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Metal–Metal Complexes

Direct Bonds Between Metal Atoms: Zn, Cd, and Hg Compounds with Metal–Metal Bonds

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cadmium · mercury · metallocenes · metal–metal interactions · zinc

The synthesis and characterization of [$Zn_2(\eta^5\text{-}C_5Me_5)_2$], a stable molecular compound with a Zn–Zn bond and the first example of a dimetallocene structure, has opened a new chapter in the organometallic chemistry of zinc and in metallocene chemistry. The existence of two directly bonded zinc atoms demonstrates that the $[Zn{-}Zn]^{2+}$ unit, the lightest Group 12 homologue of the well-known $[Hg{-}Hg]^{2+}$ ion, can be stabilized by appropriate ligands. Activity in this area has increased enormously in the few years since the determination of the structure of this molecule. Numerous theoretical studies have been devoted to the investigation of the electronic, structural, and spectroscopic properties of this and related compounds, and new metal–metal coordination and organometallic compounds of zinc, cadmium, and mercury have been synthesized and structurally characterized. This Minireview gives an overview of activity in this field during the past three to four years.

1. General Considerations

The concept of the chemical bond lies at the heart of chemistry and constitutes one of "its fundamental territories, the element from which an entire chemical universe is constructed".[1] Since Lewis formulated the hypothesis of the electron-pair bond in 1916,[2] the notion of the shared electron pair has evolved continuously thanks to experimental discoveries and theoretical developments, keeping the field fertile.[1] Metal–metal bonding is one challenge in this context, with implications in other areas of chemistry. Indeed, the study of compounds that contain metal atoms held together by one or more shared electron pairs is one of the most important and attractive chapters of modern inorganic chemistry.[3,4]

Traditionally, interest in compounds with metal–metal bonds has concentrated on the transition-metal elements, in particular in complexes that contain multiple bonds between metal atoms. As the maximum bond order exhibited by a stable molecule was thought for many decades to be three, the proposal by Cotton and co-workers in 1964 that a quadruple bond exists between the rhenium atoms[5] of the anion $[Re_2Cl_8]^{2-}$ was a landmark discovery that opened a new field of inorganic chemistry.[6] In these molecules and in others subsequently prepared, the quadruple-bond interaction can be expressed qualitatively as $\sigma^2\pi^4\delta^2$.[3–6]

For transition-metal elements, two σ bonds, one pair of π bonds, and one pair of δ bonds are possible owing to the availability of s and d orbitals. This situation leads to a maximum possible bond order of six, which has been proposed to exist in Mo_2 and especially in W_2.[7] Very recently, the quadruple interaction between two metal atoms was surpassed by Power and co-workers with the synthesis of the stable compound $Cr_2Ar'_2$ ($Ar' = C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}i\text{Pr}_2)_2$), which exhibits fivefold bonding between two chromium(I) centers.[8] This milestone in the chemistry of multiply bonded metal atoms has been the subject of an interesting theoretical discussion.[9] The quintuple bond in $Cr_2Ar'_2$ results from five metal–metal bonding molecular orbitals, which can be identified as one σ, two π, and two δ Cr–Cr bonds.

Although advancements on related compounds of main-group elements with metal–metal interactions have been somewhat slower, remarkable progress has been achieved in

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the last two decades. Two families of substances have spurred developments in this field: 1) compounds that exhibit delocalized "metal-like" bonds, and 2) compounds that feature multiple bonds between the heavier elements of Groups 13 and 14. The first family, called metalloid clusters by Schnepf and Schnöckel, contains metal atoms bearing ligands as well as "naked" ones bonded only to other metal atoms.[10] In general, these clusters display a greater number of direct metal–metal bonds than metal–ligand bonds. The second family comprises compounds with element–element multiple bonds, an area that started with the synthesis and structural characterization of the first Sn=Sn compound by Lappert and co-workers.[11a] Many reports on related molecules followed, including compounds of type RMMR featuring triple bonds between the M atoms. Some examples can be found in references [11–13]. These RMMR molecules have characteristic planar *trans*-bent geometries. For main-group atoms, only one σ and two π bonds can result from the available s and p valence atomic orbitals. Theoretical studies on molecules of this kind support the conception that the two M atoms are held together by three pair of electrons. The bond consists of one familiar σ and one π bond, plus one "slipped" π bond as a consequence of the large contribution of the p atomic orbital to the σ component, resulting in the *trans*-bent geometry.[9c] For $Cr_2Ar'_2$, the same authors[9c] propose familiar σ, 2π, and δ bonds plus a side-on δ bond constructed from sd-hybridized orbitals, resulting in the observed *trans*-bent structure of this molecule.[8] Since for the model compound Cr_2Ph_2 the *trans*-bent planar conformation is only 1 kcal mol^{-1} higher in energy than the linear structure, the preference for the observed geometry in $Cr_2Ar'_2$ could be influenced by secondary interactions between each of the chromium atoms and a flanking ring of the Ar′ ligands.[9b]

In addition to the above findings in the field of metal–metal bonds, whether of the transition metals or of the main-group elements, there is another relevant discovery to which we now direct our attention: the synthesis and structural characterization of decamethyldizincocene, $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$, the first stable compound with a Zn−Zn bond. Prior to this report,[14a] zinc was not known to form such bonds. Moreover, on the grounds of well-established chemistry for the heavier Group 12 elements cadmium and mercury (Cd is much less likely than Hg to engage in direct metal–metal bonding), the existence of molecular compounds with Zn−Zn bonds was highly questionable. Isolation of dizincocene $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ was also relevant for metallocene chemistry, which continues to attract considerable attention owing to the successful application of metal cyclopentadienyl complexes in many areas of chemistry.[15] More than fifty years after the original discovery of ferrocene, the first dimetallocene $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ was obtained. It displays a unique structure in which two metal atoms are sandwiched between two parallel cyclopentadienyl rings. The Zn−Zn bond axis is perpendicular to the C_5Me_5 rings, and in contrast to other metallocene structures with metal–metal bonds that are known for some transition metals,[4] the zinc atoms are not bonded to ligands other than C_5Me_5.

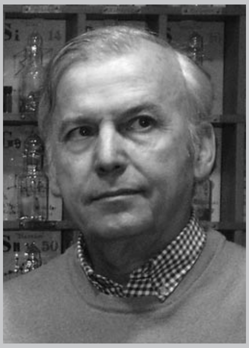
Our report on $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ was followed by several theoretical studies aimed at investigating the electronic structure and the bonding characteristics of this[16–28] and related species.[29–31] Experimental reports on other compounds with Zn−Zn bonds have also appeared,[32–35] and the first example of a molecular organometallic derivative of the $[Cd{-}Cd]^{2+}$ unit, $Cd_2Ar'_2$, has also been reported.[36] The analogous $Hg_2Ar'_2$ has been prepared recently.[36a]

In the following, we review well-characterized molecular compounds of Group 12 elements that contain M−M bonds. We first give a brief historical survey of compounds of this kind and later concentrate on dizincocenes and other Zn−Zn, Cd−Cd, and Hg−Hg compounds. The last part of this Minireview gives an overview of theoretical studies using DFT or related methodologies aimed at understanding the electronic structures and bonding properties of these molecules.

2. Experimental Studies on Group 12 Compounds with Metal–Metal Bonds

In the previous section, general considerations on the chemistry of metal–metal complexes were discussed, with reference to the position of the elements in the periodic table, that is, to their classification as transition-metal or main-group elements. It therefore seems appropriate to start this survey with comments pertaining to the consideration of Zn, Cd, and Hg as belonging to one or the other block of elements.

This is in fact an arguable, seemingly ambiguous matter, to the point that in the appropriate section of the latest edition of *Comprehensive Organometallic Chemistry*,[37] it is vaguely



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stated that "it is best to consider zinc as a privileged element, in that it partakes of chemical characteristics of both main-group and transition metals". This ambiguity is an reflection of pre-existing contradictory views: two of the main inorganic chemistry textbooks, namely "Cotton–Wilkinson"[3] and "Holleman–Wiberg"[38] have opposite perceptions, with the former firmly treating Zn, Cd, and Hg as main-group elements and the latter regarding the Zn group as "transition Group II or Group 12". We adhere to Cotton and Wilkinson's viewpoint, lucidly justified by Jensen[39] on the notion that "a d-block element is an element that uses either $(n-1)$ d electrons or empty $(n-1)$ d orbitals in its bonding" (implicitly encompassing its commonly occurring oxidation states).

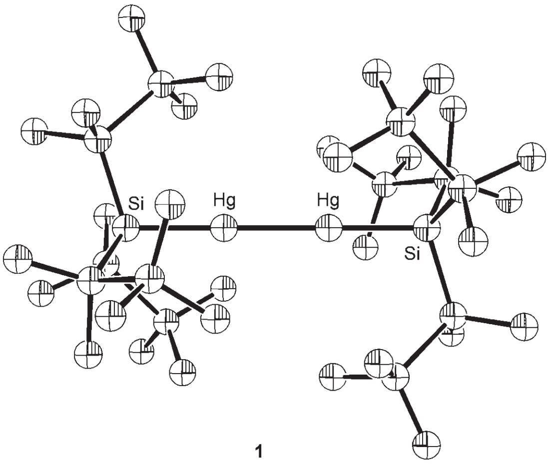
2.1. Earlier Studies on Group 12 M–M Compounds

Apart from the well-known M^{II} state common to the three Group 12 elements, the M^{I} state in the form of M_2^{2+} ions is of great importance for mercury and much rarer for zinc and cadmium. This situation is due to the large ionization enthalpy of the Hg atom, which is a consequence of the relativistic stabilization of its 6s atomic orbital. Thus, a strong Hg–Hg bond results when two Hg^+ ions share a pair of 6s electrons.[3,38]

According to Pascal's *Traité de Chimie Minérale*,[40] Hg_2Cl_2 could have been known as early as the 14th century. The other dimercury dihalides were prepared later, but detailed synthetic procedures for the four Hg_2X_2 compounds were available throughout the 19th century.[40] For many years it was thought that the Hg_2^{2+} species were unable to form many coordination compounds, as the reaction between the dimercury(I) salts and Lewis bases often induces disproportionation to form metallic mercury and a mercury(II) compound. However, a fair number of dimercury(I) coordination compounds have been synthesized and characterized by single crystal X-ray crystallography.[41] Organometallic derivatives of Hg_2^{2+} ions are uncommon, although interaction between the dication and the electron-rich C_6Me_6 aromatic ring has been demonstrated in the salt-like complex $[Hg_2(C_6Me_6)_2](AlCl_4)_2$.[42] No σ-bonded organomercury(I) compounds of the type Hg_2R_2 (R = hydrocarbyl group) have been known until recently (see Section 2.3), but some years ago the molecular σ-bonded silyl derivative **1** was prepared according to Equation (1).[43]

$$HgtBu_2 + 2\,(Me_3SiMe_2Si)_3SiH \rightarrow Hg[Si(SiMe_2SiMe_3)_3]_2\ (\mathbf{1}) \qquad (1)$$

X-ray studies revealed a Hg–Hg bond length of approximately 2.66 Å within a linear Si-Hg-Hg-Si unit (Figure 1). Further characterization of **1** was achieved by spectroscopy. Its characteristic red color is due to the presence of three bands in the UV/Vis spectrum at 334, 434, and 530 nm. Since $Hg(SiR_3)_2$ compounds and the mixed $Hg[Si(SiMe_2SiMe_3)_3]tBu$, thought to be an intermediate in the synthesis of **1** according to Equation (1), display two UV/Vis bands in the 300–400-nm range, the 530-nm absorption of **1** was assigned to the Hg–Hg moiety. Similarly, a strongly deshielded resonance of **1** at $\delta = 1142.3$ ppm in the ^{199}Hg NMR spectrum was considered characteristic of the $[Hg–Hg]^{2+}$ unit. By comparison, the most deshielded value for a Hg^{II} silyl derivative is $\delta = 987$ ppm for $Hg[Si(SiMe_3)_3]_2$.[43] An interesting tris(3,5-dimethylpyrazolyl)borate (Tp^{Me2}) derivative of Hg_2^{2+} had been reported previously, but its X-ray structure was not determined.[44] Reaction of different HgX_2 salts with KTp^{Me2} affords the Hg^{II} compounds $[Hg(Tp^{Me2})_2]$ and $[HgTp^{Me2}(X)]$, while treatment of $Hg_2(ClO_4)_2 \cdot 4H_2O$ with KTp^{Me2} yields $[Hg_2(Tp^{Me2})_2]$, which was also found to result from decomposition of some of the Hg^{II} derivatives. The resonance of the Hg^{I} compound in the ^{199}Hg NMR spectrum was deshielded by 300–600 ppm from those of the Hg^{II} derivatives.[44]



1

Figure 1. Molecular structure of $Hg_2[Si(SiMe_2SiMe_3)_3]_2$ (**1**, hydrogen atoms not shown).

In marked contrast, evidence for the existence of M^{I} compounds of the lighter Group 12 elements Zn and Cd was obtained only in the second half of the 20th century. Isolation and characterization of the first Cd_2^{2+} compound was achieved by Corbett and collaborators.[45] Dissolving Cd metal in molten cadmium halides produces dark red melts thought to contain both Cd^{I} and Cd^{II} joined by halide bridges. Addition of the strongly acidic $AlCl_3$ to such systems results in a stable Cd^{I} compound. Phase studies of $Cd/CdCl_2/2\,AlCl_3$ melts revealed the formation of $Cd_2(AlCl_4)_2$ (**2**), which was isolated and analyzed; the dimeric formulation was proposed on the basis of its diamagnetism. Separation from the Cd^{II} compound $Cd(AlCl_4)_2$ was achieved by heating at reflux in C_6H_6. Under these conditions the binuclear $Cd_2(AlCl_4)_2$ forms flat plates and sheets, which were hand-picked from the mixture. The Cd^{I} compound **2** was found to undergo disproportionation not only in common basic solvents such as H_2O and NH_3 but also with less basic solvents such as xylene, acetonitrile, and tetrahydrofuran. Subsequent studies using Raman[45d] and UV/Vis[45f] spectroscopy and electrochemical methods[45e] provided additional information, and some twenty years later two independent X-ray crystallographic studies allowed structural characterization of **2**.[46a,b] The structure consists of Cd_2^{2+} cations and approximately tetrahedral, isolated $AlCl_4^-$ anions. The $[Cd–Cd]^{2+}$ ion has a bond of 2.576(1) Å, longer than the Hg–Hg bond in the dihalides Hg_2X_2 (2.49–2.54 Å).[46c]

The first molecular compound with a Cd–Cd bond, $[Cd_2(Tp^{Me2})_2]$ (**3**) was prepared by Reger et al.[47] in 1993 by reduction of $CdCl_2$ with $LiBHEt_3$ in the presence of $TlTp^{Me2}$. Although its X-ray structure could not be determined, **3** was unambiguously characterized by mass spectrometry and by the observation of an extremely large $^{111}Cd–^{113}Cd$ coupling constant of 20 646 Hz (characteristic for a single bond). Extension of this synthetic methodology to Zn–Zn compounds was then considered feasible,[47] but $[Zn_2(Tp^{Me2})_2]$ remains the missing member of the homologous series of $[M_2(Tp^{Me2})_2]$ complexes of the Group 12 elements.

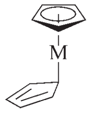
In 1963 Kerridge investigated the formation of Zn_2X_2 by reaction of Zn and the halides ZnX_2 in the gas phase. [48a] He found that the volatility of metallic zinc between 285 and 350 °C is higher in the presence of ZnX_2 vapor than in a vacuum and obtained evidence suggesting the formation of the molecular species $(ZnX)_2$, which disproportionates when cooled to room temperature. Some years later, Kerridge and Tariq[48b] measured the solubility of Zn in molten $ZnCl_2$ between 500 and 700 °C and obtained a yellow glass containing a reduced zinc species by rapid freezing of saturated melts. This yellow glass dissolves in saturated aqueous zinc chloride solution when warmed at temperatures below 80 °C to give a stable greenish-yellow solution, but in water the resulting colorless solution quickly deposits gray zinc particles. Similarly, the yellow glass was also soluble in dry methanol, acetone, and ethyl acetate, but rapid precipitation of zinc occurs from these solutions. All of these data are consistent with formation of Zn_2Cl_2, a proposal also supported by the diamagnetic nature of the yellow glass and by the observation of a Raman scattering at $175 \pm 5\ cm^{-1}$ during studies on ether solutions and the yellow glass.

Some forty years later, a microwave-discharge-powered reactive resonance lamp was found to effectively activate zinc and cadmium atoms for reaction with H_2. Different zinc hydride species were obtained in a solid argon matrix, among them the linear dizinc dihydride Zn_2H_2,[49a] proposed to form on dimerization of the monohydride ZnH. The deuterated analogue was also obtained; the two molecules were investigated by IR spectroscopy and their optimized structures calculated at the MP2 level. Zn_2H_2 also forms when laser-ablated zinc atoms react with molecular hydrogen upon condensation at 4.5 K.[49b]

Zinc clusters Zn_x^{2+} ($x \geq 2$) can be stabilized inside the cavities of a zinc-exchanged zeolite Y, prepared by passing zinc metal vapor through a cylindrical bed of water-free zeolite HY at 120 °C. Although the exact composition of the polyzinc cations could not be determined, Zn_2^{2+} was considered the most probable species.[50] An important further advance came from Seff and co-workers, who used single crystal X-ray diffraction to study the products of the reaction of zinc vapor with fully dehydrated, fully Tl^+-exchanged, zeolite X at 450 and 500 °C. At 450 °C, monoatomic Zn^+ ions were reported to form as a result of reduction of Tl^+ ions by Zn(g).[51] Another important finding that takes advantage of microspaces with oxidizing sites in zeolites and aluminophosphate-based materials is the formation of Zn^+ through reaction of Zn(g) with H^+ from a Brönsted acidic site of a silicoaluminophosphate with a characteristic chabazite structure (SAPO-CHA).[52] During the chemical vapor reaction, the generated Zn^+ ions replaced all the protons of the original SAPO-CHA structure; their existence was unequivocally demonstrated by ESR spectroscopy and variable-temperature magnetic susceptibility studies.[52]

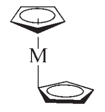
2.2. Dizincocenes $[Zn_2(\eta^5-C_5Me_5)_2]$ and $[Zn_2(\eta^5-C_5Me_4Et)_2]$

As explained in detail elsewhere,[53] the cyclopentadienyl zinc chemistry that led unexpectedly to **4** was an extension of prior work dealing with beryllocenes $BeCp_2$ ($Cp = C_5H_5$).[54] Our aim was the structural characterization of a zincocene with a rigid $\eta^5/\eta^1(\sigma)$ structure (**I**), unknown for binary metallocenes, as an alternative to the $\eta^5/\eta^1(\pi)$ or slipped-sandwich geometry (**II**) exhibited by the majority of beryllocenes and zincocenes known to date. The evident similarity between structures **I** and **III**, the latter corresponding to half-sandwich alkyl (or in general hydrocarbyl) derivatives, that were scarcely known for the $\{(\eta^5-C_5Me_5)Zn\}$ unit, advised investigating the conproportionation reaction between $[Zn(C_5Me_5)_2]$ and different organometallic zinc species ZnR_2. Much to our surprise, while corresponding reactions of the Zn^{II} reagents with R = Me, *i*Pr, and C_6H_2-2,4,6-Me_3 gave only the expected half-sandwich products $[Zn(\eta^5-C_5Me_5)R]$,[14b,55] ^1H NMR spectroscopy studies of the analogous reactions of $[Zn(C_5Me_5)_2]$ and $ZnEt_2$ or $Zn(C_6H_5)_2$ revealed the presence of a singlet at $\delta = 2.02$ ppm, arising from the C_5Me_5 protons of an unknown complex, in addition to characteristic signals of the expected $[Zn(\eta^5-C_5Me_5)R]$ molecules. Single crystals of the new complex were obtained and a low-temperature X-ray study undertaken, showing a unique dimetallocene structure **4**.



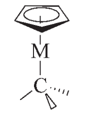
$\eta^5/\eta^1(\sigma)$

I

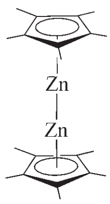


$\eta^5/\eta^1(\pi)$

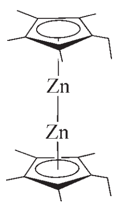
II



III



4



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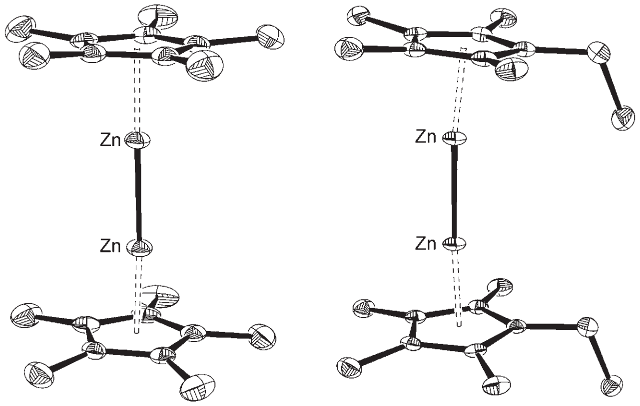
The synthesis of **4** from $[Zn(C_5Me_5)_2]$ and $ZnEt_2$ [Eq. (2)] was optimized by performing the reaction in Et_2O at −40 °C. The addition of 1,4-cyclohexadiene and of the free radical TEMPO (2,2,6,6-tetramethylpiperidin-1-yloxy) inhibits the formation of **4**, suggesting the involvement of radicals in the generation of the dimetallocene.[14b] Subsequently, dizincocene **4** was generated by reduction of $[\mathrm{Zn(C_5Me_5)_2}]$ with KH and from mixtures of the $[\mathrm{Zn(C_5Me_5)_2}]$, KH, and $\mathrm{ZnCl_2}$ [Eq. (3)].

$$[\mathrm{Zn(C_5Me_5)_2}]+\mathrm{ZnEt_2} \rightarrow [\mathrm{Zn_2(\eta^5\text{-}C_5Me_5)_2}]\ (\mathbf{4}) + [(\eta^5\text{-}\mathrm{C_5Me_5})\mathrm{ZnEt}] + \ldots \tag{2}$$

$$[\mathrm{Zn(C_5Me_5)_2}]+\mathrm{ZnCl_2} + 2\,\mathrm{KH} \xrightarrow[-\mathrm{KCl}]{\mathrm{THF},\ 20^{\circ}\mathrm{C}} [\mathrm{Zn_2(\eta^5\text{-}C_5Me_5)_2}]\ (\mathbf{4}) + \ldots \tag{3}$$

The synthetic route in Equation (3) is a convenient, straightforward procedure that allows the synthesis of **4** in 1-g or somewhat larger quantities. Extension of this procedure to the synthesis of the analogous derivatives of the parent $\mathrm{C_5H_5}$ group was not possible. Instead, action of NaH or KH on equimolar mixtures of $[\mathrm{Zn(C_5H_5)_2}]$ and $\mathrm{ZnCl_2}$ yielded the corresponding $\mathrm{M^+}$ salts of the zincates $[\mathrm{Zn(C_5H_5)_3}]^-$ and $[\mathrm{Zn_2(C_5H_5)_5}]^-$.[56] Similarly, no dizincocenes derived from the substituted cyclopentadienyl groups $\mathrm{C_5Me_4H}$, $\mathrm{C_5Me_4}t\mathrm{Bu}$, and $\mathrm{C_5Me_4SiMe_3}$ could be isolated, but a second dizincocene $[\mathrm{Zn_2(\eta^5\text{-}C_5Me_4Et)_2}]$ (**5**) was obtained following KH reduction of $[\mathrm{Zn(C_5Me_4Et)_2}]$ and $\mathrm{ZnCl_2}$ mixtures. Compound **5** shows appreciably lower thermal stability than **4**.

The novel structural characteristics of **4** and **5**, most notably their formulation as formally $\mathrm{Zn^I}$ derivatives with a $[\mathrm{Zn{-}Zn}]^{2+}$ unit, were demonstrated by a combination of structural characterization techniques and chemical reactivity studies.[14] Figure 2 shows ORTEP representations of **4** and **5**.



4 **5**

Figure 2. ORTEP views of dizincocene compounds $[\mathrm{Zn_2(\eta^5\text{-}C_5Me_5)_2}]$ (**4**) and $[\mathrm{Zn_2(\eta^5\text{-}C_5Me_4Et)_2}]$ (**5**; hydrogen atoms not shown).

The two cyclopentadienyl rings in each molecule are parallel and separated by a distance of approximately 6.40 Å, which allows adoption of an eclipsed geometry without steric interaction between their Me (or Et) substituents. The two Cp′ rings of **4** and **5** (Cp′ = $\mathrm{C_5Me_5}$ or $\mathrm{C_5Me_4Et}$) sandwich two directly bonded Zn atoms, thus providing an unprecedented dimetallocene structure. The $\mathrm{Zn{-}C_{ring}}$ separations are between 2.27 and 2.30 Å, and $\mathrm{Zn{-}Cp'_{centr.}}$ separations are approximately 2.04 Å (data for **4**). The most notable feature of these structures is the short Zn–Zn separation of approximately 2.30 Å (identical for **4** and **5** within experimental error), which, as discussed below (Section 2.3), is the shortest Zn–Zn separation found in the known Zn–Zn compounds. In characterized hydride-bridged binuclear zinc compounds $[\{\mathrm{ZnL}\}_2(\mu\text{-H})_2]$,[36a,57,58] the Zn–Zn separations are 2.40–2.45 Å.

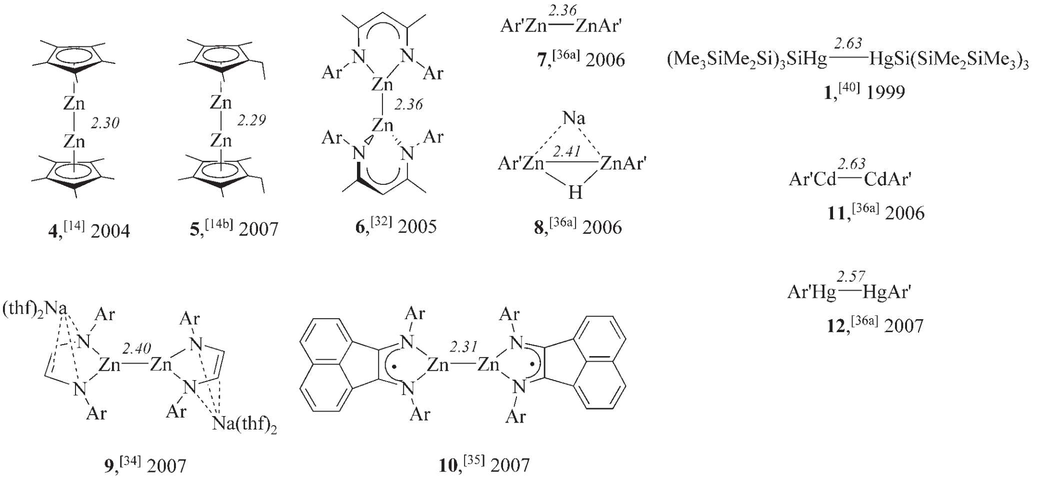
High-resolution mass spectra of **4** with natural isotopic distribution and labeled with $^{68}\mathrm{Zn}$ unambiguously favor the proposed formulation and rule out an alternative bridging hydride structure $[\{\mathrm{Zn(\eta^5\text{-}C_5Me_5)}\}_2(\mu\text{-H})_2]$.[14b] Despite the complexity of the molecular ion envelope (M^+ ca. 400 m/e), which is due to the existence of several Zn isotopes, the exact masses of its peaks are coincident with those calculated for the dimeric molecules of **4** of different zinc isotopes. Indeed, the artificially enriched $[^{68}\mathrm{Zn}]$**4** gives a simple molecular ion M^+ at 406 amu, with exact mass corresponding to that of $^{68}\mathrm{Zn_2}{}^{12}\mathrm{C_{20}}{}^{1}\mathrm{H_{30}}$. These studies also reveal that in the gas phase $[\mathrm{Zn_2(\eta^5\text{-}C_5Me_5)_2}]$ rearranges to $[\mathrm{Zn(C_5Me_5)_2}]$ and Zn.

Vibrational spectroscopy (IR and Raman) as well as ^{1}H and ^{13}C{^{1}H} NMR spectroscopy are also in accord with the dimetallocene structure of **4** and give no indication for the presence of zinc-bound hydrogen atoms. Comparison of the reactivity of $[\mathrm{Zn_2(\eta^5\text{-}C_5Me_5)_2}]$ toward $\mathrm{H_2O}$, tBuOH, and CNXyl (Xyl = $\mathrm{C_6H_3}$-2,6-$\mathrm{Me_2}$) with that of mononuclear zincocene $[\mathrm{Zn(C_5Me_5)_2}]$ unequivocally support the formulation of **4** as a derivative of the $[\mathrm{Zn{-}Zn}]^{2+}$ binuclear central unit. In all cases the Lewis base induces disproportionation of **4** into metallic zinc and a $\mathrm{Zn^{II}}$ compound identical to that resulting from the reaction of the $\mathrm{Zn^{II}}$ metallocene $[\mathrm{Zn(C_5Me_5)_2}]$ with the Lewis base.

2.3. New Metal–Metal Complexes of Zn, Cd, and Hg

Considering the state of the field prior to our first report on $[\mathrm{Zn_2(\eta^5\text{-}C_5Me_5)_2}]$ in 2004, it is indeed striking that in only a few years the number of molecular metal–metal compounds of Zn, Cd, and Hg has experienced a remarkable increase. Most noteworthy is a homologous series of complexes $\mathrm{M_2Ar'_2}$ (M = Zn, Cd, Hg) produced by Power and co-workers.[36a] Scheme 1 shows molecular compounds containing the $\mathrm{M_2}^{2+}$ unit that have been structurally characterized by X-ray crystallography. $\mathrm{Cd_2(AlCl_4)_2}$ is not included, as its structure has been described as containing $\mathrm{Cd_2}^{2+}$ cations stabilized by $\mathrm{AlCl_4}^-$ ions. Perhaps the most striking feature in Scheme 1 is the present existence of seven Zn–Zn compounds, **4**–**10**, that have been structurally characterized by X-ray crystallography. Zn–Zn bond lengths in these complexes span the relatively narrow range of 2.30–2.41 Å. In the known $[\mathrm{Zn_2X_2}(\mu\text{-H})_2]$ complexes (X = $\mathrm{HC(CMeNAr)_2}$ (Ar = $\mathrm{C_6H_3}$-2,6-$\mathrm{Me_2}$)[58] and $\mathrm{C_6H_3}$-2,6-$(\mathrm{C_6H_3}\text{-2,6-}i\mathrm{Pr_2})_2$[36a]), the Zn atoms are separated by a distance of approximately 2.45 Å.

Shortly after the characterization of **4**, Robinson et al. reported the formation of the Zn–Zn complex **6** (Scheme 1) containing a β-diketiminato ligand that had been used to stabilize other metal–metal bonds.[32] X-ray studies confirmed the dimeric nature of **6**, which despite having a lower effective coordination number than **4** features a somewhat longer Zn–



Scheme 1. Structurally characterized Zn, Cd, and Hg complexes containing metal–metal bonds. Literature references and year of publication are given, and M–M bond lengths are indicated in Ångstrom. Ar = C_6H_3-2,6-$i$$Pr_2$, Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$i$$Pr_2$)$_2$).

Zn bond of 2.3586(7) Å. Interestingly, the two β-diketiminato ligands arrange in a nearly orthogonal fashion, thus providing optimum steric protection to the bonded zinc atoms. This situation may explain the high thermal stability of **6** (m.p. 190 °C, dec.) and its somewhat lower reactivity toward oxygen and water in comparison with pyrophoric **4** and **5**.

Power and co-workers described two new Zn–Zn compounds[36] in which the Zn_2^{2+} unit was stabilized by the bulky terphenyl group (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$i$$Pr_2$)$_2$), namely $Zn_2Ar'_2$ (**7**) and the unusual hydride- and Na^+-bridged $Zn_2Ar'_2$(μ-H)(μ-Na) (**8**). They also characterized the Cd and Hg analogues of **7**, that is, $Cd_2Ar'_2$ (**11**) and $Hg_2Ar'_2$ (**12**).[36] The zinc complexes **7** and **8** were generated, together with the bishydride $(ZnAr')_2$(μ-H)$_2$, from Zn(Ar′)I by reaction with Na or NaH under appropriate conditions. Homoleptic $Zn_2Ar'_2$ (**7**) features a Zn–Zn bond length identical within experimental error to that in Robinson's complex **6** and greater by approximately 0.05 Å than in the dizincocenes **4** and **5**. For the unusual hydride **8**, which features a new type of Zn–Zn bonding, the Zn–Zn separation is lengthened by an additional 0.05 Å to approximately 2.41 Å. Once again, the two Ar′ ligands of **7** are nearly orthogonal to provide effective steric protection to the Zn–Zn bond. Complex **7** has high thermal stability and decomposes when the temperature is kept at 360 °C for several minutes. The sodium- and hydride-bridged complex **8** has a Zn–Zn bond length identical to that of **7**, but its two central aryl rings are nearly coplanar, with the bridging sodium and hydrogen atoms lying near this plane. The coordination requirements of the Na^+ ion are satisfied by strong η^6 interactions with the flanking aryl rings of the terphenyl group.

The homoleptic dicadmium diaryl complex $Cd_2Ar'_2$ (**11**) is only the second molecular compound with a Cd–Cd bond (after $[Cd_2(Tp^{Me2})_2]$[47]) and the first to be structurally characterized by X-ray crystallography (Figure 3, top). As previously discussed, $Cd_2(AlCl_4)_2$[46a,b] has a polymeric structure consisting of Cd_2^{2+} ions stabilized by $AlCl_4^-$ ions. While reaction of the Cd(Ar′)I precursor with Na and Na/naphthalene results in over-reduction to Cd metal, treatment with two equivalents of NaH allowed the isolation of **11** according to Equation (4).

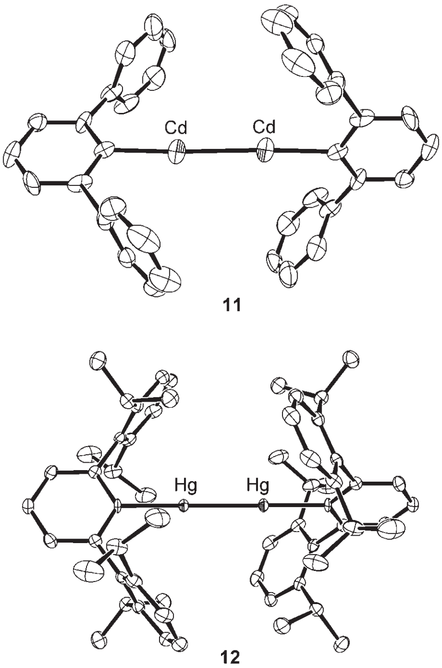


Figure 3. Molecular structures of $Cd_2Ar'_2$ (**11**, top, iPr groups and hydrogen atoms not shown) and $Hg_2Ar'_2$ (**12**, bottom, hydrogen atoms not shown); Ar′ = C_6H_3-2,6-(C_6H_3-2,6-$i$$Pr_2$)$_2$.

$$\{Cd(Ar')I\}_2 \xrightarrow[\text{THF, 25°C}]{\text{2 NaH}} Cd_2Ar'_2\ (\mathbf{11}) + \ldots \qquad (4)$$

The spatial distribution of the terphenyl ligands is similar to that in the dizinc analogue **7**, and the observed Cd–Cd distance of 2.6257(5) Å is comparable, albeit slightly longer, than the corresponding distance in $Cd_2(AlCl_4)_2$ (ca. 2.58 Å)[46a,b]. Further studies have shown that under the reaction conditions leading to **11**, the bishydride

$\{CdAr'(\mu\text{-}H)\}_2$ also forms. This complex has poor thermal stability and decomposes at ambient temperature over a period of a few hours to give **11**. This result suggests that the reaction of $\{CdAr'(\mu\text{-}I)\}_2$ with NaH [Eq. (4)] proceeds with initial formation of the $\{Cd_2(\mu\text{-}H)_2\}$ hydride, which then decomposes to yield **11** and dihydrogen.[36a]

In this same contribution,[36a] Power and co-workers describe the formation and structural characterization of the dimercury analogue $Hg_2Ar'_2$ (**12**) (Figure 3b, bottom), thus completing for the first time a series of homologous metal–metal complexes of the Group 12 elements. Compound **12** could not be obtained by direct arylation of Hg_2I_2 owing to disproportionation to Hg^0 and Hg^{II}, but reduction of Hg(Ar′)I with KC_8 provided the desired compound, albeit in low yields (less than 20%). Structural characteristics are similar to those of the lighter analogues **7** (Zn) and **11** (Cd), with the terphenyl groups in a nearly orthogonal arrangement. Comparison of the Hg–Hg and Hg–X bonds of **12** and the related silyl derivative **1** reveals the foreseen variation in bond lengths in view of the expected polarity differences between the Hg–C and Hg–Si bonds. Thus, the Hg–C bonds in **12** (ca. 2.10 Å) are significantly shorter than the 2.485(2) Å found for the Hg–Si bond in **1**, while the Hg–Hg bond length of approximately 2.57 Å is also shorter than the corresponding 2.6569(8) Å value in **1**. A more interesting comparison is offered by the M–M distances found in the $M_2Ar'_2$ complexes **7** (2.36 Å, Zn), **11** (2.63 Å, Cd), and **12** (2.57 Å, Hg). The decrease from the Cd–Cd to the Hg–Hg complex is in accord with the smaller radius of Hg than Cd, as predicted by theoretical calculations that include relativistic effects.[59] A similar contraction has been found experimentally in compounds of Cu, Ag, and Au, leading to the conclusion that for two-coordinated M^I compounds radius values of 1.13 (Cu), 1.33 (Ag), and 1.25 Å (Au) should be considered.[60] In qualitative terms, this can be explained by the "lanthanide contraction," which refers to the high effective nuclear charge of atoms of the third transition series with $4s^2p^6d^{10}f^{14}5s^2p^6d^n6s^2$ electron configurations as a consequence of the highly directional properties of f electrons and hence of their poor screening of the nuclear charge. The contribution of the directional character of d electrons to this effect becomes especially important for the late transition metals platinum and gold and for the heaviest Group 12 element mercury.[60]

Recently, the two Zn–Zn compounds **9** and **10** (Scheme 1) were prepared and their solid-state structures determined by X-ray crystallography. The successful isolation of these (and previously discussed) compounds rests largely on a rational choice of the co-ligands. Reduction of $[ZnCl_2(H_2L)]$ with Na metal (where L represents the neutral, parent α-diimine ligand of **9** in Scheme 1) permits isolation of orange crystals of the centrosymmetric dimer $[Zn_2L_2\{Na(thf)_2\}_2]$ containing the doubly reduced α-diimine ligand.[34] In contrast to the orthogonal ligand distributions in **6** and **7**, the two C_2N_2 planes of **9** are parallel with a vertical separation of approximately 1.28 Å. The two $[Na(thf)_2]^+$ units place themselves above and below the two five-membered ZnN_2C_2 metallacycles, respectively. In this compound the coordination of each of the Na^+ cations is completed by κ^4-interaction with one N–C=C–N moiety, thus providing additional steric protection to the Zn–Zn bond, which has a length of ca. 2.40 Å.

In turn, compound **10** represents the first example of a complex with a Zn–Zn bond stabilized by radical anionic ligands, $[Zn_2(\text{dpp-bian})_2]$, where dpp-bian is the radical anion of 1,2-bis[(2,6-diisopropylphenyl)imino]acenaphthene.[35] Although **10** can be obtained by potassium reduction of the $[\{Zn(\text{dpp-bian})(\mu\text{-}I)\}_2]$ dimer, the most convenient synthesis consists in the reaction of $ZnCl_2$ with the in situ generated sodium salt of the dpp-bian dianion. In this way compound **10** may be prepared on a several-gram scale in the form of deep red, almost black crystals, which are stable under inert atmosphere up to 300°C. The Zn–Zn bond length is approximately 2.33 Å, and the biradical nature of the complex has been probed by ESR spectroscopy.

3. Theoretical Studies

3.1. Simple M_2, M_2H_2, and M_2X_2 Compounds

The simplest Group 12 species that displays a metal–metal interaction is the diatomic M_2 dimer (M = Zn, Cd, Hg). Several properties of these homonuclear dimers were discussed by Morse in 1986 in a review devoted to clusters of transition-metal atoms.[61] Some Group 12 heteronuclear MM′ dimers were also considered. The Zn_2 dimer has been studied by DFT methods at various levels of computation in conjunction with other homonuclear 3d metal dimers.[62] Zn_2 is characterized by a $^1\Sigma_g^+$ ground state and a long Zn–Zn separation. In localized molecular orbitals (MOs), all the bonding and antibonding orbitals derived from 3d and 4s atomic orbitals are occupied with no chemical bonding (zero bond order) and only a small binding energy.[62b] The computed binding energies fit well with the spectroscopically determined experimental values.[63]

Recently, the spectroscopic and thermochemical parameters of the triad of dimers M_2 (M = Zn, Cd, Hg) have been computed to verify the performance of a high-level basis set.[64] The Zn_2 species has a diffuse 5s4p + 5s4p orbital which could accept an electron, but the resulting Zn_2^- anion is not stable toward dissociation. By contrast, the removal of one electron from Zn_2 leads to the formation of a single populated 4s + 4s bond in the Zn_2^+ cation ($^2\Sigma_u^+$ ground state).[62b] The existence of this bonding interaction agrees with a shorter computed Zn–Zn separation (2.60 Å) than in Zn_2 and a higher dissociation energy, which slightly overestimates the experimental value.[62b] The presence of the Zn_2^+ cation as a furan adduct appears to have been detected by high-resolution mass spectrometry.[65] The removal of a second electron produces the Zn_2^{2+} species, the electronic structure of which has been recently examined by ab initio plane-wave-based DFT calculations[23] and which is characterized by a bond length of 2.46 Å.

A second simple species that has been theoretically analyzed is the compound Zn_2H_2. According to the arguments outlined above, this compound should display a Zn–Zn single bond owing to the formal presence of the Zn_2^{2+} ion. Zn_2H_2 was detected by matrix infrared spectroscopy; calculations by

Andrews and co-workers at several levels of theory were carried out to rationalize the experimentally observed bands.[49] Linear HZnZnH is 6.7 kcal mol^{-1} more stable than the rhombic D_{2h} ring structure, and its formation from the monohydride ZnH is exothermic (59.5 kcal mol^{-1}).[49a] The analogous HCdCdH was also detected, and the DFT results also gave a linear molecule with a Cd–Cd length of 2.715 Å and a calculated IR spectrum in agreement with the observed absorptions.[49b] A comparative ab initio investigation on M_2H_2 and M_2X_2 (M = Zn, Cd, Hg; X = F, Cl) was carried out by Kaupp and von Schnering to search for the origin of the stability of the Hg_2^{2+} ion.[66] The M–M binding energies were computed at various computational levels and were all found to be around 60 kcal mol^{-1} (for the dihydride derivatives, a somewhat higher value was found for Hg than for Zn or Cd). However, the disproportionation energies are a more realistic measure of the stability of M_2H_2 than energies attributed to the dissociation into MH units. The order of stability based on the energy of disproportionation into MH_2 and M is Cd > Zn > Hg (in the gas phase).[66] Kaupp and von Schnering also found that the Hg_2X_2 (X = F, Cl) compounds are considerably less stable toward disproportionation than their Cd and particularly their Zn homologues.

Consequently, the gas-phase disproportionation energies did not provide an explanation for the observed stability of the Hg_2^{2+} species in the condensed phase. The aggregation and solvation effects in the condensed phase along with relativistic effects are important to explain such stability. In fact, these conclusions were corroborated and extended by Schwarz and co-workers in a relativistic DFT study carried out for MX, MX_2, and M_2X_2 in the solid state (M = Zn, Cd, Hg; X = F, Cl, Br, I).[67] All M_2X_2 molecules, specially Zn_2X_2, were predicted to be stable towards disproportionation in the gas phase, but the equilibrium was shifted toward MX_2, specially for Zn and Cd, by condensation of the metal. This work is also an extension of a previous study devoted specifically to mercury compounds Hg_2X_2 (X = H, F, Cl, CH_3, CF_3).[68]

3.2. Dizincocenes $[Zn_2(\eta^5\text{-}C_5R_5)_2]$ and Related Compounds

On the basis of the above considerations, proving the existence of stable Zn^+ species appears to be a difficult task. As already noted, there is evidence for the formation of Zn_2^{2+} ions in $ZnCl_2$/Zn glasses at high temperatures[48] and in zeolite matrixes,[50,51] and recently the formation of mononuclear, paramagnetic Zn^+ in a microporous crystalline silicoaluminophosphate was reported.[52] The presence of the same ion in the cavities of a zeolite was claimed in a reinterpretation of previously published results.[51b] However, $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ was the first stable compound with a Zn–Zn bond to be characterized, and following this report,[14a] the characterization of the unprecedented Zn–Zn bond and the study of its properties have been the aim of several research groups.

The first theoretical studies of $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ and the model compound $[Zn_2(\eta^5\text{-}C_5H_5)_2]$ were simultaneously published by our group[16] and by Xie et al.[17] The latter report analyzed two possible conformations (coaxial and perpendicular) of the dimetal units (M = Zn, Ni, Cu) in dimetallocenes. About a dozen subsequent studies have appeared, which we now summarize. Concerning the structural parameters, the cyclopentadienyl rings are parallel or practically parallel when no symmetry is imposed in the calculations. Similarly, the angle between the two zinc atoms and the cyclopentadienyl centroid is 180° or close to it when no symmetry is imposed. In fact, several symmetries have been analyzed (D_{5h}, D_{5d}), and they have essentially the same energy. The optimized $[Zn_2(\eta^5\text{-}C_5R_5)_2]$ molecules display Zn–Zn bonds of 2.28–2.35 Å, in good agreement with experimental values.

Taking into account the classical MO diagram of a half-sandwich main-group metallocene,[69] the frontier orbitals of a neutral $\{(\eta^5\text{-}C_5Me_5)Zn\}$ group are a singly occupied highest occupied MO, which results from the antibonding combination of a_1 (π, C_5Me_5) and the s and p_z metal orbitals, and a pair of degenerate orbitals that are the combination of e_1 (π, C_5Me_5) with the $p_{x,y}$ metal orbitals. Thus, from a qualitative point of view, the Zn–Zn bond results from the interaction of the singly occupied HOMOs of the two $\{(\eta^5\text{-}C_5Me_5)Zn\}$ fragments. These qualitative arguments are fully confirmed by the calculations of several authors, which have afforded analogous results. The frontier orbitals are four quasi-degenerate occupied orbitals (from the HOMO to the HOMO−3) that are the combinations (in-phase and out-of-phase) of the degenerate e_1 orbitals of C_5Me_5 with a very small participation of the Zn p orbitals. The HOMO−4 (Figure 4) corresponds to the Zn–Zn interaction in which the participation of Zn orbitals is high (different contributions give values of ca. 60 %,[16] 70 %[20] or even higher[25,28]). There is also agreement between the different calculations about the preponderance of Zn 4s orbitals (e.g. 86[28] or 96 %[16]), which is also expressed by hybridization of type $sp^{0.03}d^{0.01}$ [17] or $sp^{0.01}d^{0.02}$.[25]

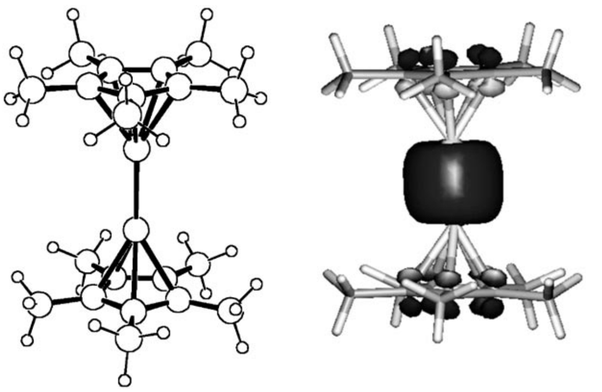


Figure 4. Optimized structure of $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ and 3D representation of the HOMO−4 orbital that accounts for the Zn–Zn interaction.

An analysis by Schnepf and Himmel[70] emphasized the importance of the disproportionation energy for the stabilization of the formally Zn^I centers and the presence of the Zn–Zn bond. This conclusion corroborates the observation by Kaupp and von Schnering[66] for M_2X_2 compounds (see Section 3.1). However, most theoretical studies have focused on the bond dissociation energy (BDE) to estimate the bond strength. Only a few contributions have determined the energy of the disproportionation reaction to Zn and Zn^{II} (e.g. $[Zn_2Cp'_2] \rightarrow Zn + [ZnCp'_2]$). For the $[Zn_2(\eta^5\text{-}C_5H_5)_2]$ model, ΔE values for this reaction of 20[17] and 17 kcal mol^{-1} have been reported. The 17-kcal mol^{-1} value[14b] corresponds to an endergonic value for ΔG of approximately 5 kcal mol^{-1}, assuming that gaseous zinc is produced, and is consistent with the stability of $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ and $[Zn_2(\eta^5\text{-}C_5Me_4Et)_2]$. Calculated values for the dissociation energy of the Zn–Zn bond cover the range 55–70 kcal mol^{-1}. In general, a computed electronic energy E(Zn–Zn) somewhat higher than 60 kcal mol^{-1} was found for $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$, which is of the same order of magnitude as the calculated value for the related Zn_2H_2 and Zn_2X_2 species (see Section 3.1). Xie and Fang pointed out that the values calculated by using the CCSD(T)/B3LYP approach are lower than those obtained with DFT/B3LYP (e.g. 41.9 and 67.2 kcal mol^{-1}, respectively, for $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$).[19] Some energy decomposition analyses have been performed for metal–metal bonds in $[Zn_2(\eta^5\text{-}C_5R_5)_2]$ and M_2R_2.[26,28] For $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$, Pandey[26] and Kan[28] come to similar conclusions. The bond dissociation energy for the Zn–Zn bond is close to 70 kcal mol^{-1} and has slightly more attractive contributions from classical electrostatic interactions than from orbital interactions (more than half ionic character).

The spectroscopic properties of decamethyldizincocene have been theoretically studied by several authors.[20,21] Kress found absorptions in the calculated Raman spectrum associated with the Zn–Zn stretching mode at 384 and 92 cm^{-1}.[20] Besides these frequencies, Richardson and co-workers found an intense peak at 1410 cm^{-1}, which was always mixed with several vibrational modes.[21] Our own experimental (IR and Raman spectroscopy) and theoretical studies show the presence of a characteristic band arising from Zn–(η^5-C_5Me_5) stretching within $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ that appears at 320 cm^{-1} in the IR (asymmetric mode) and at 370 cm^{-1} in the Raman spectrum (symmetric mode).[71] Furthermore, a weak absorption in the Raman spectrum centered at 232 cm^{-1} is assigned to the Zn–Zn stretching mode.[71]

The calculations have been extended to the heavier elements of Group 12, and the unknown $[M_2(\eta^5\text{-}C_5R_5)_2]$ compounds have been studied for M = Cd[18,19,22] and Hg.[25–28] In some cases, heterometallic species $[MM'(\eta^5\text{-}C_5R_5)_2]$, have also been considered.[18,22] For mercury, the nature of the metal–metal bond in the hypothetical $[Hg_2(\eta^5\text{-}C_5R_5)_2]$ (R = H, Me) compounds was investigated using energy decomposition analysis.[25,26,28] However, the presence of two η^5-cyclopentadienyl ligands coordinated to mercury seems unrealistic[72] (although it has been employed for comparison with the other Group 12 elements),[28] while the η^1-coordination studied by Philpott and Kawazoe in $[Hg_2(\eta^1\text{-}C_5H_5)_2]$ and mixed $[(\eta^5\text{-}C_5H_5)ZnHg(\eta^1\text{-}C_5H_5)]$ species looks more reasonable.[27] Some conclusions can be drawn by comparing the Zn and Cd derivatives of $[M_2(\eta^5\text{-}C_5R_5)_2]$. The expected longer metal–metal bond for Cd (the computed range 2.56–2.72 Å fits well with the experimental value of 2.6257(5) Å found in $Cd_2Ar'_2$) correlates with a lower dissociation energy than for Zn.

Recently, the geometries and energetics of multimetallocenes $[CpM_nCp]$ (M = Zn and some Group 2 metals) have been theoretically studied by Frenking, Merino, and co-workers.[31] In the case of zincocenes, the $[CpZn_nCp]$ compounds with $n > 2$ are thermodynamically unstable with respect to loss of one metal atom, and the interactions between Zn_n^{2+} and $(Cp^-)_2$ have a large electrostatic character.

3.3. $[Zn_2L_2]$, Zn_2Ar_2, and Related Compounds

Reports on Zn–Zn compounds **6**–**10** (Scheme 1) were accompanied by corresponding DFT studies on models or real compounds. Calculations of $[Zn_2L_2]$ (L = $(HNCH)_2CH$),[32] $Na_2[Zn_2L_2]$ (L = $(HCNH)_2$),[34] and $[Zn_2L_2]$ (L = 1,2-bis(phenylimino)acenaphthene)[35] models have been performed. These calculations mainly focused on the length of the computed Zn–Zn bond, the orbital contributions to the Zn–Zn bond, the nature of the frontier MOs, the bond dissociation energy (65.2 and 57 kcal mol^{-1} for **6** and **9**, respectively), and the disproportionation energy (5.6 kcal mol^{-1} for **6**). Each of the models share a common environment around the Zn atoms. These are tricoordinated, and besides the Zn–Zn interaction they are bonded to two N-donor atoms belonging to monoanionic (**6**), dianionic (**9**), and radical anionic ligands L (**10**). Surely this fact is related to the similar orbital composition of the Zn–Zn bond (ca. 95 % s and 4 % p) found in all cases.

Power and co-workers[36a] have characterized an homologous series of $M_2Ar'_2$ compounds (M = Zn, Cd, Hg; Ar' = C_6H_3-2,6-(C_6H_3-2,6-iPr$_2$)$_2$). The computed M–M bond lengths for corresponding M_2Ph_2 models (2.385 (Zn), 2.707 (Cd), and 2.677 Å (Hg)) are in agreement with experimental values for the $M_2Ar'_2$. The HOMO of M_2Ar_2 compounds is a metal–metal bonding orbital; its s-orbital character is less than 50 % in all cases, and the remaining contributions arise from p_z and ligand-based orbitals. The involvement of the metal p_z orbitals in the HOMO is in contrast to the bonding situation calculated for other Zn–Zn compounds (**4**, **6**, **9**, and **10**), in which the Zn–Zn bond is formed almost exclusively from 4s orbitals. The lower coordination number of metal atoms and the nature of the ligands are likely responsible for this change in hybridization. For the M_2Ph_2 model series,[36a] the p character of the HOMO gradually decreases down the group (Zn 18.8 %, Cd 16.5 %, Hg 15.8 %), and Hg has a non-negligible d_{z^2} contribution to the HOMO (5 %). In this work, the energies of the M–M bonds for the $M_2Ar'_2$ species and the BDE for M_2Ph_2 models have been computed. The BDE values are similar to those of the M–M compounds $M_2Ar'_2$ and are comparable to data reported for M_2H_2,[49,66] M_2Me_2[26,28] and $[M_2(\eta^5\text{-}C_5R_5)_2]$.[14b] The energy of the Cd–Cd bond in Cd_2Ph_2 was found to be 52.7 kcal mol^{-1}, which is lower than corresponding values for the Zn and Hg homologues (60.9 and 54.4 kcal mol^{-1}, respectively). Analogous results were observed for the energies computed in $M_2Ar'_2$ (56.3 (Zn), 48.8 (Cd), and 51.0 kcal mol^{-1} (Hg)). A similar BDE trend within M_2X_2 salts (X = halogen) was reported by Kaupp and von Schnering[66] and by Schwerdtfeger et al.[68]

Recently, Pandey analyzed $Hg_2(SiH_3)_2$,[26] a model of $Hg_2[Si(SiMe_2SiMe_3)_3]_2$,[43] in comparison with other RMMR compounds. The computed Hg–Hg bond of 2.706 Å is slightly longer than the experimental value of 2.6569(8) Å. The MO description is similar to that outlined for $M_2Ar'_2$. The HOMO accounts for the Hg–Hg σ bond resulting from the interactions of s and p_z orbitals, while LUMO and LUMO + 1 are orbitals of π symmetry derived from a combination of the empty metal p orbitals, similar to the observations of Power and co-workers.[36a]

4. Summary and Outlook

The structural characterization of the dizincocene $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ has triggered research in this field, which has resulted in remarkable growth of the experimental and theoretical chemistry of Group 12 compounds with metal–metal bonds. Studies have concentrated on the synthetic, structural, and electronic characteristics of these compounds and have led to seven Zn–Zn compounds that have been characterized by X-ray crystallography. So far, little attention has been devoted to the reactivity of these compounds, in particular to their participation in reactions that may lead to new homo- and heterometallic zinc cluster compounds. As already mentioned,[70] the tendency of $[Zn_2(\eta^5\text{-}C_5Me_5)_2]$ to disproportionate to Zn^{II} and Zn^0 opens the possibility of accessing new metalloid clusters.[10] It is also likely that Zn_2R_2 compounds may participate in oxidative addition reactions; therefore, a variety of polymetallic structures can be anticipated. Furthermore, the search for related M–M structures of this kind, for example for the lighter Group 2 elements (especially beryllium), also appears to be an attractive research target. In fact, after submission of this manuscript, the synthesis and structure of the first Mg–Mg compounds were published.[73] Other recent reports related to the content of this manuscript, including a new Zn–Zn complex,[74] can be found in the references.[75,76]

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