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■ **Organometallic Chemistry**

Diphenylberyllium Reinvestigated: Structure, Properties, and Reactivity of BePh₂, [(12-crown-4)BePh]⁺, and [BePh₃]⁻

Matthias Müller and Magnus R. Buchner*[a]

Abstract: The first synthesis of BePh₂ was accomplished almost a century ago. However, its structure has remained unknown so far, while the corresponding aryls of the elements adjacent to beryllium in the periodic table are well investigated. Herein, we present an improved synthesis for diphenylberyllium and show by X-ray diffraction that it forms a trinuclear complex in the solid state. NMR spectroscopy revealed that this structure is also retained in solution but exhibits dynamic behavior. Its stability against heat and coordinating solvents is discussed and the possible obstacles to the synthesis of BePh₂ from BeCl₂ are examined. In the process of this study two ether adducts, BePh₂·Et₂O and Be₂Ph₄·Et₂O, have been characterized as well as the previously unknown triphenylberyllate anion. From the latter several single-crystal structures were obtained under various conditions, in which [BePh₃]⁻ is either isolated or acts as a ligand for Li⁺. Furthermore, the crown ether induced selfionization of BePh₂ is described and the resulting [(12-crown-4)BePh]⁺ cation was isolated, which shows an unusual 4+1 coordination around the Be atom.

Introduction

Berylliumorganyles are together with organic aluminium compounds the textbook examples for electron-deficient organometallic compounds. However in contrast to aluminiumorganyles only scarce data is available for their beryllium counterparts. BeMe₂[1] and beryllocenes[2,3] are the only homoleptic organic beryllium compounds of which the crystal structure was known and only recently we could show NMR spectroscopically that Be*n*Bu₂ actually dimerizes in solution.[4] The reason for this lack of research is on the one hand the safety issues associated with the handling of beryllium and its compounds[5] and on the other hand the fact that only BeMe₂, beryllocenes, and BePh₂ are solids at ambient temperature. While it is known that BeMe₂ is a coordination polymer with exclusively four-coordinated beryllium atoms[1] the structure of BePh₂ remained unknown and it was speculated that it also adopts an analo-

gous polymeric structure.[6,7] In contrast to this, the structure of the beryllocenes has been extensively studied.[8]

It is surprising that the solid-state structure of diphenylberyllium has never been determined considering the fact that its synthesis from beryllium metal and HgPh₂ in sealed tubes has already been described nearly one century ago[9] and this procedure is said to yield single crystals of BePh₂.[10] With slight variation, the transmetallation remained the method of choice to obtain pure BePh₂, even though various sources mention reproducibility problems and suggest numerous additives to improve the synthesis.[6,9–12] Therefore, alternative syntheses for BePh₂ have been described, such as the phenylation of BeCl₂ either by LiPh[13] or through a Grignard reagent[14] that yield the corresponding ether adduct of BePh₂. Though, these sources mention that in contrast to the beryllium alkyls like BeMe₂,[1,9,15] BeEt₂[9] or Be*n*Bu₂,[4] it is not possible to remove the ether from BePh₂,[13,14] since it can neither be distilled nor sublimed.[14,16,17] These obstacles might be the reason why BePh₂ has hardly been investigated and compounds obtained from it are scarce. The few existing studies mention that BePh₂ readily forms adducts towards Lewis bases like PMe₃,[14] *n*Bu₂O[11] or *N*-heterocyclic carbenes (NHCs)[11] and on contact with acids it cleaves benzene and the corresponding beryllium salt is formed.[14] The same is described for the contact with MeOH.[14] If BePh₂ is reacted with beryllium halides in ether a redistribution reaction was observed,[18,19] while when an excess of Ph⁻ is available, BePh₂ is said to form triphenylberyllates.[10,20,21] However with exception of the adducts BePh₂·*n*Bu₂O and BePh₂·NHC,[11] all known diphenylberyllium compounds were characterized exclusively by elemental analysis.

To clarify these inconsistencies, we decided to reinvestigate the synthesis, structure, solution behavior, and reactivity of

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$BePh_2$. We also wanted to evaluate if $Li[BePh_3]$, which was already postulated by Wittig in 1951,[10] could be synthesized. Because we were interested, whether it features a $[BePh_3]^-$ anion that is isoelectronic to BPh_3[22] or a $[Be_2Ph_6]^{2-}$ anion that has the structure of Al_2Ph_6.[23] Herein, we present our findings, which includes the crystal structure of diphenylberyllium (**1**) as well as its reactivity towards LiPh, Et_2O, 12-crown-4, and chlorinated solvents.

Results and Discussion

$BePh_2$ was prepared from Be and $HgPh_2$ in benzene at 140 °C and was obtained as colorless rhombic crystals [Eq. (1)].

$$Be + HgPh_2 \xrightarrow[\;(C_6H_6)\;]{140°c} BePh_2 + Hg \downarrow \qquad (1)$$

It crystallizes in the triclinic space group $P\bar{1}$ (2) with two formula units per unit cell. Compound **1** consists of a linear trimer with the formula Be_3Ph_6. The three beryllium atoms are μ_2-linked to each other via two phenyl moieties each. Thus, the terminal atoms Be(1) and Be(3) are trigonal planar coordinated, whereas the middle Be(2) atom is tetrahedrally coordinated by the phenyl groups as illustrated in Figure 1.

This structure motive is known for Mn^{II} aryls[24,25] and is also reported for $Be_3(OtBu)_4Cl_2$[26] as well as $Be_3(NMe_2)_6$.[27] The Be(1/3)–C atomic distances in **1** range from 1.707(2)–1.863(2) Å while those of Be(2) towards the carbon atoms are longer by tendency (1.848(2)–1.951(2) Å), see also Table 1. For comparison, the Be–C atomic distances in $BeMe_2$ are 1.922(4) Å, which corresponds to those of Be(2), whereas the Be(1/3)–C atomic distances are in the range of the trigonal-planar coordinated beryllium aryls $BePh_2$·NHC (1.745(5)–1.758(4) Å),[11] $BePh_2$·nBu_2O (1.734(3)–1.745(2) Å)[11] and $BeMes_2$·Et_2O (1.739(3) Å).[28] Be(1) and Be(3) show a deflection of 0.045(1) and 0.057(1) Å relative to the plane spanned by their surrounding carbon atoms and the C-Be-C angles range from 110.62(8) to 126.26(9)°, which corresponds with a trigonal-planar coordination around Be(1) and Be(3). The C-Be(2)-C angles range from 106.05(7) to 120.30(8)°, which is a significant deviation from the perfect tet-
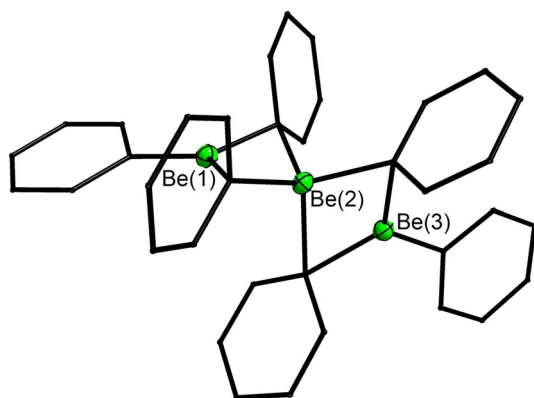
Table 1. Selected interatomic distances and angles of compounds **1–6**.

	Be–C [Å]	Be–O [Å]	d[a] [Å]	$\propto$[b] [°]
1	1.707(2)–1.951(2)		0.045(1); 0.057(1)	13.0(1)–89.6(1)
3	1.718(3)–2.008(3)	1.678(3); 1.691(3)	0.051(2); 0.061(2)	4.4(1)–81.5(1)
4	1.756(3)–1.766(3)		0.027(2)	4.6(1)–56.3(1)
5	1.754(3)–1.778(4)		0.033(2)–0.063(2)	13.0(1)–74.8(1)
6	1.777(2)–1.780(2)		0.034(1)	4.0(1)–45.6(1)
7	1.760(2)–1.766(2)	1.690(1)–1.773(2)	0.034(1)	19.9(1)–40.0(1)

[a] Deflection of Be relative to the trigonal plane. [b] Torsion angle between Ph rings and the trigonal plane (see Figure 5).

rahedral angle. The structure of **1** seemed unexpected to us, as we rather assumed a chain-like structure similar to $BeMe_2$. Therefore, we were interested in how **1** behaves in solution. Based on ${}^1H$, ${}^9Be$ as well as 2D NMR spectroscopy we were able to confirm that the molecular structure of **1** is retained in solution (Figures S1–S4). The ${}^9Be$ NMR spectrum of **1** is also illustrated in Figure 2 along with those of the other compounds that were characterized during our investigation on $BePh_2$ (vide infra). It shows two broad singlets at 8.9 ($\omega_{1/2} = 104.7$ Hz) and 21.0 ppm ($\omega_{1/2} = 281.7$ Hz), which are assigned the tetrahedrally coordinated Be(2) and to the trigonal planar coordinated beryllium atoms Be(1) and Be(3) respectively. The corresponding chemical shift region and linewidths are in the typical range of four- and three-coordinated Be nuclei.[29]

We observed exchange between the terminal and the μ_2-bridging phenyl units of **1** via exchange NMR Spectroscopy (EXSY), meaning that the phenyl groups constantly change their positions from terminal to bridging in solution. The protons within the phenyl groups do not exchange with each other. Therefore, the Be–C bond is not broken and we assume that the interchange between terminal and bridging phenyl groups occurs via dissociation and recoordination of $BePh_2$ units. This exchange of the phenyl groups in conjunction with the quadrupolar nature of the ${}^9Be$ nucleus leads to broadening of the signals in the ${}^9Be$ NMR spectrum as well as the ${}^{13}C$ NMR spectrum, especially for the signals of the carbon atoms directly bound to the Be atoms, which makes them barely noticeable. Additional line broadening is also caused by the low solubility of **1** in C_6D_6, CD_2Cl_2 and $CDCl_3$. Whereas **1** is not stable in

Figure 1. Molecular structure of $BePh_2$ (**1**) in the solid state. Ellipsoids are depicted at 70 % probability at 100 K. Protons are omitted and carbon atoms are shown as wire frame for clarity. The Be–Be atomic distances are 2.033(2) and 2.047(2) Å.

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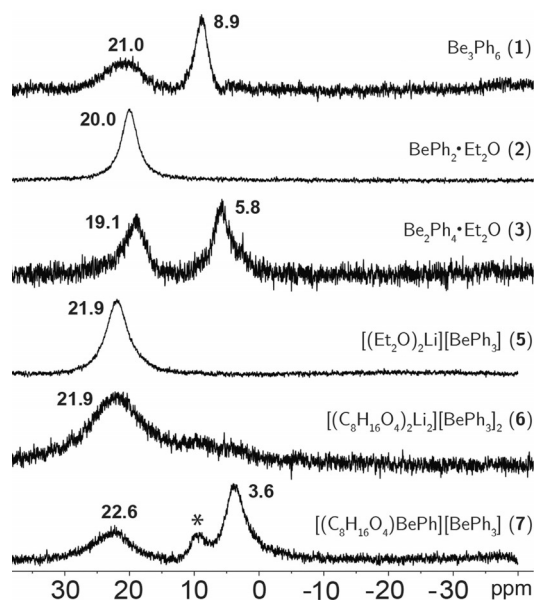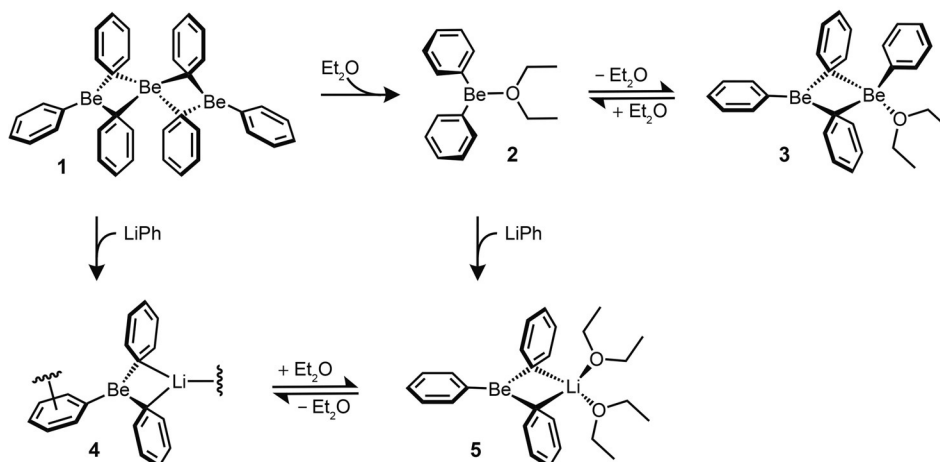
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Figure 2. ^{9}Be NMR spectra of **1**, **2**, **5–7** in CD_2Cl_2 and **3** in C_6D_6. * unknown Be-species, tentatively assigned to $BePh_2 \cdot$(12-crown-4).

the latter for more than a few days. In CD_2Cl_2, on the other hand, **1** is stable for weeks. Although a slight formation of benzene, which originates from deprotonation of the solvent by Ph^-, is observed in CD_2Cl_2 when the solution is stored for longer. More polar solvents like CD_3CN lead to the decomposition of **1**, which restricted us to the use of CD_2Cl_2. The solubility of **1** increases drastically in benzene and dichloromethane when the solutions are heated to their boiling points. We were not able to determine a significant degradation of **1** during the heat up. Therefore, dichloromethane was used to separate **1** from Be and Hg after the transmetallation reaction [Eq. (1)], which is a small but impactful modification in comparison to the literature procedure where the separation is done in benzene.[6, 11, 12, 16] If **1** is heated in substance, it already starts to decompose at 50 °C, which was observed via thermogravimetric analysis (TGA) (Figure S27). This finding is in contrast with the

reported melting / decomposition temperature of approx. 245 °C for **1**.[6, 16] However, at 260 °C a significant mass loss is observed in the TGA, which might explain the previously published data.

It was reported that the reaction of $BeCl_2$ with aryllithium reagents in ethereal solution yields the ether adducts of the corresponding beryllium aryles in crystalline form.[11, 13, 14, 28] It was also reported that $BePh_2$ undergoes a redistribution when beryllium halides are present in ethereal solution.[18, 19] However, our own efforts to synthesize **1** from $BeCl_2$ and LiPh in Et_2O resulted in opaque, viscous oils from which we were not able to isolate a distinct crystalline compound. Also the previous studies on the etherates obtained from the reaction of $BeCl_2$ with LiPh are solely based on elemental analysis.[13, 14] Therefore, we examined the reactivity of **1** towards Et_2O and LiPh. Subsequently, we dissolved **1** in C_6D_6 and added one equivalent of Et_2O to obtain a reference for the $BePh_2 \cdot Et_2O$ adduct **2**, which was observed via NMR spectroscopy (Figures S5 and S6). In its ^{9}Be NMR spectrum a broad singlet at 18.6 ppm ($\omega_{1/2} = 153.9$ Hz) indicates a trigonal planar coordinated Be nucleus, which corresponds well to the signal of $BePh_2 \cdot nBu_2O$ at 17.4 ppm ($\omega_{1/2} = 239$ Hz).[11] In the ^{1}H NMR spectrum only one signal set for a phenyl group is observed as well as a signal set for a slightly down-field shifted Et_2O. Consequently, we deduct that compound **2** is present is solution as illustrated in Scheme 1.

In order to crystallize **2**, the solvent was reduced in vacuo. However, the acquired single crystalline compound revealed the structure of $Be_2Ph_4 \cdot Et_2O$ (**3**), which is illustrated in Figure 3 and crystallizes in the monoclinic space group $P2_1/c$ (14). The structure of **3** is closely related to that of **1**. Through the substitution of one $BePh_2$ unit by an Et_2O molecule at Be(2), compound **1** can be transferred into **3**, in theory. Similar to **1**, compound **3** features two inequivalently coordinated Be atoms. Be(1) is trigonal planar coordinated by three carbon atoms of one terminal and two μ_2-phenyl groups with Be(1)–C atomic distances of 1.718(4)–1.817(3) Å and C-Be(1)-C angles of 114.4(2)–125.3(2)°. These values are in the range of those in compound **1** and reflect their similarity. For the tetrahedrally

Scheme 1. Formation of **2–5** through addition of LiPh and/or Et_2O to $BePh_2$ (**1**).
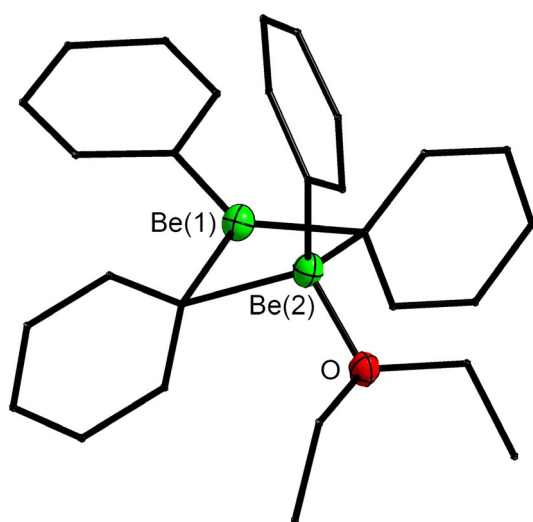
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Figure 3. Molecular structure of $Be_2Ph_4 \cdot Et_2O$ (**3**) in the solid state. Ellipsoids are depicted at 70% probability at 100 K. Protons are omitted and carbon atoms are shown as wire frame for clarity. The Be–Be atomic distance is 2.068(4) Å.

coordinated Be(2) atom the Be(2)–C atomic distances towards the μ_2-phenyl groups are 1.927(3)-2.008(4) Å, while that towards the terminal phenyl group is with 1.756(3) or 1.760(3) Å significantly shorter. The Be(2)–O atomic distance is 1.678(3) or 1.691(3) Å, which is slightly longer than those of $BePh_2 \cdot nBu_2O$ (1.647(2) Å).[11]

Since there was no evidence for **3** in the NMR spectra of **2**, the crystals of **3** were redissolved in C_6D_6. This time compound **3** could be observed in solution, but also **1** and **2** emerged in the ^1H as well as in the 2D NMR spectra (Figures S7–S11). Like for **1**, in the ^9Be NMR spectrum of **3** two broad singlets at 5.7 ($\omega_{1/2} = 119.1$ Hz) and 19.2 ppm ($\omega_{1/2} = 172.3$ Hz) are observed. Also the three chemically independent phenyl groups could be assigned via 2D NMR spectroscopy. Thus, **3** seems at least metastable in solution, because after several weeks of storage, we observed a small amount of white precipitate in the NMR tube. Therefore, we conducted additional NMR experiments, in which the intensity of the signals for **2** had increased. In the EXSY spectrum exchange peaks between the terminal phenyl group at Be(2) of **3** and the phenyl groups of **2** occurred. There is no exchange of the phenyl groups within **3**, but NOE peaks between the μ_2-Ph and the terminal Ph groups at Be(2), which in turn leads to the assumption that neither Et_2O nor a Ph group dissociates from Be(2), but the dinuclear complex molecule **3** splits into **2** and $BePh_2$. The latter then trimerizes to **1** and subsequently precipitate, due to its low solubility in benzene.

Compound **2** was formed willingly when Et_2O was offered to **1**. Hence, we were curious if additional Et_2O could coordinate towards **2**. However, adding more Et_2O to **2** did not alter the NMR spectra. Therefore, the two phenyl groups either result in steric hindrance or high electron density at the Be atom, which prevents the coordination of a second Et_2O molecule. This is in contrast to the beryllium halide etherates.[28,30,31]

Addition of one equivalent LiPh to **1** in C_6D_6 resulted in a voluminous precipitate around $BePh_2$ as soon as LiPh had dissolved. In the NMR spectra only signals of LiPh were observed. When the suspension was heated to 80 °C for several days, the precipitate completely recrystallized as colorless column-shaped crystals in the upper part of the J. Young NMR tube. Single-crystal diffraction revealed these to be $Li[BePh_3]$ (**4**), which had already been postulated in 1951.[10] It crystallizes in the orthorhombic space group $P2_12_12_1$ (19) and features a triphenylberyllate anion $[BePh_3]^-$, which is the first example of its kind. Within $[BePh_3]^-$, the Be atom is coordinated trigonal planar by three phenyl groups that tilt relative to the trigonal plane with angles that range from 4.6(1)–56.3(1)°. The Be–C atomic distances (1.756(3)–1.766(3) Å) are comparable to those of $BePh_2 \cdot NHC$[11] and the C-Be-C angles (118.5(1)–121.2(2)°) are nearly ideal for a trigonal-planar coordination sphere. The $[BePh_3]^-$ anions in **4** are coordinated by two Li^+ cations each, to build up one-dimensional chains. The Li^+ cations in turn are coordinated by two $[BePh_3]^-$ anions via a η^6-coordination towards one phenyl group of the first $[BePh_3]^-$ anion and η^1 to two μ_2-phenyl groups of the second $[BePh_3]^-$ anion as illustrated in Figure 4. A similar coordination motive for the Li^+ cation is found in LiPh[32] and was also reported for a lithium triphenylborate compound.[33] Like for Et_2O, further addition of LiPh did not lead to the formation of a $[BePh_4]^{2-}$ anion, in which the beryllium atom would be tetrahedrally coordinated. In-
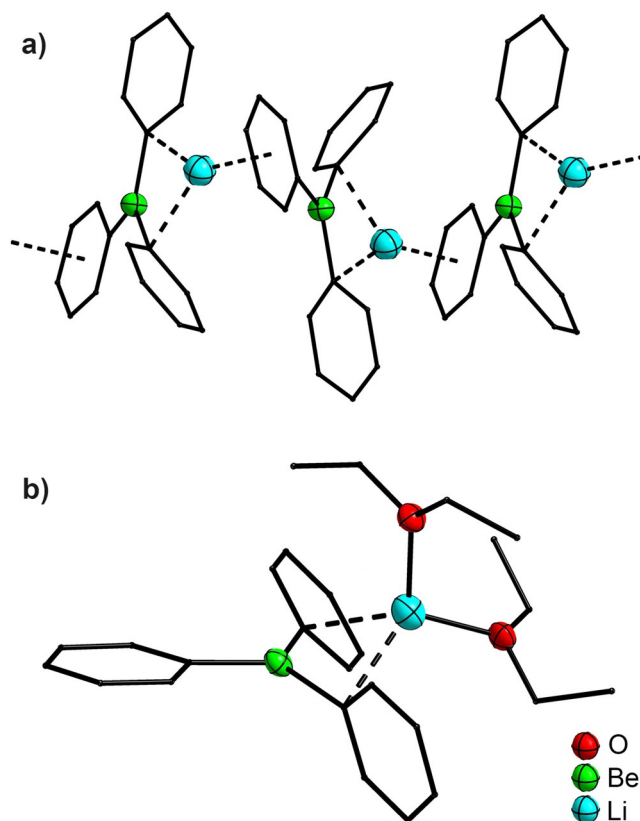

Figure 4. Section of the crystal structures of a) **4** and b) **5**. Ellipsoids are depicted at 70% probability at 100 K. Protons are omitted and carbon atoms are shown as wire frame for clarity.

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stead, **4** was received repeatedly. Since [BeMe$_4$]$^{2-}$ is known,[34] we assume that the phenyl groups are to bulky to facilitate a tetrahedral coordination around the Be atom.

The respective addition of Et$_2$O to **4** or of LiPh to **2** in C$_6$D$_6$ leads to the formation of colorless clear solutions with equal NMR spectra. In the ^{9}Be NMR spectrum a broad singlet at 23.5 ppm ($\omega_{1/2} = 241.9$ Hz) indicates trigonal coordinated beryllium nuclei. According to the ^{1}H and ^{13}C NMR spectra the Be atoms are coordinated by three identical phenyl groups. In the ^{7}Li NMR spectrum a narrow singlet at -1.2 ppm ($\omega_{1/2} = 7.1$ Hz) speaks for a highly symmetrically coordinated Li$^+$ cation. Thus we assume that the Et$_2$O is exclusively coordinated towards Li$^+$ while [BePh$_3$]$^-$ is solvent separated and shows no interaction with the ether molecules. When the solvent is removed slowly in vacuo, single crystals of (Et$_2$O)$_2$LiBePh$_3$ (**5**) in the monoclinic space group $P2_1/c$ (14) could be isolated, whose molecular structure is depicted in Figure 4. Here, the Li$^+$ cation is coordinated by two μ_2-phenyl groups of the [BePh$_3$]$^-$ anion and two Et$_2$O molecules complete the tetrahedral coordination sphere around it. A nearly analogous molecular structure is reported for (nBu$_2$O)$_2$LiZnPh$_3$.[35] The phenyl groups of [BePh$_3$]$^-$ in **5** are slightly more tilted relative to the trigonal plane compared to those in **4** (Table 1) and the Be–C atomic distances (1.754(3)–1.778(4) Å) and C-Be-C angles (118.4(2)–121.9(2)°) in **5** are within the standard deviation identical to those of **4**. It should be noted that when the solvent of the reaction mixture of **5** is removed to fast or the solution is diluted with a less polar solvent, compound **4** crystallizes exclusively, even when Et$_2$O is initially provided in excess.

Considering that the [BePh$_3$]$^-$ anion is present in solution as a trigonal-planar molecule missing further coordination through Et$_2$O, we were suspicious if the [BePh$_3$]$^-$ anion could be isolated in the solid state without direct interaction towards a counter ion and whether this would lead to the formation of dinuclear [Be$_2$Ph$_6$]$^{2-}$ ions in analogy to the chloroberyllate system[36] or Al$_2$Ph$_6$.[23] Thus, one equivalent of 12-crown-4 was added to **4** in C$_6$D$_6$. This resulted in the immediate formation of a voluminous precipitate around **4**, which is in strong contrast to the analogous reaction with Et$_2$O that led to a clear colorless solution. Only free crown ether was observed in the NMR spectra and the suspension was consequently recrystallized at 80 °C to quantitatively yield [(12-crown-4)$_2$Li$_2$][BePh$_3$]$_2$ (**6**, Scheme 2) in the monoclinic space group $P2_1/n$ (14). Here, the [BePh$_3$]$^-$ anions show no interaction with the [(12-crown-4)$_2$Li$_2$]$^{2+}$ cation, the formation of which has already been described under similar conditions.[37,38] In **6** the Ph groups of [BePh$_3$]$^-$ (Figure 5a) are tilted similarly to those of **4** with angles of 4.0(1)–45.6(1)° relative to the trigonal plane and their
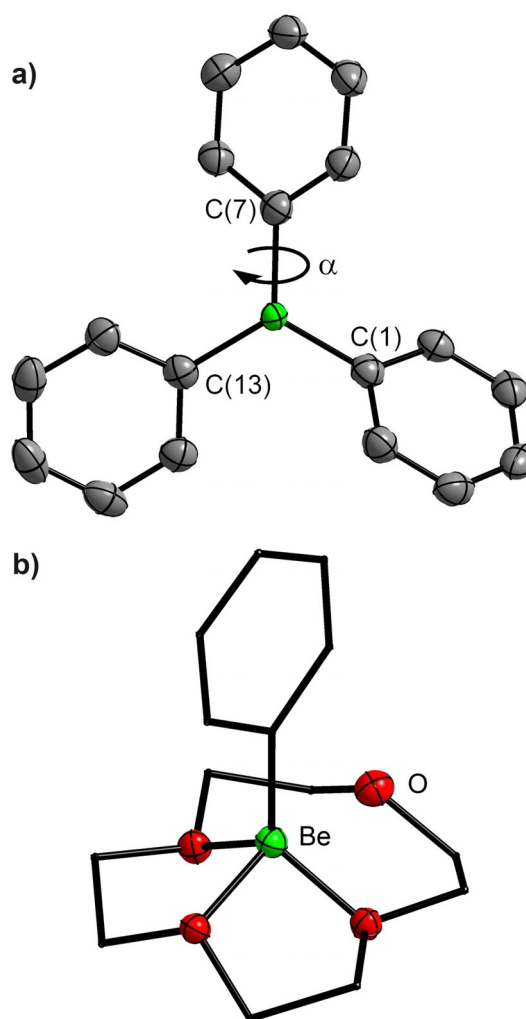

Figure 5. Molecular structure of a) the [BePh$_3$]$^-$ anion in **6** and b) the [(12-crown-4)BePh]$^+$ cation in **7**. Ellipsoids are depicted at 70 % probability at 100 K. Protons are omitted and carbon atoms in b) are shown as wire frame for clarity. Torsion angle α between the Ph groups and the trigonal plane defined by C(1), C(7), and C(13).

orientation is comparable to those of **5**. This is unlike in the structure of the isoelectronic molecule BPh$_3$, where the phenyl groups are tilted to form a paddle wheel.[22] Furthermore, the Ph groups in BPh$_3$ are tilted more evenly (28–35°) and the B–C atomic distances (1.589(5)–1.571(3) Å)[22] are significantly shorter than the corresponding Be–C distances in **6**. The Be–C atomic distances (1.777(2)–1.780(2) Å) as well as the C-Be-C angles (118.5(1)–121.1(1)°) of **6** are, however, nearly identical to those of **4** and **5**.
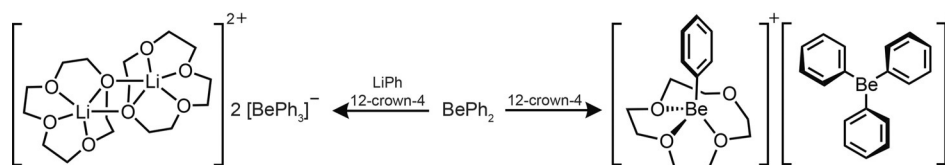
Scheme 2. Reaction of BePh$_2$ (**1**) with LiPh and 12-crown-4 to [(12-crown-4)$_2$Li$_2$][BePh$_3$]$_2$ (**6**) and [(12-crown-4)BePh][BePh$_3$] (**7**).

Single crystals of **6** were dissolved in CD_2Cl_2 and NMR spectra measured. As expected, a broad singlet at 21.9 ppm ($\omega_{1/2} = 382.0$ Hz) was observed in the ^9Be NMR spectrum, like for **5**. In the ^1H and ^{13}C NMR spectra, the signals for the Ph groups are well resolved and again indicate an isolated $[BePh_3]^-$ anion in solution. However, in the ^9Be NMR spectrum (Figure 2) as well as in the EXSY spectrum (Figure S15) of **6** small signals of an additional Be-species were observed, which shows exchange with the $[BePh_3]^-$ anion. Therefore, a control experiment without LiPh was performed to determine the reactivity of $BePh_2$ towards 12-crown-4. While a clear colorless solution was obtained in CD_2Cl_2, in C_6D_6 a viscous suspension was formed immediately. From the latter, single crystals of $[(12-crown-4)BePh][BePh_3]$ (**7**) were obtained in quantitative yield when the suspension was heated for several days to 100 °C. Compound **7** crystallizes in the monoclinic space group $P2_1/n$ (14). It again contains the $[BePh_3]^-$ anion and a $[(12-crown-4)BePh]^+$ cation (Figure 5 b), in which the beryllium atom is distorted tetrahedrally coordinated by one phenyl moiety and three oxygen atoms of the 12-crown-4 ligand. The fourth oxygen atom of the crown ether is inclined in the direction of the beryllium atom, but shows a significantly longer Be–O atomic distance of 2.347(2) Å compared to the other three oxygen atoms (1.690(1)–1.773(1) Å), whose Be–O atomic distances are in range of the corresponding distances in the very similar $[(12-crown-4)BeCl]^+$ cation reported by Dehnicke.[39] Here, one of the four coordinating O atoms also has a much longer distance to the Be atom. A closer relation between the two cations is revealed based on the O-Be-O (76.70(6)–89.75(7)°) and the C-Be-O (97.76(6)–123.02(8)°) angles of $[(12-crown-4)BePh]^+$, which are more comparable to a trigonal bipyramidal or square pyramidal than to a tetrahedral coordination sphere. This is also observed in $[(12-crown-4)BeCl]^+$, which was the first reported example of a five-fold coordinated molecular beryllium compound.[39] However, due to the large Be–O atomic distance in $[(12-crown-4)BePh]^+$, it is not possible to speak of a five-fold coordinated beryllium atom in compound **7**. In general, compounds in which beryllium is five-fold coordinated are very rare.[39,40,41] The Be–C atomic distances (1.763(2)–1.766(2) Å) of the $[BePh_3]^-$ anion in **7** are within the standard deviation identical to that of the $[(12-crown-4)BePh]^+$ cation (1.760(2) Å), which is remarkable considering the charge difference of the two molecules. The second noticeable feature of the $[BePh_3]^-$ anion in **7** is the paddle wheel arrangement of the phenyl groups with tilt angles of 19.9–40.0(1)°, that was not observed in **4** or **6**. Other than that it is quite similar to the $[BePh_3]^-$ anion found in **6**. This crown ether induced selfionization is common for magnesium organyls,[42–45] but not reported for corresponding aluminium compounds. However, cationic aluminium alkyls are known[46,47] as well as for other related elements such as boron,[48] mercury[49,50] and gallium.[51]

Compound **7** is also observed in solution when **7** is dissolved in CD_2Cl_2 or when the starting materials are reacted in it. In the ^9Be NMR spectrum, three broad signals occur, from which the singlet at 3.6 ppm ($\omega_{1/2} = 150.4$ Hz) was assigned to the $[(12-crown-4)BePh]^+$ cation while the signal at 22.6 ppm ($\omega_{1/2} = 269.1$ Hz) corresponds to the $[BePh_3]^-$ anion. The origin

of the third signal at 9.4 ppm ($\omega_{1/2} = 97.2$ Hz) remains unknown. Nevertheless, we assume that this signal is related to some kind of $BePh_2\cdot12$-crown-4 adduct since the same signals were also observed in the NMR spetra of **6** (vide supra). While compound **7** is easily assigned to signals in the ^1H and ^{13}C NMR spectra, the additional signals in those spectra give no hint about the structure of the potential $BePh_2\cdot12$-crown-4 adduct. The EXSY NMR spectrum of **7** (Figure S19) shows not only exchange of the phenyl moieties between $[(12-crown-4)BePh]^+$ and $[BePh_3]^-$ but also exchange between the protons within the phenyl rings of the $[BePh_3]^-$ anion. This process was not observed in the other phenylberyllium compounds. This proton transfer inside the phenyl rings is reminiscent of the proton chain walking of polymers triggered by Lewis acidic metal cations.[52] Since there is a $[BePh]^+$ cation in solution, this may cause the proton exchange in **7**.

Conclusions

We determined the crystal structure of $BePh_2$ (**1**), which is a trinuclear linear molecule. This structure motive is known for O-[26] and N-bridged beryllium[27] as well as aryl manganese compounds[24,25] and is related to the structures of Zn_2Ph_4[53] and Al_2Ph_6.[23] However, it clearly shows that the small size of the beryllium atom results in a unique structural chemistry. The molecular structure of **1** persists also in solution and it is stable against chlorinated solvents. This low reactivity is more comparable to organic boron compounds than to zinc, magnesium or lithium organyles. While **1** was successfully obtained from the well established synthesis through $HgPh_2$, the phenylation of $BeCl_2$ in ethereal solution did not yield a distinct product.

When Et_2O is offered to **1** it readily forms the adduct $BePh_2\cdot Et_2O$ (**2**), to which no additional ether coordinates even when provided in excess. This is proof of the Lewis acidic character of $BePh_2$, which is postulated in most text books and is in line with the reactivity of boron- and aluminium–organic compounds. Though, Et_2O can be removed from a solution of **2** to yield $Be_2Ph_4\cdot Et_2O$ (**3**), which is formally an adduct of one equivalent $BePh_2$ towards **2**. Additionally, **3** is not stable in the long term and tends to cleave into **1** and **2**. This shows that the Be–O bond strength in ether adducts of $BePh_2$ had been previously overestimated and is evidence for the high stability of the Be–C bonds in these compounds.

When **1** is reacted with LiPh, $Li[BePh_3]$ (**4**) is obtained in quantitative yield as a one-dimensional coordination polymer. It is the first isolated example of a triphenylberyllate. Within the $[BePh_3]^-$ anion the Be atom is trigonal planar coordinated and two of the phenyl moieties are tilted relative to the trigonal plane. The low solubility of **4** in non-coordinating solvents is drastically improved when small amounts of Et_2O are added, which coordinates to the Li^+ cations in solution, while the $[BePh_3]^-$ anions are not coordinated by an additional ligand. The $[BePh_3]^-$ anion is stable even in Et_2O and there is no evidence for ether coordination. The corresponding ether adduct $(Et_2O)_2LiBePh_3$ (**5**) was obtained from ethereal solutions of **4** when the solvent was removed very slowly. Otherwise **4** is re-

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ceived again. Other than in solution the [BePh$_3$]$^-$ anion in **5** is coordinated by the Li$^+$ cation in the solid state. Therefore, [BePh$_3$]$^-$ no longer acts as a Lewis acid. Quite contrary the whole anion acts as a good ligand for the Lewis acid Li$^+$ and forms Li–C bonds, which closely resemble the ones found in phenyllithium. In order to obtain an isolated [BePh$_3$]$^-$ anion in the solid state, 12-crown-4 was added to **4**. In the resulting compound **6**, the [BePh$_3$]$^-$ anion shows no direct interaction with the [(12-crown-4)$_2$Li$_2$]$^{2+}$ cation. Since the NMR spectra of **6** did show an additional species in solution 12-crown-4 was reacted with **1** as a control experiment. Thereby, **7** was obtained, in which **1** dissociated into a [BePh$_3$]$^-$ anion and a [(12-crown-4)BePh]$^+$ cation. While these autoionization processes in solution are common for magnesium organyles they are unknown for the related aluminium compounds.[42–45] Therefore, the solution behavior of BePh$_2$ is more closely related to magnesium than aluminium, which is in line with the ligand redistribution between berylliumhalides and -aryls.[18,19] The Be atom in [(12-crown-4)BePh]$^+$ is four-fold coordinated but does not show a tetrahedral coordination sphere. In the course of the coordination by the crown ether, the Be^{2+} cation is forced into a more trigonal bipyramidal coordination with a coordination number of 4+1.

In summary, it was shown that the structure and solution behavior of BePh$_2$ is unique due to the small size of the Be atom in comparison to all other metals. While some properties are closely related to the corresponding aluminium compounds others are more closely matched by organic magnesium, lithium or boron compounds. At the moment research on the structure of further beryllium organyles is conducted to put these finding into a broader context. The reactivity of BePh$_2$ is lower than in the analogous zinc and mercury compounds, which is probably due to the high Be–C bond strength. We suspect that the described reactivity of berylliumorganyles towards N–H and O–H bonds[14] is rather driven by the formation of even more stable Be–N and Be–O bonds. This is reinvestigated at the moment and will be published in due course. The solution behavior of BePh$_2$ seems to closely resemble the one of organic magnesium compounds and studies on ligand redistribution reactions in the berylliumhalide/aryl system are under way. Finally we could prove that the common assumption that berylliumorganyles behave like aluminiumorganyles is to simplistic and further studies are necessary to obtain a concise picture of this substance class.

Experimental Section

General

Please see the Supporting Information.

The following files are available free of charge: Supporting Information: Containing tables with crystallographic details, depictions of further crystal structures and selected NMR and IR spectra.

CCDC 1971538, 1971539, 1971540, 1971541, 1971542 and 1971543 contain the supplementary crystallographic data for this paper. These data are provided free of charge by The Cambridge Crystallographic Data Centre

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