A Trimetallic Compound Containing Zn−Zr Bonds: $Cp_2Zr(ZnR)_2$ ($Cp = C_5H_5$; $R = C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2$)$_2$)

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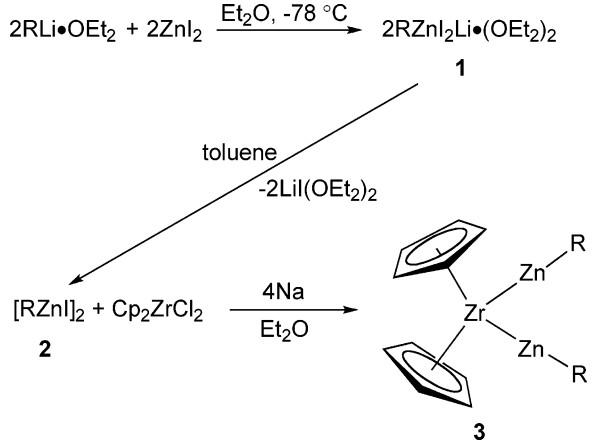
*Summary: m-Terphenylzinc iodides $RZnI_2Li(OEt_2)_2$ (**1**) and RZnI (**2**) (R = C_6H_3-2,6-(2,4,6-i-$Pr_3C_6H_2$)$_2$) were prepared and structurally characterized. The sodium metal reduction of Cp_2ZrCl_2 with **2** afforded $Cp_2Zr(ZnR)_2$ (**3**) as the first structurally characterized compound containing a Zn−Zr bond. The nature of the unique Zn−Zr bond for **3** was further probed by DFT computations.*

Our pursuit of organometallic chemistry at the main-group-metal−transition metal interface[1−4] led recently to 18-electron $Cp_2M(GaR)_2$ complexes ($Cp = C_5H_5$; M = Ti, Zr; R = C_6H_3-2,6-(2,4,6-*i*-$Pr_3C_6H_2$)$_2$),[1,3] where the :GaR units appear to mimic the neutral 2-electron-donor behavior of :CO ligands. The isolation of the first compound containing a Zn−Zn bond[5] spawned interest in the chemistry of zinc; reports of additional compounds containing the Zn−Zn bond followed.[6−8] Since zinc, a group 12 metal, and gallium, a main group 13 metal, are neighbors on the periodic table, we wondered if such $Cp_2M(ZnR)_2$ (M = Ti, Zr) complexes could be prepared. Furthermore, what would be the nature of such Zn−M bonding? Although compounds containing zinc−transition-metal (mostly groups 6−8) bonds have been known for some time,[9−14] compounds containing Zn−M (M = group 4: Ti, Zr, Hf) bonds have not been reported. We now report the synthesis and molecular structure of $Cp_2Zr(ZnR)_2$ (**3**; R = C_6H_3-2,6-(2,4,6-*i*-$Pr_3C_6H_2$)$_2$), the first structurally characterized compound containing a Zn−Zr bond. The nature of the Zn−Zr bond in **3** was probed by computations on a model system, $Cp_2Zr(ZnR')_2$ (R′ = C_6H_3-2,6-(C_6H_5)$_2$) (**3a**).

Scheme 1. Synthetic Routes to Compounds 1−3



Results and Discussion

The lithium adduct $RZnI_2Li(OEt_2)_2$ (**1**) was synthesized by reaction of RLi·OEt_2 with ZnI_2 in Et_2O. Interestingly, vigorous stirring of a toluene solution of **1** leads to the formation of $[RZnI]_2$ (**2**) as colorless crystals. The moisture- and air-sensitive title compound, **3**, was synthesized by sodium reduction of Cp_2ZrCl_2 with **2** (Scheme 1). Compounds **1**−**3** were characterized by ^{1}H NMR, elemental analyses, and single-crystal X-ray diffraction.

X-ray structural analysis (Figure 1) shows that the tricoordinate zinc atom in **1** prefers a trigonal-planar geometry and is embraced by the sterically demanding *m*-terphenyl ligand on both sides of the ZnI_2 plane. The essentially identical Zn−I distances, 2.5910(5) and 2.5950(5) Å, in **1** are only slightly shorter than those in [{(2,6-*i*-$Pr_2C_6H_3$)N(Me)C}$_2$CHZn(μ-I)$_2$Li-(OEt_2)$_2$] (**4**)[15] (2.6142(8) and 2.6648(8) Å). The Zn−C distance (1.971(3) Å) in **1** is between those of **2** and **3** from 1.952(4) to 1.997(4) Å. While the 2.804(7) and 2.800(7) Å Li−I distances in **1** are equal, those in **4** (2.784(8) and 2.919(8) Å) differ significantly.

Like the lithium adduct **1**, compound **2** (Figure 2) has two μ_2-bridging iodine atoms. However, in **2** the iodine atoms link two zinc atoms and help constitute a planar four-membered Zn_2I_2 ring, which is shielded effectively by the two nearly orthogonal-oriented *m*-terphenyl ligands. The C(1)−Zn(1)···Zn(2)−C(37)

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(1) Yang, X.-J.; Quillian, B.; Wang, Y.; Wei, P.; Robinson, G. H. *Organometallics* **2004**, *23*, 5119−5120.
(2) Wang, Y.; Quillian, B.; Yang, X.-J.; Wei, P.; Chen, Z.; Wannere, C. S.; Schleyer, P. v. R.; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 7672−7673.
(3) Yang, X.-J.; Wang, Y.; Quillian, B.; Wei, P.; Chen, Z.; Schleyer, P. v. R.; Robinson, G. H. *Organometallics* **2006**, *25*, 925−929.
(4) Quillian, B.; Wang, Y.; Wannere, C. S.; Wei, P.; Schleyer, P. v. R.; Robinson, G. H. *Angew. Chem., Int. Ed.* **2007**, *46*, 1836−1838.
(5) Resa, I.; Carmona, E.; Gutierrez-Puebla, E.; Monge, A. *Science* **2004**, *305*, 1136−1138.
(6) Wang, Y.; Quillian, B.; Wei, P.; Wang, H.; Yang, X.-J.; Xie, Y.; King, R. B.; Schleyer, P. v. R.; Schaefer, H. F.; Robinson, G. H. *J. Am. Chem. Soc.* **2005**, *127*, 11944−11945.
(7) Zhu, Z.; Wright, R. J.; Olmstead, M. M.; Rivard, E.; Brynda, M.; Power, P. P. *Angew. Chem., Int. Ed.* **2006**, *45*, 5807−5810.
(8) Grirrane, A.; Resa, I.; Rodriguez, A.; Carmona, E.; Alvarez, E.; Gutierrez-Puebla, E.; Monge, A.; Galindo, A.; Del Rio, D.; Andersen, R. A. *J. Am. Chem. Soc.* **2007**, *129*, 693−703.
(9) Burlitch, J. M.; Ferrari, A. *Inorg. Chem.* **1970**, *9*, 563−569.
(10) Denis, J. S.; Butler, W.; Glick, M. D.; Oliver, J. P. *J. Am. Chem. Soc.* **1974**, *96*, 5427−5436.
(11) Budzelaar, P. H. M.; Boersma, J.; Van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *Inorg. Chem.* **1982**, *21*, 3777−3780.
(12) Budzelaar, P. H. M.; Boersma, J.; Van der Kerk, G. J. M.; Spek, A. L.; Duisenberg, A. J. M. *Organometallics* **1985**, *4*, 680−683.
(13) Wright, C. A.; Shapley, J. R. *Inorg. Chem.* **2001**, *40*, 6338−6340.
(14) Enders, M.; Kohl, G.; Pritzkow, H. *Organometallics* **2002**, *21*, 1111−1117.
(15) Prust, J.; Most, K.; Muller, I.; Stasch, A.; Roesky, H. W.; Uson, I. *Eur. J. Inorg. Chem.* **2001**, 1613−1616.

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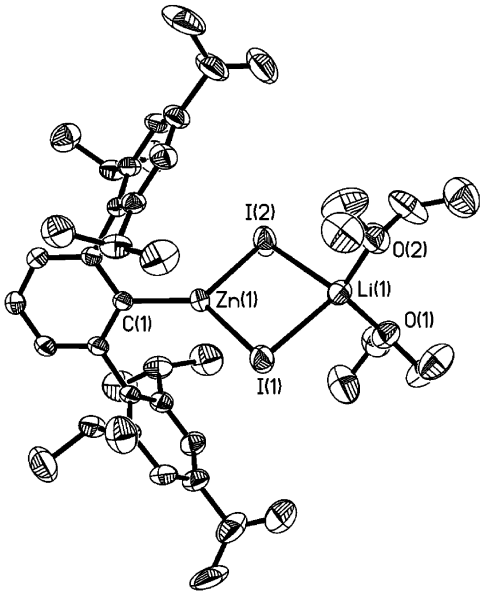

Figure 1. Molecular structure of **1** (thermal ellipsoids are shown at the 30% probability level). Selected bond distances (Å) and angles (deg): Zn(1)−C(1) = 1.971(3), Zn(1)−I(1) = 2.5910(5), Zn(1)−I(2) = 2.5950(5), I(1)−Li(1) = 2.804(7), I(2)−Li(1) = 2.800(7); I(1)−Zn(1)−I(2) = 103.053(16), Zn(1)−I(1)−Li(1) = 81.98(13), Zn(1)−I(2)−Li(1) = 81.98(14).

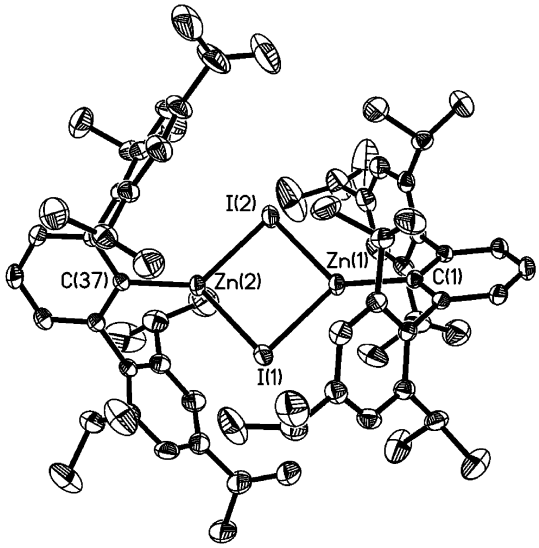

Figure 2. Molecular structure of **2** (thermal ellipsoids are shown at the 30% probability level). Selected bond distances (Å) and angles (deg): Zn(1)−C(1) = 1.960(4), Zn(2)−C(37) = 1.952(4), Zn(1)−I(1) = 2.6180(6), Zn(1)−I(2) = 2.6300(11), Zn(2)−I(1) = 2.6218-(6), Zn(2)−I(2) = 2.6355(10); I(1)−Zn(1)−I(2) = 95.21(3), I(1)−Zn(2)−I(2) = 94.99(3), Zn(1)−I(1)−Zn(2) = 85.157(18), Zn(1)−I(2)−Zn(2) = 84.65(3).

array is almost linear, with C(1)−Zn(1)···Zn(2) (175.97°) and Zn(1)···Zn(2)−C(37) (176.26°) angles. The array in RZn−ZnR (R = C_6H_3-2,6-(2,6-*i*-$Pr_2C_6H_3$)$_2$) is similar.[7] The tricoordinate zinc atoms in **2** have trigonal-planar geometries. The Zn−I bond distances in **2**, ranging from 2.6180(6) to 2.6355(10) Å, are comparable to those in **1** and **4**.[15]

Although **3** resides about a 2-fold axis, the most notable structural feature is the central trimetallic Zn−Zr−Zn core (Figure 3). This V-shaped Zn−Zr−Zn core is well protected sterically by two bulky *m*-terphenyl ligands as well as by two Cp ligands. Indeed, the Zn−Zr−Zn core represents a rare

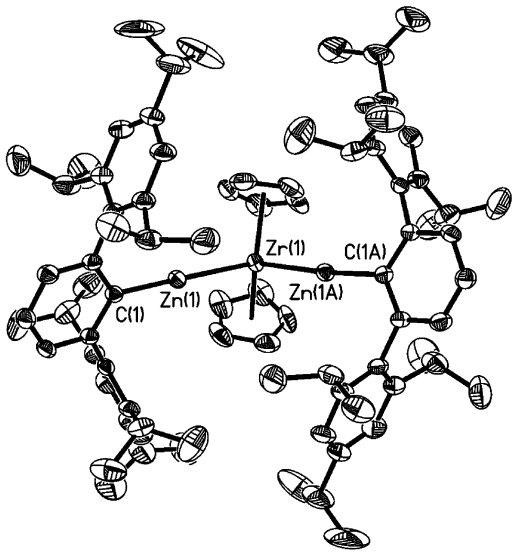

Figure 3. Molecular structure of **3** (thermal ellipsoids are shown at the 30% probability level). Selected bond distances (Å) and angles (deg): Zn(1)−C(1) = 1.997(4), Zn(1)−Zr(1) = 2.7721(7); C(1)−Zn(1)−Zr(1) = 172.84(13), Zn(1)−Zr(1)−Zn(1a) = 99.12(3).

symmetric Zn−M−Zn type of Zn−M (M = transition metal) bonding. Another reported example of this structural type is the Zn−Co−Zn linkage in $(CpZn)_2Co(Cp)PPh_3$,[11] while most examples contain either symmetric M−Zn−M or unsymmetrical M−Zn metallic cores.[9,10,12−14] The 99.12(3)° Zn−Zr−Zn bond angle of **3** is similar to the 100.39(4)° Ga−Zr−Ga angle of $Cp_2Zr(GaR)_2$ (**5**),[3] the 95.06(4)° Sn−Zr−Sn angle of $Cp_2Zr(SnR_2)_2$ (R = $CH(SiMe_3)_2$) (**6**),[16] and the In−Zr−In angle (95.37(2)°) for $Cp_2Zr(InR)_2$ (**7**)[3] but is significantly greater than the 87.70-(3)° Ga−Zr−Ga angle in $Cp_2Zr\{Ga[N(Ar)C(H)]_2\}_2][Li(THF)_4]$[17] (Ar = $C_6H_3Pr^i_2$-2,6) and especially the 74.90(2)° Zn−Co−Zn angle of $(CpZn)_2Co(Cp)PPh_3$.[11]

The novel Zn−Zr bond is the most remarkable structural feature of **3**. The Zn−Zr bond distance, 2.7721(7) Å, is close to the 2.70 Å sum of the zinc and zirconium covalent radii. While the central zirconium is four-coordinate with a pseudo-tetrahedral geometry, the two terminal zinc atoms are two-coordinate with an almost linear C−Zn−Zr angle of 172.84-(13)°. This value is nearly identical with the 172.44(16)° C−Ga−Zr angle of **5** but is between the 171.33(12)° C−In−Zr bond angle of **7** and the 179.2(1)° C−Ga−Fe bond angle of $RGaFe(CO)_4$.[18]

The nature of the Zn−Zr bond in **3** was explored by PW91PW91/LANL2DZ density functional theory (DFT) computations on the $Cp_2Zr(ZnR')_2$ (R′ = C_6H_3-2,6-(C_6H_5)$_2$) model, **3a**.[19] The Zn−Zr bond distance of 2.860 Å for **3a** is somewhat longer than the experimental value of 2.7721(7) Å for **2**, but the C−Zn−Zr angle of 176.0° for **3a** compares well with the 172.84(13)° angle of **3**. Notably, the computed 62.9° Zn−Zr−Zn bond angle for **3a** is much more acute than the 99.12(3)° experimental value for **3**. This difference may be ascribed to the substantially less steric crowding of the 2,6-diphenylphenyl

(16) Piers, W. E.; Whittal, R. M.; Ferguson, G.; Gallagher, J. F.; Froese, R. D. J.; Stronks, H. J.; Krygsman, P. H. *Organometallics* **1992**, *11*, 4015−4022.

(17) Baker, R. J.; Jones, C.; Murphy, D. M. *Chem. Commun.* **2005**, 1339−1341.

(18) Su, J.; Li, X.-W.; Crittendon, R. C.; Campana, C. F.; Robinson, G. H. *Organometallics* **1997**, *16*, 4511−4513.

(19) The structure was optimized at the PW91PW91/LANL2DZ DFT level with the Gaussian 03 program (see the reference in the Supporting Information).

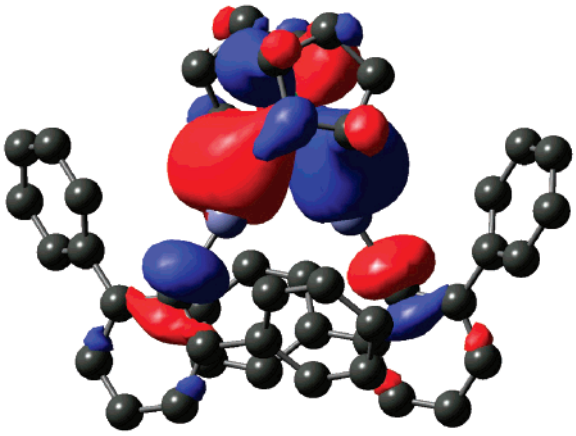

Figure 4. Representation of the HOMO of **3a** from DFT computations.

ligands employed in the **3a** model compared to the extremely bulky *m*-terphenyl ligands (C_6H_3-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$) in **3**.[3]

DFT computations reveal that the HOMO of **3a** (Figure 4) is a Zn−Zr σ-bonding orbital involving overlap of a 3d Zr orbital with the 4s orbital of the Zn atom. The Wiberg bond index (WBI), 0.514, and the 1.57e occupancy of the Zn−Zr interaction (given by natural bond orbital (NBO) analysis) also support the presence of a Zn−Zr bond. Notably, the 0.514 Zn−Zr bond index may be compared with the 0.328 and 0.333 Mo−Mo bond orders reported for $[\{Mo(\eta^5\text{-Cp})(CO)_3\}_2]$ and $[\{Mo(\eta^5\text{-Cp})(CO)_2\}_2(\mu\text{-PMe}_2)]$,[20] respectively, and the Zr−Zr bond order of 0.453 for $[\{(t\text{-}BuC_5H_4)(t\text{-}BuC_5H_3)Zr(\mu\text{-H})Na\}_2]_4$.[21] Indeed, the Zn−Zr bonding mode for **3** (Figure 4) is remarkably different from those of the rather short E−Zr bonds in **5** (E = Ga), **6** (E = Sn), and **7** (E = In), which may be described as having E→Zr donor−acceptor σ bonds supplemented by Zr→E π back-bonding.[18]

In summary, an interesting zirconocene derivative containing unique Zn−Zr bonds (Figure 3) has been synthesized and its molecular structure determined. Furthermore, the nature of the Zn−Zr bonding was probed by DFT computations.

Experimental Section

All reactions were performed under purified argon using Schlenk techniques and an inert-atmosphere drybox (M-Braun LabMaster 130). Solvents were dried and distilled under argon from Na/benzophenone prior to use. Elemental analyses were performed by Complete Analysis Laboratories, Inc. (CALI, Parsippany, NJ). ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer.

Syntheses of 1−3. Compound 1. A diethyl ether solution (50 mL) of $[(2,4,6\text{-}i\text{-}Pr_3C_6H_2)_2C_6H_3]Li{\cdot}OEt_2$ (6.04 g, 10.7 mmol), prepared as previously reported,[22] was added to a flask charged with anhydrous ZnI_2 (3.43 g, 10.7 mmol (Aldrich)) and diethyl ether (20 mL) at −78 °C. The mixture was stirred for 4 h at −78 °C and then warmed gradually to ambient temperature. After the mixture was stirred for 2 days at ambient temperature, the solvent was removed in vacuo. The white residue, recrystallized in Et_2O/hexane, gave colorless crystals of **1**. Yield: 8.35 g, 81.4%. Mp: >150 °C dec (as white solid). ^{1}H NMR (THF-d_8): δ 0.98 (d, 12H, *o*-CH(CH_3)$_2$), 1.11 (t, 12H, *o*-(CH_2CH_3)$_2$), 1.26 (d, 12H, *o*-CH(CH_3)$_2$), 1.31 (d, 12H, *p*-CH(CH_3)$_2$), 2.86 (m, 2H, *p*-C*H*(CH_3)$_2$), 3.01 (m, 4H, *o*-C*H*(CH_3)$_2$), 3.38 (q, 8H, O(CH_2CH_3)$_2$), 6.94−7.14 (m, 7H, $-C_6H_3$ and $-C_6H_2$). Anal. Calcd (found) for $C_{44}H_{69}O_2I_2ZnLi$ (956.10): C, 55.27 (55.14); H, 7.27 (7.25).

Compound 2. The white residue of **1** (5.00 g, 5.23 mmol) was dissolved in 80 mL of toluene, and this solution was stirred vigorously for 1 day. After filtration, the solution was concentrated to 10 mL. After 2 days at ambient temperature, colorless crystals of **2** (2.36 g, 67.0% yield) were observed. Mp: 282 °C. ^{1}H NMR (C_6H_6): δ 1.17 (d, 12H, *o*-CH(CH_3)$_2$), 1.27 (d, 12H, *o*-CH(CH_3)$_2$), 1.34 (d, 12H, *p*-CH(CH_3)$_2$), 2.87 (m, 2H, *p*-C*H*(CH_3)$_2$), 3.06 (m, 4H, *o*-C*H*(CH_3)$_2$), 7.13−7.24 (m, 7H, $-C_6H_3$ and $-C_6H_2$). Anal. Calcd (found) for $C_{72}H_{98}Zn_2I_2$ (1348.04): C, 64.14 (64.03); H, 7.33 (7.24).

Compound 3. A 70 mL portion of diethyl ether was added to a flask containing **2** (3.00 g, 2.22 mmol), Cp_2ZrCl_2 (0.65 g, 2.23 mmol (Strem)), and finely cut sodium (0.50 g, 21.7 mmol) at ambient temperature. After being powerfully stirred over 2 days, the dark red solution was filtered. The filtrate was concentrated to 10 mL and then kept standing at ambient temperature. Over 3 days, orange crystals of **3** (0.57 g, 18.4% yield) were observed. Mp: 273 °C. ^{1}H NMR (C_6H_6): δ 1.22 (d, 24H, *o*-CH(CH_3)$_2$), 1.32 (d, 24H, *o*-CH(CH_3)$_2$), 1.39 (d, 24H, *p*-CH(CH_3)$_2$), 2.93 (m, 4H, *p*-C*H*(CH_3)$_2$), 3.22 (m, 8H, *o*-C*H*(CH_3)$_2$), 4.33 (s, 10H, C_5H_5), 7.16−7.29 (m, 14H, $-C_6H_3$ and $-C_6H_2$). Anal. Calcd (found) for $C_{86}H_{118}OZn_2Zr$ (1389.76): C, 74.32 (74.37); H, 8.56 (8.54).

X-ray Crystal Structure Determination of 1−3. Crystals of **1**−**3** were mounted in glass capillaries under an atmosphere of argon in the drybox. The X-ray intensity data for **1**−**3** were collected at room temperature on a Bruker SMART APEX II X-ray diffractometer system with graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å), using the ω-scan technique. The structures were solved by direct methods using the SHELXTL 6.1 bundled software package.[23] Absorption corrections were applied with SADABS. All non-hydrogen atoms were refined anisotropically (except for those atoms of the disordered diethyl ether solvent molecule in crystals of **3**). Hydrogen atom positions were calculated and allowed to ride on the attached carbon atoms with the isotropic temperature factors fixed at 1.1 times those of the corresponding carbon atoms. Crystal data for **1**: $C_{44}H_{69}O_2I_2ZnLi$, fw = 956.10, monoclinic, $P2_1/n$ (No. 14), a = 14.1460(12) Å, b = 14.7776(12) Å, c = 24.150(2) Å, β = 102.0940(10), V = 4936.4(7) Å^3, Z = 4, R1 = 0.0385 for 7903 data ($I > 2\sigma(I)$), wR2 = 0.1121 (all data). Crystal data for **2**: $C_{72}H_{98}Zn_2I_2$, fw = 1348.04, triclinic, $P\bar{1}$ (No. 2), a = 13.4042(17) Å, b = 14.4142(18) Å, c = 18.520(2) Å, α = 88.019(2)°, β = 86.503(2)°, γ = 79.634(2)°, V = 3512.3(8) Å^3, Z = 2, R1 = 0.0463 for 8969 data ($I > 2\sigma(I)$), wR2 = 0.1433 (all data). Crystal data for **3**: $C_{86}H_{118}OZn_2Zr$, fw = 1389.76, orthorhombic, *Pbcn* (No. 60), a = 15.8883(17) Å, b = 17.6831(19) Å, c = 29.505(3) Å, V = 8289.6(15) Å^3, Z = 4, R1 = 0.0654 for 5205 data ($I > 2\sigma(I)$), wR2 = 0.2304 (all data).

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Supporting Information Available: CIF files giving full details of the computations and X-ray crystallographic studies. This material is available free of charge via the Internet at http://pubs.acs.org.

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(20) Hong, F.-E.; Chang, Y.-C. *Bull. Chem. Soc. Jpn.* **2004**, *77*, 115−121.

(21) Wang, Y.; Quillian, B.; Wei, P.; Wannere, C. S.; Schleyer, P. v. R.; Robinson, G. H. *Organometallics* **2006**, *25*, 3286−3288.

(22) Schiemenz, B.; Power, P. P. *Organometallics* **1996**, *15*, 958−964.

(23) Sheldrick, G. M. SHELXTL 6.1, Crystallographic Computing System; Bruker Analytical X-Ray Systems, Madison, WI, 2000.