Main-Group Chemistry

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The Reactivity of $[Zn_2Cp^*_2]$: Trapping Monovalent $\{^{\cdot}ZnZnCp^*\}$ in the Metal-Rich Compounds $[(Pd,Pt)(GaCp^*)_a(ZnCp^*)_{4-a}(ZnZnCp^*)_{4-a}]$ $(a = 0, 2)$**

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Carmona's synthesis of $[Zn_2Cp^*_2]$ (Cp* = pentamethylcyclopentadienyl), the first molecular compound exhibiting a covalent Zn–Zn bond, has generated much interest and stimulated research on low-coordinate (main-group) metal compounds.[1–3] Other derivatives with the formula $[M_2L_2]$, such as $[Zn_2\{HC(CMeNAr)_2\}_2]$ (Ar = 2,6-iPr$_2$C$_6$H$_3$) or $[Zn_2Ar_2]$ (Ar = 2,6-(2,6-iPr$_2$C$_6$H$_3$)$_2$C$_6$H$_3$) were subsequently obtained, and even magnesium analogues, such as $[Mg_2(DippNacnac)_2]$ (DippNacnac = [(2,6-iPr$_2$C$_6$H$_3$)N=CMe]$_2$CH) have been reported.[4–7] Notably, Robinson's concept of using N-heterocyclic carbenes (NHCs) as neutral, soft, and very bulky ligands for stabilizing unusual bonding states, for example, $[L{:}E{=}E{:}L]$ (E = Si, Ge; L$\mathrel{:=}$C[N(2,6-iPr$_2$-C$_6$H$_3$)CH]$_2$) relates to this progress.[8] The quite well-developed coordination chemistry of the carbenoid Group 13 metal analogues of NHC ligands, ER (E = Al, Ga, In; R = Cp* and other bulky substituents) to metal centers complements this progress.[9,10] Nevertheless, not much is known on the chemistry of the compounds $[M_2L_2]$ in general,[6,8] and only very few reports have appeared for reactions of the zinc dimers in particular.[4,5,7]

For example, $[Zn_2Cp^*_2]$ should behave as a natural source for the monovalent species $^{\cdot}$ZnCp*, which in essence contains Zn^{I}. In fact, only a few transition metal (TM) complexes with one-electron ligands $^{\cdot}$Zn^{I}R are known (R = Cp*, CH$_3$). Recently, we established an access to very zinc-rich, highly coordinated $[TM(ZnR)_n]$ compounds (TM: Group 6–10 element, n = 8–12) bridging the gap between complexes, clusters, and Hume-Rothery intermetallic phases, with the icosahedral $[Mo(ZnCp^*)_3(ZnMe)_9]$ as prototype of a novel family.[11,12] The formation reaction starts from mononuclear complexes $[TM(GaCp^*)_m]$ (m = 4–6) and ZnR$_2$ (R = Me, Et) and involves Ga/Zn and Cp*/R exchange processes. In the course of the reaction, Zn^{II} is reduced to Zn^{I} by Ga^{I}, which ends up as Ga^{III} and causes the overall substitution of one two-electron GaCp* ligand by two one-electron ZnR ligands at the TM center. If inert co-ligands at TM are present, other unusual and high nuclearity clusters, such as $[Mo_4(CO)_{12}Zn_6(ZnCp^*)_4]$, may be formed, which reveal close similarities to structural motifs of Mo/Zn intermetallic phases.[13] Herein, we present the first results of our ongoing study on reactions of $[Zn_2Cp^*_2]$ with $[L_aTM_b(GaCp)^*_c]$. Most interestingly, we found the fragment {ZnZnCp*} with the intact covalent Zn–Zn linkage being trapped as a one-electron ligand in the coordination sphere of a transition metal.

Treatment of $[Pd(GaCp^*)_4]$ with four equivalents of $[Zn_2Cp^*_2]$ in toluene at 95 °C over a period of 2 h leads to the quantitative formation of a mixture of the six-coordinate complex $[Pd(GaCp^*)_2(ZnCp^*)_2(ZnZnCp^*)_2]$ (**1**) and the eight-coordinate complex $[Pd(ZnCp^*)_4(ZnZnCp^*)_4]$ (**2**) in a molar ratio of 6:1, as revealed by in situ NMR spectroscopy (Scheme 1). Orange crystals of **1** and red needle-shaped crystals of **2** deposit from a saturated toluene solution at −30 °C overnight. Both complexes are stable in solution from room temperature up to 100 °C for prolonged periods, but decompose rapidly within a few seconds after separation of crystallized material from the supernatant mother liquor and subsequent drying. When covered by solvent, the individual crystals are more stable. First signs of decomposition were, however, seen after a few minutes. Notably, the homologous platinum compounds were obtained by treatment of $[Pt(GaCp^*)_4]$ with $[Zn_2Cp^*_2]$ (see the Supporting Information).

$$[Pd(GaCp^*)_4] \xrightarrow[\text{toluene, 95 °C, 1.5 h}]{[Zn_2Cp^*_2]} \begin{array}{c}[Pd(GaCp^*)_2(ZnCp^*)_2(ZnZnCp^*)_2]\ (\mathbf{1})\\ +\\ [Pd(ZnCp^*)_4(ZnZnCp^*)_4]\ (\mathbf{2})\end{array}$$

Scheme 1. Synthesis of compound **1** and **2** (for Pt homologues, see the Supporting Information).

By manual separation of the different crystals under a microscope in a glove box in the presence of solvent, samples of analytically pure **1** can be obtained, whereas it was not possible to collect substantial amounts of pure **2** suitable for

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C/H microanalysis or NMR spectroscopy before the crystals decompose. The molar ratio of isolated crystals of **1** and **2** was estimated to be 10:1. Nevertheless, single-crystal X-ray diffraction (XRD) studies allowed the determination of the molecular structures of **1** and **2** (see below) and also their platinum homologues. The Ga/Zn content of **1** (9.5 wt% Ga) was obtained by atomic absorption spectroscopy (AAS), and theoretical calculations at the DFT level of theory confirm the Ga/Zn assignment deduced by NMR spectroscopy and XRD (Figure 1 and Figure 2). The ^{1}H NMR spectrum of **1** in C_6D_6 recorded at room temperature reveals three sharp signals at $\delta = 1.87$, 2.15, and 2.31 ppm, with an intensity ratio of 1:1:1. The ^{13}C NMR spectrum shows the expected signal pattern for three non-equivalent Cp* groups. These three signals represent the three chemically different Cp* substituents, assigned as the {GaCp*}, {ZnCp*}, and {ZnZnCp*} moieties, which were all found in the solid-state structure of **1**.

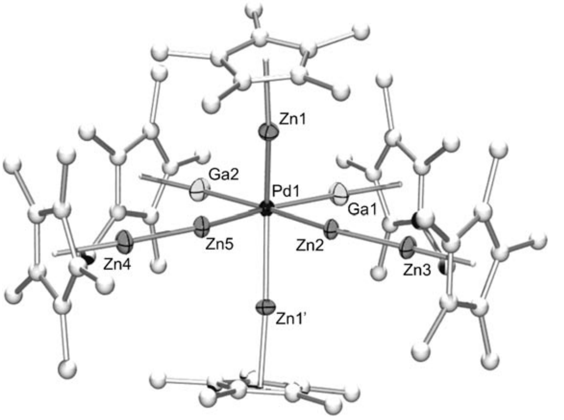

Figure 1. Molecular structure of $[Pd(GaCp^*)_2(ZnCp^*)_2(ZnZnCp^*)_2]$ (**1**) in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.[17] Selected bond lengths [Å] and angles [°]: Pd1–Ga1 2.359(1), Pd1–Ga2 2.360(1), Pd1–Zn1 2.448(1), Pd1–Zn5 2.375(1), Pd1–Zn2 2.379(1), Zn5–Zn4 2.345(1), Zn2–Zn3 2.346(1), Zn1–$Cp^*_{centroid}$ 1.954, Zn4–$Cp^*_{centroid}$ 1.938, Zn3–$Cp^*_{centroid}$ 1.941, Ga1–$Cp^*_{centroid}$ 1.954, Ga2–$Cp^*_{centroid}$ 1.969; Zn1-Pd1-Zn1′ 129.73(4), Ga2-Pd1-Ga1 103.76(4), Ga2-Pd1-Zn5 86.39(4), Zn5-Pd1-Zn2 88.29(3), Zn2-Pd1-Ga1 81.56(4), Zn4-Zn5-Pd1 170.31(5), Zn3-Zn2-Pd1 170.45(5), Ga2-Pd1-Zn2 174.68(4), Ga1-Pd1-Zn5 169.85(4), $Cp^*_{centroid}$-Zn4-Zn5 175.62, $Cp^*_{centroid}$-Zn2-Zn3 178.79, $Cp^*_{centroid}$-Zn1-Pd1 169.68, $Cp^*_{centroid}$-Ga1-Pd1 176.10, $Cp^*_{centroid}$-Ga2-Pd1 174.85.

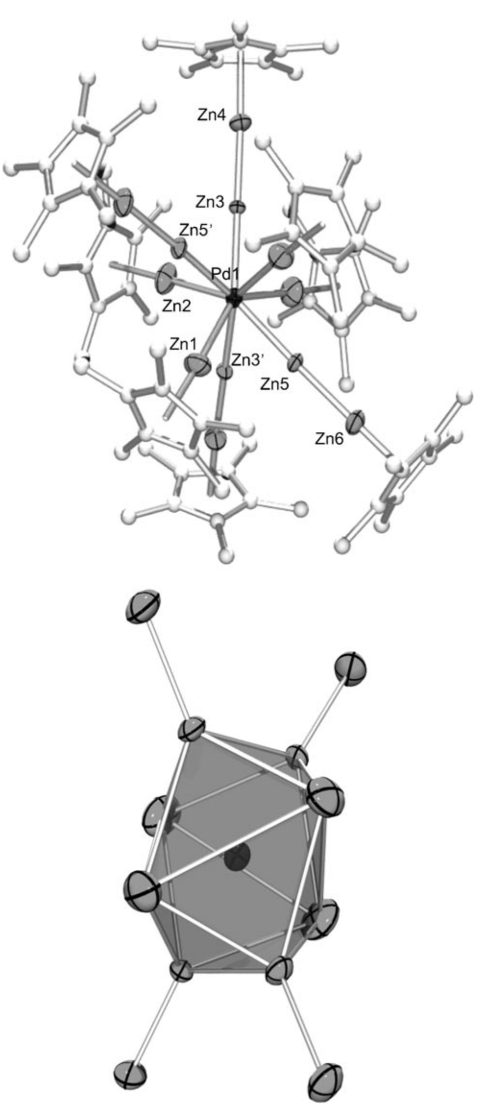

Figure 2. Top: Molecular structure of $[Pd(ZnCp^*)_4(ZnZnCp^*)_4]$ (**2**) in the solid state. Ellipsoids are set at 50% probability; hydrogen atoms are omitted for clarity.[19] Bottom: The $\{PdZn_8\}$ core of **2**. Selected interatomic distances [Å] and angles [°]: Pd1–Zn1 2.422(2), Pd1–Zn2 2.433(2), Pd1–Zn3 2.478(2), Pd1–Zn5 2.473(2), Zn3–Zn4 2.351(3), Zn5–Zn6 2.347(3), Zn1–$Cp^*_{centroid}$ 1.981, Zn2–$Cp^*_{centroid}$ 2.004, Zn4–$Cp^*_{centroid}$ 2.002, Zn6–$Cp^*_{centroid}$ 2.013; Pd1-Zn3-Zn4 179.69(13), Pd1-Zn5-Zn6 177.70(11), Zn5-Pd1-Zn5′ 134.40(12), Zn3-Pd1-Zn3′ 131.40(11), Zn3-Zn4-$Cp^*_{centroid}$ 178.00, Zn5-Zn6-$Cp^*_{centroid}$ 178.62, Pd1-Zn1-$Cp^*_{centroid}$ 176.53, Pd1-Zn2-$Cp^*_{centroid}$ 179.19.

The reaction was monitored by ^{1}H NMR in C_6D_6 by heating a mixture of the starting materials to 75 °C for 1.5 h and subsequently recording NMR spectra. By subtracting the signals of pure **1** from a ^{1}H NMR spectrum of the reaction mixture after quantitative conversion of the starting materials, two signals of **2** at $\delta = 2.19$ and 2.31 ppm with an intensity ratio of 1:1 are found, which correspond to the {ZnCp*} and {ZnZnCp*} fragments. The assignment of ^{13}C NMR data for **2** could not be carried out owing to the low concentration of **2** in the product mixture. Fulvalene species, which may result from dimerization of free Cp* radicals, were not detected. Along with the resonances for **1** and **2**, the ^{1}H NMR spectrum of reaction mixture exhibits a very broad signal at $\delta = 1.90$ ppm, which is assigned to a coalescence peak of {GaCp*} and $\{ZnCp^*_2\}$ probably via an instable fluxional intermediate, such as $\{Cp^*Ga \cdots ZnCp^*_2\}$ (see the Supporting Information).[14] Both species were not observed in our previous studies on the synthesis of $[TM(ZnR)_n]$ compounds from $[TM(GaCp^*)_m]$ and ZnR_2 mentioned in the introduction.[11,12] The observation of free [GaCp*] and $[ZnCp^*_2]$ as by-products is consistent with the expectation that the formation of **1** and **2** should not involve redox reactions between TM, Ga, and Zn, but rather proceed by dissociation of {GaCp*} from $[Pd(GaCp^*)_4]$ and addition of the Zn–Zn bond, that is, trapping of monovalent $\{^{\bullet}ZnCp^*\}$ at electronically and coordinatively unsaturated palladium centers. This reasoning is also consistent with the quite low yield of **2** with respect to **1**, assuming that the {GaCp*} dissociation equilibrium of **1** is shifted to the adduct side in the presence of free [GaCp*], thus inhibiting Pd–Zn bond formation with increasing product concentration. The formation of the novel one-electron {$^{\bullet}$ZnZnCp*} ligand with an intact Zn–Zn bond can be explained by Cp* transfer reactions between the starting compound [Zn_2Cp*_2] and the Zn centers of lower-coordinate intermediate species of the type [$L_aPd(ZnCp*)_b$] (L = {GaCp*} or {ZnCp*}), which lead to the release of [$ZnCp*_2$] as the second by-product. Interestingly, the combination of [Zn_2Cp*_2] with [GaCp*] gives no reaction, and neither adduct nor decomposition is observed by NMR spectroscopy. [Zn_2Cp*_2] is usually refered to as a Zn^I compound.[3] The Allen spectroscopic electronegativities of Pd and Zn are equal (1.59) and thus we regard **1** and **2** as Pd^0 complexes. However, we follow Parkin's arguments and rather point out the low coordination and the essentially divalent type of bonding of the Zn (and Ga) atoms in **1** and **2** and avoid mixing the discussion of (formal) oxidation states into this description.[15] Nevertheless, the Zn atoms of the {ZnZnCp*} moieties of **1** and **2** have chemically different surroundings, and the presence of [$ZnCp*_2$] as the stoichiometric by-product for each {ZnZnCp*} unit trapped as a ligand to Pd suggests the reaction in Scheme 1 is a formal disproportionation of a part of the Zn^I species into Zn^0; that is, {Zn^0Zn^ICp*}, and Zn^{II}, that is, {$Zn^{II}Cp*_2$}. Related investigations of using [Zn_2Cp*_2] as a synthetic equivalent of monovalent {$^{\bullet}$ZnCp*} to react with substitution labile transition metal complexes in the absence of {GaCp*} (and other strongly coordinating, neutral two-electron ligands) is a matter of our ongoing research. For instance, the reaction of [$M(cod)_2$] (M = Ni, Pt; cod = 1,5-cyclooctadiene) with [Zn_2Cp*_2] leads to a variety of products, two of which could be identified as [$Cp*M(ZnCp*)_3$] (M = Ni, Pt) and [$Ni(ZnCp*)_4(ZnZnCp*)_4$] (see the Supporting Information).[16]

The result of a single-crystal X-ray diffraction study of **1** is depicted in Figure 1. The molecular structure emphasizes the octahedral arrangement of the six Ga/Zn ligands around the central palladium atom. As gallium and zinc are not unambiguously distinguishable by standard X-ray crystallography owing to very the similar scattering power, the assignment of Ga/Zn in the solid-state structure of **1** was supported by DFT calculations.[31] To assign the metal (M) positions to either Zn or Ga, in a first step single-point energy calculations were performed at BP86/def2-TZVPP[32,34] for all 28 possible permutations of two Ga and six Zn atoms over the eight M positions, including the {MMCp*} moieties. The experimental structure data of **1** was used for the calculations, but the methyl groups of the Cp* moieties were replaced by hydrogen atoms to reduce the otherwise exceedingly large computational cost of calculating the full system. Cartesian coordinates of this model system **1H** are given in the Supporting Information. The lowest-energy structure of all of the calculated isomers of **1H** turned out to be the analogue of structure **1** shown in Figure 1. Four other isomers were calculated to be higher in energy by less than 15 kcal mol^{-1} (see Table S2 in the Supporting Information). Using different density functionals, single-point calculations of these five isomers were then performed using the crystal structure of **1** without replacing the methyl groups by hydrogen (see Supporting Information for details) to substantiate the conclusion of our calculations. The isomer as assigned in Figure 1 remains the lowest in energy in all cases (see Table S3 in the Supporting Information for the calculated relative energies of the isomers with different functionals). As the Pd–Zn and Pd–Ga bond lengths resulting from this assignment are in good agreement with corresponding bond lengths in other comparable compounds (see below), the calculated results strongly support the assignment of the Ga and Zn positions as given in Figure 1.

The coordination geometry around the Pd atom in **1** is best described as a distorted octahedron, with a strong deviation from linearity for the Zn1-Pd1-Zn1′ linkage of the {Cp*Zn-Pd-ZnCp*} unit (129.73(4)°). The deviations of all other characteristic bond angles from the ideal octahedral structure are small. Furthermore, the Zn-Zn-Pd groups are almost linear with 170.31(5)° for Zn4-Zn5-Pd1 and 170.45(5)° for Zn3-Zn2-Pd1, and the angles $Cp*_{centroid}$-M-Pd (M = Ga, Zn) are quite linear, with the notable exception of $Cp*_{centroid}$-Zn1-Pd1 (169.68°). These features suggest that the deviation of the inner {PdM_6} core from ideal octahedral structure can be explained by steric reasons caused by the bulky Cp* ligands at Zn1 and Zn1′. The Zn–Zn bond lengths (2.345(1) and 2.346(1) Å) are in good agreement with the Zn–Zn distance in the parent compound [Zn_2Cp*_2] (2.331 Å).[3] The Pd–Ga bonds (2.359(1) and 2.360(1) Å) match well with the average Pd–Ga bond in [$Pd(GaCp*)_4$] (2.354(1) Å).[18] Interestingly, the Pd–Zn bond lengths are significantly different. Whereas the Pd–ZnCp* distances (av. 2.448(1) Å) are similar to the Pd–Zn bond in [$Pd(ZnCp*)_4(ZnMe)_4$] (2.447(1)–2.459(1) Å),[11] the Pd–ZnZnCp* distances are distinctly shorter (2.375(1) and 2.379(1) Å). Whether this fact can be attributed only to the decreased steric demand of the {ZnZnCp*} group with respect to the {ZnCp*} ligand or also to a higher π character of the interaction between the bare Zn atom to Pd cannot be determined at this point and is part of ongoing work. The $Cp*_{centroid}$–M distances (M = Ga, Zn) are almost equal to values for $Cp*_{centroid}$–Zn1 (1.954 Å) and $Cp*_{centroid}$–Ga (av. 1.962 Å). Both data sets show only slight deviation from the reference compounds [$Pd(ZnCp*)_4(ZnMe)_4$] ($Cp*_{centroid}$–Zn 1.934 Å) and [$Pd(GaCp*)_4$] (Ga–$Cp*_{centroid}$ 2.019 Å), but are longer than the $Cp*_{centroid}$–ZnZn distances of 1.940 Å (av.). Interestingly, this latter bond distance is significantly shorter than found in the parent compound [Zn_2Cp*_2] (2.04 Å), which points to an increased ionic contribution for the coordinated {ZnZnCp*} moieties.

Figure 2 shows the molecular structure of **2** as obtained by single-crystal X-ray diffraction.[19] The presence of Ga in the actual crystal could not be unambiguously ruled out by AAS because of the small amount of **2** that could be isolated as well as rapid decomposition of crystalline material. Thus, the assumption of a {$PdZn_{12}$} composition of **2** is based on the structural and computational analysis of **1** together with heuristic reasoning based on electron counting, as all homoleptic [$M(ZnR)_x$] and heteroleptic [$M(ZnR)_x(GaR)_y$] compounds synthesized and characterized to date perfectly fulfill the eighteen valence-electron rule.[11,12] The coordination polyhedron of the inner {$PdZn_8$} core of **2** can be best described as a slightly distorted trigonal dodecahedron (Figure 2), which is comparable to [Pd(ZnCp*)$_4$(ZnMe)$_4$].[11] The Zn–Zn bond distances of the four {ZnZnCp*} units (2.347(3)–2.351(3) Å) are in line with the Zn–Zn bond parameters of [Zn$_2$Cp*$_2$] (2.331 Å) and compound **1** (2.345(1) and 2.346(1) Å).[3] With distances of 2.473(2) to 2.478(2) Å, the Pd–ZnZn interaction is distinctly longer than those in **1**, and significantly elongated in comparison to the Pd–ZnCp* distances (2.422(2)–2.433(2) Å). The Zn–Cp*$_{\text{centroid}}$ distances are all very similar, with average values of 1.993 Å for {ZnCp*} and 2.008 Å for the {ZnZnCp*} units. Interestingly, the angles of Pd-Zn-Zn and Pd-Zn-Cp*$_{\text{centroid}}$ are almost linear (Pd1-Zn3-Zn4 179.69(13)°, Pd1-Zn5-Zn6 177.70(11)°, Pd1-Zn1-Cp*$_{\text{centroid}}$ 176.53°, and Pd1-Zn2-Cp*$_{\text{centroid}}$ 179.19°). The linearity can be also observed for Zn-Zn-Cp*$_{\text{centroid}}$, giving an average value of 178.31°. As a consequence of the trigonal dodecahedral structure, a strong deviation from linearity is found for the five metal-atom chains Zn-Zn-Pd-Zn-Zn, with values of 134.40(12)° for Zn5-Pd1-Zn5′ and 131.40(11)° for Zn3-Pd1-Zn3′. Molecular compounds featuring finite metal-atom chains are well known in literature. Typically, however, the metal atoms are supported by additional bridging ligands, for example, [(NH$_3$)$_4$-Pt$_2$(C$_5$H$_5$N$_2$O$_2$)$_2$Ag(C$_5$H$_5$N$_2$O$_2$)$_2$Pt$_2$(NH$_3$)$_4$]$^{5+}$ and [Pt$_6$(μ-H)(μ-dpmp)$_4$(XylNC)$_2$]$^{3+}$[20,21] (dpmp = bis(diphenylphosphanylmethyl)phenylphosphane; Xyl = 2,6-dimethylphenyl) or [Ni$_5$(μ$_5$-tpda)$_4$Cl$_2$] and [Ru$_5$(μ$_5$-tpda)$_4$(NCS)$_2$]) (tpda = tripyridyldiamine).[22,23] Similarly, infinite mixed-metal chains are known for various metal/ligand combinations in coordination polymers.[24,25] In comparison, compound **2** is among the very few examples[26] of molecular compounds featuring oligo (hetero) metal chains without stabilization of the internal chain atoms by ligands, similar to the ligand-free, infinite metal chains in some solid state compounds, for example, Hg$_3$(AsF$_6$)$_2$ and Hg$_4$(AsF$_6$)$_2$).[27,28]

Notably, treatment of [(Pd,Pt)(GaCp*)$_4$] with a large excess of [Zn$_2$Cp*$_2$] does not lead to products with a (Ga + Zn)/(Pd,Pt) coordination number of more than eight. For example, icosahedral homoleptic molecular compounds [(Pd,Pt)(ZnR)$_{12}$] exhibiting (Pd,Pt)Zn$_{12}$ cores known from intermetallic (Pd,Pt)/Zn phases[29,30] and being similar to the MoZn$_{12}$ core of [Mo(ZnCp*)$_3$(ZnMe)$_{12}$] turn out to be notoriously inaccessible. It might be speculated that such compounds can be achieved by a substitution of all four {GaCp*} and then trapping twelve {$^{\bullet}$ZnCp*} groups supplied by six molar equivalents of [Zn$_2$Cp*$_2$] at the Pd or Pt center. However, the stability of the products in such reactions (if steric constraints are neglected) appears to be strictly predictable by the classic eighteen-electron rule, which is explained well by the frontier orbital analysis of the [TM(MR)$_n$] cores.[11] The title compounds are eighteen-electron closed-shell species if {GaCp*} is counted as two-electron and the {ZnCp*} and {ZnZnCp*} moieties are treated as one-electron ligands. Thus, the bonding situation of **2** is likely to be very similar to [Pd(ZnCp*)$_4$(ZnMe)$_4$], and the details of this comparison will be reported elsewhere. From this perspective, we suggest that even homoleptic compounds of formula [(Ni,Pd,Pt)(ZnZnCp*)$_8$] could be stable and may represent interesting targets for synthesis.

In summary, our data support the conceptual view of [Zn$_2$Cp*$_2$] as synthetic equivalent of two types of novel one-electron metal-atom ligator ligands at transition metal centers, namely $^{\bullet}$ZnCp* and $^{\bullet}$ZnZnCp* with the surprising persistence of the covalent Zn–Zn linkage in the latter. This particular structural feature of **1** and **2** and their platinum homologues further links the molecular chemistry outlined herein to the solid-state chemistry of zinc-rich Hume-Rothery solid-state phases with structures featuring interstitial zinc/transition metal polyhedra fused together by bonding Zn–Zn contacts.[29,30] Thus, the title compounds may be useful as building blocks to achieve even larger molecular units with comparable structural motifs.

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[14] The exact nature of this coalescence is not yet clear. However, a 1:1 mixture of [ZnCp*$_2$] and [GaCp*] in C$_6$D$_6$ shows only one set of broad Cp* signals, both in the ^{1}H NMR (δ = 1.89 ppm) and ^{13}C NMR spectrum (δ_C = 112.12 and 10.72 ppm). The line width of free [GaCp*] (0.46 Hz) is increased by addition of [ZnCp*$_2$] (0.83 Hz). The exact linewidth of the coalescence peak should increase with decreasing concentration, as it is reasonable to assume that the rate-determining step of the coalescence is the formation of an adduct of [GaCp*] and [ZnCp*$_2$].

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