

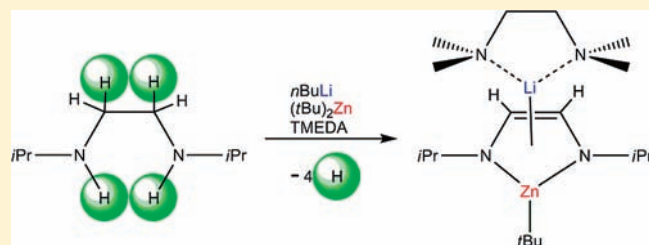
Main Group Multiple C–H/N–H Bond Activation of a Diamine and Isolation of A Molecular Dilithium Zincate Hydride: Experimental and DFT Evidence for Alkali Metal–Zinc Synergistic Effects

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S Supporting Information

ABSTRACT: The surprising transformation of the saturated diamine $(i\text{Pr})\text{NHCH}_2\text{CH}_2\text{NH}(i\text{Pr})$ to the unsaturated diazaethene $[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]^{2-}$ via the synergic mixture $n\text{BuM}$, $(t\text{Bu})_2\text{Zn}$ and TMEDA (where $M = \text{Li}, \text{Na}$; TMEDA = N,N,N',N' -tetramethylethylenediamine) has been investigated by multinuclear NMR spectroscopic studies and DFT calculations. Several pertinent intermediary and related compounds $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{NH}(i\text{Pr})]\text{Zn}(t\text{Bu})_2$ (**3**), $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})$ (**5**), $\{(\text{THF})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})\}_2$ (**6**), and $\{(\text{TMEDA})\text{Na}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})\}_2$ (**11**), characterized by single-crystal X-ray diffraction, are discussed in relation to their role in the formation of $(\text{TMEDA})\text{M}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})$ ($M = \text{Li}, \text{Na}$, **10**). In addition, the dilithio zincate molecular hydride $[(\text{TMEDA})\text{Li}]_2[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})\text{H}$ **7** has been synthesized from the reaction of $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{NH}(i\text{Pr})]\text{Zn}(t\text{Bu})$ **3** with $n\text{BuLi}(\text{TMEDA})$ and also characterized by both X-ray crystallographic and NMR spectroscopic studies. The retention of the $\text{Li}-\text{H}$ bond of **7** in solution was confirmed by $^7\text{Li}-^1\text{H}$ HSQC experiments. Also, the ^7Li NMR spectrum of **7** in C_6D_6 solution allowed for the rare observation of a scalar $^1J_{\text{Li}-\text{H}}$ coupling constant of 13.3 Hz. Possible mechanisms for the transformation from diamine to diazaethene, a process involving the formal breakage of four bonds, have been determined computationally using density functional theory. The dominant mechanism, starting from $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})$ (**4**), involves the formation of a hydride intermediate and leads directly to the observed diazaethene product. In addition the existence of **7** in equilibrium with **4** through the dynamic association and dissociation of a $(\text{TMEDA})\text{LiH}$ ligand, also provides a secondary mechanism for the formation of the diazaethene. The two reaction pathways (i.e., starting from **4** or **7**) are quite distinct and provide excellent examples in which the two distinct metals in the system are able to interact synergically to catalyze this otherwise challenging transformation.



INTRODUCTION

The field of utility organometallics is increasingly turning to more complex mixed-metal systems to deliver superior results, whether this be for metal–halogen exchange,^{1–24} alkylation,^{25–42} insertion,^{7,10,43–56} or the trapping of reactive intermediates.^{57–60} In theory, mixed-metal reagents can offer more flexible, tunable solutions to any problem compared to more traditional monometallic alternatives due to the increased number of components which can be varied. Furthermore, the different metal centers and ligand sets can exhibit cooperativity (or synergism) to produce new reactivities inaccessible to the monometallic components.

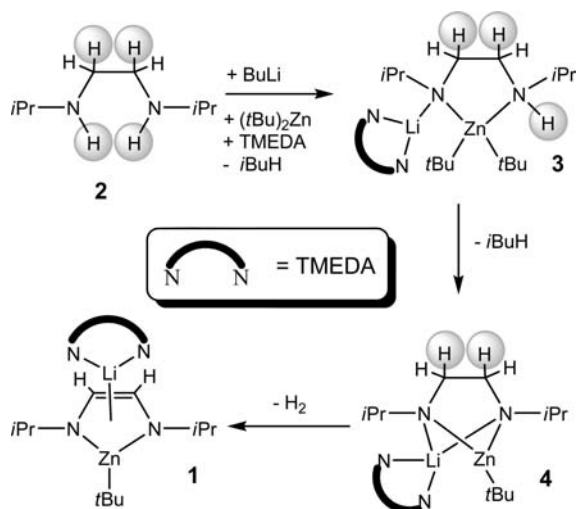
Hydrogen abstraction is an area in which the lure of such mixed-metal systems is proving to be irresistible.^{61–63} The combination of an alkali metal with a range of different subordinates (i.e., metals that would be expected to be less reactive than the alkali metals - Zn ,^{64–95} Mg ,^{96–119} Mn ,^{109,120–125} Cr ,¹²⁶ Fe ,^{126,127} Cu ,^{128,129} Cd ,^{93,101,130–133} Al ^{157,60,134–136}) have been integrated with a diverse array of ligands (alkyl, amido, alkoxy, halide) and have been efficiently deployed in both ethereal and

hydrocarbon media to overcome some of the great challenges facing deprotonation chemistry such as the incapability to metalate low Brønsted acidity substrates, lack of compatibility with sensitive functionalities, low selectivity and the need to perform reactions under cryogenic conditions. This is exemplified in the successful application of the alkylamido zincate $(\text{TMEDA})\text{Na}(\text{TMP})\text{Zn}(t\text{Bu})_2$.^{70,74,77,85,87,88} Recently our own group has started to investigate the use of diamines in a bimetallic context, reporting in a communication the synthesis of the diazaethene zincate complex $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})$ **1**.¹³⁷ 1,3-Diazabutadiene ligands, from which diazaethene ligands are often prepared, are increasingly important within coordination chemistry due to their flexible coordination modes and redox properties.^{138–149} The synthesis of this complex from the fully saturated $(i\text{Pr})\text{NHCH}_2\text{CH}_2\text{NH}(i\text{Pr})$ (diisopropylethylenediamine) **2** (Scheme 1) displayed a new

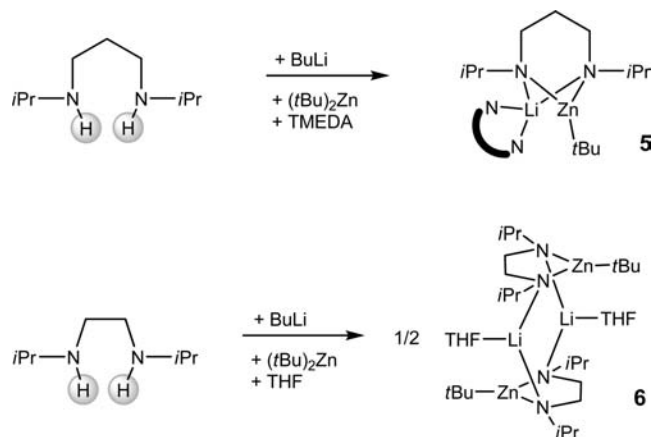
Received: June 15, 2011

Published: July 21, 2011

Scheme 1. Multiple CH Activation of Diisopropylethylenediamine **2 Using a Synergic Lithium/Zinc Mixture To Generate the Unsaturated Diazaethene Product **1****



Scheme 2. Synthesis of the Monomeric (Dinuclear) and Dimeric (Tetranuclear) Fully Saturated Complexes (TMEDA)Li[(iPr)NCH₂CH₂CH₂N(iPr)]Zn(tBu) **5 and {(THF)Li[(iPr)NCH₂CH₂N(iPr)]Zn(tBu)}₂ **6**, Respectively**



mode of hydrogen activation previously unseen within zincate chemistry. We now report a detailed mechanistic overview of this surprising transformation from both experimental and theoretical perspectives.

RESULTS

Synthesis and Molecular Structures. As reported previously, the cocomplexation of the monolithiated diamine Li[(iPr)NCH₂CH₂NH(iPr)] with (tBu)₂Zn(TMEDA) at 0 °C gives the expected product (TMEDA)Li[(iPr)NCH₂CH₂NH(iPr)]Zn(tBu)₂ **3** (Scheme 1).¹³⁷ In a fashion similar to that of the two-step mechanism for monoamido zincates originally proposed by Uchiyama et al.,^{82,150,151} the amino N–H group of **3** is rapidly deprotonated by a tBu ligand to form the dimetalated diamido (TMEDA)Li[(iPr)NCH₂CH₂N(iPr)]Zn(tBu) **4** with the evolution

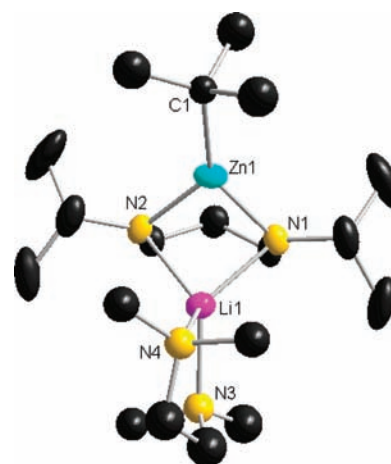


Figure 1. Molecular structure of the diamido zincate (TMEDA)-Li[(iPr)NCH₂CH₂CH₂N(iPr)]Zn(tBu) **5**. Hydrogen atoms and disordered tBu/TMEDA components have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level.

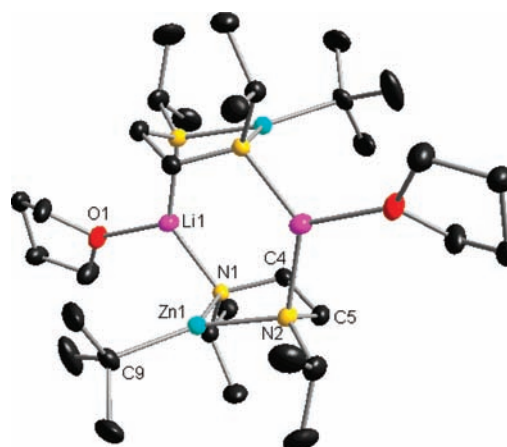
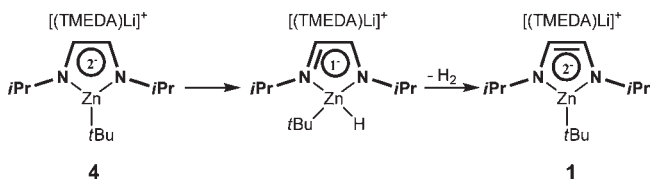


Figure 2. Molecular structure of the THF solvated lithium zincate {(THF)Li[(iPr)NCH₂CH₂N(iPr)]Zn(tBu)}₂ **6**. Hydrogen atoms and minor disordered tBu/THF components have been omitted for clarity. Symmetry operation to generate equivalent atoms: 1–x, –y, 1–z. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Zn1–N1, 2.019(2); Zn1–N2, 1.986(2); Zn1–C9, 2.019(9); Li1–N1, 2.001(4); Li1–N2(a), 2.041(4); Li1–O1, 2.004(4); N1–C4, 1.471(3); N2–C5, 1.470(3); C4–C5, 1.530(3); N1–Zn1–N2, 91.20(7); N1–Zn1–C9, 127.5(2); N2–Zn1–C9, 141.2(2); N1–C4–C5–N2, 50.0(2); N1–Li1–N2(a), 127.0(2); N1–Li1–O1, 117.7(2); N3–Li1–O1, 114.9(2).

of iBuH. Although diamido **4** has thus far not crystallized, it has been characterized by multinuclear NMR spectroscopy, and we have succeeded in the crystallographic identification of several analogous structures.

Using the homologous (iPr)NHCH₂CH₂CH₂NH(iPr) (diisopropylpropylenediamine), the dimetalated diamido (TMEDA)Li[(iPr)NCH₂CH₂CH₂N(iPr)]Zn(tBu) **5** (Scheme 2 and Figure 1) could be crystallized from the corresponding reaction of Li[(iPr)NCH₂CH₂CH₂NH(iPr)] with (tBu)₂Zn(TMEDA). Unfortunately, the crystal data are of insufficient quality to allow discussion of the geometric parameters of the structure, but the connectivity is definite. Zincate **5** contains an NCCCNZn

Scheme 3. Proposed Reaction Pathway for the Formation of 1 Highlighting the Redox Chemistry and Changing Charge Associated with the Chelating Diisopropylethylenediamide Ligand



six-membered ring in a boat-type conformation. The diamido ligand thus chelates the Zn center while its two *iPr* arms are oriented out of the plane of the ring. The (TMEDA)Li cation is coordinated to the hull of the boat, anchored exclusively to the two secondary amido groups to produce a puckered LiN₂ZnN four-membered ring. A *tBu* ligand completes the distorted trigonal planar configuration of the zinc atom. ¹H NMR spectroscopic studies confirm the fully saturated nature of the propylene bridge with methylene resonances at 3.33, 2.95, and 1.93 ppm, while no characteristic diazaethene resonances were present in the 5–6 ppm region.

On utilizing THF as a donor ligand in the absence of TMEDA, in a repeat of the synthesis of 4, the dimeric THF-solvated product $\{[(\text{THF})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})]\}_2$ 6 was isolated and subsequently crystallographically characterized (Scheme 2 and Figure 2). Lithium zincate 6 has a centrosymmetric molecular structure consisting of two $[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})$ complex anions, juxtaposed, and bridged by two (THF)Li cations to produce an eight-membered (LiN₂ZnN)₂ ring. The cyclic conformation of 6 allows for the symmetrical coordination of each amido group to one lithium and one zinc center. Both sets of metal centers occupy distorted trigonal planar geometries. The *iPr* groups on the amido ligands lie *syn* with respect to the ZnNCCN ring, while the nonplanar nature of the diamide (N1–C4–C5–N2 torsion angle of 50.0(2)°) as well as its N–C [1.471(3) Å] and C–C [1.530(3) Å] bond distances, which are comparable with those found in the ruthenium complex $[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{RuH}_2(\text{CO})_5$ [N–C, 1.48(1) Å; C–C, 1.52(1) Å],¹⁵² establish that the CH₂CH₂ backbone remains saturated.

Mechanistic Considerations. To gain mechanistic insight a detailed NMR spectroscopic study was carried out on the reaction between the monometallic compounds Li[(*iPr*)NCH₂CH₂NH(*iPr*)] and (*tBu*)₂Zn(TMEDA). A ⁷Li NMR spectrum of isolated crystals of the cocomplexation product (TMEDA)-Li[(*iPr*)NCH₂CH₂NH(*iPr*)]Zn(*tBu*)₂ 3 in C₆D₆ solution reveals two major resonances at –0.37 ppm and 0.63 ppm, suggesting a mixture of products. When this solution is gently warmed and reanalyzed, the resonance at –0.37 ppm is absent, intimating that the product associated with this low-frequency resonance has been fully consumed, and only the resonance at 0.63 ppm remains (see Figure S24 in Supporting Information). This is consistent with the disappearing resonance at –0.37 ppm representing the bisalkyl zincate 3 which, via an intramolecular deprotonation and concomitant release of *iBu*H, forms the diamido complex 4. Further support for this interpretation can be found when considering how close the signal assigned to complex 4 (0.63 ppm) comes to that of the structurally analogous propylene derivative 5 (0.75 ppm, i.e. a difference of only

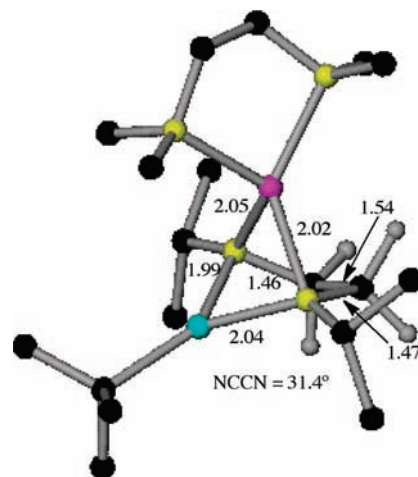


Figure 3. Optimized geometry of 4 with key distances shown in Å. All H atoms, except those involved in the reaction, are omitted for clarity. NCCN refers to the torsion angle (in degrees) of the diamido ligand.

0.12 ppm). When the reaction was repeated *in situ* at 0 °C and an aliquot removed and analyzed by ⁷Li NMR spectroscopy, two pertinent resonances at –2.39 ppm, and 1.71 ppm, as well as the resonance belonging to the previously identified intermediate 4, are present (see Figure S24 in Supporting Information). ⁷Li DOSY NMR experiments reveal that the intermediate responsible for the resonance at 1.71 ppm has a molecular weight similar to that of 4 (see Figure S25 in Supporting Information), presumably ruling out an aggregation process for the formation of this, as yet, unidentified species. Comparison with the ⁷Li NMR spectra of the diazaethene 1 in C₆D₆ reveals that the signal at –2.39 ppm is the result of a trace amount of this final product. Due to the highly reactive, transient nature of the bis-alkylzincate 3, its presence is not detected in this *in situ* NMR study. Another aliquot of the solution was removed after a 2-day stir at room temperature, but the recorded ⁷Li NMR spectrum indicated no significant compositional change had taken place. Aliquots were then removed after 5 min, 1 h, and 2 h reflux time, and the recorded spectra revealed a gradual transformation from the saturated intermediate 4 to the unsaturated final product 1. After 2 h reflux, decomposition of the reaction mixture is evidenced by the deposition of a black solid. Any further intermediates along the reaction pathway must be too short lived to be visible on the NMR time scale.

The next step in the reaction pathway 4 → 1 has been shown to likely proceed through a hydride intermediate as we successfully trapped a hydride by using the electrophilic ketone (*tBu*)₂CO. The hydride produced can then deprotonate the now allylic proton on the ethylene bridge to give the final product. This process could be described as proceeding via β-hydride elimination. The system must then find a way of solubilizing and activating the produced LiH, which is normally insoluble in hydrocarbon solvents. A more typical dehydrogenation pathway involving redox active transition metals, such as those reported by Brookhart,^{153,154} can be ruled out as there are no redox-active metals present in our alkali metal–zinc system to facilitate the transformation. Instead, the reaction could be envisaged to proceed through a ligand-sited oxidation followed by a reduction (Scheme 3). This reaction can thus be said to exploit a unique three-way cooperation, where the chemical properties of the two metals and the ethylenediamide ligand combine to allow a type of chemistry otherwise unavailable.

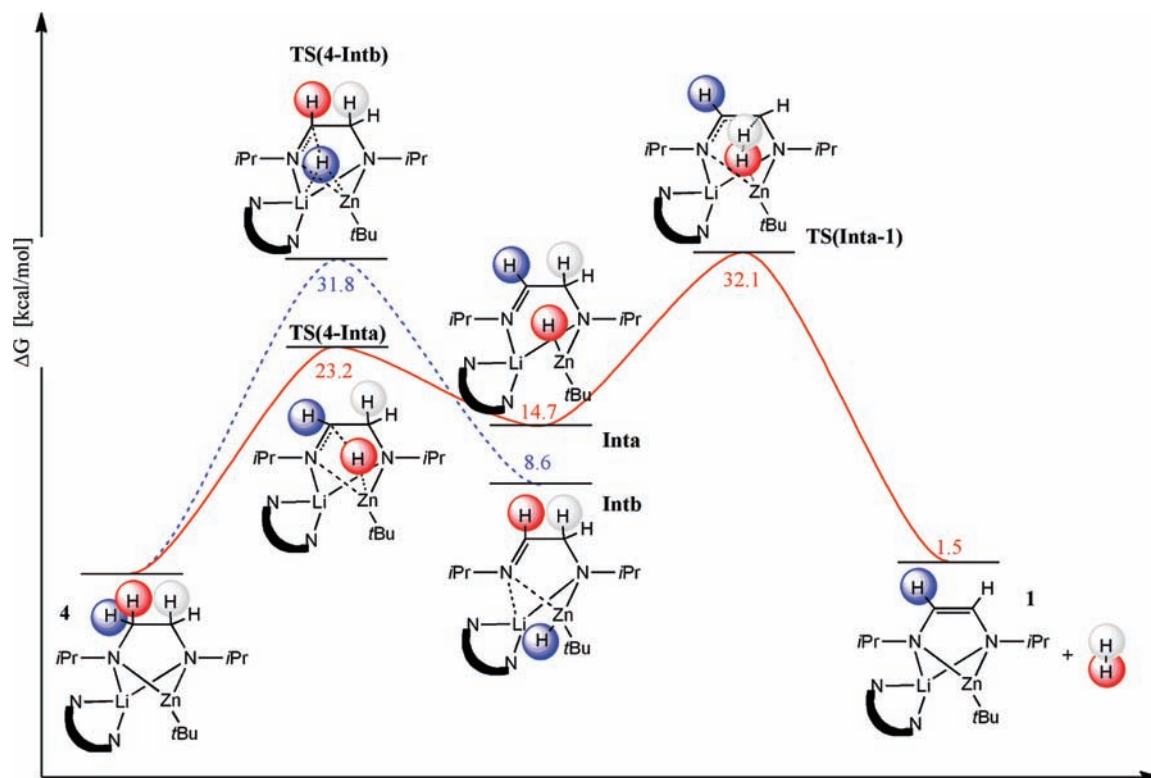


Figure 4. Free energy (ΔG) profile for the formation of **1** from **4** via a hydride intermediate. Free energies in kcal/mol. The path in red corresponds to the formation of the hydride intermediate above the ring plane (**Inta**), while the path in blue corresponds to the formation of the hydride intermediate below the ring plane (**Intb**).

DFT Calculations of Conversion of 4 to 1. In order to explore the possible pathways by which this reaction could proceed we carried out detailed mechanistic investigations using density functional theory (DFT, see the Supporting Information for full details on the level of theory employed) in order to explore the potential energy surface (PES) associated with the proposed mechanisms. We initially inspected the structure and stability of the monomer species **4** at the DFT level of theory. In agreement with the three-carbon bridge analogue (**5**, Figure 1), **4** is found to be a stable minimum on the PES with the diamido ligand coordinated to the Zn atom (N–Zn: 2.04 Å and 1.99 Å) to form a five-membered ring (NCCNZn) in a slightly twisted (NCCN torsion of 31.4°) envelope conformation with the Zn atom below the NCCN plane, (Figure 3). The (TMEDA)Li cation is coordinated directly above the two N atoms of the five-membered ring by two essentially equivalent Li–N interactions (2.02 Å and 2.05 Å, Figure 3). Based on the optimized structure of **4** two different mechanisms by which the proposed zinc hydride species could be formed are possible.

The H atom could be initially abstracted by the Li cation to form a Zn–H bond below the plane of the ring, or direct abstraction by the Zn to form the Zn–H bond above the ring plane. Optimization of the two hydride intermediate structures revealed that both were stable minima on the PES but were formed in endothermic reactions relative to **4** (Figure 4). The intermediate with the H atom above the NCCN plane (**Inta**) is destabilized by 14.7 kcal/mol (ΔG) relative to **4**, while the intermediate with the H atom below the plane (**Intb**) is destabilized by 8.6 kcal/mol (ΔG), relative to **4**. While both reactions are endothermic, the relative stabilities of the intermediates are not

sufficiently different to determine which pathway is more favorable. Therefore, we characterized the transition states leading to the intermediate structures in order to determine whether there was a kinetic preference toward either species. The activation barrier associated with the formation of **Inta** is 23.2 kcal/mol (ΔG^*), compared to a barrier of 31.8 kcal/mol (ΔG^*) for the formation of **Intb**. An activation barrier of 31.8 kcal/mol is still accessible under the experimental conditions employed in the reactivity of **4**; thus, while **Inta** is expected to be preferentially formed as an initial hydride intermediate in the formation of the diazaethene product (**1**), we also considered **Intb** as a potential intermediate from which the second hydrogen abstraction could occur. Abstraction of the second H atom from **Inta** occurs with a barrier of 17.4 kcal/mol, relative to **Inta**, (ΔG^*) in an exothermic reaction ($\Delta G = -13.2$ kcal/mol) to generate H₂ and the final product **1**. However, despite exhaustive sampling, no transition state could be located that corresponded to the formation of H₂ and **1** starting from **Intb**. Therefore, the overall reaction **4** → **1** + H₂, which is essentially thermoneutral ($\Delta G = 1.5$ kcal/mol, Figure 4), appears to preferentially occur via the hydride **Inta**.

The relative stabilities of **TS(4-Inta)** and **TS(4-Intb)** (Figure 4) are dictated by the different roles that the Li and Zn centers play in the two different mechanisms. In both transition states, in order for the Zn–H bond to be formed, one Zn–N bond must be broken such that the Zn atom is able to accommodate the incoming H and the unsaturated N=C bond can form. Within the **TS(4-Inta)** structure, the Zn–N bond breaking is facilitated by the formation of a stabilizing interaction between the N atom and the Li. This is evidenced by the rotation around the C–C bond [increase in the dihedral angle from 31.4° in **4** (Figure 3) to

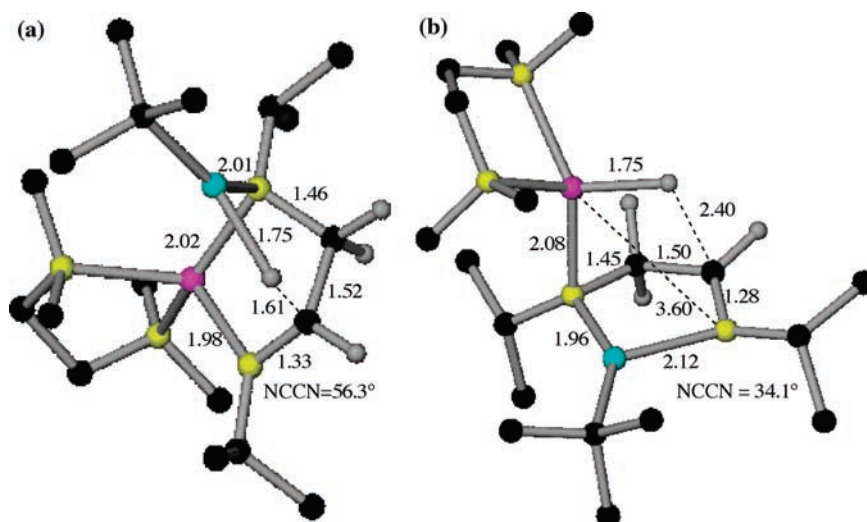
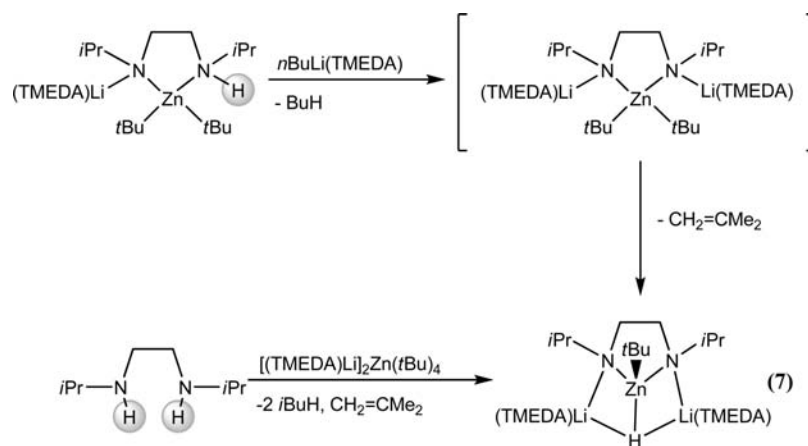


Figure 5. Optimized structures of (a) TS(4-Inta) and (b) TS(4-Intb). Distances in Å. NCCN refers to the dihedral angle (in degrees) of the diamido ligand.

Scheme 4. β -Hydride Formation and Elimination of *i*BuH from the Putative Highly Coordinated Zincate $[(\text{TMEDA})\text{Li}]_2[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})_2$ To Generate the Trapped Hydride Species 7



56.3° (Figure 5a)], which decreases the Li–N distance from 2.02 Å (Figure 3) to 1.98 Å (Figure 5a) and increases the Zn–N distance from 2.04 Å (Figure 3) to 3.39 Å (Figure 5a). In contrast, the rotation around the C–C bond in TS(4-Intb) is not as great (34.1°, Figure 5b). In addition, in TS(4-Intb) the Li atom is forced to migrate toward the second N atom in order to facilitate the transfer of the H atom beneath the plane of the ring. This movement results in a substantial elongation of the Li–N distance to 3.60 Å for the primary N (Figure 5b), and consequently, the breaking of the Zn–N bond is not facilitated (the Zn–N bond length is only slightly increased from 2.04 Å in 4 (Figure 3) to 2.12 Å in TS(4-Intb) (Figure 5b). Thus, the formation of the hydride intermediate is truly the result of the synergic interplay between the Zn (stabilizing the formation of the Zn–H bond) and Li (stabilizing the breaking of the Zn–N bond) metals.

Direct Observation of a Second Molecular Hydride Species. Returning to experimental studies, a molecular hydride species $[(\text{TMEDA})\text{Li}]_2[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})\text{H}$ 7 has been isolated by using a variation of this mixed-metal approach

with the ethylenediamide ligand, demonstrating that this system has the ability to encapsulate LiH (Scheme 4 and Figure 6). Dilithium hydrido-zincate 7 was synthesized while attempting to generate “ $[(\text{TMEDA})\text{Li}]_2[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})_2$ ” by the N–H deprotonation of $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{NH}(i\text{Pr})]\text{Zn}(t\text{Bu})_2$ 3 with a molar equivalent of $n\text{BuLi}(\text{TMEDA})$ (Scheme 4). Presumably a high degree of steric clashing in the anticipated product “ $[(\text{TMEDA})\text{Li}]_2[(i\text{Pr})\text{NCH}_2\text{CH}_2\text{N}(i\text{Pr})]\text{Zn}(t\text{Bu})_2$ ” facilitates the β -hydride formation and elimination of *i*BuH to generate the zinc hydride species 7. DFT calculations have confirmed that such a process $[4 + (\text{TMEDA})\text{LiH} \rightarrow 7]$ would be exothermic ($\Delta G = -28.4$ kcal/mol). Molecular hydride 7 can also be produced via the alternative reaction of the usually kinetically challenged base $[(\text{TMEDA})\text{Li}]_2\text{Zn}(t\text{Bu})_4$ ¹¹ with $(i\text{Pr})\text{NHCH}_2\text{CH}_2\text{NH}(i\text{Pr})$ with an improved yield of 65% relative to 35%.

Mixed-metal zincate hydrides have repeatedly demonstrated their utility in organic synthesis as reagents for chemoselective, diastereoselective, and catalytic reductions.^{155–158} Highly soluble, stable, and well-defined zincate hydride species are thus

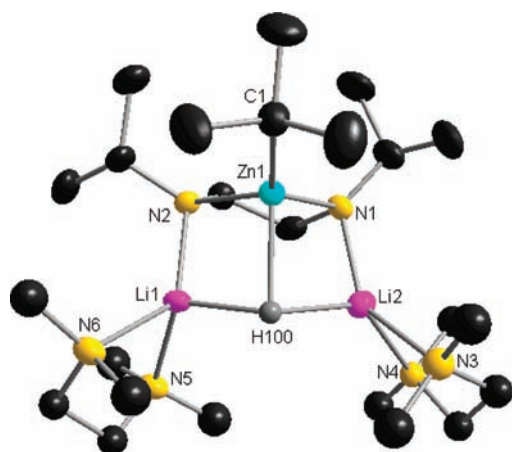


Figure 6. Molecular structure of the zincate hydride complex [(TMEDA)Li]₂[(iPr)NCH₂CH₂N(iPr)]Zn(*t*Bu)H **7** with hydrogen atoms (except for the hydride ion) omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Li1–H100, 1.96(2); Li2–H100, 2.07(2); Zn1–H100, 2.14(2); Li1–N2, 1.979(4); Li2–N1, 1.989(4); Zn1–N1, 2.043(2); Zn1–N2, 2.074(2); Zn1–C1, 2.045(3); N1–C9, 1.481(3); N2–C8, 1.448(3); C8–C9, 1.523(4); N1–Zn1–H100, 92.8(6); N1–Zn1–N2, 89.66(8); N1–Zn1–C1, 133.1(1); N2–Zn1–C1, 125.19(9); N2–Zn1–H100, 92.8(5); H100–Zn1–C1, 113.0(6); N2–Li1–N5, 121.8(2); N2–Li1–N6, 129.6(2); N2–Li1–H100, 101.5(6); N5–Li1–N6, 85.7(2); N5–Li1–H100, 115.9(6); N6–Li1–H100, 101.6(6).

highly desirable. Despite this, however, structurally characterized alkali metal zincate hydrides are extremely rare. To date the only examples on the CCDB¹⁵⁹ are the zinc–zinc bonded ArZn–(μ -H)(μ -Na)ZnAr (Ar = C₆H₃-2,6-[C₆H₃-(iPr)₂]₂),¹⁶⁰ the heterocubanes [(*t*BuOZnH)_{4–n}(LiO*t*Bu·THF)_n] (*n* = 0–3),¹⁶¹ and the higher-order zincates Na₂[(Et)₂ZnH]₂ and Na₃[(iPr)₃Zn(μ -H)Zn(iPr)₃].¹⁶² Although metal–hydride complexes are notoriously insoluble, a reputation perpetuated by common hydride reagents such as LiH and CaH₂, the hydride carrier **7** is soluble in the nonpolar solvent hexane. This high solubility is achieved despite maintaining the polar alkali metal–hydride bond. The structure of zinc hydride **7** bears a partial resemblance to that of the THF solvated dimer **6**, with a [(iPr)NCH₂CH₂N(iPr)]Zn(*t*Bu) complex anion having a lithium cation bound to each nitrogen atom. The Li–N amido bond distances in **7** (average 1.984 Å) are close to those in dimer **6** (average 2.021 Å). Likewise the Zn–N bond distances in hydride **7** [2.074(2) Å and 2.043(2) Å] are only marginally longer than those in alkylamido **6** (average 2.002 Å), owing to the increased number of anions bound to the zinc. The *t*Bu group has been pushed out of the plane of the amido ligand to allow the zinc center to enter a distorted tetrahedral geometry by binding to the hydride ligand. As in the lithium zincate **6**, the N–C [1.481(3) Å and 1.448(3) Å] and C–C [1.523(4) Å] bond lengths in **7** are consistent with an unactivated ethylene bridge. The trapped μ_3 -hydride was successfully located and freely refined in the X-ray diffraction study. It caps a Li₂Zn triangle asymmetrically with unequal Li–H bond distances [1.96(2) Å and 2.07(2) Å] and a longer Zn–H bond [2.14(2) Å]. The CCDB¹⁵⁹ at the time of writing contains only 45 compounds exhibiting a Zn–hydride bond. Excluding an anomalously long contact within a zinc borohydride compound (2.409 Å),¹⁶³ Zn–hydride bond lengths range from

1.409¹⁶⁴–2.167 Å¹⁶⁵ with an average distance of 1.771 Å. The Zn–hydride contact in **7** is thus long-range—to the best of our knowledge, the longest Zn hydride contact in a non-borohydride complex to date (the value of 2.167 Å mentioned above also comes from a borohydride complex). There are currently 147 compounds in the CCDB containing Li hydride contacts with their lengths spanning the wide range 1.607¹⁶⁶–2.802 Å.¹⁶⁷ The average distance (2.044 Å) is comparable with those found in **7**. To the best of our knowledge there are no previously reported zinc μ_3 -hydride complexes. However, there have been various dilithio μ_3 -hydride complexes reported with other metals such as Ga,^{168,169} Al,^{166,170–173} Zr,^{174–176} W,^{177,178} Sm,^{179,180} Ta,¹⁷⁸ and Fe.¹⁸¹

Variable-concentration multinuclear (¹H, ¹³C and ⁷Li) NMR spectroscopic studies of **7**, as well as exchange spectroscopic (EXSY) experiments, confirm the presence of a dynamic equilibrium in C₆D₆ solution. As well as resonances consistent with the solid state structure of **7**, resonances attributable to **4** are also observed. This suggests that LiH is associating with/dissociating from **4**. Mixed-metal zincate complex **4** can thus be described as a molecular scaffold for the molecularization of the usually insoluble polymeric LiH. An examination of the ⁷Li NMR spectrum reveals a doublet with a ¹J_{Li–H} coupling constant of 13.3 Hz, confirming the retention of the Li–H bond in solution. Observations of ¹J_{Li–H} scalar coupling constants are rare. Only a few examples have been detected since the first measurement by Bergman of (Cp*)IrH₂SiMe₃Li(PMDETA) (Cp* = C₅Me₅[–], PMDETA = N,N,N',N'',N''-pentamethyldiethylenetriamine) in 1985.^{182–186} Those detected have coupling constants ranging from ~6.4–14.7 Hz, placing our example at the upper end of the literature examples. Taking advantage of this direct Li–H coupling, a two-dimensional ⁷Li–¹H HSQC experiment was performed to determine the chemical shift of the hydride resonance. Surprisingly, two independent ¹H resonances, at 3.27 and 3.19 ppm, were detected coupling with the doublet in the ⁷Li NMR spectrum. These resonances had previously been masked by others assigned to the diamide ligand. This result can be tentatively assigned to the ⁷Li resonance for the zincate hydride **7** sharing the same chemical shift as dissociated (TMEDA)LiH, in agreement with the presence of a dynamic equilibrium in solution. Given the equilibrium between **4** and **7**, the formation of a diazaethene compound, analogous to **1**, may also occur using **7** as the starting point.

DFT Calculations on the Conversion of **7 to a Hypothetical Diazaethene Derivative.** The optimized structure of **7** closely matches the experimental X-ray structure, with a mean unsigned error of 0.07 Å between the measured and calculated bond lengths. The largest deviation between the calculated and experimental values occurs for the interactions involving the hydride ion (e.g., Zn–H: 1.94 Å calculated vs. 2.14 Å experimental, see Table S1 in Supporting Information for details). The deviations in the hydride ion distances may be due to the uncertainty inherent in the crystallographic determination of hydride positions; however, even with the shorter calculated Zn–H interaction, at 1.94 Å the Zn–H contact is clearly long-range.

The introduction of the (TMEDA)LiH ligand to **4** to form **7** results in a different mechanism for the formation of the diazaethene compound. One of the ethylene C8 hydrogen atoms from **7** (Figure 7) is aligned for abstraction by the dilithio hydride to form the intermediate (**Intc**) containing a (LiH)₂ unit. The formation of **Intc** occurs in an endothermic step (ΔG = 21.7 kcal/mol), relative to **7**, with an associated barrier of

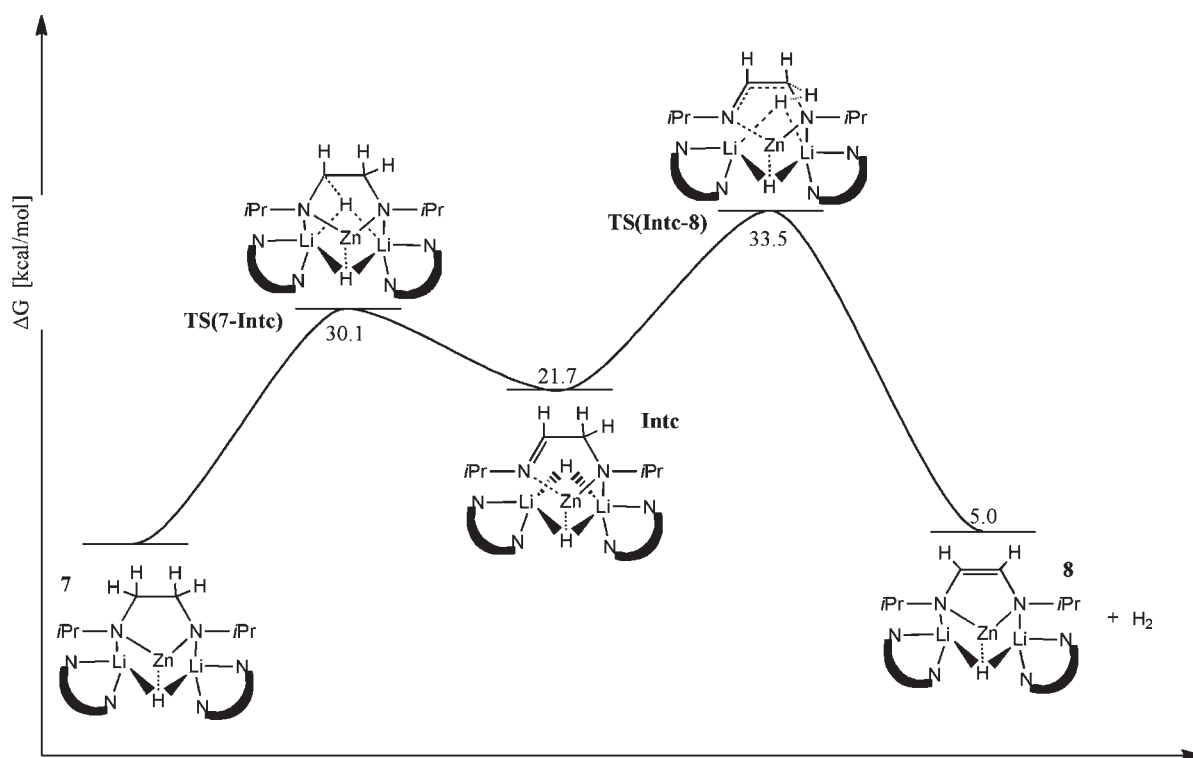


Figure 7. Free energy (ΔG) profile for the formation of **8** from **7** via a dihydride intermediate. Free energies in kcal/mol. The *t*Bu ligand attached to Zn is omitted for clarity.

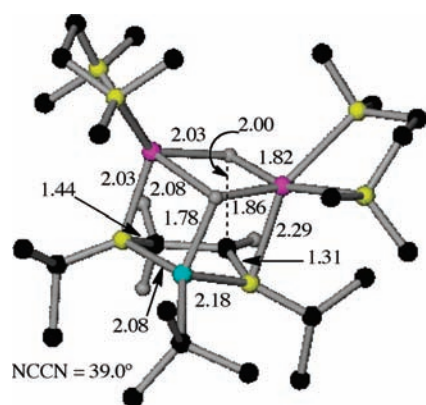


Figure 8. Optimized structures of **TS(7-Intc)**. Distances in Å. NCCN refers to the dihedral angle (in degrees) of the diamido ligand.

30.1 kcal/mol (ΔG^* , Figure 7). The subsequent abstraction of the H atom from C9 (Figure 7) to form H_2 and the diazaethene compound **8**, occurs with a barrier (ΔG^*) of 11.8 kcal/mol, relative to **Intc**, in an exothermic reaction ($\Delta G = -16.7$ kcal/mol). Overall, the reaction from **7** to form **8** is slightly endothermic ($\Delta G = 5.0$ kcal/mol, Figure 7). From the intermediate structure (**Intc**) the barriers to the forward and reverse reaction (i.e., the formation of **8** + H_2 and **7**, respectively) are comparable in energy ($\Delta\Delta G^* = 3.4$ kcal/mol). Therefore, although the equilibrium from **Intc** will be in the direction of **7**, the formation of **8** + H_2 from this structure should also occur to some extent.

The possible formation of a Zn hydride intermediate, in analogy to the mechanisms explored for the formation of **1** (via **Inta**) was also investigated. The barrier associated with the formation

of this hydride intermediate ($\Delta G^* = 28.4$ kcal/mol) is accessible under the experimental reaction conditions and the intermediate produced in this reaction is destabilized by 21.1 kcal/mol, relative to **7**. However, the barrier to the subsequent second hydrogen abstraction (i.e., the formation of **8** + H_2) is 34.4 kcal/mol, which results in a strong preference for the reverse reaction back to the reactant **7** ($\Delta\Delta G^* = 6.0$ kcal/mol). As such, the mechanism resulting in the formation of dihydride intermediate (**Intc**, Figure 7) is expected to be the dominant mechanism for the formation of **8** + H_2 , from **7**.

Despite the comparable energetics for the formation of **8** from **7** (via **Intc**) and **1** from **4** (via **Inta**), the mechanisms and the synergic interaction of the two metals are distinctly different. The presence of the second Li atom in **7** (relative to **4**) allows the Zn to stabilize the formation of the C=N bond (the Zn–N bond increases from 2.07 Å in **7** to 2.18 Å in **TS(7-Intc)**, Figure 8), while the Li atom is able to facilitate the C–H bond breaking step. Finally, the free energy associated with the loss of a (TMEDA)LiH ligand from **8** to form **1** is slightly less ($\Delta G = 24.9$ kcal/mol) than the equivalent association/dissociation reaction between **4** and **7**. Therefore, given the similar overall kinetic barriers associated with the generation of the diazaethene species starting from **4** and **7**, both reaction mechanisms described in Figures 5 and 8, should be competitive and operate in a complementary fashion to generate the observed product **1**.

Related Systems with Different Metal Combinations. The closest analogy to the synthesis of **1** was reported by Veith who formed 1,3-diaza-2-silacyclopentene by the double lithiation of (*t*Bu)NHCH₂CH₂NH(*t*Bu) (di-*tert*-butylethylenediamine) with *n*BuLi followed by an electrophilic quench with Cl₂Si(Me)N-(H)*t*Bu.¹⁸⁷ It was acknowledged at the time that the process leading to this dehydrogenation was unclear but it was noted that

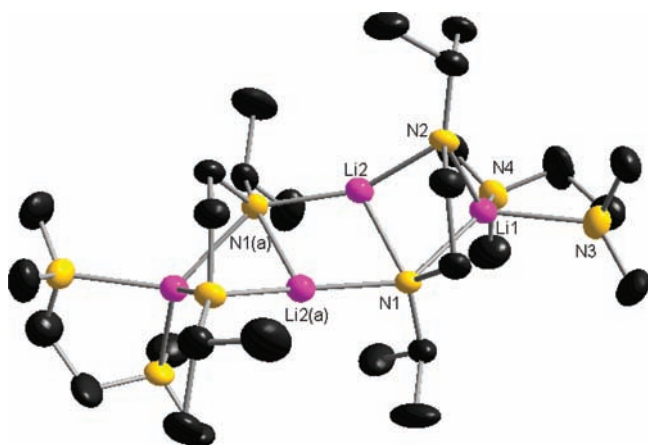


Figure 9. Molecular structure of the dilithium diamido [(TMEDA)-Li(*iPr*)NCH₂CH₂N(*iPr*)Li]₂ **9**. Hydrogen atoms and minor disordered TMEDA components have been omitted for clarity. Thermal ellipsoids are shown at the 50% probability level. Symmetry operations to generate equivalent atoms: $-x, y, 0.5-z$. Selected bond lengths [Å] and angles [deg]: Li1–N1, 2.227(2); Li1–N2, 1.977(3); Li1–N3, 2.209(3); Li1–N4, 2.199(3); Li2–N1, 2.025(2); Li2–N2, 1.971(2); Li2–N1(a), 2.057(2); N1–C2, 1.460(2); N2–C1, 1.458(2); C1–C2, 1.521(2); N1–Li1–N2, 81.23(9); N1–Li1–N3, 125.9(1); N1–Li1–N4, 129.1(1); N2–Li1–N3, 117.3(1); N2–Li1–N4, 125.26(1); N3–Li1–N4, 83.34(1); N1(a)–Li2–N1, 109.6(1); N1(a)–Li2–N2, 151.4(1); N1–Li2–N2, 86.7(1).

the reaction was highly concentration dependent. For dehydrogenation to occur the lithiation step needed to be carried out in a highly concentrated *n*BuLi hexane solution (~2 M). This concentration dependence infers a different mechanism of hydrogen activation from that which results in the synthesis of **1**, possibly involving either larger aggregates or an intermolecular process. Large aggregates of LiOtBu have previously been found to activate and retain LiH in solution.¹⁸⁴ The diamido species was never characterized in Veith's study. We have confirmed by NMR spectroscopy that (*iPr*)NHCH₂CH₂NH(*iPr*), like its homologue (*t*Bu)NHCH₂CH₂NH(*t*Bu), can be activated when refluxed in a concentrated *n*BuLi solution. When the reaction was carried out at concentrations akin to that used in the synthesis of **1**, then the dilithiated species could be crystallized as a TMEDA solvate (Figure 9). This product, [(TMEDA)Li(*iPr*)NCH₂CH₂N(*iPr*)Li]₂ **9**, has a distorted ladder structure in the solid state with the diamido ligands adopting a trans-bent conformation allowing them to bridge between opposite corners of alternate rungs. The rungs of the ladder differ little in length with Li–N bond distances in the range of 1.977(3)–2.025(2) Å. In contrast, the edges exhibit distinct variation in length with Li–N bond distances of 2.227(2) Å and 1.971(2) Å between the outer rungs and 2.057(2) Å between the inner rungs. Maintaining the C₂ axis of symmetry, the long and short edges of the ladder alternate as the ladder is ascended. The distortion in the edge lengths generates a screw twist along the ladder. Both outer lithium centers adopt distorted tetrahedral geometries, while the internal lithium atoms are three-coordinate. Gardiner postulated that donor free Li(*t*Bu)NCH₂CH₂N(*t*Bu)Li polymerized as an infinite ladder.¹⁸⁸ This trapping of a ladder segment instigated by the Lewis base TMEDA supports Gardiner's assertions.

The activation of (*iPr*)NHCH₂CH₂NH(*iPr*) has also been achieved starting from the sodium congener Na[(*iPr*)NCH₂CH₂NH(*iPr*)]

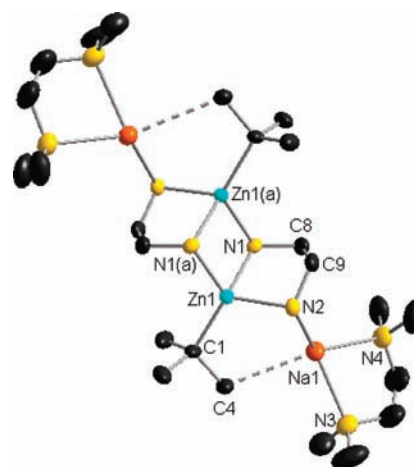


Figure 10. Molecular structure of one of the independent molecules of the dimeric sodium zincate [(TMEDA)Na(*iPr*)NCH₂CH₂N(*iPr*)]Zn(*t*Bu)₂ **11**. A weak agostic Na...C contact is denoted by a broken bond. Hydrogen atoms, *iPr* groups, and disordered hexane of crystallization have been omitted for clarity. Symmetry operations to generate equivalent atoms: $-x, 1-y, 1-z$. Thermal ellipsoids are shown at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Na1–N1, 3.720(4); Na2–N2, 2.326(5); Na1–N3, 2.490(6); Na1–N4, 2.490(5); Na1–C4, 2.977(6); Zn1–N1, 2.105(4); Zn1–N2, 2.103(4); Zn1–C1, 2.072(5); Zn1–N1(a), 2.122(4); N1–C8, 1.463(6); N2–C9, 1.452(6); C8–C9, 1.494(7); N4–Na1–N3, 75.4(2); N4–Na1–N2, 121.9(2); N4–Na1–C4, 147.7(2); N3–Na1–N2, 137.7(2); N3–Na1–C4, 91.8(2); N2–Na1–C4, 87.4(2); N2–Zn1–C1, 117.1(2); N2–Zn1–N1, 85.9(2); N2–Zn1–N1(a), 110.5(2); N1–Zn1–C1, 127.6(2); N1–Zn1–N5, 88.8(2); N5–Zn1–C1, 120.0(2).

and (*t*Bu)₂Zn(TMEDA) to generate the sodium diazaethene zincate (TMEDA)Na[(*iPr*)NCH=CHN(*iPr*)]Zn(*t*Bu) **10**. Although the initial cocomplexation adduct “(TMEDA)Na[(*iPr*)NCH₂CH₂NH(*iPr*)]Zn(*t*Bu)₂” with one N–H bond still remaining is apparently too short-lived to isolate, when the reaction was carried out at 0 °C and the resulting solution stored at –30 °C, it was possible to isolate and fully characterize the dimeric species {(TMEDA)Na[(*iPr*)NCH₂CH₂N(*iPr*)]Zn(*t*Bu)₂} **11** with no N–H bond but containing the saturated ethylene diamido backbone (Figure 10) which must exist further along the reaction pathway that ultimately produces **10**. Two independent centrosymmetric molecules of dimer **11** as well as a hexane molecule form the asymmetric unit. Sodium zincate **11** is constructed from a 5–4–5 fused ring system in a distorted ladder conformation; the two ZnNCCN rings lie *anti* about the strictly planar central ZnN₂ZnN core. The N–C [1.452(6) Å and 1.463(6) Å] and C–C [1.494(7) Å] bond distances are indicative of a fully saturated bisamide. Contrary to binding in the lithium monomer **5**, the heavier alkali metal binds to only one of the available amido groups, with the core nitrogen atoms (N1, N1a) coordinating exclusively to zinc. Despite the variety of amide environments around zinc, the Zn–N bond distances show little variation (average 2.11 Å). Due to the narrow bite angle of the diamido ligand (85.9°) the zinc center adopts a distorted tetrahedral geometry. A highly distorted tetrahedral geometry around sodium is also completed by a weak agostic interaction [2.977(6) Å] to a methyl arm of the tertiary butyl ligand on zinc. This is moderately longer than a similar interaction found in the bis-alkylamido zincate (TMEDA)Na(TMP)-Zn(*t*Bu)₂ (2.75 Å).⁷⁰ 5–4–5 fused ring systems have been

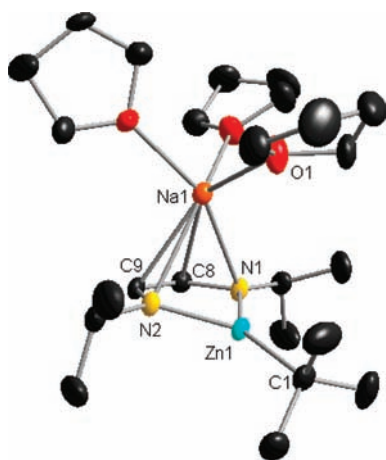


Figure 11. Molecular structure of the diazaethene sodium zincate $(\text{THF})_3\text{Na}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})$ **10A**. Hydrogen atoms and minor disordered THF components have been omitted for clarity. Thermal ellipsoids shown at the 50% probability level. Selected bond lengths [Å] and angles [deg]: Na1–O1, 2.350(2); Na1–O2, 2.312(2); Na1–O3, 2.312(2); Na1–N1, 2.587(2); Na1–N2, 2.662(2); Na1–C8, 2.612(2); Na1–C9, 2.649(2); Zn1–N1, 1.957(2); Zn1–N2, 1.971(2); Zn1–C1, 2.009(2); N1–Na1–N2, 60.81(6); N1–Zn1–N2, 85.14(8); N1–Zn1–C1, 139.88(10); N2–Zn1–C1, 134.97(10).

found before in metallate complexes containing saturated NCCN diamido ligands. Examples include the lithium lanthanide complexes $[(\text{THF})_3\text{Li}[1,2\text{-}\{\text{N}(\text{SiMe}_3)\}_2\text{-C}_6\text{H}_{10}]\text{MCl}_2]_2$ ($\text{M} = \text{Nd}, \text{Yb}$)¹⁸⁹ and the dimeric gallium species $\{(\text{Bz})\text{NCH}_2\text{-CH}_2\text{N}(\text{Bz})\}_2\text{Li}\{(\text{Bz})\text{NCH}_2\text{CH}_2\text{N}(\text{Bz})\}_2\text{GaO}$ ($\text{Bz} = \text{benzyl}, \text{CH}_2\text{C}_6\text{H}_5$).¹⁹⁰

As might be expected from polarity considerations, the sodium reagent proves more reactive than the lithium analogue, providing after a 30 min reflux in hexane, the sodium diazaethene **10** in 61% isolated yield. The lithium congener requires a 2 h reflux to achieve similar conversions. Although the TMEDA solvate **10** could be isolated as a crystalline solid, to obtain crystallographic data of adequate precision, the donor ligand THF had to be used in place of TMEDA to produce the analogous THF solvate $(\text{THF})_3\text{Na}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})$ **10A** (Figure 11). Here, the zinc atom is chelated symmetrically [Zn–N bond distances 1.957(2) Å and 1.971(2) Å] by the diamido ligand, lying below the plane defined by the NCCN core of the diazaethene ligand. The methine carbons of the isopropyl groups lie in the plane of the diazaethene ligand while their methyl groups protrude above and below this plane. The sodium atom lies above the NCCN bridge, though slightly off center, coordinating to both pairs of nitrogen and carbon atoms. Three THF molecules complete the coordination sphere of the sodium center. Comparing the C–N [1.398 Å (average)] and C–C [1.353(4) Å] bond distances of the diazaethene core with those found in the lithium analogue $(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(\text{Me})$ [1.400 (average) and 1.349(3) Å] indicates that the change in alkali metal has little effect on the diazaethene ligand. The THF ligands in **10A** can be removed under drying *in vacuo*. Dissolution of **10A** in C_6D_6 to perform an NMR spectroscopic analysis was achieved by the addition of a drop of d_8 -THF. Comparing the ^1H NMR spectra of the THF solvate **10A** with the TMEDA solvate **10** reveals only marginal shift changes of the resonances associated with the diazaethene ligand. Comparing the ^1H NMR spectra of the homologues

$(\text{TMEDA})\text{Li}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})$ **1** and $(\text{TMEDA})\text{Na}[(i\text{Pr})\text{NCH}=\text{CHN}(i\text{Pr})]\text{Zn}(t\text{Bu})$ **10** reveals a 0.24 ppm downfield shift of the signal attributable to the $\text{CH}=\text{CH}$ backbone of the diazaethene ligand on moving from lithium to sodium. Interestingly, there are two sets of doublets associated with the methyl groups of the isopropyls of the lithium compound but only one set in the sodium congener. This would suggest sterically induced hindered rotation of the isopropyl groups in the lithium compound which is relieved on switching to the larger sodium cation. The synthesis of several alkali metal zincate diazaethene complexes has been achieved previously. However, to the best of our knowledge, all previous examples were synthesized by the reduction of unsaturated bis-imino ligands.^{191–195} Therefore, the synthesis of the sodium zincate **10**, along with the lithium zincates detailed in our recent communication,¹³⁷ appear to represent the first such complexes to be synthesized via a double CH activation of a saturated diamido ligand.

CONCLUSION

Conversions of saturated diamines into unsaturated diazaethenes are usually associated with redox-amenable transition metal catalysts. However here we show through a combination of experimental (NMR spectroscopic, X-ray crystallographic) and theoretical (DFT) studies that working co-operatively in a molecular mixed-metal system, an alkali metal (lithium or sodium) and zinc can bring about such transformations under challenging redox-inactive conditions.

ASSOCIATED CONTENT

S Supporting Information. Full experimental details, NMR spectra, supporting tables, and crystallographic details. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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ACKNOWLEDGMENT

We gratefully acknowledge financial support from the UK Engineering and Physical Science Research Council, EPSRC (Award No. EP/F063733/1), and the Royal Society (Wolfson research merit award to R.E.M.).

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