

# VIP Reactivity of Diphenylberyllium as a Brønsted Base and Its Synthetic Application

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**Abstract:** Diphenylberyllium [Be<sub>2</sub>Ph<sub>4</sub>] is shown here to react cleanly as a Brønsted base with a vast variety of protic compounds. Through the addition of the simple molecules *t*BuOH, HNPh<sub>2</sub> and HPPPh<sub>2</sub>, as well as the more complex 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride, one or two phenyl groups in diphenylberyllium were protonated. As a result, the long-postulated structures of [Be<sub>3</sub>(OtBu)<sub>6</sub>] and [Be(μ-NPh<sub>2</sub>)Ph]<sub>2</sub> have finally been verified and shown to be

static in solution. Additionally [Be(μ-PPh<sub>2</sub>)(HPPPh<sub>2</sub>)Ph]<sub>2</sub> was generated, which is only the second beryllium-phosphanide to be prepared; the stark differences between its behaviour and that of the analogous amide were also examined. The first crystalline example of a beryllium Grignard reagent with a non-bulky aryl group has also been prepared; it is stabilised with an N-heterocyclic carbene.

The progress of synthetic beryllium chemistry has been notably slower than that of its neighbouring elements, such as boron, magnesium and aluminium; this is largely due to its perceived toxicity.<sup>[1,2]</sup> Consequently, there are a large number of fundamental species and bonds that have not yet been prepared with beryllium. The last five years have seen a raft of landmark compounds produced, including low-valent Be<sup>0</sup> and Be<sup>I</sup>, as well as Be=C and Be=N species.<sup>[3–6]</sup> However, in order to understand the properties of beryllium, aid chemical synthesis and explore academical and industrial applications, the field remains in need of robust routes to the preparation of equivalent fundamental species such as alkoxides, amides, phosphanides and Grignard reagents. These species have contributed so heavily to the chemical progression of similar elements,<sup>[7,8]</sup> that the same must be explored for beryllium.

Metal alkoxides have been used as starting materials across the chemical disciplines, with particular use in industry.<sup>[9,10]</sup> The initial rise of sol-gel chemistry throughout various industrial processes relied heavily on metal alkoxides, and the ever-increasing importance of this process has created a huge requirement for the development of new metal alkoxides.<sup>[11,12]</sup> Beryllium metals and alloys are widely used across the aeronautical industries, due to their lightweight, robust, and highly conducting properties.<sup>[1,13]</sup> Thus, beryllium alkoxides

could be eagerly used for such sol-gel processes. The synthesis of beryllium alkoxides was investigated by Coates et al. over half a century ago.<sup>[14–16]</sup> Following preparation of a homoleptic alkoxide, the terminal groups were replaced with a range of alternative alkyl and alkoxide groups.<sup>[14]</sup> However, the synthetic route for preparation of these alkoxides is less than ideal, and the characterisation was understandably lacking. Nevertheless, the structure of [Be<sub>3</sub>(OtBu)<sub>6</sub>] was predicted in 1967 based on NMR measurements but was never proven.<sup>[14]</sup> Given that beryllium reports from the early to mid-20th century have recently been shown to be incorrect, it is an important step to verify such fundamental research before large-scale application is possible.<sup>[17]</sup> Main group amides and phosphanides are indispensable single source precursors for modern 13–15 semiconductors.<sup>[18]</sup> However, the generation of binary species remains an important target for chemical vapour (CVPE), liquid-phase epitaxy (LPE), and further industrial processes.<sup>[19]</sup> Furthermore, beryllium is an important doping element for these semiconductors.<sup>[20]</sup> Therefore, effective, reliable, and clean synthetic routes towards such beryllium species are paramount, particularly when semiconductor applications require exceedingly pure materials.<sup>[21]</sup> Grignard reagents are arguably the most important family of organometallic compounds, with their uses spanning far and wide.<sup>[22,23]</sup> The facile preparation of these reagents has certainly aided in their widespread use, whilst similar attempts for beryllium required aggressive and terrifying experimental procedures along with ill-defined yields and species,<sup>[24–26]</sup> or require extremely bulky aryl groups.<sup>[27,28]</sup> However, due to the higher electronegativity of beryllium in comparison with magnesium and the more favourable orbital overlap with carbon, one would expect beryllium Grignard reagents to be softer nucleophiles than classical magnesium Grignard reagents. In addition, as the di- and trimerisation of Grignard reagents hugely affects the reactivity, the smaller size of beryllium is expected to result in different reactivity. These

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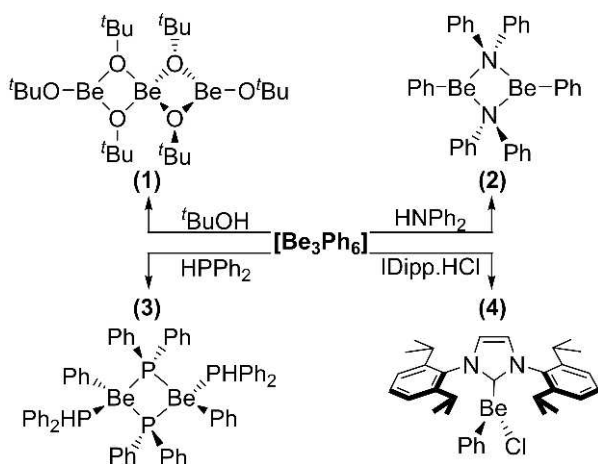
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combined factors could lead beryllium Grignard reagents to be thoroughly useful across the chemical disciplines.

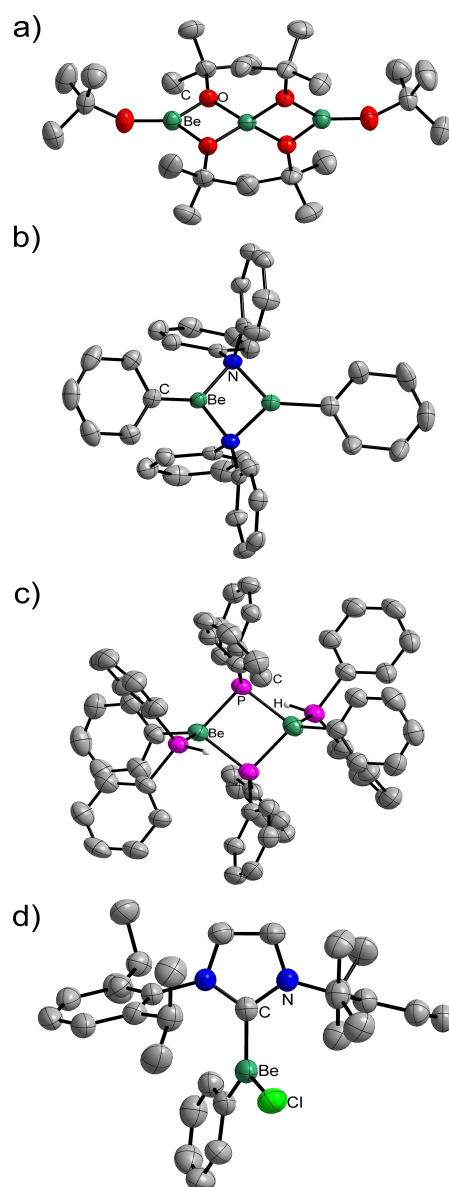
Protonolysis reactions are a fundamental aspect in the synthesis of these compound classes, with metalorganyls behaving as a Brønsted base to react with a Brønsted acidic reagent in a controllable manner. These reactions can be more favourable than salt elimination reactions, due to the generation of by-products that are innocent and easily separated. Recently, beryllium organyls have been overlooked as starting materials, with most beryllium chemical transformations starting with beryllium halides.<sup>[29,30]</sup> This is due to the difficult synthesis and purification of most organo-beryllium compounds in comparison with the easily accessible beryllium halides.<sup>[31–33]</sup> Diphenylberyllium, however, is readily prepared and purified, allowing thorough investigation and use in synthetic chemistry.<sup>[17]</sup> Before 2020, there were only two published studies on the behaviour of diphenylberyllium,<sup>[34,35]</sup> with the reactivity only recently starting to be thoroughly investigated.<sup>[17,36]</sup> Following on from the behaviour of diphenylberyllium as a Lewis acid,<sup>[36]</sup> it was logical to also investigate its reactivity as a Brønsted base. Therefore, the behaviour of  $[\text{Be}_3\text{Ph}_6]$  towards protic compounds with greatly varying Brønsted acidity and steric demand was explored. As benchmark compounds, *tert*-butanol, diphenylamine, diphenylphosphine and a C–H-acidic imidazolium halide were chosen. These were not only selected for their chemical properties, but also because the resulting alkoxides, amides, phosphanides and Grignard analogous compounds are regarded to be important reagents for potential synthetic and industrial applications (see above). In the presented study, the phenyl groups on beryllium are protonated by the Brønsted acid to produce benzene and the conjugate beryllium species (Scheme 1). These reactions were carried out in deuterated benzene or dichloromethane and can be readily followed through the occurrence of  $\text{C}_6\text{H}_6$  in the  $^1\text{H}$  NMR spectra.

Six equivalents (or excess) of  $\text{HO}t\text{Bu}$  react cleanly and fully with  $[\text{Be}_3\text{Ph}_6]$  to produce  $[\text{Be}_3(\text{O}t\text{Bu})_6]$  (**1**). Two resonances relating to the *t*Bu groups are observed in the  $^1\text{H}$  NMR spectrum



**Scheme 1.** Reaction scheme for the preparation of compounds 1–4 from  $[\text{Be}_3\text{Ph}_6]$  with  $t\text{BuOH}$ ,  $\text{HNPh}_2$ ,  $\text{HPPH}_2$  and  $\text{IDipp}\cdot\text{HCl}$ , respectively.

in a 2:1 ratio and the absence of phenyl groups shows that complete protonation of  $[\text{Be}_3\text{Ph}_6]$  has occurred, thus producing a homoleptic beryllium alkoxide. This reaction is rapid and clean, with the product highly soluble in dichloromethane (DCM) and benzene. EXSY measurements demonstrate that there is no ligand exchange in solution (Figure S4 in the Supporting Information), which is in direct contrast to the behaviour of  $\text{Be}_3\text{Ph}_6$ .<sup>[17]</sup> This behaviour is most likely due to the increased steric bulk of the *tert*-butyl groups and the stronger 3-centre-4-electron Be–O–Be interactions compared to the 3-centre-2-electron Be–C–Be bonds in diphenylberyllium. Crystals of **1** grew in DCM after storage at room temperature for 14 days (Figure 1). **1** retains almost the same structural motif as that of



**Figure 1.** Molecular structures of a)  $[\text{Be}_3(\text{O}t\text{Bu})_6]$  (**1**), b)  $[\text{Be}(\mu\text{-NPh}_2)\text{Ph}]_2$  (**2**), c)  $[\text{Be}(\mu\text{-PPh}_2)(\text{HPPH}_2)\text{Ph}]_2$  (**3**) and d)  $[(\text{IDipp})\text{BePhBr}]$  (**4**). Ellipsoids are shown at 70% probability at 100 K. Carbon-bound hydrogen atoms are omitted for clarity.

the starting material  $[\text{Be}_3\text{Ph}_6]$ , a motif that has also been observed for the heteroleptic beryllium alkoxide  $[\text{Be}_3(\text{tBuO})_4\text{Cl}_2]$ .<sup>[16]</sup> There are three beryllium centres, with the central beryllium occupying tetrahedral geometry meaning that the adjacent bridging tBuO groups are staggered. The Be–Be distance in **1** is longer than in  $[\text{Be}_3\text{Ph}_6]$  (2.284(2) vs. 2.033(2) Å), but is similar to that of  $[\text{Be}_3(\text{NMe}_2)_6]$  (2.300(9) Å).<sup>[37]</sup> Furthermore, the Be–Be–Be angle observed is almost linear at 175.5(2)°, far more so than the bent Be–Be–Be angle of  $[\text{Be}_3\text{Ph}_6]$  (141.72(8)).<sup>[17]</sup>

As two equivalents of alcohol were cleanly deprotonated by one  $\text{BePh}_2$  moiety, one and two equivalents of the less acidic amine  $\text{HNPh}_2$  were reacted with the organoberyllium species. In the  $^1\text{H}$  NMR spectrum of both reactions, Be–Ph groups remained present, even following heating at 80 °C, with  $\text{HNPh}_2$  still observed in the reaction with two-equivalents. Thus, it was clear that only one equivalent of  $\text{HNPh}_2$  is able to react with “ $\text{BePh}_2$ ”. The  $^1\text{H}$  NMR spectrum of this compound is highly symmetric and contains only aryl protons. Crystals were grown following concentration of the benzene solution, and the structure was determined to be  $[\text{Be}(\mu\text{-NPh}_2)\text{Ph}]_2$  (**2**), which is in accordance with the NMR spectra.

As analogous N and P bidentate donors can behave differently with beryllium,<sup>[36]</sup> we combined  $\text{HPPH}_2$  with  $[\text{Be}_3\text{Ph}_6]$  in various stoichiometries. The reaction of  $\text{HPPH}_2$  proceeds far, far slower than that of diphenylberyllium with  $\text{HNPh}_2$ . Following addition and sonication for 14 days, a single species is observed in the  $^1\text{H}$  and  $^9\text{Be}$  NMR spectra, with two new resonances observed in the  $^{31}\text{P}$  NMR spectra. This species is the sole product whether there is a one-, two-, three- or fourfold excess of  $\text{HPPH}_2$ . The structure of this species was determined to be  $[\text{Be}(\mu\text{-PPh}_2)(\text{HPPH}_2)\text{Ph}]_2$  (**3**). **3** represents only the second ever example of a beryllium-phosphanide, and is the first bridging-phosphanide. The other known beryllium-phosphanide,  $(\eta^5\text{-C}_5\text{Me}_5)\text{BeP}(\text{tBu})_2$ , has a Be–P bond length of 2.083(6) Å, which is significantly shorter than the Be–P distances in **3** (2.195(6) to 2.243(6) Å).<sup>[38]</sup> This is expected, with the bridging Be–P distances more in line with dative Be–P bonds.<sup>[21]</sup> The large steric bulk of the phosphanides and phosphines in **3** likely also contribute to the relatively long Be–P bonds. Each phosphorus atom in **3** can be clearly assigned in the NMR spectrum due to a comparison of proton-coupled and -decoupled spectra. Although multiple equivalents of  $\text{HNPh}_2$  and  $\text{HPPH}_2$  were combined with diphenylberyllium, only one amine or phosphine per beryllium centre was deprotonated, respectively. This is because, following coordination of one ligand, the remaining phenyl group is less Brønsted basic, and is thus not able to deprotonate the additional amine or phosphine. The structure of **3** differs from that of **2** as there is not only a deprotonated  $\text{Ph}_2\text{P}^-$  species, but also the neutral adduct  $\text{Ph}_2\text{PH}$ . The additional phosphorus atom was able to coordinate to each beryllium centre due to the elongated Be–P bonds in comparison with Be–N (2.243(6) vs. 1.703(3) Å, respectively). This means that the steric crowding around the beryllium centre is massively reduced, and that favourable tetrahedral geometry around beryllium can be achieved through the coordination of  $\text{HPPH}_2$ . The Be–Be distance in **3** is also approximately 1 Å longer than in **2**, further

highlighting this difference. Interestingly, the Be–P bond lengths of the bridging phosphanides and the terminal phosphines are statistically indistinguishable. The steric congestion in **2** causes puckering in the Be–N–Be–N motif, whereas the analogous motif in **3** is noticeably more linear.

The reaction between  $[\text{Be}_3\text{Ph}_6]$  and 1,3-bis-(2,6-diisopropylphenyl)imidazolium chloride ( $\text{IDipp}\cdot\text{HCl}$ ) also proceeds with protonation of a single phenyl group to produce benzene and  $[(\text{IDipp})\text{BePhCl}]$  (**4**). Whilst the structures of NHC-beryllium halides and borohydrides are well studied,<sup>[39,40]</sup> there is not yet an example of an NHC-berylliumaryl halide, also viewed as a Grignard analogue. **4** is well soluble in DCM and benzene, and crystallises after storage in the latter at room temperature. **4** is the only monometallic species produced here, which is due to the large steric bulk of the carbene. The structure is unsurprising given the raft of similar species in the literature, with the  $\text{C}_{\text{NHC}}\text{-Be}$  bond length also unremarkable.<sup>[41]</sup> Potentially, with a smaller NHC, bridging of the halide atoms would be observed, which could have profound effects on the reactivity, as observed for traditional Grignard reagents.<sup>[22]</sup> The preparation of this beryllium Grignard species acts as a proof of concept for the preparation of more active species. The large and strongly electron-donating NHC will no doubt prevent or complicate the nucleophilic reactivity of this species, but the synthetic route used could be modified with alternative ligands. For example, taking salts of more classical Grignard solvents, such as triethylammonium chloride in combination with diphenylberyllium, could produce an amine-substituted beryllium Grignard reagent. Oxonium salts are also a potential reagent, however the presence of fluoride-containing counterions could complicate the reactivity. An ether- or amine-stabilised beryllium Grignard would be far more useful and reactive. Such investigations, along with small NHC complexes, are currently underway in our laboratory.

The solid-state structures of the investigated species have some similar motifs, in that apart from the very sterically encumbered  $\text{IDipp}$ , there is a bridging ligand involved in every species. Whilst beryllium is generally found to be more favourable as a tetrahedral species, an increasing number of trigonal planar species are being produced.<sup>[36]</sup> These low-coordinate species are possible with small ligands due to the smaller size of beryllium in comparison to the likes of magnesium and aluminium. However, coordination number in solution can differ from that observed in the solid state, at which point bridging ligands are typically observed.<sup>[42]</sup> For complexes in **1**, **2** and **3**, the bridging of the ligands prevents less stable two and three coordinate species being formed. For each studied compound, the solid-state structure is retained in solution. This is readily observed in **1**, **3** and **4**, for which the  $^9\text{Be}$  NMR resonances are typical for 3- and 4-coordinate species respectively. As the  $^9\text{Be}$  NMR resonances of 3-coordinate species can be very broad,<sup>[36]</sup> it is not entirely surprising that it is not possible to observe a  $^9\text{Be}$  NMR resonance in **2**, even with very long experiment times. This is most likely caused by a combination of low symmetry around the  $^9\text{Be}$  nuclei and strong  $^1J_{\text{BeN}}$  coupling and not due to chemical exchange, as the  $^1\text{H}$  NMR spectra show sharp resonances.

In conclusion, with its behaviour as a Brønsted base, diphenylberyllium is shown to be an excellent starting material, and this has led to the clean preparation of fundamental species. The homoleptic beryllium alkoxide **1** retains its structure in solution, and the synthesis of beryllium Grignard **4** is a strong proof of concept for the future preparation of more active species. The large difference in Be–N and Be–P interactions is highlighted here by the differing structures in amide **2** and phosphanide **3**.

**CAUTION!** Beryllium and its compounds are regarded as toxic and carcinogenic. As the biochemical mechanisms that cause beryllium associated diseases are still unknown,<sup>[2,43]</sup> special (safety) precautions are strongly advised.<sup>[3]</sup> Details on the synthesis, experimental setup, and characterisation of the described compounds are given in the Supporting Information.

Deposition Numbers 2154434 (for **1**), 2154436 (for **2**), 2154435 (for **3**) and 2154437 (for **4**) contain the supplementary crystallographic data for this paper. These data are provided free of charge by the joint Cambridge Crystallographic Data Centre and Fachinformationszentrum Karlsruhe Access Structures service.

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## Conflict of Interest

The authors declare no conflict of interest.

## Data Availability Statement

The data that support the findings of this study are available in the supplementary material of this article.

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