

**Figure 7.18** (a) 1,4,7,10-tetraazacyclododecane triacetic acid, (LH<sub>3</sub>). (b) Structure of the 7-coordinate complex [InL]; the coordination polyhedron (shown in white) comprises a trigonal prism of 4N and 2O capped on one of its quadrilateral faces by the third O atom.

from the use of the  $\gamma$ -active  $^{111}\text{In}$  isotope ( $E_{\gamma}$  173, 247 keV,  $t_{1/2}$  2.81 d) in radio-labelled monoclonal antibodies to detect tumours. Interestingly, the 7-coordinate crystalline complex reverts to a stable neutral hexacoordinate species in aqueous solution. Other 7-coordinate macrocyclic  $\text{In}^{\text{III}}$  complexes of potential relevance in radio-pharmaceutical applications have been prepared, including [InL] where L is the triacetate of the tetraaza macrocycle shown in Fig. 7.18(a).<sup>(70)</sup> In this case the coordination polyhedron is a trigonal prism with one of its quadrilateral faces capped by a carboxylate O atom as shown schematically in Fig. 7.18(b).

Indium clusters have also recently been characterized, notably in intermetallic compounds. Thus, the Zintl phase,  $\text{Rb}_2\text{In}_3$ , (prepared by direct reaction between the two metals at 1530°C) has layers of octahedral *closo*- $\text{In}_6$  clusters joined into sheets through exo bonds at four coplanar vertices.<sup>(71)</sup> These four In atoms are therefore each bonded to five neighbouring In atoms at the corners of a square-based pyramid, whereas the remaining two (*trans*) In atoms in the  $\text{In}_6$  cluster

show pyramidal 4-fold bonding only, to contiguous In atoms in the same cluster.  $\text{Cs}_2\text{In}_3$  is isostructural. The intermetallic compound  $\text{K}_3\text{Na}_{26}\text{In}_{48}$  (synthesized from the elements in sealed Nb ampoules at 600°C) has a more complicated structure in which the In forms both *closo* icosahedral  $\text{In}_{12}$  clusters and hexagonal antiprismatic  $\text{In}_{12}$  clusters.<sup>(72)</sup> All the various  $\text{In}_{12}$  clusters are interconnected by 12 exo bonds forming a covalent 3D network (In–In 291–315 pm) and the  $\text{In}_{12}$  hexagonal antiprisms are additionally centred by single Na atoms. The phase contains several other interesting structural features and the original paper (in English) makes rewarding reading.

### 7.3.6 Organometallic compounds

Many organoaluminium compounds are known which contain 1, 2, 3 or 4 Al–C bonds per Al atom and, as these have an extensive reaction chemistry of considerable industrial importance, they will be considered before the organometallic compounds of Ga, In and Tl are discussed.

<sup>70</sup> A. RIESEN, T. A. KADEN, W. RITTER and H. A. MACKE, *J. Chem. Soc., Chem. Commun.*, 460–2 (1989).

<sup>71</sup> S. C. SEVEOV and J. D. CORBETT, *Z. anorg. allg. Chem.* **619**, 128–32 (1993).

<sup>72</sup> W. CARRILLO-CABRERA, N. CAROCA-CANALES, K. PETERS and H. G. VON SCHNERING, *Z. anorg. allg. Chem.* **619**, 1556–63 (1993).

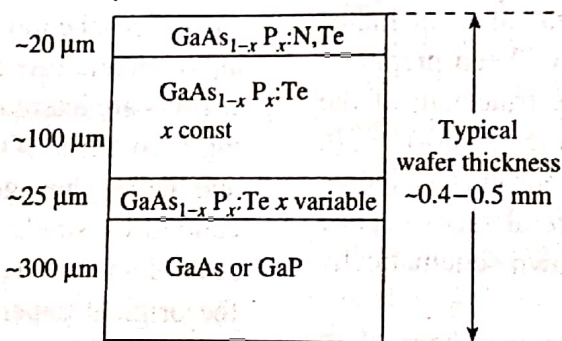
### Organoaluminium Compounds

Aluminium trialkyls and triaryls are highly reactive, colourless, volatile liquids or low-melting solids which ignite spontaneously in air and react violently with water; they should therefore be handled circumspectly and with

suitable precautions. Unlike the boron trialkyls and triaryls they are often dimeric, though with branched-chain alkyls such as  $\text{Pr}^i$ ,  $\text{Bu}^i$  and  $\text{Me}_3\text{CCH}_2$  this tendency is less marked.  $\text{Al}_2\text{Me}_6$  (mp  $15^\circ$ , bp  $126^\circ$ ) has the methyl-bridged structure shown and the same dimeric structure is found for  $\text{Al}_2\text{Ph}_6$  (mp  $225^\circ$ ).

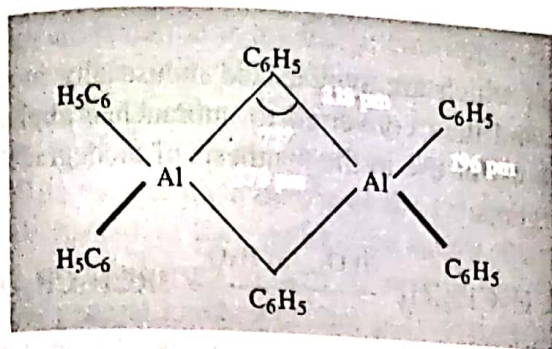
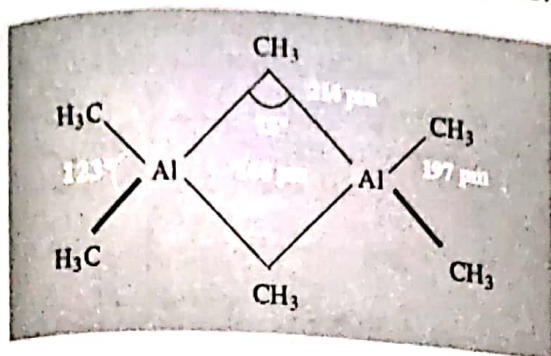
### Applications of III-V Semiconductors

The 9 compounds that Al, Ga and In form with P, As and Sb have been extensively studied because of their many applications in the electronics industry, particularly those centred on the interconversion of electrical and optical (light) energy. For example, they are produced commercially as light-emitting diodes (LEDs) familiar in pocket calculators, wrist watches and the alpha-numeric output displays of many instruments; they are also used in infrared-emitting diodes, injection lasers, infrared detectors, photocathodes and photomultiplier tubes. An extremely elegant chemical solid-state technology has evolved in which crystals of the required properties are deposited, etched and modified to form the appropriate electrical circuits. The ternary system  $\text{GaAs}_{1-x}\text{P}_x$  now dominates the LED market for  $\alpha$ -numeric and graphic displays following the first report of this activity in 1961.  $\text{GaAs}_{1-x}\text{P}_x$  is grown epitaxially on a single-crystal substrate of GaAs or GaP by chemical vapour deposition and crystal wafers as large as  $20\text{ cm}^2$  have been produced commercially. The colour of the emitted radiation is determined by the energy band gap  $E_g$ ; for GaAs itself  $E_g$  is  $138\text{ kJ mol}^{-1}$  corresponding to an infrared emission ( $\lambda\ 870\text{ nm}$ ), but this increases to  $184\text{ kJ mol}^{-1}$  for  $x \sim 0.4$  corresponding to red emission ( $\lambda\ 650\text{ nm}$ ). For  $x > 0.4$   $E_g$  continues to increase until it is  $218\text{ kJ mol}^{-1}$  for GaP (green,  $\lambda\ 550\text{ nm}$ ). Commercial yellow and green LEDs contain the added isoelectronic impurity N to improve the conversion efficiency. A schematic cross-section of a typical  $\text{GaAs}_{1-x}\text{P}_x$  epitaxial wafer doped with Te and N is shown in the diagram: Te (which has one more valence electron per atom than As or P) is the most widely used dopant to give  $n$ -type impurities in this system at concentrations of  $10^{16}$ – $10^{18}$  atoms  $\text{cm}^{-3}$  (0.5–50 ppm). The  $p$ - $n$  junction is then formed by diffusing Zn (1 less electron than Ga) into the crystal to a similar concentration.



An even more recent application is the construction of semiconductor lasers. In normal optical lasers light is absorbed by an electronic transition to a broad band which lies above the upper laser level and the electron then drops into this level by a non-radiative transition. By contrast the radiation in a semiconductor laser originates in the region of a  $p$ - $n$  junction and is due to the transitions of injected electrons and holes between the low-lying levels of the conduction band and the uppermost levels of the valence band. (Impurity levels may also be involved.) The efficiency of these semiconductor injection lasers is very much higher than those of optically pumped lasers and the devices are much smaller; they are also easily adaptable to modulation. As implied by the band gaps on p. 255, emission wavelengths are in the visible and near infrared. A heterostructure laser based on the system  $\text{GaAs}-\text{Al}_x\text{Ga}_{1-x}\text{As}$  was the first junction laser to run continuously at  $3000\text{ K}$  and above (1970).

In the two types of device just considered, namely light emitting diodes and injection lasers, electrical energy is converted into optical energy. The reverse process of converting optical energy into electrical energy (photoconductivity and photovoltaic effects) has also been successfully achieved by III-V semiconductor systems. For example, the small band-gap compound  $\text{InSb}$  is valuable as a photoconductive infrared detector, and several compounds are being actively studied for use in solar cells to convert sunlight into useful sources of electrical power. The maximum photon flux in sunlight occurs at  $75$ – $95\text{ kJ mol}^{-1}$  and GaAs shows promise, though other factors make  $\text{Cu}_2\text{S}-\text{CdS}$  cells more attractive commercially at the present time.

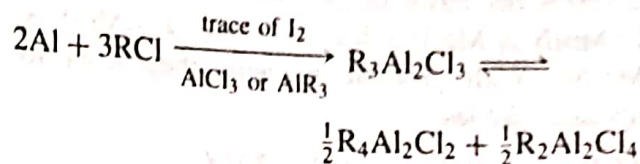


In each case  $\text{Al}-\text{C}_\mu$  is about 10% longer than  $\text{Al}-\text{C}_t$  (cf.  $\text{Al}_2\text{X}_6$ , p. 235;  $\text{B}_2\text{H}_6$ , p. 157). The enthalpy of dissociation of  $\text{Al}_2\text{Me}_6$  into monomers is  $84 \text{ kJ mol}^{-1}$ .  $\text{Al}_2\text{Et}_6$  (mp  $-53^\circ$ ) and  $\text{Al}_2\text{Pr}_6^i$  (mp  $-107^\circ$ ) are also dimeric at room temperature but crystalline trimesitylaluminium (mesityl = 2,4,5-trimethylphenyl) is monomeric with planar 3-coordinate Al; the mesityl groups adopt a propeller-like configuration with a dihedral angle of  $56^\circ$  between the aromatic ring and the  $\text{AlC}_3$  plane and with  $\text{Al}-\text{C}$  199.5 pm.<sup>(73)</sup>

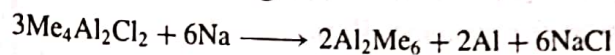
As with  $\text{Al}(\text{BH}_4)_3$  and related compounds (p. 230), solutions of  $\text{Al}_2\text{Me}_6$  show only one proton nmr signal at room temperature due to the rapid interchange of bridging and terminal Me groups; at  $-75^\circ$  this process is sufficiently slow for separate resonances to be observed.

$\text{Al}_2\text{Me}_6$  can be prepared on a laboratory scale by the reaction of  $\text{HgMe}_2$  on Al at  $\sim 90^\circ\text{C}$ .  $\text{Al}_2\text{Ph}_6$  can be prepared similarly using  $\text{HgPh}_2$  in boiling toluene or by the reaction of  $\text{LiPh}$  on  $\text{Al}_2\text{Cl}_6$ . On the industrial (kilotonne) scale Al is alkylated by means of  $\text{RX}$  or by alkenes plus  $\text{H}_2$ . In the first method the sesquichloride  $\text{R}_3\text{Al}_2\text{Cl}_3$  is formed in equilibrium with its disproportionation

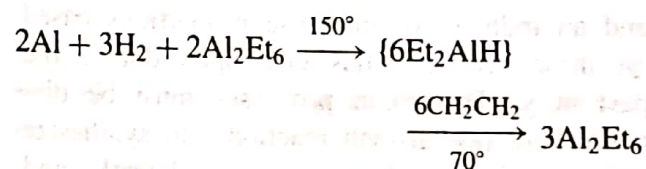
products:<sup>†</sup>



Addition of  $\text{NaCl}$  removes  $\text{R}_2\text{Al}_2\text{Cl}_4$  as the complex  $(2\text{NaAlCl}_3\text{R})$  and enables  $\text{R}_4\text{Al}_2\text{Cl}_2$  to be distilled from the mixture. Reaction with Na yields the trialkyl, e.g.:



Higher trialkyls are more readily prepared on an industrial scale by the alkene route (K. Ziegler *et al.*, 1960) in which  $\text{H}_2$  adds to Al in the presence of preformed  $\text{AlR}_3$  to give a dialkylaluminium hydride which then readily adds to the alkene:



Similarly, Al,  $\text{H}_2$  and  $\text{Me}_2\text{C}=\text{CH}_2$  react at  $100^\circ$  and 200 atm to give  $\text{AlBu}_3^i$  in a single-stage process, provided a small amount of this compound is present at the start; this is required because Al does not react directly with  $\text{H}_2$  to form  $\text{AlH}_3$  prior to alkylation under these conditions. Alkene exchange reactions can be used to transform  $\text{AlBu}_3^i$  into numerous other trialkyls.  $\text{AlBu}_3^i$  can also be reduced by potassium metal in hexane at room temperature to give the novel brown compound  $\text{K}_2\text{Al}_2\text{Bu}_6^i$  (mp  $40^\circ$ ) which is notable in providing a rare example of an Al-Al bond in the diamagnetic anion  $[\text{Bu}_3^i\text{AlAlBu}_3^i]^{2-}$ .<sup>(74)</sup>

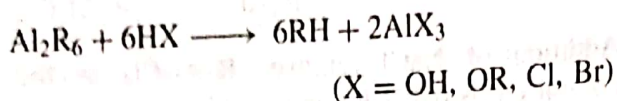
$\text{Al}_2\text{R}_6$  (or  $\text{AlR}_3$ ) react readily with ligands to form adducts,  $\text{LAlR}_3$ . They are stronger Lewis acids than are organoboron compounds,  $\text{BR}_3$ , and can be considered as 'hard' (or class a)

<sup>†</sup> It is interesting to note that the reaction of  $\text{EtI}$  with Al metal to give the sesqui-iodide " $\text{Et}_3\text{Al}_2\text{I}_3$ " was the first recorded preparation of an organoaluminium compound (W. Hallwachs and A. Schafarik, 1859).

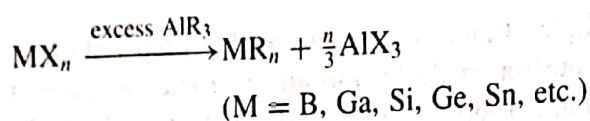
<sup>74</sup> H. HOBERG and S. KRAUSE, *Angew. Chem. Int. Edn. Engl.* 17, 949-50 (1979).

<sup>73</sup> J. J. JERIUS, J. M. HAHN, A. F. M. M. RAHMAN, O. MOLS, W. H. ISLEY and J. P. OLIVER, *Organometallics* 5, 1812-14 (1986).

acids; for example, the stability of the adducts  $\text{LAlMe}_3$  decreases in the following sequence of L:  $\text{Me}_3\text{N} > \text{Me}_3\text{P} > \text{Me}_3\text{As} > \text{Me}_2\text{O} > \text{Me}_2\text{S} > \text{Me}_2\text{Se}$ . With protonic reagents they react to liberate alkanes:

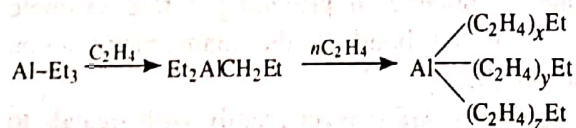


Reaction with halides or alkoxides of elements less electropositive than Al affords a useful route to other organometallics:



The main importance of organoaluminium compounds stems from the crucial discovery of alkene insertion reactions by K. Ziegler,<sup>(75)</sup> and an industry of immense proportions based on these reactions has developed during the past 40 y. Two main processes must be distinguished: (a) "growth reactions" to synthesize unbranched long-chain primary alcohols and alkenes (K. Ziegler *et al.*, 1955), and (b) low-pressure polymerization of ethene and propene in the presence of organometallic mixed catalysts (1955) for which K. Ziegler (Germany) and G. Natta (Italy) were jointly awarded the Nobel Prize for Chemistry in 1963.

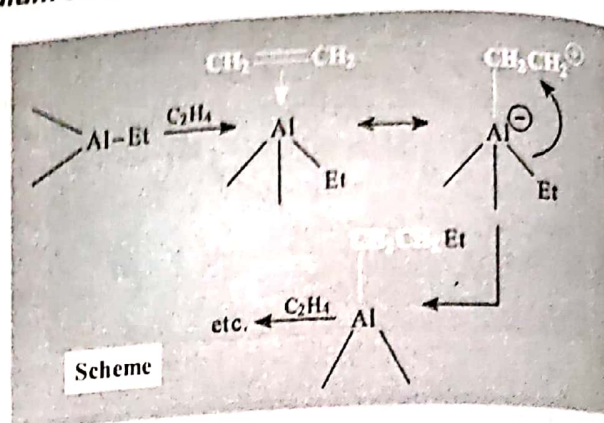
In the first process alkenes insert into the Al-C bonds of monomeric  $\text{AlR}_3$  at  $\sim 150^\circ$  and 100 atm to give long-chain derivatives whose composition can be closely controlled by the temperature, pressure and contact time:



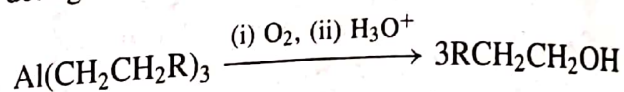
The reaction is thought to occur by repeated  $\eta^2$ -coordination of ethene molecules to Al followed by migration of an alkyl group from Al to the alkene carbon atom (see Scheme).

Unbranched chains up to  $\text{C}_{200}$  can be made, but prime importance attaches to chains of 14–20 C

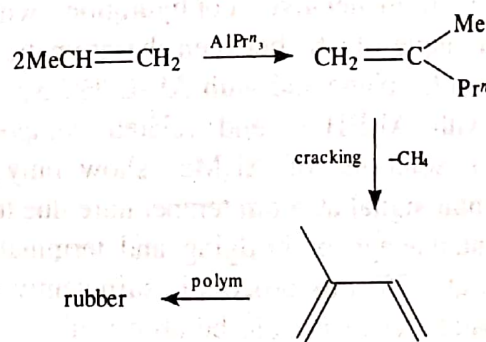
<sup>75</sup> K. ZIEGLER, *Adv. Organometallic Chem.* 6, 1–17 (1968).



atoms which are synthesized industrially in this way and then converted to unbranched aliphatic alcohols for use in the synthesis of biodegradable detergents:



Alternatively, thermolysis yields the terminal alkene  $\text{RCH}=\text{CH}_2$ . Note that, if propene or higher alkenes are used instead of ethene, then only single insertion into Al-C occurs. This has been commercially exploited in the catalytic dimerization of propene to 2-methylpentene-1, which can then be cracked to isoprene for the production of synthetic rubber (*cis*-1,4-polyisoprene):



Even more important is the stereoregular catalytic polymerization of ethene and other alkenes to give high-density polyethene ("polythene") and other plastics. A typical Ziegler-Natta catalyst can be made by mixing  $\text{TiCl}_4$  and  $\text{Al}_2\text{Et}_6$  in heptane: partial reduction to  $\text{Ti}^{\text{III}}$  and alkyl transfer occur, and a brown suspension forms which rapidly absorbs and polymerizes ethene even at room temperature and atmospheric pressure. Typical industrial conditions are  $50\text{--}150^\circ\text{C}$  and 10 atm. Polyethene

produced at the surface of such a catalyst is 85-95% crystalline and has a density of 0.95-0.98 g cm<sup>-3</sup> (compared with low-density polymer 0.92 g cm<sup>-3</sup>); the product is stiffer, stronger, has a higher resistance to penetration by gases and liquids, and has a higher softening temperature (140-150°). Polyethene is produced in megatonne quantities and used mainly in the form of thin film for packaging or as molded articles, containers and bottles; electrical insulation is another major application. Stereoregular (isotactic) polypropene and many copolymers of ethene are also manufactured. Much work has been done in an attempt to elucidate the chemical nature of the catalysts and the mechanism of their action; the active site may differ in detail from system to system but there is now general agreement that polymerization is initiated by η<sup>2</sup> coordination of ethene to the partly alkylated lower-valent transition-metal atom (e.g. Ti<sup>III</sup>) followed by migration of the attached alkyl group from transition-metal to carbon (the Cossee mechanism, see Scheme below). An alternative suggestion involves a metal-carbene species generated by α-hydrogen transfer from carbon to the transition metal.<sup>(76)</sup>

Coordination of the ethene or propene to Ti<sup>III</sup> polarizes the C-C bond and allows ready migration of the alkyl group with its bonding electron-pair. This occurs as a concerted

process, and transforms the η<sup>2</sup>-alkene into a σ-bonded alkyl group. As much as 1 tonne of polypropylene can be obtained from as little as 5 g Ti in the catalyst.

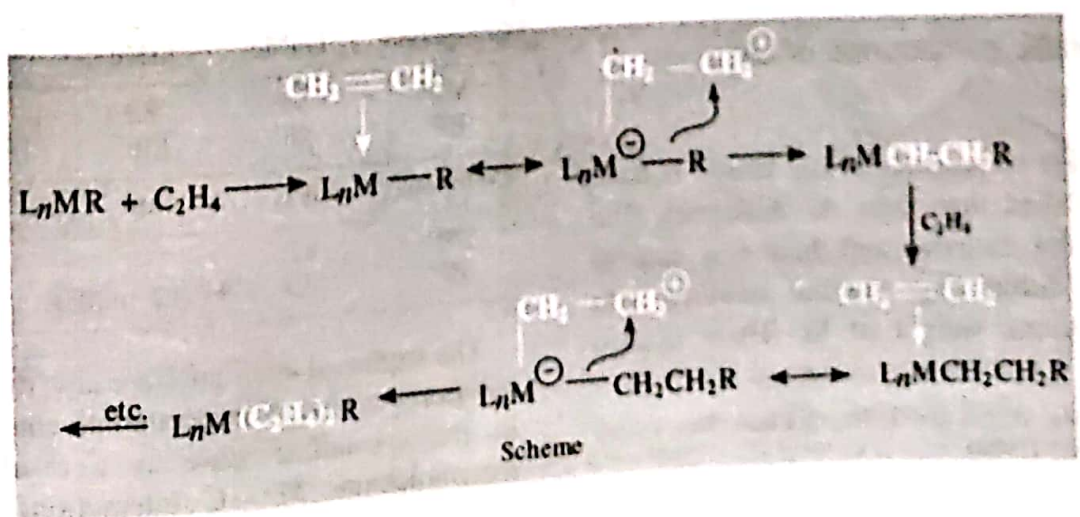
Finally, in this subsection, we mention a few recent examples of the use of specific ligands to stabilize particular coordination geometries about the organoaluminium atom (see also p. 256). (Trigonal planar stereochemistry has been achieved in R<sub>2</sub>AlCH<sub>2</sub>AlR<sub>2</sub> [R = (Me<sub>3</sub>Si)<sub>2</sub>CH-], which was prepared as colourless crystals by reacting CH<sub>2</sub>(AlCl<sub>2</sub>)<sub>2</sub> with 4 moles of LiCH(SiMe<sub>3</sub>)<sub>2</sub> in pentane.<sup>(77)</sup> It is also noteworthy that the bulky R groups permit the isolation for the first time of a molecule having the AlCH<sub>2</sub>Al grouping, by preventing the dismutation which spontaneously occurs with the Me and Et derivatives.)

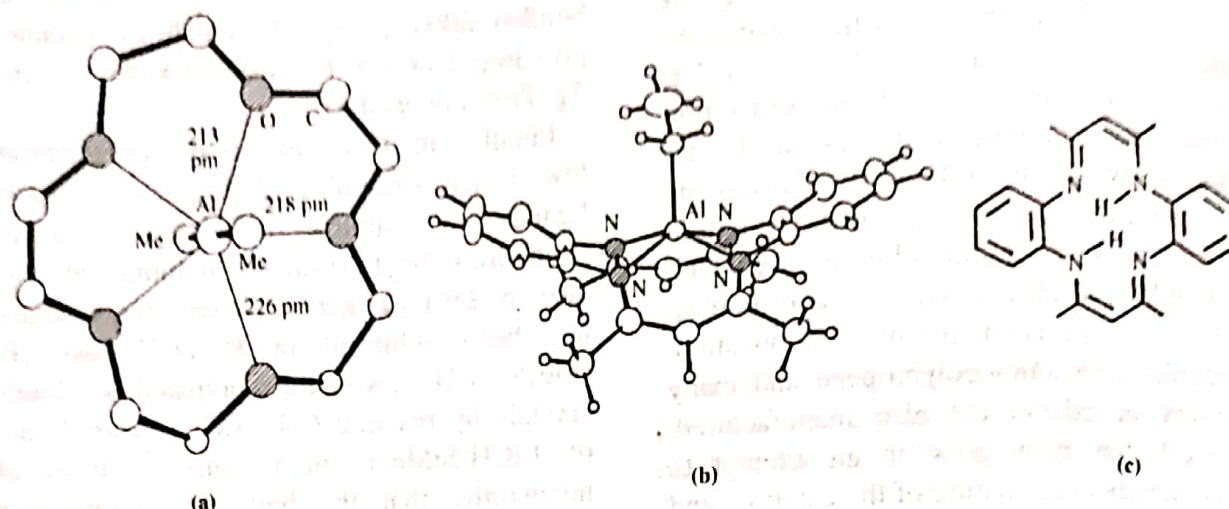
(The linear cation [AlMe<sub>2</sub>]<sup>+</sup> has been stabilized by use of crown ethers (p. 96).<sup>(78)</sup> For example, 15-crown-5 gives overall pentagonal bipyramidal 7-fold coordination around Al with axial Me groups having Al-C 200 pm and angle Me-Al-Me 178° (see Fig. 7.19a). With the larger ligand 18-crown-6, the Al atom is bonded to only three of the six O atoms to give unsymmetrical 5-fold coordination with Al-C 193 pm and angle Me-Al-Me 141°. Symmetrical (square-pyramidal) 5-coordinate Al is found

<sup>76</sup> M. L. H. GREEN, *Pure Appl. Chem.* **50**, 27-35 (1978). K. J. IVIN, J. J. ROONEY, C. D. STEWART, M. L. H. GREEN and R. MAHTAB, *J. Chem. Soc., Chem. Commun.*, 604-6 (1978).

<sup>77</sup> M. LAYH and W. UHL, *Polyhedron* **9**, 277-82 (1990).

<sup>78</sup> S. G. BOTT, A. ALVANIPOUR, S. D. MORLEY, D. A. ATWOOD, C. M. MEANS, A. W. COLEMAN and J. L. ATWOOD, *Angew. Chem. Int. Edn. Engl.* **26**, 485-6 (1987).





**Figure 7.19** (a) Structure of the cation in  $[\text{AlMe}_2(15\text{-crown-5})]^+[\text{AlMe}_2\text{Cl}_2]^-$  showing pentagonal bipyramidal coordination of Al with axial Me groups. (b) Structure of  $[\text{AlEtL}]$  where L is the bis(deprotonated) form of the macrocycle  $\text{H}_2[\text{C}_{22}\text{H}_{22}\text{N}_4]$  shown in (c).

in the complex  $[\text{AlEtL}]$  (Fig. 7.19b) formed by reacting  $\text{Al}_2\text{Et}_6$  in hexane solution with  $\text{H}_2[\text{C}_{22}\text{H}_{22}\text{N}_4]$ , i.e.  $\text{H}_2\text{L}$ , shown in Fig. 7.19c.<sup>(79)</sup> The average Al–N distance is 196.7 pm, Al–C is 197.6 pm (close to the value for the terminal Al–C in  $\text{Al}_2\text{Me}_6$ , p. 259) and the Al atom is 57 pm above the  $\text{N}_4$  plane. A further notable feature is the great stability of the Al–C bond: the compound can be recrystallized unchanged from hydroxylic or water-containing solvents and does not decompose even when heated to 300°C in an inert atmosphere.)

Heterocyclic and cluster organoaluminium compounds containing various sequences of Al–N bonds are discussed on p. 265.

### Organometallic compounds of Ga, In and Tl

Organometallic compounds of Ga, In and Tl have been less studied than their Al analogues. The trialkyls do not dimerize and there is a general tendency to diminishing thermal stability with increasing atomic weight of M. There is also

a general decrease of chemical reactivity of the M–C bond in the sequence  $\text{Al} > \text{Ga} \approx \text{In} > \text{Tl}$ , and this is particularly noticeable for compounds of the type  $\text{R}_2\text{MX}$ ; indeed, Tl gives air-stable non-hydrolysing ionic derivatives of the type  $[\text{TlR}_2]\text{X}$ , where  $\text{X} = \text{halogen}, \text{CN}, \text{NO}_3, \frac{1}{2}\text{SO}_4$ , etc. For example, the ion  $[\text{TlMe}_2]^+$  is stable in aqueous solution, and is linear like the isoelectronic  $\text{HgMe}_2$  and  $[\text{PbMe}_2]^{2+}$ .

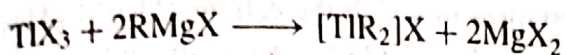
$\text{GaR}_3$  can be prepared by alkylating Ga with  $\text{HgR}_2$  or by the action of  $\text{RMgBr}$  or  $\text{AlR}_3$  on  $\text{GaCl}_3$ . They are low-melting, mobile, flammable liquids. The corresponding In and Tl compounds are similar but tend to have higher mps and bps; e.g.

Compound	$\text{GaMe}_3$	$\text{InMe}_3$	$\text{TlMe}_3$
MP	–16°	88.4°	38.5°
BP	56°	136°	147° (extrap)
Compound	$\text{GaEt}_3$	$\text{InEt}_3$	$\text{TlEt}_3$
MP	–82°	–	–63°
BP	143°	84°/12 mmHg	192° (extrap)

The triphenyl analogues are also monomeric in solution but tend to associate into chain structures in the crystalline state as a result of weak intermolecular  $\text{M} \cdots \text{C}$  interactions:  $\text{GaPh}_3$  mp

<sup>79</sup> V. L. GOEDKEN, H. ITO and T. ITO, *J. Chem. Soc., Chem. Commun.*, 1453–5 (1984).

166°, InPh<sub>3</sub> mp 208°, TIPh<sub>3</sub> mp 170°. For Ga and In compounds the primary M-C bonds can be cleaved by HX, X<sub>2</sub> or MX<sub>3</sub> to give reactive halogen-bridged dimers (R<sub>2</sub>MX)<sub>2</sub>. This contrasts with the unreactive ionic compounds of Tl mentioned above, which can be prepared by suitable Grignard reactions:



As in the case of organoaluminium compounds, unusual stereochemistries can be imposed by suitable design of ligands. Thus, reaction of GaCl<sub>3</sub> with 3,3',3''-nitrotris(propylmagnesium chloride), [N{[(CH<sub>2</sub>)<sub>3</sub>MgCl]}<sub>3</sub>], yields colourless crystals of [Ga(CH<sub>2</sub>)<sub>3</sub>N] in which intramolecular N→Ga coordination stabilizes a planar trigonal monopyramidal geometry about Ga as shown schematically in Fig. 7.20(a).<sup>(80)</sup> Because of steric constraints, the Ga-N distance of 209.5 pm is about 7% longer than the sum of the covalent radii (195 pm), although not so long as in Me<sub>3</sub>GaNMe<sub>3</sub> (220 pm). Long bonds are also a feature of the unique 6-coordinate complex of InMe<sub>3</sub> with the heterocyclic triazine ligand (Pr<sup>i</sup>NCH<sub>2</sub>)<sub>3</sub>. The air-sensitive adduct, [Me<sub>3</sub>In{η<sup>3</sup>-(Pr<sup>i</sup>NCH<sub>2</sub>)<sub>3</sub>}], can be prepared by

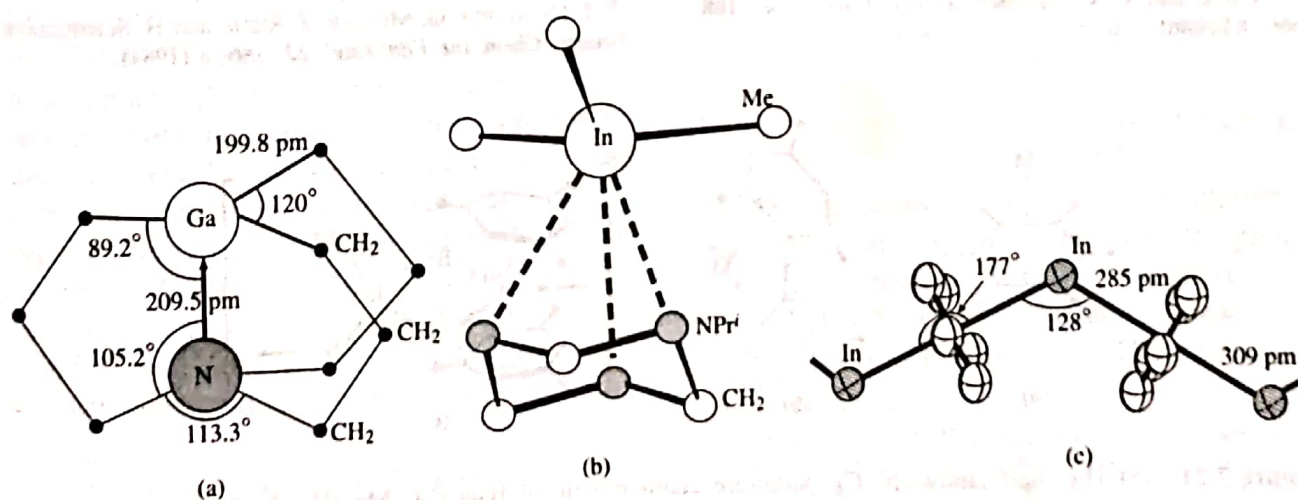
direct reaction of the donor and acceptor in ether solution, and is the first example of a tridentate cyclotriazine complex; it is also the first example of InMe<sub>3</sub> accepting three lone pairs of electrons rather than the more usual one or two.<sup>(81)</sup> The structure (Fig. 7.20b) features a shallow InC<sub>3</sub> pyramid with C-In-C angles of 114°-117° and extremely acute N-In-N angles (48.6°) associated with the long In-N bonds (278 pm). The three Pr<sup>i</sup> groups are all in equatorial positions.

Cyclopentadienyl and arene complexes of Ga, In and Tl have likewise attracted increasing attention during the past decade and provide a rich variety of structural types and of chemical diversity. [Ga(C<sub>5</sub>H<sub>5</sub>)<sub>3</sub>], prepared directly from GaCl<sub>3</sub> and an excess of LiC<sub>5</sub>H<sub>5</sub> in Et<sub>2</sub>O, was found to have simple trigonal planar Ga bonded to three η<sup>1</sup>-C<sub>5</sub>H<sub>5</sub> groups. The more elusive C<sub>5</sub>Me<sub>5</sub> derivative was finally prepared from GaCl<sub>3</sub> and an excess of the more reactive NaC<sub>5</sub>Me<sub>5</sub> in thf solution, or by reduction of Ga(C<sub>5</sub>Me<sub>5</sub>)<sub>n</sub>Cl<sub>3-n</sub> (n = 1, 2) with sodium naphthalenide in thf.<sup>(82)</sup> [Ga(C<sub>5</sub>Me<sub>5</sub>)<sub>3</sub>]

<sup>80</sup> H. SCHUMANN, U. HARTMANN, A. DIETRICH and J. PICKARDT, *Angew. Chem. Int. Edn. Engl.* **27**, 1077-8 (1988).

<sup>81</sup> D. C. BRADLEY, D. M. FRIGO, I. S. HARDING, M. B. HURSTHOUSE and M. MOTEVALLI, *J. Chem. Soc., Chem. Commun.*, 577-8 (1992).

<sup>82</sup> O. T. BEACHLEY and R. B. HALLOCK, *Organometallics* **6**, 170-2 (1987).



**Figure 7.20** (a) Structure of [Ga(CH<sub>2</sub>)<sub>3</sub>N] showing trigonal planar monopyramidal 4-fold coordination about Ga and tetrahedral coordination about N. (b) Structure of [Me<sub>3</sub>In{η<sup>3</sup>-(Pr<sup>i</sup>NCH<sub>2</sub>)<sub>3</sub>}] — see text for dimensions. (c) Structure of polymeric [In(η<sup>5</sup>-C<sub>5</sub>H<sub>5</sub>)].

is a colourless, sublimable, crystalline solid, mp 168°, and appears to be a very weak Lewis acid.

As distinct from the cyclopentadienyls of Ga<sup>III</sup>, those of In and Tl involve the +1 oxidation state of the metal and pentahapto bonding of the ligand. [In( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] is best prepared by metathesis between LiC<sub>5</sub>H<sub>5</sub> and a slurry of InCl in Et<sub>2</sub>O.<sup>(83)</sup> It is monomeric in the gas phase with a 'half-sandwich' structure, the In-C<sub>5</sub>(centroid) distance being 232 pm, but in the solid state it is a zig-zag polymer with significantly larger In-C<sub>5</sub>(centroid) distances as shown in Fig. 7.20c.<sup>(84)</sup> The crystalline pentamethyl derivative, by contrast, is hexameric and features an octahedral In<sub>6</sub> cluster each vertex of which is  $\eta^5$ -coordinated by C<sub>5</sub>Me<sub>5</sub>.<sup>(85)</sup> [Tl( $\eta^5$ -C<sub>5</sub>H<sub>5</sub>)] precipitates as air-stable yellow crystals when aqueous TlOH is shaken with cyclopentadiene. In the gas phase the compound is monomeric with C<sub>5v</sub> symmetry, the Tl atom being 241 pm above the plane of the ring (microwave), whereas in the crystalline phase there are zig-zag chains of equispaced alternating

C<sub>5</sub>H<sub>5</sub> rings and Tl atoms similar to the In homologue.

Hexahapto ( $\eta^6$ -arene) complexes of Ga<sup>I</sup> and In<sup>I</sup> can be obtained from solutions of the lower halides (p. 240) in aromatic solvents, and some of these have surprisingly complex structures.<sup>(86)</sup> With bulky ligands such as C<sub>6</sub>Me<sub>6</sub> simple adducts crystallize in which the cations [M( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)]<sup>+</sup> have the C<sub>6v</sub> 'half-sandwich' structure shown in Fig. 7.21a, e.g. [Ga( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)] [GaCl<sub>4</sub>] mp 168° and [Ga( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)] [GaBr<sub>4</sub>] mp 146°.<sup>(87)</sup> With less bulky ligands such as mesitylene (1,3,5-C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>), a 2:1 stoichiometry is possible to give cations [M( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)<sub>2</sub>]<sup>+</sup> shown schematically in Fig. 7.21b, although further ligation from the anion may also occur; e.g. [In( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)<sub>2</sub>] [InBr<sub>4</sub>] features polymeric helical chains in which bridging [ $\mu$ - $\eta^1, \eta^2$ -InBr<sub>4</sub>] units connect the cations as shown in Fig. 7.21c.<sup>(88)</sup> With still less bulky ligands such as benzene itself, discrete dimers can be formed as in the solvated complex [Ga( $\eta^6$ -C<sub>6</sub>H<sub>6</sub>)<sub>2</sub>] [GaCl<sub>4</sub>] . 3C<sub>6</sub>H<sub>6</sub>. This features tilted bis(arene)Ga<sup>I</sup> units linked through bridging GaCl<sub>4</sub> units to form the dimeric structure shown in Fig. 7.22a.<sup>(86)</sup> Mixed adducts can also be prepared. Thus, when

<sup>83</sup> C. PEPPE, D. G. TUCK and L. VICTORIANO, *J. Chem. Soc., Dalton Trans.*, 2592 (1981).

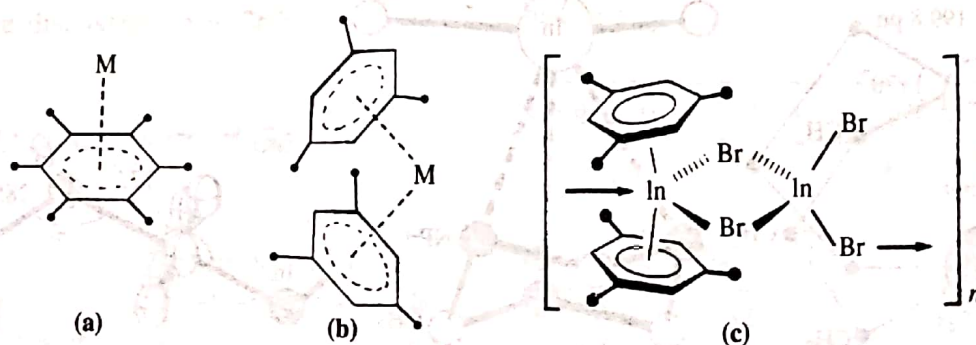
<sup>84</sup> O. T. BEACHLEY, J. C. PAZIK, T. E. GLASSMAN, M. R. CHURCHILL, J. C. FETTINGER and R. BLOM, *Organometallics* 7, 1051-9 (1988).

<sup>85</sup> O. T. BEACHLEY, M. R. CHURCHILL, J. C. FETTINGER, J. C. PAZIK and L. VICTORIANO, *J. Am. Chem. Soc.* 108, 4666-8 (1986).

<sup>86</sup> H. SCHMIDBAUR, *Angew. Chem. Int. Edn. Engl.* 24, 893-904 (1985).

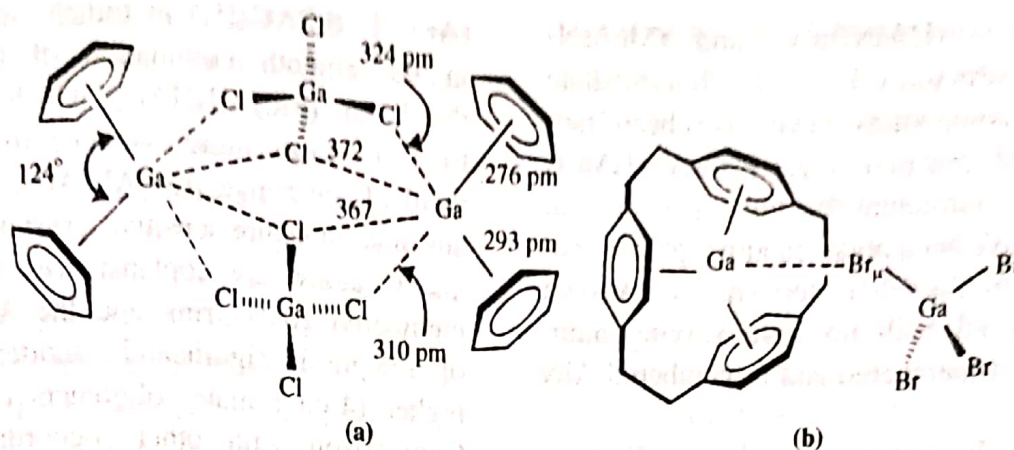
<sup>87</sup> H. SCHMIDBAUR, U. THEWALT and T. ZAFIROPOULOS, *Angew. Chem. Int. Edn. Engl.* 23, 76-7 (1984).

<sup>88</sup> J. EBENHÖCH, G. MÜLLER, J. RIEDE and H. SCHMIDBAUR, *Angew. Chem. Int. Edn. Engl.* 23, 386-8 (1984).



**Figure 7.21** (a) The 'half-sandwich' C<sub>6v</sub> structure characteristic of [Ga( $\eta^6$ -C<sub>6</sub>Me<sub>6</sub>)]<sup>+</sup>. (b) The 'bent-sandwich' structure found in ions of the type [In( $\eta^6$ -C<sub>6</sub>H<sub>3</sub>Me<sub>3</sub>)<sub>2</sub>]<sup>+</sup>. (c) A section of the helical chain in [In( $\eta^6$ -mes)<sub>2</sub>] [InBr<sub>4</sub>] showing the [ $\mu$ - $\eta^1, \eta^2$ -InBr<sub>4</sub>] unit bridging ions of the type shown in (b); the tilting angle is 133° and the ring-centres of the two arene ligands are almost equidistant from In (283 and 289 pm).





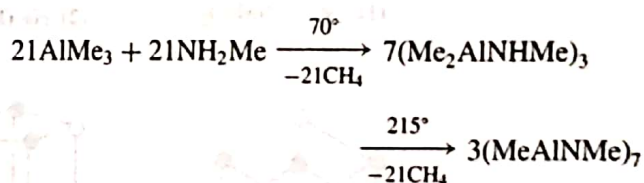
**Figure 7.22** (a) Structure of the dimeric unit in the solvated complex  $[\text{Ga}(\eta^6\text{-C}_6\text{H}_6)_2][\text{GaCl}_4]\cdot 3\text{C}_6\text{H}_6$  indicating the principal dimensions; the six benzene molecules of solvation per dimer lie outside the coordination spheres of the gallium atoms. (b) Structure of the ion-pair  $[\text{Ga}(\eta^{18}\text{-[2.2.2]paracyclophane})][\text{GaBr}_4]$ ; the four Ga-Br distances within the tetrahedral anion are in the range 230.5–233.3 pm, the distance for Ga- $\text{Br}_\mu$  being 231.9 pm; the  $\text{Ga}^1 \cdots \text{Br}_\mu$  distance is 338.8 pm.

dilute toluene solutions of  $\text{Ga}_2\text{Cl}_4$  and durene (1,2,4,5- $\text{C}_6\text{H}_2\text{Me}_4$ ) are cooled to  $0^\circ$ , crystals containing the centrosymmetric dimer  $[(\text{Ga}(\eta^6\text{-dur})(\eta^6\text{-tol}))\text{GaCl}_4]_2$  are obtained.<sup>(89)</sup> The structure resembles that in Fig. 7.22a, with each  $\text{Ga}^1$  centre  $\eta^6$ -bonded to one durene molecule at 264 pm and one toluene molecule at 304 pm. These bent-sandwich moieties are then linked into dimeric units via three of the four Cl atoms of each of the two  $\text{GaCl}_4$  tetrahedra.

An even more remarkable structure emerges for the monomeric complex of  $\text{Ga}_2\text{Br}_4$  with the tris(arene) ligand [2.2.2]paracyclophane (Fig. 7.22b).<sup>(90)</sup> the  $\text{Ga}^1$  centre is encapsulated in a unique  $\eta^{18}$  environment which has no parallels even in transition-metal coordination chemistry. The  $\text{Ga}^+$  cation is almost equidistant from the three ring centres (265 pm) but is displaced away from the ligand centre by 43 pm towards the  $\text{GaBr}_4^-$  counter anion. The complex was prepared by dissolving the dimeric benzene complex  $[(\text{C}_6\text{H}_6)_2\text{Ga}\cdot\text{GaBr}_4]_2$  (cf. Fig. 7.22a) in benzene and adding the cyclophane.

### Al-N heterocycles and clusters

Finally, in this chapter, attention should be drawn to a remarkable range of heterocyclic and cluster organoaluminium compounds containing various sequences of Al-N bonds<sup>(91)</sup> (cf. B-N compounds, p. 207). Thus the adduct  $[\text{AlMe}_3(\text{NH}_2\text{Me})]$  decomposes at  $70^\circ\text{C}$  with loss of methane to give the cyclic amido trimers *cis*- and *trans*- $[\text{Me}_2\text{AlNHMe}]_3$  (structures 2 and 3) and at  $215^\circ$  to give the oligomeric imido cluster compounds  $(\text{MeAlNMe})_7$  (structure 6) and  $(\text{MeAlNMe})_8$  (structure 7), e.g.:



Similar reactions lead to other oligomers depending on the size of the R groups and the conditions of the reaction, e.g. *cyclo*- $(\text{Me}_2\text{AlNMe}_2)_2$  (structure 1) and the imido-clusters  $(\text{PhAlNPh})_4$ ,  $(\text{HAlNPr}^i)_4$  or 6.

<sup>89</sup> H. SCHMIDBAUR, R. NOWAK, B. HUBER and G. MÜLLER, *Polyhedron* **9**, 283–7 (1990).

<sup>90</sup> H. SCHMIDBAUR, R. HAGER, B. HUBER and G. MÜLLER, *Angew. Chem. Int. Edn. Engl.* **26**, 338–40 (1987). See also H. SCHMIDBAUR, W. BUBLAK, B. HUBER and G. MÜLLER, *Organometallics* **5**, 1647–51 (1986).

<sup>91</sup> S. AMIRKHALILI, P. B. HITCHCOCK and J. D. SMITH, *J. Chem. Soc., Dalton Trans.*, 1206–12 (1979); and references 1–9 therein. See also P. P. POWER, *J. Organometallic Chem.* **400**, 49–69 (1990); K. M. WAGGONER, M. M. OLMSTEAD and P. P. POWER, *Polyhedron* **9**, 257–63 (1990); A. J. DOWNS, D. DUCKWORTH, J. C. MACHELL and C. R. PULHAM, *Polyhedron* **11**, 1295–304 (1992).