Synthesis, Solid State Structures and Computational Calculations of half-sandwich Cp*BeX (X = Cl, Br, I) compounds

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ABSTRACT. The solid state structures of half sandwich beryllium complexes Cp*BeX (X = Cl **1**, Br **2**, I **3**) are described. Any attempts to synthesize Cp*BeF **4** by reaction of **1** - **3** with several fluorinating reagents such as AgF₂, XeF₂, 4-F-C₆H₄IF₂, AgF, NaF and Me₄NF failed. However, the reaction of **3** and AgF in resulted in the unexpected synthesis of known beryllocene Cp*₂Be **5**. Quantum chemical calculations were performed to investigate the electronic structure of **1** - **4**.

Introduction

Metallocenes of group 2 metals of the type MCp_2 ($\text{Cp} = \text{C}_5\text{H}_5$) as well as those containing sterically more bulky cyclopentadienyl ligands such as Cp' ($\text{C}_5\text{Me}_4\text{H}$) and Cp^* (C_5Me_5) have been investigated in detail in recent years.^[1] The most prominent difference within this class of compounds is reflected by the different bonding situation. While metallocenes containing the heavier group 2 metals show predominantly ionic bonding contribution, which account to approximately 70–85% of the total interaction energy,^[1a,2] the corresponding beryllium complexes exhibit higher covalent bonding character. Moreover, the number of structurally characterized beryllocenes is much smaller compared to their heavier congeners.^[3] To the best of our knowledge, only Cp_2Be ,^[4,5,6d] Cp^*_2Be ,^[6a,c,d] $\text{Cp}'_2\text{Be}$,^[6c,d] and Cp^*BeCp ^[6b,c] have been structurally characterized by single crystal X-ray analysis, to date. Cp_2Be adopts a slip-sandwich η^5/η^1 structure, in which the Be atom is disordered between two crystallographically equivalent sites of 50% occupancy. The different nature of the two Cp rings is preserved in solution, as is indicated by the high dipole moment, for which different values were reported^[4] (i.e. 2.24 D in cyclohexane, 2.46D in benzene in at 25 °C^[4a]), as well as in the gas phase, as shown by gas phase electron diffraction^[7] and quantum chemical calculations.^[8] However, NMR spectroscopic studies proved that Cp_2Be undergoes fast rearrangement reactions in solution,^[9] which occur through two dynamic processes according to theoretical calculations,^[10] in fact a 1,5 sigmatropic shift of the $\eta^5\text{-CpBe}$ unit around the periphery of the $\eta^1\text{-Cp}$ ring (activation energy 5 $\text{kJ}\cdot\text{mol}^{-1}$; η^5/η^2 transition state) as well as a molecular inversion mechanism that interchanges the $\eta^5\text{-Cp}$ and the $\eta^1\text{-Cp}$ rings (activation energy 8 $\text{kJ}\cdot\text{mol}^{-1}$; η^3/η^3 transition state). The activation energy for the molecular inversion of Cp_2Be in the solid state was experimentally determined by Hung et al. to 36.9 $\text{kJ}\cdot\text{mol}^{-1}$.^[6d] Comparable slip-sandwich structures in the solid state were reported

for $\text{Cp}'_2\text{Be}^{[6c,d]}$ and $\text{Cp}^*\text{BeCp}'^{[6b,e]}$ whereas $\text{Cp}^*_2\text{Be}^{[6a,c,d]}$ adopts a regular sandwich structure with two η^5 -bonded Cp^* groups. Even more surprisingly, the solid state structures of the corresponding half-sandwich complexes Cp^*BeX (X = halide) are unknown,^[11] while heteroleptic CpBeX complexes such as CpBeCl and CpBeSiMe_3 have been structurally characterized.^[12] Very recently, Krossing et al. reported on the synthesis and structure of $\text{Cp}^*\text{Be-F-Al(OR}^{\text{F}})_3$ upon reaction of Cp^*BeBr with $\text{Ag[Al(OR}^{\text{F}})_4]$. During this reaction, one of the 36 equivalent C–F bonds of the $[\text{Al(OR}^{\text{F}})_4]^-$ anion was activated by the highly electrophilic $[\text{Cp}^*\text{Be}]^+$ cation, resulting in the formation of a $[\text{F-Al(OR}^{\text{F}})_3]^-$ anion.^[13]

We became recently interested in the synthesis of homo- and heteroleptic Be complexes and reported on the structures of several 1-tris(pyrazolyl)borate beryllium halides TpBeX as well as on the solid state structure of $\text{Be[N(SiMe}_3)_2]_2$, respectively.^[14] We herein report on the synthesis and solid state structures of heteroleptic, donor-free pentamethylcyclopentadienyl beryllium halides Cp^*BeX (X = Cl **1**, Br **2**, I **3**) as well as Cp^*_2Be and their solid state structures. In addition, their structures were investigated by quantum chemical calculation and results from NBO, ELF and LOL analyses are presented.

Results and Discussion.

Cp^*BeCl can be prepared either by reaction of $\text{BeCl}_2(\text{OEt}_2)_2$ with $\text{Cp}^*_2\text{Mg}^{[15]}$ or $\text{Cp}^*\text{Li}^{[16]}$ and Cp^*BeBr by reaction of Cp^*Na with BeBr_2 .^[11] We synthesized Cp^*BeX (X = Cl **1**, Br **2**, I **3**) in a slightly modified procedure by reaction of BeX_2 (X = Cl, Br, I) and Cp^*K (scheme 1). Both compounds were mixed as solids and suspended in dry toluene. The reaction mixture was then stirred for at least 16 h at ambient temperature to give **1** to **3** in good yields (> 50 %). Toluene was used as solvent since both starting reagents are insoluble in this solvent, but the product

dissolves very well. Coordinating solvents such as thf or Et₂O can also be used, as **1** to **3** do not show any sign of formation of the corresponding solvent-stabilized compounds. The yields can be substantially improved by stirring the reaction mixture for three days at room temperature or for 12 h at 60 °C. Pure **1** to **3** were isolated in very high yields (**1** 86 %, **2** 85 %, **3** 92 %) as large colorless block-like crystals after filtration of any insoluble material and storage of the resulting concentrated solutions at 6 °C. **1** to **3** are extremely sensitive toward oxygen or water and also decompose rapidly in the presence of impurities such as grease. Therefore, the synthesis of **1** to **3** is best performed in closed apparatuses with Young-type stopcocks such as a double Schlenk flask equipped with a glass frit.

Scheme 1. Synthesis of **1** to **3**.

¹H and ¹³C NMR spectra of **1** to **3** show the expected resonances of the Cp* ligand. The ¹H NMR spectra of **1** to **3** show a single resonance for the magnetically equivalent Me-groups (1.68 ppm (**1**), 1.67 ppm (**2**), 1.65 ppm (**3**) in C₆D₆) / (Cp*₂Be 1.81 ppm,^[6c] Cp*BeCl 1.67 ppm,^[15] Cp*BeBr 1.66 ppm,^[11] Cp*BeMe (1.76 ppm),^[17] Cp*BeCp' 1.59 ppm^[6c]). The ¹³C NMR spectra of **1** to **3** each show a single resonance for the ring carbon atoms (109.95 ppm (**1**), 110.21 ppm (**2**), 110.53 ppm (**3**) in C₆D₆), indicating η⁵-bonded Cp* groups. Comparable findings were reported for homo- and heteroleptic η⁵-Cp*BeX compounds such as Cp*₂Be (110.4 ppm),^[6c] Cp*BeCp (108.6 ppm),^[16] Cp*BeCl (109.6 ppm),^[16] Cp*BeMe (108.0 ppm),^[17] Cp*BeCp' (108.9 ppm),^[6c]

Cp*BeCNXylCp* (108.8 ppm),^[18] Cp*BeP(*t*-Bu)₂,^[19] and Cp*BeAs(*t*-Bu)₂ (109.3 ppm),^[20] respectively. In addition, ⁹Be{¹H} NMR spectra gave resonances at −14.9 ppm (**1**), −14.8 ppm (**2**) and −15.8 ppm (**3**), which compare well with values reported for Cp*₂Be (−21.7, *w*_{1/2} = 4.4 Hz)^[6c,15] and Cp*BeCp' (−19.7 ppm, *w*_{1/2} = 4.4 Hz)^[6c] and clearly show the η^5 -coordination mode of the Cp* ligand. These findings are consistent with known beryllium metallocene complexes, whereas the low field shift compared to the homoleptic organoberyllium compounds can be explained by the electron withdrawing influence of the halide substituent.

Table 1. ⁹Be NMR shifts [ppm] of homo- and heteroleptic CpBe and Cp*Be-compounds in various solvents.

	Cp*BeCl ^a	Cp*BeBr	Cp*BeI	Cp* ₂ Be ^[6c]	Cp*BeCp' ^[6c]	Cp ₂ Be ^{9b}
⁹ Be in C ₆ D ₆	−14.88	−14.81	−15.78	−21.7	−19.7	-
⁹ Be in Tol- <i>d</i> ₈	−14.94	−14.85	−15.77	-	-	-
⁹ Be in thf- <i>d</i> ₈	−15.20	−15.08	−16.00	-	-	-
⁹ Be in Cy- <i>d</i> ₁₂ ^b	-	-	-	-	-	−21.9
⁹ Be in ^{Me} Cy ^c	-	-	-	-	-	−18.3

^a this work; ^b Cy = cyclohexane; ^c ^{Me}Cy = methylcyclohexane

Attempted synthesis of Cp*BeF **4 and unexpected formation of Cp*₂Be **5**.** Several procedures were applied to synthesize Cp*BeF **4**. Heteroleptic cyclopentadienyl beryllium complexes CpBeX have been prepared by the reaction between beryllocene and the corresponding disubstituted beryllium compound BeR₂.^[3] Since previous attempts of Drew et al. on the synthesis of CpBeF by reaction of Cp₂Be and BeF₂ failed,^[21] we didn't investigated the analogous reaction with Cp*₂Be. Moreover, salt elimination reactions were expected to be rather problematic due to the insolubility of BeF₂ in organic solvents. We therefore investigated reactions of **1** to **3** with well established fluorinating reagents including oxidizing reagents such

as AgF_2 , XeF_2 and 4-F- $\text{C}_6\text{H}_4\text{IF}_2$ as well as "salt elimination" reagents like AgF , NaF and Me_4NF (scheme 2).

Scheme 2. Attempted synthesis of Cp^*BeF **4** and synthesis of Cp^*_2Be **5**.

Unfortunately, mixing of **1**, **2** or **3** with one of the oxidizing reagents as solid powders in the glovebox led to tremendous flames, even though they were under argon atmosphere, which impressively demonstrated the reactivity of these compounds and yielded in black amorphous powder and several non-identifiable organic decomposition products. Analogous reactions at low temperatures ($-78\text{ }^\circ\text{C}$) and highly diluted solutions in toluene also did not yield **4**. In contrast, reactions of suspensions of NaF or Me_4NF in toluene with **1** to **3** did not lead to any reaction as was proven with ^9Be -NMR spectroscopy and even after several days only the starting materials could be isolated. In contrast, a suspension of AgF and **3** in toluene immediately turned dark and

yielded a black insoluble powder and a yellow solution. The black solid was a mixture of elemental silver and silver iodide, whereas the yellow solution contained BeCp^*_2 **5**, which crystallized upon concentration and cooling of the toluene solution. The NMR data and the unit cell of the measured crystal were consistent with the previously described structure. We first suggested that this reaction occurred due to a light-induced redox reaction of AgI, which is formed during the salt elimination reaction, but the strict avoidance of light (brown glassware and dark fumehood) gave the same results.

Solid state structures. Single crystals of **1** to **3** were grown from solutions in toluene at $-28\text{ }^\circ\text{C}$ and figures 1 to 3 show the crystal structures. **1** to **3** crystallize with two independent molecules in the monoclinic space group $P2_1/c$ (**1** and **3**) and $P-1$ (**2**) as colorless crystals. Table S1 summarizes the crystallographic details and table 2 the most important structural parameters of **1** to **3** and of other structurally characterized Cp^*Be complexes. **1** to **3** crystallize with two independent molecules in the monoclinic space group $P2_1/c$ (**1** and **3**) and $P-1$ (**2**) as colorless crystals. Table S1 summarizes the crystallographic details and table 2 the most important structural parameters of **1** to **3** and of other structurally characterized Cp^*Be complexes. The Cp^* ligands are η^5 -bonded to the Be atoms and the $\text{Cp}^*_{\text{centr.}}\text{-Be}$ bond lengths in **1** to **3** becomes marginally shorter with increasing atomic number of the halide substituent (1.4401, 1.4393 Å **1**, 1.4241, 1.4348 Å **2**, 1.4165, 1.4254 Å **3**), while the Be-X bond lengths increase with increasing atomic number of the halide (1.879(4), 1.879(4) Å **1**, 2.031(3), 2.032(3) Å **2**, 2.251(4), 2.238(4) Å **3**). The $\text{Cp}^*_{\text{centr.}}\text{-Be-X}$ bond angles in **1** to **3** are close to 180° . Due to the lack of heteroleptic cyclopentadienyl beryllium halides, the Be-Cl bond lengths of **1** can only be compared with the one reported for CpBeCl (1.869(3) Å),^[12a] which is almost identical. The $\text{Cp}_{\text{centr.}}\text{-Be}$ (1.451(5) Å) bond length of $\eta^5\text{-CpBeCl}$ is somewhat longer than the $\text{Cp}^*_{\text{centr.}}\text{-Be}$ bond

length of **1** despite the less steric demand of the Cp ligand (table 1). The Cp*_{centr.}-Be bond length reported for Cp*₂Be (1.471(7) Å) is marginally elongated compared to those observed in **1** - **3**.^[6a,c,d] In the packing the molecules of **1** - **3** form centro-symmetric dimers connected by a CH... π interaction (Fig 4, table 3).

Figure 1. Solid state structure of **1**, thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity.

Figure 2. Solid state structure of **2**, thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity.

Figure 3. Solid state structure of **3**, thermal ellipsoids are shown at 50% probability levels. Hydrogen atoms are omitted for clarity.

Table 2. Interatomic distances [Å] and angles [°] of **1** - **4** and related Cp*BeR compounds.

	Be-X [Å]	Cp* _{centr.} -Be [Å]	Cp* _{centr.} -Be-X [°]	Ref.
1	1.879(4), 1.879(4)	1.4393, 1.4401	178.07, 178.85	
2	2.031(3), 2.032(3)	1.4241, 1.4348	177.49, 178.78	
3	2.251(4), 2.238(4)	1.4165, 1.4254	178.07, 179.14	
CpBeCl	1.869(3)	1.451(5)	178.4(3)	[12a]
Cp*Be-F-Al(OR^F)₃	1.502(7)	1.400	-	[13]
Cp*₂Be	-	1.655(1)	180	[6a,c,d]
Cp*BeCp'^[a]	-	1.471(7)	-	[6b,c]
Cp*BeC(Cp')=NR^[b]	-	1.470(4)	178.2(2)	[11]
Cp*BeC(Cp*)=NR^[b]	-	1.472(4)	178.7(5)	[11,18]
Cp*BeP(<i>t</i>-Bu)₂	-	1.48(1)	168.3(7)°	[19]
Cp*BeAs(<i>t</i>-Bu)₂	-	1.48(1)	171.9(5)	[20]
Cp*₂YbMeBeCp*	-	1.45	-	[17]

^[a] Cp' = C₅Me₄H; ^[b] R = 2,6-Me₂-C₆H₃

1 to **3** are Be-analogues of classical Grignard compound (RMgX), which are typically obtained as donor-stabilized dimeric molecules of the general type [MgCp*X(Do)]₂ (Do = donor solvent) such as [Cp*MgBr(O=CHNMe₂)]₂,^[22] [Cp*Mg(thf)μ-Cl]₂,^[23] [Cp*Mg(OEt₂)μ-Cl]₂,^[24] and [Mg₂Br₂Cp*₂(thf)].^[25] Comparable findings were reported for the heavier Ca-analogue [Cp*Ca(thf)₂μ-I]₂.^[26] However, the Lewis acidity of homoleptic cyclopentadienyl beryllium complexes is rather less and as a consequence, these complexes are typically obtained as solvent-free molecules. In addition, Schnöckel et al. reported on the solid state structures of several anionic Grignard derivatives such as [Mg₃Cl₄Cp*₃][−], [Mg₆Br₈Cp*₅][−], [Mg₂I₃Cp*₂][−],^[27] and [Mg₆Cl₈Cp*₅][−],^[28] which were claimed as final intermediate on the way to the molecular donor-free Grignard reagent Cp*MgX. Of particular interest are [Mg₆Cl₈Cp*₅][−] and [Mg₆Br₈Cp*₅][−], since these contain inverse sandwich-like MgCp*Mg moieties.

Table 3. Geometrical data of the CH⋯π interactions.

DHCp* _{centr}	Symmetry operator	H⋯Cp* _{centr}	<DHCp* _{centr}
1			
C19-H19A...Cp* _{centr.2} ^[a]	-x+2, -y+1, -z	2.74	159.0
C10-H10C...Cp* _{centr.1} ^[a]	-x+1, -y+1, -z+1	2.61	164.0
2			
C16-H16A...Cp* _{centr.2} ^[a]	-x+2, -y+1, -z	2.65	160.1
C7-H7C...Cp* _{centr.1} ^[a]	-x+1, -y, -z+1	2.75	163.5
3			
C20-H20C...Cp* _{centr.2} ^[a]	-x+1, -y, -z+1	2.68	159.6
C8-H8C...Cp* _{centr.1} ^[a]	-x+2, -y+1, -z+1	2.86	154.2

^[a] centroids of the Cp* ligands. See Figures 1 to 3.

Figure 4. Centro-symmetric dimer formed by CH $\cdots\pi$ interaction. Example taken from **1**..

Computational calculations. Gas phase structures of **1** to **4** were calculated using the crystal structures as starting points for geometry optimizations with density functional theory (DFT) methods employing the B3LYP functional^[29] on the def2-TZVPP basis set level^[30] using relativistic effective core potentials for I (def2-ecp)^[32] and the resolution of the identity (RI) approximation^[31] as implemented in the TURBOMOLE program package.^[32]

The calculated structures **1'** to **4'** each show Cp*_{centr.}-Be-X angles of approximately 180° and approximate C_{5v} symmetry with one hydrogen atom of each methyl group pointing away from the Be atom. While the Be-X distance increases from F to I, the Cp*_{centr.}-Be distance marginally decreases, which is in accordance with the trends observed in the crystal structures. Calculated distances and average distances as-obtained from the crystal structures are in good agreement with the calculated values (table 4).

Table 4. Comparison of calculated and experimental Be-X and Cp*_{centr.}-Be lengths [Å].

		F	Cl	Br	I
Be-X	calc	1.42	1.88	2.04	2.26
	XRD	-	1.879(4), 1.879(4)	2.031(3), 2.032(3)	2.251(4), 2.238(4)
Cp* _{centr.} -Be	calc	1.48	1.46	1.45	1.45
	XRD	-	1.4393, 1.4401	1.4241, 1.4348	1.4165, 1.4254

The slight deviation of the Cp*_{centr.}-Be-X angle in the crystal structure (~178–179°) from 180° seems to be due to crystal packing effects. The differences between the calculated Cp*_{centr.}-Be and Be-X distances and those observed in the crystal structures are less than 3%. The decrease of the Cp*_{centr.}-Be distance, while consistent between the calculated and the crystal structure, lies very close to the accuracy of the methods and will not be discussed any further. The increase of the Be-X distance, while dampened by increasing covalent character of the bond, is to be expected due to the increasing van-der-Waals-radius of the halide.

Natural bond orbital (NBO) analyses of **1'** to **4'** show decreasing absolute charges of the Be atom (1.72 **4'**; Cl: 1.57 **1'**; Br: 1.51 **2'**; I: 1.44 **3'**) as well as the halide atom (F: -0.87; Cl: -0.74; Br: -0.69; I: -0.62) with increasing atomic number of the halide substituent X, while the average charge on the C atoms of the Cp* ring (C_{ring}) are approximately constant (-0.21). In addition, electron localization function (ELF)^[33] and localized orbital locator (LOL)^[34] calculations were performed on the resulting structures. Fig. 4 shows 2D plots of the ELF along the C_{ring}-Be-X plane and Fig. 5 shows 3D renderings of the LOL (at $\nu = 0.525$). The decreasing charges are evidence for the increasing covalent character of the Be-X bond, which is further compounded by the ELF plots and LOL renderings.

The ELF plots clearly show that the bonding situation between Be and Cp* does not change with decreasing electronegativity of the halide substituent, while small changes are apparent between the halide and Be atom (Fig. 5). While still being predominantly ionic, which can be seen by the very low η values around Be, the beryllium-halide bond becomes more covalent, which reflects in a change of shape of the ELF around the halide in vicinity to Be. Also, the polarization of the Cp* ligand by Be is apparent from the asymmetric shape of the ELF around it concerning the ring plane. Naturally, the Cp*-Be interaction shows some covalent contributions.

Figure 5. 2D ELF plots of **1** to **4** of in the $C_{\text{ring}}\text{-Be-X}$ plane

The LOL renderings further demonstrate the increase in covalence of the beryllium-halide bond with increasing atomic number of the halide atom (Fig 6). As the rendered surfaces ($v = 0.525$) contain regions where electrons are slower than they would be in the uniform electron gas ($v = 0.5$), covalent bonding contribution can be visualized. While the surfaces around F and Cl are still attached to those occurring at the atoms themselves, they can be clearly seen in between beryllium and the halide for Br and I, which demonstrates the decreasing covalent character from

F to I in an intuitive way. As was observed in the ELF plots, the interaction between the Cp* ligand and the Be atom can also be seen and is similar for all halides. Nevertheless, no descriptive quantitative value for the amount of covalent contribution to the beryllium-halide bond can be derived from LOL visualizations.

Figure 6. 3D LOL plots of **1** to **4** with $v = 0.525$

Conclusions. Three Be-analogous Grignard compounds of the type Cp*BeX (X = Cl, Br, I) were structurally characterized. The half-sandwich beryllocenes show η^5 -bonded Cp* groups and form centro-symmetric dimers connected by CH $\cdots\pi$ interactions in the solid state. The structural parameters of geometry-optimized structures of **1** to **3** agree very well with the experimental data. Natural bond orbital (NBO) analyses show decreasing absolute charges of the Be atom and the halide atom with increasing atomic number of the halide substituent as was expected, while

the average charge on the C atoms of the Cp* ring (C_{ring}) are approximately constant. Electron localization function (ELF) and localized orbital locator (LOL) calculations show an increasing covalent character of the Be-X bond with increasing atomic number of the halide substituent.

Experimental Details.

CAUTION! Beryllium and its compounds are regarded as highly toxic^[35] and carcinogenic and have an allergenic potential if inhaled with the risk of causing chronic beryllium disease (CBD). They should therefore be handled with appropriate safety precautions and all experiments described herein were performed in fume hoods, glove boxes or with standard Schlenk techniques under an Ar atmosphere. Dry solvents were obtained from a solvent purification system (MBraun) and degassed prior to use. NMR spectra were recorded on a Bruker Avance 300 spectrometer at 25 °C at 300.1 MHz (^1H), 42.2 MHz (^9Be), 96.3 MHz (^{11}B) and 75.5 MHz (^{13}C), respectively, and referenced to internal $\text{C}_6\text{D}_5\text{H}$ (^1H : $\delta = 7.154$; ^{13}C : $\delta = 128.0$) and internal $\text{thf-}d_8$ (^1H : $\delta = 3.580, 1.730$; ^{13}C : $\delta = 25.2, 67.4$) and external BeSO_4 in D_2O ($\delta(^9\text{Be}) = 0$). Elemental analyses were not determined due to the potential toxicity of the complexes. Purity of the compounds was verified by NMR spectroscopy. BeX_2 ($\text{X} = \text{Cl, Br, I}$) was synthesized from the elements at elevated temperatures followed by high temperature high vacuum fractional sublimation.^[36]

General procedure for the synthesis of Cp^*BeX ($\text{X} = \text{Cl } \mathbf{1}$, $\text{Br } \mathbf{2}$, $\text{I } \mathbf{3}$). Equimolar amounts of Cp^*K (2.500 g, 14 mmol) and BeX_2 ($\text{X} = \text{Cl}$ 1.146 g, 14 mmol, Br 2.363 g, 14 mmol, I 3.679 g, 14 mmol) were mixed in toluene (50 mL) at ambient temperature and stirred for 16 h. After filtration of the insoluble precipitate, the solvent was reduced in vacuo to 3 mL. **1** to **3** were obtained in high yields as colorless crystalline solid after storage at $-30\text{ }^\circ\text{C}$ for 4 h. The analytical data of **1** and **2** agree with those reported in the literature.^[11]

Cp*BeCl (1): Yield 2.163 g (86 %). ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 1.68 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^9Be (C_6D_6 , 42.2 MHz): δ = -14.88 (s, $\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^{13}C NMR (125 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 9.05 ($\text{BeC}_5(\text{CH}_3)_5\text{Cl}$), 109.95 ($\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^1H NMR (300 MHz, $\text{Tol-}d_8$, 25 $^\circ\text{C}$): δ = 1.70 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^9Be ($\text{Tol-}d_8$, 42.2 MHz): δ = -14.94 (s, $\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^{13}C NMR (125 MHz, $\text{Tol-}d_8$, 25 $^\circ\text{C}$): δ = 8.61 ($\text{BeC}_5(\text{CH}_3)_5\text{Cl}$), 109.55 ($\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^1H NMR (300 MHz, $\text{thf-}d_8$, 25 $^\circ\text{C}$): δ = 1.96 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^9Be ($\text{thf-}d_8$, 42.2 MHz): δ = -15.20 (s, $\text{BeC}_5(\text{CH}_3)_5\text{Cl}$). ^{13}C NMR (125 MHz, $\text{thf-}d_8$, 25 $^\circ\text{C}$): δ = 9.00 ($\text{BeC}_5(\text{CH}_3)_5\text{Cl}$), 110.41 ($\text{BeC}_5(\text{CH}_3)_5\text{Cl}$).

Cp*BeBr (2): Yield 2.667 g (85 %). ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 1.67 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^9Be (C_6D_6 , 42.2 MHz): δ = -14.81 (s, $\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^{13}C NMR (125 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 9.10 ($\text{BeC}_5(\text{CH}_3)_5\text{Br}$), 110.21 ($\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^1H NMR (300 MHz, $\text{Tol-}d_8$, 25 $^\circ\text{C}$): δ = 1.69 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^9Be ($\text{Tol-}d_8$, 42.2 MHz): δ = -14.85 (s, $\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^{13}C NMR (125 MHz, $\text{Tol-}d_8$, 25 $^\circ\text{C}$): δ = 8.30 ($\text{BeC}_5(\text{CH}_3)_5\text{Br}$), 109.57 ($\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^1H NMR (300 MHz, $\text{thf-}d_8$, 25 $^\circ\text{C}$): δ = 1.96 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^9Be ($\text{thf-}d_8$, 42.2 MHz): δ = -15.08 (s, $\text{BeC}_5(\text{CH}_3)_5\text{Br}$). ^{13}C NMR (125 MHz, $\text{thf-}d_8$, 25 $^\circ\text{C}$): δ = 9.08 ($\text{BeC}_5(\text{CH}_3)_5\text{Br}$), 110.68 ($\text{BeC}_5(\text{CH}_3)_5\text{Br}$).

Cp*BeI (3): Yield 3.492 g (92 %). ^1H NMR (300 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 1.65 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^9Be (C_6D_6 , 42.2 MHz): δ = -15.78 (s, $\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^{13}C NMR (125 MHz, C_6D_6 , 25 $^\circ\text{C}$): δ = 9.27 ($\text{BeC}_5(\text{CH}_3)_5\text{I}$), 110.53 ($\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^1H NMR (300 MHz, $\text{Tol-}d_8$, 25 $^\circ\text{C}$): δ = 1.67 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^9Be ($\text{Tol-}d_8$, 42.2 MHz): δ = -15.77 (s, $\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^{13}C NMR (125 MHz, $\text{Tol-}d_8$, 25 $^\circ\text{C}$): δ = 8.84 ($\text{BeC}_5(\text{CH}_3)_5\text{I}$), 110.13 ($\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^1H NMR (300 MHz, $\text{thf-}d_8$, 25 $^\circ\text{C}$): δ = 1.97 (s, 15H, $\text{BeC}_5(\text{CH}_3)_5\text{I}$). ^9Be ($\text{thf-}d_8$, 42.2 MHz): δ = -16.00 (s, $\text{BeC}_5(\text{CH}_3)_5\text{I}$).

BeC₅(CH₃)₅I. ¹³C NMR (125 MHz, thf-*d*₈, 25 °C): δ = 9.29 (*BeC₅(CH₃)₅I*), 111.00 (*BeC₅(CH₃)₅I*).

Single crystal X-ray analyses. Crystallographic data of **1** to **3**, which were collected on a Bruker AXS APEX 2 diffractometer (MoK α radiation, λ = 0.71073 Å), are summarized in Table S1 (Supporting Information). Figures 1 to 3 show diagrams of the solid-state structures of **1** to **3**. Data were collected at 121(1) K (**1**), 100(1) K (**2**) and 150(1) K (**3**), respectively. The structures were solved by Direct Methods (SHELXS-97) and refined anisotropically by full-matrix least-squares on F² (SHELXL-97/SHELXL2013).^[37] Absorption corrections were performed semi-empirically from equivalent reflections on basis of multi-scans (Bruker AXS APEX2). **1** was a non-merohedral twin of two components of approximately equal size and refined against HKL5 data. Absorption correction was performed with TWINABS.

The crystallographic data of **1** to **3** (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC-1051315 (**1**), CCDC-1051317 (**2**), and CCDC-1051316 (**3**). 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).

Supporting Information. Electronic Supplementary Information (ESI) available: A CIF file giving X-ray crystallographic data of **1** to **3**. In addition, the crystallographic details of **1** to **3** and **5**, ¹H, ⁹Be and ¹³C NMR data of **1** to **3** as well as computational details (gas phase structures, NBO analyses, ELF and LOL plots) of **1** to **3** are given. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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REFERENCES

[1] a) Hanusa, T. P. *Organometallics* **2002**, *21*, 2559-2571. b) Jutzi, P.; Burford, N. *Chem. Rev.* **1999**, *99*, 969-990. b) Jutzi, P.; Burford, N. in *Metallocenes*, Vol. 1 (Eds: Togni, A.; Halterman, R. L.), Wiley **1998**, Ch. 2. c) Bell, N. A. in *Comprehensive Organometallic Chemistry II*, Vol. 1 (Eds.: Wilkinson, G.; Stone, F. G. A.; Abel E. W.), Pergamon, Oxford, **1995**, Ch. 2. d) Hays, M. L.; Hanusa, T. P. *Adv. Organomet. Chem.* **1996**, *40*, 117-170. e) Stalke, D. *Angew. Chem.* **1994**, *106*, 2256-2259; *Angew. Chem. Int. Ed. Engl.* **1994**, *33*, 2168-2171. f) Budzelaar, P. H. M.; Engelberts, J. J.; van Lenthe, J. H. *Organometallics* **2003**, *22*, 1562-1576.

[2] a) Rayon, V. M.; Frenking, G. *Chem. - Eur. J.* **2002**, *8*, 4693-4707. b) Kwon, O.; McKee, M. L. in *Computational Organometallic Chemistry* (Ed.: Cundari T. R.), Marcel Dekker, New York, **2001**, 397.

[3] Fernández, R.; Carmona, E. *Eur. J. Inorg. Chem.* **2005**, 3197-3206.

[4] a) Fischer, E. O.; Hofmann, H. P. *Chem. Ber.* **1959**, *92*, 482-486. b) Fischer, E. O.; Schreiner, S. *Chem. Ber.* **1959**, *92*, 938-948. c) W. Strohmeier, W.; von Hobe, D. *Z. Elektrochem.* **1960**, *64*, 945-951. d) Pratten, S. J.; Cooper, M. K.; Aroney, M. J.; Filipczuk, S. W. *Dalton Trans.* **1985**, 1761-1765.

[5] a) Nugent, K. W.; Beattie, J. K.; Hambley, T. W.; Snow M. R. *Aust. J. Chem.* **1984**, *37*, 1601-1606. b) Wong, C. H.; Lee, T. Y.; Chao, K. J.; Lee S. *Acta Crystallogr. Sect. B* **1972**, *28*, 1662-1665. c) Wong, C. H.; Lee, T. Y.; Lee, T. J.; Chang, T. W.; Liu C. S. *Inorg. Nucl. Chem. Lett.* **1973**, *9*, 667-673.

[6] a) del Mar Conejo, M.; Fernández, R.; Gutiérrez-Puebla, E.; Monge, Á.; Carmona, E.; *Angew. Chem.* **2000**, *112*, 2025-2027. *Angew. Chem. Int. Ed.* **2000**, *39*, 1949-1951. b) del Mar Conejo, M.; Fernández, R.; del Río, D.; Carmona, E.; Monge, Á.; Ruiz, C. *Chem. Commun.* **2002**, *23*, 2916-2917. c) del Mar Conejo, M.; Fernández, R.; del Río, D.; Carmona, E.; Monge, Á.; Ruiz, C.; Márquez, A. M.; Sanz, J. F. *Chem. - Eur. J.* **2003**, *9*, 4452-4461. d) Hung, I.; Macdonald, C. L. B.; Schurko, R. W. *Chem. - Eur. J.* **2004**, *10*, 5923-5935.

[7] Almenningen, A.; Haaland, A.; Lusztyk, J. *J. Organomet. Chem.* **1979**, *170*, 271-284.

[8] a) Marinyk, D. S. *J. Am. Chem. Soc.* **1977**, *99*, 1436-1441. b) Chiu, N. S.; Schäfer, L. *J. Am. Chem. Soc.* **1978**, *100*, 2604-2607. c) Jemmis, E. D.; Alexandratos, S.; Schleyer, P. R.;

Streitwieser, A.; Schaefer, H. F. *J. Am. Chem. Soc.* **1978**, *100*, 5695-5700. d) Gleiter, R.; Böhm, M.; Haaland, A.; Johansen, R.; Lusztyk, J. *J. Organomet. Chem.* **1979**, *170*, 285-292.

[9] a) Wong, C.; Wang, S. *Inorg. Nucl. Chem. Lett.* **1975**, *11*, 677-678. b) Nugent, K. W.; Beattie, J. K.; Field L. D. *J. Phys. Chem.* **1989**, *93*, 5371-5377.

[10] a) Margl, P.; Schwarz, K.; Blöchl, P. E. *J. Chem. Phys.* **1995**, *103*, 683-690. b) McKee, M. L. *WIREs Comput. Mol. Sci.* **2011**, *1*, 943-951.

[11] del Mar Conejo, M.; Fernández, R.; Carmona, E.; Andersen, R. A.; Gutiérrez-Puebla, E.; Monge, M. A. *Chem. - Eur. J.* **2003**, *9*, 4462-4471.

[12] a) Goddard, R.; Akhtar, J.; Starowieyski, K. B. *J. Organomet. Chem.* **1985**, *282*, 149-154. b) Saulys, D. A.; Powell, D. R. *Organometallics* **2003**, *22*, 407-413.

[13] Himmel, D.; Scheer, H.; Kratzert, D.; Krossing, I. *Z. anorg. allg. Chem.* **2015**, *641*, 655-659.

[14] a) Naglav, D.; Bläser, D.; Wölper, C.; Schulz, S. *Inorg. Chem.* **2014**, *53*, 1241-1249. b) Naglav, D.; Neumann, A.; Bläser, D.; Wölper, C.; Haack, R.; Jansen, G.; Schulz, S. *Chem. Commun.* **2015**, *51*, 3889-3891.

[15] Burns, C. J.; Andersen, R. A. *J. Organomet. Chem.* **1987**, *325*, 31-37.

[16] Pratten, S. J.; Cooper, M. K.; Aroney, M. J. *J. Organomet. Chem.* **1990**, *381*, 147-153.

[17] Burns, C. J.; Andersen, R. A. *J. Am. Chem. Soc.* **1987**, *109*, 5853-5855.

[18] del Mar Conejo, M.; Fernández, R.; Carmona, E.; Gutierrez-Puebla, E.; Monge, M. A. *Organometallics* **2001**, *20*, 2434-2436.

- [19] Atwood, J. L.; Bott, S. G.; Jones, R. A.; Koschmieder, S. U. *Chem. Commun.* **1990**, 692-693.
- [20] Battle, S. L.; Cowley, A. H.; Decken, A.; Jones, R. A.; Koschmieder, S. U. *J. Organomet. Chem.* **1999**, 582, 66-69.
- [21] Drew, D. A.; Morgan, G. L. *Inorg. Chem.* **1977**, 16, 1704-1708.
- [22] Schnöckel, H.; Duan, T. *Private Communication* **2005**, CCDC 267694, DOI: 10.5517/cc8zk92.
- [23] Cramer, R. E.; Richmann, P. N.; Gilje, J. W. *J. Organomet. Chem.* **1991**, 408, 131-136.
- [24] Dohmeier, C.; Loos, D.; Robl, C. Schnöckel H. *J. Organomet. Chem.* **1993**, 448, 5-8.
- [25] Vollet, J.; Hartig, J. R.; Schnöckel, H. *Angew. Chem.* **2004**, 116, 3248-3252; *Angew. Chem. Int. Ed.* **2004**, 43, 3186-3189.
- [26] McCormick, M. J.; Craig-Sockwell, S.; Davies, C. E. H.; Hanusa, T. P.; Huffman, J. C. *Organometallics* **1989**, 8, 2044-2049.
- [27] Kruczyński, T.; Pushkarevsky, N.; Henke, P.; Köppe, R.; Baum, E.; Konchenko, S.; Pikies, J.; Schnöckel, H. *Angew. Chem.* **2012**, 124, 9159-9163; *Angew. Chem. Int. Ed.* **2012**, 51, 9025-9029.
- [28] Vollet, J.; Hartig, J. R.; Baranowska, K.; Schnöckel, H. *Organometallics* **2006**, 25, 2101-2103.
- [29] a) Becke, A. D. *J. Chem. Phys.* **1993**, 98, 5648-5652. b) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, 98, 11623-11627.

- [30] Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **1994**, 7, 3297-3305.
- [31] a) Häser, M.; Ahlrichs, R. *J. Comput. Chem.* **1989**, 10, 104-111. b) Bauernschmitt, R.; Ahlrichs, R. *Chem. Phys. Lett.* **1996**, 256, 454-464. c) von Arnim, M.; Ahlrichs, R. *J. Comp. Chem.* **1998**, 19, 1746-1757. d) Sierka, M.; Hogeckamp, A.; Ahlrichs, R. *J. Chem. Phys.* **2003**, 118, 9136-9148. e) Weigend, F. *Phys. Chem. Chem. Phys.* **2006**, 8, 1057-1065.
- [32] Ahlrichs, R.; Bär, M.; Häser, M.; Horn, H.; Kölmel, C. *Chem. Phys. Lett.* **1989**, 162, 165-169.
- [33] Becke, A. D.; Edgecombe, K. E. *J. Chem. Phys.* **1990**, 92, 5397-5403.
- [34] Schmider, H. L.; Becke, A. D. *J. Mol. Struct. THEOCHEM* **2000**, 527, 51-61.
- [35] a) Handa, T.; Nagai, S.; Kitaichi, M.; Chin, K.; Ito, Y.; Oga, T.; Takahashi, K., Watanabe, K.; Mishima, M.; Izumi, T. *Sarcoidosis Vasculitis and Diffuse Lung Diseases* **2009**, 26, 24-31. b) Strupp, C. *Ann. Occup. Hyg.* **2011**, 55, 43-56. c) Strupp, C. *Ann. Occup. Hyg.* **2011**, 55, 30-42. d) Cummings, K. J.; Stefaniak, A. B.; Abbas Virji, M.; Kreiss, K. *Environmental Health Perspectives* **2009**, 117, 1250-1256. e) Bill, J. R.; Mack, D. G.; Falta, M. T.; Maier, L. A.; Sullivan, A. K.; Joslin, F. G.; Martin, A. K.; Freed, B. M.; Kotzin, B. L.; Fontenot, A. P. *J. Immunology* **2005**, 175, 7029-7037.
- [36] Brauer, G. (Hrsg.) in *Handbook of Preparative Inorganic Chemistry*. 2. Auflage., Vol. 1, Academic Press **1963**, p 890.
- [37] a) Sheldrick, G. M. *Acta Crystallogr. Sect. A* **1990**, 46, 467-473. b) Sheldrick, G. M., SHELXL-97, *Program for the Refinement of Crystal Structures*, University of Göttingen,

Göttingen (Germany) **1997** (see also: Sheldrick, G. M. *Acta Crystallogr. Sect. A* **2008**, 64, 112-122.).

Graphic for Table of Content.

The structures of half-sandwich complexes Cp^*BeX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) were determined by single crystal X-ray diffraction and their electronic structures investigated by quantum chemical calculations. Electron localization function (ELF) and localized orbital locator (LOL) calculations show an increasing covalent character of the Be-X bond with increasing atomic number of the halide substituent.

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