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Coordinatively Saturated Tris(oxazolinyl)borato Zinc Hydride-Catalyzed Cross Dehydrocoupling of Silanes and Alcohols

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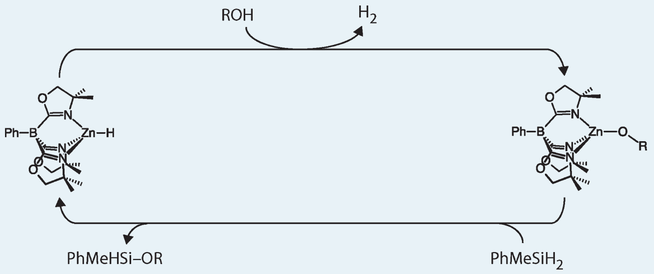
Supporting Information

ABSTRACT: The four-coordinate zinc compound To^MZnH (**1**, To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) catalyzes selective alcoholysis of substituted hydrosilanes. The catalytic reaction of $PhMeSiH_2$ and aliphatic alcohols favors the monodehydrocoupled product PhMeHSi−OR. With the aryl alcohol 3,5-$C_6H_3Me_2OH$, the selectivity for mono(aryloxy)hydrosilane $PhMeHSiOC_6H_3Me_2$ and bis(aryloxy)silane $PhMeSi(OC_6H_3Me_2)_2$ is controlled by relative reagent concentrations. Reactions of secondary organosilanes and diols provide cyclic bis(oxo)silacycloalkanes in high yield. The empirical rate law for the To^MZnH-catalyzed reaction of 3,5-dimethylphenol and $PhMeSiH_2$ is $-d[PhMeSiH_2]/dt = k'_{obs}[To^MZnH]^1[3,5\text{-}C_6H_3Me_2OH]^0[PhMeSiH_2]^1$ (determined at 96 °C) which indicates that Si−O bond formation is turnover-limiting in the presence of excess phenol.



KEYWORDS: silane alcoholysis, alkoxysilane, zinc hydride, oxazoline, dehydrocoupling

Si−O bond formation is important in materials preparations and surface derivatizations. For example, alkoxysilanes are a central component in the preparation of functionalized mesoporous silica nanospheres (MSNs), either by co-condensation routes or grafting reactions through hydrolytic Si−O bond formations.[1,2] Our interest in the catalytic preparation of alkoxysilanes was inspired by our interactions with Prof. Victor Lin, as we sought to synthesize precursors for advanced silica-based functionalized nanomaterials for catalytic applications. Silyl ethers are also important building blocks in organosilicon chemistry and in synthetic organic chemistry as protecting groups.[3] The reaction of chlorosilanes and alcohols provides a straightforward route to Si−O bonds. However, the HCl byproduct of these reactions must be trapped with base, and this method is not useful for syntheses that require neutral conditions. The degree of condensation is difficult to control when more than one Si−Cl group is present in the silicon substrate. Furthermore, chlorosilanes are water sensitive and must be kept rigorously anhydrous prior to use. Catalytic Si−H bond alcoholysis (eq 1) can avoid these problems, giving H_2 as the byproduct and bypassing acid formation and/or basic conditions. Organosilanes are not hydrolytically sensitive (in the absence of a catalyst), and catalysts can control selectivity.

$$R'_3SiH + HOR \xrightarrow{\text{catalyst}} R'_3Si - OR + H_2 \qquad (1)$$

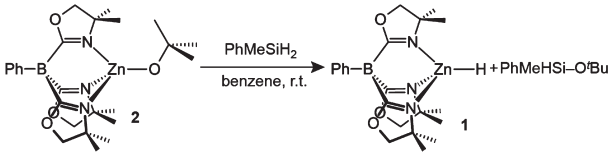
A range of homogeneous and heterogeneous catalytic systems have been developed for hydrosilane alcoholysis, including early, middle, and late transition metal complexes of titanium,[4−6] manganese,[7] rhenium,[8] iron,[9] ruthenium,[10,11] rhodium,[12] iridium,[13] nickel,[14,15] copper,[16−19] gold,[20] and platinum.[21] Strong Lewis acids, such as $B(C_6F_5)_3$, are also catalysts.[22] A number of reaction mechanisms have been proposed, including alcohol attack on η^2-hydrosilane or silyl hydride transition-metal complexes formed via oxidative addition steps.[7,13,14] In contrast, copper- and gold-catalyzed silane alcoholyses are proposed to involve discrete metal hydride and metal-alkoxide intermediates (no M−Si bond).[18,20] In situ generated zinc(II) catalysts are also proposed to follow this mechanism.[23] However, these zinc, copper, and gold catalysts are generated in situ, the catalytic speciation is unknown, and the turnover-limiting step has not been established.

Zinc(II) catalysts are particularly interesting, given the low cost, favorable biocompatibility, and high natural abundance of this main group metal. Although zinc hydrides are presumed intermediates in hydrosilane alcoholysis, the catalytic activity of the few isolable, monomeric, terminal zinc hydrides is not developed.[24−28] We recently synthesized a monomeric zinc hydride To^MZnH (**1**; To^M = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) by reaction of To^MZnO^tBu (**2**) and $PhMeSiH_2$. The byproduct of this reaction is the silyl ether $PhMeHSi-O^tBu$. Incorporation of this step into a catalytic cycle for Si−O bond formation would provide an opportunity to use a well-defined set of alkoxide and hydride intermediates, as well as stoichiometric reactions, to study and develop zinc-catalyzed transformations. Furthermore, the zinc-catalyzed reactions are mechanistically

Special Issue: Victor S. Y. Lin Memorial Issue

Received: February 23, 2011
Revised: April 20, 2011
Published: May 20, 2011

distinct from transition-metal catalyzed silane alcoholyses in that oxidative addition pathways are unlikely in the main group system.



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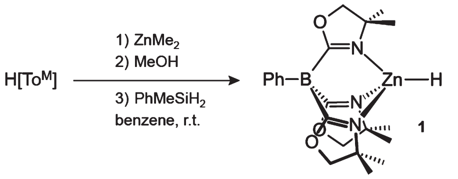
Here we present the reactivity and selectivity of **1** as a catalyst for silane alcoholysis and kinetic studies on a catalytic conversion. Although To^{M}ZnMe (**3**), *tert*-butoxide **2**, and To^{M}ZnOAryl (**4**; Aryl = $C_6H_3Me_2$) may be used as precatalysts,[29] these compounds have some limitations. For example, alkyl **3** reacts relatively slowly with some alcohols, and that step can impede efficient catalyst initiation. While *tert*-butoxide **2** is the catalyst precursor, 1 equiv of silane is wasted as R_3Si-O^tBu. Therefore, compound **1** is the precatalyst of choice for these studies, and although it is moisture sensitive, **1** does not react with O_2 under ambient conditions. The monomeric zinc hydride **1** was previously prepared following a three-step synthesis where To^{M}ZnCl and **2** intermediates were isolated from the TlCl and KCl reaction byproducts.[30] An alternative and easy one pot preparation involves sequential treatment of H[To^M] with $ZnMe_2$, MeOH, and then $PhMeSiH_2$ in benzene or toluene (eq 3).



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The byproducts of this synthesis are methane and PhMeH-Si−OMe, and evaporation of the volatile materials provides crystalline and spectroscopically pure **1**. The **3** intermediate is isolable and fully characterized, including an X-ray structure (Figure 1) that shows the pseudo-C_{3v}-symmetric four-coordinate zinc alkyl complex. The bowl-like steric properties of To^M prevent redistribution to {κ^3-To^M}$_2$Zn yet allow sufficient space for reactivity. The constitution and pseudo C_{3v}-symmetry of **1** is maintained in solution. Thus, a 2D $^1H-^{15}N$ NMR correlation experiment contained crosspeaks for the oxazoline nitrogen signal (−155.8 ppm), including one with the zinc methyl resonance that indicated both ligands are bonded in the same complex.

Compound **1** is a catalyst for reactions of aliphatic alcohols ROH (*R* = Me, Et, $CH_2{}^tBu$, ^{i}Pr, ^{t}Bu) and the secondary silane $PhMeSiH_2$ to give the monodehydrocoupled silyl ether PhMeH-Si−OR as the major product with good selectivity (Table 1). At lower temperature, selectivity is further improved although the rate is sacrificed (e.g., MeOH and $PhMeSiH_2$ react to give 90% yield of PhMeHSi−OMe at 45 °C; $PhMeHSi-OCH_2{}^tBu$ is formed with >99% selectivity at 85 °C). For comparison, the Cp_2TiCl_2/nBuLi system converts all SiH groups of secondary and primary silanes to bis- and tris-alkoxy silanes, respectively.[4] However, Wilkinson's catalyst and chiral phosphine/rhodium(I) catalysts provide alkoxy(hydro)silanes from secondary silanes and alcohols,[12] as does the chiral phosphine/copper system.[17] The selectivity observed in these systems and the oxazolinyl-borato zinc system contrast the often observed relative reactivity of organosilanes versus alkoxy hydrosilanes, where the latter are more reactive (e.g., as in titanium-catalyzed hydrosilylations).[31] Selectivity for the monoalkoxy silane product increases with increasing size of the alcohol, and sterically hindered alcohols require higher temperature and longer reaction times. Although sterics play a large role in this selectivity (in that PhMe(RO)SiH is more hindered than $PhMeSiH_2$), experiments with the tertiary organosilane $BnMe_2SiH$ (Bn = $CH_2C_6H_5$) show that the effects are subtle.

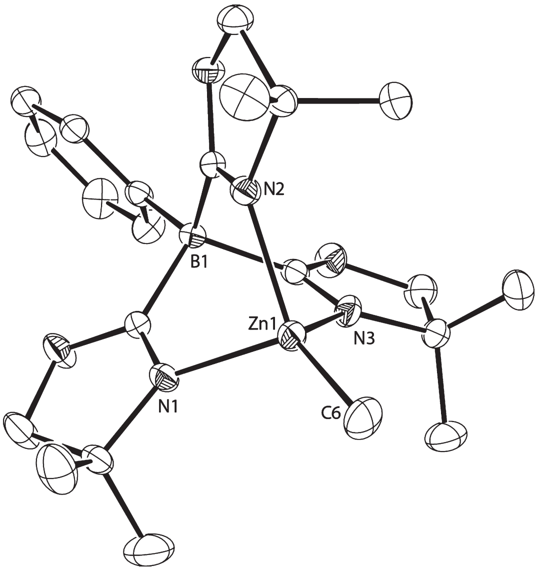


Figure 1. ORTEP diagram of To^{M}ZnMe (**3**) drawn with ellipsoids at 50% probability. Hydrogen atoms are not shown. Selected bond distances (Å): Zn1−C6, 1.972(1); Zn1−N1, 2.0574(9); Zn1−N2, 2.0797(9); Zn1−N3, 2.0955(9). Selected bond angles (deg): C6−Zn1−N1, 122.25(5); C6−Zn1−N2, 130.25(5); C6−Zn1−N3, 122.93(5).

Thus, compound **1** also catalyzes the dehydrocoupling of the tertiary silane $BnMe_2SiH$ with primary, secondary, and tertiary alcohols. Unexpectedly, the Zn-catalyzed reactions of the tertiary organosilane $BnMe_2SiH$ and alcohols are more rapid than the corresponding reactions with secondary silane $PhMeSiH_2$. All of these dehydrocoupling reactions are sensitive to the steric bulk of the alcohol. For example, $PhMeSiH_2$ reacts four times slower than $BnMe_2SiH$ under equivalent conditions (catalyst loading, reagent concentrations, temperature). ^{t}BuOH is an exception to this trend likely because of high steric congestion (see Table 1). Despite the apparently greater rate of alcoholysis of tertiary organosilanes, the secondary organosilanes react with good selectivity for the monosilyl ether products. Notably, To^{M}ZnH is observed by ^1H NMR spectroscopy during the reactions, and apparently it is thermally stable and catalytically active to even 135 °C for 64 h.

The thermal and kinetic stability of the To^{M}ZnX-complexes suggested that lower catalyst loadings could be used in larger scale reactions for the convenient isolation of alkoxysilanes. In fact, catalyst loadings as low as 0.27 mol % provide product, albeit with increased reaction times. Additionally, these catalyses are efficient for gram-scale reactions of organosilanes, and the products PhMeHSiOMe, $BnMe_2SiOMe$, PhMeHSiOEt, PhMeH-SiO^{i}Pr, and PhMeHSiO^{t}Bu are readily obtained in our catalytic system.[29]

Compound **1** also catalyzes the dehydrocoupling reaction of the substituted phenol 3,5-$Me_2C_6H_3OH$ and $PhMeSiH_2$.

Table 1. Micromolar-Scale Reactions of $PhMeSiH_2$ and $BnMe_2SiH$ with ROH

$$\mathrm{PhMeSiH_2 + HOR \xrightarrow{10\ mol\%\ To^MZnH} PhMeHSi{-}OR + H_2}$$

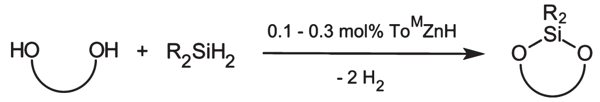
Alcohol	Product[a]	Temperature	Time (h)	Selectivity (%)[b]
MeOH	PhMeHSiOMe	45 °C	10	89 : 11[c]
MeOH	PhMeHSiOMe	60 °C	4.2	81 : 19[c]
EtOH	PhMeHSiOEt	60 °C	20	89 : 11[c]
${}^tBuCH_2OH$	$PhMeHSiOCH_2{}^tBu$	135 °C	5	93 : 7
${}^iPrOH$	$PhMeHSiO^iPr$	85 °C	45	95 : 5[c]
${}^tBuOH$	$PhMeHSiO^tBu$	135 °C	13	>99

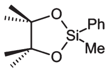
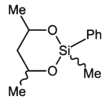
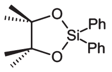
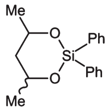
$$\mathrm{BnMe_2SiH + HOR \xrightarrow{10\ mol\%\ To^MZnH} BnMe_2Si{-}OR + H_2}$$

Alcohol	Product[a]	Temperature	Time (h)	Selectivity (%)[b]
MeOH	$BnMe_2SiOMe$	60 °C	1	n.a.
EtOH	$BnMe_2SiOEt$	60 °C	4	n.a.
${}^iPrOH$	$BnMe_2SiO^iPr$	60 °C	25	n.a.
${}^tBuOH$	$BnMe_2SiO^tBu$	135 °C	64	n.a.

[a] 10 mol % catalyst loading for the reaction of equimolar ROH and $PhMeSiH_2$ to 100% conversion in benzene-d_6. [b] Products were identified and selectivity was determined by ^1H NMR spectroscopy and GC-MS, and by comparison with isolated materials. [c] The minor product is the dialkoxylsilane $PhMeSi(OR)_2$.

Table 2. Catalytic Cyclization of Secondary Silanes and Diols



Product[a]	isolated yield[b]	product ratio
	92.2%	n.a.
	96.8%	1 : 2.11 : 2.27
	91.5%	n.a.
	93.0%	1 : 1.15

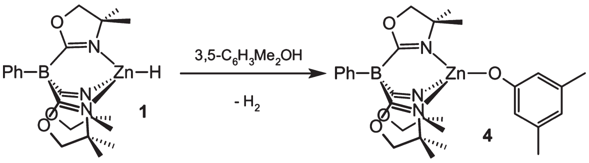
[a] Conditions for catalysis: 0.1−0.3 mol % To^MZnH, 8 mmol diol, and 7 mmol organosilane were dissolved in benzene, degassed, and stirred at 60−90 °C. [b] Products are isolated by distillation, and yield is calculated for five- or six-member ring product(s) after distillation.

Equimolar $PhMeSiH_2$ and $3,5\text{-}Me_2C_6H_3OH$ affords 1:2:1 mixtures of $PhMeSiH_2$, $PhMeHSiOC_6H_3Me_2$ and $PhMeSi(OC_6H_3Me_2)_2$ under catalytic conditions, contrasting the higher selectivity found with aliphatic alcohols. However, relative ratios of starting materials can be used to control the product distribution, and both $PhMeHSiOC_6H_3Me_2$ and $PhMeSi(OC_6H_3Me_2)_2$ are isolable in pure form in high yield. For example, 5 equiv of $PhMeSiH_2$ with respect to $3,5\text{-}Me_2C_6H_3OH$ affords $PhMeHSiOC_6H_3Me_2$ (89.2%), whereas 3 equiv of $3,5\text{-}Me_2C_6H_3OH$ versus $PhMeSiH_2$ provides $PhMeSi(OC_6H_3Me_2)_2$ (90.8%). In both cases, the excess reagent is recovered in pure form during the distillation and is not wasted.

Diols are also challenging substrates for cross-dehydrocoupling because polymers, branched oligomers, and a range of cyclic species are possible products. Titanocene complexes are catalysts for cyclization to give five, six, and seven-member rings,[4] and this provides a classic example for catalytic control over selectivity in Si−O bond forming reactions. The steric control, efficient transformations, and high selectivities observed with the convenient To^MZnH system provide small cyclic dioxasilacycles in high yield and high purity using $PhMeSiH_2$ and Ph_2SiH_2 (Table 2).[29] Additionally, the $PhMeSiH_2$/pinacol and Ph_2SiH_2/2,4-pentanediol products are crystalline at room temperature, and their identities are confirmed by X-ray crystallography (see Supporting Information).

Given the range of proposed mechanisms for metal-mediated dehydrogenative silylation of alcohols and the coordinative saturation of To^MZnH, we have examined the To^MZnH-catalyzed dehydrocoupling reactions in greater detail. The phenolic alcohols had shown the greatest dependence of product identity on concentration of substrates, and therefore we chose $3,5\text{-}C_6H_3Me_2OH$ and $PhMeSiH_2$ as the substrates to study the dehydrocoupling reaction mechanism to identify the factors that control relative rates of reactivity. Additionally, we have studied isolated **1**[30] and $To^MZnOC_6H_3Me_2$ (**4**) as likely intermediates in the dehydrocoupling of $3,5\text{-}C_6H_3Me_2OH$ and organosilanes to test their role in the catalytic cycle.

Reaction of To^MZnH and 3,5-dimethylphenol in benzene readily provides **4** (eq 4), which is isolated and fully characterized by spectroscopic, analytical and X-ray diffraction techniques.



(4)

The reaction between $To^MZnOC_6H_3Me_2$ and $PhMeSiH_2$ (benzene-d_6, 60 °C) affords a mixture of $PhMeHSi(OC_6H_3Me_2)$ and $PhMeSi(OC_6H_3Me_2)_2$ in a 61:39 ratio. Additionally, the compounds **1** and **4** show the same activity under catalytic conditions for organosilane phenolysis. Thus, stoichiometric steps have been observed that support a two-step catalytic mechanism for dehydrocoupling of organosilanes and 3,5-dimethylphenol. Related steps have also been observed for the coupling of organosilanes and *tert*-butanol.

To provide further support for the proposed mechanism, the concentrations of species in the catalytic reactions were monitored by ^1H NMR spectroscopy over the reaction course. Under initial conditions of 200 mM $[HOC_6H_3Me_2]$, 130 mM $[PhMeSiH_2]$ with 1.5−12 mol % To^MZnH in toluene-d_8 at 96.3 °C (calibrated), plots of $[HOC_6H_3Me_2]$ versus time are linear, and curves of $[PhMeSiH_2]$ versus time follow an exponential decay over three half-lives (nonlinear least-squares analysis provides k_{obs} for a particular catalyst concentration). Several reactions were attempted with a range of concentrations of phenol with constant **1**; k_{obs} does not change with $[HOC_6H_3Me_2]$ ranging from 0.2−1.2 M. This lack of dependence on phenol concentration confirms its zero-order contribution to the rate law

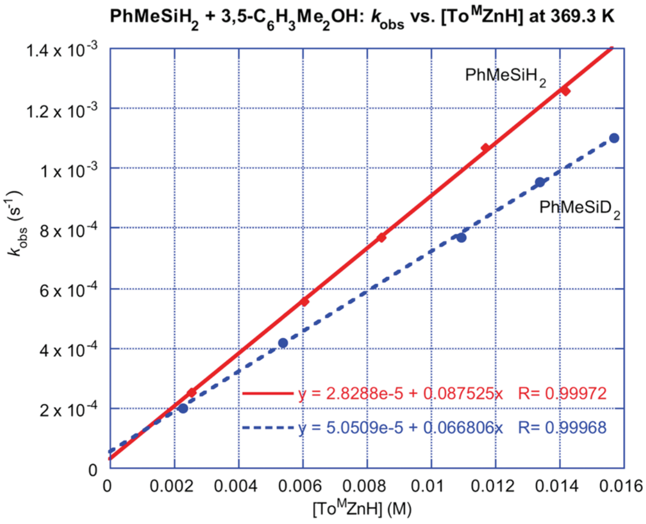


Figure 2. Plot of k'_{obs} versus [To^{M}ZnH] for the reaction of 3,5-dimethylphenol with $PhMeSiH_2$ and $PhMeSiD_2$.

with $PhMeSiH_2$ as the limiting reagent. In contrast, a plot of k_{obs} versus [To^{M}ZnH] shows a linear correlation (Figure 2) giving $k'_{obs}{}^{(PhMeSiH2)} = 8.8 \pm 0.3 \times 10^{-2}\ M^{-1}\ s^{-1}$. Under these conditions, an empirical rate law is:

$$-d[PhMeSiH_2]/dt = k'_{obs}{}^{(PhMeSiH2)}[To^{M}ZnH]^1[PhMeSiH_2]^1[Phenol]^0$$

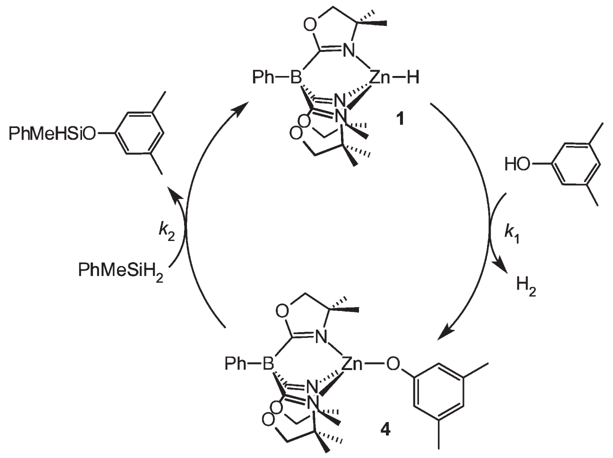
This empirical rate law is consistent with the mechanism of Scheme 1, with the turnover-limiting step (k_2) involving interaction of $PhMeSiH_2$ and the catalyst. The experimentally determined k'_{obs} corresponds to the rate constant k_2 for the interaction of **4** and $PhMeSiH_2$.

The only To^{M}Zn-species observed under these reaction conditions is **4**. This observation and the empirical rate law indicate that **4** is the resting state for the catalysis at 96 °C in the presence of excess 3,5-dimethylphenol. Thus, the rate constant (k_1) for the hydrogen elimination reaction of **1** and $HOC_6H_3Me_2$ is greater than k_2. Additionally, the kinetics reveal that under these conditions, neither step of the cycle is reversible.

To further probe the turnover-limiting step, we determined the empirical rate law and rate constant for the catalytic reaction of $PhMeSiD_2$ and $HOC_6H_3Me_2$. At 96.3 °C, $k'_{obs}{}^{(PhMeSiD2)}$ is $6.7 \pm 0.7 \times 10^{-2}\ M^{-1}\ s^{-1}$. The ratio of $k'_{obs}{}^{(PhMeSiH2)}$ to $k'_{obs}{}^{(PhMeSiD2)}$, and hence the kinetic isotope effect (k_H/k_D) was calculated to be 1.3(1). This value suggests that the Si−H (or Si−D) bond is broken during the turnover-limiting step and is consistent with a four-centered transition state for Si−O bond formation where the ∠Zn−H−Si is nonlinear. However, this relatively small value could also be interpreted as resulting from a (large) secondary isotope effect.

Therefore, the nature of the proposed turnover-limiting step was further investigated by measurement of the rate law for the stoichiometric reaction of $PhMeSiH_2$ and **4**. Under pseudo-first order conditions (10−20 equiv of $PhMeSiH_2$ at 96 °C), the reaction is too fast to be easily monitored by ^{1}H NMR spectroscopy. Instead, we measured the (stoichiometric) second-order rate constants from 24 to 61 °C under pseudo-first order conditions and calculated the rate constant at 96 °C using the Eyring equation. This calculated value, $0.1\ M^{-1}\ s^{-1}$, is close to the value measured under catalytic conditions (0.088 (3) $M^{-1}\ s^{-1}$). Thus, the stoichiometric Si−O bond forming reaction of To^{M}ZnO$C_6H_3Me_2$ and $PhMeSiH_2$ is chemically and kinetically competent for its proposed role in the catalytic cycle. The other step, namely, interaction of To^{M}ZnH and $HOC_6H_3Me_2$, is rapid at room temperature ($t_{1/2} < 5$ min), and this step is also catalytically competent and consistent with the proposed mechanisms.

Scheme 1. Proposed Cycle for To^{M}ZnH-Catalyzed Dehydrocoupling of $PhMeSiH_2$ and 3,5-Dimethylphenol



The activation parameter values obtained from the Eyring analysis, $\Delta H^{\ddagger} = 13$ kcal mol^{-1} and $\Delta S^{\ddagger} = -27$ cal mol^{-1} K^{-1}, further support a highly organized transition state for Si−O bond formation. Related four-center transition states that involve transfer of a hydrogen atom from silicon to a metal center have values for activation parameters with relatively low $\Delta H^{\ddagger}$ and highly negative $\Delta S^{\ddagger}$, as well as isotope effects that range from unity to about 3. For example, the reaction of CpCp*ClHf−SiH_2Ph and $PhSiH_3$ or $PhSiD_3$ gives CpCp*ClHf−H (or [Hf]−D) with a $k_H/k_D = 2.7(2)$ (at 70 °C) and activation parameters $\Delta H^{\ddagger} = 19$ kcal mol^{-1} and $\Delta S^{\ddagger} = -33$ e.u..[32] The isotope effect for the related reaction of Cp^*_2ScMe with Ph_2SiH_2 or Ph_2SiD_2 that gives Ph_2MeSiH or Ph_2MeSiD is 1.15(5), and the related value for the reaction of [DADMB]YMe(THF) and $PhMeSiH_2$ is 1.1(1) (at 298 K; DADMB = 2,2′-bis(*tert*-butyldimethysilylamido)-6,6′-dimethylbiphenyl).[33,34] Related four-centered transition states are proposed in titanium-catalyzed hydrosilylation of ketones,[31] in zinc-catalyzed hydrosilylations, and in gold and copper-catalyzed silane alcoholyses,[18,20,35] although isotope effects for Si−O bond formation are not reported. Thus, the studies reported here for the To^{M}ZnH-catalyzed reaction, including kinetics, isolable intermediates, stoichiometric reactions, and rate constants provide substantial support for the proposed two-step catalytic mechanism as well as concerted Si−H bond cleavage/Si−O bond formation previously suggested for in situ generated zinc, copper, and gold catalysts.

We are currently working to identify relative rates of Si−O bond formation for reactions of isolated zinc alkoxides and zinc aryloxides with a range of organosilanes to better understand the selectivity of these reactions and to better characterize the bond cleavage and formation steps. Because the isolable To^{M}ZnH can be reacted with aliphatic alcohols and phenols, the relative rate law(s) and rates of these reactions will also be used to probe the overall mechanism of catalytic silane alcoholysis and develop new bond-forming catalytic conversions.

ASSOCIATED CONTENT

Supporting Information. Experimental procedures and characterization data for zinc complexes, conditions for catalytic conversions, kinetics data, and crystallographic data files (cif). This material is available free of charge via the Internet at http://pubs.acs.org.

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Funding Sources

This research was supported by the U.S. Department of Energy, Office of Basic Energy Sciences, Division of Chemical Sciences, Geosciences, and Biosciences through the Ames Laboratory (Contract No. DE-AC02-07CH11358).

ACKNOWLEDGMENT

We thank the late Prof. Victor S.-Y. Lin for his support as a colleague, mentor, and friend. Aaron D. Sadow is an Alfred P. Sloan Fellow.

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