5-14-2010

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Abstract
An unusual β-elimination reaction involving zinc(II) and LiCl is reported. LiCl and a coordinatively saturated
disilazido zinc compound form an adduct that contains activated SiH moieties. In THF/toluene mixtures, this
adduct is transformed into a zinc hydride and 0.5 equiv. cyclodisilazane. The Li⁺ and Cl⁻ ions apparently
affect the reaction pathway of the disilazido zinc in a synergistic fashion. Thus, the zinc hydride and
cyclodisilazane products of formal β-elimination are not observed upon treatment of the zinc disilazide with
Cl⁻ or Li⁺ separately.

Keywords
Elimination reaction, Reaction pathways, zinc compounds, disilazane, lithium chloride, silane derivative,
silicon, tetrahydrofuran, toluene, biotransformation, crystal structure, cycloaddition, ion transport

Disciplines
Chemistry

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Conversion of a Zinc Disilazide to a Zinc Hydride Mediated by LiCl

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Organozinc compounds are valuable in synthetic chemistry as alkyl, aryl, and hydride transfer agents that complement organolithium and organomagnesium reagents.1 Importantly, alkali metal and alkaline earth metal salt adducts of zinc reagents give selective group transfer chemistry that is distinct from monometallic main group reagents, and related adducts facilitate selective arene, hydrocarbon, and alkylether metalations.2 Zn(II) centers also mediate physiological processes involving group transfer as in liver alcohol dehydrogenase (LADH), where hydride transfer from a zinc alkoxide to NAD+ facilitates by LiCl.

ToMZnCl (1) (To3 = tris(4,4-dimethyl-2-oxazolinyl)phenylborate) with Li(N(SiHMe2)2) in benzene readily provides To3ZnN(SiHMe2)2 (2), and no other products are detected by 1H NMR spectroscopy before or after workup. The spectroscopic features of the SiH, including its downfield chemical shift (5.26 ppm), high 1J(SH) (185 Hz), and ν(SH) (2110 cm⁻¹), are consistent with a normal disilazido ligand. An X-ray crystal structure (see Supporting Information) contains Zn···H and Zn···Si distances (2.98 Å and 3.06 Å) that are longer than the sums of van der Waals radii. Although 2 is formed quantitatively in benzene, in a benzene (10 mL) and THF (2 mL) mixture, the compounds 2, 1, and To3ZnH (3) (identified later) are present in a ratio of 20:1:8 upon workup after 24 h. Additionally, 1,3-diaza-2,4-disilacyclobutane (Me2HSiN-SiMe2)12 is observed. This cyclosilazidane is the head-to-tail dimer of silaime Me2HSiN=SiMe2; its formation and the presence of zinc hydride 3 suggest a β-elimination reaction. Reactions of lithium hydrosilazides and group 14 electrophiles (e.g., Me3SiCl) in hexane give cyclosilazidanes, and silaamines are suggested as intermediates in one of the two proposed mechanisms.13 These literature transformations require nonpolar media, and THF solvent gives substitution rather than elimination. Our zinc system contrasts with that of Me3SiCl, with nonpolar solvents giving substitution and THF favoring elimination. Neither HN(SiHMe2)2 and LiCl nor mixtures of 1, HN(SiHMe2)2, and LiCl afford the cyclosilazidane.

The identity of zinc hydride 3 is provided by its independent preparation in a two-step sequence. Reaction of 1 and KOt-Bu provides To3ZnOr-Bu (4). As shown in Scheme 1, PhMeSiH2 and 4 react to give 3. Notably, 2 and PhMeSiH2 do not readily provide 3, presumably due to the hindered, non-nucleophilic nature of the zinc disilazide. The IR spectrum of 3 contains a ν(ZnH) (1745 cm⁻¹), KBr, and the ZnH resonance appears at 4.29 ppm in the 1H NMR spectrum (cf. HB(3-Bupz)ZnH, δ(H) 5.36; ν(ZnH) 1770 cm⁻¹).13 A single crystal X-ray diffraction study reveals that 3 is monomeric and contains a terminal zinc hydride, of which there are relatively few crystallographically studied examples including the four-coordinate TpBu4ZnH and TpPh,Me4ZnH (for which the ZnH are not located)13 and a three-coordinate diketiminate ZnH (Zn−H 1.46(2) Å).10 The four-coordinate ZnH in 3 (1.52(2) Å) is longer by 0.06 Å.

Li(N(SiHMe2)2) and 1 react in THF-d6 to provide possible intermediates in the apparent β-elimination process. Two C₃ symmetric compounds are detected after 10 min, rather than C₅ symmetric 1, 2, and 3. After 12 h at room temperature, the minor species is partly converted into 3 and (Me2HSiN−SiMe2). Attempts to isolate these intermediates from toluene/THF solvent mixtures (crystallization conditions) afford crystals of 3.

We suspect that the intermediates formed from 1 and Li(N(SiHMe2)2) in THF were LiCl adducts. Therefore, LiCl and zinc disilazide 2 were allowed to interact. A crystallized sample of the 1:1 LiCl/2 adduct (5) has the same 1H NMR spectrum as 1:1...
Li\(_2\)N(SiHMe\(_2\))\(_2\) (major isomer). The \(v_{\text{SiH}}\) of this material is lower (2061 cm\(^{-1}\)) than in the case of 2, and the \(1/2\)\(v_{\text{SiH}}\) (102 Hz) is significantly lower. Compound 5 is fluxional, as it crystallizes at \(-80\) °C from THF with a \(C_2\)-symmetric structure (Figure 1). Although spectroscopic features suggest [M]–SiH interactions, there are no close contacts between the SiH moieties and the Zn or Li centers in 5. Additionally, this interesting structure contains an unusual O-Li-N-Zn-coordinated bridging oxazoline group. The phenyl group on boron and the chloride on zinc are disposed syn, as are the N-lithiated oxazoline and N(SiHMe\(_2\)) groups. Because Li\(^+\) and Cl\(^-\) are separate in 5, we investigated these ions independently to determine their role in the formal \(\beta\)-elimination.

Figure 1. ORTEP diagram of 5 drawn at 35% probability.

Treatment of 2 with \([n\text{-Bu}][\text{Cl}]\) in a mixture of benzene-\(d_6\) and THF-\(d_8\) also gives two \(C_2\)-symmetric species. One of the isomers crystallizes and was structurally characterized as \([n\text{-Bu}][\text{NH}]\)\((\text{ac}^\beta-\text{ToM})\)\(\text{ZnClN(SiHMe}_2\)\(_2\))\(_2\)) (6). The IR spectrum (KBr) of 6 shows a broad, intense \(v_{\text{SiH}}\) at 2036 cm\(^{-1}\) which is notably lower energy than in the case of 2 (2110 cm\(^{-1}\)) and 5 (2061 cm\(^{-1}\)). The \(1/2\)\(v_{\text{SiH}}\) values in 6 (178 Hz) are slightly lower than in the case of 2 (185 Hz). After 1 week, neither 3 nor (Me\(_2\)HSiN-SiMe\(_2\))\(_2\) is observed, and no change is detected in the \(1H\) NMR spectrum. Thus, although addition of Cl\(^-\) affects the \(v_{\text{SiH}}\) of the disilazide, it does not promote \(\beta\)-elimination from the Zn(II) amide.

Addition of [Li(\text{Et}_2\text{O})\(_2\)][\text{B}(\text{CF}_3)\(_2\)\(_2\)] to 2 in benzene-\(d_6\)/THF-\(d_8\) mixtures results in oxazoline ring-opening giving O=Si bond formation and formal transfer of hydrogen from silicon to the (former) imidine carbon (eq 1).

A bimolecular transformation, in which a Zn–N bond of 5 reacts with a Si–H bond of a second molecule, might also explain the \(\beta\)-H elimination chemistry. However, THF-\(d_8\) solutions of 5 and Et\(_3\)SiH (as a competitive tertiary SiH group) give To\(\text{ZnH}\) and cyclosilazilane, while the Et\(_3\)SiH is unreacted. Also, only starting materials are observed upon treatment of 2 with Et\(_3\)SiH, ruling out an intermolecular dehydrocoupling-type mechanism.

Clearly, Li\(^+\) and Cl\(^-\) have a synergistic effect in this \(\beta\)-elimination reaction through the formation of the adduct 5, and this requirement is surprising given the coordinative and electronic saturation in both 2 and 5. It is tempting to suggest that Cl\(^-\) dissociation from 5 gives a three-coordinate zinc center that undergoes \(\beta\)-elimination. However, such a mechanism requires an unlikely 2\(\times\) repetition of a Cl\(^-\) coordination and dissociation sequence since the final product, To\(\text{ZnH}\), does not form a detectable adduct with LiCl, and Cl\(^-\) appears to be necessary to inhibit oxazoline ring-opening. Cl\(^-\) also does not appear to bind to silicon, as H-transfer is not observed in the absence of Li\(^+\). Furthermore, addition of the Lewis acids BP\(_3\) or B(\text{C}_\(_6\)\text{F}_5\)\(_2\)) to 6 does not provide cyclosilazilane, suggesting that Li\(^+\) is not acting as a Lewis acid in 5 to mediate hydride transfer.

Lithium chloride also affects the electronic properties of the disilazide ligand, as shown by the spectroscopy of the \(\beta\)-SiH moiety. This electronic effect may be more significant than a low coordination number for zinc because the dicoordinate Zn(N(SiHMe\(_2\))\(_2\)\(_2\)) is not reported to undergo \(\beta\)-elimination.\(^{14}\) Therefore, we favor a mechanism in which the zinc hydride is formed from the four-coordinate \([\text{ac}^\beta\text{-ToM})\text{ZnClN(SiHMe}_2\)\(_2\])]\(. Given the importance of Zn-mediated reactions in synthetic, catalytic, and enzymatic chemistry, we are currently investigating related zinc amido, alkyl, and alkoxide compounds in \(\beta\)-H and group transfer reactions.

Acknowledgment. Dr. Bruce Fulton is thanked for valuable NMR assistance. The U.S. DOE Office of Basic Energy Science (DE-AC02-07CH11358) and the ACS Green Chemistry Institute-PRF provided financial support. A.D.S. is an Alfred P. Sloan Fellow.

Supporting Information Available: Experimental procedures and crystallographic data for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

References


JA102323G