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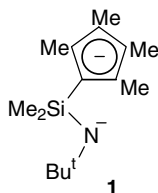
Introduction

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 $\bar{N}(R)R'$ 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 $\bar{N}H_2$, $\bar{N}(H)R$, and $\bar{N}(R)R'$, 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 $[Sn(NMe_2)(\mu-NMe_2)]_2$ and $[Cu(\mu-NMe_2)]_4$. 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- $C_6H_4(\bar{N}CH_2Bu^t)_2$ and $MeC\{Si(Me)_2\bar{N}Bu^t\}_3$ 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, guanidinates, 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 $[As(Cl)(\mu-NBu^t)]_2$. 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)	Be (2)				
	Na (1)	Mg (2)		Al (1, 3) ^c	Si (2) ^e	
	K (1)	Ca (2)	Zn (2)	Ga (1, 2, 3) ^d	Ge (2, 3) ^f	As (1, 2, 3, 5)
	Rb (1)	Sr (2)	Cd (2)	In (1, 2, 3)	Sn (2, 3) ^f	Sb (3, 5)
	Cs (1)	Ba (2)	Hg (2)	Tl (1, 3, 1/3)	Pb (2)	Bi (3, 5)
Total no. of references	260	211	114	355	388	137

^aSince 1979

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

^cAlso cluster compounds having metal oxidation states <1, e.g., [Al₇₇{N(SiMe₃)₂}₂₀]²⁻

^dAlso cluster compounds having metal oxidation states <1, e.g., [Ga₈₄{N(SiMe₃)₂}₂₀]⁴⁻

^eAlso oligomeric anions (e.g., [Si(NN)₄]⁻, [Si(NN)₄]²⁻, [Si(NN)₃]²⁻; [Si(NN)≡Si{(NR)₂C₆H₄-1,2}], R = Et, Bu[†])

^fAlso cluster compounds having metal oxidation states <1: [Ge₈{N(SiMe₃)₂}₆], [Sn₉{Sn(N(C₆H₃iPr-2,6)SiMe₂R)}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(NPrⁱ)₂]_∞, [Ti(NMe₂)₃(py)₂][BPh₄], [Pt(μ-Cl){SnCl(NR₂)₂}(PEt₃)₂] (R = SiMe₃), [Li(thf)₄][Ni(NPh₂)₃], [U(NEt₂)₂(py)₂][BPh₄]₂, [As(C₃Me₅)(NMe₂)][AlCl₄] and Li[Sb₃(μ-NCy)₄(NMe₂)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(SiMe₃)C₆H₃Mes₂-2,6}], [Si{N(Bu^t)CH=CHNBu^t}] and [As{N(H)Mes*}(=NMes*)] (Mes = C₆H₂Me₃-2,4,6; Mes* = C₆H₂Bu^t-3,2,4,6). The highest metal coordination number recorded for a homo- or heteroleptic metal amide containing only monodentate ligands is six, in [M(NMe₂)₆] (M = Mo or W), or seven, in [U(NEt₂)₂(py)₅][BPh₄]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(SiMe₃)₂]₂(thf)₂; U(NMe₂)₆ was found to be thermally labile.

Bi-, tri- and oligonuclear compounds have ring, fused ring, or cluster core geometries, which feature 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{μ-N(SiMe₃)₂}]₃ into 3[Li{N(SiMe₃)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(NPrⁱ)₂(OBuⁿ)₂] (see Chapter 3, Figure 3.5) and [Li₃(thf)₃Sb₆(NCy)₆(N)₃-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)	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 4f 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. d-Block elements (Ch. 6): 692				

^aSince 1979

^bPt, Nd, Gd,

^cSm, Eu, Yb

Tb, Dy, Ho, Er, Tm, Lu

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 $\text{M}' =$ 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, aryloxy, 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^1_2 and LiNCy_2 , are important proton-abstractors for organic synthesis, as are recently the synergic couple $\text{MN}(\text{R})\text{R}'/\text{M}'\text{R}_n$ ($\text{M}' =$ 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 *f*-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 *4f*-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 $[Zr(\mathbf{F})Cl_2]$ with KC_8 and N_2 (\mathbf{F} is a macrocyclic *P,P',N,N'*-centred bis-(amido) ligand) (see Schemes 6.3, 6.4 and 6.7 in Chapter 6).