Gallium-Bridged Dizirconocene

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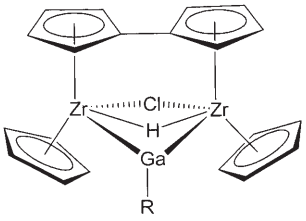
A Trimetallic Fulvalene-Bridged Dizirconocene–Gallium Complex**

*Brandon Quillian, Yuzhong Wang, Chaitanya S. Wannere, Pingrong Wei,
Paul von Ragué Schleyer, and Gregory H. Robinson**

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-iPr$_3C_6H_2)_2C_6H_3$; 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-$iPr_2C_6H_3$), was recently reported.[3] Moreover, reduction of $RBiCl_2$ (R = 2,6-$Mes_2C_6H_3$; Mes = 2,4,6-$Me_3C_6H_2$) 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 [$(C_{10}H_8)(ZrCp)_2(\mu$-H)(μ-Cl)(μ-GaR)] (**1**; R = 2,6-(4-tBu$C_6H_4)_2C_6H_3$). Compound **1** joins a small group of compounds containing 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.



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Reduction of [Cp_2ZrCl_2] with sodium amalgam has been reported to couple the two cyclopentadienyl ligands, thus generating a fulvalene ligand, to form [$(C_{10}H_8)\{CpZr(\mu$-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

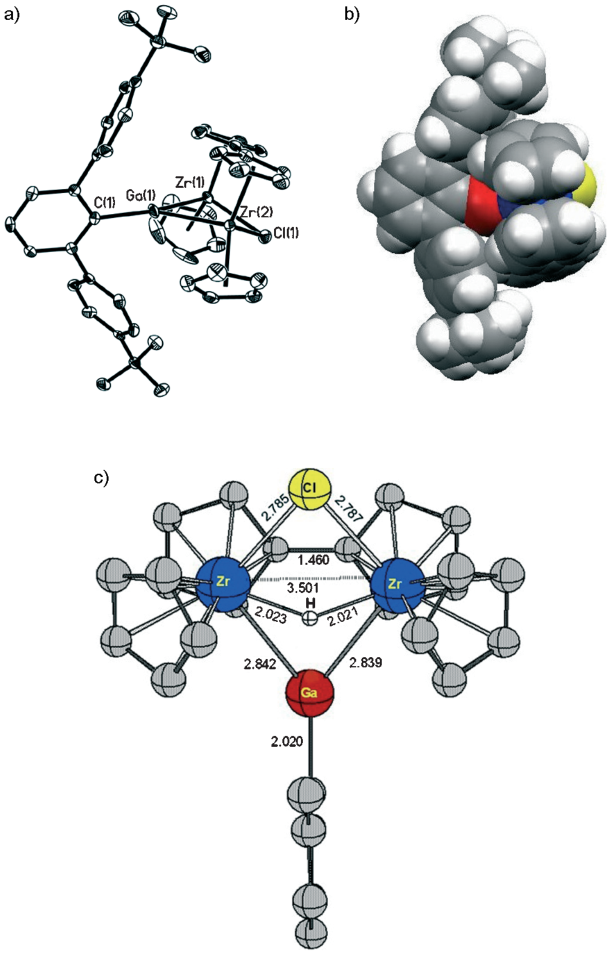

Figure 1. a) Molecular structure of **1** (thermal ellipsoids are shown at 30% probability levels). Selected bond lengths [Å] and angles [°]: Ga(1)-Zr(1) 2.7457(9), Ga(1)-Zr(2) 2.8796(10), Zr(1)-Cl(1) 2.6033(13), Zr(2)-Cl(1) 2.6141(13); Zr(1)-Ga(1)-Zr(2) 77.33(2), Zr(1)-Cl(1)-Zr(2) 84.73(4), Ga(1)-Zr(1)-Cl(1) 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 **1 a**; bond lengths are shown in Å.

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[*] B. Quillian, Dr. Y. Wang, Dr. C. S. Wannere, Dr. P. Wei,
Prof. Dr. P. v. R. Schleyer, Prof. Dr. G. H. Robinson
Department of Chemistry and
The Center for Computational Chemistry
The University of Georgia
Athens, GA 30602-2556 (USA)
Fax: (+1) 706-542-9454
E-mail: robinson@chem.uga.edu

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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 $[Cp_2Zr(GaR)_2]$ ($R = 2,6\text{-}(2,4,6\text{-}i\text{Pr}_3C_6H_2)_2C_6H_3$) (2.6350(8) Å),[2] they are comparable with those in $[Li(thf)_4][Cp_2Zr\{Ga[N(aryl)C(H)]_2\}_2]$ ($\text{aryl} = 2,6\text{-}i\text{Pr}_2C_6H_3$) (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**; $R = 2,6\text{-}Me_2C_6H_3$), 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 ($\tilde{\nu} = 1150\text{–}1500\ \text{cm}^{-1}$) 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). $2,6\text{-}(4\text{-}t\text{BuC}_6H_4)_2C_6H_3GaCl_2{\cdot}(OEt_2)$ 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: $2,6\text{-}(4\text{-}t\text{BuC}_6H_4)_2C_6H_3GaCl_2{\cdot}(OEt_2)$ (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): $\delta = 7.46\text{–}7.56$ (m, 11 H, ArH), 7.14–7.26 (m, 5 H, $C_6H_5CH_3$), 5.26 (s, 5 H, C_5H_5), 5.12 (s, 5 H, C_5H_5), 5.91, 5.62, 4.26, 4.20, 3.85, 3.79, 3.70, 3.53 (m, 1 H × 8, two ABCD spin systems, $C_{10}H_8$), 2.30 (s, 3 H, $C_6H_5CH_3$), 1.29 (s, 18 H, $C(CH_3)_3$), −4.316 ppm (s, 1 H, 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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[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, $Z = 4$, $\rho = 1.508\ \mathrm{g\,cm^{-3}}$, $\mu = 5.454\ \mathrm{mm^{-1}}$, 7213 unique reflections collected, 6134 were observed ($I > 2\sigma(I)$), $R_{\mathrm{int}} = 0.0567$, $R1 = 0.0478$ ($I > 2\sigma(I)$, $wR2 = 0.1117$(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 $\mathrm{Mo}_{\mathrm{K}\alpha}$ 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.

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