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Cp* as a removable protecting group: low valent Zn(I) compounds by reductive elimination, protolytic and oxidative cleavage of Zn–Cp*†

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Zn–Cp* bond cleavage reactions leading to novel monovalent cationic zinc species are presented (Cp* = pentamethylcyclopentadienyl). The treatment of $[Zn_2Cp^*_2]$ with two equiv. of $[H(Et_2O)_2][BAr_4^F]$ (BAr_4^F = $B\{C_6H_3(CF_3)_2\}_4$) yields the triple-decker complex $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ (**1**) *via* protolytic removal of a Cp* ligand as Cp*H, whereas the reaction with an equimolar amount of $[FeCp_2][BAr_4^F]$ (Cp = cyclopentadienyl) results in the formation of $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$ (**2**) under oxidative cleavage of a Cp* ring giving decamethylfulvalene, $(Cp^*)_2$, and $[FeCp_2]$ as by-products. The molecular structures of compounds **1** and **2** are established by single-crystal X-ray diffraction studies. A new synthetic pathway for the formation of $[Zn_2Cp^*_2]$ based on the reductive elimination of Cp*H from *in situ* formed Cp*ZnH is presented.

1. Introduction

Although $[Zn_2Cp^*_2]$ (Cp* = pentamethylcyclopentadienyl) was discovered nearly a decade ago by Carmona *et al.*,[1] a possible reaction mechanism for the formation of this remarkable Zn^I–Zn^I bonded species has not yet been fully elucidated. First postulations have been made by Schnepf and Himmel in 2005 where the authors discussed the involvement of active zinc, formed in disproportionation steps during the reaction, which reduces $ZnCp^*_2$.[2] This possibility has been ruled out by Carmona *et al.* as Rieke-zinc was not strong enough to achieve reduction and conversion into $[Zn_2Cp^*_2]$.[3] Until now, the favoured perception of the reaction scheme is based on radical mechanisms in which $[Zn_2Cp^*_2]$ is formed by dimerization of the monovalent, radical fragments $[Cp^*Zn^{\cdot}]$.[4] The first reports on $[Zn_2Cp^*_2]$ were mostly dealing with the structure and bonding situation of the Cp* stabilized Zn_2 molecule itself, recent studies also focus on the synthesis of new Zn_2 containing derivatives $[Zn_2R_2]$ ($R \neq Cp^*$)[4–17] as well as the reactivity of $[Zn_2Cp^*_2]$ towards aryl or alkyl alcohols in the presence of stabilizing nitrogen donors.[18] In contrast to neutral organo Zn^I compounds, the knowledge on related cationic species is still rather limited. The existence of $[Zn_2]^{2+}$ was first evidenced in 1967 in a zinc solution of fused $ZnCl_2$,[19] but up to now, only the dimethylaminopyridine stabilized $[Zn_2]^{2+}$ dication $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$ (dmap = 4-dimethylaminopyridine) has been isolated and characterized.[15] These results suggest that a selective removal of the stabilizing/protecting Cp* moieties from $[Zn_2Cp^*_2]$ is feasible in general and the synthetic success will depend on finding the right reaction conditions and sufficiently stabilizing ligand settings for the resulting $[Zn_2]^{2+}$ species. As for the smooth removal of Cp* groups from related GaCp* species we were able to demonstrate the suitability of $[H(Et_2O)_2][BAr_4^F]$ (BAr_4^F = $B\{C_6H_3(CF_3)_2\}_4$) and $[FeCp_2][BAr_4^F]$ (Cp = cyclopentadienyl). The first reagent allows the abstraction by protolytic splitting of Cp*H, the latter one yields selective oxidation of the Cp* moiety forming decamethylfulvalene as a by-product. Thus, the reaction of GaCp* with $[H(Et_2O)_2][BAr_4^F]$ (BAr_4^F = $B\{C_6H_3(CF_3)_2\}_4$) results in the formation of the cation $[Ga_2(C_5Me_5)]^+$.[20] Accordingly, Braun *et al.* synthesized the triple-decker complex $[Zn_2Cp^*_3][BAr_4^F]$, emerging from the reaction of $[ZnCp^*_2]$ with $[H(Et_2O)_2][BAr_4^F]$.[21] In addition, we succeeded in the oxidative cleavage of Ga–Cp* bonds with $[FeCp_2][BAr_4^F]$ in $[M(GaCp^*)_4]$ (M = Ni, Pd, Pt) yielding $[GaNi(GaCp^*_4)]^+$ and $[(\mu_2\text{-}Ga)_nM_3(GaCp^*)_6]^{n+}$ (n = 2 for M = Pd and n = 1 for M = Pt).[22] Herein, we report on selective Zn–Cp* cleavage reactions of $[Zn_2Cp^*_2]$ leading to cationic species with an intact Zn^I–Zn^I bond: $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ is accessible by protonation of $[Zn_2Cp^*_2]$ with $[H(Et_2O)_2][BAr_4^F]$, while

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oxidation with $[FeCp_2][BAr_4^F]$ selectively leads to semi-deprotected $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$. These studies of selective Cp* removal from $[Zn_2Cp^*_2]$ lead us to a new and reliable synthetic route for the preparation of $[Zn_2Cp^*_2]$ based on a Cp*H reductive elimination reaction from the precursors $[ZnCp^*_2]$ and ZnH_2(s) most likely involving *in situ* formed [Cp*ZnH].

2. Results and discussion

2.1. Protolytic cleavage of Zn–Cp* – synthesis of $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ (1)

The reaction of $[H(Et_2O)_2][BAr_4^F]$ with two equivalents of $[Zn_2Cp^*_2]$ at −25 °C in fluorobenzene leads to the novel double sandwich complex $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ (**1**) as a white powder in yields around 70% (Scheme 1). Colourless crystals of **1**·2C_6H_5F suitable for single crystal X-ray diffraction were obtained by slow diffusion of *n*-hexane into a saturated fluorobenzene solution of **1** at −30 °C. The pure solid of **1** is stable under an inert gas atmosphere at −30 °C but decomposes rapidly in the solid state at room temperature under formation of a metallic precipitate.

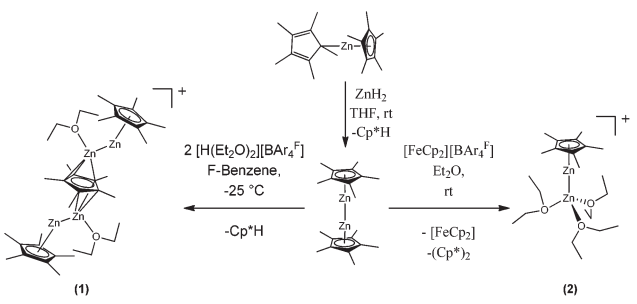
2.2. Spectroscopic features of $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ (1)

The ^{1}H NMR spectrum of **1** in CD_2Cl_2 at room temperature shows the expected set of signals for one $[BAr_4^F]^-$ anion (δ = 7.57 (s, 4H) and 7.73 (s, 8H) ppm) and two coordinated diethyl ether solvent molecules (δ = 1.22 (m, 12H) and 3.63 (m, 8H ppm)) as well as one signal for the Cp* groups at δ = 2.06 (s, 45H) ppm. Low temperature ^{1}H NMR measurements at −60 °C show no splitting of the signal which indicates a fast fluxional process interchanging the terminal and bridging Cp* units. The ^{19}F NMR spectrum exhibits one signal at δ = 62.9 ppm for the CF_3 groups of the $[BAr_4^F]^-$ anion, as expected. Owing to the instability of **1** in solution, no ^{13}C NMR spectrum could be obtained. The FTIR spectrum of **1** shows absorption bands typical of the Cp* units at 2955, 2887 and 2844 cm^{-1} and a band at 1260 cm^{-1} ascribed to the C–F vibration. Both absorption bands are well comparable to literature known examples.[23–26]

Liquid injection field desorption ionization mass spectrometry (LIFDI-MS) displays a signal at m/z = 668, which can be assigned to $[M - (Et_2O)_2]^+$ (see the ESI†). Two more signals at m/z = 602 and 536 indicate the loss of one and two zinc atoms, respectively (see the ESI†).

2.3. Molecular structure of $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ (1)

Compound **1**·2C_6H_5F crystallizes in the monoclinic space group $P2_1/c$ with four molecules in the unit cell. While Zn1 and Zn4 are η^5 bound to terminal Cp* rings, two more Zn atoms (Zn2 and Zn3) are η^3 bound to one bridging Cp* ring resulting in a "bent" triple-decker sandwich structure (Fig. 1). The bridging Cp* ligand and the terminal one bound to Zn1 are each disordered over two sites. The Zn–Zn distances are almost identical with values of 2.310(1) Å for Zn1–Zn2 and 2.307(1) Å for Zn3–Zn4. These bond distances are virtually the same as the one found in $[Zn_2Cp^*_2]$ (2.305(3) Å) or other Zn_2R_2 compounds, *e.g.* $[Zn_2Tp^{Me2}_2]$ (Tp = tris(3,5-dimethylpyrazolyl) hydridoborate).[1,14] The approximate Zn–Cp*$_{centroid}$ distances for the terminal ligands (Zn1–Cp*$_{centroid}$ 1.93 Å, Zn4–Cp*$_{centroid}$ 1.89 Å) are slightly shortened as compared to the mother compound $[Zn_2Cp^*_2]$ (2.04 Å) or other Zn_2R_2 compounds like $[\{Zn_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_5Me_5)\text{-}(pyr\text{-}py)\}_2]$ (2.004 Å) or $[Cp^*_2ZnZn(dmap)_2]$ (2.033 Å) (dmap = 4-dimethylaminopyridine).[1,18,27] However, these ZnCp*$_{centroid}$ distances are all slightly elongated in comparison to the recently published triple-decker complex of Zn^{II}, $[Zn_2Cp^*_3][BAr_4^F]$ (Zn–Cp*$_{centroid}$ 1.828 and 1.830 Å).[21] The Zn2–C_{Cp^*} and Zn3–C_{Cp^*} distances in **1** strongly vary between 2.256(3)–2.451(3) (Zn2–C_{Cp^*}) and 2.316(4)–2.572(3) (Zn3–C_{Cp^*}), due to the η^3 binding mode of the central Cp* ring. This can also be observed in the related $[Zn_2Cp^*_3]^+$, where the respective distances vary between 2.060(3) and 2.049(3) Å and 2.396(3) and 2.050(3) Å caused by an η^1 binding mode.[21] Both Zn–O bonds (Zn2–O2 2.204(4) Å, Zn3–O1 2.234(4)) are elongated as compared to literature known



Scheme 1 Synthesis of $[Zn_2Cp^*_2]$ by reductive elimination of Cp*H and formation of the cations $[Cp^*_3Zn_4(Et_2O)_2]^+$ and $[Cp^*Zn_2(Et_2O)_3]^+$ from $[Zn_2Cp^*_2]$ by selective protolysis or oxidative cleavage.

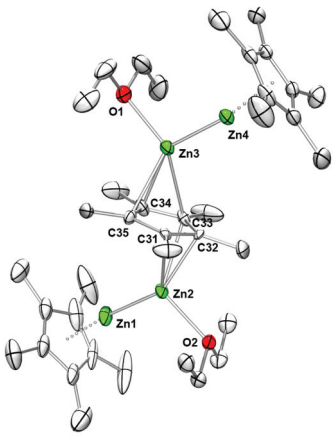


Fig. 1 Molecular structure of the cation $[Zn_4Cp^*_3(Et_2O)_2]^+$ in the crystal of **1**·2C_6H_5F. Displacement ellipsoids are drawn at the 30% probability level. For the sake of clarity, disorder of the Cp* ligands and hydrogen atoms are omitted. Selected interatomic distances (Å) and angles (°): Zn1–Zn2 2.310(1), Zn3–Zn4 2.307(1), Zn2–O2 2.204(4), Zn3–O1 2.234(4), Zn2–C31 2.442(3), Zn2–C32 2.256(4), Zn2–C33 2.402(3), Zn3–C33 2.572(3), Zn3–C43 2.316(4), Zn3–C35 2.412(4), Zn1–Cp*$_{centroid}$ 1.935, Zn4–Cp*$_{centroid}$ 1.899; Cp*$_{centroid}$–Zn1–Zn2 165.86, Cp*$_{centroid}$–Zn3–Zn4 170.92.

Zn–OEt_2 bond distances, which range from 1.997 Å in $[Ph_2SiO]_8[AlO(OH)]_2[AlO_2]_2[Zn(OH)]_2{\cdot}2(OEt_2)$ to 2.163 Å in [(*R*,*R*)-(*N*,*N*′-bis(3,5-di-*tert*-butylsalicylidene)-1,2-diphenylethylenediamino)(diethyl ether)zinc(II)], indicating a rather weak Zn–OEt_2 interaction in **1**.[28,29] The angles Zn–Zn–$Cp^*_{centroid}$ exhibit values of 165.86(4)° (Zn2–Zn1–$Cp^*_{centroid}$) and 170.92(4)° (Zn3–Zn4–$Cp^*_{centroid}$), respectively, which results in a significant deviation from linearity, possibly due to steric reasons. This deviation can also be observed in similar compounds with additional coordinated donor ligands to the ZnZnCp* unit, *e.g.* $[Zn_2Cp^*(OAr^{Mes})(pyr\text{-}py)_2]$ (175.6°) or $[Zn_2Cp^*(\mu\text{-}OC_5Me_5)(pyr\text{-}py)]_2$ (167.2°).[18]

2.4. Oxidative cleavage of Zn–Cp* – synthesis of semi-protected $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$ (2)

Treatment of $[Zn_2Cp^*_2]$ with an equimolar amount of $[FeCp_2][BAr_4^F]$ at room temperature in diethyl ether leads to an oxidative cleavage of a Cp* moiety and formation of $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$ (**2**) as a grey powder with a yield of 71% (Scheme 1). Ferrocene and decamethylfulvalene $(Cp^*)_2$ can both be observed as stoichiometric by-products by *in situ* ^{1}H NMR spectroscopy. Although the compound is stable as a microcrystalline powder at −30 °C under an inert gas atmosphere, it gradually decomposes at room temperature in the solid state and more rapidly in solutions of fluorobenzene, diethyl ether or dichloromethane under precipitation of metallic particles.

2.5. Spectroscopic features of $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$ (2)

The ^{1}H NMR spectrum of **2** in CD_2Cl_2 at room temperature exhibits two signals for the $[BAr_4^F]^-$ anion (δ = 7.56 (s, 4H) and 7.71 (s, 8H)), two resonances corresponding to the coordinated Et_2O molecules (δ = 1.25 (t, 18H) and 3.69 (q, 12H) ppm) and one peak for the Cp* moiety (δ = 2.08 (s, 15H) ppm). At room temperature additional signals are observed due to decomposition of the compound: at 8.24 and 8.02 ppm (BAr^F) in a ratio of 1 : 2.

The coordinated Et_2O molecules in **2** can be exchanged by THF molecules at room temperature: the ^{1}H NMR spectrum of **1** in THF-d_8 at room temperature shows signals for non-coordinated Et_2O at δ = 3.39 (q) and 1.12 (t) ppm as well as two resonances for the $[BAr_4^F]^-$ anion (δ = 7.58 (s, 4H) and 7.79 (s, 8H)) and one peak for the Cp* unit at δ = 2.07 (s, 15H) ppm. Solutions of **1** in THF are apparently less temperature sensitive than solutions in other solvents like fluorobenzene, CH_2Cl_2 or Et_2O. The FTIR spectrum of **2** reveals typical bands for the Cp* ring at 2963, 2889 and 2845 cm^{-1} as well as a signal due to the C–F vibration at 1265 cm^{-1}.

2.6. Molecular structure of $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$ (2)

Colourless crystals appropriate for single crystal X-ray diffraction were obtained by slow diffusion of *n*-hexane into a fluorobenzene solution of **2** at −30 °C. Compound **2** crystallizes in the orthorhombic space group *Pbca*. Note that the cation is fully disordered. The coordination geometry of the $Cp^*Zn_2O_3$ unit resembles an "elongated" piano stool (Fig. 2). One Cp*

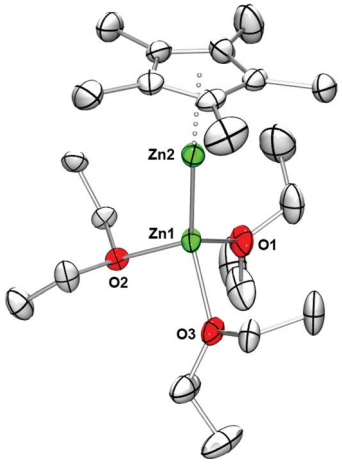
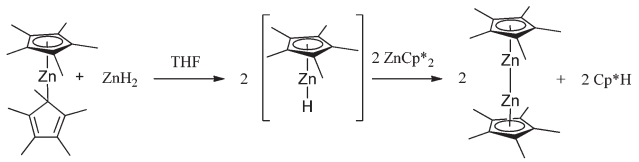


Fig. 2 Hydrogen atoms and the disorder of the complex are omitted for clarity. Selected interatomic distances (Å) and angles (°): Zn1–Zn2 = 2.324(2), *ca.* Zn2–$Cp^*_{centroid}$ = 1.92, Zn1–O1 = 2.117(4), Zn1–O2 = 2.096(4), Zn1–O3 = 2.076(4); $Cp^*_{centroid}$–Zn2–Zn1 = 174.47, Zn2–Zn1–O1 = 121.99(15), Zn2–Zn1–O2 = 120.54(12), Zn2–Zn1–O3 = 121.71(14).

ligand from the parent compound $[Zn_2Cp^*_2]$ is replaced by three Et_2O molecules, while the second Zn atom is still coordinated by an η^5-Cp* moiety. In the crystal, the entire complex is disordered over two sites. Compared to $[Zn_2Cp^*_2]$ (2.305(3) Å) the Zn–Zn bond of **2** is slightly elongated (2.324(2) Å).[1] However this value is in the range of other reported Zn^I–Zn^I bond lengths, such as $[Zn_2(dpp\text{-}bian)_2]$ (dpp-bian = 1,2-bis-[(2,6-diisopropylphenyl)imino]acenaphthene) (2.332(2) Å).[7] The Zn2–$Cp^*_{centroid}$ distance of approximately 1.92 Å is comparable with the Zn1–$Cp^*_{centroid}$ and Zn4–$Cp^*_{centroid}$ distances of compound **1** and accordingly distinctly shorter than in $[Zn_2Cp^*_2]$ (2.04 Å).[1] Compound **2** shows a deviation of the angle Zn1–Zn2–$Cp^*_{centroid}$ (170.31°) from linearity, similar to other Zn^I–Zn^I compounds with coordinated donor ligands ($[Zn_2(\eta^5\text{-}C_5Me_5)(OAr^{Mes})(pyr\text{-}py)_2]$ (175.6°), $[Zn_2(\eta^5\text{-}C_5Me_5)(\mu\text{-}OC_5Me_5)(pyr\text{-}py)]_2$ (167.2°) or $[Zn_2Cp^*_2(dmpa)_2]$ (159.6°)).[18,27] The Zn1–O1, Zn1–O2 and Zn1–O3 distances are 2.117(4), 2.096(4) and 2.076(4) Å, respectively, which are very close to those of other Zn–Et_2O complexes such as $[EtZn(OEt_2)_3][B(C_6F_5)_4]$ (2.110(2), 2.072(2) and 2.031(2) Å).[30] There is a major difference between the Zn–Zn–O angles of compound **1** with 109.66(11) and 110.2(1)° and compound **2** whose values range from 120.54(12) to 121.99(15)°.

2.7. Mechanism of the $[Zn_2Cp^*_2]$ formation *via* elimination of Cp*H

The convenient and high-yield elimination of Cp*H from $[Zn_2Cp^*_2]$ by addition of an *external* proton source (intermolecular attack on Zn–Cp*) prompted us to study the Cp*H elimination reaction also in systems with an *internal* hydrogen source, *i.e.* zinc-hydride moiety. Notably, such a very selective, intramolecular reductive elimination reaction in main group organometallic chemistry has recently been reported for the aluminium complexes $[Cp^*AlH_2]$ and $[Cp^*_2AlH]$: heating a



Scheme 2 Formation of $[Zn_2Cp^*_2]$ from $[ZnCp^*_2]$ and ZnH_2.

solution of $[Cp^*AlH_2]$ leads quantitatively to metallic aluminium, Cp*H (and presumably H_2). Accordingly, reductive elimination of Cp*H from $[Cp^*_2AlH]$ represents a new high yield access to $AlCp^*$.[31] Indeed, the reaction of $[ZnCp^*_2]$ and ZnH_2 in a 3 : 1 molar ratio in THF affords $[Zn_2Cp^*_2]$ and Cp*H in yields around 65%. As shown by ^1H NMR spectroscopy, the only observed species are the reaction products $[Zn_2Cp^*_2]$ and Cp*H as well as the starting compound $[ZnCp^*_2]$. The yield of the products depends only on the molar ratio of starting compounds. The reaction proceeds quantitatively, however, the product $[Zn_2Cp^*_2]$ itself is reactive towards ZnH_2 leading to metallic Zn and Cp*H. By suitable adjustment of reactant concentration and molar ratios this undesired decomposition can be slowed down very considerably and isolated yields of $[Zn_2Cp^*_2]$ up to 65% (based on Zn) can be obtained. The comparison with $[Cp^*_2AlH]$ suggests that the reaction mechanism is likely to involve a soluble, unstable intermediate, presumably [Cp*ZnH], which is formed *via* a heterogeneous reaction of pure, insoluble ZnH_2(s) and soluble $[ZnCp^*_2]$. This intermediate [Cp*ZnH] spontaneously reacts with another equivalent of $[ZnCp^*_2]$ to give $[Zn_2Cp^*_2]$ *via* reductive elimination of Cp*H (Scheme 2). Preliminary kinetic studies are in agreement with that reasoning (Fig. S8†), however, a more detailed analysis of this reaction is needed and currently ongoing. The results will be published elsewhere together with theoretical calculations, similar to the related $[Cp^*_2AlH]$ case.[30]

It should be noted that the possible pathway for $[Zn_2Cp^*_2]$ formation suggested herein agrees well with the literature: an appropriate mixture of $[ZnCp^*_2]$, $ZnCl_2$ and KH most likely gives a similar distribution of intermediates and products as the combination of $[ZnCp^*_2]$ with pure, preformed ZnH_2. However, the reaction of $[ZnCp^*_2]$ with ZnR_2 (R = Et, Ph) at low temperature, which is the second (and low yield) route to $[Zn_2Cp^*_2]$ known in the literature, cannot be explained by a similar (intra/intermolecular) reductive Cp*H elimination mechanism.[3]

3. Conclusions

In this contribution we presented two routes to unusual cationic low valent zinc species based on the selective cleavage of a Cp* ligand from $[Zn_2Cp^*_2]$. Protonation with $[H(Et_2O)_2][BAr_4^F]$ yields the triple-decker complex $[Cp^*_3Zn_4(Et_2O)_2]^+$ and oxidation with $[FeCp_2][BAr_4^F]$ leads to the formation of semi-protected $[Cp^*Zn_2(Et_2O)_3]^+$. Both cations exhibit intact Zn^I–Zn^I units, which are stabilized by substitution labile solvent molecules. Note that the $[Cp^*_3Zn_4(Et_2O)_2][BAr_4^F]$ (**1**) and $[Cp^*Zn_2(Et_2O)_3][BAr_4^F]$ (**2**) as well as $[Zn_2(dmap)_6][Al\{OC(CF_3)_3\}_4]_2$,[15] contain weakly coordinating anions, indicating the need of such components for a successful isolation of the di-zinc species. The selective Cp*H elimination turned out as the key step in the formation of $[Zn_2Cp^*_2]$ from ZnH_2 and $ZnCp^*_2$ whereby [ZnCp*H] is suggested to be the crucial intermediate and a new, reliable synthesis of $[Zn_2Cp^*_2]$ was developed. Apparently, efficient nucleophilic reaction mechanisms, *i.e.* intramolecular hydride migration, are possible at the Zn centre and allow selective Zn–Cp* bond splitting to yield the desired Zn^I compound. From these data it can be expected that the lability of the Zn–Cp* bond towards both, electrophilic (protonation) and nucleophilic (hydride) attack and as well single electron oxidation allow new approaches to other cationic Zn^I products. Moreover it is reasonable to assume that the reported chemistry may offer valuable precursors and reaction concepts for the formation of intermetallic Zn-rich clusters.[32]

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