Review

Modern organometallic and coordination chemistry of beryllium

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ABSTRACT

Recent developments in the coordination and organometallic chemistry of beryllium are reviewed. The primary focus is on synthetic as well as theoretical reports relevant to the synthetic chemist since 2008 on molecular Be complexes bound to C, N and P ligands.

1. Introduction and general considerations

Due to its relatively high electronegativity, beryllium is unique in comparison with the heaver alkaline earth elements with respect to the chemistry that can be accessed. However, research into beryllium chemistry is suppressed by the extreme toxicity of Be metal, Be-containing salts and beryllium compounds, which arises primarily via inhalation of dust containing Be compounds [1]. The danger is sufficiently acute as to prevent most research groups from investigating synthetic beryllium chemistry in any significant extent. There are even recent papers specifically devoted to the synthesis of beryllium dihalide starting materials less prone to producing dust [2]. A survey of the Cambridge Structural Database shows a total of 59 compounds containing C–Be bonds, 116

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Table 1
Number of Cambridge Structural Database hits for Be, Mg, Zn and Al compounds with C, N and P bonds of any type.

	C	N	P
Be	59	116	4
Mg	647	1334	39
Zn	1386	15,953	126
Al	3504	3188	195
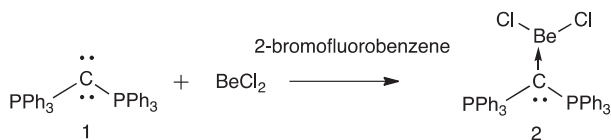
Scheme 1. Synthesis of **2** via direct coordination reaction using carbodiphosphorane **1**.

compounds containing N–Be bonds and 4 compounds containing P–Be bonds. In Table 1, the number of hits for the same bonds in Mg, Zn and Al compounds is compared, as these atoms possess chemistry that is most in common with Be. Clearly, exploration of Be chemistry is highly suppressed in comparison.

Nevertheless, there have been some major advances in the organometallic and coordination chemistry of Be in recent years, both from an experimental and a theoretical/computational perspective. This review covers advances made since Dehnicke's review on Be chemistry in 2008 (and relevant earlier examples not discussed in Dehnicke's review) in Be compounds using C-, N- and P-based ligands [3]. We also would direct the reader interested in the alkaline earth elements to Hanusa's recent review in *Comp. Inorg. Chem.*, covering developments for the entire group over approximately the last 30 years [4].

Bonds containing Be exhibit a higher degree of covalent character compared to other s-block elements due to the higher Pauling electronegativity of Be (1.57, cf. Mg 1.31, Ca 1.00, Li 0.98, Na 0.93). For example, the metallocene Cp_2Mg has the expected sandwich structure, but in Cp_2Be one of the Cp rings binds via a covalent σ interaction, albeit in a highly fluxional manner [5]. Bridging groups (i.e. Cl, H, CH_3) are also a common feature in Be chemistry, which is similar to that seen in the chemistry of Zn and Al, which are also elements often featuring electron deficient environments and having an electronegativity similar to that of Be (Zn 1.65, Al 1.61). Be has a convenient NMR handle, with ^{9}Be having a spin of 3/2 and a 100% natural abundance.

2. Be(II) chemistry

2.1. Carbon based ligands with Be(II)

#### 2.1.1. Be(II)–carbone chemistry

Carbones (e.g. carbodiphosphorane **1**) are ligands that have found increasing interest in recent years following Frenking's identification of these ligands as compounds containing carbon in a formal zero oxidation state [6,7]. Carbones exhibit two lone pairs of electrons about the central carbon atom and hence they can act as two-electron donors (Lewis bases) towards two Lewis acids, or as a four-electron Lewis base to a single acidic centre. Be(II) is an attractive element centre with which to explore coordination chemistry of carbones, as X–Be–X Lewis acids (e.g. $BeCl_2$) are formally four electron species, and can therefore accept a further four electrons.

Dehnicke and coworkers have reported on the reaction of $BeCl_2$ with carbodiphosphorane **1** (Scheme 1) [8]. In solvents typically used in such reactions (e.g. THF), only protonated **1** was isolated. Arene solvents such as toluene and benzene presented issues since $BeCl_2$ is insoluble in such solvents. However, use of

2-bromofluorobenzene allowed for facile isolation of **2**. Exposure of the isolated compound to a wide variety of organic solvents resulted in the production of either singly or doubly protonated carbodiphosphorane, indicating that solvent choice is a crucial consideration in this system.

The Be–C bond distance in **2** was found to be 1.74 Å, which is typical of a Be–C single bond. Theoretical studies indicated the π symmetric lone pair was only very weakly involved in the Be–C bonding, which may explain the ready decomposition of the complex as the Be remains electron deficient.

A theoretical study of the analogous BeH_2 complex (**3**) predicted the Be–C bond strength (28 kcal/mol) to be substantially weaker than in **2** (43 kcal/mol) [9]. Theoretical analysis of this hypothetical BeH_2 adduct indicated that the H atoms are highly hydridic, with partial charges of −0.36 e. In comparison, charges of only −0.02 are calculated for the isoelectronic and isolated $[BH_2]^+$ adduct of the carbodiphosphorane (**4**), which indicates that Be–H bonds in adducts will potentially exhibit chemistry quite different to that of related compounds having hydrogen bound to more electronegative elements. The $[BH_2]^+$ adduct was also predicted to have substantially more double bond character in the B–C bond as compared to the BeH_2 adduct, which may indicate it is the reduced electronegativity of Be that is suppressing formation of a double bond in adducts with the carbone.
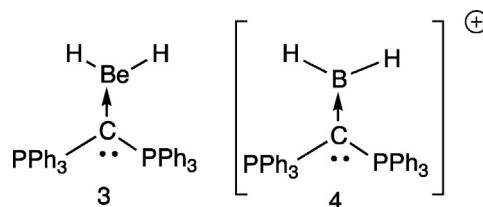
2.1.2. Be(II)–NHC chemistry

Since Arduengo's isolation of a free N-heterocyclic carbene (NHC) in 1991 there has been substantial interest in using NHCs as ligands for elements across the entire periodic table. Beryllium is no exception, but as is typical for Be, there is a limited volume of examples. Nonetheless, some of the higher profile reports in Be–C chemistry from the last two years are associated with the use of NHCs as ligands.

The first NHC adduct of Be was reported by Herrmann in 1995 where the reaction of three equivalents of Me_2NHC with $BeCl_2$ gave a cationic tris–NHC adduct of $[BeCl]^+$ as a Cl^- salt (**5**; Scheme 2) [10]. This report was also an early indication that NHC–metal adducts do not require π-backbonding to be stable complexes, as Be^{2+} lacks any electrons to contribute in this respect. Direct reaction of $BeCl_2$ with a bulkier 2,6-diisopropylphenyl substituted NHC gave the simple three-coordinate NHC–$BeCl_2$ adduct **6** [11].

The first NHC complex of a diorganoberllylium was the NHC adduct of Ph_2Be reported in 2006, which gives a three-coordinate species **7** [12]. In this compound, the C–Be bond for the NHC was found to be longer than the C–Be bonds to the phenyl rings, with distances of 1.80 and 1.75 Å, respectively.

Robinson and co-workers used **6** as a starting compound to generate an NHC stabilized analogue of beryllium borohydride by reaction of **8** with two equivalents of $LiBH_4$ (Scheme 3) [11]. The geometry about the Be atom in **8** is unusual in that it features dual bridging hydrogen atoms between the Be and B atoms along both bond axes where the chlorides were displaced. Reaction of **8** with $[Na]_2[Fe(CO)_4]$ resulted in an unusual complete reduction of one NHC ring in the isolated product and formation of an NHC–B bond (**9**), although the fate of the Be atom in this reaction was not specified.