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A transition metal–gallium cluster formed *via* insertion of "GaI"†

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The reaction between a two-coordinate Co(ii) diaryl complex and "GaI" affords 2,6-Pmp$_2$C$_6$H$_3$CoGa$_3$I$_5$, in a new geometry for a heavier group 13-transition metal cluster. Experimental and computational investigations show that this compound is best described as a *nido* metalla-group 13 cluster.
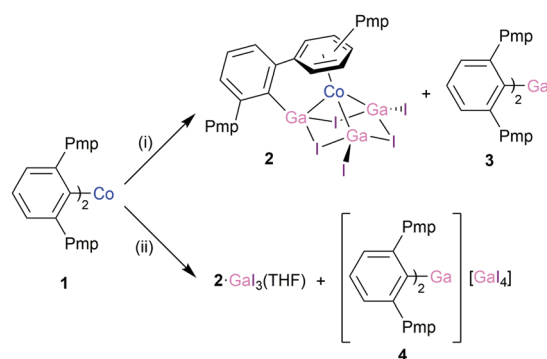
Cluster compounds featuring metal–metal bonds are of significant interest as they serve as intermediate species between discrete molecules and bulk metals.[1] Such compounds provide potentially valuable models for bulk-phase reactions, such as that seen in the reaction of Al$_{13}^-$ with dioxygen.[2] In addition to homometallic compounds, the development of mixed-metal cluster species offers potential insight into alloys and intermetallic phases.[3]

In previous work, the reaction between a 1,2-diaminoethane (en) solution of the Zintl phase precursor K$_4$Ge$_9$ with the coordinatively unsaturated *m*-terphenyl complex (2,6-Mes$_2$C$_6$H$_3$)$_2$Fe (Mes = 2,4,6-Me$_3$C$_6$H$_2$) and 2,2,2-crypt (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]-hexacosane) afforded [K(2,2,2-crypt)]$_3$[Fe@Ge$_{10}$]·2(en).[4a] The endohedral Zintl ion [Fe@Ge$_{10}$]$^{3-}$ exhibits a pentagonal prismatic 10-atom germanium cage with an interstitial Fe atom in the central cavity. An analogous Co species, [Co@Ge$_{10}$]$^{3-}$, was published at approximately the same time by a different route.[4b] This synthesis of [Fe@Ge$_{10}$]$^{3-}$ serves as one example of how low-coordinate transition metal diaryl complexes can facilitate a wide range of stoichiometric and catalytic reactvity.[5]

Further to this, the stoichiometric reactions of Fe(ii) and Co(ii) terphenyl complexes with carbon monoxide has furnished several new metal complexes[6] and ketones[7] through M–C bond breaking (M = Fe, Co) and C–C bond forming reactions. These have generated new stereogenic centres and, more recently,

squaraines featuring a C$_4$ unit entirely derived from CO through C≡O scission and homologation.[8] Given this reactivity, and the parallels in bonding that have been drawn between CO and the group 13 diyls such as the gallium monohalides GaX (X = Cl, Br, I),[9] we were interested in the chemistry between *m*-terphenyl transition metal complexes and "GaI".

A freshly prepared suspension of excess "GaI" in toluene[10] was reacted with **1** [(2,6-Pmp$_2$C$_6$H$_3$)$_2$Co, Pmp = C$_6$Me$_5$] in toluene at room temperature [Scheme 1(i)] to afford a deep red solution over a black suspension after 5 days. The removal of volatiles *in vacuo* and the extraction of the dark green/black solid into hexane yields 2,6-Pmp$_2$C$_6$H$_3$CoGa$_3$I$_5$ (**2**, 8% yield) and into diethyl ether affords (2,6-Pmp$_2$C$_6$H$_3$)$_2$GaI (**3**, 21% yield). Performing the analogous reaction in a mixture of toluene and THF [Scheme 1(ii)] again yields **2** [now co-crystallised with 1 eq. GaI$_3$(THF), denoted as **2**·GaI$_3$(THF), in 6% yield] but affords a different side product, [(2,6-Pmp$_2$C$_6$H$_3$)$_2$Ga]$^+$[GaI$_4$]$^-$ (**4**). The extractions left an insoluble black powder, which is likely to be elemental gallium, presumably originating from "GaI".[11] Linti has described the difficulties in rationalising the reactivity of the subvalent species "GaI",[12] which has been demonstrated to be a mixture of Ga(0), Ga(i) and Ga(iii) species.[13] Although we

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Scheme 1 Reactions between **1** and "GaI". Reaction conditions: (i) excess "GaI", toluene, room temperature, 5 days; (ii) excess "GaI", toluene/THF. Pmp = C$_6$Me$_5$.
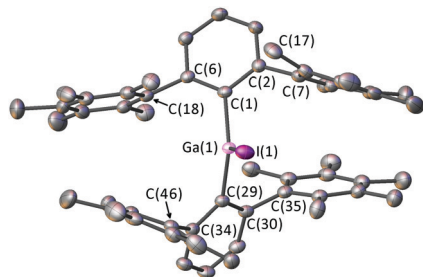
Fig. 1 Crystal structure of **3** with displacement ellipsoids set at 50% probability. Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°): Ga(1)–I(1) 2.5357(5), Ga(1)–C(1) 1.990(3), Ga(1)–C(29) 1.989(3), C(1)–Ga(1)–C(29) 131.1(1), C(1)–Ga(1)–I(1) 114.02(8), C(29)–Ga(1)–I(1) 114.89(9).

have been unable to determine an exact mechanism for the formation of the cluster **2** and its by-products from **1** and "GaI", given the previous isolation of $Ga_3I_5 \cdot (PEt_3)_3$ from "GaI",[14] one could postulate a Ga_3I_5 moiety reacting with **1** to afford **2** and the organic radical 2,6-$Pmp_2C_6H_3^\bullet$. Given their structures, it is plausible that side products **3** and **4** may result from transmetallation and/or halide abstraction reactions involving Ga(III) species in the "GaI" mixture.[15] In our hands, complexes **2–4** are consistently isolated, and these are the only compounds detected on repeated attempts.

Single crystals of **3** were obtained from a saturated solution of **3** in diethyl ether (Fig. 1). **3** features a Ga(III) centre coordinated to two *m*-terphenyl ligands and an iodide donor. **3** is highly sterically encumbered, as demonstrated by the twisting of the flanking C_6Me_5 substituents. Thus, the C(7) ring is twisted from planarity; *ortho*-methyl C(17) sits 0.382 Å and *meta*-methyl C(14) sits 0.343 Å out of the best mean plane for the phenyl ring defined by C(7), presumably to avoid a steric clash with I(1) [C(17)···I(1) = 3.506(3) Å].

4 (Fig. 2) is a rare example of an unsolvated two-coordinate gallium cation and is an analogue of the highly reactive alumenium cations (R_2Al^+).[16] The mesityl-substituted complex
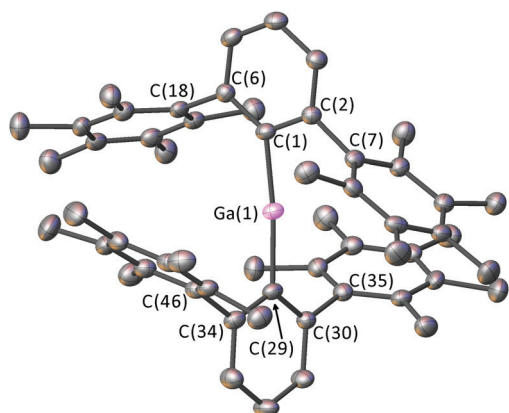

Fig. 2 Crystal structure of **4** with displacement ellipsoids set at 50% probability. Hydrogen atoms, solvent of crystallisation and [GaI_4]$^-$ omitted for clarity. Selected bond lengths (Å) and angles (°): Ga(1)–C(1) 1.920(4), Ga(1)–C(29) 1.920(4), C(1)–Ga(1)–C(29) 173.9(2).
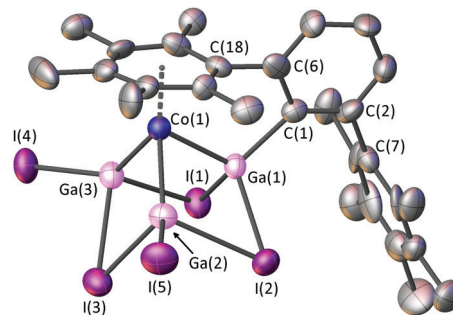

Fig. 3 Crystal structure of **2**·GaI_3(THF) with displacement ellipsoids set at 50% probability. Hydrogen atoms and lattice GaI_3·(THF) omitted for clarity. Selected bond lengths (Å): Co(1)–Ga(1) 2.374(3), Co(1)–Ga(2) 2.296(3), Co(1)–Ga(3) 2.277(3), Ga(1)–C(1) 1.96(2), Ga(1)–I(1) 2.661(2), Ga(1)–I(2) 2.698(2), Ga(2)–I(2) 2.862(3), Ga(3)–I(1) 2.917(3), Ga(2)–I(5) 2.532(3), Ga(3)–I(4) 2.540(2), Ga(1)···Ga(2) 2.966(3), Ga(2)···Ga(3) 2.948(3), Ga(1)···Ga(3) 3.017(3), Co(1)–C(arene) 2.07(2)–2.16(2).

[(2,6-$Mes_2C_6H_3$)$_2$Ga]$^+$ has been stabilised by the highly weakly-coordinating Li[Al{OCH(CF$_3$)$_2$}$_4$]$^-$,[17] but it appears from the isolation of **4** that such weakly coordinating anions[18] are unnecessary if the ligands are sufficiently bulky. The [GaI_4]$^-$ counterion is non-coordinating in **4**, with a very large separation between Ga(1) and the closest I atom (6.4541(7) Å). The Ga–C bonds [1.920(4) Å] in **4** are *ca.* 3.5% shorter than for **3**, and the C(1)–Ga(1)–C(29) angle [173.9(2)°] is deviated from linearity.

Single crystals of **2** [or **2**·GaI_3(THF)] can be obtained from the work-up of both of the reactions as detailed above (Scheme 1). **2** yielded poor quality crystals, but crystals of **2**·GaI_3(THF) obtained from hexane afforded higher quality diffraction data. The cobalt-containing moieties in the crystal structures of **2** and **2**·GaI_3(THF) are isostructural, therefore discussions will focus on the **2**·GaI_3(THF) data. The cluster adopts a cubane-type structure that contains four metal atoms and three I$^-$, with one corner of the cube remaining unoccupied, in a similar manner as that found for the anionic moiety in [Li(THF)]$^+$[$R_4Ga_4I_3$]$^-$ (R = Si(SiMe$_3$)$_3$).[12] There are close contacts between the Co centre and the three Ga atoms, with two of these exhibiting terminal Ga–I bonds, the other being bound terminally to the *m*-terphenyl ligand. The coordination sphere of the Co centre is completed by an interaction with one of the flanking aryl substituents of the terphenyl. We note that **2** is a 12e$^-$ cluster (2e$^-$ per GaI, 3e$^-$ from the Co-arene and 3e$^-$ from the bridging iodides) and adopts a *nido* geometry as predicted by Wade–Mingos rules.[19]

Within the cluster there are significant differences between the three Co–Ga distances, the longest being to Ga(1) [Co(1)–Ga(1) = 2.374(3) Å], with shorter bonds to Ga(2) and Ga(3) [Co(1)–Ga(2) = 2.296(3) Å, Co(1)–Ga(3) = 2.277(3) Å]. Concomitant with this, the bridging iodine distances to Ga(1) are shorter than those to Ga(2) or Ga(3) [2.661(2) and 2.698(2) Å *vs.* 2.862(3) and 2.917(3) Å]. These differences in Co–Ga and Ga–I distances could be due to the influence of the strong σ-donor C(1), or possibly the rigid steric restraints of the *m*-terphenyl ligand. The Co(1)–Ga(2) and Co(1)–Ga(3) distances are in the range exhibited by [Cp*Co(GaCp*)$_3$][BAr^f]$_2$ [Cp* = η^5-C$_5$Me$_5$; Ar^f = 3,5-(CF$_3$)$_2$C$_6$H$_3$] [2.2798(13)–2.3168(16) Å].[20]

The Ga(1)–C(1) distance [1.96(2) Å] is similar to those for the paramagnetic cluster $Ga_{11}(C_6H_3$-2,6-$Mes_2)_4$ [1.991(6), 1.996(6) Å], which features four-coordinate Ga–C(terphenyl) moieties.[21] There is some variation within the lengths of the three Ga···Ga edges [2.948(3)–3.017(3) Å], the shortest of these being opposite to the terphenyl moiety [Ga(2)···Ga(3)]. We also note that the Ga–I bridging distances [2.661(2)–2.917(2) Å] are significantly longer than the terminal Ga–I distances [2.532(3) and 2.540(2) Å].

The average Co–C arene ring distances (2.12 Å) is shorter than those observed in metallaboranes 2-(η^6-C_6H_5Me)-1-[$(Me_3Si)_2CH$]-2,1-$CoCB_{10}H_{10}$ (2.14 Å) and $Co(\eta^6$-$C_6H_5Me)(\eta^5$-7-NH^tBu-7-$CB_{10}H_{10}$) (2.15 Å).[22] There is a difference of *ca.* 0.09 Å between the shortest and longest Co–C distances in **2** due to the asymmetry of the η^6-arene and the rigidity of the *m*-terphenyl ligand. There is also a pronounced tilting between the planes of the η^6-arene and the Ga_3 rings of 11.6(4)°. Whilst relatively common for Co,[23] the incorporation of (η^6-arene)metal units is unknown for heavier group 13-transition metal clusters.

X-ray photoelectron spectroscopy (XPS) measurements were performed on **2** to probe its electronic structure (see ESI,† Section S4). Complex **2** shows binding energies of Ga $2p_{3/2}$ (1119.1 eV) and Ga $3d_{5/2}$ (20.7 eV), with the kinetic energy for the Ga LMM_a transition of 1061.7 eV and the Auger parameter = 1082.4 eV. Oxidation states for gallium iodides are difficult to assign from XPS parameters, potentially due to the electron-donating ability of iodide ligands or the polarisability of iodine,[24b] but **2** has broadly similar binding and kinetic energy values to other gallium iodides such as [Ga][GaI_4] and GaI_3.[24]

To support the formulation of **2**, a series of geometry optimisations were carried out on models of **2** in the $S = 0, 1,$ 2 spin-states using the ADF software package.[25] Geometry optimisation of the model of **2** in the $S = 0$ state afforded a geometry that most closely matched the experimental crystal structure (ESI,† Section S6.1), with optimisation in higher spin states resulting in significant distortion (Fig. S8 and Table S4, ESI†). This supports a diamagnetic, $S = 0$ formulation of **2** the ground state, in line with our NMR spectroscopic measurements.

The bonding in **2** was analysed using the Quantum Theory of Atoms in Molecules (QTAIM)[26] on a DFT optimised structure (see ESI,† Section S6.2).[27] A plot of located bond paths, bond critical points (BCPs) and ring critical points (RCPs) for the central [$CoGa_3I_5C$] core of compound **2** is shown in Fig. 4. Bond paths and BCPs are found linking the 3 Ga atoms to the central Co, and between the Ga and I atoms, indicating attractive interactions (which are not, necessarily, classical 2c,2e⁻ bonds). However, there is no evidence of Ga–Ga bonds, with an RCP located at the centre of each [$CoGa_2I$] face of the molecule. We also note the substantial HOMO–LUMO gap calculated for this compound (1.9501 eV), consistent with the view that **2** is a cluster compound in which all bonding MOs are filled (see ESI,† Fig. S9).

A selection of QTAIM parameters calculated for the atomic interactions in the [$CoGa_3I_5C$] core of **2** is presented in Table S5 of the ESI.† Of note are the bond degree parameter (BD = H_{BCP}/ρ_{BCP}) and the ratio $|V_{BCP}|/G_{BCP}$.[28,29] In **2**, all bonds within the cluster have $1 < |V_{BCP}|/G_{BCP} < 2$ and negative BD values,
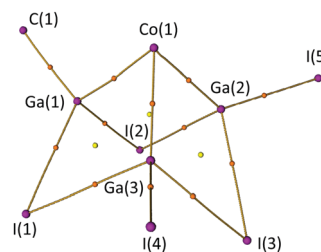

Fig. 4 Plot of computed bond paths, nuclear attractors (NAs, purple), bond critical points (BCPs, orange) and ring critical points (RCPs, yellow) for the [$CoGa_3I_5C$] core of compound **2**. Plot generated by the MultiWFN software package.[35]

indicating that they are transit shared shell interactions with a significant degree of covalency (which is typical for heavy-element interactions).[28,29] Delocalisation indices (DIs) have also been computed (ESI,† Table S5). These are a measure of the degree of electron sharing between two atoms[30] which has been proposed as a quantum mechanical measure of the classical concept of "bond order".[31] Here, we observe the terminal Ga–C (0.717) and Ga–I (0.805, 0.813) bonds have substantially higher DIs than the bridging Ga–I bonds (0.443–0.592). We also note that Co(1)–Ga(2) and Co(1)–Ga(3) have higher DIs than Co(1)–Ga(1). This suggests that Ga(2) and Ga(3) form stronger bonds to Co(1) than Ga(1), which correlates with the crystallographically observed difference in bond lengths. Conversely, Ga(1) appears to form stronger bonds with I(1) and I(2) than either Ga(2) or Ga(3) (see Table S5, ESI†).

From the experimental bond lengths (Fig. 3) and computed delocalisation indices (Table S5, ESI†), we can determine approximate bond orders for the cluster, which allows us to assign formal oxidation states using the methods outlined by Karen.[32] If we consider each Co–Ga, Ga–C, and terminal Ga–I to have a bond order of 1, while the bridging Ga–I interactions have a bond order of 0.5, we can assign charges using Allen electronegativities[33] and arrive at formal oxidation states of (−I) for C(1) and all I atoms, (+III) for the Ga atoms, and (−III) for the Co. This is consistent with the observed neutrality of **2**, as well as its diamagnetism, as it assigns 12 valence electrons to Co to fill both the 4s and 3d orbitals. This view of the oxidation states is supported by the DDEC6 computed atomic charges,[34] which show large partial positive charges on the Ga atoms (+0.321 to +0.394) and a substantial negative charge on the Co (−0.434), consistent with the assigned (+III)/(−III) oxidation states. Full data on the atomic charges is given in the ESI,† Table S6.

In conclusion, a metal-gallium cluster complex (2,6-$Pmp_2C_6H_3CoGa_3I_5$, **2**) featuring a previously unseen coordination geometry has been synthesized *via* the reaction between (2,6-$Pmp_2C_6H_3)_2Co$ and "GaI". It is formed alongside Ga-containing by-products, which are all formed consistently under the reaction conditions employed. Based on X-ray diffraction measurements, QTAIM analysis, and atomic charge calculations we conclude that the bonding in **2** is best described as a *nido* metalla-group 13 cluster with formal oxidation states of Ga(III) and Co(−III).

Conflicts of interest

There are no conflicts to declare.

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