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Preliminary communication

Solution stabilized monomeric dialkyl-aluminium and -gallium species, $[MR_2]^{\cdot}$ ($R = 2\text{-}C(SiMe_3)_2C_5H_4N$): from reduction of MR_2Cl. Crystal structure of GaR_2Cl

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Abstract

Reduction of MR_2Cl, M = Al or Ga, $R = 2\text{-}C(SiMe_3)_2C_5H_4N$, in THF yields the paramagnetic dialkylmetal species, $[MR_2]^{\cdot}$, which in the absence of solvent yields diamagnetic material shown to contain reductively coupled pyridyl groups by isolation of the corresponding 4,4′-dipyridyl after hydrolysis and oxidation. An X-ray diffraction study of $[GaR_2Cl]$ has shown the metal to be in a distorted trigonal bipyramidal environment with apical N-centres.

Despite several reports of seemingly aluminium(II) species [1–7] the only such compounds stable at ambient temperature are diamagnetic and possess metal–metal bonds [7]. The same applies to gallium(II) species [3,8], except for monomeric $[Ga(DAB)_2]$ in which one of the DAB ligands (DAB = 1,4-di-t-butyl-1,4-diazabutadiene) is in the reduced diamino form [9]. We report here the formation from MR_2Cl of monomeric paramagnetic dialkyl-aluminium and -gallium species, $[MR_2]^{\cdot}$, that are stable in solution, but reversibly associate in the solid to diamagnetic material, in a way reminiscent of the formation of the Gomberg dimer, $(trityl)_2$, from solutions containing the trityl radical, $Ph_3C^{\cdot}$ [10], although in the latter case there is head to tail association, in contrast to the tail to tail association in the Al and Ga species. The alkyl ligand used was the very bulky *N*-functionalized ligand, $2\text{-}C(SiMe_3)_2C_5H_4N^-$, R^-, which is a relatively new ligand, previously shown to stabilize a cationic aluminium(III) species, $[AlR_2]^+$ $[AlCl_4]^-$ [11]. The structure of GaR_2Cl is also reported, and establishes the nature of the metal to ligand bonding interaction prior to reduction.

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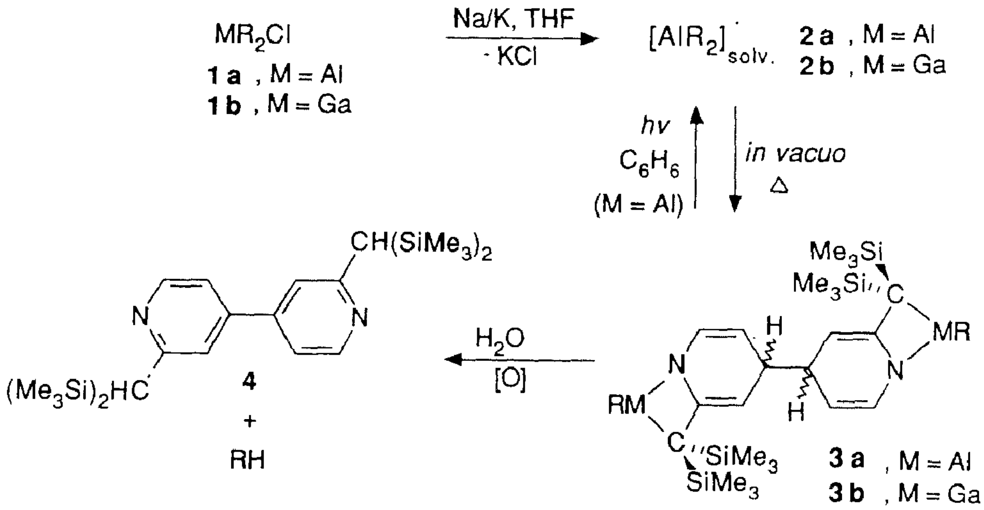
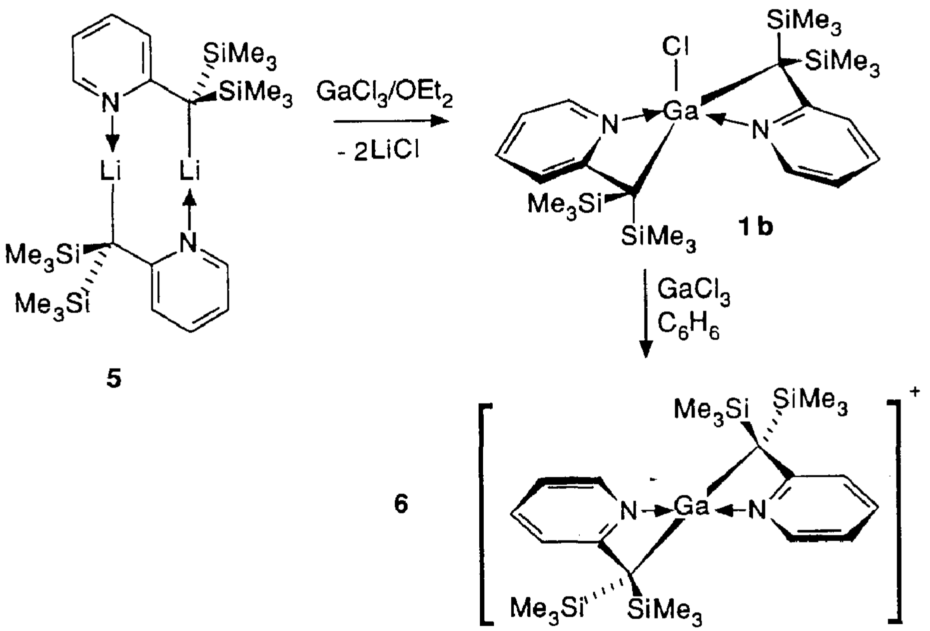


Scheme 1

Treatment of AlR$_2$Cl (**1a**) [11], with sodium/potassium alloy in (tetrahydrofuran) (THF) yielded a red solution containing paramagnetic species, **2a** (Scheme 1); there was no reaction in other solvents, including hexane, diethyl ether, and toluene, and the potassium is the only active reducing agent. Finely divided sodium alone failed to reduce **1a**, and it appears that potassium and THF are required to effect electron transfer [7]. Removal of the solvent in vacuo gave a diamagnetic cream solid AlR$_2$ (**3a**). Addition of THF afforded a red solution with the same characteristics as the initially formed red solution: ESR, singlet, g_{av} 2.0030, fluorescence spectrum (incident radiation 494 nm) λ_{max} 589 nm. The solid dissolves sparingly in benzene to yield an orange solution containing paramagnetic species (ESR broad singlet, g_{av} 2.0013); irradiation with UV (1000 Hg/Xe lamp) increased the signal, which then decayed to its preirradiation intensity, $t_{1/2}$ 6 min. On the basis of the similarity of the fluorescence spectrum in THF (above) and benzene (incident radiation 537 nm, λ_{max} 593) the paramagnetic species is assumed to be [AlR$_2$]$^{\cdot}$ (**2a**). As to the nature of the solid, the isolated products after hydrolysis and oxidation products were RH and a substituted 4,4′-dipyridyl (**4**) (isolated as a dihydrate), in the ratio 2/1, plus an intractable brown solid. In contrast, hydrolysis of THF solutions of **2a** yielded exclusively RH. Thus formation of diamagnetic species is associated with at least some reductive coupling of the pyridyl moieties to yield alkyl/amino-aluminium(III) species. Reductive coupling of pyridyl groups has precedents in some aluminium halide chemistry [5], and the structural unit has recently been authenticated in a low valent titanium compound [12].

Compound **1b** behaves similarly, yielding dark green solutions of **2b** (broad ESR singlet in THF, g_{av} 2.0037) and a pale green diamagnetic solid, **3b**. The absence of resolved hyperfine coupling in the ESR spectra of **2** precludes any notional assignment of oxidation states, i.e. a decision between whether the unpaired electron is primarily metal(II)-centred or ligand-centred in formally M^{III} species. If the electron is in a metal-centred *s* orbital the arrangement of the ligands could be symmetrical, as in the cationic species, [MR$_2$]$^+$. It is noteworthy that there is asymmetry in the structure of [Ga(DAB)$_2$] [9]; one of the ligands has been formally reduced to DAB^{2-}.



Scheme 2

Conditions for the synthesis of **1b** from $[(LiR)_2]$ (**5**) [13] (Scheme 2), must be precisely controlled in order to avoid the formation of a novel ionic compound, $[GaR_2]^+[GaCl_4]^-$ (**6**), which is isostructural [14] with the analogous aluminium compound [4], the cationic species being isolobal with MR_2 (M = Mg, Zn, Cd, Hg) [15]. Compound **6** forms a liquid clathrate with 6 molecules of benzene (^{1}H NMR) (cf. 14 molecules for $[AlR_2]^+[AlCl_4]^-$) [4].

Non-equivalence of the trimethylsilyl groups in compound **1a** is consistent with the structures being the same as that established for **1b** in the solid (see below). However, the gallium compound showed dynamic equivalence of these groups, possibly because weaker metal–N interactions allow rotation about metal–carbon bonds. This type of behaviour is known for some tin(II) compounds containing R^- [16].

Results of the X-ray diffraction study of **1b** are depicted in Fig. 1. Surprisingly the compound is isostructural with $[SnR_2]$ [16], and thus the stereochemically active tin-centered lone pair occupies the same site as the chloride. Molecules lie on crystallographic two fold axes; the metal centres have highly distorted trigonal bipyramidal geometries with the N-centres apical, mean N–Ga–N 162.6°. The related compound $[GaClMe_2(1,10\text{-phenanthroline})]$ also has a distorted trigonal bipyramidal geometry but with the halide and one N-centre in apical positions, N–Ga–Cl 161.0(2)° [17].

Synthesis and characterization of 1–6

Compound 1b. To 20 ml of $LiBu^n$ (1.7 *M*, 34 mmol) in 20 ml of OEt_2 was added RH (8.0 g, 33.7 mmol). After 1 h $GaCl_3$ (2.9 g, 17 mmol) in 40 ml of OEt_2 was added to the orange solution of **5** [13] and the mixture stirred at room temperature overnight then filtered and cooled to −30 °C. The product was recrystallized from benzene as colorless needles, m.p. 194 °C. (2.7 g, 30% yield). ^{1}H NMR (80 MHz,

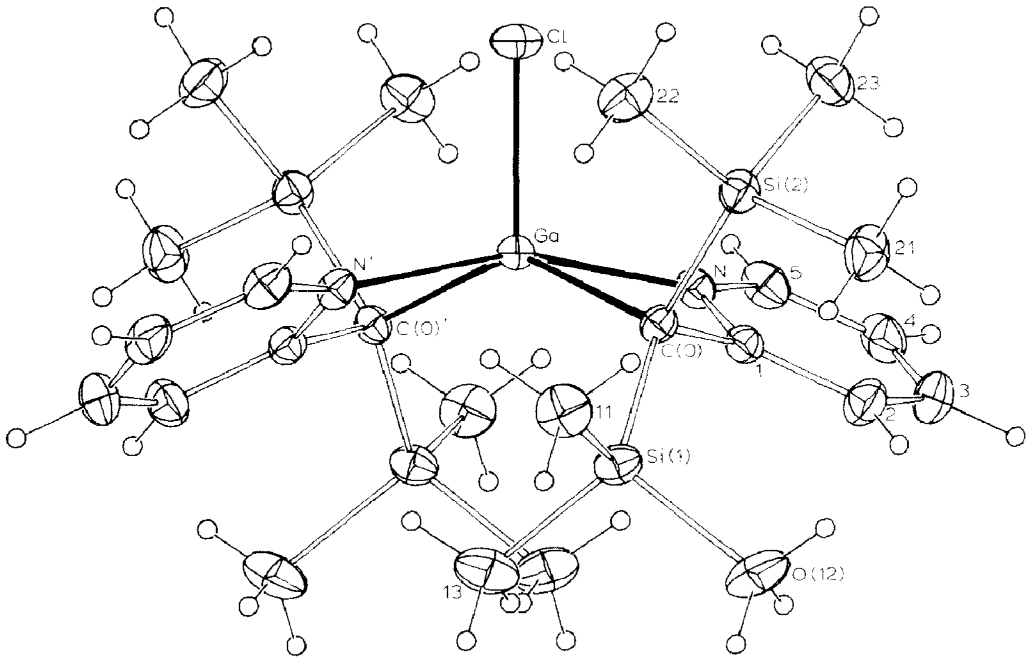


Fig. 1. Molecular projection of one of the three independent molecules of crystallographic 2 symmetry of compound **1b** showing 20% thermal ellipsoids for the non-hydrogen atoms, and arbitrary radii for hydrogen atoms. Selected bond distances (Å) and angles (°) (values for molecules 1, 2 and 3, respectively): Ga–C(0) 2.080(4), 2.059(4), 2.056(4); Ga–N 2.268(4), 2.186(3), 2.214(4); Ga–Cl 2.211(2), 2.212(2), 2.231(2); C(0)–Ga–N 65.6(1), 67.2(2), 67.2(2); C(0)–Ga–C(0)′ 149.5(2), 132.7(2), 136.6(2); C(0)–Ga–Cl 105.2(1), 113.7(1), 111.7(1); N–Ga–Cl 96.5(1), 99.5(1), 100.1(1); N–Ga–N′ 167.1(1), 161.0(1), 159.8(1); N–Ga–C(0)′ 110.7(2), 104.8(2), 104.9(2); Ga–N–C(1) 88.7(3), 89.7(3), 89.1(3); Ga–N–C(5) 151.3(3), 149.3(3), 151.3(3); Ga–C(0)–C(1) 92.5(2), 90.9(3), 91.4(3); Ga–C(0)–Si(1) 115.9(2), 117.4(2), 117.8(2); Ga–C(0)–Si(2) 111.4(2), 110.8(2), 110.5(2).

C_6D_6), δ (rel. TMS) −0.34 (36H, s, $SiMe_3$) 6.10 (H, s) 6.60 (2H, m) 7.70 (H, m); MS *m/z* 577; IR: ν(Ga–Cl) 328 (s) cm^{-1}.

Compound 3a. To a slurry of Na/K (7.03 mmol, K) in 400 ml THF, 3.32 g of **1a** (6.21 mmol) in 50 ml of THF was added during 15 min. After 2 days the red solution was filtered and the solvent removed in vacuo to leave a brown glass, to which 100 ml of hexane was added. The mixture was stirred for 12 h and the pyrophoric cream solid then collected and dried in vacuo (3.28 g, 53% yield). Found: C, 50.7; H, 8.11, Al; 5.10; N, 4.63. $C_{24}H_{44}Al_2N_2Si_4$ calcd.: C, 56.7; H, 9.07; Al, 5.41; N, 5.73%.

Compound 3b. This was prepared in the way described for **3a**. (20% yield).

Compound 4. Water (1 ml) was added to a stirred solution of 1.59 g of **3a** (1.59 mmol) in 30 ml of benzene. After 30 min the mixture was filtered and solvent removed in vacuo, 20 ml hexane was added, and the solution dried (Na_2SO_4). Distillation in vacuo yielded 2-bis(trimethylsilyl)methylpyridine (51 mg) [13]. The solid residue was recrystallized from hexane to yield 2,2′-bis[bis(trimethylsilyl)-methyl]-4,4′-bipyridine (50 mg), m.p. 136 °C. ^1H NMR (300 MHz, C_6D_6), δ (rel. TMS) 0.09 (36 H, s, $SiMe_3$) 2.01 (2H, s, CHSi) 4.30 (H, d, H(6)) 7.15 (2H, m, H(3,5)); MS *m/z* 472. Found: C, 56.0; H, 9.15; N, 5.10. $C_{24}H_{44}N_2Si_4 \cdot 2H_2O$ calcd.: C, 56.6; H, 9.51; N, 5.50%.

Compound 6. To 0.88 g of **1b** (1.52 mmol) in 1.52 ml of benzene was added 0.27 g $GaCl_3$ (1.53 mmol). Two liquid phases immediately separated. The solvent was removed in vacuo and the solid recrystallized as colorless plates from 5 ml of THF (0.8 g, 70% yield). ^1H NMR (80 MHz, C_6D_6), δ (rel. TMS) -0.47 (36H, s, $SiMe_3$) 6.30 (2H, m) 7.3 (2H, m); IR: ν(Ga–Cl) 375 (s) cm^{-1}.

Crystal structure determination, compound 1b (capillary). (T 295 K; Enraf–Nonius CAD- diffractometer). $C_{24}H_{44}ClGaN_2Si_4$, $M = 578.1$, monoclinic, space group $C2/c$ a 15.953(60, b 27.939(5), c 21.593(4) Å, β 103.36(3)°, U 9364(9) Å^3, $F(000) = 3672$; $Z = 12$, $D_c = 1.23$ g cm^{-3} $\mu(\text{Mo-}K_\alpha)$ 11.0 cm^{-1}, $A^* = 1.19–1.56$, specimen $0.43 \times 0.16 \times 0.46$ mm, 7689 unique reflections, 4735 with $I > 2\sigma(I)$ used in the refinement, $2\theta_{max}$ 50°; $R = 0.040$, $R' = 0.041$.

Lists of atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre.

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