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Notes

The First Carbene Complex of a Diorganoberyllium: Synthesis and Structural Characterization of Ph_2Be(*i*-Pr-carbene) and Ph_2Be(*n*-Bu_2O)

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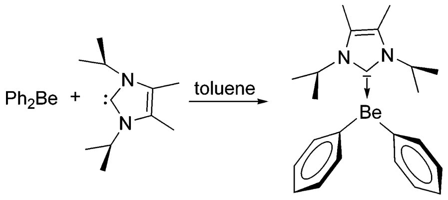
*Summary: The reaction of base-free Ph_2Be with 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene (i-Pr-carbene) in toluene gave the carbene adduct Ph_2Be(i-Pr-carbene) (**1**) as colorless crystal blocks. For comparison, the di-n-butyl ether adduct $Ph_2Be(n\text{-}Bu_2O)$ (**2**) was prepared from $BeCl_2$ and PhLi in a mixture of Et_2O and n-Bu_2O. Single-crystal X-ray determinations reveal monomeric solid-state structures for both complexes.*

Introduction

Beryllium chemistry has received the least attention among the nonradioactive group 2 elements. The main reason for this is the exceptionally high toxicity of beryllium and its compounds.[1,2] Nevertheless, the chemistry of beryllium was already studied in the early years of organometallic chemistry. The synthesis of diphenylberyllium was first reported in 1927 by Gilman et al. starting from elemental Be and $Hg(C_6H_5)_2$ in a sealed tube at 225 °C.[3] Various other ways to prepare diphenylberyllium have been described using different methods such as the Grignard, organolithium, or organomercury method.[4] Several Lewis base adducts were studied, such as $Ph_2Be(Et_2O)_2$[5−7], $Ph_2Be(TMEDA)_2$ (TMEDA = tetramethylethylenediamine),[7] and $Ph_2Be(DME)_2$ (1,2-dimethoxyethane).[5,7] Furthermore, reactivity studies of diphenylberyllium with ketones, aldehydes, and azomethine compounds were performed.[8] More recently, the synthesis and structure of $Mes_2Be(Et_2O)$ (Mes = 2,4,6-$Me_3C_6H_2$)[9] was reported as well as detailed studies of heteroleptic $ArBeX(Et_2O)$ complexes (Ar = 2,6-$Mes_2C_6H_3$, X = Cl, Br) including ^{9}Be NMR.[10] No single-crystal X-ray structures are known of Lewis base adducts of the simple diphenylberyllium. A nucleophilic carbene complex of beryllium is known only for the reaction of $BeCl_2$ that forms the beryllium carbene complex [(Me-carbene)$_3$BeCl]Cl (Me-carbene = 1,3-dimethylimidazol-2-ylidene).[11,12] Also, sophisticated theoretical studies of a series of beryllium-carbene complexes were performed.[13] Herein we report the synthesis and structure determination of novel diphenylberyllium complexes containing 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene and di-*n*-butyl ether as Lewis bases. The former represents the first well-defined carbene complex of a diorganoberyllium.

Results and Discussion

Diphenylberyllium reacts with the stable nucleophilic carbene 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene in toluene at room temperature to give the nucleophilic carbene complex Ph_2Be(*i*-Pr-carbene) (**1**) in high yield in the form of colorless crystals (eq 1).



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(1)

In contrast to the starting material Ph_2Be, which is only poorly soluble in nonpolar organic solvents, the carbene adduct **1** is highly soluble in toluene and pentane. The corresponding di-*n*-butyl ether adduct $Ph_2Be(n\text{-}Bu_2O)$ (**2**) was obtained from $BeCl_2$ dissolved in diethyl ether and PhLi dissolved in di-*n*-butyl ether at room temperature (eq 2). This synthetic route provides straightforward access to Lewis base adducts of diphenylberyllium.

$$2\ PhLi + BeCl_2 \xrightarrow{n\text{-}Bu_2O/Et_2O} Ph_2Be(n\text{-}Bu_2O)\ (\mathbf{2}) + 2\ LiCl \qquad (2)$$

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Compound **2** is also freely soluble in nonpolar solvents as well as in Et_2O and THF. Both compounds form colorless crystals and exhibit high air- and moisture-sensitivity. The ^1H NMR data show the phenyl signals for both compounds in the expected area, whereas the signal for the proton in *ortho* position to beryllium in **1** is shifted downfield by 0.2 ppm in contrast to **2**. The ^{13}C NMR resonance shows the typical upfield shift of the carbene carbon from 207.4 ppm in the "free" carbene to 173.6 ppm in **1** and is in good agreement with the value determined for $[(Me\text{-}carbene)_3BeCl]Cl$.[11] The resonance of the CH_3 groups of the isopropyl groups is shifted to high field by over 0.4 ppm in the ^1H NMR and 2 ppm in the ^{13}C NMR compared to the corresponding free carbene. This might be due to an interaction of the methyl groups with the metal, which was also observed for a series of carbene complexes of the heavier alkaline earth metals.[14] The ^9Be NMR resonances for **1** and **2** relative to $Be(H_2O)_4^{2+}$ as external standard were found at 21.05 ppm ($\omega_{1/2} = 464$ Hz) and 17.4 ppm ($\omega_{1/2} = 239$ Hz), respectively. Generally, an increasing coordination number of beryllium results in a chemical shift at higher field, whereas the chemical shifts of ^9Be are in the range from δ ca. -25 to δ $+25$ ppm.[15,16] The results for **1** and **2** are in good agreement with a coordination number of 3 (e.g., $\delta = 20.8$ ppm for $Me_2Be(Et_2O)$[15] and are at lower field than the ^9Be shifts for the heteroleptic complexes $ArBeX(Et_2O)$ ($Ar = 2,6\text{-}Mes_2C_6H_3$, $X = Cl$, Br) (12.8 and 13.4 ppm, respectively), which also possess a coordination number of 3 in solution.[10]

Single-crystal X-ray structure determinations of **1** and **2** reveal monomeric molecular structures in the solid state (Figures 1 and 2). Compound **1** crystallizes in the space group $P2_1$ with two different molecules in the asymmetric unit, whose distances and angles are nearly identical. Refinement in the centrosymmetric space group $P2_1/n$ was not possible. Compound **2** crystallizes in the space group $P2_1/c$. The beryllium centers in both complexes exhibit a distorted trigonal planar coordination sphere with nearly equivalent angles around the metal center (C(7)−Be−C(1) = 126.6(3)°, C(7)−Be−C(13) = 115.9(2)°, C(1)−Be−C(13) = 117.4(2)°/C(7′)−Be′−C(1′) = 125.7(2)°, C(7′)−Be′−C(13′) = 117.6(2)°, C(1′)−Be′−C(13′) = 116.5(2)° for **1** and O(1)−Be(1)−C(1) = 116.80(12)°, O(1)−Be(1)−C(7) = 115.40(13)° for **2**, respectively). The Be−C(aryl) bond lengths in **1** (1.75−1.76 Å) and **2** (1.73−1.75 Å) are in the typical range for beryllium aryl distances and are in good agreement with the known values for $Mes_2Be(Et_2O)$ (1.739(3) Å)[9] and $ArBeX(Et_2O)$ (1.74−1.78 Å).[10] The Be−C(carbene) bond in **1** is slightly longer (1.787(4) and 1.807(4) Å) and is thus in good agreement with the distance found in the only other known beryllium carbene complex, $[(Me\text{-}carbene)_3BeCl]Cl$ (Me-carbene = 1,3-dimethylimidazol-2-ylidene) (1.807(3) and 1.822(3) Å).[11,12] Beryllium−oxygen distances normally vary from 1.60 to 1.69 Å. The value of the Be−O bond (1.647(2) Å) in **2** resulting from the coordination of the di-*n*-butyl ether to the beryllium is within this range. The corresponding bond lengths in $Mes_2Be(Et_2O)$ (1.638(5) Å)[9] and $ArBeX(Et_2O)$ (1.60−1.61 Å)[10] are in the same range and match well with the Be−O distance in **2**.

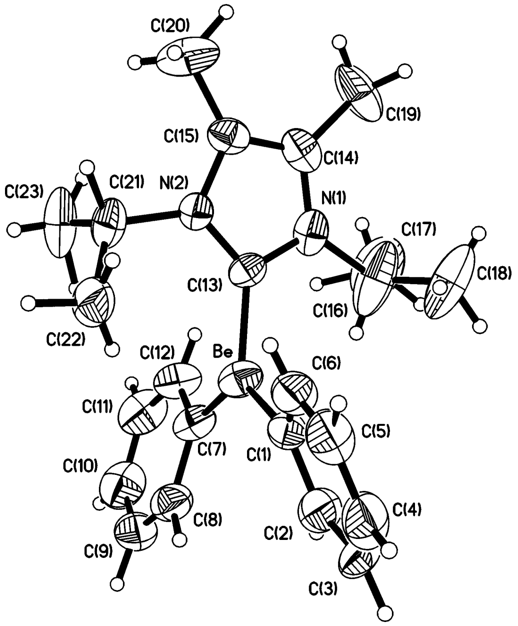

Figure 1. ORTEP plot of **1** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Be−C(7) = 1.745(4), Be−C(1) = 1.757(4), Be−C(13) = 1.807(4), N(1)−C(13) = 1.342(3), N(2)−C(13) = 1.340(3), C(7)−Be−C(1) = 126.6(3), C(7)−Be−C(13) = 115.9(2), C(1)−Be−C(13) = 117.4(2), N(2)−C(13)−N(1) = 105.6(2); Be′−C(7′) = 1.749(4), Be′−C(1′) = 1.752(4), Be′−C(13′) = 1.787(4), N(1′)−C(13′) = 1.350(3), N(2′)−C(13′) = 1.353(3), C(7′)−Be′−C(1′) = 125.7(2), C(7′)−Be′−C(13′) = 117.6(2), C(1′)−Be′−C(13′) = 116.5(2), N(1′)−C(13′)−N(2′) = 104.7(2).

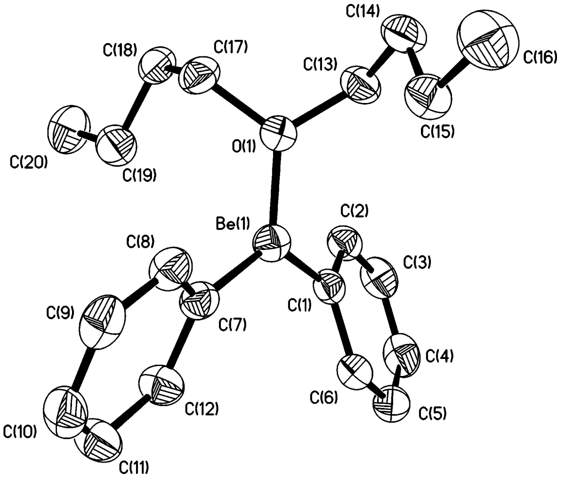

Figure 2. ORTEP plot of **2** with 50% probability thermal ellipsoids. Selected bond lengths (Å) and angles (deg): Be(1)−O(1) = 1.647(2), Be(1)−C(1) = 1.734(2), Be(1)−C(7) = 1.745(2), O(1)−Be(1)−C(1) = 116.80(12), O(1)−Be(1)−C(7) = 115.40(13), C(1)−Be(1)−C(7) = 127.79(13).

In summary we achieved the first structural characterization of a diorganoberyllium carbene complex. In addition, we have demonstrated that diphenylberyllium Lewis base adducts possess a coordination number of 3 even when employing unsubstituted phenyl groups, which are sterically less bulky than the mesityl groups in $Mes_2Be(Et_2O)$.[9] The presented complexes with their straightforward synthetic routes should facilitate further development of this largely neglected class of compounds.

Experimental Section

Cautionary note: Beryllium and its compounds are extremely toxic. Any work with these materials should be conducted according to the established safe-handling procedures.

General Procedures. The reactions were carried out in an inert atmosphere of dry argon using standard drybox and Schlenk

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techniques. The melting points were determined in a sealed capillary without correction. NMR spectra were recorded on a Bruker DPX 400 or AVANCE 600 NMR spectrometer. All chemical shifts are reported in ppm. ^{1}H and ^{13}C chemical shifts are referenced to tetramethylsilane as internal standard, and ^{9}Be chemical shifts are referenced to $BeCl_2$, 0.1 mol/L in D_2O. The mass spectra (EI, 70 eV) were obtained using a Finnigan SSQ 7000. Only characteristic fragments containing the isotopes of the highest abundance are listed. The elemental analysis was performed on a LECO CHNS932 apparatus. The starting materials beryllium powder, beryllium chloride, and diphenylmercury were purchased from Aldrich Chemical Co. and used as received. Solvent-free Ph_2Be was synthesized according to literature procedures[17] without any activation of the beryllium powder, which was used as received. Beryllium powder and diphenylmercury were mixed in a Schlenk flask in the glovebox, and 200 mL of xylene was added. The reaction mixture was heated at reflux conditions under argon for 3 days under formation of metallic mercury.

Ph_2Be(*i*-Pr-carbene) (1). A 0.5 g (3.1 mmol) amount of Ph_2Be was suspended in 30 mL of toluene, and 0.56 g (3.1 mmol) of 1,3-di-isopropyl-4,5-dimethylimidazol-2-ylidene, dissolved in 20 mL of toluene, was added. The unsolvated Ph_2Be dissolved immediately under formation of a clear solution. After stirring for another 12 h, the solvent was reduced in vacuo to 10 mL. The product crystallized at −20 °C as colorless crystal blocks (0.91 g, 85%). Mp: 172 °C (dec). Anal. Calcd for [$C_{23}H_{30}N_2Be$]: C 80.42, H 8.80, N 8.16. Found: C 80.61, H 8.91, N 8.02. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 8.21 (dd, $^3J(^1H,^1H) = 6.8$ Hz, $^5J(^1H,^1H) = 1.4$ Hz, 4H, o-Ph*H*), 7.53 (m, 4H, m-Ph*H*), 7.41 (m, 2H, p-Ph*H*), 3.89 (sept, $^3J(^1H,^1H) = 6.4$ Hz, 2H, CH_3CH), 1.49 (s, 6H, NC(CH_3)), 1.06 (d, $^3J(^1H,^1H) = 6.4$ Hz, 12H NCH(CH_3)). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 173.6 (N*C*N), 160.2 (Be*C*(Ar)), 140.3 (2-*C*(Ar)), 126.8 (3-*C*(Ar)), 126.1 (4-*C*(Ar)), 123.8 (N*C*CH_3), 50.9 (N*C*HCH_3), 22.5 (NCH*C*H_3), 8.7 (NC*C*H_3). ^{9}Be NMR (56.2 MHz, C_6D_6, 25 °C): δ 21.05 ($\omega_{1/2} = 464$ Hz). MS (EI, ^{9}Be): *m*/*z* (%) 344 (38) $[M]^{+\bullet}$, 329 (12) $[M - CH_3]^+$, 267 (100) $[M - Ph]^+$.

Ph_2Be(*n*-Bu_2O) (2). A 0.5 g (6.3 mmol) portion of $BeCl_2$ was dissolved in 50 mL of diethyl ether, and 12.6 mmol of PhLi, dissolved in di-*n*-butyl ether (5 mL, $c = 2.5$ mol/L), was added dropwise via a syringe at room temperature. After stirring the solution for 12 h, the solvents were removed in vacuo and the resulting white solid was dissolved in 10 mL of pentane. The product crystallized at −20 °C as colorless crystals (1.4 g, 76%). Mp: 45 °C. Anal. Calcd for [$C_{20}H_{28}OBe$]: C 81.86, H 9.62. Found: C 81.34, H 9.33. ^{1}H NMR (400 MHz, C_6D_6, 25 °C): δ 7.98 (m, 4H, o-Ph*H*), 7.47 (m, 4H, m-Ph*H*), 7.38 (m, 2H, p-Ph*H*), 3.65 (t, $^3J(^1H,^1H) = 7.3$ Hz, 4H, OCH_2), 1.24 (pent, $^3J(^1H,^1H) = 7.3$ Hz, 4H, OCH_2CH_2), 0.94 (d, $^3J(^1H,^1H) = 7.3$ Hz, 4H, CH_2-CH_3), 0.59 (d, $^3J(^1H,^1H) = 7.3$ Hz, 6H CH_2CH_3). ^{13}C NMR (100.6 MHz, C_6D_6, 25 °C): δ 154.8 (Be*C*(Ar)), 138.9 (2-*C*(Ar)), 127.4 (3-*C*(Ar)), 127.2 (4-*C*(Ar)), 73.4 (O*C*H_2CH_2), 30.2 (OCH_2*C*H_2), 18.6 (*C*H_2CH_3), 13.6 (CH_2*C*H_3). ^{9}Be NMR (56.2 MHz, C_6D_6, 25 °C): δ 17.4 ($\omega_{1/2} = 239$ Hz). MS (EI, ^{9}Be): *m*/*z* (%) 155 (100) $[C_{12}H_{11}]^{+\bullet}$.

X-ray Crystal Structure Determination. X-ray crystal data for **1**: $C_{23}H_{30}BeN_2$, $M = 343.50$, T (K), 200(2), $\lambda = 0.71073$ Å, monoclinic, $P2_1$, $a = 9.3630(3)$ Å, $b = 25.2755(8)$ Å, $c = 9.6082(3)$ Å, $\alpha = 90°$, $\beta = 112.7240(10)°$, $\gamma = 90°$, $V = 2097.32(11)$ Å^3, $Z = 4$, density 1.088 mg/m^3, abs coeff = 0.062 mm^{-1}, $F(000) = 744$, θ range = 2.30° to 28.67°, 16 367 reflections, 9130 unique, [R(int) = 0.0301], completeness to $\theta = 27.96° = 92.1\%$, absorption correction: SADABS, max./min. transmission = 0.9755 and 0.9636, refinement method: full-matrix least-squares on F^2, 679 parameters, GOF = 1.109, R1 $[I > 2\sigma(I)] = 0.0589$, wR2 = 0.1563, R1 (all data) = 0.0787, wR2 = 0.1686. X-ray crystal data for **2**: $C_{20}H_{28}BeO$, $M = 293.43$, T (K), 200(2), $\lambda = 0.71073$ Å, monoclinic, $P2_1/c$, $a = 9.4993(9)$ Å, $b = 10.5282(10)$ Å, $c = 18.7174(18)$ Å, $\alpha = 90°$, $\beta = 103.118(2)°$, $\gamma = 90°$, $V = 1823.1(3)$ Å^3, $Z = 4$, density 1.069 mg/m^3, abs coeff = 0.062 mm^{-1}, $F(000) = 640$, θ range = 3.31° to 28.29°, 12 185 reflections, 4258 unique, [R(int) = 0.0409], completeness to $\theta = 27.96° = 94.0\%$, absorption correction: SADABS, max./min. transmission = 0.9877 and 0.9695, refinement method: full-matrix least-squares on F^2, 311 parameters, GOF = 1.000, R1 $[I > 2\sigma(I)] = 0.0515$, wR2 = 0.1284, R1 (all data) = 0.0905, wR2 = 0.1485. CCDC 603138 (**1**) and CCDC 603137 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data_request/cif, by e-mailing data_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U.K.; fax: +49 1223 336033.

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Supporting Information Available: Crystallographic information files (CIFs). This material is available free of charge via the Internet at http://pups.acs.org.

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