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Activation of olefins with low-valent gallium compounds under ambient conditions†

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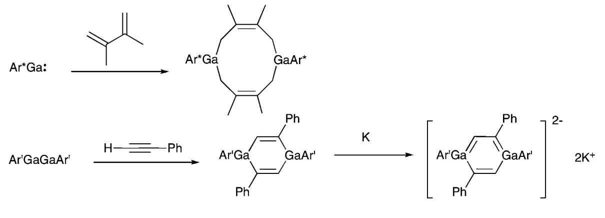
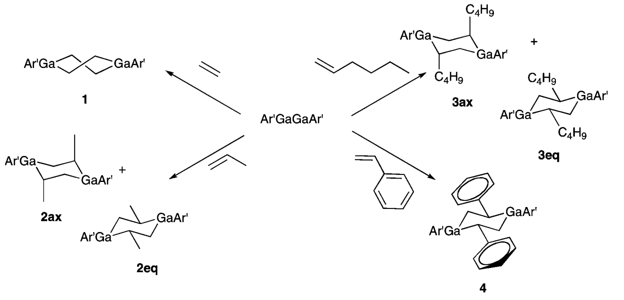
The reactions of Ar′GaGaAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$) with alkenes revealed the addition of two olefins per Ar′GaGaAr′ under ambient conditions for ethylene, propene, 1-hexene and styrene but no reactions with more hindered or cyclic olefins.

The reaction of unactivated olefins with main group element compounds under ambient conditions is rare.[1] Others workers and this group, have reported on olefin reactivity of Group 14 homonuclear dimetallynes, RMMR[2–7] and dimetallenes, R_2MMR_2 (R = organic ligand, M = Si, Ge, Sn)[8–15] and have shown that they can undergo cycloaddition reactions with alkenes[16–20,5] and alkynes.[21–24,5] The reactions of low-valent Group 13 M(I) (M = Al, Ga, In, Tl) compounds with alkenes are poorly investigated although Uhl has shown that single bonded M(II) R_2MMR_2 (M = Al or Ga, R = alkyl) species undergo interesting reactions with alkynes.[25] To our knowledge, there are no reactions of Group 13 dimetallenes with non-congugated, unactivated olefins reported to date. The cycloaddition of :GaAr* (Ar* = C_6H_3-2,6-(C_6H_2-2,4,6-^{i}Pr$_3$)$_2$) with 2,3-dimethyl-1,3-butadiene has been reported to afford a digalla-macrocycle (Scheme 1).[13] The reaction of Ar′GaGaAr′ (Ar′ = C_6H_3-2,6-(C_6H_3-2,6-^{i}Pr$_2$)$_2$) with phenylacetylene afforded the 1,4-digallatacyclohexadiene {Ar′GaC(Ph)CH}$_2$, which upon reduction gives K_2{Ar′GaC(Ph)-CH}$_2$OEt$_2$ (Scheme 1).[26] Roesky[27] and Cui[28] demonstrated that *in situ* reduction of $LAlI_2$ (L = HC{(CMe)-(N(2,6-^{i}Pr$_2C_6H_3$)}$_2$ or C_6H_3-2,6-(2,6-^{i}Pr$_2C_6H_3$)$_2$) with K in the presence of an alkyne formed aluminacyclopropene and 1,2-dialuminacyclobutene, however, no reactions with olefins were reported. Herein, we report an investigation of the general reactivity of the Group 13 dimetallene Ar′GaGaAr′ with several non-conjugated olefins.



Scheme 1 Known reactions of Group 13 dimetallenes with 2,3-dimethyl-1,3-butadiene and phenylacetylene.[13,26]



Scheme 2 Summary of the reactions of Ar′GaGaAr′ with alkenes.

The reaction of Ar′GaGaAr′ with ethylene occurred readily at *ca.* 25 °C at 1 atm. to afford colourless crystals of Ar′Ga(CH_2CH_2)$_2$GaAr′ (**1**). Unlike the similar Group 14 dimetallynes RMMR (R = organic ligand, M = Ge, Sn)[20] which gave strained four-membered metallacycles, two equivalents of the alkene react to form a 6-membered ring with cleavage of the M–M bond (Scheme 2).

The X-ray structure of **1** reveals a twist-boat conformation for the central 1,4-digallacyclohexane core, with Ga–C bond lengths between 1.966(4) and 1.974(4) Å and with C–Ga–C angles of 114.2(2) and 114.4(6)°, respectively (Fig. 1). The central ring C–C distances of 1.544(5) and 1.546(5) Å are typical for C–C single bonds.[29] The internal ring angles at three-coordinate Ga(III) centres are 109.1(2) and 112.7(3)° which conform to the internal C–C–C angles of the sp^3-hybridized ring carbons. We believe that the twist-boat conformation of the core is favoured over the, usually lower energy, chair conformation because of the bulk of the flanking terphenyl substituents.

Treatment of a solution of Ar′GaGaAr′ with excess propene gas at 25 °C and 1 atm. also afforded a colourless solution. Cooling yielded colourless crystals whose X-ray crystal structure showed that the product ArGa{$(CH_2CH(CH_3)$}$_2$GaAr′ (**2**) had a 2,5-dimethyl-1,4-diagallacyclohexane core. The central

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† Electronic supplementary information (ESI) available: Synthetic procedures for **1–4** and crystallographic details for **1**, **2** and **4**. CCDC 818771–818773. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c1cc11676b

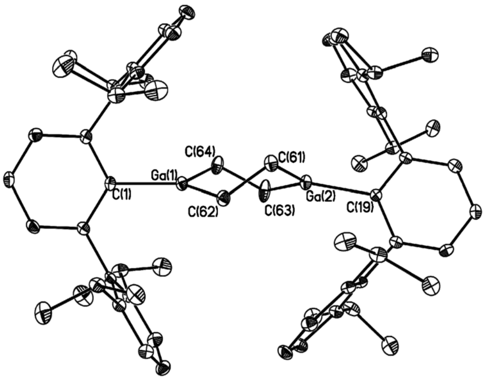


Fig. 1 Thermal ellipsoid (30%) plot of **1**. H atoms are not shown. Selected bond distances (Å) and angles (°): Ga(1)–C(1) 1.964(3), Ga(1)–C(62) 1.971(3), Ga(1)–C(64) 1.968(4), C(61)–C(62) 1.544(5), C(63)–C(64) 1.546(5), C(62)–Ga(1)–C(64) 114.6(2), C(61)–C(62)–Ga(1) 109.1(2), C(63)–C(64)–Ga(1) 112.7(3), C(62)–Ga(1)–C(1) 123.4(1), C(64)–Ga(1)–C(1) 121.8(1).

ring has a chair conformation, with two conformers, $\mathbf{2_{ax}}$ and $\mathbf{2_{eq}}$, present in the solid state in a 54 : 46 ratio (Fig. 2). These conformers can interconvert by a chair flip, which places methyl groups in either axial or equatorial positions. The ^{1}H NMR spectrum shows the presence of the two conformers in solution at room temperature. This implies some flexibility in the structure despite the fact that none of the statistically expected regioisomer where propene reacted to form a 2,6-dimethyl-1,4-digallacyclohexane core, in which both methyl groups substitute the carbons adjacent to the same gallium. We attribute this to the inability of the second equivalent of propene to interact with the metal with this regiochemistry due to the protection afforded by the bulky terphenyl ligands. The reaction of propene with Ar′GaGaAr′ may be contrasted with the behaviour of Ar′SnSnAr′ which reacts with ethylene but not propene.[30]

Attempts to add more highly substituted olefins to Ar′GaGaAr′ were unsuccessful under ambient conditions. Treatment of Ar′GaGaAr′ with 2-methylpropene, *trans*-2-butene, *cis*-2-butene, 2,3-dimethyl-2-butene and 3,3-dimethyl-1-butene, afforded no colour change and ^{1}H NMR spectroscopy showed that the reactants were unchanged. A reaction was observed when Ar′GaGaAr′ was treated with an excess of the longer chain terminal alkene, 1-hexene. Analysis of the ^{1}H NMR spectrum revealed a pattern similar to that of **2** and indicated that the compound existed as a mixture of axial and equatorial conformers with a cyclic core. Unfortunately, crystals suitable for X-ray diffraction studies could not be obtained.

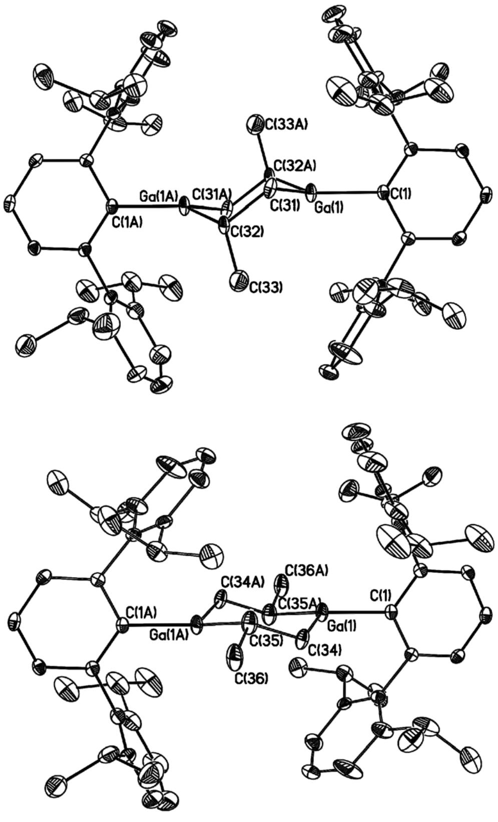


Fig. 2 Thermal ellipsoid (30%) plot of $\mathbf{2}_{\boldsymbol{ax}}$ (top) and $\mathbf{2}_{\boldsymbol{eq}}$ (bottom). H atoms are not shown. Selected bond lengths (Å) and angles (°): $\mathbf{2}_{\boldsymbol{ax}}$: Ga(1)–C(1) 1.983(2), Ga(1)–C(31) 1.972(5), Ga(1)–C(32A) 1.982(5), C(31)–C(32) 1.544(7), C(1)–Ga(1)–C(31) 124.9(2), C(1)–Ga(1)–C(32A) 124.3(14), C(31)–Ga(1)–C(32A) 107.7(3), Ga(1)–C(31)–C(32) 113.6(4), Ga(1)–C(32A)–C(31A) 107.8(4); $\mathbf{2}_{\boldsymbol{eq}}$: Ga(1)–C(34) 1.964(6), C(34)–C(35) 1.526(7), C(35)–C(36) 1.558(1), C(34)–Ga(1)–C(1) 120.4(3), C(34)–Ga(1)–C(35A) 114.8(3), C(1)–Ga(1)–C(35A) 119.98(19), C(34)–C(35)–Ga(1A) 110.9(6), C(35)–C(34)–Ga(1) 118.8(5).

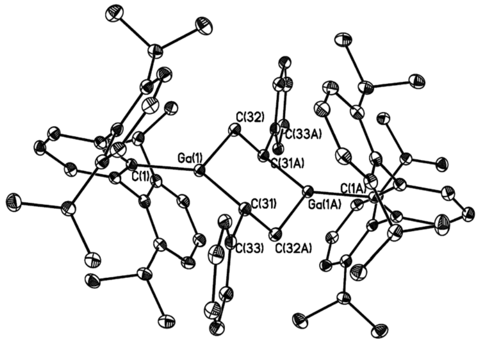
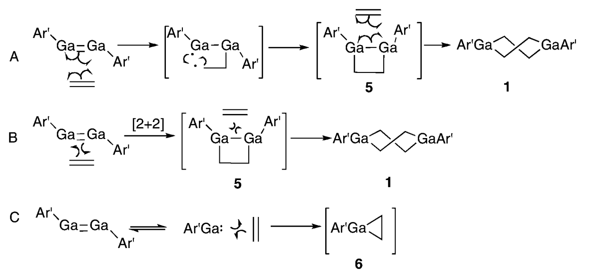


Fig. 3 Thermal ellipsoid (30%) plot of **4**. Hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Ga(1)–C(1) 1.995(2), Ga(1)–C(31) 2.008(2), Ga(1)–C(32) 1.999(2), C(31)–C(32A) 1.559(3), C(1)–Ga(1)–C(32) 114.16(9), C(1)–Ga(1)–C(31) 137.38(8), C(31)–Ga(1)–C(32) 108.46(8), Ga(1)–C(31)–C(32A) 106.38(13).

Treatment of Ar′GaGaAr′ with styrene induced a colour change from dark green to pale yellow after stirring at *ca.* 25 °C for 12 h. The X-ray structure revealed that product **4** had a 2,5-diphenyl-1,4-digallacyclohexane structure similar to **2** (Fig. 3). In this case, the central ring adopted a chair conformation with the phenyl groups residing exclusively in equatorial positions. The ^{1}H NMR spectrum confirmed that there was only one conformer present in solution at room temperature. The Ga–C bond lengths and the C–Ga–C angles displayed noteworthy differences. The C(1)–Ga(1)–C(31) bond angle (137.38(8)°) is > 20° wider than the others (C(1)–Ga(1)–C(32) 114.16(9)° and C(31)–Ga(1)–C(32) 108.46(8)°) to accommodate the space required for the additional phenyl ring adjacent to the bulky terphenyl ligand. The Ga_2C_4 core ring C–C bonds were 1.518(3) to 1.559(3) Å, within the range expected for C–C single bonds (~1.54 Å).



Scheme 3 Possible mechanisms for the cycloaddition reactions.

Several trends are noteworthy from the metrical parameters of the three structures. The average Ga–C bond length becomes elongated (1.968 Å in **1**; 1.978 Å in $\mathbf{2_{ax}}/\mathbf{2_{eq}}$; 2.000 Å in **4**) in order to accommodate the increasing size of substituents ($H < CH_3 < Ph$) at the 1,4-digallacyclohexane core. The average C(Ar)–Ga–C(ring) bond angles also increase as steric bulk increases (122.6° for **1**; 124.6° for $\mathbf{2_{ax}}$; 120.2° for $\mathbf{2_{eq}}$; 125.8° for **4**). The most dramatic increase is in the C(1)–Ga(1)–C(31) bond angle to 137.38(8)° in **4** (*vs.* 121.8(1)° in **1**; 119.98(19)° in $\mathbf{2_{eq}}$; 124.3(14)° $\mathbf{2_{ax}}$) which is up to 17° wider than in the other structures.

A further increase in substitution at the aryl olefin prevents reaction. Thus, *trans*- or *cis*-stilbene, gave no reaction upon overnight stirring with Ar′GaGaAr′ at room temperature. Heating to 110 °C for 3 h also produced no reaction and ^{1}H NMR spectroscopy showed unchanged reactants. We also tested the reaction of some cyclic olefins (cyclopentene, cyclohexene and norbornene) thinking that their lower steric bulk might permit these reactions to occur. No reaction was observed with these olefins.

The mechanism of the cycloaddition reaction is currently under experimental and computational investigation and may involve an initial radical stepwise addition to the Ga–Ga π-bond followed by reaction with a second equivalent of olefin and cleavage of the Ga–Ga σ-bond (Scheme 3A). Other possibilities include two sequential symmetry forbidden [2+2] cycloadditions (B) or direct cyclization with monomeric Ar′Ga: present in equilibrium with Ar′GaGaAr′ (C). No evidence for the formation of gallacyclopropane (**6**) was observed.

In summary, we have shown that the reactivity of Ar′GaGaAr′ is highly dependent on the substitution of the olefin fragments. Treatment of Ar′GaGaAr′ with small terminal alkenes (ethylene, propene, 1-hexene and styrene) under ambient conditions gave 1,4-digallacyclohexane structures while larger and/or branched alkenes did not react. Further insights into the reaction mechanism are currently under investigation.

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