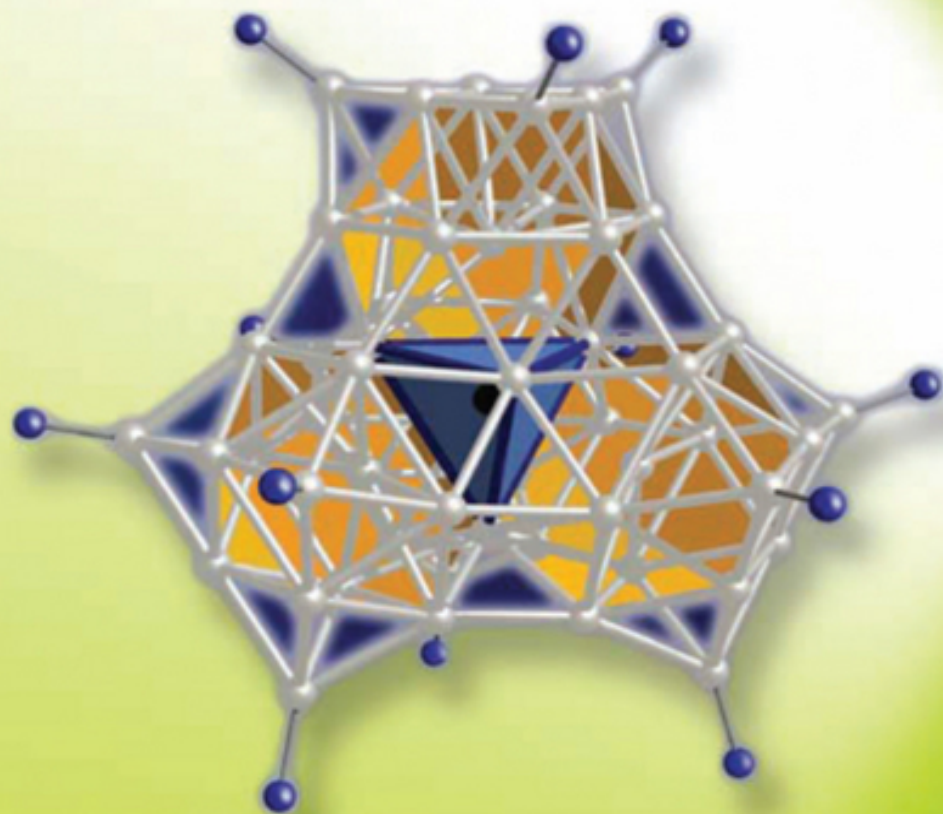


THE GROUP 13 METALS ALUMINIUM, GALLIUM, INDIUM AND THALLIUM

Chemical Patterns and Peculiarities



Editors | SIMON ALDRIDGE | ANTHONY J. DOWNS

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The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities

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A John Wiley and Sons, Ltd., Publication

This edition first published 2011

© 2011 John Wiley & Sons, Ltd.

Registered office

John Wiley & Sons Ltd, The Atrium, Southern Gate,
Chichester, West Sussex, PO19 8SQ, United Kingdom

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Library of Congress Cataloging-in-Publication Data

The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities / editors
Simon Aldridge, Anthony J. Downs.

p. cm.

Includes bibliographical references and index.

ISBN 978-0-470-68191-6 (cloth)

1. Group 13 elements. I. Aldridge, Simon II. Downs, Anthony J., 1936- III.

Title: The Group 13 Metals Aluminium, Gallium, Indium and Thallium: Chemical Patterns and Peculiarities.

QD466.C495 2011

546'.67-dc22

2010034290

A catalogue record for this book is available from the British Library.

ISBN 9780470681916

e-book - 9780470976555

o-book - 9780470976562

e-pub - 9780470976685

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, 3, 4, 5, 6, 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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Chapter 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 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 B₁₂ 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, $\text{H}_3\text{B}_3\text{N}_3\text{H}_3$, 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.

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 ($^{12}\text{C} = 12.0000$)	10.811(7)	26.9815386(8)	69.723(1)	114.818(3)	204.3833(2)
Ground-state electron configuration (term)	$[\text{He}]2s^2 2p^1$ ($^2P_{1/2}$)	$[\text{Ne}]3s^2 3p^1$ ($^2P_{1/2}$)	$[\text{Ar}]3d^{10} 4s^2 4p^1$ ($^2P_{1/2}$)	$[\text{Kr}]4d^{10} 5s^2 5p^1$ ($^2P_{1/2}$)	$[\text{Xe}]4f^{14} 5d^{10} 6s^2 6p^1$ ($^2P_{1/2}$)
Ionisation energies (kJ mol^{-1})					
$M \rightarrow M^+$	800.637	577.539	578.844	558.299	589.351
$M^+ \rightarrow M^{2+}$	2427.07	1816.68	1979.41	1820.71	1971.03
$M^{2+} \rightarrow M^{3+}$	3659.75	2744.78	2963	2704	2878
$M^{3+} \rightarrow M^{4+}$	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/\hbar)	^{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
	1.53 [B ^I], 2.28 [B ^{III}]	0.84 [Al ^I], 1.71 [Al ^{III}]	0.86 [Ga ^I], 2.42 [Ga ^{III}]	0.71 [In ^I], 2.14 [In ^{III}]	0.99 [Tl ^I], 2.25 [Tl ^{III}]
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) 1.31 ^b [646] (3)	1.57 ^c (3) 1.51(13) ^d [260] (4) 1.71 ^b [602] (3) 1.95(7) ^d (6)	1.74 ^c (3) 1.79(17) ^d [225] (4) 2.10(4) ^d [ca.525] (6)	1.76 ^c [181] (3)
M-F	1.74 ^b [444] (3)	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) 1.94(5) ^d (4)	1.91(8) ^d [ca. 430] (4) (4) 1.96(5) ^d (6) 2.26(5) ^d (4)	2.15(10) ^d [ca. 360] (4) 2.18(10) ^d (6) 2.48(7) ^d (4)	2.38(11) ^d [375] (6)
M-S	1.58 ^b [376] (3) 1.63(4) ^d (4)	1.97 ^b [245] (3) 1.985(38) ^d (4)	2.16 ^b [162] (3) 2.18(4) ^d (4)	2.48(2) ^d (4) 2.21 ^b [125] (3) 2.17(4) ^d (4)
M-C [≡]	1.58 ^b [376] (3) 1.63(4) ^d (4)	1.96 ^b [280] (3) 1.97(3) ^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]	2.70 [115]	2.97 [78]	3.41 [59]
M-H	1.232 [342]	1.662 [265]	1.836 [243]	1.873 [195]
M-F	1.263 [732]	1.774 [584]	1.985 [507]	2.084 [439]
M-Cl	1.715 [427]	2.202 [463]	2.401 [430]	2.485 [373]
M-Br	1.888 [391]	2.352 [416]	2.543 [388]	2.618 [331]
M-I	2.131 [361]	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, orthorhombic	Face-centred tetragonal	α -Tl, hexagonal
β -B, tetragonal	High pressure form	β -Ga, monoclinic		β -Tl, cubic
α -B, rhombohedral	β -Al, hexagonal	γ -Ga, rhombic		γ -Tl, f.c.c.
β -B, rhombohedral		δ -Ga, rhombohedral		Tl($\alpha \rightarrow \beta$) 503 K

(continued)

Property	B	Al	Ca	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), b.c.c. Ga(III), b.c. tetragonal Ga(IV), f.c.c. ^b		
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	11850, 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⁺ (Å)	(0.27)	0.535	0.620	0.800	0.885
M ⁺ (Å)	–	(ca. 1.00)	1.13	1.32	1.50
$\Delta H^\circ[\text{M}^{3+}(\text{g})]$ (kJ mol ⁻¹)	7468.8	5484.0	5816	5345.3	5639.2
$\Delta H^\circ[\text{M}^+(\text{g})]$ (kJ mol ⁻¹)	1369.6	910.09	861.9	807.8	777.73
Thermodynamic properties for aqueous species (kJ mol ⁻¹)					
$\Delta_f G^\circ[\text{M}^{3+}(\text{aq})]$ std state, $m = 1$	–967.7 [B(OH) ₃]	–485.0	–159.0	–98.0	+214.6
$\Delta_f H^\circ[\text{M}^{3+}(\text{aq})]$ std state, $m = 1$	–1072.8 [B(OH) ₃]	–531.0	–211.7	–105.0	+196.6
$\Delta_{\text{hydration}} G^\circ[\text{M}^{3+}(\text{g})]$, single ion	n.a.	–4540	–4550	–4020	–4000
$\Delta_{\text{hydration}} H^\circ[\text{M}^{3+}(\text{g})]$, single ion	n.a.	–4680	–4690	–4110	–4110

Standard reduction potentials,

E° (V):



$a_H^+ = 1$



$a_{OH}^- = 1$



$a_H^+ = 1$

(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, $\text{Na}_2\text{B}_4\text{O}_5(\text{OH})_4 \cdot x\text{H}_2\text{O}$; colemanite, $\text{Ca}_2\text{B}_3\text{O}_4(\text{OH})_3 \cdot 2\text{H}_2\text{O}$	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 aluminium 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 ₂ SO ₄ manufacture
World production (tonnes year ⁻¹)	ca. 2×10^6 (B ₂ O ₃)	ca. 4×10^7 (Al)	ca. 100 (Ga)	ca. 450 (In)	ca. 30 (Tl)
Reserves (tonnes)	270×10^6 (as B ₂ O 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 MH₃, MF₃, MCl₃, M(OH)₃ and M(CH₃)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 TlF₃ (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.

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]3 d^{10} , [Kr]4 d^{10} and [Xe]4 f^{14} 5 d^{10} . 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

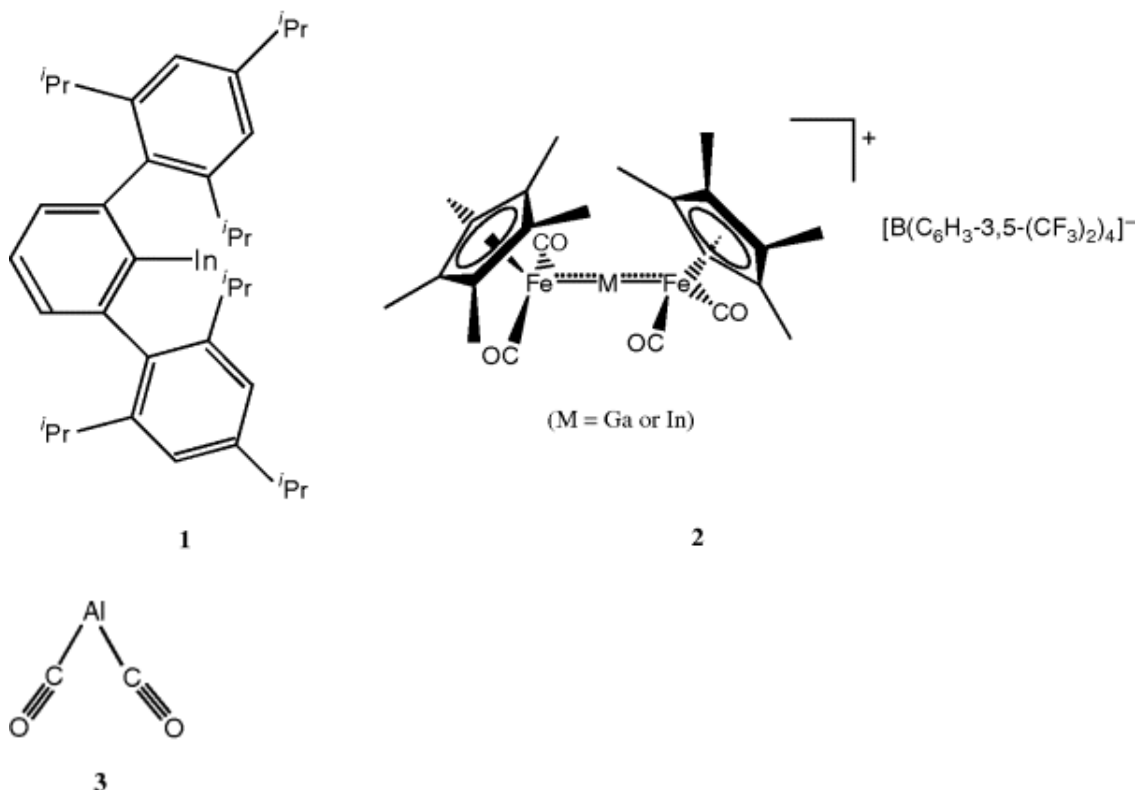
Developments in Group 13 metal chemistry in the past two decades have often been driven, at least ostensibly, by the promise of practical applications, for example in realms as diverse as the sourcing and storage of energy;

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.

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.



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.

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 MA₅, for M = Ga or In);^{64^a} in other cases, they have offered a rationale for the instability of a compound (e.g. MH₃, where M = In or Tl).^{64^{b-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 $\text{Al}(\text{BH}_4)_3$ and GaMe_3 ,^{10,12} and otherwise to high-energy species such as the metal atoms, M, metal clusters and their ions, and the diatomic molecules $\text{M}^{\text{I}}\text{X}$ [M = Al, Ga, In or Tl; X = H, F, Cl, Br or I].^{12,21,22} Some M^{I} compounds, such as InCl or $(\eta^5\text{-C}_5\text{R}_5)\text{M}$ [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 GaCl_3 and In_2O_3 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 Cl_2 , HCl or GaCl_3 at 800–1000 °C,⁷⁰ and InF is formed by heating together the metal and InF_3 .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 AlCH_3 (formed in a discharge reaction between aluminium vapour and HgMe_2),⁷⁴ is of interest as a potential carrier of the metal in the