

Metal–Metal Bonds

Theoretical and Synthetic Studies on $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$: Analysis of the Zn–Zn Bonding Interaction**

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Recently we have characterized $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1**), a molecular compound of zinc with a Zn–Zn bond.^[1] The unique nature of this compound warrants a study of its bonding and electronic properties. Herein, we provide details of a theoretical investigation of the Zn–Zn bonding interaction in **1**, along with further synthetic studies that result in the direct preparation of the compound on a gram scale.

Complex **1** formed unexpectedly during attempts to generate the half-sandwich ethyl derivative $[\text{Zn}(\text{C}_2\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ (**2**) from $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ ^[2] and $[\text{Zn}(\text{C}_2\text{H}_5)_2]$. At -60°C

in pentane the reaction produced compound **2**, whereas upon mixing diethyl ether solutions of the two reactants at -10°C the dizinc compound **1** was isolated in moderate yields.^[1] Notably, compound **1** is also generated when $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ is treated with $[\text{Zn}(\text{C}_6\text{H}_5)_2]$ ^[3] in diethyl ether, under similar conditions; the related half-sandwich complex $[\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_5)]$ is the other organometallic product of this transformation (see Experimental Section). The limitations of this synthesis of **1** prompted us to search for a more convenient procedure. Whereas $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ is recovered unaltered upon attempted reduction with Rieke zinc, the use of Na, K, K/naphthalene, or KH produces **1** in variable yields. Of these materials, potassium hydride appears to be the most useful reagent and allows the synthesis of **1** by an experimentally simple procedure, namely the reduction of $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ in tetrahydrofuran at -20°C , over a period of 2–3 h. Moreover, isolation of $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ is not necessary—the dizinc compound **1** may be prepared in quantities of over 1 g by the direct reaction of ZnCl_2 , KC_5Me_5 , and KH at room temperature (see Experimental Section).

The electronic structure and bonding properties of **1** were computed by a density functional theory approach at the B3LYP level (see Experimental Section and Supporting Information). The simplest model, the parent compound $[\text{Zn}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ (**3**), was also calculated (see the Supporting Information). In view of the structural diversity of main-group metallocenes,^[4] several starting geometries, with and without symmetry, were investigated, resulting in different optimized structures. The use of the atomic coordinates obtained from the X-ray study,^[1] but with imposed C_{5h} and S_{10} symmetries, yielded optimized structures that are characterized by four and five imaginary frequencies, respectively. Subsequent optimization without symmetry constraints still gave four imaginary frequencies, all smaller than $30i\text{ cm}^{-1}$, but involving displacement of the Zn atoms. In an attempt to eliminate them, the optimization was repeated with the GDHIS algorithm and a finer grid for the integration step (see Supporting Information). The resulting optimized structure $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1a**), is displayed in Figure 1.

However, two small imaginary frequencies of $13i$ and $12i\text{ cm}^{-1}$, which involve deviation of the two Zn atoms from the η^5 coordination mode, were still found. For the parent molecule **3** a related optimized structure, $[\text{Zn}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ (**3a**), was obtained with three imaginary frequencies; $[\text{Zn}_2(\eta^3\text{-C}_5\text{H}_5)_2]$ (**3b**) was found to be a real minimum. In light of this

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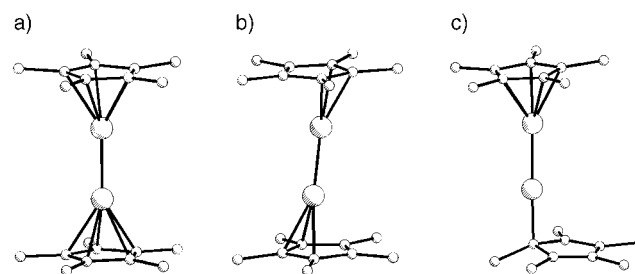


Figure 1. Optimized structures for $[\text{Zn}_2(\text{C}_5\text{Me}_5)_2]$: a) $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1a**); b) $[\text{Zn}_2(\eta^3\text{-C}_5\text{Me}_5)_2]$ (**1b**); c) $[\text{Zn}_2(\eta^1\text{-C}_5\text{Me}_5)(\eta^5\text{-C}_5\text{Me}_5)]$ (**1c**). (H atoms omitted for clarity.)

result, the analogous structure for **1**, $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1b**), was optimized and found to correspond to a real minimum on the potential energy surface (Figure 1).

To complete these studies, and having in mind the propensity of zirconocenes to adopt a slipped-sandwich or $\eta^5/\eta^1(\pi)$ structure,^[5] the optimization of a starting point with one η^5 - and one $\eta^1\text{-C}_5\text{Me}_5$ ring was considered appropriate. The resulting structure, **1c**, is also a real minimum (NImag = 0), and is presented in Figure 1. It is worth pointing out that the C_5H_5 analogue **3c** is not a stationary point; instead, all optimization attempts converge to the pseudoallylic structure **3b**.

The energy differences between the optimized structures of **1** are negligible ($\leq 0.1 \text{ kcal mol}^{-1}$), thereby indicating a flat energy surface in the gas phase. Therefore, the optimized structure **1a** can be employed for the description of the molecules of **1** despite the existence of two imaginary frequencies. It seems reasonable to assume that the specific packing found in the crystals of **1** may overcome this small energy difference (Supplementary Information). For this structure the computed bond distances and angles match the experimental values closely. In particular, the calculated Zn–Zn bond distance of 2.331 Å, without a doubt the most salient feature of this compound, compares very well with the value of 2.305(3) Å found by X-ray diffraction methods. Furthermore, the computed $(\text{C}_5\text{Me}_5)_{\text{centr.}}\text{-Zn-Zn}$ angle of 178.9° is also in excellent agreement with the average experimental value of 177.4(1)°. The calculated Zn–Zn bond length may be compared with values computed for other dizinc species that have been studied theoretically. For instance, the dizinc dihalides Zn_2X_2 (X = F, Cl, Br, I), computed at various levels of theory, display Zn–Zn bond lengths in the range 2.28–2.42 Å.^[6,7] In addition, ab initio studies for Zn_2H_2 lead to Zn–Zn distances of about 2.38 Å.^[7,8]

An important objective of the present study was the investigation of the unprecedented Zn–Zn bond of **1**. On the basis of previous analysis of $\{\text{M}(\text{C}_5\text{H}_5)\}$ fragments,^[9] including $\{\text{Zn}(\text{C}_5\text{H}_5)\}$,^[5a,10,11] the frontier orbitals for a $\{\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)\}$ unit are the singly occupied HOMO (an antibonding combination of the a_1 , $\pi\text{-C}_5\text{Me}_5$ orbital and the zinc s and p_z orbitals) and a pair of degenerate orbitals that result from the combination of the e_1 $\pi\text{-C}_5\text{Me}_5$ and the $p_{x,y}$ metal orbitals. These qualitative arguments lead to a Zn–Zn bond derived from the interaction of the singly occupied HOMOs of two $\{\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)\}$ fragments. However, DFT calculations reveal that the Zn–Zn bonding interaction resides in the HOMO–4, and that even if it has a contribution of Zn orbitals close to 60%, the metal–metal bond involves mostly the Zn 4s orbitals (more than 96%), with only a small contribution from the 4p orbitals (less than 4%). A simplified MO diagram that includes the HOMO–4 is provided in the Supporting Information. The higher-energy occupied orbitals (from HOMO–3 to HOMO) are quasi-degenerate and result from the in-phase and out-of-phase combinations of the e_1 C_5Me_5 orbitals, with very little participation from the d (<2%) and p (<0.5%) orbitals of Zn. The LUMO represents the antibonding zinc–zinc interaction and its major contributors are the 4s orbitals (89%), with minor participation of the C_5Me_5 (9%) and the Zn d orbitals (2%).

Figure 2 shows the calculated overlap population density of states (OPDOS) for **1a**.

The next target of this analysis was the estimation of the Zn–Zn bond energy in **1a**. A fragment-oriented approach^[12]

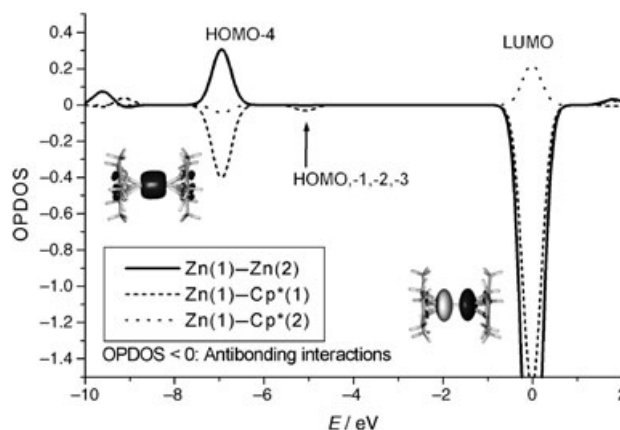


Figure 2. Calculated overlap population density of states (OPDOS) for $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1a**). The insets display 3D representations of the HOMO–4 and the LUMO. The former clearly has a positive overlap population between the Zn atoms.

was adopted in which the metal–metal bond-dissociation energy (BDE) was calculated in two steps. Firstly, we computed the energy needed for “snapping” the metal–metal bond, $E(\text{Zn-Zn})$, and then the energy ER, gained when the isolated fragment relaxes from its original conformation to the optimal ground-state structure with imposed C_5 and C_{5v} symmetries for **1a** and **3a**, respectively (see Supporting Information). This approach allows the basis set superposition error (BSSE) associated with the Zn–Zn bond energy to be computed directly by the counterpoise method.^[13] The calculated BDEs for complexes **1a** and **3a** are given in Table 1, wherein they are broken down into their various

Table 1: Calculated Zn–Zn bond dissociation energy (BDE) for complexes **1a** and **3a**, with energy contributions [kcal mol^{-1}].

	$E(\text{Zn-Zn})^{\text{[a]}}$	ER	BSSE	BDE ^[b]
$[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (1a)	66.3	–1.2	–0.9	62.1
$[\text{Zn}_2(\eta^5\text{-C}_5\text{H}_5)_2]$ (3a)	66.7	–1.3	–0.8	62.5

[a] The computed bonding energies represent only the electronic contribution to the reaction enthalpies and do not include ZPE corrections. [b] Corrected for BSSE.

energy contributions (for further details, see the Supporting Information). The results obtained for the Zn–Zn bond energy in both complexes are analogous and are actually similar to the energies computed previously for related Zn–Zn bonds (about 59 kcal mol^{-1} for Zn_2H_2 ,^[7,8] and in the range 57–67 kcal mol^{-1} for the dihalides Zn_2X_2 with X = F, Cl, Br, I).^[6,7]

The final objective of our theoretical study was to ascertain the viability of a possible bridging hydride structure, $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-H})_2]$ (**4a**). Attempts to optimize the structure of such a complex proved unsuccessful as the stationary

point found in all cases consists of two molecules of $[\text{Zn}(\eta^1\text{-C}_5\text{Me}_5)(\text{H})]$ (**5a**) that are kept together by means of dipole–dipole interactions. A graphical representation of the final optimized structure can be found in the Supporting Information. In contrast, if the optimization of the model $[\text{Zn}_2(\eta^5\text{-C}_5\text{H}_5)_2(\mu\text{-H})_2]$ is done under C_{2h} symmetry, complex **4b** can be found as a stationary point. However, this is characterized by six imaginary frequencies that involve displacement of the Zn atoms and breaking of the imposed molecular symmetry. If the symmetry constraints are removed the optimization converges, as in the case of C_5Me_5 , to two molecules of $[\text{Zn}(\eta^1\text{-C}_5\text{H}_5)(\text{H})]$ (**5b**). Even if the structure of complex **4b** is not a minimum on the potential energy surface we consider it useful to compare some of the structural parameters of this calculated model complex with the observed experimental values of **1**. In particular, the calculated Zn–Zn bond distance for **4b**, 2.498 Å, is appreciably longer than the experimentally observed value of 2.305(3) Å. This fact provides additional theoretical support for the $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ structure of **1**.

In summary, a rational, simple synthesis of $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1**) has been developed. As **1** is so far the only organometallic compound of zinc that contains a Zn–Zn bond, it is expected that its availability will allow not only the study of its chemical properties but also its use as a starting material for the preparation of other Zn–Zn compounds, thereby contributing to the development of this previously unforeseen area of the chemistry. Theoretical calculations reveal that the Zn–Zn bond of **1** ($\approx 60 \text{ kcal mol}^{-1}$) is relatively strong, and derives mostly from the zinc 4 s orbitals, with very little participation of the zinc 4 p orbitals. Furthermore, a bridging hydride structure, $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2(\mu\text{-H})_2]$, appears to be unattainable, whereas the calculated bond distances and angles for the optimized structure, $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$, match the experimental X-ray diffraction values very closely.

Experimental Section

1: Tetrahydrofuran (50 mL) was added to a mixture of KC_5Me_5 (2.78 g, 16 mmol), ZnCl_2 (1.09 g, 8 mmol), and KH (0.32 g, 8 mmol) with careful exclusion of oxygen and moisture. The resulting suspension was stirred for about 3 h at room temperature and the solvent was then evaporated under reduced pressure. The residue was extracted with three portions of pentane (30 mL each). Crude $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1**) was obtained as a pale yellow solid in about 60–80% yield (between 0.9 and 1.2 g) upon removal of the solvent in vacuo. This product was sufficiently pure for chemical studies but could be further purified by recrystallization from pentane, at -20°C , as reported previously.^[1] This operation provided highly crystalline material. We routinely followed the above synthetic procedure starting with 4–10 mmol of ZnCl_2 . $^1\text{H NMR}$ (C_6D_6 , 20°C): $\delta = 2.02 \text{ ppm}$; $^{13}\text{C}\{^1\text{H}\}$ NMR (C_6D_6 , 20°C): $\delta = 10.0$ (C_5Me_5), 108.8 ppm (C_5Me_5).^[1]

Reactions of $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ and ZnR_2 ($\text{R} = \text{C}_2\text{H}_5$, C_6H_5): Equimolar solutions of $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ and $[\text{Zn}(\text{C}_2\text{H}_5)_2]$ in $(\text{C}_2\text{D}_5)_2\text{O}$ were mixed in an NMR tube at -20°C . $^1\text{H NMR}$ monitoring revealed the formation of $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ (**1**) together with minor amounts of the half-sandwich compound $[\text{Zn}(\text{C}_2\text{H}_5)(\eta^5\text{-C}_5\text{Me}_5)]$.^[1] The formation of ethane was ascertained by GC analysis of the volatiles produced during different reaction runs. Similarly, $(\text{C}_2\text{D}_5)_2\text{O}$ solutions of $[\text{Zn}(\text{C}_5\text{Me}_5)_2]$ react readily with $[\text{Zn}(\text{C}_6\text{H}_5)_2]$ dissolved in the same solvent. However, in this case approximately equimolar mixtures of $[\text{Zn}_2(\eta^5\text{-C}_5\text{Me}_5)_2]$ and $[\text{Zn}(\eta^5\text{-C}_5\text{Me}_5)(\text{C}_6\text{H}_5)]$ were always generated.

The structures of all calculated complexes were computed within the density functional theory at the B3LYP^[14] level with the 6-31G** basis set for C and H atoms and 6-311G* for the Zn atoms. All the calculations were performed with the Gaussian-98 package.^[15] The GDIIS algorithm^[16] and a finer integration grid were used. Several starting geometries, with and without symmetry, were investigated for each complex, resulting in different optimized structures. For all of them vibrational frequency calculations by diagonalization of the analytically computed Hessian were computed. The number of imaginary frequencies (NImag) of each optimized structure is given in the text. The MO analysis was performed with the AOMix program.^[17] Further details are included in the Supporting Information.

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- [1] I. Resa, E. Carmona, E. Gutiérrez-Puebla, A. Monge, *Science* **2004**, 305, 1136.
- [2] R. Blom, J. Boersma, P. H. M. Budzelaar, B. Fischer, A. Haaland, H. V. Volden, J. Weidlein, *Acta Chem. Scand. Ser. A* **1986**, 40, 113.
- [3] a) D. K. Bretinger, C. E. Zybilla, in *Synthetic Methods of Organometallic and Inorganic Chemistry*, Vol. 5 (Eds.: D. K. Bretinger, W. A. Herrmann), Thieme, Stuttgart, **1999**, pp. 150–153; b) P. R. Markies, G. Schat, O. S. Akkerman, F. Bickelhaupt, W. J. J. Smeets, A. L. Spek, *Organometallics* **1990**, 9, 2243.
- [4] a) P. H. M. Budzelaar, J. J. Engelberts, J. H. van Lenthe, *Organometallics* **2003**, 22, 1562; b) T. P. Hanusa, *Organometallics* **2002**, 21, 2559; c) P. Jutzi, N. Burford, *Chem. Rev.* **1999**, 99, 969; d) P. Jutzi, N. Burford, *Metallocenes*, Wiley-VCH, Weinheim, Germany, **1998**.
- [5] a) A. Haaland, S. Samdal, N. V. Tverdova, G. V. Girichev, N. I. Giricheva, S. A. Shlykov, O. G. Garkusha, B. V. Lokshin, *J. Organomet. Chem.* **2003**, 684, 351; b) D. J. Burke, T. P. Hanusa, *J. Organomet. Chem.* **1996**, 512, 165; c) B. Fischer, P. Wijkens, J. Boersma, G. van Koten, W. J. J. Smeets, A. L. Spek, P. H. M. Budzelaar, *J. Organomet. Chem.* **1989**, 376, 223.
- [6] M.-S. Liao, Q.-E. Zhang, W. H. E. Schwarz, *Inorg. Chem.* **1995**, 34, 5597.
- [7] M. Kaupp, H. G. von Schnering, *Inorg. Chem.* **1994**, 33, 4179.
- [8] T. M. Greene, W. Brown, L. Andrews, A. J. Downs, G. V. Chertihin, N. Runeberg, P. Pyykkö, *J. Phys. Chem.* **1995**, 99, 7925.
- [9] E. Canadell, O. Eisenstein, *Organometallics* **1984**, 3, 759.
- [10] B. V. Lokshin, O. G. Garkusha, Yu. A. Borisov, N. E. Borisova, *Russ. Chem. Bull. Int. Ed.* **2003**, 52, 831.
- [11] V. M. Rayón, G. Frenking, *Chem. Eur. J.* **2002**, 8, 4693.
- [12] A. Rosa, A. W. Ehlers, E. J. Baerends, J. G. Snijders, G. te Velde, *J. Phys. Chem.* **1996**, 100, 5690.
- [13] S. F. Boys, F. Bernardi, *Mol. Phys.* **1970**, 19, 553.
- [14] a) A. D. Becke, *J. Chem. Phys.* **1993**, 98, 5648; b) C. Lee, Y. Wang, R. G. Parr, *Phys. Rev. B* **1988**, 37, 785.
- [15] Gaussian98 (Revision A.7), M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, V. G. Zakrzewski, J. A. Montgomery, R. E. Stratmann, J. C. Burant, S. Dapprich, J. M. Millam, A. D. Daniels, K. N. Kudin, M. C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G. A. Petersson, P. Y. Ayala, Q. Cui, K. Morokuma, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. Cioslowski, J. V. Ortiz, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, C. Gonzalez, M.

Challacombe, P. M. W. Gill, B. G. Johnson, W. Chen, M. W. Wong, J. L. Andres, M. Head-Gordon, E. S. Replogle, J. A. Pople, Gaussian, Inc., Pittsburgh, PA, **1998**.

- [16] a) P. Csaszar, P. Pulay, *J. Mol. Struct.* **1984**, *114*, 31; b) Ö. Farkas, H. B. Schlegel, *J. Chem. Phys.* **1999**, *111*, 10806.
- [17] a) S. I. Gorelsky, A. B. P. Lever, *J. Organomet. Chem.* **2001**, *635*, 187; b) S. I. Gorelsky, AOMix program, rev. 5.62. <http://www.obligato.com/software/aomix>