Preliminary communication

Synthesis and structure of an ionic beryllium–"carbene" complex ☆

Wolfgang A. Herrmann *, Oliver Runte, Georg Artus

Anorganisch-chemisches Institut der Technischen Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

Abstract

The Lewis-acidic metal ion Be^{2+} forms stable adducts with the carbene 1,3-dimethylimidazolin-2-ylidene (L). The pronounced nucleophilicity of the ligand is encountered in the cleavage of the polymeric structure of $BeCl_2$ with consecutive heterolysis to yield the ionic coordination compound $[L_3BeCl]^+Cl^-$.

Keywords: Beryllium; Heterocyclic carbene; Crystal structure

1. Introduction

Among the alkaline-earth metals, beryllium exhibits specific features in its chemistry. The large charge-to-radius ratio makes beryllium one of the hardest known Lewis acids and the character of its compounds is mainly influenced by this property [1]. In recent times main-group metal–carbene adducts were prepared by the reaction of nucleophilic carbenes with Lewis acidic compounds [2]. With the exception of magnesium [3], alkaline–earth metal complexes have not yet been reported. We now show that nucleophilic carbenes can split the polymeric structure of beryllium chloride to form a cationic "carbene" complex [4].

2. Results and discussion

The beryllium "carbene" complex **3** was prepared in 73% yield by treatment of beryllium chloride **1** with three equivalents of 1,3-dimethylimidazolin-2-ylidene in toluene solution (Eq. (1)). Attempts to introduce four carbene ligands into beryllium chloride failed. The isolable product is **3**, even in case of a large excess of the free ligand **2**.

Compound **3** is a pale yellow, moisture and temperature sensitive solid. The proposed composition is in accord with the elemental analysis and spectroscopical data. The ^9Be-NMR spectrum exhibits one signal at 0.9 ppm, which value is typical for tetracoordinated beryllium [5]. The electric conductivity of **3** confirms the ionic structure. The ^{13}C resonances show the typical upfield shift of the carbene atom (C-2) from 213 ppm in **2** to 174.8 ppm upon metal coordination in **3**. As compared to the "carbene complexes" of hydrogen (H^+) [6], boron [7], aluminium [8], magnesium [3] and titanium [9], the tendency of the upfield shift follows the order H > Be ≈ Al > Mg ≈ Ti, thus relating to the sequence of Lewis acidity of the central atoms. The upfield shift of the ^{14}N resonances from −199 ppm in **2** to −209 in **3** indicates some withdrawal of π-electron density towards the positively polarized carbene carbon (C-2) [10].

A crystallographic structure determination proved that the nucleophilic carbene not only splits the polymeric structure of $BeCl_2$ but also causes heterolysis to yield an ionic complex of type $[ClBeL_3]^+Cl^-$. Beryllium exhibits a distorted tetrahedral coordination. There are two independent molecules in the asymmetric unit of the cubic unit cell. Both molecules lie on a threefold main axis for which reason the three carbene ligands within one molecule are symmetry-equivalent. The independent molecules differ in the sign of the torsional angle Cl–Be–Cl–(N1,N11) and must therefore be considered as a pair of enantiomers. The compound crystallizes as a racemate in the acentric space group $P2_13$.

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* Corresponding author.
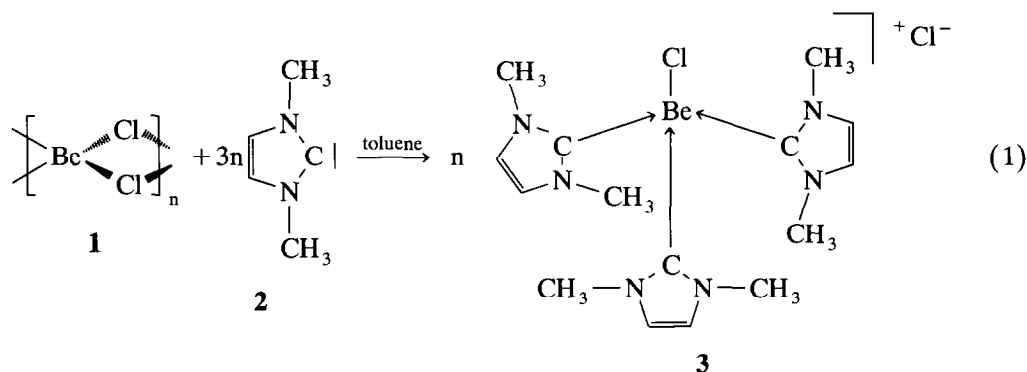
The bond lengths and angles in both molecules are similar (Fig. 1).

The angles at the carbene and all ring distances (Table 1) are very similar to those in the free carbene [2]. Since an interaction of the π-system of the ligand with d-orbitals can clearly be excluded in the case of beryllium, it is interesting to see that all bond lengths and angles are slightly shorter than those in transition metal complexes of this ligand [12,21]. This again shows that possible backbonding in complexes of imidazol-2-ylidene with d-block metals must be small to negligible.

The beryllium–chlorine distances of 2.091(7) Å and 2.076(6) Å are strikingly long. Other tetracoordinated beryllium complexes show distances in the range 1.86–1.99 Å [13]. Even in solid [BeCl₂]∞ the distance from beryllium to the bridging chlorine atom is shorter (2.02 Å) [4]. The bond distances of 1.339(4) Å (C3–C4) and 1.322(5) Å (C13–C14) clearly indicate undistorted dou-

ble bonds. The beryllium–carbon distances (1.807(3) Å and 1.822(3) Å) are at the upper end of the range of single bond lengths [14]. These vary from 1.708(6) Å to 1.85(3) Å (Be–CH₃). With regard to the different radii of carbon, nitrogen and oxygen, the bond distances Be–C are also comparable to those in Be–(N,O) adducts [15]. The beryllium–oxygen distances vary from 1.60 Å to 1.69 Å and the beryllium–nitrogen distances from 1.732 Å (Be–NCCH₃) to 1.92 Å (Be–quinuclidine) [16,17].

It is quite clear from these and other findings that the N-heterocyclic carbenes derived from imidazole do not depend on backbonding upon forming stable complexes. In this respect, they cannot be compared with conventional metal–carbene complexes such as (CO)₅W[C-
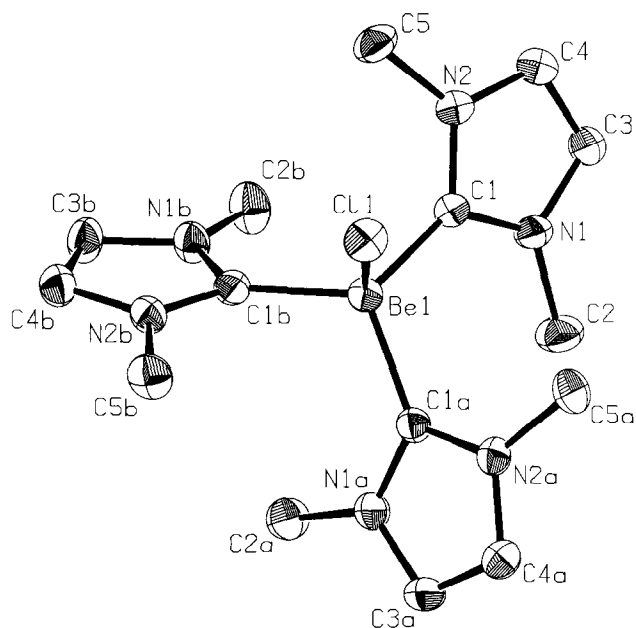

Fig. 1. PLATON [11] drawing of the crystal and molecular structure of 3. The thermal ellipsoids correspond to 50% probability. Hydrogens and the chloride ion are omitted for clarity.

Table 1
Bond distances (Å) and angles (deg) of chlorotris(1,3-dimethylimidazolin-2-ylidene)beryllium chloride 3

Bond distances			
C(5)–N(2)	1.464(4)	Cl(1)–Be(1)	2.091(7)
C(11)–N(11)	1.348(4)	Cl(11)–Be(11)	2.076(6)
C(11)–N(12)	1.367(3)	C(1)–N(1)	1.358(3)
C(12)–N(11)	1.456(4)	C(1)–N(2)	1.345(3)
C(13)–C(14)	1.322(5)	C(2)–N(1)	1.467(4)
C(13)–N(11)	1.376(4)	C(3)–C(4)	1.339(4)
C(14)–N(12)	1.382(4)	C(3)–N(1)	1.381(4)
C(15)–N(12)	1.459(4)	C(4)–N(2)	1.380(4)
Be(11)–C(11)	1.807(3)	Be(1)–C(1)	1.822(3)
Bond angles			
N(1)–C(3)–C(4)	106.6(3)	C(2)–N(1)–C(1)	125.7(3)
N(2)–C(4)–C(3)	106.7(3)	C(3)–(1)–C(1)	111.6(2)
N(11)–C(11)–Be(11)	125.6(2)	C(3)–N(1)–C(2)	122.5(2)
N(11)–C(11)–Be(11)	125.6(2)	C(4)–N(2)–C(1)	111.7(2)
N(11)–C(11)–Be(11)	125.6(2)	C(5)–N(2)–C(1)	125.3(2)
N(12)–C(11)–Be(11)	130.8(2)	C(5)–N(2)–C(4)	122.8(2)
N(12)–C(11)–Be(11)	130.8(2)	C(12)–N(11)–C(11)	124.9(3)
N(12)–C(11)–Be(11)	130.8(2)	C(13)–N(11)–C(11)	111.5(3)
N(12)–C(11)–N(11)	103.5(2)	C(13)–N(11)–C(12)	123.6(3)
N(11)–C(13)–C(14)	107.3(3)	C(14)–N(12)–C(11)	110.8(3)
N(12)–C(14)–C(13)	106.9(3)	C(15)–N(12)–C(11)	125.9(3)
C(1)–Be(1)–CL(1)	105.5(2)	C(15)–N(12)–C(14)	123.2(3)
C(1)–Be(1)–C(1)	113.1(2)	N(1)–C(1)–Be(1)	130.0(2)
C(11)–Be(11)–CL(11)	106.9(2)	N(2)–C(1)–Be(1)	126.0(2)
C(11)–Be(11)–C(11)	111.9(2)	N(2)–C(1)–N(1)	103.5(2)

(OCH$_3$)CH$_3$] and (C$_5$H$_5$)$_2$Ta(CH$_2$)CH$_3$. We rather conclude that carbenes of type **2** are similar, in terms of both their coordination chemistry and metal-bonding, to electron-rich donor ligands such as phophines, ethers and amines. "Carbenes" of this type seem to be universal ligands in coordination chemistry.

3. Experimental section

All reactions were performed in an inert gas atmosphere using standard Schlenk techniques. All solvents were freshly distilled, degassed and dried prior to use. NMR spectra were recorded on a Jeol-GX 400. Chemical shifts are reported in ppm with respect to TMS. All spectra are referenced to the residual protons of deuterated solvents. ^{9}Be-NMR data are reported in ppm with respect to 1 M BeCl$_2$ in D$_2$O. ^{14}N-NMR is reported with respect to CD$_3$NO$_2$. IR spectra were recorded in the range 4000–400 cm^{-1} on a Perkin Elmer 1650 FT-IR spectrometer. Elemental analyses were determined on a Heraeus-CHN-Rapid in the Microanalytical Laboratory of the authors' institute. 1,3-Dimethylimidazolin-2-ylidene was prepared according to the literature [18], while beryllium chloride was used as received form Fluka Chemicals.

3.1. Chlorotris(1,3-dimethylimidazolin-2-ylidene)beryllium chloride 3

A suspension of 190 mg (2 mmol) BeCl$_2$ **1** in 50 ml of toluene was treated with 3 equivalents of 1,3-dimethyl-imidazolin-2-ylidene **2** in 80 ml of toluene. A pale yellow precipitate forms instantaneously. The solvent was removed under vacuum and the product was extracted with CH$_2$Cl$_2$. The yellow solution was covered with a layer of *n*-hexane. Crystals formed overnight at room temperature, yielding 535 mg (73%) of the title compound **3**. IR (film, cm^{-1}): 3140 m, 3052 vs, 1572 s, 1173 vs, 623 s. ^{1}H-NMR (400 MHz, CDCl$_3$): $\delta = 3.62$ (s, 18 H), 7.14 (s, 6 H). ^{13}C-NMR (100.61 MHz, CDCl$_3$): $\delta = 174.9$ (N–C–N), 124.3 (N–N–C), 36.5 (CH$_3$). ^{14}N-NMR (28.56 MHz, CDCl$_3$): $\delta = -209$ ppm. ^{9}Be-NMR (56.05 MHz, CDCl$_3$): $\delta = 0.9$ ppm. Anal. calcd. for C$_{15}$H$_{24}$BeCl$_2$: C 48.92; H 6.57; N 22.82; found: C 48.35; H 6.54; N 22.49.

3.2. Single-crystal X-ray diffraction study

The title compound **3** of formula C$_{15}$H$_{24}$BeCl$_2$N$_6$ ($F_w = 368.31$ g mol^{-1}, $F_{000} = 1552$, $\mu = 3.4$ cm^{-1}) crystallizes at room temperature from CH$_2$Cl$_2$/hexane solution in colourless to light yellow single crystals in the space group $P2_13$ (Int. Tab. No. 198). Lattice constants were obtained by least-squares refinement of 25 well-centered reflections in the range $30.1° < 2\theta <$

$40.7°$ ($\lambda = 0.70930$ Å, Mo Kα_1)): $a = 15.707(1)$ Å, $V = 3874.8(2)$ Å^3, $Z = 8$, $\rho_{calc} = 1.26$ g cm^{-3}. A single crystal was prepared in an argon gas atmosphere in a glove box and was mounted in a glass capillary on a CAD4 diffractometer (Enraf Nonius) with graphite monochromator ($\lambda = 0.71073$ Å, Mo Kα_1). Temperature, -110 ± 5 °C; range $1.0° < \theta < 25.0°$; scan mode, ω; scan time, max. 120 s; scan width $(1.2 + 0.2 \tan\theta)°$; 3271 data measured, 18 systematic absent, 238 with negative intensity, 1467 reflections merged, out of 2141 independent reflections 2054 reflections with ($I > 1.0\sigma(I)$) used for refinement. All data were corrected for Lorentz and polarization terms. Structure solution with direct methods [18], refinement with standard difference Fourier techniques [11,20]. All hydrogen atoms were calculated and freely refined: 210 parameters refined, $w = 1$, 9.8 data per parameter, shift/error: < 0.0001, residual electron density: max. $+0.68$ e Å^{-3} 0.96 Å near Cl2; min. -0.29 e Å^{-3}, $R = \Sigma(\| F_o \| - \| F_c \|)/\Sigma \| F_o \| = 0.032$, $Rw = [\Sigma w(\| F_o \| - \| F_c \|)^2/\Sigma wF_o^2]^{1/2} = 0.034$. Further details are given in the Supplementary Material deposited at the Fachinformationszentrum Karlsruhe.

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Note added in proof

Rh–C distances of the same type of "carbene" complexes are at ca. 2.03 Å. The covalent radii of Be and Rh are 1.12 and 1.34 Å, respectively. This difference is also seen in the bond lengths of **3** (Be) and a series of Rh complexes [12d].