A Metallocene with Ga−Zr Bonds: $Cp_2Zr(GaR)_2$ ($Cp = C_5H_5$; $R = -C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$)

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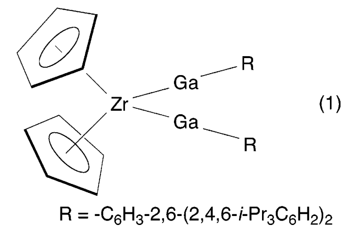
Summary: The reaction of sodium metal with Cp_2ZrCl_2 and $RGaCl_2$ in hexane affords $Cp_2Zr(GaR)_2$ ($R = -C_6H_3$-2,6-(2,4,6-i-$Pr_3C_6H_2)_2$) as deep green-black air-sensitive crystals. Essentially, $Cp_2Zr(GaR)_2$ is isoelectronic with the well-known 18-electron zirconocene dicarbonyl, $Cp_2Zr(CO)_2$, complex. The title compound is the first example of an organometallic compound containing Ga−Zr bonds (Ga−Zr = 2.6350(8) Å).

Although the chemistry of metallocenes has been extensively developed, examples of direct transition-metal−main-group-metal bonds involving metallocene complexes have not been reported.[1−3] Herein, we report the synthesis and molecular structure of $Cp_2Zr(GaR)_2$ ($R = -C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$) as the first example of a structurally characterized organometallic compound containing a gallium−zirconium bond. Moreover, $Cp_2Zr(GaR)_2$ is the first compound containing a main-group-metal−transition-metal bond with a sandwich metallocene complex. The fact that the donor properties of :GaR seem to mimic those of :CO also is intriguing.

The utilization of sterically demanding ligands has proven to be particularly effective in the stabilization of novel main-group compounds.[1,4−6] In particular, *m*-terphenyl ligands have been successfully employed for this purpose in developing the organometallic chemistry of the heavier main-group metals.[7−9] We have utilized such ligands to prepare metalloaromatic gallium ring compounds, $M'_2[GaR]_3$ (M' = Na, K; $R = -C_6H_3$-2,6-$Mes_2C_6H_2$),[10−14] and the provocative $Na_2[GaR]_2$ digallyne compound ($R = -C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$).[15−22] The present study was undertaken to explore early-transition-metal metallocenes as partners in transition-metal−main-group-metal bonding, facilitated by sterically demanding ligands.

The air- and moisture-sensitive title compound was prepared by sodium reduction of zirconocene dichloride, Cp_2ZrCl_2, with $RGaCl_2$[23] (eq 1).[24]



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A number of points are noteworthy regarding structure and bonding. The *m*-terphenyl ligands effectively

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(1) Fischer, R. A.; Weiss, J. *Angew. Chem., Int. Ed.* **1999**, *38*, 2830−2850.

(2) Uhl, W.; Melle, S.; Frenking, G.; Hartmann, M. *Inorg. Chem.* **2001**, *40*, 750−755.

(3) Baker, R. J.; Jones, C.; Platts, J. A. *J. Am. Chem. Soc.* **2003**, *125*, 10534−10535.

(4) West, R.; Fink, M. J.; Michl, J. *Science* **1981**, *214*, 1343−1344.

(5) Linti, G.; Schnöckel, H. *Coord. Chem. Rev.* **2000**, *206−207*, 285−319.

(6) Stürmann, M.; Saak, W.; Marsmann, H.; Weidenbruch, M. *Angew. Chem., Int. Ed.* **1999**, *38*, 187−189.

(7) Cotton, F. A.; Cowley, A. H.; Feng, X. *J. Am. Chem. Soc.* **1998**, *120*, 1795−1799.

(8) Phillips, A. D.; Wright, R. J.; Olmstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 5390.

(9) Pu, L.; Twamley, B.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 3524−3525.

(10) Li, X.-W.; Pennington, W. T.; Robinson, G. H. *J. Am. Chem. Soc.* **1995**, *117*, 7578−7579.

(11) Li, X.-W.; Xie, Y.; Schreiner, P. R.; Gripper, K. D.; Crittendon, R. C.; Campana, C. F.; Schaefer, H. F.; Robinson, G. H. *Organometallics* **1996**, *15*, 3798−3803.

(12) Xie, Y.; Schreiner, P. R.; Schaefer, H. F.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1996**, *118*, 10635−10639.

(13) Xie, Y.; Schreiner, P. R.; Schaefer, H. F.; Li, X.-W.; Robinson, G. H. *Organometallics* **1998**, *17*, 114−122.

(14) Robinson, G. H. *Acc. Chem. Res.* **1999**, *32*, 773−782.

(15) Su, J.; Li, X.-W.; Crittendon, R. C.; Robinson, G. H. *J. Am. Chem. Soc.* **1997**, *119*, 5471−5472.

(16) Xie, Y.; Grev, R. S.; Gu, J.; Schaefer, H. F.; Schleyer, P. v. R.; Su, J.; Li, X.-W.; Robinson, G. H. *J. Am. Chem. Soc.* **1998**, *120*, 3773−3780.

(17) Xie, Y.; Schaefer, H. F.; Robinson, G. H. *Chem. Phys. Lett.* **2000**, *317*, 174−180.

(18) Robinson, G. H. *Chem. Commun.* **2000**, 2175−2181.

(19) Robinson, G. H. *Adv. Organomet. Chem.* **2001**, *47*, 283−294.

(20) Klinkhammer, K. W. *Angew. Chem., Int. Ed.* **1997**, *36*, 2320−2322.

(21) Bytheway, I.; Lin, Z. *J. Am. Chem. Soc.* **1998**, *120*, 12133−12134.

(22) Grützmacher, H.; Fässler, T. F. *Chem. Eur. J.* **2000**, *6*, 2317−2325.

(23) Su, J.; Li, X.-W.; Robinson, G. H. *Chem. Commun.* **1998**, 2015−2016.

(24) Under an inert atmosphere of dry argon a solution of $RGaCl_2$ (2.22 g, 3.55 mmol) in hexane (40 mL) was added to a flask containing finely cut sodium metal (0.50 g, 21.7 mmol) and Cp_2ZrCl_2 (1.04 g, 3.55 mmol). With stirring at room temperature, the color of the solution gradually changed to dark green-black and some gray solid precipitated. After filtration and concentration of the solution (to approximately 10 mL), in vacuo, dark green-black crystals of $Cp_2Zr(GaR)_2$ (0.59 g; 25% yield) were isolated (upon standing for several days). Mp: 218−220 °C dec. Anal. (E+R Microanalytical Laboratories, Corona, NY) Calcd (found) for $C_{82}H_{108}Ga_2Zr$ (1324.40): C, 74.36 (74.29); H, 8.22 (8.55). ^1H NMR (C_6D_6): δ 1.19 (d, 24H, J = 6.8 Hz, *o*-CH(CH_3)), 1.35 (d, 24H, J = 6.8 Hz, *o*-CH(CH_3)), 1.51 (d, 24H, J = 6.8 Hz, *p*-CH(CH_3)), 2.92 (m, 12H, $CH(CH_3)$), 4.01 (s, 10H, η^5-C_5H_5), 7.14 (m, 6H, $-C_6H_3$), 7.26 (s, 8H, $-C_6H_2$). X-ray intensity data were collected on a Bruker SMART TM 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 an orthorhombic crystal system, with unit cell parameters a = 15.829(2) Å, b = 17.574(3) Å, c = 29.319(4) Å, V = 8156(2) Å^3, D_{calcd} = 1.079 g cm^{-3}, and Z = 8 for $C_{41}H_{54}GaZr_{0.5}$. The structure was solved in the space group *Pbcn* (No. 60) by direct methods using the SHELXTL 6.1 bundled software package. Using 3522 observed reflections ($I > 2\sigma(I)$), refinement converged at R1 = 0.064 and wR2 = 0.157.

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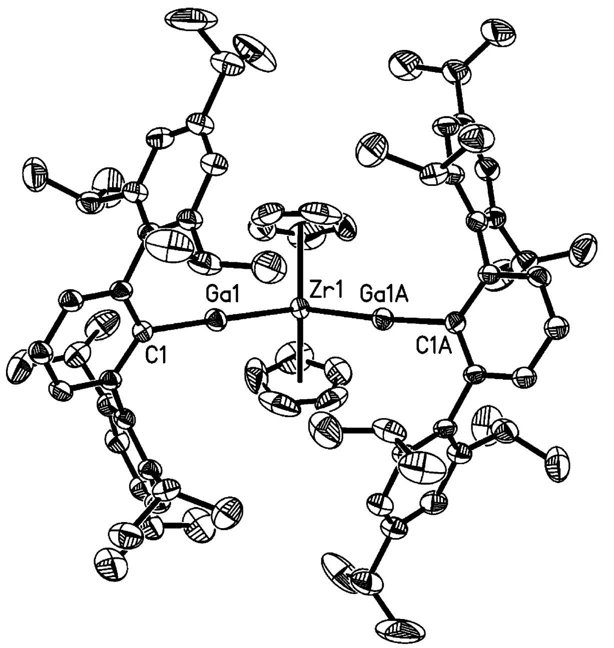

Figure 1. Molecular structure of $Cp_2Zr(GaR)_2$ (thermal ellipsoids are shown at 30% probability levels). Selected bond distances (Å) and angles (deg): Ga(1)−C(1), 2.003(5); Ga(1)−Zr(1), 2.6350(8); C(1)−Ga(1)−Zr(1), 172.44(16); Ga(1)−Zr(1)−Ga(1a), 100.39(4); $Cp_{centroid}$−Zr−$Cp_{centroid}$, 137.4.

dominate the molecular structure of $Cp_2Zr(GaR)_2$ (Figure 1), as the central Cp_2Zr unit is essentially dwarfed by the two GaR units. The molecule resides about a two-fold axis. Other notable structural features of $Cp_2Zr(GaR)_2$ are the Ga−Zr bonds. As $Cp_2Zr(GaR)_2$ is the first structurally characterized organometallic compound containing Ga−Zr bonds, it is difficult to place the Ga−Zr bond distance of 2.6350(8) Å in perspective. However, it is noteworthy that the sum of the gallium and zirconium covalent radii approaches 2.850 Å. The pseudo-tetrahedral environment about zirconium in $Cp_2Zr(GaR)_2$ is easily compared with those of zirconocene dichloride, Cp_2ZrCl_2,[25] and zirconocene dicarbonyl, $Cp_2Zr(CO)_2$.[26] The $Cp_{centroid}$−Zr−$Cp_{centroid}$ bond angle of 137.4° in $Cp_2Zr(GaR)_2$ compares to values of 129.3 and 143.4° in Cp_2ZrCl_2 and $Cp_2Zr(CO)_2$, respectively. The Ga−Zr−Ga bond angle of 100.39(4)° in $Cp_2Zr(GaR)_2$ is only slightly wider than the Cl−Zr−Cl bond angle of 97.0° in Cp_2ZrCl_2. The C−Zr−C bond angle in $Cp_2Zr(CO)_2$, however, is more acute at 89.0°. The Ga−Ga separation of 4.049 Å in $Cp_2Zr(GaR)_2$ is well beyond any significant metal−metal interaction.

The gallium atoms in $Cp_2Zr(GaR)_2$ are unambiguously two-coordinate. While other organometallic compounds containing two-coordinate gallium atoms recently have been reported,[27−30] the literature reveals a paucity of organometallic compounds containing terminal two-coordinate R−Ga−M (M = transition metal) moieties.[31,32] The title compound is similar to $RGaFe(CO)_4$ (R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$),[32] in which the gallium atom also is two-coordinate. The Ga−C bond distance of 2.003(5) Å in $Cp_2Zr(GaR)_2$ is slightly longer than that observed in RGa−$Fe(CO)_4$ (1.943(3) Å). The slightly distorted C−Ga−Zr bond angles observed for $Cp_2Zr(GaR)_2$ of 172.44(16)° compare with the almost perfectly linear C−Ga−Fe bond angle of 179.2(1)° for $RGaFe(CO)_4$. While a proposal for multiple Ga−Fe bond character in $RGaFe(CO)_4$ was initially suggested,[32] an alternative interpretation involving a Ga−Fe single bond was subsequently proposed.[33] Still others[34] concluded that common chemical bonding models may simply be “inappropriate” to adequately describe the Ga−Fe bond in $RGaFe(CO)_4$. The nature of the Ga−Zr bonds in $Cp_2Zr(GaR)_2$, however, appears to be similar to that of the Ga−Fe bond in $RGaFe(CO)_4$: in both compounds the :GaR fragments seem to mimic the neutral two-electron Lewis base donor properties of :C≡O.

The gallium atoms appear to have been reduced by sodium from Ga(III) in $RGaCl_2$ to Ga(I) in the :GaR moieties, while zirconium is reduced from Zr(IV) in Cp_2ZrCl_2 to Zr(II) in $Cp_2Zr(GaR)_2$. Indeed, the preparation of $Cp_2Zr(GaR)_2$ bears some resemblance to the preparation of $Cp_2Zr(CO)_2$: the formal 16-electron zirconocene dichloride was reduced by Na/Hg in the presence of carbon monoxide to give the formal 18-electron $Cp_2Zr(CO)_2$ complex.[35] Similarly, the 16-electron Cp_2ZrCl_2 complex in this study is readily converted to the 18-electron $Cp_2Zr(GaR)_2$ complex. However, :GaR may be regarded as an electron-deficient species, while :C≡O is saturated.

The title compound will be useful as a benchmark as we further explore the fascinating organometallic chemistry at the transition-metal−main-group-metal interface.

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Supporting Information Available: Full details of the 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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(25) Corey, J. Y.; Zhu, Z.-H.; Brammer, L.; Rath, N. P. *Acta Crystallogr.* **1995**, *C51*, 565−567.

(26) Atwood, J. L.; Rogers, R. D.; Hunter, W. E.; Floriani, C.; Fachinetti, G.; Chiesi-Villa, A. *Inorg. Chem.* **1980**, *19*, 3812−3817.

(27) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667−2679.

(28) Wehmschulte, R. J.; Steele, J. M.; Young, J. D.; Khan, M. A. *J. Am. Chem. Soc.* **2003**, *125*, 1470−1471.

(29) Bunn, N. R.; Aldridge, S.; Coombs, D. L.; Rossin, A.; Willock, D. J.; Jones, C.; Ooi, L.-L. *Chem. Commun.* **2004**, 1732−1733.

(30) Ueno, K.; Watanabe, T.; Tobita, H.; Ogino, H. *Organometallics* **2003**, *22*, 4375−4377.

(31) Weiss, D.; Winter, M.; Merz, K.; Knüfer, A.; Fischer, R. A.; Fröhlich, N.; Frenking, G. *Polyhedron* **2002**, *21*, 535−542.

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

(33) Cotton, F. A.; Feng, X. *Organometallics* **1998**, *17*, 128−130.

(34) Boehme, C.; Frenking, G. *Chem. Eur. J.* **1999**, *5*, 2184−2189.

(35) Thomas, J. L.; Brown, K. T. *J. Organomet. Chem.* **1976**, *111*, 297−301.