# Activation of N-Heterocyclic Carbenes by {BeH₂} and {Be(H)(Me)} Fragments

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Ⓢ Supporting Information

ABSTRACT: A stable three-coordinate dimethylberyllium species coordinated by the 1,3-bis(2,4,6-trimethylphenyl)-imidazol-2-ylidene (IMes) ligand is readily converted to the corresponding methylhydrido derivative through metathetical reaction with phenylsilane. Attempts to synthesize the corresponding molecular dihydrides are, however, unsuccessful and result in ring opening of an IMes ligand through hydride transfer to the donor carbon atom and the consequent formation of a heterocyclic beryllium organoamide. In agreement with previous calculations, we suggest that this process occurs via a Schlenk-type equilibration process and formation of a four-coordinate bis-NHC beryllium dihydride. These species are not observed, however, as the steric pressure exerted by coordination of the two sterically demanding IMes ligands is sufficient to induce hydride transfer. The latter deduction is supported by the observation that a similar ring-opened product, but derived from methyl and hydride transfer, is available through the introduction of a further equivalent of IMes to the isolated beryllium methyl hydride species. In the latter case the ring-opening process is more facile, which we ascribe to the increased steric pressure achieved upon the formation of four-coordinate beryllium. In a further striking reaction under more forcing thermal conditions, the carbene carbon center of an IMes ligand is observed to be completely eliminated with selective formation of a three-coordinate diamidoberyllium species.
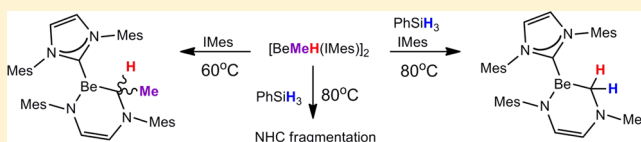
INTRODUCTION

While the past decade has witnessed significant advances in the chemistry of the heavier alkaline earth elements (Mg, Ca, Sr, and Ba),[1] their lightest congener, beryllium, maintains its role as the black sheep of the family. Central to recent progress in heavier group 2 element reactivity has been the exploitation of well-defined molecular hydride species[2] such as the μ-hydrido magnesium and calcium β-diketiminate derivatives [HC{(Me)-CN(2,6-^{i}Pr₂C₆H₃)₂MH(THF)$_n$]₂ (M = Mg, n = 0;[3] M = Ca, n = 1[4]) and several magnesium hydride cluster molecules supported by either polynucleating β-diketiminate or neutral N-heterocyclic carbene (NHC) ligands.[5−7] Although the synthesis and structural characterization of several molecular beryllium monohydrides has been described during the past four decades,[2,8−16] impeded by its reputation as among the most toxic of the nonradioactive elements,[17] concerted study of the reaction chemistry of even these simplest beryllium derivatives has been unsurprisingly sporadic. Derived from the smallest group 2 element, however, the Be²⁺ cation may be expected to display unique characteristics as a consequence of its high charge density and resultant polarizing capacity, variations of which have been implicated in the ability of its heavier congeners to effect a variety of cross metathetical[18] and heterofunctionalization catalyses.[1,19]

Motivated by these considerations, we have previously described attempts to synthesize an NHC-supported molecular beryllium dihydride by silane metathesis with the three-coordinate dimethyl species [Me₂Be·(IPr)] (**I**, IPr = 1,3-bis(2,6-di-isopropylphenyl)imidazol-2-ylidene).[20] Although re-

action with one stoichiometric equivalent of PhSiH₃ was observed to proceed with the smooth formation of the desired methyl monohydride derivative [Me(μ-H)Be·(IPr)]₂ (**II**), further attempts to form the putative dihydride species were thwarted by a previously unobserved NHC degradation pathway in d_8-THF at 80 °C over 6 h involving ring opening by C−N bond cleavage of the imidazolylidene framework to form the heterocyclic organoamido species **III** (Scheme 1).[21] Subsequent to this initial report the groups of Rivard and Radius described analogous reactions between IPr and the aminoborane [H₂B(NHDipp)] (**IV**)[22] and 1,3-dialkyl- and 1,3-diarylimidazolin-2-ylidenes and Ph$_n$SiH$_{4-n}$ (**V**, n = 1, 2, 3),[23] respectively, although these reactions required higher temperatures (100 °C) and longer reaction times (up to 3 days) to proceed. Computational analyses by Dutton,[24] Su,[25] Fang,[26] and Brown[27] of the silane- and borane-mediated processes have highlighted a common mechanism involving initial hydrogen atom migration to the carbene carbon followed by ring expansion through insertion of the main group hydride into the ring prior to the hydrogen transfer process. Dutton and co-workers deduced a similar mechanism for the beryllium-centered reaction based on calculations performed on a simplified model featuring IMes ligands (IMes = 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene) and from a starting point of our initial postulate that the ring-opening reactivity occurs via the *in situ* formation of a [H₂Be·NHC]
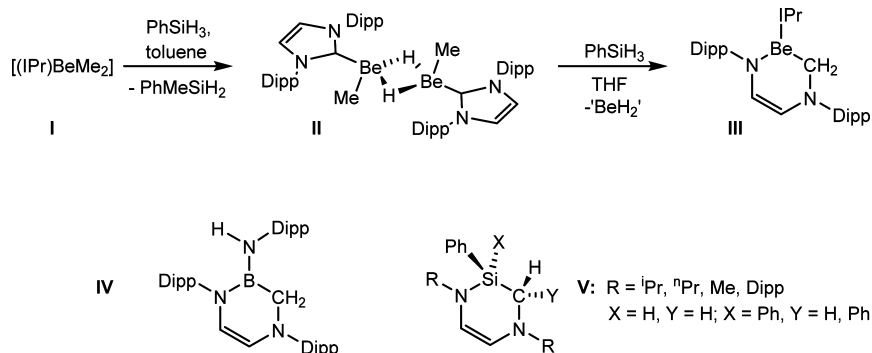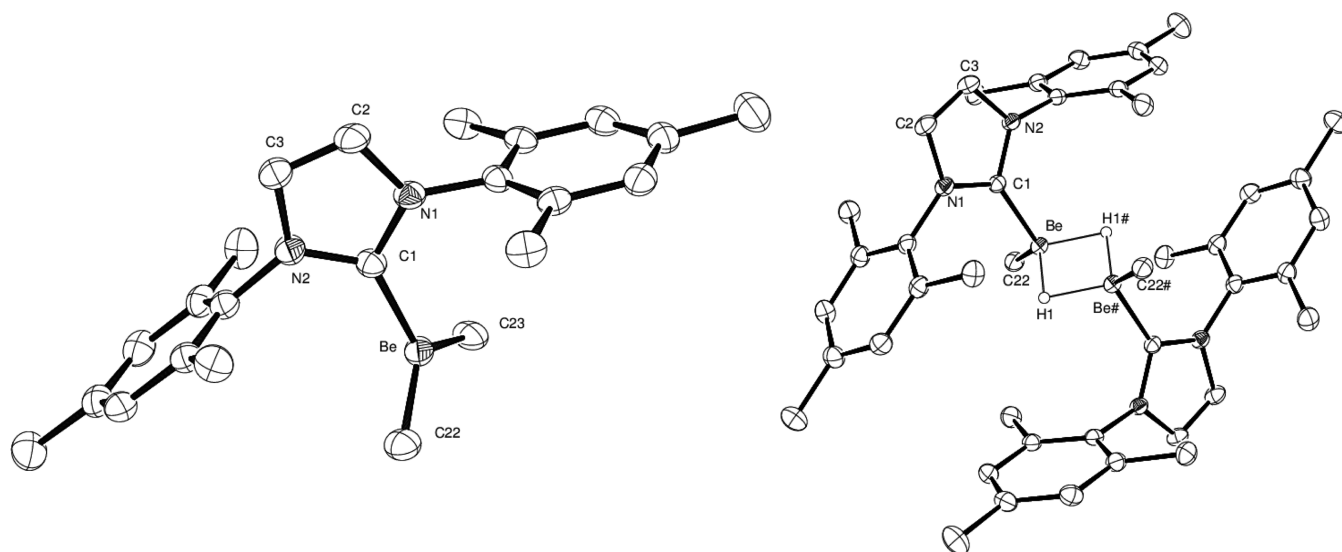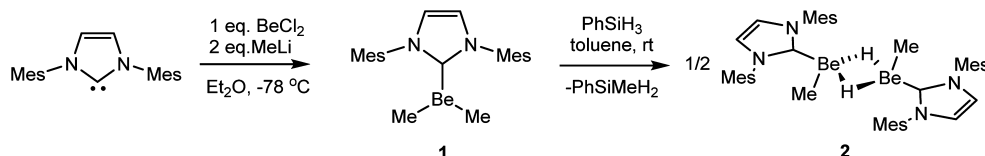
Scheme 1

Scheme 2

Figure 1. ORTEP representations of compounds **1** (left) and **2** (right). Ellipsoids are drawn at 20% probability. Hydrogen atoms are omitted for clarity, except for the bridging hydride atom H1 in **2**. Symmetry transformations used to generate equivalent atoms in **2**: #1 −x, −y, −z+1; #2 −x+1, −y+1, −z+1.

compound.[24b] Their calculations suggested that this monomeric species would preferentially bind a second NHC prior to the first hydrogen atom transfer step. While this latter observation is consistent with the products derived from the reaction stoichiometry depicted in Scheme 1 and deuterium labeling studies described in our initial communication, further synthetic mechanistic interrogation was hampered by the virtual insolubility of the intermediate methylhydrido beryllium species, **II**, in all but the donor solvent THF at elevated (80 °C) temperatures. In this contribution we describe the synthesis of highly soluble analogues of compounds **I**–**III**, which are more amenable to mechanistic analysis.

■ RESULTS AND DISCUSSION

The IMes-stabilized dimethylberyllium NHC adduct **1** (IMes = N,N′-bis(2,4,6-trimethylphenyl)imidazol-1-ylidene) was synthesized by a salt metathesis route in diethyl ether, following

the same procedure used to obtain **I** (Scheme 2).[20] Extraction into toluene and filtration away from the dense white LiCl precipitate yielded a clear yellow solution. Recrystallization from a saturated toluene solution at −18 °C afforded a crop of large colorless crystals of compound **1** (58% yield). The yield could be improved to 80% by reacting the IMes precursor with a premade stock solution of BeMe$_2$ in toluene obtained by salt metathesis between BeCl$_2$ and two equivalents of methyllithium. The ^{1}H NMR spectrum of compound **1** displayed a characteristic upfield (6H) singlet at −0.73 ppm attributed to the beryllium-coordinated methyl groups, 0.24 ppm downfield of the analogous resonance observed for **I**. Comparison with NMR data of the free NHC precursor also confirmed the presence of a single beryllium-coordinated NHC ligand. The ^{13}C{^{1}H} NMR spectrum comprised a distinctive downfield resonance at 184.9 ppm for the carbenoid carbon as well as an upfield signal at −3.7 ppm assigned to the beryllium-bound

methyl carbons (confirmed by an HMQC experiment), which was broadened by coupling with the adjacent quadrupolar beryllium atom. As was the case for **I**, compound **1** also provided a single broad ^{9}Be NMR resonance around 25 ppm, comparable to that of the previously reported NHC-stabilized organoberyllium compound $[Ph_2Be\cdot\{C(N(^iPr)CMe)_2\}]$ (δ_{9Be} 21.1 ppm).[28] A ^{1}H$-^9$Be HMQC experiment showed a two-bond correlation between this ^{9}Be NMR shift and the upfield BeCH_3 protons at −0.73 ppm.

Highly air-sensitive single crystals of compound **1** suitable for X-ray diffraction analysis were obtained from saturated toluene solutions stored at low temperature. The structure of compound **1** is displayed in Figure 1, and selected bond lengths and angles are provided in Table 1, together with

Table 1. Selected Bond Lengths and Angles for Compounds I, 1, II, and 2

	I[a]	1[b]	II[c]	2[d]
Be−C1	1.816(2)	1.820(4)	1.822(2)	1.8002(19)
Be−X	1.734(2)	1.736(5)	1.813(2)	1.777(2)
Be−Y	1.749(2)	1.739(5)	1.552(18)	1.456(15)
Be−H1#			1.630(18)	1.496(15)
C1−N1	1.3555(15)	1.359(3)	1.3608(16)	1.3579(16)
C1−N2	1.3568(16)	1.353(3)	1.3622(16)	1.3558(15)
N1−C2	1.3887(17)	1.387(3)	1.3858(17)	1.3897(16)
N2−C3	1.3853(16)	1.394(3)	1.3878(17)	1.3923(16)
C2−C3	1.3430(19)	1.341(4)	1.344(2)	1.340(2)
C1−Be−X	118.07(12)	113.6(2)	115.47(11)	114.49(10)
C1−Be−Y	113.95(11)	118.6(3)	107.6(7)	106.9(6)
C1−Be−H1#			103.5(7)	105.7(6)
X−Be−Y	127.70(12)	127.8(3)	113.9(7)	118.6(6)
X−Be−H1#			117.9(7)	119.5(6)
H1−Be−H1#			96.3(7)	88.6(6)
Be−H1−Be#			83.7(7)	91.4(6)
N1−C1−Be	131.46(11)	127.0(2)	127.27(11)	129.14(10)
N2−C1−Be	123.91(10)	129.1(2)	129.21(11)	126.85(10)
N1−C1−N2	103.87(10)	103.7(2)	103.42(11)	103.98(10)
C1−N1−C2	111.26(10)	111.5(2)	111.45(11)	111.33(11)
C1−N2−C3	111.65(10)	111.8(2)	111.89(11)	111.34(10)
N1−C2−C3	106.80(11)	106.9(2)	107.09(12)	106.73(11)
N2−C3−C2	106.40(12)	106.2(2)	106.15(12)	106.61(11)

[a]X = C28, Y = C29. [b]X = C22, Y = C23. [c]X = C28, Y = H1. [d]X = C22, Y = H1.

structural data for $[Me_2Be\cdot(IPr)]$ (**I**) for comparative purposes. Although structurally very similar, compounds **I** and **1** crystallize in different space groups (**I** monoclinic $P2_1/n$; **1** orthorhombic $Pcab$) as three-coordinate monomers. In both cases the beryllium centers adopt a trigonal planar geometry with C−Be−C angles close to 120° [**I** C1−Be−C28 118.07(12)°; C1−Be−C29 113.95(11)°; C28−Be−C29 127.70(12)°; **1** C1−Be−C22 113.6(2)°; C1−Be−C23 118.6(3)°; C28−Be−C29 127.8(3)°]. The BeMe$_2$ fragment in compound **1** subtends an angle of ca. 78° with the planar NHC framework, the beryllium atom lying ca. 0.27 Å above the ligand plane. In compound **1** this distance is reduced to ca. 0.12 Å, inducing a rotation of the BeMe$_2$ fragment such that the angle with the ligand plane becomes more acute (ca. 62°). As a result, the N−C1−Be angles around the carbene carbon (C1) differ greatly between the two compounds [**I** 131.46(11)°, 123.91(10)°; **1** 127.0(2)°, 129.1(2)°]. These variations may be rationalized as a consequence of the differing steric compression exerted on the BeMe$_2$ fragment by the respective isopropyl and methyl *ortho*-substituents of the NHCs' pendant aryl groups. All other angles and bond lengths in the two compounds are otherwise very similar. The Be−C bond lengths [**I** Be−C1 1.816(2); Be−C28 1.734(2); Be−C29 1.749(2) Å; **1** Be−C1 1.820(4); Be−C22 1.736(5); Be−C23 1.739(5) Å], in particular, are comparable to those in the only other crystallographically characterized NHC-supported diorganoberyllium compound $[Ph_2Be\cdot\{C(N(^iPr)CMe)_2\}]$ [Be−C$_{carbene}$ 1.807(4); Be−CPh 1.745(4), 1.757(4) Å][28] and Robinson's beryllium chloride and borohydride adducts of the IPr ligand [1.773(5), 1.765(2) Å].[29]

As was the case for **I**, the reaction between **1** and two equivalents of phenylsilane in toluene at room temperature did not yield the desired dihydridoberyllium compound but the dimeric NHC-stabilized methylhydridoberyllium compound, **2**, together with one equivalent of the metathesis byproduct PhSiMeH$_2$. In contrast to the analogous IPr compound, **II**, which was virtually insoluble in both noncoordinating and coordinating hydrocarbon solvents, precluding the acquisition of meaningful ^{13}C NMR data, compound **2** was highly soluble in C$_6$D$_6$ and d_8-toluene. Figure 2 shows annotated ^{1}H NMR and ^{1}H$-^9$Be HMQC spectra of the *in situ* reaction after full consumption of **1**. The IMes ^{1}H NMR resonances were very similar to those of compound **1**, with the exception of the 6H singlet of the mesityl *ortho*-substituents, which underwent a
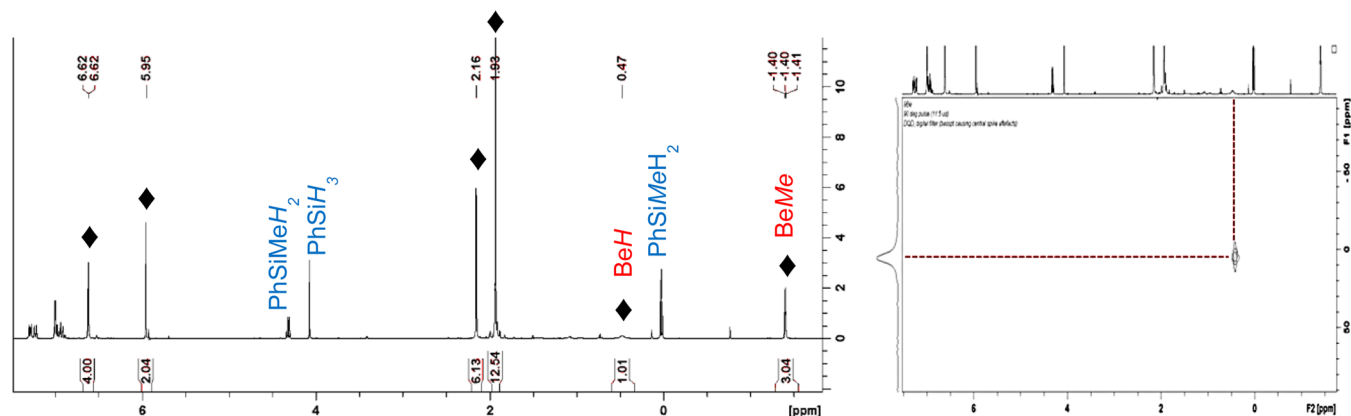
Figure 2. ^{1}H NMR (left) and ^{1}H−^{9}Be HMQC (right) spectra recorded in C$_6$D$_6$ after completion of the reaction between **1** and two equivalents of PhSiH$_3$. ◆ indicates the resonances of the methylhydrido dimer, **2**.

downfield shift of 0.24 ppm. The characteristic 6H Be(CH_3)$_2$ singlet at −0.73 ppm was replaced with a triplet further upfield at −1.26 ppm (^3J = 1.9 Hz), integrating to three protons relative to the IMes ligand and suggesting the retention of a dimeric hydride-bridged compound in solution. A new broad resonance corresponding to 1H by integration was observed to appear concomitantly at 0.61 ppm, which was correlated with the protons of the beryllium-bound methyl group in the corresponding COSY experiment. The ^{9}Be NMR spectrum displayed a single new resonance at 5.6 ppm, significantly upfield from that of the starting material **1** (25.4 ppm), displaying a ^{1}H−^{9}Be HMQC interaction with the 1H resonance at δ_{1H} 0.61 ppm.

An unstirred preparative-scale reaction between **1** and one equivalent of PhSiH$_3$ in benzene yielded a crop of large colorless crystals of compound **2** (85% yield), suitable for X-ray diffraction analysis. The resulting crystal structure, displayed in Figure 1, revealed a dimeric IMes-supported methylhydroberyllium compound with bridging hydride atoms, which were located and freely refined. Table 1 presents selected bond lengths and angles for **2** and its previously reported IPr analogue, **II**. In both compounds the beryllium centers display a pseudotetrahedral geometry [**II** C1−Be−C28 115.47(11)°; C1−Be−H1 107.6(7)°; C1−Be−H1# 103.5(7)°; **2** C1−Be−C22 114.49(10)°; C1−Be−H1 106.9(6)°; C1−Be−H1# 105.7(6)°]. While the Be−C$_{carbene}$ bond length [1.822(2) Å] of **II** is similar to that in the lower coordinate dimethylberyllium precursor, **I** [1.816(2) Å], the corresponding bond in compound **2** is somewhat shortened [**2** 1.8002(19); **1** 1.820(4) Å]. The Be−C$_{Me}$ bond lengths, however, increase by ca. 0.08 Å in **II** and 0.04 Å in compound **2** relative to the respective dimethylberyllium NHC precursors. The central planar Be$_2$H$_2$ units of both dimers form quasi-square arrays [**II** Be−H−Be 96.3(7)°, H−Be−H 83.7(7)°; **2** Be−H−Be 88.6(6)°, H−Be−H 91.4(6)°]. While the Be−H bond lengths in compounds **II** and **2** are strongly dependent on the steric demands of the NHC coligand [**II** 1.552(18) and 1.630(18) Å; **2** 1.456(15) and 1.496(15) Å], all these distances are somewhat longer than those in the similarly four-coordinate hydridoberyllium tris-(pyrazolyl)borate reported by Parkin and co-workers [1.228(70) Å][16] and Shearer's dimeric *N,N,N′*-trimethylethylenediamido beryllium hydride compound [1.39(2) Å],[30] both of which contain a terminal hydride ligand. The Be−H distances in **II** and **2** are, however, similar to the bridging interactions reported for the dimeric ate-compound [Na$_2${Be$_2$Et$_4$H$_2$}·2Et$_2$O] [1.53(3) Å].[14]

In a similar manner to that observed previously for compound **II** in THF solution, a d_8-toluene reaction mixture of compound **2** and a further equivalent of PhSiH$_3$ heated at 80 °C for 6 h yielded a clear dark red solution. Analysis by ^{1}H NMR spectroscopy evidenced full conversion of PhSiH$_3$ to the expected metathesis byproduct PhMeSiH$_2$ (Scheme 3) as well as the formation of a single well-defined product, compound **3**, containing one coordinated NHC ligand and another NHC-

derived environment characterized by a distinctive AB spin system at δ_{1H} 5.02 and 4.79 ppm and a set of unsymmetrical mesityl methyl resonances. Comparison with NMR data recorded for the previously reported ring-expanded IPr derivative, **III**, confirmed the product as the analogous IMes-supported six-membered alkylamidoberyllium ring system [{MesNCH=CHN(Mes)CH$_2$}Be·(IMes)] (**3**). Similarly to compound **III**, HMQC data for compound **3** revealed coupling between an otherwise unobserved ^{13}C NMR resonance at 40.2 ppm, broadened by ^{9}Be−^{13}C coupling, and a ^{1}H NMR resonance at 2.32 ppm, overlapping with a mesityl methyl singlet, which was attributed to the beryllium-bound methylene fragment (Figure 3).

X-ray quality crystals of compound **3** were obtained through recrystallization of the product of the NMR-scale reaction in d_8-toluene at room temperature. The results of the X-ray diffraction experiment are displayed in Figure 4. Selected bond length and angle data are provided in Table 2, along with the equivalent parameters for compound **III**. The apparent asymmetry of the ligand backbone observed in the NMR spectra is caused by what can be effectively considered as the insertion of a BeH$_2$ unit into a C$_{carbene}$−N bond with transfer of the hydrogens onto the carbenoid carbon atom. The result is a six-membered BeC$_3$N$_2$ ring with a flattened boat conformation, in which the three-coordinate beryllium center is bound to a bidentate amidoalkyl ligand and a single unchanged IMes ligand. The beryllium centers in both compounds are trigonal planar with little variation in the bond lengths and angles, except for the Be−N1 distance, which is shorter in **3** [1.560(5) Å] than the corresponding measurement in one of the two independent molecules observed in structure **III** [Be(2)−N(8) 1.592(5) Å]. This may be ascribed to the differences in steric bulk of the respective N1-aryl groups. As expected, the newly formed Be−C3 bond to the dianionic alkylamido ligand [**III** 1.741(5), 1.744(5); **3** 1.756(5) Å] is significantly shorter than the Be−C$_{carbene}$ bond to the neutral NHC ligand [**III** 1.803(5), 1.805(5); **3** 1.807(5) Å]. The geometry around C3 clearly indicates sp^3 hybridization and a C3−N2 single bond [Be−C3−N2: **III** 112.5(2)°, 113.0(2)°; **3** 111.1(2)°; C3−N2: **III** 1.471(4), 1.473(4); **3** 1.462(4) Å]. It is also notable that the N1−C1 [**III** 1.422(4), 1.414(4); **3** 1.406(3) Å] and N2−C2 bond lengths [**III** 1.389(4), 1.396(4); **3** 1.379(4) Å] are no longer identical and are significantly longer than in the parent NHC ligands (ca. 1.35 Å), suggesting some loss of delocalization. While NHC compounds have been shown to be generally stable under catalytic conditions, they are also susceptible to various decomposition processes involving C−H, C−C, and C−N bond-activation reactions at peripheral and exocyclic positions.[21] The reactions leading to compounds **III** and **3**, however, are particularly unusual, as they involve loss of possible aromatic character, reduction of the carbene carbon atom, and ring expansion. The C−C and C−N bond lengths and angles within the alkylamido ligands in the borane and silane ring-opened products (**IV** and **V**) are closely comparable to those in compounds **III** and **3**.[22,23]

It is notable that the amidoalkylberyllium fragments of compounds **III** and **3** are isomeric to the target [H$_2$Be·(NHC)] compounds. The presence of a second equivalent of unreacted IPr or IMes ligand to complete the beryllium coordination sphere therefore requires the formal loss of "BeH$_2$" during the reaction. Indeed, examination of the ^{9}Be NMR spectra for the *in situ* formation of both **III** in d_8-THF and **3** in d_8-toluene revealed additional resonances at 0.7 and −3.9 ppm,
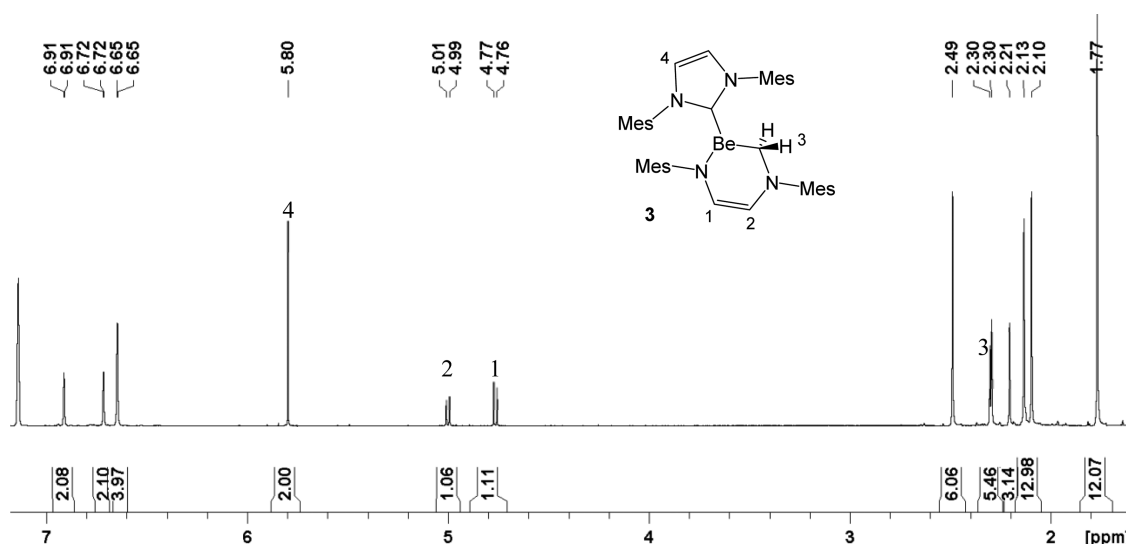
Scheme 3

2   3
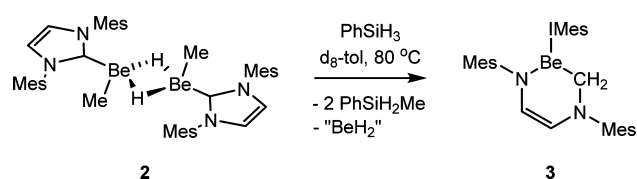
Figure 3. Annotated ^{1}H NMR spectrum of isolated crystals of compound **3**.
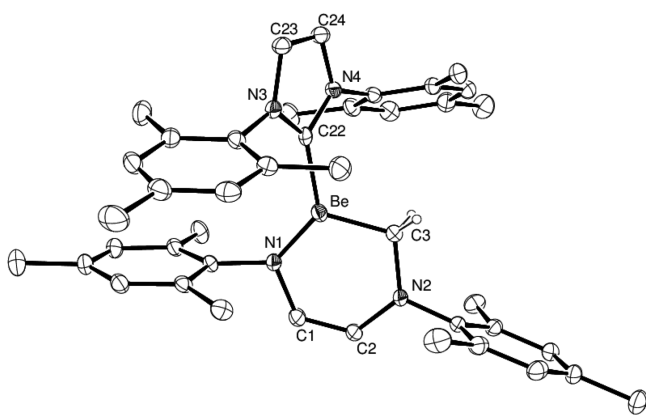

Figure 4. ORTEP representation of compound **3**. Ellipsoids are drawn at 20% probability. Hydrogen atoms are omitted for clarity, except for those on the methylene carbon C3.

Table 2. Selected Bond Lengths and Angles for Compounds III, 3, and 4

|	III	3	4
Be–C$_{carbene}$	1.803(5), 1.805(5)	1.807(5)	1.808(3)
Be–N1	1.587(5), 1.592(5)	1.560(5)	1.577(3)
Be–C3	1.741(5), 1.744(5)	1.756(5)	1.766(3)
N1–C1	1.422(4), 1.414(4)	1.406(3)	1.419(2)
C1–C2	1.343(4), 1.339(4)	1.344(4)	1.342(3)
C2–N2	1.389(4), 1.396(4)	1.379(4)	1.391(2)
N2–C3	1.471(4), 1.473(4)	1.462(4)	1.481(2)
C3–C4			1.535(3)
C$_{carbene}$–Be–N1	130.4(3), 129.1(3)	128.9(2)	128.08(16)
C$_{carbene}$–Be–C3	113.7(2), 114.8(3)	115.1(3)	115.52(15)
N1–Be–C3	115.7(3), 115.6(3)	116.0(2)	116.19(15)
Be–N1–C1	112.8(2), 113.4(2)	116.4(2)	114.32(15)
Be–C3–N2	112.5(2), 113.0(2)	111.1(2)	111.81(14)
Be–C3–C4			109.57(15)
N2–C3–C4			110.13(15)
N1–C1–C2	126.5(3), 126.6(3)	125.5(3)	127.00(17)
C1–C2–N2	125.5(3), 126.5(3)	126.4(3)	127.55(17)
C2–N2–C3	117.9(2), 118.3(2)	121.9(2)	120.66(14)

respectively, alongside the broad singlet of the alkylamidoberyllium compounds at 16.9 ppm (compound **III**) and 11.0 ppm (compound **3**). In the case of the formation of compound **3** this additional resonance appeared as a poorly defined multiplet, indicating likely ^{1}H–^{9}Be coupling. Although it seems likely that a solvated mononuclear constitution for BeH$_2$ is readily attributed in a coordinating solvent such as THF, solutions in less basic hydrocarbon solvents do not appear to have been studied. Crystalline beryllium hydride has been shown to comprise a body-centered orthorhombic unit cell, containing a network of corner-sharing {BeH$_4$} tetrahedra,[31] while studies of the amorphous form also find that it consists of a network of corner-shared tetrahedra.[32] It seems likely, therefore, that smaller oligomers built around similar interactions are likely to persist under the conditions of the formation of compounds **III** and **3** in nonbasic media. Repetition of the reaction with two equivalents of PhSiD$_3$ in place of PhSiH$_3$ led to the exclusive formation of [**D$_2$**]-**3**, comprising a fully deuterated beryllium-bound methylene fragment. In this case the ^{9}Be NMR resonance of the "*Be*D$_2$" byproduct appeared as an ill-defined multiplet at −1.4 ppm. The slight downfield shift of this ^{9}Be nucleus compared to "*Be*H$_2$" is consistent with its interaction with the marginally reduced effective nuclear charge of the deuteride ligands. Furthermore, ^{2}H NMR data revealed, alongside the deuterated methylene resonance of **3** (2.11 ppm) and the resonance of the PhSiMeD$_2$ byproduct (4.38 ppm), a third resonance at 1.20 ppm, which may be attributed to "BeD_2" (see Figure S1 in the Supporting Information). Unfortunately ^{1}H–^{9}Be HMQC experiments failed to confirm the location of the corresponding, presumably highly broadened, hydride resonance in the ^{1}H NMR spectrum.

In an analogous fashion to compound **III**, compound **3** was also formed through heating a C$_6$D$_6$ solution of **2** in the absence of PhSiH$_3$ under forcing thermal conditions (110 °C, 5 days) as depicted in Scheme 4. In this case the formation of compound **3** was accompanied by the appearance of two molar equivalents of the dimethylberyllium compound **1** as identified by ^{1}H NMR spectroscopy. This latter process may be a consequence of thermally induced Schlenk-type ligand redistribution to the unreactive dimethylberyllium compound **1** and an unobserved dihydridoberyllium species, which then

Scheme 4
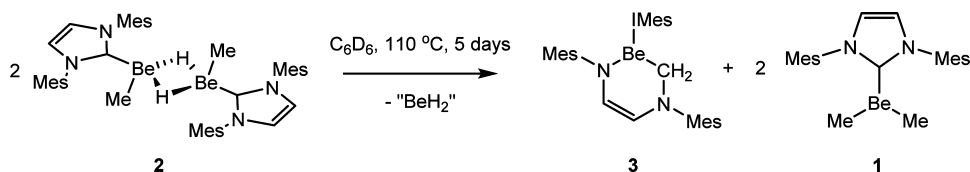
Scheme 5
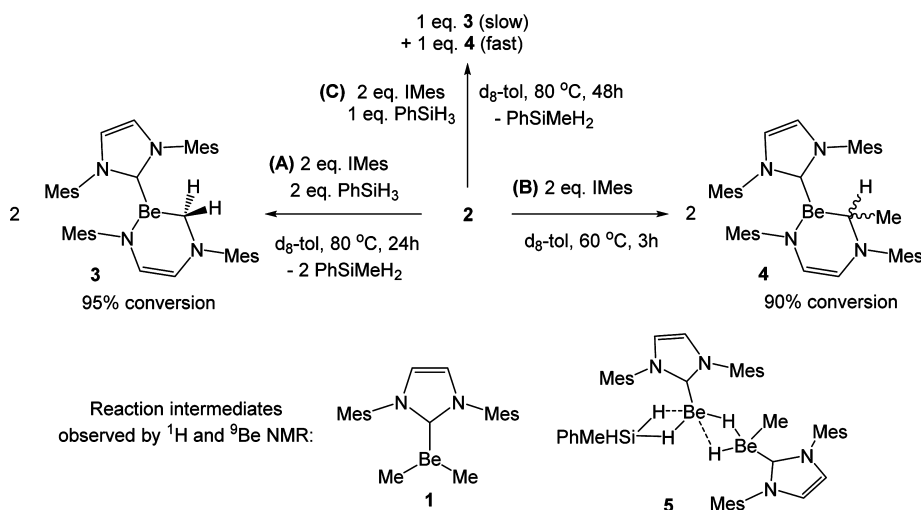
reacts further to yield the ring-opened product **3**, releasing "BeH$_2$".

These observations confirm that the presence of phenylsilane is unnecessary for the formation of either **3** or **III**. It is also apparent from the reaction stoichiometries depicted in Schemes 3 and 4 that the addition of two further equivalents of IMes during these reactions should allow the remaining "BeH$_2$" to generate a further equivalent of the ring-opened alkylamidoberyllium compound, **3**. Accordingly the reaction of **2** with two equivalents of both PhSiH$_3$ and IMes at 80 °C over 24 h led to the consumption of all reactants and the exclusive formation of **3** and two equivalents of PhSiMeH$_2$ without any other byproducts (Scheme 5, pathway A). From this observation we postulate that this process, involving the formation of a species of the form [H$_2$Be(IMes)$_2$] similar to the [H$_2$Be-(NHC)$_2$] intermediates invoked in the computational DFT study reported by Dutton and co-workers,[24] is a prerequisite to allow the ring-opening process for the formation of **3**.

An identical reaction in the presence of an additional equivalent of IMes but *without* added phenylsilane induced a rapid color change in the reaction mixture to orange at 60 °C, again suggestive of N−C bond cleavage and beryllium insertion. Notably, this process occurred under significantly less energetic conditions than had been the case in the presence of PhSiH$_3$, implying an inhibitory effect of the silane. Thus, after 3 h at 60 °C, ^{1}H NMR analysis indicated near-quantitative consumption of all reactants with clean formation (90%) of a single ring-expanded product reminiscent of compound **3**. In this case the AB spin system arising from the desymmetrized ligand backbone methine centers was found to have undergone a 0.07 ppm downfield shift (δ_{1H} 4.86 vs 4.79 ppm in **3**), and the spectrum did not exhibit the expected methine singlet at δ_{1H} 2.32 ppm. Rather, the appearance of a distinctive 3H doublet at 1.36 ppm was observed, which was shown to couple to a resonance at 2.07 ppm overlapping with the IMes methyl

resonances through a COSY experiment. Moreover, the methyl and *meta*-aryl proton resonances of both the neutral bound IMes and the ring-opened alkylamido ligands were observed to become magnetically inequivalent, suggesting the presence of a chiral center within the reaction product. ^{13}C{^{1}H} NMR analysis and HMQC and HMBC experiments led to the identification of this new product as compound **4**, in which both methyl and hydride ligands had been transferred to the carbenoid carbon atom during the ring-expansion process (Scheme 5, pathway B). In addition, it appears that the formation of the methylated compound **4** is kinetically favored over that of **3**, a hypothesis that was confirmed through monitoring of a further reaction between dimer **2**, two equivalents of IMes, and a single equivalent of PhSiH$_3$ at 80 °C. In this case the rapid formation of one molar equivalent of compound **4** was observed over a period of 2 h, while compound **3** was formed much more slowly over a period of 48 h (Scheme 5, pathway C). We suggest that these observations provide corroborative evidence for the deductions of Dutton and co-workers that the ring-opening process necessitates the formation of a four-coordinate and bis-NHC ligated Be center. Furthermore, the kinetic facility of the methyl/hydride transfer resulting in the formation of compound **4** is enhanced by the greater steric compression induced in the putative [(IMes)$_2$BeMeH] intermediate compound versus the corresponding dihydrido species invoked during the synthesis of compound **3**.

Large crimson single crystals of compound **4** were obtained from a saturated toluene solution at room temperature over several days. The structure of compound **4** is displayed in Figure 5, while selected bond lengths and angles are provided in Table 2. The Be−C$_{carbene}$ bond length [1.808(3) Å] is very similar to that in the other two ring-expanded compounds, **III** and **3**, and the bond lengths and angles around C3 [Be−C3 1.766(3); C3−N2 1.481(2); C3−C4 1.535(3) Å; Be−C3−N2 111.81(14)°; Be−C3−C4 109.57(15)°; N2−C3−C4
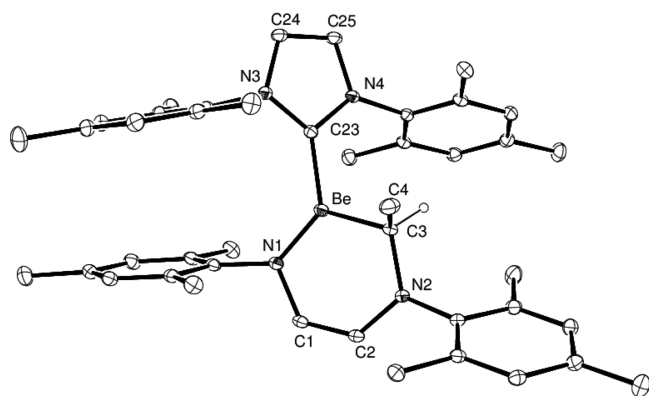
Figure 5. ORTEP representation of compound **4**. Ellipsoids are drawn at 20% probability. Hydrogen atoms are omitted for clarity, except for that on the methine carbon C3.

110.13(15)°] are clearly indicative of sp^3 hybridization. Furthermore, the higher steric demands of the C3-methyl functionality of **4** compared to the hydrogens of the methylene fragment of compound **3** result in a lengthening of all bonds within the six-membered BeN$_2$C$_3$ ring by 0.010 to 0.019 Å, except for the C1−C2 vinylene backbone. The ring itself is only slightly distorted from planarity and subtends a 47° angle with the planar framework of the neutral IMes ligand.
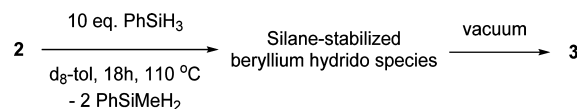
Careful monitoring of the formation of compounds **3** and **4** by ^{1}H and ^{1}H−^{9}Be HMQC NMR experiments revealed the formation and consumption of small amounts of the dimethylberyllium compound **1** as well as a new compound characterized by a distinctive upfield triplet at δ_{1H} −1.32 ppm. COSY analysis indicated a coupling of this latter signal to a resonance overlapping with the methyl protons of PhSiMeH$_2$ at ca. 0.3 ppm, which, in turn, correlated with a very broad resonance at ca. 2.8 ppm. Furthermore, a ^{1}H−^{9}Be HMQC NMR experiment performed on the reaction mixture revealed a new ^{9}Be NMR resonance at ca. 2.0 ppm, which coupled to both the ^{1}H NMR resonances at 0.3 and 2.8 ppm (see Figures S2 and S3 in the Supporting Information). The integrity of this new compound (**5**) was demonstrated by the observation of a single diffusion coefficient for these resonances in the corresponding ^{1}H DOSY NMR spectrum, leading to its tentative identification as the dimeric methyldihydrido diberyllium silanate [(IMes)·BeMe(μ-H$_2$)Be(SiH$_2$MePh)·(IMes)], compound **5** (see Scheme 5). Attempts to isolate compound **5** failed due to its solution instability at the given reaction temperatures. The appearance of both **1** and **5** during both of these reactions emphasizes that Schlenk-type ligand exchange is a key process during the formation of both **3** and **4** in the absence of PhSiH$_3$.

The role of phenylsilane was further investigated with a proton−deuterium crossover experiment. Addition of two equivalents of PhSiD$_3$ to a solution of **2** led to H/D exchange to form PhSiD$_{3-n}$H$_n$ ($n = 1–3$) and a 2:3 mixture of **D$_2$-2** and **2** after 30 min at room temperature as determined by NMR spectroscopy. Five minutes of heating at 100 °C resulted in full deuteration of **2** without any evidence for Be−C/Si−H σ-bond metathesis. After a further 30 min at 100 °C, however, the appearance of the σ-bond metathesis product PhSiMeD$_{2-n}$H$_n$ ($n = 0–2$) was observed, alongside compounds **1** and **5**. Notably, discernible evidence for the commencement of the ring-opening process was observed only after several hours' heating at 110 °C, with the diprotio product, **3**, being formed

first followed by the mixed H/D species, **D-3**, and finally the fully deuterated product, **D$_2$-3**. These observations indicate facile H/D exchange between silane and any beryllium hydrido species present in solution, as well as a marked kinetic isotope effect upon the overall ring expansion reaction.

The reaction of 10 molar equiv of PhSiH$_3$ with **2** also evidenced a marked suppression of the ring-opening reactivity. Less than 10% conversion to compound **3** was observed after 18 h of heating at 110 °C despite over 90% of the beryllium methyl groups having undergone σ-bond metathesis (Scheme 6). While ^{1}H NMR resonances were too broad to

Scheme 6

$$\textbf{2} \xrightarrow[\substack{d_8\text{-tol, 18h, 110 °C} \\ -\ 2\ \text{PhSiMeH}_2}]{10\ \text{eq. PhSiH}_3} \substack{\text{Silane-stabilized} \\ \text{beryllium hydrido species}} \xrightarrow{\text{vacuum}} \textbf{3}$$

unambiguously identify the beryllium-containing product(s) in solution, the near-quantitative conversion of beryllium methyl groups suggests the formation of a potentially dimeric NHC- and silane-stabilized dihydridoberyllium species. Attempts to isolate the latter species by removing volatiles were unsuccessful, with the reaction mixture rapidly turning dark red, whereupon NMR analysis of the redissolved solid residue evidenced near-quantitative conversion to **3**. The presence of excess silane, while promoting σ-bond metathesis and the formation of a dihydridoberyllium species, can, thus, be deduced to inhibit hydride transfer and NHC ring opening. In the absence of the stabilizing influence of the silane, however, the dihydridoberyllium NHC adduct is unstable and undergoes spontaneous decomposition to **3**.

Heating of the methylhydrido compound **2** in d_8-toluene under more forcing thermal conditions (110 °C) led to the formation of one equivalent of compound **3** and half an equivalent of a new species apparently displaying two distinct symmetrical IMes environments in a 1:1 ratio in the ^{1}H NMR spectrum (see Figure 6). Heating of a sample of **2** with one equivalent of PhSiH$_3$ in d_8-toluene at 110 °C also led to exclusive and quantitative conversion to this same compound, which a DOSY experiment confirmed to be a single species, compound **6**. ^{9}Be NMR data indicated the presence of a single major beryllium-containing product with a broad singlet at 4.4 ppm, as well as a series of low-intensity and ill-defined overlapping resonances further upfield. An X-ray diffraction experiment performed on single crystals of this orange compound yielded the unexpected structure of an NHC-supported beryllium compound of the diamido ligand [{CHNMes}$_2$]$^{2-}$. Although the crystals diffracted too weakly to collect data beyond $\theta = 24°$, the structure provided unambiguous connectivity (Figure 7) and confirmed the loss of the formerly carbene carbon atom in one of the IMes ligands.

Monitoring of the formation of **6** from **2** and PhSiH$_3$ revealed the appearance and disappearance of compound **3** as a reaction intermediate. Heating of a d_8-toluene solution of isolated crystals of compound **3** to 150 °C for several hours, however, did not result in any reactivity. It was therefore inferred that the byproduct of the formation of **6** from **2** and PhSiH$_3$, formally [BeH$_2$], had to be present for the reaction to occur. Polymeric [H$_2$Be(THF)$_n$]$_m$ was, thus, obtained by precipitation from the reaction of BeMe$_2$ with excess PhSiH$_3$ in boiling THF and added to the sample of **3** in d_8-toluene. Heating at 150 °C for a week indeed provided about 70%
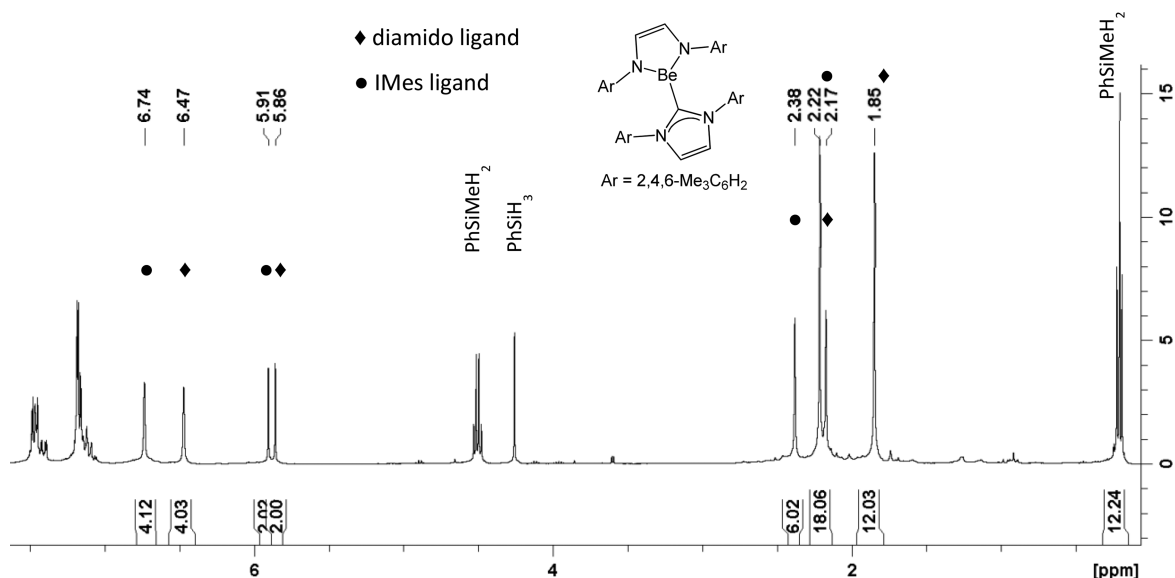
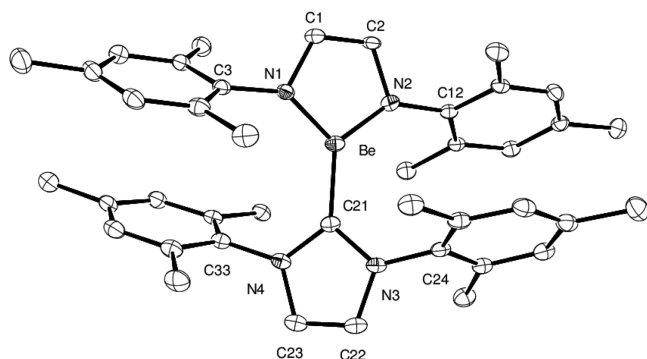**Figure 6.** Annotated ^{1}H NMR spectrum of the reaction leading to the formation of compound **6**.

Figure 7. ORTEP representation of compound **6**. Ellipsoids are drawn at 20% probability. Hydrogen atoms are omitted for clarity.

conversion to compound **6** as well as a few minor unidentified decomposition products, indicating the involvement of [BeH$_2$] in the reaction. Although the fate of the remaining elements required to provide mass balance during the formation of compound **6** could not been definitively resolved, this observation of activation of both N–C bonds within an N-heterocyclic carbene is, to the best of our knowledge, unique.

CONCLUSION

We have observed that dimethylberyllium NHC adducts are stable species and readily form the methylhydrido derivatives upon silane-mediated methyl for hydride exchange. Attempts to synthesize the corresponding molecular dihydrides were unsuccessful, however, and resulted in the formation of heterocyclic beryllium organoamides as a consequence of hydride transfer to the donor carbon atom of a coordinated NHC ligand. In agreement with previous calculations, we suggest that this process is likely to occur via the formation of a four-coordinate bis-NHC beryllium dihydride, whereupon the steric congestion of the Be center is sufficient to induce hydride transfer. The latter deduction is supported by the observation that similar ring-opened products, but derived from methyl and hydride transfer, are available through the introduction of a further equivalent of NHC to the isolated beryllium methyl hydride species. In this case, however, the ring-opening process

is more facile, which we ascribe to the greater relief of steric pressure achieved after the formation of four-coordinate beryllium. Schlenk-type redistribution is evidently a vital process throughout this chemistry, both between the individual Be centers and between the beryllium hydride and silane reaction partners. Although the full scope of this reactivity requires further investigation, these unusual transformations and the fragmentation process leading to compound **6** suggest that beryllium hydrido and organometallic species are worthy of more concerted study than that currently sanctioned by their somewhat fearsome reputation.

■ EXPERIMENTAL SECTION

All reactions dealing with air- and moisture-sensitive compounds were carried out under an argon atmosphere using standard Schlenk line or glovebox techniques in an MBraun Labmaster glovebox at O$_2$, H$_2$O < 0.1 ppm. NMR experiments using air-sensitive compounds were conducted in Youngs tap NMR tubes prepared and sealed in a glovebox under argon. All NMR data were acquired on Bruker 300 or 400 Ultrashield spectrometers for ^{1}H (300/400 MHz), COSY, ^{13}C{^{1}H} (75.48 MHz), and ^{9}Be (56.23 MHz) spectra at room temperature. ^{1}H/^{13}C NMR spectra were referenced using residual solvent resonances, and ^{9}Be NMR spectra were referenced to an external standard of aqueous beryllium chloride. Elemental analyses of all moisture- and air-sensitive compounds were performed by Stephen Boyer of London Metropolitan Enterprises. Solvents for air- and moisture-sensitive reactions were provided by an Innovative Technology Solvent Purification System. C$_6$D$_6$, d_8-toluene, and d_8-THF were purchased from Fluorochem and dried over molten potassium prior to vacuum transfer into a sealed ampule and storage in the glovebox under argon. BeCl$_2$ was purchased from Sigma-Aldrich. 1,3-Bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) was synthesized by a literature procedure.[33]

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 them.*

Synthesis of [Me$_2$Be·IMes], 1. IMes (0.5 g, 1.64 mmol) was combined with BeCl$_2$ (131 mg, 1.64 mmol) and 1.6 M MeLi in Et$_2$O (2.1 mL, 3.36 mmol) at −78 °C. The reaction mixture was allowed to warm to room temperature and stirred overnight. Removal of the solvent *in vacuo*, followed by extraction into hot toluene and filtration, yielded a clear, pale yellow solution. Compound **1** was isolated as colorless crystals from a concentrated toluene solution stored at −18

°C (0.33 g, 0.96 mmol, 58% yield). ^{1}H NMR (300 MHz, 298 K, d_8-tol): 6.67 (s, 4H, m-Ar-H), 6.09 (s, 2H, MesNCH), 2.06 (s, 12H, o-CH_3), 2.05 (s, 6H, p-CH_3), −0.73 (s, 6H, BeCH_3). ^{13}C{^{1}H} NMR (75 MHz, 298 K, d_8-tol): 184.9 (C$_{carbene}$), 139.5, 135.6, 135.5, 129.7, 121.8, 21.3, 18.0, −3.7 (br, BeCH_3). ^{9}Be (56 MHz, 298 K, d_8-tol): 25.4 ppm. Anal. Calcd for C$_{23}$H$_{30}$BeN$_2$ (MW = 353.5): C, 80.42; H, 8.80; N, 8.16. Found: C, 80.30; H, 8.75; N, 8.13.

Synthesis of [MeHBe·IMes]$_2$, 2. Compound **1** (30 mg, 87.3 μmol) and PhSiH$_3$ (10.8 μL, μmol) were combined in C$_6$D$_6$. Quantitative conversion to **2** was reached after 5 h at room temperature. Colorless crystals of **2** were obtained after storing the reaction mixture at 4 °C overnight. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): 6.76 (s, 4H, m-Ar-H), 6.09 (s, 2H, MesNCH), 2.29 (s, 6H, p-CH_3), 2.07 (s, 12H, o-CH_3), 0.61 (br s, 1H, BeH), −1.26 (t, 3H, BeCH_3, ^3J = 1.9 Hz). ^{13}C{^{1}H} NMR (75 MHz, 298 K, C$_6$D$_6$): 179.6 (C$_{carbene}$), 137.5 (i-Ar-C), 136.9, 136.4, 129.0, 121.3 (MesNCH), 21.7, 18.9, −8.2 (br, BeCH_3). ^{9}Be (56 MHz, 298 K, C$_6$D$_6$): 5.6 ppm (cross-peak in ^{9}Be−^{1}H HMQC spectrum at δ_{1H} 0.61 ppm). Anal. Calcd for C$_{22}$H$_{28}$BeN$_2$ (MW = 329.5): C, 80.20; H, 8.57; N, 8.50. Found: C, 80.13; H, 8.48; N, 8.37.

Synthesis of [{MesN(CH)$_2$NMesCH$_2$}Be·IMes], 3. Compound **2** (29 mg, 87.3 μmol) was heated with one equivalent of PhSiH$_3$ (10.8 μL, μmol) in d_8-toluene for 5 h at 80 °C. NMR data showed full conversion to the ring-opened product. Orange-red crystals of compound **3** were obtained from a saturated toluene solution at room temperature. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): 6.93 (s, 2H, $H6/6'$), 6.74 (s, 2H, $H6/6'$), 6.67 (s, 4H, $H14$), 5.82 (s, 2H, $H11$), 5.02 (d, 1H, $H2$, ^3J = 6.3 Hz), 4.79 (d, 1H, $H3$, ^3J = 6.3 Hz), 2.51 (s, 6H, $H8/8'$), 2.32 (s, 2H, $H1$), 2.31 (s, 3H, $H9/9'$), 2.23 (s, 3H, $H9/9'$), 2.15 (s, 6H, $H17$), 2.12 (s, 6H, $H8/8'$), 1.79 (s, 12H, $H16$). ^{13}C{^{1}H} NMR (75 MHz, 298 K, C$_6$D$_6$): 176.2 (C10), 152.4, 150.8 (C4/4'), 139.2 (C15), 136.2 (C5/5'), 135.2 (C12), 134.9 (C13), 131.9 (C7/7'), 129.5 (C14), 128.4, 128.2 (C6/6'), 122.8 (C11), 116.0 (C2), 115.7 (C3), 40.2 (C1), 21.2, 21.0 (C9/9'), 20.0 (C17), 18.7 (C8/8'), 17.7 (C16). ^{9}Be NMR (56 MHz, 298 K, C$_6$D$_6$): 16.9 ppm (br). Anal. Calcd for C$_{42}$H$_{50}$BeN$_4$ (MW = 619.9): C, 81.38; H, 8.13; N, 9.04. Found: C, 81.37; H, 8.38; N, 8.85.

Synthesis of [{MesN(CH)$_2$NMesCHMe}Be·IMes], 4. Compound **4** was stirred in toluene with one equivalent of PhSiH$_3$ at 50 °C for 1 week. The solution slowly turned red. Analysis of the crude showed about 50% conversion to compound **7**. Removal of volatiles and fractional crystallization in hexanes allowed recovery of the unreacted methylhydrido compound **4**. Orange-red crystals of the ring-opened product were obtained from a saturated 9:1 hexanes/toluene solution at room temperature in 34% yield. ^{1}H NMR (300 MHz, 298 K, C$_6$D$_6$): 6.95 (s, 1H, $H6/6'$), 6.89 (s, 1H, $H6/6'$), 6.79 (s, 1H, $H6/6'$), 6.67 (s, 2H, $H6/6'$), 6.61 (s, 1H, $H14$), 6.54 (s, 2H, $H14$), 5.83 (s, 2H, $H11$), 5.02 (d, 1H, $H2$, ^3J = 6.3 Hz), 4.86 (d, 1H, $H3$, ^3J = 6.3 Hz), 2.64 (s, 3H, $H8/8'$), 2.32 (s, 3H), 2.29 (s, 3H), 2.27 (s, 3H), 2.16 (s, 3H), 2.15 (s, 6H), 2.07 (m, 4H, $H1$/Mes-CH_3), 1.98 (s, 6H), 1.66 (s, 6H), 1.36 (d, 3H, $H18$, ^3J = 6.3 Hz). ^{13}C{^{1}H} NMR (75 MHz, 298 K, C$_6$D$_6$): 176.4 (C10), 152.7, 147.8 (C4/4'), 139.2 (C15), 136.5, 136.3, 136.1 (C5/5'), 135.1 (C12), 134.8 (C13), 134.4, 131.1, 130.0 (C7/7'), 129.8 (C14), 129.4, 129.3, 129.0, 128.4 (C6/6'), 123.0 (C11), 117.4 (C2), 114.2 (C3), 45.0 (C1), 21.2, 21.0 (C9/9'), 20.7, 20.2 (C17), 20.0, 19.9, 19.2 (C8/8'), 18.0, 17.7 (C16). ^{9}Be NMR (56 MHz, 298 K, C$_6$D$_6$): 14.7 ppm (br). Anal. Calcd for C$_{43}$H$_{52}$BeN$_4$ (MW = 633.9): C, 81.47; H, 8.27; N, 8.84. Found: C, 81.36; H, 8.38; N, 8.79.

Synthesis of [{(CH)$_2$(NMes)$_2$}Be·IMes], 6. Compound **2** (29 mg, 87.3 μmol) was heated overnight with one equivalent of PhSiH$_3$ (10.8 μL, 88 μmol) in d_8-toluene at 110 °C. Analysis by NMR spectroscopy showed full conversion to the diamidoberyllium compound, **6**. Flaky orange crystals of **6** were obtained from slow vapor diffusion of hexanes into a saturated toluene solution at room temperature over a period of 2 weeks. ^{1}H NMR (300 MHz, 298 K, d_8-tol): 6.63 (s, 4H, m-Ar-H_{NHC}), 6.43 (s, 4H, m-Ar-H_{DAB}), 5.90 (s, 2H, MesNCH_{NHC}), 5.71 (s, 2H, MesNCH_{DAB}), 2.32 (s, 6H, p-CH_{3-NHC}), 2.16 (s, 6H, p-CH_{3-DAB}), 2.11 (s, 12H, o-CH_{3-NHC}), 1.82 (s, 12H, o-CH_{3-DAB}). ^{13}C{^{1}H} NMR (75 MHz, 298 K, d_8-tol): 173.6 (C$_{carbene}$), 151.1 (i-Ar-C$_{DAB}$), 138.8, 135.5, 135.1 (i-Ar-C$_{NHC}$), 134.2, 129.8, 129.7, 128.6,

123.6 (MesNCH$_{DAB}$), 120.8 (MesNCH$_{NHC}$), 21.6, 21.5, 20.3, 18.3. ^{9}Be (56 MHz, 298 K, d_8-tol): 4.4 ppm. Acceptable CHN microanalysis could not be obtained for this compound. Best values obtained: Anal. Calcd: C, 81.28; H, 7.99; N, 9.25. Found: C, 78.10; H, 8.26; N, 8.71.

X-ray Crystallography. Data for compounds **1**−**4** and **6** were collected at 150 K on a Nonius KappaCCD diffractometer equipped with an Oxford Cryosystem, using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Data were processed using the Nonius Software.[34] Crystal parameters and details of data collection, solution, and refinement for the compounds are provided in Table S1 in the Supporting Information. Structure solution, followed by full-matrix least-squares refinement, was performed using the WINGX-1.70 suite of programs throughout.[35] Due to a very weakly diffracting crystal, data of **6** were truncated to 48° in 2θ.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Crystallographic information files (CIF) for **1**−**4** and **6**, details of the X-ray analyses (Table S1), and additional figures of selected NMR spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

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