JACS JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Article

Cite This: J. Am. Chem. Soc. 2019, 141, 16024−16032

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# Silylpalladium Cations Enable the Oxidative Addition of C($sp^3$)−O Bonds

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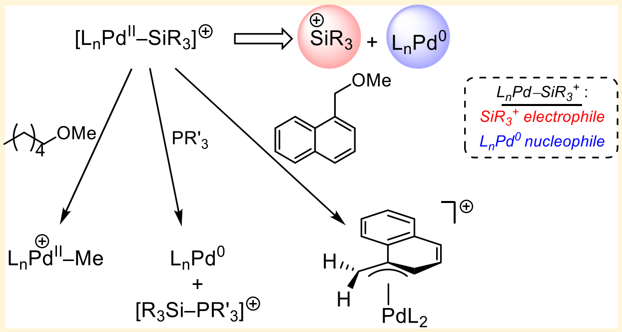
Supporting Information

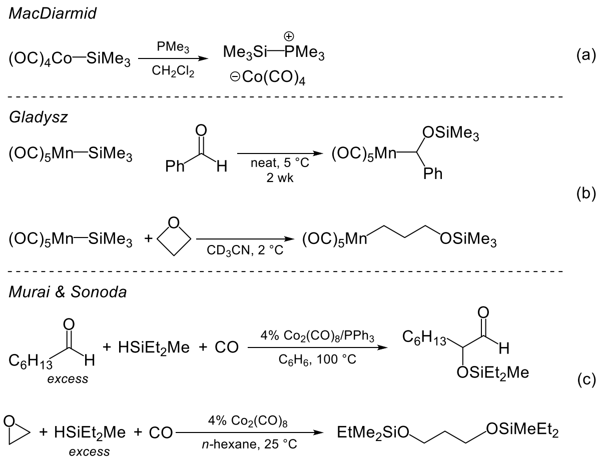
**ABSTRACT:** The synthesis and characterization of the room-temperature and solution-stable silylpalladium cations $(PCy_3)_2Pd{-}SiR_3^+(C_6F_5)_4B^-$ ($SiR_3$ = $SiMe_2Et$, $SiHEt_2$) and (Xantphos)Pd−$SiR_3^+(BAr^f_4)$ ($SiR_3$ = $SiMe_2Et$, $SiHEt_2$; Xantphos = 4,5-bis(diphenylphosphino)-9,9-dimethylxanthene; $BAr^f_4$ = $(3,5\text{-}(CF_3)_2C_6H_3)_4B^-$) are reported. Spectroscopic and ligand addition experiments suggest that silylpalladium complexes of the type $(PCy_3)_2Pd{-}SiR_3^+$ are three-coordinate and T-shaped. Addition of dialkyl ethers to both the $PCy_3$ and Xantphos-based silylpalladium cations resulted in the cleavage of C($sp^3$)−O bonds and the generation of cationic Pd−alkyl complexes. Mechanistically enabling is the ability of silylpalladium cations to behave as sources of both electrophilic silylium ions and nucleophilic $L_nPd(0)$.



## INTRODUCTION

Since the first reported synthesis of a transition-metal−silyl complex, $Cp(CO)_2FeSiMe_3$ by Wilkinson in 1953,[1] the number of compounds containing a formal metal−silicon bond have grown to include nearly every transition metal.[2−7] The synthesis and study of silylmetal complexes has been driven, in part, by the development of homogeneous transition-metal catalysts for olefin hydrosilylation.[8,9] The most commonly proposed mechanisms for this process, the Chalk−Harrod and modified Chalk−Harrod mechanisms, invoke silylmetal complexes as key catalytic intermediates. While the most familiar reactivity of silylmetal complexes is the insertion of C═X (X = C, O, N) bonds into the M−Si bond (to formally cleave the π-bond), silylmetal complexes are also known to react with nucleophiles to heterolytically cleave the M−Si bond and transfer the silyl group as the Lewis acidic silylium ion ($SiR_3^+$) to the Lewis base.[2,3,9]

### Scheme 1. Examples of C−O Bond Cleavage by Silylmetal Complexes



In the early 1970s, MacDiarmid isolated the first reported silylphosphonium salts with $(CO)_4Co^-$ counteranions by adding phosphines to $(CO)_4CoSiMe_3$ (Scheme 1a).[10,11] Their seminal work demonstrated the ability of certain silylmetal complexes to behave as sources of both $SiR_3^+$ and low-valent transition-metal nucleophiles. Related studies by Corriu on the transfer of $SiR_3^+$ to alcoholic and hydridic nucleophiles from neutral Mn− and Co−$SiR_3$ complexes bearing chiral silyl ligands demonstrated that $SiR_3^+$ transfer to the nucleophile occurs predominantly with inversion (i.e., $S_N2$) at the stereogenic silicon center.[9,12−16] With the aim of generating M−C bonds from C−O bonds, Gladysz exploited the ability of silylmetal complexes to be sources of $SiR_3^+$ and metal nucleophiles to oxidatively add to C−O bonds.[17−21] They demonstrated that metal−(α-silyloxy)alkyl and metal−alkyl compounds can be generated from the reaction of carbonyl compounds and dialkyl ethers with silylmetal complexes, respectively (Scheme 1b). This type of silylmetal-mediated C−O bond cleavage has also been exploited in catalytic applications by Murai and Sonoda, who established the catalytic generation of α-siloxyaldehydes from aldehydes,

**Received:** July 30, 2019
**Published:** September 18, 2019

DOI: 10.1021/jacs.9b08178
J. Am. Chem. Soc. 2019, 141, 16024−16032

and silylated 1,*n*-diols from cyclic ethers, by the application of an *in situ* generated silylcobalt catalyst in the presence of CO and excess hydrosilane (Scheme 1c).[22−24] The mechanisms proposed by Gladysz, Murai, and Sonoda all involve the nucleophilic attack of oxygen at the electrophilic silyl ligand. The resulting silyloxocarbenium(silyloxonium) electrophiles and metal nucleophiles recombine to cleave the C−O bond and forge a new M−C bond.

These examples illustrate the ability of silylmetal complexes to cleave C−O bonds, particularly those that are unactivated, aliphatic, unstrained, and thus typically described as inert. Their ability to cleave C−O bonds is an important property, as the oxidative addition of "inert" C($sp^3$)−O bonds by transition metals remains a challenge.[25−30] The ability of silylmetal complexes to simultaneously generate metal nucleophiles and $SiR_3^+$, the latter being well established as electrophiles for C−X (X = O, N) bond activation,[31−34] demonstrates that silylmetal complexes can serve as powerful but underutilized reagents for organometallic synthesis.

The heterolytic cleavage of a M−Si bond to produce $SiR_3^+$ is defined by Djukic as a complex's intrinsic silylicity.[35] Djukic computed the silylicity of a number of complexes, and as expected, this parameter depends on the nature of the supporting ligands, metal, and oxidation state. In cases where M−Si complexes exhibit silylicity, the silyl ligand is best described as cationic, Lewis acidic, and of the *Z*-type.[36,37] Conceptually related to the notion of a heterolyzed silylmetal complex are Coates' bimetallic catalysts for the carbonylation of epoxides (e.g., $[(salen)Al(THF)_2]^+[Co(CO)_4]^-$).[38,39] In this ion pair, the Lewis acidic aluminum cation activates the ethereal oxygen atom for attack by the cobalt nucleophile/counteranion, generating the Co−C intermediate.[38,39]

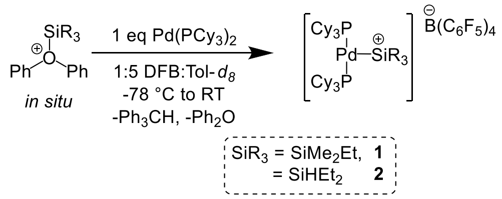
Literature cases of neutral M−Si complexes able to transfer a metal-bound $SiR_3^+$ to exogenous nucleophiles are predominantly limited to complexes bearing CO ligands.[9,12,21−24,13−20] Metal−silyl complexes that exhibit silylicity but lack *π*-acidic CO ligands are of interest, as this obviates the possibility of carbonyl insertion into any M−C bonds that may form, while also enhancing the nucleophilicity of the metal nucleofuge.[9] The reactivity of the few cases of M−Si cations (with the exception of metal silane adducts, M−H−Si) is mostly limited to the insertion of unsaturated bonds into the M−Si bond, silylative decyanation, or ligand displacement reactions.[2,3,40−47]

In this work, we report the synthesis and characterization of two types of silylpalladium *cations* lacking CO ligands, demonstrate that they are sources of $SiR_3^+$ and nucleophilic $L_nPd(0)$, detail their reactions with phosphino and ethereal Lewis bases, and demonstrate that this new class of silylmetal complex can enable the oxidative addition of typically inert C($sp^3$)−O bonds to generate alkylpalladium cations.

## ■ RESULTS AND DISCUSSION

### Preparation and Characterization of $(PCy_3)_2Pd{-}SiR_3^+$.

The general synthesis of $(PCy_3)_2Pd{-}SiR_3^+$ is presented in eq 1



(1)

and proceeds by the addition of a stabilized silylium source to Pd(0). Smooth reactivity required premixing the trityl $(C_6F_5)_4B^-$ salt, $Ph_2O$, and hydrosilane to generate a solution-stable $Ph_2O{-}SiR_3^+$ salt.[48] The mixture of *o*-difluorobenzene (DFB) and toluene provided a good combination of solubility and reactivity, and silylium stabilization by diphenyl ether was essential for clean $SiR_3^+$ transfer to $Pd(PCy_3)_2$. Although **1** and **2** were observable in solution for several hours at room temperature, both decomposed in solution and in the solid state, hampering the crystallographic characterization of their structures. Multinuclear NMR spectroscopy was therefore a key characterization tool. By $^{31}P\{^1H\}$ NMR spectroscopy, solutions of **1** and **2** presented one major singlet for the pair of chemically equivalent phosphorus atoms (34.8 and 32.7 ppm, respectively). No clear coupling between the phosphorus atoms and the protons of the silyl moiety of **1** was discernible in the one-dimensional $^1H$ NMR spectra. The P,H-HMBC experiment, however, revealed weak $^4J_{PH}$ coupling between the $-SiMe_2$ and $-SiCH_2CH_3$ protons and the phosphorus atoms (Figures 1 and 2). More obvious was $J_{PH}$ coupling between the Si−H proton and the phosphorus atoms of **2** in the $^1H$ NMR spectrum (tp, *J* = 16.2, 2.3 Hz): the triplet from coupling to the ligand phosphorus atoms and the pentet from coupling to the adjacent methylene protons of the ethyl substituents. The Si−H proton of **2** also showed coupling to $^{29}Si$, discernible as satellites ($^1J_{HSi}$ = 190 Hz). The low natural abundance and low detection sensitivity of $^{29}Si$ hampered its direct detection; however, $^{29}Si$ chemical shifts could be obtained indirectly at even low concentrations (~0.04 M) via the Si,H-HMBC experiment. The extracted $^{29}Si$ chemical shifts of **1** and **2** are 73.2 and 58.0 ppm, respectively. In the $^{13}C\{^1H\}$ spectra, both **1** and **2** showed coupling between the $-SiMe_2$ and $-SiCH_2CH_3$ carbon atoms and two chemically equivalent phosphorus atoms, splitting the resonances into triplets. Finally, the methyne carbon atoms of $PCy_3$ for both **1** and **2** presented as 1:2:1 virtual triplets, which is characteristic of

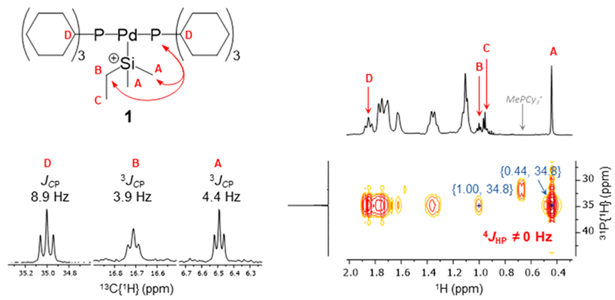


**Figure 1.** Selected spectroscopic data for **1** in 1:5 DFB−toluene-$d_8$.

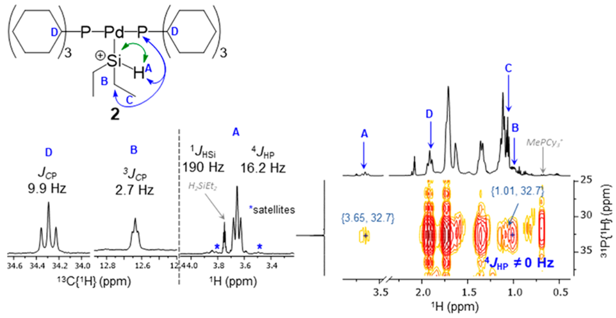


**Figure 2.** Selected spectroscopic data for **2** in 1:5 DFB−toluene-$d_8$.

mutually *trans* and chemically equivalent phosphorus atoms.[49−51]

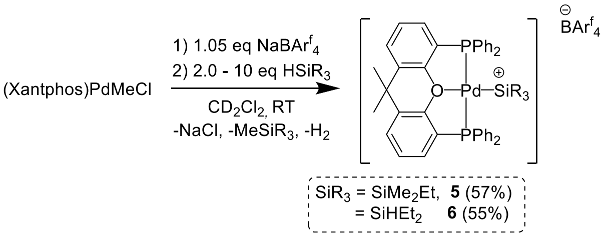
Taken together, the NMR data for **1** and **2** indicated that the silyl ligand is bound to Pd and is *cis* to two chemically equivalent and mutually *trans* phosphine ligands. Along with the lack of an obvious fourth ligand, the data suggested that **1** and **2** are three-coordinate, formally 14-electron, and T-shaped with an open coordination site *trans* to the silyl ligand. Several examples of T-shaped, coordinatively unsaturated, group 10 cationic complexes with bulky phosphine ligands are known. Uttinger showed $(PCy_3)_2Pt(BCat)^+$ (BCat = catecholboryl) to be T-shaped by X-ray crystallography.[52] Low-temperature $^1H$ and $^{31}P\{^1H\}$ NMR spectra additionally revealed features characteristic of agostic interactions between a cyclohexyl C−H bond and the metal center. The agostic C−H breaks the symmetry and generates a pair of strongly coupled doublets in the $^{31}P\{^1H\}$ NMR spectra ($^2J_{PP}$ = 258 Hz), consistent with the phosphines being mutually *trans*. Interestingly, Uttinger noted a lack of evidence for agostic interactions in the solid state or in solution, with complexes bearing boryl ligands more electron donating than BCat, despite also adopting T-shaped geometries. They attributed this difference to the greater *trans* influence of the more donating boryl ligands.[52,53] We have also shown that the thermally unstable $(PCy_3)_2PdMe^+$ complex displayed NMR spectra indicative of a T-shaped geometry with stabilizing agostic interactions *trans* to the methyl ligand (*vide infra*). Although we propose that **1** and **2** are isostructural to $(PCy_3)_2PdMe^+$, we have observed no spectroscopic signatures for agostic interactions in the former complexes. This observation may be due to the higher *trans* influence of silyl over methyl, in analogy to the $(PCy_3)_2Pt{-}boryl^+$ systems described by Uttinger.

The spectroscopic data for **1** and **2** combined with the reactivity described in the following sections thus indicate that T-shaped, 14-electron, $(PCy_3)_2Pd{-}SiR_3^+$ cations can be formed by oxidative addition of a suitably stabilized silylium ion to $Pd(PCy_3)_2$.

**Coordination of MeCN-$d_3$ to 1.** To probe the suggestion that **1** was T-shaped with a vacant site *trans* to $SiR_3$, we investigated whether added nitrile would coordinate to this site. As expected, adding one equivalent of acetonitrile-$d_3$ to **1** rapidly generated a new complex (**3**) with a $^{31}P\{^1H\}$ NMR chemical shift of 37.3 ppm (eq 2). The $^2H$ NMR spectrum for this new complex indicates a $CD_3CN$ downfield chemical shift change of 1.48 ppm relative to uncomplexed $CD_3CN$, characteristic of nitrile binding to an electrophilic center.[43,44] By $^{13}C\{^1H\}$ NMR spectroscopy, the carbon resonances for the $-SiMe_2$ and $-SiCH_2CH_3$ carbon atoms have lost their coupling to phosphorus. Weak cross peaks between the $-SiMe_2$ protons and the phosphorus resonances in the P,H-HMBC spectrum indicated that the complex still contained a bound silylium. The extracted $^{29}Si$ NMR resonance of **3** was shifted 60 ppm upfield of **1** to 13.2 ppm. The attenuation of $^4J_{HSi}$ coupling is consistent with nitrile coordination, as Kubas has shown that for *trans*-$L(^iPr_3P)_2PtH^+$ complexes the donating ability of ligand L influences $J_{HPt}$, with stronger binding ligands reducing this coupling.[54] All evidence thus indicates that the nitrile coordinates *trans* to silicon.

(2)

**Preparation and Characterization of (Xantphos)Pd−$SiR_3^+$.** Optimal for the synthesis of (Xantphos)Pd−$SiR_3^+$ was the hydrosilylative approach presented in eq 3. Combining $NaBAr^f_4$ and (Xantphos)PdMeCl generated $(Xantphos)PdMe^+$ (**4**) *in situ*, as evidenced by a singlet in the $^{31}P\{^1H\}$ NMR spectrum (19.1 ppm). Since $BAr^f_4{}^-$ and $(C_6F_5)_4B^-$ are known to be inert counteranions in reactions involving silylium when Lewis bases are present, we will not be discussing them further.[55,56] The xanthene carbon atoms directly bound to phosphorus and the *ipso* carbon atoms of the $-PPh_2$ moieties each present as 1:2:1 virtual triplets and suggest a meridionally coordinated Xantphos ligand, as shown in the crystallographically characterized structure of $(Xantphos)Pd(4\text{-}CN\text{-}C_6H_5)^+$ by van Leeuwen.[57,58]



(3)

Addition of hydrosilane to **4** resulted in its conversion to (Xantphos)Pd−$SiR_3^+$. The ambidentate nature of Xantphos was hypothesized to facilitate the generation of **5** and **6** from $(Xantphos)PdMe^+$, as a putative $\kappa^3$-*P,O,P* to $\kappa^2$-*P,P* isomerization of the ligand would open a coordination site *cis* to the methyl ligand.[41,43,44,59,60] While two equivalents of silane were necessary to fully convert to the silylpalladium cation, excess hydrosilane speeds the formation of **5** and **6**. Both products are stable in solution for days but decompose slowly in the solid state. Once again, spectroscopic methods were crucial to confirming their structure (Figures 3 and 4). Particularly informative was the measurable coupling between the proton and carbon atoms of the silyl ligand with the phosphorus atoms, as this coupling confirms a P−Pd−Si array. Additionally, splitting of the ligand P−<u>C</u> atoms into 1:2:1 virtual triplets confirmed the mutually *trans* nature of P coordination. The data thus suggest a square planar geometry with the Xantphos ligand adopting the pincer form.

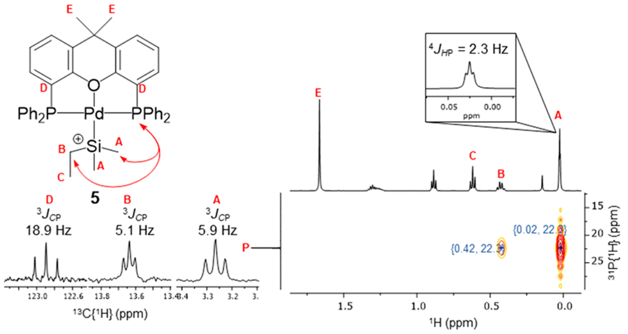


Figure 3. Selected spectroscopic data for **5** in $CD_2Cl_2$.

*In situ* spectroscopic analysis of the formation of **5** and **6** revealed that the extra equivalent of silane forms $Me_3SiEt$ and $HSiEt_2Me$, respectively (see Supporting Information Figure S1). Dihydrogen was also spectroscopically observed and visibly bubbles from the solution. The organosilane and $H_2$ byproducts suggested that Pd−Si formation involves a putative

DOI: 10.1021/jacs.9b08178
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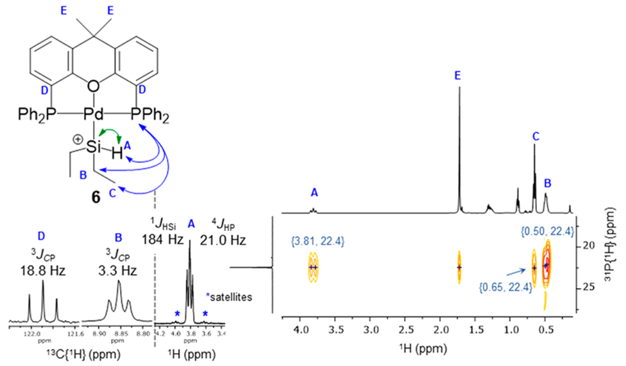
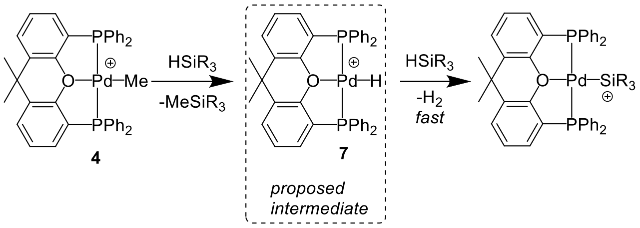


**Figure 4.** Selected spectroscopic data for **6** in $CD_2Cl_2$.

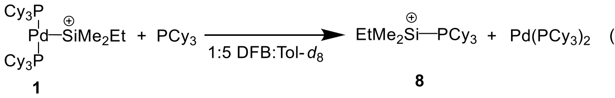
Pd−H intermediate. We hypothesize that oxidative addition of the Si−H bond to **4**, followed by Si−C reductive elimination, forms the observed organosilanes and (Xantphos)$PdH^+$ (**7**). While the reaction is discussed as proceeding via oxidative addition of Si−H, a σ-bond metathesis-type transformation cannot be ruled out.[4] The reactive hydride **7**, which was not spectroscopically observed, is surmised to rapidly react with hydrosilane to evolve hydrogen gas and produce the silylpalladium cation (Scheme 2). Schubert has shown that a similar mechanism is operative in the generation of neutral silylplatinum complexes from the reaction of neutral platinum−methyl complexes with hydrosilanes.[60] This picture is additionally supported by experiments showing that *in situ* generated **7** rapidly reacts with hydrosilane to generate (Xantphos)Pd−$SiR_3^+$ (*vide infra*).

**Scheme 2. Proposed Mechanism for (Xantphos)Pd−$SiR_3^+$ Generation Involving a Palladium−Hydride Intermediate**



SiMe$_2$Et; $\Delta G_{calc.}$ = -25.8 kcal/mol*
SiHEt$_2$; $\Delta G_{calc.}$ = -27.1 kcal/mol*
*calculated free energies; see Supporting Information

**Silylium Transfer from 1 to $PCy_3$.** Evidence that **1** is a source of $SiR_3^+$ was obtained from its reaction with $PCy_3$, in analogy to MacDiarmid's silylphosphonium synthesis with $(CO)_4CoSiMe_3$.[10,11] Addition of $PCy_3$ to *in situ* generated **1** at room temperature resulted in the formation of the silylphosphonium salt **8** and the $Pd(PCy_3)_2$ nucleofuge (eq 4; see Supporting Information Figure S2). The assignment of the signals to **8** was confirmed by its independent synthesis (see Supporting Information). The quantitative transfer of $SiMe_2Et^+$ from **1** to $PCy_3$ confirmed that **1** is a source of $SiR_3^+$ and a neutral and zerovalent Pd complex. The analogous reaction between $PCy_3$ and **3** also provided **8** and $Pd(PCy_3)_2$, revealing that the nitrile adduct **3** is also a source of $SiR_3^+$ (see Supporting Information Figure S3).

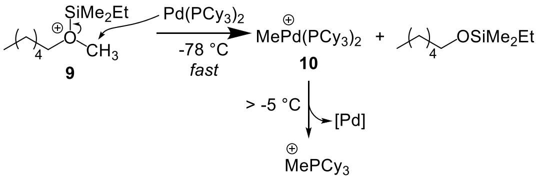


$$(Cy_3P)_2Pd^{\oplus}{-}SiMe_2Et + PCy_3 \xrightarrow[\text{1:5 DFB:Tol-}d_8]{} EtMe_2Si{-}PCy_3^{\oplus} + Pd(PCy_3)_2 \quad (4)$$

**Stoichiometric Silyloxonium C−O Cleavage by $Pd(PCy_3)_2$.** To confirm that $Pd(PCy_3)_2$, the leaving group of silylium transfer from **1** to a Lewis base, is a suitable nucleophile for silylium-activated oxygenates, we next looked to react a stable dialkylsilyloxonium ion ($R_2O−SiR_3^+$) with $Pd(PCy_3)_2$. We surmised that the nucleophilic $Pd(PCy_3)_2$ would be able to cleave the methyl C−O bond of hexyl(methyl)(silyl)oxonium (**9**) by oxidative addition to furnish an alkoxysilane and a Pd−Me cation.

In a glovebox, a solution of $Pd(PCy_3)_2$ was added to a solution of *in situ* generated **9** frozen in a liquid nitrogen cooled cold well. The reaction was mixed and warmed to −78 °C before being placed into an NMR spectrometer probe precooled to −80 °C. Low-temperature NMR spectral data of the reaction mixture revealed that even at −70 °C complete and rapid demethylation of **9** occurred to form silyl ether and a Pd−Me cation (**10**) (Scheme 3). Diagnostic of methyl C−O bond cleavage was the appearance of the silyl ether $R_3SiOCH_2−$ resonance and the disappearance of the silyloxonium methyl resonance. Up to −5 °C, both the $^1H$ and $^{31}P\{^1H\}$ NMR spectra indicated that $MePCy_3^+$ was not formed, clearly demonstrating that the methyl C−O bond of **9** was not cleaved by dissociated phosphine. Only above −5 °C was the gradual formation of $MePCy_3^+$ observed. The complete demethylation of **9** at low temperatures thus indicated that oxidative addition of the silyloxonium methyl C−O bond to $Pd(PCy_3)_2$ was rapid and kinetically formed **10**. The conclusion is therefore that $Pd(PCy_3)_2$ is a suitable nucleophile for silyloxonium electrophiles and that the reaction between **9** and $Pd(PCy_3)_2$ is fast.

**Scheme 3. Stoichiometric Silyloxonium Methyl C−O Bond Cleavage by $Pd(PCy_3)_2$**



Despite not being stable at room temperature $(PCy_3)_2Pd−Me^+$ (**10**) could be characterized by low-temperature NMR spectroscopy (Figure 5; see Supporting Information Figures S4 and S5). At −60 °C, three signals were observed in the $^{31}P\{^1H\}$ NMR spectrum: two coupled doublets at 29.0 and 47.0 ppm ($^2J_{PP}$ = 318 Hz) and a singlet at 24.0 ppm. Warming to 0 °C resulted in signal broadening and coalescence into a broad singlet at 30.2 ppm. The signals in the variable-temperature $^{31}P\{^1H\}$ NMR spectra were consistent with two equilibrating species, only one of which had equivalent phosphine ligands.[50,53] At temperatures below −40 °C, the singlet at 24.0 ppm was assigned to the symmetric Pd−Me complex **10a**, and the pair of coupled doublets to the asymmetric Pd−Me complex **10b**. The large $^2J_{PP}$ coupling constant for **10b** indicated that the phosphine ligands remain mutually *trans*,[50] a scenario accommodated by a cyclohexyl C−H agostic interaction that rendered the phosphorus nuclei chemically inequivalent.[52,61] At temperatures below −40 °C, a broad signal was observed at −1.13 ppm in the $^1H$ NMR spectrum, consistent with the proposed agostic C−H.[52,61] As

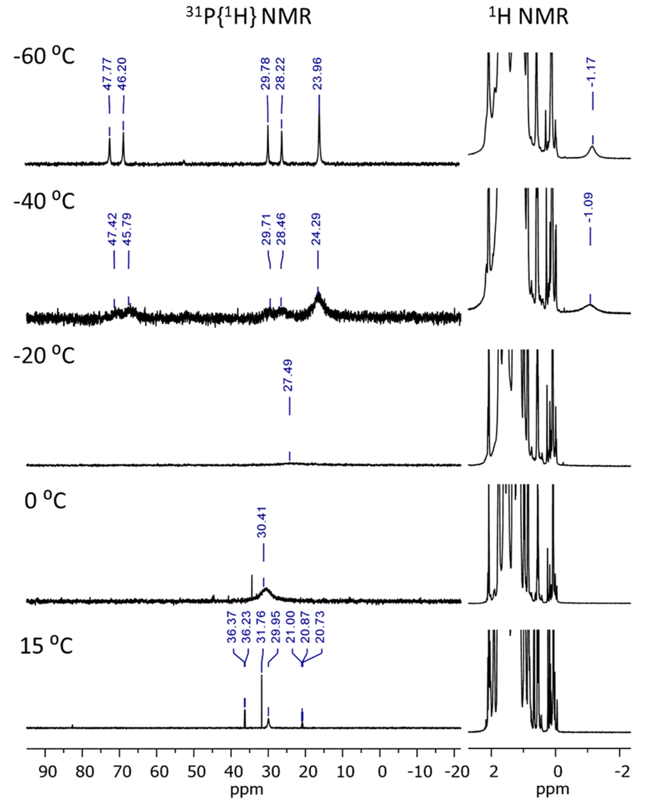
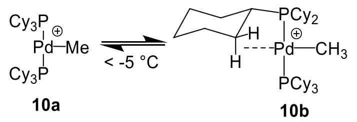


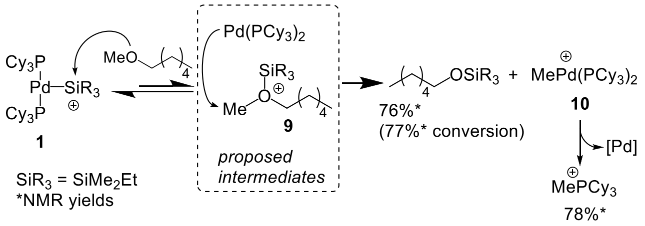
**Figure 5.** Low-temperature $^{31}$P{$^1$H} and $^1$H NMR spectra of the reaction depicted in Scheme 3, highlighting the diagnostic phosphorus and agostic proton resonances of *in situ* generated **10**. Spectrometer frequency: 202 MHz ($^{31}$P{$^1$H}), 500 MHz ($^1$H). Solvent: 1:5 DFB–toluene-$d_8$.

the temperature increased, the rate of equilibration between **10a** and **10b** also increased, leading to signal broadening in the $^{31}$P{$^1$H} NMR spectra and the eventual coalescence into a peak at the weighted average of the three resonances observed below −40 °C. Above −5 °C, $MePCy_3^+$ begins to form and is observed as a sharp singlet at 31.8 ppm in the $^{31}$P{$^1$H} NMR spectrum.

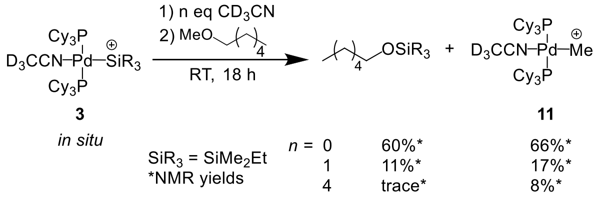


**Stoichiometric Ether Demethylation by 1.** Having demonstrated that $Pd(PCy_3)_2$ is a suitable nucleophile for a model silyloxonium salt, we tested whether **1** and hexyl methyl ether could transiently generate **9** and $Pd(PCy_3)_2$ for subsequent methyl C−O bond cleavage. Gratifyingly, addition of hexyl methyl ether to *in situ* generated **1** formed silyl ether and methylphosphonium over 4 h (Scheme 4; see Supporting Information Figure S6). During the room-temperature demethylation reaction, **10** could be observed by $^{31}$P{$^1$H} NMR spectroscopy, confirming the viability of silylium transfer from **1** to hexyl methyl ether (the reverse of Scheme 3) to form the reactive pair highlighted in Scheme 4. The instability of **10** eventually leads to $MePCy_3^+$. Although the slow decomposition of **10** complicates a kinetic analysis, one can glean informative data from the time scale of the ether demethylation. Since demethylation of **9** is rapid (Scheme 3), the observed rate of hexyl methyl ether demethylation (~4 h) likely reflects the kinetics of silylium transfer from **1** to ether.

**Scheme 4. Stoichiometric Demethylation of Hexyl Methyl Ether by 1**



**Stoichiometric Ether Demethylation by 3.** Since $CD_3CN$ coordinates to **1** to generate the nitrile-ligated silylpalladium cation **3**, we sought to determine if **3** can similarly demethylate hexyl methyl ether. Addition of the hexyl methyl ether to *in situ* generated **3** gave partial demethylation (60% NMR yield) over 18 h at room temperature (eq 5; see Supporting Information Figure S7). Under these conditions the stable palladium−methyl cation (**11**) forms. Repeating this reaction with excess nitrile slowed the demethylation and suggested that the mechanism likely involves dissociation of nitrile from **3** (to form **1**) prior to silylium transfer.

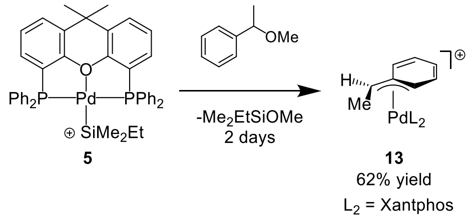


(5)

**Silylium Transfer from 5 to $PCy_3$.** Reacting **5** with $PCy_3$ yields silylphosphonium **8** in analogy to eq 4 and demonstrates that **5** is also a viable source of $SiR_3^+$. In this case, full conversion required two equivalents of $PCy_3$ to yield **8** and the stable zerovalent palladium complex **12** (eq 6; see Supporting Information Figure S8). The expected nucleofuge of this reaction, (Xantphos)Pd$^0$, sequesters an equivalent of phosphine to form **12**, which presented NMR spectra identical to authentically prepared material (see Supporting Information). The $^{31}$P{$^1$H} NMR spectrum for **12** displayed a coupled triplet and doublet at 35.0 and 1.8 ppm ($^2J_{PP}$ = 107 Hz) in a 1:2 ratio, consistent with the expected trigonal geometry.[50]

(6)

**Stoichiometric Benzyl Ether C−O Bond Cleavage by 5.** Unlike silylpalladium complex **1**, which reacted to cleave the methyl C(sp$^3$)−O bond of hexyl methyl ether (Scheme 4), complex **5** did not react with this ether, even at elevated temperatures. The *secondary* benzylic C−O bond of (1-methoxyethyl)benzene, however, was more prone to oxidative addition by **5** and yielded the palladium−($\eta^3$-phenethyl) cation **13** (eq 7). Interestingly, no evidence for methyl C−O bond cleavage was observed, pointing to a higher reactivity of the benzylic C−O bond toward oxidative addition. Complex **13**,



(7)

which is surprisingly stable to air, moisture, and silica gel, was isolated as needle-like crystals. Its $^{31}P\{^1H\}$ NMR spectrum showed a single broad resonance at 9.0 ppm, and the benzylic and methyl proton and carbon atoms of the phenethyl ligand showed discernible coupling to two chemically equivalent phosphorus atoms in both the $^1H$ and $^{13}C\{^1H\}$ NMR spectra. The *ipso* carbon atom of the phenethyl ligand is split into a triplet in the $^{13}C\{^1H\}$ NMR spectrum due to $^2J_{CP}$ coupling, consistent with metal-ring association. The carbon atoms of the xanthene backbone directly attached to the phosphorus atoms are split into doublets, indicating that unlike complexes **4**−**6**, the phosphorus atoms of **13** are not mutually *trans*. The crystal structure of **13** confirmed the $\eta^3$ binding mode, and the metrical parameters were similar to the related [(Xantphos)-Pd($\eta^3$-benzyl)][OTf] complex reported by Hartwig (Figure 6; see Supporting Information).[62]

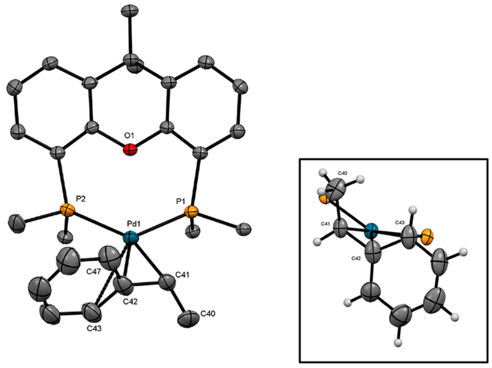
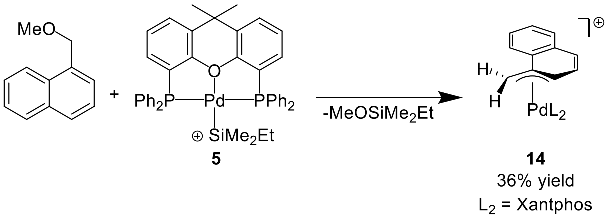


**Figure 6.** ORTEP plot of **13** at the 30% probability level (hydrogen atoms, $CH_2Cl_2$, and $BAr^f_4$ counteranion omitted for clarity; ligand phenyl groups represented by the *ipso* carbon atoms for clarity). The view along the benzallyl−palladium interaction is shown in the inset. Selected bond lengths and angles: Pd1−P1 = 2.315(1) Å, Pd1−P2 = 2.409(1) Å, Pd1−O1 = 3.490(4) Å, Pd1−C41 = 2.109(8) Å, Pd1−C42 = 2.228(9) Å, Pd1−C43 = 2.81(1) Å, Pd1−C47 = 2.85(1) Å, P1−Pd1−P2 = 107.76(5)°.

Cleavage of the *primary* $C(sp^3)$−O bond of (1-methoxymethyl)naphthalene also occurs on addition to **5** at room temperature. The resulting Pd−($\pi$-naphthalen-1-ylmethyl) complex **14** was also stable to air, moisture, and silica gel (eq 8). While the $^{31}P\{^1H\}$ NMR spectrum of **14** exhibits significant broadening due to a fluxional process, acquiring spectra at 40 °C sharpens the resonances into a singlet. Single crystals of **14** enabled X-ray crystallography to confirm that this complex adopts a geometry analogous to that of **13** (Figure 7; see Supporting Information).



(8)

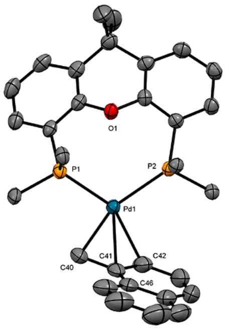
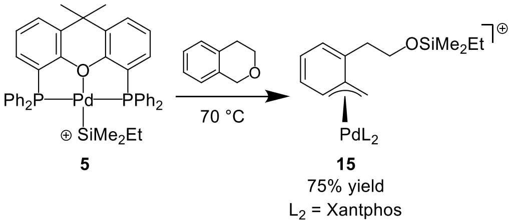


**Figure 7.** ORTEP plot of **14** at the 50% probability level (hydrogen atoms, pentane, and $BAr^f_4$ counteranion omitted for clarity; ligand phenyl groups represented by the *ipso* carbon atom for clarity). Selected bond lengths and angles: Pd1−P1 = 2.331(1) Å, Pd1−P2 = 2.412(1) Å, Pd1−O1 = 3.383(3) Å, Pd1−C40 = 2.114(6) Å, Pd1−C41 = 2.239(5) Å, Pd1−C42 = 2.448(6) Å, Pd1−C46 = 3.150(4) Å, P1−Pd1−P2 = 108.82(4)°.

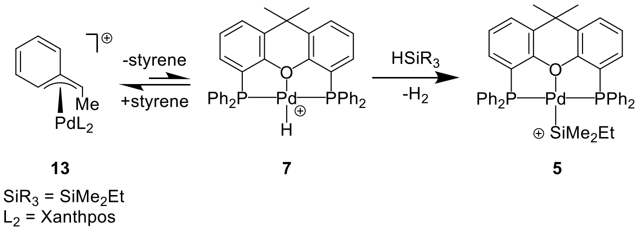
The primary benzylic C−O bond of isochroman is also cleaved by **5** with mild heating (eq 9). The organometallic product isolated from this reaction was characterized by NMR spectroscopy and determined to be the Pd−($\pi$-benzyl) complex (**15**) by its spectroscopic similarities to **14** (see Supporting Information).



(9)

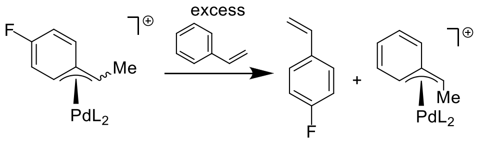
**Evidence for Palladium−Hydride 7.** Addition of excess ethyldimethylsilane to isolated **13** resulted in the slow generation of **5** and styrene (Scheme 5; see Supporting Information Figure S9). This is conveniently accounted for by a mechanism where **13** undergoes *net* $\beta$-hydride elimination to produce styrene and palladium hydride (**7**). The metal hydride then subsequently reacts with hydrosilane to generate **5** and hydrogen gas. It has been established that palladium−($\eta^3$-benzyl)-type complexes can undergo net $\beta$-hydride elimination from a $\sigma$-benzylic intermediate.[63] The observation of ethylbenzene by NMR spectroscopy suggested that hydrosilane may also react directly with **13**; however, the transfer of hydride

**Scheme 5. Proposed Mechanism for the Generation of 5 from the Reaction of Hydrosilane and 13**



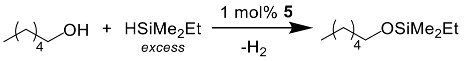
from **7** to **13** to produce ethylbenzene cannot be ruled out. Addition of excess hydrosilane to (Xantphos)Pd($\eta^3$-(CHOSiMe$_2$Et)C$_6$H$_5$)$^+$ (**16**), a Pd−($\pi$-benzyl) complex lacking $\beta$-hydrogens, provided only trace amounts of **5** and silyl-protected benzyl alcohol over 3 days (see Supporting Information Figure S10). The lower reactivity of **16** toward hydrosilane compared to **13** supports the notion that $\beta$-hydride elimination is the initiating step in Scheme 5.

To buttress the mechanism presented in Scheme 5, complex **17**, a fluorinated congener of **13**, was synthesized and treated with excess styrene. After 1 day, all of **17** was converted to **13** and *p*-fluorostyrene (eq 10; see Supporting Information Figure S11). This exchange of phenethyl ligands supported the intermediacy of **7** and demonstrated that it can be intercepted by styrene. Both the mechanism for the synthesis of **5** and **6** and the reactivity of **13** with hydrosilane and **17** with styrene implied the existence of reactive hydride **7**. We surmised that the dehydrogenative silylation of an alcohol would also involve the intermediacy of **7**, which could be generated by deprotonation of the silyloxonium ion by the L$_n$Pd(0) that would form from silylium transfer from **5** to an alcohol. To test this hypothesis, we carried out the catalytic dehydrogenative silylation of 1-hexanol with excess hydrosilane at a 1 mol % loading of **5** (eq 11; see Supporting Information Figure S12).



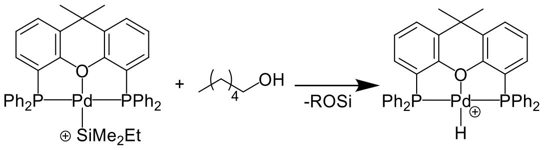
**17** **13** (10)

L$_2$ = Xantphos



(11)

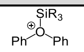
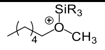
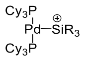
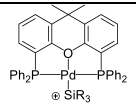
Addition of the alcohol to a mixture of **5** and hydrosilane resulted in immediate and vigorous gas evolution. NMR spectroscopy confirmed the generation of the expected silyl ether and H$_2$; however, the only phosphine-containing species observable by $^{31}$P{$^1$H} NMR spectroscopy was **5**. The palladium hydride **7** could be directly generated by stoichiometrically reacting **5** with 1-hexanol, resulting in a new broad phosphorus resonance at 25.3 ppm (eq 12; see Supporting Information Figure S13). Diagnostic for the generation of **7** was the new upfield resonance at −14.40 ppm in the $^1$H NMR spectrum, which we attribute to the hydridic proton. Addition of excess hydrosilane to the reaction mixture containing **7** resulted in its rapid conversion to **5**, demonstrating that **7** rapidly reacts with hydrosilane to generate a silylpalladium cation. Similarly, adding styrene to *in situ* generated **7** led to the rapid formation of **13**, proving that styrene readily inserts into the Pd−H bond (see Supporting Information Figure S14). The instability of (Xantphos)PdH$^+$, determined by its decomposition in solution over several hours, prevented its isolation and independent characterization.



**5** **7** (12)

**DFT-Calculated Geometries and Silylicities (Π).** Density functional theory (DFT) was used to obtain gas-phase geometry-optimized structures of (PCy$_3$)$_2$Pd−SiR$_3^+$, (Xantphos)Pd−SiR$_3^+$, and the silyloxonium cations synthesized and generated in this study (Table 1; see Supporting Information Table S1). The optimized geometries agree with those proposed by experimental spectroscopic observations. Additionally, the method used by Djukic to compute the "relative intrinsic silylicity" (Π) of Lewis base-silylium adducts was used to compute Π for several of the compounds generated in this study.[35] Silylicities > 1 reflect a silicon that is more electrophilic than it is in R$_3$SiOTf; all compounds in Table 1 have silylicities > 1. The relative ordering of Π also agrees with experimentally observed silylicities. First, the silylium ion in Ph$_2$O−SiMe$_2$Et$^+$ stoichiometrically transfers to hexyl methyl ether (by NMR), and second, the Π of Ph$_2$O−SiMe$_2$Et$^+$ is higher than **1**, befitting its role as stoichiometric silylium source for (PCy$_3$)$_2$Pd (eq 1). Although direct experimental comparisons of the silylicities of **1** and **5** were not possible, we note that **5** does not demethylate hexyl methyl ether, while **1** is capable of this reactivity.

**Table 1. DFT-Calculated Silylicities of Lewis Base Silylium Adducts**[a]

| Compound | SiR$_3$ | Π |
|---|---|---|
|  | SiMe$_2$Et | 2.68 |
|  | SiMe$_2$Et (**9**) | 2.56 |
|  | SiMe$_2$Et (**1**)<br>SiHEt$_2$ (**2**) | 1.42<br>1.36 |
|  | SiMe$_2$Et (**5**)<br>SiHEt$_2$ (**6**) | 1.29<br>1.28 |

[a] Following Djukic's procedure, silylicities were calculated according to the equation Π = [Δ$E_{int}$(TfO−SiR$_3^+$)]/[Δ$E_{int}$(LB−SiR$_3^+$)], where Δ$E_{int}$ is the basis set superposition error corrected interaction energy and LB is the Lewis base.

## ■ CONCLUSIONS

Herein, we present the synthesis of two different types of silylpalladium cations, (PCy$_3$)$_2$Pd−SiR$_3^+$ and (Xantphos)Pd−SiR$_3^+$, both of which are sources of silylium cations and L$_n$Pd(0) nucleophiles. Silylium transfer to phosphines and aliphatic ethereal oxygen atoms occurs to generate stable silylphosphonium ions or reactive silyloxonium ions, respectively. In the case of silyloxonium generation, C(sp$^3$)−O bonds are activated toward oxidative addition by the concomitantly generated L$_n$Pd(0) and thereby provides synthetically versatile palladium−alkyl cations. When the resulting Xantphos-based palladium−alkyl cations bear $\beta$-hydrogens, reversible $\beta$-hydride elimination to a cationic palladium−hydride intermediate was noted. This palladium−hydride could be independently generated, and it rapidly reacts with excess hydrosilane to regenerate a silylpalladium complex or insert styrene. In summary, cationic L$_n$Pd−SiR$_3$ complexes can be heterolytically cleaved to generate a synergistic combination of silylium ions (for O activation) and nucleophilic $L_nPd(0)$ complexes. Together, these components enable the oxidative addition/activation of otherwise difficult to react $C(sp^3){-}O$ bonds.

## ■ ASSOCIATED CONTENT

### Ⓢ Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/jacs.9b08178.

Experimental details, computational details, and NMR spectra used for characterization (PDF)

Crystallographic data for **13** (CIF)

Crystallographic data for **14** (CIF)

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### Notes

The authors declare no competing financial interest.

## ■ ACKNOWLEDGMENTS

This research was supported by the U.S. Army Research Office (ARO) (W911NF-15-2-0119). The mass spectrometer used in these studies was purchased with the support of the National Science Foundation under Grant No. CHE-1726291.

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DOI: 10.1021/jacs.9b08178
*J. Am. Chem. Soc.* 2019, 141, 16024−16032