

Metal Amide Chemistry

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Biographies

Michael Lappert is Emeritus Research Professor of Chemistry at the University of Sussex. A graduate of Northern Polytechnic, his B.Sc. was followed by a Ph.D. (with W. Gerrard) to which in 1960 he added a D.Sc. (University of London). He has been at Sussex since 1964, having previously been at UMIST (1959–1964). He was the recipient of the first Chemical Society Award for Main Group Metal Chemistry (1970) and then of the Organometallic Award (1978). He won the ACS – F. S. Kipping Award for Organosilicon Chemistry (1976); with the RSC (he was its Dalton Division President, 1989–1991), he has been a Tilden (1972), Nyholm (1994), and Sir Edward Frankland (1998) Medallist and Lecturer. In 2008, he was awarded the GDCh Alfred-Stock Prize. He was elected FRS in 1979 and was awarded an honorary doctorate from Ludwig-Maximilians-Universität (München, 1989). With co-workers he has published 2 books, edited 4 others, and more than 780 papers and reviews and a few patents on various aspects of inorganic and organometallic chemistry.

Philip Power received a B. A. from Trinity College Dublin in 1974 and a D. Phil. under M. F. Lappert from the University of Sussex in 1977. After postdoctoral studies with R. H. Holm at Stanford University, he joined the faculty at the Department of Chemistry at the University of California at Davis in 1981, where he is a Distinguished Professor of Chemistry. His main interests lie in the exploratory synthesis of new main-group and transition-metal complexes. A major theme of his work has been the use of sterically crowded ligands to stabilize species with new types of bonding, low coordination numbers, and high reactivity. He has been the recipient of several awards including the A. P. Sloan Foundation Fellow (1985), Alexander von Humboldt Fellowship for Senior U. S. Scientists (1992), Ludwig Mond Medal of the Royal Society of Chemistry (2005), F.A. Cotton Award in Synthetic Inorganic Chemistry of the American Chemical Society (2005) and was elected Fellow of the Royal Society of London (FRS) (2005).

Andrey Protchenko was born in 1961 in Rostov-on-Don, Russia. A graduate of the Moscow State University (Russia) in 1983, he carried out his doctoral work at the Karpov Institute of Physical Chemistry (Moscow) and completed his Ph.D. in chemistry (1997) at the Razuvaev Institute of Organometallic Chemistry (Nizhny Novgorod) under the supervision of Prof. M. N. Bochkarev studying naphthalene complexes of the lanthanides. In 1998 he joined the group of Prof. M. F. Lappert at the University of Sussex (England) working on a series of projects (Royal Society, EPSRC and Leverhulme Trust grants) involving lanthanide redox chemistry based on cyclopentadienyl, N- and N,N'-centred ligands.

Alexandra Seeber, née Pickering, was born in 1979 in Lichfield, UK. After graduating in Chemistry at Keele University in 2001 and completing a Ph.D. in Inorganic Chemistry into the design and synthesis of ligands for the controlled self-assembly of transition metal complexes at the University of Glasgow (Scotland) in 2004, she carried out postdoctoral research into nanoparticle synthesis at the University of California, Davis with Prof. Philip Power under a Department of Energy grant for the design of high surface area materials as hydrogen storage vessels. Alexandra Seeber has worked since 2006 in Research and Development in the catalysis department at BASF in Ludwigshafen (Germany).

Preface

In 1980, Ellis Horwood Ltd (with John Wiley & Sons, Ltd) were the publishers of a book entitled *Metal and Metalloid Amides*, by M. F. Lappert, P. P. Power, A. R. Sanger and R. C. Srivastava. This comprehensive treatise, which gathered together for the first time information on this important subject, is still occasionally referenced: for example, there have been more than 10 citations per annum in the major American Chemical Society journals during 2003–2007. However, the intervening three decades (from 1980) have witnessed a massive interest in the area, as evident in the more than 3000 papers; and to bring the subject up to date was a substantial undertaking.

The present volume arose from discussions during the end of 2004 with the late Ellis Horwood, who urged us to take up this challenge. Two of us (MFL and PPP, with our respective research groups; we thank our able collaborators for their contributions) have continued to publish extensively in the area. MFL and PPP were fortunate to have dedicated colleagues AVP (at Sussex) and ALS (at Davis) to join in this enterprise and to have the encouragement of Paul Deards, Richard Davies and their colleagues especially Nicole Elliott of John Wiley & Sons, Ltd, Chichester.

The first drafts of Chapters 1, 4, 5, 9 and 10 were written by MFL and AVP, while Chapters 2, 3, 6, 7 and 8 owe their origin to PPP and ALS; however, there have been ongoing consultations between the Sussex and Davis groups.

M. F. Lappert
P. P. Power
A. V. Protchenko
A. L. Seeber

1

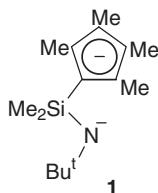
Introduction

1.1 Scope and Organisation of Subject Matter

Our principal focus is to describe the synthesis, structure, reactions and applications of metal amides and related compounds which are stable at ambient temperatures, and particularly those which are mono-, di- or oligonuclear. Thus, the main thrust is on compounds having one or more $\bar{\text{N}}(\text{R})\text{R}'$ ligands attached to a metal M. Such species are now known for all the natural elements (and Np and Pu), except for the lighter rare gases. In the present treatise, M is restricted to an element of Groups 1, 2, 3 and a 4*f* metal, a lighter 5*f* metal, and a metal of Groups 4 to 11, 12, 13 (except B), 14 (excluding M^{IV} compounds as reagents), and 15 (excluding P); these are described in Chapters 2 to 10, respectively.

The amido ligand may be $\bar{\text{N}}\text{H}_2$, $\bar{\text{N}}(\text{H})\text{R}$, and $\bar{\text{N}}(\text{R})\text{R}'$, in which R and R' are the same or different, and each is an alkyl, aryl, or silyl (particularly SiMe_3) group; selected NH_2 -metal compounds feature mainly in Chapters 2, 3, 6, 7 and 8. The amido ligand may be bound to the metal in a terminal or bridging (double or single) fashion; examples of the latter are $[\text{Sn}(\text{NMe}_2)(\mu\text{-NMe}_2)]_2$ and $[\text{Cu}(\mu\text{-NMe}_2)]_4$. Within our scope for main group and *f*-elements are bi- and tri-dentate ligands, including not only *N,N'*- and *N,N',N''*-centred species such as 1, 2- $\text{C}_6\text{H}_4(\bar{\text{N}}\text{CH}_2\text{Bu}^t)_2$ and $\text{MeC}\{\text{Si}(\text{Me})_2\bar{\text{N}}\text{Bu}^t\}_3$ but also others with a single amido site such as **1**. Tetradentate encapsulating ligands are excluded; their more natural home is to be found for the most part in textbooks of organic and biological chemistry and, more recently, materials chemistry. Amide-free metal complexes containing some *N,N'*-bidentate ligands which are neutral (e.g. bipy) or monoanionic (e.g. amidinates, guanidines, or β -diketiminates) are also outside our scope.

Imides are usually included for main group elements because bi- and oligonuclear metal imides are ubiquitous and were often developed in parallel with the amides. They generally feature trivalent nitrogen, as in $[\text{As}(\text{Cl})(\mu\text{-NBu}^t)]_2$. Imido derivatives of the transition



metals are not widely covered, as their chemistry is quite extensive and distinct from that of the amides. In general mononuclear metal imides are more frequent in *d*- and *f*-block chemistry; examples are $[\text{Ti}(=\text{NC}_6\text{H}_3\text{Pr}^i_{2-2,6})(\text{NMe}_2)(\text{NHMe}_2)_3][\text{B}(\text{C}_6\text{F}_5)_4]$ or $[\text{U}\{(\text{N}(\text{SiMe}_2\text{Bu}^t)\text{CH}_2\text{CH}_2)_3\text{N}\}(=\text{NSiMe}_3)]$, but rare examples are also found in main group metal compounds having bulky ligands, as in $[\text{In}\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_3\text{Pr}^i_{2-2',6'})_2-2,6\}-\{\text{=NC}_6\text{H}_3(\text{C}_6\text{H}_3\text{Me}_2-2',6')_2-2,6\}]]$. The majority of metal amides and related compounds are neutral, but cationic and anionic complexes have featured; examples are $[\text{Bi}\{\text{N}(\text{Bu}^t)\text{Si}(\text{Me})_2\text{NBu}^t\}][\text{GaCl}_4]$ and $[\text{Li}(\text{OEt}_2)_2[\text{Zr}(\text{NMe}_2)_6]]$. Compounds considered are mainly homometallic, but several are heterometallic such as the inverse crown complex $[\text{Na}_4\text{Mn}_2(\text{tmp})_6(\text{C}_6\text{H}_4)]$ [$\text{tmp} = \text{NC}(\text{Me})_2(\text{CH}_2)_3\text{CMe}_2$].

1.2 Developments and Perspectives

In 1980, metal and metalloid amides were already known for 57 elements, but then excluded were amides of the following elements: Sr, Ba, Tb, Dy, Er, Tm, Ru, Os, Rh, Ir and Pd (for several others, the first publications were post-1970: Sc, Y, La, Ce, Pr, Nd, Sm, Eu, Gd, Ho, Yb, Lu, Re, In and Tl). Since then, these lacunae have been filled. The variety of metal oxidation states for metal amides has also greatly expanded since 1980. The literature on metal amides has likewise burgeoned. For example, in the 1980 book there were 119 and 317 bibliographic citations for Group 1 and a conglomerate of Group 3 and 4/*f* and *d*-metal amides, respectively, whereas there are now 263 and 1110 for these two sections, respectively. Our aim has been to provide a comprehensive, but not exhaustive, coverage of the field of metal amides, with emphasis on the post-1980 developments through to the end of 2007. The total number of references for the succeeding Chapters 2 to 10 is in excess of 2500, while for these topics there were 923 citations in 1980.

Tables 1.1 and 1.2, laid out in the form of a Periodic Table, provide (i) a list of the elements, (ii) in brackets after each entry, the metal oxidation states for its amides, and (iii) the number of literature citations for each group of metals. Highlighted in bold are those metals for which amides were reported in the post-1979 period, while in italics are those metal oxidation states which likewise are of more recent date.

The variety of amido ligands now in use is very large. Many are bulky and often are free of β -hydrogen atoms. Among the newer monodentate amides are $\bar{\text{N}}\text{Cy}_2$ (Cy = cyclohexyl), $\bar{\text{N}}(\text{SiHMe}_2)_2$, $\bar{\text{N}}(\text{SiMe}_2\text{Bu}^t)_2$, $\bar{\text{N}}[(\text{SiMe}_3)\text{C}_6\text{H}_3\text{Pr}^i_{2-2,6}]$, $\bar{\text{N}}[(\text{SiMe}_3)\{\text{C}_6\text{H}_3(\text{C}_6\text{H}_2\text{Me}_3-2',4',6')_2-2,6\}]]$, and $\bar{\text{N}}[\text{Ad}(\text{C}_6\text{H}_3\text{Me}_2-3,5)]$. Bi- and tridentate amides include not only those which are solely *N*-centred such as $\bar{\text{N}}(\text{R})\text{CH}=\text{CH}\bar{\text{N}}\text{R}$ or $\text{X}\{\text{CH}_2\text{CH}_2\bar{\text{N}}\text{Bu}^t\}_3$ (X = SiBu^t or N), but others in which the ligating atoms are not exclusively nitrogen: for illustrations of such ligands see 6–12 and 26–54 in Chapter 4.

Table 1.1 List of metal amides of Group 1, 2, 12, 13 (not B), 14 (not M^{IV}) and 15 (not P) in various oxidation states (shown in brackets) and number of literature citations: new^a metals and oxidation states are shown in bold and italics, respectively

Group no.	1	2	12	13 (not B)	14 (subvalent) ^b	15 (not P)
Chapter no.	2	3	7	8	9	10
	Li (1) Na (1) K (1) Rb (1) Cs (1)	Be (2) Mg (2) Ca (2) Sr (2) Ba (2)	Zn (2) Cd (2) Hg (2)	Al (1, 3) ^c Ga (1, 2, 3) ^d In (1, 2, 3) Tl (1, 3, 1/3)	Si (2) ^e Ge (2, 3) ^f Sn (2, 3) ^f Pb (2)	As (1, 2, 3, 5) Sb (3, 5) Bi (3, 5)
Total no. of references	260	211	114	355	388	137

^aSince 1979

^b M^{IV} compounds for Group 14 metal (M) amides are not discussed

^cAlso cluster compounds having metal oxidation states <1, e.g., $[Al_{77}\{N(SiMe_3)_2\}_{20}]^{2-}$

^dAlso cluster compounds having metal oxidation states <1, e.g., $[Ga_{84}\{N(SiMe_3)_2\}_{20}]^{4-}$

^eAlso oligomeric anions (e.g., $[(Si(NN))_4]^-$, $[(Si(NN))_4]^{2-}$, $[(Si(NN))_3]^{2-}$; $[Si(NN) \equiv Si\{(NR)_2C_6H_4-1,2\}]$, R = Et, Bu^t)

^fAlso cluster compounds having metal oxidation states <1: $[Ge_8\{N(SiMe_3)_2\}_6]$, $[Sn_9\{Sn(N(C_6H_3iPr_2-2,6)SiMe_2)_6\}]$ (R = Me, Ph)

Numerous amidometallates (several as cluster compounds) and, more rarely, cationic complexes, are well established. Representative examples of such salts are $[KMg(NPr^i_2)_3]_\infty$, $[Ti(NMe_2)_3(py)_2][BPh_4]$, $[Pt(\mu-Cl)\{SnCl(NR_2)_2\}(PEt_3)_2]$ (R = SiMe₃), $[Li(thf)_4][Ni(NPh_2)_3]$, $[U(NEt_2)_2(py)_2][BPh_4]_2$, $[As(C_5Me_5)(NMe_2)][AlCl_4]$ and $Li[Sb_3(\mu-NCy)_4(NMe_2)_2]$.

A feature of the post-1980 literature on mononuclear metal amides has been the discovery of numerous low-coordinate metal complexes. Significant examples among neutral compounds are the crystalline uniconordinate Group 13 metal and the dicoordinate Si^{II} and Group 15 metal amides $[Ga\{N(SiMe_3)C_6H_3Mes_{2-2,6}\}]$, $[Si\{N(Bu^t)CH=CHNBu^t\}]$ and $[As\{N(H)Mes^*\}(=NMes^*)]$ (Mes = C₆H₂Me₃-2,4,6; Mes* = C₆H₂Bu^t₃-2,4,6). The highest metal coordination number recorded for a homo- or heteroleptic metal amide containing only monodentate ligands is six, in $[M(NMe_2)_6]$ (M = Mo or W), or seven, in $[U(NEt_2)_2(py)_5][BPh_4]_2$, respectively. The highest metal oxidation state of +6 is found not only in the Mo and W hexa(dimethylamides) but also for U, originally in *trans*- $[U(O)_2\{N(SiMe_3)_2\}_2(thf)_2]$; $U(NMe_2)_6$ was found to be thermally labile.

Bi-, tri- and oligonuclear compounds have ring, fused ring, or cluster core geometries, which feature $\bar{N}(R)R'$ as bridging ligands. For oligonuclear aggregates, the fused rings are often arranged as ladders or stacks, descriptions which were originally coined in the context of such alkali metal amides. The addition of a neutral ligand often fragments such an aggregate, a simple example being the conversion of $[Li\{\mu-N(SiMe_3)_2\}]_3$ into $3[Li\{N(SiMe_3)_2\}(tmeda)]$ (tmeda = Me₂NCH₂CH₂NMe₂).

A wider range of amido-containing complexes is of mixed metals, while others have imido bridges. Illustrations are provided by $[NaMg(NPr^i_2)_2(OBu^n)]_2$ (see Chapter 3, Figure 3.5) and $[Li_3(thf)_3Sb_6(NCy)_6(N)_3\cdot Li(N=NH)]$ (see **29** in Chapter 10). In the latter compound, each of the bridging cyclohexylimido or nitrido ligands has a coordination number ≥ 3 and hence may be regarded as a bis- or tris-(metallo)amide, respectively; the

Table 1.2 List of Group 3–11 metal amides in various metal oxidation states (shown in brackets) and number of literature citations: new^a metals and oxidation states are shown in bold and italics, respectively

Sc (3)	Ti (2, 3, 4; 1/3)	V (3, 4, 5; 3/5)	Cr (2, 3, 4, 5, 6; 3/4)	Mn (2, 3)	Fe (2, 3; 2/3)	Co (2, 3)	Ni (1, 2)	Cu (1)
Y (3)	Zr (4)	Nb (4, 5)	Mo (1, 2, 3, 4, 5, 6; 4/5)		Ru (1, 2)	Rh (1, 3; 1/3)	Pd (2)	Ag (1)
La (3)	Hf (4)	Ta (4, 5)	W (2, 3, 5, 6; 4/5)	Re (1, 2, 5)	Os (1, 2, 4)	Ir (2, 3)	Pt (2, 4)	Au (1, 3)
Ce (3, 4, 3/4)		Th (4)		Total number of references:				
Ln ^b (3)		U (2, 3, 4, 5, 6; 3/4)		1. Sc, Y, La and 4 <i>f</i> elements (Ch. 4): 268				
Ln ^c (2, 3)		Np (3)		2. Th, U (Ch. 5): 116				
		Pu (3)		3. Np, Pu (Ch. 5): 3				
				4. <i>d</i> -Block elements (Ch. 6): 692				

^aSince 1979

^bPr, Nd, Gd, **Tb**, **Dy**, Ho, **Er**, **Tm**, Lu

^cSm, Eu, Yb

diradicaloid compound $[\text{SnCl}(\mu\text{-NSiMe}_3)_2]$ is a simpler compound having bridging imido ligands in which the nitrogen atoms are three-coordinate.

Prior to 1980, 11 methods of synthesis of metal (M) amides were described and continue to be used. The salt elimination procedure $[\text{L}_n\text{MX} + \text{M}'\{\text{N}(\text{R})\text{R}'\}]$ is the most general, usually with $\text{X} = \text{Hal}$ and $\text{M}' = \text{an alkali metal}$; whereas lithium is often the metal of choice, employing $\text{M}' = \text{Na}$ or K has the advantage of easier separation of the alkali metal halide from the target metal amide. More recently used leaving groups are tosylate, triflate, aryloxide, or a cyclopentadienyl (e.g. in Al^{I} or Pb^{II} chemistry). Newer sources of an amido ligand are $\text{BrN}(\text{SiMe}_3)_2$ and a *N,N'*-dihydrocarbyl-1,4-diazabuta-1,3-diene.

Molecular structure elucidation, principally by single crystal X-ray diffraction, has become almost routine and is now available for the majority of the metal amides presently discussed. In the 1980 book, however, such data were provided for just 112 compounds, 54 of which were for *d*- and *f*-block metals and 41 for the Group 13 metal amides. The contrast with the developing situation is illustrated by reference to Group 1 metal amides: from four X-ray data sets in 1980 there were more than 200 by the end of 2007.

Among other physicochemical techniques which now feature prominently are those based on vibrational, electronic, NMR (including ^2H , ^{13}C , ^6Li , ^7Li , ^9Be , ^{27}Al , ^{29}Si , ^{113}Cd , ^{119}Sn and ^{171}Yb) and EPR spectroscopy and magnetic measurements. Computational studies are increasingly significant, particularly for subvalent metal-nitrogen compounds. The nitrogen environment is almost invariably close to trigonal, or distorted trigonal, planar for homo- and heteroleptic metal amides having terminal $\bar{\text{N}}(\text{R})\text{R}'$ ligands, respectively. This fact, as well as the generally relatively short M–N bond lengths (compared with the sum of the covalent radii of M and N) has often been interpreted in terms of the $\bar{\text{N}}(\text{R})\text{R}'$ ligand being both a σ - and a π -donor. However, as has increasingly become evident, other factors should also be considered, as discussed, for example, in the context of transition metal amides and bis(amino)silylenes in Chapter 6 (Section 6.2.3.1) and Chapter 9 (Section 9.2.3), respectively.

Several metal amides are much employed as reagents, ligand transfer reagents or precursors for more complex molecules. Alkali metal, and mainly lithium, bulky amides, including $\text{LiN}(\text{SiMe}_3)_2$, LiNPr_2 and LiNCy_2 , are important proton-abstractors for organic synthesis, as are recently the synergic couple $\text{MN}(\text{R})\text{R}'/\text{M}'\text{R}_n$ ($\text{M}' = \text{a Group 2, 12 or 13 metal}$). Magnesium, aluminium, tri(methyl)tin and, particularly, alkali metal amides are valuable ligand transfer reagents, being the most useful precursors to amides of other metals. The ready cleavage of the highly polar M–N(R)R' bond, especially by protic reagents, make several metal amides important as (i) synthons for a wide range of that metal's compounds, and (ii) materials. Examples of (i) are $\text{Sn}(\text{NMe}_2)_2$ or $\text{Sb}(\text{NMe}_2)_3$ as the source of unusual Sn–N and Sn–P complexes such as the cubane $[\{\text{Sn}(\mu\text{-NBu}^t)\}_4]$ and $[\text{Li}_2\text{Sn}_2(\text{PR})_4(\text{tmeda})_2]$ (**53** in Chapter 9), or related Sb compounds, such as $[\text{Li}_4\{\text{Sb}_2(\text{NCy})_4\}_2]$ (**30** in Chapter 10). Illustration of (ii) is provided by Tables 4.1 and 4.2 of Chapter 4, showing $[\text{Ce}\{\text{N}(\text{SiMe}_3)_2\}_3]$ as a starting material for a heteroleptic β -diketiminato compound and $[\text{Y}\{\text{N}(\text{SiHMe}_2)_2\}_3(\text{thf})_2]$ as a substrate for the formation of yttrium-centred catalysts, usually immobilised, for various organic transformations. A valuable feature for (i) and (ii) is that the amine co-product, NHMe_2 or $\text{NH}(\text{SiHMe}_2)_2$, is volatile. Metal amide-catalysed hydroamination/cyclisation of *N*-unprotected alkenes to form heterocyclic nitrogen compounds is exemplified by the role of an optically active Sm^{III} amide as an enantioselective catalyst for such a process (e.g. see Equations (4.8) and (4.12) in Chapter 4). Various *d*- and *4f*-block metal amides have been shown to be catalysts for

some important processes, including olefin di-, oligo- or polymerisation, olefin hydroamination and hydrosilylation, copolymerisation of an oxirane and carbon dioxide, and ring-opening polymerisation of lactides or ϵ -caprolactam. Certain *d*- and 4*f*-block metal amides are unusual in their ability to 'activate' N_2 or N_2O , as in the conversion of $[Mo\{N(Ad)R\}_3]$ into $[Mo(X)\{N(Ad)R\}_3]$, respectively ($R = C_6H_3Me_{2-3,5}$ and $X = N$ or NO), or in the reactions of $[Zr(F)Cl_2]$ with KC_8 and N_2 (**F** is a macrocyclic *P,P',N,N'*-centred bis-(amido) ligand) (see Schemes 6.3, 6.4 and 6.7 in Chapter 6).

2

Alkali Metal Amides

2.1 Introduction

Amido derivatives of the alkali metals enjoy the most widespread use of all metal amides. This is a result of their central importance as amido ligand transfer agents for the synthesis of other element amido derivatives throughout the Periodic Table. In addition, they are widely used in organic chemistry as powerful Bronsted bases and they are preferred bases for the formation of ketone enolates. Despite their importance in these fields, the primary focus of this chapter is on their synthesis and structures. In particular, the number of known structural types has undergone great expansion since 1980. It is instructive to compare knowledge of alkali metal diaorganoamides described in Chapter 2 of our 1980 book¹ with currently available data. At that time, a comprehensive listing of the known alkali metal amides, including the parent metal amides MNH_2 ($M = Li - Cs$), totalled less than 40 compounds with less than 100 citations from the primary literature. The detailed structures of just three compounds – $[LiN(SiMe_3)_2]_3$,^{2,3} $[NaN(SiMe_3)_2]_\infty$ ⁴ and $[(dioxane)_2KN(SiMe_3)_2]_\infty$ ⁵ had been published. The lithium salt $[Li(tmp)]_4$ ($tmp = 2,2,6,6$ -tetramethylpiperidine), was also listed as structurally characterized but as unpublished work (see below).¹

The intervening years have seen huge growth in the number of well-characterized compounds, the vast majority of which are lithium, sodium or potassium salts. Their structural chemistry has proven to be especially rich and the number of structures of alkali metal amides currently available exceeds 200. These involve a wide selection of structural motifs that were mostly unknown in 1980.

There have been several reviews on alkali metal amide structural chemistry.^{6–12} Most of these deal with lithium amides but there is also significant coverage of the heavier elements^{9–12} and other topics such as derivatives of primary amides and hydrazides.¹² Two comprehensive reviews^{6,8} for lithium amides and related salts published in 1991 and 1995 include extensive tables of structural data. There have also been reviews of the solution behaviour^{13–15} of lithium amides as well as of the extensive use of alkali metal

amides in organic synthesis.^{16–19} In addition, there have been a large number of related lithium complexes that incorporate chelating or multidentate amido ligands or ligands related to amides in which nitrogen is part of a delocalized array incorporating carbon, nitrogen, sulfur, or phosphorus atoms, exemplified by azallyl anions, guanidines, benzamidines, β -diketiminates, phosphoraneiminates, sulfaminides, and related ligands. However, these complexes lie outside our current scope and are thus not covered in this chapter. The present coverage focuses on the most important structural findings for alkali metal complexes of monodentate diorganoamido ligands with emphasis on the more recent developments.

2.2 Lithium Amides

2.2.1 Introduction

Lithium amides are the most important of the alkali metal amides. This is mainly due to the facility with which they can be prepared in solution by the simple reaction of the amine with commercially available LiBu^n . An analogous reaction with heavier metal alkyls is much more difficult due to the high reactivity of heavier alkali metal alkyls which attack many solvents. Another advantage of lithium amides is that they tend to be more soluble in hydrocarbons than their heavier element congeners. This is due to the small size (and hence greater polarizing power) of the lithium ion, which induces greater covalent character.

The parent lithium amide, LiNH_2 , was discovered in 1894²⁰ but crystal data were not refined until 1972.²¹ Unfortunately, the variation in NH_2 group orientation and the crystal packing of the ions in the unit cell made it impossible to fully determine the crystal structure. The crystal structure of LiNH_2 was reinvestigated more recently by powder neutron diffraction.²² It was found to crystallize in the tetragonal space group $I4$. The distances between the nearest nitrogen and hydrogen atoms lie between 0.986 and 0.942 Å. The H-N-H bond angle was estimated to be 99.97° . These results differ significantly from those reported in the previous studies. The structure of the deuterated analogue LiND_2 also has the tetragonal space group $I4$ and a structure in which the lithium ions are coordinated by four amido (ND_2^-) ions in a distorted tetrahedral geometry (Li-N distances lie between 2.06 and 2.21 Å).²³ The LiN_4 tetrahedra are connected by edge-sharing interactions to form a three-dimensional network. The two N-D distances (av. 0.98 Å) are similar to those previously published. The crystal structure of a bromide ion-supported Li-NH_2 lattice in $\text{Li}_2\text{Br}(\text{NH}_2)$ has been determined.²⁴ It has an infinite array of $[\text{Li}_4(\text{NH}_2)_2]^{2+}$ rods held within a three-dimensional crystal lattice via coordinative interactions with the Br^- ions. The Li-N distances are between 2.01 and 2.17 Å, and the Li-Br distances lie between 2.50 and 2.63 Å.

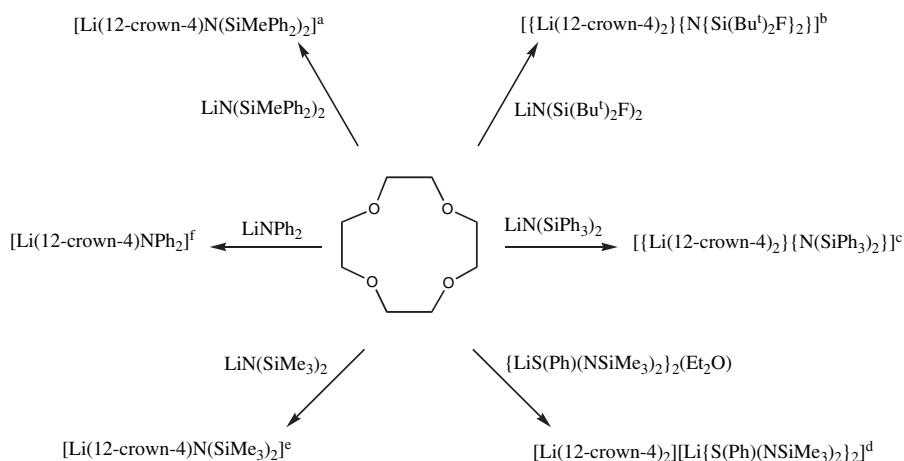
In the vapor phase it is possible to obtain LiNH_2 as a monomer and its structure has been determined by millimeter/submillimeter – wave spectroscopy.²⁵ The r_0 structure of LiNH_2 has Li-N and NH distances of 1.736(3) Å and 1.022(3) Å as well as H-N-H angle of $106.9(1)^\circ$. The Li-N distance is the shortest measured for a lithium amide, and it is in good agreement with theoretical predictions.^{26–29} There have also been theoretical investigations of the lower aggregates $(\text{LiNH}_2)_n$ ($n = 2, 3, 4$, etc.).^{30–33} In recent work it has been shown that, with use of complexing agents at both lithium and boron, it is possible to stabilize

monomeric LiNH_2 in the solid state.³⁴ The use of 12-crown-4 to complex lithium and of $\text{B}(\text{C}_6\text{F}_5)_3$ to coordinate nitrogen allowed the isolation of the unique $[(12\text{-crown-4})\text{LiNH}_2\text{-}\{\text{B}(\text{C}_6\text{F}_5)_3\}]$ which has an average Li–N bond length of 2.048(1) Å.

Parent lithium amide derivatives are also attracting attention due to their potential applications in hydrogen storage.^{35–39} For example, the complex hydride system $\text{LiNH}_2\text{-LiH}^{40}$ can undergo reversible, thermally induced hydrogenation and dehydrogenation transformations and represents a material with a potential to provide over 10 wt. % hydrogen storage.^{40–42} There is also interest in the reduction of the hydrogen desorption temperature by destabilization of complex hydrides via full or partial cationic substitutions with heterometallic atoms.^{43–53} For example, a substitution of $\text{M}=\text{Li}$ with $\text{M}=\text{Li}_{0.9}\text{Mg}_{0.1}$ results in a decrease of dehydrogenation temperature from 550 to 500 K.^{54–56} Interest in the chemical hydrogen storage problem has also led to the isolation of several new complex hydrides. For example, $\text{Li}_2\text{BH}_4\text{NH}_2$ has a hexagonal array of distinct $(\text{LiNH}_2)_6$ clusters dispersed in a LiBH_4 matrix.⁵⁷ The lithium amide-borohydride system is dominated by a bcc compound of formula $\text{Li}_4\text{BH}_4(\text{NH}_2)_3$.⁵⁸

2.2.2 Monomeric Lithium Amides

The simplest substituted lithium amide structures are mononuclear. Some of the earliest examples were isolated through the use of the multidentate ligand 12-crown-4 to complex the lithium and prevent oligomerization (Scheme 2.1). The reaction of lithium complexes LiNR_2 (where $\text{R}=\text{SiMe}_3$, Ph or SiMePh_2), obtained by treatment of the amine with LiBu^n , with 12-crown-4 forms the corresponding monomer $[\text{Li}(12\text{-crown-4})\text{NR}_2]$ ^{59,60} with Li–N bond distances in the range 1.97 to 2.06 Å. Each monomer features a five-coordinate Li^+ ion in an approximately square pyramidal environment complexed by one nitrogen and four oxygen donor atoms. It is also possible to induce ion pair separation⁶¹ by the addition of 12-crown-4 to lithium amide complexes LiNR_2 when R is very large, for example, $[\{\text{Li}(12\text{-crown-4})_2\}\{\text{N}(\text{SiPh}_3)_2\}]$ ⁶² and $[\{\text{Li}(12\text{-crown-4})_2\}\{\text{N}\{\text{Si}(\text{Bu}^t)_2\text{F}_2\}_2\}]$.⁶³ The crown



Scheme 2.1 Lithium amido complexes formed upon addition of 12-crown-4: ^a,⁶⁰ ^b,⁶³ ^c,⁶² ^d,⁶⁵ ^e,⁵⁹ ^f,⁶⁰

ether acts as a stronger donor ligand to the lithium ion and ion pair separation allows minimization of the steric pressure within the bulky amido anion.⁶³ An interesting structure is observed upon addition of 12-crown-4 to the dimeric lithium amide $[\{\text{LiS(Ph)(NSiMe}_3)_2\}_2(\text{OEt}_2)]$,⁶⁴ which results in the ion pair separated compound $[\text{Li(12-crown-4)}_2][\text{Li}\{\text{S(Ph)(NSiMe}_3)_2\}_2]$, where the anion and cation each contain a complexed lithium ion.⁶⁵ One of the lithium ions is sandwiched between two crown ether molecules to afford 8-coordinate Li^+ and the other is coordinated by the two chelating anions in a spirocyclic fashion. The Li–N bond lengths are relatively long (2.09 to 2.17 Å) due to the increased interelectronic repulsion within the anionic component.

Other monomeric silylamido complexes have also been obtained by the addition of tmeda (*N,N,N',N'*-tetramethylethylenediamine) or pmdeta (*N,N,N',N'',N''*-pentamethyldiethylenetriamine) to afford $[(\text{tmeda})\text{LiN}(\text{SiMe}_3)_2]$ which has three coordinate lithium Li–N(amide) = 1.893(3) Å and $[(\text{pmdeta})\text{LiN}(\text{SiMe}_3)_2]$ with 4-coordinate Li and Li–N(amide) = 1.988(6) Å.⁶⁶ The use of very large substituents at the amido ligand can also afford monomeric structures. Examples include $[\text{Li}(\text{thf})_3\text{N}(\text{SiMe}_2\text{Ph})_2]$,⁶⁰ $[\text{Li}(\text{thf})_2\text{N}(\text{SiPh}_3)_2]$,⁶⁰ $[\text{Li}(\text{thf})_2\text{N}(\text{SiBu}^t_2\text{F})_2]$,⁶³ $[\text{Li}(\text{thf})_2\text{N}\{(\text{C}_6\text{F}_5)(\text{SiBu}^t_2\text{F})\}]$ ⁶⁷ and $[\text{Li}(\text{thf})_3\{\text{NMes}^*(\text{SiPr}^i_2\text{X})\}]$ ($\text{Mes}^* = \text{C}_6\text{H}_2\text{Bu}^t_{3-2,4,6}$; $\text{X} = \text{F}$ or Cl).⁶⁸ A more recent example is given by the monomeric $[\text{Li}\{\text{N}[\text{Si}(\text{NCH}_2\text{Bu}^t)_2\text{C}_6\text{H}_4\text{-1,2-SiMe}_2\text{Ph}][\text{Si}(\text{NCH}_2 = \text{Bu}^t)_2\text{C}_6\text{H}_4\text{-1,2-SiMe}_3](\text{thf})]$.⁶⁹ The lithium ion is three-coordinate and is bound by two amido nitrogen atoms (average Li–N bond length is 1.96 Å) and one tetrahydrofuran donor molecule.

Monomeric structures are also observed in sterically crowded borylamides such as $[(\text{Et}_2\text{O})_2\text{LiN(R)BMes}_2]$ ($\text{R} = \text{Ph}^{70}$ or Mes^{71}) or $[(\text{tmeda})\text{LiN}(\text{Bu}^t)\text{BBu}^t_2]$ ⁷² where B–N π bonding may lower the basicity of the nitrogen lone pair and disfavour aggregation.

Monomeric amido complexes were also obtained through the use of other large nitrogen substituents in combination with various donor ligands. For example, the mononuclear primary amide $[\text{Li}(\text{NHMes}^*)(\text{tmeda})]$ ⁷³ formed by addition of tmeda to a toluene solution of the dimeric $[\{\text{Li}(\text{NHMes}^*)(\text{OEt}_2)\}_2]$.⁷⁴ The lithium ion in this structure has a very distorted trigonal planar coordination environment (Figure 2.1) because of an additional

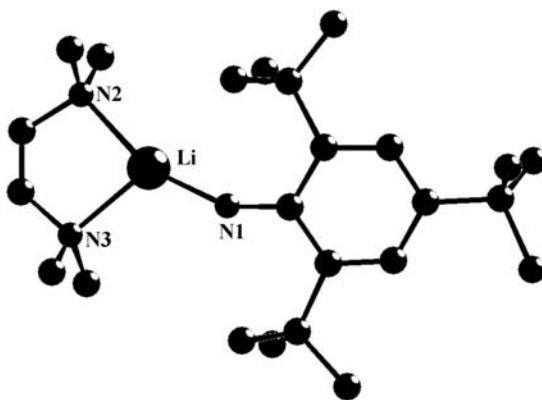
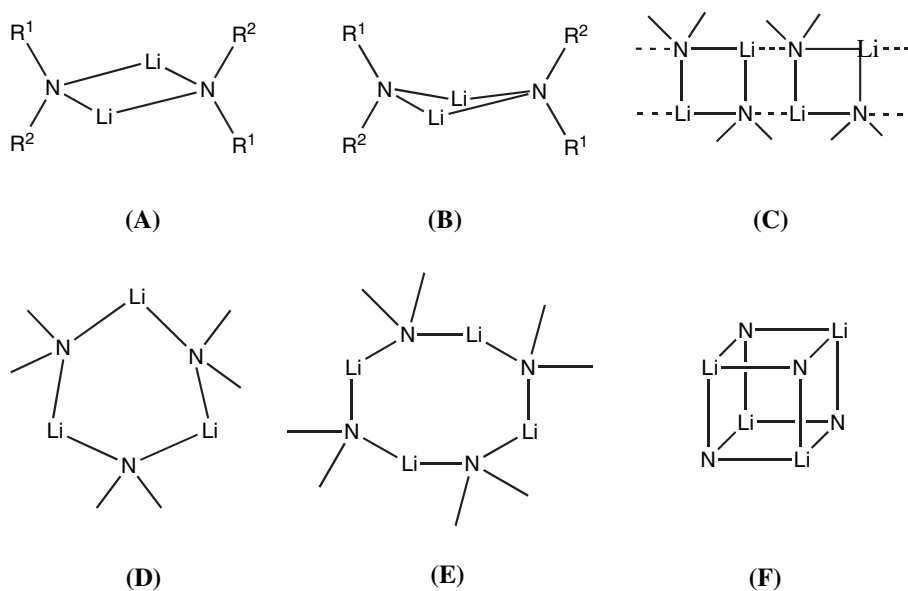


Figure 2.1 Illustration of the monomeric primary amido complex $[\text{Li}(\text{NHMes}^*)(\text{tmeda})]$ ⁷³ showing the distorted trigonal planar geometry at the lithium ion. Selected bond lengths: Li–N1: 1.895(8) Å, Li–N2: 2.137(9) Å and Li–N3: 2.165(9) Å

C-H...Li interaction. The lithium ion has a much shorter bond to the amido nitrogen ($\text{Li}-\text{N} = 1.897(5) \text{ \AA}$) in comparison with the tmeda nitrogens (av. $\text{Li}-\text{N}$ distance is $2.15 \text{ \AA}$). This strategy has been further employed in the synthesis of the monomeric complexes $[\text{Li}\{\text{NPh}(\text{naphthyl})\}(\text{tmeda})]$ and $[\text{Li}\{\text{NPh}(\text{naphthyl})\}(\text{pmdeta})]$, which have a trigonal ($\text{Li}-\text{N}$ bond lengths between 1.97 and $2.13 \text{ \AA}$) and tetrahedral ($\text{Li}-\text{N}$ distances between 2.00 and $2.22 \text{ \AA}$) coordination of the lithium ion, respectively,⁷⁵ and $[\text{Li}\{\text{N}(\text{CH}(\text{Me})\text{Ph})-(\text{CH}_2\text{Ph})\}(\text{pmdeta})]$,⁷⁶ which has tetrahedral lithium coordination with $\text{Li}-\text{N}$ bond lengths between 1.96 and $2.31 \text{ \AA}$. Each of the above complexes has shorter contacts to the nitrogen from the aryl group than to the amino groups of the multidentate donor ligands. Furthermore, reaction of NCBu^t with a pentane solution of $[(\text{tmeda})\text{Li}\{\text{C}_6\text{H}_7(\text{SiMe}_3)_2\}]$ at room temperature yielded the monomeric chelated lithium amido complex $[(\text{tmeda})\text{LiN}(\text{SiMe}_3)-\{\text{C}(\text{Bu}^t)\text{C}_6\text{H}_7\text{SiMe}_3\}]$.⁷⁷ The presence of relatively bulky substituents at the amido ligand is an important factor in the preferential formation of monomers.⁷⁵⁻⁷⁷ Smaller substituents on N facilitate higher aggregate species even in the presence of donor ligands, as exemplified by the formation of the dimeric species $[\{\text{LiNMePh}(\text{tmeda})\}_2]$ ⁷⁵ and $(R)-[\text{Li}\{\text{N}(\text{CH}_2\text{Ph})-\text{CH}(\text{Me})\text{Ph}\}(\text{pmdeta})]$.⁷⁶

2.2.3 Dimeric Lithium Amides

Dimeric and higher aggregate lithium amides can generally be classified into the coordination motifs illustrated in Scheme 2.2. The four-membered $(\text{LiN})_2$ ring is ubiquitous in lithium amide chemistry and is observed both in discrete dimeric structures in either planar (Scheme 2.2, A) or non-planar (Scheme 2.2, B) geometries as well as in oligomeric and polymeric (ladder) frameworks (Scheme 2.2, C). Trimeric six-membered $(\text{LiN})_3$ ring

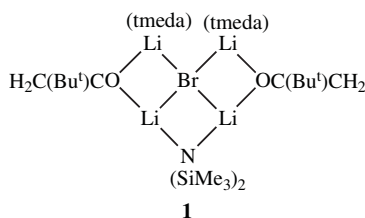


Scheme 2.2 Common aggregation motifs of lithium amides

(Scheme 2.2, D) and tetrameric eight-membered $(\text{LiN})_4$ ring and cubane (Scheme 2.2, E and F) structures are also known. Comprehensive reviews of dimeric and other lithium amido structures were published in the 1990s. As a result only selected examples from the preceding literature are covered.^{6,8}

The most common lithium amide structures are dimeric although in solution the dimers often exist in equilibrium with other structures.^{13–15,78} The simplest are derived from monodentate, primary amido ligands, $-\text{NHR}$. For example, the solvated structures $[\{\text{Li}(\text{OEt}_2)\text{NHR}\}_2]$ (where $\text{R} = \text{Mes}^*$ or Dipp ($\text{C}_6\text{H}_3\text{Pr}^i\text{-2,6}$)) contain a planar Li_2N_2 framework (Structure A) with $\text{Li}-\text{N}$ bonds of 1.987(5) and 2.041(6) Å for $[\{\text{Li}(\text{OEt}_2)\text{NHMe}^*\}_2]$,⁷⁴ and an average $\text{Li}-\text{N}$ distance of 2.00 Å for $[\{\text{Li}(\text{OEt}_2)\text{NHDipp}\}_2]$. The lithiums are bridged by the two amido ligands, and the trigonal coordination geometry at the lithium atoms is completed by coordination of one (diethyl ether) molecule.

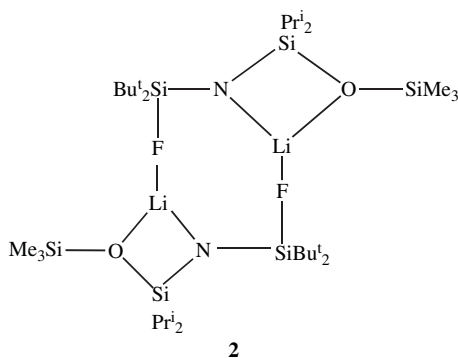
There are several simple dimeric structures of less crowded lithium derivatives of primary amides. Among these are $[\{\text{Li}(\text{thf})_2\text{NHPH}\}_2]$,⁷⁹ and $[\{\text{Li}(\text{thf})_2\text{NHC}_6\text{F}_5\}_2]$,⁷⁹ $[\{\text{Li}(\text{py})_2\text{NHPH}\}_2]$ ⁸⁰ and $[\{\text{Li}(\text{C}_6\text{H}_4\text{-NMe}_2\text{-4})_2\text{NHPH}\}_2]$,⁸⁰ the silylamides $[\{\text{Li}(\text{tmeda})\text{-NH}(\text{SiBu}^t_2\text{F})\}_2]$ ⁸¹ and $[(\text{LiNH}(\text{SiBu}^t\text{OSi}(\text{F})\{\text{N}(\text{SiMe}_3)\text{Pr}^i\}_2)_2)]$.⁸² It has already been mentioned that $\text{LiN}(\text{SiMe}_2)_2$ is a trimer in the solid state.^{2,3} However, in the vapor phase it has the dimeric formula $[\{\text{LiN}(\text{SiMe}_3)_2\}_2]$ (Structure A) with two coordinate Li and $\text{Li}-\text{N} = 1.99(3)$ Å.⁸³ The more crowded $[\{\text{LiN}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})\}_2]$ ⁸⁴ is a dimer in the solid state. The extensive use of the lithium amide $\text{LiN}(\text{SiMe}_3)_2$ has led to great interest in the structures of its complexes with various Lewis bases and the various factors that control its aggregation tendency. Several crystal structures of the general formula $[\{(\text{L})\text{LiN}(\text{SiMe}_3)_2\}_2]$ ($\text{L} = \text{Et}_2\text{O}$,^{85,86} thf ,⁸⁷ $\text{NMe}_2\text{CH}_2\text{Ph}$,⁶⁶ and $\text{MeOCH}_2\text{CH}_2\text{OMe}$ (dme)⁶⁶ or 1,4-dioxane⁶⁶) are known. In addition, $\text{LiN}(\text{SiMe}_3)_2$ forms an unusual cationic species in the salt $[\text{Li}(\mu\text{-NSiMe}_3)(\mu\text{-tempo})(\text{tempo})_2][\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_3]$ when it is treated with tempo (tetramethylpiperidine-N-oxide) and $\text{Mg}\{\text{N}(\text{SiMe}_3)_2\}_2$.⁸⁸ In addition, an unusual triple anion complex with three different types of anion shown in **1** was obtained from a solution containing a 1:1:1:2 ratio of LiBr , $\text{LiN}(\text{SiMe}_3)_2$, $\text{LiOC}(\text{Bu}^t)\text{CH}_2$ and tmeda .⁸⁹ The behaviour of lithium silylamides in solution in various solvents and in the presence of a range of donors has been studied by ^6Li and ^{15}N NMR spectroscopy.^{13–15}



The borylamide derivative $[\{\text{Li}(\text{OEt}_2)\text{NHBMe}_2\}_2]$ also has a bridged dimeric structure despite the reduction in nitrogen lone pair character by $\text{B}-\text{N}$ π -bonding.⁹⁰ A dimeric structure containing a crown ether moiety was formed upon monodeprotonation of 1,7-diaza-12-crown-4, $[\{1\text{-Li-1,7-N-12-crown-4}\}_2]$.⁹¹ The lithium atom is coordinated to the macrocycle through four oxygen and one nitrogen donor ($\text{Li}-\text{N}$ is 2.19 Å; $\text{Li}-\text{O} = 2.23$ and 2.26 Å). There is an additional, shorter bond to the deprotonated N atom ($\text{Li}-\text{N}$ bond length, 2.00 Å). Two such units are dimerized through $\text{Li}-\text{N}$ interactions to form a regular $(\text{LiN})_2$ core.

Similar, isolated diamond-shaped $(\text{LiN})_2$ frameworks are observed for many of the dimeric lithium amide complexes formed from monodentate,^{75,76,92–105} bidentate,^{102,106–113} or tridentate^{114–118} amido ligands or ligands with multiple amido functions.^{119–129} These ring systems are generally planar (Structure A), but puckering of the ring can occur (Structure B), as is seen in the compound $[(\text{Li}(\text{OEt}_2)c\text{-}\{\text{NCH}(\text{n-Bu})\text{CHCH-2,3-C}_{10}\text{H}_6\})_2]^{130}$ formed by the reaction of 7,8-benzoquinoline with *n*-BuLi. The lithiums are three coordinate and bridge two benzoquinoline ligands and are coordinated to one diethyl ether ligand. The Li–N bond lengths are 2.038(3) and 2.104(2) Å. The lithium and nitrogen atoms in the $(\text{LiN})_2$ ring in $[\{\text{LiN}(\text{SiMe}_3)(\text{SiMe}_2\text{Ph})\}_2]^{84}$ alternate above and below the ring plane by approximately 0.033 Å, with Li–N bond lengths between 1.98 and 2.02 Å. Each lithium ion has an additional contact to the *ipso* carbon of the aryl group (2.45 Å). Likewise, the $(\text{LiN})_2$ cores in the compounds $[\text{Li}\{1,2\text{-(N}(\text{SiMe}_3)_2\text{C}_{20}\text{H}_{12})\}(\text{thf})_2]$ and $[\text{Li}\{1,2\text{-(N}(\text{CH}_2\text{Bu}^t)_2\text{C}_{20}\text{H}_{12})\}(\text{thf})_2]$ are folded, and have Li–N distances of 1.85–2.25 and 1.92–2.24 Å, respectively.¹³¹ Each lithium ion is four-coordinate with coordination by one tetrahydrofuran ligand (av. Li–O distance is 1.88 Å) and an additional short contact with an *ipso* carbon (Li–C contact, 2.24 Å).

An unusual variation of the $(\text{LiN})_2$ core structure is observed in the lithium fluorosilylamide $[\{\text{LiN}(\text{Bu}^t\text{Si}(\text{Bu}^t)_2\text{F})\}_2]^{132}$. The fluorine atoms coordinate to the lithium atoms from the central $(\text{LiN})_2$ ring in a boat-like conformation (Structure B, av. Li–N distance is 2.04 Å), which forms two four-membered Si–N–Li–F rings fused to the central $(\text{LiN})_2$ core. Other examples of fluoride coordination to the $(\text{LiN})_2$ core have been reported, for example in the complexes $[\{\text{LiFSi}(\text{Bu}^t)_2\text{NSi}(\text{Pr}^i)_2\text{OSiMe}_3\}_2]^{133}$ (**2**) and $[\{\text{LiFSi}(\text{Pr}^i)_2\text{NSi}(\text{Bu}^t)\text{OSi}(\text{Me})\{\text{N}(\text{SiMe}_3)_2\}_2\text{F}\}_2]^{134}$. In contrast, the fluorine atom in $[\{\text{LiN}(\text{H})\text{Si}(\text{Bu}^t)_2\text{F}(\text{tmeda})\}_2]^{81}$ does not display coordinative interactions, and a regular $(\text{LiN})_2$ framework (Structure B) is observed with average Li–N distances of 2.06 Å for the fluorosilylamido nitrogens and significantly longer contacts with the bidentate tmeda ligands (average Li–N = 2.27 Å).



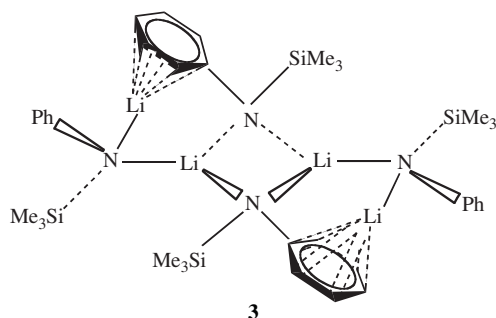
2.2.4 Trimeric Lithium Amides

The structure of $[\{\text{LiN}(\text{SiMe}_3)_2\}_3]^{2,3}$ (**1**), was originally reported in 1969;² it has a planar Li_3N_3 array and it represented the first substituted lithium amide to be structurally characterized. The Li–N bond lengths range from 1.98 to 2.02 Å (Structure D).³ The

germanium analogue $[\{\text{LiN}(\text{GeMe}_3)_2\}_3]^{135}$ has an almost identical structure, with shorter Li–N contacts (average 1.96 Å), possibly as a result of lower steric crowding. The dibenzylamido derivative $[\{\text{LiN}(\text{CH}_2\text{Ph})_2\}_3](\mathbf{2})^{90}$ also has a planar six-membered Li_3N_3 ring. The methylene linkers of the amido ligand effectively block delocalization, resulting in a low coordination number of two around the Li atoms (Li–N distances range between 1.91 and 2.04 Å). The trimer $[\{\text{LiN}(\text{SiMe}_3)(\text{CH}_2\text{Ph})\}_3]$ can be seen as a hybrid structure of compounds **1** and **2** as it contains a planar $(\text{LiN})_3$ ring with two coordinate lithium atoms and short Li–N bond lengths (*ca.* 1.95 Å).¹³⁶ The internal ring angles at Li and N average 93.7 and 146.2° and the SiMe_3 and CH_2Ph substituents are disposed at opposite sides of the almost planar Li_3N_3 ring. Its treatment with $\text{OP}(\text{NMe}_2)_3$ yielded $[\{(\text{Me}_3\text{N})_3\text{POLiN}(\text{SiMe}_3)-\text{CH}_2\text{Ph}\}_2]^{136}$. The trimetallic primary amido derivative $[\{(\text{pmdeta})_2(\text{LiNHPh})_3\}]$ features a central $\{\text{Li}(\text{NHPh})_3\}^{2-}$ unit, one $\{\text{Li}(\text{pmdeta})^+\}$ cation coordinates to one of the NHPh nitrogens and the other bridges the two remaining nitrogens.¹³⁷ The two related complexes $[\{\text{Bu}^t\text{Si}(\text{OSiMe}_2\text{N}[\text{Li}]\text{Bu}^t)_3\}]$ and $[\{\text{Bu}^t\text{Si}(\text{OSiMe}_2\text{N}[\text{Li}]\text{SiMe}_3)_3\}]$ feature a trimetallic, six-membered ring in which the tripodal ligand coordinates to three lithium ions with average Li–N bond lengths of 1.99 and 1.98 Å, respectively.¹³⁸ Other trimeric lithium amide structures have also been reported, which feature chelating ligands.^{139,140}

2.2.5 Tetrameric Lithium Amides

The most common structure observed for tetrameric lithium amides is the ladder structure **C** as shown in Scheme 2.2, in which edge bridged (Li_2N_2) units form a corrugated, generally linear, array. This is exemplified by the structures of $[\{\text{LiNH}\{\text{Si}(\text{NMe}_2)_3\}_4\}]^{141,142}$ and $[(\text{LiNHPh})_4(\text{py}-\text{Bu}^t-4)_6]^{80}$, chelated $[\text{LiNH}(8\text{-quinolyl})_4(\text{Et}_2\text{O})_2]^{143}$, $[\{\text{LiN}(\text{SiMe}_3)(8\text{-quinolyl})\}_4(\text{Et}_2\text{O})_2]^{143}$ and $[\{\text{LiN}(\text{SiMe}_3)(\text{furfuryl})\}_4]^{144}$. A variation of the regular ladder structure is observed for the complex $2\text{-Li}(\text{Me}_3\text{Si})\text{NC}_6\text{H}_4\text{CH}_2\text{N}(\text{SiMe}_3)\text{Li}$ and its thf solvate which displays an ‘arched-ladder’ motif probably as a result of the chelating effect to the amido ligand.¹⁴⁵ In contrast, the more sterically crowded $[\{\text{LiNH}(\text{SiBu}^t\text{Me}_2)_4\}]^{146}$ has a Li_4N_4 cubane structure. Further increases in steric crowding can induce other structural changes. For example, the tetramer $[\{\text{LiN}(\text{SiMe}_3)\text{Ph}\}_4]^{84}$ has the structure illustrated in **3** in which there is a dimeric



$\{\text{LiN}(\text{SiMe}_3)\text{Ph}\}_2$ core wherein each lithium is also bound to the nitrogen of another $\text{LiN}(\text{SiMe}_3)\text{Ph}$ unit whose lithium has η^6 by the phenyl contacts from the core $\{\text{LiN}(\text{SiMe}_3)\text{Ph}\}_2$ dimer. The Li–N core distances are 2.057(9) and 2.183(9) Å and the ‘terminal’ Li–N distances are slightly shorter at 1.983(1) and 2.004(9) Å. There have also been several