Journal Name

COMMUNICATION

Solvent-induced ion separation of a beryllium scorpionate complex

Received 00th January 20xx,
Accepted 00th January 20xx

Dominik Naglav,^a Briac Tobey,^a Kevin Dzialkowski,^a Dieter Bläser,^a Christoph Wölper,^a Georg Jansen^a and Stephan Schulz^{*a}

DOI: 10.1039/x0xx00000x

www.rsc.org/

Spontaneous ion separation of the scorpionate beryllium complex TpBeI 1 (Tp = 1-trispyrazolylborate) occurs upon treatment with THF, yielding [TpBe(thf)]I 2, which was characterized by heteronuclear NMR spectroscopy (¹H, ⁹Be, ¹³C) and structurally characterized by single crystal X-ray diffraction. 2 represents a rare example of a structurally characterized monocationic beryllium complex and to the best of our knowledge, the synthesis of 2 by a solvent-induced ion separation has previously only been observed in reactions of beryllium dihalides with strong Lewis bases.

Several cationic alkaline earth metal complexes have been prepared, to date.^{1–3} They are often highly reactive species due to their high Lewis acidity caused by the positive charge of the cationic metal atoms. Sterically demanding, chelating substituents with strong N-donor centres, i.e. diimines, β -diketimines, amidines, and guanidines, are known to effectively stabilize reactive metal complexes containing low-valent and/or cationic metal centres. The same is true for trispyrazolylborate (Tp) ligands, which can serve as tridentate N,N',N''-chelating ligand in coordination chemistry.

We are interested in beryllium complexes containing N-donor ligands and reported on the synthesis, structure and reactivity of several homoleptic and heteroleptic complexes,⁴ including beryllium scorpionate complexes with trispyrazolylborate (Tp) ligands.^{5,6} The chemical reactivity of TpBe halide complexes was intensely studied in our group and we now observed the spontaneous solvent-induced formation of the monocationic complex [TpBe(thf)]I 2, which is formed upon gently heating of a solution of TpBeI in THF for an abbreviated period of time (scheme 1). Comparable findings have been reported for

several solvent stabilized calcium cations such as [Cp*(PhPO)₃Ca]⁺, [Ph(dme)₃Ca]⁺, and [(Car^{Mes}PyCar^{Mes})₂(thf)Ca]²⁺ (Car^{Mes}PyCar^{Me} = 2,6-bis(3-mesitylimidazol-2-ylidene)-pyridine),² respectively, which were formed as solvent separated cations in reactions of the respective calcium iodide compounds with the specific Lewis base. In addition, monocationic beryllium complexes [(pyrr)₃BeCl]Cl and [py(HNPPH₃)₂BeCl]Cl were obtained from reactions of (L)₂BeCl₂ (L = thf, HNPPH₃) with pyrrolidine (pyrr) and pyridine (py),⁷ respectively, as well as in reactions of polymeric [BeCl₂]_x with strong Lewis bases such as the carbene 1,3-dimethylimidazolin-2-ylidene (L')⁸ and N,N,N',N'',N''-pentamethyldiethylentriamine (PMDETA),⁹ which were found to split the coordination polymer into monomeric units containing the beryllium monocations [L'₃BeCl]Cl and [PMDETABeCl]Cl, respectively. An analogous finding was reported for the reaction of BeCl₂ with an equimolar amount of 12-crown-4 and SbCl₅, yielding the cationic complex [BeCl(12-crown-4)][SbCl₄].¹⁰

Scheme 1: Reaction scheme for the synthesis of 2 – 5.

^a University of Duisburg-Essen and Center for Nanointegration Duisburg-Essen (Cenide), Universitätsstr. 5-7, S07 S03 C30, 45117 Essen, Germany. Fax: Int (+)201 1833830; Tel: Int (+)201 1834635; E-mail: stephan.schulz@uni-due.de.

Electronic Supplementary Information (ESI) available: Crystallographic data of 2; ¹H, ⁹Be and ¹³C NMR data of 2 and ⁹Be NMR data of 3–5; quantum chemical calculations of TpBeF, TpBeCl, TpBeBr, 1 and 2'. See DOI: 10.1039/x0xx00000x
CCDC 1836979 (2) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

The ^1H and ^{13}C NMR spectra of **2** in $\text{thf-}d_8$ show the expected resonances of the Tp ligand as well as resonances due to the presence of a coordinated thf molecule. The ^9Be NMR spectrum of **2** clearly reveals the ion separation of **2** in thf solution, since the ^9Be signal of **2** (3.14 ppm) is shifted to higher field compared to TpBeI **1** (4.66 ppm). $[(\text{pyrr})_3\text{BeCl}]\text{Cl}$ and $[\text{L}'_3\text{BeCl}]\text{Cl}$ show ^9Be NMR shifts of 1.64 and 0.9 ppm, which are both significantly highfield shifted compared to **2**.^{7a,8} Dicationic complexes with tetrahedrally-coordinated beryllium atoms such as $[\text{Be}(\text{NH}_3)_4]^{2+}$ (3.3 ppm)¹¹ and $[\text{Be}(\text{OH}_2)_4]^{2+}$ (0.0 ppm) show comparable ^9Be NMR chemical shifts.¹²

The reason for the solvent-induced ion separation might be that the bonding interaction between beryllium and iodine is rather covalent and highly polarized toward the metal center as is typical for small metal cations ("hard" Lewis acids) such as Li^+ and Be^{2+} .^{13,14} In addition, the bond dissociation energy (BDE) in TpBeI is expected to be lower compared to the lighter homologues TpBeX (X = F, Cl, Br), which is also expected due to the classical HSAB (Hard and Soft Acids and Bases) concept, since iodine is softer than the lighter halides.

Crystals of **2** suitable for a single crystal X-ray analysis were formed upon storage of a solution of TpBeI in THF at 40 °C for 6h. **2** crystallizes in the orthorhombic space group $Pnma$ with one ion pair placed on a mirror plane (Wyckoff 4c) and one THF molecule disordered via mirror plane in the asymmetric unit (Table S1). Bond lengths and angles are given in Table S2.

Figure 1: Molecular structure of **2**, H-atoms are omitted for clarity. Displacement ellipsoids at 50% levels.

The THF ligand in **2** is also disordered by mirror symmetry. The shortest Be...I distance of ~ 5.5 Å clearly proves the full ion separation of the TpBe⁺ fragment from the iodide (I⁻) counterion (Fig. 1), which shows non-classical hydrogen bonds with donor CH groups of the residual groups of the ligand and THF molecules (Table S3). The Be atom is tetrahedrally coordinated by the Tp ligand via the nitrogen atoms and an additional THF molecule via the oxygen atom. The average Be-N bond lengths of **1** (1.718(3) Å) and **2** (1.717(6) Å) as well as TpBeCl (1.731(4) Å), TpBeBr (1.723(5) Å) and TpBeF (1.755(5) Å) are almost identical within the standard deviation.^[4] The Be-O bond length of **2** (1.595(6) Å) is comparable to values previously reported for thf-coordinated complexes with fourfold-coordinated Be atoms.¹⁵ The Lewis basicity of THF obviously is too low to induce the bond dissociation between beryllium and these lighter halide atoms, while the weaker bonded iodide substituent can be replaced more easily. This explains why we never observed any ion separation in TpBeCl and TpBeBr, because these complexes exhibit a higher ionic Be-X bonding interaction.

Encouraged by this observation we tried to synthesize other cationic $[\text{TpBe}^+][\text{A}^-]$ complexes with various counter anions ($[\text{A}^-] = [\text{PF}_6]^-$ **3**, $[\text{B}(\text{C}_6\text{F}_5)_4]^-$ **4**, $[\text{Al}(\text{O}(\text{C}(\text{CF}_3)_3)_4]^-$ **5**, scheme 1). The reaction products isolated from the reactions of **2** with different reagents MA (M = Li, Ag, Tl) showed slightly different ^9Be NMR shifts (2.91 ppm **3**, **4**; 2.98 ppm **5**) compared to **2** (3.14 ppm). These findings also indicate the formation of ion pairs, even though we expected the NMR chemical shifts of **2** to **5** to be identical since the cation ($[\text{TpBe}(\text{thf})]^+$) should be identical in all cases. We therefore can't exclude cation-anion interactions, in particular with the small iodine anion in **2**, which might influence the ^9Be NMR shift of **2** - **5**. In addition, we frequently observed concentration dependency of the ^9Be NMR shifts of beryllium complexes, which might also explain the small differences observed for **2** - **5**.

Unfortunately, we did not obtain single crystals of **3** - **5** upon recrystallization in different solvents (thf, toluene). In all cases, we only observed a phase separation upon concentration of the solutions of **3** - **5**. The upper phase contained the pure solvent, while the bottom phase contained the respective $[\text{TpBe}]\text{A}$ complex with a minimum amount of solvent. We never obtained the product as solids even upon evacuating the residue with an oil diffusion pump at 10^{-6} mbar for 24h. Complexes **3** - **5** are stable in solution and as isolated liquid residue for several days under inert gas atmosphere at ambient temperature. They were found to react rapidly with strong Lewis bases such as 4-dimethylaminopyridine (DMAP) as well as pyridine with formation of white insoluble powders. To the best of our knowledge, an analogous behaviour has not been observed for alkaline earth metal complexes, to date.

Quantum chemical calculations

The bonding nature of $\text{TpBe}(\text{THF})^+$ **2'** was investigated by quantum chemical calculations and compared to that of TpBeX (X = F, Cl, Br, I **1'**). The structures of the molecules were optimized using density functional theory (DFT) with the def2-TZVPP basis set^{16a} and the B3LYP-functional^{16b-d}, using

relativistic effective core potentials (def2-ecp)^{16e-i} for iodine and the resolution of the identity (RI) approximation in addition to the third generation Becke-Johnson dispersion correction^{16j} as implemented in the Turbomole program package.^{16k} Selected bond lengths are given in table 1.

Table 1: Computed and experimental (XRD) bonding distances (Be-N average values).

	TpBeF	TpBeCl	TpBeBr	TpBeI 1	2
Be-N _{calc.}	1.770	1.747	1.740	1.734	1.719
Be-N _{exp.} ^[a]	1.755(3)	1.731(2)	1.723(2)	1.718(3)	1.717(6)
Be-X _{calc.}	1.444	1.927	2.098	2.329	1.618
Be-X _{exp.}	1.453(2)	1.931(2)	2.092(2)	2.330(2)	~ 5.5

[a] average values

Bond dissociation energies (BDE) of the compounds were calculated using counterpoise correction to estimate the basis set superposition error, while accounting for the relaxation of the fragments (TpBe⁺, THF). Table 2 summarizes the BDEs and compares the values to literature data.¹⁷

Table 2: Bond dissociation energies (BDE).

Compound	BDE in kJ·mol ⁻¹	Literature data BDE ⁸
TpBe...F	806	Be...F 573
TpBe...Cl	973	Be...Cl 384
TpBe...Br	922	Be...Br 316
TpBe...I 1	857	Be...I 261
TpBe...(THF) 2'	229	

The calculated BDEs of the heteroleptic beryllium halide complexes TpBeX (X = Cl, Br, I 1') steadily decrease with increasing atomic number of the halide substituent as was expected. However, in remarkable contrast, the BDE of TpBeF does not fit into this trend since it is even lower than that of TpBeI. Be²⁺ is typically described in the HSAB concept as hard Lewis acid and was therefore expected to form a rather strong bond (stabilized by significant ionic contribution) with the hard fluoride anion, whereas the heavier halides are typically regarded as weaker Lewis bases, which can be also more easily polarized and tend to form bonds with higher covalent bonding character. The low BDE of TpBeF is therefore contraindicative. A suitable explanation for this unexpected finding considers, that the chelating Tp ligand provides enough electron density for the Lewis acidic Be atom, resulting in a somewhat softer metal center, that prefers to interact with weaker halide anions. This is corroborated by the BDE for TpBe...THF containing the weak Lewis base thf (compared to the strong fluoride base), which is rather high for a metal THF adduct.

In addition, the partial charges of all atoms in TpBe(THF)⁺ 2' and TpBeX (X = F, Cl, Br, I 1') were calculated by natural population analysis (NPA) and the results are summarized in table 3.

Table 3: Computed NPA charges of Be, X and THF.

	TpBeF	TpBeCl	TpBeBr	TpBeI 1'	TpBe(THF) ⁺ 2'
Be	1.69	1.58	1.55	1.51	1.68
X	-0.87	-0.77	-0.74	-0.68	–
THF	–	–	–	–	0.07

Even though the differences in charges and Be-X bond lengths between TpBeF and TpBeCl is more pronounced than the differences between the other beryllium halides, this does not mean that the nature of the bond is very different. An interaction of the bigger halides with the closest hydrogens of the ligand could be excluded via shared electron numbers (SEN) analysis and by comparing plots of the LOL function along the N-Be-X plane. However, the LOL plots for TpBeX (X = F - I) (Fig. 2) underline the slowly decreasing ionic nature of the Be-X bonds. SEN data are given in the electronic supplement.

Figure 2: LOL plots of TpBeX (X = F, Cl, Br, I) in the N-Be-X plane.

Experimental details

Caution!!! Beryllium and its compounds are regarded as highly toxic and carcinogenic and they also have an allergic potential if inhaled with the risk of causing chronic beryllium disease (CBD).¹⁸ They should therefore be handled with appropriate safety precautions.¹⁹ All experiments described herein were performed in well-ventilated fume hoods, in gloveboxes, or with advanced Schlenk techniques under dry and oxygen-free Ar atmosphere. Argon was dried by passing it over Sicapent®, 4 Å molar sieve, and over a BASF catalyst and *vice versa*. Toluene and THF were dried over Na/K-alloy and degassed prior to use. TpBeI was prepared by literature method.⁵ NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300.1 MHz (¹H), 42.4 MHz (⁹Be), 75.5 MHz (¹³C). ¹H and ¹³C{¹H} NMR spectra were referenced to internal thf-d₈ (δ(¹H) = 1.72, 3.58 ppm; δ(¹³C) = 67.2, 25.3 ppm),²⁰ ⁹Be NMR spectra were referenced to external BeSO₄ in D₂O (δ(⁹Be) = 0 ppm). Elemental analyses were not determined due to the potential toxicity of the complexes. The purity of the compounds was verified by NMR spectroscopy. All reactions were performed under Argon atmosphere. The NMR experiments were performed in J-Young type NMR tubes.

Synthesis of TpBe(thf)I 2. 100 mg (0.28 mmol) TpBeI 1 were dissolved in 500 µL of thf-d₈ and heated to 40 °C for 20 minutes. The solution was then concentrated to approximately 70 µL and stored at 4 °C for 12h. 2 was obtained as colourless block-shaped crystals in almost quantitative yield.

TpBe(thf)I **2**. yield 99% (120 mg / 0.28 mmol). ^1H NMR (300.1 MHz, 25 °C, THF- d_8): δ = 1.77 (m, HB(N(CHCHCH)N) $_3$ Be(THF)I), 3.62 (m, HB(N(CHCHCH)N) $_3$ Be(THF)I), 6.21 (s (broad), 3H, HB(N(CHCHCH)N) $_3$ Be(THF)I), 7.51 (s (broad), 6H, HB(N(CHCHCH)N) $_3$ Be(THF)I). $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, 25 °C, THF- d_8): δ = 105.0 HB(N(CHCHCH)N) $_3$ Be(THF)I, 133.7 HB(N(CHCHCH)N) $_3$ Be(THF)I). ^9Be NMR (42.2 MHz, 25 °C, THF- d_8): δ = 3.14.

Single crystal X-ray analyses. Crystallographic data of **2**, which were collected on a Bruker AXS SMART diffractometer (MoK α radiation, λ = 0.71073 Å) at 100(1) K (**2**), are summarized in Table S1. The solid-state structure of **2** is shown in Figure 1. The structure was solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F 2 (SHELXL-97/SHELXL-2013).²¹ Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2).

The crystallographic data of **2** (excluding structure factors) has been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. 1836979 (**2**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB21EZ (fax: (+44) 1223/336033; e-mail: deposit@ccdc.cam.ac.uk).

Conclusions

We observed the formation of an ion separation reaction in the reaction of TpBeI **1** with the strong σ -donor solvent THF, yielding [TpBe(thf)]I **2** containing a beryllium monocation. The formation of **2** can be explained by the classical HSAB-concept, in which the stronger and harder Lewis-basic oxygen atom from the THF base binds to the rather hard Lewis acid Be $^+$. Complex **2** was fully characterized by heteronuclear NMR spectroscopy and single crystal X-ray diffraction. In addition, several attempts to generate similar monocationic beryllium complexes were made. These findings might be the start of a new field in beryllium chemistry, as we could show that these “cationic” complexes are highly reactive.

Conflicts of interest

There are no conflicts to declare.

Notes and references

‡ Footnotes relating to the main text should appear here. These might include comments relevant to but not central to the matter under discussion, limited experimental and spectral data, and crystallographic data.

§ This work was supported by the MPI-CEC within the International Max-Planck Research School (IMPRS) Recharge.

References

- a) J. Steinbauer, A. Spannenberg and T. Werner, *Green Chem.*, 2017, **19**, 3769–3779; b) L. S. Fitts, E. J. Bierschen, T. P. Hanusa, A. L. Rheingold, M. Pink and V. G. Young, *New J. Chem.*, 2016, **40**, 8229–8238; c) K. M. Fromm and W. Maudez, *Eur. J. Inorg. Chem.*, 2003, 3440–3444; d) C. Lichtenberg, P. Jochmann, T. P. Spaniol and J. Okuda, *Angew. Chem. Int. Ed.* 2011, **50**, 5753–5756.
- a) K. C. Jayaratne, L. S. Fitts, T. P. Hanusa and V. G. Young, *Organometallics*, 2001, **20**, 3638–3640; b) A. Koch, S. Kriech, H. Görls and M. Westerhausen, *Organometallics*, 2017, **36**, 994–1000; c) J. Langer, M. Köhler, J. Hildebrand, R. Fischer, H. Görls and M. Westerhausen, *Angew. Chem. Int. Ed.*, 2013, **52**, 3507–3510.
- D. Himmel, H. Scherer, D. Kratzert and I. Krossing, *Z. Anorg. Allg. Chem.*, 2015, **641**, 655–659.
- a) M. Bayram, D. Naglav, C. Wölper and S. Schulz, *Organometallics*, 2016, **35**, 2378–2383; b) M. Bayram, D. Naglav, C. Wölper and S. Schulz, *Organometallics*, 2017, **36**, 467–473.
- D. Naglav, D. Bläser, C. Wölper and S. Schulz, *Inorg. Chem.*, 2014, **53**, 1241–1249.
- D. Naglav, B. Tobey, C. Wölper, D. Bläser, G. Jansen and S. Schulz, *Eur. J. Inorg. Chem.*, 2016, 2424–2431.
- a) M. P. Dressel, S. Nogai, R. J. F. Berger and H. Schmidbaur, *Z. Naturforsch.* 2003, **58b**, 73–182; b) B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.* 2004, **630**, 369–376.
- W. A. Herrmann, O. Runte and G. Artus, *J. Organomet. Chem.* 1995, **501**, C1–C4.
- B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.* 2005, **631**, 1029–1031.
- B. Neumüller and K. Dehnicke, *Z. Anorg. Allg. Chem.* 2006, **632**, 1681–1686.
- F. Kraus, S. A. Baer, M. R. Buchner and A. J. Karttunen, *Chem. Eur. J.* 2012, **18**, 2131–2142.
- A review on ^9Be NMR shifts are given by: P. G. Plieger, K. D. John, T. S. Keizer, T. M. McCleskey, A. K. Burrell and R. L. Martin, *J. Am. Chem. Soc.* 2004, **126**, 14651–14658.
- N. D. Winter, *J. Phys. Chem. B* 2016, **120**, 12371–12378.
- For a general introduction into light main group metal chemistry see: T. P. Hanusa in *The Lightest Metals: Science and Technology from Lithium to Calcium*, John Wiley & Sons, 2015.
- Cambridge Structural Database V5.38 (update May 2017); see also: F. H. Allen, *Acta Crystallogr., Sect. B: Struct. Sci.* **2002**, B58, 380–388. The search for tetrahedrally-coordinated Be-thf complexes gave five hits. Be–O bond lengths range from 1.654 to 1.737 Å (mean value 1.688 Å).
- a) F. Weigend, R. Ahlrichs, *Phys. Chem. Chem. Phys.*, 2005, **7**, 3297–3305; b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785–789; c) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098–3100; d) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 1372–1377; e) M. Buhl, C. Reimann, D. A. Pantazis, T. Bredow and F. Neese, *J. Chem. Theory Comput.*, 2008, **4**, 1449–1459; f) D. A. Pantazis, X.-Y. Chen, C. R. Landis and F. Neese, *J. Chem. Theory Comput.*, 2008, **4**, 908–919; g) D. A. Pantazis and F. Neese, *J. Chem. Theory Comput.*, 2009, **5**, 2229–2238; h) D. A. Pantazis and F. Neese, *J. Chem. Theory Comput.*, 2011, **7**, 677–684; i) D. A. Pantazis and F. Neese, *Theor. Chem. Acc.*, 2012, **131**, 1292; j) S. Grimme, J. Antony, S. Ehrlich and S. Krieg, *J. Chem. Phys.*, 2010, **132**, 154104; k) R. Ahlrichs, M. Bär, M. Häser, H. Horn and C. Kölmel, *Chem. Phys. Lett.*, 1989, **162**, 165–169.
- CRC Press and Y.-R. Luo, eds., *Comprehensive Handbook of Chemical Bond Energies // Comprehensive handbook of chemical bond energies*, Taylor & Francis, Boca Raton, Fla, 2007.
- K. Dehnicke and B. Neumüller, *Z. Anorg. Allg. Chem.*, 2008, **634**, 2703–2728.
- a) D. Naglav, M. R. Buchner, G. Bendt, F. Kraus and S. Schulz, *Angew. Chem. Int. Ed.*, 2016, **55**, 10562–10576.

- 20 G. R. Fulmer, A. J. M. Miller, N. H. Sherden, H. E. Gottlieb, A. Nudelman, B. M. Stoltz, J. E. Bercaw and K. I. Goldberg, *Organometallics* 2010, **29**, 2176–2179.
- 21 a) G. M. Sheldrick, *Acta Crystallogr.* 1990, **A46**, 467–473; b) C. R. Groom, I. J. Bruno, M. P. Lightfoot and S. C. Ward, *Acta Crystallogr. B*, 2016, **72**, 171–179; c) C. B. Hübschle, G. M. Sheldrick and B. Dittrich, *J. Appl. Cryst.*, 2011, **44**, 1281–1284; d) G. M. Sheldrick, *Acta Crystallogr. A*, 2008, **64**, 112–122; e) PLATON/SQUEEZE, P. van der Sluis, A. L. Spek, *Acta Crystallogr.* **1990**, *A46*, 194–201.

DuEPublico

Duisburg-Essen Publications online

UNIVERSITÄT
DUISBURG
ESSEN

Offen im Denken

ub

universitäts
bibliothek

This text is made available via DuEPublico, the institutional repository of the University of Duisburg-Essen. This version may eventually differ from another version distributed by a commercial publisher.

DOI: 10.1039/c8dt01640b

URN: urn:nbn:de:hbz:464-20201218-091716-1

Accepted Manuscript. The final article was published in: *Dalton Trans.*, 2018, 47, 12511-12515 and is available at: <https://doi.org/10.1039/C8DT01640B>

All rights reserved.