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+ is proposed.3 A connection between synthetic and physiological zinc chemistry is provided by molecular coordination complexes such as tris(pyrazolyl)borato zinc alkoxides and hydroxide that model LADH,4 carbonic anhydrase,5 and phosphatase.6 Likewise, hydrolase-like transesterifications are catalyzed by tris-1,1,1-(oxazolinyl)ethane zinc dicarboxylato and ditrifluoro compounds for kinetic resolution of chiral esters.7

Given the importance of zinc-mediated group transfer chemistry, it is interesting that β-hydrogen elimination is not a common pathway for organozinc compounds. For example, ZnEt2 undergoes β-elimination only upon IR laser pyrolysis at 600–650 °C, whereas thermal treatment results in Zn-C bond homolysis.8 Few solution phase β-eliminations have been suggested, most notably in the thermolysis of [NaZnEt3] under reducing conditions.9 A three-coordinate diketiminate zinc hydride is prepared from the corresponding zinc chloride and KNH heteroleptic zinc 1,2 intermediate.10 β-Elimination was also proposed as an initiation step in a zinc-catalyzed ketone hydroisilylation.11 Identification of conditions that favor or disfavor β-H elimination in zinc(II) compounds may have important implications in group transfer reactions in synthetic and enzymatic chemistry. Here, we report a coordinatively saturated oxazolinylborato disilazidozinc(II) compound that undergoes a formal β-H elimination at room temperature facilitated by LiCl.

Treatment of To³ZnCl (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 JSiH (185 Hz), and νSiH (2110 cm⁻¹), are consistent with a normal disilazide 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 cyclodisilazide is the head-to-tail dimer of sililam 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 cyclodisilazanes, 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 cyclodisilazane.

The identity of zinc hydride 3 is provided by its independent preparation in a two-step sequence. Reaction of 1 and Koh-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 νZnH (1745 cm⁻¹) and a νSiH (1770 cm⁻¹).14 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 Tp³BuZnH and Tp²MeZnH (for which the ZnH are not located)15 and a three-coordinate diketiminate ZnH (Zn-H 1.46(2) Å).16 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-δ6 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)2. Attempts to isolate these intermediates from toluene/THF solvent mixtures (crystallization conditions) afford crystals of 3.

We suspected that the intermediates formed from 1 and LiN(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(N(SiHMe₂)₂)/I (major isomer). The νSiH of this material is lower (2061 cm⁻¹) than in the case of 2, and the 1/JSiH (102 Hz) is significantly lower. Compound 5 is fluxional, as it crystallizes at −80 °C from THF with a C₅-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(SiHMe₂)₂ groups. Because Li⁺ and Cl⁻ are separate in 5, we investigated these ions independently to determine their role in the formal β-elimination.

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

Treatment of 2 with [n-Bu₂N]Cl in a mixture of benzene-d₆ and THF-d₆ also gives two C₅-symmetric species. One of the isomers crystallizes and was structurally characterized as [n-Bu₂N][κ²-ToMo]ZnClN(SiHMe₂)₂] (6). The IR spectrum (KBr) of 6 shows a broad, intense νSiH 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/JSiH values in 6 (178 Hz) are slightly lower than in the case of 2 (185 Hz). After 1 week, neither 3 nor (Me₂HSiN-SiMe₂)₂ is observed, and no change is detected in the ¹H NMR spectrum. Thus, although addition of Cl⁻ affects the νSiH of the disilazide, it does not promote β-elimination from the Zn(II) amide.

Addition of [Li(Et₂O)[B(C₆F₅)₄] to 2 in benzene-d₆/THF-d₆ 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 β-H elimination chemistry. However, THF-d₆ solutions of 5 and Et₃SiH (as a competitive tertiary SiH group) give To³ZnH and cyclodisilazane, while the Et₃SiH is unreacted. Also, only starting materials are observed upon treatment of 2 with Et₃SiH, ruling out an intermolecular dehydrocoupling-type mechanism.

Clearly, Li⁺ and Cl⁻ have a synergistic effect in this β-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 β-elimination. However, such a mechanism requires an unlikely 2× repetition of a Cl⁻ coordination and dissociation sequence since the final product, To³ZnH, 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 BP₃ or (C₆F₅)₃Sn to 6 does not provide cyclodisilazane, 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 β-SiH moiety. This electronic effect may be more significant than a low coordination number for zinc because the dicoordinate Zn(N(SiHMe₂)₂)₂ is not reported to undergo β-elimination.14 Therefore, we favor a mechanism in which the zinc hydride is formed from the four-coordinate [(κ²-ToMo]ZnClN(SiHMe₂)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 β-H and group transfer reactions.

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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


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