

## Progress report

Michael F. Lappert \*

The Chemical Laboratory, University of Sussex, Brighton, East Sussex BN1 9QJ, UK

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### Abstract

This paper provides a brief resumé of our current researches in organometallic chemistry. The first deals with non-classical organolanthanoid chemistry, which has, as targets, subvalent compounds of the early 4f elements (La, Ce, Pr, Nd) and cationic organosamarium(II) and -ytterbium(II) complexes. The second is concerned with new aspects of metal amide chemistry including (a) silver(I) amides and isonitrile complexes of lithium amides; (b) derivatives of aromatic diamides such di(metalamino)cyclophanes; (c) metal silyl complexes derived from insertion of a stable silylene into  $M(II)-N(SiMe_3)_2$  ( $M = Ge, Sn$  or  $Pb$ ) bonds; and (d) reactions of  $M'-X$  compounds with 1,3,5-triazine [ $M' = Li$  or  $Na$  and  $X = N(SiMe_3)_2, C(SiMe_3)_3$  or  $CH(SiMe_3)_2$ ]. The two other present areas (on subvalent compounds of Group 14 elements and metal 1-azaallyls,  $\beta$ -diketimines and 1,3-diazaallyls) are reported more cursorily. The Introduction is divided into three sections entitled 'Relationship to the *Journal of Organometallic Chemistry*', 'Reviews (from 1956 to 1995)' and 'An outline of principal contributions'. © 2000 Elsevier Science S.A. All rights reserved.

**Keywords:** Ligand design;  $MX_2$  ( $M = Si, Ge, Sn, Pb$ ); 1-Azaallyl;  $\beta$ -Diketiminates; Amides; Lanthanides

### 1. Introduction

#### 1.1. Relationship to the *Journal of Organometallic Chemistry*

I am pleased to have been asked to contribute to this 600th volume of the *Journal of Organometallic Chemistry*, a periodical for which I have a close affection for a number of reasons. First, because I regard myself almost to have been its begetter. This claim is based on the following facts. In the autumn of 1960, Jeffrey Leigh and I organised a course of postgraduate lectures on *Inorganic Polymers* in our then department of chemistry of the Manchester College of Science and Technology. An outcome was an edited book on the subject [1], probably the first of its kind in that field, which appeared in 1962, published by Elsevier with the encouragement of its Dr W. Gaade. He suggested to me that a journal on this topic might be viable. I advised against it, but proposed that if he wished to fill a lacuna in the chemical journals' publishing

market, then organometallic chemistry was a fast-growing discipline. After a few months, Dr Gaade invited me to be a founding editor; I was flattered but declined. I was delighted when I learned that my then future colleague and good friend, Colin Eaborn, was to become the UK Regional Editor, a position which he filled with great distinction until quite recently.

Volume 1 appeared in 1963. I was happy, not only to have joined the Editorial Advisory Board, but also to have a paper (on haloboration and phenylboration of acetylenes [2]) in that volume. I have been a regular contributor over the years, most recently in 1999 on the synthesis and structure of  $Na(TMP)$ ,  $[Na\{\mu-NC(Me)_2(CH_2)_3CMe_2\}]_4$  [3].

A companion journal (now extinct), *Organometallic Chemistry Reviews*, was first published in 1966; for volume 1, we contributed two reviews (on organic B–S [4] and on organoSn–N compounds [5]). I was privileged to be able to present further reviews for the *Journal of Organometallic Chemistry*: for volume 100 (1975) (on the coordination chemistry of bivalent Group 14 donors, nucleophilic carbene and dialkylstannylenes complexes [6]) and volume 500 (1995) (on metal and metalloid bis(trimethylsilyl)methyls and the trans-

\* Fax: +44-1273-677196.

E-mail address: m.f.lappert@sussex.ac.uk (M.F. Lappert)

formation of the  $^{-}\text{CH}(\text{SiMe}_3)_2$  into 1-azaallyl and  $\beta$ -diketiminato ligands [7].

### 1.2. Reviews (from 1956 to 1995)

We have written reviews regularly, enabling us to place various aspects of our research in a wider context. In chronological order, they dealt with the following topics. (1) Organic compounds of boron, 1956 [8]; (2) reactions of boron trichloride with organic compounds, 1958 [9]; (3) polymers containing B and N, 1962 [10]; (4) B–S compounds, 1966 [4]; (5) Sn–N compounds, 1966 [5]; (6) pseudohalides of Group 13 and 14 elements, 1966 [11]; (7) insertion reactions of compounds of metals and metalloids involving unsaturated substrates, 1967 [12]; (8) organoboron compounds, 1967 [13]; (9)  $\alpha$ -heterodiazalkanes and reactions of diazalkanes with derivatives of metals and metalloids, 1970 [14]; (10) organoSn–N compounds, 1971 [15]; (11) transition-metal–carbene complexes, 1972 [16]; (12) organometallic complexes with Si–transition-metal or Si–C–transition-metal bonds, 1973 [17]; (13) the chemistry of transition-metal–carbene complexes and their role as reaction intermediates, 1973 [18]; (14) stable homoleptic metal alkyls, 1974 [19]; (15)  $\text{CX}_2$ - and  $\text{SnX}_2$ -metal complexes, 1976 [6]; (17) metal  $\sigma$ -hydrocarbyls, 1976 [20]; (18) free radicals in organometallic chemistry, 1976 [21]; (19) metal and metalloid bis(trimethylsilyl)amides and  $\text{Bu}'(\text{Me}_3\text{Si})\text{N}$  analogues, 1976 [22]; (20) studies on the mechanism of reactions catalysed by ethanolamine ammonialyase-coenzyme  $\text{B}_{12}$ , 1979 [23]; (21) metal and metalloid amides, 1980 [24]; (22) organoZr and -Hf chemistry, 1982 [25]; (23) bridged hydrocarbyl or hydrocarbon binuclear transition-metal complexes, 1983 [26]; (24) organoZr and -Hf compounds, 1986 [27]; (25) the coordination chemistry of electron-rich alkenes (enetetramines), 1988 [28]; (26) the role of Group 14 element carbene analogues in transition-metal chemistry, 1990 [29]; (27) bis(trimethylsilyl)methylmetal complexes, 1991 [30]; (28) chemistry of bivalent organic compounds of germanium, tin and lead, 1993, 1994 [31]; (29) 1-azaallyl- and  $\beta$ -diketiminato–metal complexes, 1995 [7]; and (30) new spectator ligands in transition-metal complexes and their application in catalysis [32].

### 1.3. An outline of principal contributions

Our group is perhaps best known for introducing several new ligands, some extensively used world-wide. Often, they confer lipophilicity on their complexes, by virtue of their bulk, the presence of one or more  $\text{SiMe}_3$  ( $\equiv\text{R}$ ) or  $\text{Bu}'$  groups and their freedom from  $\beta$ -hydrogen. Notable carbon-centred examples have been  $^{-}\text{CHR}_2$  ( $\equiv\text{R}'$ ),  $[\eta\text{-C}_5\text{H}_3\text{R}_2\text{-1,3}]^{-}$  ( $\equiv[\text{Cp}''\text{R}']^{-}$ ),  $[\text{CN}_2]^{2-}$ , carbenes  $\overline{\text{CN}}(\text{R}'')(\text{CH}_2)_2\text{NR}''$  ( $\equiv\text{LR}''$ ),  $[\text{CH}_2=\text{CHSi}(\text{Me})_2]_2\text{O}$ , the

allyl  $[\{\text{C}(\text{SiMe}_2\text{Bu}')\text{H}\}_2\text{CH}]^{-}$ , and, most recently, 1-azaallyls,  $[\text{C}_6\text{H}_6]^{2-}$  and  $[\text{C}_6\text{H}_6]^{-}$ . Group 14 metal-centred ligands have included  $\text{MX}_2$  [ $\text{M} = \text{Ge}$  or  $\text{Sn}$  and  $\text{X} = \text{CHR}_2$  or  $\text{NR}_2$ ,  $\text{R} = \text{SiMe}_3$ ; or  $\text{MX}_2 = \text{Si}(\text{NCH}_2\text{Bu}')_2\text{C}_6\text{H}_4\text{-1,2}$ ]; *N*-, *P*-, *O*- and *S*-centred ligands were represented by  $[\overline{\text{NC}}(\text{Me})_2(\text{CH}_2)_3\text{CMe}_2]^{-}$ ,  $[\text{RNC}(\text{H})\text{NC}(\text{H})\text{NC}(\text{H})\text{CR}_2]^{-}$ , the  $\beta$ -diketiminato  $[\{\text{N}(\text{R})\text{C}(\text{Ph})\}_2\text{CH}]^{-}$ ,  $[\text{PC}_6\text{H}_2\text{Bu}'_3\text{-2,4,6}]^{2-}$   $[\text{OC}_6\text{H}_2\text{Bu}'_3\text{-2,6-R}''\text{-4}]^{-}$  ( $\text{R}'' = \text{H}$ ,  $\text{Me}$  or  $\text{Bu}'$ ),  $[\text{SC}_6\text{H}_2\text{Bu}'_3\text{-2,4,6}]^{-}$  and  $[\text{S}_2\text{CPR}_2]^{-}$ .

Stable homoleptic alkyls of the transition metals (TMs) were unknown in the late 1960s. In 1969 we reported (in a patent [33]) that the ligands  $^{-}\text{CH}_{3-n}\text{R}_n$  ( $n = 1, 2$  or  $3$ ) were capable of generating a host of stable alkyls, including the first homoleptic (a term we coined in 1974 [19]) d- and f-block metal alkyls {e.g.  $[\text{CrR}'_3]$  [34] and  $[\text{LaR}'_3]$  [35]} and of  $\text{R}'_2\text{M}=\text{MR}'_2$  ( $\text{M} = \text{Ge}$  [36] or  $\text{Sn}$  [37], the first compounds having a double bond between two heavier metals),  $\text{PbR}'_2$  [38] and persistent radicals  $\text{MR}'_3$  [39],  $\text{PR}'_2$  [40] and  $\text{AsR}'_2$  ( $\text{R}' = \text{CHR}_2$ ).

Our group was the first to prepare carbenometal complexes from a carbenoid, an electron-rich olefin  $\text{L}_2^{\text{R}''}$  [41] or a Vilsmeier reagent [42], and in 1973, provided the first model demonstration that a carbene–metal complex was an initiator in olefin metathesis [43]. We prepared and characterised the first crystalline, heavier Group 14 element analogues of a carbene:  $\text{M}[\text{N}(\text{SiMe}_3)_2]_2$  ( $\text{M} = \text{Ge}$ ,  $\text{Sn}$  or  $\text{Pb}$ ) [44] and  $\text{Si}[\text{N}(\text{CH}_2\text{Bu}')_2\text{C}_6\text{H}_4\text{-1,2}]$  [45] (another silylene had been reported previously by Denk et al. [46]).

We discovered numerous other mononuclear, crystalline metal complexes in formerly unknown oxidation states, including those of Zr(III), Th(III) and La(II) in  $[\text{ZrCp}''\text{X}_2]^{-}$  ( $\text{X} = \text{Cl}$  or  $\text{Br}$ ) [47],  $[\text{ThCp}''_3]$  [48],  $[\text{K}(\text{18-crown-6})(\eta\text{-C}_6\text{H}_6)_2][(\text{LaCp}''_2)(\mu\text{-C}_6\text{H}_6)]$  [49] and provided EPR spectral evidence for labile organoLa(II) complexes [50]. We characterised the first stable metal phosphinidene  $[\text{MoCp}_2(=\text{PAr})]$  ( $\text{Ar} = \text{C}_6\text{H}_2\text{Bu}'_3\text{-2,4,6}$ ) [51].

We elucidated the reaction pathway in the commercially important Karstedt modification of Speier hydrosilylation and identified the initiator as  $[\{\text{Pt}(\text{LL})\}_2(\mu\text{-LL})]$ , from  $\text{H}_2[\text{PtCl}_6] \cdot x\text{H}_2\text{O}$  and LL [ $\text{LL} = (\text{Me}_2\text{ViSi})_2\text{O}$ ] [52]. Previously we had shown that many oxidative addition reactions proceed by a free radical pathway, as in  $[\text{Pt}(\text{PPh}_3)_3] \rightarrow \text{trans-}[\text{PtI}(\text{Me})(\text{PPh}_3)_2]$  [53] or  $\text{Sn}(\text{CHR}_2)_2 \rightarrow \text{Sn}(\text{CHR}_2)_2\text{I}(\text{Me})$  [54].

We provided the first measurements of TM M–C bond energies ( $\bar{D}$ ) and noted that in any group,  $\bar{D}$  increases with *Z* only for M being d-block metals [55]. We used He(I) photoelectron spectroscopy to define valence orbitals, e.g. in the context of  $\text{MX}_2$  species ( $\text{M} = \text{Ge}$ ,  $\text{Sn}$  or  $\text{Pb}$ ) [56] and  $[\text{ThCp}''_3]$  (having the remarkably low HOMO of 4.87 eV [48]). The first EPR

spin-trapping experiments of paramagnetic TM complexes were carried out in 1974 [57]; and the use of  $^{171}\text{Yb}$ -NMR spectroscopy was demonstrated in 1989 [58]. Among other papers on organometallic chemistry were those concerning the first alkyl-bridged d- or f-metal complexes:  $[\{\text{Cu}(\mu\text{-CH}_2\text{R})\}_4]$  [59] and  $[\{\text{YbCp}_2(\mu\text{-Me})\}_2]$  [60]; and the polymerisation of strained organosilicon heterocycles [61].

The group's early reputation rested on contributions to boron chemistry, including the discovery of  $[\text{BCl}_4]^-$  [62], the BN cyclobutadiene analogues  $(\text{XBNY})_2$  [63],  $\text{ClB}(\text{OC}_6\text{H}_4\text{O-1,2})$  [64], the tri(boryl)amines [65], the facile cleavage of ethers by  $\text{BCl}_3$  [66], the  $\text{BCl}_3$ -catalysed *ortho*-Claisen rearrangement [67] and the first demonstration of restricted NB rotation in aminoboranes [68]. In the 1960s attention turned to tin, especially organotin amides [5]. Insertion reactions, initially with the latter, were generalised in an important review [12]. Free radical processes included the first TM  $\text{S}_{\text{H}2}$  reaction [for Pt(II) chemistry] [69], and the spin-trapping of the 5'-deoxy-5'-adenosyl radical from coenzyme B<sub>12</sub> [70].

Over the years there have been fruitful interactions with a number of chemical companies, most prominently ICI (Runcorn), Dow Corning (Barry) and, recently, BASF (Ludwigshafen). Accordingly, several patent applications were filed, including two dealing with novel  $\alpha$ -olefin polymerisation catalysts based on early TM homoleptic alkyls [33] or  $\beta$ -diketimines [71].

## 2. Some recent results

### 2.1. General objectives and strategy

The central theme of our current (and much of our earlier) researches is concerned with the synthesis of novel, aprotic, organometallic and coordination complexes  $\text{M}(\text{L})_n(\text{L}')_m$ , in which M is a metal or metalloid, L is usually but not invariably a spectator ligand (often new) and  $(\text{L}')_m$  represents the sum of other ligands.

The target complexes  $\text{M}(\text{L})_n(\text{L}')_m$  are unusual, lipophilic, reactive but thermally stable compounds, the structures and chemical behaviour of which are further goals of the enterprise. The term unusual is intended to encompass novel features of bonding, structure and reactivity. Simple illustrations include a hydrocarbon-soluble sodium alkyl, a low-molecular-weight crystalline organotin(III) complex (a target for the year 2000) and oligomeric metal oligo(azaethynidene)s  $\text{M}(\text{CH}=\text{N})_n\text{R}'$  (a goal for the first decade of the new millennium; for initial steps see Section 2.3).

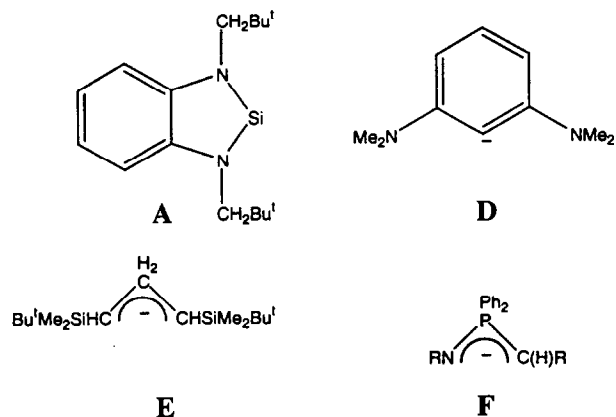
The role of the spectator ligand is a central task and may require ligand design (this will briefly be illustrated in Sections 2.2 and 2.3). The ligand L is chosen for its

strong binding to M and its capacity to confer lipophilicity upon  $\text{M}(\text{L})_n(\text{L}')_m$ . These properties generally require L to be bulky, free from  $\beta$ -hydrogen and to contain a multiplicity of methyl groups. Such criteria are often met by the presence in L of one or more  $\text{SiMe}_3$  (abbreviated hereafter as R) or  $\text{CMe}_3$  groups, which for diamagnetic molecules has the additional bonus of providing convenient NMR spectroscopic markers.

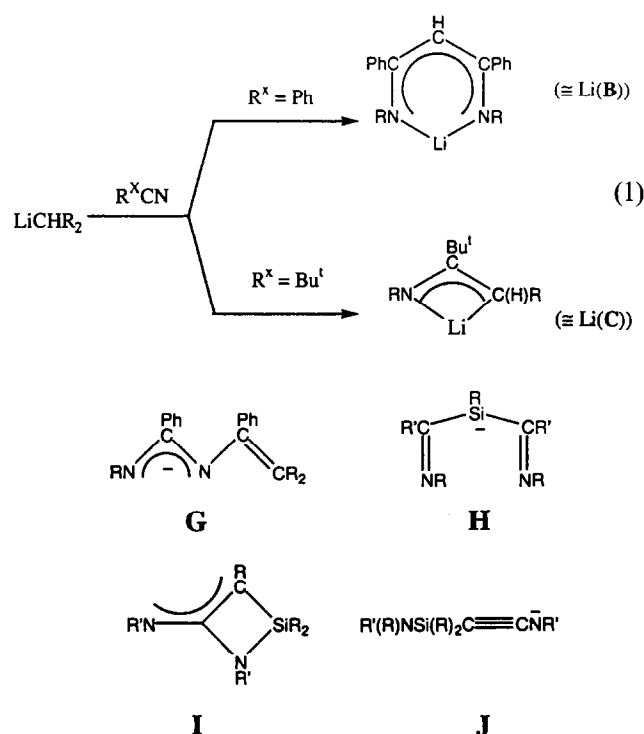
Scheme 1 summarises the above matters, which will be exemplified in Sections 2.2 and 2.3.

In order to keep this review within reasonable bounds, other areas of our current research will be omitted. These deal with (a) subvalent Group 14 element chemistry and (b) complexes of ligands derived from reactions between  $\text{LiCHR}_2$  or a related Li alkyl, or  $\text{LiSiR}_3$ , and a nitrile or isonitrile free from  $\alpha$ -hydrogen ( $\text{R} = \text{SiMe}_3$ ). Work on noble metal or nickel complexes of vinylsilanes or vinylsiloxanes, carried out most recently by Dr Calum MacBeath (now with Procter and Gamble, Pescara) is now discontinued, as is that on metal triflates by Dr Andrew Frankland (now with VCH-Wiley, Weinheim) and borylcyclopentadienyl-metal complexes by Dr Michael Davies (now with British Energy Generation, Gloucester).

As for (a), studies on the thermally stable silylene A were pioneered by Dr Barbara Gehrhus (who since January 1st, 2000 is an independent EPSRC five-year fellow) with contributions from Drs Hieronim Maciejewski (recently returned as lecturer to the University in Poznan) and Xiaoping Cai (rejoined the Jilin Chemical Company, PRC), and most currently Chris Sloopweg (a visiting undergraduate from the Free University of Amsterdam). Recent advances in the chemistry of the heavier Group 14 metal(II) complexes owe much to Drs Luc Piersens (now with the Euratom Safeguards Directorate, Luxembourg), Christian Drost (preparing for his Habilitation in the University of Leipzig) and Zhongxia Wang (now a lecturer at the University of Science and Technology, Hefei, PRC), and currently Patrick Uiterweerd (a graduate of Groningen University). They developed, inter alia, the chemistry of the ligands D (L.P., C.D. and P.U.), E (Z.W.) and F (Z.W. and P.U.).



Regarding (b), our work rests on the initial discovery by Diansheng Liu (now Professor at Shanxi University, PRC) of the data shown in Eq. (1) [7], which have been much elaborated upon, particularly by Dr Marcus Layh (now a senior lecturer at the University of the Witwatersrand), but also by Drs Catherine Caro (now with Unilever), Frederic Coslédan (now at Toulouse University), B.-J. Deelman (now at Utrecht University), Jin Hu (now in Midland, MI), Rafael Sablong (now at the University of Amsterdam), and John Severn (currently at the University of Eindhoven). Presently engaged on the topic are Dr Laurence Bourget (formerly at Montpellier University) and James Farwell (a Sussex graduate). Some interesting ligands, other than A–F of Eq. (1) are G–J.



Publications in areas (a) and (b) can be traced through our most recent papers: for (a) [72–75], and for (b) [76,77].

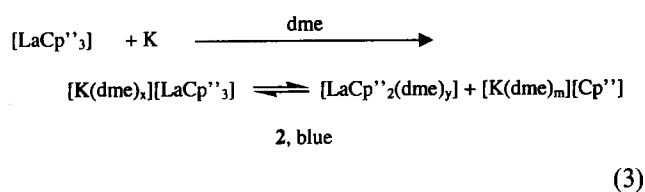
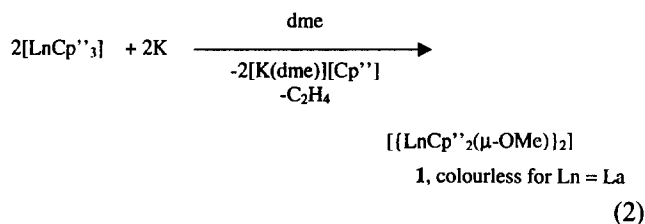
## 2.2. Non-classical organolanthanoid chemistry

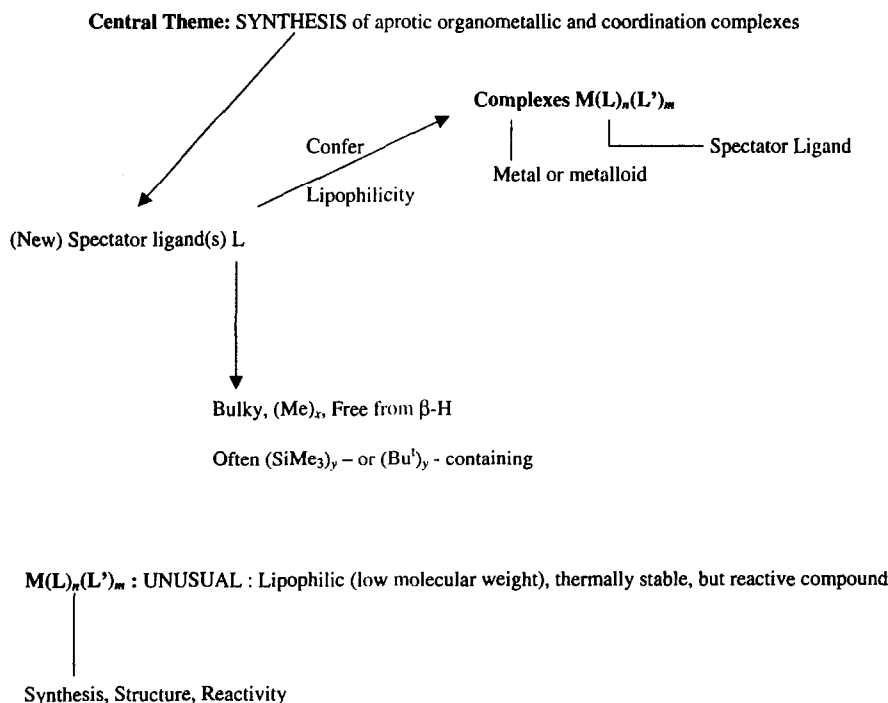
The term non-classical is intended to differentiate between the classical areas of organolanthanoid chemistry, which deal with the organic derivatives of the 4f metals (Ln) either in the ubiquitous Ln(III) oxidation state, or Sm(II) (4f<sup>6</sup>), Eu(II) (4f<sup>7</sup>) or Yb(II) (4f<sup>14</sup>) complexes. As for these Ln(II) complexes, only neutral [or a few ate(II)] complexes are well documented. Accordingly, during the last 4 years we have sought to obtain and study non-classical organoLn(II) complexes either

of the early 4f elements La, Ce, Pr, and Nd, or of cationic Sm(II) and Yb(II) species. The researches were carried out by Drs Yurii Gun'ko and Cristina Cassani (now lecturers at Trinity College, Dublin, and University of Bologna, respectively) and currently by Drs Andrey Protchenko (shortly to return to the Institute of Organometallic Chemistry, Nizhny Novgorod) and Alex Hulkes (formerly of Imperial College). Unrelated 4f element chemistry was studied by Drs Hans van den Hende (now in commerce in Malaysia) and Tian Shun (now at Northwestern University, Evanston, IL).

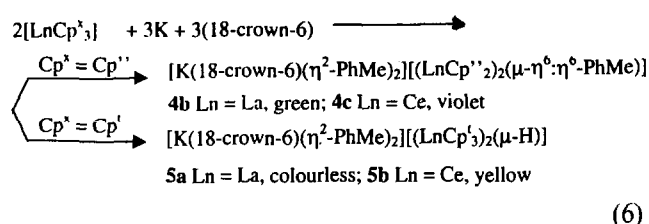
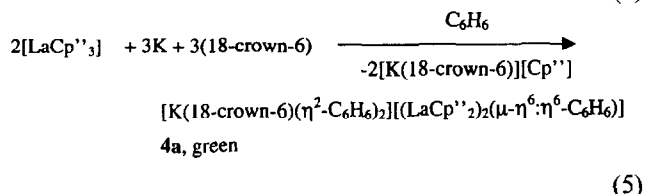
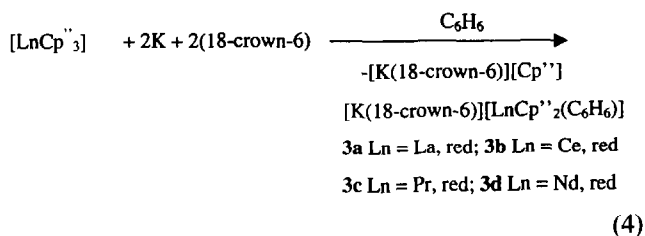
### 2.2.1. Approaches to organoLn(II) chemistry of the early 4f metals

The strategy was to use, as precursor, an appropriate homoleptic cyclopentadienyllanthanoid(II) complex [LnCp<sub>3</sub>]. For Cp<sup>x</sup>, we selected η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>(SiMe<sub>3</sub>)<sub>2</sub>-1,3 (≡Cp<sup>''</sup>), η<sup>5</sup>-C<sub>5</sub>H<sub>3</sub>Bu<sub>2</sub><sup>''</sup>-1,3 (≡Cp<sup>'''</sup>) or η<sup>5</sup>-C<sub>5</sub>H<sub>4</sub>SiMe<sub>2</sub>Bu<sup>'</sup> (≡Cp<sup>'</sup>); and Ln was La, Ce, Pr or Nd, but most frequently La or Ce. The reducing agent was a potassium mirror, in the presence of a neutral donor (dme or 18-crown-6), with benzene or toluene as solvent, at or below ambient temperature. The choice of each component and stoichiometry was crucial, as demonstrated by the synthetic observations, summarised in Eq. (2) (Ln = Ce or Nd [78] or La [79]), Eq. (3) [79], Eq. (4) [80], Eq. (5) [81] and Eq. (6) [82]. The d<sup>1</sup> La(II) character of the blue solution **2** was established by variable-temperature EPR spectroscopy (<sup>139</sup>La: 99.91% natural abundance, μ = +2.776, I = 7/2) (Fig. 1) [79]. The selection of the various Cp<sup>x</sup> ligands was based not only on their bulk and ability to confer lipophilicity on their metal complexes, but also in order to test the notion that silyl substituents might stabilise anionic charge in metallate complexes. This was confirmed by cyclic voltammetry experiments on [LaCp<sup>'</sup><sub>3</sub>] in THF at a vitreous carbon electrode using [NBu<sub>4</sub>][PF<sub>6</sub>] as supporting electrolyte at 25°C, which showed that La<sup>3+</sup> → La<sup>2+</sup> was more facile with Cp<sup>x</sup> = Cp<sup>''</sup> than Cp<sup>'</sup>, E<sub>1/2</sub> = −2.8 V for [LaCp<sup>'</sup><sub>3</sub>] [79] and −3.1 V for [LaCp<sup>''</sup><sub>3</sub>] [81] (relative to [FeCp<sub>2</sub>]<sup>+</sup> → [FeCp<sub>2</sub>]) and reversible.





Scheme 1.

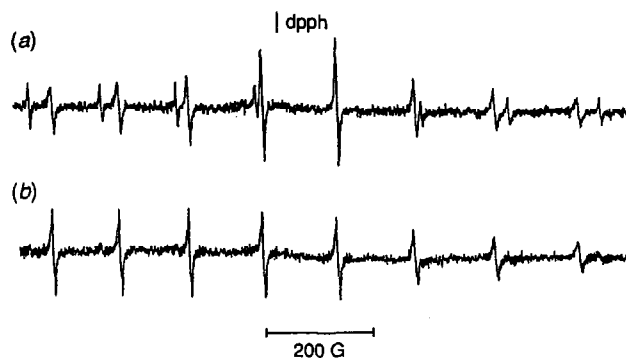


The molecular structure of each of the crystalline complexes **1**, **3a**, **3b**, **3d**, **4a**, **4c**, **5a** and **5b** was determined by single-crystal X-ray diffraction. Particularly novel are those of types **3**, **4** and **5**, illustrated in Figs. 2–4. Each compound **3** was regarded as containing a Ln(III) $Cp''_2$  moiety bound to a boat-shaped 1,4-cyclohexa-3,5-dienyl  $[C_6H_6]^{2-}$  ligand on the basis of (i) their molecular structures; (ii) the diamagnetism of **3a** [ $d^0$  La(III)]; and (iii) their protonolysis yielding cyclohexa-1,4-diene [80]. Thus, a reaction shown in Eq. (4) fol-

lowed by protonolysis of the product is similar to a Birch reduction of benzene. The paramagnetic ion pair **4a** was assigned to contain in the centrosymmetric anion two La(II) $Cp''_2$  fragments bridged by a planar  $[C_6H_6]^-$  ligand.

The electron-localised, boat-shaped conformation of the  $[C_6H_6]^{2-}$  ligand of **3a** is to be contrasted with the essentially delocalised, planar conformation of the  $[C_6H_6]^-$  ligand of **4a**, as shown schematically in **3a'** and **4a'** (bond lengths in Å, angles in degrees). Whereas the six La–C bond lengths in **4a** are essentially identical ( $2.77 \pm 0.02$  Å) [81], in **3a** they vary from  $2.54 \pm 0.02$  Å (for C-1 and C-4) and  $2.73 \pm 0.01$  Å [80].

Although the proposed  $H^-$  in the anions **5** was not located by X-ray crystallography, its presence was inferred from (i) the Ln...Ln separation of 4.52 Å (**5a**) and 4.51 Å (**5b**); (ii) the  $^1H$ -NMR spectrum of the

Fig. 1. EPR spectrum of solution **2** in dme at (a) 295 and (b) 275 K.

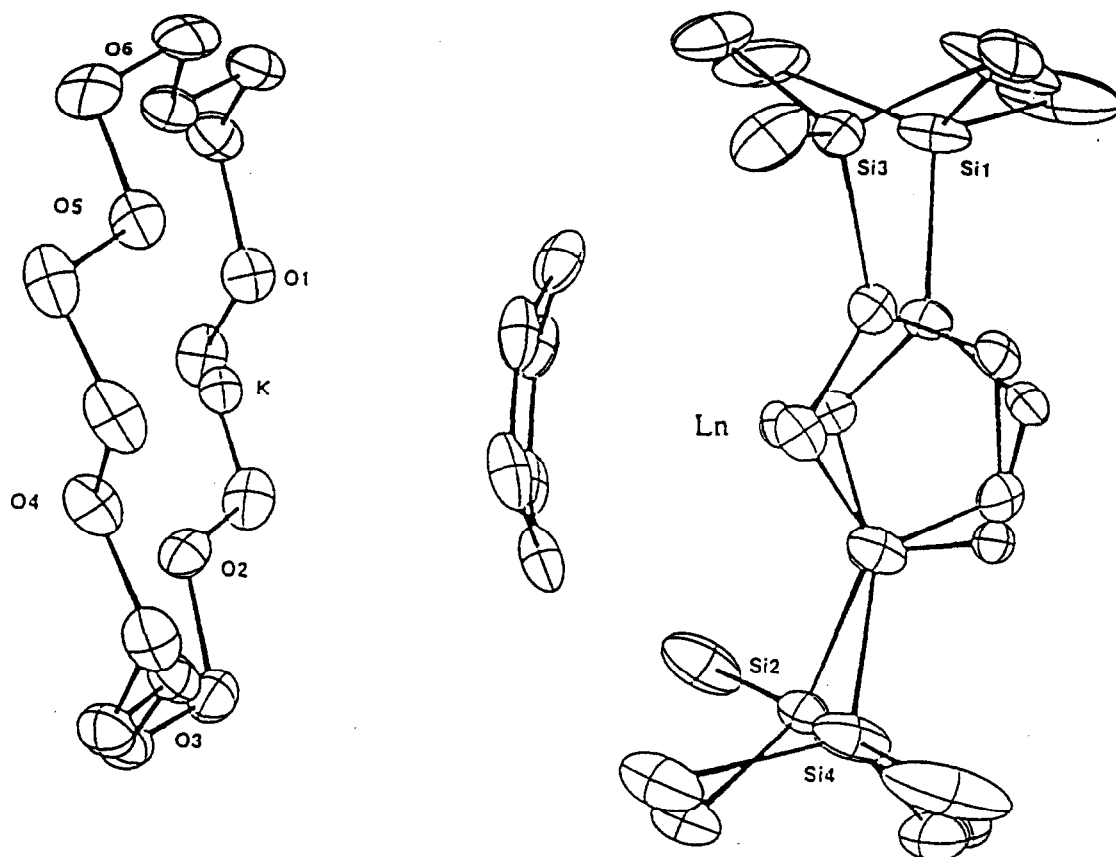


Fig. 2. The molecular structure of a complex 3 (Ln = La, Ce or Nd).

diamagnetic La(III) complex **5a** and comparison with its  $\mu\text{-}^2\text{H}$ -isotopomer [82]; and (iii) the existence of a related complex  $[\text{Na}(\text{THF})_6][\{(\text{LuCp}_3)_2(\mu\text{-H})\}]$  (obtained from  $2\text{LuCp}_3 + \text{NaH}$  in THF [83]).

The diversity of outcome of apparently similar reactions of Eq. (6), depending on choice of the  $\text{-Cp}^x$  ligand as  $\text{-Cp}''$  or  $\text{-Cp}'$  was attributed to the proposition that a Ln(II) intermediate was more readily prone to abstract a hydrogen atom from toluene if it contained the less sterically demanding  $\text{-Cp}'$  ligand [82]. When the reaction of  $[\text{LaCp}''_3]$  according to Eq. (4) was monitored by EPR spectroscopy, four La(II) intermediates were identified [80].

A unified reaction pathway to each of the products of Eqs. (2)–(6) is shown in Scheme 2 (products in bold), with Ln(II) complexes as crucial intermediates.

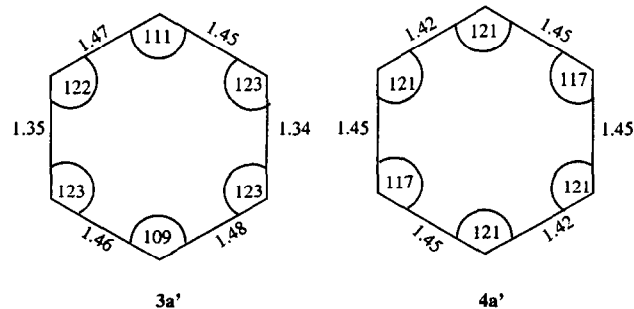
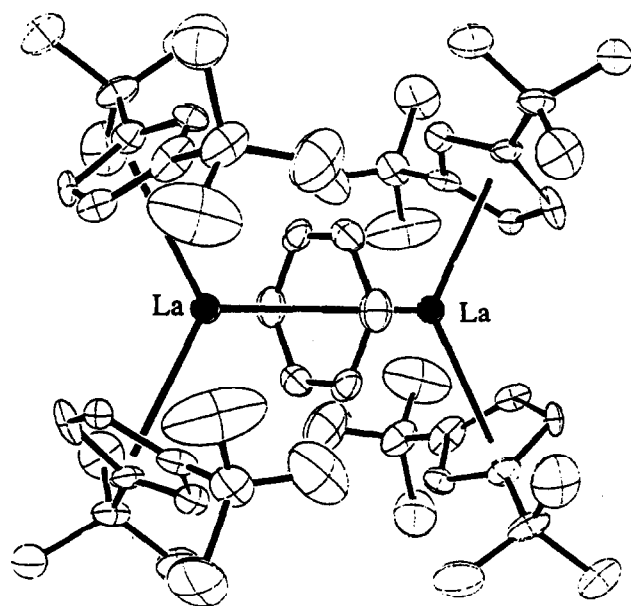


Fig. 3. The crystal structure of the anion of **4a**.

### 2.2.2. Cationic organolanthanoid(II) complexes

The objective was to prepare and study the unknown (in 1997) cationic organolanthanoid(II) complexes, which were sought in the expectation that they would



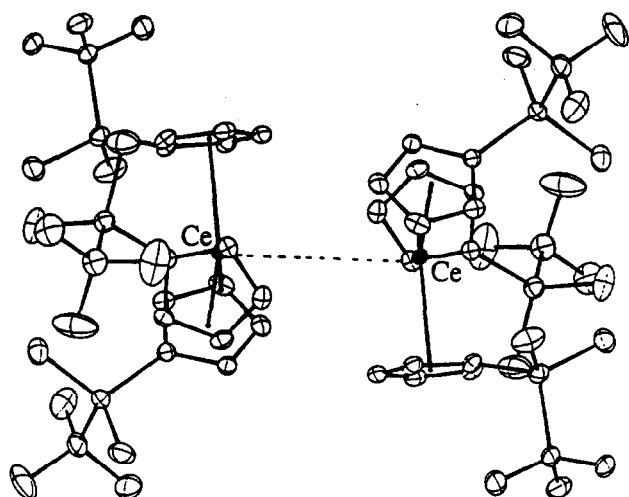
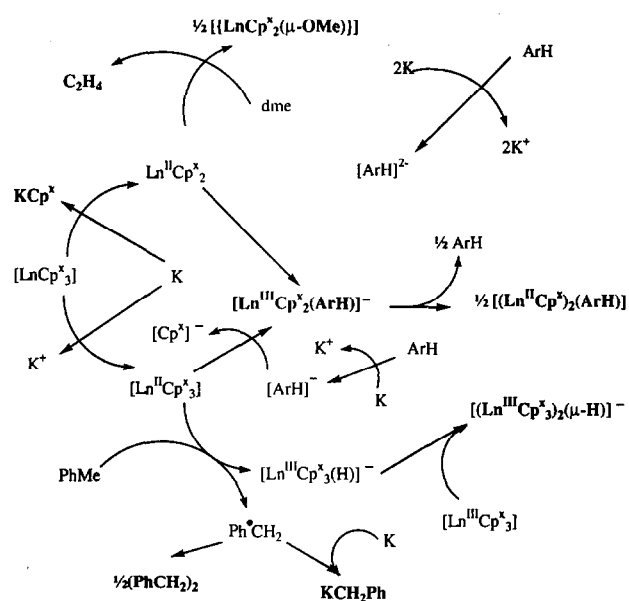


Fig. 4. The crystal structure of the anion of 5b.



be exceptionally electrophilic and that consequently Ln-centred reactions of olefins, in particular, would be favoured. The latter aspect still awaits further investigation.

Thus far, studies have concerned Sm(II) and Yb(II) complexes. The strategy was to use a homoleptic Sm(II) or Yb(II) neutral complex  $\text{LnX}_2$  and to displace an anionic  $-\text{X}$  ligand by a neutral donor  $\text{K}$ . For  $-\text{X}$ , a cyclopentadienyl was regarded as a suitable leaving group by virtue of its aromaticity, and the use of  $-\text{Cp}^*$  was taken as helpful, in the expectation that it would provide much-needed lipophilicity. For  $\text{K}$  to displace an anionic ligand, its multidentate character and strong binding to  $\text{Ln}^{2+}$  was a prerequisite; thus the choice fell upon the 18-crown-6. The results of reactions, carried out in toluene at or below ambient temperature, sum-

marised in Eq. (7), provided the crystalline complexes 6 and 7 [84].

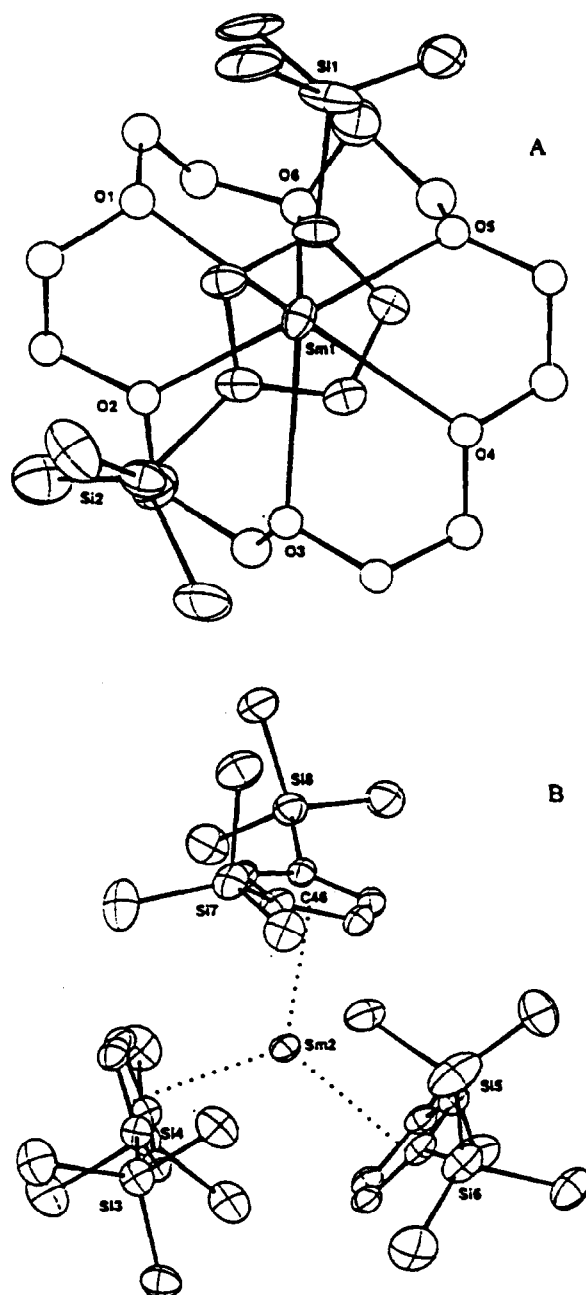
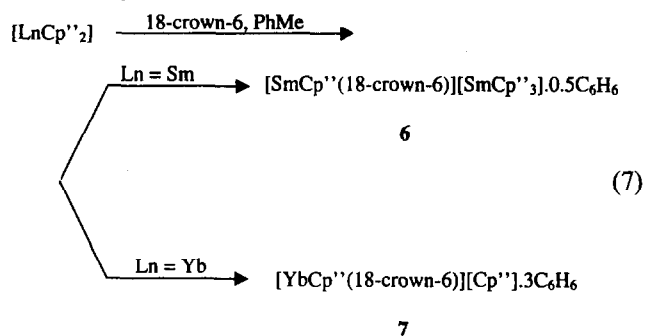
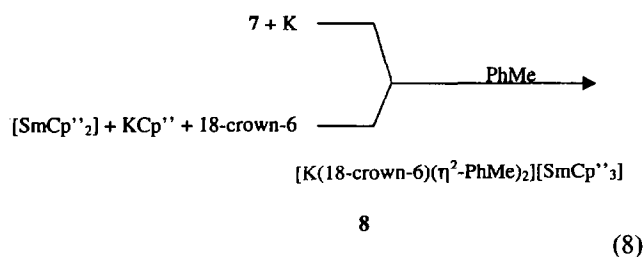


Fig. 5. The crystal structure of the cation (A) and anion (B) of 6.

The crystalline complex **6** consists of well-separated ions (Fig. 5). The cation (Fig. 5(A)) has a sandwich-like structure; the Sm atom is located within the cavity of the quasi-parallel Cp'' and the crown ligand, the latter being distorted due to strong O(6) atom deviation. The centroid of the Cp'' ring and six oxygen atoms of the crown ether form a strongly distorted pentagonal bipyramidal arrangement around Sm. The [SmCp''<sub>3</sub>]<sup>-</sup> anion (Fig. 5(B)) has the Sm in an almost trigonal planar arrangement with respect to the centroids of the three -Cp'' ligands. Crystalline **7**, likewise, has well-separated ions, the nearest Yb contact to the anion being 6.58 Å. The cation of **7** is very similar to that of **6**, with Ln-C<sub>sp</sub><sup>2</sup> distances ranging from 2.74 to 2.81 Å for Ln=Yb and 2.83–2.91 Å for Ln=Sm. The disordered anion of **7** is such that two Cp'' groups lie across inversion centres.

The different anions in the reactions of Eq. (7) were believed to arise as a consequence of the larger size of Sm<sup>2+</sup> than Yb<sup>2+</sup>. Thus, it was proposed that the salt **6** was formed via an isostructural analogue of **7**, the anion of which was able to capture a further molecule of the electrophile [SmCp''<sub>3</sub>].

In an attempt to reduce **6** by treatment with potassium in toluene at ca. 20°C, the product was the salt **8**, also accessible from its factors (Eq. (8)).



### 2.3. Metal amide and related chemistry

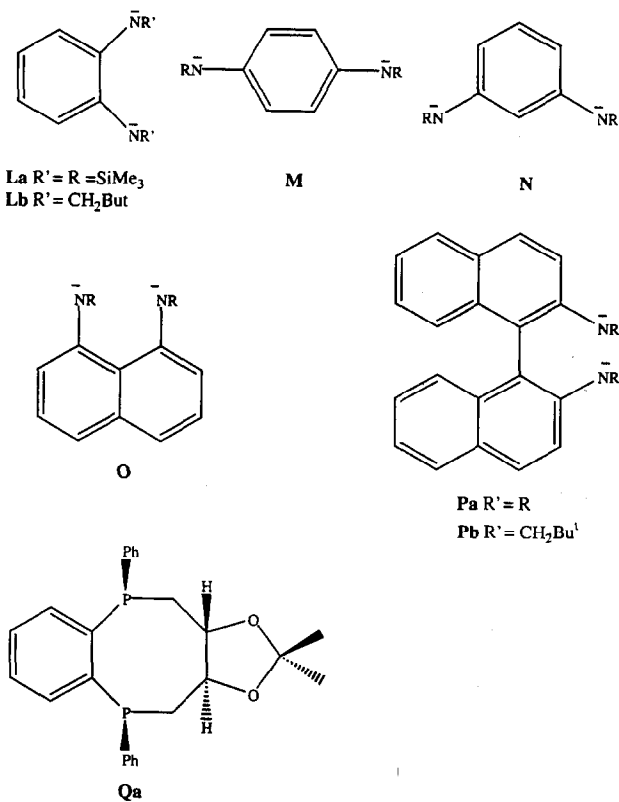
Our recent work in this area involved complexes based on three classes of ligands: (a) the monoanionic; (b) the dianionic (Section 2.3.1); and (c) the monoanionic oligo(azaethynidido) ligands derived from triazine (Section 2.3.2).

As for (a), our first publication (on dimethylamino-boranes) was in 1957 [85], but work on the bulky -NR<sub>2</sub> (R' = R = SiMe<sub>3</sub>, or NR<sub>2</sub> = TMP) ligands (which meet the criteria outlined in Scheme 1) began in the early 1970s (cf. [22]). During the last 4 years, we have had just four publications: Dr Eunseok Jang (now with Lucky Chemicals, Seoul) studied the reactions of M(NR<sub>2</sub>)<sub>2</sub> (M = Ge or Sn) with chalcogens; among interesting compounds obtained were the crystalline oxidative adducts [Sn(NR<sub>2</sub>)<sub>2</sub>(μ-E)]<sub>2</sub> (E = S, Se or Te) and [Ge(NR<sub>2</sub>)<sub>2</sub>(μ-E')<sub>2</sub>Sn(NR<sub>2</sub>)<sub>2</sub>] (E' = Se or Te) [86]. Dr Luc Pierssens prepared the crystalline tetranuclear silver(I) amide [{Ag(μ-NR<sub>2</sub>')}]<sub>4</sub> from the appropriate M(NR<sub>2</sub>')<sub>2</sub>

(M = Sn, Pb or Yb) and AgNCO [87]. A collaborative effort with Rab Mulvey's group revealed the crystal structure of [Na(μ-TMP)]<sub>4</sub> [3]. Dr Catherine Caro showed that mixing LiNR<sub>2</sub> and Bu'NC in pentane afforded the crystalline adduct [Li(NR<sub>2</sub>)(μ-CN Bu')]<sub>2</sub>, a rare example of a Main Group metal complex containing a coordinated isonitrile [88]. Work on new monoanionic metal amides is being continued by Flavia Antolini (a graduate Bologna University) and Dr Philippe Merle (formerly at Montpellier University).

#### 2.3.1. Metal complexes derived from di(amido) ligands

The ligands used in these studies are shown in L–P. The first experiment, dealing with the formation of the crystalline complex [Mg{(NR)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,2}]<sub>2</sub> from the hydrocarbon-soluble MgBu<sup>s</sup>Bu<sup>s</sup> and (HNR)<sub>2</sub>C<sub>6</sub>H<sub>4</sub>-1,2, appeared in 1985 [89]. The *o*-, *m*-, and *p*-1,2-benzenedi-amido ligands L–N were next employed in a wider context, initially by Dr Holger Braunschweig (now Dozent at the Technical University of Aachen). [The related carbene ligands CN(R')(CH<sub>2</sub>)<sub>2</sub>NR', derived from diamines HNR'(CH<sub>2</sub>)<sub>2</sub>NHR', featured in our work from 1971 (cf. Ref. [28]).] The ligands L are members of a larger family 1,2-C<sub>6</sub>H<sub>4</sub>(-X)<sub>2</sub>, in which -X was also -CH<sub>2</sub> or -C(H)R [90], or -PR' (R' = R or Ph). As for the latter, 1,2-C<sub>6</sub>H<sub>4</sub>{P(Ph)Li(tmeda)}<sub>2</sub> was converted by Dr Ping Yin (now at the University of Sydney) into (+) (*R, R, R*\*, *S*\*) (**Qa**) and (-) (*S, S, R*\*, *S*\*) enantiomers of the chiral diphosphine **Q** [91].





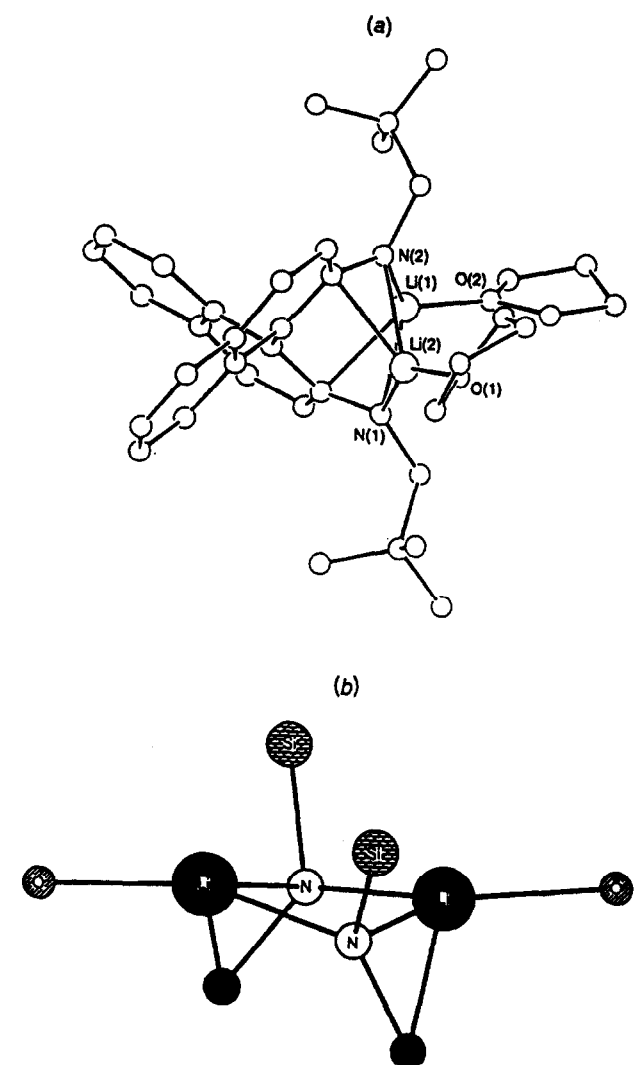
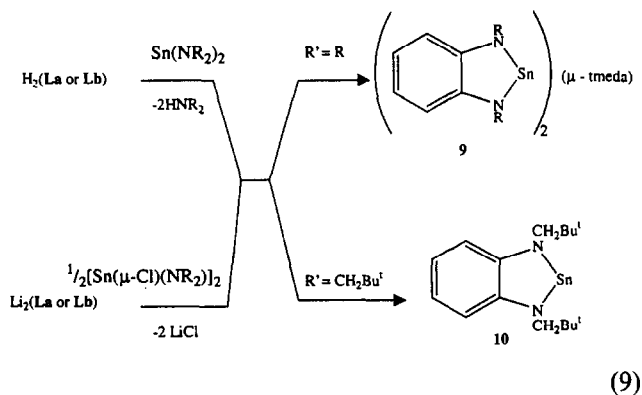
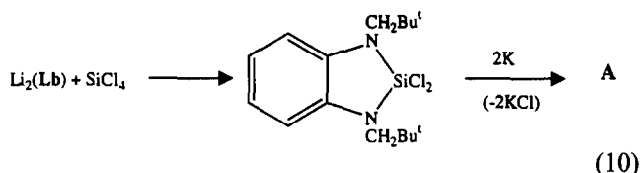


Fig. 6. Molecular structure of (a)  $\{[\text{Li}(\text{THF})]_2\{\text{C}_{20}\text{H}_{12}(\text{NR})_2\}\}$  (2) ( $\text{R} = \text{CH}_2\text{Bu}^t$ ) and (b) the central skeletal arrangement for  $\{[\text{Li}(\text{THF})]_2\{\text{C}_{20}\text{H}_{12}(\text{NR})_2\}\}$  ( $\text{R} = \text{SiMe}_3$  (1) or  $\text{CH}_2\text{Bu}^t$ ).

The crystalline tin(II) complexes **9** and **10**, derived from the *o*-diamido ligands **L**, were obtained as shown in Eq. (9) [92]. The silicon analogue **A** of **9b** was prepared as shown in Eq. (10) [45]; its chemistry has been much studied by Dr Gehrhus [72].

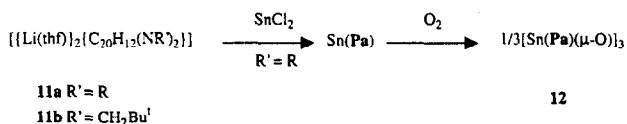


(9)



(10)

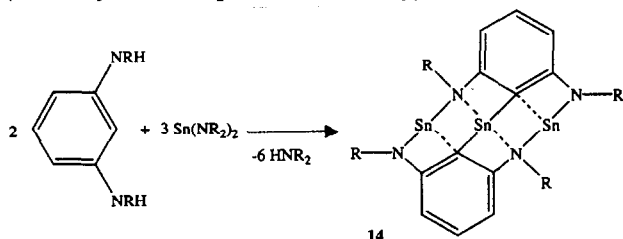
The crystalline dilithium diamides *R*-, *S*- or *R,S*- $\{[\text{Li}(\text{THF})]_2\{\text{C}_{20}\text{H}_{12}(\text{NR}')_2\}\}$  ( $\text{R}' = \text{R}$  (**11a**) or  $\text{CH}_2\text{Bu}^t$  (**11b**)) (Fig. 6) were prepared from the appropriate 2,2'-diamino-1,1'-binaphthyl  $\text{C}_{20}\text{H}_{12}(\text{NH}_2)_2$ , via  $\text{H}_2(\text{Pa})$  or  $\text{H}_2(\text{Pb})$ , by treatment with, successively,  $2\text{LiBu}^t$  in hexane and THF [93]. Compound **11a** was converted into the tin(II) amide **Sn(Pa)** which, upon treatment with  $\text{O}_2$ , gave the crystalline cyclotristannoxane  $[\text{Sn}(\text{Pa})(\mu\text{-O})]_3$  **12** (Eq. (11)).

11a  $\text{R}' = \text{R}$ 11b  $\text{R}' = \text{CH}_2\text{Bu}^t$ 

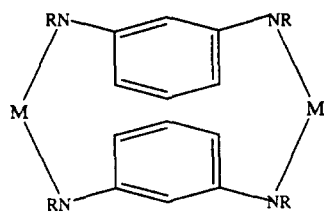
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(11)

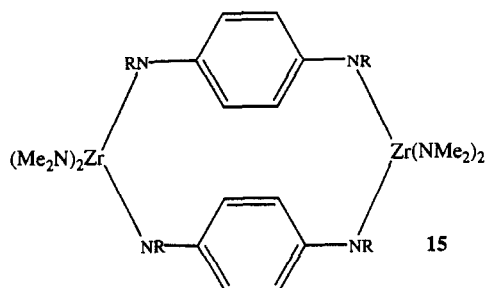
From the *m*-diamide  $\text{Li}_2(\text{N})$  and an equivalent portion of  $[\text{Sn}(\mu\text{-Cl})(\text{NR}_2)]_2$ , the crystalline *m*-bis(stannylamino)cyclophane was obtained **13a** [94]. A related crystalline bis(dimethylamido)zirconium complex **13b** was prepared from  $\{[\text{Zr}(\text{NMe}_2)_3(\mu\text{-NMe}_2)]_2\}$  by transamination with the *m*-diamine  $\text{H}_2(\text{N})$  [95]. By contrast, in the tin(II) system, the similar procedure of Eq. (12) yielded the crystalline dimeric trinuclear tin(II) cluster **14**; selected bond distances are shown in **14a** [94]. From the *p*-diamine  $\text{H}_2(\text{M})$  and the homoleptic zirconium(IV) dimethylamide, a similar crystalline *p*-cyclophane **15** was obtained (Fig. 7) [95]. In the above transamination reactions of the Zr systems, the crystalline, open-chain, binuclear complexes  $\text{C}_6\text{H}_4[\text{N}(\text{R})\text{Zr}(\text{NMe}_2)_3]_2$ -1,3 (**16a**) or -1,4 (**16b**) were isolated. The bis(zircona)cyclophanes (**13b** and **15**) were effective catalysts, in the presence of methylaluminoxane, for the polymerisation of ethylene. This property was enhanced when a 10 molar excess of  $\text{Me}_3\text{SiCl}$  was present; the polymer had very high average molecular weight. The X-ray molecular structures of each of the di(metalla)cyclophanes show that the two aromatic rings are parallel, the planes separated by 3.1 Å (**13a**), 3.4 Å (**13b**) or 3.5 Å (**15**) and a sideways displacement of 0.75 Å (**13a**), 0.75 Å (**13b**) or 0.15 Å (**15**) [94,95]. Researches in this area are being continued by Dr Jean-Philippe Bezombes (formerly at Montpellier University).



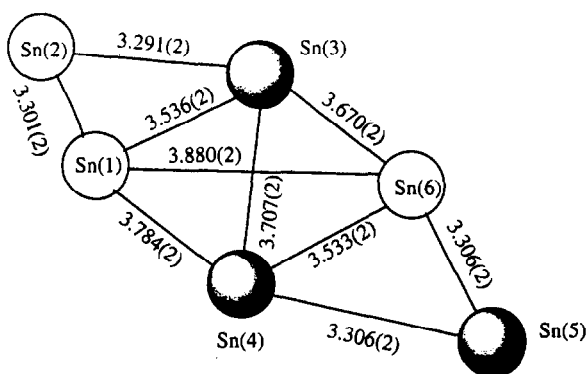
(12)



13a M = Sn  
13b M = Zr(NMe<sub>2</sub>)<sub>2</sub>

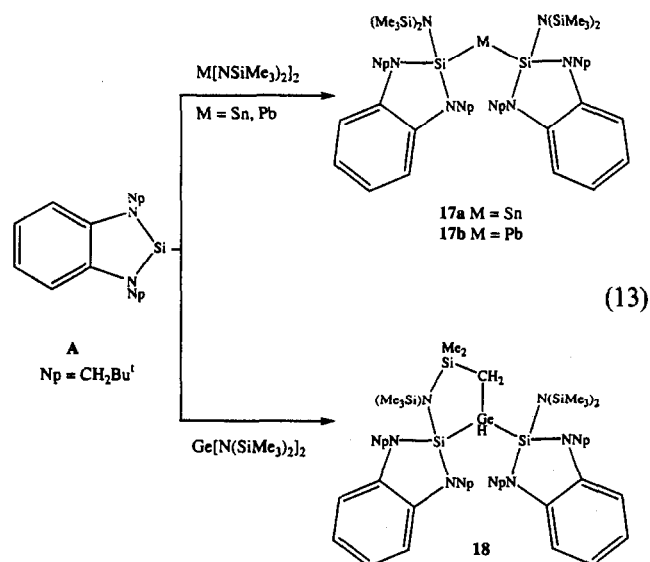


15



14a

The heavier Group 14 metal(II) amides  $M(NR_2)_2$  underwent insertion reactions with the silylene **A**, yielding the crystalline tin(II) (**17a**) or lead(II) (**17b**) but germanium(IV) (**18**) products (Eq. (13)) [96]. The crys-



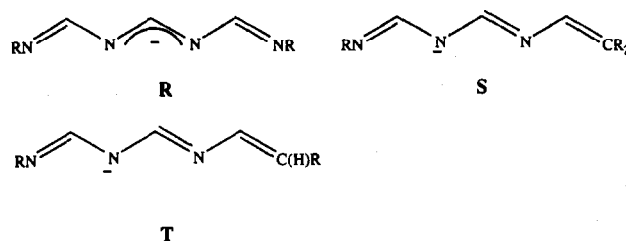
(13)

talline 1:1 adducts ( $M = \text{Ge}$  (**19a**) or  $\text{Sn}$  (**19b**)) were obtained from  $MAr_2$  [ $Ar = C_6H_3(NMe_2)_2-2,6$ ] and the tin(II) amide  $\text{Sn}(\text{O})$ ; complex **19b** has a long  $Ar_2\text{Sn}-\text{Sn}(\text{O})$  bond (Fig. 8) indicative of dative bonding with  $\text{Sn}(\text{O})$  being the acceptor moiety [97]. A similar 1:1 adduct was obtained from the carbene  $C(\text{Lb})$  and the silylene  $\text{Si}(\text{Lb}) (\equiv \text{A})$ , the latter being the acceptor. The reaction between **A** and  $\text{Sn}(\text{Ar})\text{X}$  yielded the crystalline insertion product  $\text{Sn}(\text{Ar})\{\text{Si}(\text{Lb})\text{X}\}$  ( $\text{X} = \text{Ar}$  or  $\text{NR}_2$ ) [98].

### 2.3.2. Complexes of monoanionic oligo(azaethynido) ligands

Our initial aim in examining reactions of 1,3,5-triazine with various lithium trimethylsilyl-substituted methyls or amides was to gain access to new lithium 1-azaallyls and  $\beta$ -diketiminates. Thus, by analogy with the results presented in Eq. (1), we anticipated that the triazine might behave as an HCN synthon, which with, for example,  $\text{LiCHR}_2$  would furnish  $\text{Li}[\text{N}(\text{R})\text{C}(\text{H})\text{C}(\text{H})\text{R}]$  or  $\text{Li}\{[\text{N}(\text{R})\text{C}(\text{H})]_2\text{CH}\}$ . This expectation proved to be unfounded; Dr Boesveld observed that using  $\text{LiNR}_2$ ,  $\text{LiCR}_3$  or  $\text{LiCHR}_2$ , under diverse conditions, the triazine ring was cleaved, although the predicted  $\text{Me}_3\text{Si} (\equiv \text{R})$  migrations from  $\text{N} \rightarrow \text{N}$  or  $\text{C} \rightarrow \text{N}$  did occur, yielding the final products **20–22**. These were lithium salts of the 1,3,5,7-tetraazaheptatrienyl ligand **R** or the 1,3,5-triazaheptatrienyl ligands **S** or **T**, respectively.

Hence, our revised objective has been to explore such chemistry by (i) establishing the structures and chemical behaviour of **20–22** especially their reactions with electrophiles such as metal and metalloid halides; (ii) using a wider range of silyl-substituted metal amides, alkyls or related compounds; and (iii) attempting to gain access to higher-molecular-weight linear metal oligo(azaethynide)s, such as  $\text{Li}\{[\text{NCH}]_n\text{Y}\}$  ( $n > 3$ ). We have made some progress with areas (i) and (ii), but much remains for us a continuing quest, as is (iii). Our results published recently are outlined below.



Treatment of 1,3,5-triazine with the lithium hydrocarbyl  $\text{LiR}'$  ( $\text{R}' = \text{Me}$ ,  $\text{Bu}^n$ ,  $\text{Ph}$ ,  $\text{CH}_2\text{R}$  or  $\text{CHR}_2$ ) in diethyl ether, at or below ambient temperature, yielded the appropriate 1:1 adducts **23a–23e**, which upon hydrolysis gave the corresponding 1,4-dihydrotriazine [99]. The molecular structure of the crystalline **23e** was determined by X-ray crystallography; in toluene-*d*<sub>8</sub>,

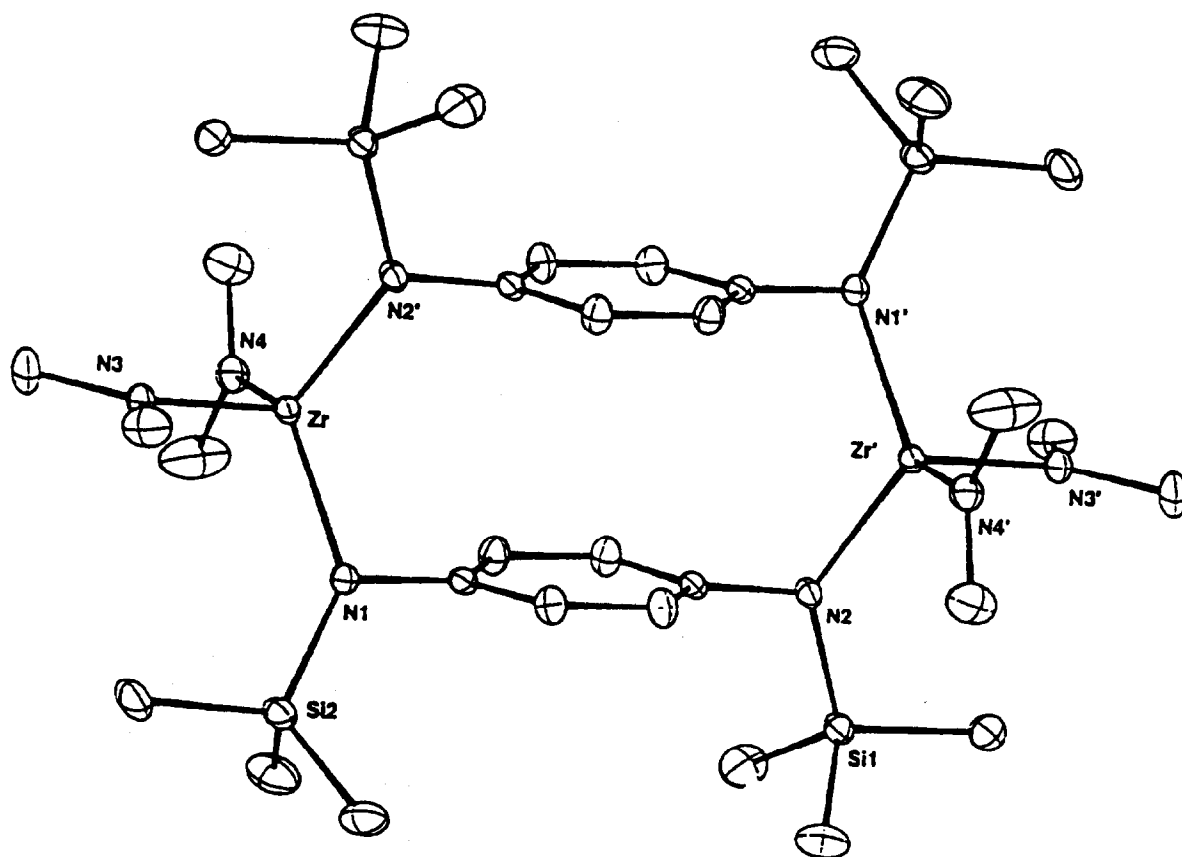
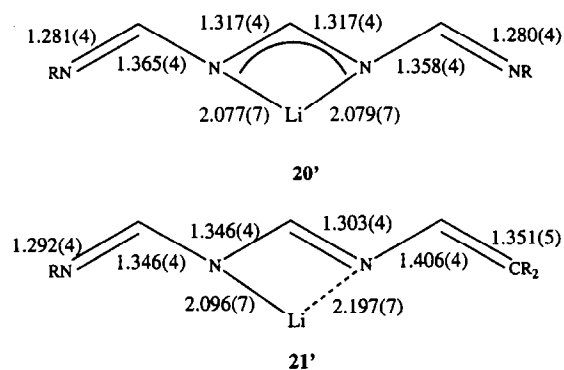


Fig. 7. The molecular structure of crystalline 15.

it was shown to be in equilibrium with its 1,2-dihydro-tautomer (ca. 50:1 at 295 K). Monosubstituted dihydro-triazines were believed previously to be thermally labile.

By contrast, under the same reaction conditions but with  $\text{LiNR}_2$  or  $\text{LiCR}_3$  as reagent, the crystalline product was **20** or **21**, respectively. Moreover, by heating **23e** at  $140^\circ\text{C}$ , the related ring-scission product **22** (Fig. 9) was obtained [99,100]. Complex **21** with  $\text{MeN}(\text{CH}_2\text{CH}_2\text{NMe}_2)_2$  furnished **24**. The results are summarised in Scheme 3. The proposed pathway leading to the ring-cleaved products **20–22** and **24** is illustrated in Scheme 4 for the case of **20**. Evidence for the intermediate Meisenheimer complex **U** was provided by a  $^1\text{H-NMR}$  spectroscopic experiment monitoring the formation of **20** from its factors, which revealed an intermediate having chemical shifts and coupling patterns resembling those of the dihydrotriazines such as **23e**.

The molecular structures of the crystalline complexes **20–22** and **24** have been determined [100]. The ligand CN (or CC) bond lengths are rather similar, shown schematically for **20** in **20'** and **21** in **21'**.



1,3,5-Triazine yielded the crystalline trimeric sodium (**25**) or octameric (**26**) thallium(I) 1,3,5,7-tetraazaheptatrienyl, upon treatment with  $\text{NaNR}_2$  in THF or  $\text{TlNR}_2$  in toluene at  $-80^\circ\text{C}$  (Eq. (14)) [101]. The sodium complex **25** was remarkably thermally stable, showing (i) two distinct  $^{23}\text{Na-NMR}$  spectral signals (ratio ca. 1:2) in toluene- $d_8$  at ambient temperature, which coalesced at ca. 370 K; and (ii) the parent trinuclear molecular ion in the EI mass spectrum.

Compounds **25** and **26** have the molecular structures shown in Figs. 10 and 11. The former illustrates the

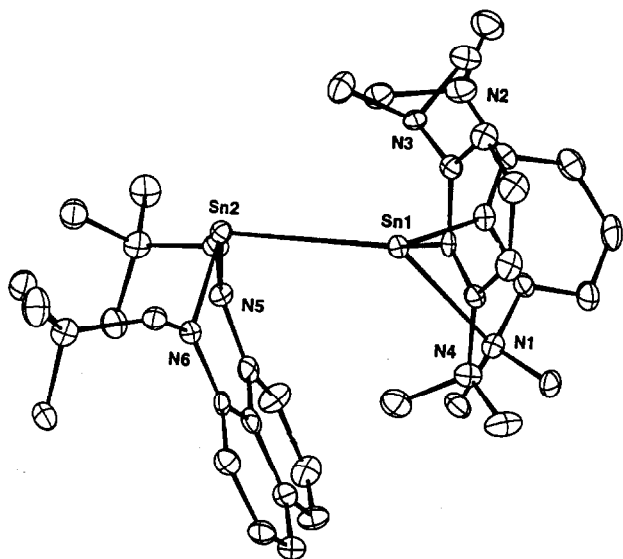


Fig. 8. The molecular structure of crystalline 19b.

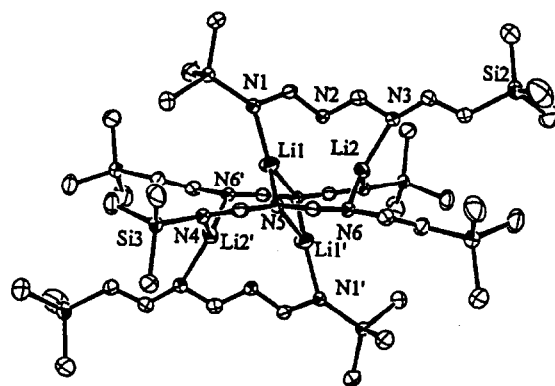
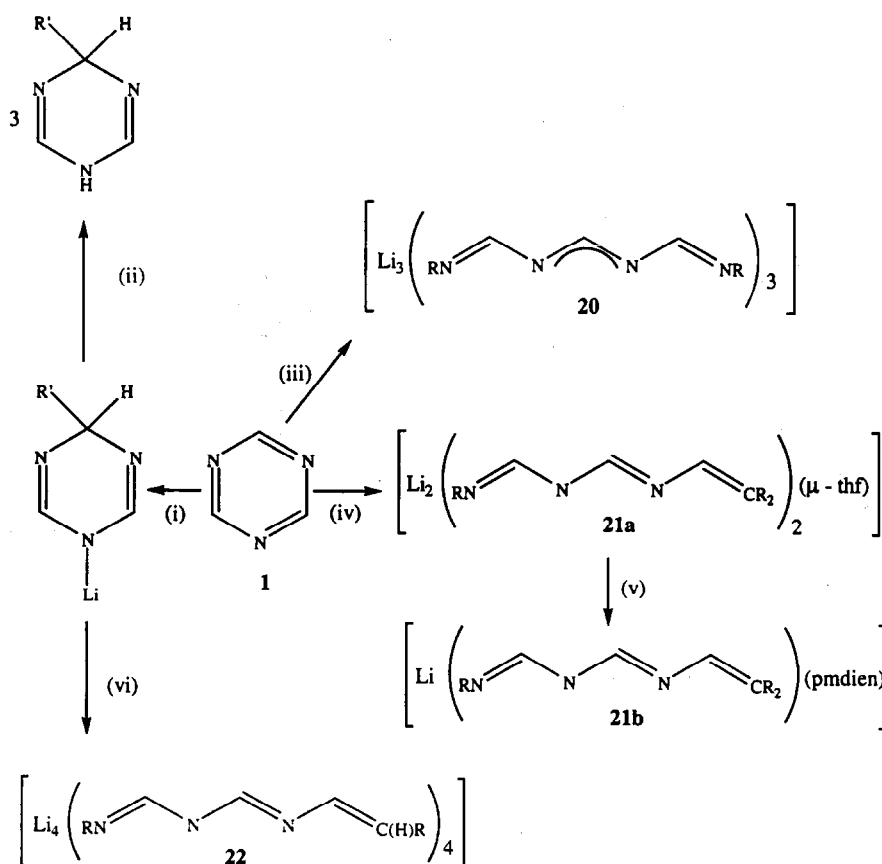
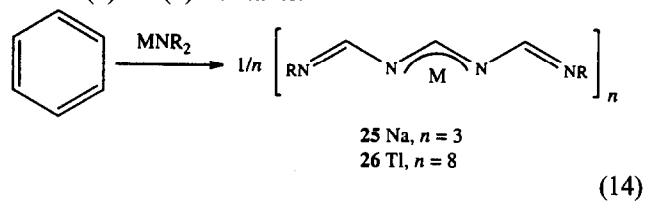


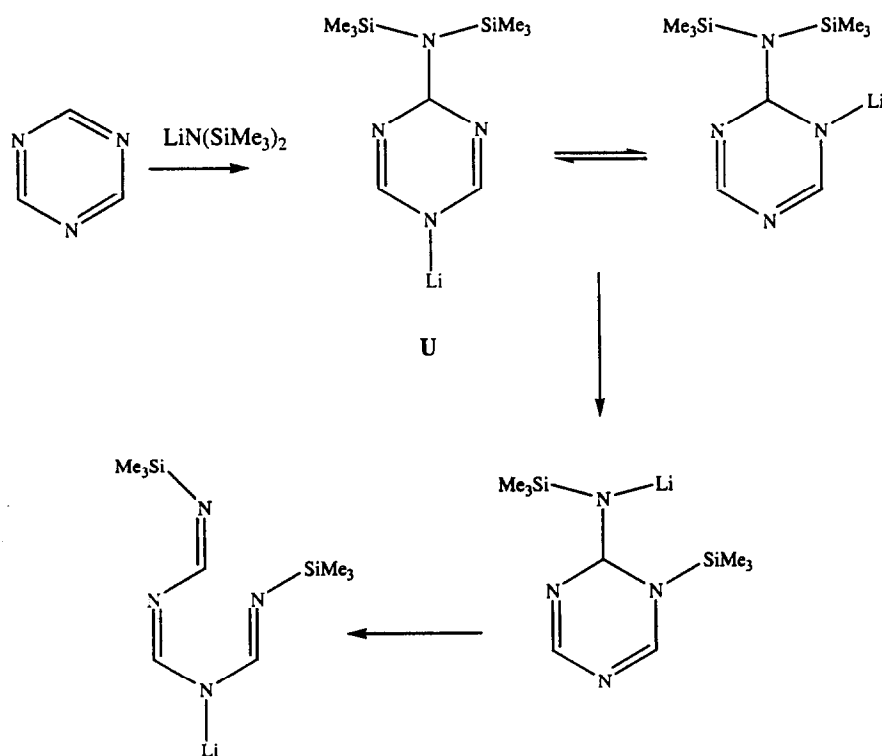
Fig. 9. The molecular structure of crystalline 22.

projection of **25** along its Na–Na–Na axis, showing the molecule to have close to  $C_3$  symmetry. Crystalline **26** consists of two symmetry-related tetranuclear units, having a rather unsymmetric structure, which is best described as comprising four units, each of two Ti

atoms and two ligands  $-R$ . Each ligand binds to two Ti atoms and each Ti atom to two ligands; thus, two  $R$ s to Ti(1) and Ti(3) and two others to Ti(2) and Ti(4). There are short internuclear Ti(1)⋯Ti(2), Ti(1)⋯Ti(3) and Ti(3)⋯Ti(4) contacts.



Scheme 3. The formation of compounds from triazine. Reagents and conditions: [(I)–(iv) ca. 20°C, benzene] and: (I) LiR' (R' = a CH<sub>2</sub>R, b CHR<sub>2</sub>, c SiR<sub>3</sub>; R = SiMe<sub>3</sub>); (ii) one equivalent MeOH; (iii) LiNR<sub>2</sub>, 4 h; (iv) LiCR<sub>3</sub>(THF)<sub>2</sub>, 24 h; (v) pmdien, pentane; (vi) 140°C, 10<sup>−3</sup> mbar, 5 min.



Scheme 4.

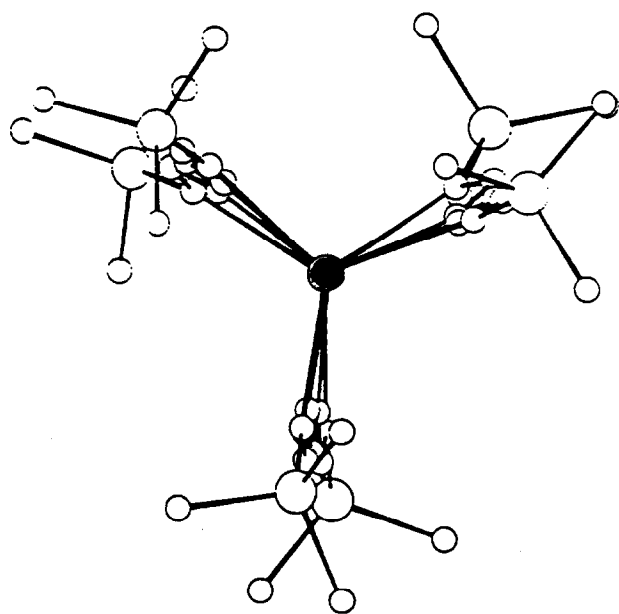


Fig. 10. The molecular structure of crystalline 25.

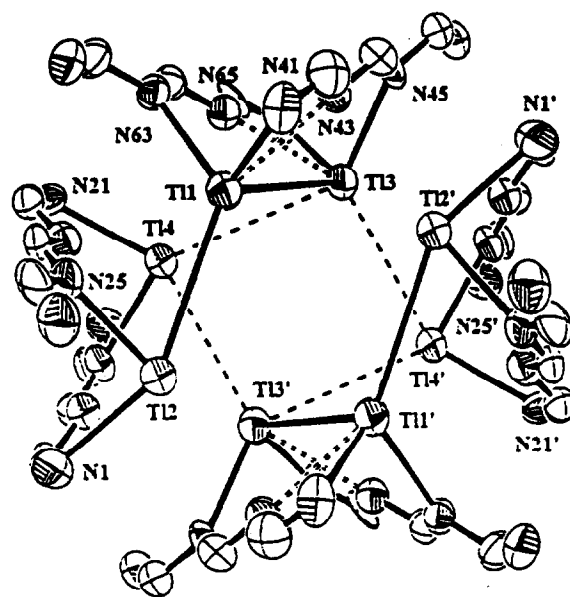


Fig. 11. The molecular structure of crystalline 26.

### 3. Concluding remarks and outlook

We have outlined in Scheme 1 our general approach to the synthesis of unusual lipophilic metal and metalloid complexes. This has been elaborated upon in the

context of two particular areas of our current researches. It is evident that our researches can be described as ligand orientated. Several new ligands have been synthesised, if anionic, first as their alkali metal or magnesium complexes and then by ligand transfer to a

wide range of metals and metalloids. Problems of structure, bonding, and reactivity (including as catalysts) are central to our study of target unusual compounds. Given time, this strategy still has a substantial future.

### Acknowledgements

The greatest privilege available to an academic researcher is to be able to work with able and dedicated young co-workers. I have been particularly fortunate in this regard and offer them my sincere thanks for their contributions, stimulation and friendship. It is a pleasure also to acknowledge the generous support made available by EPSRC, the Royal Society, the European Commission, and various industrial partners — currently BASF (Ludwigshafen).

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