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On the Chemistry of Zn−Zn Bonds, RZn−ZnR (R = [{(2,6-$Pr^i_2C_6H_3$)N(Me)C}$_2$CH]): Synthesis, Structure, and Computations

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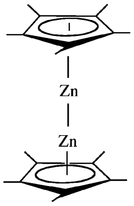
The recent preparation of the first compound containing a Zn−Zn bond, Cp*Zn−ZnCp* (Cp* = C_5Me_5), **1**,[1,2] is a remarkable achievement. The characterization of other such compounds is desirable for further exploration of Zn−Zn bond chemistry.[3−6] To this end, we now report the synthesis and molecular structure[7] of the second compound with a Zn−Zn bond, RZn−ZnR (R = [{(2,6-$Pr^i_2C_6H_3$)N(Me)C}$_2$CH]), **2** (Dipp = 2,6-diisopropylphenyl).



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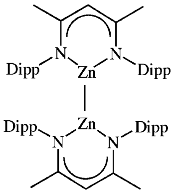

2

Our route to **2** began with the preparation of the lithium derivative, RLi (R = [{(2,6-$Pr^i_2C_6H_3$)N(Me)C}$_2$CH])[8] followed by its reaction with ZnI_2 in Et_2O to give RZn(μ-I)$_2$Li(OEt_2)$_2$.[9] Potassium reduction of RZn(μ-I)$_2$Li(OEt_2)$_2$ affords **2** as colorless, air- and moisture-sensitive crystals (eq 1).

$$\mathrm{RZn}(\mu\text{-I})_2\mathrm{Li}(\mathrm{OEt}_2)_2 \xrightarrow{K} \mathbf{2} \quad (1)$$

Supporting computations on related RZn−ZnR systems provide insight into the nature of the Zn−Zn bond.

Compounds with homonuclear metal−metal bonds of the heavier group 12 metals, cadmium[10,11] and mercury,[12] are well-known. Alkali or alkaline earth metal reduction of metal halides, complexed by sterically demanding ligands, has proven to be a fruitful synthetic approach to compounds containing main group metal−metal bonds[13−16] and main group metal−transition metal bonds.[17−19] We applied this approach to the preparation of **2** by utilizing the well-known sterically encumbered β-diketiminate ligand, [{(2,6-$Pr^i_2C_6H_3$)N(Me)C}$_2$CH]$^-$.[20−22] This β-diketiminate ligand has been used to stabilize an In−In bond, R(Cl)In−In(Cl)R,[23] and a recently reported Mn−Mn bond, RMn−MnR.[24]

X-ray structure analysis confirms the dimeric nature of **2** and the central Zn−Zn bond (Figure 1). The two ligands are arranged in a nearly orthogonal orientation with a N(1)−Zn(1)−Zn(2)−N(3) torsion angle of 86.6°, thus providing effective steric protection of the Zn−Zn bond (Figure 1b). The Zn−Zn distance in **2**, 2.3586(7) Å, is only about 0.05 Å longer than that of 2.305(3) Å reported for **1**. However, the Zn−Zn bond lengths for **1** and **2** are notably shorter than the Zn···Zn separation of 2.4513(9) Å in the related zinc hydride dimer, RZn(μ-H)$_2$ZnR (R = [{(2,6-$Me_2C_6H_3$)N(Me)C}$_2$CH]).[25] Moreover, the ^{1}H NMR resonance for the bridging zinc hydride in RZn(μ-H)$_2$ZnR was found at 4.59 ppm. This value is close to the 4.56 ppm reported for a tris(pyrazolyl)hydroborato complex with a terminal Zn−H.[26] The fact that no such zinc hydride ^{1}H resonance was observed for **2**, coupled with supporting structural and computational data (*vide infra*), further affirms **2**.

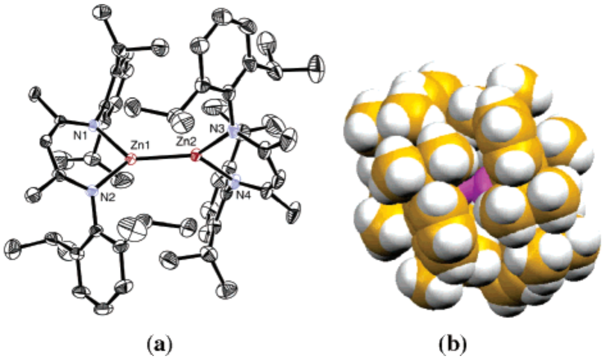

Figure 1. (a) Molecular structure of **2** (thermal ellipsoids are shown at 30% probability levels). Selected bond distances (Å) and angles (deg): Zn(1)−Zn(2) 2.3586(7), Zn(1)−N(1) 2.005(3), Zn(1)−N(2) 2.013(3), Zn(2)−N(3) 2.014(3), Zn(2)−N(4) 2.010(3); N(1)−Zn(1)−N(2) 93.65(13), N(1)−Zn(1)−Zn(2) 131.12(9), N(2)−Zn(1)−Zn(2) 134.10(9), N(3)−Zn(2)−N(4) 93.43(13), N(3)−Zn(2)−Zn(1) 132.62(9), N(4)−Zn(2)−Zn(1) 132.76(10). (b) Space filling model of **2**.

The six-membered C_3N_2Zn rings of **2** are not planar but adopt a puckered conformation with the zinc atom residing 0.65 Å out of the N−C−C−C−N plane. A similarly puckered C_3N_2Zn ring in RZnN($SiMe_3$)$_2$ (R = [{(2,6-$Pr^i_2C_6H_3$)N(Me)C}$_2$CH])[27] has been reported. However, the C_3N_2Zn rings are planar in RZn(μ-H)$_2$ZnR (R = [{(2,6-$Me_2C_6H_3$)N(Me)C}$_2$CH]).[25] The zinc atoms in **2** adopt a trigonal planar geometry, while the Zn−N bond distances of 2.005(3) and 2.014(3) Å are among the longest on record.[28]

The Zn−Zn bond of **2** was probed by B3LYP/DZP^{++} and BP86/DZP^{++} density functional theory (DFT) computations on the RZn−ZnR (R = [(HNCH)$_2$CH]) model compound, **2H** (Figure 2a). As found in **2**, the perpendicular D_{2d} conformation of **2H** is slightly favored, with the D_{2h} rotation transition state being only 0.26 (B3LYP) or 0.37 kcal/mol (BP86) higher in energy than the D_{2d} minimum. The C_3N_2Zn rings of **2H** are planar, rather than having the zinc atoms puckered out-of-plane, as observed experimentally in **2**. Indeed, **2H** may be regarded as an isoelectronic and a potentially *metalloaromatic*[29] analogue of biphenyl with a central Zn−Zn bond: two C−C−C fragments of each ring having been replaced by isoelectronic N−Zn−N units. Aromaticity was probed by computing nucleus-independent chemical shifts (NICS)[30] on the simple benzene-like cyclic $C_3H_5N_2ZnH$ monomer. The refined NICS(0)$_{\pi\,zz}$ value of −7.6 (based on the tensor component perpendicular to the ring)[31] reveals weak aromatic character (compare the −36.6 benzene and the −1.0 1,4-cyclohexadiene NICS(0)$_{\pi\,zz}$ values at the same level).

10.1021/ja053819r CCC: $30.25

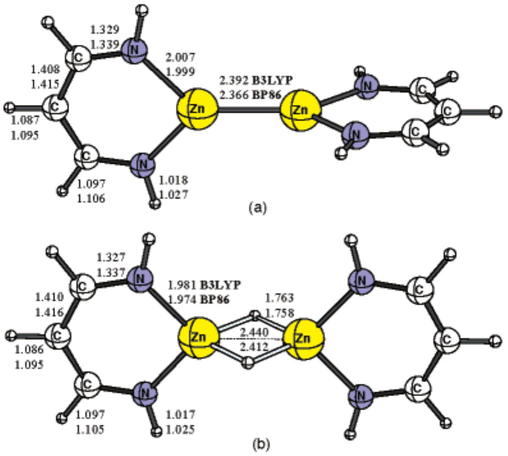

Figure 2. Model compounds **2H** computed (a) with D_{2d} symmetry and **2H(*μ*-H)₂** (b) with D_{2h} symmetry (all bond distances are in Å).

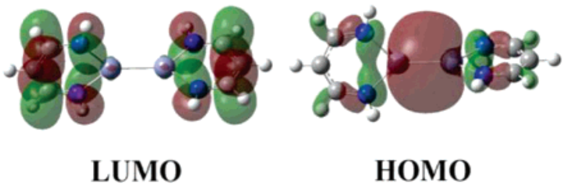

Figure 3. Representation of the frontier molecular orbitals of **2H** from DFT calculations.[33]

The bulky substituents contribute to the puckered conformation of the C_3N_2Zn rings in **2**. Indeed, the C_3N_2Sn ring of $SnCl(Me)_2[CH(CPhNSiMe_3)_2]$ is puckered, while that of the less sterically encumbered $SnCl(Me)_2[CH(CPhNH)_2]$ approaches planarity.[32] The computed Zn−Zn distances of 2.392 (B3LYP) and 2.366 Å (BP86) for **2H** agree well with the experimental Zn−Zn value of 2.3586(7) Å for **2**. The corresponding hydride-bridged $RZn(\mu\text{-}H)_2ZnR$ (R = [(HNCH)$_2$CH]) model compound, **2H(*μ*-H)$_2$**, was also examined. The D_{2h} **2H(*μ*-H)$_2$** minimum has coplanar C_3N_2Zn rings (Figure 2b). The Zn−Zn distances of 2.440 (B3LYP) and 2.412 Å (BP86) in model **2H(*μ*-H)$_2$** approach the experimental value of 2.4513(9) Å for $RZn(\mu\text{-}H)_2ZnR$ (R = [{(2,6-$Me_2C_6H_3$)N(Me)C}$_2$CH])[25] but are notably longer than those computed for **2H** and found experimentally for **2**. These computational results of the model compounds **2H** and **2H(*μ*-H)$_2$** provide further support for the structure of **2**. Bubbling of H_2 into a toluene solution of **2**, however, did not result in hydride formation.

While the **2H** LUMO (Figure 3) is entirely ligand-based with π-symmetry, the **2H** HOMO corresponds to the Zn−Zn σ-bonding orbital. Natural bond orbital (NBO) analysis shows that the natural charge of the zinc atoms in **2H** is +0.85, consistent with the +1 oxidation state of the zinc atoms in **2** and **2H**. The 65.2 kcal/mol Zn−Zn bond dissociation energy of **2H** compares well with the 67.7 kcal/mol reported for **1**.[6] The disproportionation energy of **2** to R_2Zn and Zn is 5.56 kcal/mol (B3LYP). The Zn−Zn bond has 95% s, 4% p, and 1% d character. The NLMO/NPA Zn−Zn bond order of 0.87 and the electron occupancy of the Zn−Zn bonding orbital of 1.9542 are supportive of the intriguing Zn−Zn single bond.

Acknowledgment. G.H.R., R.B.K., P.v.R.S., and H.F.S. are grateful to the National Science Foundation (CHE-0209857).

Supporting Information Available: Full details of the computations and X-ray crystallographic studies, including a cif file. This material is available free of charge via the Internet at http://pubs.acs.org.

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(7) Synthesis and structure: Under an inert atmosphere of dry argon, a solution of $RZnI_2Li(OEt_2)_2$ (R = [{(2,6-$Pr^i{}_2H_3C_6$)N(Me)C}$_2$CH]) (2.75 g, 3.080 mmol) in 50 mL of toluene was added to a flask containing finely cut potassium (0.120 g, 3.080 mmol) at ambient temperature. After being stirred over 2 days, the solution was filtered. The filtrate was concentrated to 8 mL and kept standing at ambient temperature. Over 1 day, colorless crystals of RZn−ZnR (0.70 g; 47% yield) were isolated. Mp: 190 °C (dec). ^1H NMR (C_6D_6): δ 0.76 [d, 12H, $CH(CH_3)_2$], 1.06 [d, 12H, $CH(CH_3)_2$], 1.19 [d, 12H, $CH(CH_3)_2$], 1.24 [d, 12H, $CH(CH_3)_2$], 1.58 (s, 12H, CCH_3), 2.99 [m, 4H, $CH(CH_3)_2$], 3.44 [m, 4H, $CH(CH_3)_2$], 4.84 (s, 2H, CH), 7.03−7.18 (m, 12H, Ar-H). Anal. (E+R Microanalytical Laboratories, Corona, NY) Calcd (found) for $C_{58}H_{82}N_4Zn_2$ (966.08): C, 72.11 (72.06); H, 8.56 (8.65). X-ray intensity data were collected on a Bruker SMART CCD-based X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). Cell parameters and an orientation matrix for data collection corresponded to a monoclinic crystal system, with unit cell parameters $a = 11.6783(15)$ Å, $b = 18.775(3)$ Å, $c = 28.507(4)$ Å, $\beta = 97.760(3)°$, $V = 6193.2(15)$ Å^3, $D_{calcd} = 1.135$ g cm^{-3}, and $Z = 4$ for $C_{58}H_{82}N_4Zn_2$ (toluene). The structure was solved in the space group $P2_1/c$ (No. 14) by direct methods using the SHELXTL 6.1 bundled software package. Using 8033 observed reflections ($I > 2\sigma(I)$), refinement converged at $R1 = 0.0572$ and $wR2 = 0.1493$.
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(33) Computations: All the structures were optimized at the DFT level (B3LYP and BP86) with DZP++ basis set with the Gaussian-94 program (reference in Supporting Information).

JA053819R