▮ Organometallic chemistry

Lithiated Primary Amine—A New Material for Hydrogen Storage

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Abstract: A facile method for synthesizing crystalline lithiated amines by ball milling primary amines with LiH was developed. The lithiated amines exhibit an unprecedented endothermic dehydrogenation feature in the temperature range of 150–250 °C, which shows potential as a new type of hydrogen storage material. Structural analysis and mechanistic studies on lithiated ethylenediamine (Li$_2$EDA) indicates that Li may mediate the dehydrogenation through an α,β-LiH elimination mechanism, creating a more energy favorable pathway for the selective H$_2$ release.

Thermal cracking of hydrocarbons normally leads to the break of the C—C bond (~246 kJ mol^{-1}) rather than C—H bond (~363 kJ mol^{-1}). For cyclic hydrocarbons, on the other hand, dehydrogenation can be achieved with minimal C—C bond rupture with the aid of proper catalysts.[1] For example, in the presence of Pt or [IrH$_2$(PCP)] (where PCP = C$_6$H$_3$(CH$_2$PtBu$_2$)$_2$-2,6) pincer catalysts, cyclohexane releases three equivalents of H$_2$ to benzene at temperatures above 200 °C.[2] The relatively high temperature may be due to the unfavorable dehydrogenation thermodynamics ($\Delta H^\circ = 205.9$ kJ mol^{-1}) and the high energy barrier in activating the C—H bond.[3] Theoretical and experimental studies show that partial substitution of carbon atoms by heteroatom(s) (O, N, S, etc.) promotes low temperature dehydrogenation.[4] A series of key patents have been generated by Pez et al.[5] More recently, Campbell et al. reported that

(iPr)NHCH$_2$CH$_2$NH(iPr) transformed to [(iPr)NCH=CHN(iPr)]$^{2-}$ at ambient temperature catalyzed synergistically by two distinct metals of Li and Zn in the system.[6] It is worth pointing out that no matter which heteroatom is applied, dehydrogenation is normally occurs from the breaking of the C—H bond. Little investigation has been given to the direct dehydrogenation of aliphatic amines by cracking both N—H and C—H bonds. Our experimental data show that ethylenediamine (EDA), for example, undergoes decomposition giving rise to NH$_3$, CH$_x$, and CH$_x$N$_y$ species at elevated temperatures (see Figure S1 in the Supporting Information), which, similar to hydrocarbons, is relevant to the relatively weaker C—C bond and C—N bond (~331 kJ mol^{-1}).[7] The situation changes when oxidative dehydrogenation is implemented by a transition metal (Ru, Pt, Ni, Mo, etc.) or a pincer complex catalyst by dihydrogen transfer to proper acceptors (O^{2-}, MnO$_2$, tert-butylethylene, etc.).[8] Catalyzed by molten Zn, n-butylamine and benzylamine give off gaseous hydrogen and convert to n-butyronitrile and benzonitrile.[9] H$_2$ is regarded as a clean energy carrier, and aliphatic amines are H-rich compounds; however, little success has yet been made for their dehydrogenations. Therefore, it is of both scientific and practical importance to investigate whether dehydrogenation can be achieved by a noncatalytic process under mild conditions.

The H atom in the —NH$_2$ group is acidic, resembling to that of NH$_3$ and metal amides (LiNH$_2$, Mg(NH$_2$)$_2$, etc.). There have been over 10 years' worth of activities in probing hydrogen release from the interaction of amides and hydrides, in which the chemical potential of the combination of acidic H in amide and basic H in hydride into H$_2$ is regarded as the driving force.[10] It is rational to extend such an interaction to amines and hydrides composites.

A few primary mono- and diamines, that is, ethylamine (EA), ethylenediamine (EDA), propylamine (PA), 1,3-propanediamine (PDA), benzylamine (BA), and p-xylylenediamine (PX) were chosen as representatives and were ball milled with LiH in a molar ratio of [—NH$_2$] group/LiH = 1:1, separately. The gas evolution from each sample was monitored by a pressure gauge and then was identified as H$_2$ by a mass spectrometer (see Figure S2 in the Supporting Information). As shown in Figure 1, with prolonged ball milling and in some cases post-ball-milling heat treatment, nearly one equivalent H$_2$ per LiH was generated from each sample. The characterization of solid residues reveals the formation of new phases (see Figure S3 in the Supporting Information). The detailed crystallographic study on lithiated EDA (Li$_2$EDA for short) is given below while the structural analyses on other lithiated amines are currently underway. Summarizing the experimental results above, it can

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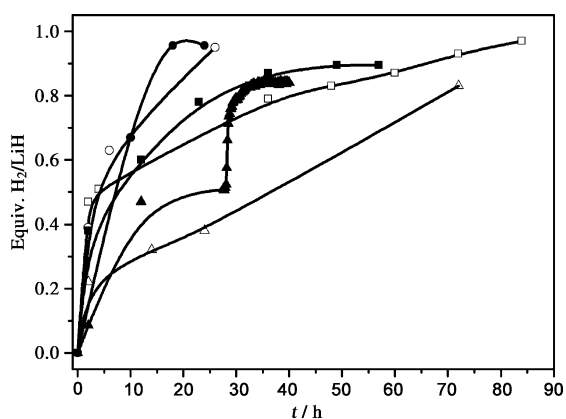🖳 Supporting information for this article is available on the WWW under http://dx.doi.org/10.1002/chem.201402543.

Figure 1. Time dependence of H_2 release from the amine–LiH mixtures during ball milling at 200 rpm. EDA, PA, and PDA were ball milled with LiH at room temperature, separately; EA, BA, and PX were ball milled with LiH at 60 °C, separately; ball milled BA–LiH mixture was further heated to 100 °C for 13.5 h to release the remaining hydrogen (□ = EDA + 2 LiH; ● PA + LiH; ○ = PDA + 2 LiH; ▲ = BA + LiH; △ = PX + 2 LiH; ■ = EA + LiH).

Figure 2. Enthalpy changes for the formation of lithiated amines determined theoretically and their dehydrogenation determined experimentally.

be derived that Equation (1) takes place in the RNH$_2$–LiH mixtures giving rise to N-lithiated amines, which are normally used as selective proton abstractors and convenient anion exchange reagents.[11] The conventional synthetic method is by metathesis of amines (R$_2$NH, in which R = H or hydrocarbon group) with *n*-butyllithium (*Li*Bu) following Equation (2).[12] A recent report by Mulvey and Robertson gave a systematic review on the syntheses, structures, and applications of alkali hexamethyldisilazides, diisopropylamides, and tetramethylpiperidides etc.[13]

$$R(NH_2)_n + nLiH \rightarrow R(NHLi)_n + nH_2 \qquad (1)$$

$$R_2NH + LiBu \rightarrow R_2NLi + BuH \qquad (2)$$
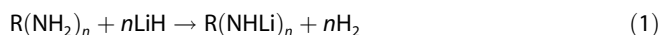
It should be highlighted that the reaction in Equation (1) can also be applied to other alkali and alkaline earth hydrides. In fact, NaH or KH readily react with the amines listed above giving rise to hydrogen and Na or K-amines. MgH$_2$ and CaH$_2$, on the other hand, would require longer times and higher temperatures to achieve the complete conversion. Although the synthetic parameters are the subjects for further optimization, the advantages of the present route lie in the following: 1) the overall process is solvent-free, 2) the only solid product is metalated amines, and 3) metal hydrides are cheaper, more stable and less reactive than *Li*Bu etc.

The next question is whether the released H$_2$ can be charged back, that is, the reversibility of Equation (1) under normal conditions. As direct thermal analyses can hardly be done under the present reaction conditions, we employed molecular calculations to determine the heat of formation of those lithiated amines. As shown in Figure 2 and Table S1 in the Supporting Information, all the lithiated amine molecules are more stable than the starting amines plus LiH, taking into consideration that the crystallization energy of those ionic lithiated amines will add weight to the exothermicity, the reaction in Equation (1) is thus a thermodynamically favorable one-way
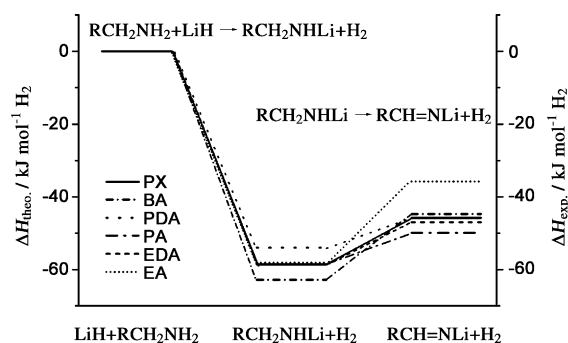
reaction. In other words, a direct hydrogen restoration under normal conditions is unlikely.

The "hydrogen story" does not stop here. The presence of Li significantly changes the chemical nature of the amines. Markedly different from the thermal decomposition of EDA, a rapid H$_2$ desorption from Li$_2$EDA upon heating it to approximately 177 °C was observed (see Figure S4 in the Supporting Information). Moreover, all lithiated amines studied in this work exhibit similar dehydrogenation behaviors around 150–250 °C. Quantitative analyses on hydrogen desorption are shown in Figure 3
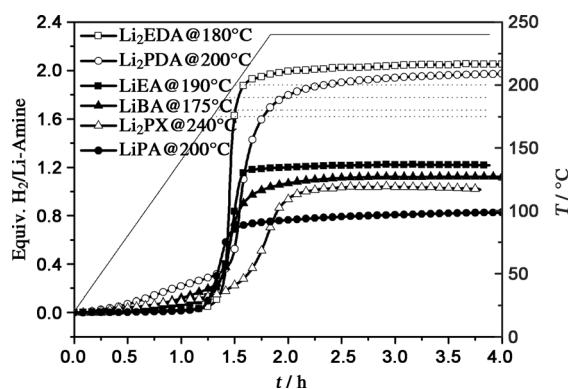

Figure 3. Volumetric releases of lithiated amines. Samples were heated to the desired temperature with a ramping rate of 2 °C min^{-1}. It needed approximately 1.2–1.7 h to reach the specified temperatures.

and S5 in the Supporting Information. Generally, dilithiated diamines samples (Li$_2$EDA and Li$_2$PDA) gave off approximately two equivalents of H$_2$ at 180 and 200 °C, respectively. Monolithiated monoamines, on the other hand, released approximately one equivalent of H$_2$. It appears that the amount of the desorbed H$_2$ depends on the number of [NH–CH$_2$] units [Eq. (3)]. In other words, direct cracking of C–H and N–H bonds with H$_2$ formation may be achieved. Our hypothesis is supported by the observation of N=C=N stretches at around 2100 cm^{-1} (the FTIR spectrum is shown in Figure S6 in the Supporting Information) as well as solid-state ^{13}C CPMAS NMR spectroscopic signals at around $\delta = 173$ ppm belonging to C in C=N or N=C=N environments (see Figure S7 in the Supporting Information).

$$R(CH_2NHLi)_n \rightarrow R(HC=NLi)_n + nH_2 \qquad (3)$$
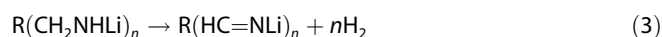
As shown in Table S1 in the Supporting Information, the lithiated amines are stabilized by approximately 150 kJ mol^{-1} from the corresponding amines. It is thus interesting to look into the thermal effect of the dehydrogenation of these stable lithiated amines. As all the post-dehydrogenated solid residues are essentially amorphous (see Figure S8 in the Supporting Information), calculation can hardly be done without any defined structures. Differential scanning calorimetry (DSC) was employed to measure the heat flow during the dehydrogenation. Figure S9 in the Supporting Information shows the DSC curves manifesting endothermic nature of dehydrogenation. The measured heat of desorption ranges from 8 to 22 kJ mol^{-1} H$_2$. Comparatively, monolithiated monoamines require more energy to release hydrogen than the dilithiated diamines.

Literature reports show that lithiated alkanes, such as *Li*Bu, eliminate LiH, easily forming the corresponding alkenes.[14] Lithiated secondary amines, such as lithium dimethylamide, lithium diethylamide, and lithium diisopropylamide, follow the same manner decomposing to LiH and *N*-methyenemethyla-mine, *N*-ethylidenethyamine, and *N*-isopropylideneisopropyla-mine, respectively.[15] Such an α,β-LiH elimination mechanism manifests the important role of lithium in activating the C–H bond in the thermal decomposition of lithiated alkanes and secondary amines. In contrast, lithiated primary amines give off H$_2$, which is most likely due to the presence of α-hydrogen at the N site. It is, therefore, of interest to figure out how dehydrogenation takes place in these lithiated primary amines. We chose Li$_2$EDA as a case for study. In a previous report, the monomeric, dimeric, and trimeric structure of Li$_2$EDA has been studied by theoretical calculations.[16] In this work, we determined the crystal structure of Li$_2$EDA from experimental data for the first time. Li$_2$EDA possesses a monoclinic structure (space group *C2/c*) with lattice parameters of $a = 11.128(1)$, $b = 12.518(1)$, $c = 8.069(1)$ Å, $\beta = 134.022(3)°$, $V = 808.3(1)$ Å^3 (see Figure S11 in the Supporting Information), determined from Rietveld refinement by using high-resolution XRD data (see Figure S10 in the Supporting Information). Figure 4 shows the coordination environment in Li$_2$EDA in which the shortest Li–β-
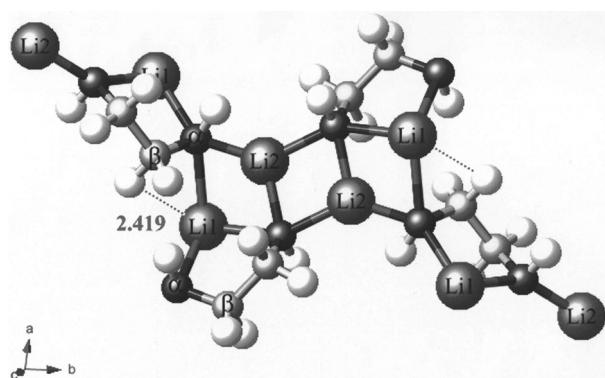
H (C) distance is 2.419 Å calculated from the relaxed structure. It is very likely that the β-H would first transfer from C to Li forming a –(H)N–Li–H moiety, and then, it reacts with the α-H on the nearby N atom giving rise to H$_2$ and [LiN=CHR].

A similar mechanism was proposed by Kim et al. and Lee et al. in the interpretation of hydrogen release from LiNH$_2$BH$_3$, in which β-H(B) transfers to Li forming a LiH intermediate. LiH, then, reacts with the α-H atom (from –NH$_2$) giving rise to H$_2$ and [LiNHBH$_2$].[17] Lithiated primary amines may follow a similar dehydrogenation pathway as that of LiNH$_2$BH$_3$ by forming a [LiN=CHR] unit, which may have chance to partially disproportionate to LiH and N≡CR. Therefore, the α,β-LiH elimination mechanism also manifests the important role of lithium in dehydrogenation of lithiated primary amines. Both [LiN=CHR] and [N≡CR] are likely to polymerize into amorphous matter at elevated temperatures. At temperatures higher than 300 °C, Li$_2$CN$_2$ and amorphous [LiCNH] species were observed (see Table S2 and Figure S12 in the Supporting Information).

It was found that the dehydrogenation was inhibited when heating Li$_2$EDA under a high initial H$_2$ pressure (720 psi; see Figure S13 in the Supporting Information) showing that at least partial reversibility can be achieved. However, the direct re-hydrogenation has not been performed successfully on the amorphous solid residues, which is due to the kinetic and thermodynamic constraints. The relatively small endothermicity reflects that the hydrogenation can only be allowed at low temperatures or under high H$_2$ pressure. There are a few ways to overcome this challenging task: 1) developing suitable catalysts to facilitate the re-hydrogenation, 2) destabilizing the dehydrogenated product(s) by preventing them from polymerization, 3) altering the composition by forming bi- or multimetallic amines in the hope to stabilize the reactant(s). Those strategies have been employed in complex hydrides,[18] amide–hydride composites,[19] and amidoboranes.[20] With the diversity of C–N chemistry and the large less-probed area of organometallic compounds, the chance of materials development for hydrogen storage is considerably high.

In summary, a novel type of hydrogen carrier has been identified, which was facilely synthesized by ball milling primary amines with LiH. Compared to the intensively studied B–N containing hydrogenous compounds,[21] the thermodynamically favorable dehydrogenation in these lithiated amines can be tailored by the presence of C–N and C–C bonds, whereas the involvement of Li is the key to facilitate the unprecedented endothermic dehydrogenation of N–H and C–H bonds under the mild conditions. Continuous efforts are necessary in the understanding, design, and optimization of this new system.

Acknowledgements

Figure 4. Structure schematic diagram of Li$_2$EDA.[22] Hydrogen atoms are represented by white spheres; nitrogen and carbon atoms are labeled by α and β, respectively.

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[22] CCDC-930314 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.