Bimetallic Aluminium and Gallium Derivatives of 1,1,1,5,5,5-Hexafluoropentane-2,4-dione *via* Selective Metallation/Hydrometallation

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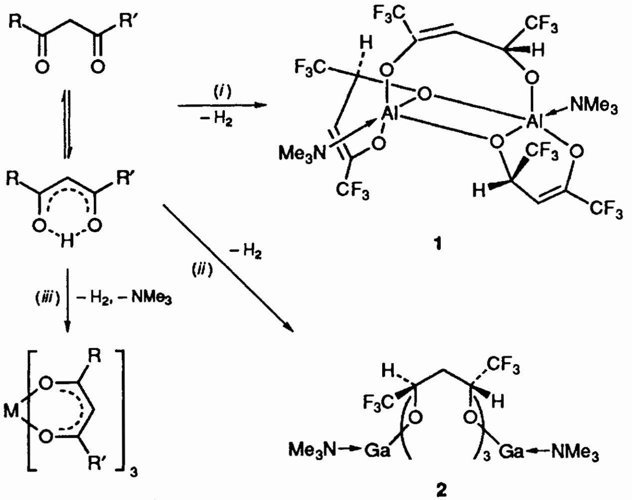
Reaction of $H_3M{\cdot}NMe_3$, M = Al or Ga, with 1,1,1,5,5,5-hexafluoropentane-2,4-dione resulted in metallation/reduction, M = Al, or reduction, M = Ga, of the β-diketone, both products being isolated as binuclear species, $[Al_2\{OC(CF_3){=}CHCH(CF_3)O\}_3(NMe_3)_2]$ (structurally authenticated for the *RRS/SSR* diastereoisomer), and $[Ga_2\{rac\text{-}OCH(CF_3)CH_2CH(CF_3)O\}_3(NMe_3)_2]$ (D_3 symmetry) containing five- or four-co-ordinate metal centres respectively; pentane-2,4-dione, 1,1,1-trifluoropentane-2,4-dione and 2,2,6,6-tetramethylheptane-3,5-dione afford exclusively metallation products, isolated as the tris(β-diketonato)metal(III) complexes.

Alane, AlH_3, and gallane, GaH_3, form adducts with a wide variety of Lewis bases, including tertiary amines and phosphines.[1] These adducts are useful reagents for metallation,[2–6] and reduction of unsaturated compounds.[5,7] Recently we established some unusual reactions for the trimethylamine adducts of both alane and gallane, $H_3M{\cdot}NMe_3$, M = Al or Ga, including deprotonation of *p-tert*-butylcalix[4]arene (4,11,18,25-tetra-*tert*-butyl[1.1.1.1]metacyclophane-7,14,21,28-tetrol),[3] and reduction of both double bonds in $Bu^tN{=}CHCH{=}NBu^t$.[5] In further exploring the synthetic utility of these hydrides we have investigated the reactions of $H_3M{\cdot}NMe_3$ with a variety of pentane-2,4-diones (β-diketones) including fluorinated derivatives. Unusual results were obtained for 1,1,1,5,5,5-hexafluoropentane-2,4-dione, notably (*i*) metallation/reduction or exclusive reduction depending on the choice of metal hydride, (*ii*) the isolation of bimetallic species for both metals, with five- and four-fold co-ordination for aluminium and gallium respectively, and (*iii*) diastereoselectivity of the reaction involving gallane.

Reactions are summarised in Scheme 1.† The product derived from $H_3Al{\cdot}NMe_3$ and 1,1,1,5,5,5-hexafluoropentane-2,4-dione is based on deprotonation and reduction of the β-diketone, *viz.* the aluminium enolate/alkoxide of the corresponding β-hydroxy ketone; spectroscopic data are consistent with the presence of several species, the bimetallic *RRS/SSR* diastereoisomer **1** being characterised in the solid state. The analogous gallium hydride yields a product based exclusively on reduction, with the gallium centres attached to a 1,3-bis(alkoxide). Reactions with pentane-2,4-dione, 1,1,1-trifluoropentane-2,4-dione and 2,2,6,6-tetramethylheptane-3,5-dione under similar conditions results in deprotonation only, with the products isolated as tris(β-diketonato)metal(III) complexes,[8] and thus here the hydrides are acting as unconventional bases for deprotonation of β-diketones. Interestingly, a tungsten hydride reduction of 1,1,1,5,5,5-hexafluoropentane-2,4-dione yields uncomplexed β-hydroxy ketone,[9] and the deprotonated β-diketone is susceptible to nucleophilic attack by OH^- [10] and MeO^-.[11] Furthermore, the highly reactive double bonds in



R = R′ = Me or Bu^t
R = Me, R′ = CF_3
M = Al or Ga

Scheme 1 (*i*) $H_3Al{\cdot}NMe_3$; (*ii*) $H_3Ga{\cdot}NMe_3$; (*iii*) $H_3M{\cdot}NMe_3$

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† 1,1,1,5,5,5-Hexafluoropentane-2,4-dione (0.74 cm^3, 5.22 mmol) was added slowly to a diethyl ether solution (30 cm^3) of trimethylamine–alane (1/1) (0.31 g, 3.48 mmol) at 0 °C. After stirring at room temperature for 1 h the solution was concentrated *in vacuo* and placed at −30 °C to afford colourless crystals of compound **1** (1.04 g, 55%), m.p. 130 °C (decomp.); ^{19}F NMR (188.1 MHz, C_6D_6), δ −78.6 (m), −80.9 (m) and −85.3 (s) (ratio 35 : 8 : 4); IR: 1680 cm^{-1} (C=C) (Found: C, 31.70; H, 3.05; N, 3.50. Calc. for $C_{21}H_{24}Al_2F_{18}N_2O_6$: C, 31.65; H, 3.05; N, 3.50%).

The dione (0.5 cm^3, 3.53 mmol) was added slowly to an ether solution (30 cm^3) of trimethylamine–gallane (1/1) (0.47 g, 3.53 mmol) at 0 °C. After stirring at room temperature for 1 h the solution was concentrated *in vacuo* and placed at −30 °C to afford a white powder of compound **2** (1.45 g, 69%), m.p. 117 °C. NMR (C_6D_6): ^1H (200 MHz), δ 1.72 (18 H, s, NMe_3), 3.48 (6 H, m, CH_2) and 3.96 (6 H, m, FCCH); ^{13}C (50.3 MHz), δ 46.3 (NMe_3), 125.9 (q, $^1J_{CF}$ 283, CF), 66.8 (q, $^2J_{CF}$ 33, OCH) and 29.8 (CH_2); ^{19}F (188.1 MHz), δ −83.47 (d, $^3J_{FH}$ 6.9 Hz) (Found: C, 28.4; H, 3.55; N, 3.60. Calc. for $C_{21}H_{30}F_{18}Ga_2N_2O_6$: C, 28.40; H, 3.40; N, 3.15%).

1,1,1,5,5,5-hexafluoropentane-2,4-dione are susceptible to attack by water yielding a tetrol.[12]

Even in the presence of an excess of metal hydride ($H_3M{\cdot}NMe_3$:β-diketone 1:1) it is only the hexafluoro-β-diketone that gives both metallation and reduction, M = Al, or reduction, M = Ga. This implies that for the hexafluoro-β-diketone either (*i*) reduction precedes metallation, in accordance with activation of C=O bonds by adjacent electron-withdrawing CF_3 groups and by complexation, or (*ii*) metallation is the initial reaction, the two CF_3 groups then collectively activating the resulting conjugated β-diketonate system towards nucleophilic attack. The latter has been noted for other nucleophiles.[10,11] For either mechanism, complexation of an oxygen-containing centre forming a trigonal-bipyramidal species with the hydrides in the equatorial plane is possibly the primary process in reactions involving alane and gallane.[2,13,14] The reduction of both double bonds of the hexafluoro-β-diketone rather than metallation using $H_3Ga{\cdot}NMe_3$ is consistent with the lower polarity of Ga–H relative to Al–H bonds.

Molecules of compound **1** are unsymmetrical, with one as the asymmetric unit, as for **2** but here the molecules have non-crystallographic D_3 symmetry, Fig. 1.* For **1** there are two types of ligands, two forming a chelate ring with the oxygen atom attached to the chiral carbon centre bridging to the other metal, and a unique ligand with both oxygen centres terminal, each oxygen associated with one metal centre. The chirality of the carbon centre in this ligand is opposite to that in the other two ligands, so that the molecules in the solid state constitute an enantiomeric mixture of the *RRS*/*SSR* diastereoisomer. Despite the lack of symmetry both metal centres have similar five-co-ordinate environments, namely distorted trigonal bipyramids with the nitrogen centre and a bridging oxygen in apical positions. While the central Al_2O_2 four-membered ring core [O–Al–O (mean) 80.0, Al–O–Al (mean) 99.4°, Al···Al 2.912(8) Å] is a common structural feature for aluminium alkoxides,[16–18] the presence of five-co-ordinate metal centres is unusual;[19] normally four- and six-co-ordination geometries are favoured.[18] The Al–O distances are similar for the two types of anionic centres within each ligand, except for the bridging oxygens where they are variable, and are unexceptional, alternating around the Al_2O_2 ring, Al–O 1.80(1), 2.04(1), 1.80(1), 2.00(1) Å, *cf.* 1.73(1)–1.78(1) Å for terminal Al–O.

Despite the presence of two metal centres in molecules of compound **2**, they are devoid of oxygen bridging and the molecules have a highly symmetrical cage-like structure with all ligands *rac* and of the same chirality within each molecule. The M–O distances are now less dispersed [1.785(6)–1.806(6) Å]. Assignment of the anionic ligands in **1** as alkoxide/enolate species is consistent with the C=C distances of the enolate moiety, 1.31(2)–1.32(2) Å; $C_{methylene}$–C distances in **2** are 1.52 Å in support of bis(alkoxide) ligands.

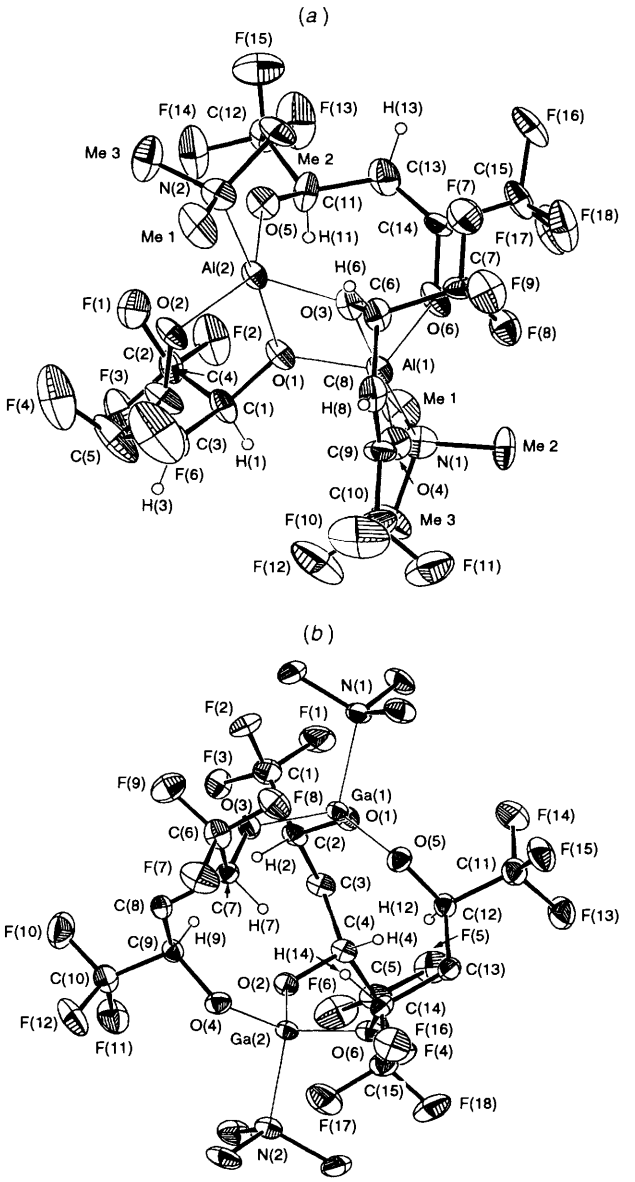

Fig. 1 Molecular projections showing atom labelling: (*a*) $[Al_2\{OC(CF_3){=}CHCH(CF_3)O\}_3(NMe_3)_2]$ **1**; (*b*) $[Ga_2\{$*rac*-$OCH(CF_3)CH_2CH(CF_3)O\}_3(NMe_3)_2]$ **2** (arbitrary radii for H atoms where shown and 20% ellipsoids for others). Selected bond distances (Å) and angles (°): **1**, Al(1)–N(1) 2.09(1), Al(1)–O(1,3,4,6) 1.80(1), 2.00(1), 1.74(1), 1.78(1), Al(2)–N(2) 2.07(1), Al(2)–O(1,2,3,5) 2.04(1), 1.75(1), 1.80(1), 1.73(1); N(1)–Al(1)–O(1,3,4,6) 104.5(5), 174.6(6), 86.1(6), 86.9(5), O(1)–Al(1)–O(3,4,6) 80.6(6), 114.9(5), 109.0(6), O(3)–Al(1)–O(4,6) 90.1(5), 93.0(6), O(4)–Al(1)–O(6) 135.9(5), N(2)–Al(2)–O(1,2,3,5) 174.6(6), 85.6(5), 105.7(6), 88.4(5), O(1)–Al(2)–O(2,3,5) 90.5(5), 79.4(5), 91.6(5), O(2)–Al(2)–O(3,5) 115.4(6), 133.8(6), O(3)–Al(2)–O(5) 110.3(5); **2**, Ga(1)–O(1,3,5) 1.806(6), 1.798(6), 1.795(6), Ga(1)–N(1) 2.024(7), Ga(2)–O(2,4,6) 1.793(5), 1.805(6), 1.785(6), Ga(2)–N(2) 2.033(7); N(1)–Ga(1)–O(1,3,5) 107.2(3), 107.1(3), 103.9(3), O(1)–Ga(1)–O(3,5) 110.9(3), 112.6(3), O(3)–Ga(1)–O(5) 114.3(5), N(2)–Ga(2)–O(2,4,6) 106.9(3), 107.1(3), 113.8(3), O(2)–Ga(2)–O(4,6) 110.3(3), 113.8(3), O(4)–Ga(2)–O(6) 113.5(3)

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* Structures determined at 297 K on an Enraf–Nonius CAD4 diffractometer, with the crystals mounted in capillaries and Mo-Kα radiation (λ = 0.710 69 Å). Crystal data: **1**, $C_{21}H_{24}Al_2F_{18}N_2O_6$, *M* = 796.4, monoclinic, space group *C*2/*c*, *a* = 31.510(5), *b* = 11.812(5), *c* = 17.596(2) Å, β = 106.36(2)°, *U* = 6284 Å^3, *F*(000) = 3248, *Z* = 8, D_c = 1.696 g cm^{-3}, μ(Mo-Kα) = 2.31 cm^{-1}, specimen 0.45 × 0.30 × 0.30 mm, 4674 unique reflections, 1865 with $I > 3.0\sigma(I)$ used in the refinement, $2\theta_{max}$ = 40°; **2**, $C_{21}H_{30}F_{18}Ga_2N_2O_6$, *M* = 887.9, triclinic, space group $P\bar{1}$, *a* = 10.868(1), *b* = 12.020(1), *c* = 15.328(2) Å, α = 91.51(1), β = 108.85(1), γ = 114.98(1)°, *U* = 1686.5 Å^3, *F*(000) = 884, *Z* = 2, D_c = 1.655 g cm^{-3}, μ(Mo-Kα) = 1.8 cm^{-1}, specimen 0.20 × 0.30 × 0.30 mm, 3407 unique reflections, 2745 with $I > 3\sigma(I)$ used in the refinement, $2\theta_{max}$ = 44°. The structures were solved by direct methods and refined by full-matrix least-squares refinement using SHELXS 86[15] with non-hydrogen atoms anisotropic; H atoms were included as invariants in **1**, U_{iso} 0.08 Å^2, and refined in *x*,*y*,*z* with U_{iso} 0.047 Å^2 for **2**. Unit weights were used and the final residuals were *R* 0.097, 0.045 and *R'* 0.099, 0.052 for **1** and **2** respectively. Atomic coordinates, thermal parameters and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

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