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TEMPO: a novel chameleonic ligand for s-block metal amide chemistry†

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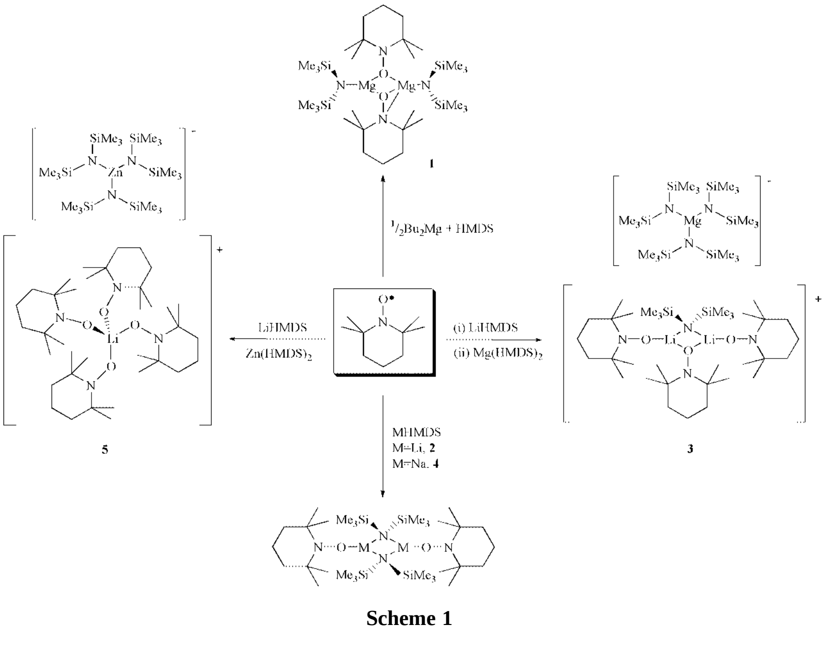
The first structurally characterised examples of the nitroxide TEMPO acting as a ligand towards Li, Na or Mg are described, through a series of hexamethyldisilazide complexes which reveals a remarkable breadth of variety in structure and in the mode of ligation.

TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) is a molecule which attracts a phenomenal level of interest. A stable nitroxide free radical, it is utilised within a remarkably diverse assortment of areas. A key ingredient in the development of 'living' free radical polymerisations,[1] it is employed also as a spin label in the study of biological systems.[2] Often the reagent of choice for effecting the mild and selective oxidation of primary and secondary alcohols,[3] TEMPO also finds utility as a radical trapping agent.[4] It is also well established as a Lewis base in d-block coordination chemistry,[5] with crystal structures known where it binds to Co, Cu, Mn, Mo or Pd atoms. Surprisingly, however, the s-block group of metals has hitherto been a virgin territory for TEMPO in this regard.[6] Here this situation is redressed with the disclosure of the first reported TEMPO complexes of Li, Na, Mg or Zn. This series establishes that TEMPO is a versatile new ligand for these electropositive metal atoms, offering more flexibility in its modes of ligation and electronic structures than the conventional O-based donor molecules usually encountered in s-block chemistry.

To minimise the number of variables that could influence structure, the study was confined to 1,1,1,3,3,3-hexamethyldisilazide [HMDS, $(Me_3Si)_2N^-$] derivatives and reactions were carried out in the same bulk solvent (hexane). Hence the predominant discriminating factor in the structures obtained would be the particular metal cation/TEMPO combination/s used. Furthermore since this was explicitly a structural study, product yields were not optimised as the immediate aim was to perfect crystals of a quality suitable for X-ray crystallographic study. As revealed in Scheme 1, five crystalline products **1**–**5** were successfully obtained using this approach. This scheme also lists the components of each reaction mixture studied. The details of the synthesis of **3** serve to illustrate the similar methodology used for each new complex: under argon gas in a Schlenk tube, a 1:1 mixture of crystalline LiHMDS and TEMPO was dissolved in hexane and stirred at ambient temperature for one day, from which orange crystals of $[\{Li(\mu\text{-}HMDS)\cdot TEMPO\}_2]$ **2** were isolated; these crystals were then mixed with an equimolar amount of crystalline $Mg(HMDS)_2$ and redissolved in warm hexane solution which, when surrounded by a hot water Dewar flask and left to cool slowly to ambient temperature, deposited orange–yellow crystals of $[\{Li_2(\mu\text{-}HMDS)(\mu\text{-}TEMPO)\cdot 2TEMPO\}^+\{Mg(HMDS)_3\}^-]$ **3**.

X-Ray crystallographic studies have been carried out on all five new complexes. ChemWin representations of their structures are shown in Scheme 1.‡ The structures of the aforementioned **2** and its sodium analogue $[\{Na(\mu\text{-}HMDS)\cdot TEMPO\}_2]$ **4** warrant only a brief mention here as they belong to a familiar structural type. Filling the terminal coordination site on the alkali metal atom within a planar, dimeric $(MN)_2$ ring, TEMPO is acting here as an orthodox neutral, monodentate O donor molecule in the mould of THF (*cf.* the structure of $[\{Li(\mu\text{-}HMDS)\cdot THF\}_2]$[7]). The third homometallic structure $[\{Mg(HMDS)(\mu\text{-}TEMPO^-)\}_2]$ **1** (Fig. 1) is also a dimer, but it is as remarkable and unpredictable as the first



Scheme 1

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† Electronic supplementary information (ESI) available: experimental, synthesis and characterisation data. See http://www.rsc.org/suppdata/cc/b1/b104937m/

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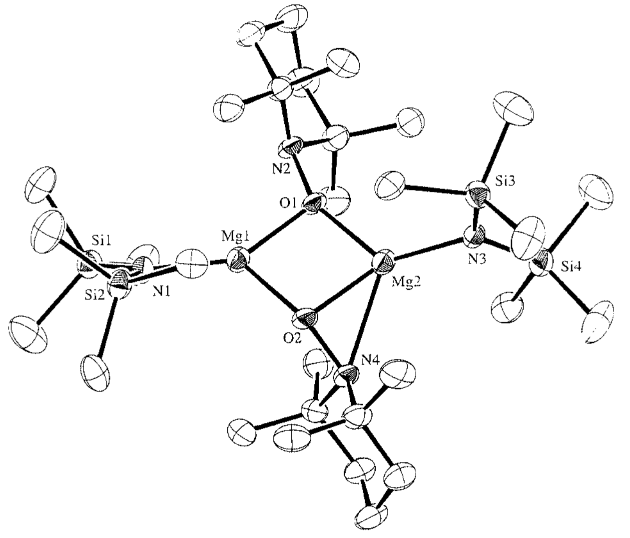

Fig. 1 Molecular structure of **1** without hydrogen atoms. Key dimensions (Å and °): Mg1–O1 1.944(3), Mg1–O2 1.946(3), Mg2-O1 1.967(3), Mg2–O2 1.979(3), Mg1–N1 1.952(3), Mg2–N3 1.965(3), Mg2–N4 2.395(3), O1–Mg1–O2 84.28(10), O1–Mg2-O2 82.80(10), Mg1–O1–Mg2 96.69(11), Mg1–O2–Mg2 96.22(11).

two structures are unremarkable and predictable. First, the positions of its ligands are mutually reversed relative to those in **2** and **4**, with HMDS occupying a terminal site and TEMPO occupying a bridging site. Second, there are two distinct types of TEMPO ligation: one involves a μ_2-O bonding mode through O(1), while the other involves a combination of μ_2-O bonding and η^2-O/N chelation through O(2)/N(4). Third, whereas in **2** and **4** the TEMPO ligands are neutral, free radicals, in **1** they must both be monoanionic (*i.e.*, reduced with respect to normal free TEMPO) to balance the charge of the $[Mg(HMDS)]_2^{2+}$ fragment: thus **1** contains a heteroleptic (anionic) ligand set. Several Lewis base complexes of this Mg bis(amide) have been structurally characterised,[8] but none in which the donor molecule bridges a pair of Mg atoms. TEMPO has therefore changed its ligating role here to be more like that of an anionic O donor such as the aldolate ligand in $[\{Mg(HMDS)[\mu\text{-}OC(Me)Bu^tCH_2C(Bu^t){=}O]\}_2]$.[9] Furthermore, there also appears to be no precedent in the library of d-block metal TEMPO complexes for the nitroxide functioning as a μ_2-O donor ligand in either its neutral or anionic form, though the η^2-O/N chelating mode has been observed previously.[5] The dimensions of **1** show that the N–O and Mg–O bond lengths are insensitive to the TEMPO ligating mode with values of 1.461(3) and 1.471(3) Å for the former, and of 1.955 (mean) and 1.979(3) Å for the latter, for the monodentate O and didentate O/N types, respectively. There is significantly more discrimination between these bridging anionic ligands and the terminal radical type found in **2** and **4** in both N–O bond lengths (mean values: in **2**, 1.279 Å; in **4**, 1.275 Å) and the geometry of the N atom {sum of bond angles (mean): in **1**, 333.5° [discounting those involving Mg(2)]; in **2**, 357.9°; in **4**, 356.4°}. This ability of the N atom to oscillate between a highly pyramidal and a planar geometry is one important factor in TEMPO's coordinative flexibility. Yet another variation is revealed in the first heterometallic structure, **3**. Here, TEMPO acts simultaneously as a bridging and terminal ligand within an unusual dinuclear asymmetrical cation $[\{Li_2(\mu\text{-}HMDS)(\mu\text{-}TEMPO)\cdot 2TEMPO\}^+]$ (Fig. 2). Its Li–O bond lengths [(mean): bridging, 1.969 Å; terminal, 1.816 Å] are in accord with the different coordination numbers involved, but again the N–O bond lengths [bridging, 1.301(3) Å; (mean) terminal, 1.284 Å] appear rather insensitive to such differences. However, the N(5) atom of the bridging TEMPO ligand adopts a near-planar geometry (sum of bond angles, 357.8°) in contrast to the highly pyramidalised geometries of its bridging counterparts in **1**: hence the major discriminating factor is the electronic nature of the N–O unit (*i.e.*, free radical or anionic). The other half of the discrete ion pair structure of **3**, $[\{Mg(HMDS)_3\}^-]$, is also special. Examples are known where this metallate species is tethered to Li as in $[pyr\cdot Li(\mu\text{-}HMDS)_2Mg(HMDS)]$,[10] but this discrete arrangement is unprecedented. This comparison highlights the effectiveness of TEMPO relative to even strong donors such as pyridine. A more emphatic demonstration of this point is provided by the final structure, $[(Li\cdot 4TEMPO)^+\{Zn(HMDS)_3\}^-]$ **5**. Substituting Zn for Mg takes place with retention of the trigonal planar anionic moiety, but surprisingly the cationic moiety changes to a simple mono-nuclear arrangement with Li tetrahedrally surrounded by TEMPO radicals. Here the four TEMPO ligands co-operate to sequester a Li^+ cation and separate it from the anionic moiety.

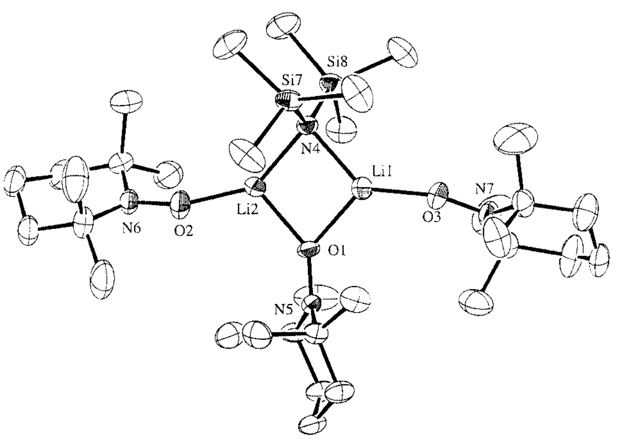

Fig. 2 The cationic moiety of **3** without hydrogen atoms. Key dimensions (Å and °): Li1–O1 1.982(6), Li1–O3 1.812(6), Li2–O1 1.957(6), Li2–O2 1.821(6), Li1–N4 1.993(6), Li2–N4 1.951(6), Li1–O1–Li2 83.0(2), Li1–N4–Li2 82.8(2), O1–Li1–N4 96.0(3), N4–Li2-O1 98.2(3).

In conclusion, using a single amido system as a case study, TEMPO has been established as a promising versatile new ligand for the s-block metals.

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‡ CCDC reference numbers 160882–160886. See http://www.rsc.org/suppdata/cc/b1/b104937m/ for crystallographic data in CIF or other electronic format.

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