

Reaction of tris-aryl gallium(III) with water: biaryl coupling *versus* Ga–C hydrolysis

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Reaction of toluene solutions of tris(aryl)gallium(III) compounds with water results in intra-molecular biaryl coupling (70% yield) and an oligomeric organogallium(III) hydroxide/oxide $[\text{Ga}_{12}\text{O}_{14}\text{H}_4(\text{aryl})_{12}]$, whereas reaction in THF with water leads to hydrolysis, formation of arylH, and for aryl = Ph the trimeric THF hydrogen bonded trimer, $[\text{Ph}_2\text{Ga}(\mu\text{-OH})_3]\cdot 3\text{THF}$.

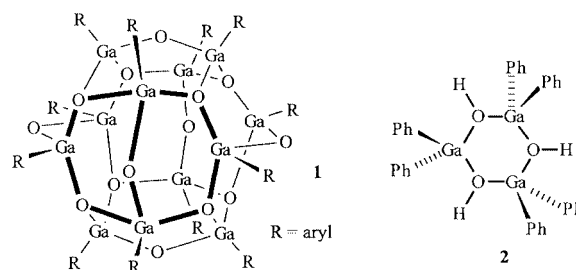
Recent years have seen major developments in the synthesis and characterisation of galloxane (organogallium(III) oxide) and organogallium(III) hydroxide/oxide compounds.^{1–13} Controlled hydrolysis reactions of organogallium(III) compounds, GaR_3 , and reactions with excess water lead to the formation of hydroxide or mixed hydroxide/oxide species. These include (a) dimeric species, $[\text{Ga}(\text{Mes})_2(\mu\text{-OH})_2]$, Mes = 1,3,5-trimethylphenyl,¹¹ and $[\text{Ga}_2\{\text{C}(\text{SiMe}_3)_3\}_2\text{Me}_2(\text{OH})(\mu\text{-OH})(\text{H}_2\text{O})]$,⁸ (b) trimeric species, $[\text{RR}'\text{Ga}(\mu\text{-OH})_3]$, R = R' = Bu^t,^{4,5} = Me,⁶ and R = Me, R' = C(SiMe₃)₃,⁸ and (c) clusters, $[\text{Ga}_6(\text{Mes})_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$,⁷ $[\text{Ga}_{12}\text{Bu}^{t}_{12}(\mu_3\text{-O})_8(\mu\text{-O})_2(\mu\text{-OH})_4]$,² and $[\text{Ga}_4\{\text{C}(\text{SiMe}_3)_3\}_4(\mu\text{-O})_2(\mu\text{-OH})_4]$.⁸ Thermolysis of $[\text{Ga}(\text{Mes})_2(\mu\text{-OH})_2]$ gives $[\text{Ga}_9(\text{Mes})_9\text{O}_9]$ as a unique, structurally authenticated galloxane.⁸

All of the condensation reactions of GaR_3 with water arise from hydrolysis of one or more of the Ga–C bonds. We now show that treatment of tris-aryl gallium(III) compounds, $\text{Ga}(\text{aryl})_3$,[†] in toluene with water results in the formation of C–C bi-aryl coupled compounds and oligomeric arylgallium(III) hydroxide/oxide species. In contrast, treatment of the same compounds with excess water using tetrahydrofuran as a phase transfer reagent leads to Ga–C hydrolysis of one or two aryl groups with only a trace of the bi-aryl coupled compound being formed. These results are summarised in Scheme 1. The formation of bi-aryl coupled compounds has implications in organic synthesis, and is relevant to the actively pursued Suzuki aryl coupling reactions involving boronic acids and esters,^{14,15} which require a transition metal catalyst in the presence of oxygen, unlike in the present reactions. Moreover, the reaction of organometallics with water is of interest in the search for environmentally benign synthetic protocols.¹⁶

For the two phase toluene/water reactions the bi-aryl coupled compounds are isolated from the organic phase, and the gallium(III) hydroxide/oxide cluster compounds are isolated from the aqueous phase. The bi-aryls are formed in yields exceeding 70% (based on two aryl groups being converted to the bi-aryl) with a trace of the expected hydrolysis product, R = H, Me (*o*-, *m*-, *p*-), and *p*-Ph (GC). Conversely the single phase

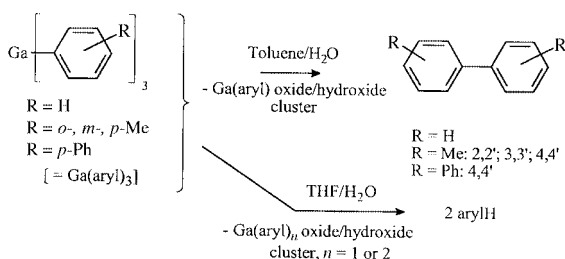
reaction in THF gives mainly hydrolysis products and a trace of the bi-aryl product.

The metal containing by-products of these reactions were investigated as part of a detailed understanding of the mechanism of the reactions. Mass spectrometry (electrospray: methanol/methylene chloride) of the rapidly formed white micro-crystalline product obtained from the coupling reactions revealed the formation of singly and positively charged clusters of composition $[\text{Ga}_{12}\text{O}_{14}\text{H}_4(\text{aryl})_{12}]$, **1**. The dominance of these



ions in the mass spectra shows the stability of the ions, and that the dominant species in solution is a single cluster. The same clusters are also formed in mildly acidic and basic solutions. A likely structure for these clusters is a central polyhedral core of twelve fused six-membered rings, **1**, as found in the structure of $[\text{Ga}_{12}\text{Bu}^{t}_{12}(\mu_3\text{-O})_8(\mu\text{-O})(\mu\text{-OH})_4]$,² albeit with the position of hydrogen atoms on the bridging hydroxy groups not defined. For the reaction of GaPh_3 with water in THF we were able to intercept and isolate some of the intermediate hydrolysis species, trimeric $[\text{Ph}_2\text{Ga}(\mu\text{-OH})_3]$, **2**, the final product being **1**. Compound **2** was authenticated using X-ray diffraction data as the hydrogen bonded tris-THF adduct.[‡] While bis-alkyl analogues of the trimer are known,^{4–6,8} this is the first example of a bis-aryl system. $[\text{Ph}_2\text{Ga}(\mu\text{-OH})_3]$ crystallises in the monoclinic space group *C2/c*, and consists of diphenylgallium bridged to two other diphenylgallium units *via* two $\mu\text{-OH}$ bridges with each gallium in a distorted tetrahedral geometry, Fig. 1. THF molecules are H-bonded to the OH bridges with two THF molecules related by a crystallographic *C*₂ symmetry axis disordered equally over two positions. Phenyl groups are close to being co-planar with an adjacent Ga–O bond and this allows maximum access to the OH groups for hydrogen bonding to THF.

As to the mechanism of the bi-aryl coupling reactions we have established that it is an intra-molecular process since hydrolysis of a mixture of the two compounds, $\text{Ga}(\text{aryl})_3$, aryl = Ph or *p*-tolyl, in toluene gave exclusively the symmetrical bi-aryls. This also implies that $\text{Ga}(\text{aryl})_3$ species themselves are non-labile and that the synthesis of mixed tris-aryl gallium(III) species is possible which would be a route to unsymmetrical bi-aryl compounds on hydrolysis. Competition experiments, bi-aryl coupling *versus* hydrolysis, were investigated for the reaction of $\text{Ga}(\text{C}_6\text{H}_4\text{Ph-}p)_3$ in THF with excess water with increasing amounts of toluene relative to THF. The bi-aryl coupling diminishes dramatically only when the THF concentration is *ca.* 30% in toluene, even for two-phase reactions. Thus the THF plays an important role in initially coordinating to the



Scheme 1

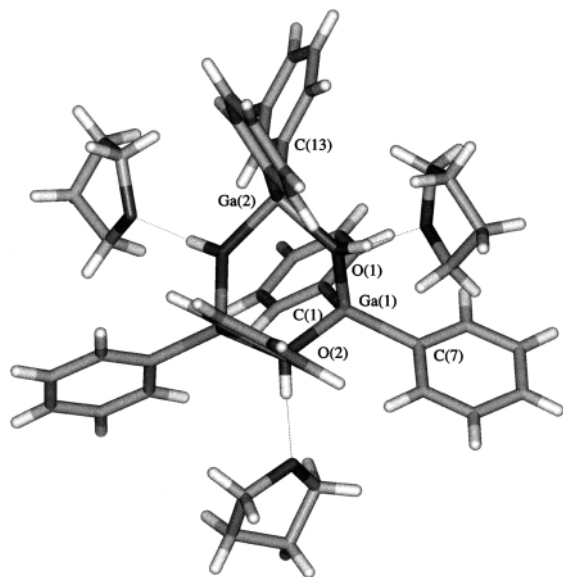


Fig. 1 Molecular structure of $[\text{Ph}_2\text{Ga}(\mu\text{-OH})]_3 \cdot 3\text{THF}$; important bond distances (Å) and angles (degrees): Ga(1)–O(1), 1.908(3); Ga(1)–O(2), 1.916(2); Ga(2)–O(1), 1.911(3); Ga(1)–C(1), 1.993(5); Ga(1)–C(7), 1.977(5); Ga(2)–C(13), 1.962(5); O(1)–Ga(1)–O(2), 97.9; O(1)–Ga(1)–C(7), 111.7; O(1)–Ga(1)–C(1), 110.8(2); C(1)–Ga(1)–C(7), 122.4(2). THF oxygen to hydroxy oxygen distances are 2.64(1) and 2.69(1) Å. (Corresponding Ga₂OH⁺···O 1.71, 1.74 Å).

metal centre and/or hydrogen bonding to a water molecule on the metal centre as found in $[\text{Ga}(\text{Mes})_3(\text{OH}_2)] \cdot 2\text{THF}$ ¹¹ and in the structure of **2**. The oxidant in the aryl coupling reactions is water with evolution of one equivalent of hydrogen gas (experimentally determined); note also that controlled experiments excluding oxygen afforded the same products. The hydrolysis reactions are rapid and under these conditions there would be insufficient oxygen delivered to account for the bi-aryl formation. The bi-aryl coupling is likely to proceed through a five coordinate bis-water adduct, $[\text{Ga}(\text{aryl})_3(\text{OH}_2)]$, at the interface between the water and toluene, leading to a bis-hydroxide, $[\text{Ga}(\text{aryl})(\text{OH})_2]$, on elimination of the biphenyl, which then oligomerizes. However a reductive elimination of bi-aryl leading to a Ga(I) species which is then oxidized by water cannot be ruled out. In the presence of THF competition between complexation of THF and water would block such a bi-molecular water process.

Roesky *et al.*¹¹ have established that the controlled reaction of $[\text{Ga}(\text{Mes})_3]$ in THF with water initially gives a four coordinate adduct of water, then a proposed five coordinate bis-adduct, followed by $[\text{Ga}(\text{Mes})_2(\mu\text{-OH})_2]$ then $[\text{Ga}_6(\text{Mes})_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4]$, and that the latter compound is formed on reaction of $[\text{Ga}(\text{Mes})_3]$ with water in toluene. The lack of aryl coupling here presumably relates to the steric impediment of two bulky aryl groups connecting at the metal centre and/or two water molecules coordinating to the metal centre necessary to effect a bimolecular water process for aryl coupling. Steric hindrance is also noteworthy in giving a smaller cluster, $[\text{Ga}_6(\text{Mes})_6(\mu_3\text{-O})(\mu_3\text{-OH})_4]$,⁷ either as an unstable hexa-tetrahydrofuran solvate⁷ or its mono-tetrahydrofuran solvate which was isolated in the present study. § We note that substitution of one of the *o*-positions of the aryl groups by Me still gives the biaryl, R = Me, Scheme 1. For *o*-OMe and *o*-Ph, however, the amount of coupling is reduced, 40 and 35% respectively. Substitution in both positions (aryl = mesitylene) gives arylH. This is consistent with some steric influence, including the formation of chelate rings in the gallium complex which may shut down the coupling reaction by blocking binding of two water molecules to the metal centre.

It is thus possible to prepare symmetrical bi-aryl compounds from tris-arylgallium(III) species. An inherent problem from the organic synthesis perspective, however, is the loss of one of the aryl groups to the gallium(III) hydroxide/oxide species. This

aspect is being addressed along with developing the method for the synthesis of unsymmetrical bi-aryls.

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Notes and references

† Compounds $\text{Ga}(\text{aryl})_3$, aryl = Ph, *o*-, *m*-, *p*-tolyl, were prepared by reacting the Grignard or lithium reagent of an arylbromide with GaCl_3 in diethyl ether (yields 65–80%), and melting points checked with the same compounds prepared from $\text{Hg}(\text{aryl})_2$ and gallium metal.^{17,18} $\text{Ga}(\text{aryl})_3$, aryl = $\text{C}_6\text{H}_4\text{OMe-}o$, $\text{C}_6\text{H}_4\text{Ph-}o$ and $\text{C}_6\text{H}_4\text{Ph-}p$, were similarly prepared from their corresponding lithium reagents but were difficult to obtain pure. The hydrolysis reactions involved addition of a $\text{Ga}(\text{aryl})_3$ toluene solution at ca. 25 °C to excess water followed by stirring for 5 min. The two layers were separated and the respective products isolated; $\text{Ga}_{12}\text{O}_{10}(\text{OH})_4(\text{aryl})_{12}$, aryl = Ph, $\text{C}_6\text{H}_4\text{Me-}o$, *m*-, *p*-, from the aqueous layer, yields 30–40%, $M/2^+$ and M^+ (FTMS) 995.81, 1990.64, Ph; 1079.7, 2158.8, *o*-tolyl, *m*-tolyl, *p*-tolyl; 1175.6, 2350.7, $\text{C}_6\text{H}_4\text{OMe-}o$; M^+ 1549.0, $\text{C}_6\text{H}_4\text{Ph-}p$, $\text{C}_6\text{H}_4\text{Ph-}o$.

‡ X-Ray crystallography. A prismatic crystal of dimensions $0.15 \times 0.15 \times 0.1$ mm was mounted under a stream of argon onto a glass capillary under oil. X-Ray data were collected at 123(1) K on an Enraf-Nonius KappaCCD single crystal diffractometer with Mo-K α radiation ($\lambda = 0.71073$ Å). Data were corrected for Lorentzian and polarisation effects, but not absorption. The structure was solved using Fourier techniques with teXsan and refined by full matrix least-squares on *F* using teXsan: $[\text{Ph}_2\text{Ga}(\mu\text{-OH})]_3 \cdot 3\text{THF}$ $\text{C}_{48}\text{H}_{57}\text{O}_6\text{Ga}_3$, $M_r = 939.13$ g mol⁻¹, monoclinic, *C2/c* (no. 15), $a = 16.3050(3)$, $b = 17.6498(3)$, $c = 15.9096(2)$ Å, $\beta = 100.777(1)^\circ$, $V = 4497.7(1)$ Å³, $\rho_{\text{calc}} = 1.387$ g dm⁻³, $\mu = 18.30$ cm⁻¹ (no correction), $Z = 4$, 33253 reflections were collected (6400 unique), $2\theta_{\text{max}} = 60.1^\circ$ (4917 observed), $I > 3\sigma(I)$, $R = 0.067$, $R_w = 0.082$. The non-hydrogen atoms were refined anisotropically and hydrogen atoms were included at geometrically estimated positions but not refined. CCDC 182/1643. See <http://www.rsc.org/suppdata/cc/b0/b002422h/> for crystallographic files in .cif format.

§ Crystal structure of $[\text{Ga}_6(\text{Mes})_6(\mu_3\text{-O})_4(\mu_3\text{-OH})_4] \cdot \text{THF}$, the same cluster being previously authenticated as the hexakis-THF adduct;⁷ crystals were obtained from THF: $M_r = 1121.37$ g mol⁻¹, trigonal $R\bar{3}$ (no. 148), $a = 22.5232(2)$, $c = 20.8835(2)$ Å, $V = 9174.7(0.1)$ Å³, $\rho_{\text{calc}} = 1.218$ g dm⁻³, $\mu = 26.41$ cm⁻¹ (no correction), $Z = 6$, 45092 reflections, $2\theta_{\text{max}} = 60.1^\circ$ (3576 observed), $I > 3\sigma(I)$, $R = 0.061$, $R_w = 0.060$. The THF molecule is disordered over two positions.

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