

## Article

# N-Heterocyclic Carbene-Supported Aryl- and Alkoxides of Beryllium and Magnesium

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**Abstract:** Recently, we have witnessed significant progress with regard to the synthesis of molecular alkaline earth metal reagents and catalysts. To provide new precursors for light alkaline earth metal chemistry, molecular aryloxide and alkoxide complexes of beryllium and magnesium are reported. The reaction of beryllium chloride dietherate with two equivalents of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (sIPr) results in the formation of a bis(*N*-heterocyclic carbene) (NHC) beryllium dichloride complex, (sIPr)<sub>2</sub>BeCl<sub>2</sub> (**1**). Compound **1** reacts with lithium diisopropylphenoxide (LiODipp) or sodium ethoxide (NaOEt) to form the terminal aryloxide (sIPr)Be(ODipp)<sub>2</sub> (**2**) and alkoxide dimer [(sIPr)Be(OEt)Cl]<sub>2</sub> (**3**), respectively. Compounds **2** and **3** represent the first beryllium alkoxide and aryloxide species supported by NHCs. Structurally related dimers of magnesium, [(sIPr)Mg(OEt)Br]<sub>2</sub> (**4**) and [(sIPr)Mg(OEt)Me]<sub>2</sub> (**5**), were also prepared. Compounds **1–5** were characterized by single crystal X-ray diffraction studies, <sup>1</sup>H, <sup>13</sup>C, and <sup>9</sup>Be NMR spectroscopy where applicable.

**Keywords:** N-heterocyclic carbenes; alkoxides; aryloxides; beryllium; magnesium

## 1. Introduction

The chemistry of alkaline earth metal oxides has historically been associated with materials of high thermal stability and poor solubility [1]. For example, beryllium and magnesium oxide melt at extremely high temperatures (up to 2852 °C) and are completely insoluble in organic solvents [2]. Indeed, the inherent chemical and physical properties of Ae-O (Ae = alkaline earth) heterogeneous materials preclude the use of these types of compounds as precursors for molecular chemistry. As such, chemists routinely employ synthetic strategies to decorate Ae-O bonds with various aryl or alkyl functionalities and/or bulky ligands to impart both stability and solubility. Even under these strict conditions, Ae-O moieties have a propensity to form insoluble polymeric structures, particularly after loss of stabilizing ligands [3,4]. Consequently, the literature contains a relatively small number of structurally characterized compounds containing Ae-O fragments beyond weakly bound Ae←O dative interactions resulting from coordination of ethereal solvents [5–9].

Early work by Bell on the reactions of beryllium chloride with lithium salts led to the reactive beryllium alkoxide dimer (ClBeO<sup>t</sup>Bu•OEt)<sub>2</sub> and tetramer (ClBeO<sup>t</sup>Bu)<sub>4</sub> [7]. Power reported a beryllium aryloxide [Be(OMes\*)<sub>2</sub>(OEt<sub>2</sub>)] (Mes\* = 2,4,6-<sup>t</sup>Bu<sub>3</sub>C<sub>6</sub>H<sub>2</sub>), which is protected by sterically demanding groups [10]. More recently, Hill reported a series of beryllium aryl- and alk-oxides (NacNac-BeOR; R = Me, <sup>t</sup>Bu, Ph) stabilized by the bulky β-diketiminato (NacNac) ligand, as well as the first tricoordinate beryllium hydroxide (NacNac-BeOH) [11]. In a subsequent report, Hill detailed the synthesis of

tricoordinate  $\beta$ -diketiminato beryllium alkoxide species,  $[\text{NacNac-BeO}(\text{CH}_2)_4\text{I}]$ , which was generated by ring opening insertion of tetrahydrofuran into a beryllium-iodide bond [12].

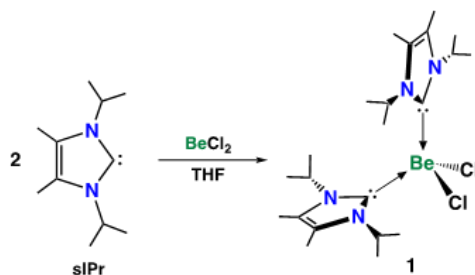
As expected, there are considerably more Ae oxides of magnesium. Over five decades ago, Shearer structurally characterized the dimeric magnesium alkoxide  $[\text{BrMgO}^t\text{Bu}\bullet\text{OEt}]_2$  [13]. Chisholm described the synthesis of  $\text{NacNac-MgO}^t\text{Bu}$ , where dimerization is prevented by THF coordination to magnesium in combination with ligand steric demand [14]. Kemp reported the  $\text{MgOR}$  dimers and trimers where R is the bulky 1,1-di-*penylethoxide* substituent [15]. Fedushkin synthesized  $\text{MgO}^t\text{Bu}$  dimer stabilized by 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene [16]. Recently, Jones reported a series of  $\text{NacNac-Mg}$  acyl dimers bridged by  $\text{O}^t\text{Bu}$  groups [17].

The molecular compounds described thus far continue to play an important role in Ae-mediated bond activation and catalysis, and this is consistent with the recent surge in interest regarding the study of Ae metal complexes as cost-effective mediators for important organic transformations [18–34]. Indeed, compounds containing Ae-R functionalities also facilitate energy-relevant bond activation events. Recently, Schulz reported that a beryllium alkyl dimer,  $[\text{Be}(\mu\text{-CH}_2\text{CH}_3)]_2$ , undergoes O-atom insertion to form a beryllium ethoxy dimer  $[\text{Be}(\mu\text{-OCH}_2\text{CH}_3)]_2$ , which is stabilized by two  $\text{N,N'}$ -chelating amidinate ligands [35]. Lewiński reported that  $\text{NacNac-Mg}$  alkyl compound is susceptible to oxygenation with  $\text{O}_2$ , affording the corresponding alkylperoxide dimer, which then converts to the alkoxide [9]. It is noteworthy that the majority of the compounds described thus far has relied on the utilization of strongly bound formally anionic ligands to control the chemistry around the metal center, as heteroleptic alkaline earth complexes are notorious for facile ligand exchanges and disproportionations [29].

Recently, the utilization of neutral carbenes in Ae metal chemistry has attracted a significant amount of attention, which has resulted in a substantial amount of new chemistry [36,37]. Might these ligands play a role in the formation of Ae oxides? Thus far, only two examples of NHC–magnesium alkoxide- or aryloxide-containing complexes have been crystallographically characterized [38,39]. The first example,  $[\text{Mg}(\mu\text{-OR})(\text{Mes})]_2$ , where OR is 1-methyl-3-(4,6-di-*tert*-butyl-2-hydroxybenzyl)imidazolium (Figure 1B), is the first reported s-block complex with an aryloxide-NHC chelating ligand [39]. The second example,  $[\text{Mg}(\text{L}^R)\text{N}(\text{SiMe}_3)_2]_2$  (where  $\text{L}^R = [\text{OCMe}_2\text{CH}_2(\text{CNCH}_2\text{CH}_2\text{NR})]$ ), features a magnesium atom supported by a bidentate alkoxide-NHC ligand [38]. It is noteworthy that magnesium complexes with  $\text{Mg-OR}$  units have been shown catalyze the formation of polylactide [14,38,40–44], the ring opening polymerization of  $\epsilon$ -caprolactone [45], as well as the hydroboration of aldehydes and ketones [46]. The chemistry of beryllium continues to be severely understudied relative to the heavier group 2 elements and NHC-beryllium oxides are hitherto unknown. Herein, we report the synthesis of  $(\text{sIPr})_2\text{BeCl}_2$  (**1**), which was used to access molecular aryloxides and alkoxides of beryllium,  $[(\text{sIPr})\text{Be}(\text{OEt})\text{Cl}]_2$  (**2**) and  $(\text{sIPr})\text{Be}(\text{ODipp})_2$  (**3**). In addition, we have prepared related magnesium alkoxide dimers,  $[(\text{sIPr})\text{Mg}(\text{OEt})\text{Br}]_2$  (**4**) and  $[(\text{sIPr})\text{Mg}(\text{OEt})\text{Me}]_2$  (**5**). In nearly all of these cases, the synthetic route began with the preparation of a ligand stabilized metal halide complexes of Be or Mg, of which a number of examples are known [47,48].

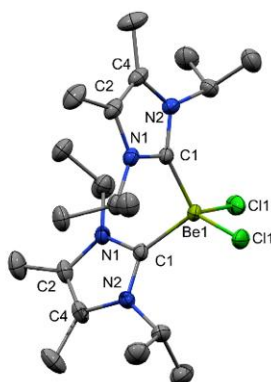
## 2. Results and Discussion

In THF, the reaction of 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (*sIPr*) and  $(\text{Et}_2\text{O})_2\text{BeCl}_2$  produces a white suspension after stirring for 1 h at room temperature (Scheme 1). After workup, compound **1** is isolated as a white solid in 84% yield. The  $^1\text{H}$  NMR spectrum revealed a new septet at 6.34 ppm which was attributed to the methine protons of compound **1**. Due to the strongly deshielding Be center, this peak is significantly downfield from free ligand (3.96 ppm).



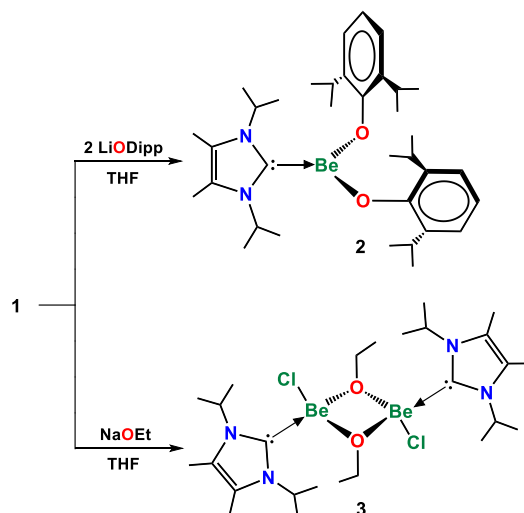
**Scheme 1.** Synthesis of a complex containing two untethered NHCs bound to a mononuclear beryllium halide.

Colorless crystals of compound **1** were obtained from toluene at  $-37\text{ }^{\circ}\text{C}$ . The structure features a unit of  $\text{BeCl}_2$  coordinated by two sIPr ligands. The beryllium atom is featured in a distorted tetrahedral environment with the widest bond angle being  $\text{C1}-\text{Be1}-\text{Cl1}$  at  $118.13(6)^{\circ}$ , with two NHC ligands bound to  $\text{BeCl}_2$  (Figure 1). The  $^{\text{carbene}}\text{C}-\text{Be}$  bond distance of **1** is  $1.849(3)\text{ \AA}$  falls within the range of other  $^{\text{carbene}}\text{C}-\text{Be}$  bonds ( $1.779\text{--}1.856(4)$ ) [49–56]. Additionally, the  $^{\text{carbene}}\text{C}-\text{Be}$  bond of **1** is longer than those of  $(\text{CDC})\text{BeCl}_2$  ( $1.748\text{ \AA}$ ) [57], and  $(\text{CDP})\text{BeCl}_2$  ( $1.742\text{ \AA}$ ) [58]. Compound **1** is structurally similar to the recently reported  $(\text{PMe}_3)_2\text{BeCl}_2$  and  $(\text{NHC})_2\text{BeCl}_2$  complexes [50,59].



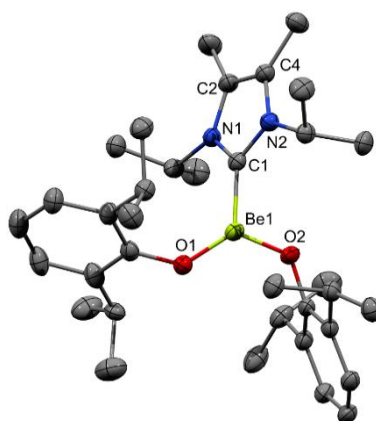
**Figure 1.** Molecular structure of **1** (thermal ellipsoids at 50% probability; H atoms and toluene solvent molecules omitted for clarity). Selected bond distances ( $\text{\AA}$ ) and angles ( $^{\circ}$ ):  $\text{Cl1}-\text{Be1}$ :  $2.0445(19)$ ;  $\text{C1}-\text{Be1}$ :  $1.849(3)$ ;  $\text{N1}-\text{C1}$ :  $1.367(2)$ ;  $\text{N1}-\text{C2}$ :  $1.397(2)$ ;  $\text{C2}-\text{C4}$ :  $1.354(3)$ ;  $\text{N2}-\text{C4}$ :  $1.397(2)$ ;  $\text{N2}-\text{C1}$ :  $1.357(2)$ .  $\text{N2}-\text{C1}-\text{Be1}$ :  $132.29(14)$ ;  $\text{N1}-\text{C1}-\text{Be1}$ :  $123.10(14)$ ;  $\text{C1}-\text{Be1}-\text{Cl1}$ :  $105.37(19)$ ;  $\text{C1}-\text{Be1}-\text{Cl1}$ :  $118.13(6)$ ;  $\text{C1}-\text{Be1}-\text{Cl1}$ :  $103.79(6)$ .

In THF, two equivalents of lithium diisopropylphenoxide ( $\text{LiODipp}$ ) were stirred with **1** for 18 h at room temperature. After workup,  $(\text{sIPr})\text{Be}(\text{ODipp})_2$  (**2**) was obtained as a white solid in 34% yield (Scheme 2). The  $^1\text{H}$  NMR spectra shows two new heptets at 4.87 ppm and 3.55 ppm, representative of new methine environments for sIPr and ODipp, respectively. We also performed the reaction of **1** with one equivalent of  $\text{LiODipp}$ . The  $^1\text{H}$  NMR spectrum revealed peaks for **1**, **2**, and uncoordinated sIPr (Figure S12). It is clear that the reaction is highly selective for producing **2**, and therefore, no heteroleptic monosubstituted molecules could be isolated.



**Scheme 2.** Synthesis of (sIPr)Be(ODipp)<sub>2</sub> and [(sIPr)BeCl(EtO)]<sub>2</sub>.

Colorless, needlelike crystals of **2** were obtained at  $-37\text{ }^{\circ}\text{C}$  from a toluene solution (Figure 2). The crystal structure revealed one sIPr ligand bound to beryllium *bis*(diisopropylphenoxide), (sIPr)Be(ODipp)<sub>2</sub> (**2**). The beryllium is centered in a distorted trigonal planar geometry, with the largest angle being O1–Be1–C1 at  $124.99(17)^{\circ}$ . The <sup>carbene</sup>C–Be bond ( $1.797\text{ }\text{\AA}$ ) falls within the range of known <sup>carbene</sup>C–Be bond distances [50,53,54].

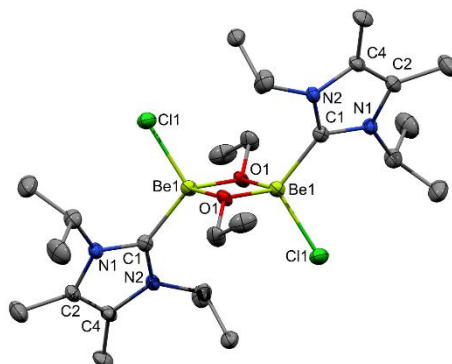


**Figure 2.** Molecular structure of **2** (thermal ellipsoids at 50% probability; H atoms omitted for clarity). Selected bond distances ( $\text{\AA}$ ) and angles ( $^{\circ}$ ): Be1–O2:  $1.497(3)$ ; Be1–O1:  $1.507(3)$ ; Be1–C1:  $1.797(3)$ ; N1–C2:  $1.393(2)$ ; N1–C1:  $1.353(2)$ ; N1–C2:  $1.359(2)$ ; N2–C4:  $1.391(2)$ ; C2–C4:  $1.362(3)$ . O2–Be1–O1:  $122.34(17)$ ; O2–Be1–C1:  $112.66(15)$ ; O1–Be1–C1:  $124.99(17)$ .

We reasoned that the reaction of **1** with a less sterically demanding alkoxide salt would give the heteroleptic halo-beryllium alkoxide dimer. Therefore, we reacted **1** with sodium ethoxide in THF for two days. After removing insoluble NaCl and concentration of the filtrate, compound **3** was obtained as colorless block-like crystals at  $-37\text{ }^{\circ}\text{C}$  from a toluene solution. The <sup>1</sup>H NMR spectra revealed a septet at 6.47 ppm for a methine environment of a new sIPr containing product, which is downfield from the starting material **1** (6.34 ppm). Due to very similar solubilities, crystals of compounds **1** and **3** were obtained in the bulk product and could not be separated despite considerable effort.

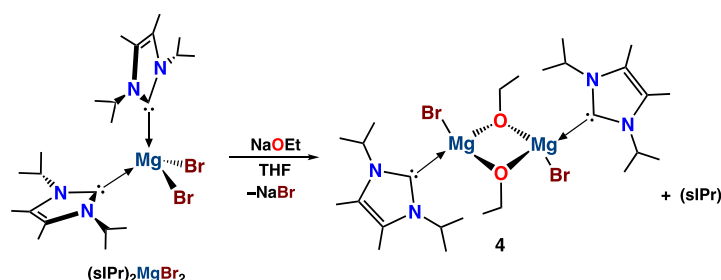
The crystal structure revealed a bridging ethoxide beryllium complex, **3**, where one chloride remains on each beryllium atom (Figure 3). These complexes represent the first examples of beryllium alkoxide species stabilized by a neutral carbene ligand. The beryllium atoms are each in a distorted tetrahedral environment. The <sup>carbene</sup>C–Be bond length is  $1.855(4)\text{ }\text{\AA}$ , which is slightly longer than the starting material **1**. The Be–O bond distances ( $1.621(4)\text{ }\text{\AA}$  and  $1.641(4)\text{ }\text{\AA}$ ) are within the range of the

Be–O bond distances of the known amidinate supported  $[\text{Be}(\mu\text{-OEt})]_2$  dimer (1.602 Å and 1.631 Å) [35], and the ketiminate supported  $[\text{Be}(\text{OEt})\text{Cl}]_2$  dimer (1.631 Å and 1.666 Å) [47].



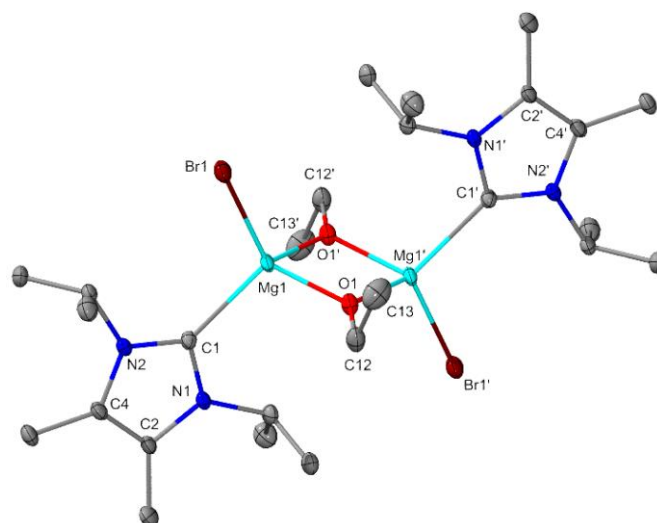
**Figure 3.** Molecular structure of **3** (thermal ellipsoids at 50% probability; H atoms omitted for clarity). Selected bond distances (Å) and angles (deg): Be1–O1: 1.621(4); Be1–O1': 1.641(4); Be1–C1: 1.855(4); Be1–Cl1: 2.044(3); N1–C1: 1.362(3); N1–C2: 1.391(3); 1.362(3); N2–C4: 1.393(3); C2–C4: 1.355(4). O1–Be1–O1': 89.99(18); O1–Be1–C1: 113.9(2); O1–Be1–Cl1: 119.0(2); C1–Be1–Cl1: 109.11(18).

In contrast to the chemistry of beryllium, magnesium halides and related molecules stabilized by neutral ligands are well-established, and the literature contains a variety of starting materials to access molecular magnesium compounds [36,60]. To obtain solvent-free and terminal magnesium(II) reagents supported by “normal” NHCs [61], we recently detailed a dual carbene stabilization strategy [62]. Due to the limited examples of NHC stabilized magnesium alkoxide dimers, we were interested in synthesizing magnesium complexes analogous to compound **3**. It is noteworthy that the reaction of  $(\text{sIPr})_2\text{MgBr}_2$  with lithium LiODipp resulted in a mixture of products which were not isolated. Therefore,  $(\text{sIPr})_2\text{MgBr}_2$  was reacted with sodium ethoxide. After stirring the starting materials for two days at room temperature,  $[\text{sIPrMgBr}(\mu\text{-OEt})]_2$ , **4** was produced in 54% yield (Scheme 3). The  $^1\text{H}$  NMR spectrum showed a broad signal attributed to the methine protons of **4** at 5.67 ppm, which only differs by 0.01 ppm from the starting material (5.68 ppm) [62].



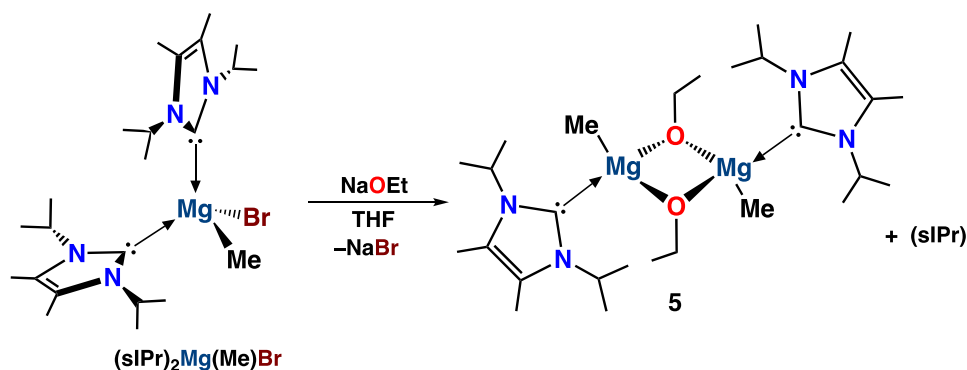
**Scheme 3.** Synthesis of bromo-substituted oxo-bridged dimer from bis-NHC magnesium dibromide.

Colorless block-shaped crystals of **4** suitable for X-ray diffraction were obtained from toluene at  $-37^\circ\text{C}$  (Figure 4). As in compound **3**, the molecular structure of **4** shows two ethoxides bridging two magnesium atoms, which are each in a distorted tetrahedral environment. The O1–Mg1–O1' bond angle is  $82.48(7)^\circ$ , which is smaller than that of **3** ( $89.99^\circ$ ). The  $\text{carbeneC-Mg}$  bond distance is  $2.236(2)$  Å, which is within the range of reported sIPr coordinated magnesium compounds ( $2.202$  Å to  $2.258$  Å) [62]. The Mg–O bond lengths ( $1.9558(17)$  Å and  $1.9666(17)$  Å) are in agreement with the known  $[(\text{dioxane})\text{Mg}(\text{Mes})(\mu\text{-OEt})]_2$  ( $1.961$  Å and  $1.966$  Å) [63].



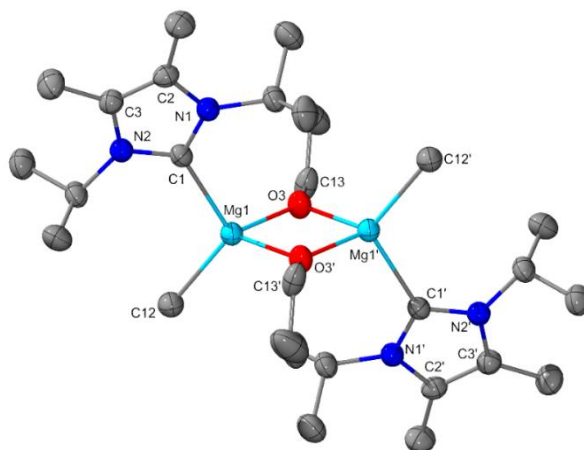
**Figure 4.** Molecular structure of **4** (thermal ellipsoids at 50% probability; H atoms omitted for clarity). Selected bond distances (Å) and angles (°): Mg1–O1: 1.9558(17); Mg1–O1': 1.9666(17); Mg1–C1: 2.236(2); N1–C1: 1.364(3); N2–C1: 1.357(3); Mg1–Br1: 2.4931(8); C2–C4: 1.346(3); N2–C4: 1.399(3); N1–C2: 1.404(2). C1–Mg1–Br1: 111.53(6); O1–Mg1–Br1: 116.30(5); O1'–Mg1–Br1: 113.13(5); O1–Mg1–O1': 82.48(7); Mg1–O1–Mg1': 97.52(7).

We also reacted (sIPr)<sub>2</sub>MgMeBr [62] with sodium ethoxide in THF (Scheme 4). After stirring for 2 days, the product and sIPr was extracted with hexanes. Colorless block-shaped crystals of compound **5** were grown from hexanes at −37 °C. The <sup>1</sup>H NMR spectrum revealed a new septet at 5.65 ppm, which is attributed to the methine protons of the sIPr ligand. With the exception of a singlet at −0.68 ppm for the Mg–Me protons, the <sup>1</sup>H NMR for compound **5** is comparable to that of **4**.



**Scheme 4.** Synthesis of methyl-substituted alkoxide-bridged dimer from a bis-NHC Grignard reagent.

The molecular structure of **5** (Figure 5) is isostructural to **4**. The <sup>carbene</sup>C–Mg bond length is 2.299 Å, which is longer than our previously reported sIPr coordinated magnesium complexes (2.202 Å to 2.258 Å) [62]. The Mg–O bond length in **5** (1.9761 Å and 1.9903 Å) are slightly longer than the Mg–O bond length in **4**. The longer Mg–O bond length in **5** is a result of the more inductively electron donating methyl group.



**Figure 5.** Molecular structure of **5** (thermal ellipsoids at 50% probability; H atoms omitted for clarity). Selected bond distances (Å) and angles (°): N1–C1: 1.361(2); N2–C1: 1.362(3); Mg1–C12: 2.160(2); Mg1–O3: 1.9761(16); Mg1–O3: 1.9903(16); Mg1–C1: 2.299(2); C2–C3: 1.352(3); N1–C2: 1.395(3); N2–C3: 1.400(3); C1–Mg1–C12: 112.58(8); O3–Mg1–C1: 112.70(7); O3–Mg1–O3': 80.99(7); O3–Mg1–C12: 121.41(8); Mg1–O3–Mg1': 99.01(7).

### 3. Materials and Methods

#### 3.1. General Procedures

All manipulations were carried out under an atmosphere of purified argon using standard Schlenk techniques or in a MBRAUN LABmaster glovebox equipped with a  $-37\text{ }^{\circ}\text{C}$  freezer (M. BRAUN INERTGAS-SYSTEME GMBH, Dieselstr. 31, D-85748 Garching, Germany). Dichloromethane was purified by distillation over calcium hydride. All other solvents were distilled over sodium/benzophenone. Glassware was oven-dried at  $190\text{ }^{\circ}\text{C}$  overnight. The NMR spectra were recorded at room temperature on a Varian Inova 500 MHz ( $^1\text{H}$ : 500.13 MHz), a Bruker Avance 600 MHz ( $^1\text{H}$ : 600.13 MHz,  $^{13}\text{C}$ : 150.90 MHz, and  $^9\text{Be}$ : 84.28 MHz), and an 800 MHz spectrometer (Bruker AXS GmbH, Oestliche Rheinbrueckenstr. 49, 76187 Karlsruhe, Germany) ( $^1\text{H}$ : 800.13 MHz and  $^{13}\text{C}$ : 201.193 MHz). Proton and carbon chemical shifts are reported in ppm and are referenced using the residual proton and carbon signals of the deuterated solvent ( $^1\text{H}$ ;  $\text{C}_6\text{D}_6$ ,  $\delta$  7.16,  $^{13}\text{C}$ ;  $\text{C}_6\text{D}_6$ ,  $\delta$  128.06;  $^1\text{H}$ ;  $\text{CD}_2\text{Cl}_2$ ,  $\delta$  5.32,  $^{13}\text{C}$ ;  $\text{CD}_2\text{Cl}_2$ ,  $\delta$  53.84). All  $^9\text{Be}$  NMR spectra were referenced to the reported diethyl ether beryllium dichloride  $\text{BeCl}_2(\text{Et}_2\text{O})_2$ ,  $\delta$  1.15 [64]. Reference samples were sealed in a capillary tube and placed in the NMR sample tube. Single crystal X-ray diffraction data were collected on a Bruker Kappa APEXII Duo diffractometer (Bruker AXS GmbH, Oestliche Rheinbrueckenstr. 49, 76187 Karlsruhe, Germany) running the APEX3 software suite. The crystal data and additional details regarding data collection are summarized in the supporting information. Deuterated solvents were purchased from Acros Organics and Cambridge Isotope Laboratories dried the same way as their protic analogues. Due to the toxicity of the beryllium compounds no combustion analysis was performed. Instead, purity was accessed by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^9\text{Be}$  NMR. CAUTION! Beryllium and its compounds are regarded as highly toxic and carcinogenic. Please adhere to protocols outlined in safety data sheets including using a respirator/mask and working in a well-ventilated fume hood.

#### 3.2. Synthesis of Lithium 2,6-Diisopropylphenolate

2,6-diisopropylphenol (5.2 mL, 0.028 mmol) was added to dry *n*-hexane (40 mL) and cooled to  $-15\text{ }^{\circ}\text{C}$ . While stirring vigorously, a solution of *n*-butyllithium in hexanes (2.5 M, 12 mL, 0.031 mmol) was added dropwise, yielding a white precipitate. The reaction was allowed to warm to RT and was stirred for 2 d. The reaction mixture was filtered through a medium fritted filter tube, and the resulting solids were washed with hexane (30 mL). These solids were dried under vacuum to yield the product as an off-white powder (4.384 g, 85%).  $^1\text{H}$  NMR (600.13 MHz,  $\text{THF}-d_8$ , 298K)  $\delta$  6.80–6.79 (d, 2H,

LiODipp-*H<sub>meta</sub>*), 6.31 (br, 1H, LiODipp-*H<sub>para</sub>*), 3.57 (br, 2H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.18–1.17 (d, 12H, CH(CH<sub>3</sub>)<sub>2</sub>). Note: Lithium 2,6-diisopropylphenolate was previously synthesized using a different method [65].

### 3.3. Synthesis of Compound 1

To a 100 mL round bottom flask, (Et<sub>2</sub>O)<sub>2</sub>BeCl<sub>2</sub> (63.2 mg, 0.277 mmol) was dissolved in dry THF. 1,3-diisopropyl-4,5-dimethylimidazol-2-ylidene (100 mg, 0.554 mmol) was dissolved in dry THF and added to the stirring suspension. The reaction was allowed to stir for 1 h before filtration to obtain a crude solid. After subsequent filtration drying *in vacuo*, compound 1 was obtained white air- and moisture-sensitive solid (103 mg, 84% yield). Colorless block-like crystals suitable for X-Ray diffraction were obtained from a toluene solution at −37 °C. <sup>1</sup>H NMR (800.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 6.34 (hept, *J* = 6.9 Hz, 4H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.69 (s, 12H, C-CH<sub>3</sub>), 1.19 (d, *J* = 6.9 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 177.8(C<sub>carbene</sub>), 124.4, 50.3, 21.7, 10.2; <sup>9</sup>Be NMR (84.28 MHz, C<sub>6</sub>D<sub>6</sub>) δ 0.5.

### 3.4. Synthesis of Compound 2

To a 20 mL scintillation vial, lithium diisopropylphenoxide (83.6 mg, 0.454 mmol) was added and stirred in dry THF. A slurry of compound 1 (100 mg, 0.227 mmol) in dry THF was added to the stirring suspension. The reaction was allowed to stir for 18 h. After filtration, the crude solid was washed with hexanes to remove uncoordinated sIPr ligand. Compound 2 was obtained as a white solid after drying *in vacuo* for 1 h (42 mg, 34% yield). Colorless rod-shaped crystals suitable for X-Ray diffraction were obtained from a toluene solution at −37 °C. <sup>1</sup>H NMR (800.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 7.20 (d, 4H, *H<sub>meta</sub>*-2,6-diisopropylphenyl), 6.98 (t, 2H, *H<sub>para</sub>*-2,6-diisopropylphenyl), 4.87 (br, 2H, N-CH(CH<sub>3</sub>)<sub>2</sub>), 3.55 (hept, *J* = 6.7 Hz, 4H, C-CH(CH<sub>3</sub>)<sub>2</sub>), 1.44 (s, 6H, C-CH<sub>3</sub>), 1.28 (d, *J* = 6.8 Hz, 24H, C-CH(CH<sub>3</sub>)<sub>2</sub>), 1.25 (d, *J* = 6.8 Hz, 12H, N-CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 156.16, 136.74, 128.35, 123.13, 117.94, 52.12, 27.85, 23.64, 22.12, 9.41; <sup>9</sup>Be NMR (84.28 MHz, C<sub>6</sub>D<sub>6</sub>) δ 3.14.

### 3.5. Synthesis of Compound 3

To a 20 mL vial, a slurry of compound 1 (200 mg, 0.554 mmol) was added to a stirring suspension of sodium ethoxide (31 mg, 0.554 mmol) in dry THF. The reaction was allowed to stir for two days before drying *in vacuo*. The resulting white crude solid was washed with hexanes, then extracted with toluene. Colorless crystals of compound 3 were obtained from a toluene solution at −37 °C. Note: It is important that only one equivalent of NaOEt be used. An excess produces other unidentified products. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 6.46 (hept, *J* = 7.0 Hz, 4H, N-CH(CH<sub>3</sub>)<sub>2</sub>), 4.30 (m, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 3.96 (m, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 1.71 (s, 12H, C-CH<sub>3</sub>), 1.47 (t, *J* = 7.0 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.44 (d, *J* = 7.0 Hz, 24H, C-CH(CH<sub>3</sub>)<sub>2</sub>).

### 3.6. Synthesis of Compound 4

To a flask containing (sIPr)<sub>2</sub>MgBr<sub>2</sub> (0.600 g, 1.101 mmol) and sodium ethoxide (0.066 g, 0.990 mmol), 50 mL of THF was added. The brown suspension was stirred for 48 h at room temperature before solvent was removed in *vacuo*. 50 mL of toluene was added and stirred for 1 h. A brown solution was formed and filtered. Solvent in filtrate was removed in *vacuo* and 50 mL of hexane was added. The brown suspension was stirred at room temperature for 1 h. Filtration of the brown suspension and subsequent drying of the residue *in vacuo* result in a brown powder. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 5.67 (br, 4H, N-CH(CH<sub>3</sub>)<sub>2</sub>), 4.16 (q, *J* = 6.9 Hz, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 1.62 (s, 12H, C-CH<sub>3</sub>), 1.47 (t, *J* = 6.8 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.45 (d, *J* = 7.0 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>); <sup>13</sup>C NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298K) δ 178.75(C<sub>carbene</sub>), 125.65, 58.65, 53.47, 22.93, 22.64, 10.14, 1.54. Anal. Calcd. for C<sub>22</sub>H<sub>40</sub>Cl<sub>2</sub>MgN<sub>4</sub>: C, 57.97; H, 8.85; N, 12.29%. Found: C, 57.95; H, 8.79; N, 12.11%.

### 3.7. Synthesis of Compound 5

To a flask containing (sIPr)<sub>2</sub>MgMeBr (0.500 g, 1.042 mmol) and sodium ethoxide (0.071 g, 1.042 mmol), 50 mL of THF was added. The white suspension was stirred for 48 h at room temperature before the solvent was removed *in vacuo*. The crude product was suspended in 50 mL of toluene and stirred for 1 h followed by filtration and drying *in vacuo*. The resulting white solid was then stirred in 40 mL of cold hexanes, then filtered. After drying *in vacuo*, compound 5 was obtained as a white powder. <sup>1</sup>H NMR (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) δ 5.65 (hept, *J* = 7.0 Hz, 4H, N-CH(CH<sub>3</sub>)<sub>2</sub>), 4.21 (q, *J* = 6.9 Hz, 4H, OCH<sub>2</sub>CH<sub>3</sub>), 1.68 (s, 12H, C-CH<sub>3</sub>), 1.49 (t, *J* = 6.9 Hz, 6H, OCH<sub>2</sub>CH<sub>3</sub>), 1.43 (d, *J* = 7.0 Hz, 24H, CH(CH<sub>3</sub>)<sub>2</sub>), −0.68 (s, 6H, MgCH<sub>3</sub>); <sup>13</sup>C NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>) δ 184.8 (C<sub>carbene</sub>), 124.5, 58.5, 52.4, 22.8, 10.1, 1.4, −12.9.

## 4. Conclusions

The chemistry surrounding the alkaline earth metals has flourished in part due to recent advances in their use as reagents for bond activation and catalysis. In order to expand the library of molecular precursors available for chemical synthesis, including complexes relevant to catalysis, we have synthesized NHC-supported BeCl<sub>2</sub>, Be-OR and Mg-OR complexes. Extensive studies probing the reactivity of these molecules are currently underway in our laboratory.

**Supplementary Materials:** The following are available online at <http://www.mdpi.com/2073-4344/9/11/934/s1>, Figure S1: <sup>1</sup>H NMR spectrum (800.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 1, Figure S2: <sup>13</sup>C{<sup>1</sup>H}NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 1, Figure S3: <sup>9</sup>Be NMR (84.28 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 1, Figure S4: <sup>1</sup>H NMR spectrum (800.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 2, Figure S5: <sup>13</sup>C{<sup>1</sup>H}NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 2, Figure S6: <sup>9</sup>Be NMR (84.28 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 2, Figure S7: <sup>1</sup>H NMR spectrum (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 3 mixed with compound 1, Figure S8: <sup>1</sup>H NMR spectrum (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 4, Figure S9: <sup>13</sup>C{<sup>1</sup>H}NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 4, Figure S10: <sup>1</sup>H NMR spectrum (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 5, Figure S11: <sup>13</sup>C{<sup>1</sup>H}NMR (201.19 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 5, Figure S12: <sup>1</sup>H NMR spectrum (500.13 MHz, C<sub>6</sub>D<sub>6</sub>, 298 K) of compound 1 reaction with one equivalent of LiODipp, Figure S13: <sup>1</sup>H NMR spectrum (600.13 MHz, THF-d<sub>8</sub>, 298 K) of LiODipp, Table S1: Crystallographic Data for 1–5.

**Author Contributions:** J.E.W. performed the synthesis and characterization for the beryllium complexes (1, 2, and 3). Y.-O.W. isolated and characterized the magnesium compounds 4 and 5. L.A.F. synthesized the starting material lithium 2,6-diisopropylphenoxide using a new method. D.A.D. performed the X-ray data collection and refinement. J.E.W., Y.-O.W., L.A.F. and R.J.G.J. analyzed the data and wrote the paper. R.J.G.J. administered and supervised the project.

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**Conflicts of Interest:** There are no conflicts to declare.

## References

- Mokkelbost, T.; Kaus, I.; Haugrud, R.; Norby, T.; Grande, T.; Einarsrud, M.-A. High-Temperature Proton-Conducting Lanthanum Ortho-Niobate-Based Materials. Part II: Sintering Properties and Solubility of Alkaline Earth Oxides. *J. Am. Chem. Soc.* **2008**, *130*, 879–886. [\[CrossRef\]](#)
- Haynes, W.M. *CRC Handbook of Chemistry and Physics: A Ready-Reference Book of Chemical and Physical Data: 2011–2012*, 92nd ed.; CRC: Boca Raton, FL, USA, 2011.
- Diao, Y.; Walawender, W.P.; Sorensen, C.M.; Klabunde, K.J.; Ricker, T. Hydrolysis of Magnesium Methoxide. Effects of Toluene on Gel Structure and Gel Chemistry. *Chem. Mater.* **2002**, *14*, 362–368. [\[CrossRef\]](#)
- Perera, L.C.; Raymond, O.; Henderson, W.; Brothers, P.J.; Plieger, P.G. Advances in beryllium coordination chemistry. *Coord. Chem. Rev.* **2017**, *352*, 264–290. [\[CrossRef\]](#)
- Bell, N.A.; Shearer, H.M.M.; Twiss, J. Dimeric tert-butoxyberyllium bromide-diethyl ether adduct, [Be<sub>2</sub>Br<sub>2</sub>(C<sub>4</sub>H<sub>9</sub>O)<sub>2</sub>(C<sub>4</sub>H<sub>10</sub>O)<sub>2</sub>], and a comparison with the magnesium analogue. *Acta Crystallogr.* **1984**, *40*, 605–607. [\[CrossRef\]](#)

6. Bell, N.A.; Coates, G.E.; Shearer, H.M.M.; Twiss, J.  $\pi$ -Bonding in three-co-ordinate beryllium compounds. Structure of tetra- $\mu$ -t-butoxydichlorotriberyllium. *Chem. Commun.* **1983**, *15*, 840–841. [[CrossRef](#)]
7. Bell, N.A.; Coates, G.E.; Schneider, M.L.; Shearer, H.M.M. Terminal beryllium–hydrogen bonding. X-Ray crystal structure of the (2-dimethylamino-N-methylethylamido)hydridoberyllium dimer. *Chem. Commun.* **1983**, *15*, 828–829. [[CrossRef](#)]
8. Naglav, D.; Tobey, B.; Wölper, C.; Bläser, D.; Jansen, G.; Schulz, S. On the Stability of Trimeric Beryllium Hydroxide Scorpionate Complexes. *Eur. J. Inorg. Chem.* **2016**, *2016*, 2424–2431. [[CrossRef](#)]
9. Pietrzak, T.; Kubisiak, M.; Justyniak, I.; Zelga, K.; Bojarski, E.; Tratkiewicz, E.; Ochal, Z.; Lewiński, J. Oxygenation Chemistry of Magnesium Alkyls Incorporating  $\beta$ -Diketiminato Ligands Revisited. *Chem. Eur. J.* **2016**, *22*, 17776–17783. [[CrossRef](#)]
10. Ruhlandt-Senge, K.; Bartlett, R.A.; Olmstead, M.M.; Power, P.P. Synthesis and structural characterization of the beryllium compounds  $[\text{Be}(2,4,6\text{-Me}_3\text{C}_6\text{H}_2)_2(\text{OEt}_2)]$ ,  $[\text{Be}\{\text{O}(2,4,6\text{-tert-Bu}_3\text{C}_6\text{H}_2)\}_2(\text{OEt}_2)]$ , and  $[\text{Be}\{\text{S}(2,4,6\text{-tert-Bu}_3\text{C}_6\text{H}_2)\}_2(\text{THF})]$ . *Inorg. Chem.* **1993**, *32*, 1724–1728. [[CrossRef](#)]
11. Arrowsmith, M.; Hill, M.S.; Kociok-Köhn, G.; MacDougall, D.J.; Mahon, M.F.; Mallov, I. Three-Coordinate Beryllium  $\beta$ -Diketiminates: Synthesis and Reduction Chemistry. *Inorg. Chem.* **2012**, *51*, 13408–13418. [[CrossRef](#)]
12. Arrowsmith, M.; Crimmin, M.R.; Hill, M.S.; Kociok-Köhn, G. Beryllium derivatives of a phenyl-substituted  $\beta$ -diketiminato: A well-defined ring opening reaction of tetrahydrofuran. *Dalton Trans.* **2013**, *42*, 9720–9726. [[CrossRef](#)] [[PubMed](#)]
13. Moseley, P.T.; Shearer, H.M.M. The crystal structure of the addition product of a Grignard reagent with a ketone. *Chem. Commun.* **1968**, *5*, 279–280. [[CrossRef](#)]
14. Chisholm, M.H.; Huffman, J.C.; Phomphrai, K. Monomeric metal alkoxides and trialkyl siloxides:  $(\text{BDI})\text{Mg}(\text{OtBu})(\text{THF})$  and  $(\text{BDI})\text{Zn}(\text{OSiPh}_3)(\text{THF})$ . Comments on single site catalysts for ring-opening polymerization of lactides. *Dalton Trans.* **2001**, *3*, 222–224. [[CrossRef](#)]
15. Zechmann, C.A.; Boyle, T.J.; Rodriguez, M.A.; Kemp, R.A. Synthesis, characterization, and structural study of sterically hindered magnesium alkoxide and siloxide compounds. *Inorg. Chim. Acta* **2001**, *319*, 137–146. [[CrossRef](#)]
16. Fedushkin, I.L.; Morozov, A.G.; Hummert, M.; Schumann, H. Alkylmagnesium Complexes with the Rigid dpp-bian Ligand [dpp-bian = 1,2-Bis[(2,6-diisopropylphenyl)imino]acenaphthene]. *Eur. J. Inorg. Chem.* **2008**, *2008*, 1584–1588. [[CrossRef](#)]
17. Boutland, A.J.; Lamsfus, C.A.; Maitland, B.; Maron, L.; Stasch, A.; Jones, C. Accessing Stable Magnesium Acyl Compounds: Reductive Cleavage of Esters by Magnesium(I) Dimers. *Chem. Eur. J.* **2017**, *23*, 14049–14055. [[CrossRef](#)]
18. Wilson, A.S.S.; Hill, M.S.; Mahon, M.F.; Dinoi, C.; Maron, L. Organocalcium-mediated nucleophilic alkylation of benzene. *Science* **2017**, *358*, 1168–1171. [[CrossRef](#)]
19. Wilson, A.S.S.; Dinoi, C.; Hill, M.S.; Mahon, M.F.; Maron, L. Heterolysis of Dihydrogen by Nucleophilic Calcium Alkyls. *Angew. Chem. Int. Ed.* **2018**, *57*, 15500–15504. [[CrossRef](#)]
20. Green, S.P.; Jones, C.; Stasch, A. Stable Magnesium(I) Compounds with Mg–Mg Bonds. *Science* **2007**, *318*, 1754–1757. [[CrossRef](#)]
21. Jones, C. Dimeric magnesium(I)  $\beta$ -diketiminates: A new class of quasi-universal reducing agent. *Nat. Chem. Rev.* **2017**, *1*, 0059. [[CrossRef](#)]
22. Bonyhady, S.J.; Collis, D.; Frenking, G.; Holzmann, N.; Jones, C.; Stasch, A. Synthesis of a stable adduct of dialane(4) ( $\text{Al}_2\text{H}_4$ ) via hydrogenation of a magnesium(I) dimer. *Nat. Chem.* **2010**, *2*, 865. [[CrossRef](#)] [[PubMed](#)]
23. Sidiropoulos, A.; Jones, C.; Stasch, A.; Klein, S.; Frenking, G. N-Heterocyclic Carbene Stabilized Digermanium(0). *Angew. Chem. Int. Ed.* **2009**, *48*, 9701–9704. [[CrossRef](#)] [[PubMed](#)]
24. Jones, C.; Sidiropoulos, A.; Holzmann, N.; Frenking, G.; Stasch, A. An N-heterocyclic carbene adduct of diatomic tin, Sn [double bond, length as m-dash] Sn. *Chem. Commun.* **2012**, *48*, 9855–9857. [[CrossRef](#)] [[PubMed](#)]
25. Rit, A.; Campos, J.; Niu, H.; Aldridge, S. A stable heavier group 14 analogue of vinylidene. *Nat. Chem.* **2016**, *8*, 1022. [[CrossRef](#)]

26. Arras, J.; Kruczyński, T.; Bresien, J.; Schulz, A.; Schnöckel, H. Magnesium(I) Halide versus Magnesium Metal: Differences in Reaction Energy and Reactivity Monitored in Reduction Processes of P–Cl Bonds. *Angew. Chem. Int. Ed.* **2019**, *58*, 716–721. [[CrossRef](#)] [[PubMed](#)]
27. Bakewell, C.; White, A.J.P.; Crimmin, M.R. Addition of Carbon–Fluorine Bonds to a Mg(I)–Mg(I) Bond: An Equivalent of Grignard Formation in Solution. *J. Am. Chem. Soc.* **2016**, *138*, 12763–12766. [[CrossRef](#)] [[PubMed](#)]
28. Stasch, A.; Jones, C. Stable dimeric magnesium(i) compounds: From chemical landmarks to versatile reagents. *Dalton Trans.* **2011**, *40*, 5659–5672. [[CrossRef](#)]
29. Hill, M.S.; Liptrot, D.J.; Weetman, C. Alkaline earths as main group reagents in molecular catalysis. *Chem. Soc. Rev.* **2016**, *45*, 972–988. [[CrossRef](#)]
30. Rosch, B.; Gentner, T.X.; Elsen, H.; Fischer, C.A.; Langer, J.; Wiesinger, M.; Harder, S. Nucleophilic Aromatic Substitution at Benzene with Powerful Strontium Hydride and Alkyl Complexes. *Angew. Chem. Int. Ed.* **2019**, *58*, 5396–5401. [[CrossRef](#)]
31. de Bruin-Dickason, C.N.; Sutcliffe, T.; Alvarez Lamsfus, C.; Deacon, G.B.; Maron, L.; Jones, C. Kinetic stabilisation of a molecular strontium hydride complex using an extremely bulky amidinate ligand. *Chem. Commun.* **2018**, *54*, 786–789. [[CrossRef](#)]
32. Causero, A.; Ballmann, G.; Pahl, J.; Zijlstra, H.; Färber, C.; Harder, S. Stabilization of Calcium Hydride Complexes by Fine Tuning of Amidinate Ligands. *Organometallics* **2016**, *35*, 3350–3360. [[CrossRef](#)]
33. Pahl, J.; Brand, S.; Elsen, H.; Harder, S. Highly Lewis acidic cationic alkaline earth metal complexes. *Chem. Commun.* **2018**, *54*, 8685–8688. [[CrossRef](#)] [[PubMed](#)]
34. Pahl, J.; Friedrich, A.; Elsen, H.; Harder, S. Cationic Magnesium  $\pi$ -Arene Complexes. *Organometallics* **2018**, *37*, 2901–2909. [[CrossRef](#)]
35. Bayram, M.; Naglav, D.; Wölper, C.; Schulz, S. Syntheses and Structures of Homo- and Heteroleptic Beryllium Complexes Containing  $N,N'$ -Chelating Ligands. *Organometallics* **2017**, *36*, 467–473. [[CrossRef](#)]
36. Nesterov, V.; Reiter, D.; Bag, P.; Frisch, P.; Holzner, R.; Porzelt, A.; Inoue, S. NHCs in Main Group Chemistry. *Chem. Rev.* **2018**, *118*, 9678–9842. [[CrossRef](#)] [[PubMed](#)]
37. Bellemin-Laponnaz, S.; Dagorne, S. Group 1 and 2 and Early Transition Metal Complexes Bearing N-Heterocyclic Carbene Ligands: Coordination Chemistry, Reactivity, and Applications. *Chem. Rev.* **2014**, *114*, 8747–8774. [[CrossRef](#)]
38. Arnold, P.L.; Casely, I.J.; Turner, Z.R.; Bellabarba, R.; Tooze, R.B. Magnesium and zinc complexes of functionalised, saturated N-heterocyclic carbene ligands: Carbene lability and functionalisation, and lactide polymerisation catalysis. *Dalton Trans.* **2009**, *35*, 7236–7247. [[CrossRef](#)]
39. Zhang, D.; Kawaguchi, H. Deprotonation Attempts on Imidazolium Salt Tethered by Substituted Phenol and Construction of Its Magnesium Complex by Transmetalation. *Organometallics* **2006**, *25*, 5506–5509. [[CrossRef](#)]
40. Drouin, F.; Whitehorne, T.J.J.; Schaper, F. Nacnac  $\text{BnMgOtBu}$ : A diketiminate-based catalyst for the polymerisation of rac-lactide with slight isotactic preference. *Dalton Trans.* **2011**, *40*, 1396–1400. [[CrossRef](#)]
41. Chamberlain, B.M.; Cheng, M.; Moore, D.R.; Ovitt, T.M.; Lobkovsky, E.B.; Coates, G.W. Polymerization of Lactide with Zinc and Magnesium  $\beta$ -Diiminato Complexes: Stereocontrol and Mechanism. *J. Am. Chem. Soc.* **2001**, *123*, 3229–3238. [[CrossRef](#)]
42. Dove, A.P.; Gibson, V.C.; Marshall, E.L.; White, A.J.P.; Williams, D.J. Magnesium and zinc complexes of a potentially tridentate  $\beta$ -diketiminato ligand. *Dalton Trans.* **2004**, *4*, 570–578. [[CrossRef](#)] [[PubMed](#)]
43. Chen, H.-Y.; Huang, B.-H.; Lin, C.-C. A Highly Efficient Initiator for the Ring-Opening Polymerization of Lactides and  $\epsilon$ -Caprolactone: A Kinetic Study. *Macromolecules* **2005**, *38*, 5400–5405. [[CrossRef](#)]
44. Chisholm, M.H.; Gallucci, J.C.; Phomphrai, K. Comparative Study of the Coordination Chemistry and Lactide Polymerization of Alkoxide and Amide Complexes of Zinc and Magnesium with a  $\beta$ -Diiminato Ligand Bearing Ether Substituents. *Inorg. Chem.* **2005**, *44*, 8004–8010. [[CrossRef](#)] [[PubMed](#)]
45. Raghavendra, B.; Shashank, P.V.S.; Pandey, M.K.; Reddy, N.D.  $\text{CO}_2$ /Epoxide Coupling and the ROP of  $\epsilon$ -Caprolactone: Mg and Al Complexes of  $\gamma$ -Phosphino-ketiminates as Dual-Purpose Catalysts. *Organometallics* **2018**, *37*, 1656–1664. [[CrossRef](#)]
46. Arrowsmith, M.; Hadlington, T.J.; Hill, M.S.; Kociok-Köhn, G. Magnesium-catalysed hydroboration of aldehydes and ketones. *Chem. Commun.* **2012**, *48*, 4567–4569. [[CrossRef](#)]
47. Paparo, A.; Jones, C. Beryllium Halide Complexes Incorporating Neutral or Anionic Ligands: Potential Precursors for Beryllium Chemistry. *Chem. Asian J.* **2019**, *14*, 486–490. [[CrossRef](#)]

48. Freeman, L.A.; Walley, J.E.; Obi, A.D.; Wang, G.; Dickie, D.A.; Molino, A.; Wilson, D.J.D.; Gilliard, R.J., Jr. Stepwise Reduction at Magnesium and Beryllium: Cooperative Effects of Carbenes with Redox Non-Innocent  $\alpha$ -Diimines. *Inorg. Chem.* **2019**, *58*, 10554–10568. [[CrossRef](#)]
49. Walley, J.E.; Obi, A.D.; Breiner, G.; Wang, G.; Dickie, D.A.; Molino, A.; Dutton, J.L.; Wilson, D.J.D.; Gilliard, R.J., Jr. Cyclic(alkyl)(amino) Carbene-Promoted Ring Expansion of a Carbodicarbene Beryllacycle. *Inorg. Chem.* **2019**, *58*, 11118–11126. [[CrossRef](#)]
50. Schuster, J.K.; Roy, D.K.; Lenczyk, C.; Mies, J.; Braunschweig, H. New Outcomes of Beryllium Chemistry: Lewis Base Adducts for Salt Elimination Reactions. *Inorg. Chem.* **2019**, *58*, 2652–2658. [[CrossRef](#)]
51. Arrowsmith, M.; Braunschweig, H.; Celik, M.A.; Dellermann, T.; Dewhurst, R.D.; Ewing, W.C.; Hammond, K.; Kramer, T.; Krummenacher, I.; Mies, J.; et al. Neutral zero-valent s-block complexes with strong multiple bonding. *Nat. Chem.* **2016**, *8*, 890. [[CrossRef](#)]
52. Wang, G.; Freeman, L.A.; Dickie, D.A.; Mokrai, R.; Benkő, Z.; Gilliard, R.J., Jr. Isolation of Cyclic(Alkyl)(Amino) Carbene-Bismuthinidene Mediated by a Beryllium(0) Complex. *Chem. Eur. J.* **2019**, *25*, 4335–4339. [[CrossRef](#)] [[PubMed](#)]
53. Herrmann, W.A.; Runte, O.; Artus, G. Synthesis and structure of an ionic beryllium-“carbene” complex. *J. Organomet. Chem.* **1995**, *501*, C1–C4. [[CrossRef](#)]
54. Gilliard, R.J.; Abraham, M.Y.; Wang, Y.; Wei, P.; Xie, Y.; Quillian, B.; Schaefer, H.F.; Schleyer, P.v.R.; Robinson, G.H. Carbene-Stabilized Beryllium Borohydride. *J. Am. Chem. Soc.* **2012**, *134*, 9953–9955. [[CrossRef](#)] [[PubMed](#)]
55. Arrowsmith, M.; Hill, M.S.; Kociok-Kohn, G.; MacDougall, D.J.; Mahon, M.F. Beryllium-induced C-N bond activation and ring opening of an N-heterocyclic carbene. *Angew. Chem. Int. Ed.* **2012**, *51*, 2098–2100. [[CrossRef](#)] [[PubMed](#)]
56. Arrowsmith, M.; Hill, M.S.; Kociok-Köhn, G. Activation of N-Heterocyclic Carbenes by  $\{\text{BeH}_2\}$  and  $\{\text{Be}(\text{H})(\text{Me})\}$  Fragments. *Organometallics* **2015**, *34*, 653–662. [[CrossRef](#)]
57. Walley, J.E.; Breiner, G.; Wang, G.; Dickie, D.A.; Molino, A.; Dutton, J.L.; Wilson, D.J.D.; Gilliard, R.J., Jr. s-Block carbodicarbene chemistry: C(sp<sup>3</sup>)-H activation and cyclization mediated by a beryllium center. *Chem. Commun.* **2019**, *55*, 1967–1970. [[CrossRef](#)] [[PubMed](#)]
58. Petz, W.; Dehnicke, K.; Holzmann, N.; Frenking, G.; Neumüller, B. The Reaction of  $\text{BeCl}_2$  with Carbodiphosphorane  $\text{C}(\text{PPh}_3)_2$ ; Experimental and Theoretical Studies. *Z. Anorg. Allg. Chem.* **2011**, *637*, 1702–1710. [[CrossRef](#)]
59. Buchner, M.R.; Spang, N.; Müller, M.; Rudel, S.S. Formation and Properties of the Trichloroberyllate Ion. *Inorg. Chem.* **2018**, *57*, 11314–11317. [[CrossRef](#)]
60. Hopkinson, M.N.; Richter, C.; Schedler, M.; Glorius, F. An overview of N-heterocyclic carbenes. *Nature* **2014**, *510*, 485. [[CrossRef](#)]
61. Arduengo, A.J.; Harlow, R.L.; Kline, M. A stable crystalline carbene. *J. Am. Chem. Soc.* **1991**, *113*, 361–363. [[CrossRef](#)]
62. Wong, Y.O.; Freeman, L.A.; Agakidou, A.D.; Dickie, D.A.; Webster, C.E.; Gilliard, R.J. Two Carbenes versus One in Magnesium Chemistry: Synthesis of Terminal Dihalide, Dialkyl, and Grignard Reagents. *Organometallics* **2019**, *38*, 688–696. [[CrossRef](#)]
63. Langer, J.; Kriek, S.; Fischer, R.; Görls, H.; Walther, D.; Westerhausen, M. 1,4-Dioxane Adducts of Grignard Reagents: Synthesis, Ether Fragmentation Reactions, and Structural Diversity of Grignard Reagent/1,4-Dioxane Complexes. *Organometallics* **2009**, *28*, 5814–5820. [[CrossRef](#)]
64. Nöth, H.; Schlosser, D. The Aminolysis of Beryllium Dichloride with Diisopropylamine and Reactions of Some Aminoberyllium Chlorides. *Eur. J. Inorg. Chem.* **2003**, *12*, 2245–2254. [[CrossRef](#)]
65. Hanna, T.A.; Ghosh, A.K.; Ibarra, C.; Zakharov, L.N.; Rheingold, A.L.; Watson, W.H. Facile Formation of Molybdenum(VI) Monooxo Aryloxides  $\text{MoO}(\text{OAr})_4\text{-nCl}_n$  from Molybdenum Dioxo Dichloride. *Inorg. Chem.* **2004**, *43*, 7567–7569. [[CrossRef](#)]

