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Synthesis, Reactivity and Applications of Zinc-Zinc Bonded Complexes

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Abstract

The discovery of decamethyldizincocene [$Zn_2(\eta$-Cp*$)_2$] (Cp* = C_5Me_5), the first complex containing a covalent zinc-zinc bond, by Carmona in 2004 initiated the search for this remarkable class of compounds. Low-valent organozinc complexes can either be formed by ligand substitution reactions of [$Zn_2(\eta$-Cp*$)_2$] or by reductive coupling reactions of Zn(II) compounds. To the best of our knowledge, until now 25 low-valent Zn-Zn bonded molecular compounds stabilized by a variety of sterically demanding, very often chelating, organic ligands have been synthesized and characterized. There are two major reaction pathways of [$Zn_2(\eta$-Cp*$)_2$]: It can either react with cleavage of the Zn-Zn bond or by ligand substitution. In addition, upon reaction with late transition metal complexes, [$Zn_2(\eta$-Cp*$)_2$] was found to form novel intermetallic complexes with Cp*Zn and Cp*Zn_2 acting as unusual one-electron donor ligands. Very recently, the potential capability of [$Zn_2(\eta$-Cp*$)_2$] to serve as suitable catalyst in hydroamination reactions was demonstrated. Finally, the recent work on Cd-Cd bonded coordination compounds is reviewed.

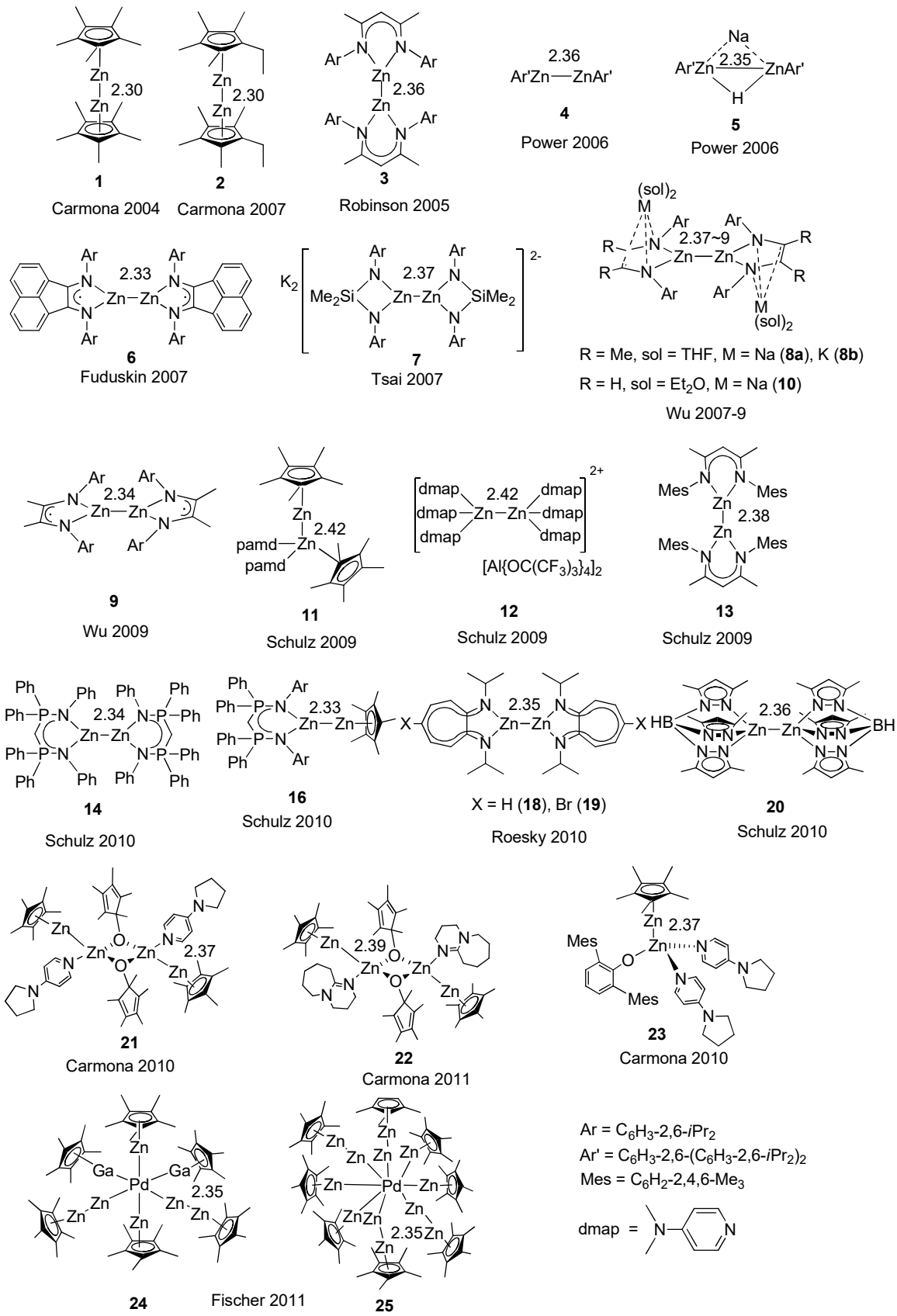
1. Introduction

Metal-to-metal bonds in clusters and molecules are of fundamental interest in many areas of natural science.[1, 2] In coordination chemistry of transition metals, single and multiple metal-to-metal bonds are well established since the pioneering work in the mid-1960s.[3] The frontiers of new and unusual combinations of metal-to-metal bonds are now being explored rapidly.[4-6] Thus, the synthesis of gallium-gallium multiple bonds,[7, 8] stable chromium compounds with fivefold bonding between the two chromium centers,[9-16] the unexpected coordination of early main group metals with the *f*-elements,[17] and the recently published Mg-Mg bond[18] opened new opportunities in this area.

A covalent zinc-zinc bond was not known until the landmark discovery of the dimetallic sandwich compound decamethyldizincocene, $[Zn_2(\eta\text{-Cp*})_2]$ (**1**) (Cp* = C_5Me_5), by Carmona and coworkers in 2004.[19] Prior to this study, only a single report on the synthesis of Zn_2Cl_2, obtained in a $Zn/ZnCl_2$ melt, pointed to the possible formation of low-valent Zn species.[20]

This stands in remarkable contrast to salt-like inorganic compounds containing the $[Hg_2]^{2+}$ dication such as as Hg_2Cl_2, whereas structurally characterized compounds containing the $[Cd_2]^{2+}$ dication are also still limited to $[Cd_2][AlCl_4]_2$.[21-23] In addition, a very few molecular Hg_2R_2 (R = $Si(SiMe_2SiMe_3)_3$,[24] C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$,[25] and $[Cd_2R_2]$ (R = C_6H_3-2,6-(C_6H_3-2,6-Pr^i_2)$_2$)[25] complexes have been structurally characterized. In the following years, several studies were performed in order to understand the formation of Zn-Zn bonded complexes and to reveal the nature of the Zn-Zn bonds. To the best of our knowledge, 25 low-valent Zn-Zn bonded molecular compounds stabilized by a variety of organic ligands, as shown in Scheme 1, have been synthesized and characterized since then. Moreover, the chemical reactivity of dizincocene has been studied in detail.

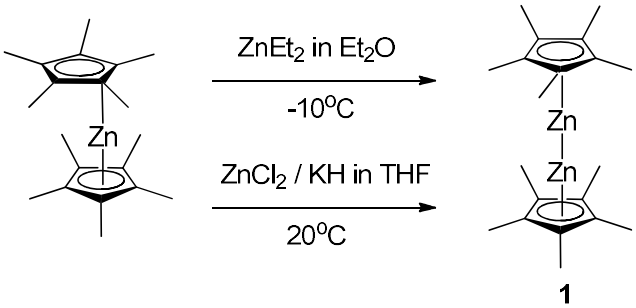
Dizincocene and other Zn-Zn complexes, which have been reviewed before, will be described only briefly.[26-28] In this review, we will focus on the most recent development of Zn-Zn bonded complexes, which include the reactivity of dizincocene, the synthesis and structure of novel Zn-Zn bonded complexes and the catalytic application of dizincocene.



Scheme 1. Structurally characterized low valent Zn-Zn bonded complexes. Authors and year of publication are shown. Zn-Zn bond lengths are given in Ångstrom.

2. Synthesis, structure, and properties of dizincocenes

$[Zn_2(\eta\text{-Cp*})_2]$ (**1**), which has the unusual formal oxidation state +1, was unexpectedly formed in rather low yield via reductive coupling reaction of $ZnEt_2$ and $[Zn(\eta\text{-Cp*})_2]$. In contrast, the reductive coupling reaction between $ZnCl_2$, $[Zn(\eta\text{-Cp*})_2]$ and KH as the reducing agent at 1:1:2 molar ratio gives **1** in higher yield (Scheme 2).[29] The possible formation of a hydride-bridged zincocene $[(\eta\text{-Cp*})ZnH]_2$ has been eliminated by high-resolution mass spectrometry. NMR, IR and Raman spectroscopy also support the dizincocene formulation.[19]



Scheme 2

The electrochemical behavior of **1** and $[Zn(\eta\text{-Cp*})_2]$ has been studied by cyclic voltammetry. Two similar mono-electronic oxidation steps have been observed for both **1** ($E_{1/2}$ = -0.195 and 0.300 V) and $[Zn(\eta\text{-Cp*})_2]$ ($E_{1/2}$ = -0.230 and 0.270 V). Compound **1** shows slightly more positive potentials than $[Zn(\eta\text{-Cp*})_2]$.[30]

The only other example of a dizincocene, $[Zn_2(\eta\text{- }C_5Me_4Et)_2]$ (**2**), was reported in 2007. It was obtained by reduction of $Zn(C_5Me_4Et)_2/ZnCl_2$ with KH.[29] Both **1** and **2** are air and moisture sensitive. The less symmetric compound **2** is less thermally stable than **1** and decomposes between 0 and 20 °C. Several attempts to synthesize other dizincocenes $[Zn_2(\eta\text{-Cp'})_2]$ (Cp' = C_5H_5, C_5Me_4H, $C_5Me_4SiMe_3$, C_5Me_4tBu) by the same synthetic method failed. Surprisingly, the substituents on the Cp ring have strong impact on the stability and therefore formation of dizincocenes. X-ray diffraction studies showed that **1** (Figure 1) and **2** have

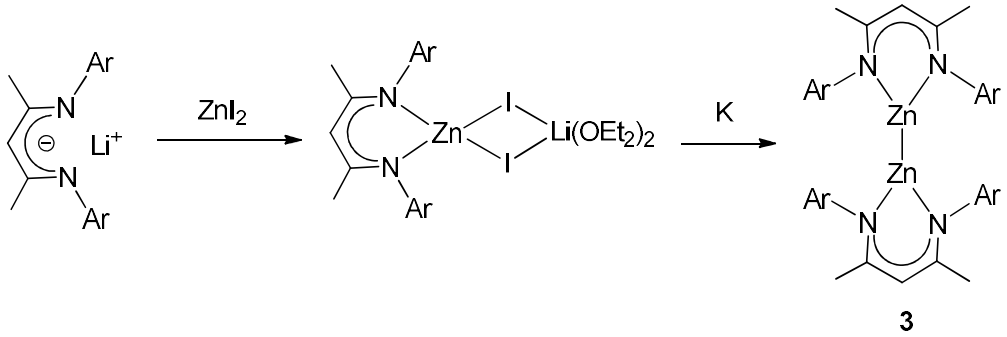
almost identical structures in the solid state. The Zn_2 moiety is sandwiched by two parallel Cp* rings and the Zn-Zn bond distances of approximately 2.30 Å are shorter than the sum of the covalent radii of 2.36 Å,[31] which indicates a bonding interaction between two zinc atoms. The Cp^*_{centr}-Zn-Zn- Cp^*_{centr} arrangement is almost linear.[29] Computational calculations clearly showed that the Zn-Zn bond is mostly formed by an overlap between the Zn 4s orbitals, while the Zn 4p orbitals mainly interact with the η^5-Cp* ligand.[32-34]

Figure 1

here

3. Synthesis and structure of other zinc-zinc bonded complexes

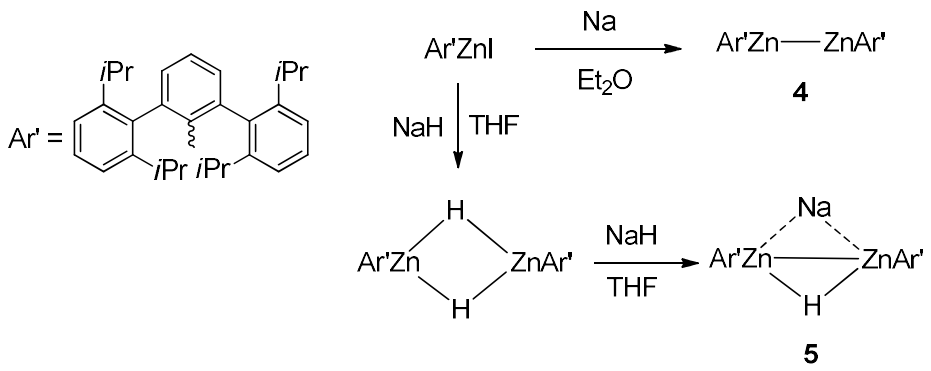
Sterically demanding as well as chelating organic ligands have been proven to be successful candidates for kinetically stabilizing the metal-metal bond in low-valent metal complexes.[7, 35-37] In 2005, Robinson and coworkers prepared the second Zn-Zn bonded complex bearing a sterically demanding β-diketiminate ligand L' ([{(C_6H_3-2,6-*i*Pr_2)N(Me)C}$_2$CH]$^-$). [L'Zn-ZnL'] (**3**) was synthesized by reductive coupling reaction of [LZn(μ-I)$_2$Li(OEt$_2$)$_2$], which was obtained from the reaction of LiL with ZnI_2 in Et_2O, with potassium (Scheme 3).[38]



Scheme 3

^{1}H NMR studies confirmed the formation of **3**, whereas no indication on the formation of a bridging or terminal zinc hydride complex was found. A single crystal X-ray structure determination of **3** showed that each zinc atom is coordinated by two nitrogen atoms from the bidentate β-diketiminate ligand and another zinc atom, hence leading to a trigonal-planar coordination mode. The Zn-Zn bond length of 2.3586(7) Å is only 0.05 Å longer than that of **1**. It is clear that the Zn-Zn bond length strongly depends on the type of ligands. The six-membered C_3N_2Zn ring adopts a puckered configuration with the Zn atom out of the plane by 0.65 Å. DFT calculation suggested the Zn-Zn bond mainly derives from the s orbital overlap (95 %).[38]

Power and coworkers have synthesized a Zn-Zn bonded complex stabilized by a monodentate, sterically demanding aryl ligand Ar' (C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$).[25] The reduction of [Ar'ZnI] with sodium gave [Ar'Zn-ZnAr'] (**4**) in good yield. In addition, the bridging hydride complex [Ar'Zn(μ-H)$_2$ZnAr'] as well as the unprecedented sodium hydride bridging complex [Ar'Zn(μ-Na)(μ-H)ZnAr'] (**5**) with a new type of Zn-Zn interaction were prepared by reducing [Ar'ZnI] with different amounts of NaH in THF (Scheme 4).[25]

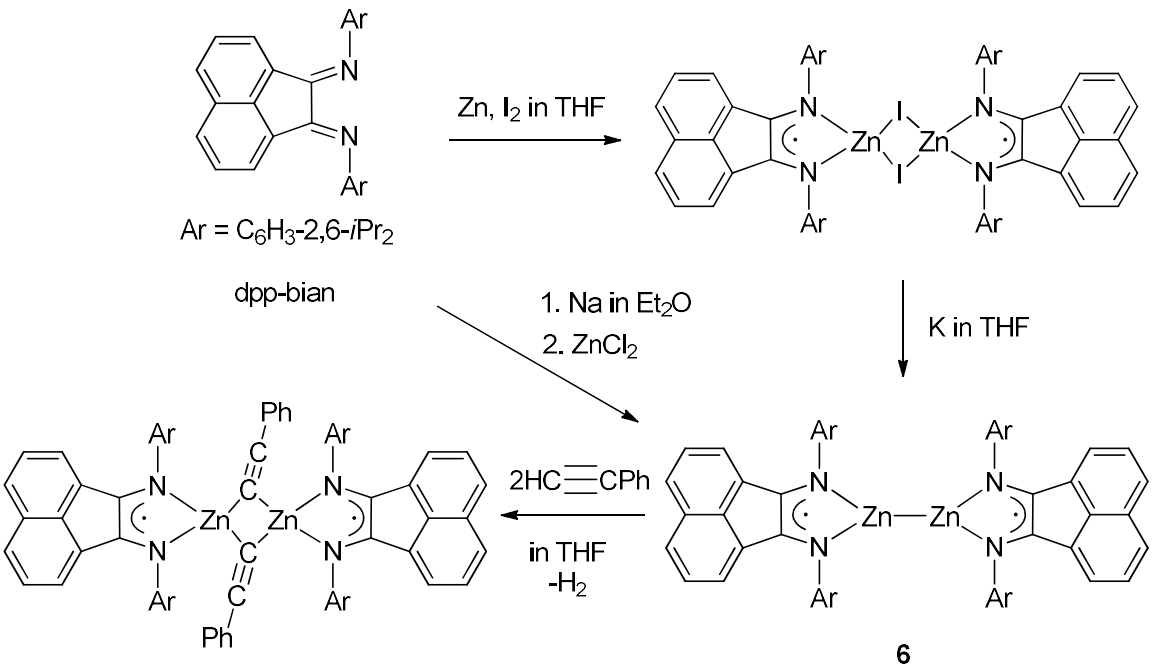


Scheme 4

X-ray diffraction studies showed that the Zn-Zn bond lengths in **4** (2.3591(9) Å) and **5** (2.352(2) Å) were essentially the same as that in compound **3**. In addition, the perpendicular

orientation of the two Ar' ligands in **4** is very similar to that in **3**. In contrast to **3** and **4**, the two central aryl rings of the ligand in **5** are almost in the same plane. The interior C-Zn-Zn-C in **4** and **5** arranges almost linearly. DFT calculation showed that the $4p_z$ orbitals were mainly used in Zn-Zn bond formation in **4**, in remarkable contrast to the mainly s-orbital contribution in **1** and **3**. A new type of Zn-Zn bond formed by a delocalized orbital from the bridging hydride and two Zn atoms was observed in **5**.[39]

Fedushkin and coworkers prepared the Zn-Zn bonded complex **6** containing a radical anionic ligand, 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene (dpp-bian). As seen from Scheme 5, the formation of complex **6** can be obtained in two ways: 1) by reduction of $[\{(dpp\text{-}bian)ZnI\}_2]$ with K in THF; 2) by the direct reaction of $ZnCl_2$ with in situ generated [Na(dpp-bian)] from dpp-bian and Na in Et_2O.[40] The redox reaction of **6** with PhC≡CH occurred with formation of a dinuclear acetylene bridged Zn(II) complex $[\{(dpp\text{-}bian)Zn(\mu\text{-}C{\equiv}CPh)\}_2]$ with elimination of hydrogen by reducing the proton from PhC≡CH.[41]



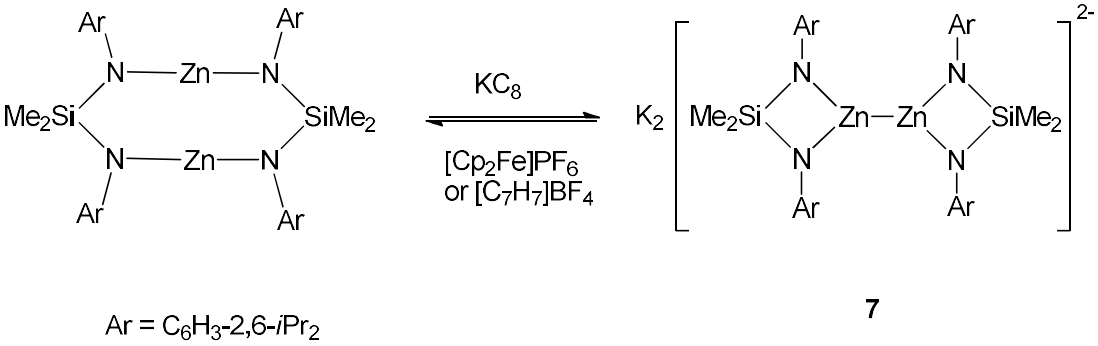
Scheme 5

The single crystal X-ray structure of **6** as shown in Figure 2 confirms that two metallacycles ZnC_2N_2 adopt an almost coplanar orientation to each other. DFT calculations confirmed the radical anionic nature in **6** and revealed that the metal s-orbital was contributing with 93.9% to the Zn-Zn bond, which is slighter shorter (2.3321(2) Å) than those in **3**-**5**.[40]

Figure 2

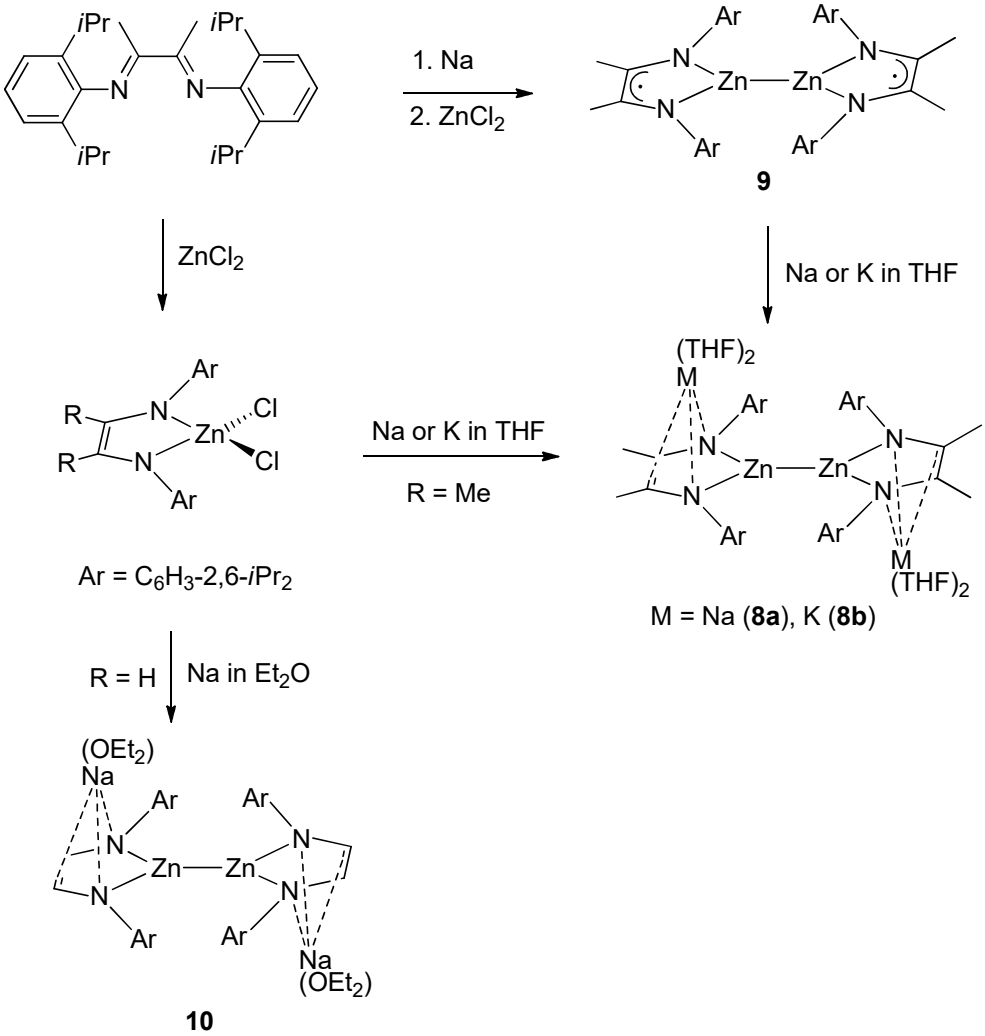
here

Based on their previous findings on the synthesis of a quadruply bonded Mo-Mo complex stabilized by a dianionic diamide ligand, $[Me_2Si(NC_6H_3\text{-}2,6\text{-}iPr_2)_2]^{2-}$,[42] Tsai and coworkers prepared a neutral dinuclear Zn(II) precursor $[Zn_2(\mu\text{-}\eta^2\text{-}Me_2Si(NC_6H_3\text{-}2,6\text{-}iPr_2)_2)_2]$,[43] from which the Zn-Zn bonded complex **7** was obtained by reductive coupling reaction with 4 equiv of KC_8. Interestingly, the oxidation of **7** with weak oxidants, such as $[Cp_2Fe]PF_6$ or $[C_7H_7]BF_4$, partially reverted to the precursor complex (Scheme 6). The single crystal X-ray structure of **7** revealed a slightly longer Zn-Zn bond distance of 2.370(2) Å than those of **3**-**5**.[43]



Scheme 6

Wu and coworkers have synthesized several new Zn-Zn bonded complexes stabilized by a dianionic α-diimine ligand L ($[(C_6H_3\text{-}2,6\text{-}i\text{Pr}_2)NC(Me)]_2^{2-}$). The neutral α-diimine complex $[LZnCl_2]$ was doubly reduced by Na or K in THF to form two Zn-Zn bonded complexes $[M(THF)_2]_2[L\text{-}Zn\text{-}Zn\text{-}L]$, **8a** (M = Na) and **8b** (M = K) (Scheme 7).[44, 45] One electron reduction of the *in situ* generated Na_2L and $ZnCl_2$ formed a new Zn-Zn complex **9** with a monoanionic radical ligand, $[(C_6H_3\text{-}2,6\text{-}i\text{Pr}_2)NC(Me)]_2^{-}$. Further reduction of **9** with Na or K in THF led to **8a** or **8b**.[46] However, by using a similar ligand, ($[(C_6H_3\text{-}2,6\text{-}i\text{Pr}_2)NCH]_2^{2-}$, simply by alternating the backbone of diimine from methyl to hydrogen, the Zn-Zn bonded complex **10** could only be obtained by doubly reduction of $[LZnCl_2]$ with Na but not with K, which resulted in disproportionation reaction (Scheme 7). A formal replacement of the phenyl substituents on the ligands from 2,6-iPr$_2$ to 2,6-Me$_2$, 2,6-Et$_2$, or 2,4,6-Me$_3$ led to mononuclear Zn(II) complexes.[47]



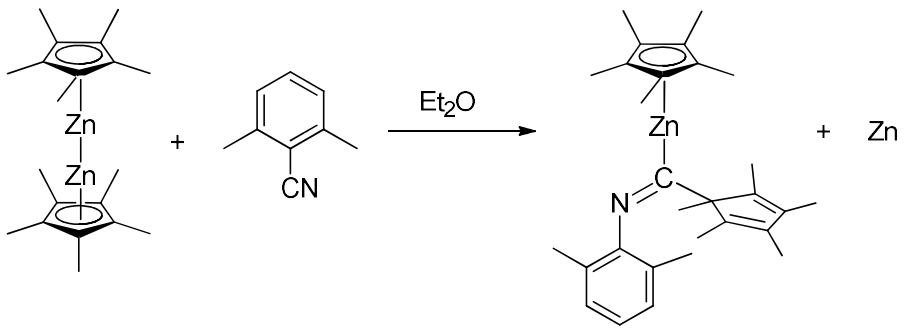
Scheme 7

The Zn-Zn bonded complexes containing non-innocent diimine ligands **8a**, **8b**, **9** and **10** were characterized by single crystal X-ray diffraction. **8a** and **8b** were found to have an almost identical structure and Zn-Zn bond lengths of 2.399(1) and 2.393(1) Å, respectively. The two C_2N_2Zn planes are nearly coplanar in **8a** and **8b**, whereas those in **9** are twisted with a dihedral angle of 46.4°. As a result, the Zn-Zn bond length in **9** (2.340(2) Å) is shorter than those in **8a** and **8b**, but comparable to those observed in **3**-**6**. DFT calculation showed that the Zn-Zn bond in **9** was formed by 4s-orbitals with a nearly 96% contribution. Although **10** has a similar structure as **8a** and **8b**, the Zn-Zn bond length of 2.3673(6) Å in **10** is shorter than those in **8a** and **8b**.[44-47]

4. Reactivity studies of dizincocene

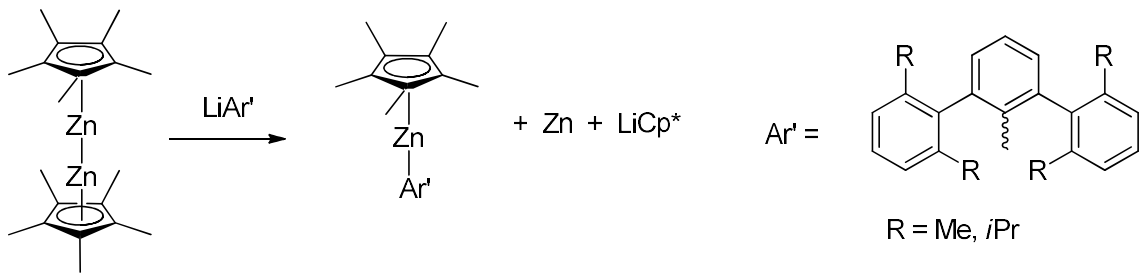
4.1 Reactions of dizincocene with cleavage of the zinc-zinc bond

Compound **1** was found to be inert under H_2, CO or CO_2 and did not react with many common Lewis bases containing nitrogen or phosphorus donors, i.e. NEt_3, $Me_2NCH_2CH_2NMe_2$, pyridine, bipyridine, PMe_3 or PPh_3. In contrast, **1** reacts with protonic reagents such as H_2O or *t*BuOH with disproportionation and formation of Zn metal, $Zn(OH)_2$ or $Zn(O\mathit{t}Bu)_2$ and HCp*. Disproportionation reaction was also observed in the reaction of **1** and CNXyl (Xyl = C_6H_3-2,6-Me_2), which yielded Zn metal and the Zn(II) iminoacyl complex as shown in Scheme 8.[19] The latter was also obtained from the reaction of zincocene, Cp^*_2Zn, with CNXyl. In contrast, the redox reaction of **1** with I_2 led to the corresponding Zn(II) products ZnI_2 and $[Zn(\eta\text{-}Cp^*)_2]$.



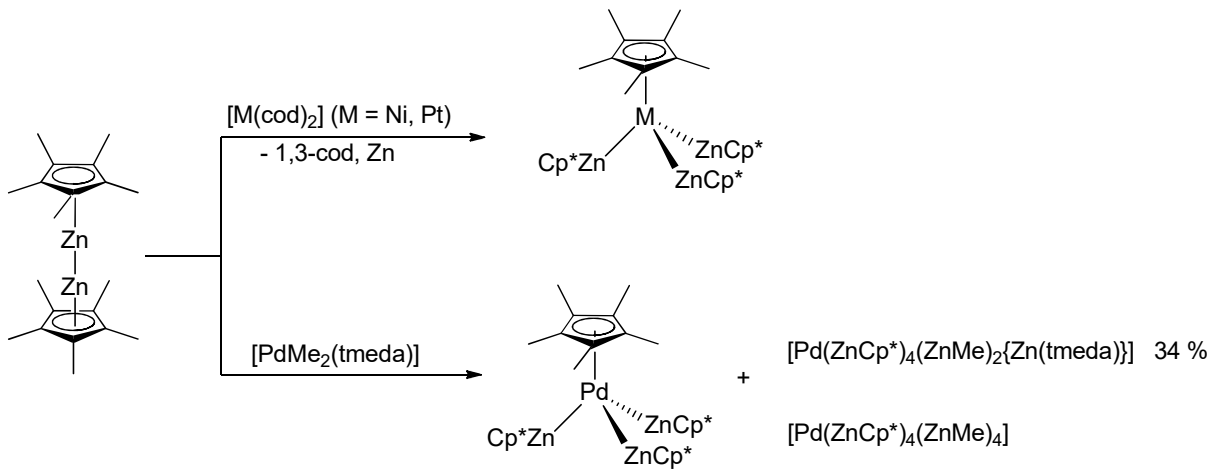
Scheme 8

Several attempts by Carmona and coworkers to synthesize a heteroleptic Zn-Zn bonded complex $[(\eta^5\text{-}Cp^*)Zn\text{-}Zn(Ar')]$ (Ar' = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$ or C_6H_3-2,6-(C_6H_3-2,6-Me_2)$_2$) were unsuccessful. No ligand exchange reaction was observed in the deuterated benzene solution of **1** and $[Zn_2Ar'_2]$. Moreover, the reaction of **1** and LiAr' occurred with disproportionation and formation of the corresponding Zn(II) complex $[(\eta^5\text{-}Cp^*)Zn(Ar')]$ (Scheme 9).[30]



Scheme 9

Recently, Fischer and coworkers reported on the reactivity of **1** toward transition metal complexes. Substitution reactions of labile d^{10} metal complexes $[M(cod)_2]$ (M = Ni, Pt; cod =1,5-cyclooctadiene) with 2 equiv of **1** led to $[Cp^*M(ZnCp^*)_3]$ (M = Ni, Pt) with the release of 1,3-cyclooctadiene (Scheme 10). The homolytic splitting of Zn-Zn bond and Cp* ligand transfer from Zn(I) to the transition-metal centers occurred in these reaction. The formation of compounds $[Cp^*M(ZnCp^*)_3]$ is accompanied by an oxidation of M(0) to M(I) and reduction of 1 equiv of Zn(I) to Zn(0), i.e. $2[Zn_2Cp^*_2] + M^0 \rightarrow Zn^0 + \{Cp^*M^I\} + 3\{ZnCp^*\}$. The reaction of $[PdMe_2(tmeda)]$ (tmeda = *N*,*N*,*N'*,*N'*-tetramethylethane-1,2-diamine) with 4 equiv of **1** led to the Pd homologue $[Cp^*Pd(ZnCp^*)_3]$ and various side products such as $[Pd(ZnCp^*)_4(ZnMe)_4]$ and $[Pd(ZnCp^*)_4(ZnMe)_2(Zn\{tmeda\})]$ resulting from complex competing redox reactions.[48] $[Pd(ZnCp^*)_4(ZnMe)_2\{Zn(tmeda)\}]$ could be isolated as yellow crystals in 34 % yield. The Pd center coordinates to three different types of Zn ligands.[49]



Scheme 10

Both reactions demonstrate the capability of **1** to serve as a Cp* and Cp*Zn transfer reagent in low oxidation state transition metal chemistry.[48]

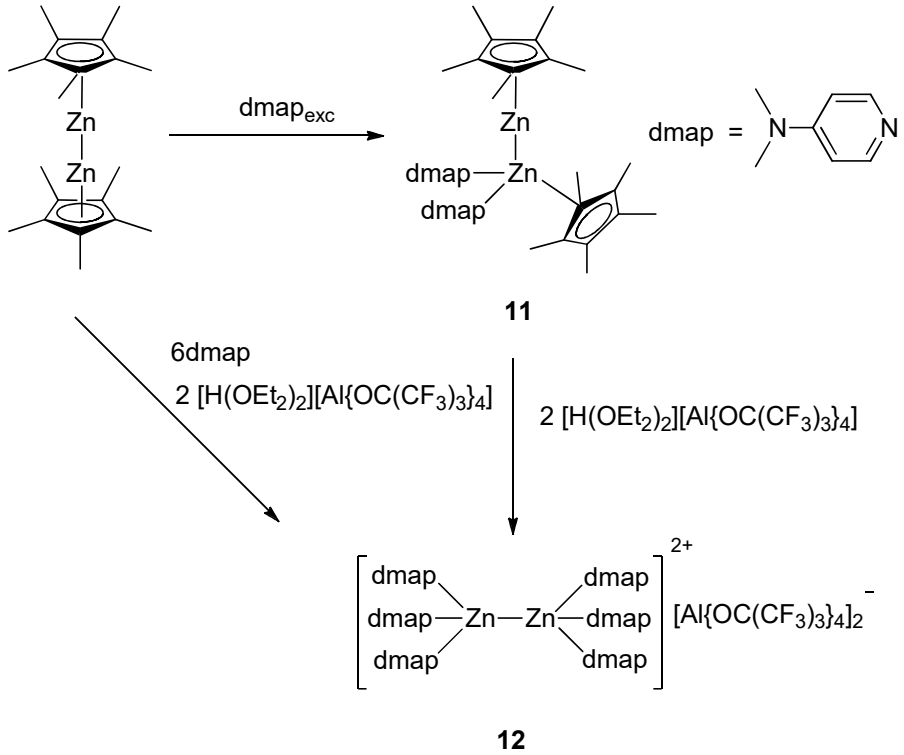
4.2 Reactions with preservation of the Zn-Zn bond

Schulz and coworkers have shown that the reaction of **1** with the strong Lewis base 4-dimethylaminopyridine (dmap; pK_a value of Hdmap$^+$ = 17.95) [50] proceeded with preservation of the Zn-Zn bond and formation of the adduct [(η^5-Cp*)Zn-Zn(dmap)$_2$(η^1-Cp*)] (**11**) (Scheme 11), which is in remarkable contrast to reactions with weaker Lewis bases as mentioned before. Two dmap molecules unexpectedly coordinate in a geminal mode to a single Zn atom rather than in a vicinal mode to both Zn atoms. The increase of the coordination number on one Zn atom leads to a significant elongation of Zn-Zn bond from 2.305(3) to 2.418 (1) Å. Moreover, the bond length elongation results from a partial population of the LUMO orbital, which exhibits Zn-Zn antibonding character. DFT calculations revealed that the formation of **11** is strongly exothermic and the Zn-Zn bond has 96.7% of s orbital contribution.[51] Further reaction of **11** with 2 equiv of the protonic acid [H(OEt$_2$)$_2$][Al{OC(CF$_3$)$_3$}$_4$] resulted in a protonation of the formally anionic Cp* ligand and

formation of the dmap-stabilized Zn_2^{2+} dication $[Zn_2(dmpa)_6][Al\{OC(CF_3)_3\}_4]_2$ (**12**) as shown in Scheme 11. **12**, which is the first structurally characterized compound containing the $[Zn_2]^{2+}$ dication,[52] can also be synthesized by an *in situ* reaction of **1**, 6 equiv of dmap, and 2 equiv of the protonic acid $[H(OEt_2)_2][Al\{OC(CF_3)_3\}_4]$. The Zn-Zn bond length in **12** (2.419 (1) Å) is significantly longer than those in **1**, clearly resulting from the increased coordination number (Figure 3).

Figure 3

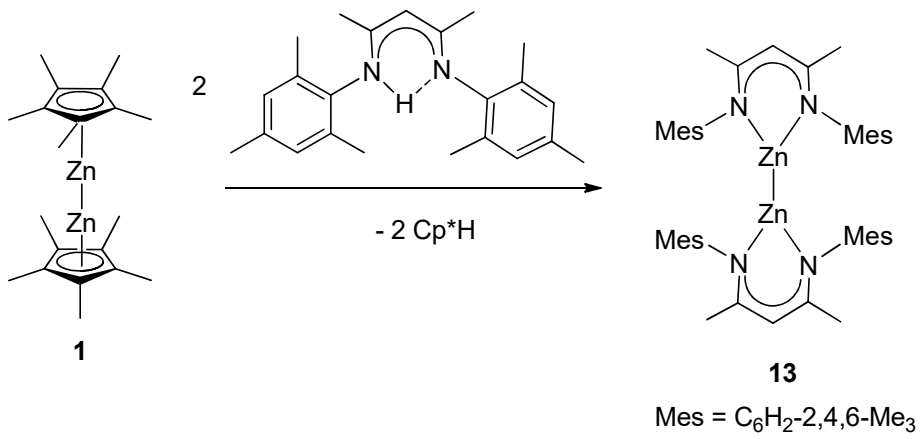
here



Scheme 11

Although the Zn-Zn bonded complex **3**, [L'Zn-ZnL'] (L' = $[\{(C_6H_3\text{-}2,6\text{-}iPr_2)N(Me)C\}_2CH]^-$), bearing a sterically demanding β-diketiminate ligand has been prepared

by reductive coupling reaction (see Scheme 3),[38] several attempts to synthesize the Zn-Zn bonded complex **13** with a mesityl functionalized β-diketiminate ligand L ([{(C_6H_2-2,4,6-Me_3)N(Me)C}$_2$CH]$^-$) by reduction of [LZn(II)X] were unsuccessful. In contrast, Schulz and coworkers obtained complex **13** from the reaction of **1** with two equiv LH. As shown in Scheme 12, the acidic N-H group in LH protonates the Cp* ligand in **1**, resulting in the ligand substitution reaction with subsequent formation **13** in high yield.[53] This reaction pathway shows several advantages compared with reduction reactions, since the latter typically proceed with formation of sometimes hard to separate by-products. In addition, reduction reactions typically gave the low-valent complexes in rather low yield, whereas the ligand exchange reaction gave **13** in almost quantitative yield.

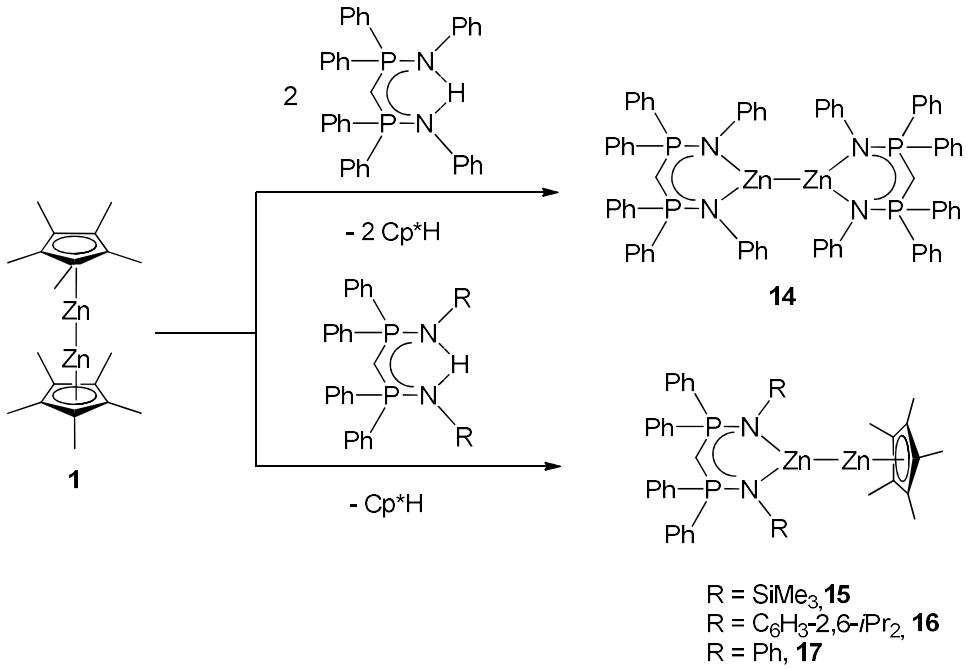


Scheme 12

The single crystal X-ray study of **13** proved that the Zn-Zn bond was preserved with a bond distance of 2.3813(8) Å, which is 0.023 Å longer than the sterically more hindered β-diketiminate complex **3**. Differently from complex **3** with the Zn atom out of the C_3N_2Zn-plane, the C_3N_2Zn rings in complex **13** are arranged in an almost planar fashion. The Zn-Zn bond has almost exclusive s-character (94.5%) as was typically observed for Zn-Zn bonded

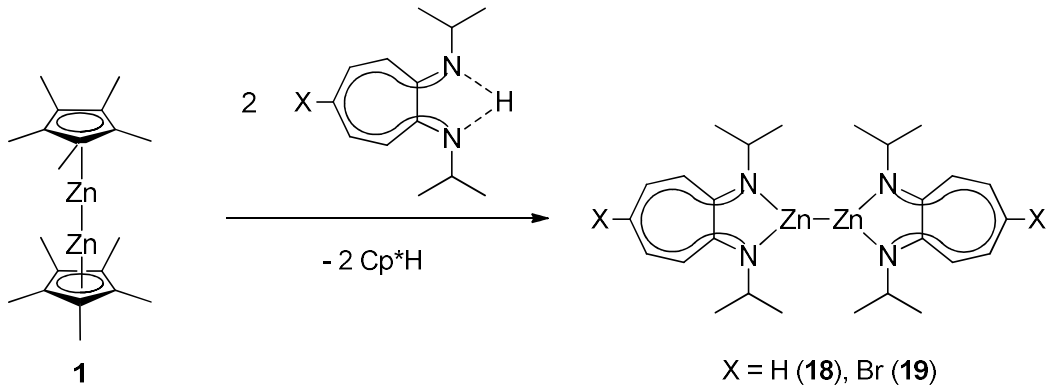
complexes.[54] The formation of a hydride bridged Zn(II) dimer was excluded. LZnH was independently prepared and structurally characterized.[55]

Soon after, six new Zn-Zn bonded complexes **14-19** were prepared by protonation of Cp* in dizincocene **1** with an *H*-acidic ligand followed by the replacement of Cp* with the mono-anionic chelating ligand. Schulz and coworkers have obtained complexes **14-17** by reacting **1** with bis(iminophosphorano)methanes [$H_2C(PPh_2NR)_2$] (R = Ph, $SiMe_3$, C_6H_3-2,6-*i*Pr_2) (Scheme 13). The reaction of [$Cp^*_2Zn_2$] and 2 equiv of [$H_2C(PPh_2NR)_2$] led to the homoleptic complex **14** only with the sterically less demanding *N*-substituents, i.e. R = Ph. In contrast, heteroleptic Zn-Zn bonded complexes **15-17** were obtained when bulkier *N*-substituents (R = $SiMe_3$, C_6H_3-2,6-*i*Pr_2) were used or in reactions with only one equivalent of the bis(iminophosphorano)methanes. Compounds **14-17** were characterized by NMR and IR spectroscopy as well as by single crystal X-ray diffraction (**14**, **16**). The six-membered rings CP_2N_2Zn in both **14** and **16** adopt distorted boat-type conformations. The Zn-Zn bond distance of 2.3272(2) Å in **16** is slightly shorter than that in **14** (2.3409(1) Å). **16** represents the first structurally characterized heteroleptic Zn-Zn bonded complex.[56]



Scheme 13

Roesky and coworkers have reacted **1** with protonic aminotroponimine ligands, *N*-isopropyl-2-(isopropylamino)troponimine (iPr$_2$ATI), yielding two Zn-Zn bonded complexes [{(iPr)$_2$ATI}$_2$Zn$_2$] (**18**, Figure 4) and [{4-Br(iPr)$_2$ATI}$_2$Zn$_2$] (**19**) as shown in Scheme 14.[57] Single crystal X-ray diffraction studies for **18** and **19** confirmed the preservation of Zn-Zn bond with typical Zn-Zn bond lengths of 2.3534(7) and 2.3570(8) Å, respectively. As shown in Figure 4, two ligands are arranged in a nearly orthogonal orientation with a N1-Zn1-Zn1'-N1' torsion angle of 79.2°. NMR and IR spectra were consistent with the solid state structure. Compound **18** exhibited a stretching motion of the Zn-Zn bond at 330.4 cm^{-1} (calcd 322 cm^{-1}) in the Raman spectrum, which was almost uncoupled to other vibrations.[57] In contrast for **1** Raman bands at 373 and 236 cm^{-1} were observed. With the help of a normal coordinate analysis the authors assigned both vibrations to the Zn-Zn stretching mode each strongly coupled to deformation motions.[58] The theoretically deduced Raman spectrum of Zn_2Cl_2 can be explained in a similar way.[52]

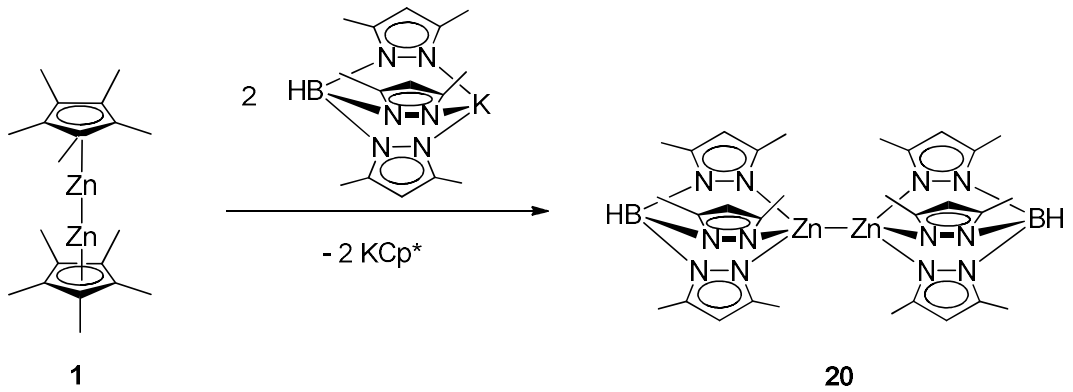


Scheme 14

Figure 4 here

A novel synthetic pathway for the synthesis of Zn-Zn bonded complexes was established by Schulz and coworkers in 2010.[59] The reaction of **1** and the potassium salt of tris(3,5-dimethylpyrozolyl)hydridoborate K(Tp^{Me2}) occurred under mild reaction conditions with

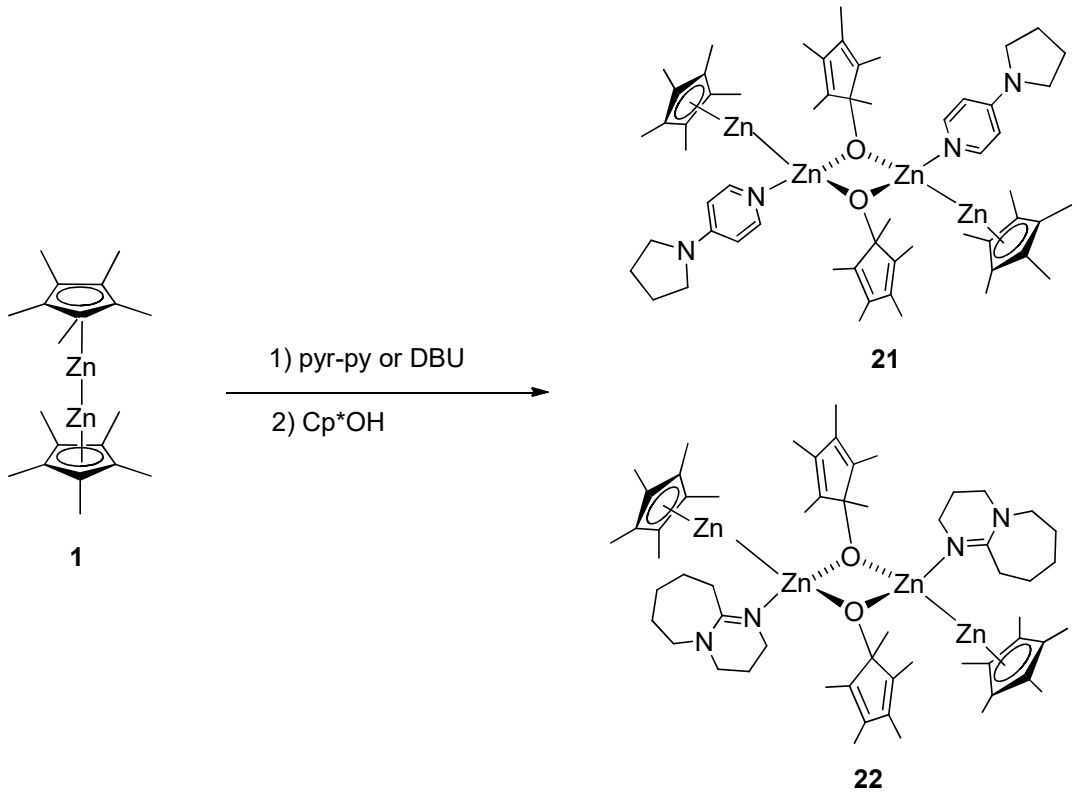
elimination of KCp* and subsequent formation of $[Zn_2(Tp^{Me2})_2]$ (**20**) in almost quantitative yield (Scheme 15). Due to the excellent shielding of the sterically demanding tridentate ligand, compound **20** is thermally and chemically more stable than most other Zn-Zn bonded complexes. The single crystal X-ray structure of **20** showed that the Tp^{Me2} ligand coordinates to a Zn atom in a tridentate mode and the Zn atoms adopt tetrahedral coordination spheres. The Zn-Zn bond length of 2.3560(9) Å is comparable to those observed for **13**, **18** and **19**.[59]



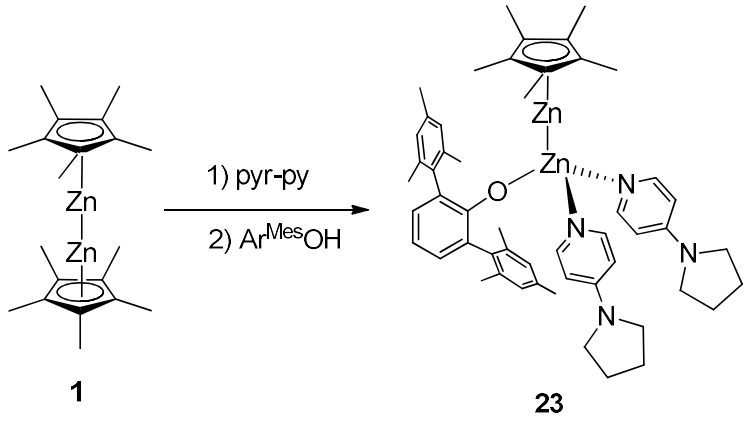
Scheme 15

Inspired by the isolation of **11**, Carmona and coworkers[30] studied the reactivity of **1** with other related but stronger Lewis bases pyr-py (4-pyrrolidinopyridine, pK_a value of Hpyr-py$^+$ = 18.33) and DBU (1,8-diazabicyclo[5.4.0]undec-7-ene, pK_a value of HDBU$^+$ = 24.34).[50] The formation of the Lewis acid-base adducts [Cp*Zn-Zn$(DBU)_2$Cp*] and [Cp*Zn-Zn$(pyr\text{-}py)_2$Cp*] were observed in the ether solution of **1** and the Lewis base. Due to their poor stability in the solid state, no single crystal X-ray structures were obtained. Both [Cp*Zn-Zn$(DBU)_2$Cp*] and [Cp*Zn-Zn$(pyr\text{-}py)_2$Cp*] were characterized by NMR spectroscopy and showed similarities to compound **11**. The Zn-Zn complexes [Cp*Zn-Zn$(DBU)_2$Cp*] and [Cp*Zn-Zn$(pyr\text{-}py)_2$Cp*] were used as precursors to prepare the first oxygen donor containing Zn-Zn complexes.[30, 60] Treating [Cp*Zn-Zn$(pyr\text{-}py)_2$Cp*] or [Cp*Zn-Zn$(DBU)_2$Cp*] with Cp*OH at -25 °C yielded tetrametallic compounds **21** and **22**, which

consist of two Cp*Zn-Zn(pyr-py) or Cp*Zn-Zn(DBU) units bridged by two Cp*O$^-$ moieties (Scheme 16). A similar reaction of [Cp*Zn-Zn(pyr-py)$_2$Cp*] with the bulkier terphenol Ar^{Mes}OH yielded the bimetallic compound **23** (Scheme 17). Single crystal X-ray structures for **21**-**23** displayed identical Zn-Zn bond distances of 2.366(1) Å in **21** and **23**, both containing pyr-py as the stabilizing Lewis base. A Zn-Zn bond length of ca. 2.39 Å was observed in compound **22**.[30, 60]

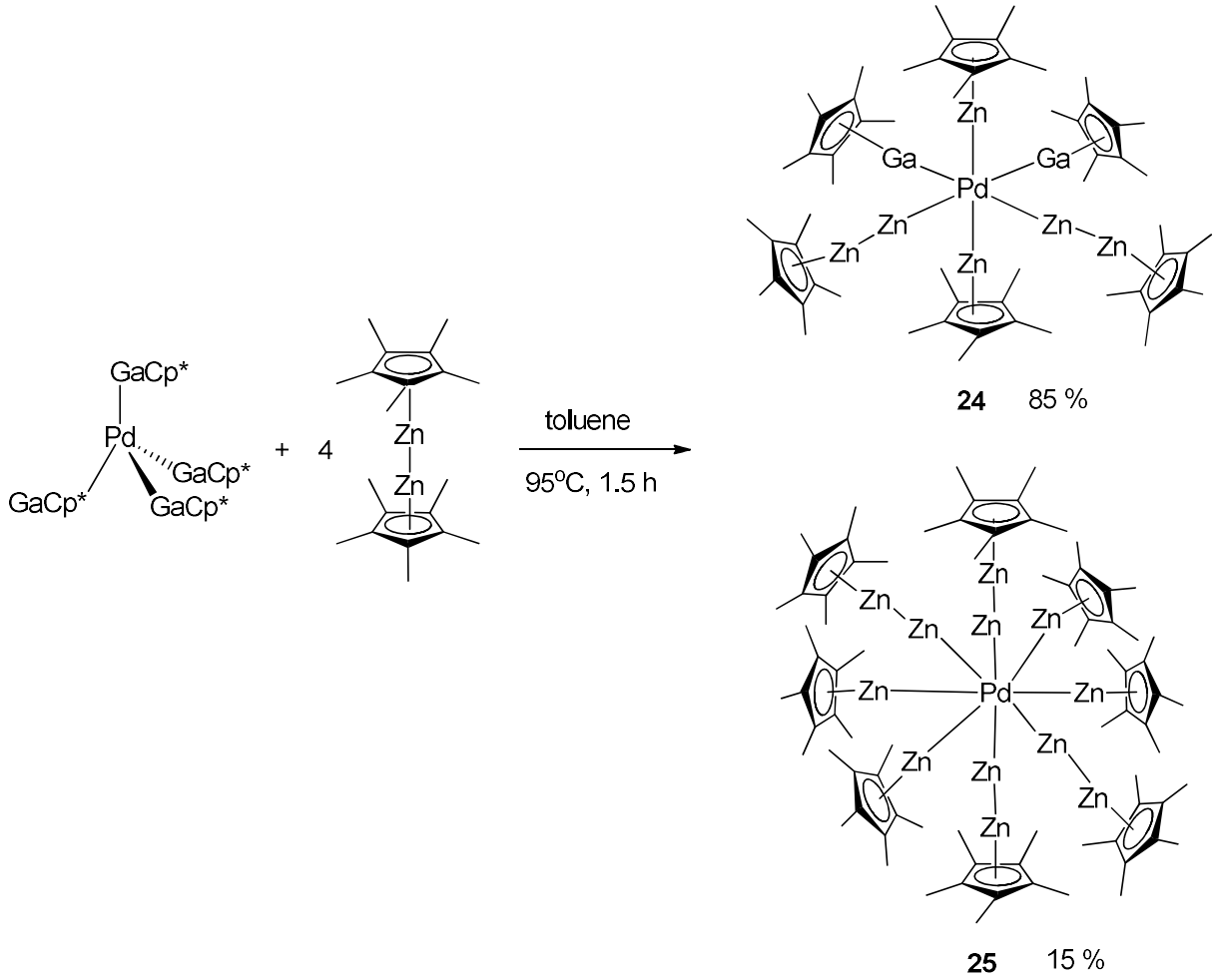


Scheme 16



Scheme 17

Very recently, Fischer and coworkers synthesized and structurally characterized two metal rich intermetallic complexes, in which the central Pd atom is either sixfold-([Pd(GaCp*)$_2$(ZnCp*)$_2$(ZnZnCp*)$_2$] (**24**)) or eightfold-coordinated ([Pd(ZnCp*)$_4$(ZnZnCp*)$_4$] (**25**)).[61] Both complexes contain Cp*Zn ligands as well as Cp*Zn$_2$ ligands with an intact Zn-Zn bond. As shown in Scheme 18, the reaction of [Pd(GaCp*)$_4$] with 4 equiv of **1** led to the formation of **24** and **25** in a molar ratio of 6:1 with free [GaCp*] and [ZnCp*$_2$] as side-products. The Zn atoms in {ZnZnCp*} moieties were believed to have different oxidation states. In this reaction, the disproportionation reaction of [Zn(I)$_2$Cp*$_2$] resulted in the formation of [Zn(II)Cp*$_2$], {Zn(0)Zn(I)Cp*} and {Zn(I)Cp*} fragments. The {ZnZnCp*} and {ZnCp*} fragments can be described as novel one-electron donor ligands. The Pd metal centers in **24** and **25** obey the 18-electron rule.



Scheme 18

The single crystal X-ray structure of **24** (Figure 5) suggested a distorted octahedral geometry around the Pd metal center and an almost linear arrangement of the Zn-Zn-Pd groups. The Zn-Zn bond distances of 2.345(1) and 2.346(1) Å were elongated by 0.05 Å from the starting compound [$Zn_2Cp^*_2$]. Similarly to [$Pd(ZnCp^*)_4(ZnMe)_4$],[62] the molecular structure of **25** was described as a distorted trigonal dodecahedron with the inner {$PdZn_8$} core. All four Pd-Zn-Zn units were almost linear and the Zn-Zn bond distances in four {ZnZnCp*} range from 2.347(1) to 2.351(3) Å, which is comparable to compound **24**.[61]

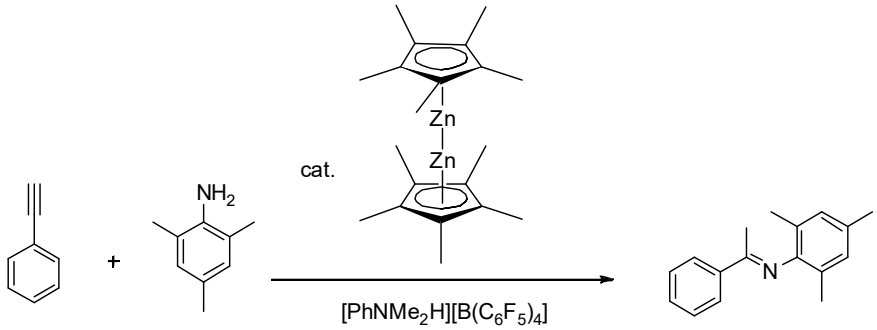
Figure 5

here

5. Catalytic applications of low-valent organozinc complexes

Twenty five Zn-Zn bonded complexes have been structurally characterized and reported since Carmona firstly reported on the synthesis of the dizincocene **1** in 2004 (Scheme 1). Many efforts have been focused on the synthesis and reactivity of the new complexes. Only very recently, the catalytic potential of compound **1** was investigated.[63] It is well known that important reactions in organic chemistry such as the Reformatsky reaction,[64] the Negishi cross coupling,[65] the Simmons-Smith cyclopropanation,[66] the copolymerisation of carbon dioxide and epoxides,[67] and the hydroamination[68-71] catalytically or stoichiometrically are mediated by zinc. Roesky, Blechert, and coworkers have investigated dizincocene **1** and recently reported on its catalytic properties as a homogenous catalyst for inter- and intramolecular hydroamination reactions.[63] Hydroamination describes the addition of an N-H bond of an amine to an alkene or alkyne in one step with subsequent formation of nitrogen containing compounds.[72]

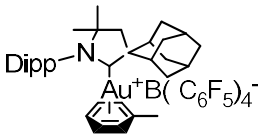
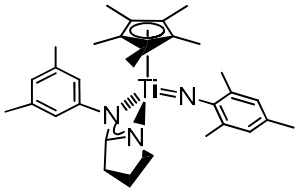
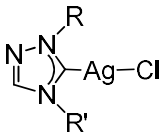
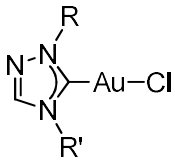
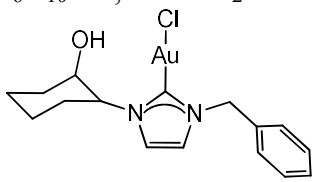
In the catalytic studies the activity of dizincocene **1** was compared with previous published catalysts [73-79] by using the standard reaction, the addition of 2,4,6-trimethylaniline to phenylethyne (Scheme 19). These studies clearly showed the high potential of **1** for this type of reaction. Compound **1** is so far the most active system by yield and rate (Table 1). Compound **1** catalyzes the this reaction at room temperature, whereas other systems only proceeded at elevated temperatures.



Scheme 19

In general, compound **1** was found to catalyze the intermolecular hydroamination reaction of primary and secondary anilines with different functional groups and different arylethynes.[63] In this screening an amine to alkyne ratio of 1:1 was used. Quantitative Markovnikov regioselectivity was observed for all reactions. Many functional groups such as halides, methoxy, and even OH groups were tolerated. The reactions were run in benzene at 80 °C with the exception of 2,4,6-trimethylaniline and some reactions of 3-methoxyaniline, which already reacted in acceptable rates at room temperature. With a few exceptions all reactions run with a conversion of 90-100%. Kinetic measurements showed that the steric demand of the aniline had no influence on the reaction rate. Moreover, neither any induction period nor an unstable conversion was observed. Obviously a stable catalytic species is formed *in situ* but in the present stage the exact nature and the oxidation state of the catalytic active species is not known.[63]

Table 1. Intermolecular Hydroamination of Phenylethyne with 2,4,6-Trimethylaniline[63]

Ref.	Cat.	*T*[°C]	*t*[h]	Yield [%]	mol% cat.	Ratio amine/ alkyne
63	$[(\eta^5\text{-Cp*})_2Zn_2]$	23	5.5	quant.	2.5	1:2
73		40	16	81	5	1:1
74		105	24	80	5	1:1
75	CuSTA[a]	110	8	95		2:1
76	CuAlSBA-15	110	6	37		2:1
77	Cu-K-10[b]	110	20	95	10 wt%	2:1
78	$(Ph_3P)AuCH_3 + H_3PW_{12}O_{40}$	70	2	93	0.2:1	1.1:1
79		90	12		2	1:1.5
	R = CH_2CO*t*Bu, R' = CH_2Ph R = CH_2CONH*t*Bu, R' = CH_2Ph R = CH_2CO*t*Bu, R' = CH_2CO*t*Bu R = $C_6H_{10}OH$, R' = CH_2Ph			7 0 16 1		
79		90	12		2	1:1.5
	R = CH_2CO*t*Bu, R'= CH_2Ph R = CH_2CONH*t*Bu, R'= CH_2Ph R = CH_2CO*t*Bu, R'= CH_2CO*t*Bu R = $C_6H_{10}OH$, R'= CH_2Ph			84 75 80 58		
79		90	12	46	2	1:1.5

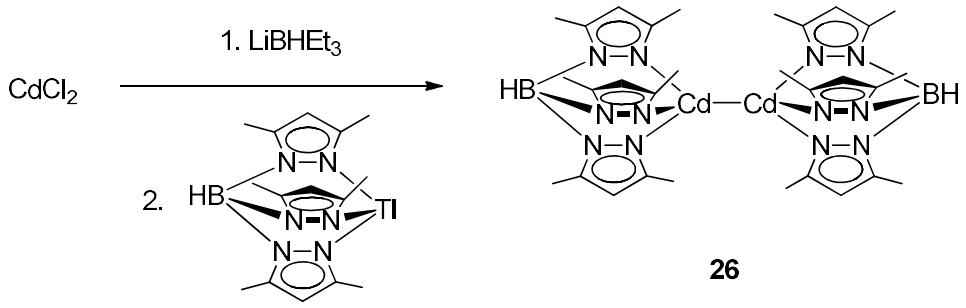
[a] Copper salt of silicotungstic acid, [b] Montmorillonite K-10

Further investigations of intermolecular hydroamination reactions of various substituted primary or secondary aniline and *meta*- or *para*- substituted arylethynes afforded quantitative Markovnikov regioselectivity for all cases. The catalytic activities of **1** in intramolecular cyclizations of secondary amino olefins reactions have shown very promising rates and yields as well.[63]

6. Related metal-metal bonded complexes

Accessibility to the metal-metal bonded oxidation state +1 for group 12 metals increases from top to bottom of the group. Due to the large ionization enthalpy of the Hg atom, two Hg^{+} ions can share a pair of 6s electrons to form a stable Hg-Hg bond.[28] Thus, the $[Hg_2]^{2+}$ cation is a well known species, in contrast to the corresponding $[Cd_2]^{2+}$ unit[21-23] which has been rarely reported in solid state compounds. Therefore in this chapter, we focus on reviewing molecular complexes containing a cadmium-cadmium bond only.

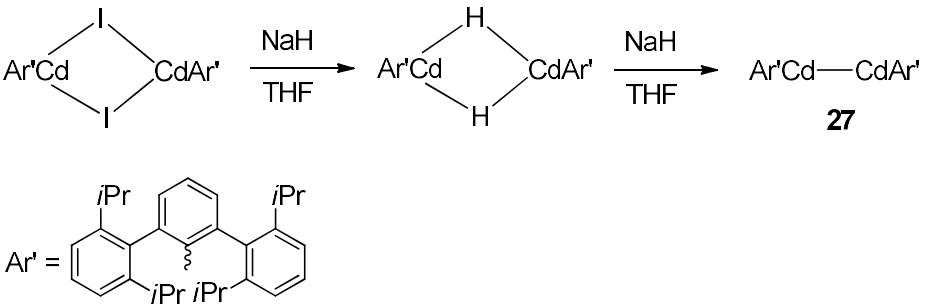
In 1993, Reger and Mason reported on the first molecular Cd-Cd bond containing complex, $[(Tp^{Me2})Cd]_2$ (**26**). **26** was prepared by reaction of $CdCl_2$ with $LiBHEt_3$ followed by addition of $Tl(Tp^{Me2})$ (Scheme 20).[80] Although no crystal structure of **26** was obtained to prove the formation of a Cd-Cd bond, ^{113}Cd NMR spectroscopy showed an extremely large ^{111}Cd-^{113}Cd coupling constant of 20646 Hz, suggesting a strong bond between the two cadmium atoms.[80]



Scheme 20

As shown previously for compound **20**, Schulz and coworkers applied the same ligand $(Tp^{Me2})^-$ for the stabilization of a Zn-Zn bond.[59]

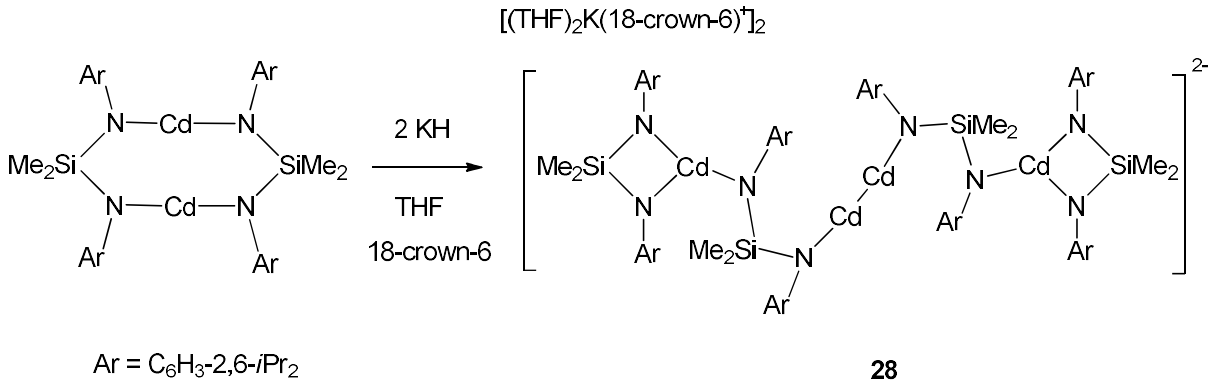
Power and coworkers described the synthesis and characterization of a series of molecular group 12 compounds [Ar'M-MAr'] (M = Zn (**4**), Cd (**27**) and Hg; Ar' = C_6H_3-2,6-(C_6H_3-2,6-*i*Pr_2)$_2$). **27** was obtained by reduction reaction of [Ar'CdI] with NaH in THF and was the first structural characterized molecular compound containing Cd-Cd bond. The reaction mechanism involved the initial formation of the dimeric complex [Ar'Cd(μ-H)$_2$CdAr'] containg two bridging hydride units, followed by elimination of hydrogen and subsequent formation of the more stable compound **27** (Scheme 21). The single crystal X-ray structure of **27** revealed a Cd-Cd bond distance of 2.6257(5) Å and a nearly linear arrangement of C-Cd-Cd-C in the core structure, which is very similar to the geometry of the zinc analogue compound **4**. The ^{113}Cd NMR spectroscopy indicated the large ^{111}Cd-^{113}Cd coupling constant of 8650 Hz. Similarly to the Zn analogue compound **4** as well, DFT calculations showed significant p-character in the Cd-Cd bonding orbital.[25, 81]



Scheme 21

After the successful characterization of the Zn-Zn bonded complex **7** stabilized by the diamide ligand $[Me_2Si(NC_6H_3\text{-}2,6\text{-}iPr_2)_2]^{2-}$, Tsai and coworker switched their attention to cadmium and recently reported the new Cd-Cd bonded complex **28**. Surprisingly unlike the Zn-Zn complex, the reduction of the neutral dinuclear Cd(II) precursor [Cd_2(μ-η^2-

$Me_2Si(NC_6H_3\text{-}2,6\text{-}iPr_2)_2)_2]$ by KH with the presence of 18-crown-6 in THF led to a tetranuclear mixed-valent complex **28** containing a Cd-Cd bond in the center of the molecule (Scheme 22).[82]



Scheme 22

In contrast to the stable Cd-Cd bonded complex **27**, compound **28** is thermally unstable in organic solvents and decomposes in THF at room temperature to cadmium metal, free ligand and other unidentified species. The X-ray diffraction study showed that the Cd-Cd bond distance of 2.6103(9) Å in **28** is slightly shorter than that in **27** (2.6257(5) Å).[82]

The reductive cleavage of the Cd-C bond in dimesitylcadmium by the Zintl phase K_4Pb_9 in an ethylenediamine (en) solution resulted in the formation of the dimeric Zintl ion $[Pb_9Cd\text{-}CdPb_9]^{6-}$ (**29**) with $[K(2,2,2\text{-crypt})]_6$ as the counterion. As shown in the single crystal X-ray structure (Figure 6), the $[Pb_9Cd\text{-}CdPb_9]^{6-}$ anion displays a pseudo-D_{4h} point symmetry. The Cd-Cd bond distances of 2.697(1) Å and 2.715(2) Å were observed for the two cluster moieties in the single crystal X-ray structure, which is ca. 0.08 Å longer than that in **27**.[83]

Figure 6

here

7. Conclusions

In the period immediately following the discovery of [$Zn_2(\eta$-Cp*$)_2$] **1**, the low valent Zn-Zn bonded complex was mostly considered as a lab curiosity. The research dealing with these compounds was majorly focused on studies of the nature of Zn-Zn bond. Early attempts to use these compounds in synthetic chemistry resulted mostly in disproportionation to Zn(II) and Zn(0). This situation has changed dramatically in the last five years. Now, [$Zn_2(\eta$-Cp*$)_2$] is a firmly established reagent and numerous compounds containing Zn-Zn bond(s) have been discovered.

A variety of innovative synthetic approaches went beyond the pure synthesis of new Zn-Zn bond species, e.g. the use of the {ZnZnCp*} fragment as a novel one-electron donor ligands opens the opportunity of a new cluster chemistry. Moreover, the first catalytic applications of [$Zn_2(\eta$-Cp*$)_2$] was published recently. Based on this fast development, we expect a rich synthetic chemistry of Zn-Zn bond species as well as new applications of these compounds in catalysis and material science in the near future.

8. Acknowledgement

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9. References

1. F. A. Cotton, L. A. Murillo and R. A. Walton, *Multiple Bonds Between Metal Atoms*, 3 edn., Springer, Berlin, 2005.
2. G. Schmid, M. Baumle, M. Geerkens, I. Heim, C. Osemann and T. Sawitowski, *Chem. Soc. Rev.*, 1999, **28**, 179-185.

3. F. A. Cotton, N. F. Curtis, C. B. Harris, B. F. G. Johnson, S. J. Lippard, J. T. Mague, W. R. Robinson and J. S. Wood, *Science*, 1964, **145**, 1305-1307.

4. M. H. Chisholm, *Philos. Trans. R. Soc. London, Ser. A*, 2008, **366**, 101-112.

5. H. Schnöckel, *Dalton Trans.*, 2008, 4344-4362.

6. Y. Wang and G. H. Robinson, *Chem. Commun.*, 2009, 5201-5213.

7. X.-W. Li, W. T. Pennington and G. H. Robinson, *J. Am. Chem. Soc.*, 1995, **117**, 7578-7579.

8. J. Su, X.-W. Li, R. C. Crittendon and G. H. Robinson, *J. Am. Chem. Soc.*, 1997, **119**, 5471-5472.

9. A. Noor, F. R. Wagner and R. Kempe, *Angew. Chem. Int. Ed.*, 2008, **47**, 7246-7249.

10. A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko and R. Kempe, *Z. Anorg. Allg. Chem.*, 2009, **635**, 1149-1152.

11. A. Noor, G. Glatz, R. Müller, M. Kaupp, S. Demeshko and R. Kempe, *Nat Chem*, 2009, **1**, 322-325.

12. C.-W. Hsu, J.-S. K. Yu, C.-H. Yen, G.-H. Lee, Y. Wang and Y.-C. Tsai, *Angew. Chem. Int. Ed.*, 2008, **47**, 9933-9936.

13. T. Nguyen, A. D. Sutton, M. Brynda, J. C. Fettinger, G. J. Long and P. P. Power, *Science*, 2005, **310**, 844-847.

14. G. Frenking, *Science*, 2005, **310**, 796-797.

15. F. R. Wagner, A. Noor and R. Kempe, *Nat. Chem.*, 2009, **1**, 529-536.

16. R. Wolf, C. Ni, T. Nguyen, M. Brynda, G. J. Long, A. D. Sutton, R. C. Fischer, J. C. Fettinger, M. Hellman, L. Pu and P. P. Power, *Inorg. Chem.*, 2007, **46**, 11277-11290.

17. P. W. Roesky, *Dalton Trans.*, 2009, 1887-1893.

18. S. P. Green, C. Jones and A. Stasch, *Science*, 2007, **318**, 1754-1757.

19. I. Resa, E. Carmona, E. Gutierrez-Puebla and A. Monge, *Science*, 2004, **305**, 1136-1138.

20. D. H. Kerridge and S. A. Tariq, *J. Chem. Soc. A*, 1967, 1122-1125.

21. J. D. Corbett, W. J. Burkhard and L. F. Druding, *J. Am. Chem. Soc.*, 1961, **83**, 76-80.

22. R. Faggiani, R. J. Gillespie and J. E. Vekris, *J. Chem. Soc., Chem. Commun.*, 1986, 517-518.

23. T. Staffel and G. Meyer, *Z. Anorg. Allg. Chem.*, 1987, **548**, 45-54.

24. D. Bravo-Zhivotovskii, M. Yuzefovich, M. Bendikov, K. Klinkhammer and Y. Apeloig, *Angew. Chem. Int. Ed.*, 1999, **38**, 1100-1102.

25. Z. Zhu, M. Brynda, R. J. Wright, R. C. Fischer, W. A. Merrill, E. Rivard, R. Wolf, J. C. Fettinger, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 2007, **129**, 10847-10857.

26. S. Schulz, *Chem. Eur. J.*, 2010, **16**, 6416-6428.

27. A. Grirrane, I. Resa, A. Rodríguez and E. Carmona, *Coord. Chem. Rev.*, 2008, **252**, 1532-1539.

28. E. Carmona and A. Galindo, *Angew. Chem. Int. Ed.*, 2008, **47**, 6526-6536.

29. A. Grirrane, I. Resa, A. Rodriguez, E. Carmona, E. Alvarez, E. Gutierrez-Puebla, A. Monge, A. Galindo, D. del Rio and R. A. Andersen, *J. Am. Chem. Soc.*, 2007, **129**, 693-703.

30. M. Carrasco, R. Peloso, I. Resa, A. Rodríguez, L. Sánchez, E. Álvarez, C. Maya, R. Andreu, J. J. Calvente, A. Galindo and E. Carmona, *Inorg. Chem.*, 2011, **50**, 6361-6371.

31. P. Pyykkö and M. Atsumi, *Chem. Eur. J.*, 2009, **15**, 186-197.

32. Y. Xie, H. F. Schaefer, III and R. B. King, *J. Am. Chem. Soc.*, 2005, **127**, 2818-2819.

33. J. W. Kress, *J. Phys. Chem. A*, 2005, **109**, 7757-7763.

34. D. del Río, A. Galindo, I. Resa and E. Carmona, *Angew. Chem. Int. Ed.*, 2005, **44**, 1244-1247.

35. B. Twamley, C. D. Sofield, M. M. Olmstead and P. P. Power, *J. Am. Chem. Soc.*, 1999, **121**, 3357-3367.

36. Y. Wang, B. Quillian, X.-J. Yang, P. Wei, Z. Chen, C. S. Wannere, P. v. R. Schleyer and G. H. Robinson, *J. Am. Chem. Soc.*, 2005, **127**, 7672-7673.

37. X.-J. Yang, B. Quillian, Y. Wang, P. Wei and G. H. Robinson, *Organometallics*, 2004, **23**, 5119-5120.

38. Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R. B. King, P. v. R. Schleyer, H. F. Schaefer and G. H. Robinson, *J. Am. Chem. Soc.*, 2005, **127**, 11944-11945.

39. Z. Zhu, R. J. Wright, M. M. Olmstead, E. Rivard, M. Brynda and P. P. Power, *Angew. Chem., Int. Ed.*, 2006, **45**, 5807-5810.

40. I. L. Fedushkin, A. A. Skatova, S. Y. Ketkov, O. V. Eremenko, A. V. Piskunov and G. K. Fukin, *Angew. Chem. Int. Ed.*, 2007, **46**, 4302-4305.

41. I. L. Fedushkin, O. V. Eremenko, A. A. Skatova, A. V. Piskunov, G. K. Fukin, S. Y. Ketkov, E. Irran and H. Schumann, *Organometallics*, 2009, **28**, 3863-3868.

42. Y.-C. Tsai, Y.-M. Lin, J.-S. K. Yu and J.-K. Hwang, *J. Am. Chem. Soc.*, 2006, **128**, 13980-13981.

43. Y.-C. Tsai, D.-Y. Lu, Y.-M. Lin, J.-K. Hwang and J.-S. K. Yu, *Chem. Commun.*, 2007, 4125-4127.

44. J. Yu, X.-J. Yang, Y. Liu, Z. Pu, Q.-S. Li, Y. Xie, H. F. Schaefer and B. Wu, *Organometallics*, 2008, **27**, 5800-5805.

45. X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H. F. Schaefer, Y. Liang and B. Wu, *Chem. Commun.*, 2007, 2363-2365.

46. Y. Liu, S. Li, X.-J. Yang, P. Yang, J. Gao, Y. Xia and B. Wu, *Organometallics*, 2009, **28**, 5270-5272.

47. P. Yang, X.-J. Yang, J. Yu, Y. Liu, C. Zhang, Y.-H. Deng and B. Wu, *Dalton Trans.*, 2009, 5773-5779.

48. T. Bollermann, K. Freitag, C. Gemel, R. W. Seidel and R. A. Fischer, *Organometallics*, 2011, **30**, 4123-4127.

49. T. Bollermann, K. Freitag, C. Gemel, M. Molon, R. W. Seidel, M. von Hopffgarten, P. Jerabek, G. Frenking and R. A. Fischer, *Inorg. Chem.*, 2011, **50**, 10486-10492.

50. I. Kaljurand, A. Kütt, L. Sooväli, T. Rodima, V. Mäemets, I. Leito and I. A. Koppel, *J. Org. Chem.*, 2005, **70**, 1019-1028.

51. D. Schuchmann, U. Westphal, S. Schulz, U. Flörke, D. Bläser and R. Boese, *Angew. Chem. Int. Ed.*, 2009, **48**, 807-810.

52. S. Schulz, D. Schuchmann, I. Krossing, D. Himmel, D. Bläser and R. Boese, *Angew. Chem. Int. Ed.*, 2009, **48**, 5748-5751.

53. S. Schulz, T. Eisenmann, D. Bläser and R. Boese, *Z. Anorg. Allg. Chem.*, 2009, **635**, 995-1000.

54. S. Schulz, D. Schuchmann, U. Westphal and M. Bolte, *Organometallics*, 2009, **28**, 1590-1592.

55. S. Schulz, T. Eisenmann, D. Schuchmann, M. Bolte, M. Kirchner, R. Boese, J. Spielmann and S. Harder, *Z. Naturforsch.*, 2009, **64b**, 1397-1400.

56. S. Schulz, S. Gondzik, D. Schuchmann, U. Westphal, L. Dobrzycki, R. Boese and S. Harder, *Chem. Commun.*, 2010, **46**, 7757-7759.

57. H. P. Nayek, A. Lühl, S. Schulz, R. Köppe and P. W. Roesky, *Chem. Eur. J.*, 2011, **17**, 1773-1777.

58. D. del Rio, I. Resa, A. Rodriguez, L. Sánchez, R. Köppe, A. J. Downs, C. Y. Tang and E. Carmona, *J. Phys. Chem. A*, 2008, **112**, 10516-10525.

59. S. Gondzik, D. Bläser, C. Wölper and S. Schulz, *Chem. Eur. J.*, 2010, **16**, 13599-13602.

60. M. Carrasco, R. Peloso, A. Rodríguez, E. Álvarez, C. Maya and E. Carmona, *Chem. Eur. J.*, 2010, **16**, 9754-9757.

61. T. Bollermann, K. Freitag, C. Gemel, R. W. Seidel, M. von Hopffgarten, G. Frenking and R. A. Fischer, *Angew. Chem. Int. Ed.*, 2011, **50**, 772-776.

62. T. Cadenbach, T. Bollermann, C. Gemel, M. Tombul, I. Fernandez, M. v. Hopffgarten, G. Frenking and R. A. Fischer, *J. Am. Chem. Soc.*, 2009, **131**, 16063-16077.

63. A. Lühl, H. Pada Nayek, S. Blechert and P. W. Roesky, *Chem. Commun.*, 2011, **47**, 8280-8282.

64. S. Reformatsky, *Berichte der deutschen chemischen Gesellschaft*, 1887, **20**, 1210-1211.

65. A. O. King, N. Okukado and E.-i. Negishi, *J. Chem. Soc., Chem. Commun.*, 1977, 683-684.

66. H. E. Simmons and R. D. Smith, *J. Am. Chem. Soc.*, 1958, **80**, 5323-5324.

67. G. W. Coates and D. R. Moore, *Angew. Chem. Int. Ed.*, 2004, **43**, 6618-6639.

68. T. E. Müller, M. Grosche, E. Herdtweck, A.-K. Pleier, E. Walter and Y.-K. Yan, *Organometallics*, 2000, **19**, 170-183.

69. A. Zulys, M. Dochnahl, D. Hollmann, K. Löhnwitz, J.-S. Herrmann, P. W. Roesky and S. Blechert, *Angew. Chem. Int. Ed.*, 2005, **44**, 7794-7798.

70. M. Dochnahl, K. Löhnwitz, J.-W. Pissarek, M. Biyikal, S. R. Schulz, S. Schön, N. Meyer, P. W. Roesky and S. Blechert, *Chem. Eur. J.*, 2007, **13**, 6654-6666.

71. M. Dochnahl, J.-W. Pissarek, S. Blechert, K. Löhnwitz and P. W. Roesky, *Chem. Commun.*, 2006, 3405-3407.

72. T. E. Müller, K. C. Hultzsch, M. Yus, F. Foubelo and M. Tada, *Chem. Rev.*, 2008, **108**, 3795-3892.

73. X. Zeng, G. Frey, S. Kousar and G. Bertrand, *Chem. Eur. J.*, 2009, **15**, 3056-3060.

74. K. Weitershaus, B. D. Ward, R. Kubiak, C. Müller, H. Wadepohl, S. Doye and L. H. Gade, *Dalton Trans.*, 2009, 4586-4602.

75. G. V. Shanbhag, K. Palraj and S. B. Halligudi, *Open Org. Chem. J.*, 2008, **2**, 52-57.

76. G. V. Shanbhag, T. Joseph and S. B. Halligudi, *J. Catal.*, 2007, **250**, 274-282.

77. G. V. Shanbhag, S. M. Kumbar, T. Joseph and S. B. Halligudi, *Tetrahedron Lett.*, 2006, **47**, 141-143.

78. E. Mizushima, T. Hayashi and M. Tanaka, *Org. Lett.*, 2003, **5**, 3349-3352.

79. C. Dash, M. M. Shaikh, R. J. Butcher and P. Ghosh, *Inorg. Chem.*, 2010, **49**, 4972-4983.

80. D. L. Reger, S. S. Mason and A. L. Rheingold, *J. Am. Chem. Soc.*, 1993, **115**, 10406-10407.

81. Z. Zhu, R. C. Fischer, J. C. Fettinger, E. Rivard, M. Brynda and P. P. Power, *J. Am. Chem. Soc.*, 2006, **128**, 15068-15069.

82. D.-Y. Lu, J.-S. K. Yu, T.-S. Kuo, G.-H. Lee, Y. Wang and Y.-C. Tsai, *Angew. Chem. Int. Ed.*, 2011, **50**, 7611-7615.

83. B. Zhou, M. S. Denning, T. A. D. Chapman, J. E. McGrady and J. M. Goicoechea, *Chem. Commun.*, 2009, 7221-7223.

Figures and Captions:

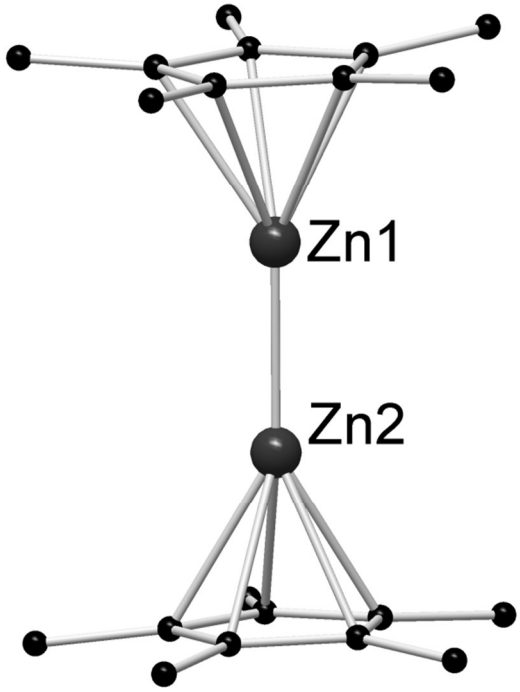


Fig.1: Solid-state structure of **1**. Hydrogen atoms are omitted for clarity.

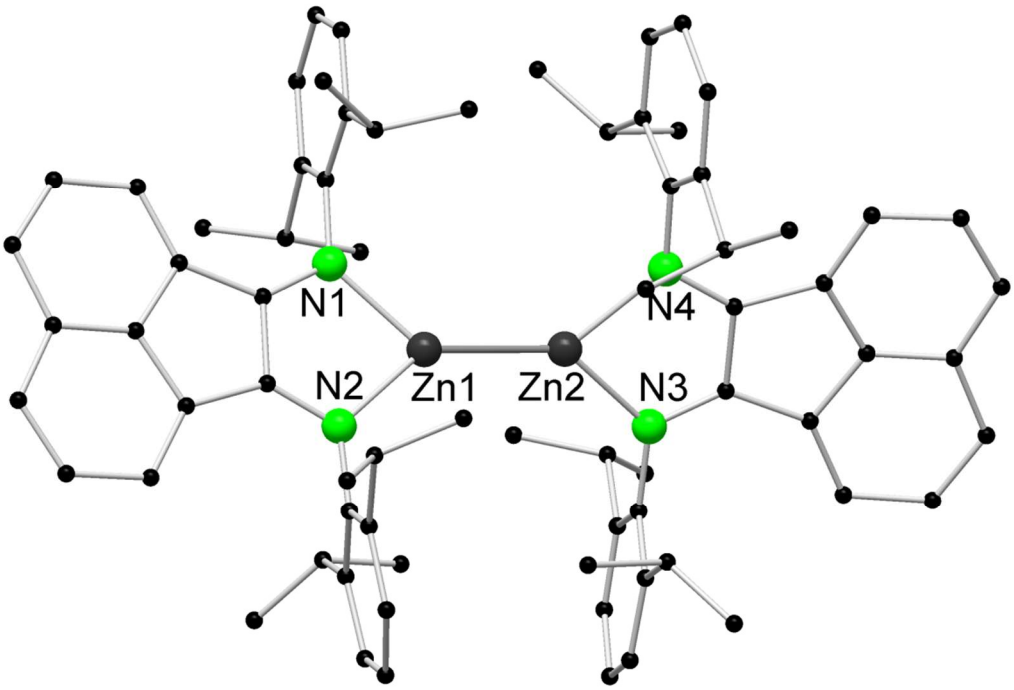


Fig.2: Solid-state structure of **6**. Hydrogen atoms are omitted for clarity.

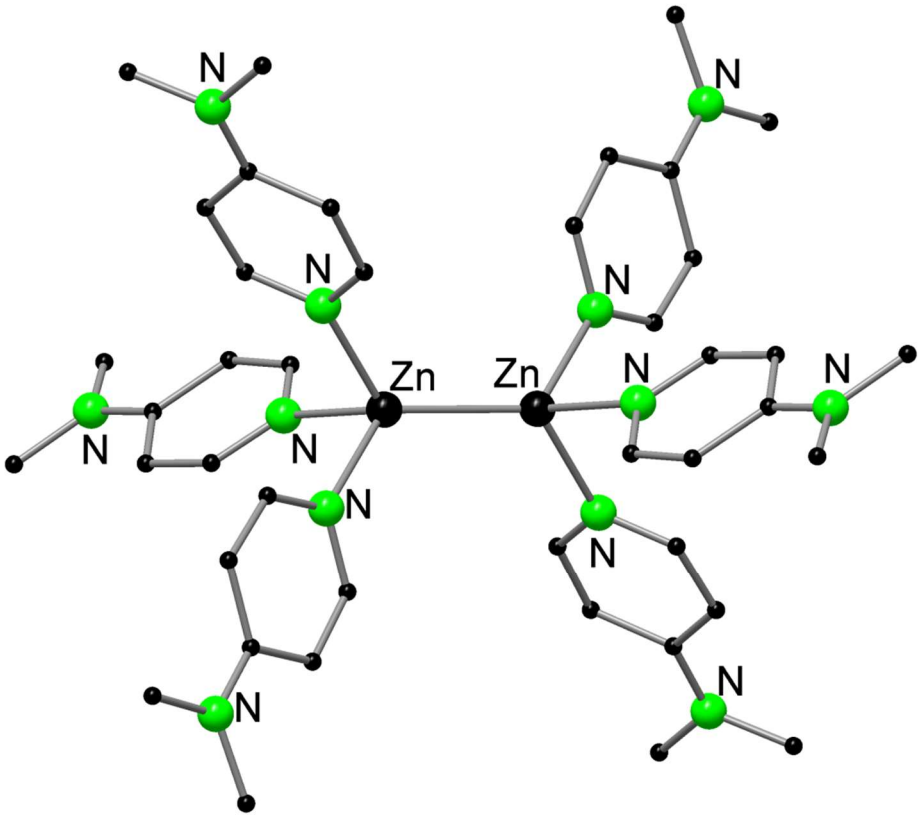


Fig.3: Solid-state structure of the base stabilized dication $[Zn_2(dmap)_6]^{2+}$ of **12**. Hydrogen atoms and the two anions $[Al(OC(CF_3)_3)_4]$ are omitted for clarity.

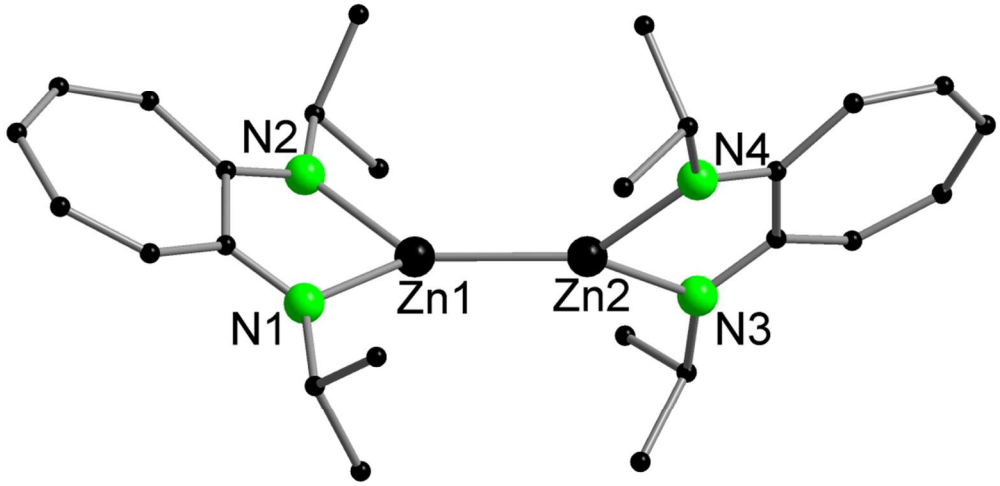


Fig.4: Solid-state structure of **18**. Hydrogen atoms are omitted for clarity.

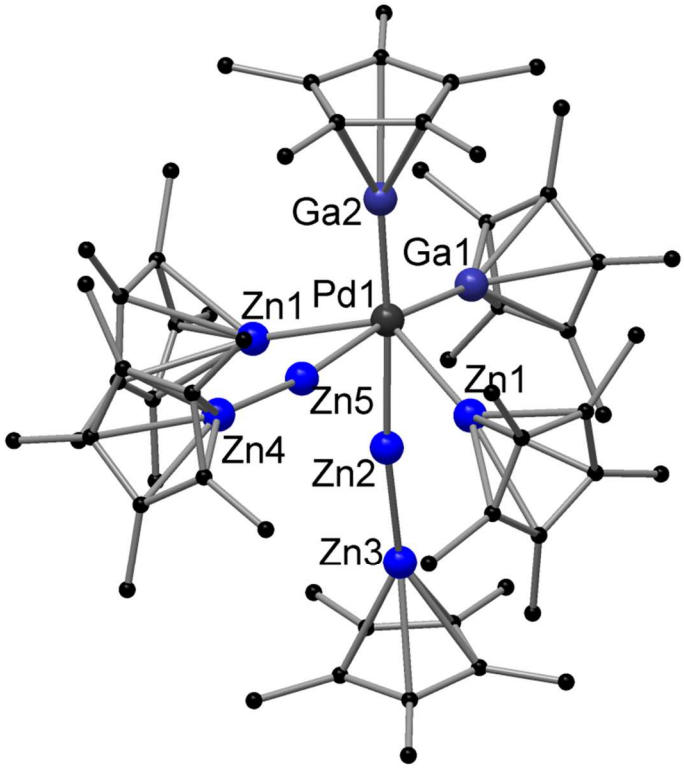


Fig.5: Solid-state structure of **24**. Hydrogen atoms are omitted for clarity.

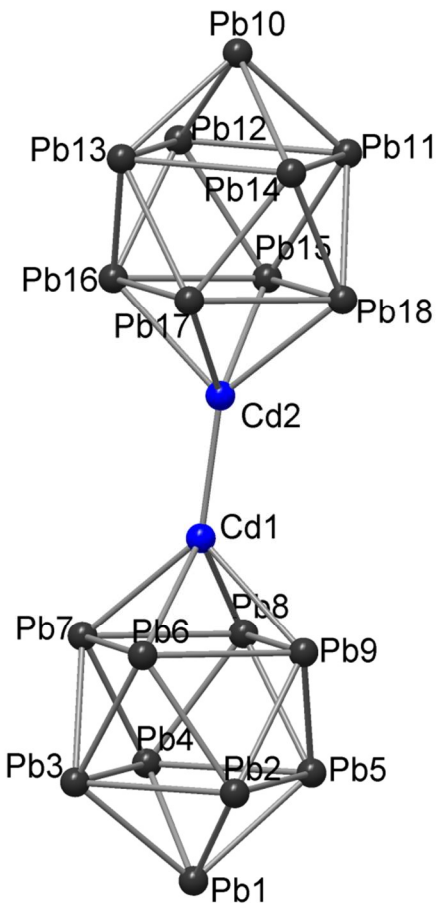
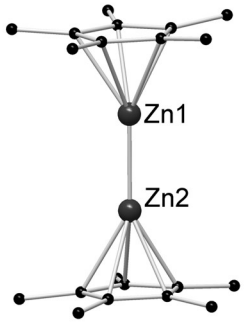


Fig.6: Solid-state structure of **28**. Hydrogen atoms are omitted for clarity.

Text for the Table of Contents

This review deals with the synthesis and reactivity of low-valent organozinc complexes. These compounds can either be formed by ligand substitution reactions of [Zn_2(η-Cp*)$_2$] or by reductive coupling reactions of Zn(II) compounds.



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Stephan Schulz obtained his PhD with Herbert W. Roesky at the University of Göttingen in 1994. After a postdoctoral work with R. F. Jordan at the University of Iowa (USA), he completed his habilitation at the University of Bonn in 2001. He then joined the faculty of chemistry at the University of Paderborn as an associate professor. Since 2007, he holds the chair for inorganic chemistry at the University of Duisburg-Essen. He received in 1996 a Liebig-Stipendium and in 1998 a DFG-Stipendium. His research focus is on organometallic chemistry including subvalent metal complexes and the bottom-up synthesis of nanomaterials via solution and gas phase processes.

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