Journal of Organometallic Chemistry, 475 (1994) 15–24

Invited Lecture

Recent developments in the chemistry of alane (AlH_3) and gallane (GaH_3) *

Colin L. Raston

Faculty of Science and Technology, Griffith University, Nathan, Qld. 4111 (Australia)

(Received January 11, 1994)

Key words: Aluminium; Gallium; Alane; Gallane; Hydride

1. Introduction

There has been a recent resurgence of interest in the chemistry of alane and gallane. This is due mainly to the potential application of volatile, Lewis base adducts in chemical vapour deposition (= CVD) technology, related materials science, synthesis [1–11], and the novelty of their structures [12,13]. The advantages of these adducts in CVD over conventional group 13 alkyl compounds includes the ease of cleavage of M–H bonds relative to M–C bonds [9] resulting in a reduction in the amount of carbonaceous material in the metal deposit. Research at Griffith University and in collaboration with Atwood *et al.* at the University of Alabama, and Lamb *et al.* at the University of New South Wales, constitutes an integrated study of Lewis base adducts of alane and gallane involving synthetic strategies coupled with structural elucidation and theoretical considerations. Applications include CVD, surface modification of oxidised silicon, and the utility of these adducts in synthesis [3,14–27].

Relevant pioneering structural elucidations include the characterisation of polymeric alane [28], polymeric $H_3Al(TMEDA)$ (TMEDA = tetramethylethylenediamine) [29], and H_3MNMe_3 (M = Al, Ga (gas phase)) [30,31]. More recent structural contributions from other groups include dimeric $[H_2Al(\mu\text{-}H)(THF)]_2$ and monomeric $H_3Al(THF)_2$ [12], a carbene adduct of alane [13], and dimeric gallane (gas phase) [32] which is structurally analogous to diborane. Indeed, aspects of the chemistry of gallane are more akin to the chemistry of borane. This is related to the periodic anomaly for the Group 13 elements, notably the increase in electronegativity of gallium over aluminium (1.8 Ga, 1.5 Al, *cf.* 2.0 B, Allred Rochow), and the associated lower polarising influence of gallium. Differences between the chemistry of alane and gallane also relate to the back-bonding of the d^{10} core for gallium, the frailty of the Ga–H bonds relative to Al–H bonds, and the stronger tendency of aluminium to form hyper-valent structures compared with gallium, *viz.* greater than four fold coordination.

2. Synthesis, structure, stability and theoretical studies

The synthesis of adducts of alane and gallane can be achieved by (i) the reaction of an amine hydrochloride or a 1:1 mixture of Lewis base and HCl with $LiMH_4$, or (ii) ligand displacement reactions whereby Lewis base adducts such as readily available H_3MNMe_3 are treated with other Lewis bases, resulting in metathetical exchange. In the case of gallium, the treatment of $LiGaH_4$ with tertiary phosphines can result in the elimination of LiH and concomitant formation of the phosphine adduct [21]. For alane a range of structural types have been identified in the solid state, with representatives illustrated in Fig. 1. The dimeric species have unsymmetrical bridging hydrides, for example in the dimethylbenzyl amine adduct, depicted in Fig. 2. These species can be viewed as tertiary amine stabilised adducts of dialane. It is noteworthy that borane and gallane form symmetrical hydride bridged structures, albeit unsolvated by Lewis bases. The THF adduct of alane is also an unsymmetrical hydride bridged dimer, and a monomeric bis(THF) adduct is analogous to that of tertiary amine adducts [12]. Tertiary amine adducts of alane usually decompose to

---

* Dedicated to Professor Ernst Otto Fischer on the occasion of his 75th birthday.

0022-328X/94/$7.00
SSDI 0022-328X(94)24508-G

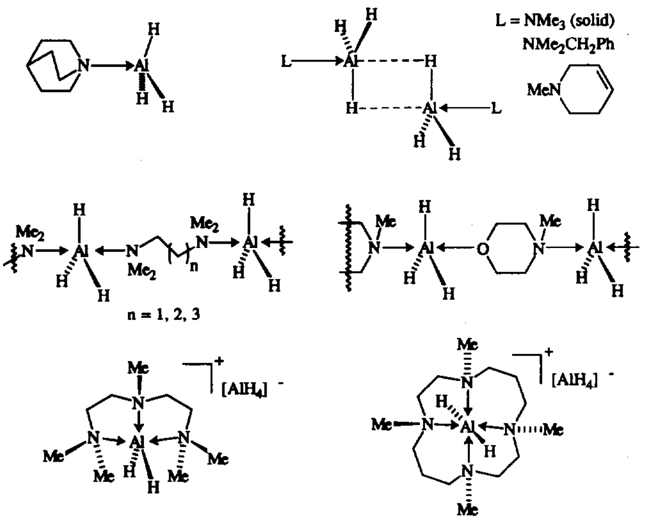


Fig. 1. Structural types for alane derivatives of tertiary amines.

aluminium, hydrogen and amine above *ca.* 100°C (see below), unlike adducts of 1,3,5-trimethylhexahydro-1,3,5-triazine which undergo C–N cleavage [16].

The computed structures for the model compound $[H_2Al(\mu\text{-}H)NH_3]_2$ agree well with experimental dimeric structures, Fig. 1, as does the calculated structure of H_3AlNH_3 with H_3Al(quinuclidine) [17], DZP [38] TZ2P + *f* basis. Calculations determined that a monomeric structure is favoured over a dimeric structure by only 0.4 kcal mol^{-1} which is within the realms of crystal packing forces and is consistent with the existence of both structural types in the solid state. Determined structures for the five coordinate bis (amine) adducts of alane, Fig. 1, have geometries close to the computed structure of $H_3Al(NH_3)_2$, which has D_{3h} symmetry [16]. A starting geometry of C_{2v} and C_s for the same system results in fragmentation to H_3AlNH_3 and NH_3 (HF/DZP-ECP) [16]. This highlights the inherent stability of planar H_3Al moieties in

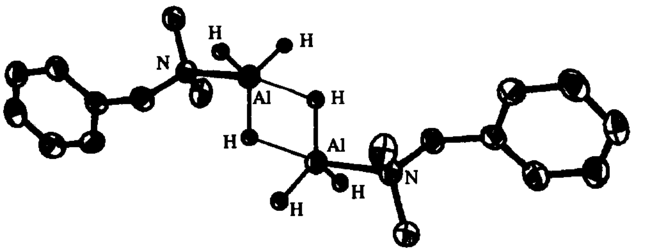
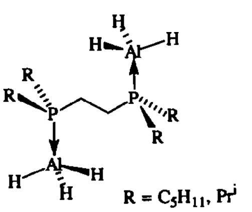
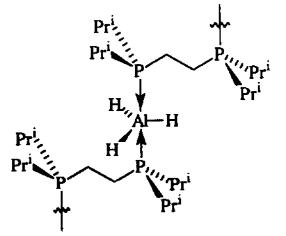


Fig. 2. Dimeric structure of $[H_2Al(\mu\text{-}H)(NMe_2CH_2Ph)]_2$; Al–N 2.088(2) Å, Al–μ-H 1.56, 2.07 Å, Al–H 1.56 Å (mean), Al···Al 2.883 Å, H–Al–H 122(1); Al–μ-H–Al 104.7(5)°; μ-H–Al–μ-H 75(1)° [14].





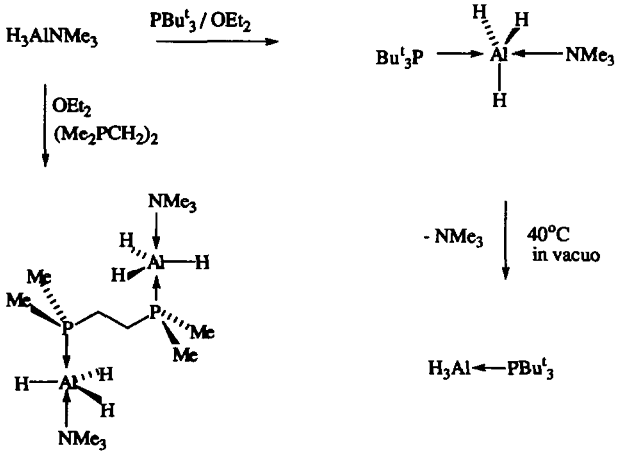
bis(amine) adducts and the hydride bridged dimeric structures where the weak secondary interactions are in apical positions of trigonal bypyramids, the other apical positions being occupied by N-centres, Fig. 2.

Tertiary phosphines with bulky substituents are required to stabilise phosphine adducts of alane with respect to decomposition to polymeric alane. For example, H_3AlPEt_3 decomposes at −20°C to polymeric AlH_3 whereas H_3AlPR_3, R = C_6H_{11}, ^tBu, decompose above 160°C, but directly to aluminium, hydrogen and phosphine. Steric hindrance about the P-centres seemingly blocks the formation of hyper-valent species and restricts the metal centres to four coordination even using an excess of the phosphine, as established for $(PR_2CH_2)_2$, R = C_6H_{11} [17,19,20]. The exception is for R = ^iPr which forms a five coordinate polymeric structure in the solid state, $H_3Al(P^iPr_2CH_2)_2$. Here the arrangement of ligands around the metal centre is analogous to that found for the bis(tertiary amine) adducts of alane, with exceptionally long Al–P distances, 2.755(3) Å [19].

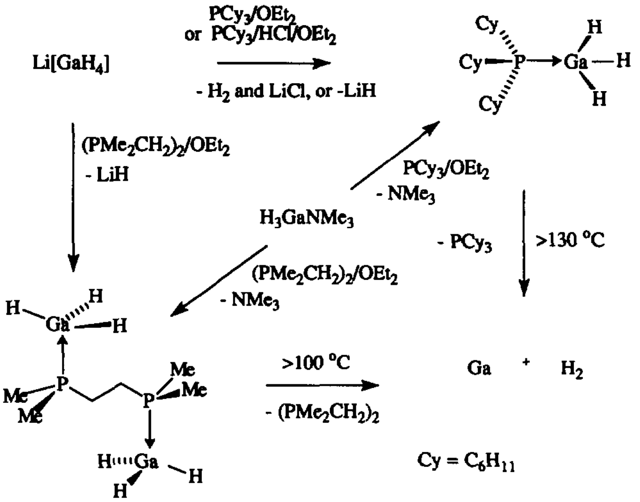
The computed stabilisation energy of H_3AlPH_3 over free AlH_3 and PH_3 is 13.2 kcal mol^{-1} (6-31 G^* + DZP) [19]. However, the potential energy hypersurface of $(H_3AlPH_3)_2$ results in convergence on dialane $H_2Al(\mu\text{-}H)_2AlH_2$ and free phosphine, favoured by 5.84 kcal mol^{-1} relative to H_3AlPH_3 [19]. This is consistent with the instability of phosphine adducts of alane relative to polymeric alane, unless steric hindrance at the phosphine suppresses association *via* hydride bridges. Theory on the model compound $H_3Al(PH_3)_2$ (D95*) predicts a trigonal bypyramidal structure, as found in the solid state structure of $H_3Al(P^iPr_2CH_2)_2$ [20].

Synthetic procedures involve treating etheral solutions of $LiAlH_4$ with dry HCl in the presence of phosphine. The ligand displacement method employing H_3AlNMe_3 either fails, notably for aryl phosphines, or gives mixed donor adducts, Scheme 1. The $(PMe_2CH_2)_2$ adduct is sublimable at 50°C *in vacuo* whereas under the same conditions the P^tBu_3 adduct affords H_3AlP^tBu. Here facile loss of NMe_3 is surprising given theory on the $H_3N/AlH_3/PMe_3$ system predicts a stabilisation energy of 9.02 kcal mol^{-1} for $H_3Al(NH_3)PMe_3$ relative to H_3AlPMe_3 and NH_3, and 2.72 kcal mol^{-1} relative to H_3AlNH_3 and PMe_3, ignoring zero point energy corrections (D95*//D95*) [20]. The loss of amine is also surprising on consideration of relative donor strengths of the ligands towards alane, and the thermal stability of the mixed donor for $(PMe_2CH_2)_2$ (Scheme 1) [17].

Tertiary amine adducts of gallane are readily prepared from the reaction of $LiGaH_4$ and the hydrochloride salt of the amine, or by ligand displacement [33]. These adducts usually decompose at room temperature to metal, hydrogen and ligand, H_3Ga(quinuclidine) excepted which is stable up to 100°C due to the relatively higher basicity of quinuclidine [18]. Polydentate tertiary amines destabilise gallane relative to H_3GaNMe_3. The 1:1 reaction of TMEDA with H_3GaNMe_3 yields an unstable intermediate H_3Ga(TMEDA) [18], presumably five coordinate, which readily loses half an equivalent of TMEDA affording the gallane rich species $(H_3Ga)_2$(TMEDA) [10,18], which decomposes above −10°C in diethyl ether. Adducts of PMDETA (= *N,N,N′,N″,N″*-pentamethyldiethylenetriamine), *N*-methylmorpholine and *N*-methylthiomorpholine rapidly decompose above *ca.* −20°C. As is usual for gallane the metal centres in the gallane rich TMEDA species are four coordinate in the solid state. Five coordination in gallane chemistry has precedence in $H_3Ga(NMe_3)_2$ which is a stable species below −23°C. *Ab initio* molecular orbital calculations (HF/D95* + DZP) yields the five coordinate species $H_3GaNH_3(OH_2)$ as energetically favoured relative to H_3GaNH_3 and H_2O by only 0.67 kcal mol^{-1}, and H_3GaOH_2 and NH_3 by 7.8 kcal mol^{-1} [22]. This has implications in surface chemistry (see below). No bridging hydride species are evident in an extensive search of the potential hypersurface for H_3GaNH_3 (ECP-DZP), in contrast to calculations on H_3AlNH_3 (see above) which gives the dimer to be of comparable energy to the monomer [21].



Scheme 1. Synthesis of mixed donor phosphine/amine adducts of alane.



Scheme 2. Synthesis and thermal stability of some tertiary phosphine adducts of gallane.

The synthesis of phosphine adducts of gallane is simpler, with selected examples presented in Scheme 2. There is no formation of five coordinate species, and steric hindrance at the phosphorus is not essential to impart stability of the complex with respect to formation of digallane or higher oligomers of gallane [18] and free phosphine. However, steric hindrance results in less air sensitive materials, highlighted by the tricyclohexylphosphine adduct which is air stable. This feature makes it an attractive reagent to develop for use in organic synthesis [34]. Displacement of NMe_3 and H^-, as well as the use of the hydrochloride of the phosphine generated *in situ* also feature in the syntheses of a range of phosphine adducts of gallane [20,21]. A substantial survey of the potential energy surface of H_3GaPH_3 using ECP-DZ basis set gives the monomer as the only minimum, as for H_3GaNH_3 [21].

Trialkylphosphine adducts of gallane are usually more stable than trialkyl amine adducts, decomposing above 100°C to gallium, hydrogen and phosphine, Table 1, Scheme 2 [19,35]. Corresponding phosphine adducts of alane have higher stability only if the *P*-centre is sterically demanding, otherwise decomposition is to polymeric alane above *ca.* −20°C [19,20] (see above). Aryl phosphine adducts of alane and gallane have low thermal stabilities yielding polymeric alane or gallium metal, Table 1. Lower stabilities here are consistent with the lower base strengths of aryl-substituted phos-

TABLE 1. Decomposition temperatures of selected Lewis base adducts of alane and gallane, $H_3ML \rightarrow M + H_2 + L$

H_3AlNMe_3	> 100°C
$H_3Al(Quinuclidine)$	> 190°C
$H_3Al(TMEDA)$	> 170°C
$H_2Al(PMDETA)^+AlH_4^-$	> 182°C
H_3AlPCy_3	> 160°C
$\{H_3Al(PPh_2CH_2)\}_2$	> 0°C [a]
$\{(Me_3N)H_3Al(PMe_2CH_2)\}_2$	> 50°C
H_3GaNMe_3	> 0°C
$H_3Ga(Quinuclidine)$	> 100°C
$\{H_3Ga\}_2(TMEDA)$	> −10°C
H_3GaPCy_3	> 130°C
$\{H_3Ga(PMe_2CH_2)\}_2$	> 100°C
$\{H_3Ga(PPh_2CH_2)\}_2$	> 0°C

[a] Decomposition to polymeric AlH_3 and free phosphine.

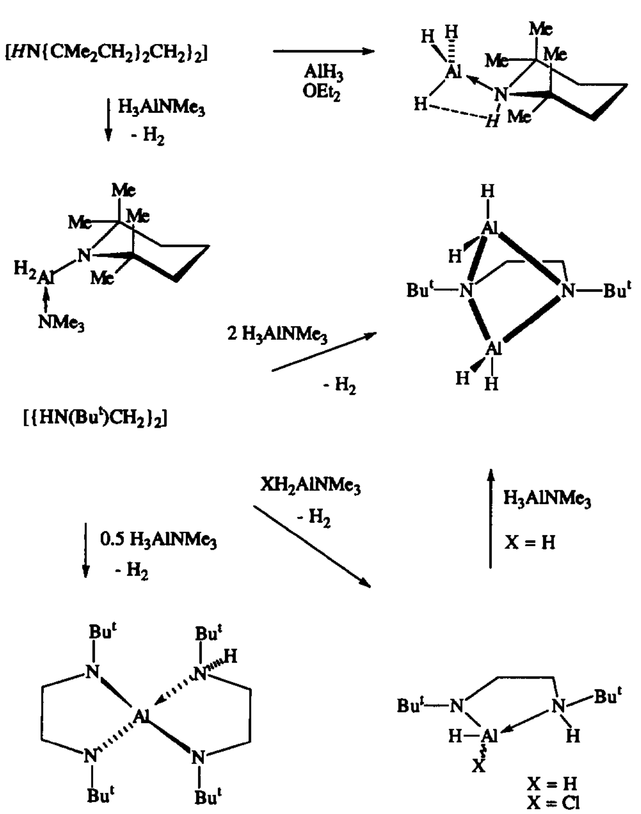
phines. The mechanisms for the decomposition of adducts of alane and gallane are poorly understood, despite the emerging importance of the adducts in CVD technology, especially for their tertiary amine adducts [1]. The mono-tertiary amine adducts of alane yield aluminium mirrors above *ca.* 100°C depending on the nature of the amine; base strength increases the decomposition temperature as does the incorporation of additional N-centres. However, with only methylene linkages between N-centres, decomposition is *via* N–C bond scission, for example for adducts of 1,3,5-trimethylhexahydro-1,3,5-triazine [16]. In general tertiary amine adducts of gallane decompose at lower temperatures than analogous alane species. This is due to the weaker metal–nitrogen bonds in the gallane adducts, which in turn is a consequence of the lower acidity of GaH_3 [31], the apparent restriction of gallane to four coordinate species, and also because of the frailty of Ga–H bonds [36].

3. Reactions

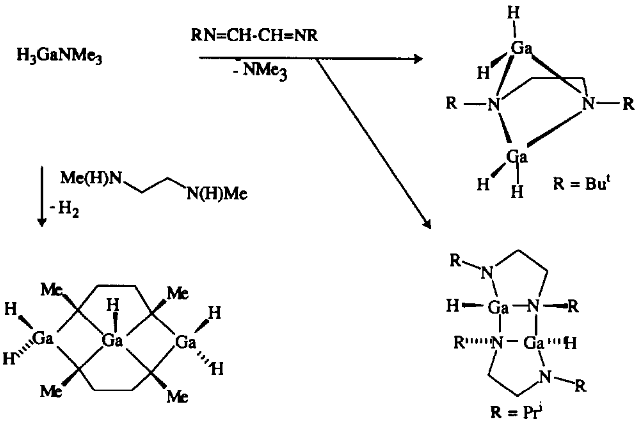
Primary and secondary amine adducts of alane are usually thermally unstable, a consequence of the high reactivity of the hydrido groups towards acidic amine protons resulting in hydrogen elimination and formation of N-bridging oligomeric amides [37–39]. However, the bulky amine 2,2,6,6-tetramethylpiperidine $[\mathit{H}N(CMe_2CH_2)_2CH_2\ (= L\mathit{H})]$ forms a remarkably stable secondary amine adduct of alane, $[H_3AlL\mathit{H}]$, at least in the reaction with diethyl ether solvated alane, generated *in situ* from $LiAlH_4$ and HCl, Scheme 3. In contrast, the reaction of H_3AlNMe_3 with the same amine yields a stable monomeric Lewis base stabilised amidoalane $[Me_3NAlH_2L]$ [40]. Interestingly Klein *et al.* recently reported that the reaction of $LiAlH_4$ with $L\mathit{H} \cdot HCl$ gave $[\{H(\mu\text{-}H)Al\{N(CMe_2CH_2)_2CH_2\}\}_3]$ as a trimeric H-bridged species, and that H_3AlNMe_3 with two equivalents of $L\mathit{H}$ results in dimeric $[\{(\mu\text{-}H)Al\{N(CMe_2CH_2)_2CH_2\}_2\}_2]$, also associated *via* H-bridges [41].

If the primary process for the formation of $[Me_3NAlH_2L]$ is complexation of the bulky amine, then subsequent metallation without loss of trimethylamine may be favoured by release of steric strain and formation of a four coordinate species. In the absence of trimethylamine any weakly bound diethyl ether may dissociate at the expense of complexation of the secondary amine. Seemingly here there is no steric impetus for elimination of hydrogen from the four coordinate species, $[H_3AlL\mathit{H}]$, with stabilisation of any amidoalane by amido bridging being sterically suppressed. Compound $[H_3AlL\mathit{H}]$ initially melts at 115–117°C with evolution of a gas, presumably arising from hydrogen elimination and amidometal formation.

The novelty of the structure of $[H_3AlL\mathit{H}]$ is the presence of adjacent $N\text{–}H^{\delta+} \ldots {}^{\delta-}H\text{–}Al$ groups with H...H(1) at 2.31 Å, Scheme 3. While this is at the Van der Waal's limit, and despite the relative inaccuracy of the structure determination, it represents a transition

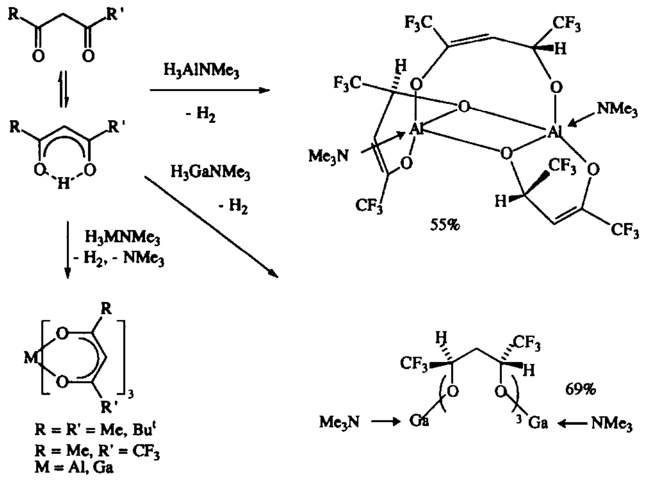


Scheme 3. Reactions of secondary amines with alane in diethyl ether at −80°C.



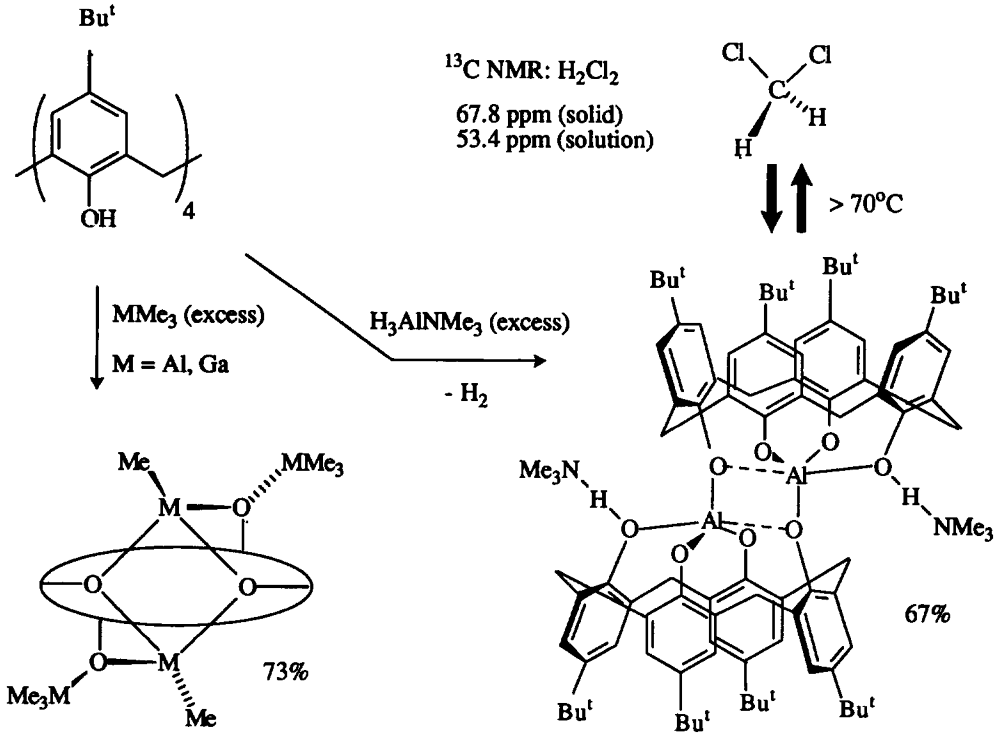
Scheme 4. Synthesis of gallium amides.

state prior to dihydrogen evolution *en route* to an amidometal species. Further credence for this is the eclipsed geometry of the AlH_3 moiety with respect to the ligand, along the Al–N bond. It is noteworthy that all other structures of alane amine species to date exhibit a staggered arrangement about this bond, and in theoretical calculations involving AlH_3 and NH_3 the eclipsed geometry represents a first order transition state [42].



Scheme 5. Reactions of trimethylamine adducts of alane and gallane with β-diketones.

Steric demand is also important in the formation of alane-rich amido species $[(H_2Al)_2\{\mu\text{-}N(^tBu)CH_2\}_2]$ on the reaction of 1,4-*N*,*N*′-bis-t-butylethylenediamene with excess alane, Scheme 3 [43]. This most likely proceeds *via* an amido/amine complex, at least on the basis of the formation of a stable, intramolecularly coordinated secondary amine adduct of aluminium dihydride, $[H_2Al\{N(H)(^tBu)CH_2CH_2N^tBu\}]$; the mono-



Scheme 6. Reaction of *p*-t-butylcalix[4]arene with excess H_3AlNMe_3 and for comparison, the reactions with excess MMe_3, M = Al and Ga.

chloro analogue $[Cl(H)Al\{N(H)(^tBu)CH_2CH_2N^tBu]$, is accessible using ClH_2AlNMe_3, as a mixture of diastereoisomers in solution.

Oligomeric amidogallium species have been prepared *via* metallation or hydrometallation, Scheme 4; the compound isolobal with $[(H_2Al)_2\{\mu\text{-}N(^tBu)CH_2\}_2]$, is conveniently prepared *via* hydrometallation involving 1,4-bis-t-butyl-1,4-diazabutadiene, even with a deficiency of H_3GaNMe_3 [3,18]. ^1H NMR on this compound is unusual in yielding structural information. The magnetically distinct hydrido groups on each gallium show an AB spin system albeit with broad peaks in consequence of the quadrupolar nature of $^{69,71}Ga$, *J*(HH) 44 Hz.

β-Diketones react with trimethyl amine adducts of alane and gallane in several ways, either as an unconventional source of metallating agent, a combination of metallation and hydrometallation or exclusively hydrometallation, Scheme 5 [44]. Thus reaction of H_3MNMe_3, M = Al or Ga, with 1,1,1,5,5,5-hexafluoropentane-2,4-dione results in metallation/ hydrometallation, M = Al, or hydrometallation, M = Ga, of the β-diketone. Both products can be isolated as binuclear species, $[Al_2\{OC(CF_3)=CHCH(CF_3)O\}_3(NMe_3)_2]$ (structurally authenticated for the *RRS*/*SSR* diastereoisomer), or $[Ga_2\{rac\text{-}OCH(CF_3)CH_2CH(CF_3)\text{-}O\}_3(NMe_3)_2]$, ($D_3$ symmetry) containing five or four coordinate metal centres respectively. Pentane-2,4-dione, 1,1,1-trifluoropentane-2,4-dione, and 2,2,6,6-tetramethylheptane-3,5-dione give metallation products, isolated as the tris(β-diketonato)metal(III) complexes.

Metallation of *p*-t-butylcalix[4]arene, with $H_3Al\text{-}NMe_3$ results in trimetallation and deprotonation by the tertiary amine, yielding a fused bis(calix[4]arene), Scheme 6, isolated with included methylene chloride in the slightly flattened cones of the calixarenes [26]. The methylene chloride H-atoms reside over two opposite aromatic rings in each cone, as $C\text{–}H\cdots\pi$-arene ring hydrogen bonds at 2.46 Å, Fig. 3. For comparison, the reaction of excess MMe_3, M = Al, Ga, with the same calixarene gives trimethylmetal rich adducts, Fig. 4 [45]. Here all the phenolic protons are removed yielding four membered M_2O_2 rings which are coordinated *via* the attached oxygen atoms to two further MMe_3 molecules. The now doubly flattened partial cone conformations are not conducive to the formation of molecular inclusion complexes.

The reduction of a variety of unsaturated functional groups with the Lewis base adducts H_3ML (M = Al; M = Ga; M = B; L = NMe_3; quinuclidine; $P(C_6H_{11})_3$) in toluene have been examined [34]. Whereas H_3Al(quinuclidine) reduces *p*-bromophenacyl bromide predominantly to 1-(4′-bromophenyl)-1-ethanol, the gallane H_3GaNMe_3 reduces the same compound with very little concomitant debromination, Scheme 7. Interestingly, H_3BNMe_3 did not react under these conditions. Hydrometallation of styrene oxide with H_3Al(quinuclidine) yielded a mixture of 1- and 2-phenylethanol (63:37) whereas $H_3GaP(C_6H_{11})_3$ gives exclusively Markovnikov addition. Overall these results are consistent with the increased electronegativity of gallium and the associated decreased reactivity of the less polar M–H bond relative to aluminium.

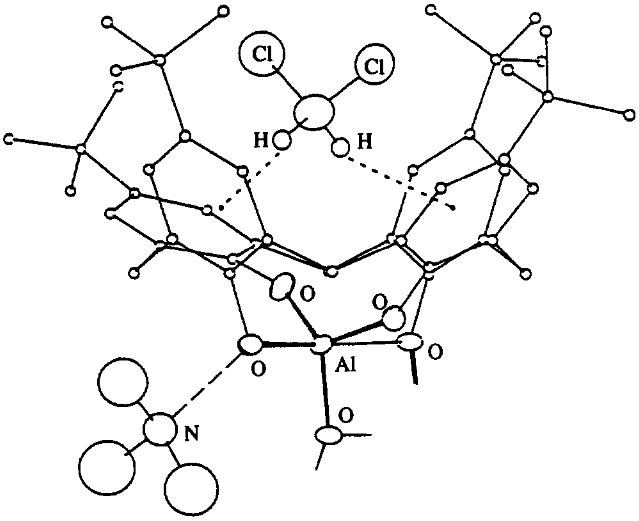


Fig. 3. Projection of half the centrosymmetric dimer formed from the reaction of H_3AlNMe_3 with *p*-t-butylcalix[4]arene.

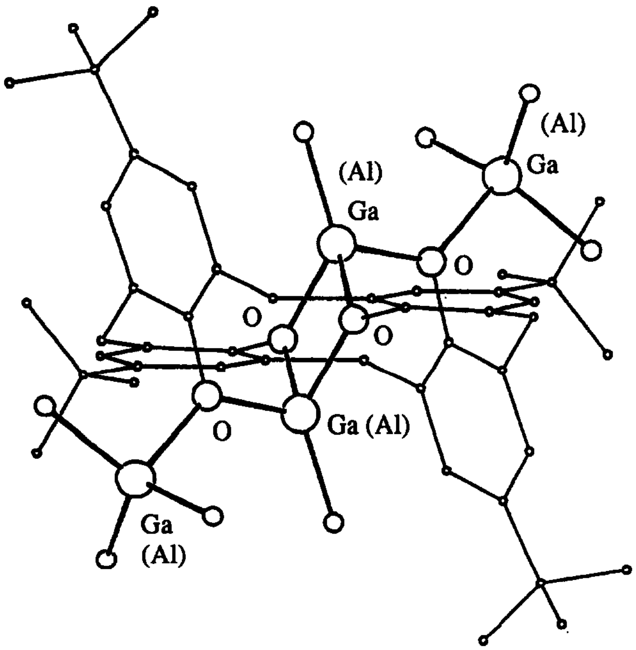
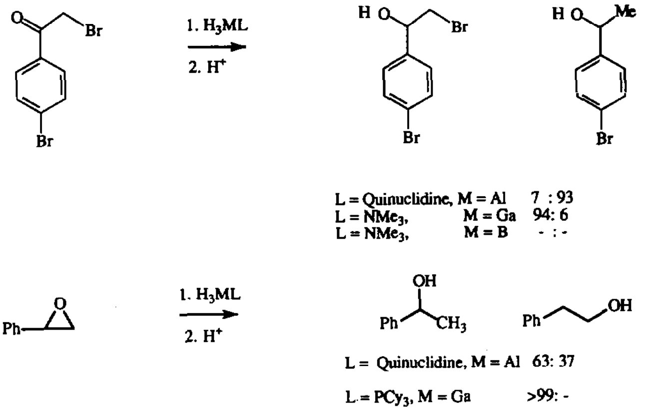


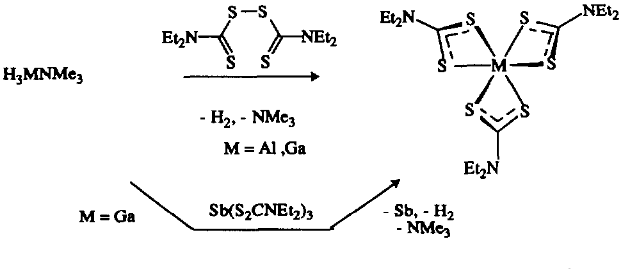
Fig. 4. Molecular structure of reaction product of *p*-t-butylcalix[4]arene with $GaMe_3$; the aluminium analogue is isolobal.



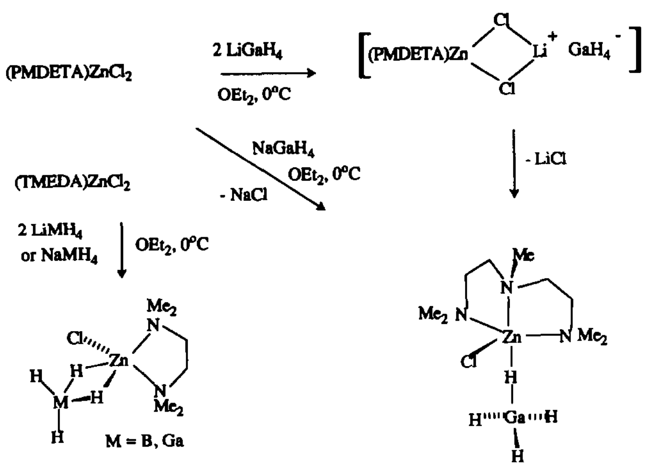
Scheme 7. Reactions of various adducts of alane and gallane (and borane) with selected functional groups.

Extending the work to sulfur containing systems we find that H_3MNMe_3, M = Al and Ga, reacts with the thiuram disulfide, $(Et_2NCS_2)_2$, to give the corresponding tris(diethyldithiocarbamato)metal(III) species, Scheme 8 [46]. While the gallium compound has previously been prepared by conventional methods [47], this is the first synthesis of tris(diethyldithiocarbamato)aluminium(III); the two compounds are isostructural [46,47]. The reaction of H_3GaNMe_3 with tris(diethyldithiocarbamato)antimony(III) also gives the same gallium compound, along with antimony, hydrogen and trimethylamine, Scheme 8.

As part of a study targeting the synthesis of heterobimetallic species based on alane or gallane and another metal centre, we have prepared some mixed gallium and zinc hydrido species which are shown in Scheme 9 [48]. Reaction of $(TMEDA)ZnCl_2$ or $(PMDETA)ZnCl_2$ requires two equivalents of $LiGaH_4$ to give the mono-gallate species, otherwise it appears mixed lithium chloride adducts are formed. In contrast only one equivalent of $NaGaH_4$ is required to form the same compounds, and indeed using two equivalents of $NaGaH_4$ intrinsically unstable species are formed, rapidly decomposing to grey metallic powders. The structure of $(PMDETA)ZnCl(\mu\text{-}H)GaH_3$ has been established by single crystal X-ray diffraction studies, Fig. 5. The compound $(TMEDA)ZnCl(\mu\text{-}H)_2GaH_2$ slowly decomposes to a grey powder at room temperature and the structure has been inferred from the authenticated structure of the corresponding borane analogue.



Scheme 8. Synthesis of alumunium and gallium dithiocarbamates from alane and gallane derivatives.



Scheme 9. Synthesis of tertiary amine/mixed zinc and gallium hydrides.

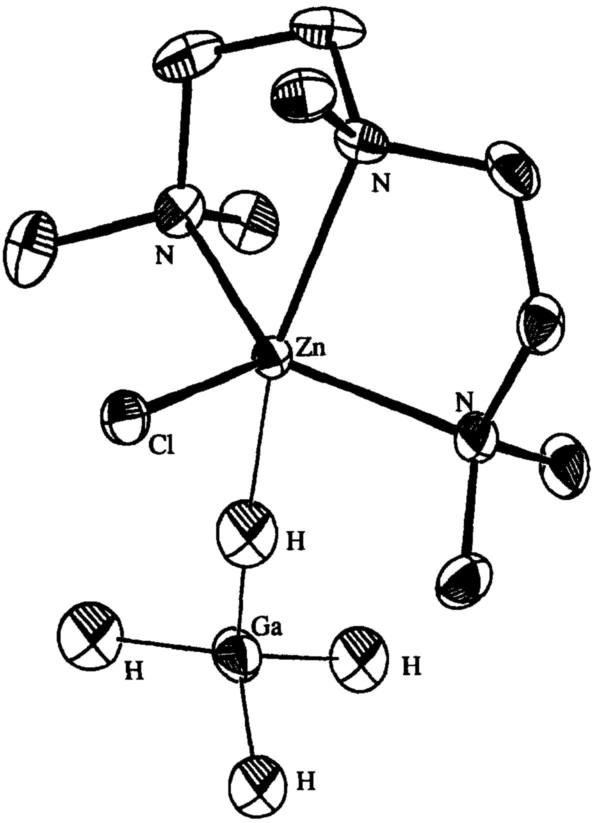
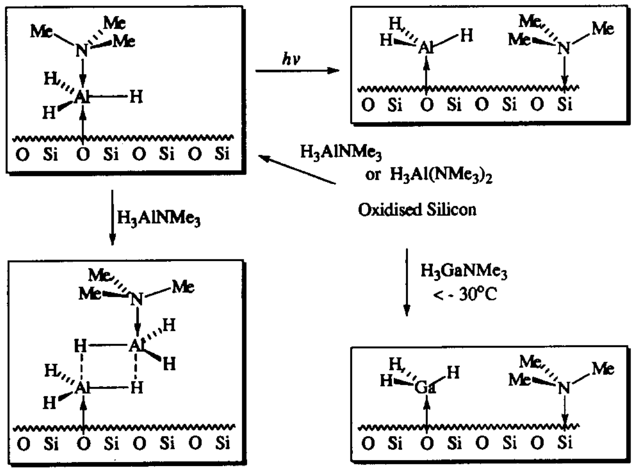


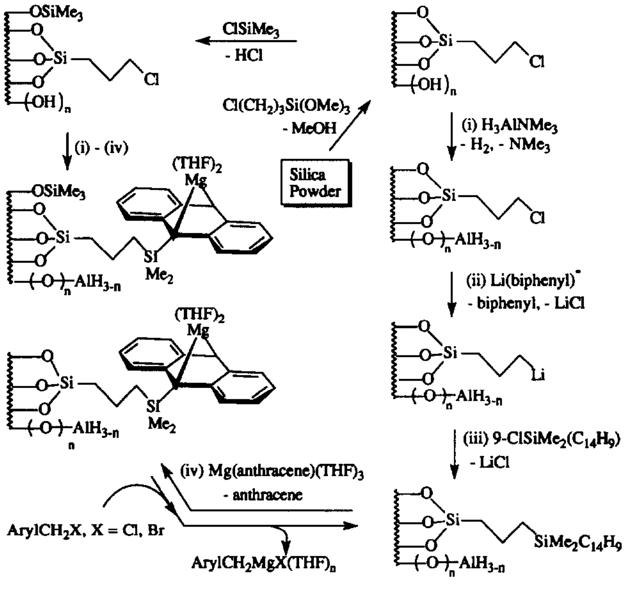
Fig. 5. Molecular structure of $(PMDETA)ZnCl(\mu\text{-}H)GaH_3$; Ga–H 1.54–1.61(5) Å, Ga–μ-H 1.42 Å, Zn–μ-H 2.01 Å, Zn–Cl 2.235(1) Å, Zn–N 2.146–2.232(3) Å; Ga–μ-H–Zn 177(3)°.

Tertiary amine adducts of alane and gallane are useful precursors for delivering metal to surfaces, because of their useful vapour pressure, and the absence of direct metal–carbon bonds thus minimising the amount of carbonaceous materials being formed [8]. In addition, the compounds are less air sensitive than trialkylmetal compounds which have been used extensively in CVD technology [7,9,49].

As part of a study of the structure of adsorbed alane and gallane species on surfaces prior to thermal degradation we have investigated the uptake of both H_3AlNMe_3 [23] and H_3GaNMe_3 on oxidised silicon [22]. The results are summarised in Scheme 10. For aluminium molecular adsorption prevails at a dosing pressure of *ca.* 5.0×10^{-7} mbar, the aluminium centres expanding their coordination spheres by complexation with surface O-centres. High XPS X-ray flux (> 240 W) results in migration of NMe_3 to silicon centres. For dosing pressures $> 10^{-7}$ mbar an aluminium rich species is formed, with Al:N ratio close to 2:1. This possibly corresponds with hydride bridge formation. Theoretical studies show the energetics of the process are feasible, at least for model systems based on H_3AlNH_3, $H_3Al(OH_2)NH_3$, H_3AlOH_2 and the appropriate dimer [1,50]. Adsorption of H_3GaNMe_3 also on oxidised silicon and under UHV conditions is different [22]. For temperatures below *ca.* −30°C dissociative adsorption occurs with some trimethyl amine adsorbed on silicon sites. This is in accordance with the preference for gallane to maintain four fold coordination, although the primary process is likely to be the formation of five coordinate mixed donor species. Calculations on the model compound $H_3Ga(OH_2)NH_3$ show it to be energetically favoured relative to H_3GaNH_3 and H_20 by only 0.67 kcal mol^{-1}, and H_3GaOH_2 and NH_3 by 7.8 kcal mol^{-1} [22].



Scheme 10. Models for the adsorption of H_3MNMe_3, M = Al, Ga, on oxidised silicon.



Scheme 11. Synthesis of silica supported "magnesium(anthracene)" and its reaction with benzylic halides.

As an extension of earlier studies on "magnesium (anthracene)" chemistry, including the development of polymer supported "magnesium(anthracene)" for use in generating Grignard reagents from benzylic halides [51], we have prepared a silica supported version for the same application [52]. The success of this work depended on the use of alane in eliminating surface hydroxyl groups, Scheme 11. Hydroxyl depleted silica surfaces derived from treating chloropropylsilyl (or chloropropylsilyl/ trimethylsilyl) functionalised silica with H_3AlNMe_3 affords the corresponding organolithium reagent when treated with $Li^+(biphenyl)^{\cdot-}$. Successive treatment with 9-(chlorodimethylsilyl) anthracene and $Mg(anthracene)(THF)_3$ generates anthracene and silica supported "magnesium anthracene". This gives Grignard reagents of benzylic chlorides in THF in excellent yield with the spent silica supported anthracene readily recycled.

4. Conclusions

In recent years new developments in the synthesis, structure and reactivity of Lewis base adducts of alane and gallane have emerged as part of our systematic study of these classes of compounds, and studies from other groups. Different characteristics between alane and gallane are (i) the ability of alane but not gallane to readily form hyper-valent species, gallium achieving four fold coordination whereas aluminium prefers five fold coordination, (ii) the frailty of the Ga–H bond relative to the Al–H bond, and (iii) the polarizing influence/back bonding participation of the d^{10} core for gallium. Applications of the Lewis base adducts are in synthesis and in materials science. Exploitation of the differences already noted between the reactivity of alane and gallane towards various functional groups is a current research effort. New applications in materials sciences we are concerned with include developing heterobimetallic compounds as precursors for alloys, and further use of the hydrides in surface modification, in wet chemistry and under UHV conditions.

Acknowledgements

The author gratefully acknowledges contributions to the research from Professor Jerry Atwood (University of Alabama), Professor Robert Lamb and Dr. Paul Pigram (University of New South Wales), Dr. David Young, Dr. George Koutsantonis, Dr. Mark Henderson, Dr. Cameron Jones, Dr. Kirk Butz, Tania van den Ancker, Fiona Elms, Michael Gardiner, Stacey Lawrence, Carolyn Tranter and Fred Bennett (Griffith University), and Barry Wood (University of Queensland). Financial support from the Australian Research Council and the Department of Industry, Technology and Commerce is also gratefully acknowledged.

References

1 C. Jones, G.A. Koutsantonis and C.L. Raston, *Polyhedron*, *12* (1993) 1829.

2 (a) E.M. Marlett and W.S. Park, *J. Org. Chem.*, *55*, (1990) 2968 and references cited therein; (b) B.M. Bulychev, *Polyhedron*, *9* (1990) 387.

3 M.J. Henderson, C.H.L. Kennard, C.L. Raston and G. Smith, *J. Chem. Soc.*, *Chem. Commun.*, (1990) 1203.

4 L.H. Dubois, B.R. Zegarski, M.E. Gross and R.G. Nuzzo, *Surf. Sci.*, *244* (1991) 89 and references cited therein.

5 P. Zonella, G. Rossetto, N. Brianese, F. Ossola and M. Porchia, *Chem. Mater.*, *3* (1991) 225 and references cited therein.

6 A.A. Melas, *US Patent 4740606*, 1988; *Chem. Abstr.*, *109* (1988) 121598d.

7 W.L. Gladfelter, D.C. Boyd and K.F. Jensen, *Chem. Mater.*, *1* (1989) 339.

8 T.H. Baum, C.E. Larson and R.L. Jackson, *Appl. Phys. Lett.*, *55* (1989) 1264.

9 A.T.S. Wee, A.J. Murrell, N.K. Singh, D. O'Hare and J.S. Foord, *J. Chem. Soc.*, *Chem. Commun.*, (1990) 11.

10 D. O'Hare, J.S. Foord, T.C. Page and T.J. Whitaker, *J. Chem. Soc.*, *Chem. Commun.*, (1991) 1445 and references cited therein.

11 (a) T.E. Daenen, *UK Patent*, *GB 2021646*, 1979; (b) E.M. Marlett, *US Patent*, *4474743*, 1984.

12 I.B. Gorrell, P.B. Hitchcock and J.D. Smith, *J. Chem. Soc.*, *Chem. Commun.*, (1993) 189.

13 A.J. Ardruengo, H.V.R. Dias, J.C. Calabrese and F. Davidson, *J. Am. Chem. Soc.*, *114* (1992) 9724.

14 M.R. Mason and A.R. Barron, *Chemtracts* (*Inorg. Chem.*), (1992) 179.

15 J.L. Atwood, F.R. Bennett, F.M. Elms, C. Jones, C.L. Raston and K.D. Robinson, *J. Am. Chem. Soc.*, *113* (1991) 8183.

16 J.L. Atwood, F.R. Bennett, C. Jones, G.A. Koutsantonis, C.L. Raston and K.D. Robinson, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 541.

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

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

19 J.L. Atwood, F.R. Bennett, F.M. Elms, G.A. Koutsantonis, C.L. Raston and D.J. Young, *Organometallics*, *11* (1992) 1475.

20 F.M. Elms and M.G. Gardiner, G.A. Koutsantonis, C.L. Raston, J.L. Atwood and K.D. Robinson, *J. Organomet. Chem.*, *449* (1993) 45.

21 J.L. Atwood, K.D. Robinson, F.R. Bennett, F.M. Elms, G.A. Koutsantonis, C.L. Raston and D.J. Young, *Inorg. Chem.*, *31* (1992) 2674.

22 K.W. Butz, F.M. Elms, C.L. Raston, R.N. Lamb and P.J. Pigram, *Inorg. Chem.*, *32* (1993) 3985.

23 F.M. Elms, R.N. Lamb, P.J. Pigram, M.G. Gardiner, B.J. Wood and C.L. Raston, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 1423.

24 J.L. Atwood, K.D. Robinson, C. Jones and C.L. Raston, *J. Chem. Soc.*, *Chem. Commun.*, (1991) 1697.

25 J.L. Atwood, S.G. Bott, F.M. Elms, C. Jones and C.L. Raston, *Inorg. Chem.*, *30* (1991) 4868.

26 J.L. Atwood, S.G. Bott, C. Jones and C.L. Raston, *J. Chem. Soc.*, *Chem. Commun.*, (1992) 1349.

27 F.G.N. Cloke, C.I. Dalby, M.J. Henderson, P.B. Hitchcock, C.H.L. Kennard, R.N. Lamb and C.L. Raston, *J. Chem. Soc.*, *Chem. Commun.*, (1990) 1394.

28 J.W. Turley and H.W. Rinn, *Inorg. Chem.*, *8* (1969) 18.

29 G.J. Palenik, *Acta Crystallogr.*, *17* (1964) 1573.

30 A. Almenningen, G. Gundersen, T. Haugen and A. Haaland, *Acta Chem. Scand.*, *26* (1972) 3928.

31 P.L. Baxter, A.J. Downs and D.W.H. Rankin, *J. Chem. Soc.*, *Dalton Trans.*, (1984) 1755.

32 C.R. Pulham, A.J. Downs, M.J. Goode, D.W.H. Rankin and H.E. Robertson, *J. Am. Chem. Soc.*, *113* (1991) 5149.

33 E. Wiberg and E. Amberger, *Hydrides of the Elements of Main Groups I–IV*, Elsevier, London, 1971, Chap. 6.

34 C.L. Raston, C. Tranter and D.J. Young, unpublished results.

35 E. Wiberg and H. Nöth, *Z. Naturforsch.*, *Teil B*, *10* (1955) 237.

36 C.R. Pulham, A.J. Downs, D.W.H. Rankin and H.E. Robertson, *J. Chem. Soc.*, *Dalton Trans.*, (1992) 1509.

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

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

39 C. Cucinella, T. Salvatori, C. Busseto, G. Perego and A. Mazzei, *J. Organomet. Chem.*, *78* (1974) 185.

40 J.L. Atwood, G.A. Koutsantonis, Fu-Chin Lee and C.L. Raston, *J. Chem. Soc.*, *Chem. Commun.*, (1994) 91.

41 C. Klein, H. Noth, M. Tacke and M. Thomann, *Angew. Chem.*, *Int. Ed. Engl.*, *32* (1993) 886.

42 F.R. Bennett, M.G. Gardiner and C.L. Raston, unpublished results.

43 J.L. Atwood, S.M. Lawrence and C.L. Raston, *J. Chem. Soc.*, *Chem. Commun.*, (1994) 73.

44 J.L. Atwood, Fu-Chin Lee, C.L. Raston and K.D. Robinson, unpublished results.

45 J.L. Atwood, S. Bott, C. Jones and C.L. Raston, unpublished results.

46 S.M. Lawrence, G.A. Koutsantonis and C.L. Raston, unpublished results.
47 K. Dymock, G.J. Palenik, J. Slezak, C.L. Raston and A.H. White, *J. Chem. Soc., Dalton Trans.*, (1976) 28.
48 Fu-Chin Lee and C.L. Raston, unpublished results.
49 B.E. Bent, R.G. Nuzzo and L.H. Dubois, *J. Am. Chem. Soc.*, *111* (1989) 1634.
50 F.M. Elms, R.N. Lamb, P.J. Pigram, M.G. Gardiner, B.J. Wood and C.L. Raston, unpublished results.
51 S. Harvey and C.L. Raston, *J. Chem. Soc., Chem. Commun.*, (1988) 652.
52 T. van den Ancker, R.N. Lamb and C.L. Raston, unpublished results.