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Unexpected Role of Zinc Hydride in Catalytic Hydrosilylation of Ketones and Nitriles

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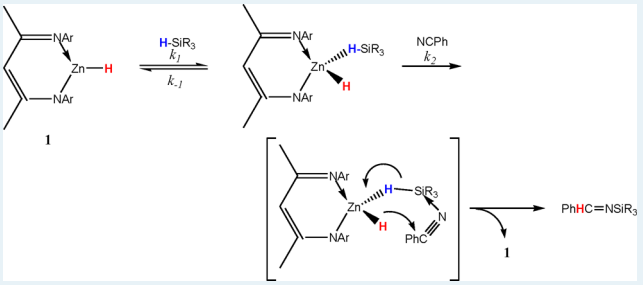
Supporting Information

ABSTRACT: The hydride compound DippNacNacZnH (**1**) catalyzes chemoselective hydrosilylation of ketones and aldehydes under mild conditions and chemoselective reduction of nitriles to imines. Mechanistic studies showed that the product of nitrile insertion into the Zn−H bond of **1**, DippNacNacZn-N═C(H)(Ph) (**2**), is not a potent catalyst. Kinetic studies under catalytic conditions suggest a reversible coordination of silane to **1** to form an intermediate which then reacts with the substrate (nitrile or ketone) via a cyclic transition state to give the silylated product.

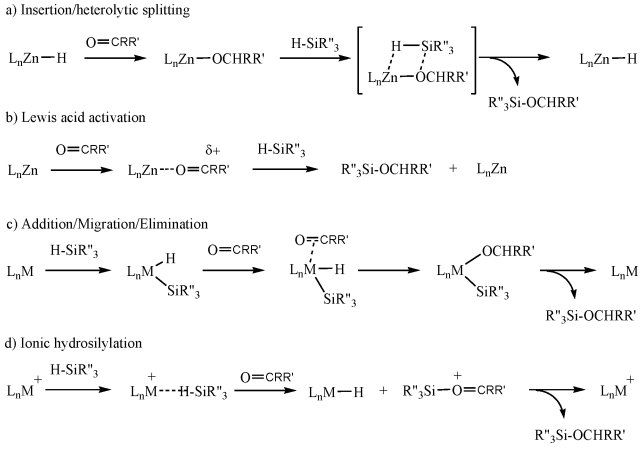


KEYWORDS: *hydrosilylation, zinc hydride, mechanism, nitrile, ketone*

There is a strong current interest in the replacement of precious metal catalysts with cheaper and more environmentally benign systems.[1,2] In this regard, the use of main group metals is very appealing.[3,4] For example, in the field of catalytic hydrosilylation, calcium,[5] boron,[6,7] and aluminum[8] catalysts have been reported. In this context, zinc, an inexpensive, earth abundant and biocompatible[9] post-transition element appears to be an excellent candidate.[10] Although zinc-catalyzed hydrosilylation has been studied for a few decades,[11−13] it is limited mainly to aldehydes, ketones, and imines, and only very recently have applications to more challenging substrates, such as esters,[14] amides,[15] and CO_2,[16] been reported. It is usually postulated that these hydrosilylations proceed via intermediate formation of a zinc hydride,[10,11a,b,d,h,o,12a,c,15] but only in very few cases were well-defined hydride catalysts used.[11m,16] For the latter reactions, it is usually assumed that the substrate (e.g., ketone) inserts into the Zn−H bond followed by the reaction of the product (e.g., zinc alkoxide) with silane (Scheme 1a).[11b,h,m,16a,17,18] As an alternative, Lewis acid activation of the substrate by zinc followed by hydride transfer from the silane is also proposed (Scheme 1b).[11g,j,k] Given the recent finding of a nonhydride mechanism for a variety of metal catalysts,[19] elucidation of the exact role of zinc hydrides in catalysis is of importance.

Another impetus for our research was the recent discovery of chemoselective hydrosilylation of nitriles to synthetically useful *N*-silyl imines, a process that required the use of a Ru catalyst.[20] Given the recent progress in the application of Ca and Mg hydrides in hydrosilylation,[3a,f] and in particular the stoichiometric insertion of such a challenging substrate as pyridine into the Mg−H bond, we became interested in exploring the related zinc hydrides. The well-defined zinc hydride, DippNacNacZnH

Scheme 1. Most Common Mechanisms for Metal-Catalyzed Hydrosilylation



(**1**; DippNacNac = {(ArN=)CMe-CH═CMe-NAr}$^-$ and Ar = 2,6-$Pr^i_2C_6H_3$) is known, but its reactivity has not been studied.[21] Here, we report chemoselective hydrosilylation of ketones and reduction of nitriles to imines catalyzed by **1** and disclose unusual cyclic mechanisms for these reactions.

We found that **1** brings about chemoselective hydrosilylation of aldehydes and ketones at room temperature. Primary ($PhSiH_3$) and secondary ($PhMeSiH_2$) silanes work well in this reaction, whereas tertiary silanes ($PhMe_2SiH$, Et_3SiH) and silicones (TMDS and PMHS) are less effective. Fortunately,

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Table 1. Hydrosilylation of Carbonyls Catalyzed by 1[a]

	substrate	time	yield[b]	product
1	PhCHO	15 min	>98%	$PhCH_2OSiR_3$
2	*p*-NCC_6H_4CHO	15 min	>98%	*p*-$NCC_6H_4CH_2OSiR_3$
3	PhCH=CHCHO	20 min	>98%	$PhCH{=}CHCH_2OSiR_3$
4	PhC(O)Me	7 h	84%	$PhCHMeOSiR_3$
5	*p*-$NCC_6H_4C(O)Me$	2 h	60%[c]	*p*-$NCC_6H_4CHMeOSiR_3$
6	*m*-$NCC_6H_4C(O)Me$	4.5 h	55%[c]	*m*-$NCC_6H_4CHMeOSiR_3$
7	*p*-$MeOC_6H_4C(O)Me$	24 h	82%	*p*-$MeOC_6H_4CHMeOSiR_3$
8	*m*-$NH_2C_6H_4C(O)Me$	24.3 h	86%	*m*-$NH_2C_6H_4CHMeOSiR_3$
9	*p*-$NO_2C_6H_4C(O)Me$	2.3 h	96%	*p*-$NO_2C_6H_4CHMeOSiR_3$
10	*p*-$EtO_2CC_6H_4C(O)Me$	5 h	82%	*p*-$EtO_2CC_6H_4CHMeOSiR_3$
11	Ph_2CO	22.3 h	38%	$Ph_2CHOSi(OEt)_3$
12	$C_5H_{10}CO$	2 d	0%	N.R.
13	$MeCO_2Et$	18 d	0%	N.R.
14	PhC(=NPh)H	24 h	0%	N.R.

[a]3% of **1**, $HSi(OEt)_3$, 0.6 mL of C_6D_6. [b]Determined by ^1H NMR. [c]Complete conversion after 21 h to a mixture of silanes $(EtO)_{4-x}Si(OCHMeC_6H_5CN)_x$ (x = 0−4).

Table 2. Hydrosilylation of Nitriles Catalyzed by 1[a]

	substrate	time	yield[b]	product
1	PhCN	7 h	86%	$PhCH{=}NSiR_3$
2	CH_3CN	5 h	12%	$CH_3CH{=}NSiR_3$, $CH_3CH_2N(SiR_3)_2$
3	$NCCHMeCH_2CH_2CN$	0.5 h	3%	$NCCHMeCH_2CH_2CH{=}NSiR_3$, $R_3SiN{=}CHCHMeCH_2CH_2CN$
4	*t*BuCN	2 d	>98%	*t*$BuCH{=}NSiR_3$
5	*m*-$O_2NC_6H_4CN$	3.3 h	89%	*m*-$O_2NC_6H_4CH{=}NSiR_3$
6	*p*-$MeOC_6H_4CN$	24 h	75%	*p*-$MeOC_6H_4CH{=}NSiR_3$
7	*p*-$NH_2C_6H_4CN$	4 d	0%	N.R.
8	*p*-$NCC_6H_4CO_2Et$	3 d	0%	N.R.
9	*m*-$NCC_6H_4CO_2Me$	4 d	0%	N.R.
10	$CH_2{=}CHCN$	30 h	0%	N.R.
11	3-$NC(C_5H_4N)$	7 d	0%	N.R.

[a]3% of **1**, $HSi(OEt)_3$, 0.6 mL of C_6D_6. [b]Determined by ^1H NMR.

the relatively inexpensive silane $HSi(OEt)_3$ is active, and thus it was chosen for reactivity screening. Benzaldehyde, 4-cyanobenzaldehyde and cinnamaldehyde were reduced to the corresponding silyl ethers in 15−20 min (Table 1, entries 1−3). Acetophenone was hydrosilylated in high yield at a good rate (entry 4). It is noteworthy that this catalytic system tolerates the presence of several important functionalities, such as cyano- (entries 2, 5−6), amino- (entry 8), nitro- (entry 9), and ester groups (entry 10). Electron-donating substituents in the aryl ring cause slower reaction rates (entries 7−8). On the other hand, the presence of electron-withdrawing groups resulted in faster hydrosilylation (entries 5, 9−10). Even the bulky benzophenone was reduced, albeit at a much slower rate and lower conversion (entry 11). However, attempted hydrosilylation of alkyl ketone (cyclohexanone, entry 12), ester (ethyl acetate, entry 13), and aldimine (entry 14) were unsuccessful.

Rewardingly, **1** also catalyzes chemoselective monoreduction of nitriles to *N*-silyl imines (Table 2), which is the first example of such catalysis without a transition metal. Benzonitrile was reduced rapidly at room temperature (entry 1), whereas alkyl nitriles containing a labile α-CH bond resulted in catalyst deactivation (entries 2−3). In contrast, *t*BuCN was successfully hydrosilylated, albeit at a much slower rate (entry 4). Like for aryl ketones, a withdrawing group in the ring facilitates the reduction (entry 5), whereas a donating group slows it down. However, the scope of functionalities that are tolerated is limited, and amino-, ester-, olefin-, and pyridine-containing substrates are not reduced (entries 8−11).

To elucidate the origin of chemoselectivity, and to understand the reactivity pattern, mechanistic studies were attempted. As a foreword, it is relevant to note that there are four main mechanistic scenarios in catalytic hydrosilylation (Scheme 1): (a) substrate insertion into the M-H bond followed by heterolytic cleavage of the Si−H bond on the M-X bond;[22] (b) Lewis acid activation of substrate on the metal followed by hydride transfer;[23] (c) substrate insertion into the M-H bond followed by oxidative addition of silane, migration, and reductive elimination (the Ojima mechanism);[24] and (d) ionic hydrosilylation via silane coordination to metal and hetrolytic splitting of the Si−H bond.[6a−c,25,26] We first established that stoichiometric reactions of compound **1** with silanes ($PhSiH_3$, $PhMeSiH_2$, and $HSi(OEt)_3$) do not take place, nor is there any H/D exchange between **1** and $PhSiD_3$ or $PhMeSiD_2$. In contrast, benzonitrile does react with **1** to give a vinylidenamido derivative **2** (Figure 1). Remarkably, kinetic studies showed that this reaction is second order in **1** and first order in nitrile concentration, which is at odds with the conventional insertion mechanisms shown in Scheme 1, a and c. The study of temperature dependence afforded a large negative entropy of activation ($\Delta S^{\ddagger}$ = −272.0 ± 1.7 J·mol^{-1}·K^{-1}, $\Delta H^{\ddagger}$ = 17.7 ± 0.5 kJ·mol^{-1}) suggesting an associative mechanism.

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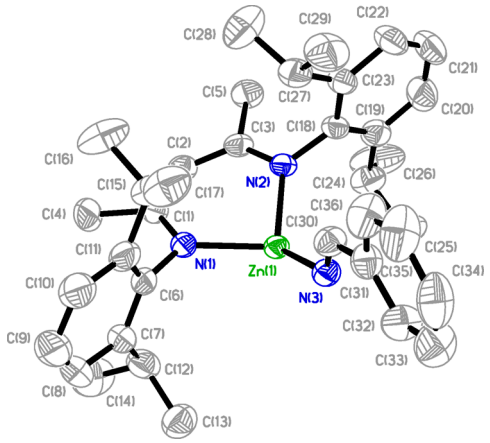
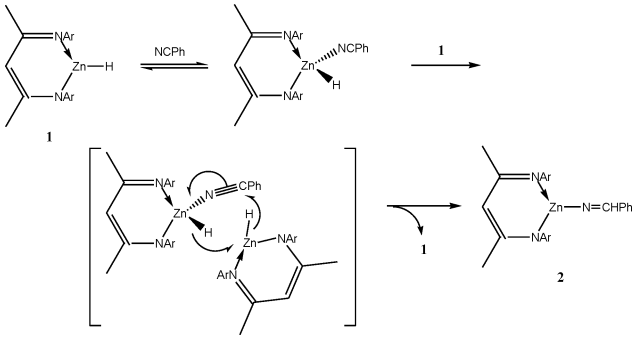


Figure 1. Molecular structure of compound **2** (thermal ellipsoids are shown at 50%, hydrogen atoms are omitted for clarity).

These kinetic data can be rationalized by a novel cyclic, six-membered mechanism shown in Scheme 2. The unusual

Scheme 2. Possible Mechanism for the Formation of Complex 2



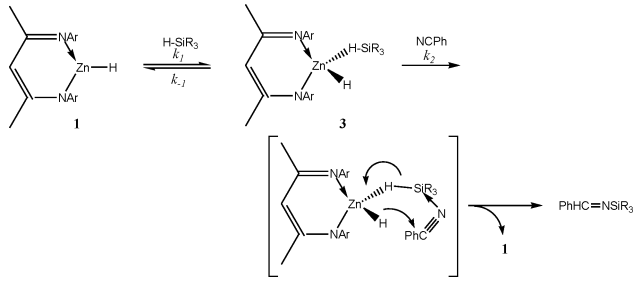
feature of this mechanism is that the zinc hydride plays a dual role as a Lewis acid activator and as a hydride transfer reagent. However, unlike transition metal catalysis where the reduction happens by coordination to the metal followed by hydride migration at the same metal center, reduction by zinc hydride requires the cooperative action of two zinc centers. Six-membered transition states in main group chemistry have precedents, for example in Meerwein–Ponndorf–Verley transfer hydrogenation[27] and in reduction of unsaturated substrates by aluminum alkyls.[28]

Although **2** looks like a possible first product in the insertion/silylation pathway of Scheme 1a, the reaction of **2** with silanes to regenerate the catalyst **1** does not occur, and indeed **2** is not a potent catalyst for nitrile hydrosilylation. Since the stoichiometric reactions were not consistent with any known mechanistic scenario, kinetic studies under catalytic conditions (3% of **1**) were performed. The kinetic data were linearized in the coordinates $-\ln([\text{silane}]/[\text{silane}]_0)$/time indicating first order kinetics in silane. The dependence of the k^{eff} on the amount of nitrile shows saturation behavior at large nitrile concentration ($k^{\text{eff}} = 1.3 \times 10^{-4}$ s^{-1}), which allowed us to derive the following kinetic law:[29]

$$\text{rate} = \frac{k_1 k_2[\mathbf{1}][\text{HSi(OEt)}_3][\text{nitrile}]}{k_{-1} + k_2[\text{nitrile}]}$$

Furthermore, carrying out the test for a nonhydride mechanism, that is, reacting complex **1** with 1 equiv of nitrile and 1 equiv of $DSiMe_2Ph$,[19] resulted in the formation of deuterated complex $\mathbf{1}_D$ and complete hydride transfer to the product $PhHC{=}NSiMe_2Ph$. Taken together, these kinetic and labeling experiments are consistent with the cyclic mechanism shown in Scheme 3. Complex **1** is in fast equilibrium with silane

Scheme 3. Proposed Cyclic Mechanism for 1-Catalyzed Hydrosilylation of Nitriles



to give the adduct **3**. However, unlike the ionic hydrosilylation shown in Scheme 1d, the silylium ion abstraction from the neutral species does not take place in nonpolar media. Rather, the substrate attacks **3** via a cyclic, 6e σ-aromatic transition state. Consistent with the Si–H cleavage in the rate-determining step, we found a kinetic isotope effect (KIE) of 1.4 for the reaction with the secondary silane $H_2SiMePh$ ($D_2SiMePh$). Further evidence for the existence of silane equilibrium shown in Scheme 3 comes from the observation of significant shifts of ^{1}H NMR resonances of groups proximal to the Zn center when **1** is treated with 20-fold excess silane (e.g., the Zn–H signal shifts from 4.392 to 4.328 ppm and the isopropyl Me shifts from 1.255 to 1.232 ppm), whereas other signals remain intact.

Similar kinetic studies for acetophenone afforded a k^{eff} of 2.0×10^{-4} s^{-1} and a KIE of 1.5, suggesting an analogous cyclic mechanism for hydrosilylation of ketones. We further carried out a catalytic competition experiment between benzonitrile and acetophenone. Despite the k^{eff} for both substrates being comparable, we observed preferential hydrosilylation of acetophenone (>50% conversion for acetophenone vs <2.5% for benzonitrile after 7 h), which suggests that the kinetic differentiation comes from the difference in k_2 in eq 1, that is, the rate of the reaction with substrate.

In summary, we discovered the first zinc-catalyzed chemoselective hydrosilylation of nitriles to *N*-silyl imines, and revealed a novel type of hydride mechanism involving activation of silane by a Lewis acidic zinc catalyst followed by an out-of-sphere zinc hydride transfer to the substrate via a concerted 6-membered cyclic transition state.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Details of kinetic studies and substrate screening. This material is available free of charge via the Internet at http://pubs.acs.org.

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Author Contributions

§Author I.K. performed the X-ray study.

Notes

The authors declare no competing financial interest.

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■ DEDICATION

Dedicated to Prof. Dr. Lutz Gade on the occasion of his 50th birthday/

■ ABBREVIATIONS

KIE kinetic isotope effect; TMDS tetramethyldisiloxane; PMHS polymethylhydrosiloxane

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