

The reaction of 'GaI' with a 1,3-diyne: synthesis, characterisation and reactivity of a novel C–C coupled ene–diyne–bis(*gem*-organodigallium(III)) complex†

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Treatment of 'GaI' with a 1,3-diyne, $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$, leads to C–C coupling reactions and the isolation of the novel organogallium species, $[\text{Ga}_4\text{I}_8\{\text{C}_8(\text{SiMe}_3)_4\}]$, as two isomeric forms; their X-ray crystal structures show them to contain the first structurally authenticated *gem*-organodigallium fragments and to exhibit rare examples of Ga–alkyne π -interactions.

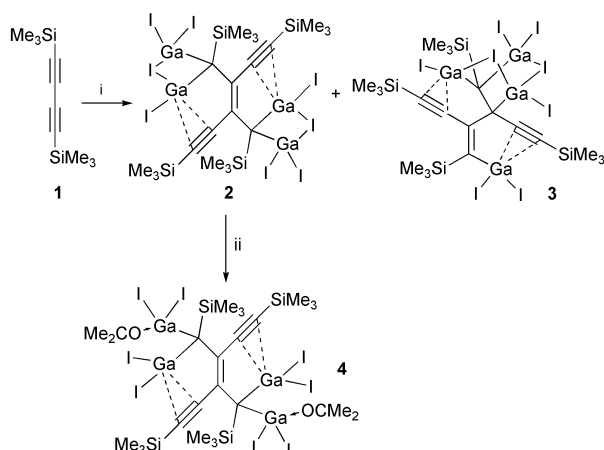
The use of indium and its salts as reagents in organic synthesis is a rapidly expanding area.¹ Within this field indium(I) halides have found a niche as either stoichiometric or catalytic reagents in a variety of C–C coupling reactions.² To the best of our knowledge no efforts have been made to investigate the use of gallium(I) halides in organic synthesis, presumably because these are not commercially available. To address this paucity, we have begun examining the interaction of Green's 'GaI'³ with unsaturated substrates. Its reactions with 1,4-diazabutadienes have led to the facile preparation of paramagnetic gallacycles, *e.g.* $[\text{I}_2\text{Ga}\{\text{N}(\text{R})\text{C}(\text{H})\text{C}(\text{H})\text{N}(\text{R})\}]$, R = alkyl or aryl, which are readily reduced to diamagnetic gallium(I) carbene analogues, $[\text{:Ga}\{\text{N}(\text{R})\text{C}(\text{H})\text{C}(\text{H})\text{N}(\text{R})\}]$.⁴ In an extension of this work the reactivity of the 1,3-diyne, $\text{Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3$ **1**, toward 'GaI' has been examined. This substrate is known to undergo C–C coupling reactions within the coordination sphere of early transition metal fragments.⁵ In the present study a main group metal mediated diyne coupling is reported to give two novel ene–diyne–bis(*gem*-organodigallium(III)) complexes, the characterisation and reactivity of which are discussed.

The reaction of **1** with 4 equivalents of 'GaI' in toluene afforded a deep red solution and gave rise to gallium metal deposition. Upon recrystallisation the C–C coupled product, **2**, was isolated in moderate yield (33%) (Scheme 1). A less symmetrical isomeric form of this compound, *viz.* **3**, was also

formed in trace amounts (<2%) but not reproducibly. In addition, if the reaction was carried out in a 1:1 or 1:8 stoichiometry compound **2** was again formed, but in reduced yields. The mechanism of formation of **2** and **3** is unknown but it seems that, as has been proposed for the formation of the gallacycles $[\text{I}_2\text{Ga}\{\text{N}(\text{R})\text{C}(\text{H})\text{C}(\text{H})\text{N}(\text{R})\}]$, there is an initial complexation of the diyne with GaI which in turn initiates a series of ligand reduction, C–C coupling and disproportionation reactions to give the observed products. The amount of gallium deposited in the reaction appears consistent with this proposal though the possibility exists that GaI disproportionation initially occurs in the presence of the diyne (*cf.* Lewis base initiated GaI disproportionation⁶), then C–C coupling takes place. To test this possibility **1** was reacted with varying stoichiometries of Ga(I) and Ga(III) halides and either no reaction occurred or the product mixtures did not contain **2** or **3**. It is also noteworthy that no reaction occurred between InI and **1**, an observation that is indicative of a weaker reducing ability for this reagent relative to GaI.

The spectroscopic data‡ for **2** are consistent with its proposed structure. Its infrared spectrum exhibits a weak absorption at 2041 cm^{-1} which has been assigned to the $\text{C}\equiv\text{C}$ bond stretch whilst a $\text{C}=\text{C}$ stretching absorption is visible at 1584 cm^{-1} . The former absorption is at lower frequency than that in **1** (2067 cm^{-1})⁷ which suggests that the alkyne bonds have weakened upon coordination to the gallium centres. A similar weakening has been observed in a calcium complex of **1**, *viz.* $[\text{Cp}^*\text{Ca}\{\eta^2\text{-Me}_3\text{SiC}\equiv\text{CC}\equiv\text{CSiMe}_3\}]$.⁷ The ^{13}C NMR spectrum of **2** displays resonances which have been assigned to its alkenic (124.3 ppm) and alkyne (89.3, 85.9 ppm) carbons, the latter of which are only slightly shifted from the corresponding resonances in **1** (89.2, 86.8 ppm), thus suggesting that the Ga–alkyne interactions are only weak. The chemical shift of the digallium substituted quaternary carbon centres occurs at 20.0 ppm, a value in keeping with related examples of *gem*-organodimetallics.⁸ Little spectroscopic data could be obtained for the isomer, **3**, due to the very low yield of this compound.

The X-ray crystal structures§ of both **2** and **3** (Figs. 1 and 2) represent the first for *gem*-organodigallium species and show that they both form *via* coupling of two molecules of **1** at carbon centres β - to one of the trimethylsilyl groups of each diyne unit. The positioning of the resultant double bond of the more symmetrical, major isomer, **2**, is different to that in **3**. In **2** the Ga–C–Ga angles [$98.5(2)^\circ$] are significantly more acute than that in **3** [$106.4(4)^\circ$] and those generally seen for M–C–M fragments in related compounds, *e.g.* $129.6(2)^\circ$ in $[\text{H}_2\text{C}\{\text{Al}\{\text{CH}(\text{SiMe}_3)_2\}_2\}_2]$.⁹ This observation arises from the strained nature of the Ga_2CI ring in **2** in which the Ga–I–Ga angle [$67.80(3)^\circ$] is the most acute yet reported (mean angle from previously reported compounds: $85(2)^\circ$).¹⁰ This strain is also borne out in the dative I(3)–Ga(1) interaction which is considerably longer than the covalent Ga(2)–I(3) bond length and all other terminal Ga–I bond lengths in this compound. Examples of Ga(III)– π interactions are very rare and there is only one previously reported alkyne–Ga interaction, an intermolecular alkyne coordination in the dimer $[(\text{Me}_2\text{GaC}\equiv\text{CPh})_2]$.¹¹ In this compound, however, the two Ga–C intermolecular interactions are very different [2.375(7) and



Scheme 1 Reagents and conditions: i, 'GaI', toluene, – Ga_(s); ii, $\text{Me}_2\text{C}=\text{O}$, toluene.

† Electronic supplementary information (ESI) available: full synthetic details for **2**–**4**. Molecular structure of **4**. See <http://www.rsc.org/suppdata/cc/b2/b210868m/>

2.722(7) Å]. This contrasts with **2** and **3** in which the Ga centres sit approximately central to the C≡C bonds with very similar bond lengths within each C₂Ga fragment [*e.g.* 2.359(6) and 2.362(5) Å in **2**]. The C≡C bond lengths in both compounds are close to those in uncoordinated alkynes and other main group element-alkyne complexes, *e.g.* 1.21(1) Å in [Cp*₂Ca{η²-Me₃SiC≡CC≡CSiMe₃}], which again is suggestive of weak Ga-alkyne interactions.

Considering the unusual nature of **2** we have begun to examine its reactivity. When it was treated with acetone, cleavage of the GaIga bridge and coordination of the ketone to two gallium centres occurred to give the complex, **4**, in high yield (94%) (Scheme 1). This is not surprising given the strained nature of the iodide bridges in **2** but it is interesting that

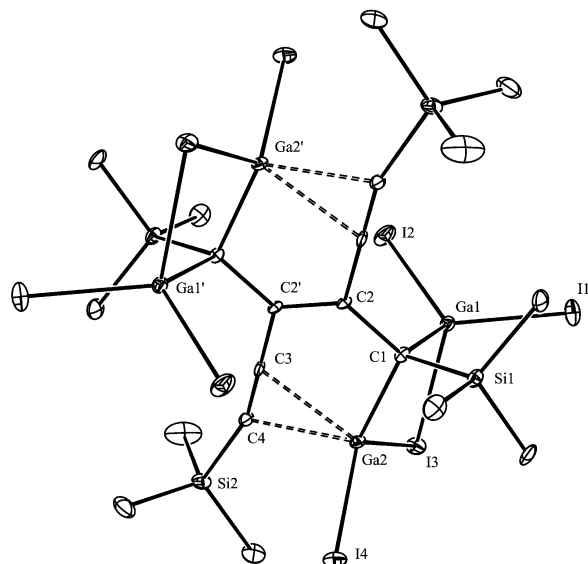


Fig. 1 Molecular structure of **2**. Selected bond lengths (Å) and angles (°): I(1)–Ga(1) 2.5167(8), I(2)–Ga(1) 2.5113(9), I(3)–Ga(2) 2.6154(9), I(3)–Ga(1) 2.8472(12), I(4)–Ga(2) 2.4935(9), Ga(1)–C(1) 2.032(5), Ga(2)–C(1) 1.996(5), Ga(2)–C(4) 2.359(6), Ga(2)–C(3) 2.362(5), C(2)–C(2') 1.372(11), C(3)–C(4) 1.220(8), Ga(2)–I(3)–Ga(1) 67.80(3), Ga(2)–C(1)–Ga(1) 98.5(2), I(2)–Ga(1)–I(1) 109.86(3), I(4)–Ga(2)–I(3) 115.99(4).

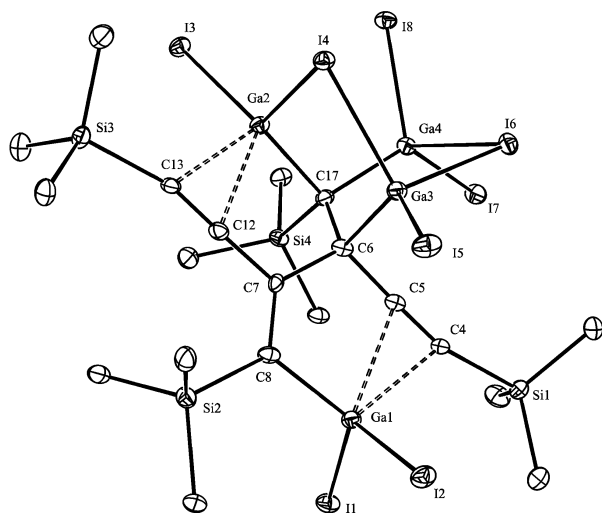


Fig. 2 Molecular structure of **3**. Selected bond lengths (Å) and angles (°): I(1)–Ga(1) 2.5206(13), Ga(1)–C(8) 1.983(10), Ga(1)–C(4) 2.433(9), Ga(1)–C(5) 2.475(9), Ga(1)–I(2) 2.5097(13), Ga(2)–C(17) 1.991(9), Ga(2)–C(13) 2.470(9), Ga(2)–C(12) 2.472(9), Ga(2)–I(3) 2.4773(13), Ga(2)–I(4) 2.6621(13), Ga(3)–C(6) 2.067(9), Ga(3)–I(5) 2.4752(13), Ga(3)–I(6) 2.6104(13), Ga(3)–I(4) 2.6752(13), Ga(4)–C(17) 2.024(9), Ga(4)–I(7) 2.5337(13), Ga(4)–I(8) 2.5378(13), Ga(4)–I(6) 2.7793(13), C(4)–C(5) 1.221(12), C(12)–C(13) 1.216(12), I(2)–Ga(1)–I(1) 114.59(5), I(3)–Ga(2)–I(4) 112.86(4), I(5)–Ga(3)–I(6) 115.29(5), I(7)–Ga(4)–I(8) 111.00(4), Ga(2)–I(4)–Ga(3) 79.25(4), Ga(3)–I(6)–Ga(4) 80.96(4).

this cleavage occurs in preference to the displacement of the η²-coordinated alkyne moieties from the gallium centres. Indeed, when **2** is treated with an excess of acetone the alkyne–Ga interactions remain intact and **4** is the only product. The spectroscopic data for **4** are similar to those for **2**, as are the metrical parameters within its crystal structure.¹² The one exception here are the Ga–C–Ga angles [104.2(5)°] which are much more open than in **2**, presumably due to the relief of strain in the acetone adduct.

In conclusion, we have reported main group metal mediated diyne coupling reactions which have given rise to complexes containing the first crystallographically characterised examples of *gem*-organodigallium fragments and rare examples of gallium–alkyne π-interactions. In view of the well known utility of *gem*-organodimetals in organic synthesis¹³ we are exploring the reactivity of **2** toward a variety of electrophiles, in addition to examining reactions of GaI with conjugated diynes, poly-yne and poly-ene. The outcomes of these studies will be reported in a forthcoming publication.

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Notes and references

‡ Selected data for **2**: Mp 103–105 °C; ¹H NMR (400 MHz, C₆D₆, 300 K) δ 0.31 (s, 18H, SiMe₃), 0.62 (s, 18H, SiMe₃); ¹³C NMR (400 MHz, C₆D₆, 300 K) δ –1.37 (SiMe₃), 0.55 (SiMe₃), 20.01 (Ga–C–Ga), 124.27 (C=C), 89.32 (C≡C), 85.91 (C≡C); MS FAB: *m/z* (%) 1556 [M⁺ – I, 1%], 1035 [M⁺ – 2 GaI₂, 10%]; IR (Nujol) ν/cm^{–1} 2041 (w), 1584 (w), 1462 (s), 1376 (s), 1249 (sh), 1115 (m), 1010 (m), 842 (br), 760 (w), 725 (w), 480 (s); **4**: Mpt 126–132 °C; ¹H NMR (400 MHz, C₆D₆, 300 K) δ 0.22 (s, 18H, SiMe₃), 0.59 (s, 18H, SiMe₃), 1.61 (s, 12H, (CH₃)₂CO); ¹³C NMR (400 MHz, C₆D₆, 300 K) δ –1.35 (SiMe₃), –1.55 (SiMe₃), 21.16 (Ga–C–Ga), 30.11 ((CH₃)₂CO), 125.43 (C=C), 87.21 (C≡C), 85.93 (C≡C) 189.63 ((CH₃)₂CO); MS APCI: *m/z* (%) 1556 [M⁺ – I – 2(CH₃)₂CO, 100%]; IR (Nujol) ν/cm^{–1} 2081 (w), 1689 (m), 1503 (w), 1460 (s), 1376 (s), 1259 (m), 1091 (m), 1022 (m).

§ Crystal data for **2**: C₂₀H₃₆Ga₄I₈Si₄ *M* = 1682.93 monoclinic, space group P2₁/c, *a* = 10.504(2), *b* = 18.886(4), *c* = 12.232(2) Å, β = 115.43(3)°, *V* = 2191.5(8) Å³, *Z* = 2, *D_c* = 2.550 g cm^{–3}, *F*(000) = 1520, μ(Mo–Kα) = 8.18 mm^{–1}, 150(2) K, 4845 unique reflections [*R*(int) 0.1146], *R* (on *F*) 0.0386, *wR* (on *F*²) 0.0812 (*I* > 2σ*I*); **3**: C₂₀H₃₆Ga₄I₈Si₄ *M* = 1682.93 orthorhombic, space group *Pbca*, *a* = 19.676(4), *b* = 20.606(4), *c* = 21.642(4) Å, *V* = 8775(3) Å³, *Z* = 8, *D_c* = 2.548 g cm^{–3}, *F*(000) = 6080, μ(Mo–Kα) 8.18 mm^{–1}, 150(2) K, 7739 unique reflections [*R*(int) 0.1580], *R* (on *F*) 0.0471, *wR* (on *F*²) 0.0823 (*I* > 2σ*I*); **4**:(toluene)₂: C₄₀H₆₄Ga₄I₈O₂Si₄ *M* = 1983.35 monoclinic, space group P2₁/c, *a* = 11.973(2), *b* = 22.496(5), *c* = 11.547(2) Å, β = 94.52(3)°, *V* = 3100.4(11) Å³, *Z* = 2, *D_c* = 2.124 g cm^{–3}, *F*(000) = 1848, μ(Mo–Kα) = 5.81 mm^{–1}, 150(2) K, 5377 unique reflections [*R*(int) 0.0613], *R* (on *F*) 0.0642, *wR* (on *F*²) 0.1532 (*I* > 2σ*I*). CCDC 197051–197053.

See <http://www.rsc.org/suppdata/cc/b2/b210868m/> for crystallographic data in CIF or other electronic format.

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