Gallium-Bridged Dizirconocene

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A Trimetallic Fulvalene-Bridged Dizirconocene–Gallium Complex**

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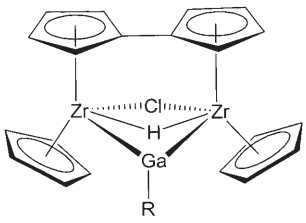
The investigation of alkali-metal reductions of Group 4 metallocene dichlorides, $[Cp_2MCl_2]$ ($Cp = C_5H_5$; M = Ti, Zr), in the presence of Group 13 organometallic chlorides, $RECl_2$ (R = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$; E = Ga, In), in our laboratory gave $[Cp_2M(ER)_2]$ compounds containing "V-shaped" E-M-E trimetallic cores.[1,2] In addition to our studies, a paramagnetic complex with a "V-shaped" Ga-Zr-Ga core, $[Li(thf)_4][Cp_2Zr\{Ga[N(aryl)C(H)]_2\}_2]$ (aryl = 2,6-*i*Pr$_2$C$_6$H$_3$), was recently reported.[3] Moreover, reduction of $RBiCl_2$ (R = 2,6-Mes$_2$C$_6$H$_3$; Mes = 2,4,6-Me$_3$C$_6$H$_2$) with sodium metal in the presence of $[Cp_2ZrCl_2]$ yielded $[Cp_2Zr(BiR)_2]$.[4] This compound was significant as it contained the first Bi–Zr bonds and the first $\{ZrBi_2\}$ ring system. Indeed, trimetallic complexes wherein one Group 13 metal fragment bridges two transition-metal centers are of increasing interest.[5–10] Herein, we report the synthesis and molecular structure of $[(C_{10}H_8)(ZrCp)_2(\mu\text{-H})(\mu\text{-Cl})(\mu\text{-GaR})]$ (**1**; R = 2,6-(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$). Compound **1** joins a small group of compounds containing



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Ga–Zr bonds and is the first example of a gallium atom bridging two zirconium atoms. There are bridging chlorine and hydrogen anions in this complex as well.

Reduction of $[Cp_2ZrCl_2]$ with sodium amalgam has been reported to couple the two cyclopentadienyl ligands, thus generating a fulvalene ligand, to form $[(C_{10}H_8)\{CpZr(\mu\text{-Cl})\}_2]$ ($C_{10}H_8$ = fulvalene).[11] Reduction of $[Cp_2ZrCl_2]$ with sodium in the presence of $RGaCl_2{\cdot}(OEt_2)$,[12] however, yielded compound **1** as air- and moisture-sensitive purple-black crystals. Compound **1** is stable for months under an argon atmosphere without significant decomposition and has high thermal stability (melting above 253 °C). Compound **1** is readily soluble in THF, sparingly soluble in diethyl ether and toluene, and insoluble in hexane.

The X-ray crystal structure[13] of **1** (Figure 1 a) reveals two Zr atoms each bonding in an η^5 fashion to a dianionic fulvalenediyl ligand and one Cp ligand. The two zirconium

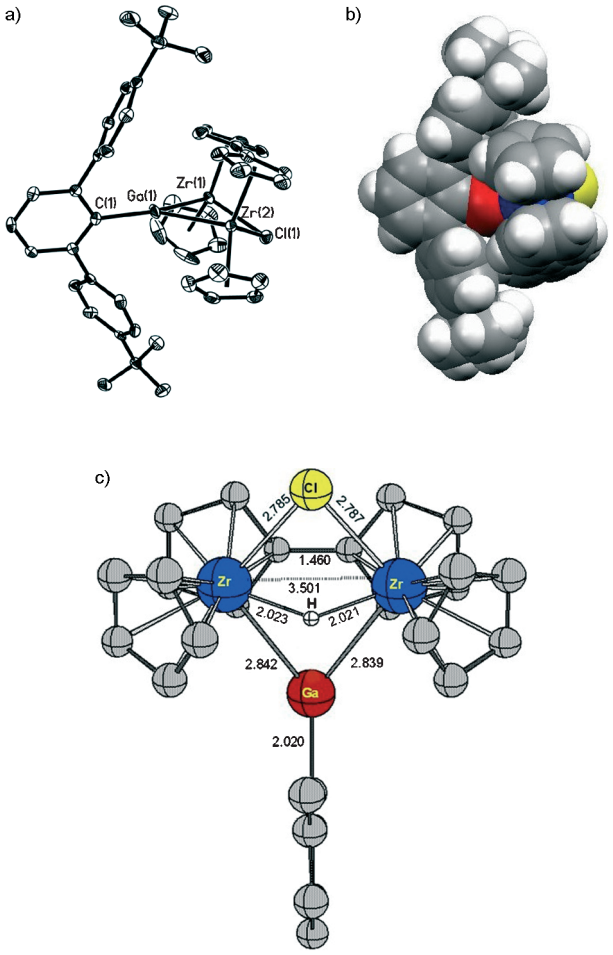

Figure 1. a) Molecular structure of **1** (thermal ellipsoids are shown at 30% probability levels). Selected bond lengths [Å] and angles [°]: Ga(1)-Zr(1) 2.7457(9), Ga(1)-Zr(2) 2.8796(10), Zr(1)-Cl(1) 2.6033(13), Zr(2)-Cl(1) 2.6141(13); Zr(1)-Ga(1)-Zr(2) 77.33(2), Zr(1)-Cl(1)-Zr(2) 84.73(4), Ga(1)-Zr(1)-Cl(1) 96.17(4), Ga(1)-Zr(2)-Cl(1) 92.76(4). b) Space-filling model of **1**; Ga red, Zr blue, Cl yellow. c) PW91PW91/LANL2DZ-optimized structure of **1a**; bond lengths are shown in Å.

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centers in **1** have a formal oxidation state of +4 and are bridged by a $\{RGa\}^{2-}$ moiety as well as by the chloride and hydride ions. The X-ray structural analysis reveals a $\{Zr_2GaCl\}$ butterfly (bent) core. While attempts to detect the bridging Zr-H-Zr hydride in **1** by single-crystal diffraction techniques were unsuccessful, other evidence of this structural feature was obtained (see below). The Zr···Zr separation in **1** (3.516 Å) is slightly longer than the sum of the covalent radii (3.4 Å).[14] Notably, computational studies have suggested that through-space metal–metal interactions may occur up to a Zr···Zr separation of 4.25 Å.[15] The Ga(1)–Zr(1) bond length (2.7457(9) Å) is somewhat shorter than the Ga(1)–Zr(2) bond length (2.8796(10) Å) in **1**. The gallium atom in **1** resides in a trigonal-planar environment, and bonds to the *ipso* carbon atom of the *meta* terphenyl ligand and two zirconium atoms. The space-filling view of **1** (Figure 1b) clearly demonstrates that inherent steric congestion could be manifest in this fashion.

The central phenyl ring of the *meta* terphenyl ligand in **1** resides at an angle of 63.41° relative to the $\{GaZr_2\}$ plane. Although both Ga–Zr bond lengths in **1** (2.7457(9) and 2.8796(10) Å) are longer than those bonds found in $[Cp_2Zr(GaR)_2]$ (R = 2,6-(2,4,6-*i*Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$) (2.6350(8) Å),[2] they are comparable with those in $[Li(thf)_4][Cp_2Zr\{Ga[N(aryl)C(H)]_2\}_2]$ (aryl = 2,6-*i*Pr$_2$C$_6$H$_3$) (2.7417(7) and 2.7349(8) Å).[3] The literature reveals only two somewhat related aluminum-based compounds: $[(C_{10}H_8)(CpTi)_2(\mu\text{-}H)(H_2AlEt_2)]$[16] and $[\{Cp_2Zr(\mu\text{-}H)\}_2(\mu\text{-}H)AlCl_2]$.[17]

The Zr(1)–Cl(1) and Zr(2)–Cl(1) bond lengths in **1** (2.6033(13) and 2.6141(13) Å) are similar to those in $[(C_{10}H_8)\{CpZr(\mu\text{-}Cl)\}_2]$ (2.568(2) and 2.591(2) Å),[18] but longer than that of the terminal Zr–Cl bond in $[(C_{10}H_8)(CpZrCl)_2(\mu\text{-}O)]$ (2.471(1) Å).[11] The Ga(1)-Zr(2)-Cl(1) bond angle in **1** (92.76(4)°) is slightly smaller than the Ga(1)-Zr(1)-Cl(1) bond angle (96.17(4)°). The Zr(1)-Cl(1)-Zr(2) bond angle in **1** (84.73(4)°) is greater than the corresponding angles in $[(C_{10}H_8)\{CpZr(\mu\text{-}Cl)\}_2]$ (av 77.35°).[18] Notably, the Zr(1)-Ga(1)-Zr(2) bond angle in **1** (77.33(2)°) is comparable to the Zr-Cl-Zr bond angles in $[(C_{10}H_8)\{CpZr(\mu\text{-}Cl)\}_2]$ (av 77.35°).

The diamagnetic nature of **1** is supported by the fact that this compound is EPR-inactive. The ^{1}H NMR spectrum of **1** reveals a singlet at $\delta = -4.316$ ppm, which may be ascribed to the bridging hydride ligand. This value compares well with the value of $\delta = -4.67$ ppm reported for the bridging hydride ligand in $[(C_{10}H_8)(CpZr)_2(\mu\text{-}Cl)(\mu\text{-}H)(CH_2C{\equiv}CSiMe_3)][BMe(C_6F_5)_3]$.[19] Other ^{1}H NMR signals for bridging zirconium hydrides range from $\delta = -5.32$ to 0.95 ppm,[20–23] whereas terminal zirconium hydride ^{1}H NMR signals may range from $\delta = 3.03$ to 7.25 ppm.[20–24] The computed ^{1}H NMR spectrum of a model of **1**, $[(C_{10}H_8)(CpZr)_2(\mu\text{-}H)(\mu\text{-}Cl)(\mu\text{-}GaR)]$ (**1a**; R = 2,6-Me$_2$C$_6$H$_3$), at the GIAO-PW91PW91/LANL2DZ/-/PW91/LANL2DZ level showed that the computed hydride δ value of −5.00 ppm is comparable to the experimental value observed for **1**. The characteristically broad Zr–H IR stretch ($\tilde{\nu} = 1150$–1500 cm^{-1}) was obscured in the spectrum of **1**. This phenomenon—in which a hydride was clearly observed in the ^{1}H NMR spectrum as a singlet at $\delta = -9.3$ ppm but was undetected by X-ray or IR analyses—was reported for $[(Cp_2Zr)_2(\mu\text{-}C_{10}H_7)(\mu\text{-}H)]$.[25] It should be noted that the ^{1}H NMR spectrum of **1** displays two singlets for the Cp ligands and eight well-resolved multiplets (see the Experimental Section) for the fulvalene ligand (resulting in two ABCD spin systems).[19,26] We did not observe a Ga–H IR stretch in the expected region (1800–2100 cm^{-}).[27–30]

In an effort to better elucidate the nature of the hydride, we performed density functional theory (DFT) computations on **1a**, in which the *meta* terphenyl ligand of **1** has been replaced with a 2,6-dimethylphenyl ligand. Two different methods, B3LYP and PW91PW91, were used in conjunction with the LANL2DZ basis set for the optimization of **1a** (Figure 1c). The hydride ligand, arbitrarily positioned in **1a**, was ultimately optimized as a Zr-H-Zr bridging hydride as illustrated in Figure 1c.[31] The computed Zr···Zr separation in **1a** (3.501 Å) agrees well with that in **1** (3.516 Å). The Ga–Zr bond lengths in **1** (2.7457(9) and 2.8796(10) Å) span a greater range than those computed for the more symmetrical **1a** (2.842 and 2.839 Å). Certainly, the steric bulk of the *meta* terphenyl ligand in **1** contributes to this manifestation.

Future contributions from this laboratory will address other fascinating aspects of the chemistry at the main-group-metal–transition-metal interface.

Experimental Section

All reactions were performed under purified argon using Schlenk techniques in conjunction with an inert-atmosphere drybox (Vacuum Atmospheres HE-493). 2,6-(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$GaCl$_2$·(OEt$_2$) was prepared by a literature procedure.[12] $[Cp_2ZrCl_2]$ was purchased from Aldrich Chemical Co. and was used as received. Solvents were dried and distilled under argon from Na/benzophenone prior to use. ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. EPR spectra were recorded on a Bruker ESP 300E EPR spectrometer. IR spectra were recorded on a Nicolet-Avatar 360 FT-IR spectrometer. Elemental analysis was carried out at Complete Analysis Laboratories, Inc., Parsippany, NJ.

1: 2,6-(4-*t*BuC$_6$H$_4$)$_2$C$_6$H$_3$GaCl$_2$·(OEt$_2$) (5.54 g, 10 mmol) in diethyl ether (75 mL) was transferred to a flask containing $[Cp_2ZrCl_2]$ (2.92 g, 10 mmol) and finely divided sodium metal (1 g, 43.5 mmol) and stirred at room temperature. The initial colorless solution turned brown after 24 h. After 5 days, a reddish-brown solution was filtered from the precipitate. The filtrate was collected, and its solvent removed in vacuo, resulting in a brownish-black residue. The residue was extracted with toluene (15 mL), and the solution was filtered at about −78 °C. The solution was stored at 5 °C, whereupon purple-black crystals formed overnight. The crystals were recrystallized in a solvent mixture of toluene and diethyl ether (1:1 ratio, 20 mL total). After 2 weeks at room temperature, purple-black, flat, rectangular X-ray quality crystals formed (0.615 g, 0.627 mmol, 6.3% yield). M.p. 253–255 °C. Elemental analysis (%) calcd for $C_{53}H_{56}ClGaZr_2$ (980.64): C 64.91, H 5.76; found: C 64.75, H 5.33. ^{1}H NMR (400 MHz, [D$_8$]THF): $\delta = 7.46$–7.56 (m, 11H, ArH), 7.14–7.26 (m, 5H, C$_6$*H*$_5$CH$_3$), 5.26 (s, 5H, C$_5$H$_5$), 5.12 (s, 5H, C$_5$H$_5$), 5.91, 5.62, 4.26, 4.20, 3.85, 3.79, 3.70, 3.53 (m, 1H × 8, two ABCD spin systems, C$_{10}$H$_8$), 2.30 (s, 3H, C$_6$H$_5$C*H*$_3$), 1.29 (s, 18H, C(CH$_3$)$_3$), −4.316 ppm (s, 1H, Zr-H-Zr); IR (KBr): $\tilde{\nu} = 3114.83$ (w), 3044.64 (w), 2960.68 (s), 2902.51 (w), 2864.98 (w), 1529.43 (m), 1507.98 (m), 1461.08 (m), 1438.41 (m), 1393.85 (m), 1362.21 (m), 1289.88 (m), 1115.86 (m), 1042.00 (s), 1014.85 (s), 797.20 (vs), 729.69 (s), 693.98 (m), 574.88 cm^{-1} (w).

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[1] X.-J. Yang, Y. Wang, B. Quillian, P. Wei, Z. Chen, P. von R. Schleyer, G. H. Robinson, *Organometallics* **2006**, *25*, 925.

[2] X.-J. Yang, B. Quillian, Y. Wang, P. Wei, G. H. Robinson, *Organometallics* **2004**, *23*, 5119.

[3] R. J. Baker, C. Jones, D. M. Murphy, *Chem. Commun.* **2005**, 1339.

[4] Y. Wang, B. Quillian, X.-J. Yang, P. Wei, Z. Chen, C. S. Wannere, P. von R. Schleyer, G. H. Robinson, *J. Am. Chem. Soc.* **2005**, *127*, 7672.

[5] R. A. Fischer, J. Weib, *Angew. Chem.* **1999**, *111*, 3002; *Angew. Chem. Int. Ed.* **1999**, *38*, 2830.

[6] G. Linti, L. G. , H. Pritzkow, *J. Organomet. Chem.* **2001**, *626*, 82.

[7] W. Uhl, S. Melle, G. Frenking, M. Hartmann, *Inorg. Chem.* **2001**, *40*, 750.

[8] N. R. Bunn, S. Aldridge, D. L. Kays, N. D. Coombs, A. Rossin, D. J. Willcock, J. K. Day, C. Jones, L.-L. Ooi, *Organometallics* **2005**, *24*, 5891.

[9] E. Leiner, O. Hampe, M. Scheer, *Eur. J. Inorg. Chem.* **2002**, 584.

[10] K. Ueno, T. Watanabe, H. Ogino, *Organometallics* **2000**, *19*, 5679.

[11] T. V. Ashworth, T. C. Agreda, E. Herdtweck, W. A. Herrmann, *Angew. Chem.* **1986**, *98*, 278; *Angew. Chem. Int. Ed. Engl.* **1986**, *25*, 289.

[12] B. Quillian, Y. Wang, P. Wei, A. Handy, G. H. Robinson, *J. Organomet. Chem.* **2006**, *691*, 3765 – 3770.

[13] Crystal data for **1**: monoclinic, space group $P2(1)/c$ (No. 14), $a = 17.9545(3)$, $b = 13.3890(3)$, $c = 18.1881(5)$ Å, $\beta = 99.2920(10)°$; $V = 4314.92(17)$ Å^3, $Z = 4$, $\rho = 1.508$ g cm^{-3}, $\mu = 5.454$ mm^{-1}, 7213 unique reflections collected, 6134 were observed ($I > 2\sigma(I)$), $R_{int} = 0.0567$, $R1 = 0.0478$ ($I > 2\sigma(I)$), $wR2 = 0.1117$(all data), 514 refined parameters. Crystals of **1** were mounted in glass capillaries under an argon atmosphere. The X-ray intensity data were collected at 100(2) K on a Bruker SMART Apex II X-ray diffractometer system with graphite-monochromated $Mo_{K\alpha}$ radiation ($\lambda = 0.710\ 73$ Å) using the ω-scan technique. The structure was solved by direct methods by using the SHELXTL 6.1 bundle software package. Absorption corrections were applied with SADABS. The remaining non-hydrogen atoms were located from successive difference Fourier map calculations. In the final cycles of each refinement, the non-hydrogen atoms were refined anisotropically. The hydrogen atom positions were calculated and allowed to ride on the carbon atom to which they are bonded by assuming a C–H bond length of 0.95 Å. Hydrogen atom temperature factors were fixed at 1.10 times the isotropic temperature factor of the carbon atom to which they are bonded. CCDC-618791 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

[14] M.-M. Rohmer, M. Bénard, *Organometallics* **1991**, *10*, 157.

[15] M. Bénard, M.-M. Rohmer, *J. Am. Chem. Soc.* **1992**, *114*, 4785.

[16] L. J. Guggenberger, F. N. Tebbe, *J. Am. Chem. Soc.* **1973**, *95*, 7870.

[17] A. I. Sizov, T. M. Zvukova, V. K. Belsky, B. M. Bulychev, *J. Organomet. Chem.* **2001**, *619*, 36.

[18] S. Gambarotta, M. Y. Chiang, *Organometallics* **1987**, *6*, 897.

[19] E. Royo, P. Royo, T. Cuenca, M. Galakhov, *Organometallics* **2000**, *19*, 5559.

[20] C. J. Curtis, R. C. Haltiwanger, *Organometallics* **1991**, *10*, 3220.

[21] S. H. Jones, J. L. Petersen, *Inorg. Chem.* **1981**, *20*, 2889.

[22] P. J. Chirik, L. M. Henling, J. E. Bercaw, *Organometallics* **2001**, *20*, 534.

[23] G. Bai, P. Müller, H. W. Roesky, I. Usón, *Organometallics* **2000**, *19*, 4675.

[24] J. A. Pool, E. Lobkovski, P. J. Chirik, *Organometallics* **2003**, *22*, 2797.

[25] G. P. Pez, C. F. Putnik, S. L. Suib, G. D. Stucky, *J. Am. Chem. Soc.* **1979**, *101*, 6933.

[26] E. Royo, P. Royo, T. Cuenca, M. Galakhov, *J. Organomet. Chem.* **2001**, *634*, 177.

[27] J. F. Janik, R. L. Wells, V. G. Young, Jr., *Organometallics* **1997**, *16*, 3022.

[28] P. C. Andrews, M. G. Gardiner, C. L. Raston, V.-A. Tolhurst, *Inorg. Chim. Acta* **1997**, *259*, 249.

[29] R. B. Hallock, O. T. Beachley, Jr., Y.-J. Li, W. M. Sanders, M. R. Churchill, W. E. Hunter, J. L. Atwood, *Inorg. Chem.* **1983**, *22*, 3683.

[30] X.-W. Li, P. Wei, B. C. Beck, Y. Xie, H. F. Schaefer III, J. Su, G. H. Robinson, *Chem. Commun.* **2000**, 453.

[31] Both B3LYP/LANL2DZ and PW91PW91/LANL2DZ optimization of a structure starting with the H atom bridged to the two Zr atoms and Cl also lead to **1a** as in Figure 1c.

