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Chalcogenides of aluminium(III) and gallium(III) derived from Lewis base adducts of alane and gallane

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Reductive cleavage of $(ER)_2$ by $[GaH_3L]$, L = NMe_3 or $P(C_6H_{11})_3$, afforded $[Ga(TePh)_3(NMe_3)]$, $[Ga(SeEt)_3(NMe_3)]$ and $[Ga(TePh)_3\{P(C_6H_{11})_3\}]$; the latter was also prepared by the reaction of $[GaH_2Cl\{P(C_6H_{11})_3\}]$ with LiTePh. They have slightly disordered tetrahedral metal centres, established in the solid for $[Ga(TePh)_3(NMe_3)]$ and $[Ga(TePh)_3\{P(C_6H_{11})_3\}]$, and in the structure of the aluminium analogue, $[Al(SePh)_3(NMe_3)]$, which was also determined. Reaction of $[GaH_2Cl\{P(C_6H_{11})_3\}]$ with Li_2Se afforded dinuclear *trans*-$[\{GaCl(\mu\text{-Se})[P(C_6H_{11})_3]\}_2]$ (minor product) which is centrosymmetric with distorted tetrahedral metal centres associated with a planar Ga_2Se_2 ring system. Treatment of *trans*-$[\{AlH(\mu\text{-Se})(NMe_3)\}_2]$ with tmen (=*N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine), or $[\{AlH_3(tmen)\}_\infty]$ with elemental selenium, afforded polymeric $[\{[AlH(\mu\text{-Se})]_2(tmen)\}_\infty]$. Cleavage of $(EPh)_2$ by *trans*-$[\{AlH(\mu\text{-Se})(NMe_3)\}_2]$ gave *trans*-$[\{Al(\mu\text{-Se})(EPh)(NMe_3)\}_2]$, E = S, Se or Te, also as centrosymmetric dinuclear species with planar Al_2Se_2 ring systems. Reaction of *trans*-$[\{AlH(\mu\text{-Se})(NMe_3)\}_2]$ with 2 equivalents of $NH(SiMe_3)_2$ or 6-methyl-2-trimethylsilylaminopyridine gave the secondary amine metallated products *trans*-$[\{Al(\mu\text{-Se})[N(SiMe_3)_2](NMe_3)\}_2]$ (structurally authenticated as a centrosymmetric dinuclear species) and $[\{Al(\mu\text{-Se})(NC_5H_3NSiMe_3\text{-}2\text{-}Me\text{-}6)\}_2]$.

Complexes containing aluminium or gallium bound to the heavier chalcogen elements have recently gained prominence in synthesis,[1–3] and as single source precursors for generating films of binary metal chalcogenides. 1:1 Lewis base adducts of MMe_3 (M = Al or Ga) with dimethylchalcogens are available,[4,5] as are a variety of mono-, di- and tetra-nuclear chalcogenido- and chalcogenolato-complexes.[6–28] Mononuclear complexes containing anionic chalcogenolate ligands, ER^-, are either three-co-ordinate, in $[Ga\{Se(2,4,6\text{-}Bu^t_3C_6H_2)\}_2]$[6] and $[Ga\{TeSi(SiMe_3)_3\}_3]$,[7] or four-co-ordinate, in $[AlMe_2(SePh)(PPh_3)]$[8] and $[M(ER)_3(NMe_3)]$ (M = Al, E = Se, R = Et, Ph or CH_2Ph; E = Te, R = Ph; and M = Ga, E = Se, R = Ph).[9]

Dinuclear complexes containing μ-bridging chalcogenide ligands across two aluminum or gallium centres include $[\{M[(Me_3Si)_2HC]\}_2E]$ (M = Al or Ga; E = S, Se or Te),[10–15] $[\{Ga(mes)(NC_5H_4Me\text{-}4)(\mu\text{-Se})\}_2]$ (mes = 1,3,5-$Me_3C_6H_2$),[16] *trans*-$[\{AlH(\mu\text{-E})(NMe_3)\}_2]$ (E = Se or Te),[17] and *trans*-$[\{Al(\mu\text{-E})(EPh)(NMe_3)\}_2]$ which also has terminal chalcogenide ligands.[18] Then there are complexes with μ-bridging chalcogenolate ligands, such as $[\{GaBu^t_2(\mu\text{-EBu}^t)\}_2]$ (E = Se or Te),[19] $[\{Ga(Me_3CCH_2)_2(\mu\text{-TePh})\}_2]$,[20] $[\{AlBu^t_2(\mu\text{-TeBu}^t)\}_2]$,[21] and $[\{Al(mes)(\mu\text{-SeMe})\}_2]$.[8]

Tetranuclear clusters containing μ_3-bridging chalcogenides have cubane structures, $[\{M(\eta^n\text{-}C_5Me_5)(\mu_3\text{-Se})\}_4]$ (M = Al, *n* = 5; M = Ga, *n* = 1),[22,23] $[\{Al(Me_2EtC)(\mu_3\text{-Se})\}_4]$[24] and $[\{Ga(\eta^5\text{-}C_5Me_5)(\eta_3\text{-Te})\}]$.[12] Higher oligomers involving hexanuclear and octanuclear complexes are also known.[19,25] Tetranuclear clusters with μ-bridging chalcogenide ligands across two metal centres have recently been reported, notably $[Al_4(\mu\text{-S})_6(NMe_3)_4]$[26] in which each S^{2-} bridges two metal centres along an edge of a tetrahedron of metal centres, and the closely related complexes $[Al_4H_2(\mu\text{-E})_5(NMe_3)_4]$ (E = S[26] or Se)[18] where one edge of the tetrahedron is open with the associated metal centres each bearing a hydride. Finally, several ionic group 13/16 metal complexes have been structurally elucidated, $K[(AlMe_3)_3SeMe]$,[27] $K_2[S(GaMe_3)_2]$,[28] and $[PPh_4][GaTe_2\{(CH_2NH_2)_2\}_2]$.[29]

Herein we report an extension of our studies on the reaction of $(RE)_2$, E = Se or Te, with Lewis base adducts of alane and gallane showing that the reaction is general, leading to $[M(ER)_3(NMe_3)]$. An earlier study dealt with the complexes where M = Al, E = Se, R = Et, Ph or CH_2Ph; E = Te, R = Ph; and M = Ga, E = Se, R = Ph, and included the structural elucidation of $[Al(ER)_3(NMe_3)]$ (E = Se, R = Et; E = Te, R = Ph).[9] We also report (i) reactions of *trans*-$[\{AlH(\mu\text{-Se})(NMe_3)\}_2]$ with $(RE)_2$, *N*,*N*,*N*′,*N*′-tetramethylethane-1,2-diamine (tmen), and bulky secondary amines, and (ii) the structure of *trans*-$[\{GaCl(\mu\text{-Se})[P(C_6H_{11})_3]\}_2]$, isolated as a minor product from a reaction of Li_2Se with $[GaH_2Cl\{P(C_6H_{11})_3\}]$. This is further to our report on the reaction of *trans*-$[\{AlH(\mu\text{-Se})(NMe_3)\}_2]$ with *N*,*N*,*N*′,*N*″,*N*″-pentamethyldiethylenetriamine (pmdien) to give the aforementioned tetranuclear cluster, $[Al_4H_2(\mu\text{-Se})_5(NMe_3)_4]$, the sulfur analogue being independently prepared by the reaction of $[AlH_3(NMe_3)]$ with $S(SiMe_3)_2$.[26] This was also the route to $[Al_4(\mu\text{-S})_6(NMe_3)]$, the nature of the metal chalcogen core, Al_4S_5 or Al_4S_6, depending on the ratio of reactants. The only other reported reaction of the dinuclear species is that of *trans*-$[\{AlH(\mu\text{-Se})(NMe_3)\}_2]$ with $(TePh)_2$ resulting in the formation of *trans*-$[\{Al(\mu\text{-Se})(TePh)(NMe_3)\}_2]$.[18] The compounds *trans*-$[\{AlH(\mu\text{-E})(NMe_3)\}_2]$, E = Se or Te, are formed on treating $[AlH_3(NMe_3)]$ with elemental selenium or tellurium.[17]

Results and Discussion

Mononuclear tris(chalcogenolato)-aluminium(III) and -gallium(III) complexes

Treatment of (trimethylamine) alane, $[AlH_3(NMe_3)]$, and (trimethylamine) gallane, $[GaH_3(NMe_3)]$, with the diorganyl

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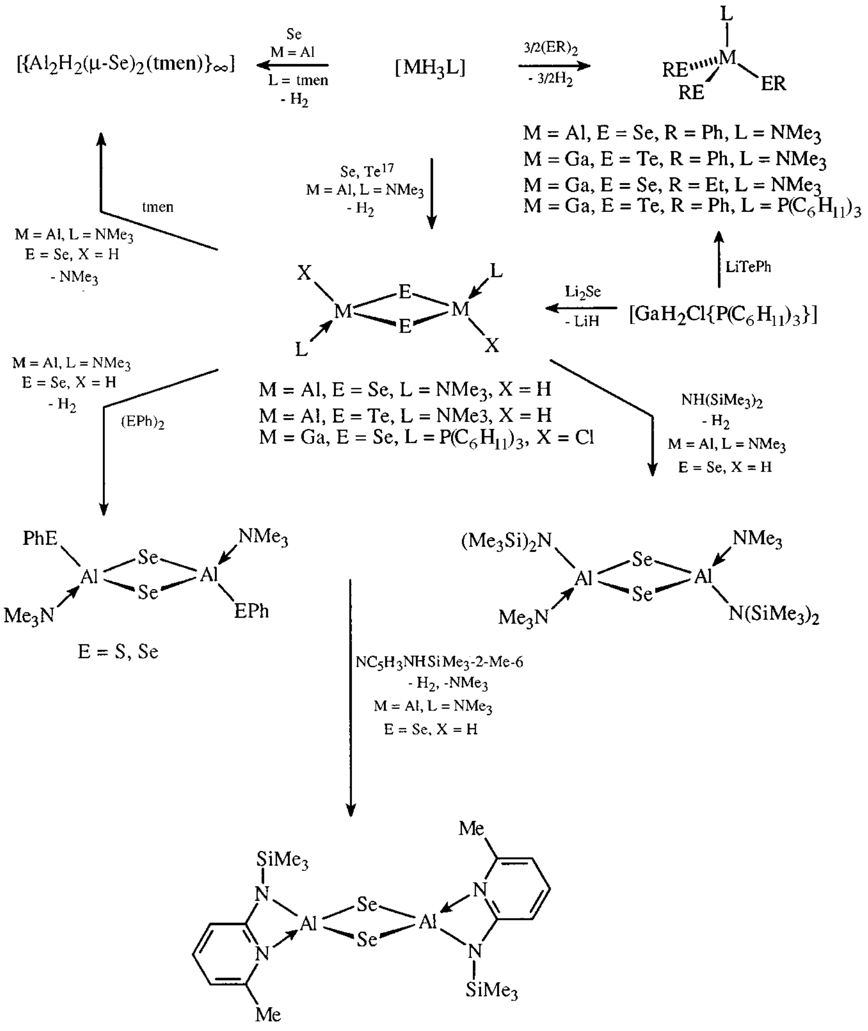
dichalcogenides $(RE)_2$ (E = Se or Te, R = alkyl or aryl) results in chalcogen–chalcogen bond cleavage and the elimination of hydrogen affording colourless, trichalcogenolato-aluminium(III) and -gallium(III) complexes as mononuclear adducts of trimethylamine.[9] This method is a convenient one step synthesis of Lewis base adducts of tris(chalcogenolato) Group 13 metal complexes. New compounds reported here are $[Ga(TePh)_3(NMe_3)]$ and $[Ga(SeEt)_3(NMe_3)]$; previous work focused on using $[AlH_3(NMe_3)]$ and one example using $[GaH_3(NMe_3)]$, *viz.* $[Ga(SePh)_3(NMe_3)]$. A limiting factor in using $[GaH_3(NMe_3)]$ is its decomposition above 0 °C which necessitates the use of freshly prepared material.[30] The tricyclohexylphosphine adduct of gallane is, in contrast, thermally stable, and indeed is stable in air. It similarly reacts with $(TePh)_2$ affording yellow $[Ga(TePh)_3\{P(C_6H_{11})_3\}]$. The same complex has also been isolated from the reaction of $[GaH_2Cl\{P(C_6H_{11})_3\}]$ with LiTePh at room temperature in thf, and has been structurally authenticated, along with $[Ga(TePh)_3(NMe_3)]$ and a previously prepared aluminium compound $[Al(SePh)_3(NMe_3)]$.[9] The new complexes have also been characterised using NMR spectroscopy and microanalysis. The ^{31}P NMR chemical shift for $[Ga(TePh)_3\{P(C_6H_{11})_3\}]$, δ 68.6, contrasts with δ 11.8 for $[GaH_3\{P(C_6H_{11})_3\}]$ and δ 9.2 for $P(C_6H_{11})_3$, and may be related to steric compression within the complex,[31] which is reflected in the crystal structure (see below).

All reactions were carried out at room temperature in either diethyl ether or toluene, depending on the solubility of $(ER)_2$. Reactions involving $[GaH_3(NMe_3)]$ were sluggish whereas those involving $[AlH_3(NMe_3)]$ were often vigorous with evolution of a gas,[9] presumably hydrogen. The difference in the reactivity of the two complexes reflects the difference in the polarity of the M–H bonds in $[MH_3(NMe_3)]$, M = Al or Ga.[31] Using an excess of $[MH_3(NMe_3)]$, M = Al or Ga, gave tris(chalcogenolato)-products rather than the redistribution compounds, $[MH(ER)_2(NMe_3)]$ and $[MH_2(ER)(NMe_3)]$. The new complexes, including those previously reported, were obtained in moderate to good yields. They exhibit good to high thermal stability being stable to room temperature for weeks, and are moisture and air sensitive, with the selenolato-complexes decomposing to red products and tellurolato-complexes to black materials which were not investigated.

The reactions most likely proceed *via* initial complexation of the dichalcogen forming a mixed donor hypervalent metal centre, at least for aluminium for which five-co-ordinate mixed donor adducts have been reported.[32,33] Hypervalent species involving gallane are stable only at low temperature,[30] and the reluctance of gallium to be five-co-ordinate may account for the different rates of formation of the tris(chalcogenolato)-complexes.

No reaction was evident between $BH_3(NMe_3)$ and $(SePh)_2$, $(SeCH_2Ph)_2$ or $(TePh)_2$ in diethyl ether or toluene at room temperature for times up to 17 h. We note that very few boron chalcogenolato-complexes are known.[33–35] The lack of reaction is consistent with steric considerations, *viz.* the inability of boron to form five-co-ordinate species, and the lower polarisation of B–H bonds (<Ga–H < Al–H). Surprisingly no reaction was evident between $[AlH_3(NMe_3)]$ and $(SCH_2Ph)_2$ in diethyl ether at room temperature over several hours. Here the high S–S bond energy may be the problem, 425.01 kJ mol^{-1}, *cf.* 332.6 kJ mol^{-1} for Se–Se, 264.4 kJ mol^{-1} for Te–Te, but we



Scheme 1

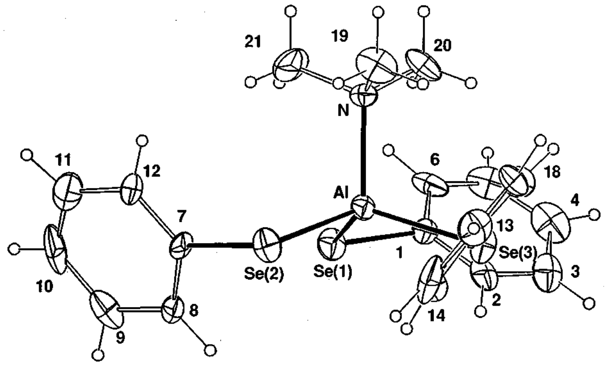


Fig. 1 Projection of [Al(SePh)$_3$(NMe$_3$)] with 20% thermal ellipsoids for non-hydrogen atoms (as in other Figures); hydrogen atoms have arbitrary radii of 0.1 Å. Selected bond distances (Å) and angles (°): Se(1)–Al 2.343(8), Se(1)–C(1) 1.93(2), Se(2)–Al 2.365(8), Se(2)–C(7) 1.95(3), Se(3)–Al 2.355(8), Se(3)–C(13) 1.95(1) and Al–N 2.00(2); Al–Se(1)–C(1) 101.3(8), Al–Se(2)–C(7) 100.1(8), Al–Se(3)–C(13) 100.0(8), Se(1)–Al–Se(2,3) 109.5(3), 114.0(3), Se(2)–Al–Se(3) 113.4(4), N–Al–Se(1,2,3) 106.2(7), 106.3(7), 106.9(7) and Al–N–C(19,20,21) 111(2) (×3)

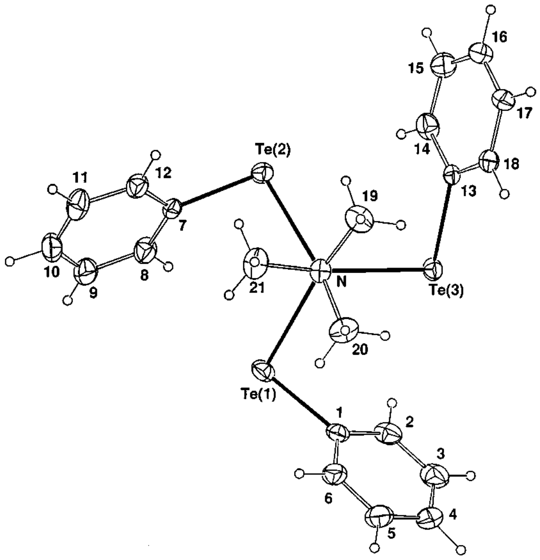


Fig. 2 Projection of [Ga(TePh)$_3$(NMe$_3$)] down the Ga–N bond. Selected bond distances (Å) and angles (°): Te(1)–Ga 2.5804(9), Te(1)–C(1) 2.135(6), Te(2)–Ga 2.5725(9), Te(2)–C(7) 2.127(5), Te(3)–Ga 2.575(1), Te(3)–C(13) 2.133(5) and Ga–N 2.095(4); Ga–Te(1)–C(1) 97.6(1), Ga–Te(2)–C(7) 96.8(1), Ga–Te(3)–C(13) 96.9(1), Te(1)–Ga–Te(2,3) 112.66(3), 111.74(3), Te(2)–Ga–Te(3) 111.83(3), N–Ga–Te(1,2,3) 105.7(1), 106.6(1), 107.8(1) and Ga–N–C(19,20,21) 110.1(4), 109.8(3), 109.8(3)

note that the dimeric species [{AlH(μ-Se)(NMe$_3$)}$_2$] reacts with (SPh)$_2$ (see below).

The crystal structures of [Al(SePh)$_3$(NMe$_3$)], [Ga(TePh)$_3$(NMe$_3$)] and [Ga(TePh)$_3${P(C$_6$H$_{11}$)$_3$}], are shown in Figs. 1–3. They are all mononuclear species with distorted tetrahedral (N or P)ME$_3$ metal centres. The compound [Ga(TePh)$_3$(NMe$_3$)] is isostructural with [Al(TePh)$_3$(NMe$_3$)],[9] having similar cell dimensions in the monoclinic space group $P2_1/c$; [Al(SePh)$_3$(NMe$_3$)], in contrast, crystallises in the monoclinic space group *Cc* and with dissimilar dimensions.

In all three structures the asymmetric unit is the mononuclear species in which the metal centres are in slightly flattened tetrahedral environments and possessing a staggered conformation about the M–N bond (M = Al or Ga) with the phenyl groups in a propeller like arrangement. Other Group 13 metal tris(selenolato)-complexes with a co-ordinated Lewis base are [In(SePh)$_3$(PPh$_3$)$_2$][36] and [{In[SeSi(SiMe$_3$)$_3$]$_3$}$_2$(μ-dmpe)].[7] Mononuclear three-co-ordinate trichalcogenolato Group 13 metal(III) complexes have been reported, *e.g.* [Ga{TeSi(SiMe$_3$)$_3$}$_3$],[7] [In{SeC(SiMe$_3$)$_3$}$_3$],[7] and [Ga{Se(2,4,6-Bu$^t_3$C$_6$H$_2$)}$_3$],[6] but these are stabilised by the bulky nature of the ligands. In this context we note that the structure of In(SePh)$_3$ is polymeric with six-co-ordinate metal centres and forms mononuclear complexes on the addition of Lewis bases.[37]

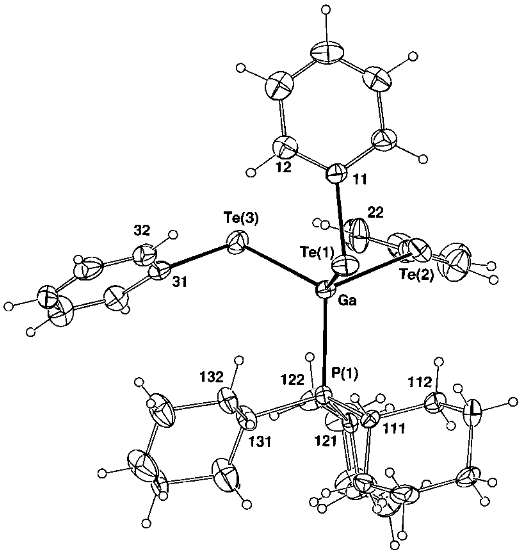


Fig. 3 Projection of [Ga(TePh)$_3${P(C$_6$H$_{11}$)$_3$}]. Selected bond distances (Å) and angles (°): Te(1)–Ga 2.598(2), Te(1)–C(11) 2.12(2), Te(2)–Ga 2.604(2), Te(2)–C(21) 2.12(2), Te(3)–Ga 2.576(2), Te(3)–C(31) 2.09(1) and Ga–P(1) 2.419(5); Ga–Te(1)-C(11) 97.0(4), Ga–Te(2)–C(21) 110.3(3), Ga–Te(3)–C(31) 109.0(5), Te(1)–Ga–Te(2,3) 102.46(5), 119.66(7), Te(2)–Ga–Te(3) 106.96(8), P(1)–Ga–Te(1,2,3) 102.3(1), 110.7(1), 114.13(9) and Ga–P(1)–C(111,121,131) 106.9(5), 109.8(5), 107.3(6)

The Al–Se bond distances in [Al(SePh)$_3$(NMe$_3$)], 2.343(8)–2.365(8) Å, compare with 2.394(1) Å in [AlMe$_2$(SePh)(PPh$_3$)][8] and 2.37 Å in Al$_2$Se$_3$.[38] The Ga–Te bond distances in [Ga(TePh)$_3$(NMe$_3$)], 2.5725(9)–2.5804(9) Å, are similar to the analogous distances in the aluminium complex, 2.518(2)–2.589(2) Å. This is consistent with two metals having almost identical covalent radii. As expected, the Ga–Te distances are significantly shorter than those of the dinuclear complex [{Ga(Me$_3$CCH$_2$)$_2$(μ-TePh)}$_2$], 2.755 Å (mean),[20] and the cubane tetranuclear complex [{Ga(η^1-C$_5$Me$_5$)(μ$_3$-Te)}$_4$], 2.671 Å (mean).[40] In contrast they are longer than the Ga–Te bond distances in the mononuclear three-co-ordinate species [Ga{TeSi(SiMe$_3$)$_3$}$_3$], 2.488(4)–2.531 Å[7] and [Ga{(Me$_3$Si)$_2$CH}$_2${TeSi(SiMe$_3$)$_3$}], 2.535(1) Å.[10] All the above Ga–Te distances are significantly shorter than those in Ga$_2$Te$_5$, 2.62 Å (mean).[39]

The Al–N distance in [Al(SePh)$_3$(NMe$_3$)], 2.00(2) Å, is similar to that in the tellurium analogue, 2.018(5) Å,[9] both of which are within the range typical for four-co-ordinate, monotertiary amine adducts of aluminium species bearing strongly electron withdrawing or electron releasing substituents attached to the aluminium centres,[41,42] and also with Al–N distances in [{AlH(μ-E)(NMe$_3$)}$_2$] [E = Se, 2.0115(5) Å; Te, 2.011(9) Å]. The Ga–N distance in [Ga(TePh)$_3$(NMe$_3$)], 2.095(4) Å, is also typical for four-co-ordinate monotertiary amine adducts of gallium species,[43,44] but is longer than in the aluminium complex. This is also the case for M–N distances in mononuclear quinuclidine adducts of alane and gallane, 1.991(4)[32] and 2.063(4) Å,[45] respectively, and is related to the lower Lewis acidity of gallane relative to alane.[30]

The metal centres in [Al(SePh)$_3$(NMe$_3$)] and in the SeEt analogue[9] have slightly distorted flattened tetrahedral geometries, marginally more than in the TePh analogue,[9] but similar to those in [Ga(TePh)$_3$(NMe$_3$)]: Se–Al–Se, 109.5(3), 113.4(4) and 114.0(3), N–Al–Se 106.2(7), 106.3(7) and 106.9(7)°; *cf.*

Te–Ga–Te 111.74(3), 111.83(3) and 112.66(3)°, N–Ga–Te 105.7(1), 106.6(1) and 107.8(1)° in [Ga(TePh)$_3$(NMe$_3$)]. The Ga–Te–C angles in [Ga(TePh)$_3$(NMe$_3$)], 96.8(1)–97.6(1)°, compare with those in the aluminium analogue, 97.4(2)–97.6(2)°;[9] Al–Se–C angles in [Al(SePh)$_3$(NMe$_3$)] are significantly larger at 100.0(8), 100.1(8) and 101.3(8)° which is a common feature between analogous selenolato- and tellurolato-complexes, for example in [{[Al(Me$_3$Si)$_2$HC]$_2$}$_2$E] (E = CH$_2$, S, Se or Te).[15] The N–M–E–C dihedral angles in both complexes range over 74.7(3)–87(1)° thus reflecting the quasi-C_3 symmetry of the molecules. In contrast, for the P(C$_6$H$_{11}$)$_3$ adduct, the corresponding P–Ga–Te–C dihedral angles are −174.1(3), 81.5(6) and 58.3(4)°.

The compound [Ga(TePh)$_3${P(C$_6$H$_{11}$)$_3$}] crystallises from toluene in the monoclinic space group $P2_1/c$. The metal environment is also a distorted tetrahedral PGaTe$_3$ metal core with a staggered conformation about the Ga–P bond. The Ga–Te bond distances of 2.576(2)–2.604(2) Å are similar to those in the trimethylamine adduct, and are elongated relative to those in three-co-ordinate species.[7,10] The Ga–P distance, 2.419(5) Å, is significantly shorter than that of the starting complex [GaH$_3${P(C$_6$H$_{11}$)$_3$}], 2.460(2) Å,[46] but is typical for Ga–P bond distances found in complexes with higher Lewis acidity at the gallium centre such as in the monochlorogallane complex [GaH$_2$Cl{P(C$_6$H$_{11}$)$_3$}], 2.403(4) Å.[47]

The Te–Ga–Te bond angles are quite varied at 102.46(5), 106.96(8) and 119.66(7)°, with the largest, Te(1)–Ga–Te(3), having the phenyl substituent on Te(3) orientated towards the Te(1) group, Fig. 3. The average of these angles, 109.7°, is smaller than the narrower range of the corresponding angles in the trimethylamine analogue, 111.74(3)–112.66(3)°. The larger range of bond distances in the phosphine adduct can be attributed to the bulky nature of P(C$_6$H$_{11}$)$_3$ resulting in different orientations of the phenyl substituents on the tellurium centres. The P–Ga–Te bond angles are also varied at 102.3(1), 110.7(1) and 114.13(9)°, the latter associated with Te(1) which has its phenyl substituent orientated away from the Te(3) plane to alleviate steric congestion within the molecule [*e.g.* the P–Ga–Te(1)–C(11) dihedral angle is −174.1(3)°]. Overall the gallium has an unsymmetrically distorted tetrahedral geometry.

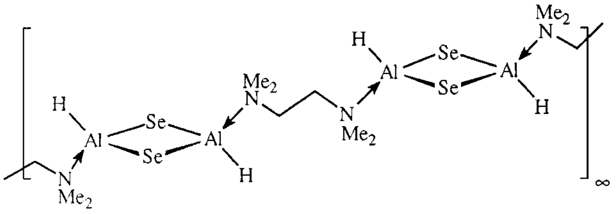
The Ga–Te–C angles in [Ga(TePh)$_3${P(C$_6$H$_{11}$)$_3$}], 97.0(4), 109.0(5) and 110.0(3)°, are significantly larger than those found in the trimethylamine adduct, 96.8(1)–97.6(1)°, again most likely due to the larger steric interactions within the molecule. The smallest, 97.0(4)°, is associated with the tellurolate ligand which deviates most from the approximately C_3 symmetry of the molecule, and is intuitively the angle closest to those in the related, less strained, trimethylamine analogue.

Dinuclear selenido- and tellurido-complexes

The starting complexes here are *trans*-[{AlH(μ-E)(NMe$_3$)}$_2$], E = Se or Te, which are prepared from the reaction of [AlH$_3$(NMe$_3$)] with an excess of elemental selenium or tellurium powder.[17] The related chlorogallium selenido complex *trans*-[{GaCl(μ-Se)[P(C$_6$H$_{11}$)$_3$]}$_2$], Scheme 1, was prepared as a minor product in the reaction of [GaH$_2$Cl{P(C$_6$H$_{11}$)$_3$}] and Li$_2$Se. An interesting aspect of this reaction is the preferential elimination of LiH rather than of LiCl, although elimination of LiH has previously been observed in the formation of the phosphine adducts of gallane, [GaH$_3${P(C$_6$H$_{11}$)$_3$}] and [(GaH$_3$)$_2${(CH$_2$PMe$_2$)$_2$}] from the treatment of LiGaH$_4$ with P(C$_6$H$_{11}$)$_3$ and (CH$_2$PMe$_2$)$_2$, respectively,[46] and in the synthesis of [Ga(TePh)$_3${P(C$_6$H$_{11}$)$_3$}] (see above).

In the solid state, molecules of dinuclear [{GaCl(μ-Se)[P(C$_6$H$_{11}$)$_3$]}$_2$] are centrosymmetric and are thus in the *trans* arrangement, as for the aluminium chalcogenide complexes *trans*-[{AlH(μ-E)(NMe$_3$)}$_2$], E = Se or Te.[17] The central core has μ-bridging seleniums in a strictly planar Ga$_2$Se$_2$ ring, with distorted tetrahedral gallium centres. Only one related gallium selenido complex has been previously reported, *trans*-[{Ga(mes)(μ-Se)(NC$_5$H$_4$Me-4)}$_2$].[16] The formation of dimers in these complexes possessing Lewis base adducts contrasts with tetranuclear cubane structures for alkyl/cyclopentadienyl metal derivatives devoid of such bases,[19,21,24,40] and [{(η-C$_5$H$_5$)(OC)$_2$Fe(μ$_3$-E)Ga}$_4$] (E = S, Se or Te).[48]

Theoretical studies on [{AlH(μ$_3$-E)}$_2$] give an association energy to the Al/Se tetramer of −42.58 kJ mol^{-1} and formation of a Lewis base solvated dimer, *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$], from the unsolvated dimer has an association energy of −136.11 kJ mol^{-1}.[17] Co-ordinative saturation of a monomeric species [AlH(Se)(NMe$_3$)$_2$] is only 51.46 kJ mol^{-1} less stable than the formation of a Lewis base dimer and free amine. The anion [GaTe$_2${(CH$_2$NH$_2$)$_2$}$_2$]$^{-}$[29] with formal Ga=Te double bonds helps to support the feasibility of this type of structure. However, attempts to prepare Lewis base adducts of 'HAl=Se' were unsuccessful. Treating *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$] with tmen yielded a polymeric complex of composition [{[AlH(Se)]$_2$(tmen)}$_\infty$], Scheme 1. The same complex was also prepared by treating [{AlH$_3$(tmen)}$_\infty$] with elemental selenium in toluene at room temperature. It is only sparingly soluble in hydrocarbon solvents and is involatile *in vacuo*, and most likely has a polymeric structure with the tmen bridging metal centres from different dimers, in a similar mode to that found in the solid state structure of [{AlH$_3$(tmen)}$_\infty$].[49] The presence of Al–H was confirmed by IR [ν(Al–H) 1786 cm^{-1}]. The reaction of complex [{AlH(μ-Se)(NMe$_3$)}$_2$] and the tridentate ligand pmdien results in the formation of [Al$_4$H$_2$Se$_5$(NMe$_3$)$_4$] and possibly the ionic complex [{AlH$_2$ (pmdien)}$_2$Se].[18]



Treating [AlH$_3${P(C$_6$H$_{11}$)$_3$}] with elemental selenium and tellurium results in oxidation of the phosphine to (C$_4$H$_{11}$)$_3$P=E rather than forming the corresponding dimeric phosphine/hydride/selenide species, [{AlH(μ-Se)[P(C$_6$H$_{11}$)$_3$]}$_2$]. Attempts to synthesize dimeric species by treating [AlH$_2$Cl(NMe$_3$)] with elemental tellurium in a similar method to the synthesis of [{AlH(μ-Te)(NMe$_3$)}$_2$] gave an unidentifiable complex, containing Al–H bonds (IR), which decomposed to a black material on exposure to air. Similar reactions with Lewis base adducts of gallane failed to give the analogous gallium chalcogenide complexes. No reaction was evident between [GaH$_3$(NMe$_3$)] and excess of tellurium powder prior to the gallane decomposing. Using the more thermally robust Lewis base adducts of gallane, namely [GaH$_3$(quin)] (quin = quinuclidine) and [GaH$_3${NMe$_2$(CH$_2$Ph)}], also gave no reactions, even after heating in toluene. The gallane reagents were recovered in high yield. In addition, treating [GaH$_3${P(C$_6$H$_{11}$)$_3$}] with either selenium or tellurium powder also resulted in formation of (C$_6$H$_{11}$)$_3$P=E (E = Se or Te) as for reactions of [AlH$_3${P(C$_6$H$_{11}$)$_3$}].

The mixed chalcogen aluminium complexes [{Al(μ-Se)(EPh)(NMe$_3$)}$_2$], E = S, Se or Te, were prepared by treating *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$] with (EPh)$_2$ and are associated with cleavage of the E–E bonds and elimination of dihydrogen, Scheme 1. Colourless crystals of the sulfur and selenium compounds, and red crystals of the tellurium compound, were grown from toluene solutions on slow cooling to 4 °C, the latter being previously reported along with its crystal structure.[18] The structures of the sulfur and selenium compounds are reported herein. Interestingly (SPh)$_2$ is unreactive towards [AlH$_3$(NMe$_3$)]

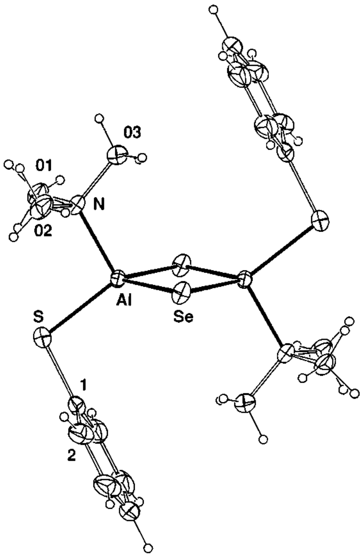


Fig. 4 Projection of *trans*-[{Al(μ-Se)(SPh)(NMe$_3$)}$_2$]. Selected bond distances (Å) and angles (°): Se–Al,Al′ 2.344(2), 2.340(2), Al–N,S 1.998(4), 2.243(2); Al–Se–Al′ 76.67(6), Se–Al–N,S,Se′ 108.3(1), 119.96(7), 103.33(6), N–Al–S, Se′ 98.7(1), 107.8(1), S–Al–Se′ 118.03(9), Al–N–C(01,02,03) 109.5(3), 111.5(3), 110.9(3), Al–S–C(1) 100.1(2). Values for *trans*-[{Al(μ-Se)(SePh)(NMe$_3$)}$_2$]: Se(1)–Al 2.344(4), Al–Se(2) 2.378(6) and Al–N(1) 2.01(2); Al–Se(1)–Al′ 76.7(2), C(1)–Se(2)–Al 96.3(6), N(1)–Al–Se(1) 108.8(3), Se(1)–Al–Se(1′) 103.3(2), N(1)–Al–Se(2) 99.3(5) and Se(1)–Al–Se(2) 118.0(2)

under the conditions studied (see above) yet reacts with *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$]. This is despite the Al–H bonds in the dimer being less polarised as judged by the difference in ν(Al–H) 1780 cm^{-1} for [AlH$_3$(NMe$_3$)] *cf.* 1805 cm^{-1} for the dimer.[17,50]

The compounds *trans*-[{Al(μ-Se)(EPh)(NMe$_3$)}$_2$], E = S, Se or Te, are air and moisture sensitive decomposing to brown solids. They have high thermal stability, being stable up to their melting points. They have been characterised using ^{1}H and ^{13}C NMR spectroscopy (although low solubility of the sulfur analogue precluded obtaining satisfactory ^{13}C NMR data), elemental microanalysis, and crystal structure determinations. Crystals of the sulfur compound were mounted under an atmosphere of argon and sealed in capillary tubes and the data collected at room temperature, whereas those of the selenium compound were coated in paraffin oil and the data collected at −100 °C. They are the first authenticated complexes which exhibit both bridging and terminally bound Group 16 moieties with a Group 13 : Group 16 element ratio of 1 : 2. The compounds with E = S or Te are the first mixed chalcogen aluminium complexes structurally elucidated where both chalcogen moieties are bound to aluminium, and the compound with E = Se is the first aluminium selenide complex where the Al : Se ratio is 1 : 2 and the complex exhibits both μ-bridging selenide groups and terminally bound selenolato moieties.

The compounds *trans*-[{Al(μ-Se)(EPh)(NMe$_3$)}$_2$], E = S or Se, are dimeric in the solid state, as is the tellurium analogue.[18] All complexes are centrosymmetric and thus the chalcogenolato substituents have *trans* arrangements with respect to each other, and the four-membered Al$_2$Se$_2$ ring core is strictly planar, Fig. 4. This type of arrangement is common within Group 13/Group 16 compounds, *e.g.* [{Ga(mes)(μ-Se)(NC$_5$H$_4$-Me-4)}$_2$][16] and [{AlBu$^t{}_2$(μ-TeBu^t)}$_2$].[21]

The compound *trans*-[{Al(μ-Se)(SPh)(NMe$_3$)}$_2$] is isostructural with *trans*-[{Al(μ-Se)(TePh)(NMe$_3$)}$_2$],[18] crystallising in space group $P2_1/c$ ($P2_1/n$). The molecules have crystallographic imposed inversion centres but they approximate to 2/*m* symmetry with the Se–Se vector defining the rotation axis. The compound *trans*-[{Al(μ-Se)(SePh)(NMe$_3$)}$_2$] crystallises as a toluene solvate in *C*2/*m* with the dimers now having crystallographically imposed 2/*m* symmetry. The toluene molecules are disordered over two sites across twofold rotation axes, each site with a 0.5 site occupancy.

The four-membered ring cores are planar, as found in the dimeric aluminium selenolate complex [{Al(mes)(μ-SeMe)}$_2$],[8] where there is a methyl group attached to selenium. However, the present complexes, along with *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$], are the only complexes with μ-Se bridging two aluminium centres which have been structurally authenticated.

The Al–(μ-Se) distances are uniform across the three complexes, 2.344(2) [2.340(2)], 2.344(4) [2.344(4)], and 2.347(2) [2.347(2)] Å for terminal S, Se, and Te, respectively, and thus the presence of different chalcogenolate ligands does not significantly influence the geometry of the four membered Al$_2$Se$_2$ cores. The distances are slightly shorter than the corresponding Al–Se distances, 2.359(2) Å, in *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$]. The Al–N distances are similar for the three complexes, 1.998(4), 2.01(2) and 1.998(5) Å, respectively, and comparable to the Al–N distance of 2.011(5) Å in *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$].

The Al–E (terminal) distances, 2.243(2), 2.378(6) and 2.610(2) Å, respectively, vary according to increasing covalent radii from sulfur to tellurium. The Al–S distance is longer than that in the monomeric three-co-ordinate aluminium complexes [Al{S(2,4,6-Bu$^t{}_3$C$_6$H$_2$)}$_3$] and [AlBu^n{S(2,4,6-Bu$^t{}_3$C$_6$H$_2$)}$_2$], 2.185(7) and 2.13(1) Å,[51] respectively, but shorter than those of the five-co-ordinate aluminium complex [AlH(SCH$_2$CH$_2$-NEt$_2$)$_2$], 2.271(1) and 2.278(1) Å.[52] It is also shorter than that in the four-co-ordinate dinuclear thiolato complex [{AlMe$_2$-(μ-SC$_6$F$_5$)}$_2$], 2.405(8) Å.[53] The Al–Se (terminal) distance in *trans*-[{Al(μ-Se)(SePh)(NMe$_3$)}$_2$] is significantly longer than the Al–Se distances in the Al$_2$Se$_2$ core, but comparable with the upper limit observed in [Al(SePh)$_3$(NMe$_3$)], and is considerably shorter than that in the dinuclear complex [{Al(mes)$_2$-(μ-SeMe)}$_2$], 2.519(2) Å.[8] The Al–Te (terminal) distance is slightly elongated compared to Al–Te in *trans*-[{AlH-(μ-Te)(NMe$_3$)}$_2$], 2.586(4) and 2.580(4) Å, and [Al(TePh)$_3$-(NMe$_3$)], 2.581(2)–2.589(2) Å, but shorter than in [{AlBu$^t{}_2$-(μ-TeBu^t)}$_2$], 2.732(3) Å.[21]

The (PhE)Al–Se–Al(EPh) angles, 76.67(6), 76.7(2) and 76.37(6)°, respectively for E = S, Se or Te are slightly smaller than that of the parent dimer *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$], 76.90(7)°. The μ-Se–Al–μ-Se angles, 103.33(6), 103.3(2) and 103.63(6)°, respectively, are correspondingly slightly larger than that of the parent dimer, 103.10(7)°. The μ-Se–Al–E angles are considerably larger than ideal tetrahedral values and decrease slightly in the series E = S, 119.6(7) and 118.03(9), Se, 118.0(2), and Te, 117.16(7) and 117.31(7)°. In the same series the Al–E′–C angles decrease, 100.1(2), 96.3(6) and 94.6(1)°, due to the increasing influence of the stereochemically active lone pair of electrons on the chalcogen centres. The Al–N–C angles are close to ideal tetrahedral values at 109.5(3)–111.5(3), 109.6(9) and 109.8(4)–110.2(4)°, respectively, and are slightly smaller than the corresponding angles in the parent dimer *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$], 113.0(4)°. All other bond distances, including S, Se, Te-C, and angles within the molecules are unexceptional.

Treatment of [{AlH(μ-Se)(NMe$_3$)}$_2$] with 2 equivalents of the secondary amines NH(SiMe$_3$)$_2$ or 6-methyl-2-trimethylsilylaminopyridine in toluene at room temperature results in metallation of the secondary amine to form the amidoaluminium selenide complexes [{Al(μ-Se)[N(SiMe$_3$)$_2$](NMe$_3$)}$_2$] and [{Al(μ-Se)(NC$_5$H$_3$NSiMe$_3$-2-Me-6)}$_2$], respectively, with the expulsion of dihydrogen, Scheme 1. Both complexes are air and moisture sensitive, decomposing to red material, and were isolated in modest to good yields. They were characterised by ^{1}H and ^{13}C NMR spectroscopy (a pure NMR sample was not obtained for the latter complex and a ^{13}C NMR spectrum could not be obtained), and by crystal structure determination for [{Al(μ-Se)[N(SiMe$_3$)$_2$](NMe$_3$)}$_2$].

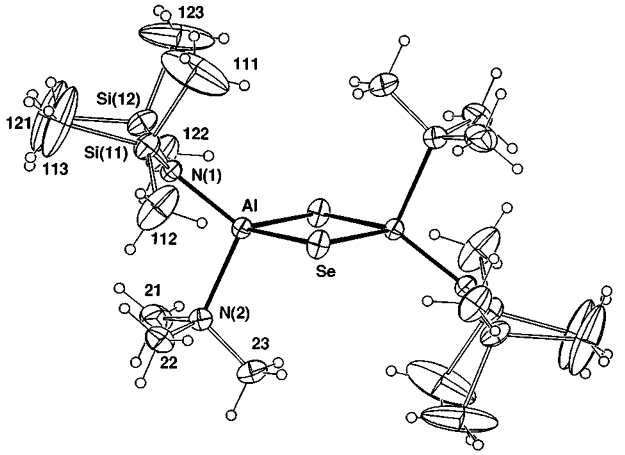


Fig. 5 Projection of *trans*-[{Al(μ-Se)[N(SiMe$_3$)$_2$](NMe$_3$)}$_2$]. Selected bond distances (Å) and angles (°): Se–Al,Al′ 2.357(1), 2.353(1), Al–N(1),N(2) 1.842(3), 2.033(3), N(1)–Si(11,12) 1.730(3), 1.740(4); Al–Se–Al′ 80.09(4), Se–Al–N(1,2),Se′ 119.6(1), 104.6(1), 99.91(5), N(1)–Al–N(2),Se′ 105.6(1), 120.7(1), N(2)–Al–Se′ 104.7(1), Al–N–Si(11,12) 120.2(2), 120.6(2), Al–N(2)–C(21,22,23) 110.9(3), 109.9(3), 112.1(3)

The complex crystallises from toluene in space group $P\bar{1}$ with the dinuclear molecules disposed about inversion centres, and the aluminium centres in distorted tetrahedral geometries, Fig. 5. The complex possesses non-crystallographic $2/m$ symmetry with the two selenium centres defining the quasi-C_2 rotation axis. The amide ligands are arranged *trans* with respect to each other and the four-membered Al_2Se_2 ring core, analogous to the parent compound [{AlH(μ-Se)(NMe$_3$)}$_2$],[17] and the above dimers. The compound [{Al(μ-Se)(NC$_5$H$_3$NSiMe$_3$-2-Me-6)}$_2$] is likely to have a similar dimeric structure, Scheme 1, with the N-donor groups of the amide displacing trimethylamine forming strained four-membered chelate rings for which there is precedence in some antimony and bismuth chemistry.[54]

The planar M_2Se_2 core of *trans*-[{Al(μ-Se)[N(SiMe$_3$)$_2$](NMe$_3$)}$_2$] is related to the analogous core of *trans*-[{Ga(mes)(μ-Se)(NC$_5$H$_3$Me-4)}$_2$],[16] as is the arrangement of donor ligands. The Al–Se distances, 2.357(1), 2.353(1) Å, are unchanged from those of the parent dimer *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$], 2.359(2), 2.359(2) Å, but are slightly longer than *trans*-[{Al(μ-Se)(EPh)(NMe$_3$)}$_2$] which range from 2.340(2) to 2.347(2) Å.

The Al–N (amido) distance, 1.842(3) Å, is comparable to that in [{AlMe$_2$[N(SiMe$_3$)$_2$]}$_2$(diox)] (diox = 1,4-dioxane), 1.848(8) Å,[55] and [AlH(Cl){N(SiMe$_3$)$_2$}(NMe$_3$)], 1.823(4) Å,[56] and as expected[57] is shorter than that in the amido-bridged complex [{Al(NMe$_2$)$_2$(μ-NMe$_2$)}$_2$], 1.959(2) and 1.980(2) Å.[58] The Al–N (amine) distance is considerably longer at 2.033(3) Å, and longer than in the parent complex, the above dinuclear compounds, and [AlH(Cl){N(SiMe$_3$)$_2$}(NMe$_3$)], 2.016(5) Å.[56] The N–Si distances [1.730(3), 1.740(4) Å] are comparable to those in other [bis(trimethylsilyl)amido]aluminium complexes such as [Al{N(SiMe$_3$)$_2$}$_3$], 1.75(1) Å,[59] [{AlMe$_2$[N(SiMe$_3$)$_2$]}$_2$(diox)], 1.715(8) Å,[57] and [AlH(Cl){N(SiMe$_3$)$_2$}(NMe$_3$)] 1.748(4), 1.731(4) Å.[56] Moreover they are longer than in the essentially ionic Group 1 metal amide complexes such as {Na[N(SiMe$_3$)$_2$]}$_\infty$, 1.687(2) and 1.694(2) Å.[60]

The Al–Se–Al angle, 80.09(4)°, and Se–Al–Se angle, 99.91(5)°, correspond to a diamond shaped ring core which is significantly different to that observed in the Al_2Se_2 ring core of the parent complex, *trans*-[{AlH(μ-Se)(NMe$_3$)}$_2$], Al–Se–Al and Se–Al–Se at 76.90(7) and 103.10(7)°,[17] and also the ring core in the above dinuclear complexes. This is likely to be due to the large steric hindrance around the aluminium centre imposed by N(SiMe$_3$)$_2$ which also manifests itself in the overall flattened tetrahedral geometry of the metal centres. The N (amine)–Al–Se and N (amine)–Al–N (amide) bond angles of 104.6(1) and 104.7(1) and 105.6(1)°, respectively, are close to tetrahedral values, N (amide)–Al–Se angles being much larger, 119.6(1) and 120.7(1)°.

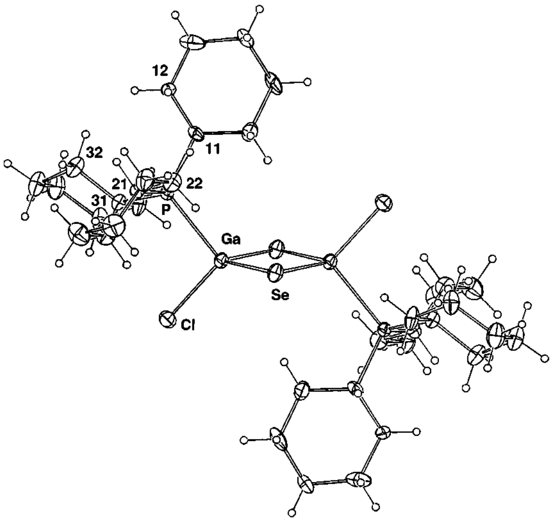


Fig. 6 Projection of *trans*-[{GaCl(μ-Se)[P(C$_6$H$_{11}$)$_3$]}$_2$]. Selected bond distances (Å) and angles (°): Se–Ga,Ga′ 2.365(2), 2.375(2), Ga–Cl,P 2.211(4), 2.418(4), P–C(11,12,13) 1.84(1), 1.84(1), 1.85(1); Ga–Se–Ga′ 77.06(6), Se–Ga–Cl,P,Se′ 114.2(1), 115.1(1), 102.94(7), Cl–Ga–P,Se′ 99.3(1), 114.3(1), P–Ga–Se′ 111.6(1), Ga–P–C(11,21,31) 113.3(4), 112.8(4), 105.8(4)

The compound *trans*-[{GaCl(μ-Se)[P(C$_6$H$_{11}$)$_3$]}$_2$] crystallises as yellow prisms from toluene in space group $P\bar{1}$, with the centrosymmetric molecules disposed about inversion centres, and with a planar four-membered Ga_2Se_2 ring core as for the above dinuclear species, Fig. 6. A toluene of crystallisation is disordered over inversion centres, over two sites of equal population. The complex approximates to $2/m$ symmetry with the rotation axis passing through the two selenium centres.

The complex is best described as a tricyclohexylphosphine Lewis base stabilised chloro, selenide-bridged gallium(III) species with the metal centres in distorted tetrahedral geometries. The selenium atoms are μ-bridging two gallium centres and only one such gallium complex has been reported, *viz*. [{Ga(mes)(μ-Se)(NC$_5$H$_4$Me-4)}$_2$],[16] which has similar Ga–Se distances to these in the present structure, 2.3872(13) and 2.3784(12) Å,[51] *cf*. 2.635(2) and 2.375(2) Å. As expected these are shorter than in the triply bridged system [{Ga(η-C$_5$Me$_5$)(μ_3-Se)}$_4$], 2.4454(8)–2.4992(8) Å.[23] The selenolate-bridged dinuclear complex [Ga{Ph$_2$(μ-SeMe)}$_2$][8] also has Ga–Se distances considerably longer, as expected, at 2.493(1) and 2.509(1) Å.[8] However, the Ga–Se bond distances in [{(Me$_3$Si)$_2$CH}$_2$Ga(μ-Se)Ga{CH(SiMe$_3$)$_2$}$_2$], 2.3439(5) Å,[15] are significantly shorter than in the present structure, which may be related to the absence of strain associated with a Ga_2Se_2 ring core in [{(Me$_3$Si)$_2$CH}$_2$Ga(μ-Se)Ga{CH(SiMe$_3$)$_2$}$_2$].

The Se–Ga–Se angle, 102.94(7)°, compares with 100.13(4)° in {Ga(mes)(μ-Se)(NC$_5$H$_4$Me-4)}$_2$];[16] the associated Ga–Se–Ga′ angles are 76.06(6) and 79.87(4)° respectively. The Se–Ga–Se and Ga–Se–Ga angles in [{GaPh$_2$(μ-SeMe)}$_2$] are 96.93(2) and 83.07(2)°,[8] respectively, giving a more nearly square four-membered ring core. In the less strained complex [{(Me$_3$Si)$_2$CH}$_2$Ga(μ-Se)Ga{CH(SiMe$_3$)$_2$}$_2$] the Ga–Se–Ga angle is 113.45(3)°.[15] The Cl–Ga–Se and P–Ga–Se angles in the present compound are more open at 114.2(1) and 114.3(1) and 115.1(1) and 111.6(1)°, respectively, but the Cl–Ga–P bond angle is smaller at 99.3(1)°. All other bond distances, including Ga–Cl and Ga–P, and angles within the molecule are unexceptional.

Conclusion

We have shown that Lewis base adducts of alane and gallane are useful reagents for a one step synthesis of tris(chalcogenolato)-complexes of the two metals, *via* reductive cleavage of $(ER)_2$. The reactions of *trans*-[{AlH(μ-Se)(NMe_3)}$_2$] with $(ER)_2$, also reductive cleavages, represent a simple route to mixed chalcogen containing species, with the integrity of the dinuclear core maintained. This offers scope for the synthesis of a wide range of mixed chalcogenides. In addition we have shown that *trans*-[{AlH(μ-Se)(NMe_3)}$_2$] is a useful reagent for building up novel mixed amido/chalcogenide species and the simple metallation reaction has potential for generating other mixed anionic ligand/chalcogenide species.

Experimental

General procedure

Preparative work was routinely carried out under an atmosphere of high purity argon. Proton spectra were recorded on Varian Gemini 200 and Mercury spectrometers operating at 200 and 300 MHz, respectively, or on Bruker AC200 and AM300 spectrometer operating at 200 and 300 MHz, respectively, ^{13}C NMR spectra on the same spectrometers operating at 50.3 and 75.7 MHz, using broad band decoupling or DEPT pulse sequences, and ^{31}P NMR spectra on a Varian Gemini spectrometer operating at 81.0 MHz or a Bruker AM300 spectrometer operating at 121.5 MHz. Elemental analyses were performed by Chemical and Microanalytical Services Pty, Ltd. (CMAS), Melbourne. Melting points were determined in sealed glass capillaries under argon or *in vacuo*, where appropriate, and are uncorrected.

Materials

Tetrahydrofuran, toluene, hexane, and diethyl ether were refluxed over sodium wire or Na/K alloy. Benzene was refluxed over sodium wire. All solvents were freshly distilled, freeze-degassed prior to use and stored over a potassium mirror. Selenium and tellurium powder, diphenyl ditelluride, diphenyl diselenide, diphenyl disulfide, dibenzyl diselenide, dibenzyl disulfide, tricyclohexylphosphine, lithium aluminium hydride, gallium chloride, lithium hydride, bis(trimethylsilyl)amine, tmen and pmdien were from Aldrich; tmen was purified and dried by distillation over sodium wire before use. Other reagents were used as received. The compounds [Al(SePh)$_2$(NMe_3)],[9] *trans*-[{AlH(μ-E)(NMe_3)}$_2$], E = Se or Te,[17] (trimethylamine)alane,[61] lithium gallium hydride and (trimethylamine)gallane,[62] tricyclohexylphosphine alane,[63] (tricyclohexylphosphine)gallane,[46] (tricyclohexylphosphine)gallane monochloride,[47] 6-methyl-2-trimethylsilylaminopyridine[64] and Li_2Se[65] were prepared using variations of the literature procedures.

Syntheses

[Ga(TePh)$_3$(NMe_3)]. A red solution of $(TePh)_2$ (0.60 g, 1.47 mmol) in diethyl ether (*ca.* 10 cm^3) was slowly added to a stirred solution of [GaH_3(NMe_3)] (0.13 g, 0.99 mmol) in diethyl ether (*ca.* 20 cm^3) at 25 °C. Slight gas evolution was observed upon addition. The red mixture was stirred for 14 h whereupon it was filtered and the solvent removed *in vacuo*. Recrystallisation from diethyl ether (*ca.* 10 cm^3) at 4 °C afforded yellow crystals (0.72 g, 62%), m.p. decomp. > 101 °C (Found: C, 35.18; H, 3.66; N, 1.78. Calc. for $C_{21}H_{24}GaNTe_3$: C, 33.95; H, 3.26; N, 1.89%). ^1H NMR (300 MHz, C_6D_6, 25 °C); δ 7.65 (6 H, m, OH of C_6H_5), 6.83 (9 H, m, *m*- and *p*-H of C_6H_5) and 2.05 (9 H, s, NCH_3). ^{13}C NMR (75.4 MHz, C_6D_6, 25 °C): δ 141.7, 137.8, 129.2, 108.3 (C_6H_5) 47.9 (NCH_3).

[Ga(SeEt)$_3$(NMe_3)]. Orange $(SeEt)_2$ (0.38 cm^3, 1.76 mmol) was syringed dropwise into a colourless solution of [GaH_3(NMe_3)] (0.16 g, 1.21 mmol) in toluene (*ca.* 30 cm^3) at room temperature. Slight gas evolution was observed upon addition. The mixture was stirred for 16 h whereupon it was filtered and the solvent removed *in vacuo*. Recrystallisation from toluene (*ca.* 10 cm^3) at 4 °C afforded pale yellow crystals (0.23 g, 66%), m.p. 90–91 °C (Found: C, 23.77; H, 5.42; N, 3.02. Calc. for $C_9H_{24}GaNSe$: C, 23.87; H, 5.34; N, 3.09%). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 2.83 (6 H, q, $^3J_{HH}$ 7.4, CH_2), 1.96 (9 H, s, NCH_3) and 1.52 (9 H, t, $^3J_{HH}$ 7.4 Hz, CH_3). ^{13}C NMR (50.3 MHz, C_6D_6, 25 °C): δ 46.9 (NCH_3), 20.2 (CH_2) and 14.3 (CH_3).

[Ga(TePh)$_3${P(C_6H_{11})$_3$}]. A red solution of $(TePh)_2$ (0.36 g, 0.89 mmol) in toluene (*ca.* 20 cm^3) was slowly added to a stirred solution of [GaH_3{P(C_6H_{11})$_3$}] (0.21 g, 0.60 mmol) in diethyl ether (*ca.* 20 cm^3) at room temperature. The red mixture was stirred for 11 h whereupon it was filtered and the solvent removed *in vacuo*. Recrystallisation from diethyl ether (*ca.* 10 cm^3) at −30 °C afforded yellow crystals (0.30 g, 52%), m.p. > 100 °C (decomp.) (Found: C, 44.08; H, 6.17; P, 3.35. Calc. for $C_{36}H_{48}GaPTe_3$: C, 44.84; H, 5.02; P, 3.21%). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 8.12–8.08 (6 H, m, *o*-H of C_6H_5), 7.17–6.90 (9 H, m, *m*- and *p*-H of C_6H_5) and 1.82–0.83 (33 H, m, PC_6H_{11}). ^{13}C NMR (50.3 MHz, C_6D_6, 25 °C): δ 141.3, 129.0, 129.0 (d, *J* = 4.02), 126.7 (d, *J* = 5.48 Hz), 125.6 (C_6H_5), 39.2, 35.1, 34.0, 28.8–25.8 (m) and 21.4 (C_6H_{11}). ^{31}P NMR (121.5 MHz, C_6D_6, 25 °C): δ 68.6.

[{GaCl(μ-Se)[P(C_6H_{11})$_3$]}$_2$]. Superhydride ($LiBHEt_3$) (2.55 cm^3 of a 1.0 M solution in thf, 2.55 mmol) was added to a slurry of selenium powder (0.48 g, 6.08 mmol) in toluene (*ca.* 10^3) at room temperature. A white precipitate formed upon addition. The reaction mixture was allowed to stir at room temperature for 30 min. To this was added a solution of [GaH_2Cl{P(C_6H_{11})$_3$}] (0.92 g, 2.37 mmol) in toluene (*ca.* 20 cm^3) at room temperature. The reaction mixture was allowed to stir for 17 h at room temperature. The resulting yellow solution was filtered leaving a white precipitate when the solvent volume was reduced *in vacuo* (*ca.* 15 cm^3). Recrystallisation from toluene (*ca.* 5 cm^3) at −30 °C afforded a yellow prismatic crystal of [{GaCl(μ-Se)[P(C_6H_{11})$_3$]}$_2$] as a minor product.

[{Al(μ-Se)(SPh)(NMe_3)}$_2$]. A colourless solution of $(SPh)_2$ (0.53 g, 2.43 mmol) in toluene (*ca.* 10 cm^3) was added to a colourless solution of [{AlH(μ-Se)(NMe_3)}$_2$] (0.80 g, 2.41 mmol) in toluene (*ca.* 30 cm^3) at room temperature. Gas evolution was observed. The resulting white solution was allowed to stir for 17 h whereupon it was filtered. Recrystallisation from toluene (*ca.* 15 cm^3) afforded colourless crystals (0.71 g, 54%). m.p. 235–238 °C (Found: C, 39.33; H, 5.13; N, 5.46. Calc. for $C_9H_{14}AlNSSe$: C, 39.42; H, 5.15; N, 5.11%). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 7.03 (10 H, m, C_6H_5) and 2.08 (s, NCH_3).

[{Al(μ-Se)(SePh)(NMe_3)}$_2$]. A yellow solution of $(SePh)_2$ (0.57 g, 1.83 mmol) in toluene (*ca.* 10 cm^3) was added to a colourless solution of [{AlH(μ-Se)(NMe_3)}$_2$] (0.61 g, 1.84 mmol) in toluene (*ca.* 30 cm^3) at room temperature. Gas evolution was observed. The resulting colourless solution was allowed to stir for 17 h whereupon it was filtered. Recrystallisation from toluene (*ca.* 15 cm^3) afforded colourless crystals (0.30 g, 26%). m.p. 211–213 °C (Found: C, 36.54; H, 5.06; N, 4.20. Calc. for $C_{18}H_{28}Al_2N_2Se_4 \cdot 0.5C_7H_8$: C, 37.52; H, 4.69; N, 4.07%). ^1H NMR (200 MHz, C_6D_6, 25 °C): δ 8.10–8.05 (2 H, m, C_6H_5), 7.04–6.93 (3 H, m, C_6H_5) and 2.04 (9 H, s, NCH_3); ^{13}C NMR (50.3 MHz, C_6D_6, 25 °C): δ 134.0, 131.7, 129.4, 128.9, 125.8 (C_6H_5) and 47.3 (NCH_3).

[{AlH(μ-Se)(tmen)}$_\infty$]. The compound tmen (0.30 cm^3, 1.96 mmol) was added dropwise to a colourless solution of [{AlH-

Table 1 Crystal data and details of the data collection and structure refinement for [Al(SePh)$_3$(NMe$_3$)] **1**, [Ga(TePh)$_3$(NMe$_3$)] **2**, [Ga(TePh)$_3${P(C$_6$H$_{11}$)$_3$}] **3**, *trans*-[{Al(μ-Se)(SPh)(NMe$_3$)}$_2$] **4**, *trans*-[{Al(μ-Se)(SePh)(NMe$_3$)}$_2$] **5**, *trans*-[{Al(μ-Se)[N(SiMe$_3$)$_2$](NMe$_3$)}$_2$] **6** and *trans*-[{Ga(Cl)(μ-Se)[P(C$_6$H$_{11}$)$_3$]}$_2$] **7***

	1	**2**	**3**	**4**	**5**·2C$_6$H$_5$Me	**6**	**7**·C$_6$H$_5$Me
Formula	$C_{21}H_{24}AlNSe_3$	$C_{21}H_{24}GaNTe_3$	$C_{36}H_{48}GaPTe_3$	$C_{18}H_{28}Al_2N_2S_2Se_2$	$C_{32}H_{44}Al_2N_2Se_4$	$C_{18}H_{54}Al_2N_4Se_2Si_2$	$C_{43}H_{74}Cl_2Ga_2P_2Se_2$
M	554.3	743.0	964.3	548.5	826.5	650.9	1021.3
Crystal system	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Triclinic	Triclinic
Space group	*Cc* (no. 9)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$P2_1/c$ (no. 14)	$C2/m$ (no.12)	$P\bar{1}$ (no. 2)	$P\bar{1}$ (no. 2)
a/Å	10.966(2)	7.317(2)	9.928(3)	9.507(4)	16.37(1)	12.458(1)	14.891(3)
b/Å	18.973(4)	13.948(5)	33.933(9)	10.596(4)	10.461(9)	9.120(1)	9.761(5)
c/Å	11.300(8)	24.215(6)	12.655(2)	12.111(4)	10.447(8)	8.543(1)	8.562(2)
α/°						66.23(1)	76.04(3)
β/°	99.02(4)	91.06(2)	120.88(2)	100.29(3)	93.38(7)	72.87(1)	84.07(2)
γ/°						85.73(1)	84.15(3)
U/Å^3	2322(2)	2471(1)	3659(2)	1200.3(7)	1786(2)	847.8(2)	1197.4(8)
Crystal size/mm	0.48 × 0.40 × 0.21	0.45 × 0.37 × 0.24	0.32 × 0.13 × 0.34	0.12 × 0.60 × 0.40	0.25 × 0.20 × 0.15	0.074 × 0.25 × 0.48	0.08 × 0.18 × 0.30
D_c/g cm^{-3}	1.58_5	1.99_7	1.75_0	1.51_7	1.53_6	1.27_5	1.41_6
Z	4	4	4	2	2	1	1
μ/cm^{-1}	48.0	45.9	31.6	33.3	41.2	23.9	28.5
$A^*_{\mathrm{(min,max)}}$	2.29, 4.07	2.28, 3.01	1.59, 2.32	1.47, 2.54	—	1.19, 1.75	1.25, 2.03
$2\theta_{\mathrm{max}}$/°	50	55	50	50	45	65	50
No. unique reflections	2042	5665	6328	2106	1264	5051	4220
No. observed data	1165	3705	3714	1477	748	2941	1858
R	0.064	0.031	0.061	0.036	0.065	0.042	0.059
R'	0.060	0.032	0.064	0.038	0.117	0.045	0.054

* Data collected at *ca*. 297 K on a ENRAF-Nonius CAD 4 or at *ca*. 100 K on a Nicolet R3m/V diffractometer (compound **5** only); graphite-monochromated Mo-Kα radiation ($\lambda = 0.7107_3$ Å); statistical weights; anisotropic thermal parameters refined for all non-hydrogen atoms, C(1) for **1** excepted, for absorption corrected ‘observed’ data, with $I > 3\sigma(I)$ [$2\sigma(I)$, **5**]; hydrogen atoms were inserted at calculated positions and constrained, with isotropic thermal parameters at $1.25U_{\mathrm{eq}}$ of the attached carbon; R, R' for other hand for **1** 0.067, 0.064; for **5** and **7** toluene molecules are disordered about twofold rotation axes and inversion centres respectively.

(μ-Se)(NMe$_3$)}$_2$] (0.65 g, 1.96 mmol) in toluene (*ca.* 60 cm^3) at room temperature. A white precipitate started forming upon addition. The cloudy reaction mixture was allowed to stir for 12 h at room temperature whereupon it was filtered leaving a white insoluble product (0.53 g, 82%). m.p. > 350 °C (Found: C, 21.89; H, 5.21; N, 8.27. Calc. for C_3H_9AlNSe: C, 21.83; H, 5.50; N, 8.49%). ν(Al–H) 1786 cm^{-1}.

[{Al(μ-Se)[N(SiMe$_3$)$_2$](NMe$_3$)}$_2$]. A solution of NH(SiMe$_3$)$_2$ (0.45 g, 2.8 mmol) in toluene (*ca.* 10 cm^3) was added to a colourless solution of [{AlH(μ-Se)(NMe$_3$)}$_2$] (0.46 g, 1.4 mmol) in toluene (*ca.* 30 cm^3) at room temperature. Gas evolution was observed. The resulting colourless solution was allowed to stir for 11 h whereupon it was filtered. Recrystallisation from toluene (*ca.* 10 cm^3) afforded colourless needles (0.36 g, 40%), m.p. > 300 °C (Found: C, 34.97; H, 8.23; N, 8.71. Calc. for $C_9H_{27}AlN_2SeSi$: C, 36.35; H, 9.15; N, 9.42%). ^{1}H NMR (200 MHz, C_6D_6, 25 °C): δ 2.25 (18 H, s, NMe) and 0.52 (36 H, s, SiCH$_3$). ^{13}C NMR (50.3 MHz, C_6D_6, 25 °C): δ 46.5 (NCH$_3$) and 2.1 (SiCH$_3$).

[{Al(μ-Se)(NC$_5$H$_3$NSiMe$_3$-2-Me-6)}$_2$]. A solution of 6-methyl-2-trimethylsilylaminopyridine (0.28 g, 1.55 mmol) in toluene (*ca.* 5 cm^3) was added dropwise to a solution of [{AlH(μ-Se)(NMe$_3$)}$_2$] (0.26 g, 0.78 mmol) in toluene (*ca.* 30 cm^3) at room temperature. Gas evolution was observed and a white precipitate gradually formed. The resulting cloudy reaction mixture was allowed to stir for 16 h whereupon the colourless solution was filtered and the toluene removed *in vacuo* affording a white powder which was washed with hexane and dried (0.27 g, 49%) m.p. > 160 °C (decomp.) (Found: C, 37.50; H, 5.45; N, 9.56. Calc. for $C_{15}H_9AlN_2SeSi$: C, 37.90; H, 5.30; N, 9.82%). ^{1}H NMR (major component) (200 MHz, C_6D_6, 25 °C): δ 7.05–5.70 (m, 3 H, C_6H_5N), 2.03 (s, 3 H, CH$_3$) and 0.30 (s, 9 H, SiCH$_3$).

Crystallography

Suitable crystals were sealed in capillaries under argon. Crystallographic data are summarised in Table 1. Refinements were carried out using XTAL,[66] SHELXS and SHELXL[67] program systems.

CCDC reference number 186/1026.

See http://www.rsc.org/suppdata/dt/1998/2547/ for crystallographic files in .cif format.

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References

1 T. Inoue, N. Kambe, I. Ryu and N. Sonoda, *J. Org. Chem.*, 1994, **59**, 8209.

2 T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *J. Org. Chem.*, 1994, **59**, 5824.

3 T. Inoue, T. Takeda, N. Kambe, A. Ogawa, I. Ryu and N. Sonoda, *Organometallics*, 1994, **13**, 4543.

4 Brown and Davidson, *J. Am. Chem. Soc.*, 1942, **64**, 316.

5 G. E. Coates, *J. Chem. Soc.*, 1951, 2003.

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

7 S. P. Wuller, A. L. P. Seligson and G. Arnold, *Inorg. Chem.*, 1995, **34**, 4854.

8 R. Kumar, D. G. Dick, S. U. Ghazi, M. Taghiof, M. J. Heeg and J. P. Oliver, *Organometallics*, 1995, **14**, 1601.

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

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

11 W. Uhl, A. Vester and W. Hiller, *J. Organomet. Chem.*, 1993, **443**, 9.

12 W. Uhl and U. Schütz, *Z. Naturforsch., Teil B*, 1994, **49**, 931.

13 W. Uhl, U. Schütz, W. Hiller and M. Heckel, *Organometallics*, 1995, **14**, 1073.

14 W. Uhl, R. Graupner and H. Reuter, *J. Organomet. Chem.*, 1996, **523**, 227.

15 W. Uhl, R. Gerding, I. Hahn, S. Pohl, W. Saak and H. Reuter, *Polyhedron*, 1996, **15**, 3987.

16 H. Rahbarnoohi, R. L. Wells, L. M. Liable-Sands, G. P. A. Yap and A. L. Rheingold, *Organometallics*, 1997, **16**, 3959.

17 M. G. Gardiner, C. L. Raston and V.-A. Tolhurst, *J. Chem. Soc., Chem. Commun.*, 1995, 2501.

18 P. D. Godfrey, C. L. Raston, B. W. Skelton, V.-A. Tolhurst and A. H. White, *Chem. Commun.*, 1997, 2235.

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

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

21 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.

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

23 S. Schulz, E. G. Gillan, J. L. Ross, L. M. Rodgers, R. D. Rodgers and A. R. Barron, *Organometallics*, 1996, **15**, 4880.

24 C. J. Harlan, E. G. Gillian, S. G. Bott and A. R. Barron, *Organometallics*, 1996, **15**, 5479.

25 M. B. Power, J. W. Ziller and A. R. Barron, *Organometallics*, 1992, **11**, 2783.

26 R. J. Wehmschulte and P. P. Power, *J. Am. Chem. Soc.*, 1997, **119**, 9566.

27 J. L. Atwood and S. K. Seale, *J. Organomet. Chem.*, 1976, **114**, 107.

28 H. v. Dahlen and K. Dehnicke, *Chem. Ber.*, 1977, **110**, 383.

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

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

31 A. R. Barron, *J. Chem. Soc., Dalton Trans.*, 1988, 3047.

32 J. L. Atwood, K. W. Butz, M. G. Gardiner, C. Jones, G. A. Koutsantonis, C. L. Raston and K. D. Robinson, *Inorg. Chem.*, 1993, 3482.

33 E. Hanecker, H. Nöth and U. Wietelmann, *Chem. Ber.*, 1986, **119**, 1904.

34 G. Yagupsky, W. Mowart, A. Shortland and G. Wilkinson, *Chem. Commun.*, 1970, 1369.

35 H. Horn, F. Rudolph, R. Ahlrichs and K. Merzweiler, *Z. Naturforsch., Teil B*, 1992, **47**, 1.

36 R. Kumar, H. E. Mabrouk and D. G. Tuck, *J. Chem. Soc., Dalton Trans.*, 1988, 1045.

37 T. A. Annan, R. Kumar, H. E. Marbrouk and D. G. Tuck, *Polyhedron*, 1989, **7**, 865.

38 V. A. Schneider and G. Gattow, *Z. Anorg. Allg. Chem.*, 1954, **277**, 49.

39 M. Julien-Pouzol, S. Jaulmes and F. Alapini, *Acta Crystallogr., Sect B*, 1977, **33**, 2270.

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

41 D. F. Grant, R. C. G. Killean and J. L. Lawrence, *Acta Crystallogr., Sect. B*, 1969, **25**, 377.

42 C. D. Whitt, L. M. Parker and J. L. Atwood, *J. Organomet. Chem.*, 1971, **32**, 291.

43 H. Schumann, T. D. Seuss, O. Just, R. Weimann and H. Hemling, *J. Organomet. Chem.*, 1994, **479**, 171.

44 H. S. Isom, A. H. Cowley, A. Decken, F. Sissingh, S. Corbelin and R. J. Lagow, *Organometallics*, 1995, **14**, 2400.

45 J. L. Atwood, S. G. Bott, F. M. Elms, C. Jones and C. L. Raston, *Inorg. Chem.*, 1991, **30**, 3792.

46 J. L. Atwood, K. D. Robinson, F. R. Bennett, F. M. Elms, G. A. Koutsantonis, C. L. Raston and D. J. Young, *Inorg. Chem.*, 1992, **31**, 2673.

47 F. M. Elms, G. A. Koutsantonis and C. L. Raston, *J. Chem. Soc., Chem. Commun.*, 1995, 1669.

48 U. App and K. Merzweiler, *Z. Anorg. Allg. Chem.*, 1997, **623**, 478.

49 C. Jones, Ph.D. Thesis, Griffith University, 1992.

50 H. Roszinski, R. Dautel and W. Zeil, *Z. Phys. Chem. Neue Folge*, 1963, **36**, 26.

51 K. Ruhlandt-Senge and P. P. Power, *Inorg. Chem.*, 1991, **30**, 2633.

52 C. Jones, F. Lee, G. A. Koutsantonis, M. G. Gardiner and C. L. Raston, *J. Chem. Soc., Dalton Trans.*, 1996, 829.

53 V. S. J. De Mel, R. Kumar and J. P. Oliver, *Organometallics*, 1990, **9**, 1303.

54 C. L. Raston, B. W. Skelton, V.-A. Tolhurst and A. H. White, *Polyhedron*, 1998, **17**, 935.

55 T. Her, C. Chang, S. Peng and Y. Wang, *Inorg. Chem.*, 1994, **33**, 99.

56 M. G. Gardiner, G. A. Koutsantonis, S. M. Lawrence, F. Lee and C. L. Raston, *Chem. Ber.*, 1996, **129**, 545.

57 J. J. Byers, W. T. Pennington and G. H. Robinson, *Polyhedron*, 1990, **9**, 2205.

58 K. von Ouzounis, H. Riffel, H. Hess, U. Kohler and J. Weidlein, *Z. Anorg. Allg. Chem.*, 1983, **504**, 67.

59 G. M. Sheldrick and W. S. Sheldrick, *J. Chem. Soc. A*, 1969, 2279.

60 R. Grüning and J. L. Atwood, *J. Organomet. Chem.*, 1977, **137**, 101.

61 J. K. Ruff and M. F. Hawthorne, *J. Am. Chem. Soc.*, 1960, **82**, 2141.

62 C. A. Grob, A. Kaiser and E. Renk, *Chem. Ind.*, 1957, 598.

63 F. R. Bennett, F. M. Elms, M. G. Gardiner, G. A. Koutsantonis, C. L. Raston and N. K. Roberts, *Organometallics*, 1992, **11**, 1457.

64 L. M. Engelhardt, G. E. Jacobsen, P. C. Junk, C. L. Raston, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1988, 1011.

65 J. A. Gladysz, J. L. Hornby and J. E. Garbe, *J. Org. Chem.*, 1978, **43**, 1204.

66 S. R. Hall, H. D. Flack and J. M. Stewart, *The XTAL 3.2 Reference Manual*, Universities of Western Australia, Geneva and Maryland, 1992.

67 G. M. Sheldrick, SHELXS 86 and SHELXL 93, Programs for crystal structure solution and refinement, University of Göttingen, 1986 and 1993.

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