Hydrosilane σ-Adduct Intermediates in an Adaptive Zinc-Catalyzed Cross-Dehydrocoupling of Si–H and O–H Bonds

Smita Patnaik
*iowa State University and Ames Laboratory*

Uddhav Kanbur
*iowa State University*, uakanbur@iastate.edu

Arkady Ellern
*iowa State University*, ellern@iastate.edu

Aaron D. Sadow
*iowa State University and Ames Laboratory*, sadow@iastate.edu

Follow this and additional works at: https://lib.dr.iastate.edu/chem_pubs

Part of the Catalysis and Reaction Engineering Commons, and the Materials Chemistry Commons

The complete bibliographic information for this item can be found at https://lib.dr.iastate.edu/chem_pubs/1307. For information on how to cite this item, please visit http://lib.dr.iastate.edu/howtocite.html.

This Article is brought to you for free and open access by the Chemistry at Iowa State University Digital Repository. It has been accepted for inclusion in Chemistry Publications by an authorized administrator of Iowa State University Digital Repository. For more information, please contact digirep@iastate.edu.
Hydrosilane $\sigma$-Adduct Intermediates in an Adaptive Zinc-Catalyzed Cross-Dehydrocoupling of Si–H and O–H Bonds

Abstract
Three-coordinate Ph BOX Me2 ZnR (Ph BOX Me2 = phenyl-(4,4-dimethyl-oxazolinato; R = Me 2a, Et 2b) catalyzes the dehydrocoupling of primary or secondary silanes and alcohols to give silyl ethers and hydrogen, with high turnover numbers (TON), up to 10^7, under solvent-free conditions. Primary and secondary silanes react with small, medium, and large alcohols to give varying degrees of substitution, from mono-alkoxylation to tri-alkoxylation, while tri-substituted silanes do not react with MeOH under these conditions. The effect of coordinative unsaturation on the behavior of the Zn catalyst is revealed through a dramatic variation of both rate law and experimental rate constants, which depend on the concentrations of both the alcohol and silane reactants. That is, the catalyst adapts its mechanism access the most facile and efficient conversion. In particular, either alcohol or silane bind to the open coordination site on the Ph BOX Me2 ZnOR catalyst to form a Ph BOX Me2 ZnOR(HOR) complex under one set of conditions or an unprecedented $\sigma$-adduct Ph BOX Me2 ZnOR(H–SiR' 3) under other conditions. Saturation kinetics provide evidence for the latter species, in support of the hypothesis that $\sigma$-bond metathesis reactions, involving four-centered electrocyclic 2$\sigma$-2$\sigma$ transition states, are preceded by $\sigma$-adducts.

Keywords
$\sigma$-adduct, Silyl Ether, dehydrogenative cross-coupling, adaptive zinc catalysis, saturation kinetics

Disciplines
Catalysis and Reaction Engineering | Materials Chemistry

Comments

Creative Commons License
This work is licensed under a Creative Commons Attribution 4.0 International License.
Hydrosilane σ-Adduct Intermediates in an Adaptive Zinc-Catalyzed Cross-dehydrocoupling of Si–H and O–H Bonds

Smita Patnaik,[a, b] Uddhav Kanbur,[a, b] Arkady Ellern,[a] and Aaron D. Sadow[a, b]

Abstract: Three-coordinate $^3$BuBOX$^{Me}$ZnR ($^3$BuBOX$^{Me}$ = phenyl-(4,4-dimethyl-oxazolinato; R=Me: 2 a, Et: 2 b) catalyzes the dehydrocoupling of primary or secondary silanes and alcohols to give silyl ethers and hydrogen, with high turnover numbers (TON; up to 10$^7$) under solvent-free conditions. Primary and secondary silanes react with small, medium, and large alcohols to give various degrees of substitution, from mono- to tri-alkylation, whereas tri-substituted silanes do not react with MeOH under these conditions. The effect of coordinative unsaturation on the behavior of the Zn catalyst is revealed through a dramatic variation of both rate law and experimental rate constants, which depend on the concentrations of both the alcohol and hydrosilane reactants. That is, the catalyst adapts its mechanism to access the most facile and efficient conversion. In particular, either alcohol or hydrosilane binds to the open coordination site on the $^3$BuBOX$^{Me}$ZnOR catalyst to form a $^3$BuBOX$^{Me}$ZnOR(HOR) complex under one set of conditions or an unprecedented σ-adduct $^3$BuBOX$^{Me}$ZnOR(H–SiR)$^-$ under other conditions. Saturation kinetics provide evidence for the latter species, in support of the hypothesis that σ-bond metathesis reactions involving four-centered electrocyclic 2σ–2σ transition states are preceded by σ-adducts.

Introduction

Silicon-oxygen bond formation has wide-ranging impact in synthetic applications, ranging from the construction of organic-inorganic hybrid materials to the assembly of complex molecules. Silyl ethers themselves have important roles in cross-coupling as templates for cyclization and as protecting groups. These moieties are conventionally formed from alcohols and chlorosilanes; this approach, however, is hindered by the formation of HCl or salts as by-products, moisture sensitivity and competing hydrolysis of chlorosilanes, as well as the limited reactivity of bulky tertiary alcohols and bulky chlorosilanes. Incompatibilities with base-sensitive reactants. That is, the dehydrocoupling reactions; however, in some cases these systems also mediate isomerization or hydrolysis of C=C or C=O moieties. Basic catalysts such as sodium hydroxide overcome this limitation but are restricted to secondary and tertiary silanes, as B(C$_6$F$_5$)$_3$-catalyzed reactions also catalyze these cross-dehydrocouplings however, a divergent picture of the fundamental nature of hydridozinc catalysts has emerged, obscuring design principles. In particular, catalytic product formation is observed with coordinatively saturated (ZnX$_2$, 8-electron) hydride and super-saturated (ZnX$_3$, 10-electron) alkoxide pre-catalysts, as well as with dimeric hydride-bridged N-heterocyclic carbene-coordinated zinc pre-catalysts which likely access lower coordinate catalytic sites (ZnX$_2$, 6-electron). For example, the interconverting four-coordinate [L$_2^-$Tptm]ZnH and five-coordinate [L$_2^-$Tptm]ZnOR (Tptm = tris(2-pyridylthio)methyl) catalyzes the methanalysis of phenylsilane with high turnover number (TON) of 10$^5$ and turnover frequency of 10$^6$ h$^{-1}$.[26] These pre-catalysts also mediate carbonyl hydrolysis, which involves related Si–O bond formations. In hydrolysylations, however, TON and rates do not necessarily benefit from coordinatively unsaturated zinc pre-catalysts. Such behavior suggests that complex reaction pathways underpin deceptively simple transformations.

Alternatively, catalytic dehydrogenative cross-coupling of hydrosilanes and alcohols can provide partly substituted products by influencing reaction rates, the H$_2$ by-product is inert, and alkyl- and arylsilanes can be stored in air prior to dehydrocoupling. Late-transition-metal complexes based on Re$^{[14]}$, Rh$^{[11,18]}$, Ni$^{[19]}$, and Ir$^{[20]}$ are catalysts for these cross-dehydrocoupling reactions; however, in some cases these systems also mediate isomerization or hydrolysis of C=C or C=O moieties. Basic catalysts such as sodium hydroxide overcome this limitation but are restricted to secondary and tertiary silanes, as B(C$_6$F$_5$)$_3$-catalyzed reactions also catalyze these cross-dehydrocouplings however, a divergent picture of the fundamental nature of hydridozinc catalysts has emerged, obscuring design principles. In particular, catalytic product formation is observed with coordinatively saturated (ZnX$_2$, 8-electron) hydride and super-saturated (ZnX$_3$, 10-electron) alkoxide pre-catalysts, as well as with dimeric hydride-bridged N-heterocyclic carbene-coordinated zinc pre-catalysts which likely access lower coordinate catalytic sites (ZnX$_2$, 6-electron). For example, the interconverting four-coordinate [L$_2^-$Tptm]ZnH and five-coordinate [L$_2^-$Tptm]ZnOR (Tptm = tris(2-pyridylthio)methyl) catalyzes the methanalysis of phenylsilane with high turnover number (TON) of 10$^5$ and turnover frequency of 10$^6$ h$^{-1}$.[26] These pre-catalysts also mediate carbonyl hydrolysis, which involves related Si–O bond formations. In hydrolysylations, however, TON and rates do not necessarily benefit from coordinatively unsaturated zinc pre-catalysts. Such behavior suggests that complex reaction pathways underpin deceptively simple transformations.

A two-step catalytic cross-dehydrocoupling mechanism has been proposed based on kinetic studies of conversions catalyzed by the four-coordinate To$^{[16]}$ZnH (To$^{[16]}$ = tris(4,4-dimeth-
yl-2-oxazolinylphenyborate,\textsuperscript{22} structurally and spectroscopically characterized hydridozinc and alkoxizinc intermediates, and kinetically well-defined elementary steps (Scheme 1). The key turnover-limiting silicon-oxygen bond formation is proposed to occur by \( \sigma \)-bond metathesis,\textsuperscript{31} involving cleavage of Zn–OR and Si–H bonds and formation of Zn–H and Si–O bonds via a four-centered, concerted, electrocyclic transition state. Related steps are generally accepted for C–H and Si–H bond activations by \( d^2 \) early transition metal and rare earth organometallic compounds,\textsuperscript{32–34} and these elementary steps are ubiquitous in catalytic transformations including alkane hydrogentlylations,\textsuperscript{35,36} silane polymerization,\textsuperscript{37} hydrosilylations,\textsuperscript{38–41} alkane silylation,\textsuperscript{42} and hydromethylation of alkenes.\textsuperscript{43} Theoretical results suggest that Si–H or C–H \( \sigma \)-coordination precedes the four-centered transition state,\textsuperscript{34–46} although experimental evidence for \( \sigma \)-complexes as intermediates is limited to kinetic isotope effects (KIEs).

KIEs in \( \sigma \)-bond metathesis type E–E bond formations vary considerably, with Si–N and Si–C bond forming steps characterized by \( k_D/k_C = 1\textsuperscript{,47,48} \) whereas the \( k_D/k_0 \) for Si–Si and P–P bond forming steps are typically \( \sim 3\textsuperscript{,31,40} \). The latter, non-unity KIEs likely result from the long M–E and E–E bonds in the cyclic transition state, involving a M–H–E angle that approaches linearity. In contrast, either transfer of H in a bent geometry or a rate-determining step which does not break the E–H bond could lead to the KIE \( \sim 1\). For example, the nearly unitary primary \( k_D/k_0 \) in the reaction of Cp\textsubscript{2}HfHCl and the stannane Mes\textsubscript{3}SnH\textsubscript{2} (Mes = 2,4,6-C\textsubscript{6}H\textsubscript{3}Me\textsubscript{2}) or Mes\textsubscript{3}SnD\textsubscript{2} to form a HF–Sn bond, was interpreted in terms of a \( \sigma \)-coordinated intermediate prior to H–H bond formation.\textsuperscript{49} Also, the near unity isotope effect in reaction of Todi\textsubscript{Mg}NHBDu and PhMeSiH\textsubscript{3} or PhMeSiD\textsubscript{3}, along with a companion Hammet study, were instead interpreted as the resulting from an asynchronous \( \sigma \)-bond metathesis sequence involving rate-controlling N–Si bond formation prior to H migration to Mg via \( \beta \)-H elimination-like step.\textsuperscript{47}

Noting that To\textsuperscript{Mg}ZnH is an 8-electron species, a strategy for increasing catalytic performance could involve electronically unsaturated, three-coordinate zinc centers. To investigate this idea, we targeted zinc species supported by bidentate, monoanionic bis(4-R-oxazolinato) ligands (BOX),\textsuperscript{53,54} which are the LX analogues of common neutral bis(oxazoline) ligands.\textsuperscript{55} The C1-phenyl ligand was chosen to impede undesired ancillary ligand redistribution reactions, observed for BOXZnOR and diketiminatozinc in the presence of alcohols\textsuperscript{54,56} without hindering access to the active site. Here, we report the catalytic properties of \( \text{\textsuperscript{10}} \text{BOX} \) alkylzinc compounds in dehydrocoupling of alcohols and hydrosilanes. The straightforward syntheses of the alkylzinc pre-catalysts, mild conditions, solvent-free reactions and high TONs make this methodology attractive. Furthermore, detailed kinetic investigations reveal that multiple catalytic pathways become accessible under varying conditions, as a consequence of three-coordinate electronically unsaturated zinc pre-catalysts.

Results and Discussion

Pre-catalyst synthesis and characterization

Reactions of \( \text{\textsuperscript{10}} \text{BOX} \text{Ph} \) and dimethylzinc or diethylzinc provide the heteroleptic compounds \( \text{\textsuperscript{10}} \text{BOX} \text{Ph} \text{Me} \text{ZnMe} \) (2a) and \( \text{\textsuperscript{10}} \text{BOX} \text{Ph} \text{Me} \text{ZnEt} \) (2b) in high yield after 12 h at room temperature [90–92%: Eq. (1)]. 

\[
\text{[1]} \quad \text{[To}^\text{Mg} \text{ZnH}]^+ \text{[PhMeSiH}_2] \quad \text{[PhMeSiH}_2] \quad \text{[PhMeSiH}_2] \\
\]

Theoretical results suggest that \( \sigma \)-bond metathesis-type E–E bond formations vary considerably, with Si–N and Si–C bond forming steps characterized by \( k_D/k_C = 1\textsuperscript{,47,48} \) whereas the \( k_D/k_0 \) for Si–Si and P–P bond forming steps are typically \( \sim 3\textsuperscript{,31,40} \). The latter, non-unity KIEs likely result from the long M–E and E–E bonds in the cyclic transition state, involving a M–H–E angle that approaches linearity. In contrast, either transfer of H in a bent geometry or a rate-determining step which does not break the E–H bond could lead to the KIE \( \sim 1\). For example, the nearly unitary primary \( k_D/k_0 \) in the reaction of Cp\textsubscript{2}HfHCl and the stannane Mes\textsubscript{3}SnH\textsubscript{2} (Mes = 2,4,6-C\textsubscript{6}H\textsubscript{3}Me\textsubscript{2}) or Mes\textsubscript{3}SnD\textsubscript{2} to form a HF–Sn bond, was interpreted in terms of a \( \sigma \)-coordinated intermediate prior to H–H bond formation.\textsuperscript{49} Also, the near unity isotope effect in reaction of Todi\textsubscript{Mg}NHBDu and PhMeSiH\textsubscript{3} or PhMeSiD\textsubscript{3}, along with a companion Hammet study, were instead interpreted as the resulting from an asynchronous \( \sigma \)-bond metathesis sequence involving rate-controlling N–Si bond formation prior to H migration to Mg via \( \beta \)-H elimination-like step.\textsuperscript{47}

\[
\begin{align*}
\text{Rate expression of proposed cycle:} \\
\frac{-d[\text{PhMeSiH}_2]}{dt} &= k_1 [\text{To}^\text{Mg} \text{ZnH}]^+ [\text{PhMeSiH}_2]^+ \\
\end{align*}
\]

Experimental rate law:

\[
\frac{-d[\text{PhMeSiH}_2]}{dt} = k_{obs} [\text{To}^\text{Mg} \text{ZnH}]^+ [\text{PhMeSiH}_2]^+ \\
\]

\[
\begin{align*}
\text{Scheme 1. Proposed cycle for To}^\text{Mg} \text{-catalyzed cross-dehydrocoupling of hydrosilanes and alcohols.}
\end{align*}
\]
than in the free proligand ($\nu_{C_{10}H_{18}} = 1648 \text{ cm}^{-1}$). X-ray crystallographic analysis of complexes $2\,a$ (Figure 1) and $2\,b$ (see the Supporting Information) were obtained from pentane solutions cooled at $-30^\circ\text{C}$.

\[ \text{Ph-CH=NO} + \text{ZnR}_2 \xrightarrow{1.5 \text{ equiv}} \text{C}_{11}\text{N-Zn-R} \quad \text{C}_6\text{H}_6, \text{RT, 12 h} \quad 2a: \text{R} = \text{Me} (90\%) \quad \text{BOXZnMe-ZnOR}\]

Single-crystal X-ray diffraction studies reveal that the approximately $C_2$symmetric asymmetric zinc compounds $2\,a$ (Figure 1) and $2\,b$ are three-coordinate, with $\text{Zn}1$, two oxazoline $C\text{--N}$ and the backbone $C_{11}$ as vertices in a nearly planar six-membered ring. All torsion angles of this planar and symmetrical chelate ring are less than $10^\circ$, with equivalent distances for $\text{Zn}--\text{N}$ pairs, $\text{N}--\text{C}$ pairs, and $\text{C}--\text{N}$ pairs. The $C1$ and $C6$ dimethyl substituents of the oxazoline rings are pseudoequatorial, whereas $C3$ and $C8$ are pseudo-axial in $2\,a$, as defined by transannular torsion angles $\angle C1$–$C2$–$C7$–$C6 \approx (0\%)$ and $\angle C3$–$C2$–$C7$–$C8 \approx (165.0(9)^\circ)$.

Reactions of $2\,a$ with methanol, isopropanol, or 3,5-dimethylaniline provide $\text{BOX}^{\text{Me}}\text{ZnOR}$ compounds ($R^* = \text{Me}$ $3\,a$, $i\text{C}_3\text{H}_7$ $3\,b$, $\text{C}_8\text{Me}_2\text{H}_3$ $3\,c$) in fewer than 5 mins in $[D]$benzene or $[D]$chloroform, as determined by $^1\text{H}$ NMR spectroscopy. The dimeric products ($3\,a$–$c$) precipitate from the benzene reaction mixture over 1 h at room temperature and are easily isolated in excellent yield (Scheme 2). The qualitative trend in precipitation rate depends on the alcohol substituent ($\text{Me} > i\text{C}_3\text{H}_7 > \text{C}_8\text{Me}_2\text{H}_3$). The solids are insoluble in $[D]$benzene, but dissolve in $[D]$ methylene chloride or $[D]$chloroform. In addition, the compounds may be generated and used in situ in $[D]$benzene. $^1\text{H}$ and $^{13}\text{C}([\text{H}])$ NMR spectra of isolated species, dissolved in $[D]$ chloroform, consisted of singlet resonances assigned to oxazoline methyl and methylene groups. These spectra are identical to those obtained by in situ reaction of $2\,a$ and $\text{R}^*\text{OH}$ in $[D]$ chloroform. 2D DOSY NMR measurements performed on a mixture of zinc ethyl $2\,b$ and zinc methoxy $3\,a$ in $[D]$benzene revealed their similar diffusion constants (ca. $2.1 \times 10^{-6}$ and $1.6 \times 10^{-6}$ m$^2$/s, respectively). Because the molecular weight of $2\,b$ differs by only 2 amu from that of the monomeric form of $3\,a$, these results suggest that the soluble form of $3\,a$ is mostly monomeric.

Single-crystal X-ray diffraction studies of $3\,a$, and $3\,b$, reveal that the isolated dimeric species contain planar $\text{Zn}_2\text{O}_2$ cores composed of four-coordinate zinc centers bridged by alkoxide ligands (see Figure 2 for $3\,a$, and Supporting Information for $3\,b$). Both structures contain a crystallographic inversion center at the center of the $\text{Zn}_2\text{O}_2$ core, relating the two $\text{BOX}^{\text{Me}}\text{Zn}$ units and the two alkoxide ligands. The $\text{Zn}--\text{O}$ distances (mean 1.975 Å) within both compounds are equivalent within 3σ error, giving rhombohedral-shaped cores. In addition, the $\text{BOX}^{\text{Me}}\text{Zn}$ moieties form a similar planar six-member chelate ring as in the zinc alkyls; however, the methyl substituents are more symmetrically disposed about the plane of the chelate ring compared to the twisted conformations in $2\,a$ and $2\,b$. That is, the torsion angles in $3\,a$, $\angle C1$–$C2$–$C7$–$C8 \approx (115.7(4)^\circ)$ and $\angle C3$–$C2$–$C7$–$C8 \approx (121.5(3)^\circ)$ provide an approximate $C_2\text{v}$ conformation. These different conformations likely reflect low energy barriers (flexibility) in the BOXZn motif, despite the rigid six-member chelate ring.

- Figure 1. Thermal ellipsoid plot of $\text{BOX}^{\text{Me}}\text{ZnMe}(2\,a)$ at 50% probability. H atoms are excluded for clarity. Selected interatomic distances (Å): Zn1–C18, 1.931(1); Zn1–N1, 1.947(9); Zn1–N2, 1.947(9); N1–C5, 1.31(2); N2–C10, 1.31(2); C5–C11, 1.44(2); C10–C11, 1.39(2).

- Figure 2. Thermal ellipsoid plot of $\text{BOX}^{\text{Me}}\text{Zn}(\mu\text{OMe})(3\,a)$ at 50% probability. H atoms are not included in the plot. Selected interatomic distances (Å): Zn1–O3, 1.976(2); Zn1–N1, 1.973(2); Zn1–N2, 1.989(3).
Catalytic alcohol/hydrosilane dehydrocoupling reactions

The monomeric species 2a is a pre-catalyst for the dehydrocoupling of primary, secondary, or tertiary alcohols and primary or secondary organosilanes to give trialkoxysiloxane, dialkoxy, or monoalkoxy organosilanes and H₂ as the by-product (Eq. 2; Table 1). Catalytic conversions occur readily at room temperature, although a few examples are improved upon mild heating. In addition, solvent-free reactions provide products efficiently.

\[
\text{PhH}_2 Si + ROH \stackrel{10 \text{ mol} \% \text{PhH}_2 \text{MeMe} \text{PhN-Zn-} \text{Me} \text{H}}{\text{25 - 50 °C, 10 min - 24 h benzene or neat}} \rightarrow \text{PhH}_2 \text{Si} \text{OR} + \text{H}_2
\]

(2)

Methanol gives quantitative substitution of all silicon hydrides with 10 mol% 2a, producing Ph(SiMe_3)_2 or PhSiH_2(OMe)_2 within 10 min at room temperature in benzene or under solvent-free conditions. In addition, 2a provides a long-lived and effective catalyst, resulting in up to 10^5 turnovers (3 x 10^5 equiv. of Ph(SiMe_3)_2) with low catalyst loading. Likewise, the reaction of PhSiH₃ and excess i-C₃H₇OH provides PhSi(Oi-C₃H₇)₃ after 1 day under neat conditions at room temperature or after 4 h in benzene at 60°C.

Attempts to synthesize mono-methoxy PhH₂SiMeO by Zn-catalyzed reactions of 1 equivalent of MeOH and PhSiH₃ afforded a mixture of PhH₂SiMeO and PhSiH₃(OMe)₂. Instead, monoalkoxy species such as PhH₂SiOEtBu, PhMeH₂SiOIPr, PhMeH₂SiOIPr, and PhMeH₂SiOIPr₃ and PhMeH₂SiOIPr₃ are synthesized by Zn-catalyzed reactions of i-PrOH or BuOH. Secondary silanes easily provide monoalkoxy silane products, such as PhMeH₂SiOIPr. Even in the presence of excess i-PrOH after 1 day at room temperature, the tertiary silane PhH₂SiOIPr is obtained rather than PhSi(OiPr)_3. Remarkably, the reactions involving tBuOH can be performed solvent-free to access partially substituted silanes directly. Tertiary silanes such as triethylysilane and methylphenylsilane are inert toward dehydrocoupling reactions with methanol using 2a under these conditions. Clearly, tri-substituted silane intermediates such as Ph(MeO)₂SiH, PhMeH₂SiOIPr, and PhH₂(MeO)₂SiH are reactive toward MeOH in the presence of catalytic zinc. Because there are only minor differences in the sterics properties at the silicon centers in Ph₂MeSiH and Ph₂(MeO)₂SiH, the greater reactivity of the monoalkoxy silane is most likely the result of its greater electrophilicity.

Kinetics and mechanism of zinc-catalyzed dehydrocoupling reactions

The kinetic behavior of 2a-catalyzed dehydrocoupling of 3,5-dimethylphenol and PhMeH₂SiO by Zn-catalyzed dehydrocoupling of 3,5-dimethylphenol and PhMeH₂SiO as described below, indicates that this reaction follows two distinct mechanisms. The two proposed mechanisms are distinguished by coordination of the aryl alcohol (Kinetic Regime 1: Phenol first) or hydrosilane (Kinetic Regime 2: Silane first) to the zinc aryloxide catalytic species (Scheme 3). The relative concentration of aryl alcohol and silane substrates appears to be the primary factor that determines which pathway is dominant. In addition, the observed rate constants in both mechanistic regimes are affected by saturation behavior by one or both of the reactants. The saturation in organosilane leads to the important conclusion that a σ-complex Zn—H—Si forms prior to the σ-bond metathesis step that produces the Si—O bond. Saturation kinetics in aryl alcohol indicates that a ZnOAr⁻(HOAr) adduct is formed prior to creation of the Si—O bond under conditions of excess arylalcohol. We propose that these mechanisms are a consequence of the three-coordinate nature of the monomeric tBuOX Me₂Zn—X catalytic species. This coordinative unsaturation allows.

Table 1. 2a-Catalyzed dehydrogenative cross-coupling of hydrosilanes and alcohols.

<table>
<thead>
<tr>
<th>Reactants</th>
<th>Products</th>
<th>Conditions</th>
<th>Yield [b] [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhSiH₃ + 1.1 MeOH</td>
<td>PhH₂SiMeO + PhSiH₃(OMe)₂</td>
<td>RT, &lt; 10 min</td>
<td>15:50</td>
</tr>
<tr>
<td>PhSiH₃ + 3.5 MeOH</td>
<td>PhSi(OiPr)₂</td>
<td>RT, &lt; 10 min</td>
<td>100 (98)</td>
</tr>
<tr>
<td>PhSiH₃ + 3.5 MeOH</td>
<td>PhSi(OEtBu)₂</td>
<td>RT, neat, &lt; 10 min</td>
<td>100</td>
</tr>
<tr>
<td>PhSiH₃ + 3.5 MeOH</td>
<td>PhSi(OiPr)₂</td>
<td>0.000001 mol % 2a, RT, neat, 1 h</td>
<td>100</td>
</tr>
<tr>
<td>PhSiH₃ + 3.5 i-PrOH</td>
<td>PhSi(OiPr)₂</td>
<td>60°C, 4 h</td>
<td>95 (90)</td>
</tr>
<tr>
<td>PhSiH₃ + 3.5 tBuOH</td>
<td>PhH₂SiOEtBu</td>
<td>RT, neat, 24 h</td>
<td>98</td>
</tr>
<tr>
<td>PhSiH₃ + 1.1 tBuOH</td>
<td>PhH₂SiOEtBu</td>
<td>RT, 24 h</td>
<td>88</td>
</tr>
<tr>
<td>PhSiH₃ + 1.1 tBuOH</td>
<td>PhSi(OiPr)₂</td>
<td>RT, neat, 24 h</td>
<td>100</td>
</tr>
<tr>
<td>PhMeSiH₃ + 1.1 MeOH</td>
<td>PhMeH₂SiOIPr + PhMeSi(OMe)₂</td>
<td>RT, 1 h</td>
<td>42:30</td>
</tr>
<tr>
<td>PhMeSiH₃ + 3.5 MeOH</td>
<td>PhMeH₂SiOIPr + PhMeSi(OMe)₂</td>
<td>RT, &lt; 10 min</td>
<td>88</td>
</tr>
<tr>
<td>PhMeSiH₃ + 3.5 MeOH</td>
<td>PhMeH₂SiOIPr</td>
<td>RT, neat, 30 min</td>
<td>100 (92)</td>
</tr>
<tr>
<td>PhMeSiH₃ + 3.5 MeOH</td>
<td>PhMeH₂SiOIPr</td>
<td>60°C, 4 h</td>
<td>73 (68)</td>
</tr>
<tr>
<td>PhMeSiH₃ + 1.1 i-PrOH</td>
<td>PhMeH₂SiOIPr</td>
<td>60°C, 4 h</td>
<td>80</td>
</tr>
<tr>
<td>PhMeSiH₃ + 1.1 i-PrOH</td>
<td>PhMeH₂SiOIPr</td>
<td>RT, neat, 24 h</td>
<td>100 (82)</td>
</tr>
<tr>
<td>PhMeSiH₃ + 1.1 i-PrOH</td>
<td>PhMeH₂SiOIPr</td>
<td>60°C, 3 h</td>
<td>100 (65)</td>
</tr>
<tr>
<td>Aryl = C₆Me₆H₄</td>
<td>PhSi(OEtBu)₂</td>
<td>RT, neat, 10 min</td>
<td>100 (94)</td>
</tr>
<tr>
<td>PhSiH₃ + 3.5 MeOH</td>
<td>PhSi(OiPr)₂</td>
<td>RT, 24 h</td>
<td>100</td>
</tr>
<tr>
<td>PhSiH₃ + 1.1 i-PrOH</td>
<td>PhSi(OiPr)₂</td>
<td>RT, 24 h</td>
<td>100 (89)</td>
</tr>
<tr>
<td>PhSiH₃ + 1.1 i-PrOH</td>
<td>PhSi(OiPr)₂</td>
<td>RT, 24 h</td>
<td>100 (65)</td>
</tr>
</tbody>
</table>

[a] Standard conditions unless specified: 10 mol% 2a pre-catalyst, benzene (2 mL) or solvent-free (neat), 0.9 mmol hydrosilane. Reactions performed with 3.15 mmol MeOH, 3.15 mmol i-C₃H₇OH, 0.99 mmol i-C₃H₇OH, 0.99 mmol tBuOH. [b] (Isolated yield).
the catalyst to adapt its structure to the reaction conditions, to maintain high reactivity.

First, initiation of the pre-catalyst 2a involves its rapid reaction with ArylOH to produce the aryloxido-zinc 3c, or with MeOH or iC₂H₅OH to give 3a or 3b, respectively, as described above. In contrast, solutions of 2a and PhMeSiH₂ contained only starting materials after standing at room temperature for 4 d. In addition, NMR spectra and gas chromatograms of reaction mixtures lacking the PhMeSiO-Aryl and H₂ products were not detected. The rate laws determined under a wide range of reactant concentrations also show first-order dependence on the initial [2a], suggesting the active catalytic species is monomeric.

Kinetic Regime 1

In the presence of excess 3,5-dimethylphenol ([ArylOH]/[PhMeSiH₂] = 1.55:1), with [ArylOH] = 0.18 ± 0.01 M, 60 °C) plots of [PhMeSiH₂] against time (Figure 3) analyzed by nonlinear least-squares regression provide second-order rate constants k₁obs. A plot of second-order rate constants k₁obs against [2a] from 2.1 to 25.1 mM reveals a linear correlation (Figure 3, inset), with the slope corresponding to the observed ternary rate constant k₁obs. The small but non-zero value for the y-intercept of 6 × 10⁻⁴ M⁻¹s⁻¹ suggests a catalyst-free background reaction, in conflict with the lack of background reaction under catalyst-free conditions. Instead, the dependence of this y-intercept on [ArylOH] results from a [ArylOH]-dependent displacement of the equilibrium between PhBOX₆⁵⁵ZnMe and PhBOX₆⁵⁵ZnOaryl (HOaryl). As further evidence, a subsequent series of kinetic experiments revealed that the slope and intercept of the plot of k₁obs against [2a] were affected by the concentration of 3,5-dimethylphenol, with [ArylOH] / [PhMeSiH₂] = 8:1 giving a flatter slope (k₁obs = 0.015 M⁻²s⁻¹) and smaller y-intercept (7.6 × 10⁻⁵ M⁻¹s⁻¹).

Together, this observation and the unlikely representation of the ternary rate law by a single termolecular elementary step suggest a mechanism involving a two-step sequence, in which the first reactant and the catalyst form an adduct in a reversible step, followed by reaction of the complex intermediate with the second reactant. This two-step reaction mechanism is further supported by kinetic saturation of initial rates at high [ArylOH]. The initial rates of product formation (d[PhMeHSiOAryl]/dt) increase with increasing concentrations of 3,5-dimethylphenol until 0.44 M, at which point the reaction rate decreases (Figure 4). The latter effect is attributed to catalyst inhibition by coordination of a second equivalent of phenol. This observation of inhibition by ArylOH provides additional important evidence reinforcing the proposed catalytically relevant sequence involving reversible coordination of one arylalcohol molecule to zinc, followed by reaction with hydrosilane. In particular, the reverse order (coordination by hydrosilane then Si–O bond formation by reaction with ArylOH) would require, unreasonably, ArylOH to simultaneously inhibit the intermediate and react with that same intermediate in a productive catalytic step.

An experimental rate law combining these observations is given in Equation (3), where k₁cat corresponds to the product of the two forward steps, Kₘ is related to the Michaelis constant (rates consuming the intermediate divided by the rate constant for the first step), and K₀inh is the inhibition equilibrium constant.

\[
\frac{d[\text{PhMeHSiOAryl}]}{dt} = \frac{k_{\text{cat}}[^{[\text{PhMeHSiOAryl}][\text{Ar}][\text{PhMeSiH}_2]]}{1 + K_m[^{[\text{Ar}][\text{PhMeSiH}_2]] + k_{\text{inh}}[^{[\text{Ar}][\text{PhMeSiH}_2]]}^2}}
\]  

(3)

At low [ArylOH], a ternary rate law is observed, and the observed order of [ArylOH] dependence becomes zero and then inverse as its concentration increases.

Kinetic Regime 2

At lower ArylOH concentrations, the time dependences of both [PhMeSiH₂] and [ArylOH] follow an exponential decay (Figure 5A; 1.4 > [ArylOH]/[PhMeSiH₂] > 1.2; average [ArylOH]₀ = 0.12 M, average [PhMeSiH₂]₀ = 0.096 M), indicating that the
transformation is first-order in only one of the reactants. These data indicate that either PhMeSiH$_2$ or ArylOH is present in the turnover-limiting step, in a remarkable contrast to the behavior in Kinetic Regime 1. Experiments varying [2 a], with [PhMeSiH$_2$]$_{ini}$ and [ArylOH]$_{ini}$ kept constant, reveal first-order dependence on catalyst concentration. At high [PhMeSiH$_2$]$_{ini}$, 2a-catalyzed dehydrocoupling shows zero-order kinetic dependence on the ArylOH limiting reactant (Figure 5B). These data indicate that under conditions of moderate [PhMeSiH$_2$]$_{ini}$ the catalytic reaction follows the second-order rate law of Equation (4) ($k_{obs}^{2 a} = 9.8 \pm 0.4 \times 10^{-3} \text{M}^{-1} \cdot \text{s}^{-1}$) in Kinetic Regime 2.

$$
\frac{d[\text{ArylOH}]}{dt} = k_{obs}^{2 a} [2 \text{a}] [\text{PhMeSiH}_2]^{1}
$$

(4)

For comparison, the observed second-order rate constant for To$_2$ZnH-catalyzed dehydrocoupling is 0.014 M$^{-1} \cdot \text{s}^{-1}$. 

Figure 3. A) Plots of [PhMeSiH$_2$] vs. time for its dehydrocoupling reaction with ArylOH catalyzed by $^{18}$BOX-Me$_2$ZnMe at 60 °C, with catalytic concentration ranging from 1.14 to 25.1 mM. [ArylOH]$_{ini} = 0.18 \pm 0.01 \text{M}, [\text{PhMeSiH}_2]_{ini} = 0.115 \pm 0.008 \text{M}. B)$ Plot of second-order rate constants $k_{obs}^{2 a}$ vs. [2 a]. The slope corresponds to the ternary rate constant $k_{obs}^{2 a} = 0.086 \pm 0.005 \text{M}^{-2} \cdot \text{s}^{-1}$.

Figure 4. Plot of the initial rate of PhMeHSiOAr formation vs. [ArylOH] showing decreasing rate constant.

Figure 5. Plots of [ArylOH] and [PhMeSiH$_2$] vs. time in 2a-catalyzed dehydrocoupling reactions in Kinetic Regime 2 follow A) exponential time dependence indicative of first-order behavior or B) linear time dependence indicative of zero-order behavior, with the observed rate constant $k_{obs}^{2 a}$. 

A) Plots of [PhMeSiH$_2$] vs. time for its dehydrocoupling reaction with ArylOH catalyzed by $^{18}$BOX-Me$_2$ZnMe at 60 °C, with catalytic concentration ranging from 1.14 to 25.1 mM. [ArylOH]$_{ini} = 0.18 \pm 0.01 \text{M}, [\text{PhMeSiH}_2]_{ini} = 0.115 \pm 0.008 \text{M}. B)$ Plot of second-order rate constants $k_{obs}^{2 a}$ vs. [2 a]. The slope corresponds to the ternary rate constant $k_{obs}^{2 a} = 0.086 \pm 0.005 \text{M}^{-2} \cdot \text{s}^{-1}$.
Thus, the experimental rate law, rate constant, and reactivity, as well as Si–O bond formation as the turnover-limiting step for 2a-catalyzed dehydrocoupling of ArylOH and PhMeSiH₂ in Kinetic Regime 2 are comparable to the catalytic features of four-coordinate To⁹ZnH. A first major consequence, then, of the coordinative unsaturation of 2a is the creation of the new catalytic mechanism in Kinetic Regime 1, rather than increasing the catalytic rate.

Zero-order dependence on [ArylOH] in Figure 5b, however, is ambiguous with respect to the dependence of rate on [PhMeSiH₂] at that high concentration. Unexpectedly, initial rates of product formation (d[PhMeHSiOAryl]/dt) reveal saturation behavior as [PhMeSiH₂] increase is given, leading to zero-order dependence on [PhMeSiH₂] at high initial concentrations (Figure 6). Thus, Equation (4) represents the lower-concentration limiting case of the bimolecular Michaelis-Menten-type description of the catalytic kinetics in Equation (5).

\[
\frac{\text{d}[\text{PhMeHSiOAryl}]}{\text{dt}} = \frac{k_{\text{cat}}[2a][\text{PhMeSiH}_2]}{K_m + [\text{PhMeSiH}_2]} \tag{5}
\]

This rate law is consistent with the bimolecular reaction of \(\text{BOX}^{16}\text{ZnOAr}_2\) and PhMeSiH₂ occurring in two steps: reversible association of PhMeSiH₂ and \(\text{BOX}^{16}\text{ZnOAr}_2\) to give an adduct, followed by extrusion of the product in an irreversible step (Scheme 3, right). These data, which lead to the revised mechanism of Kinetic Regime 2, reveal this second consequence of the coordinative unsaturation of pre-catalyst 2a.

The structure of the alkoxyzinc-silane adduct could involve hydrosilane coordination to the zinc center (Scheme 4a). As noted in the Introduction, M=H–Si adducts prior to the four-centered electrocyclic transition have been postulated in o-bond metathesis-type on the basis of DFT calculations, but these species are typically fleeting. Although hydrosilane adducts to d⁷ transition metal centers \((n \neq 0)\) are well established, including in silane/alcohol dehydrocoupling reactions, the core-like 3d orbitals of zinc are unable to provide the stabilizing back-donating interaction important to transition metal o-adducts.

Alternatively, coordination of the nucleophilic alkoxide to silicon would give a five-coordinate silane adduct (Scheme 4b). Formation of this intermediate could also rationalize the higher reactivity of alkoxy-substituted silanes through stabilization of the higher-coordinate silicon center by electronegative substituents. Several experimental observations, however, disfavor this kind of intermediate. The formation of such a hyper-coordinated silane intermediate does not require a coordinatively unsaturated metal center, which appears to be the significant feature of the chemistry of \(\text{BOX}^{16}\text{ZnX}\). Moreover, the saturation in hydrosilane in Kinetic Regime 2 parallels saturation with excess ArylOH in Kinetic Regime 1, where coordination of phenol to zinc is reasonably established. Finally, the distinct rate laws of the two Kinetic Regimes suggest that their mechanisms are inequivalent, which would also imply that a zinc-silane adduct is reasonable.

DFT calculations also favor the Zn=H–Si adduct over a hyper-coordinate silane adduct preceding the four-centered transition state during o-bond metathesis. In particular, the energy of the system increases as the alkoxyxigen approaches the silicon center of PhMeSiH₂ and a local minimum involving a Zn=O–SiPhMeH₂ interaction could not be located. In contrast, the Zn=H–Si, involving a side-on interaction, is a local minimum (Figure 7). In particular, the Zn–H distance of 2.23 Å in this adduct is longer than Zn–H in three coordinate \((\text{DIPP-nacnac})\text{ZnH} \ (1.46(2) \text{Å}; \text{DIPP-nacnac} = \text{HCCHN} (2,6-\text{C}_6\text{H}_4\text{Pr}_2))\) and in four-coordinate To⁹\text{ZnH} \ (1.52(2) \text{Å}) \(\text{[31]}\) and \((\text{k}^3-\text{Tptm})\text{ZnH} \ (1.51(3) \text{Å})\). The calculated Zn–H, as well as Zn–Si and Si–O distances (3.32 and 2.95 Å, respectively), are also longer than the sum of covalent radii. The Zn–H–Si angle (124.5°) is far from linear, the Zn–O–Si–H torsion is −11.8°, and the silicon center is tetrahedral. In addition, the terminal (1.48 Å) and bridging (1.50 Å) Si–H distances are very similar, although the calculated vibrational frequencies of 2147 and 2072 cm⁻¹, respectively, are not equivalent.

![Figure 6](image-url)  
**Figure 6.** Initial rates vs. [PhMeSiH₂]₀ reveals saturation behavior. \(k_{\text{cat}}\) (often defined as \(k_{\text{obs}}\)) is equal to the rate at saturation \(v_{\text{max}}\) divided by catalyst concentration.

![Scheme 4](image-url)  
**Scheme 4.** Possible equilibria that could lead to saturation kinetics in \([\text{PhMeSiH}_2]_0\).


These are not the final page numbers!
This Zn—H—Si adduct is connected, as shown by an IRC calculation, to the four-centered transition state, which is characterized by one negative vibrational mode. The calculated energy coordinate diagram for Si—OMe bond formation is shown in Scheme 5. In the transition state, the Zn—H and O—Si distances are shortened (2.12 and 2.30 Å, respectively) and the Si—H and Zn—O distances are slightly longer (1.52 and 1.89 Å, respectively) than in the adduct. The calculated zinc · silane adduct is an intermediate leading to a four-centered transition state associated with σ-bond metathesis. The phenyl group and all H atoms bonded to carbon were included in the calculation, but not in the illustration for clarity.

Figure 7. The calculated zinc-silane adduct is an intermediate leading to a four-centered transition state associated with σ-bond metathesis. The phenyl group and all H atoms bonded to carbon were included in the calculation, but not in the illustration for clarity.

Scheme 5. Reaction free energies (298.16 K) showing the σ-bond metathesis step for Si—O bond formation.

Conclusions

Three-coordinate zinc complexes provide highly active and long-lived catalysts for dehydrocoupling of primary or secondary silanes and alcohols. Selectivity for partial substitution to monoalkoxy silanes is influenced by the steric properties of the alcohol, and extremely fast and efficient conversion of primary silanes and methanol gives a high degree of substitution.

While the previously reported kinetic behavior of four-coordinate To[ZnH/To][ZnOAr] implies a simple, two-step mechanism, comparison with BOX-ZnMe-initiated dehydrocoupling provides evidence for several accessible mechanisms. These mechanisms are established under conditions in which one reactant is in excess, as is often the case under pseudo-first-order conditions employed in kinetic studies. In contrast, typical reaction conditions for synthetic applications in these dehydrogenative cross-couplings, as well in other cross-coupling reactions, match the concentration of reagents to the desired stoichiometry of the conversion. Under such synthetic conditions, it is probable that both the phenol-first and silane-first pathways are concurrently operative. This variation of mechanism as a function of reactant concentrations has important consequences for assessing and comparing the performance of catalysts, in typical terms of activity and selectivity, and eventually designing more efficient and effective complexes.

The reactivity of BOX-ZnX is dominated by its open coordination site, which is satisfied in BOX-ZnOR by dimerization upon crystallization, formation of alkoxyzinc-alcohol intermediates at high alcohol concentrations, and formation of alkoxy-zinc-silane intermediates at high hydrosilane concentrations. Kinetic experiments, corroborated by DFT calculations, provide powerful evidence in support of hydrosilane σ-complexes as intermediates prior to the σ-bond metathesis transition state.

We also note that phenol is a catalyst inhibitor at high concentration, as depicted in the phenol-first cycle in Scheme 3. This inhibition, either by coordinating to zinc or hydrogen-bonding to the reactive phenoxide group, likely blocks interaction with the hydrosilane reactant. Such structures undoubtedly affect related catalytic transformations involving organozinc and coordinating reactants because the zinc center is able to effectively adapt its coordination sphere to reaction conditions.

Acknowledgements

This research was supported by the U.S. Department of Energy (DOE), Office of Science, Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences. Ames Laboratory is operated for the DOE by Iowa State University under Contract no. DE-AC02-07CH11358.

Conflict of Interest

The authors declare no conflict of interest.

Keywords: dehydrogenative cross-coupling · saturation kinetics · sigma-adducts · silyl ethers · zinc catalysis
σ-Silane adducts and alcohol adducts are kinetically detected intermediates in zinc-catalyzed σ-bond metathesis-type dehydrocoupling reactions. These intermediates feature prominently in the reactivity of coordinatively unsaturated zinc centers, which efficiently mediate Si–O bond formation. The catalyst is responsive to reaction conditions, adapting as a function of concentration to follow the kinetically preferred mechanism.