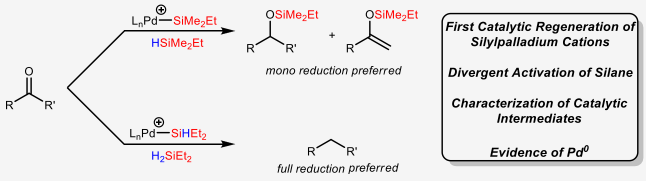
ABSTRACT: The catalytic use of silylpalladium cations has been developed for the hydrosilylation of ketones. Product outcome was heavily influenced by hydrosilane identity with tertiary silanes providing silyl ethers and secondary silanes, alkanes. Stoichiometric studies suggest a key differentiating feature is the ability to transfer silylium from XantPhosPd-SiR_3^+ to silyl ether intermediates in the case of secondary silanes but not tertiary. Formation of a bimetallic Pd species during catalysis with secondary silanes points to silylpalladium cations behaving as a source of both electrophilic silylium ions and nucleophilic Pd(0).

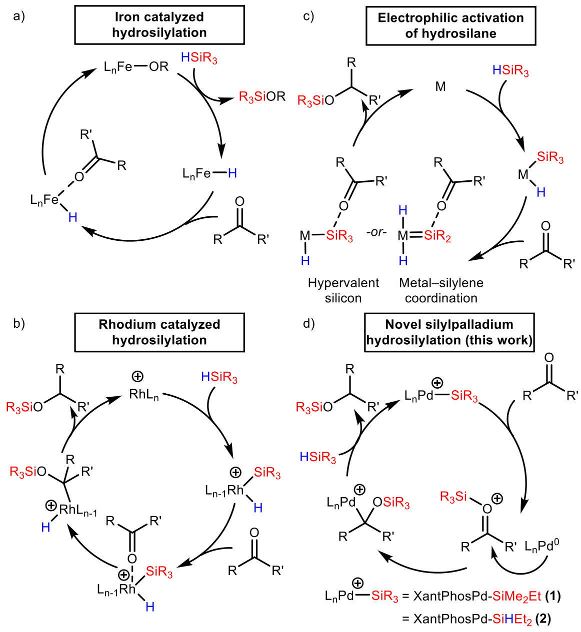


INTRODUCTION

The catalytic hydrosilylation of ketones through the intervention of metal-silyl complexes has yielded powerful methods for the synthesis of alcohols. Since Ojima's use of Wilkinson's catalyst,[1] numerous complexes have emerged as competent catalysts for the hydrosilylation of ketones, including ruthenium, rhodium-, iron-, and iridium-based systems.[2,3] Despite sharing similar M−SiR_3 intermediates, vastly different mechanisms have been reported across these systems.[4] Iron complexes typically activate silane by σ-bond metathesis across the Fe−OR bond, leading to metal-hydrides and silyl ether products (Scheme 1a).[5,6] Late metal species, especially rhodium catalysts, are thought to follow the mechanistic steps proposed by Ojima et al. and are closely related to the Chalk−Harrod and modified Chalk−Harrod mechanisms.[7,8] Oxidative addition of hydrosilane followed by ketone coordination to rhodium allows for silyl transfer and subsequent C−H reductive elimination to yield product (Scheme 1b). Metal identity is important in these transformations as discrete metal−carbon bonds can be formed and oxidative addition/reductive elimination cycles can be utilized to create the product.

Another mechanism frequently invoked in the metal-silyl reduction of ketones is the electrophilic activation of silane (Scheme 1c). Ionic activation of hydrosilane has been proposed for a variety of transition metal hydrosilylation catalysts.[9−11] Oestreich's exploration of Brookhart's Ir catalyst deconvoluted a nuanced role for high valent Ir intermediates and the reversibility of silane transfer,[12,13] which differ from traditional Lewis acid-catalyzed processes.[14] Another mechanistic pathway initiates by oxidative addition of hydrosilane followed by coordination of the carbonyl oxygen to the silicon, made possible by either the creation of a hypervalent silicon

Scheme 1. General Mechanisms for Metal-Based Ketone Hydrosilylation



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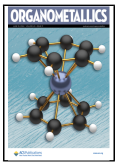

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species or the coordination to a metal-silylene species, the former having been proposed as intermediates in Lewis-base-catalyzed hydrosilylations,[15−17] ring-strain-promoted aldol condensations,[18,19] and Si−H hydrolysis,[20] and in ketone hydrosilylations.[21,22]

Tilley's isolation of hexacoordinate silicon upon the addition of Lewis bases to a silyl-ruthenium complex is important evidence to the viability of these intermediates in ketone hydrosilylations.[23] Metal-silylene complexes are made by oxidative addition of a Si−H bond, followed by creation of the M═Si bond through subsequent α-hydrogen migration. Ketone coordination to the $\pi^*_{\text{M-Si}}$ initiates the subsequent reduction.[24−27] In these scenarios, the metal's primary function is to activate the H−Si bond to generate electrophilic silicon species, rather than direct activation of the carbonyl.[28]

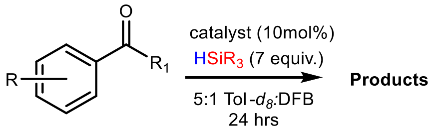
Our previous studies of silylpalladium cations showed their ability to act as a source of electrophilic Si by its transfer from Pd(II)-SiR_3 to ethereal Lewis bases to yield a reactive silyloxonium and Pd(0) pair,[29] recombination of which cleaved the C−O bond to forge reactive Pd−C species. By applying these concepts to the hydrosilylation of ketones, we envisioned the creation of a reactive Pd(0)/silyl−oxocarbenium pair (Scheme 1d), whose subsequent recombination would yield a Pd−C species susceptible to reduction with hydrosilane. We report herein the first catalytic function of silylpalladium cations in the hydrosilylation of ketones and detail how the mechanisms differ depending on whether the silane is tertiary or secondary.

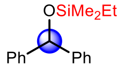
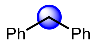
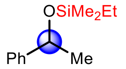
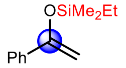
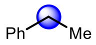
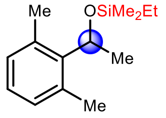
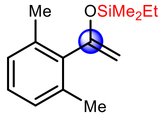
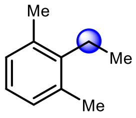
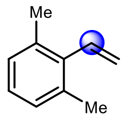
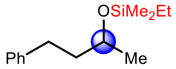
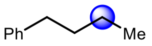
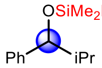
RESULTS AND DISCUSSION

We began our study of the reduction using excess hydrosilane and catalytic quantities of [(XantPhos)Pd−SiR_3^+][$BArF_{24}^-$], R_3═Me_2Et (**1**), R_3=HEt_2 (**2**) to observe the full conversion of ketones (see the Supporting Information for more details). As reported in Table 1 catalyst **1** preferentially makes silylether products at elevated temperatures (silylenol ethers also minor products) while catalyst **2** provides the alkane at room temperature. This product divergence was not expected as **1** and **2** possess similar relative intrinsic silylicity (Π_1 = 1.29, Π_2 = 1.28) and can be viewed as similarly electrophilic.[29,30] The full reduction of ketones to alkanes is a challenging transformation that typically requires harsh conditions such as a Wolff−Kishner reduction,[31,32] Clemmensen reduction,[33,34] or hydrogenation using platinum or palladium catalysts[35] and hydrosilane identity rarely yields products with different levels of reduction[4,5,36,37] despite playing a key role in the rates of hydrosilylation.[38,39] Most importantly, the ability of **2** to reduce silylethers is reactivity not reported by more electrophilic metal-silyl complexes.[36,40] Our interest in these findings led us to perform several mechanistic experiments.

Mechanistic Studies of Catalyst 1. In situ monitoring of the catalytic reduction of benzophenone revealed **1** to be the catalytic resting state. To gather evidence for putative Pd-benzyl intermediates in the cycle, a series of stoichiometric experiments was undertaken. Addition of 1 equiv of **1** to benzophenone (no added silane) provided a new species consistent with palladium-π-benzyl species **3** and confirmed by HRMS (Figure S35). It was characterized by a broad resonance in the $^{31}P\{^1H\}$ NMR (9 ppm), indicative of the ligand dynamics seen in complexes undergoing η^3−η^1−η^3 benzyl ligand interconversion.[41,42] The single broad peak in the $^{31}P\{^1H\}$ NMR at room temperature decoalesced into two broad peaks at −78 °C (Figure 1), an observation ascribed to a desymmetrization of the two P ligands by slowing the benzyl ligand's η^3−η^1−η^3 interconversion. The previously reported [(XantPhos)Pd(η^3-phenethyl)][$BArF_{24}^-$] complex, bearing an η^3 benzyl ligand,[29] was similarly cooled and revealed analogous benzyl ligand dynamics (Supporting Information Figure S1). As judged by $^{31}P\{^1H\}$ and ^1H NMR spectroscopy, complex **3** proved catalytically viable as the addition of 70 equiv of $HSiMe_2Et$ (catalysis conditions) furnished a 91% yield of the silylether and regeneration of **1** (eq 1).

Table 1. Catalytic Reduction of Ketones with (XantPhos)Pd-SiR_3^+ Catalysts 1 and 2



L_nPd-$SiMe_2Et$ (**1**) at 110°C	L_nPd-$SiHEt_2$ (**2**) at RT
 57% yield[a]  40% yield[a]	 78% yield[ab]
 59% yield[a]  9% yield[a]	 65% yield[a]
 43% yield[a]  51% yield[a]	 84% yield[ac]  11% yield[ac]
 98% yield[a]	 10% yield[d]
 74% yield[a]	 58% yield[a]

[a]Yield determined by ^1H NMR spectroscopy using bibenzyl as an internal standard. [b]DCM-d_2, 48 h, 70 °C. [c]72 h. [d]Yield determined by ^1H NMR spectroscopy using mesitylene as an internal standard.

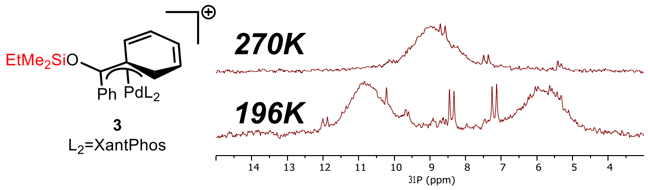
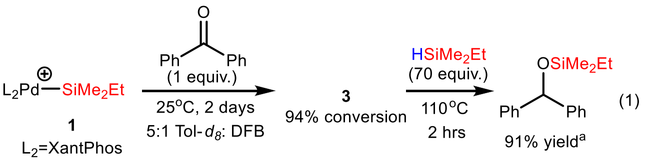


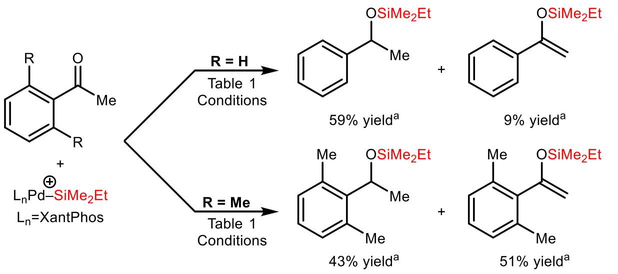
Figure 1. Variable-temperature $^{31}P\{^1H\}$ NMR spectrum of *in situ* generated **3**. Solvent: CD_2Cl_2.



^{a}Yield determined by ^{1}H NMR spectroscopy using bibenzyl as an internal standard

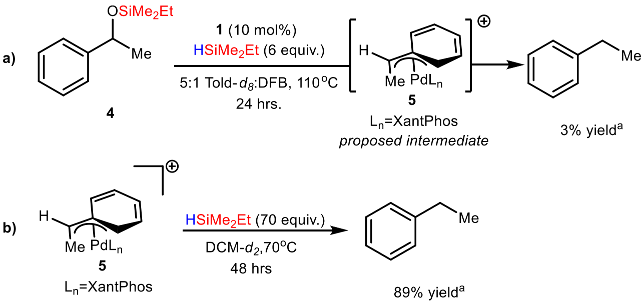
In ketone hydrosilylations, it has been noted that an increase in steric hindrance can increase the proportion of silyl enol ether product,[43] presumably by accelerating a unimolecular β-H elimination over a bimolecular reaction with silane. A similar effect was observed in the current system, as 2,6-dimethylacetophenone provided a substantially increased proportion of silyl enol ether over silylether (Scheme 2), suggesting that the σ-form of the Pd-benzyl intermediate is accessible in the catalytic cycle.

Scheme 2. Steric Hindrance Effect on Product Formation



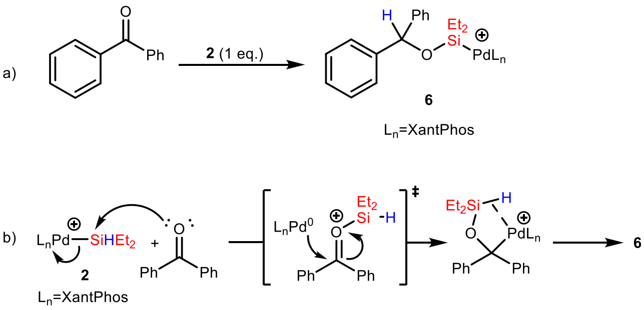
One possibility for the preference of catalyst **1** for ketone monoreduction is a lack of reactivity toward the intermediate silyl ether. Complex **1** was previously demonstrated to react with phenethyl methyl ether to yield **5**, which was additionally susceptible to Pd–C reduction with silane (Scheme 3b). A similar reaction with silylether **4** only returned 3% ethylbenzene (Scheme 3a). Since palladium-π-benzyl **5** reacts with 70 equiv of HSiMe$_2$Et to produce ethylbenzene in 89% yield, it is apparent that the silylium character of **1** is not enough to overcome the diminished Lewis basicity of silylether **4**.[44−46]

Scheme 3. Reduction of Silyl Ethers by 1



Mechanistic Studies of Catalyst 2 (Pd–SiHEt$_2$). Catalyst **2**'s preference for the full reduction of ketones was probed by the addition of benzophenone to 1 equiv of **2**. This did not generate the expected Pd-π-benzyl system, and instead, a silylpalladium species **6** incorporating partially reduced ketone was observed (Scheme 4a), reminiscent of a complex isolated by Tilley from benzophenone addition to a ruthenium–silyene complex.[40]

Scheme 4. Proposed Mechanism for the Formation of 6



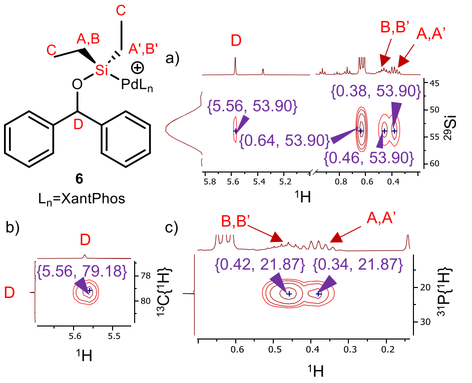
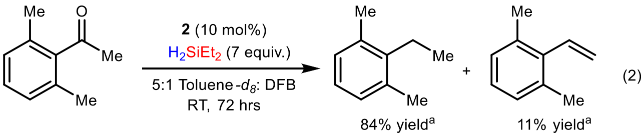


Figure 2. Selected NMR spectra of **6** in CD$_2$Cl$_2$: (a) ^{1}H,^{29}Si-HMBC (400 MHz, 80 MHz) at 25 °C; (b) ^{1}H,^{13}C-HSQC (400 MHz, 100 MHz) at 25 °C; (c) ^{1}H,^{31}P-HMBC (400 MHz, 162 MHz) at 25 °C.

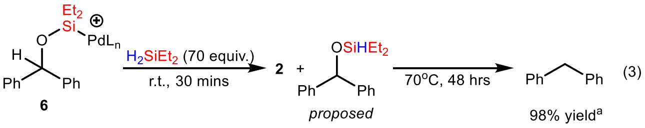
Compound **6** was characterized via NMR spectroscopy (Figure 2) and its constitution confirmed by HRMS. A new ^{31}P resonance at 21 ppm was observed, which coupled to the methylene peaks of the ethyl groups as confirmed by ^{1}H,^{31}P-HMBC. The ^{1}H,^{29}Si-HMBC spectrum established connectivity between the benzylic CH and silicon. The activation of the internal Si–H bond and regeneration of a Pd–Si bond constitute one difference between catalysts **1** and **2**.

We again tested the possibility of an intermediate Pd-benzyl structure by enhancing the steric congestion of the ketone. In our control reaction with acetophenone, no styrene was observed under our standard conditions with **2**; however, it was detectable (11%) with 2,6-dimethylacetophenone (eq 2), suggesting the feasibility of a Pd-σ-benzyl intermediate, which could either react with silane to generate alkane or perform β-H elimination to yield styrene. We hypothesize that the route to **6** is initiated by ketone displacement of silicon[12,36] to create a silyloxonium ion and Pd^0 pair, which then recombine to give a Pd-benzyl species. Pd activation of the internal Si–H bond would then yield **6** (Scheme 4b).



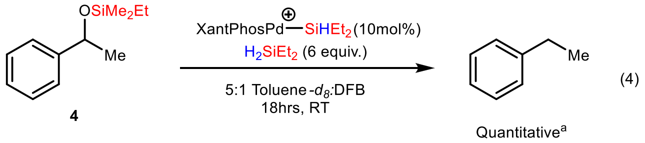
^{a}Yield determined by ^{1}H NMR spectroscopy using bibenzyl as an internal standard

The rapid conversion of **2** to **6** established the feasibility of a process wherein the internal Si–H bond is consumed for the first reduction of acetophenone (Scheme 3a). Complex **6** also reacts with 70 equiv of H_2SiEt_2 to regenerate **2** and a proposed silylether. Continued heating provides high conversion to diphenylmethane (eq 3) and points to the viability of **6** as a



^{a}Yield determined by ^1H NMR spectroscopy using bibenzyl as an internal standard

catalytic intermediate. Despite their similar relative intrinsic silylicities, **2** is more reactive toward relatively nonbasic C−O bonds than **1**. To illustrate, complex **2** readily reacts with silylether **4** and H_2SiEt_2 to quantitatively produce ethylbenzene over 18 h (eq 4).



^{a}Yield determined by ^1H NMR spectroscopy using bibenzyl as an internal standard

Unlike catalyst **1**'s reduction of silylether **4** (Scheme 3a), analysis of the $^{31}P\{^1H\}$ NMR spectrum of catalyst **2**'s reduction at completion revealed only 27% of **2**, with the remaining 73% relative yield belonging to an unknown species, **7**. We surmised that characterization of **7** could provide key insight into the mechanism of the reduction of silylether **4** by **2**.

Characterization of Bimetallic Complex 7. Based on similarities to a binuclear XantPhosPd(I)-hydridocarbonyl species,[47] we suggest that this unknown compound is the bimetallic complex **7** (Figure 3). Most distinctively, the ^1H NMR spectra show a quintet at −7.5 ppm ($^2J_{HP}$ = 30.7 Hz), indicative of a metal hydride coupling to four near equivalent ^{31}P nuclei. Assuming a square planar geometry at Pd, symmetry considerations would suggest an AA′XX′ spin system with distinct J_{H-P} values, but rapid cleavage of a Pd−Si or Pd−H bond followed by rotation could provide the observed A_4 spin system. This behavior mirrors that seen in binuclear Pd(I)-hydridocarbonyl species at room temperature.[47,48] Low-temperature NMR studies of **7** further support our characterization. When cooled to −90 °C, the Pd−H, a quintet at 25 °C, forms a triplet of triplets ($J_{HP(trans)}$ = 76.4 Hz, $J_{HP(cis)}$ = 12.9 Hz), indicative of inequivalent phosphorus atoms in **7**. Although the $^{31}P\{^1H\}$ NMR resonance of **7** split into multiple resonances at −90 °C, the resulting multiplicity of these species made it difficult to confirm the results seen by ^1H NMR, a finding also observed by Hartwig in his studies of a binuclear Pd(I)−hydridocarbonyl complex (Figure S15).[49]

Viewing **7** as a 1:1 combination of (XantPhos)Pd(0) and (XantPhos)Pd-$SiHEt_2^+$ suggested an approach to independently synthesize **7**. We previously showed PCy_3 could abstract silylium cation from (XantPhos)Pd-$SiMe_2Et^+$ to form (XantPhos)Pd(0), which then associated with another equivalent of PCy_3 to generate (XantPhos)Pd-PCy_3.[29] Repeating this reaction with only 0.5 equiv of PCy_3 cleanly generated **7**, suggesting that it indeed forms by the interception of **2** with in situ generated (XantPhos)Pd(0) (eq 5). It is worth noting that we have never directly observed XantPhosPd(0) and presume that it is highly prone to decomposition.

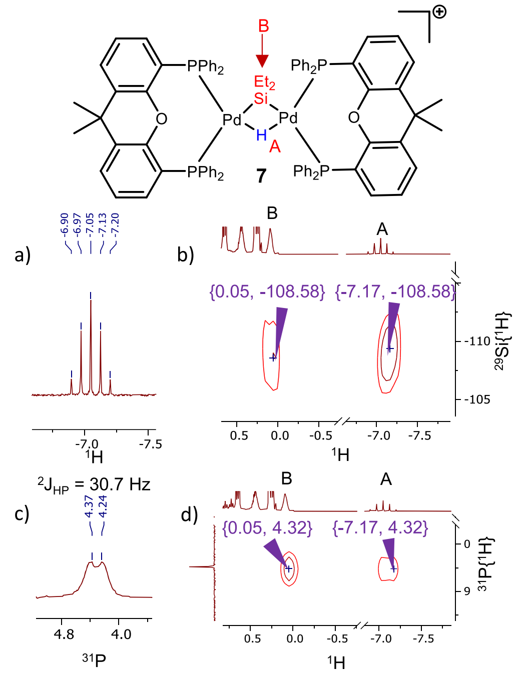
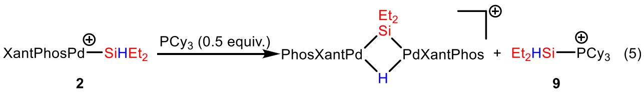
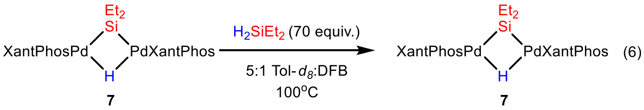


Figure 3. Selected NMR spectra of **7** in CD_2Cl_2. (a) ^1H (400 MHz) at 25 °C, (b) $^1H,^{29}Si$-HMBC (400 MHz, 80 MHz) at 25 °C; (c) ^{31}P (162 MHz) at 25 °C; (d) $^1H,^{31}P$-HMBC (400 MHz, 162 MHz) at 25 °C.



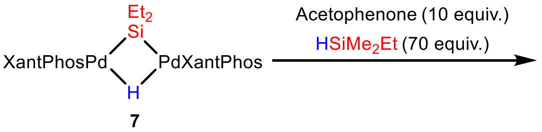
Reactivity of Bimetallic Complex 7. The upfield shifting of **7**'s ^{29}Si NMR resonance (−108 ppm) was indicative of decreased silicon electrophilicity compared to **2** (35 ppm), making **7** an unlikely source of R_3Si^+ in the reduction of ketones.[50] However, the ability of **2** to reduce silylethers, reactivity not reported by much more electrophilic metal-silyl complexes,[36,40] pointed to the possibility of **7** playing a key role in this reactivity. The formation of **7** by the clean reaction of 0.5 equiv of Pd^0 with 0.5 equiv of **2** provided insight into the hydrosilylation mechanism of complex **2**. That is, transfer of R_3Si^+ from **2** would generate equal amounts of silyloxonium ion and (undetected) XantPhosPd(0), which could either productively trap the oxocarbenium ion to form a Pd−C intermediate or react with **2** to form **7**. Under catalytic conditions, the concentration of **7** was found to increase as ketone was consumed (Table S1). Qualitatively, it was noted that the reduction of silylethers to alkanes was significantly limited when large quantities of **7** were present in catalytic mixtures (Figure S9), suggesting that it is off-cycle.

To test the ability of **7** to form **2**, a series of high-temperature NMR experiments were conducted. Addition of **2** to large excesses of volatile 2-butanone and H_2SiEt_2 cleanly generated **7** upon concentration and trituration with pentanes. Heating a solution of **7** and H_2SiEt_2 (70 equiv) to 100 °C failed to regenerate **2** via $^{31}P\{^1H\}$ NMR (eq 6). However,



monometallic palladium (either **1** or **2**, indistinguishable) was generated when acetophenone was added to the mixture (Table 2). These results parallel those of Hartwig, who established the need for excess base in the generation of active $Pd(CO)_2$ complexes from a bimetallic Pd(I)−hydridocarbonyl complex.[49] Although this result could potentially provide a method for generation of **2** from **7**, the elevated temperatures and extent of catalyst degradation suggest this route is not likely viable under catalytic conditions (RT).

Table 2. Conversion of 7 to Monometallic Palladium Was Observed at Various Times and Temperatures



7

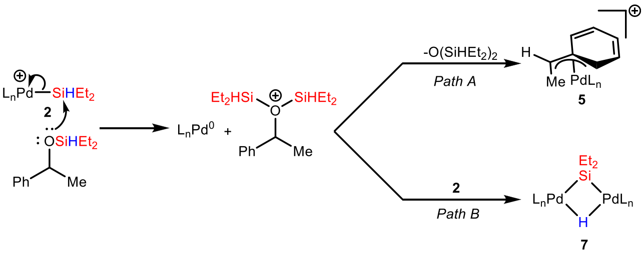
	yield of monometallic palladium[a,b]	
temperature	5:1 Tol-d_8:DFB	DFB
25 °C	0%	0%
70 °C	1%	3%
90 °C 30 min	14%	12%
90 °C 60 min	18%	17%

[a] Either **1** (^{31}P NMR δ = 22.3) or **2** (^{31}P NMR δ = 22.4). [b] Catalyst degradation observed.

Although catalyst degradation made it difficult to fully delineate the role of **7** in catalysis, the observation of generated monometallic palladium led us to reexamine our reaction conditions to see if heating might allow bimetallic **7** to reenter the catalytic cycle and enhance the rates of reaction. Heating at 70 °C caused the reaction color to change from a pale orange to red with improved yield and a decreased buildup of **7**, possibly due to generation of **2** from **7** (Table 3, entries 1 and 2). Additional heating to 110 °C, however, led to a darker-red mixture lacking peaks in the ^{31}P{^{1}H} NMR spectrum, both indicative of catalyst degradation (entry 3).[51] Although we were encouraged by the increase in yield, the catalyst degradation was concerning.

The effect of solvent polarity was then tested, with increasing proportions of DFB improving yields and with less **7** being formed throughout the reaction (entries 5 and 10). Additionally, heating a mixture of **7**, acetophenone, and $HSiMe_2Et$ generated monometallic palladium at a rate similar to that of a 5:1 Tol-d_8:DFB mixture. Combined, these results suggest that DFB encourages the productive addition of Pd^0 to the silyloxonium (Scheme 5, path A) rather than deleterious formation of **7** (path B), potentially by improving the stability of the palladium/silyloxonium pair.

Scheme 5. Proposed Pathway for the Creation of 5 (Path A) and 7 (Path B)[a]

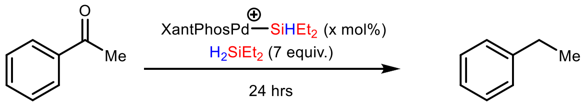


[a] L_n = XantPhos.

The optimized conditions in entry 5 were confirmed at a lower catalyst loading (entries 7−9) and applied to additional substrates (Table 4). 2-Acetonaphthone, (4-CF_3)-acetophenone and 4-phenyl-2-butanone were chosen as catalyst **2** performed poorly when subjected to the reaction conditions outlined in Table 1. In all three cases, improved yields of these problematic substrates were noted.

Mechanistic Proposal. These results outline two distinct mechanistic scenarios for the hydrosilylation of ketones depending on whether the silane is secondary or tertiary. In the case of **1**, monoreduction to silylethers is preferred, predominantly because the product is insufficiently basic to abstract silylium from **1** to initiate deoxygenation (Scheme 1d). Silylpalladium cation **2**, on the other hand, is reactive enough to transfer Et_2SiH^+ to the secondary silyl ether, which enables double reduction (Scheme 6 and Figure S4). Consistent with this picture, **8** is an observable product in our catalytic trials (Figure S17). In situ ^{31}P{^{1}H} NMR spectroscopy revealed the presence of **2**, **5**, and **7** under catalytic conditions and strongly supports their intermediacy in our proposed mechanism (Figure S14).

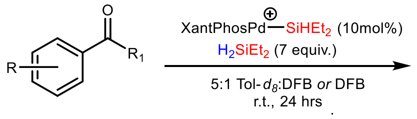
Table 3. Reoptimization of Acetophenone Reduction with Catalyst 2

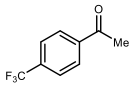
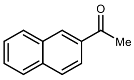
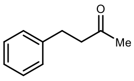


entry	solvent	catalyst loading (mol %)	*T*	yield of ethylbenzene %[a]	relative yield of **7** (%)[b,c]	relative yield of **2** (%)[b]
1	**5:1 Tol-d_8:DFB**	**10**	**r.t.**	**65**	**83**	**17**
2	5:1 Tol-d_8:DFB	10	70 °C	85	78	22
3	5:1 Tol-d_8:DFB	10	110 °C	80	-	-
4	1:1 Tol-d_8:DFB	10	r.t.	89	50	50
5	**DFB**	**10**	**r.t.**	**91**	**52**	**48**
6	DFB	10	70 °C	84	73	27
7	1:1 Tol-d_8:DFB	2.5	r.t.	45	~100	~0
8	DFB	2.5	r.t.	57	90	10
9	5:1 Tol-d_8:DFB	2.5	r.t.	31	98	2
10[d]	DFB	2.5	r.t.	36	33	67

[a] Yields were determined by ^{1}H NMR spectroscopy using bibenzyl as an internal standard. [b] Relative yield was determined by ^{31}P{^{1}H} NMR spectroscopy between **7** and **2**. [c] Contains 2 equiv of XantPhos(Pd) per percentage. [d] Run for 90 min.

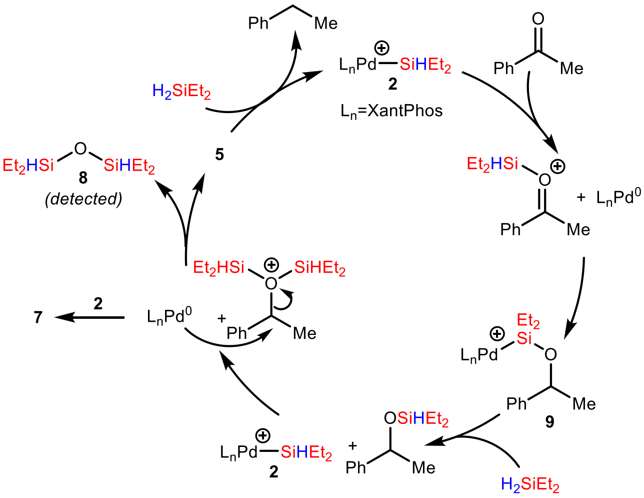
Table 4. Reduction of Poorly Performing Ketones with Reoptimized Conditions 2



entry	Ketone	Solvent	yield of alkane(%)[a]	relative yield of **7** (%)[bc]	relative yield of **2** (%)[b]
1		5:1 Tol-d_8:DFB	11	22	78
2		DFB	30	44	56
3		5:1 Tol-d_8:DFB	15	73	27
4		DFB	65	64	36
5		5:1 Tol-d_8:DFB	10	37	63
6		DFB	38	43	57

[a]Yields were determined by ^{1}H NMR spectroscopy using bibenzyl as an internal standard. [b]Relative yield was determined by ^{31}P{^{1}H} NMR spectroscopy between **7** and **2**. [c]Contains two equiv of XantPhos(Pd) per percentage.

Scheme 6. Proposed Mechanism for Reduction of Ketones with 2



The buildup of bimetallic complex **7** points to its role as an off-cycle intermediate but more importantly sheds light on some of the competitive processes occurring under catalytic conditions, namely, the ability of XantPhosPd(0) to react with either **2** (nonproductive) or silyloxonium (productive).

■ CONCLUSIONS

In conclusion, we report the catalytic function of silylpalladium cations for ketone hydrosilylation, detail two mechanisms, and demonstrate the mechanistic divergence between tertiary and secondary silanes. Both mechanisms are proposed to activate the ketone by an initiating silylium transfer, with concomitantly generated Pd(0) recombining to yield distinct palladium cations. These catalysts ultimately differ in their propensity to transfer silylium to silylether intermediates of reduced basicity. Tertiary (XantPhos)Pd-SiMe$_2$Et$^+$ does not readily transfer silylium to silyl ethers while secondary (XantPhos)Pd-SiHEt$_2$$^+$ is able to do so. The similarity in intrinsic silylcity suggests that the ultimate difference in reactivity may be steric in origin (secondary silylium transferring to secondary silyl ether). This study additionally provides a deeper understanding of the difference in product selectivity observed in an underexplored class of ketone hydrosilylation catalysts.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acs.organomet.4c00104.

Experimental details and NMR spectra used for characterization (PDF)

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Notes

The authors declare no competing financial interest.

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