Syntheses, structures, and bonding of Cp 2M(ER) 2 compounds (Cp = C 5H 5; M = Ti, Zr; e = Ga, In; R = C 6H 3-2,6-(2,4,6-i-Pr 3C 6H 2) 2)

7 AUTHORS, INCLUDING:

Yuzhong Wang
University of Georgia
50 PUBLICATIONS **2,136** CITATIONS

SEE PROFILE

Brandon Quillian
Armstrong State University
25 PUBLICATIONS **722** CITATIONS

SEE PROFILE

Zhongfang Chen
University of Puerto Rico at Rio Piedras
220 PUBLICATIONS **8,015** CITATIONS

SEE PROFILE

Syntheses, Structures, and Bonding of Cp$_2$M(ER)$_2$ Compounds (Cp = C$_5$H$_5$; M = Ti, Zr; E = Ga, In; R = C$_6$H$_3$-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$)

Xiao-Juan Yang, Yuzhong Wang, Brandon Quillian, Pingrong Wei, Zhongfang Chen, Paul v. R. Schleyer, and Gregory H. Robinson*

Department of Chemistry and the Center for Computational Chemistry, The University of Georgia, Athens, Georgia 30602-2556

Sodium or magnesium metal reduction of Cp$_2$MCl$_2$ (Cp = C$_5$H$_5$; M = Zr, Ti) with RECl$_2$ (E = Ga, In; R = C$_6$H$_3$-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$) affords heteronuclear organometallic compounds, Cp$_2$M(ER)$_2$, with new types of group 4−group 13 M−E bonds (Zr−Ga (**1**), Ti−Ga (**2**), Zr−In (**3**), Ti−In (**4**)). These compounds have been characterized by elemental analyses, ^{1}H and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction analyses. The structures of **1**−**4** have V-shaped E−M−E trimetallic linkages with quite short M−E bonds (Zr−Ga, 2.6350(8) Å; Ti−Ga, 2.4921(7) Å; Zr−In, 2.7916(5) Å; Ti−In, 2.6685(8) Å). The transition metal (M = Zr, Ti) centers adopt a pseudo-tetrahedral coordination geometry, while the main group metal (E = Ga, In) atoms reside in a two-coordinate, almost linear environment. Density functional theory (DFT) computations on the model compounds Cp$_2$M(EPh)$_2$ (**1Ph**−**4Ph**) suggest significant π-back-bonding from the group 4 metals (Zr, Ti) to the group 13 metals (Ga, In) in these compounds.

Introduction

Not only is the nature of the bonding between transition metals (M) and main group elements (E) intriguing, but also compounds with M−E bonds have potential applications in a variety of important catalytic processes.[1−10] Many complexes with the general formula of L$_n$M(ER)$_m$, where L$_n$M denotes transition metal-based moieties (M = Fe, Ni, W, Cr; L = Cp, CO) and ER represents group 13 fragments (E = B, Al, Ga, In, Tl; R = organic ligands), have been synthesized and studied theoretically.[11−24] However, there have been few reports of compounds containing direct early transition metal (group 4, Ti, Zr, Hf)−group 13 metal bonds.[25,26] We have been exploring the organometallic chemistry at the transition metal−main group metal interface by utilizing alkali or alkaline earth metal reduction of group 4 metallocene halides and *m*-terphenyl-stabilized main group metal halides.[26,27] Compound **1**, Cp$_2$Zr-(GaR)$_2$ (Cp = C$_5$H$_5$, R = C$_6$H$_3$-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$), which contained the first Zr−Ga bond, was synthesized by sodium reduction of Cp$_2$ZrCl$_2$ with RGaCl$_2$.[26] The Zr−Ga bonds (2.6350(8) Å) in **1** are shorter than the sum of the covalent radii of gallium (1.26 Å) and zirconium (1.46 Å), 2.72 Å, suggesting possible M→E π-back-bonding.[28,29] To gain further insight into the structure and bonding of group 4 metallocene units bearing

* To whom correspondence should be addressed. E-mail: robinson@chem.uga.edu.

(1) Compton, N. A.; Errington, R. J.; Norman, N. C. *Adv. Organomet. Chem.* **1990**, *31*, 91−182.

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

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

(4) Braunschweig, H.; Colling, M.; Kollann, C.; Merz, K.; Radacki, K. *Angew. Chem., Int. Ed.* **2001**, *40*, 4198−4200.

(5) Aldridge, S.; Coombs, D. L. *Coord. Chem. Rev.* **2004**, *248*, 535−559.

(6) Bollwein, T.; Brothers, P. J.; Hermann, H. L.; Schwerdtfeger, P. *Organometallics* **2002**, *21*, 5236−5242.

(7) Macdonald, C. L. B.; Cowley, A. H. *J. Am. Chem. Soc.* **1999**, *121*, 12113−12126.

(8) Jutzi, P.; Neumann, B.; Reumann, G.; Stammler, H.-G. *Organometallics* **1998**, *17*, 1305−1314.

(9) Haubrich, S. T.; Power, P. P. *J. Am. Chem. Soc.* **1998**, *120*, 2202−2203.

(10) Jutzi, P.; Neumann, B.; Reumann, G.; Schebaum, L. O.; Stammler, H.-G. *Organometallics* **1999**, *18*, 2550−2552.

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

(12) Weiss, J.; Stetzkamp, D.; Nuber, B.; Fischer, R. A.; Boehme, C.; Frenking, G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 70−72.

(13) Boehme, C.; Frenking, G. *Chem. Eur. J.* **1999**, *5*, 2184−2190.

(14) Uhl, W.; Benter, M.; Melle, S.; Saak, W.; Frenking, G.; Uddin, J. *Organometallics* **1999**, *18*, 3778−3780.

(15) Coombs, D. L.; Aldridge, S.; Jones, C.; Willock, D. J. *J. Am. Chem. Soc.* **2003**, *125*, 6356−6357.

(16) Uddin, J.; Frenking, G. *J. Am. Chem. Soc.* **2001**, *123*, 1683−1693.

(17) Frenking, G.; Froehlich, N. *Chem. Rev.* **2000**, *100*, 717−774.

(18) Boehme, C.; Uddin, J.; Frenking, G. *Coord. Chem. Rev.* **2000**, *197*, 249−276.

(19) Chen, Y.; Frenking, G. *J. Chem. Soc., Dalton Trans.* **2001**, 434−440.

(20) Uddin, J.; Boehme, C.; Frenking, G. *Organometallics* **2000**, *19*, 571−582.

(21) Frenking, G.; Wichmann, K.; Frohlich, N.; Loschen, C.; Lein, M.; Frunzke, J.; Rayon, V. M. *Coord. Chem. Rev.* **2003**, *238−239*, 55−82.

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

(23) Aldridge, S.; Rossin, A.; Coombs, D. L.; Willock, D. J. *Dalton Trans.* **2004**, 2649−2654.

(24) Gemel, C.; Steinke, T.; Cokoja, M.; Kempter, A.; Fischer, R. A. *Eur. J. Inorg. Chem.* **2004**, 4161−4176.

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

(26) Yang, X.-J.; Quillian, B.; Wang, Y.; Wei, P.; Robinson, G. H. *Organometallics* **2004**, *23*, 5119−5120.

(27) 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.
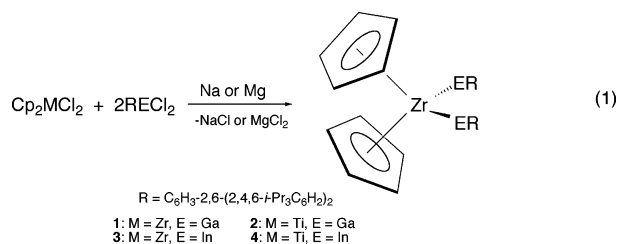
(28) Whittal, R. M.; Ferguson, G.; Gallagher, J. F.; Piers, W. E. *J. Am. Chem. Soc.* **1991**, *113*, 9867−9868.

(29) 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.

unsupported M−E bonds, and to examine the generality of the synthetic method employed for **1**, we have extended this strategy to titanium and indium. We now report the syntheses, molecular structures, and bonding of $Cp_2M(ER)_2$ (**2**, M = Ti, E = Ga; **3**, M = Zr, E = In; **4**, M = Ti, E = In; Cp = C_5H_5; R = C_6H_3-2,6-(2,4,6-i-$Pr_3C_6H_2)_2$). These compounds represent the first structurally characterized organometallic compounds with Zr−Ga,[26] Ti−Ga, Zr−In, and Ti−In bonds. Only a few group 4 transition metal metallocene−main group metal compounds are known; noteworthy examples include $Cp'_2Zr(SnR_2)_2$ (R = CH-(SiMe_3)_2; Cp' = C_5H_5, **5**; R = CH(SiMe_3)_2; Cp' = C_5H_4Me, **6**),[28,29] $[Cp_2Zr\{Ga[N(Aryl)C(H)]_2\}_2][Li(THF)_4]$ (Aryl = C_6H_3-2,6-i-Pr_2) (**7**),[25] and $Cp_2Zr(BiR)_2$ (R = C_6H_3-2,6-$Mes_2C_6H_2$) (**8**).[27] Density functional theory (DFT) computations on the corresponding model complexes $Cp_2M(EPh)_2$ (**1Ph**−**4Ph**) were performed to further probe the M−E bonding.

Results and Discussion

Syntheses. Compounds **1**−**4**, isolated as dark green or blue-black crystals, were prepared by sodium or magnesium reduction of the metallocene dichloride, Cp_2MCl_2 (M = Zr, Ti), with $RECl_2$ (R = C_6H_3-2,6-(2,4,6-i-$Pr_3C_6H_2)_2$; E = Ga, In)[30] (eq 1). The title compounds were characterized by elemental analyses, ^1H and ^{13}C NMR spectroscopy, and single-crystal X-ray diffraction. These compounds are readily soluble in hexane,

$$Cp_2MCl_2 + 2RECl_2 \xrightarrow[\text{-NaCl or MgCl}_2]{\text{Na or Mg}} \quad (1)$$

R = C_6H_3-2,6-(2,4,6-i-$Pr_3C_6H_2)_2$

1: M = Zr, E = Ga   **2**: M = Ti, E = Ga
**3**: M = Zr, E = In   **4**: M = Ti, E = In

ether, and toluene. Although these products are extremely air- and moisture-sensitive (as the intensely green- or blue-colored solutions of the samples rapidly change to colorless when exposed to air), they exhibit considerable thermal stability, decomposing or melting only above 200 °C.

The synthetic strategy for the title compounds combines the utilization of sterically demanding m-terphenyl ligands to stabilize the low-valent, low-coordinate main group species[2,3,11,31−35] with the "one-pot" reduction of the two starting materials, Cp_2MCl_2 and $RECl_2$. Indeed, the alkali or alkaline earth metal reduction of the organometallic halides REX_n has been widely used in the syntheses of novel main group compounds.[36−46] Furthermore, the reduction of metallocene

dichlorides Cp_2MCl_2 with Mg, Na/Hg has also been studied, and the products include the useful intermediate "Cp_2M"[47,48] for the preparation of a variety of metallocene complexes.[49,50] In the present work, the synthetic approach facilitates a facile, reduction of the two reactants in the same reaction vessel and thus the formation of the E−M−E adducts. During the preparative processes, the group 13 metals (Ga and In) were reduced from E(III) in $RECl_2$ to E(I) in the ER moieties, while the transition metals (Zr and Ti) were reduced from M(IV) in Cp_2MCl_2 to M(II) in $Cp_2M(ER)_2$. Accordingly, the formal 16-electron metallocene dichlorides, Cp_2MCl_2, were converted to the 18-electron $Cp_2M(ER)_2$ complexes. The $Cp_2M(ER)_2$ compounds bear some resemblance to zirconocene dicarbonyl, $Cp_2Zr(CO)_2$:[51] two ER fragments coordinate to the M center, which mimics the two-electron donor properties of :C≡O.

We also reduced $RECl_2$ in the presence of $CpZrCl_3$ instead of Cp_2ZrCl_2. Surprisingly, the sodium reduction of $RGaCl_2$ with $CpZrCl_3$ led to the isolation of the known digallyne compound $Na_2[GaR]_2$ (R = C_6H_3-2,6-(2,4,6-i-$Pr_3C_6H_2)_2$) (eq 2),[37,40−46] while magnesium reduction of $RGaCl_2$ and $CpZrCl_3$ resulted in the unexpected formation of compound **1**, $Cp_2Zr(GaR)_2$ (R = C_6H_3-2,6-(2,4,6-i-$Pr_3C_6H_2)_2$) (eq 2).[26] Although the

$$CpZrCl_3 + 2RGaCl_2 \xrightarrow[Mg]{Na} \quad (2)$$
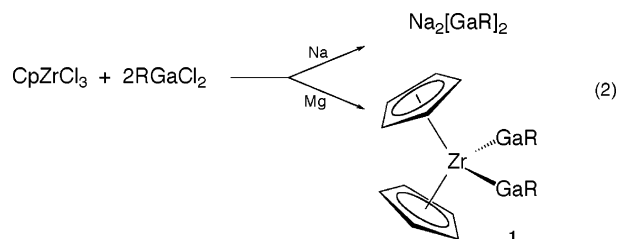
mechanism of this system is still under consideration, the formation of $Na_2[GaR]_2$, from the sodium reduction of $CpZrCl_3$ and $RGaCl_2$, is intriguing. Furthermore, the formation of **1** by magnesium reduction is also very interesting since an intermolecular migration of Cp ligands[52−55] may have been involved. This led to the transformation of the mono(cyclopentadienyl) starting material $CpZrCl_3$ to the bis(cyclopentadienyl) "Cp_2Zr" moiety in the product. This result also reveals that $Cp_2Zr(GaR)_2$ is a relatively stable structure. Indeed, the formation of different products from Na or Mg reduction of $CpZrCl_3$ and $RGaCl_2$ is in contrast to the Na/Mg reductions of Cp_2MCl_2 and $RGaCl_2$ (eq 1) (wherein the same products were obtained by either Na or Mg reduction).

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

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

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

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

(34) Pu, L.; Twamley, B.; Haubrich, S. T.; Olmstead, M. M.; Mork, B. V.; Simons, R. S.; Power, P. P. *J. Am. Chem. Soc.* **2000**, *122*, 650−656.

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

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

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

(38) Tokitoh, N.; Arai, Y.; Okazaki, R.; Nagase, S. *Science* **1997**, *277*, 78−80.

(39) Twamley, B.; Sofield, C. D.; Omlstead, M. M.; Power, P. P. *J. Am. Chem. Soc.* **1999**, *121*, 3357−3367.

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

(41) 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.

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

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

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

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

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

(47) Watt, G. W.; F. O. Drummond, J. *J. Am. Chem. Soc.* **1966**, *88*, 5926−5927.

(48) Watt, G. W.; Baye, L. J.; F. O. Drummond, J. *J. Am. Chem. Soc.* **1966**, *88*, 1138−1140.

(49) Song, L.-C.; Han, C.; Hu, Q.-M.; Zhang, Z.-P. *Inorg. Chim. Acta* **2004**, *357*, 2199−2204.

(50) Song, L.-C.; Liu, P.-C.; Han, C.; Hu, Q.-M. *J. Organomet. Chem.* **2002**, *648*, 119−125.

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

(52) Jutzi, P. *Pure Appl. Chem.* **2003**, *75*, 483−494.

(53) Schiffer, M.; Leiner, E.; Scheer, M. *Eur. J. Inorg. Chem.* **2001**, 1661−1663.

(54) Johnson, B. P.; Schiffer, M.; Scheer, M. *Organometallics* **2000**, *19*, 3404−3409.

(55) Scheer, M.; Leiner, E.; Kramkowski, P.; Schiffer, M.; Baum, G. *Chem.--Eur. J.* **1998**, *4*, 1917−1923.

Table 1. Crystallographic Data and Structure Refinement Details for Compounds 1−4

	1	**2**	**3**	**4**
formula	$C_{82}H_{108}Ga_2Zr$	$C_{82}H_{108}Ga_2Ti$	$C_{82}H_{108}In_2Zr$	$C_{82}H_{108}In_2Ti$
fw	1324.34	1281.02	1414.54	1371.22
T, K	298(2)	298(2)	173(2)	298(2)
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	*Pbcn*	*Pbcn*	*Pbcn*	*Pbcn*
a, Å	15.829(2)	15.935(3)	15.6959(15)	15.7984(8)
b, Å	17.574(3)	17.504(3)	17.7203(17)	17.7455(9)
c, Å	29.319(4)	29.098(5)	29.497(3)	29.5189(15)
V, Å³	8156(2)	8116(3)	8204.3(13)	8275.6(7)
Z	4	4	4	4
$F(000)$	2808	2736	2952	2880
D_{calcd}, g/cm³	1.079	1.048	1.145	1.101
cryst size, mm	0.50 × 0.35 × 0.30	0.45 × 0.40 × 0.30	0.30 × 0.30 × 0.20	0.50 × 0.40 × 0.35
θ range, deg	1.87−25.00	1.86−25.00	1.87−25.00	1.86−25.00
no. of rflns collected	38 167	46 519	39 326	47 729
no. of indep rflns	6847 [R(int) = 0.0480]	7052 [R(int) = 0.0312]	7074 [R(int) = 0.0327]	7249 [R(int) = 0.0215]
refinement method	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2	full-matrix least squares on F^2
final R indices [$I > 2\sigma (I)$]	R1 = 0.0640, wR2 = 0.1567	R1 = 0.0502, wR2 = 0.1394	R1 = 0.0423, wR2 = 0.1052	R1 = 0.0490, wR2 = 0.1564
R indices (all data)	R1 = 0.1234, wR2 = 0.2206	R1 = 0.0773, wR2 = 0.1747	R1 = 0.0741, wR2 = 0.1333	R1 = 0.0678, wR2 = 0.1999
no. of data/restraints/params	6847/0/384	7052/0/384	7074/0/384	7249/0/384
goodness of fit on F^2	1.049	1.072	1.040	1.088
largest diff peak and hole, e Å⁻³	0.984/−0.515	0.622/−0.256	0.926/−0.490	0.775 /−0.250

Table 2. Selected Bond Distances (Å) and Angles (deg) of Compounds 1−4[a]

	1[b] [*1Ph*] Ga−Zr−Ga	**2** [*2Ph*] Ga−Ti−Ga	**3** [*3Ph*] In−Zr−In	**4** [*4Ph*] In−Ti−In
E−M	2.6350(8) [*2.636*]	2.4922(7) [*2.473*]	2.7916(5) [*2.806*]	2.6685(8) [*2.653*]
E−C	2.003(5) [*2.007*]	2.025(3) [*2.010*]	2.204(4) [*2.177*]	2.209(4) [*2.183*]
E···E	4.049 [*3.228*]	3.767 [*3.069*]	4.129 [*3.531*]	3.908 [*3.372*]
C−E−M	172.44(16) [*171.6*]	171.02(9) [*172.7*]	171.33(12) [*172.1*]	169.99(11) [*173.4*]
E−M−E	100.39(4) [*75.5*]	98.18(4) [*76.7*]	95.37(2) [*78.0*]	94.16(4) [*78.9*]
Cp(cen)−M−Cp(cen)	137.4 [*142.9*]	141.9 [*142.3*]	138.7 [*140.1*]	138.3 [*140.2*]

[a] The computed geometric parameters for the model compounds are also shown [in brackets] for comparison. [b] Ref 26.

Crystal Structures of 1−4. Single crystals suitable for X-ray diffraction analysis were obtained from saturated diethyl ether or hexane solutions at room temperature. The crystallographic data, summarized in Table 1, show that **1−4** are isostructural, crystallizing in the same space group *Pbcn* with very similar unit cell dimensions. The asymmetric unit contains half of the molecule with the formula $C_{41}H_{54}EM_{0.50}$. The zirconium or titanium center is coordinated by two Cp ligands and two ER fragments in a pseudo-tetrahedral geometry. A two-fold axis bisects the Cp−M−Cp and E−M−E angles. A representative molecular structure (compound **4**) is shown in Figure 1; selected bond distances and angles for **1−4** are given in Table 2.
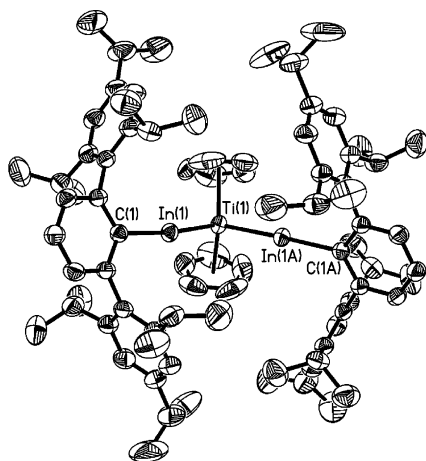

Figure 1. Molecular structure of **4** (thermal ellipsoids are shown at 30% probability levels). Compounds **2** and **3** have similar numbering schemes.

The M−E bonds are the most notable structural features of **1−4**. However, it is difficult to place these bond distances in proper perspective due to the lack of available structural data for the M−E (Zr−In, Ti−Ga, and Ti−In) bonds. However, the M−E bond lengths in **1−4** (Zr−Ga, 2.6350(8) Å; Ti−Ga, 2.4922(7) Å; Zr−In, 2.7916(5) Å; Ti−In, 2.6685(8) Å, respectively) are notably shorter than the sums of the covalent radii (Zr−Ga, 2.72 Å; Ti−Ga, 2.62 Å; Zr−In, 2.90 Å; Ti−In, 2.80 Å, respectively). This suggests that the E→M donor−acceptor σ-bond may be augmented by M→E π-back-bonding. The Zr−Ga bond distance of 2.6350(8) Å in **1** is 0.103 Å shorter than the only other reported Zr−Ga bond (2.738 Å) in compound **7**, [Cp₂Zr{Ga[N(Aryl)C(H)]₂}₂][Li(THF)₄] (Aryl = C₆H₃-2,6-*i*-Pr₂).[25] While the latter compound may have negligible back-bonding from the d¹-Zr into the empty p-orbitals of the gallyl ligands,[25] in contrast, both the d²-Zr configuration and the orientation of the Ga p-orbitals in **1** favor back-donation from Zr to Ga. Our computational studies on the related model compounds **1Ph−4Ph** support this hypothesis (vide infra). Although there are no available bond lengths for comparison for **2−4**, these compounds have a M−E bonding mode similar to that in **1**. Theoretical methods reveal the back-bonding from M to E (e.g., Pt→Ga, In;[56] Fe→Ga, etc.[16,22]) in a variety of transition metal−group 13 metal bonded complexes, $L_nM\text{-}(ER)_x$. Moreover, in Cp′₂Zr(SnR₂)₂ (R = CH(SiMe₃)₂; Cp′ = C₅H₅, **5**), where the same Cp₂Zr fragment as in **1−4** is present, the Zr→Sn back-donation is supported by extended Hückel molecular orbital (EHMO) calculations.[28,29]

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

The coordination of the group 13 metals is intriguing: the metal atoms adopt an unambiguous two-coordinate, almost linear geometry with C−E−M bond angles around 170° (172.44(16)° for **1**, 171.02(9)° for **2**, 171.33(12)° for **3**, and 169.99(11)° for **4**, see Table 2). Numerous interesting organometallic compounds containing two-coordinate group 13 atoms have recently been reported,[15,22,23,57−65] including those featuring terminal two-coordinate group 13 metal−transition metal R−E−M moieties (E = Ga, In; M = transition metal).[9,56,66] For **1−4**, the slightly distorted C−E−M bond angles compare well with the C−In−Mn angle of 175.39(9)° in RInMn(Cp)(CO)$_2$ (R = C$_6$H$_3$-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$)[9] and the almost perfectly linear C−Ga−Fe bond angle of 179.2(1)° in RGaFe(CO)$_4$ (R = C$_6$H$_3$-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$).[66] The Ga−C and In−C bond distances in **1−4** are comparable to those in the compounds bearing the same ER unit. For example, the Ga−C bond lengths in **1** (2.003(5) Å) and **2** (2.025(3) Å) are similar to those reported in Na$_2$-[GaR]$_2$ (2.06(2), 2.028(14) Å),[40] RGaFe(CO)$_4$ (1.943(3) Å),[66] RGa[B(C$_6$F$_5$)$_3$] (1.943(3) Å),[57] and the starting material RGaCl$_2$ (1.949(8) Å).[30] The In−C bond lengths in **3** (2.204(4) Å) and **4** (2.209(4) Å) are comparable to the values reported for the monomeric InR compound (2.260(7) Å), its manganese complex, RInMn(Cp)(CO)$_2$ (2.155(3) Å),[9] and RInCl$_2$ (2.129(5) Å).[30]

Other structural data concern the steric crowding of the bulky *m*-terphenyl ligands in the molecules. The ligands effectively dominate the structure of Cp$_2$M(ER)$_2$ (**1−4**), and the central Cp$_2$M (M = Zr, Ti) units are essentially dwarfed by the two ER (E = Ga, In) units (Figure 1), while the ER units are bent away from the M center with the E−M−E bond angles from 94.16(4)° to 100.39(4)°. Significantly, these angles are wider than the L−M−L bond angles in other d^2 metallocene compounds Cp$_2$ML$_2$ bearing less crowding ligands (e.g., C−Zr−C angle of 89.0° in Cp$_2$Zr(CO)$_2$[67] and C−Ti−C angle of 87.6° in Cp$_2$Ti(CO)$_2$[68]). Similar widening of the L−M−L angle caused by steric repulsion was also observed in compound **5**, where the Sn−Zr−Sn bond angle (95.06 (4)°) is comparable to the E−M−E angles in **1−4**. In the [Cp$_2$Zr{Ga[N(Aryl)C(H)]$_2$}$_2$]-[Li(THF)$_4$] (Aryl = C$_6$H$_3$-2,6-*i*-Pr$_2$) compound, **7**,[25] where the transition metal center has a d^1 electron configuration, the Ga−Zr−Ga angle is more acute (87.7°). The Cp$_{(centroid)}$−Zr−Cp$_{(centroid)}$ bond angles in **1−4** (137.4−141.9°) are readily compared to that in Cp$_2$Zr(CO)$_2$ (143.4°),[67] Cp$_2$Ti(CO)$_2$ (138.6°),[68] and **7** (136.1°), while the Cp$_{(centroid)}$−Zr−Cp$_{(centroid)}$ angle in **5** (131.5°) is much smaller. Another structural feature of **1−4** is that the two carbons (C1 and C1A) attached to the E atoms are
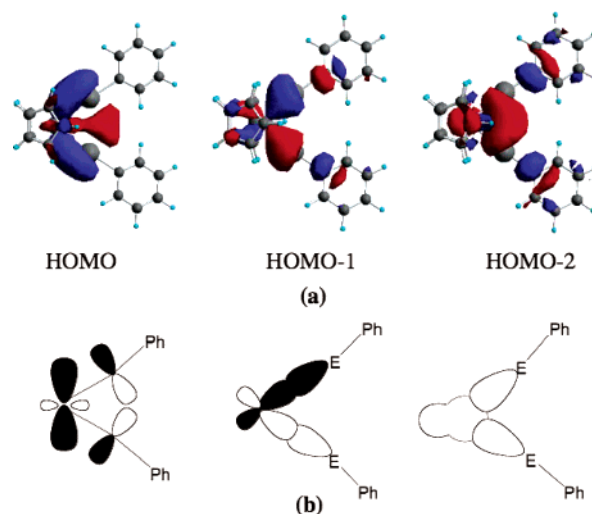
(57) Hardman, N. J.; Wright, R. J.; Phillips, A. D.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 2667−2679.

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

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

(60) Nakata, N.; Izumi, R.; Lee, V. Y.; Ichinohe, M.; Sekiguchi, A. *J. Am. Chem. Soc.* **2004**, *126*, 5058−5059.

(61) Hill, M. S.; Hitchcock, P. B. *Chem. Commun.* **2004**, 1818−1819.

(62) Wright, R. J.; Phillips, A. D.; Allen, T. L.; Fink, W. H.; Power, P. P. *J. Am. Chem. Soc.* **2003**, *125*, 1694−1695.

(63) Coombs, D. L.; Aldridge, S.; Rossin, A.; Jones, C.; Willock, D. J. *Organometallics* **2004**, *23*, 2911−2926.

(64) Wright, R. J.; Phillips, A. D.; Hino, S.; Power, P. P. *J. Am. Chem. Soc.* **2005**, *127*, 4794−4799.

(65) Wright, R. J.; Phillips, A. D.; Hardman, N. J.; Power, P. P. *J. Am. Chem. Soc.* **2002**, *124*, 8538−8539.

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

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

(68) Atwood, J. L.; Stone, K. E.; Alt, H. G.; Hrncir, D. C.; Rausch, M. D. *J. Organomet. Chem.* **1977**, *132*, 367−375.

Figure 2. (a) HOMO, HOMO−1, and HOMO−2 orbitals of Cp$_2$-Ti(InPh)$_2$ (**4Ph**). (b) Schematic representations of the molecular orbitals resulting from the interaction of Cp$_2$Ti fragment molecular orbitals[69] and p- or sp-orbitals of the InR ligands. Other model compounds have similar orbitals.

not located in the plane defined by the E−M−E core; that is, C1−E−M−E−C1A are not coplanar, with C1 and C1A slightly above and below the E−M−E plane (the perpendicular distances of C1 to the E−M−E plane are 0.087 Å for **1**, 0.051 Å for **2**, 0.169 Å for **3**, and 0.151 Å for **4**, respectively). This arrangement may minimize the steric repulsion between the two *m*-terphenyl ligands. It is also notable that the E···E separations of 4.129 to 3.767 Å in compounds **1−4** (see Table 2) are well beyond any significant E−E interactions.

DFT Computations. DFT calculations were carried out at the PW91PW91/Lanl2DZ level for model systems, Cp$_2$M(EPh)$_2$ (**1Ph−4Ph**), in which the phenyl ligand replaces the *m*-terphenyl ligand in compounds **1−4**. Selected computed structural parameters for **1Ph−4Ph**, together with the corresponding X-ray experimental data of **1−4**, are shown in Table 2. Most of the key structural data calculated for **1Ph−4Ph**, such as E−M, E−C bond distances and C−E−M bond angles, are in good agreement with the corresponding experimental X-ray structural values of **1−4**. However, there are considerable differences between some geometry parameters for **1Ph−4Ph** and **1−4**. The E−M−E angles of the model compounds **1Ph−4Ph** (75−79°) are about 20° more acute than those of **1−4** (94−100°). Consequently, the E···E separations calculated for **1Ph−4Ph** (3.069−3.531 Å) are significantly closer than those observed for **1−4** (3.767−4.129 Å, Table 2). This may simply be a consequence of the substantially less steric crowding of the phenyl ligands in **1Ph−4Ph** compared to the bulky *m*-terphenyl ligands in **1−4**.

The M−E bonds can be described as E→M donor−acceptor σ-bonds supplemented by M→E π-back-bonding. The M−E σ-bonds originate from the symmetric (HOMO−2) and antisymmetric (HOMO−1) combinations of the sp orbitals of E donating electrons to the vacant fragment molecular orbitals of the Cp$_2$M units (Figure 2). The orientation of the EPh ligands (nearly linear M−E−C(Ph) configuration) allows for maximum π-overlap of the filled d-orbitals of M with the unhybridized empty p-orbitals on the E atoms of the ER fragments. This π-back-bonding is clearly evident in the computed HOMO (Figure 2) indicated by the red and blue areas on opposite sides of the E atoms.

Summary

A series of novel group 4 transition metal−group 13 main group metal (M−E) bonded compounds were synthesized by "one-pot" reductions of mixtures of RECl$_2$ and Cp$_2$MCl$_2$ precursors dissolved in ether by sodium or magnesium metal. Single-crystal X-ray diffraction of the Cp$_2$M(ER)$_2$ products revealed short M−E bonds. The sterically demanding *m*-terphenyl ligands −C$_6$H$_3$-2,6-(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$ not only help stabilize these compounds but also influence their structures and conformations. This is shown by DFT computations on the related model systems with the much less sterically demanding phenyl ligands. Although the E−M, E−C bond lengths and C−E−M, Cp$_{(centroid)}$−Zr−Cp$_{(centroid)}$ bond angles of **1Ph−4Ph** are very close to those of **1−4**, the computed E−M−E bond angles and E···E separations are much smaller than those in **1−4**. The M−E bonds are constituted by E→M σ-bonding and significant M→E π back-bonding.

Experimental Section

General Procedures. All reactions were performed under purified argon using Schlenk techniques in conjunction with an inert atmosphere drybox (M-Braun LabMaster 130). Anhydrous GaCl$_3$, InCl$_3$ (Aldrich), Cp$_2$TiCl$_2$, and Cp$_2$ZrCl$_2$ (Strem) were purchased and used as received. Solvents were dried and distilled under argon from Na/benzophenone prior to use. [(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]GaCl$_2$ and [(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]InCl$_2$[30] were prepared as previously reported. Elemental analyses were performed by E+R Micro-analytical Laboratories (Parsippany, NJ). ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AC-300 spectrometer.

Syntheses of 2−4. Compounds **2−4** were synthesized by a method similar to that reported for **1**.[26] To a flask charged with finely cut sodium metal (0.50 g, 21.7 mmol) or activated magnesium turnings (0.52 g, 21.7 mmol) and metallocene dichloride, Cp$_2$TiCl$_2$ (0.88 g, 3.55 mmol), or Cp$_2$ZrCl$_2$ (1.04 g, 3.55 mmol), was added a solution of [(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]GaCl$_2$ (2.22 g, 3.55 mmol) or [(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]InCl$_2$ (2.37 g, 3.55 mmol) in diethyl ether (50 mL). The suspension was stirred at room temperature for 2−3 days to give a dark blue or green-black solution along with some gray precipitate. The mixture was allowed to settle overnight and filtered, and the filtrate concentrated to ca. 10 mL. Upon standing at room temperature for several days, dark green or blue crystals of compounds **2−4** were obtained from the solutions. In the initial preparation of **1**, the two reagents Cp$_2$ZrCl$_2$ and RGaCl$_2$ were added in a stoichiometric ratio of 1:1. However, only the 1:2 product, Cp$_2$Zr(GaR)$_2$, was isolated. When the reaction was performed in a 1:2 ratio (Cp$_2$ZrCl$_2$:2RGaCl$_2$), the same product, **1**, was obtained in lower yield. Similarly, higher yields of **2−4** were obtained with the molar ratio of [Cp$_2$MCl$_2$] to [RECl$_2$] being 1:1 (i.e., using an excess of Cp$_2$MCl$_2$).

Compound 2. Yield: 1.45 g (64%). Mp: 216 °C. Anal. Calc (Found) for C$_{82}$H$_{108}$Ga$_2$Ti: C, 76.88 (76.82); H, 8.50 (8.34). ^{1}H NMR (C$_6$D$_6$): δ 1.17 ppm (d, 24H, *J* = 6.8 Hz, *o*-CH(C*H*$_3$)), 1.38 (d, 24H, *J* = 6.8 Hz, *o*-CH(C*H*$_3$)), 1.43 (d, 24H, *J* = 6.8 Hz, *p*-CH-(C*H*$_3$)), 2.95 (sept, 4H, *J* = 6.8 Hz, *p*-C*H*(CH$_3$)), 3.13 (sept, 8H, *J* = 6.8 Hz, *o*-C*H*(CH$_3$)), 3.60 (s, 10H, η^5-C$_5$H$_5$), 7.15 (s, 6H, −C$_6$H$_3$), 7.26 (s, 8H, −C$_6$H$_2$). ^{13}C NMR (C$_6$D$_6$): δ 24.24, 24.40, 25.41, 30.64, 34.87, 78.84, 121.41, 128.13, 128.89, 138.74, 141.73, 147.28, 148.54.

Compound 3. Yield: 1.05 g (42%). Mp: 228 °C (dec). Anal. Calc (Found) for C$_{82}$H$_{108}$In$_2$Zr: C, 69.62 (69.37); H, 7.70 (7.94).

^{1}H NMR (C$_6$D$_6$): δ 1.21 ppm (d, 24H, *J* = 6.8 Hz, *o*-CH(C*H*$_3$)), 1.36 (d, 24H, *J* = 6.8 Hz, *o*-CH(C*H*$_3$)), 1.50 (d, 24H, *J* = 6.8 Hz, *p*-CH(C*H*$_3$)), 2.94 (sept, 4H, *J* = 6.8 Hz, *p*-C*H*(CH$_3$)), 3.20 (sept, 8H, *J* = 6.8 Hz, *o*-C*H*(CH$_3$)), 4.09 (s, 10H, η^5-C$_5$H$_5$), 7.20 (s, 6H, −C$_6$H$_3$), 7.26 (s, 8H, −C$_6$H$_2$). ^{13}C NMR (C$_6$D$_6$): δ 24.31, 24.81, 25.18, 30.58, 34.82, 81.73, 121.37, 126.43, 128.94, 138.35, 142.38, 147.35, 148.28.

Compound 4. Yield: 1.17 g (48%). Mp: 220 °C. Anal. Calc (Found) for C$_{82}$H$_{108}$In$_2$Ti: C, 71.82 (71.67); H, 7.94 (7.89). ^{1}H NMR (C$_6$D$_6$): δ 1.20 ppm (d, 24H, *J* = 6.8 Hz, *o*-CH(C*H*$_3$)), 1.38 (d, 24H, *J* = 6.8 Hz, *o*-CH(C*H*$_3$)), 1.44 (d, 24H, *J* = 6.8 Hz, *p*-CH-(C*H*$_3$)), 2.97 (sept, 4H, *J* = 6.8 Hz, *p*-C*H*(CH$_3$)), 3.17 (sept, 8H, *J* = 6.8 Hz, *o*-C*H*(CH$_3$)), 3.73 (s, 10H, η^5-C$_5$H$_5$), 7.20 (s, 6H, −C$_6$H$_3$), 7.27 (s, 8H, −C$_6$H$_2$). ^{13}C NMR (C$_6$D$_6$): δ 24.33 ppm, 24.58, 25.20, 30.52, 34.85, 78.51, 121.40, 126.20, 129.22, 139.25, 141.99, 147.19, 148.35.

Reduction of [(2,4,6-*i*-Pr$_3$C$_6$H$_2$)$_2$C$_6$H$_3$]GaCl$_2$ with CpZrCl$_3$ by Sodium or Magnesium. Procedures similar to those in the above preparations were followed except that cyclopentadienylzirconium trichloride, CpZrCl$_3$, was used instead of Cp$_2$MCl$_2$. Reduction by Na: dark red, almost black crystals of Na$_2$[GaR]$_2$ were isolated in about 23% yield. Reduction by Mg: crystals of compound **1** were obtained from hexane in 20% yield.

Crystal Structure Determinations. Crystals of **2−4** were mounted in glass capillaries under an atmosphere of argon in the drybox. The X-ray intensity data were collected at room temperature (**2** and **4**) or 173 K (**3**) on a Bruker SMART TM CCD-based 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.[70] Absorption corrections were applied with SADABS. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atom positions (except for those on the Cp rings in compound **2**) 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. Crystallographic data for **1−4** are summarized in Table 1, while the molecular structure of **4** is depicted in Figure 1.

DFT Computations. Full geometry optimizations and frequency analyses were performed for model compounds Cp$_2$M(EPh)$_2$ (**1Ph−4Ph**) in the given symmetry (C_2) at the PW91PW91/Lanl2DZ density functional level of theory. Vibrational frequencies were all real and characterized all the stationary points as minima. All calculations were carried out with the Gaussian03 program.[71]

Supporting Information Available: Detailed information of the X-ray crystal structure analyses of compounds **2−4** and the computational results using model systems (**1Ph−4Ph**). This material is available free of charge via the Internet at http://pubs.acs.org.

(69) Lauher, J. W.; Hoffmann, R. *J. Am. Chem. Soc.* **1976**, *98*, 1729−1742.

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

(71) Computations: All the structures were optimized at the PW91PW91/Lanl2DZ density functional level of theory with the Gaussian-03 program (reference in Supporting Information).