Monomeric Selenolato- and Tellurolato-aluminium(III) and -gallium(III) [$Me_3NM(ER)_3$] (E = Se, Te; R = Alkyl, Aryl), *via* Trimethylamine Alane/Gallane Cleavage of Diorgano-dichalcogens

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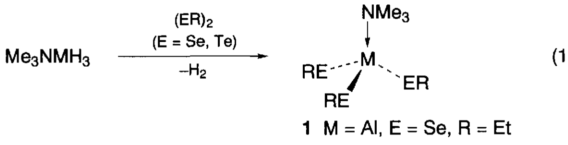
The reaction of diorgano-dichalcogens $(ER)_2$ (E = Se or Te) with trimethylamine adducts of alane or gallane yields trimethylamine adducts of the tris(selenolato- or tellurolato-)metal (III) species [$Me_3NM(ER)_3$] (M = Al, Ga; E = Se, Te; R = Et, Ph, CH_2Ph); two of which have been structurally authenticated as four coordinate, monomeric species in the solid state.

Main Group 16 complexes of the group 13 elements are of interest as potential precursors for generating films of binary metal chalcogenides with useful electronic and optoelectronic properties,^{1,2} *e.g.* gallium sulfide films from [{$Bu^tGa(\mu_3\text{-}S)$}$_4$].^{3} They are also of interest as selective reagents in synthesis, *e.g.* for the conversion of aldehydes to thiols, selenols and tellurols esters by the reaction with Bu^i_2AlER (R = alkyl, E = S, Se, Te).^{4,5}

As an extension of our research on the heavier Group 13 metal hydrides^6 we have investigated the reactions of trimethylamine adducts of alane and gallane Me_3NMH_3 (M = Al, Ga) with diorgano-dichalcogens $(ER)_2$ (E = Se, Te). Highlights of the findings include: (*a*) the reactions offer a facile, convenient route to tris(selenolato- or tellurolato-)- metal(III) species [$Me_3NM(ER)_3$] **1–5** (M = Al, Ga; E = Se, Te; R = Et, Ph, CH_2Ph) eqn. (1); (*b*) the method dispenses with the perceived need to use bulky selenolato- tellurolato- ligands to prevent oligomerisation of Group 13 derivatives *via* utilisation of empty p-orbitals and lone pairs of electrons, which was noted for the synthesis of monomeric [Ga{Se(2,4,6-$Bu^t_3C_6H_2$)}$_3$];^{7} and (*c*) the structures established for two of these products, **1** and **4**, add to the limited structural data available on chalcogenolato (RE^-) aluminium(III) species in general, *viz.* [{$Bu^t_2Al(\mu\text{-}TeBu^t)$}$_2$].^{8} There is also little structural data available for related chalcogenido (E^{2-}) species, being limited to the heterocubanes [{$RAl(\mu_3\text{-}E)$}$_4$] (R = η^5-C_5Me_5; E = Se, Te^9) and for gallium(III) RE^-, and E^{2-} species which includes analogues of the above heterocubanes (R = η^5-C_5Me_5, E = Te;^{10} R = Bu^t, E = Se^{11}) and other classes of selenato,^{7} tellurolato,^{12,13} and tellurido^{14,15} compounds.

Compounds **1–5** were prepared in diethyl ether or toluene, eqn. (1).‡ The metal hydride cleavage of diorgano-diselenides



(1)

1 M = Al, E = Se, R = Et
2 M = Al, E = Se, R = Ph
3 M = Al, E = Se, R = CH_2Ph
4 M = Al, E = Te, R = Ph
5 M = Ga, E = Se, R = Ph

or -ditellurides *via* hydrogen extrusion is also effective in the formation of Bu^i_2AlER (R = alkyl, E = S, Se, Te) using Bu^i_2AlH.^{4,5} Related to this is the cleavage of diorgano-tellurides by [In(2,4,6-$Me_3C_6H_2$)$_3$] affording [{In(2,4,6-$Me_3C_6H_2$)$_2$(μ-TeR)}$_2$] (R = Ph, Et), possibly with formation of telluro ethers.^{16} The mechanism of the present reaction yielding hydrogen as the byproduct is complex but most likely proceeds *via* initial complexation of a Group 16 donor yielding a hypervalent metal centre which is common for alane, and only transient species for gallane.^{6} Other methods of formation of selenolato and tellurolato aluminium(III) and gallium(III) species include metal halogen exchange,^{7,13} chlorotrimethylsilane elimination,^{10} insertion into metal alkyl bonds,^{8,11} and redistribution.^{13}

Compounds **1–5** are highly crystalline, colourless solids which are extremely air/moisture sensitive, decomposing to red (from **4**) and yellow (from **1–3**, **5**) solids on exposure to minute

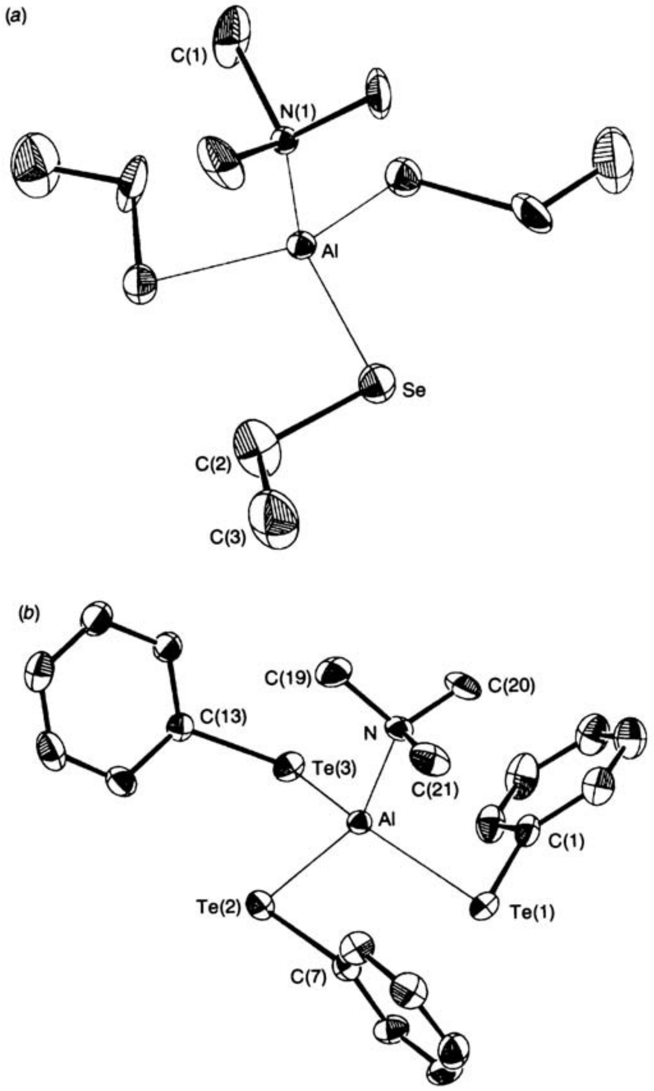


Fig. 1 Projections of (*a*) [$Me_3NAl(SeEt)_3$] **1** and (*b*) [$Me_3NAl(TePh)_3$] **4**, with 20% thermal ellipsoids for non-hydrogen atoms, hydrogen atoms have been omitted for clarity. Selected bond distances (Å) angles and dihedral angles (°): (*a*) Al–Se 2.357(8), Al–N(1) 1.99(6), Se–C(2) 1.93(3), N(1)–Al–Se 107.3(6), Al–Se–C(2) 98.0(9), Al–N(1)–C(1) 120(2), Se–Al–Se′ 111.5(5), N(1)–Al–Se–C(2) 87(1); (*b*) Al–Te(1) 2.589(2), Al–Te(2) 2.585(2), Al–Te(3) 2.581(2), Al–N 2.018(5), Te(1)–C(1) 2.121(8), Te(2)–C(7) 2.131(7), Te(3)–C(13) 2.142(7), N–Al–Te(1) 106.9(2), N–Al–Te(2) 108.6(2), N–Al–Te(3) 109.5(2),Al–Te(1)–C(1) 97.6(2), Al–Te(2)–C(7) 97.4(2), Al–Te(3)–C(13) 97.4(4), Al–N–C(19) 110.7(4), Al–N–C(20) 111.0(5), Al–N–C(21) 109.7(4), Te(1)–Al–Te(2) 111.21(7), Te(1)–Al–Te(3) 110.47(8), Te(2)–Al–Te(3) 110.11(7), N–Al–Te(1)–C(1) –77.7(3), N–Al–Te(2) –77.4(3), N–Al—Te(3) –74.7(3).

traces of oxygen/water. Compounds **1–5** are involatile, thermally decomposing without sublimation when heated *in vacuo*. Results of the X-ray structure determinations of **1** and **4**§ are shown in Fig. 1. The solid state structures of **1** and **4** comprise discrete monomeric species containing tetrahedrally coordinated aluminium atoms. Molecules of **1** possess crystallographic C_3 symmetry while the same symmetry is non-crystallographic in the case of **4**. Notable geometries include the Al–N distances of, **1** (mean) 2.05 and **4** 2.018(5) Å which are intermediate in the range typically observed in four-coordinate, mono-tertiary amine adducts of aluminium species bearing strongly electron withdrawing/releasing substituents attached to the aluminium atoms.[17] The Al–Se, Te distances of, **1** (mean) 2.353 and **4** (mean) 2.584 Å are with only one precedence for the two coordinate group 16 elements in the datively bound species [$Cl_3Al.Se{=}PPh_3$] in which the Al–Se distance (mean) is 2.437 Å,[18] and are the shortest known, *c.f.*, dimeric [{$Bu^t_2Al(\mu\text{-}TeBu^t)$}$_2$], 2.732(3) Å,[8] and the tetrameric cubane species [{(η^5-C_5Me_5)Al(μ_3-E)}$_4$] (E = Se and Te) in which Al–E distances (mean) are 2.477 and 2.710 Å, respectively.[9]

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Footnotes

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‡ *Typical experiment*: To a stirred solution of Me_3NAlH_3 (0.58 g, 6.51 mmol) in toluene (10 ml) at 25 °C was slowly added $(SeEt)_2$ (1.11 g, 5.14 mmol) and the mixture stirred for 18 h whereupon it was filtered and the solvent removed *in vacuo*. Recrystallisation from diethyl ether (*ca.* 10 ml) afforded colourless crystals of **1** (0.33 g, 24%). Mp 85–88 °C; δ_H (200 MHz, C_6D_6, 25 °C) 1.54 (9 H, t, $^3J_{H-H}$ 7.5 Hz, CH_2Me), 2.80 (6 H, q, $^3J_{H-H}$ 7.5 Hz, CH_2), 2.90 (9 H, s, NMe); δ_c (50.3 MHz, C_6D_6, 25 °C) 13.1 (CH_2Me), 20.4 (CH_2), 47.2 (NMe).

Selected data for: **2** Crystallised from benzene, yield 55%. Mp 137–140 °C (decomp.); δ_H (200 MHz, C_6D_6, 25 °C) 1.85 (9 H, s, NMe), 6.97 (9 H, m, *m*- and *p*-Ph), 7.83 (6 H, m, *o*-Ph); δ_C (50.3 MHz, C_6D_6, 25 °C) 48.0 (NMe), 126.4, 127.0, 129.4, 137.0 (Ph).

Selected data for **3**: Crystallised from toluene, yield 69%. Mp 65–69 °C (decomp.); δ_H (200 MHz, C_6D_6, 25 °C) 1.77 (9 H, s, NMe), 4.06 (6H, s, CH_2), 6.97–7.18 (9 H, m, *m*- and *p*-Ph), 7.52 (6 H, d, $^3J_{H-H}$ 7.2 Hz, *o*-Ph); ^{13}C NMR (50.3 MHz, C_6D_6, 25 °C) δ 22.6 (CH_2), 47.1 (NMe), 126.5, 128.7, 129.4, 143.9 (Ph).

Selected data for **4**: Crystallised from toluene, yield 59%. Mp 157–161 °C (decomp.); δ_H (200 MHz, C_6D_6, 25 °C) 1.94 (9 H, s, NMe), 6.88 (9 H, m, *m*- and *p*-Ph), 7.91 (6 H, dd, $^3J_{H-H}$ 8.1 Hz, $^4J_{H-H}$ 1.6 Hz, *o*-Ph); δc (50.3 MHz, C_6D_6, 25 °C) 48.2 (NMe), 106.8, 127.1, 129.3, 141.7 (Ph).

Selected data for **5**: Crystallised from toluene, yield 81%. Mp 106–109 °C; δ_H (200 MHz, C_6D_6, 25 °C) 1.86 (9 H, s, NMe), 6.97 (9 H, m, *m*- and *p*-Ph), 7.88 (6 H, m, *o*-Ph); δc (50.3 MHz, C_6D_6, 25 °C) 47.1 (NMe), 126.6, 129.0, 136.1, 136.9 (Ph).

§ *Crystal Structure Determinations*: T = 298 K; Rigaku AFC7R diffractometer, crystal mounted in capillaries. *Data* for **1**: $C_9H_{24}NAlSe_3$, M = 410.16, trigonal, space group $P\bar{3}$, $a = b$ = 11.548(4), c = 7.082 Å, V = 817(1) Å^3, $F(000)$ = 364, Z = 2, D_c = 1.519 g cm^{-3}, Mo-Kα λ = 0.71069 Å, μ (Mo-K$_\alpha$) = 67.66 cm^{-1} (no absorption correction), specimen 0.4 × 0.4 × 0.6 mm, 603 unique reflections, 244 with $I > 3.00\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°.

For **4**: $C_{21}H_{24}NAlTe_3$, M = 700.21, monoclinic, space group $P2_1/c$, a = 7.318(3), b = 13.984(5), c = 24.297(5) Å, β = 91.44(3)°, V = 2485.6(9) Å^3, $F(000)$ = 1304, z = 4, D_c = 1.871 g cm^{-3}, Mo-Kα λ = 0.71069 Å, μ (Mo-Kα) = 35.38 cm^{-1} (absorption correction), specimen 0.2 × 0.2 × 0.6 mm, 4588 unique reflections, 2557 with $I > 3.00\sigma(I)$ used in the refinement, $2\theta_{max}$ = 50°.

The structures were solved by direct methods and refined by full-matrix least-squares refinement using the TEXSAN program system. Compound **1** was disordered along the threefold axis such that two sites of 50% occupancy were located for the aluminium and nitrogen atoms with one of the two sets shown in Fig. 1(*a*). The nitrogen atoms were refined isotropically, while the aluminium atoms and the other non-hydrogen atoms not involved in the disorder were refined anisotropically. Hydrogen atoms attached to the ethyl carbons were calculated and constrained in x,y,z and u_{iso}. Hydrogen atoms were not included for the disordered NMe_3 group. Hydrogen atoms for **4** were calculated and constrained in x, y, z and U_{iso}. Sigma weights were used and the final residuals were R = 0.046, 0.029, R' = 0.047, 0.030, for **1** and **4**, respectively. Atomic coordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Information for Authors, Issue No. 1.

References

1 A. M. Mancini, G. Micoccin and A. Rizzo, *Mater. Chem. Phys.*, 1983, **9**, 29.

2 N. N. Greenwood and A. Earnshaw, *The Chemistry of the Elements*, Pergamon, New York, 1989, p. 285.

3 A. N. MacInnes, M. B. Power and A. R. Barron, *Chem. Mater.*, 1992, **4**, 11.

4 K. Sasaki, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1989, 60; K. Sasaki, T. Mori, Y. Doi, A. Kawachi, Y. Aso, T. Otsubo and F. Ogura, *Chem. Lett.*, 1991, 415; A. P. Kozikowaski and A. Ames, *J. Org. Chem.*, 1978, **13**, 2737.

5 T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *J. Org. Chem.*, 1994, **59**, 5824; *Organometallics*, 1994, **13**, 4543.

6 C. Jones, G. A. Koutsantonis and C. L. Raston, *Polyhedron*, 1993, **12**, 1829; C. L. Raston, *J. Organomet. Chem.*, 1994, **475**, 15.

7 K. Ruhlandt-Senge and P. P. Power, *Inorg. Chem.*, 1991, **30**, 3683.

8 A. H. Cowley, R. A. Jones, P. R. Harris, D. A. Atwood, L. Contreras and C. J. Burek, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 1143.

9 S. Schulz, H. W. Roesky, H. J. Koch, G. Sheldrick, D. Stalke and A. Kuhn, *Angew. Chem., Int. Ed. Engl.*, 1993, **32**, 1729.

10 S. Schulz, M. Andruh, T. Pape, T. Heinze, H. W. Roesky, L. Haming, A. Kuhn and R. Herbst-Irmer, *Organometallics*, 1994, **13**, 4004.

11 M. B. Power, J. W. Ziller, A. N. Tyler and A. R. Barron, *Organometallics*, 1992, **11**, 1055.

12 M. A. Banks, O. T. Beachley, H. J. Gysling and H. R. Luss, *Organometallics*, 1990, **9**, 1979.

13 W. Uhl, M. Lahy, G. Becker, K. W. Klinkhammer and T. Hildenbrand, *Chem. Ber.*, 1992, **125**, 1547.

14 C. J. Warren, D. M. Ho, R. C. Haushalter and A. B. Bocarsly, *J. Chem. Soc., Chem. Commun.*, 1994, 361.

15 W. Uhl, U. Schutz, W. Hiller and M. Heckel, *Organometallics*, 1995, **14**, 1073.

16 H. Rahbarnoohi, R. Kumar, M. J. Heeg and J. Oliver, *Organometallics*, 1995, **14**, 502.

17 See for example, D. F. Grant, R. C. G. Killean and J. L. Lawrence, *Acta Crystallogr., Sect. B, Struct. Crystallogr.*, 1969, **25**, 377; C. D. Whitt, L. M. Parker and J. L. Atwood, *J. Organomet. Chem.*, 1971, **32**, 291.

18 N. Burford, B. W. Royan, R. E. H. Spence and R. D. Rogers, *J. Chem. Soc., Dalton Trans.*, 1990, 2111.