N-Heterocyclic Carbenes

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Beryllium-Induced C–N Bond Activation and Ring Opening of an N-Heterocyclic Carbene**

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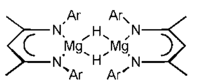
The widespread use of N-heterocyclic (imidazol-2-ylidene) carbenes (NHCs) has been driven by their ease of synthesis and their ability to act as robust two-electron σ-donor ligands.[1] While this latter attribute has proven to be especially advantageous in homogeneous catalytic applications, a variety of NHC activation and catalyst deactivation pathways have also been identified.[2] A number of groups have observed that N-alkyl and N-aryl-substituted NHCs are prone to both C–H and C–N activation of the peripheral organic substituents within the coordination sphere of transition-metal centers.[3,4] Herein we report that the imidazol-2-ylidene ring is prone to reductive ring opening in the presence of reactive hydride compounds; observations that may be of particular relevance to hydride poisoning of NHC-based catalysts.

Recent studies of the Group 2 elements below beryllium in the periodic table have shown a striking variability in their chemistries, which has been suggested to result from the different charge densities of the corresponding M^{2+} cations.[5] The exploitation of reactive but well-defined species, such as the μ-hydrido magnesium compounds $[HC\{(Me)CN(2,6\text{-}iPr_2C_6H_3)\}_2MgH]_2$ (**I**),[6] $[Mg_4H_6\{N(SiMe_3)_2\}_2(IPr)_2]$ (**II**, IPr = 1,3-bis(2,6-diisopropylphenyl)imidazol-2-ylidene),[7] and a recently reported octanuclear $\{Mg_8H_{10}\}$ cluster (**III**) that is supported by a binucleating and *para*-phenylene-bridged β-diketiminate ligand, has been central to these advances.[8]



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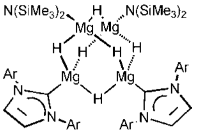
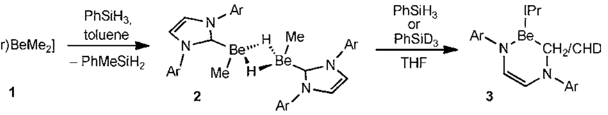


II

Initial attempts to extend this chemistry to the lightest member of Group 2, beryllium, through direct reaction of IPr and BeH_2 in THF were unsuccessful. No reaction was observed, most likely because of the polymeric nature and the consequent insolubility of the isolated main-group dihydride even at elevated temperatures (120 °C). The isolation of the hydridomagnesium compounds **I**–**III** was dependent upon the use of $PhSiH_3$ as a hydride source in the reaction with magnesium alkyl or amido starting materials.[6–8] We thus carried out the reaction of two molar equivalents of methyl lithium with an equimolar solution of IPr and $BeCl_2$ in diethyl ether. This procedure resulted after work-up in the isolation of compound **1** ($[BeMe_2(IPr)]$) as a colorless microcrystalline material in 56 % yield. Like the previously reported $[BePh_2(i\text{Pr-carbene})]$ (*i*Pr-carbene = 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene),[8] compound **1** was shown to maintain its three-coordinate geometry; in the solid state by an X-ray diffraction analysis and in solution through a combination of ^1H, ^{13}C, ^9Be, and diffusion (DOSY) NMR spectroscopic techniques (see the Supporting Information).

Although an NMR-scale reaction of compound **1** with two molar equivalents of $PhSiH_3$ in $[D_8]$toluene at room temperature indicated formation of the expected metathesis side product $PhMeSiH_2$, all the signals attributed to the IPr ligand were depleted from solution as the reaction proceeded while half of the $PhSiH_3$ remained unreacted. The origin of these observations was deduced through a preparative-scale reaction, whereupon an unstirred solution of an excess of $PhSiH_3$ and compound **1** deposited large colorless crystals, which were identified by single-crystal X-ray diffraction analysis as a Be–H–Be-bridged dimeric adduct (**2**, 78 % yield; Scheme 1 and Figure 1) of IPr and MeBeH. Although the structure will not be described further here, compound **2** is the first crystal structure of an organoberyllium hydride, which is somewhat surprising, given that compounds with the general formulation RBeH are well known.[10]



Scheme 1. Preparation of organoberyllium compound **3**. Ar = 2,6-diisopropylphenyl.

Once isolated, compound **2** could not be re-dissolved in weakly coordinating aromatic hydrocarbon solvents, but was sufficiently, though sparingly, soluble in the O-donor solvent $[D_8]$THF ($< 1\ mg\,mL^{-1}$) to enable solution NMR studies (see the Supporting Information). This sparing solubility in THF motivated a reaction of compound **2** with $PhSiH_3$ in a further attempt to access the IPr adduct of BeH_2. In an NMR-scale

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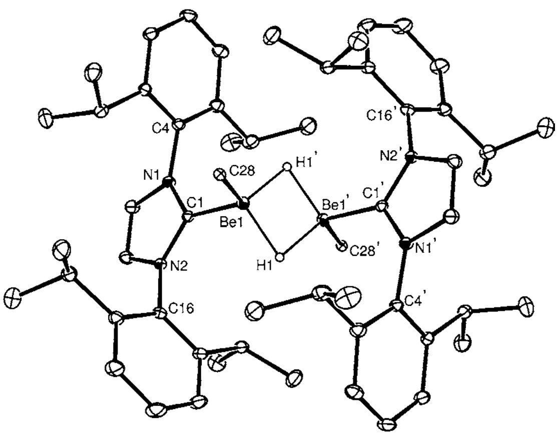

Figure 1. ORTEP representation (ellipsoids at 20% probability) of the X-ray crystal structure of compound **2**. Hydrogen atoms except those bound directly to beryllium were removed for clarity. Symmetry transformations used to generate primed-labeled atoms $-x+1,-y,-z$. Selected bond lengths [Å] and bond angles [°]: C1–Be1 1.822(2), C28–Be1 1.813(2), Be1–H1 1.552(18); C28-Be1-C1 115.47(11), C28-Be1-H1 113.9(7), C1-Be1-H1 107.6(7).

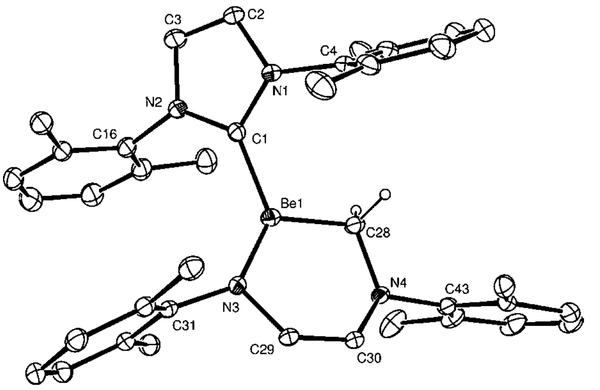

Figure 2. ORTEP representation (ellipsoids at 20% probability) of the X-ray crystal structure of compound **3**. Hydrogen atoms except those bound to C28 and isopropyl methyl groups are removed for clarity. Selected bond lengths [Å] and bond angles [°]: Be1–C1 1.803(5), Be1–C28 1.741(5), Be1–N3 1.587(5), C28–N4 1.471(4), N4–C30 1.389(4), C29–C30 1.343(4), C29–N3 1.422(4); N3-Be1-C28 115.7(3), N3-Be1-C1, 130.4(3), C28-Be1-C1 113.7(2).

reaction, heating a suspension of compound **2** and a further two equivalents of $PhSiH_3$ in [D$_8$]THF at 80 °C for 6 hours resulted in the formation of an orange/red solution with complete dissolution of the beryllium species and the clean conversion of one molar equivalent of $PhSiH_3$ to the expected product of Be–Me/Si–H metathesis, $PhMeSiH_2$. This NMR spectrum was further characterized by the appearance of an unexpected asymmetry in the IPr ring and isopropyl methine resonances, manifested as an AB spin system and as a well resolved pair of 1H heptet resonances, respectively. A further notable feature was a sharp 2H singlet resonance at $\delta =$ 2.01 ppm, which was correlated with a new methylene resonance in the ^{13}C NMR spectrum by an HMQC experiment. A preparative-scale reaction in THF provided large red crystals of compound **3** (Scheme 1), which were suitable for a single-crystal X-ray diffraction analysis. This analysis showed that the beryllium atom had effectively inserted into one of the C–N bonds of an IPr-ligand heterocycle (Figure 2). The beryllium center is thus three-coordinate with a coordination sphere provided by a chelating dianionic amidoalkyl ligand and a further equivalent of the unchanged neutral IPr ligand. Although generally noted for their stability, particularly under catalytic conditions, NHC complexes are susceptible to degradation by a variety of C–H, C–C, and C–N bond-activation reactions at peripheral and/or extracyclic positions.[2–4] The reaction to produce compound **3** is unprecedented, however, as it involves complete disruption of the σ and π systems of the imidazolylidene framework.

The formation of compound **3** occurred in stoichiometric quantities with respect to the amount of IPr present (80% yield of isolated product based on IPr), while complete stoichiometric conversion to the silane-containing metathesis product $PhMeSiH_2$ was observed during the reaction. It may also be noted that the amidoalkylberyllium component of **3** is isomeric to the target IPr adduct of BeH_2, which then requires the presence of free IPr to crystallize. This scenario also requires the production of half a molar equivalent of the initial beryllium added as compound **2** to be present as an as yet unidentified beryllium species, possibly THF-solvated BeH_2, a supposition that is reinforced by the observation of an additional resonance in the ^{9}Be{^{1}H} NMR spectrum at $\delta =$ 0.65 ppm alongside the signal attributed to compound **3** at $\delta =$ 16.9 ppm.

While the precise mechanism of the formation of compound **3** is yet to be established, further evidence for the intermediacy of the putative dihydrido species [BeH_2(IPr)] was provided by the observation that compound **3** was also formed upon heating of a THF solution of **2** under more forcing thermal conditions (120 °C, 24 h). In this case, the appearance of **3** was accompanied by the formation of an equimolar quantity of [$BeMe_2(THF)_n$], which was easily identified by ^{1}H NMR spectroscopy. We suggest that this diorganoberyllium species and the ring opening of the IPr occurs through the unobserved formation of [BeH_2(IPr)] by a Schlenk-type equilibration process. Use of $PhSiD_3$ in place of $PhSiH_3$ in the reaction sequence employed to produce compounds **2** and **3** led to the exclusive incorporation of deuterium at the beryllium-bound methylene group of [D$_2$]-**3**, while crossover experiments between [D$_2$]-**2** and $PhSiH_3$ provided evidence for the formation of [D$_1$]-**3** (see Scheme 1 and the Supporting Information). Thus, we also discount the possibility of a radical-initiated process in which the methylene group of **3** arises by hydride abstraction from the reaction solvent. We suggest instead that the formation of compound **3** occurs through the direct interaction of an IPr ligand with the highly polarizing dihydridoberyllium center, either during or subsequent to its interaction with $PhSiH_3$.

In summary, we have observed that direct insertion of a BeH_2 unit into a C–N bond of an N-heterocyclic carbene may be effected under mild conditions. We are currently attempting to clarify the mechanism of this process and to assess the generality of this reactivity with other NHC ligands.

Experimental Section

CAUTION: Beryllium and its compounds are extremely toxic. Suitable precautions (e.g., use of protective clothing, breathing apparatus, and a well-ventilated fume cupboard) should be taken for all manipulations involving these species. Details of the synthesis, characterization data, and the crystallographic protocols employed in this study are given in the Supporting Information. CCDC 848117, 848118, and 848119 contain 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.

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