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Review

Synthesis and structural characterization of dizincocenes $Zn_2(\eta^5\text{-}C_5Me_5)_2$ and $Zn_2(\eta^5\text{-}C_5Me_4Et)_2$

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Contents

Abstract

The synthesis and structural characterization of the dimetallocenes $Zn_2(\eta^5\text{-}C_5Me_5)_2$ and $Zn_2(\eta^5\text{-}C_5Me_4Et)_2$ are reviewed together with unsuccessful attempts to obtain analogous complexes containing other cyclopentadienyl ligands. The possibility of preparing related dimetallocenes structures for the late-transition elements is also examined and an overview of known metal–metal bonded molecular compounds of the group 12 elements is given.

Keywords: Metallocenes; Zinc; Metal–metal bond

1. Introduction

Recent work carried out in our laboratory has resulted in the synthesis and characterization of $Zn_2(\eta^5\text{-}C_5Me_5)_2$ **1**, the first stable molecular compound that contains a Zn–Zn bond [1a]. Decamethyldizincocene was unique at that time not only because of the presence of a Zn–Zn bond but also because of its unprecedented metallocene structure that consists of a pair of directly bonded metal atoms sandwiched between two parallel cyclopentadienyl rings, such that the metal–metal bond is collinear with the C_5 axis of the C_5Me_5 rings. At variance with related structures known for some transition elements, the zinc atoms of **1** do not bear additional ligands, either bridging or terminal.

The structural characterization of **1** was shortly followed by a number of theoretical studies of the bonding and electronic properties of this and related dimetallocenes structures [2], including our own one [3]. Experimental reports on new Zn–Zn [4] (and also Cd–Cd [5]) bonded compounds followed also in due course. Our attempts to extend the synthesis of **1** to dimetallocenes of other cyclopentadienyl groups found limited success, although a second dizincocene, $Zn_2(\eta^5\text{-}C_5Me_4Et)_2$ **2**, with lower thermal stability than **1**, was prepared and structurally characterized [1b].

In this contribution we provide an account of how this work developed, how compound **1** was unexpectedly obtained and subsequently prepared by a rational, gram-scale route. We will also discuss the difficulties encountered for the characterization

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of **1**, in particular the distinction between its correct structure and the alternative formulation as a putative bridging dihydride structure, $[Zn_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}H)_2]$.

To place our results in context, we first make a brief discussion of compounds that possess metal–metal bonds, encompassing derivatives of both the transition and the main group elements, with particular reference to clusters containing cyclopentadienyl ligands. Since transition metal compounds that hold two metal–metal bonded $(\eta^5\text{-}C_5Me_5)M$ units complemented by other ligands, e.g., hydride, halide, oxo and others, i.e., $[(\eta^5\text{-}C_5Me_5)M]_2(\mu\text{-}L)_n$, are potentially useful precursors for the synthesis of so far unknown transition metal dimetallocenes $M_2(\eta^5\text{-}C_5R_5)_2$, some binuclear complexes of this kind will also be considered. Then the synthesis and characterization of **1** and **2** will be examined.

2. Compounds with metal–metal bonds

A distinctive characteristic of inorganic chemistry is the wide occurrence of compounds that present direct bonds between metallic elements [6]. This notion was not recognized in the early years of Werner but started to become familiar in the late 1930s and in the following decades, when the subject of many such compounds was determined by X-ray crystallographic techniques. The field quickly expanded, a landmark discovery being the structural characterization of transition metal compounds that possess multiple metal–metal bonds. [7,8] The seminal recognition by Cotton in 1964 of the Re–Re quadruple bond was followed by many contributions made by his own group. Indeed, Cotton and co-workers have provided much of our present knowledge of this important class of compounds over the years. Progress on related derivatives of main group elements was comparatively slower but nowadays the study of compounds that contain single or multiple bonds between elements of groups 13 and 14 is a very important area of research [9]. Interest has centred in part on clusters that exhibit delocalized bonds among the metal atoms [10], some of which are ligand bearing whereas others are only bonded to other metal atoms [12,13]. In general, these clusters exhibit more direct metal–metal bonds than metal–ligand bonds. They are called metalloid clusters [12c] and until recently they were known only for the noble transition metals, e.g., the nanosized Pd clusters $Pd_{59}(CO)_{32}(PMe_3)_{21}$ or $Pd_{145}(CO)_x(PEt_3)_{30}$ [14]. Following the synthesis and characterization of $[Al_{77}(N(SiMe_3)_2)_{20}]^{2-}$ by Schnöckel and co-workers [12a] many compounds of this kind have been made for the heavier elements of groups 13 and 14.

Dinuclear compounds of main group elements with multiple element–element bonds have also attracted a great deal of attention. The first compound with a Sn=Sn double bond was reported by Davidson and Lappert [15], but it is only in the last 10 years that compounds that feature E≡E triple bonds have been obtained [16–18] for many of the groups 13 and 14 heavier elements. Nevertheless, despite the triple bond formulation, there is usually nonbonding lone-pair electron density character at the central E atoms that result in a decrease in the bond order.

Most of the cluster compounds mentioned above are organometallic in nature as they contain M–C bonds to different hydrocarbon-based ligands. An important group of dinuclear M–M bonded compounds is that containing cyclopentadienyl ligands (in general Cp′). Some of these compounds, like for instance $(\eta^5\text{-}C_5H_5)_2Fe_2(CO)_4$ and $(\eta^5\text{-}C_5H_5)_2Mo_2(CO)_6$ are known since the early years of metal cyclopentadienyls [19]. Some compounds of this type containing bridging hydride, halide or related ligands will be briefly mentioned in the following section. Higher nuclearity cyclopentadienyl clusters are well known, in many cases containing bridging hydride and carbonyl ligands [20]. But clusters containing only Cp′ ligands have also been described and they can be exemplified by the interesting hexameric molecule $Ni_6(\eta^5\text{-}C_5H_5)_6$ [21] and by the mixed-metal cluster $Ni_2Zn_4(\eta^5\text{-}C_5H_5)_6$ [22]. Compounds of composition $(\eta^5\text{-}Cp')E$, where E is a group 13 element, are monomeric in the gas phase but adopt highly symmetric cluster arrangement in the solid state [23]. For instance, $Al(\eta^5\text{-}C_5Me_5)$ is tetrahedral, i.e., $Al_4(\eta^5\text{-}C_5Me_5)_4$, while the Ga and In analogs display octahedral hexameric structure $M_6(\eta^5\text{-}C_5Me_5)_6$. However, in contrast with $Al_4(\eta^5\text{-}C_5Me_5)_4$ that has Al–Al distances of 2.77 Å, somewhat shorter than in aluminum metal [24], the M–M separation in the Ga_6 (ca. 4.10 Å) and In_6 (3.95 Å) clusters are very long indicating that M···M interactions are of little importance, the cluster structure being defined by ligand–ligand interactions [25]. $Al_4(\eta^5\text{-}C_5Me_5)_4$ exhibits a very rich and diverse chemistry [11,24] and has been cited as a milestone in modern organometallic chemistry [9a]. Indeed, the Al/C_5Me_5 combination has given rise to a number of unusual structures, among them a cluster core of 50 aluminum atoms protected by 12 $\eta^5\text{-}C_5Me_5$ ligands in the compound $Al_{50}(\eta^5\text{-}C_5Me_5)_{12}$ [26].

3. Some metal–metal bonded $[M(\eta^5\text{-}Cp')]_2(L)_n$ and related compounds

Binuclear cyclopentadienyl complexes of mid- and late-transition metal halides, oxides and hydrides are well known and appear as possible precursors for the synthesis of dimetallocene structures by means of chemical reduction, dehydrogenation or decarbonylation reactions. For example, halide-bridged molybdenum and tungsten compounds analogous to the known $(\eta^5\text{-}C_5H_4R)_2Mo_2(\mu\text{-}X)_4$, which are halide-bridged, probably singly bonded dimolybdenum(III) species, or to $W_2(\eta^5\text{-}C_5H_4Pr^i)_2Cl_4$, that contains terminal chloride and a triple W≡W bond of length 2.368(1) Å [27] seem suitable candidates for this purpose. While this might appear somewhat unrealistic in view of the high degree of unsaturation in the purported dimetallocenes, the successful isolation by Power and co-workers of the quintuply bonded ArCrCrAr [28], derived from the sterically encumbering monoanionic terphenyl ligand $C_6H_3\text{-}2,6\text{-}(C_6H_3\text{-}2,6\text{-}Pr_2^i)_2$, clearly shows that suitable design of the system to be investigated, particularly of the ligands, can allow synthetic achievements previously considered unattainable. On these grounds, Mo and W compounds of the above type containing bulky *supracyclopentadienyl* ligands [29] are good candidates to investigate this possibility.

Apart from the halide, the related metal–metal bonded cyclopentadienyl carbonyls deserve consideration. Complete loss of carbon monoxide from poly(carbonyl) derivatives of

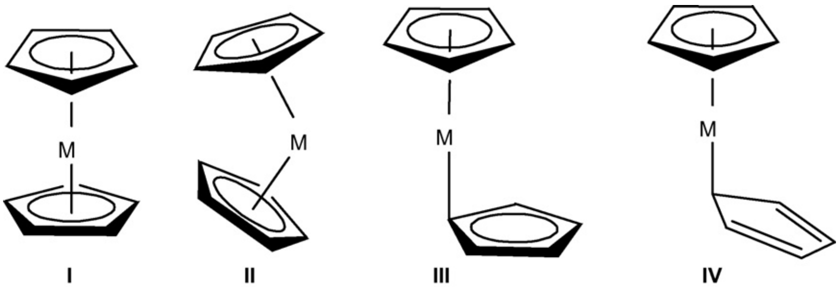


Fig. 1. Structural types for divalent metallocenes.

metals in low oxidation states, e.g., group 6 triply bonded $M_2(\eta^5\text{-}Cp')_2(CO)_4$ [30], or group 8 singly bonded $M_2(\eta^5\text{-}Cp')_2(CO)_4$ [31] derivatives does not seem feasible. However, as already hinted by DFT calculations, Ni≡Ni bonded dinickelocenes are reasonable synthetic objectives [2a] and they could be obtained by thermal or photochemical decarbonylation of suitable $Ni_2(\eta^5\text{-}Cp')_2(CO)_2$ precursors. Nickelocene reactivity provides further support to this hypothesis [32]. For example, reduction of $Ni(\eta^5\text{-}C_5H_5)_2$ with the Ni(0) isocyanide complex $Ni(CNC_6H_5)_2$ yields the Ni–Ni bonded $Ni_2(\eta^5\text{-}C_5H_5)_2(\mu\text{-}CNC_6H_5)_2$.

As discussed in the following section, the reduction of $Zn(C_5Me_5)_2$ gives $Zn_2(\eta^5\text{-}C_5Me_5)_2$. Thus, the reduction of late-transition metal metallocenes is also a viable choice in the search for other $M_2(\eta^5\text{-}Cp')_2$ structures. It has been shown [33] that under mild reduction conditions partial degradation of MCp'_2 compounds occurs with the formation of reactive, albeit isolable, products [33]. Thus, potassium reduction of $Co(\eta^5\text{-}C_5Me_5)(\eta^5\text{-}C_5H_5)$ under ethylene yields $(\eta^5\text{-}C_5Me_5)Co(C_2H_4)_2$. As mentioned briefly, treatment of $Ni(\eta^5\text{-}C_5H_5)_2$ with sodium naphthalenide yields $Ni_6(\eta^5\text{-}C_5H_5)_6$ [21]. It would be of interest to examine the effect of substituents in the Cp′ ring particularly if one considers that while the reduction of zincocenes $Zn(C_5H_4R)_2$ with $Ni(cod)_2$ gives hexameric, octahedrally derived $Ni_2Zn_4(\eta^5\text{-}C_5H_4R)_6$ clusters, the analogous reaction of the bulkier zincocene $Zn(C_5Me_5)_2$ and $Ni(cod)_2$ gives the zinc-free $[(\eta^5\text{-}C_5Me_5)Ni]_2(C_{16}H_{24})$ complex of a 16 carbon diene ligand that results from the dimerization of two molecules of cod. Metallic zinc was also produced as a consequence of complete decomposition of an intermediate $Zn–C_5Me_5$ radical [34].

A low temperature (−120 °C) cobalt atom reaction with C_5Me_5H was initially reported to give decamethyldicobaltocene $Co_2(\eta^5\text{-}C_5Me_5)_2$, together with a mononuclear complex and the triple-decker compound $Co_2(\eta^5\text{-}C_5Me_5)_3$ [35a]. However, a study of the electronic structure of model $Co_2(\eta^5\text{-}C_5H_5)_2$, along with consideration of the reactivity reported for the purported dicobaltocene, led Bursten and co-workers [35b] to suggest the presence of hydride ligands in the observed structure and this proposal was subsequently confirmed experimentally [35c], with the characterization of the complex as $Co_2(\eta^5\text{-}C_5Me_5)_2(\mu\text{-}H)_3$. Neutron diffraction studies confirmed this structure [36a] and more recently a closely related compound, $Co_2(\eta^5\text{-}C_5H_2Bu^t_5)(\mu\text{-}H)_3$ has also been studied by neutron diffraction techniques [36b].

4. Zincocenes and dizincocenes. general considerations

The zincocene chemistry our group has developed over the past years started as an extension of previous research that concentrated on beryllocenes, $BeCp'_2$ [37]. Contrary to the molecular divalent metallocenes of transition elements, that exhibit invariably the classical sandwich structure **I** (either staggered or eclipsed), those of main group elements may exhibit a variety of structures (Fig. 1), that in addition to **I** encompass the bent sandwich structure **II** and the slipped sandwich geometry **III** [9a,23]. Interestingly the three structural types are encountered among methyl-substituted metallocenes of the alkaline-earth metals. For example, $Mg(\eta^5\text{-}C_5Me_5)_2$ and $Be(\eta^5\text{-}C_5Me_5)_2$ are classical sandwich metallocenes, while $M(\eta^5\text{-}C_5Me_5)_2$ (Ca, Sr and Ba) posses structure of type **II** and $Be(C_5Me_4H)_2$ exhibits structure **III**. The slipped sandwich structure **III** is actually characteristic of beryllocenes (with the exception of $Be(\eta^5\text{-}C_5Me_5)_2$) and of zincocenes [9a,23]. This unusual geometry [38] is often referred to as $\eta^5/\eta^1(\pi)$ and its characterized by a long, relatively weak bond between the metal and the η^1 ring and by significant π-electron delocalization within this ring. The alternative $\eta^5/\eta^1(\sigma)$ structure **IV** is unknown for binary metallocenes but has been demonstrated in the cation $[B(C_5Me_5)_2]^+$ [39].

Reasons justifying the adoption of geometries **I**–**III** by a particular metallocene MCp'_2 have been lucidly analyzed by Beattie and co-workers [38]. Very briefly and in what concerns this discussion, an element like B or Si that forms strong bonds with carbon prefers the $\eta^1(\sigma)$ structure despite the loss of electron delocalization within the ring, that becomes of diene nature (Fig. 2). The heavier alkaline-earth elements that form very weak M–C bonds give rise to mostly ionic structures, with long M–C bonds but with extensive electron delocalization within the η^5-Cp′ ring. Be, Zn, Al and other elements that form bonds with carbon of intermediate strength adopt the compromise structure $\eta^1(\pi)$, where the relative weakness of the E–C bond

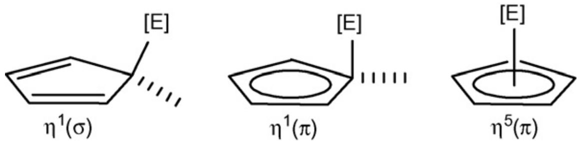
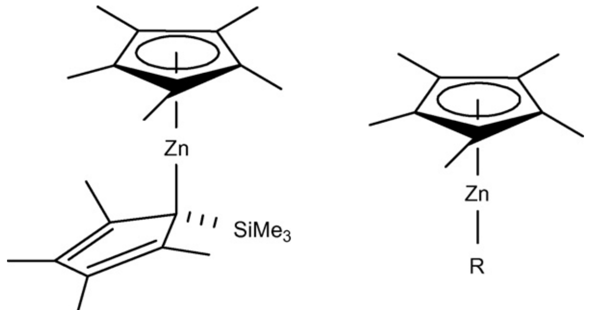


Fig. 2. Different cyclopentadienyl-main group element (E) coordinations.



V **VI**

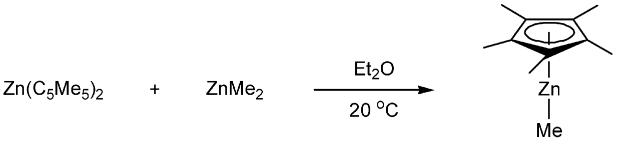
Fig. 3. Half-sandwich zincocene structures.

is compensated by some π-electron delocalization in the ring [38].

Our initial goal was the synthesis and structural characterization of a divalent metallocene MCp'_2, with a rigid $\eta^5/\eta^1(\sigma)$ structure. As explained elsewhere [40] zinc was significantly a better option than beryllium. In addition, considering structural features of $SiMe_3$ substituted cyclopentadienyl ligands, $C_5Me_4SiMe_3$ appeared as the Cp′ ring choice. An initial objective was the synthesis of $Zn(C_5Me_4SiMe_3)_2$ that was found to have a solid-state structure very close to the desired $\eta^5/\eta^1(\sigma)$ [40]. However, in solution it undergoes facile exchange between the η^5- and η^1-$C_5Me_4SiMe_3$ rings. A second synthetic target was complex $(\eta^5\text{-}C_5Me_5)Zn(\eta^1\text{-}C_5Me_4SiMe_3)$ for which structure **V** was anticipated (Fig. 3). The evident similarity between **V** and the half-sandwich derivatives **VI** advised the extension of this chemistry to $Zn(\eta^5\text{-}C_5Me_5)R$ compounds, which, somewhat surprisingly, were scarcely known at the outset of this work.

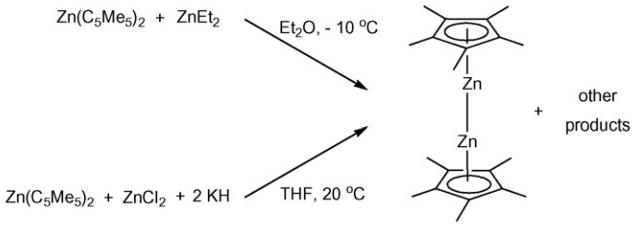
5. Synthesis of dizincocenes $Zn_2(\eta^5\text{-}C_5Me_5)_2$ (1), and $Zn_2(\eta^5\text{-}C_5Me_4Et)_2$ (2)

Treatment of $Zn(C_5Me_5)_2$ with $ZnMe_2$ gives the expected methyl derivative $Zn(\eta^5\text{-}C_5Me_5)Me$ **3** (Eq. (1)), isolable as an air-sensitive volatile, highly crystalline solid. Compound **3** can be readily characterized by spectroscopy and its solid-state structure has been determined by X-ray crystallography [41].



3 (1)

In contrast with this simple rearrangement, the analogous reaction of $ZnEt_2$ proves more complex. As for $ZnMe_2$, mixing of the reagents was effected at −20 °C and the reaction mixture was then allowed to warm to room temperature and stirred for ca. 30 min. In this case, however, a black, finely divided precipitate of metallic zinc was observed. Following the filtration and the removal of the volatiles under vacuum, ^{1}H NMR analysis of the crude reaction mixture revealed the presence of signals at δ 1.98 (singlet, 15H), 1.20 (triplet, 3H) and 0.38 (quartet, 2H) that could be attributed to the expected half-sandwich ethyl derivative $Zn(\eta^5\text{-}C_5Me_5)CH_2CH_3$ **4**. These resonances were accompanied by a singlet at δ 2.02 due to the C_5Me_5 protons of an unknown species that seemed to exhibit no other ^{1}H resonances. Similar results were obtained from the reaction of $Zn(C_5Me_5)_2$ with $Zn(C_6H_5)_2$, the ^{1}H NMR signal at δ 2.02 always appearing, in addition to another one at δ 2.11 attributed to the ring methyl protons of $Zn(\eta^5\text{-}C_5Me_5)C_6H_5$. Crystallization of these solutions provided colourless crystals of a pyrophoric solid that was identified by low-temperature X-ray crystallography as $Zn_2(\eta^5\text{-}C_5Me_5)_2$ **1**.



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Scheme 1.

Low-temperature ^{1}H NMR monitoring of the $Zn(C_5Me_5)_2$ plus $ZnEt_2$ reaction permitted the optimization of this procedure to obtain dimetallocene **1** or half-sandwich ethyl derivative **4**, as the major reaction product. Good, selective conversion into **1** was achieved when $Zn(C_5Me_5)_2$ and $ZnEt_2$ were reacted in Et_2O at −10 °C (Scheme 1). In the search for a more efficient synthetic methodology, strong reductants like Na, K, NaH, KH, CaH_2 or potassium naphthalenide were found to reduce the mononuclear zincocene $Zn(C_5Me_5)_2$ to the binuclear metallocene $Zn_2(\eta^5\text{-}C_5Me_5)_2$ **1**. Further optimization of this synthesis was attained by the use of a 1:1 mixture of $Zn(C_5Me_5)_2$ and $ZnCl_2$, and the equivalent amount of KH as the reducing agent (Scheme 1), a procedure that provides 1–2 g of **1** in a relatively short period of time. This method has been used to generate samples of the ^{68}Zn-labelled dimetallocene, $^{68}Zn_2(\eta^5\text{-}C_5Me_5)_2$ employed for high-resolution mass spectrometric experiments (*vide infra*) as well as for other studies. To this end, commercial ^{68}ZnO was converted into $^{68}ZnCl_2$ and the chloride partially transformed into $^{68}Zn(C_5Me_5)_2$. Ulterior reduction of mixtures of the mononuclear ^{68}Zn-labelled metallocene and $^{68}ZnCl_2$ gave the desired $^{68}Zn_2(\eta^5\text{-}C_5Me_5)_2$, **1**-^{68}Zn [1b].

The formation of dizincocene **1** in the reaction of $Zn(C_5Me_5)_2$ and $ZnEt_2$ was completely unexpected. For the group 12 elements, Zn, Cd and Hg, only the heaviest element Hg, forms metal–metal bonded compounds in formal oxidation state +1. The $[Hg–Hg]^{+2}$ unit has been known for a long time and it is present in many Hg(I) compounds, e.g., the dihalides Hg_2X_2 [6]. Interestingly, whereas coordination compounds of the $Hg_2{}^{+2}$ cation are known, i.e., Hg_2Tp^{Me2} [42], most dimercury compounds have appreciable ionic character and possess complex oligomeric structures. No sigma-bonded organometallic derivatives of $Hg_2{}^{2+}$ are known, the silyl $Hg_2[Si(SiMe_2SiMe_3)_3]_2$ representing a very unusual example of a molecular σ-bonded complex of $Hg_2{}^{2+}$ [43]. Early research provided evidence for the $Cd_2{}^{2+}$ ion [44], later characterized by X-ray crystallography in $Cd_2[AlCl_4]_2$ [45] and by ^{113}Cd NMR in Cd_2Tp^{Me2} [46]. In the

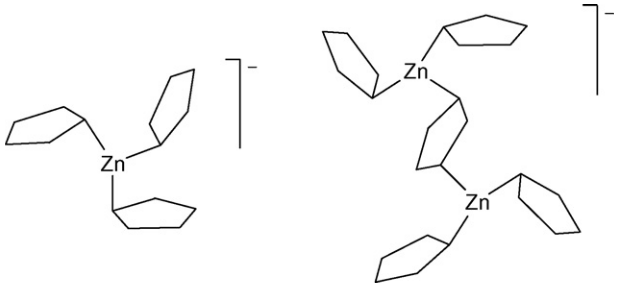

Fig. 4. Schematic representation of the structural unit of the anions $Zn(C_5H_5)_3^-$ and $Zn_2(C_5H_5)_5^-$ [48].

case of zinc, there were indications for the formation of Zn_2^{2+} ions in $ZnCl_2$/Zn glasses at high temperature [47a] and in zeolite matrices [47b]. The dihydride Zn_2H_2 had been isolated in argon matrices and characterized by vibrational spectroscopy, deuterium substitution and MP2 calculations [47c]. The paramagnetic mononuclear Zn^+ ion had been shown to form in a microporous crystalline silicoaluminophosphate environment [47d].

As examined below, unequivocal characterization of **1** as a zinc–zinc bonded dimetallocene was achieved by a combination of structural and analytical determinations, as well as by reactivity studies. Before discussing this problem, it is worth considering the attempts that were made to prepare other dizincocenes. The reactions of $ZnEt_2$ with the zincocenes $Zn(C_5Me_4H)_2$, $Zn(C_5Me_4Bu^t)_2$ and $Zn(C_5Me_4SiMe_3)_2$ yielded only the half-sandwich ethyl organometallics $Zn(\eta^5\text{-}Cp')C_2H_5$ [1b]. Similarly, reduction of equimolar mixtures of the above zincocenes and $ZnCl_2$ with KH originated extensive decomposition and a deposit of metallic zinc. Interestingly, the NaH and KH reduction of equimolar mixtures of $Zn(C_5H_5)_2$ and $ZnCl_2$ failed to give the parent $Zn_2(C_5H_5)_2$, that remains an unknown compound, but allowed the isolation of the cyclopentadienyl zincates $MZn(C_5H_5)_3$ (Na, K) and $Na[Zn_2(C_5H_5)_5]$ [48]. The sodium and potassium salts of the $Zn(C_5H_5)_3^-$ anion exhibit polymeric structures in the solid state while the structure of the dizincate $Zn_2(C_5H_5)_5^-$ can be explained as consisting of two $Zn(\eta^1\text{-}C_5H_5)_2$ units symmetrically bridged by a C_5H_5 group that binds to each Zn atom through a single carbon atom (Fig. 4) [48].

Despite our failure to obtain dimetallocenes $Zn_2(\eta^5\text{-}Cp')_2$ for the C_5H_5, C_5Me_4H, $C_5Me_4SiMe_3$ and $C_5Me_4Bu^t$ cyclopentadienyl rings, we succeeded in isolating a second dizincocene, $Zn_2(\eta^5\text{-}C_5Me_4Et)_2$ **2**, by KH reduction of $Zn(C_5Me_4Et)_2/ZnCl_2$ mixtures:

$$Zn(C_5Me_4Et)_2 + ZnCl_2 + 2KH \xrightarrow{THF} Zn_2(C_5Me_4Et)_2 \qquad (2)$$

Like **1**, compound **2** is a crystalline solid, exceedingly reactive toward oxygen and water. In solution it exhibits moderate thermal stability at room temperature but the pure crystalline solid decomposes slowly at temperatures between 0 and 20 °C to give a brown oily material. Decomposition to metallic zinc is evident when crystalline samples of **2** are heated at 40 °C.

6. Structural characterization of $Zn_2(\eta^5\text{-}C_5Me_5)_2$ (1), and $Zn_2(\eta^5\text{-}C_5Me_4Et)_2$ (2)

As briefly mentioned, the first experimental evidence for the dimetallocene nature of **1** was provided by low-temperature X-ray crystallographic studies. Despite the poorer thermal stability of **2**, crystals suitable for X-ray determination could be produced by slow evaporation of its pentane solutions at −20 °C, or by rapidly cooling very concentrated solutions from 20 to −78 °C. Fig. 5 shows schematic representations of the structure of the two compounds. The most relevant and attractive characteristic of these structures is the short Zn–Zn distance of ca. 2.30 Å exhibited by the two molecules, appreciably smaller than twice Pauling's single bond metallic radius for zinc (2.50 Å). In $Cd_2(AlCl_4)_2$ the Cd–Cd distance is 2.58 Å and in Hg_2Cl_2 the two mercury atoms are separated by 2.53 Å. Clearly, comparable bonding interactions exist in all these compounds. A second important structural feature of the molecules of **1** and **2** is the existence of a direct metal–metal bond between the two zinc atoms that are sandwiched between two planar, nearly parallel cyclopentadienyl rings. The ring centroid-zinc–zinc angles are very close to 180° (177.4(1)° and 175.2(1)°, average values for **1** and **2**, respectively) and therefore the metal–metal bond axis is nearly perpendicular to the cyclopentadienyl rings.

Spectroscopic data, while not conclusive, support the dimetallocene formulation for **1** and **2**. ^1H and $^{13}C\{^1H\}$NMR spectra of the two complexes are very simple but of limited structural value. To simplify the discussion we refer to compound **1**, data for **2** can be found in reference **1b**. The ^1H NMR spectra of **1**, consists of a single resonance at δ 2.02 (*vide supra*). No changes are observed in the temperature range from −80 to +80 °C. Similarly, the $^{13}C\{^1H\}$NMR is very simple, as it comprises a resonance at δ 10.03 for the methyl groups and another one at 108.5 ppm attributed to the ring carbon atoms.

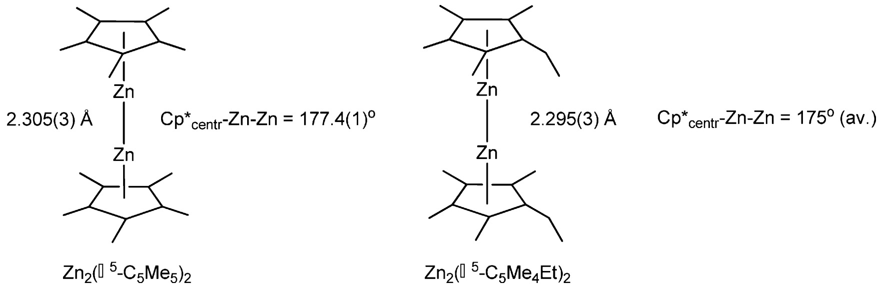

Fig. 5. Structures of **1** and **2**.

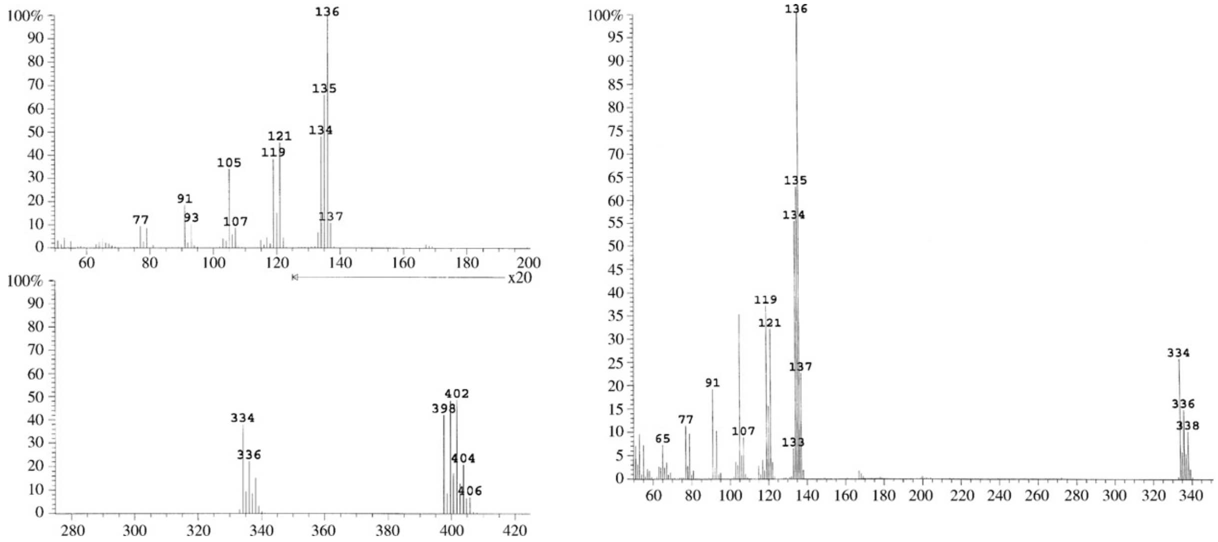

Fig. 6. High resolution mass spectra for **1** (left), and $Zn(C_5Me_5)_2$ (right).

No ^1H resonances attributable to an alternative bis(hydride) bridging structure, namely $[Zn(\eta^5\text{-}C_5Me_5)]_2(\mu\text{-}H)_2$, could be found in the ^1H NMR spectrum of **1**. High-resolution mass spectrometric studies of **1** and the ^{68}Zn-labelled dimetallocene, **1**-^{68}Zn, provide unequivocal support for the dimetallocene formulation without additional H atoms. The first measurement was carried out by Prof. R.A. Andersen at the University of California Berkeley with the result of a complex molecular ion envelope, M^+ around 400 m/e, due to the existence of several zinc isotopes [1a]. Subsequent determinations were effected in Sevilla and provided identical results. As shown in Fig. 6 it is evident that dimer **1** yields a well-behaved molecular ion in the gas phase. The exact masses of the peaks at 398 and 400 amu are coincident with those calculated for $^{64}Zn_2{}^{12}C_{20}{}^1H_{30}$ and $^{64}Zn^{66}Zn\ {}^{12}C_{20}{}^1H_{30}$, respectively, while **1**-^{68}Zn yields a simple molecular ion M^+ at 406 amu, with exact mass corresponding to that of $^{68}Zn_2{}^{12}C_{20}{}^1H_{30}$ (duplicate measurements at Berkeley and Sevilla). Fig. 6 also contains the high-resolution spectrum of the mononuclear zincocene, $Zn(C_5Me_5)_2$. Clearly, fragment ion patterns due to $Zn(C_5Me_5)_2$ are observed in the spectrum of $Zn_2(\eta^5\text{-}C_5Me_5)_2$ (the same applies to $^{68}Zn_2(\eta^5\text{-}C_5Me_5)_2$) indicating that in the gas phase the molecules of $Zn_2(\eta^5\text{-}C_5Me_5)_2$ rearrange to $Zn(\eta^5\text{-}C_5Me_5)_2$ and Zn.

Experimental and theoretical vibrational studies (infrared and Raman spectra) to be reported in due course also support the dimetallocene formulation and give no indication for the existence of Zn–H bonds, either terminal or bridging. Reactivity studies, in particular the Lewis base induced disproportionation reactions of **1** to Zn(0) and Zn(II) [1] evidently reinforce formulation of **1** as a compound of Zn(I) with a Zn–Zn bond.

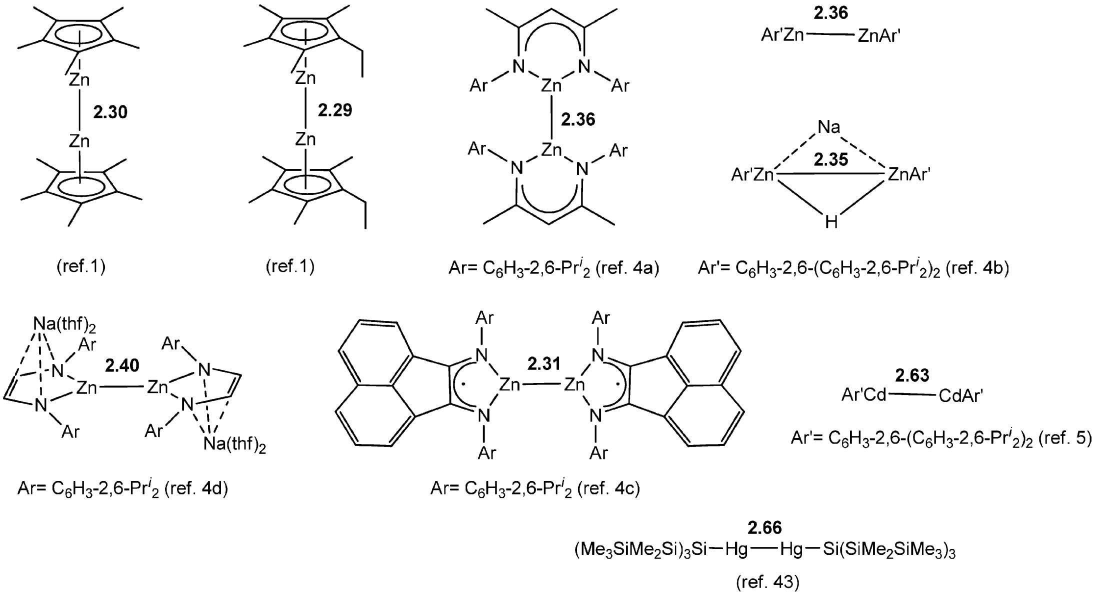

Fig. 7. Structurally characterized molecular compounds of the $M_2{}^{+2}$ unit (Zn, Cd, Hg). M–M bond lengths are in Å. The cadmium compound $Cd_2[AlCl_4]_2$ is not included since its structure may be described as containing $Cd_2{}^{2+}$ cations stabilized by $AlCl_4{}^-$ anions [45].

7. Conclusions

Our work has resulted in the first representatives of the dimetallocene structure, $M_2(\eta^5\text{-}Cp')_2$, and has provided examples of previously unknown molecular complexes of Zn(I) containing the binuclear metal–metal bonded $[Zn–Zn]^{2+}$ unit. The original synthesis of **1** suggested that related complexes of Cd(I) and Hg(I) could be isolated. At that time [1a] it also appeared plausible that the stabilization of the $[Zn–Zn]^{2+}$ unit would not require the existence of Zn–C bonds. In other words, classical coordination compounds of the Zn_2^{2+} central unit were considered reasonable targets for future synthetic and structural studies. Despite the short period of time elapsed since then, some of these objectives have already been accomplished and new coordination and organometallic derivatives of zinc and cadmium containing M_2^{2+} units have been structurally characterized [4,5]. To conclude this contribution, Fig. 7 shows schematic representations of the molecular compounds of Zn, Cd and Hg that contain the M_2^{2+} unit and have been authenticated by X-ray methods. Considering only homometallic compounds (i.e., with the exclusion of those that contain Na^+ ion as a part of the dimeric structure), Zn–Zn bond lengths cluster in the narrow interval of 2.30–2.36 Å (five Zn–Zn bonded complexes). Naturally, the dicadmium and dimercury representatives feature somewhat longer metal–metal bonds (the Pauling's single-bond metallic radii for Zn, Cd and Hg have values of 1.25 (Zn), 1.41 (Cd) and 1.44 (Hg) Å). A comparative discussion of the structural parameters and electronic structures of all these compounds will be the subject of a future publication from our laboratory. Finally, Refs. [49–51] list recent contributions to this field that appeared after the submission of this manuscript.

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References

[1] (a) I. Resa, E. Carmona, E. Gutiérrez-Puebla, A. Monge, Science 305 (2004) 1136;
(b) A. Grirrane, I. Resa, A. Rodríguez, E. Carmona, E. Alvarez, E. Gutiérrez-Puebla, A. Monge, A. Galindo, D. del Río, R.A. Andersen, J. Am. Chem. Soc. 129 (2007) 693.
[2] (a) Y. Xie, H.F. Schaefer III, R.B. King, J. Am. Chem. Soc. 127 (2005) 2818;
(b) Y. Xie, H.F. Schaefer III, E.D. Jemmis, Chem. Phys. Lett. 402 (2005) 414;
(c) A. Timoshkin, H.F. Schaefer, Organometallics 24 (2005) 3343;
(d) Z.-Z. Liu, W.Q. Tian, J.K. Feng, G. Zhang, W.-Q. Li, J. Mol. Struct.: THEOCHEM 758 (2006) 127;
(e) G. Merino, H.I. Beltrán, A. Vela, Inorg. Chem. 45 (2006) 1091;
(f) M.R. Philpott, Y. Kawazoe, Chem. Phys. 327 (2006) 283;
(g) B. Pathak, S. Pandian, N. Hosmane, E.D. Jemmis, J. Am. Chem. Soc. 128 (2006) 10915;
(h) S.L. Richardson, T. Barnah, M.R. Pederson, Chem. Phys. Lett. 415 (2005) 141;
(i) Z.-Z. Xie, W.-H. Fang, Chem. Phys. Lett. 404 (2005) 212;
(j) H.S. Kang, J. Phys. Chem. A 109 (2005) 4342;
(k) J.W. Kress, J. Phys. Chem. A 109 (2005) 7757;
(l) J. Zhou, W.-N. Wang, K.-N. Fan, Chem. Phys. Lett. 424 (2006) 247;
(m) Z.-Z. Liu, W.Q. Tian, J.-K. Feng, G. Zhang, W.-K. Li, Y.-H. Cui, Ch. Sun, Eur. J. Inorg. Chem. (2006) 2808;
(n) Y. Kan, J. Mol. Struct.: THEOCHEM 805 (2007) 127;
(o) M.R. Philpott, Y. Kawazoe, Chem. Phys. 333 (2007) 201;
(p) K.K. Pandey, J. Organomet. Chem. 692 (2007) 1058.
[3] D. del Río, A. Galindo, I. Resa, E. Carmona, Angew. Chem. Int. Ed. 117 (2005) 1270.
[4] (a) Y. Wang, B. Quillian, P. Wei, H. Wang, X.-J. Yang, Y. Xie, R.B. King, P.v.R. Schleyer, H.F. Schaefer III, G.H. Robinson, J. Am. Chem. Soc. 127 (2005) 11944;
(b) Z. Zhu, R.J. Wright, M.M. Olmstead, E. Rivard, M. Brynda, P.P. Power, Angew. Chem. Int. Ed. 45 (2006) 5807;
(c) I.L. Fedushkin, A.A. Skatova, S.Y. Ketkov, O.V. Eremenko, A.V. Piskunov, G.K. Fukin, Angew. Chem. Int. Ed. 46 (2007) 4302;
(d) X.-J. Yang, J. Yu, Y. Liu, Y. Xie, H.F. Schaefer, Y. Liang, B. Wu, Chem. Commun. (2007) 2363.
[5] Z. Zhu, R.C. Fischer, J.C. Fettinger, E. Rivard, M. Brynda, P.P. Power, J. Am. Chem. Soc. 128 (2006) 15068.
[6] (a) F.A. Cotton, G. Wilkinson, C.A. Murillo, M. Bochmann, Advanced Inorganic Chemistry, 6th ed., Wiley, New York, 1999;
(b) N. Wiberg, Holleman-Wiberg (Eds.), Inorganic Chemistry, 34th ed., Academic Press, New York, 2001.
[7] (a) F.A. Cotton, Q. Rev. Chem. Soc. 20 (1966) 397;
(b) F.A. Cotton, J. Chem. Ed. 60 (1983) 713.
[8] F.A. Cotton, C.A. Murillo, R.A. Walton (Eds.), Multiple Bonds between Metal Atoms, 3rd ed., Springer, New York, 2005.
[9] (a) C. Elschenbroich, Organometallics, 3rd ed., Wiley–VCH, Weinheim, 2006;
(b) R.H. Crabtree, D.M.P. Mingos, C.E. Housecroft (Eds.), Comprehensive Organometallic Chemistry III, vol. 3, Elsevier, Oxford, 2007.
[10] (a) W. Uhl, Z. Naturforsh. B: Chem. Sci. 43 (1998) 1113;
(b) W. Uhl, M. Layh, T. Hildenbrand, J. Organomet. Chem. 364 (1989) 289;
(c) W. Uhl, M. Layh, W. Hiller, J. Organomet. Chem. 368 (1989) 139;
(d) W. Uhl, W. Hiller, M. Layh, W. Schwarz, Angew. Chem. Int. Ed. 31 (1992) 1364.
[11] (a) S. Schulz, H.W. Roesky, H.J. Koch, G.M. Sheldrick, D. Stalke, A. Khun, Angew. Chem. Int. Ed. 32 (1993) 1729;
(b) H.W. Roesky, S.S. Kumer, Chem. Commun. (2005) 4027.
[12] (a) A. Ecker, E. Weckert, H. Schnöckel, Nature 387 (1997) 379;
(b) A. Schnepf, G. Stösser, H. Schnöckel, J. Am. Chem. Soc. 122 (2000) 9178;
(c) A. Schnepf, H. Schnöckel, Angew. Chem. Int. Ed. 41 (2002) 3532;
(d) H. Schnöckel, Dalton Trans. (2005) 3131.
[13] (a) A.F. Richards, H. Hope, P.P. Power, Angew. Chem. Int. Ed. 42 (2003) 4071;
(b) A. Schnepf, R. Köppe, Angew. Chem. Int. Ed. 42 (2003) 911;
(c) A. Schnepf, Angew. Chem. Int. Ed. 42 (2003) 2624;
(d) A. Schnepf, Angew. Chem. Int. Ed. 43 (2004) 664.
[14] (a) N.T. Tran, M. Kawano, D.R. Powell, L.F. Dahl, J. Am. Chem. Soc. 120 (1998) 10986;
(b) N.T. Tran, D.R. Powell, L.F. Dahl, Angew. Chem. Int. Ed. 39 (2000) 4121.
[15] P.J. Davidson, M.F. Lappert, J. Chem. Commun. (1973) 317.
[16] J. Su, X.-W. Li, C. Crittendon, G.H. Robinson, J. Am. Chem. Soc. 119 (1997) 5471.
[17] (a) L. Pu, B. Twanley, P.P. Power, J. Am. Chem. Soc. 122 (2000) 3524;
(b) M. Stender, A.D. Phillips, R.J. Wright, P.P. Power, Angew. Chem. Int. Ed. 41 (2002) 1785;
(c) L. Pu, A.D. Phillips, A.F. Richards, M. Stender, R.S. Simons, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 125 (2003) 11626;
(d) R.J. Wright, M. Brynda, P.P. Power, Angew. Chem. Int. Ed. 45 (2006) 5953.
[18] A. Sekiguchi, R. Kiujo, M. Ichinohe, Science 305 (2004) 1755.

[19] G. Wilkinson, F.A. Cotton, Prog. Inorg. Chem. 1 (1959) 3.

[20] (a) D.F. Shriver, H.D. Kaesz, R.D. Adams, The Chemistry of Metal Cluster Complexes, VCH, Weinheim, 1990;
(b) B.F.G. Johnson (Ed.), Transition Metal Clusters, John Wiley & Sons, New York, 1980.

[21] M.S. Paquette, L.F. Dahl, J. Am. Chem. Soc. 102 (1980) 6623.

[22] P.H.M. Budzelaar, J. Boersma, G.J.M. Van der Kerk, Angew. Chem. Int. Ed. 22 (1983) 329.

[23] (a) P. Jutzi, N. Burford, Chem. Rev. 99 (1999) 969;
(b) P. Jutzi, N. Burford, in: A. Togni, R.L. Halterman (Eds.), Metallocenes: Synthesis, Reactivity, Applications, vol. 1, Wiley–VCH, New York, 1998.

[24] C. Dohmeier, C. Roble, M. Tacke, H. Schnöckel, Angew. Chem. Int. Ed. 30 (1991) 564.

[25] (a) O.T. Beachley, R. Blom, M.R. Churchill, K. Faegri, J.C. Fettinger, J.C. Pazik, L. Victoriano, Organometallics 8 (1989) 346;
(b) O.T. Beachley, M.R. Churchill, J.C. Fettinger, J.C. Pazik, L. Victoriano, J. Am. Chem. Soc. 108 (1986) 4666.

[26] J. Vollet, J.R. Hartig, H. Schnöckel, Angew. Chem. Int. Ed. 43 (2004) 3186.

[27] (a) P.D. Grebenik, M.L.H. Green, A. Izquierdo, V.S.B. Mtetwa, K. Prout, J. Chem. Soc. Dalton Trans. (1987) 9;
(b) M.L.H. Green, J.D. Hubert, P. Mountford, J. Chem. Soc. Dalton Trans. (1990) 3793.

[28] T. Nguyen, A.D. Sutton, M. Brynda, J.C. Fettinger, G.J. Long, P.P. Power, Science 310 (2005) 844.

[29] C. Janiak, H. Schumann, Adv. Organomet. Chem. 33 (1991) 291.

[30] (a) R.B. King, A. Efraty, J. Am. Chem. Soc. 93 (1971) 4950;
(b) R.B. King, M.B. Bisnette, J. Organomet. Chem. 8 (1967) 287;
(c) R.B. King, M.Z. Iqbal, A.D. King Jr., J. Organomet. Chem. 171 (1979) 53.

[31] T.S. Piper, G. Wilkinson, J. Inorg. Nucl. Chem. 6 (1956) 104.

[32] P.W. Jolly, G. Wilke, The Organic Chemistry of Nickel, vol. 1, Academic Press, New York, 1974 (Chapter VII).

[33] K. Jonas, Angew. Chem. Int. Ed. 24 (1985) 295.

[34] (a) B. Fisher, J. Boersma, B. Kolié-Prodić, A.L. Spek, J. Chem. Soc. Chem. Commun. (1985) 1237;
(b) B. Fischer, J. Boersma, G. van Koten, New J. Chem. 12 (1988) 613.

[35] (a) J. Wachter, Angew. Chem. Int. Ed. 30 (1991) 1120;
(b) H.B. Abrahamson, G.P. Niccolai, D.M. Heinekey, C.P. Casey, B.E. Bursten, Angew. Chem. Int. Ed. 31 (1992) 471.

[36] (a) F. Lutz, R. Bau, P. Wu, T.F. Koetzle, C. Krüger, J.J. Schneider, Inorg. Chem. 35 (1996) 2698;
(b) M. Bortz, R. Bau, J.J. Schneider, S.A. Mason, J. Clust. Sci. 12 (2001) 285.

[37] (a) M.M. Conejo, R. Fernández, E. Gutiérrez-Puebla, A. Monge, C. Ruiz, E. Carmona, Angew. Chem. Int. Ed. 39 (2000) 1949;
(b) M.M. Conejo, R. Fernández, D. del Río, E. Carmona, A. Monge, C. Ruiz, A.M. Márquez, J.F. Sanz, Chem. Eur. J. 9 (2003) 4452;
(c) R. Fernández, E. Carmona, Eur. J. Inorg. Chem. (2005) 3197.

[38] K.W. Nugent, J.K. Beattie, T.W. Hambley, M.R. Snow, Aust. J. Chem. 37 (1984) 1601.

[39] A. Voigt, S. Filipponi, C.L.B. Macdonald, J.D. Gorden, A.H. Cowley, Chem. Commun. (2000) 911.

[40] R. Fernández, I. Resa, D. del Río, E. Carmona, E. Gutierrez-Puebla, A. Monge, Organometallics 22 (2003) 381.

[41] I. Resa, E. Alvarez, E. Carmona, Z. Anorg. Allg. Chem. 633 (2007).

[42] G.G. Lobbia, F. Bonati, P. Cecchi, C. Pettinari, Gaz. Chim. Ital. 121 (1991) 355.

[43] D. Bravo-Zhivotovskii, M. Yuzefovich, M. Bendikov, K. Klinkhammer, Y. Apeloig, Angew. Chem. Int. Ed. 38 (1999) 1100.

[44] (a) K. Grjotheim, F. Grönwold, J. Krogh-Moe, J. Am. Chem. Soc. 77 (1955) 5824;
(b) J.D. Corbett, W.J. Burkhard, L.F. Druding, J. Am. Chem. Soc. 83 (1961) 76;
(c) T.C.F. Munday, J.D. Corbett, Inorg. Chem. 5 (1966) 1263;
(d) R.A. Potts, R.D. Barnes, J.D. Corbett, Inorg. Chem. 7 (1987) 2558.

[45] (a) R. Faggiani, R.J. Gillespie, J.E. Vekris, J. Chem. Soc. Chem. Commun. (1986) 517;
(b) T. Staffel, G. Meyer, Z. Anorg. Allg. Chem. 548 (1987) 45.

[46] D.L. Reger, S.S. Mason, A.L. Rheingold, J. Am. Chem. Soc. 115 (1993) 10406.

[47] (a) D.H. Kerridge, S.A. Tariq, J. Chem. Soc. A (1967) 1122;
(b) F. Rittner, A. Seidel, B. Boddenberg, Micropor. Mesopor. Mater. 24 (1998) 127;
K. Seff, S. Zhen, D. Bae, J. Phys. Chem. B 104 (2000) 515;
(c) T.M. Greene, W. Brown, L. Andrews, A.J. Downs, G.V. Chertihin, N. Runeberg, P. Pyykkö, J. Phys. Chem. 99 (1995) 7925;
X. Wang, L. Andrews, J. Phys. Chem. A 108 (2004) 11006;
(d) Y. Tian, G.D. Li, J.S. Chen, J. Am. Chem. Soc. 125 (2003) 6622.

[48] E. Alvarez, A. Grirrane, I. Resa, D. del Río, A. Rodríguez, E. Carmona, Angew. Chem. Int. Ed. 46 (2007) 1296.

[49] Z. Zhu, M. Brynda, R.J. Wright, R.C. Fischer, W.A. Merrill, E. Rivard, R. Wolf, J.C. Fettinger, M.M. Olmstead, P.P. Power, J. Am. Chem. Soc. 129 (2007) 10847.

[50] Y-Ch. Tsai, D.-Y. Lu, Y.-M. Lin, J.-K. Hwang, J-S.K. Yu, Chem. Commun. (2007) 4125.

[51] S.P. Green, C. Jones, A. Stasch, Science 318 (2007) 1754.