

Syntheses, Structures, and Bonding of Cp₂M(ER)₂ Compounds (Cp = C₅H₅; M = Ti, Zr; E = Ga, In; R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂)

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Sodium or magnesium metal reduction of Cp₂MCl₂ (Cp = C₅H₅; M = Zr, Ti) with RECl₂ (E = Ga, In; R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂) affords heteronuclear organometallic compounds, Cp₂M(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, ¹H and ¹³C 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 Cp₂M(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_nM(ER)_m, where L_nM 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**, Cp₂Zr-(GaR)₂ (Cp = C₅H₅, R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂), which contained the first Zr–Ga bond, was synthesized by sodium reduction of Cp₂ZrCl₂ with RGaCl₂.²⁶ 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

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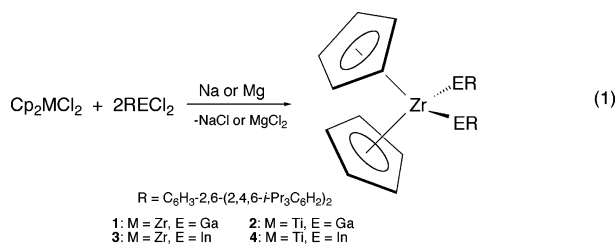
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unsupported M–E bonds, and to examine the generality of the synthetic method employed for **1**, we have extended this strategy to titanium and indium. We now report the syntheses, molecular structures, and bonding of Cp₂M(ER)₂ (**2**, M = Ti, E = Ga; **3**, M = Zr, E = In; **4**, M = Ti, E = In; Cp = C₅H₅; R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)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(SnR₂)₂ (R = CH(SiMe₃)₂; Cp′ = C₅H₅, **5**; R = CH(SiMe₃)₂; Cp′ = C₅H₄Me, **6**),^{28,29} [Cp₂Zr{Ga[N(Aryl)C(H)]₂}₂][Li(THF)₄] (Aryl = C₆H₃-2,6-*i*-Pr₂) (**7**),²⁵ and Cp₂Zr(BiR)₂ (R = C₆H₃-2,6-Mes₂C₆H₂) (**8**).²⁷ Density functional theory (DFT) computations on the corresponding model complexes Cp₂M(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, Cp₂MCl₂ (M = Zr, Ti), with RECl₂ (R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂; E = Ga, In)³⁰ (eq 1). The title compounds were characterized by elemental analyses, ¹H and ¹³C NMR spectroscopy, and single-crystal X-ray diffraction. These compounds are readily soluble in hexane,

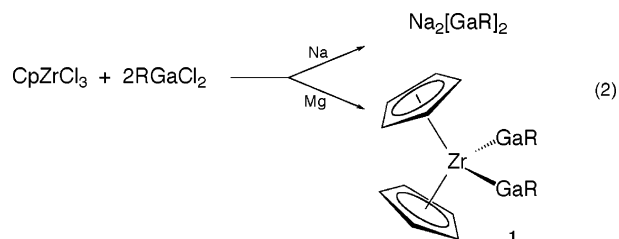


ether, and toluene. Although these products are extremely air- and moisture-sensitive (as the intensely green- or blue-colored solutions of the samples rapidly change to colorless when exposed to air), they exhibit considerable thermal stability, decomposing or melting only above 200 °C.

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, Cp₂MCl₂ and RECl₂. 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 Cp₂MCl₂ with Mg, Na/Hg has also been studied, and the products include the useful intermediate “Cp₂M”^{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 RECl₂ to E(I) in the ER moieties, while the transition metals (Zr and Ti) were reduced from M(IV) in Cp₂MCl₂ to M(II) in Cp₂M(ER)₂. Accordingly, the formal 16-electron metallocene dichlorides, Cp₂MCl₂, were converted to the 18-electron Cp₂M(ER)₂ complexes. The Cp₂M(ER)₂ compounds bear some resemblance to zirconocene dicarbonyl, Cp₂Zr(CO)₂:⁵¹ two ER fragments coordinate to the M center, which mimics the two-electron donor properties of :C≡O.

We also reduced RECl₂ in the presence of CpZrCl₃ instead of Cp₂ZrCl₂. Surprisingly, the sodium reduction of RGeCl₂ with CpZrCl₃ led to the isolation of the known digallyne compound Na₂[GaR]₂ (R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂) (eq 2),^{37,40–46} while magnesium reduction of RGeCl₂ and CpZrCl₃ resulted in the unexpected formation of compound **1**, Cp₂Zr(GaR)₂ (R = C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)₂) (eq 2).²⁶ Although the



mechanism of this system is still under consideration, the formation of Na₂[GaR]₂ from the sodium reduction of CpZrCl₃ and RGeCl₂ 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 CpZrCl₃ to the bis(cyclopentadienyl) “Cp₂Zr” moiety in the product. This result also reveals that Cp₂Zr(GaR)₂ is a relatively stable structure. Indeed, the formation of different products from Na or Mg reduction of CpZrCl₃ and RGeCl₂ is in contrast to the Na/Mg reductions of Cp₂MCl₂ and RGeCl₂ (eq 1) (wherein the same products were obtained by either Na or Mg reduction).

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

	1	2	3	4
formula	C ₈₂ H ₁₀₈ Ga ₂ Zr	C ₈₂ H ₁₀₈ Ga ₂ Ti	C ₈₂ H ₁₀₈ In ₂ Zr	C ₈₂ H ₁₀₈ In ₂ Ti
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	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>	<i>Pbcn</i>
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, Å ³	8156(2)	8116(3)	8204.3(13)	8275.6(7)
Z	4	4	4	4
F(000)	2808	2736	2952	2880
D _{calcd} , g/cm ³	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 > 2σ(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 C₄₁H₅₄EM_{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.

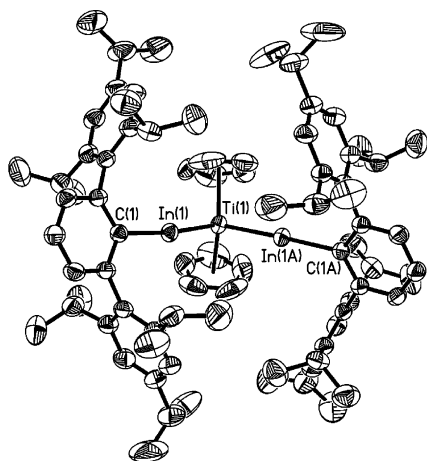


Figure 1. Molecular structure of 4 (thermal ellipsoids are shown at 30% probability levels). Compounds 2 and 3 have similar numbering schemes.

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–(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}

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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° ($172.44(16)^\circ$ for **1**, $171.02(9)^\circ$ for **2**, $171.33(12)^\circ$ for **3**, and $169.99(11)^\circ$ 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 $175.39(9)^\circ$ in $\text{RInMn}(\text{Cp})(\text{CO})_2$ (R = $\text{C}_6\text{H}_3\text{-2,6-(2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2$)⁹ and the almost perfectly linear C–Ga–Fe bond angle of $179.2(1)^\circ$ in $\text{RGaFe}(\text{CO})_4$ (R = $\text{C}_6\text{H}_3\text{-2,6-(2,4,6-}i\text{-Pr}_3\text{C}_6\text{H}_2)_2$).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 $\text{Na}_2\text{-[GaR]}_2$ (2.06(2), 2.028(14) Å),⁴⁰ $\text{RGaFe}(\text{CO})_4$ (1.943(3) Å),⁶⁶ $\text{RGa[B(C}_6\text{F}_5)_3]$ (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, $\text{RInMn}(\text{Cp})(\text{CO})_2$ (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 $\text{Cp}_2\text{M}(\text{ER})_2$ (**1–4**), and the central Cp_2M (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 $94.16(4)^\circ$ to $100.39(4)^\circ$. Significantly, these angles are wider than the L–M–L bond angles in other d^2 metallocene compounds Cp_2ML_2 bearing less crowding ligands (e.g., C–Zr–C angle of 89.0° in $\text{Cp}_2\text{Zr}(\text{CO})_2$ ⁶⁷ and C–Ti–C angle of 87.6° in $\text{Cp}_2\text{Ti}(\text{CO})_2$ 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 ($95.06(4)^\circ$) is comparable to the E–M–E angles in **1–4**. In the $[\text{Cp}_2\text{Zr}\{\text{Ga}[\text{N}(\text{Aryl})\text{C}(\text{H})]_2\}_2\text{-[Li}(\text{THF})_4]$ (Aryl = $\text{C}_6\text{H}_3\text{-2,6-}i\text{-Pr}_2$) 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 $\text{Cp}_{(\text{centroid})}\text{-Zr-Cp}_{(\text{centroid})}$ bond angles in **1–4** ($137.4\text{--}141.9^\circ$) are readily compared to that in $\text{Cp}_2\text{Zr}(\text{CO})_2$ (143.4°),⁶⁷ $\text{Cp}_2\text{Ti}(\text{CO})_2$ (138.6°),⁶⁸ and **7** (136.1°), while the $\text{Cp}_{(\text{centroid})}\text{-Zr-Cp}_{(\text{centroid})}$ 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

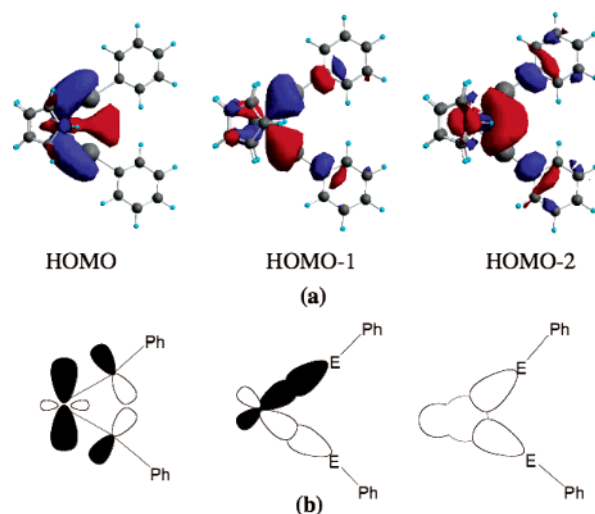


Figure 2. (a) HOMO, HOMO–1, and HOMO–2 orbitals of $\text{Cp}_2\text{-Ti}(\text{InPh})_2$ (**4Ph**). (b) Schematic representations of the molecular orbitals resulting from the interaction of Cp_2Ti fragment molecular orbitals⁶⁹ and p- or sp-orbitals of the InR ligands. Other model compounds have similar 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, $\text{Cp}_2\text{M}(\text{EPh})_2$ (**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** ($75\text{--}79^\circ$) are about 20° more acute than those of **1–4** ($94\text{--}100^\circ$). 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 anti-symmetric (HOMO–1) combinations of the sp orbitals of E donating electrons to the vacant fragment molecular orbitals of the Cp_2M 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.

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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 RECl₂ and Cp₂MCl₂ precursors dissolved in ether by sodium or magnesium metal. Single-crystal X-ray diffraction of the Cp₂M(ER)₂ products revealed short M–E bonds. The sterically demanding *m*-terphenyl ligands –C₆H₃-2,6-(2,4,6-*i*-Pr₃C₆H₂)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 GaCl₃, InCl₃ (Aldrich), Cp₂TiCl₂, and Cp₂ZrCl₂ (Strem) were purchased and used as received. Solvents were dried and distilled under argon from Na/benzophenone prior to use. [(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃][GaCl₂ and [(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃][InCl₂]³⁰ were prepared as previously reported. Elemental analyses were performed by E+R Micro-analytical Laboratories (Parsippany, NJ). ¹H and ¹³C 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, Cp₂TiCl₂ (0.88 g, 3.55 mmol), or Cp₂ZrCl₂ (1.04 g, 3.55 mmol), was added a solution of [(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃][GaCl₂ (2.22 g, 3.55 mmol) or [(2,4,6-*i*-Pr₃C₆H₂)₂C₆H₃][InCl₂ (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 Cp₂ZrCl₂ and RGaCl₂ were added in a stoichiometric ratio of 1:1. However, only the 1:2 product, Cp₂Zr(GaR)₂, was isolated. When the reaction was performed in a 1:2 ratio (Cp₂ZrCl₂:2RGaCl₂), the same product, **1**, was obtained in lower yield. Similarly, higher yields of **2–4** were obtained with the molar ratio of [Cp₂MCl₂] to [RECl₂] being 1:1 (i.e., using an excess of Cp₂MCl₂).

Compound 2. Yield: 1.45 g (64%). Mp: 216 °C. Anal. Calc (Found) for C₈₂H₁₀₈Ga₂Ti: C, 76.88 (76.82); H, 8.50 (8.34). ¹H NMR (C₆D₆): δ 1.17 ppm (d, 24H, *J* = 6.8 Hz, *o*-CH(CH₃)), 1.38 (d, 24H, *J* = 6.8 Hz, *o*-CH(CH₃)), 1.43 (d, 24H, *J* = 6.8 Hz, *p*-CH(CH₃)), 2.95 (sept, 4H, *J* = 6.8 Hz, *p*-CH(CH₃)), 3.13 (sept, 8H, *J* = 6.8 Hz, *o*-CH(CH₃)), 3.60 (s, 10H, η⁵-C₅H₅), 7.15 (s, 6H, –C₆H₃), 7.26 (s, 8H, –C₆H₂). ¹³C NMR (C₆D₆): 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 C₈₂H₁₀₈In₂Zr: C, 69.62 (69.37); H, 7.70 (7.94).

¹H NMR (C₆D₆): δ 1.21 ppm (d, 24H, *J* = 6.8 Hz, *o*-CH(CH₃)), 1.36 (d, 24H, *J* = 6.8 Hz, *o*-CH(CH₃)), 1.50 (d, 24H, *J* = 6.8 Hz, *p*-CH(CH₃)), 2.94 (sept, 4H, *J* = 6.8 Hz, *p*-CH(CH₃)), 3.20 (sept, 8H, *J* = 6.8 Hz, *o*-CH(CH₃)), 4.09 (s, 10H, η⁵-C₅H₅), 7.20 (s, 6H, –C₆H₃), 7.26 (s, 8H, –C₆H₂). ¹³C NMR (C₆D₆): 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 C₈₂H₁₀₈In₂Ti: C, 71.82 (71.67); H, 7.94 (7.89). ¹H NMR (C₆D₆): δ 1.20 ppm (d, 24H, *J* = 6.8 Hz, *o*-CH(CH₃)), 1.38 (d, 24H, *J* = 6.8 Hz, *o*-CH(CH₃)), 1.44 (d, 24H, *J* = 6.8 Hz, *p*-CH(CH₃)), 2.97 (sept, 4H, *J* = 6.8 Hz, *p*-CH(CH₃)), 3.17 (sept, 8H, *J* = 6.8 Hz, *o*-CH(CH₃)), 3.73 (s, 10H, η⁵-C₅H₅), 7.20 (s, 6H, –C₆H₃), 7.27 (s, 8H, –C₆H₂). ¹³C NMR (C₆D₆): 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*-Pr₃C₆H₂)₂C₆H₃][GaCl₂ with CpZrCl₃ by Sodium or Magnesium. Procedures similar to those in the above preparations were followed except that cyclopentadienylzirconium trichloride, CpZrCl₃, was used instead of Cp₂MCl₂. Reduction by Na: dark red, almost black crystals of Na₂[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 Cp₂M(EPh)₂ (**1Ph–4Ph**) in the given symmetry (C₂) 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

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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>.

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