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COMMUNICATION

NEW SYNTHETIC PATHWAYS INTO THE ORGANOMETALLIC CHEMISTRY OF GALLIUM

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Abstract—Ultrasonic irradiation of gallium metal with di-iodine and alkyl iodides, RI, rapidly gives high yields of $[RGaI_2]$ via a reactive intermediate material "GaI". "GaI" also inserts into the metal–iodine bonds of $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ and $[Mo(\eta\text{-}C_5H_4Me)(CO)_3I]$ as witnessed by the synthesis of $[Fe(\eta\text{-}C_5H_5)(CO)_2Ga(\eta^1\text{-}C_5H_4Me)_2\cdot\text{pyridine}]$ and $[Mo(\eta\text{-}C_5H_4Me)(CO)_3GaI_2\cdot Et_2O]$, whose crystal structures have been determined.

We report an improved and very convenient synthesis for monoalkylgallium di-iodide compounds $[RGaI_2]$. Previous routes to these compounds have involved the exchange reaction between the reactive and costly Me_3Ga and GaI_3,[1] or prolonged thermal reaction (1–2 weeks) between Ga and I_2 or thermally prepared "GaI" with RI.[2] A metal vapour synthesis route gave mixtures of the mono- and di-alkylated derivatives.[3]

We have found that sonication of liquid gallium metal with di-iodine and alkyl iodides (RI) rapidly gives high yields of the monoalkylgallium di-iodides $[RGaI_2]$. Typically, gallium metal (0.70 g, 10 mmol), di-iodine (1.27 g, 5 mmol) and the alkyl halide (*ca* 2 cm^3) in toluene (10 cm^3) were sonicated under N_2 using a Heat-Systems Ultrasonics cell disruptor direct immersion horn sonicator, supplying *ca* 375 W, 20 kHz.[4]

The mixture was warmed to melt the gallium (m.p. 30°C) before sonication. Upon sonication the gallium metal dispersed, the initially purple mix becoming first grey and then, after 2–8 min, turning into a colourless solution. Recrystallization of the products from toluene gave high yields of white crystalline $[RGaI_2]$ [**1(a)**; R = Me (70%) (**b**); R = Et (82%) (**c**); R = ^{n}Pr (80%) (**d**); R = ^{i}Pr (55%) (**e**); R = ^{n}Bu (90%) (**f**); R = n-pentyl (76%); **1e**, **1f** liquid at room temperature]. Cryoscopic molecular weight determinations in *p*-xylene for **1a–c** indicate a degree of association of 1.6–1.9 (for *ca* 0.06–0.3 M in monomer equivalents).

Many Lewis adducts are known for alkylgallium dichlorides,[5] but adducts of $[RGaI_2]$ are confined largely to those of $MeGaI_2$ with R′SH (R′ = Me, Et, ^{n}Pr and ^{t}Bu).[6] Therefore, we have explored further reactions of $[RGaI_2]$.

Treatment of **1a–f** with Lewis bases [Et_2O, THF, pyridine, acridine, PMe_3, PPh_3, $P(OPh)_3$ and $AsPh_3$] gave 1 : 1 adducts, characterized by ^1H NMR and IR spectroscopy and mass spectrometry, all adducts showing a band near 540 cm^{-1} in the IR spectrum associated with ν(Ga—C). The adducts of **1b** with PPh_3 and $AsPh_3$ dissociate on subjection to EI mass spectrometry, but cryoscopic molecular weight determinations in *p*-xylene showed them to be essentially monomeric in this solvent.

Sonication of gallium metal and di-iodine in toluene in the absence of alkyl iodide gave a pale green powder "GaI" (**2**). This material is surprisingly reactive and behaves as a monovalent gallium system. Thus treatment of **2** with excess RI and stirring at room temperature overnight or sonicating for a few minutes gave the monoalkylgallium di-iodides (**1**). Treatment of **2** with toluene solutions of tetrahydrofuran or PPh_3 gave apparent disproportionation to products that analysed as $GaI_2\cdot THF$ and $GaI_3\cdot PPh_3$, respectively,

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together with the corresponding quantity of gallium metal.*

The "GaI" prepared by sonication has a powder diffraction pattern that does not correspond either to that reported previously by Corbett or Chadwick and their co-workers,[7,8] or to those for low-valent gallium iodides reported by Gerlach *et al.*[9] It may, however, be similar to the thermally-prepared "GaI" of Wilkinson and Worral, which they showed to contain at least Ga, Ga_2I_3 and Ga_2I_4 by Raman spectroscopy.[2] Their "GaI" reacted much more slowly than our sonicated "GaI" with RI, possibly due to particle size effects. We were interested to see whether "GaI" (**2**) would undergo oxidative addition reactions with metal–iodine bonds. Room temperature reaction with $[Fe(\eta\text{-}C_5H_5)(CO)_2I]$ and recrystallization of the product from ether gave $[Fe(\eta\text{-}C_5H_5)(CO)_2GaI_2\cdot(Et_2O)_n]$ (**3a**). A similar but heated reaction of **2** with $[Mo(\eta\text{-}C_5H_4Me)(CO)_3I]$ gave large amber crystals of $[Mo(\eta\text{-}C_5H_4Me)(CO)_3GaI_2\cdot Et_2O]$ (**4a**). $[Mo(\eta\text{-}C_7H_7)(CO)_2I]$ and $[Mo(\eta\text{-}C_5H_4Me)(CO)_3]_2$ gave $[Mo(\eta\text{-}C_7H_7)(CO)_2GaI_2\cdot THF]$ (**5**) and $[(Mo(\eta\text{-}C_5H_4Me)(CO)_3)_2GaI]$ (**6**) by essentially analogous reactions. The adducts **3a** and **4a** readily lose some ether, although the last traces are retained tenaciously. As with the simple alkylgallium di-iodides, both **3a** and **4a** readily undergo displacement of Et_2O to form 1 : 1 adducts with pyridine (**3b, 4b**).

Treatment of **3a** with 2 equivalents of NaC_5H_4Me followed by reaction with pyridine

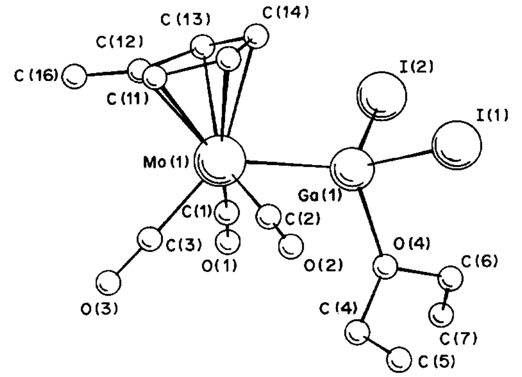

Fig. 1. Molecular structure of $[Mo(\eta\text{-}C_5H_4Me)(CO)_3GaI_2\cdot Et_2O]$ (**4a**). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) as follows:

Mo(1)—Ga(1)	2.582(2)	Mo(1)—$Cp_{cent.}$	1.99
Mo(1)—C(1)	1.99(2)	Ga(1)—I(1)	2.593(2)
Mo(1)—C(2)	1.98(2)	Ga(1)—I(2)	2.582(2)
Mo(1)—C(3)	1.99(2)	Ga(1)—O(1)	2.04(1)

Mo(1)—Ga(1)—O(1)	115.8(3)
Mo(1)—Ga(1)—I(1)	122.06(9)
Mo(1)—Ga(1)—I(2)	113.88(9)
I(1)—Ga(1)—I(2)	106.20(9)
I(1)—Ga(1)—O(1)	96.9(3)
I(2)—Ga(1)—O(1)	98.4(3)
$Cp_{cent.}$—Mo(1)—Ga(1)	108.9

where $Cp_{cent.}$ refers to the computed centroid of the η-C_5H_4Me ring.

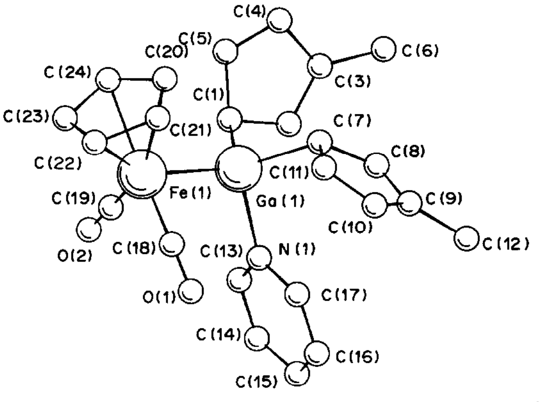

Fig. 2. Molecular structure of $[Fe(\eta\text{-}C_5H_5)(CO)_2Ga(\eta^1\text{-}C_5H_4Me)_2\cdot pyridine]$ (**7**). Hydrogen atoms omitted for clarity. Selected bond lengths (Å) and angles (°) as follows:

Fe(1)—Ga(1)	2.4272(9)	Ga(1)—N(1)	2.101(4)
Fe(1)—C(18)	1.734(8)	Ga(1)—C(1)	2.076(5)
Fe(1)—C(19)	1.744(7)	Ga(1)—C(7)	2.058(5)
Fe(1)—$Cp_{cent.}$	1.73		

Fe(1)—Ga(1)—N(1)	108.9(1)
Fe(1)—Ga(1)—C(1)	113.6(2)
Fe(1)—Ga(1)—C(7)	119.1(2)
$Cp_{cent.}$—Fe(1)—G(1)	119.5

where $Cp_{cent.}$ refers to the computed centroid of the η-C_5H_5 ring.

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* Satisfactory analyses have been obtained for all compounds except the Et_2O adducts, where all ether was removed before analysis. Compounds **1** and their adducts with Lewis bases were characterized by ^1H NMR, mass spectrometry and IR, all compounds showing bands in the Ga—C stretching region. ^1H NMR data for selected compounds {benzene[$^2H_6$]} at 300 MHz; chemical shifts (δ) in ppm.

3b: 9.12 (d, 2H, pyridine), 6.46 (t, 1H, pyridine), 6.23 (t, 2H, pyridine), 4.30 (s, 5H, η-C_5H_5). (**3c**; ether-free **3a**): 3.99 (s).

4a: 4.72 (d, 4H, η-$C_5\mathit{H}_4Me$), 3.80 (q, 4H, $(MeC\mathit{H}_2)_2O$), 1.59 (s, 3H, η-$C_5H_4\mathit{Me}$), 0.92 (t, 6H, $(\mathit{Me}CH_2)_2O$). **4b**: 9.03 (d, 2H, pyridine), 6.42 (t, 1H, pyridine), 6.16 (t, 2H, pyridine), 4.91, 4.84 (AA′, BB′, 4H, η-$C_5\mathit{H}_4Me$), 1.69 (s, 3H, η-$C_5H_4\mathit{Me}$).

5: 4.69 (s, 7H, η-C_7H_7), 3.95 (t, 2H, THF), 1.21 (m, 2H, THF).

6: 4.88, 4.77 (AA′, BB′, 4H, η-$C_5\mathit{H}_4Me$), 1.47 (s, 3H, η-$C_5H_4\mathit{Me}$).

7: 8.28 (d, 2H, pyridine), 6.71 (t, 1H, pyridine), 6.43 (br. s, 4H, η^1-$C_5\mathit{H}_4Me$), 6.41 (br., 2H, pyridine), 5.74 (br. s, 4H, η^1-$C_5\mathit{H}_4Me$), 4.35 (s, 5H, η-C_5H_5), 2.25 (s, 6H, η^1-$C_5H_4\mathit{Me}$).

gives pale diamond-shaped crystals of [Fe(η-C_5H_5)$(CO)_2$Ga(η^1-C_5H_4Me)$_2$·pyridine] (**7**) in modest yield.

The crystal structures of **4a** (Fig. 1) and **7** (Fig. 2) have been determined* and they confirm the presence of a transition metal–gallium bond in each compound. The Ga—Fe bond length of 2.4272(9) Å in **7** is comparable to those in [(CH$_2$=CH)Ga(THF)Fe$(CO)_4$]$_2$ of 2.510(1) and 2.521(2) Å.[10]

In conclusion, we have shown that sonication is a most convenient way of making alkylgallium diiodides. Sonochemically-produced "GaI" behaves as a highly-reactive monovalent gallium system and can provide a new route to compounds containing transition metal–gallium bonds.

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*Crystal data for **4a**: $C_{13}H_{17}GaI_2MoO_4$, crystal dimensions *ca* $0.3 \times 0.4 \times 0.5$ mm, triclinic, space group $P\bar{1}$, $a = 12.570(5)$, $b = 10.049(14)$, $c = 11.919(18)$ Å, $\alpha = 138.47(7)$, $\beta = 91.12(7)$, $\gamma = 94.31(7)°$, $3 \leqslant 2\theta \leqslant 46°$, $V = 988.9$ Å^3, $D_c = 2.209$ g cm^{-3}, $Z = 2$, $\mu = 50.84$ cm^{-1}, $F(000) = 612$, $R = 0.068$, $R_w = 0.061$ for 2071 observed reflections $[I > 3\sigma(I)]$.

Crystal data for **7**: $C_{24}H_{24}FeGaNO_2$, crystal dimensions *ca* $0.2 \times 0.2 \times 0.4$ mm, triclinic, space group $P\bar{1}$, $a = 9.828(2)$, $b = 10.134(3)$, $c = 12.955(7)$ Å, $\alpha = 121.29(3)$, $\beta = 96.34(3)$, $\gamma = 90.13(2)°$, $3 \leqslant 2\theta \leqslant 48°$, $V = 1093.1$ Å^3, $D_c = 1.474$ g cm^{-3}, $Z = 2$, $\mu = 19.15$ cm^{-1}, $F(000) = 496$, $R = 0.045$, $R_w = 0.057$ for 2303 observed reflections $[I > 3\sigma(I)]$.

Data were collected using an Enraf–Nonius CAD4-F diffractometer employing graphite-monochromated Mo-K_α radiation ($\lambda = 0.71069$ Å). The heavy-atom positions were located using direct methods and the other non-hydrogen atoms located from subsequent difference syntheses. The structures were refined using full-matrix least-squares procedures with anisotropic thermal parameters for all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions (C—H = 0.96 Å) with an isotropic thermal parameter of 1.3 times that of their supporting carbon atom, and refined riding on that carbon atom. Crystallographic calculations were carried out using the Oxford CRYSTALS package.[11] Atomic coordinates, bond lengths and angles, observed and calculated structure factors, and thermal parameters have been deposited at the Cambridge Crystallographic Centre.