Alane Reduction of Selenium and Tellurium: Tertiary Amine Stabilised Dimeric Chalcogenides, trans-[{Me₃N(H)Al(μ-E)}₂] (E = Se, Te)

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Elemental selenium or tellurium react with trimethylamine alane, [Me₃NAlH₃], in toluene affording the bis-trimethylamine adducts of the dimeric chalcogenidoalanes, [{HAl(μ-E)}₂] (E = Se, Te) isolated as the *trans*-isomers; *ab initio* molecular orbital calculations on model species show that N-donor Lewis-base solvated dimeric species are the energetically most favourable structures for these chalcogenidoalane species.

In further exploring the applications of alane[1] we have investigated the reactions of its trimethylamine adduct, [Me₃-NAlH₃], with elemental selenium and tellurium and find both reactions afford a new class of compound, *viz.* the bis-trimethylamine adducts of the dimeric chalcogenidoalanes, [{Me₃N(H)Al(μ-E)}₂] (E = Se, Te), structurally authenticated as the *trans*-isomers in the solid state. Overall, there is limited structural chemistry available on compounds for aluminium, and also gallium, with heavier group 16 compounds of selenium and tellurium. This includes the heterocube, chalcogenido complexes [{RM(μ₃-E)}₄], M = Al, R = η⁵-C₅Me₅, E = Se, Te,[2] M = Ga, R = η⁵-C₅Me₅, E = Te,[3] and R = Buᵗ, E = Se,[4] and related chalcogenolato complexes [Me₃NM(ER)₃], M = Al, Ga, E = Se, Te, R = alkyl or aryl,[5] [Ga{Se(C₆H₂Buᵗ₃-2,4,6)}₃],[6] [Te{Ge[CH(SiMe₃)₂]₂}₂],[7] and dialkylchalcogeno-latometal(III) species.[3,4,8–11]

The reactions of [Me₃NAlH₃] with elemental selenium and tellurium† yielding *trans*-[{Me₃N(H)Al(μ-E)}₂] (E = Se 1 or

Te 2), and hydrogen were effective in toluene (Scheme 1). The cleavage of group 16 bonds by an aluminium hydride source has precedence in the reaction of the same alane adduct with diorgano-diselenides or -ditellurides, affording [Me₃NAl(ER)₃] (E = Se, Te, R = alkyl or aryl) and similarly for the gallane adduct,[5] and the formation of Buⁱ₂Al(ER) (R = alkyl, E = S, Se, Te) from (ER)₂ using Buⁱ₂AlH.[8,9] The foregoing hetero-cubanes, [{RM(μ₃-E)}₄], have been prepared by the reaction of the group 16 element with tris(alkyl)metal(III)[10] or alkyl-metal(I)[2] species, or the reaction of bis(trimethylsilyl)tellurium with (η⁵-C₅Me₅)GaCl₂.[3]

The reactions forming 1 and 2 offer a simple route to a new class of compound under mild conditions and in modest yield. The complexes have been characterised by IR and NMR spectroscopy, microanalyses and X-ray structure determinations. Both complexes display high thermal stability, being stable up to their melting points, but are extremely air-sensitive, decomposing to red and black solids respectively on exposure to traces of oxygen.

The solid-state structure of 1 is shown in Fig. 1‡ and 2 is isostructural. Molecules of 1 and 2 lie on inversion centres, which dictate flat Al₂E₂ four-membered rings with a *trans* geometry for the coordinating NMe₃ molecules. The compounds can be regarded as tertiary amine stabilised adducts of the simplest of selenido– and tellurido–aluminium(III) species. Contrary to the literature, bulky groups attached to group 13 metal centres are not essential to gain access to low-order aggregates of chalcogenidoaluminium(III) species, at least in the presence of a Lewis-base; rather a small hydrido group and a trimethylamine attached to the metal centre is seemingly more
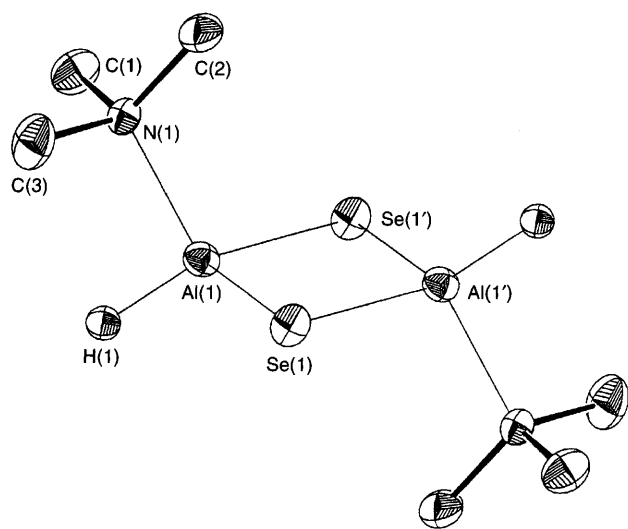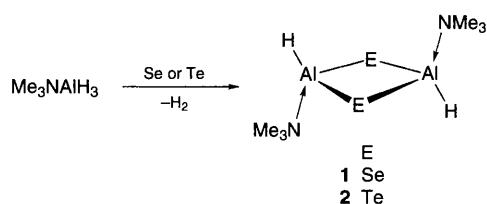
Scheme 1

Fig. 1 Crystal structure of 1. Selected distances (Å) and angles (°) (values in square brackets are for 2): Al(1)–Se(1)[Te(1)] 2.359(2) [2.586(4)], Al(1)–Se(1′)[Te(1′)] 2.359(2) [2.580(4)], Al(1)–H(1) 1.50(5) [1.40], Al(1)–N(1) 2.011(5) [2.011(9)], Al(1)–Se(1)[Te(1)]–Al(1′) 76.90(7) [76.4(1)], Se(1)[Te(1)]–Al(1)–Se(1′)[Te(1′)] 103.10(7) [103.6(1)], N(1)–Al(1)–Se(1)[Te(1)] 108.3(2) [108.0(3)], N(1)–Al(1)–Se(1′)[Te(1′)] 107.8(2) [108.2(3)], H(1)–Al(1)–Se(1)[Te(1)] 119(1) [108.0], H(1)–Al(1)–Se(1′)-[Te(1′)] 118(1) [130.1], N(1)–Al(1)–H(1) 99(1) [98], Al(1)–N(1)–C(1) 108.0(4) [108.4(7)], Al(1)–N(1)–C(2) 113.0(4) [114.0(7)], Al(1)–N(1)–C(3) 107.5(5) [109.2(8)].
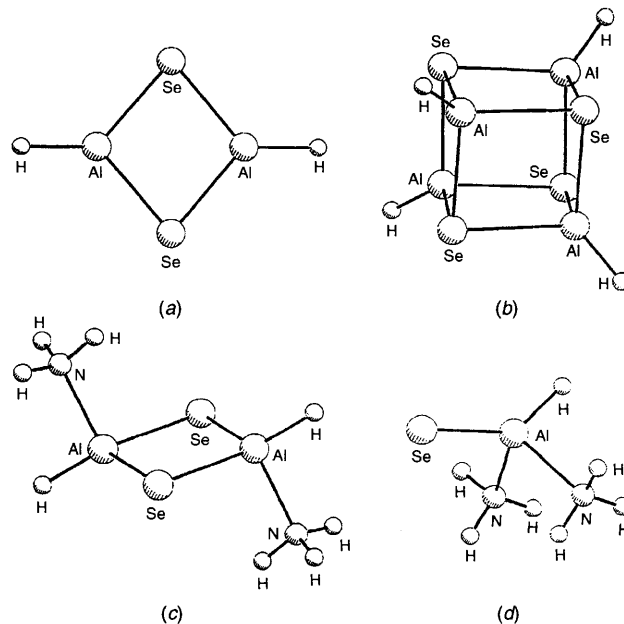
Fig. 2 Computed structures of model chalcogenidoalanes; (a) [{HAl(μ-Se)}₂], (b) [{HAl(μ₃-Se)}₄], (c) [{H₃N(H)Al(μ-Se)}₂], (d) [(H₃N)₂(H)AlSe]

effective in limiting the degree of association to dimeric species, cf. tetramers for bulky alkyl groups.[2,3,10]

Ab initio molecular orbital calculations[12]§ on model species (NMe₃ replaced by NH₃ for computational feasibility) have been performed to investigate the relative stability of unsolvated higher oligomers versus Lewis-base solvated dimers and coordinatively saturated monomeric species. The computed structures of the chalcogenidoalanes (E = Se) are shown in Fig. 2(a)–(d). The calculations show that N-donor Lewis-base solvated dimeric species are the most favourable products of the species investigated for both the selenide and telluride cases. Further association of the unsolvated dimers, [{HAl(μ-E)}₂], to tetramers, [{HAl(μ_3-E)}₄], gives association energies of −10.17 (E = Se) and −5.42 kcal mol⁻¹ (E = Te) (cal = 4.184 J). Whereas the formation of Lewis-base solvated dimers, [{H₃N(H)Al(μ-E)}₂], from the unsolvated dimers has association energies of −32.51 (E = Se) and −30.80 kcal mol⁻¹ (E = Te), coordinative saturation of the aluminium centres by the Lewis-base donors to give monomeric species, [(H₃N)₂(H)AlE], is 12.29 (E = Se) and 5.53 kcal mol⁻¹ (E = Te) less stable than the formation of Lewis-base solvated dimers and free amine. We are currently investigating the possibility of preparing monomeric chalcogenidoalanes species by the use of polydentate tertiary amines.

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Footnotes

† Typical experiment: **1**; to a stirred slurry of selenium (0.64 g, 8.11 mmol) at 25 °C, a toluene solution of [Me₃NAlH₃] (0.77 g, 8.64 mmol) was added and the mixture stirred for 16 hours at 100 °C. The mixture was filtered leaving finely divided grey metal. The colourless solution was recrystallised from toluene (ca. 10 ml) to give colourless crystals of **1** (0.73 g, 54% yield). Mp > 256 °C (decomp.); ¹H NMR (200 MHz, [²H₆]benzene) δ = 2.12 (s, 18H, NMe₃); ¹³C NMR (50 MHz, [²H₆]benzene) δ = 46.51 (NMe₃); IR (Nujol) v/cm⁻¹ 1805 m (Al–H) (Found C, 21.36; H, 6.22; N, 8.78, Calc. for C₆H₂₀Al₂N₂Se₂ C, 21.70; H, 6.07; N, 8.44%).

2; to a stirred slurry of tellurium (0.84 g, 6.58 mmol) at 25 °C, a toluene solution of [Me₃NAlH₃] (0.55 g, 6.17 mmol) was added and the mixture stirred for 16 hours at room temperature. The mixture was filtered leaving finely divided grey metal. The colourless solution was recrystallised from toluene (ca. 10 ml) to give colourless crystals of **2** (0.88 g, 66% yield). Mp 215–218 °C; ¹H NMR (200 MHz, [²H₆]benzene) δ = 2.13 (s, 18H, NMe₃); ¹³C NMR (50 MHz, [²H₆]benzene) δ = 46.53 (NMe); IR (Nujol) v/cm⁻¹ 1796m (Al–H) (Found C, 16.98; H, 4.77; N, 6.62. Calc. for C₆H₂₀Al₂N₂Te₂ C, 16.85; H, 4.71; N, 6.55%).

‡ Crystal structure determinations: T = 298 K; Rigaku AFC7R diffractometer, crystals mounted in capillaries. Compound **1**: C₆H₂₀Al₂N₂Se₂, monoclinic, space group $P2_1/n$, a = 6.650(2), b = 10.062(2), c = 10.745(1) Å, β = 90.96(1)°, U = 718.9(2) Å³, Z = 2, D_c = 1.534 g cm⁻³, μ(Mo-Kα) = 52.3 cm⁻¹ (semi-empirical correction, ψ-scans, $A_{min,max}$ = 0.935,0.998, Mo-Kα radiation, 1345 unique reflections [744 observed, I > 3.0$\sigma(I)$], refinement on F^2, 87 parameters, R = 0.032, wR = 0.028 (sigma weights). Solution by direct methods. Compound **2**: C₆H₂₀Al₂N₂Te₂, monoclinic, space group $P2_1/n$, a = 6.901(4), b = 10.189(3), c = 11.130(1) Å, β = 91.10(3)°, U = 782.4(5) Å³, Z = 2, D_c = 1.822 g cm⁻³, μ(Mo-Kα) = 38.1 cm⁻¹ (semi-empirical correction, ψ-scans, $A_{min,max}$ = 0.834, 0.999, Mo-Kα radiation, 1091 unique reflections [663 observed, I > 3.0$\sigma(I)$], refinement on F^2, 55 parameters, R = 0.035, wR = 0.034 (sigma weights). Solution by direct methods. 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.

§ Calculations used the standard LANL1DZ basis set. The structures were adapted from the crystal structure data of **1** and **2** and minimised directly with the LANL1DZ basis set. The energies do not include zero-point energy corrections. All structures were fully refined within the point groups D_{2h}, [{HAl(μ-E)}₂]; T_c [{HAl(μ_3-E)}₄]; C_{2h}, [{H₃N(H)Al(μ-E)}₂]; and C_s [(H₃N)₂(H)AlE].

References

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

2 S. Schulz, H. W. Roesky, H. J. Koch, G. Sheldrick, D. Stalke and A. Kuhn, Angew. Chem., 1993, **105**, 1828; Angew. Chem., Int. Ed. Engl., 1993, **32**, 1729.

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

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

5 M. G. Gardiner, C. L. Raston and V.-A. Tolhurst, J. Chem. Soc., Chem. Commun., 1995, 1457.

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

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

8 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.

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

10 A. H. Cowley, R. A. Jones, P. R. Harris, D. A. Atwood, L. Contreras and C. J. Burek, Angew. Chem., 1991, **103**, 1164; Angew. Chem., Int. Ed. Engl., 1991, **30**, 1143.

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

12 Gaussian 92/DFT, Revision G.4, M. J. Frisch, G. W. Trucks, H. B. Schlegel, P. M. W. Gill, B. G. Johnson, M. W. Wong, J. B. Foresman, M. A. Robb, M. Head-Gordon, E. S. Replogle, R. Gomperts, J. L. Andres, K. Raghavachari, J. S. Binkley, C. Gonzalez, R. L. Martin, D. J. Fox, D. J. Defrees, J. Baker, J. J. P. Stewart and J. A. Pople, Gaussian, Inc., Pittsburgh PA, 1993.