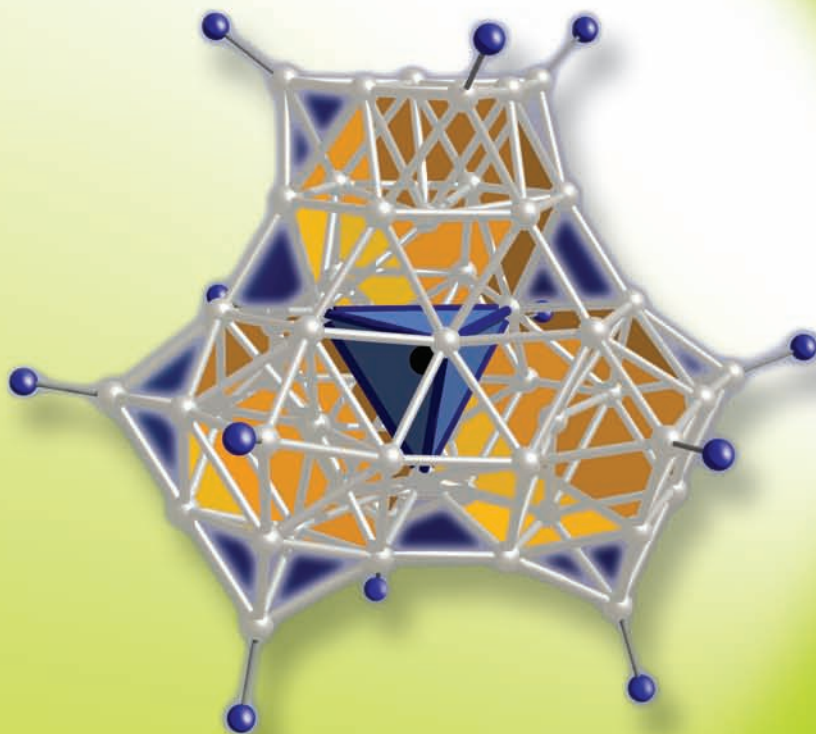


THE GROUP 13 METALS ALUMINIUM, GALLIUM, INDIUM AND THALLIUM

Chemical Patterns and Peculiarities



Editors | SIMON ALDRIDGE | ANTHONY J. DOWNS

 WILEY

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Editors

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Contents

Preface	ix
List of Contributors	xi
1 New Light on the Chemistry of the Group 13 Metals	1
<i>Anthony J. Downs and Hans-Jörg Himmel</i>	
1.1 Reprise of the General Features of Group 13 Elements	1
1.2 Developments in Methodology	6
1.3 Redox Chemistry of the Group 13 Metals: Access to Oxidation States Lower than +3	25
1.4 Bonding Aspects	28
1.5 Solid Compounds with Specific Electronic, Structural or Other Properties	38
1.6 Coordination Chemistry of M(III) Compounds	43
1.7 Mediation of Organic Transformations by Group 13 Metal Compounds	57
References	60
2 The Chemistry of the Group 13 Metals in the +3 Oxidation State: Simple Inorganic Compounds	75
<i>Simon Aldridge</i>	
2.1 Introduction	75
2.2 Hydrides	76
2.3 Halides and Pseudo-Halides	99
2.4 Oxides and Oxo- Derivatives	107
2.5 Chalcogenides and Chalco-Derivatives	118
2.6 Compounds with Bonds to Group 15 Atoms	122
References	132
3 Formal Oxidation State +3: Organometallic Chemistry	148
<i>Simon Aldridge, Anthony J. Downs and Deborah L. Kays</i>	
3.1 Introduction	148
3.2 Organo Derivatives with a Metal–Carbon Primary Framework	151
3.3 Derivatives with Bonds to Group 15 Elements	168
3.4 Derivatives with Bonds to Group 16 Elements	192
3.5 Organometal Halides	210
3.6 Organometal Hydrides	215
3.7 d-Block and f-Block Compounds with Organo-Group 13 Metal(III) Fragments	220
References	227

4	Formal Oxidation State +2: Metal–Metal Bonded Versus Mononuclear Derivatives	246
	<i>Werner Uhl and Marcus Layh</i>	
4.1	Introduction	246
4.2	Subhalides Containing M–M Bonds	247
4.3	Homoleptic Chalcogen Compounds	250
4.4	Homoleptic Dielement Compounds with Pnicogen Atoms Coordinated to the M–M Bonds	251
4.5	Heteroleptic Compounds Containing Donor Atoms of Groups 15 to 17	254
4.6	Homoleptic Dinuclear Organoelement(II) Compounds	257
4.7	Heteroleptic Organoelement(II) Compounds	265
4.8	Mononuclear Element(II) Compounds	274
	References	277
5	The Chemistry of the Group 13 Metals in the +1 Oxidation State	285
	<i>Cameron Jones and Andreas Stasch</i>	
5.1	Introduction	285
5.2	Aluminium	286
5.3	Gallium	298
5.4	Indium	310
5.5	Thallium	317
	References	329
6	Mixed or Intermediate Valence Group 13 Metal Compounds	342
	<i>Benjamin F. T. Cooper and Charles L. B. Macdonald</i>	
6.1	Mixed Valency	342
6.2	Halides	346
6.3	Arene-stabilised Mixed Valent Species	353
6.4	Chalcogenide and Other Non-Halide Salts	363
6.5	Discretely Bonded Systems	368
6.6	Donor–Acceptor Compounds	390
6.7	Conclusions	396
	References	397
7	Aluminium and Gallium Clusters: Metalloid Clusters and their Relationship to the Bulk Phases, to Naked Clusters and to Nanoscaled Materials	402
	<i>Hansgeorg Schnöckel and Andreas Schnepf</i>	
7.1	Introduction	402
7.2	Explanations of Special Terms	404
7.3	The Naked Al_{13}^- Cluster	407
7.4	Metalloid Al/Ga Clusters	416
7.5	Interactions between Cluster Species within the Crystal	471
7.6	Summary and Outlook	480
	References	482
8	Simple and Mixed Metal Oxides and Hydroxides: Solids with Extended Structures of Different Dimensionalities and Porosities	488
	<i>Andrew M. Fogg</i>	
8.1	Introduction	488
8.2	The Parent Oxides and Hydroxides	489

8.3 Layered Materials	494
8.4 Framework Materials	502
References	509
9 Coordination and Solution Chemistry of the Metals: Biological, Medical and Environmental Relevance	519
<i>Penelope J. Brothers and Christy E. Ruggiero</i>	
9.1 Introduction	519
9.2 Hydrides	521
9.3 Halides	542
9.4 Group 13 Complexes of N-donor Ligands	548
9.5 Complexes of the Monovalent M(I) Group 13 Metals	557
9.6 Divalent M(II) Complexes	568
9.7 Chemistry Relevant to Environmental and Biological Systems	569
9.8 Environmental Abundances, Uses and Sources	572
9.9 Biological Systems	576
References	593
10 III–V and Related Semiconductor Materials	612
<i>Mohammad Azad Malik and Paul O'Brien</i>	
10.1 Introduction	612
10.2 III–Nitrides	619
10.3 III–Phosphides	627
10.4 III–Arsenides	631
10.5 III–Antimonides	636
References	645
11 Group 13 Metal-Mediated Organic Reactions	654
<i>Samuel Dagonne and Stéphane Bellemin-Laponnaz</i>	
11.1 Aluminium	654
11.2 Gallium	675
11.3 Indium	681
11.4 Thallium	688
References	692
Index	701

Preface

“Evolution . . . is – a change from an indefinite, incoherent homogeneity, to a definite, coherent heterogeneity.”

Herbert Spencer, *First Principles*, 1862, Chapter 16.

It was homogeneity, modulated by predictable variations, that enabled Mendeleev in 1870 to anticipate with celebrated fidelity the properties of gallium, then the missing link in what we now call Group 13. While the kinship of the elements has never been in doubt with the evolution of our knowledge of their chemistry, it is the peculiarities which have more often left their mark – for example, the discovery of a wide variety of compounds in which the Group 13 element M assumes a formal oxidation state other than +3; the identification of diverse compounds with M–M-bonded frameworks; the finding of catalytic activity in compounds that varies radically according to the nature of M; the mediation of organic reactions in ways that differ widely from one Group 13 element to another; and the development of solids with extended structures and absorption properties more or less specific to a particular member of the Group.

So eccentric is boron, the non-metal with its propensity for forming strong localised or delocalised covalent bonds, that it is most aptly separated from the other members of Group 13. Its chemistry has been comprehensively reviewed, for example in volumes of the Gmelin Handbook up to the later years of the 20th century and in numerous other books. This contrasts with the generally meagre and piecemeal treatment of the heavier members of the Group, all of them metals forming a more closely knit family, but each with its own distinctive personality. For none of these does the Gmelin Handbook offer more than a specific volume or two dating beyond the first half of the 20th century.

This book seeks to remedy the imbalance with a definitive, wide-ranging and up-to-date review of major aspects of the chemistry of these elements. It has two obvious reference points. The first is the book entitled *The Chemistry of Aluminium, Gallium, Indium and Thallium*, written by Wade and Banister, published first in 1973 as part of *Comprehensive Inorganic Chemistry*, and appearing as a separate volume in 1975. The second is a book bearing the same title and edited by one of us and that first saw the light of day roughly two decades later (1993). With the passage of nearly two more decades that have seen a wealth of activity, it seemed to us timely once again to take stock. This we have sought to do not as a mere catalogue, but within a framework designed to present a wider picture that places new facts, developments and applications in the context of more general patterns of physical and chemical behaviour – that is, with an eye to *both* the homogeneity and heterogeneity displayed by the elements. The various chapters have been written by members of an international team of authors selected as experts with practising research experience in the particular field under review.

Chapter 1 sets the scene with an outline of the areas of Group 13 metal chemistry that have seen most progress in the past two decades. Chapters 2–7 are organised according to the formal oxidation state of the metal, a concept which, for all its imperfections, is likely to be most widely appreciated. After treatments of first the inorganic and then the organic derivatives of the metals in the dominant +3 state in Chapters 2 and 3, respectively, Chapter 4

addresses the +2 state with its prevailing theme of M–M bonding, while Chapter 5 is concerned with the +1 state, which has gained hugely in significance in recent years. Chapter 6 is devoted to compounds in which M occurs in more than one oxidation state, as exemplified by the classical case of $\text{Ga}^{\text{I}}\text{Ga}^{\text{III}}\text{Cl}_4$. Mixed oxidation states are also a feature of many of the remarkable cluster compounds, including so called metalloid clusters, that have lately caused such a storm, particularly through the pioneering research of the Karlsruhe group led by Schnöckel. An authentic and challenging account of this area is presented in Chapter 7. There follows in Chapter 8 a review of simple and mixed Group 13 metal oxides and hydroxides including zeolites, detailing the extended structures of different dimensionalities and porosities that they form in the solid state. If this is preoccupied with the solid state, the coordination chemistry of the metals, as described in Chapter 9, is intimately related to their behaviour in solution, with its relevance in biology, medicine, and the environment. The solid state is again to the fore in Chapter 10 which deals with III-V and related semiconductor materials. Last but far from least, the role of the Group 13 metals and their compounds as reagents or mediators in organic synthesis is taken up in Chapter 11.

A book on this scale cannot possibly emulate Gmelin. Even with references to some 5000 original papers, books, and review articles, some published as recently as 2010, it makes no pretence of being comprehensive. All the authors have been given licence to treat their subjects as they see fit. We are well aware that some compounds and some topics have as a result received little or no attention. Such is the case, for example, with Zintl and related phases containing more or less negatively charged clusters and networks of Group 13 metal atoms. Nor is the bonding in Group 13 metal compounds made the exclusive preserve of any one chapter. We are aware too of the overlap existing between some of the chapters, all having been written as self-sufficient accounts. While it may mean that our coverage is not everywhere as efficient as it might be, we dare to hope that there are compensations from the different perspectives, as well as the cross-linking between chapters, that will actually help to broaden any appeal the book may have.

In aiming for a clear and structured treatment with the bare minimum of specialist jargon and annoying acronyms, we have tried also to achieve an accessible style in a text that is generally readable by non-specialist no less than specialist readers. We see the book therefore not just as a contemporary source-book on Group 13 metal chemistry, but as a monograph that can be read with some profit by scientists in different walks of life. It is of course directed mainly at chemists, but includes sections likely to be of interest to physicists, biochemists, and materials, environmental and industrial scientists.

S.A.
A.J.D.

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1

New Light on the Chemistry of the Group 13 Metals

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A little learning is a dangerous thing;
Drink deep, or taste not the Pierian spring:
There shallow draughts intoxicate the brain,
And drinking largely sobers us again.

Alexander Pope, *An Essay on Criticism*, 1711

1.1 Reprise of the General Features of Group 13 Elements

First impressions may seize upon the commonality of the Group 13 elements – boron, aluminium, gallium, indium and thallium – arising out of the common configuration ns^2np^1 shared by the valence electrons in the ground state of each of the atoms. Witness, for example, the dominance of the formal oxidation state +3 and the acceptor properties that characterise the resulting derivatives, arising partly from the positive charge, partly from the inability of the Group 13 atom effectively to engage all its valence orbitals in bonding. There is harmony in the variation of properties dictated by the generally increasing atomic size and decreasing hold of the nucleus on the valence electrons as the atomic number increases from boron to thallium. But there is also counterpoint, reflecting the discontinuous build-up of the Periodic Table. Hence, each member of the Group has its own individual personality, ‘with quirks of character and not always evident dispositions’,¹ manifesting the infinite variety of the Periodic Kingdom that is perhaps the most remarkable phenomenon in the universe.

Quirkiest of the Group 13 elements is undoubtedly boron.^{2–11} As revealed in the numerical properties summarised in Table 1.1, the boron atom is disproportionately smaller and its valence electrons are more tightly held in relation to

Table 1.1 Some properties of the Group 13 elements boron, aluminium, gallium, indium and thallium¹²⁻²³

Property	B	Al	Ga	In	Tl
(i) Properties of the isolated atom					
Atomic number	5	13	31	49	81
Naturally occurring isotopes	¹⁰ B (19.9%) ¹¹ B (80.1%)	²⁷ Al (100%)	⁶⁹ Ga (60.108%) ⁷¹ Ga (39.892%)	¹¹³ In (4.29%) ¹¹⁵ In (95.71%)	²⁰³ Tl (29.524%) ²⁰⁵ Tl (70.476%)
Relative atomic mass (¹² C = 12.0000)	10.811(7)	26.9815386(8)	69.723(1)	114.818(3)	204.3833(2)
Ground-state electron configuration (term)	[He]2s ² 2p ¹ (² P _{1/2})	[Ne]3s ² 3p ¹ (² P _{1/2})	[Ar]3d ¹⁰ 4s ² 4p ¹ (² P _{1/2})	[Kr]4d ¹⁰ 5s ² 5p ¹ (² P _{1/2})	[Xe] 4f ¹⁴ 5d ¹⁰ 6s ² 6p ¹ (² P _{1/2})
Ionisation energies (kJ mol ⁻¹)					
M → M ⁺	800.637	577.539	578.844	558.299	589.351
M ⁺ → M ²⁺	2427.07	1816.68	1979.41	1820.71	1971.03
M ²⁺ → M ³⁺	3659.75	2744.78	2963	2704	2878
M ³⁺ → M ⁴⁺	25 025.9	11 577.46	6175	5210	(4900)
Thermal neutron capture cross- section (barns)	¹⁰ B 3840, ¹¹ B 0.005	0.230	⁶⁹ Ga 1.68, ⁷¹ Ga 4.7	¹¹³ In 12, ¹¹⁵ In 205	²⁰³ Tl 11, ²⁰⁵ Tl 0.11
Nuclei accessible to NMR measurements (nuclear spin <i>I</i>) ^a	[¹⁰ B(3)], ¹¹ B (3/2)	²⁷ Al (5/2)	[⁶⁹ Ga (3/2)], ⁷¹ Ga (3/2)	[¹¹³ In (9/2)], ¹¹⁵ In (9/2)	[²⁰³ Tl (1/2)], ²⁰⁵ Tl (1/2)
(ii) Properties of the bound atom					
Electronegativity, χ					
Pauling scale	2.04	1.61	1.81	1.78	1.62[Tl ^I], 2.04 [Tl ^{III}]
Allred scale	2.01	1.47	1.82	1.49	1.44
Sanderson scales	1.88	1.54	2.10	1.88	1.96
Pearson scale (eV)	4.29	3.23	3.2	3.1	3.2
Atomic (metallic) radius (Å)	0.80–0.90	1.431	1.22–1.40	1.62–1.68	1.704 (α -form)
Singlebond covalent radius for M ^{III} (Å)	0.88	1.25	1.25	1.50	1.55
van der Waals radius (Å)	2.08	2.05	1.90	1.90	2.00

Covalent bonds in M^{III}

compounds:

 length (Å) [mean bond
enthalpy (kJ mol⁻¹)]
{coordination number}

M–H	1.19 ^b [377] {3} 1.06(9) ^d {4}	1.58 ^c {3} 1.56(11) ^d [282] {4}	1.57 ^c {3} 1.51(13) ^d [260] {4}	1.74 ^c {3} 1.79(17) ^d [225] {4}	1.76 ^c [181] {3}
M–F	1.31 ^b [646] {3}	1.63 ^b [591] {3} 1.815(46) ^d {6}	1.71 ^b [602] {3} 1.95(7) ^d {6}	2.10(4) ^d [ca. 525] {6}	2.28(13) ^e [460] {8}
M–Cl	1.74 ^b [444] {3}	2.07 ^b [426] {3} 2.14(6) ^d {4}	2.10 ^b [363] {3} 2.20(8) ^d {4}	2.26 ^b [327] {3} 2.40(5) ^d {4} 2.48(10) ^d {6}	2.43(5) ^d [368] {4} 2.52(6) ^d {6}
M–O	1.37 ^b [559] {3} 1.48(4) ^d {4}	1.77(6) ^d [585] {4} 1.89(6) ^d {6}	1.91(8) ^d [ca. 430] {4} 1.96(5) ^d {6}	2.15(10) ^d [ca. 360] {4} 2.18(10) ^d {6}	2.38(11) ^d [375] {6}
M–S	1.94(5) ^d {4}	2.25(7) ^d {4}	2.26(5) ^d {4}	2.48(7) ^d {4}	2.48(2) ^f {4}
M–C ^g	1.58 ^b [376] {3} 1.63(4) ^d {4}	1.96 ^b [280] {3} 1.97(3) ^d {4}	1.97 ^b [245] {3} 1.985(38) ^d {4}	2.16 ^b [162] {3} 2.18(4) ^d {4}	2.21 ^b [125] {3} 2.17(4) ^d {4}

 Covalent bonds in diatomic
molecules: length (Å) [D_{298}°
(kJ mol⁻¹)]

M–M	1.590 [290]	2.466 [133]	2.70 [115]	2.97 [78]	3.41 [59]
M–H	1.232 [342]	1.645 [288]	1.662 [265]	1.836 [243]	1.873 [195]
M–F	1.263 [732]	1.654 [675]	1.774 [584]	1.985 [507]	2.084 [439]
M–Cl	1.715 [427]	2.130 [502]	2.202 [463]	2.401 [430]	2.485 [373]
M–Br	1.888 [391]	2.295 [429]	2.352 [416]	2.543 [388]	2.618 [331]
M–I	2.131 [361]	2.537 [370]	2.575 [334]	2.754 [331]	2.814 [285]

(iii) Properties of the elements

Crystal structure

α-B , tetragonal	α-Al , f.c.c.	α-Ga ,	Face-centred	α-Tl , hexagonal
β-B , tetragonal	High pressure form	orthorhombic	tetragonal	β-Tl , cubic
α-B ,	β-Al , hexagonal	β-Ga , monoclinic		γ-Tl , f.c.c.
rhombohedral		γ-Ga , rhombic		$T(\alpha \rightarrow \beta)$ 503 K
β-B ,		δ-Ga ,		
rhombohedral		rhombohedral		

(continued)

Table 1.1 (Continued)

Property	B	Al	Ga	In	Tl
	Other polymorphs reported and partially characterised, e.g. cubic, rhombic, monoclinic and hexagonal forms		$T(\gamma \rightarrow \alpha)$ 238 K High pressure forms: Ga(II) , <i>b.c.c.</i> Ga(III) , <i>b.c. tetragonal</i> Ga(IV) , <i>f.c.c.</i> ^h		
Melting point (K)	2348	933.47	302.92	429.75	577
Normal boiling point (K)	4273	2792	2477	2345	1746
ΔH° atomisation at 298.15 K (kJ mol ⁻¹)	565	330.9	271.96	243	182.2
Density (kg m ⁻³)	2340 (β -rhomb), 293 K	2698, 293 K	5907, 293 K	7310, 298 K	11 850, 293 K
Electrical resistivity at 273 K (Ω m)	1.8×10^4	2.417×10^{-8}	13.6×10^{-8}	8.0×10^{-8}	15×10^{-8}
(iv) Cationic and redox behaviour					
Ionic radius for six-fold coordination					
M^{3+} (\AA) ⁱ	(0.27)	0.535	0.620	0.800	0.885
M^+ (\AA)	–	(ca. 1.00)	1.13	1.32	1.50
$\Delta_f H^\circ[M^{3+}(\text{g})]$ (kJ mol ⁻¹)	7468.8	5484.0	5816	5345.3	5639.2
$\Delta_f H^\circ[M^+(\text{g})]$ (kJ mol ⁻¹)	1369.6	910.09	861.9	807.8	777.73
Thermodynamic properties for aqueous species (kJ mol ⁻¹)					
$\Delta_f G^\circ[M^{3+}(\text{aq})]$ std state, $m = 1$	–967.7 [B(OH) ₃]	–485.0	–159.0	–98.0	+ 214.6
$\Delta_f H^\circ[M^{3+}(\text{aq})]$ std state, $m = 1$	–1072.8 [B(OH) ₃]	–531.0	–211.7	–105.0	+ 196.6
$\Delta_{\text{hydration}} G^\circ[M^{3+}(\text{g})]$, single ion	n.a.	–4540	–4550	–4020	–4000
$\Delta_{\text{hydration}} H^\circ[M^{3+}(\text{g})]$, single ion	n.a.	–4680	–4690	–4110	–4110

Standard reduction potentials,

 E° (V):

$M^{III}(aq) + 3e^- \rightarrow M(s)$, $a_H^+ = 1$	-0.870	-1.662	-0.549	-0.3382	+0.741
$M^{III}(aq) + 3e^- \rightarrow M(s)$, $a_{OH^-} = 1$	-1.79	-2.328	-1.219	-1.007	-0.163 { Tl_2O_3 }
$M^I(aq) + e^- \rightarrow M(s)$, $a_H^+ = 1$	—	{[$OB(OH)_2$] $^-$ }	{[$Al(OH)_4$] $^-$ }	{[$OGa(OH)_2$] $^-$ }	{[$In(OH)_4$] $^-$ }
$M^{III}(aq) + 2e^- \rightarrow M^I(aq)$, $a_H^+ = 1$	—	(+0.3)	-0.2	-0.129	-0.334
		(-2.7)	-0.72	-0.443	+1.279

(v) Environmental properties

Abundances

Continental crust (ppb)	10^4	8.2×10^7	1.8×10^4	2.5×10^2	8.5×10^2
Ocean (ppb)	4.4×10^3	2	3×10^{-2}	3×10^{-4}	1.3×10^{-2}
Chief ores and sources	Borax and kernite, $Na_2[B_4O_5(OH)_4] \cdot xH_2O$; colemanite, $Ca_2[B_3O_4(OH)_3]_2 \cdot 2H_2O$	Bauxite, found as boehmite and diaspore, $AlO(OH)$, and gibbsite and hydrargillite, $Al(OH)_3$	Occurs up to 1% in other minerals; recovered as a by-product of zinc and alu- minium refining	Occurs up to 1% in zinc and lead sulphide ores; obtained as a by- product of zinc and lead smelting	Rare; dispersed in potash, feldspar and pollucite; by- product of zinc and lead smelting and H_2SO_4 manufacture
World production (tonnes year $^{-1}$)	ca. 2×10^6 (B_2O_3)	ca. 4×10^7 (Al)	ca. 100 (Ga)	ca. 450 (In)	ca. 30 (Tl)
Reserves (tonnes)	270×10^6 (as B_2O_3)	6×10^9	—	>1500	—

^a Nuclei enclosed in square brackets are seldom used in NMR studies.^b Refers to a specific gaseous molecule, that is MH_3 , MF_3 , MCl_3 , $M(OH)_3$ and $M(CH_3)_3$ ($M = B, Al, Ga, In$ or Tl).^c Calculated value (Ref. 21, p. 3313).^d Average length of a terminal bond determined for numerous compounds by single crystal X-ray diffraction studies,²⁰ numbers in parentheses are the standard deviations of the last digits.^e Refers to a single crystal structure, that of TlF_3 (Ref. 12, p. 3).^f Refers to a single crystal structure containing 3 terminal $Tl-S$ bonds to non-chelating ligands.²⁴^g C is an alkyl carbon atom.^h Reference 25, and references cited therein.ⁱ Reference 26.

the atoms of its vertical neighbours. Accordingly, the element itself is not a metal but a semiconductor with several hard and refractory allotropic forms characterised by unique and elaborate structures based on the B_{12} icosahedron. Here and in metal borides and boron hydrides, too, evidence is found of boron's propensity to form polyboron branched and unbranched chains, cages, planar networks and three-dimensional arrays. These typify an extensive and unusual type of covalent (molecular or macromolecular) chemistry in which multicentre bonding is one of the most distinctive features. Moreover, the relatively compact 2p orbitals of the boron atom share with those of the carbon atom the ability to engage in relatively efficient π -type interactions, providing a mechanism for supplementing substantially the bonding to electron-rich centres. Such interactions subscribe to the relative abundance and stability of three-coordinate environments for the boron atom, as in the trihalides, boric acid, amidoboranes and borazine, $H_3B_3N_3H_3$, formally analogous to benzene. Another feature peculiar to boron is the relative closeness in energy of the valence 2s and 2p orbitals, which favours a major contribution from the 2s orbital to the bonding of boron(III) compounds. This, combined with the inherent strengths of the bonds that boron forms, acts against the univalent state; accordingly, boron(I) is rarely encountered outside the realm of 'high temperature' molecules such as BF and BCl.

In these and other respects, boron must be seen as a special case, with many idiosyncracies that separate it from the other Group 13 elements. Although it serves as a vital reference point for understanding and evaluating the chemistries of these elements, reasons of space and balance defy its inclusion, except by allusion, in this volume. Otherwise, there would be the risk of having something of 'an elephant in the living room'. This view finds support in the precedents of not only two earlier books treating exclusively the metallic members of Group 13,^{12,27} but also an extensive literature devoted specifically to boron²⁻⁹ (including the only reasonably up-to-date coverage in Gmelin² for any member of the Group).

All the other members of the Group are then metals. If they show a closer kinship to one another than they do to boron, their properties are, however, far from uniform. Symptomatic of the irregularities are the ionisation potentials of the atoms which, unlike those of the corresponding metals of Groups 1 and 2, vary in a discontinuous way as a function of atomic number (Table 1.1),¹²⁻²² so that I_3 , for example, follows the order $B \gg Al < Ga > In < Tl$. This sawtooth variation is a consequence of changes in the makeup and shielding of the electron core, that is [He], [Ne], [Ar]3d¹⁰, [Kr]4d¹⁰ and [Xe]4f¹⁴5d¹⁰. That it is more marked for the valence *ns* than for the *np* electrons reflects the superior penetration of the core by the *ns* electrons. Relativistic effects²³ make a significant contribution to the binding energies for the later elements but do not change the overall pattern. The energies of the valence electrons of the free atom are a major, but not exclusive, influence on the strengths of the bonds and on the type of compounds it forms. They account, at least in part, for the chemical reactivity of the elements under normal conditions and the emergence in each case of a relatively well defined cationic chemistry.^{8,12,27,28}

The Group 13 metals are now acknowledged to have rich and distinctive chemical lives of their own, no longer overshadowed by that of boron. Salient features of these lives are: (i) their varied redox chemistry with what is now seen to be a wide range of formal oxidation states (including not only non-integral but also negative ones); (ii) the natural acidity and associated coordination chemistry of their M^{III} compounds; and (iii) the great variety of structures and other properties displayed by their compounds. The drive for new discoveries and a fuller understanding has been urged not so much by the familiar commercial importance of aluminium and alumina-based solids,¹² but by a number of other developments of more recent origin.

1.2 Developments in Methodology

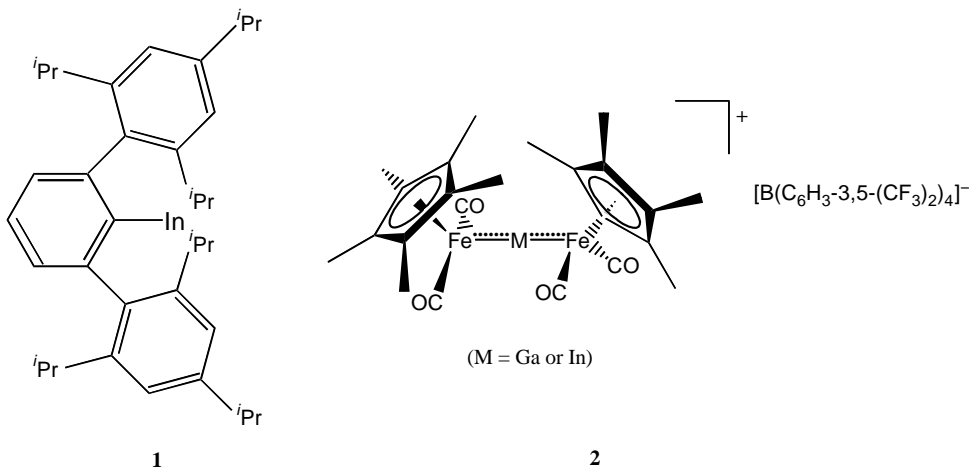
'I keep six honest serving-men
(They taught me all I knew);
Their names are What and Why and When
And How and Where and Who.'

Rudyard Kipling, *Just So Stories*, 'The Elephant's Child', 1902.

1.2.1 Introduction

Developments in Group 13 metal chemistry in the past two decades have often been driven, at least ostensibly, by the promise of practical applications, for example in realms as diverse as the sourcing and storage of energy; the production and elaboration of materials with specific electronic, structural, thermal or chemical properties; and medical diagnosis and therapy. While some important discoveries have indeed been made in pursuit of such pragmatic causes, disinterested scientific curiosity continues to be the main life force of progress. Advances have come in three principal areas.

(i) *Synthesis.* New compounds of a variety of sorts have been prepared. Most notable, perhaps, have been those in which the Group 13 metal assumes a low formal oxidation state (i.e. $< +3$),^{12,21,22,29} and may engage in metal–metal bonding (as in so-called ‘metalloid’ derivatives).^{11,22,30–32} Other compounds are made notable by the presence of weak, reactive M–H bonds;^{12,21,22} by the coordination environment of the metal, which may display an unusual geometry or an uncharacteristically low coordination number (e.g. **1**³³ or **2**^{34,35}); by the nature of the bonding, which sometimes challenges conventional wisdom regarding primary or secondary interatomic interactions;^{36–38} or by their lability under normal conditions.^{21,29} At the same time, much effort and ingenuity have been expended on the synthesis of solid materials with extended frameworks in which homo- or hetero-nuclear assemblies, including the metal atoms, are bridged by non-metal atoms, typically from Groups 15 and 16.^{8,12,39–50} Specific objectives have included the achievement of particular topologies and/or morphologies. The coordination chemistry of the metals has also expanded materially, with the preparation of new complexes.^{8,10,12,51–53} Here the metal centre, as M^{III} , usually plays its conventional acceptor role, but there is now ample evidence, usually involving M^I compounds, to show that the metal can also function predominantly as a donor.^{22,35,54–60} How different synthetic approaches have sought to achieve their respective targets is reviewed briefly in the Section 1.2.2.



(ii) *Experimental characterisation.* Closer, more extensive physical scrutiny, using new or established experimental techniques (e.g. electronic, vibrational, microwave, mass and photoelectron spectroscopies, and X-ray, neutron and electron diffraction) has extended knowledge of the structures, bonding and other properties of both new and known compounds.⁶¹ Some of the major techniques in question are identified in Section 1.2.3.

(iii) *Theoretical studies.* With improvements in reliability, sophistication, scope and accessibility, quantum chemical methods have played an increasingly important part in the advancement of the chemistry of this group of metals.⁶² In some cases, they have pointed the way to the stable existence of a hitherto unknown compound

(e.g. Ga₂H₂),⁶³ or to the intermediacy of species in vapour transport (e.g. MP₅ and MAs₅, for M = Ga or In);^{64a} in other cases, they have offered a rationale for the instability of a compound (e.g. MH₃, where M = In or Tl).^{64b–66} More often, they have been invoked to assist in the identification and characterisation of a new compound that experiments have brought to light. To an increasing extent, they are now being exploited in the effort to gain a better understanding of the *reactivity* of Group 13 metal species, for example Ga₂^{63,67} and AlCl.⁶⁸ It is theoretical methods that must also be deferred to in any questions of intramolecular or intermolecular bonding.^{36–38,69} This particular theme is taken up in Section 1.4.

1.2.2 Synthetic methods

‘All progress is based upon a universal innate desire on the part of every organism to live beyond its income.’

Samuel Butler, *Notebooks*, Chapter 1, 1912

In an attempt to encompass a topic as vast and diffuse as this, it seems appropriate to treat it phase by phase, that is according to whether the reaction takes place in the gas phase, involves the solid phase exclusively (as in a matrix, for example) or in part, or is hosted by the liquid phase (as is most commonly the case).

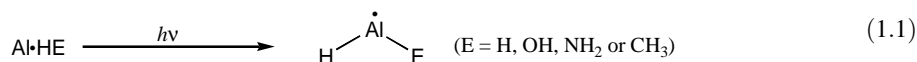
1.2.2.1 Gas Phase Synthesis

The gas phase is home to the limited number of Group 13 metal compounds that are substantially volatile at ambient temperatures, for example Al(BH₄)₃ and GaMe₃,^{10,12} and otherwise to high-energy species such as the metal atoms, M, metal clusters and their ions, and the diatomic molecules M^IX [M = Al, Ga, In or Tl; X = H, F, Cl, Br or I].^{12,21,22} Some M^I compounds, such as InCl or (η⁵-C₅R₅)M [M = Al, Ga, In or Tl; R = H or Me], vaporise on heating without decomposition or disproportionation. At sufficiently high temperatures, the entropy advantage drives even robust M^{III} molecules such as GaCl₃ and In₂O₃ to decompose, at least partially, to the corresponding M^I compound and elemental non-metal. Other M^I compounds require high-energy reactions for their formation in the gas phase. For example, GaCl is generated by the reaction of the metal with Cl₂, HCl or GaCl₃ at 800–1000 °C,⁷⁰ and InF is formed by heating together the metal and InF₃.⁷¹ The reaction of the laser-ablated metal vapour with cyanogen or acetonitrile in an argon carrier gas affords the two isomers MCN and MNC [M = Al, Ga or In].⁷² Similarly, with ethyne in a helium or neon carrier gas, laser-ablated aluminium vapour forms the linear AlCCH molecule.⁷³ This, together with the molecules AlNC and AlCH₃ (formed in a discharge reaction between aluminium vapour and HgMe₂),⁷⁴ is of interest as a potential carrier of the metal in the interstellar medium. The remarkable dialuminium compound Al₂(η⁵-C₅H₅), with a half-sandwich structure and an Al₂ dimer unit located on the fivefold axis of the C₅H₅ ring, has been prepared in a pulsed supersonic molecular beam by the reaction of laser-ablated aluminium vapour with cyclopentadiene.⁷⁵

The vapour formed by normal heating of a Group 13 metal consists mainly of atoms with only a low concentration of dimers M₂ and still lower concentrations of larger clusters. Spectroscopic and theoretical studies of the M₂ species indicate weakly bound molecules having a triplet ground state ³Π_u.^{76,77} Laser evaporation or ion bombardment (sputtering) of the metal or a compound of the metal can deliver to the gas phase not only atoms and dimers, but also larger clusters in either neutral or charged states.^{11,38,78–80} These gaseous species have been investigated experimentally by different types of mass spectrometry (e.g. secondary ion mass spectrometry (SIMS) and Fourier transform (FT) ion cyclotron resonance (ICR) mass spectrometry), photoionisation spectroscopy, or even calorimetric measurements, and theoretically at levels ranging from simple shell models to more sophisticated DFT methods. Thus, aluminium clusters^{78,79} and, to a lesser degree, gallium⁸⁰ and indium^{81,82} clusters have excited considerable interest in the general search for a better understanding of how the transition is made from the atomic/molecular state to the bulk metal. How the physical and chemical properties of the clusters vary as a function of size

has, therefore, been a primary focus of enquiry, with the constantly teasing issue of just when a cluster can be justifiably described as a ‘metal’. Intriguingly, density functional theory (DFT) calculations for Al_n clusters suggest that icosahedral packing is favoured only for $n = 13$, whereas decahedral packing is most stable with n near 55, and fcc packing is energetically preferred for $n > 80$.⁷⁹ Neutral and charged In_n clusters with n up to 200 have been produced by bombarding a pure indium surface with 15 keV Xe^+ ions,⁸² but with yields that depend only partially, and to an indeterminate extent, on their intrinsic thermodynamic properties.

Low concentrations and long mean-free-paths make the gas phase generally ill suited to useful synthetic reactions, the predominant reactions being either simple addition or bond breaking. For example, spectroscopic studies involving laser fluorescence excitation, one-photon and resonance-enhanced multiphoton ionisation (REMPI), or zero electron kinetic energy (ZEKE) spectroscopy have revealed, typically in a supersonic beam, the formation of such weakly bound adducts of aluminium atoms as $\text{Al}\cdot\text{H}_2$,⁸³ $\text{Al}\cdot\text{N}_2$,⁸⁴ $\text{Al}\cdot\text{OH}_2$,⁸⁵ $\text{Al}\cdot\text{NH}_3$,⁸⁶ $\text{Al}\cdot\text{CH}_4$ ⁸⁷ and $\text{Al}\cdot\text{ether}$ [ether = Me_2O , Et_2O or thf].⁸⁸ Some of these are potential precursors to further change, for example as represented by Equation 1.1, but, irrespective of thermodynamic considerations, such a change is usually opposed by a substantial activation barrier. While the provision of additional energy – for example, to promote the metal atom to an excited electronic state – may overcome this barrier,^{29,89} the surplus energy carried by the product is likely, in the absence of an efficient means of relaxation, to result in its rapid disintegration. Cation complexes, such as $\text{Al}^+\cdot\text{H}_2$,⁹⁰ $\text{Al}^+(\text{OH}_2)_n$ ($n = 1$ or 2)⁹¹ and $\text{Al}^+(\text{CH}_3\text{OH})_n$ ($n = 1-4$),⁹² which have also been characterised, are rather more strongly bound and may be more prone to undergo spontaneous metal-insertion reactions analogous to that in Equation 1.1.^{22,29} Particularly fascinating, though, are the recent experimental studies carried out to explore the primary reaction steps of the unusually stable cluster $[\text{Al}_{13}]^-$ and involving severally Cl_2 , HCl and O_2 (Chapter 7);⁹³ these provide what may be regarded as ‘snapshots’ of the reactions likely to take place on the base metal surface. Thermal decomposition of gaseous complexes such as $\text{Me}_3\text{Al}\cdot\text{NH}_3$ and quinuclidine- GaH_3 or of gaseous mixtures of Me_3Ga and AsH_3 is important for the chemical vapour deposition (CVD) of epitaxial films of III–V compounds or composites on an appropriate substrate.^{46,94} It is difficult, however, to distinguish between the reactions that occur strictly in the gas phase (and are likely mainly to feature bond rupture) and those occurring on the surface of the substrate.



The gas phase alone offers, then, few opportunities for the rational synthesis of compounds, and certainly on a scale exceeding a few milligrammes. Instead, condensation is needed in order to take advantage of the greater control that is afforded by the denser condensed phases. For example, the vapour of the metal or of a metal compound may be condensed with a potential reagent and/or solvent to exploit any reactions occurring during condensation or on subsequent warming of the reaction mixture. Such methods, pioneered in particular by Timms and Skell,⁹⁵ have been deployed with great success by Schnöckel *et al.* to capitalise on the inherent reactivity of aluminium(I) and gallium(I) halides.⁷⁰ Little is likely to happen in the gas phase, and while some interaction between the reagents may occur during condensation, most, if not all, of the action occurs once the reagents have entered the liquid phase; the course of events is accordingly subject to the usual considerations of choice of solvent, involvement of protective functions, temperature, and so on (Section 1.2.2.3). Alternatively, the vapour may be co-condensed with an excess of an inert gas doped with a potential reagent, as in the technique of matrix isolation.^{29,96} Spectroscopic analysis of the resulting solid matrix then provides the means of monitoring the reactions of the trapped species that may be activated either thermally or photolytically. Matrix isolation, which is therefore primarily concerned with the *solid* phase (Section 1.2.2.2), is not a method of synthesis in the conventional sense, but it has led to the first sighting and characterisation of numerous Group 13 metal compounds that are too labile to be isolated under ambient conditions, for example MH_2 , MH_3 [$\text{M} = \text{Al}, \text{Ga}, \text{In}, \text{ or } \text{Tl}$],^{65,66,97} M_2H_2 [$\text{M} = \text{Ga} \text{ or } \text{In}$]⁶³ and H_2MNH_2 [$\text{M} = \text{Al}, \text{Ga}, \text{ or } \text{In}$].⁹⁸

1.2.2.2 *Synthesis with Solids*

Group 13 metals and their solid compounds with extended, strongly bound frameworks are seldom wholly compatible with homogeneous solution chemistry, at least under ambient conditions.^{45,99} Synthetic reactions in which they feature, whether as reagents or as products, are most likely to be heterogeneous and to depend on the presence of one or more solids. The simplest and most common way of preparing Group 13 metal compounds when all the components are solids is the so-called ‘ceramic’ method.⁹⁹ Stoichiometric amounts of the solid reagents are ground together to give a uniform small particle size and heated to whatever temperature is needed to initiate reaction. Used widely both industrially and in the laboratory, this method gives access to a whole range of materials, such as mixed metal oxides, sulfides, selenides, nitrides and aluminosilicates. Representative examples of compounds recently made in this way are: LaGaO₃ and related compounds (from La₂O₃ and Ga₂O₃),¹⁰⁰ LiGa₅O₈ and LiGaO₂ (from Li₂CO₃ and Ga₂O₃),¹⁰¹ In_{4+x}Sn_{3-2x}Sb_xO₁₂ (a new transparent conductor, prepared from In₂O₃, SnO₂ and Sb₂O₃ in air)¹⁰² and Pt₂In₁₄Ga₃O₈F₁₅ (containing [PtIn₆]¹⁰⁺ moieties, prepared from InF₃, platinum powder and Ga₂O₃).¹⁰³ The case for such solid state synthesis has also been advanced for the formation of molecular organic and inorganic products and of materials with microporous metal–organic frameworks.¹⁰⁴ It has been urged, in part, by the desire to avoid the use of organic solvents, whether for reasons of reactivity and contamination or out of concern for the environment. For example, the labile gallanes Ga₂H₆,¹⁰⁵ H₂GaBH₄¹⁰⁶ and H₂GaB₃H₈¹⁰⁷ have all been prepared by mixing together the powdered solids [H₂GaCl]₂ and MX, where M = Li or N^{*n*}Bu₄ and X = GaH₄, BH₄ and B₃H₈, respectively.¹⁰⁸ In the same vein, the tetrahydaborates Al(BH₄)₃,¹⁰⁹ Me₂GaBH₄¹¹⁰ and HGa(BH₄)₂¹¹¹ are most easily synthesised from appropriate solid reactants without the intervention of a solvent.

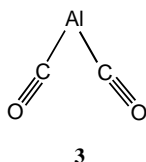
The ceramic method suffers from several disadvantages. As the entire reaction occurs between solid components and later by diffusion of the constituents through the product phase, diffusion paths necessarily become longer and longer with the progress of the reaction, and the reaction rate correspondingly slower and slower. Separation of a desired solid product from the solid mixture is liable to be difficult, if not impossible. Furthermore, the securing of a compositionally homogeneous product can be problematic, even when the reaction proceeds almost to completion. Various modifications of the technique have been devised to overcome some of its limitations. One of the main aims has been to decrease the diffusion path lengths by reducing the particle size, thus effecting more intimate mixing of the reactants, and this has been the purpose of introducing freeze drying, spray drying, coprecipitation and sol–gel techniques.⁹⁹ Microwave irradiation has also been deployed with some success in place of conventional heating techniques,¹¹² as exemplified by the formation of the diamond-like semiconductor AgInSe₂ from the powdered elements.¹¹³

Reactions involving solids are likely to be accelerated when heating results in melting of one or more components. For example, heating together indium and molybdenum metals with MoO₂ at 1150 °C must result in melting of the indium *en route* to the mixed metal oxide In₅Mo₁₈O₂₈.¹¹⁴ The same applies to the synthesis of intermetallic phases, including so-called Zintl phases,¹¹⁵ from the appropriate elements, for example K₁₀Tl₇,¹¹⁶ K₃₉In₈₀,¹¹⁷ YbGaGe (a material with zero thermal expansion)¹¹⁸ and the thermoelectric material Ba₈Ga₁₆Ge₃₀.¹¹⁹ With microwave activation, gas–solid reactions may also be turned to advantage, as with the conversion of Al₂O₃ admixed with carbon to AlCl₃ by the action of HCl.¹²⁰ Similarly, AlN and GaN have been prepared by the direct action of nitrogen on a mixture of aluminium and charcoal powder in the first case,¹²¹ and by that of ammonia on a Ga₂O₃/amorphous carbon mixture in the second.¹²²

Water commonly plays a central role as both medium and reagent in the synthesis of solids with frameworks composed of oxygen atoms bridging either metal atoms or metal and non-metal atoms such as silicon or phosphorus. ‘Hydrothermal’ synthesis is the generic term for various techniques which involve the crystallisation of solids from aqueous mixtures raised to high temperatures (typically 350–600 K) and under high vapour pressure.^{99,123} The formation of a crystalline product rather than a powder stands in marked contrast to the normal outcome of ceramic methods. The process, which is usually a heterogeneous one, occurs in nature, and numerous minerals, including naturally occurring zeolites, owe their origin to it. Zeolites are also generally prepared in the laboratory by hydrothermal methods,^{41,124} and such methods also provide the main means of entry to Group 13 metal phosphates^{43,44} and a variety of other microporous and mesoporous materials.^{41,45} A typical synthetic mixture

for making a specific aluminium phosphate consists of alumina, phosphoric acid, water and an organic material such as a quaternary ammonium salt or an amine, which are heated together in an autoclave at 373–573 K.^{43,99} It may be necessary to cater for large differences in solubility of the reactants, as exemplified by the synthesis of yttrium aluminium garnet, YAG, $\text{Y}_3\text{Al}_5\text{O}_{12}$, for which the more soluble Y_2O_3 needs to be placed in a cooler part and the less soluble Al_2O_3 (as sapphire) in a hotter part of the autoclave; YAG crystals form where the two zones meet. Hydrothermal methods, in common with ceramic methods, have benefited from the introduction of microwave, in place of conventional thermal, activation;¹¹² sonochemical methods have also been turned to advantage, notably for the synthesis of porous metal oxides.¹²⁵

Solids may act not only as reagents but also as mediators of chemical reactions. So the interstices of an open framework material, such as a zeolite, are potential reaction chambers with the physical and chemical capacity to catalyse specific modes of reaction.^{41,42} The same principle of confinement of reagents applies to a solid matrix composed of noble gas atoms or simple molecules such as hydrogen, nitrogen, or methane.^{29,61,96} Necessarily maintained at a low temperature (typically 2–20 K), such a matrix is rigid enough to immobilise any foreign atoms or molecules that may be entrained at high dilution within the interstices, inert enough to keep perturbation of these guests to a minimum, and transparent enough to broad regions of electromagnetic radiation to admit interrogation by various spectroscopic techniques. In practice, infrared measurements have been the principal agent of detection, identification and characterisation, with crucial support often coming from the response to changes of isotopic composition. Final decisions on the identity and properties of a new molecule are then likely to depend on the synergy between experiment and quantum chemical calculations at an appropriate level of theory. Given the low thermal energy available under the conditions of the matrix experiment, only simple addition reactions of the guest species opposed by little or no activation barrier are likely to occur spontaneously. Hence, for example, it has been possible to observe the formation of adducts of the metal atoms, such as $\text{M}\cdot\text{NH}_3$ ^{29,98,126} and $\text{M}(\text{CO})_n$ ($n = 1$ or 2),^{29,127} where $\text{M} = \text{Al}, \text{Ga}$ or In . These adducts range in their estimated total binding energies from a mere 7 kJ mol^{-1} for $\text{In}\cdot\text{N}_2$ to a highly respectable 176 kJ mol^{-1} for $\text{Al}(\text{CO})_2$. The latter is believed to have the intriguing structure **3** with a tight C–Al–C angle (near 70°) and $\text{Al}-\text{C}\equiv\text{O}$ arms that are bent outwards in such a way as to suggest that the two carbon atoms are drawn towards



each other.^{127,128} By contrast, a much higher price in activation has usually to be paid for changes that involve bond dissociation, insertion into a bond or isomerisation. Photons are then the only currency usually available to matrix-isolated species, and practical provision must therefore be made to enable the matrix deposit to be irradiated with light spanning an appropriate range of wavelengths. With an imagery suggestive of Coleridge's *Kubla Khan*,

‘It was a miracle of rare device,
A sunny pleasure dome with caves of ice.’

Group 13 metal atoms, once promoted to their ^2S or ^2D excited electronic states (by ultraviolet radiation in the wavelength range 290–340 nm), are capable of spontaneous insertion into an H–H or H–C bond to give authentic, paramagnetic $\text{M}(\text{II})$ molecules $\text{M}^*(\text{H})\text{X}$ (e.g. $\text{X} = \text{H}$ ^{29,97} or CH_3 ^{29,129}), which have been identified by their IR and EPR spectra. The pervasive role of photoactivation is revealed by the results of matrix experiments involving thermally evaporated gallium atoms, summarised schematically in Figure 1.1. By contrast, laser ablation of the metal gives rise to atoms of high energy, trapping of which, together with potential reagents, in an appropriate solid matrix is likely to result in spontaneous changes beyond the reach of thermally evaporated metal atoms. Co-condensing laser ablated metal atoms with hydrogen (H_2) has led, for example, to the first detailed characterisation of the Al_2H_6

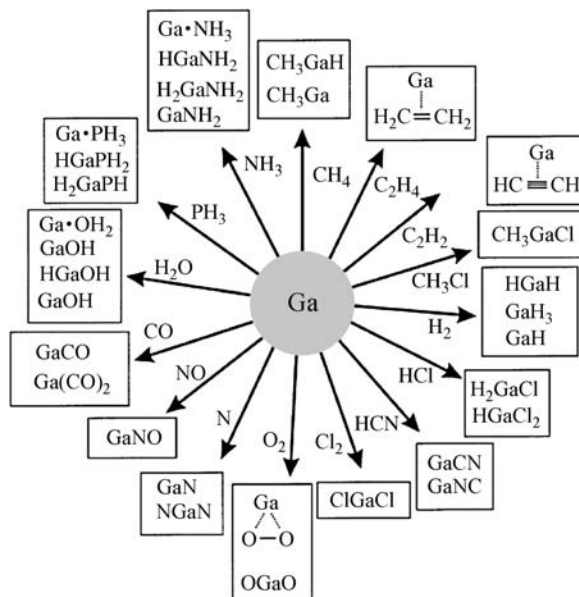


Figure 1.1 Some reactions of matrix-isolated gallium atoms in their ground or, more often, excited electronic states. Reprinted with permission from [29]. Copyright 2002 American Chemical Society

molecule¹³⁰ and of various indium hydrides, including the polymeric solid $[\text{InH}_3]_n$, which decomposes to the elements at 160–180 K.⁶⁵ Whereas gallium atoms require a substantial stimulus before they will react with hydrogen, the Ga_2 dimer reacts *spontaneously* with hydrogen at about 15 K to form the dimeric gallium(I) hydride, $\text{Ga}(\mu\text{-H})_2\text{Ga}$.⁶³ In_2 does not, however, follow suit, requiring UV photoactivation before it will form an analogous product. Both $\text{Ga}(\mu\text{-H})_2\text{Ga}$ and $\text{In}(\mu\text{-H})_2\text{In}$ prove to be photolabile under visible light ($\lambda > 450$ nm), undergoing the changes outlined in Figure 1.2. These and other Group 13 metal species characterised in recent matrix studies are listed in Table 1.2.

1.2.2.3 Liquid Phase Synthesis

Whatever the merits of the gas or solid phases in one form or another, homogeneous processes in the liquid phase have maintained their supremacy as the means of useful chemical synthesis. Nor can custom stale the infinite variety that a suitable solvent is able to bring to a reaction mixture by way of support, intimate and efficient mixing, control and potential thermodynamic and/or kinetic influence. Reagents and target compounds often being susceptible to attack by moisture, organic solvents such as ethers have been the mainstay of much of the synthetic effort. In that derivatives of the Group 13 metals in oxidation states lower than +3 are invariably weaker Lewis acids than are the corresponding M^{III} derivatives, they are vulnerable to disproportionation under basic conditions, so that the role of the solvent may be far from innocent. For example, tetrahydrofuran (thf), used quite frequently to support an indium monohalide in the presence of various reagents, tends to induce disproportionation rather than the expected metathesis or addition.²² Thus, indium metal is a common product of all the following reactions: ${}^t\text{Bu}_3\text{SiNa} + \text{InBr}$ giving the indium(II) product $({}^t\text{Bu}_3\text{Si})_2\text{InIn}(\text{Si}{}^t\text{Bu}_3)_2$;¹⁴⁹ $\text{Na}[\text{MeGa}(\text{Pz})_3]$ (Pz = pyrazolyl) + InI giving $[\{\text{MeGa}(\text{Pz})_3\}\text{In}][\text{InI}_4]$;¹⁵⁰ $\text{RLi}\cdot\text{thf} + \text{InBr}$ giving $\text{Br}(\text{R})\text{InInBr}(\text{R})$, where R is the 1-aza-allyl ligand $(\text{Me}_3\text{Si})_2\text{C}(\text{Ph})\text{C}(\text{Me}_3\text{Si})\text{N}$;¹⁵¹ $\text{LiC}(\text{SiMe}_3)_3\cdot 2\text{thf} + \text{InBr}$ giving $[\text{Li}(\text{thf})_3][\text{In}_3\text{Br}_3\{\text{C}(\text{SiMe}_3)_3\}_3]$;¹⁵² and $\text{ArN}=\text{CHPy}$ [$\text{Ar}=\text{C}_6\text{H}_3\text{-2,6-}i\text{Pr}_2$; $\text{Py}=2\text{-pyridyl}$] + InCl giving $\text{InCl}_3(\text{thf})\{\eta^2\text{-ArN}=\text{CHPy}\}$.¹⁵³ Nevertheless, basic organic solvents have played an important part in opening up the chemistry of the univalent metal halides

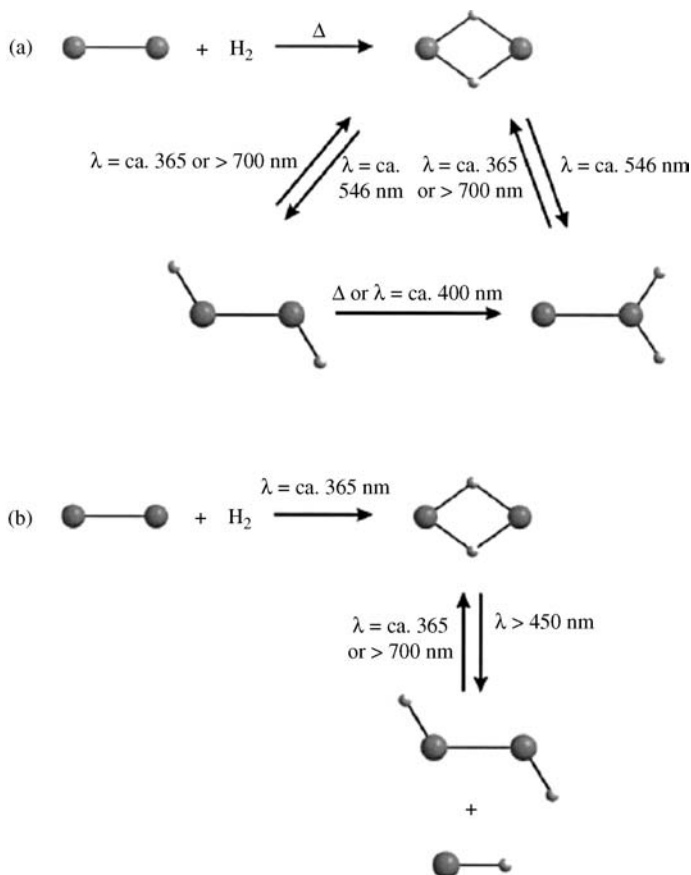


Figure 1.2 Pathways for the matrix reactions of Ga_2 and In_2 molecules with H_2 . Reprinted from [128], with permission from Elsevier

MX [$\text{M} = \text{Al}, \text{Ga}$ or In]. Toluene/ether or similar mixtures give metastable solutions of aluminium(I) and gallium(I) halides, which survive at low temperatures (190–250 K) and have proved to be invaluable synthons for new compounds of these metals in low formal oxidation states.⁷⁰ In the same vein, the less tractable indium(I) halides can be made to dissolve to a limited extent in a toluene/tmeda mixture (tmeda = $\text{Me}_2\text{NCH}_2\text{CH}_2\text{NMe}_2$), and the metastable solution formed by InI disproportionates, for example, to form indium metal and the indium sub-halide cluster complex $\text{In}_6\text{I}_8(\text{tmeda})_4$ (**4**).¹⁵⁴

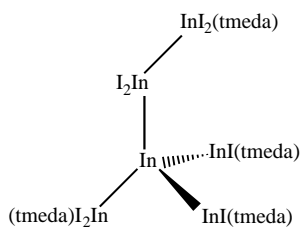


Table 1.2 *Group 13 metal atoms, dimers and molecular compounds featuring in recent matrix-isolation studies*

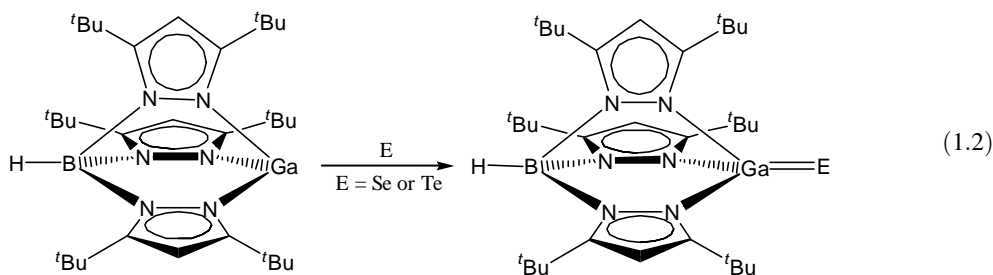
Species	Method of formation	Method of characterisation	Reference
Al, Ga, In or Tl atoms	co-deposition of metal vapour with noble gas	UV-Vis	29
Al ₂	mass selection of sputtered Al cluster ions, neutralisation and co-deposition with Ar	resonance Raman	131
Ga ₂	co-deposition of metal vapour with Ar	resonance Raman; UV-Vis	132
Ga·N ₂	co-deposition of metal vapour with N ₂	Raman; UV-Vis	133
M·OH ₂ (M = Al, Ga, In or Tl)	co-deposition of metal vapour with noble gas doped with H ₂ O	IR; UV-Vis	29
M·NH ₃ (M = Al, Ga or In)	co-deposition of metal vapour with Ar doped with NH ₃	IR; UV-Vis; EPR	29, 98, 126
M·PH ₃ (M = Al, Ga or In)	co-deposition of metal vapour with Ar doped with PH ₃	IR; UV-Vis	29, 134
M(CO) _n , M ₂ (CO) _n (M = Al, Ga or In; n = 1 or 2)	co-deposition of metal vapour with CO or noble gas doped with CO	IR; EPR	29, 127
M·SiH ₄ (M = Al or Ga)	co-deposition of metal vapor with Ar doped with SiH ₄	IR; UV-Vis	135
MH _n (M = Al, Ga or In; n = 1–3)	co-deposition of metal vapour with H ₂ or H atoms in an Ar matrix + UV photolysis	IR	97
AlH _n (n = 1–3), H ₂ ·AlH ₃ , Al ₂ H ₄ , Al ₂ H ₅ , Al ₂ H ₆ , Al ₃ H ₉	co-deposition of laser ablated Al vapour with H ₂ + UV photolysis	IR	130
GaH _n (n = 1–3), Ga ₂ H _n (n = 2, 4 or 6), GaH _n [–] (n = 2 or 4)	co-deposition of laser ablated Ga vapour with H ₂ + UV photolysis	IR	136
Ga ₂ H ₆	co-deposition of gallane vapour with noble gas	IR; Raman	105, 137
InH _n (n = 1–3), H ₂ ·InH ₃ , In ₂ H _n (n = 2, 4 or 6), [InH ₃] _x	co-deposition of laser ablated In vapour with H ₂ or Ne doped with H ₂ + UV photolysis	IR; UV-Vis emission	65
TlH _n (n = 1–3), Tl ₂ H ₂	co-deposition of laser-ablated Tl vapour with H ₂ or noble gas doped with H ₂ + UV photolysis	IR	66
Ga ₂ H ₂ , In ₂ H ₂	co-deposition of metal vapour with Ar doped with H ₂ + UV-Vis photolysis	IR; Raman	63
HMNH ₂ , MNH ₂ , H ₂ MNH ₂ (M = Al, Ga or In)	UV photolysis of Ar matrix doped with M atoms and NH ₃	IR	98
HMPH ₂ , H ₂ MPh (M = Al, Ga or In)	UV photolysis of Ar matrix doped with M atoms and PH ₃	IR	29, 134
HMCH ₃ , MCH ₃ (M = Al, Ga or In)	UV photolysis of M atoms trapped in CH ₄ or noble gas matrix doped with CH ₄	IR; EPR	29, 129
HMSiH ₃ , MSiH ₃ (M = Al or Ga)	UV photolysis of an Ar matrix doped with M atoms and SiH ₄	IR	135

Table 1.2 (Continued)

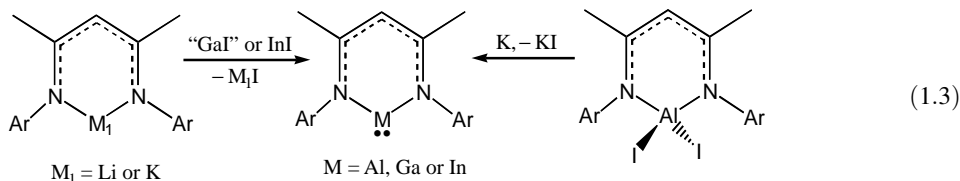
Species	Method of formation	Method of characterisation	Reference
HMSnH ₃ , H ₂ M(μ-H) ₂ Sn (M = Al or Ga)	co-deposition of metal vapour with Ar doped with SnH ₄ + UV photolysis	IR	138
H _n MX _{3-n} (M = Al, Ga or In; X = Cl or Br; n = 1 or 2)	UV photolysis of a noble gas matrix doped with MX and either H ₂ or HX	IR	21, 139
CH ₃ GaH ₂ , (CH ₃) ₂ GaH	co-deposition of volatile thermolysis products of (CH ₃) ₂ N(CH ₂) ₃ Ga (CH ₃) ₂ with Ar	IR; mass spectrometry	21
(η ⁵ -C ₅ Me ₅)AlH ₂	UV photolysis of Ar matrix doped with (η ⁵ -C ₅ Me ₅)Al and H ₂	IR	140
RAI(H)Cl (R = CH ₃ or C≡CH)	UV photolysis of Ar matrix doped with AlCl and RH	IR	141
MH ₂ (M = Al or Ga), HAICl, HAlOH, CH ₃ GaH	co-deposition of metal vapour with noble gas doped with H ₂ , HCl, H ₂ O or CH ₄ + UV photolysis	EPR	29
AlCl, Al(μ-Cl) ₂ Al, ClAl(μ-Al)(μ-Cl)AlCl	co-deposition of AlCl vapour with Ar	IR	142
AlX ₂ (X = F, Cl, Br or I)	co-deposition of laser ablated Al vapour with Ar doped with X ₂	IR	29
MOM, (η ² -O ₂)M, OMO, MOMO, M(μ-O) ₂ M, M(O ₂) ⁻ (M = Al, Ga, In or Tl)	co-deposition of metal vapour with noble gas doped with O ₂	IR	29, 143
(η ² -O ₂) _n Al (n = 1, 2 or 3)	co-deposition of Al vapour with Ar doped with O ₂	IR	144
O ₂ M(η ¹ -O ₂) (M = Ga or In)	co-deposition of metal vapour with Ar doped with O ₂	IR	145
XAl(O ₂) _n (X = F, Cl or Br; n = 1 or 2)	co-deposition of AlX vapour with Ar doped with O ₂	IR	146
M(OH) _n (M = Al, Ga, In or Tl; n = 1, 2 or 3)	co-deposition of laser-ablated metal vapour with Ar doped with H ₂ O ₂ or H ₂ + O ₂	IR	147
NMN (M = Al, Ga, In or Tl)	co-deposition of laser ablated metal vapour with N ₂ or Ar doped with N ₂	IR	29
MNO (M = Ga, In or Tl)	co-deposition of laser ablated metal vapour with Ar doped with NO	IR	29
(η ² -C ₂ H ₂)M (M = Al, Ga or In)	co-deposition of metal vapour with Ar doped with C ₂ H ₂	IR	29
(CH ₃) ₃ Al·NH ₃ , (CH ₃) ₂ AlNH ₂	co-deposition of (CH ₃) ₃ Al·NH ₃ vapour with Ar + UV photolysis	IR	148

The motivation for synthesis has commonly centred on the support of the Group 13 metal atom in an unusual oxidation state (< + 3) or coordination environment (featuring a coordination number < 4), and been influenced, too, by the need to control the partial charge carried by the metal. A metal fragment of this sort is usually reactive through its exposure to associative attack that results in aggregation, coordination, oxidation or disproportionation. With matrix isolation, protection from such attack is provided *physically* by trapping the fragment in an inert, solid matrix at low temperature. For conventional synthetic operations, however, protection must be achieved by *chemical* means, namely by the adoption of ligands with appropriate steric and/or electronic properties. Thus, labile species such as

AlH_3 , GaH_3 or InH_3 may be intercepted by a suitable donor and preserved in the form of thermally more robust adducts, such as $\text{HC}(\text{CH}_2\text{CH}_2)_3\text{N}\cdot\text{MH}_3$ [$\text{M} = \text{Al}$ or Ga]^{94,155} and $\text{Mes}(\overline{\text{NCH}=\text{CHN}(\text{Mes})\text{C}})\cdot\text{InH}_3$ ($\text{Mes} = \text{mesityl}$)¹⁵⁶ (Section 1.6.1). One of the main guiding principles in recent years has been the recognition of bulk and specific design as properties of supporting ligands that can be crucial to manipulating the reactivity of the metal centre and to stabilising previously unknown or unfamiliar bonding types, geometries or electron configurations. The ligands in question include substituted η^5 -cyclopentadienyl groups (e.g. C_5Me_5);¹⁵⁷ bulky alkyl and supersilyl groups (e.g. $\text{CH}(\text{SiMe}_3)_2$, $\text{C}(\text{SiMe}_3)_3$, and Si^tBu_3);¹⁵⁸ substituted aryl groups (e.g. C_6H_2 -2,4,6- $^t\text{Bu}_3$), terphenyl and related substituents;¹⁵⁹ β -diketiminate or amidinate derivatives (e.g. $\{\text{ArNC}(\text{Me})\}_2\text{CH}$ and $\text{Cy}_2\text{NC}(\text{NAr})_2$, with $\text{Cy} = \text{cyclohexyl}$ and $\text{Ar} = \text{C}_6\text{H}_3$ -2,6- $^i\text{Pr}_2$);^{160–163} substituted diazabutadiene derivatives (e.g. $\text{RNCH}=\text{CHNR}$ with $\text{R} = ^t\text{Bu}$ or C_6H_3 -2,6- $^i\text{Pr}_2$);^{160,164} and poly(pyrazolyl)borate groups,¹⁶⁵ as represented, for example, in Equation 1.2 showing the oxidation of a gallium(I) compound to a discrete molecular gallium(III) compound containing what may reasonably be regarded as a ‘semipolar metal–chalcogen double bond’.¹⁶⁶ A notable example is provided by the unusually encumbering *o*-terphenyl ligand $-\text{C}_6\text{H}_3$ -2,6-(C_6H_2 -2,4,6- $^i\text{Pr}_3$)₂; hence, the indium(I) compound



InC_6H_3 -2,6-(C_6H_2 -2,4,6- $^i\text{Pr}_3$)₂ has been prepared and shown to form crystals composed of well separated monomers (**1**), which are unique in the *one*-coordination of the metal.³³ Even relaxing the bulk of the ligand seemingly quite slightly in the change from $-\text{C}_6\text{H}_3$ -2,6-(C_6H_2 -2,4,6- $^i\text{Pr}_3$)₂ to $-\text{C}_6\text{H}_3$ -2,6-(C_6H_3 -2,6- $^i\text{Pr}_2$)₂ gives not a monomer but a ‘dimetalene’ dimer $[\text{InC}_6\text{H}_3$ -2,6-Dipp₂]₂ with bi-coordinated metal atoms linked by a metal–metal bond.¹⁶⁷ A similar structure is adopted by the so-called ‘gallyne’ compound $\text{Na}_2[\text{GaC}_6\text{H}_3$ -2,6-(C_6H_2 -2,4,6- $^i\text{Pr}_3$)₂]₂, superficially analogous to an alkyne and remarkable for displaying a short Ga–Ga bond, the multiple nature of which has been heatedly debated.^{36,168,169} Twofold coordination of the M^{I} centre is also found in the neutral six-membered heterocycles $\text{M}[\eta^2\text{-(NArCMe)}_2\text{CH}]$ [$\text{M} = \text{Al}$, Ga or In ; $\text{Ar} = \text{C}_6\text{H}_3$ -2,6- $^i\text{Pr}_2$] formed by either reduction or metathesis, as in Equation 1.3.^{160,161} The role of ligand bulk is particularly felt in the disproportionation of M^{I} compounds [$\text{M} = \text{Al}$, Ga or In], which normally leads to the elemental metal M^0 and the corresponding M^{III}



compound. With a bulky ligand such as Si^tBu_3 , however, the products may be M^0 and a metal–metal-bonded M^{II} derivative, for example $(^t\text{Bu}_3\text{Si})_2\text{InIn}(\text{Si}^t\text{Bu}_3)_2$.¹⁴⁹ More spectacularly still, similar ligands may frustrate the formation of the metal in such a disproportionation, yielding instead metalloid cluster species,^{29–32} such as $\text{Al}_{50}(\eta^5\text{-C}_5\text{Me}_5)_{12}$ ¹⁷⁰ and $\text{Ga}_{22}(\text{P}^t\text{Bu}_2)_{12}$.¹⁷¹

Much of the ‘variety’ of solution chemistry arises from the diversity of reaction types that can be accommodated through the greater freedom enjoyed both in the approach of reagents and the separation of products from the