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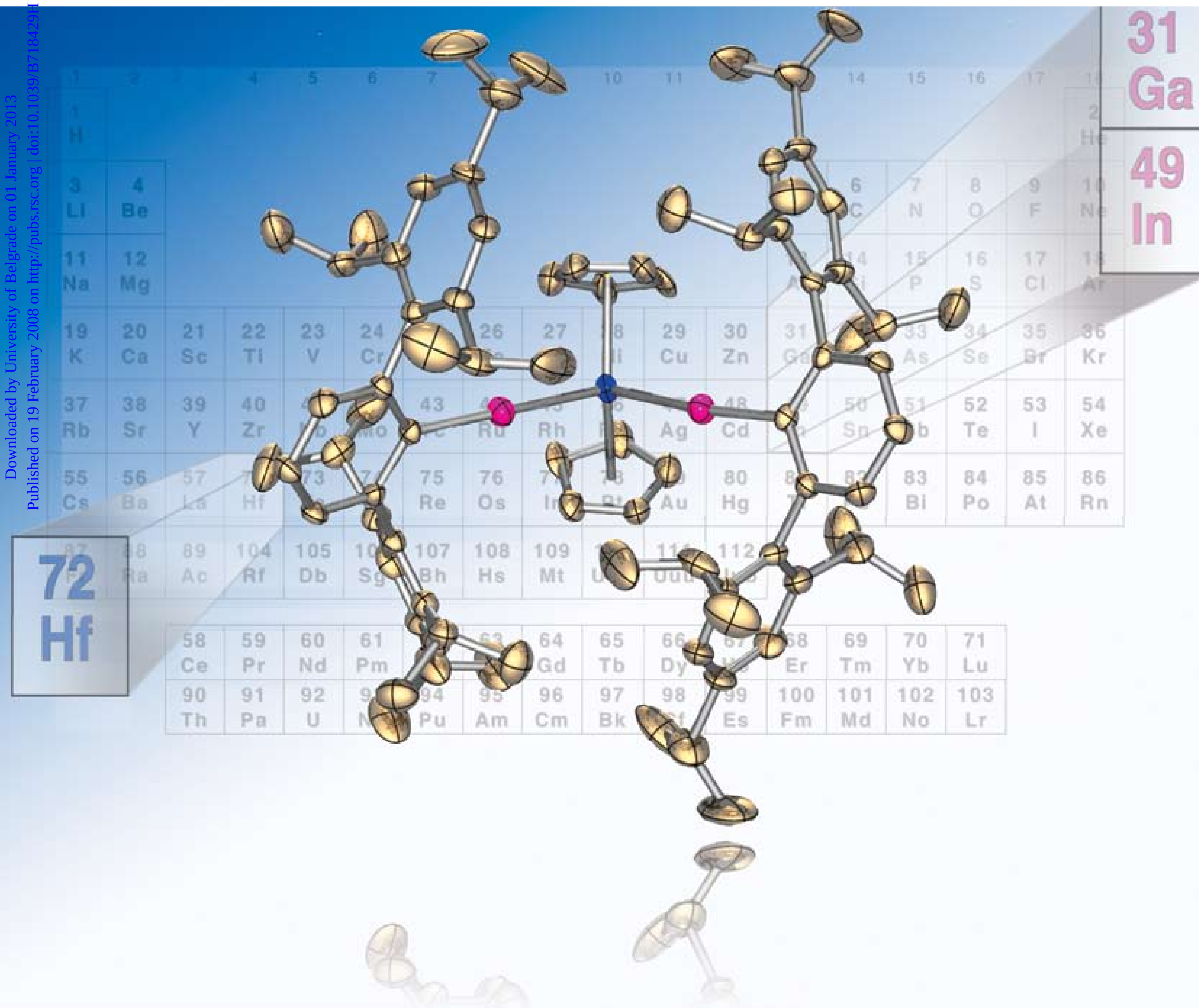

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LETTER

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Organometallic compounds containing new Hf–Ga and Hf–In bonds: $Cp_2Hf(ER)_2$ ($Cp = C_5H_5$; E = Ga, In; $R = –C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$)

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Organometallic compounds containing new Hf–Ga and Hf–In bonds: $Cp_2Hf(ER)_2$ ($Cp = C_5H_5$; E = Ga, In; R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$)†‡

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Sodium metal reduction of $RECl_2$ (E = Ga, In; R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$) with Cp_2HfCl_2 gives $Cp_2Hf(ER)_2$ compounds, which represent the first Hf–E bonds.

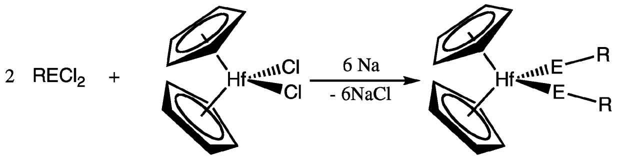
Due to their interesting bonding motifs and potential applications in various catalytic processes, compounds containing M–E bonds (M = transition metal; E = main group metal) have fascinated chemists for some time.[1–12] Thus, considerable effort has been focused on synthesizing compounds containing a variety of M–E bonds.[13–22] Among them, the group 4–group 13 bonded species are particularly interesting in this regard.[23–27] In 2004, this laboratory reported the synthesis and molecular structure of $Cp_2Zr(GaR)_2$ (R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$), the first compound containing a Zr–Ga bond.[27] Subsequently, we reported a series of $Cp_2M(ER)_2$ compounds (M = Ti, Zr; E = Ga, In) containing unprecedented Zr–In, Ti–Ga, Ti–In bonds.[25] Herein we report the syntheses and molecular structures of $Cp_2Hf(ER)_2$ (E = Ga (**1**), In (**2**); R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$). Compounds **1** and **2** are noteworthy as the first compounds containing Hf–group 13 bonds and join the small group of compounds containing group 4–group 13 bonds.[23–27]

Compounds **1** and **2** were prepared by sodium metal reduction of $RECl_2$ (E = Ga, In) with Cp_2HfCl_2 in Et_2O (Scheme 1) and isolated as dark green and dark purple crystals, respectively. Both compounds exhibit relatively high thermal stability, melting or decomposing above 270 °C.§

The reduction of Cp_2HfCl_2 with $RECl_2$ has interesting ramifications for the oxidation states of the respective metals. It appears that in **1** and **2**, the Hf^{IV} atom in Cp_2HfCl_2 is converted to Hf^{II}, while the group 13 metal in $RECl_2$ is formally reduced from E^{III} to E^{I}. Indeed, compounds **1** and **2** are quite similar to the 18-electron species hafnocene dicarbonyl, $Cp_2Hf(CO)_2$,[28] in that the RE fragments essentially act as two-electron donating species to the Hf metal.

The crystal structures of **1** and **2** are both isostructural and isomorphous (Fig. 1), crystallizing in the orthorhombic (*Pbcn*) space group.¶ Though a molecule of Et_2O crystallizes in the unit cell, the $Cp_2Hf(ER)_2$ core structure in **1** and **2** possesses a twofold axis about the central hafnium atom. Selected bond distances and angles for **1** and **2** are given in Table 1. A particularly notable feature of the title compounds is the V-shaped E–Hf–E bonding motif. The E–Hf–E bond angles in **1** (100.76(6)°) and **2** (95.26(4)°) compare well with the corresponding bond angles of their respective titanium and zirconium isostructural analogues, $Cp_2Zr(ER)_2$ (E = Ga, 100.39(4)°; E = In, 95.37(2)°), and $Cp_2Ti(ER)_2$ (E = Ga, 98.18(4)°; E = In, 94.16(4)°). However the Ga–Hf–Ga bond angle in **1** is somewhat larger than the Ga–Zr–Ga angle (87.70(3)°) in $Cp_2Zr\{Ga[N(Ar)C(H)]_2\}_2][Li(THF)_4]$.[26] Interestingly, the E–Hf–E bond angles of **1** and **2** are also comparable to the analogous bond angle in the group 4–group 12 metal bonded compound, $Cp_2Zr(ZnR)_2$ (Zn–Zr–Zn = 99.12(3)°),[29] and also to the Sn–Zr–Sn bond angle (95.06(4)°) of $Cp_2Zr(SnR)_2$ (R = $CH(SiMe_3)_2$), a group 4–group 14 trimetallic compound.[30,31]

The *m*-terphenyl ligands dwarf the Cp ligands and provide substantial steric protection for the core of labile metal centres. The most intriguing structural feature of the title compounds, however, is the Hf–E bonds (Hf(1)–Ga(1) = 2.6198(13) Å; Hf(1)–In(1) = 2.7667(10) Å). The literature reveals a paucity of compounds containing Hf–group 13 metal bonds. As opposed to the cases of $Cp_2Zr(ZnR)_2$[29] and $Cp_2Zr\{Ga[N(Ar)C(H)]_2\}_2][Li(THF)_4]$,[26] where the experimental Zr–Zn (2.7721(7) Å) and Zr–Ga (2.738 Å) bond distances are marginally longer than the corresponding sums of the covalent radii (Zr–Zn, 2.70 Å; Zr–Ga, 2.72 Å, respectively), the Hf–E bonds distances in **1** and **2** are considerably shorter than the sum of their covalent radii (Hf–Ga = 2.76 Å; Hf–In = 2.94 Å). This is consistent with other $Cp_2M(ER)_2$ (M = Ti, Zr; E = Ga, In; R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$) compounds, which showed that the M ←: E bond is augmented by M → E π-back-bonding. The two-coordinate, almost linear, geometry of the group 13 atoms in **1** and **2** (Hf(1)–Ga(1)–C(1)



E = Ga (**1**), In (**2**) R = $-C_6H_3$-2,6-(2,4,6-*i*-$Pr_3C_6H_2)_2$

Scheme 1

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† Dedicated to Professor Jerry Atwood on the occasion of his 65th birthday.

‡ CCDC reference numbers CCDC 666750 (**1**) and 666751 (**2**). For crystallographic data in CIF or other electronic format see DOI: 10.1039/b718429h

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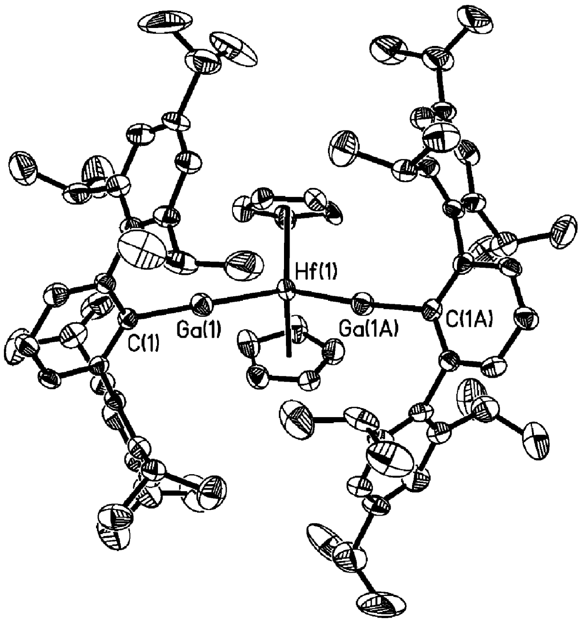

Fig. 1 Molecular structure of **1**. Thermal ellipsoids are shown at 30% probability levels and hydrogen atoms are omitted for clarity. Substituting In for Ga, compound **2** has the same numbering scheme as **1**.

171.7(3)°; Hf(1)–In(1)–C(1) 171.3(3)°, respectively) perhaps enhances such back-bonding.

As expected,[32] the Hf(1)–Ga(1) bond distances (2.6198(13) Å) in **1** are 0.0152 Å shorter than the Zr–Ga bonds distance (2.6350(8) Å) in $Cp_2Zr(GaR)_2$. Furthermore, the Hf–In bond distance (2.7667(10) Å) in **2** is 0.0249 Å shorter than the Zr–In bond length (2.7916(5) Å) in $Cp_2Zr(InR)_2$. An insightful comparison of the Hf(1)–Ga(1) bond distance in **1** with the Zr–Ga bond distances (2.7457(9) and 2.8796(9) Å) in $(C_{10}H_8)(ZrCp)_2(\mu\text{-H})(\mu\text{-Cl})(\mu\text{-GaR})$, (R = 2,6-(-$C_6H_3$-4-*t*-$BuC_6H_4)_2$),[24] is difficult to assess.

Interestingly, the nature of the M–E bond has minimal effect on the E–C bond distance. For example, the Ga–C (2.021(10) Å) bond distance in **1** is very similar to the Ga–C bond distances (M = Ti, 2.025(3) Å; M = Zr, 2.003(5) Å) in the $Cp_2M(GaR)_2$ compounds. Similarly, the In–C bond distance (2.194(13) Å) in **2** coincides with the In–C bond distances (M = Ti, 2.209(4) Å; M = Zr, 2.204(4) Å) of the $Cp_2M(InR)_2$ compounds. Finally, the group 13 elements in **1** and **2** are well separated (Ga···Ga = 4.036 Å, In···In = 4.088 Å, respectively), eliminating the possibility of an E–E bond.

In conclusion, we have prepared the first compounds containing Hf–Ga and Hf–In bonds. We are continuing to study this fascinating chemistry at the main group–transition metal interface.

Table 1 Selected bond distances (Å) and angles (°) for compounds **1** and **2**

Bonds lengths and bond angles	**1** (E = Ga)	**2** (E = In)
E–Hf	2.6198(13)	2.7667(10)
E–C	2.021(10)	2.194(13)
E···E	4.036	4.088
E–Hf–E	100.76(6)	95.26(4)
Hf–E–C	171.7(3)	171.3(3)

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§ *Syntheses*: All manipulations were performed under purified argon using Schlenk techniques in conjunction with an inert atmosphere drybox (Vacuum Atmospheres HE-493). Solvents were dried and distilled under argon from Na–benzophenone prior to use. Elemental analyses were performed by Complete Analysis Laboratories, Inc. (CALI, Parsippany, NJ). ^{1}H NMR spectra were recorded on a Varian Mercury Plus 400 MHz spectrometer. Cp_2HfCl_2 was purchased (Aldrich) and used as received without any further purification. Compounds **1** and **2** were synthesized by similar methods. $RGaCl_2$[33] (2.00 g, 4.00 mmol) or $RInCl_2$[33] (2.40 g, 3.75 mmol), Cp_2HfCl_2 (1.52 g, 4.00 mmol and 1.42 g, 3.75 mmol, respectively), and finely divided sodium metal (0.500 g, 22.0 mmol) were placed in a flask and charged with diethyl ether (80 mL). The resultant slurry was stirred for three days. The solution was filtered from the precipitant and reduced in volume by 50%. Upon standing at −25 °C for 3 days, small green-black crystals of **1** or dark purple crystals of **2** were obtained. Data **1**: (1.83 g, 33%; mp 274 °C. Anal. calc. for $C_{86}H_{118}OGa_2Hf$: C, 69.05; H, 7.82%. Found: C, 69.48; H 8.17%. ^{1}H NMR (C_6D_6): δ/ppm 1.29 (d, 24H, *o*-CH($CH_3)_2$), 1.35 (d, 24H, *o*-CH($CH_3)_2$), 1.51 (d, 24H, *p*-CH($CH_3)_2$), 2.98 (sept, 4H, *p*-$CH(CH_3)_2$), 3.26 (sept, 8H, *o*-$CH(CH_3)_2$), 3.87 (s, 10H, C_5H_5), 7.21 (s, 6H, $-C_6H_3$), 7.26 (s, 8H, $-C_6H_2$). **2**: (1.24 g, 21%; mp 174 °C (wets) 284 °C (decomp.) Anal. calc. for $C_{86}H_{118}OIn_2Hf$: C, 64.99; H, 7.36%. Found: C, 65.53; H, 7.72%. ^{1}H NMR (C_6D_6): δ/ppm 1.29 (d, 24H, *o*-CH($CH_3)_2$), 1.35 (d, 24H, *o*-CH($CH_3)_2$), 1.51 (d, 24H, *p*-CH($CH_3)_2$), 2.96 (sept, 4H, *p*-$CH(CH_3)_2$), 3.26 (sept, 8H, *o*-$CH(CH_3)_2$), 3.96 (s, 10H, C_5H_5), 7.21 (s, 6H, $-C_6H_3$), 7.25 (s, 8H, $-C_6H_2$).

¶ *Crystallographic data*: **1**: $C_{86}H_{118}OGa_2Hf$ (1485.74), orthorhombic, space group *Pbcn*, a = 15.879(4), b = 17.556(4), c = 29.381(6) Å, V = 8191(3) Å^3, Z = 4, μ = 1.958 mm^{-1}, D = 1.205 g cm^{-3}, $F(000)$ = 3104. Final R indices for 3120 observed reflections are $R1$ = [$I > 2\sigma(I)$] are R = 0.0613, w$R2$ = 0.1555 and those for all unique reflections are $R1$ = 0.1600, w$R2$ = 0.2302. **2**: $C_{86}H_{118}OIn_2Hf$ (1575.94), orthorhombic, space group *Pbcn*, a = 15.748(4), b = 17.855(5), c = 29.708(8), V = 8354(4) Å^3, Z = 4, μ = 1.827 mm^{-1}, D = 1.253 g cm^{-3}, $F(000)$ = 3248. Final R indices for 2891 observed reflections are $R1$ = [$I > 2\sigma(I)$] are R = 0.0653, w$R2$ = 0.1453 and those for all unique reflections are $R1$ = 0.1888, w$R2$ = 0.2080.‡

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