Communication

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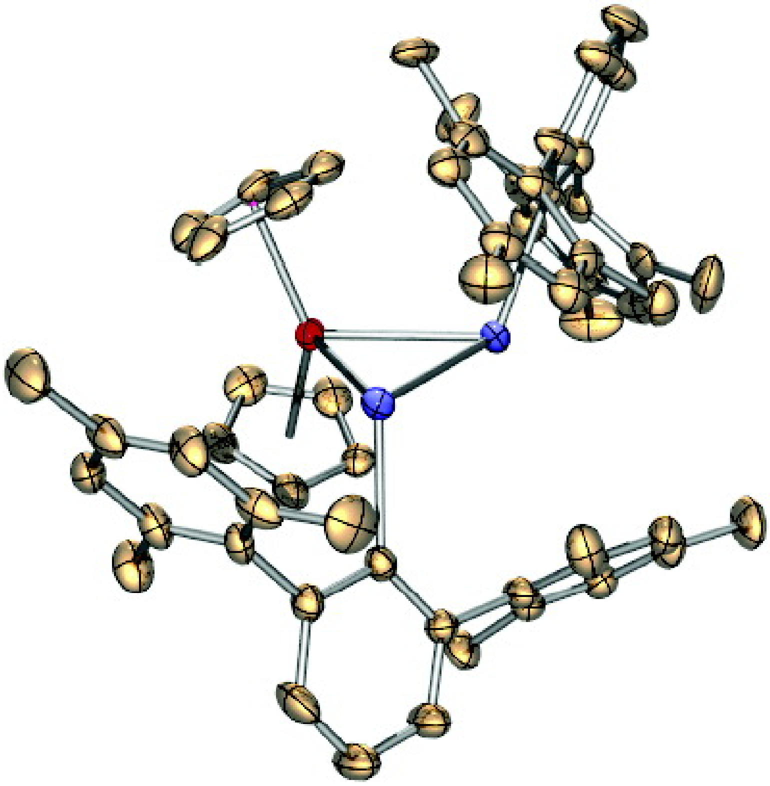

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A Metallocene-Complexed Dibismuthene: $Cp_2Zr(BiR)_2$ ($Cp = C_5H_5$; $R = C_6H_3$-2,6-Mes_2)

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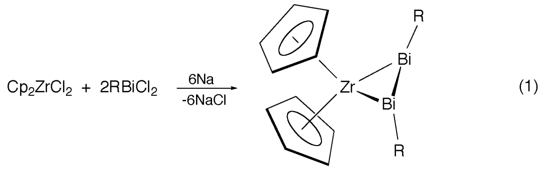
Although zirconocene dichloride may be best known as a critical component in homogeneous Ziegler−Natta catalytic systems, zirconocene derivatives also show promise in disparate processes, such as nitrogen fixation,[1,2] where, notably, dinitrogen interacts side-on with zirconium. While similar side-on zirconocene-coordinated diphosphene derivatives have been described,[3,4] the corresponding zirconocene-complexed heavier dipnictenes (diarsene, distibene, or dibismuthene) are unknown. We now report the synthesis and molecular structure of $Cp_2Zr(BiR)_2$ ($Cp = C_5H_5$; $R = C_6H_3$-2,6-Mes_2), **1**. This air- and moisture-sensitive dark reddish/brown compound was prepared by the sodium metal reduction of Cp_2ZrCl_2 with $RBiCl_2$[5] (eq 1).[6]



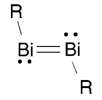
1

(1)

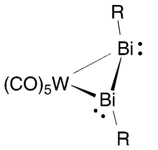
This zirconocene-complexed dibismuthene is significant as it is the first organometallic compound containing Bi−Zr bonds and the only example of a $ZrBi_2$ ring. Moreover, our computations on associated model systems offer insight into the nature of the interaction of the heaviest dipnictene with a metallocene center.

Examples of direct bonding between main group and transition metals involving zirconocene complexes are rare;[7−9] $Cp'_2Zr(SnR_2)_2$ ($Cp' = C_5H_4Me$; $R = CH(SiMe_3)_2$)[10,11] and $Cp_2Zr(GaR)_2$ ($R = C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$)[12] are most relevant to **1**. Although Sn−Sn bonding was lacking, $Cp'_2Zr(SnR_2)_2$ featured short Sn−Zr bonds (2.8715(11) Å). Similarly, while Ga−Ga bonding was absent in the 18-electron $Cp_2Zr(GaR)_2$ complex, the Ga−Zr bonds (2.6350(8) Å) were also short. The synthetic procedure for $Cp_2Zr(GaR)_2$[12] suggested a facile route to other interesting compounds at the transition metal−main group metal interface. The realization of the title compound further affirms this hypothesis.

The preparation of a stable compound with a homonuclear double bond involving bismuth, the heaviest nonradioactive element, presented a particularly desirable, if stubbornly elusive, target. The first stable dibismuthene, RBi═BiR (R = Tbt = 2,4,6-tris[bis(trimethylsilyl)methyl]phenyl), **2**, was only reported in 1997.[13] The second dibismuthene, RBi═BiR ($R = C_6H_3$-2,6-Mes_2), **3**,[5] utilized the same ligand, 2,6-dimesitylphenyl, which was successfully employed herein for the synthesis of **1**. The title compound provides an unprecedented opportunity to examine a dibismuthene "before" (**3**) and "after" (**1**) coupling to a metallocene center.



2: R = Tbt
3: $R = C_6H_3$-2,6-Mes_2



4: $R = CH_2(SiMe_3)_2$

The two *m*-terphenyl ligands dominate the structure of **1** (Figure 1) as the two cyclopentadienyl rings complete the coordination sphere of the $ZrBi_2$ metallic core. While **1** has a trans-bent, nonplanar conformation with a C(1)−Bi(1)−Bi(2)−C(25) torsion angle of −152.0°, the corresponding trans-bent C−Bi−Bi−C segment in **3** is planar (i.e., 180° C−Bi−Bi−C torsion angle). The Bi−Bi−C bond angles in **1** (109.3(2) and 109.54(18)°) are considerably greater than that in **3** (92.5(4)°). However, the Bi−C bond distances in **1** (2.324(7) and 2.312(7) Å) are only slightly longer than that in **3** (2.257(17) Å).

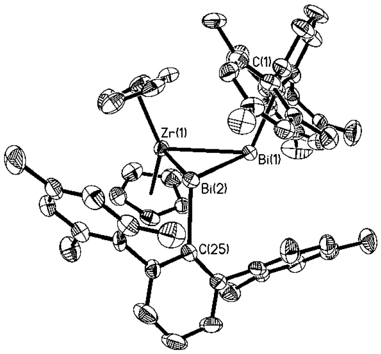


Figure 1. Molecular structure of $Cp_2Zr(BiR)_2$, **1** (thermal ellipsoids are shown at 30% probability levels). Selected bond distances (Å) and angles (deg): Bi(1)−C(1) 2.324(7), Bi(1)−Zr(1) 2.9903(10), Bi(1)−Bi(2) 3.1442(7), Bi(2)−C(25) 2.312(7), Bi(2)−Zr(1) 3.0044(11); C(25)−Bi(2)−Bi(1) 109.54(18), C(1)−Bi(1)−Bi(2) 109.3(2).

The Bi═Bi double bond distances in **2** (2.8206(8) Å) and **3** (2.8327(14) Å) are nearly the same, but are only about 0.04 Å shorter than the Bi−Bi bond (2.8769(5) Å) in the pentacarbonyltungsten−dibismuthene complex $(CO)_5W(BiR)_2$ ($R = CH_2SiMe_3$), **4**.[14] These distances compare to 2.990(2) Å for the Bi−Bi single bond distance in $Ph_2Bi{-}BiPh_2$.[15] The Bi−Bi bond distance in **1** (3.1442(7) Å), while longer than those for these compounds, is shorter than the Bi−Bi distances reported for $[Bi_4Fe_4(CO)_{13}]^{2-}$ (3.473(2) and 3.453(2) Å).[16] While **1** is the first structurally characterized organometallic compound containing Bi−Zr bonds, its Bi−Zr bond lengths (2.9903(10) and 3.0044(11) Å) may only be compared with 3.190 Å, the sum of the bismuth and zirconium

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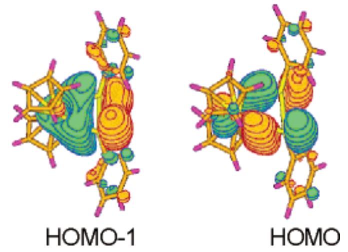
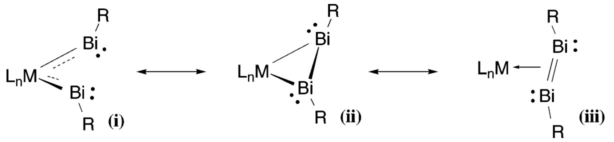


Figure 2. Representation of the frontier molecular orbitals of $Cp_2Zr(BiPh)_2$ from DFT calculations.[17]

covalent radii, and 3.002 Å, the Bi−Zr distance computed here (at the mPW1PW91/LANL2DZ DFT level, as implemented in the Gaussian 03 program[17]) for dimethyl, **1Me**, and diphenyl, **1Ph**, models of **1**.

The nature of the dibismuthene−zirconium interaction of **1** is particularly intriguing. The Bi−Bi bond is lengthened appreciably (3.1442(7) Å in **1**; 2.8327(14) Å in **3**). Although the two *m*-terphenyl ligands are bent away from the Cp_2Zr moiety, the unusually large Bi−Bi lengthening in **1** may be partly steric in origin. While the "open" $L_nM(BiR)_2$ derivative (**i**) represents an extreme bonding model, we conclude that **1** is best depicted as a $L_nM(BiR)_2$ metallocycle (**ii**).



In contrast, the short Bi−Bi bond (2.8769(5) Å) in **4** suggests a $L_nM(BiR)_2$ π-complex involving a Bi═Bi double bond (**iii**). There are two important differences between the Zr and W complexes. (1) Cp_2Zr is a 14-electron fragment in **1**, while $(CO)_5W$ is a 16-electron moiety in **4**; and (2) electron-rich Cp ligands (as in **1**) tend to donate electron density to transition metals, whereas the strong π-acid (electron accepting) CO ligands (as in **4**) decrease the electron density at the metal. Consequently, the Bi−Bi double bond character of **4** (and the contribution of (**iii**) to the resonance hybrid) is enhanced by negligible back-donation from $(CO)_5W$ to the π*-orbital of the dibismuthene moiety.[17] In contrast, the Cp_2Zr moiety donates more electron density into the π*-orbital of the RBiBiR moiety in **1** (HOMO, Figure 2). This relatively strong back-donation of electron density from Cp_2Zr into the π*-orbital of RBiBiR contributes to the Bi−Bi bond elongation in **1**.

This interpretation is also supported by our model computations, which used methyl and phenyl groups as the bismuth ligands. While HOMO-1 (Figure 2) indicates electron donation from the filled π-orbital of RBiBiR to the empty d-orbital of Cp_2Zr, HOMO demonstrates a back-donation of electron density from Cp_2Zr to the antibonding π*-orbital of RBiBiR. Our computed 3.039 Å (**1Me**) and 3.014 Å (**1Ph**) BiBi distances are much longer than all of the other Bi−Bi bond lengths in **2**, **3**, and **4** or computed Bi−Bi bond lengths of their corresponding model compounds (**2**,**3**)**Ph** and **4Me**. This elongation of Bi−Bi bonds in model compounds of **1** agrees well with our experimental observation, supporting the assignment of **1** to resonance form (**ii**). Although the computed Bi−Bi distances in **1Me** and **1Ph** are shorter than that in **1** (3.1442(7) Å), this further lengthening may be attributed to the steric repulsion between two bulky *m*-terphenyl ligands and the relatively weak binding between bismuth atoms.

In model $(CO)_5Zr(BiMe)_2$, where the two Cp ligands in **1Me** were replaced with five CO ligands, the BiBi bond length was shortened from 3.039 to 2.876 Å, due to the decrease in back-donation to the π*-orbital of RBiBiR. In contrast, replacing the W metal in **4Me** by Zr had no effect on the BiBi bond length and only slightly decreased the MeBi═BiMe complexation energy. These results can be attributed to the predominance of resonance contributor (**iii**) when carbonyl ligands are present.

In sum, the interactions between transition metal moieties and dibismuthenes favor disparate resonance forms: (**ii)** for **1**, but (**iii**) for **4**. We are continuing to study this fascinating chemistry at the main group−transition metal interface.

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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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(6) Synthesis/Structure: Under an inert atmosphere of dry argon, a solution of $RBiCl_2$ (2.54 g, 4.28 mmol) in 80 mL of toluene/diethyl ether (1:1) was added to a flask containing finely cut sodium metal (0.800 g, 34.7 mmol) and Cp_2ZrCl_2 (1.25 g, 4.28 mmol). With stirring at room temperature over 2 days, the color of the solution gradually changed to dark reddish/brown. After filtration of the solution, the solvent was removed in vacuo. The dark residual was then extracted with toluene (40 mL). The toluene solution was concentrated to 10 mL and kept standing at ambient temperature. Over several days, dark reddish/brown crystals of $Cp_2Zr(BiR)_2$ (0.97 g; 36% yield) were isolated. Mp 185−188 °C. ^1H NMR (C_6D_6): δ 2.07 (s, 24H, *o*-CH_3), 2.28 (s, 12H, *p*-CH_3), 5.28 (s, 10H, C_5H_5), 6.87 (s, 8H, C_6H_2), 7.00 (d, 4H, *m*-C_6H_3), 7.24 (t, 2H, *p*-C_6H_3). 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 triclinic crystal system, with unit cell parameters $a = 11.380(3)$ Å, $b = 12.774(3)$ Å, $c = 20.598(6)$ Å, $\alpha = 97.506(5)°$, $\beta = 100.016(6)°$, $\gamma = 111.150(3)°$, $V = 2688.6(12)$ Å^3, $D_{calcd} = 1.621$ g cm^{-3}, and $Z = 2$ for $C_{58}H_{60}Bi_2Zr\cdot0.5$(toluene). The structure was solved in the space group $P1$ (No. 2) by Patterson methods using the SHELXTL 6.1 bundled software package. Using 6195 observed reflections ($I > 2\sigma(I)$), refinement converged at $R1 = 0.0453$ and $wR2 = 0.0841$.

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