

## Author Manuscript

**Title:** New Avenues in s-Block Chemistry - Zero Oxidation State Beryllium Complexes

**Authors:** Jason Laurence Dutton; Gernot Frenking

This is the author manuscript accepted for publication and has undergone full peer review but has not been through the copyediting, typesetting, pagination and proofreading process, which may lead to differences between this version and the Version of Record.

**To be cited as:** 10.1002/anie.201606244

**Link to VoR:** <http://dx.doi.org/10.1002/anie.201606244>

# New Avenues in s-Block Chemistry – Zero Oxidation State Beryllium Complexes

Jason L. Dutton<sup>\*,[a]</sup> and Gernot Frenking<sup>\*,[b]</sup>

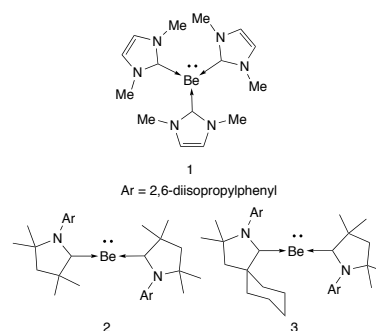
**Keywords:** Beryllium • s-block • low valent • carbenes

Beryllium is surely the least investigated chemical element of the first octal row of the periodic table excepting inert neon. Part of the reason is that Be containing molecules are highly toxic which makes experimental studies potentially dangerous in unskilled hands. Beryllium compounds and salts are carcinogenic and they exhibit extreme long-term and potentially acute toxicity when they are inhaled. However, the element Be also plays a unique role among the s-block atoms. The combination of a closed-shell electronic ground state  $^1S(1s^22s^2)$  and the relatively high excitation energy  $^1S \rightarrow ^3P(1s^22s^12p^1)$  of 62.8 kcal/mol<sup>[1]</sup> makes it relatively difficult to form compounds with covalent electron-sharing bonds. This can be achieved with electronegative atoms such as halogen or oxygen, but the molecules in the condensed phase are either polymeric solids or they form complexes with a Lewis base. However, given the relatively high electronegativity of beryllium (1.57, *c.f.* Mg 1.31, Li 0.98) it likely has the richest potential for covalent organometallic chemistry of the s-block elements. Due to issues surrounding toxicity this chemistry is not well developed. Comparing elements with the greatest similarities to Be in terms of valence and electronegativity, in the Cambridge Structural Database (2014) there are 3504 entries for compounds containing Al-C bonds, 1386 for Zn-C, 647 for Mg-C and only 59 for compounds containing Be-C bonds.<sup>[2]</sup>

A very fruitful area of beryllium chemistry takes advantage of the high Lewis acidity of beryllium compounds, which exceeds that of most other main group atom centered compounds. Beryllium oxide BeO is the strongest neutral main group Lewis acid that is known.<sup>[3]</sup> Beryllium dihalides BeX<sub>2</sub> with X = F, Cl form very stable complexes with Lewis bases<sup>[4]</sup> that were systematically studied by Dehnicke and coworkers.<sup>[5]</sup> The naked beryllium atom also exhibits strong Lewis acid character. Two theoretical studies predicted in 2013 that tricoordinated beryllium complexes [Be(L<sub>3</sub>)] with ligands L = CO, PR<sub>3</sub>, NHC (N-heterocyclic carbene), yielding an electron octet at beryllium, could be potentially synthesized and isolated, either as free molecules (L = NHC, **1**)<sup>[6]</sup> or as ligands in transition metal complexes [TM←Be(L<sub>3</sub>)] (see Scheme 1).<sup>[7]</sup> The theoretical work pointed in a direction where ingenious experiments, which were recently carried out by Braunschweig and coworkers have succeeded in a yet unexpected way.<sup>[8]</sup>

The authors synthesized the complexes [Be(cAAC<sup>Me</sup>)<sub>2</sub>] (**2**) and

[Be(cAAC<sup>Me</sup>)(cAAC<sup>Cy</sup>)] (**3**) where two cyclic alkyl amino carbene (cAAC) ligands stabilize a beryllium atom in the formal zero oxidation state with the Be dicoordinated rather than tricoordinated as had been predicted for the NHC complexes (Figure 1). The cAAC ligand that was introduced by Bertrand<sup>[9]</sup> into synthetic chemistry has proved very successful for isolating mono-,<sup>[10]</sup> di-<sup>[11]</sup> and triatomic<sup>[12]</sup> adducts [E<sub>n</sub>(cAAC)<sub>m</sub>] (n = 1 - 3) for zero-valent atoms of groups 13 and 14.<sup>[13]</sup> cAACs are better  $\sigma$  donors and  $\pi$  acceptors than NHCs<sup>[9]</sup>, which leads to distinguishably different properties in their complexes.<sup>[14]</sup> The usage of cAAC complements the field of ligand stabilized adducts [E<sub>n</sub>(NHC)<sub>2</sub>] of group 13 - 15 atoms that have been of ongoing interest for the past decade.<sup>[13b, 15]</sup> Braunschweig has now extended the range of such carbene stabilized zero oxidation state species to the s-block with these new complexes of beryllium. The synthesis consists of only 2 steps – first coordination of one cAAC<sup>Me</sup> ligand with commercially available BeCl<sub>2</sub>. The second step is elegant, involving a reduction using KC<sub>8</sub> in the presence of an added 2<sup>nd</sup> equivalent of cAAC<sup>Me</sup> to give the complex **2**. Attempts at reduction without the added ligand resulted in complicated mixtures. This method also allowed for the synthesis of heteroleptic complexes [Be(cAAC<sup>R1</sup>)(cAAC<sup>R2</sup>)], as the 2<sup>nd</sup> equivalent of cAAC could be varied, using the cyclohexyl substituted version in this case to give **3**. Compound **3** is not however the first heteroleptic bis main-group carbene complex as claimed; these have recently been reported for carbodicarbenes C(NHC)(NHC).<sup>[16]</sup> Importantly, this short synthesis minimizes the need for handling as well as the generation of Be containing waste.

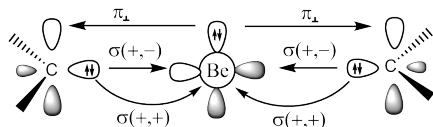


The authors made great efforts to elucidate the nature of the metal-ligand bonding in the beryllium complexes **2** and **3**. Figure 1 shows the essential features of the bonding situation which can be explained with the Dewar-Chatt-Duncanson (DCD) model<sup>[17]</sup> that is well known from transition metal chemistry.<sup>[18]</sup> Inspection of the occupied molecular orbitals and calculations with different electronic states and charges suggest that the interacting fragments are a beryllium atom in the excited  $^1D(1s^22s^02p^2)$  state and two cAAC ligands in the ground state. The latter electronic states are perfectly suited for  $\sigma$ -donation and  $\pi$ -backdonation following the DCD model. The  $\sigma$  lone-pair orbitals of the cAAC ligands donate into the vacant 2s AO (in-

[a] Dr. Jason L. Dutton  
Department of Chemistry and Physics  
La Trobe Institute for Molecular Sciences, La Trobe University  
Melbourne, Victoria, Australia  
E-mail: j.dutton@latrobe.edu.au

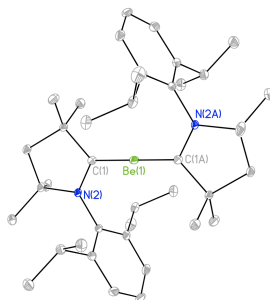
[b] Prof. Dr. Gernot Frenking  
Fachbereich Chemie, Philipps-Universität Marburg, Hans-Meerwein-  
Strasse 1, D-35032 Marburg, Germany  
Email: frenking@chemie.uni-marburg.de

phase combination +,+) and the 2p( $\sigma$ ) AO (out-of-phase +,- donation) of beryllium. The doubly occupied out-of-plane p( $\pi_{\perp}$ ) AO of Be provides  $\pi$ -backdonation into the vacant p( $\pi_{\perp}$ ) AOs of the carbene carbon atoms. The plane is defined by the rings of the cAAC ligands which are nearly coplanar. The calculations indicate that the (cAAC) $\leftarrow$ Be $\rightarrow$ (cAAC)  $\pi$ -backdonation is stronger than the total of (cAAC) $\rightarrow$ Be $\rightarrow$ (cAAC)  $\sigma$ -donation. This is in agreement with the calculated partial charges, which gave a positive charge of +0.87 e at beryllium.



**Figure 1.** Bonding situation in  $[\text{Be}(\text{cAAC})_2]$

The strong  $\pi$  component of the Be-C bonds indicates significant multiple bonding character which agrees with the rather short bond lengths of approximately 1.65 Å and the perfectly linear arrangement about the Be atom (Figure 2). The measured values for the two compounds are between the standard Be-C single bond (1.77 Å) and Be=C double bond (1.57 Å).<sup>[19]</sup> The authors ascribe the stability of the molecules to the strong 3-center-2-electron  $\pi$  bond across the C-Be-C moiety.



**Figure 2.** Solid-state X-ray structure of **2**. Selected bond distances [Å] and angles [°]: Be(1)-C(1) 1.664(1), C(1)-Be(1)-C(1A) 180.0.

The beryllium atom of the cAAC complexes still has a vacant p( $\pi_{\parallel}$ ) AO which is not shown in Figure 1. The bonding analysis of Braunschweig et al. suggests that the hyperconjugative donation of the cyclic cAAC ligands to the p( $\pi_{\parallel}$ ) AO is very weak, which should leave the Be atom open to further coordination. However, it appears that nucleophilic attack to the beryllium centre is sterically hindered by the bulky substituents which are in the plane of the five-membered rings (Figure 1). The complexes decompose with strong Brønsted acids but react cleanly with selenium and CO<sub>2</sub> giving elemental beryllium and known adducts of the cAAC ligand with Se and CO<sub>2</sub>, respectively. These facile ligand exchange reactions also point to the validity of considering these compounds as carbene adducts of Be<sup>0</sup>.

The last paradigm shifting advance in s-block chemistry was the 2007 report from Jones of Mg(I) dimers stabilized by anionic  $\beta$ -diketiminato or guanidinate ligands.<sup>[20]</sup> The Jones reagent is now used by many chemists worldwide as a soluble, powerful, yet highly controllable reducing agent. It will be interesting to see in the coming years if this new class of beryllium compound will

unlock extensive new reactivity for the s-block or if the challenges associated with working on Be will see its potential perhaps go unfulfilled.

- [1] C. E. Moore, Natl. Bur. Stand. Circ. 467, U. S. GPO, Washington, D.C. 1952.
- [2] Via searching for any structure containing any E-C bond (E = Be, Mg, Al, Zn) in the Cambridge Structural Data Bank, 2014 version.
- [3] (a) G. Frenking, W. Koch, J.R. Collins, *J. Chem. Soc. Chem. Commun.* **1988**, 1147. (b) G. Frenking, J. Gauss, D. Cremer, *J. Am. Chem. Soc.* **1988**, *110*, 8007. (c) C. A. Thompson, L. Andrews, *J. Am. Chem. Soc.* **1994**, *116*, 423. (d) L. Andrews, T. J. Tague, *J. Am. Chem. Soc.* **1994**, *116*, 6856. (e) A. Veldkamp, G. Frenking, *Chem. Phys. Lett.* **1994**, *226*, 11.
- [4] (a) S. Metz, M.C. Holthausen, G. Frenking, *Z. Anorg. Allg. Chem.* **2006** *632*, 814. (b) N. Fröhlich, U. Pidun, M. Stahl, G. Frenking, *Organometallics* **1997**, *16*, 442.
- [5] Systematic experimental studies about structure and reactivity of beryllium compounds have been reported by Dehnicke and coworkers in more than 40 publications (mostly written in German) between 2003 - 2011. Representative examples are: a) W. Petz, K. Dehnicke, N. Holzmann, G. Frenking, B. Neumüller, *Z. Anorg. Allg. Chem.* **2011**, *637*, 1702. b) Review: K. Dehnicke, B. Neumüller, *Z. Anorg. Allg. Chem.* **2008**, *634*, 2703. c) For a review on recent advances in organometallic Be chemistry see: K. J. Iversen, S. A. Couchman, D. J. D. Wilson, J. L. Dutton *Coord. Chem. Rev.* **2015**, *297-298*, 40.
- [6] S. A. Couchman, N. Holzmann, G. Frenking, D. J. D. Wilson, J. L. Dutton *Dalton Trans.* **2013**, *42*, 11375.
- [7] S. De, P. Parameswaran, *Dalton Trans.* **2013**, *42*, 4650.
- [8] M. Arrowsmith, H. Braunschweig, M. A. Celik, T. Dellermann, R. D. Dewhurst, W. C. Ewing, K. Hammond, T. Kramer, I. Krummenacher, J. Mies, K. Radacki, J. K. Schuster, *Nature Chem.* **2016**, doi:10.1038/nchem.2542.
- [9] M. Melaimi, M. Soleilhavoup, G. Bertrand, *Angew. Chem. Int. Ed.* **2010**, *49*, 8810.
- [10] (a) K.C. Mondal, H. W. Roesky, F. Klinke, M. C. Schwarzer, G. Frenking, B. Niepötter, H. Wolf, R. Herbst-Irmer, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, *52*, 2963. (b) Y. Li, K. C. Mondal, H. W. Roesky, H. Zhu, P. Stollberg, R. Herbst-Irmer, D. Stalke, D. M. Andrade, *J. Am. Chem. Soc.* **2013**, *135*, 12422
- [11] J. Böhne, H. Braunschweig, W. C. Ewing, C. Hörl, T. Kramer, I. Krummenacher, J. Mies, A. Vargas, *Angew. Chem. Int. Ed.* **2014**, *53*, 9082.
- [12] K. C. Mondal, S. Roy, B. Dittrich, D. M. Andrade, G. Frenking, H. W. Roesky, *Angew. Chem. Int. Ed.* **2016**, *55*, 3158.
- [13] (a) M. Soleilhavoup, G. Bertrand, *Acc. Chem. Res.* **2015**, *48*, 256. (b) G. Frenking, M. Hermann, D.M. Andrade, N. Holzmann, *Chem. Soc. Rev.* **2016**, *45*, 1129.
- [14] K. C. Mondal, H. W. Roesky, M. C. Schwarzer, G. Frenking, S. Neudeck, I. Tkach, H. Wolf, D. Kratzert, R. Herbst-Irmer, B. Niepötter, D. Stalke, *Angew. Chem. Int. Ed.* **2013**, *52*, 1801
- [15] Y. Wang, G. H. Robinson, *Inorg. Chem.* **2014**, *53*, 11815.
- [16] W.-C. Chen, J.-S. Shen, T. Jurca, C.-J. Peng, y.-H. Lin, Y.-P. Wang, W.-C. Shih, G.P.A. Yap, T.-G. Ong, *Angew. Chem. Int. Ed.* **2015**, *54*, 15207
- [17] a) M.J.S. Dewar, *Bull. Soc. Chim. Fr.* **1951**, *18*, C79; b) J. Chatt, L.A. Duncanson, *J. Chem. Soc.* **1953**, 2929. c) G. Frenking, *J. Organomet. Chem.* **2001**, *635*, 9; d) *Modern Coordination Chemistry: The Legacy of Joseph Chatt*; G. J. Leigh, N. Winterton, Eds.; The Royal Society: London, **2002**.
- [18] G. Frenking, N. Fröhlich, *Chem. Rev.* **2000**, *100*, 717.
- [19] P. Pyykkö, M. Atsumi, *Chem. Eur. J.* **2009**, *15*, 12770.
- [20] a) S. P. Green, C. Jones, A. Stasch, *Science* **2007**, *318*, 1754 b) C. Jones and A. Stasch in *Alkaline Earth Metals in Synthesis, Topics in Organometallic Chemistry*, S. Harder (ed.), Springer, Heidelberg, 2013, **45**,

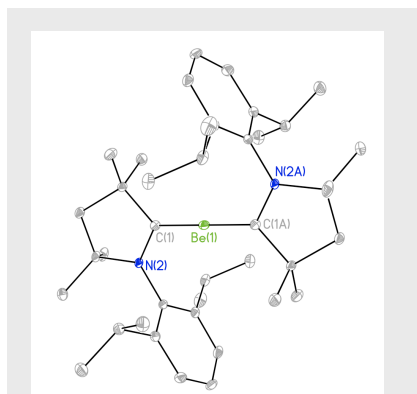
WILEY-VCH

**Entry for the Table of Contents (Please choose one layout)**

Layout 1:

**HIGHLIGHT**

Braunschweig and co-workers have recently extended the chemistry of ligand stabilized zero oxidation state complexes to the s-block with the discovery of bis- cyclic alkyl amino carbene stabilized Be<sub>0</sub>. Through combined experimental and theoretical studies they have conclusively demonstrated that the complex is low-valent at beryllium.

*Gernot Frenking\*, Jason L. Dutton\****Page No. – Page No.****Title**

Layout 2:

**HIGHLIGHT**

((Insert TOC Graphic here))

*Author(s), Corresponding Author(s)\****Page No. – Page No.****Title**

Text for Table of Contents