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A new route to sulfur polyimido anions S(NR)$_n^{m-}$: reactivity and coordination behavior

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Contents

Abstract

In a reaction sequence of amide addition followed by halogen oxidation the triazasulfite S(NR)$_3^{2-}$ and the tetrazasulfate S(NR)$_4^{2-}$ are readily accessible from sulfur diimide S(NR)$_2$ via sulfur triimide S(NR)$_3$. Addition of lithium organics to sulfur triimide provides a general route to triazasulfonates RS(NR)$_3^-$. All these anions resemble potential tripodal coordination behavior because of their nitrogen donor centers. Furthermore, the sulfur polyimido ligands are capable of responding to the various requirements of different metals (even in mixed metal species) by charge (de)localization. This review deals with the synthetic routes to the sulfur nitrogen anions and with their coordination behavior. The reactivity mainly

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towards main group metal synthons is discussed.

Keywords: Reaction sequence; Sulfur polyimido anions; Amide addition; Halogen oxidation

1. Introduction

Sulfur nitrogen compounds attracted interest from the 1950s to the 1980s, with particular activity in the 1970s and a number of reviews have appeared [1,2]. Since the structural characterization of these compounds is difficult, due to the lack of suitable physical techniques (both ^{14,15}N- and ^{33}S-NMR spectroscopic experiments are non-standard techniques), X-ray crystallography plays a major role in providing essential structural information.

The isoelectronic sulfur nitrogen analogues of the simple sulfur oxygen compounds have shown to be very fruitful synthons in inorganic and organic synthesis [3,4]. Many sulfur oxygen/nitrogen compounds and their acids have been synthesized. In these compounds, the oxygen atoms are formally, either fully or partially isoelectronically substituted by NR groups (R = H, alkyl, aryl, silyl, sulfonyl, and others) (see Table 1).

Table 1
Sulfur oxygen compounds and their sulfur nitrogen analogues

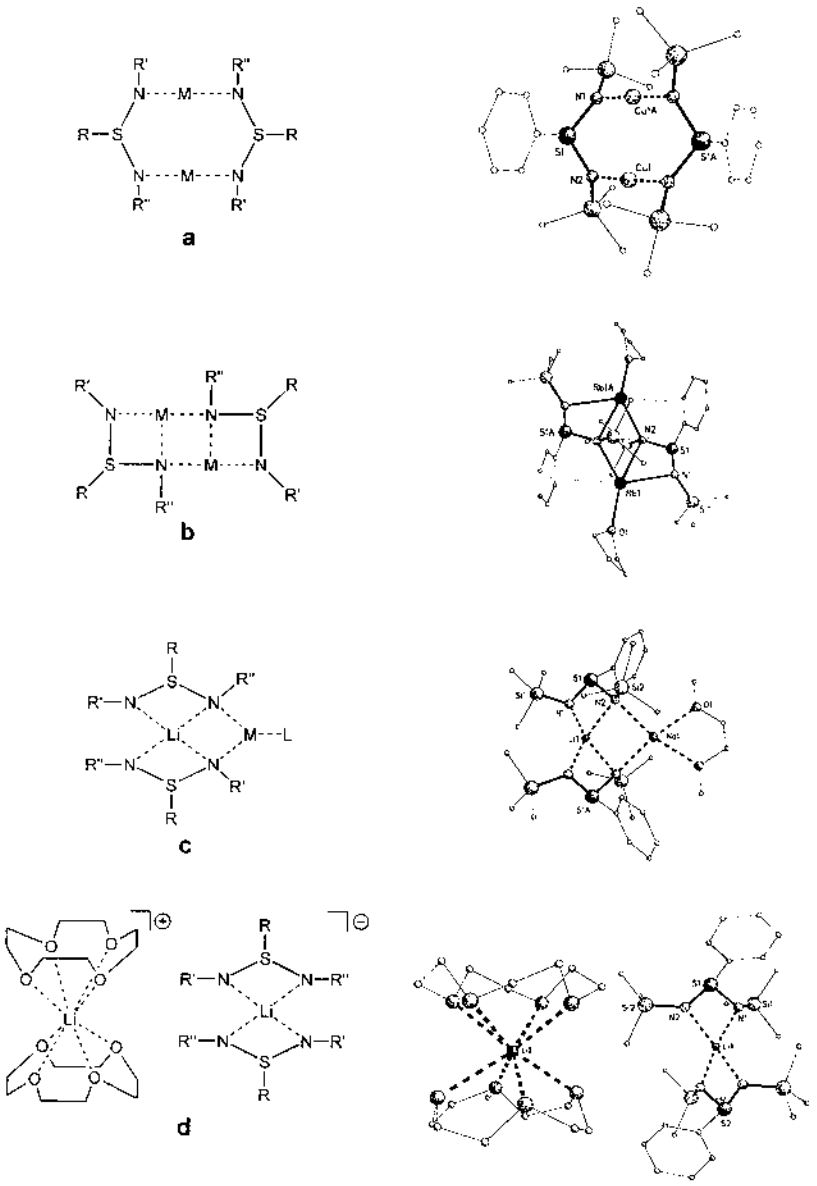
S–O	S–N
SO_2	$S(NR)_2$
SO_3^{2-}	$S(NR)_3^{2-}$
RSO_2^-	$RS(NR)_2^-$
R_2SO	R_2SNR
SO_3	$S(NR)_3$
SO_4^{2-}	$S(NR)_4^{2-}$
RSO_3^-	$RS(NR)_3^-$
R_2SO_2	$R_2S(NR)_2$
SO_4	*$S(NR)_4$*

Compounds in italics have not been reported yet.

This review is limited to anionic sulfur nitrogen species. It does not include the mixed sulfur oxygen/nitrogen compounds. For a survey of the chemistry of sulfurdiimides see Meij et al. [5]. There has also been a recent review on three coordinate sulfur(VI) species in this journal, including a detailed overview on the chemistry of sulfurtriimides [6].

2. Sulfur(IV) nitrogen compounds

The double bonds in sulfurdiimides easily undergo nucleophilic addition reactions. Due to the considerable $S^{+}-N^{-}$ bond polarization, the nucleophile always bonds to the sulfur. Up until now, the anionic sulfur(IV)-nitrogen analogues of the



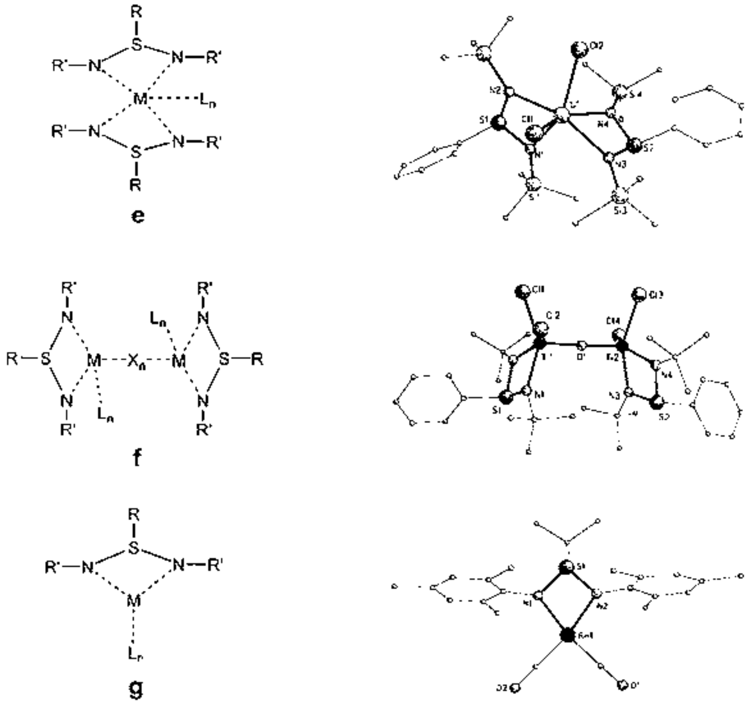


Fig. 1. Coordination patterns of $RS(NR')_2^-$ anions.

sulfur(IV)-oxygen acids can only be obtained via reactions of sulfurdiimides or reduction of sulfurtriimides.

2.1. *S-alkyl-iminosulfinamides ($RS(NR)_2^-$)*

Addition of lithium organyls to a formal double bond of sulfurdiimides gives *S*-organyl-iminosulfinamides $RS(NR')_2^-$ (R = alkyl, aryl; R′ = alkyl, aryl, trimethylsilyl), which have become versatile building blocks in main group [7–19] and transition metal [16,20–22] chemistry. A great variety of their complexes are known and in several cases their structural properties in coordination chemistry have been investigated. Fig. 1 highlights the structural variety in these complexes. The structures can be classified into an eight-membered ring structure **a**, a ladder or step structure **b**, and a twisted tricyclic structure with C_2 symmetry **c**. Also, a structure of the lithium lithiate compound $[Li(12\text{-crown-}4)_2]^+[Li\{(NSiMe_3)_2SPh\}_2]^-$ has been reported and classified as structural type **d**. It consists of a crown ether complexed lithium cation and an anionic moiety in which lithium is coordinated by two chelating iminosulfinamide anions, affording an overall singly charged anion of the 'ate' type. In one case a reorganisation of a type **c** structure to a type **b** structure, after release of the donor molecule (L), has been monitored by solid state NMR methods [16].

Table 2
Summary of $RS(NR')_2^-$ complexes

Compound	Metal	Type	References
$[Li(NSiMe_3)_2S^tBu]$	Li	b	[13]
$Li(NSiMe_3)(N^tBu)S^tBu]$	Li	a	[13]
$[Li(NSiMe_3)(NCy)S_tBu]$	Li	b	[16]
$[Et_2OLi(NSiMe_3)_2SPh]$	Li	c	[15]
$[Et_2OLi(NSiMe_3)(N_tBu)SPh]$	Li	c	[15]
$[Et_2OLi(NSiMe_3)(NCy)SPh]$	Li	c	[16]
$[thfLi(NSiMe_3)_2SPh]$	Li	b	[15]
$[(12c4)Li(NSiMe_3)_2SPh]$	Li	d	[14]
$[thfNa(NSiMe_3)(N^tBu)SPh]$	Na	b	[13]
$[dmeLiNa\{(NSiMe_3)_2SPh\}_2]$	Li/Na	c	[16]
$[thfK(NSiMe_3)(N^tBu)SPh]$	K	b	[13]
$[dmeK(NSiMe_3)_2SPh]$	K	b	[16]
$[thfRb(NSiMe_3)_2SPh]$	Rb	b	[13]
$[thfCs(NSiMe_3)_2SPh]$	Cs	b	[13]
$[thfMgBr(NSiMe_3)_2SPh]$	Mg	f	[16]
$[thfMg\{(NSiMe_3)_2SPh\}_2]$	Mg	e	[14]
$[thf_2Ca\{(NSiMe_3)_2SPh\}_2]$	Ca	e	[17]
$[thf_2Sr\{(NSiMe_3)_2SPh\}_2]$	Sr	e	[17]
$[thf_2Ba\{(NSiMe_3)_2SPh\}_2]$	Ba	e	[17]
$[SnCl_3(N^tBu)_2SCp_2Fe]$	Sn	g	[18]
$[SnMe_3(NSO_2CF_3)_2SMe$	Sn	g	[19]
$[O\{TiCl_2(N^tBu)_2SPh\}_2]$	Ti	f	[18]
$[Cu(NSiMe_3)_2SPh]$	Cu(I)	a	[16]
$[(CO)_2Rh(NMes)_2S^tBu]$	Rh	g	[21]
$[UCl_2\{(NSiMe_3)_2SPh\}_2]$	U	e	[22]

Cy = Cyclohexyl; 12c4 = 12-crown-4; Cp = Cyclopentadienyl (C_5H_5).

Careful hydrolysis of the alkali metal complexes of *S*-alkyl-iminosulfinamides affords the 'free acids' ($H(NR)_2SR'$), which show dimeric structures of the type **a** complexes in the solid state (Fig. 1). The free acid can easily be deprotonated by strong bases like the alkaline earth bis[bis(trimethylsilyl)amides], to yield the corresponding alkaline earth metal complexes [17]. Table 2 gives an overview of known $RS(NR')_2^-$ complexes.

In all these complexes, the ligand backbone is quite rigid. In most cases the negative charge is more or less delocalized over the two nitrogen atoms of the ligand backbone. Only the NH-compounds show clearly localized single (168.1 pm) and double (158.8 pm) S–N bonds. Neither the nature of the coordinated metal nor the steric or electronic properties of the organic substituents effect the structural features of the SN_2-moiety. The S–N bond lengths (av. 161 pm) and N–S–N angles (av 106°) are nearly the same in all complexes.

2.2. Iminosulfindiamides ($R_2NS(NR)_2^-$ and $S(NR)_3^{2-}$)

Various compounds containing a $S^{IV}(NR)_3$ unit have been synthesized. They can be neutral ($(R_2N)_2SNR'$; R,R′ = alkyl, aryl, sulfonyl, benzoyl) [23–26], monoanionic ($R_2NS(NR')_2^-$; R = alkyl, $SiMe_3$, R′ = tosyl, $SiMe_3$) [17,27], or dianionic ($S(NR)_3^{2-}$; R = alkyl, tosyl, $SO_2C_6H_5$) [28–32]. In the following only the anionic systems shall be discussed in detail.

In 1975 Gieren and Narayanan [28] reported on the synthesis and solid state structure of the first iminosulfindiamide, $S(NR)_3^{2-}$ (R = $SO_2(C_6H_4)Me$). Roesky et al. [29,30] reported a similar compound (R = $SO_2C_6H_5$). These compounds were obtained by the reaction of the sulfurdiimide ($S(NR)_2$ (R = $SO_2C_6H_5$, $SO_2(C_6H_4)Me$) with $NaNH_2$ in liquid ammonia. In 1992, Pauer et al. [31,32], succeeded in the synthesis of an alkyl substituted iminosulfindiamide (R = ^{t}Bu). By analogy with the addition of alkali metal alkyls to sulfurdiimides, iminosulfindiamides can be obtained by the addition of alkali metal amides to a double bond of sulfurdiimides. As with primary amides, secondary amides can be added to the S=N double bond. The synthetic strategies to obtain iminosulfindiamides are shown below:

$$3S(NR)_2 + 2NH_2^- \xrightarrow{NH_{3(l)}} S(NR)_3^{2-} + 2SNR^- + H_2NR \quad \begin{array}{l} R = SO_2(C_6H_4)Me \\ \quad\;\;\, SO_2(C_6H_5) \end{array} \qquad [28,29]$$

$$2S(N^tBu)_2 + 4LiHN^tBu \longrightarrow \left[Li_4\{(N^tBu)_3S\}_2\right] + 2H_2N^tBu \qquad [31,32]$$

$$S(NR)_2 + 2HNR_2' \longrightarrow [\{H_2NR_2'\}\{R_2'NS(NR)_2\}] \quad \begin{array}{l} R\; = SO_2(C_6H_4)Me; \\ R' = \text{alkyl} \end{array} \qquad [27]$$

$$S(NSiMe_3)_2 + LiN(SiMe_3)_2 \xrightarrow{thf} [thf_2Li(NSiMe_3)_2SN(SiMe_3)_2]$$

(Fleischer and Stalke, unpublished results)

$$S(NSiMe_3)_2 + M\{N(SiMe_3)_2\}_2 \xrightarrow{thf} [thf_nM\{(NSiMe_3)_2SN(SiMe_3)_2\}_2]$$

$M = Mg,Ca,Sr$

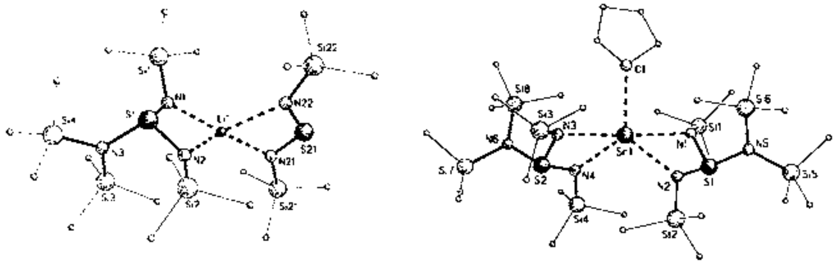
$n = 0,1,1$ [17]

$$2S(N^tBu)_3 + 4Li \xrightarrow{thf} \left[thfLi_4\{(N^tBu)_3S\}_2\right] \qquad [31,32]$$

$$3S(N^tBu)_2 + 6M \xrightarrow{thf} \left[thf_6M_6(\mu_6\text{-}S)\{(N^tBu)_3S\}_2\right] \quad M = Li,Na$$

(Fleischer et al., unpublished results).

In the monoanionic iminosulfindiamides ($R_2NS(NR)_2^-$; R = $SiMe_3$), one of the imide groups of $S^{IV}(NR)_3^{2-}$ (R = $SiMe_3$) is substituted by an additional trimethylsilyl group, which prevents this tricoordinated nitrogen atom from coordination to any metal atom in the related metal complexes. Therefore only chelating dipodal coordination can be observed (Fig. 2). The iminosulfindiamides resemble the *S*-organyl-iminosulfinamides in their coordination behavior [17].



[S(Me$_3$SiN)$_2$Li(NSiMe$_3$)$_2$SN(SiMe$_3$)$_2$]

[thfSr{(NSiMe$_3$)$_2$SN(SiMe$_3$)$_2$}$_2$]

Fig. 2. Structural examples of monoanionic iminosulfindiamides.

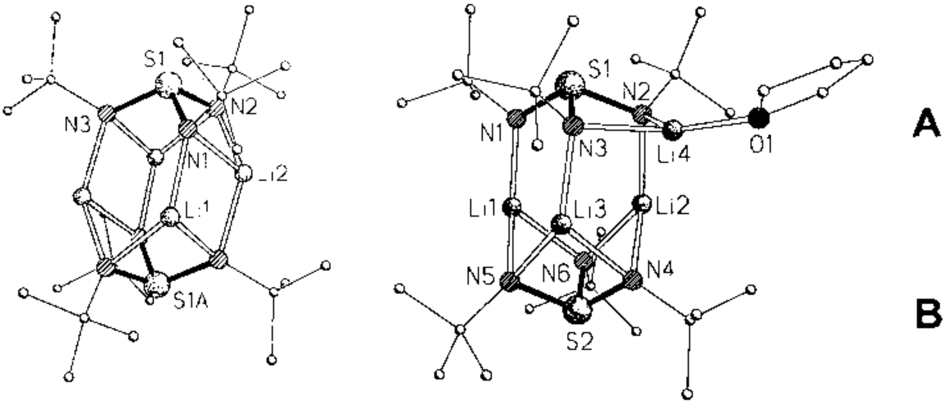


Fig. 3. Solid state structures of $[\{Li(N^tBu)_3S\}_2]$ and $[(thf)Li_4\{(N^tBu)_3S\}_2]$.

The dianionic iminosulfindiamides $S(NR)_3^{2-}$ show totally different behavior. Their cap-shaped geometry together with their dianionic character make them unique in the coordination chemistry of polyimido anions. The lithium salt $[\{Li_4(N^tBu)_3S\}_2]$ exhibits a dimeric structure, comprising two cap-shaped dianions, the concave sides of which face each other (Fig. 3, left) [31,32]. The four lithium atoms between these two caps are each coordinated by three nitrogen atoms. The S–N bond lengths (mean = 165.0 pm) are equal within standard deviations, indicating a complete delocalization of the negative charges over the nitrogen atoms of the SN_3 backbone. In the thf coordinated complex only one lithium atom is donated by a solvent molecule and about to leave the complex. This induces considerable changes in the structural parameters. While the lower cap (B in Fig. 3, right) is almost C_3-symmetrical coordinated (mean S-N 163.8 pm), the upper cap (A in Fig. 3, right) displays one short S-N bond (S1-N1: 160.7 pm) and two longer ones (mean 168.1 pm).

The iminosulfindiamides have several very intriguing properties, which provide many further opportunities for both synthesis and coordination chemistry. The most important properties are:

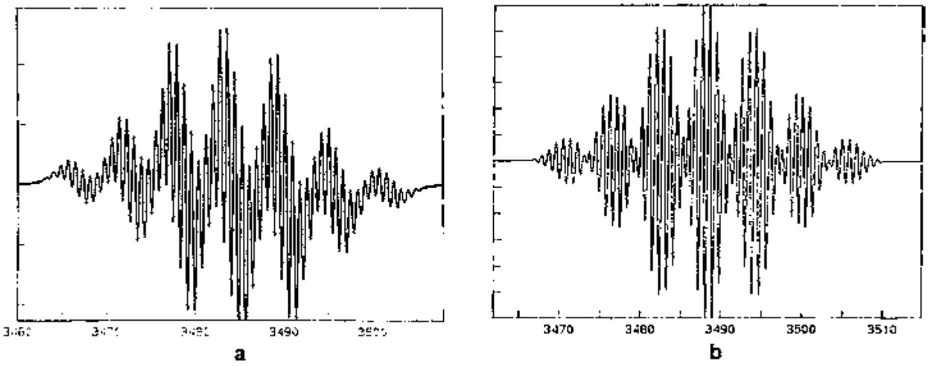
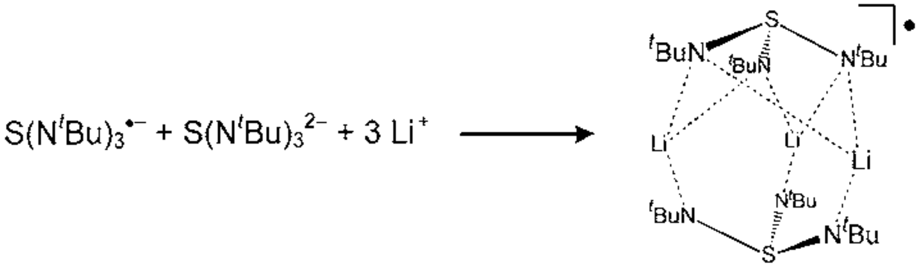


Fig. 4. Experimental ESR-spectrum (a) from oxidized $[Li_4\{N^tBu)_3S\}_2]$ in hexane solution in comparison to the calculated spectrum of $[Li\{(N^tBu)_3S\}_2]^\bullet$ (b).

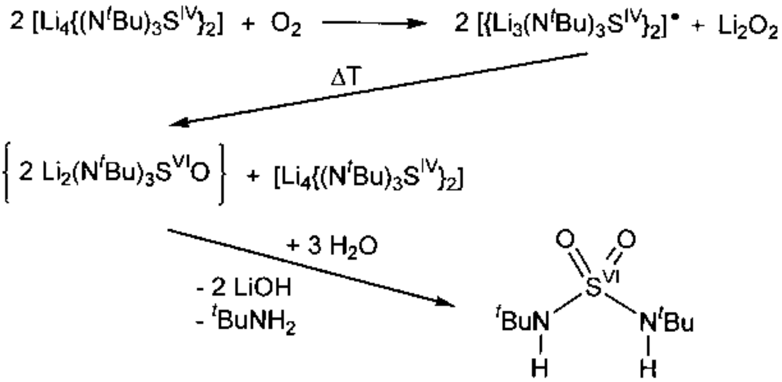
(1) *Easy oxidation*: Metal activation in the $S(NR)_3^{2-}$ complexes enables facile oxidation. Even traces of oxygen, e.g. if handled in an Argon 5.0 atmosphere without additional oxygen absorption, leads to a dark blue color of the solution and in the solid state, indicating the presence of radicals. In the case of $[Li_4\{(N^tBu)_3S\}_2]$ the resulting radical has been investigated by ESR spectroscopy. It is as stable as the $S(NR)_2^{\bullet-}$ radical [33] and can be stored for several weeks. The hyperfine splitting of the signal in the ESR-spectrum (Fig. 4a) gives a septet (a = 8 G, intensity ratio 1:3:6:7:6:3:1) which confirms that the single electron is interacting with three equivalent ^{14}N nuclei ($I = 1$). A second hyperfine splitting could be assigned to an interaction of the single electron with three equivalent ^7Li nuclei ($I = 3/2$, decet with a = 0.8 G).

Simulation of the spectrum confirmed this assignment (Fig. 4b). The structure therefore can be deduced from the ESR spectrum: in the dimer of the radical monoanion $S(N^tBu)_3^{\bullet-}$ and the dianionic $S(N^tBu)_3^{2-}$, three lithium cations are located between the cap-shaped ligands (Scheme 1).



Scheme 1. Proposed structure of $[Li_3\{(N^tBu)_3S\}_2]^\bullet$ in solution.

Oxidation of $[Li_4\{(N^tBu)_3S\}_2]$ was carried out using oxygen and halogens (bromine and iodine) [34]. Although in all reaction sequences a radical is formed in the first step, the reaction pathways differ considerably. If dry oxygen is bubbled through a solution of $[Li_4\{(N^tBu)_3S\}_2]$ in hexane under otherwise inert gas conditions, the mixture instantaneously turns dark blue. Fast interruption of the oxygen gas supply and heating of the dark blue solution causes a color change to green, then reddish brown and finally colorless again. The same sequence of colors can be initiated by using a continuous oxygen gas supply to the solution of $[Li_4\{(N^tBu)_3S\}_2]$, although it stops at the reddish brown level. Unfortunately, the product could not be purified either by distillation or recrystallization, however, hints towards the existence of such a compound are given by other reactions, which shall be discussed later, only after hydrolysis could $O_2S(^tBuNH)_2$ be isolated and characterized. Nevertheless, Scheme 2 shows a tentative mechanism for the oxidation of $[Li_4\{(N^tBu)_3S\}_2]$ by oxygen.



Scheme 2. Tentative mechanism for the oxidation of $[Li_4\{(N^tBu)_3S\}_2]$ by $O_{2(g)}$.

Two products can be isolated if bromine (or iodine) is used in the oxidation of $[Li_4\{(N^tBu)_3S\}_2]$. Dependent upon the stoichiometry, a lithium halide adduct of monomeric $[Li_2(N^tBu)_3S]$ and $S(N^tBu)_3$ can be isolated in variable yields. Following the addition of the halogen to a solution of $[Li_4\{(N^tBu)_3S\}_2]$ in thf/hexane, the mixture immediately turns dark blue, as in the reaction with oxygen, and a precipitate is formed. Unlike the reaction with oxygen the radical formed in this reaction is not stable. If addition of the halogen is interrupted, the color slowly vanishes, leaving a white suspension. The solution again turns blue with additional halogen, but the color continues to disappear until two equivalents of halogen are added.

Although oxidation of $[Li_4\{(N^tBu)_3S\}_2]$ with oxygen and halogens yields a radical after the first step, both reactions differ considerably in their character. Whilst in the first case the radical is quite stable, in the latter it is not. Presumably the structure of the radical is the same in both reactions, i.e. a dimer of the radical monoanion $S(N^tBu)_3^{\bullet -}$ and the dianionic $S(N^tBu)_3^{2-}$ with three lithium cations between the cap-shaped ligands, the crucial difference must be due to another species also present in the reaction mixture. If the dimeric structure of the radical is broken down by formation of the lithium halide adduct, a destabilized monomeric radical ($[Li(N^tBu)_3S]^\bullet$) is left. This radical monomer, in contrast to the dimer, easily undergoes redox disproportion to yield the sulfurtriimide and monomeric $[Li_2(N^tBu)_3S]$. In the reaction of halides with $[Li_4\{(N^tBu)_3S\}_2]$, four steps can be distinguished.

$$2\left[Li_4\{(N^tBu)_3S\}_2\right] + X_2 \longrightarrow 2\left[Li_3\{(N^tBu)_3S\}_2\right]^\bullet + 2LiX$$

$$2\left[Li_3\{(N^tBu)_3S\}_2\right]^\bullet + 2LiX \longrightarrow 2\left[Li_3X(N^tBu)_3S\right] + 2[Li(N^tBu)_3S]^\bullet$$

$$2[Li(N^tBu)_3S]^\bullet \longrightarrow 1/2\left[Li_4\{(N^tBu)_3S\}_2\right] + S(N^tBu)_3$$

$$2\left[Li_3X(N^tBu)_3S\right] + X_2 \longrightarrow 2[Li(N^tBu)_3S]^\bullet + 4LiX$$

with X = Br, I.

The first step of the reaction is a fast, one-electron oxidation of $[Li_4\{(N_tBu)_3S\}_2]$, to yield the dimeric radical $[Li_3\{(N^tBu)_3S\}_2]^\bullet$ and LiX (X = Br, I). In the second step, the dimeric structure of the radical is broken down by formation of the halide adduct and the radical monomer ($[Li(N^tBu)_3S]^\bullet$), followed by a redox disproportion to give $S(N^tBu)_3$ and the monomeric starting material $[Li_2(N^tBu)_3S]$. Upon further addition of the halogen, the halide adduct itself can undergo a similar one-electron oxidation, as for $[Li_4\{(N^tBu)_3S\}_2]$, resulting in the same radical monoanion. However, this seems stable enough to be isolated and characterized. The reaction of $[Li_4\{(N^tBu)_3S\}_2]$ with oxygen is very different. Instead of breaking down the dimeric structure of the radical by formation of an adduct, Li_2O_2 oxidatively adds to the S=N double bond of the radical upon heating. If the oxidation of $[Li_4\{(N^tBu)_3S\}_2]$ with iodine is performed in the presence of oxygen,

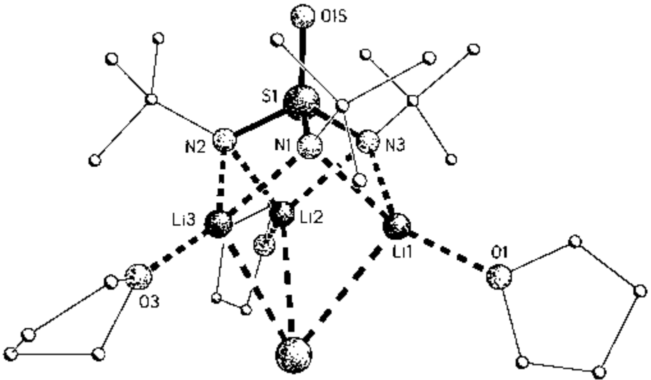


Fig. 5. Solid state structure of $[thf_3Li_3\{\mu_3\text{-I})(N^tBu)_3SO]$.

Scheme 3. $S(NR)_3^{2-}$ vs. $C(NR)_3^{2-}$.

both oxidation reactions proceed simultaneously and a lithium iodide adduct (Fig. 5) can be isolated, further supporting the proposed mechanism for the oxidation reaction with oxygen.

(2) Their *cap-shaped geometry* and *variable electronic structure*: The coordination chemistry of the iminosulfindiamides is unique among the chelating nitrogen ligands due to the two negative charges and it's cap-shaped geometry. In contrast to the $S(NR)_3^{2-}$ dianion the analogous carbon compounds (guanidines $C(NR)_3^{2-}$) are planar (Scheme 3).

While the iminosulfindiamides facilitate cage type complexes [35,36] the corresponding guanidines form polymers [37,38] due to their planar structure. The cap-shaped geometry together with the steric demand of the nitrogen bonded substituents should even enable homoleptic metal(II) complexes. Unfortunately, up until now, no such complexes of $S(NR)_3^{2-}$ are known, owing to a lack of synthetic access. Because of the ability of the ligand to simultaneously stabilize different cations, which in addition are coordinated by the anions of the starting material mixed metal complexes are formed by coordination expansion, rather than complete transmetallation occurring. This is exemplified by several transmetallation products obtained in reactions with alkali *tert*.-butoxides and some main group metal amides.

$$\left[Li_4\{(N^tBu)_3S\}_2\right] + 2MO^tBu \xrightarrow{thf} \left[thf_2Li_4M_2(O^tBu)_2\{(N^tBu)_3S\}_2\right] \quad M = Na,K$$

[36]

$$\left[Li_4\{(N^tBu)_3S\}_2\right] + [Ca\{N(SiMe_3)_2\}_2] \xrightarrow{thf} 2LiN(SiMe_3)_2 + \left[thf_2CaLi_2\{(N^tBu)_3S\}_2\right]$$

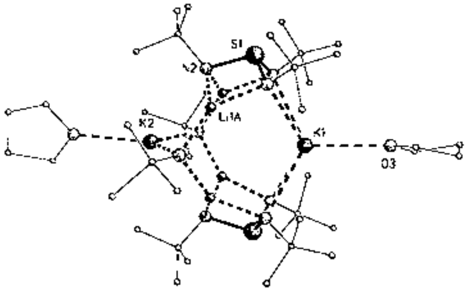
[35]

$$\left[Li_4\{(N^tBu)_3S\}_2\right] + 2[Ba\{N(SiMe_3)_2\}_2] \xrightarrow{thf} 3LiN(SiMe_3)_2 + \left[thf_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2\right]$$

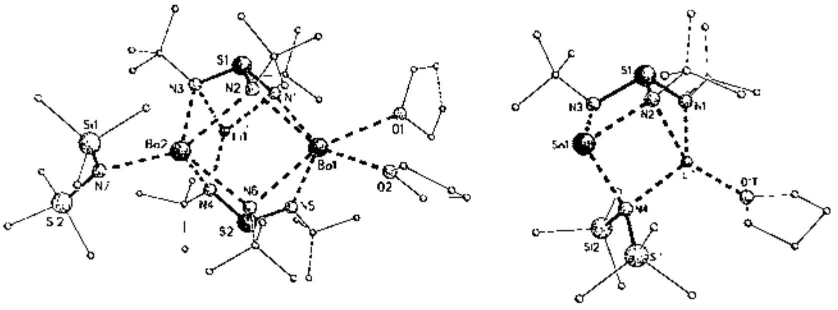
[35]

$$\left[Li_4\{(N^tBu)_3S\}_2\right] + 2[Sn\{N(SiMe_3)_2\}_2] \xrightarrow{thf} 2LiN(SiMe_3)_2 + 2[thfSnLi\{N(SiMe_3)_2\}\{(N^tBu)_3S\}]$$

[35]



$[\mathrm{thf_2Li_4K_2(O^tBu)_2\{(N^tBu)_3S\}_2}]$



$[\mathrm{thf_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2}]$ $[\mathrm{thfSnLi\{N(SiMe_3)_2\}\{(N^tBu)_3S\}}]$

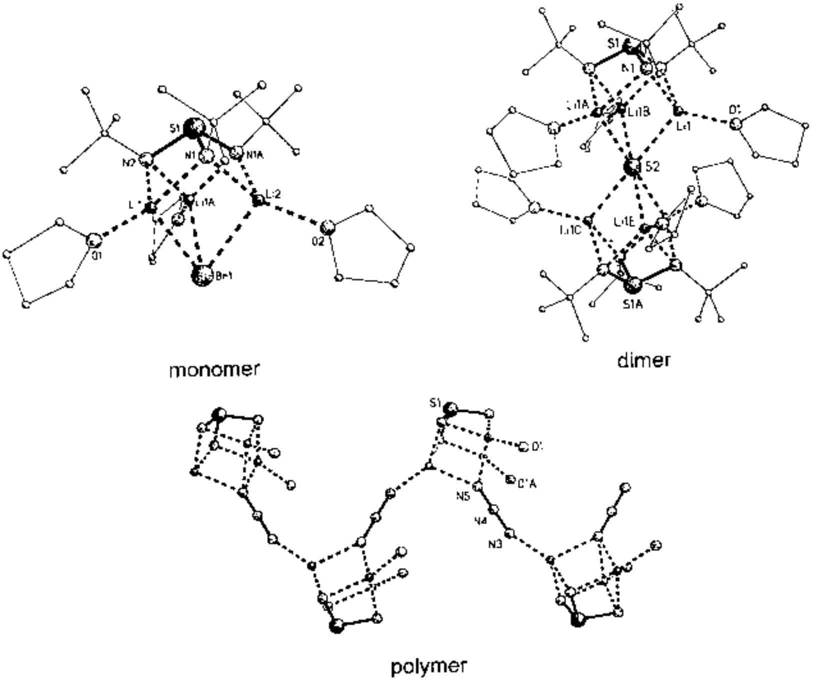
Fig. 6. Mixed metal complexes of $S(NR)_3 2^-$.

Fig. 6 shows some examples of mixed metal cage type complexes of the $S(NR)_3^{2-}$ ligand.

Another effect of the cap-shaped geometry and the electronic flexibility is the tendency to build adducts with metal salts (M_nX). Depending on the nature of the anion (X^-) in these salts, the resulting adducts can be monomers (MX = LiBr, LiI) [33], dimers ($M_2X = Li_2S$, Na_2S) (Fleischer et al., unpublished results) or polymers ($MX = LiN_3$) [39] (see Fig. 7).

A driving force in the formation of these adducts is the tendency of the ligand to coordinate three lithium anions rather than two, resulting in complete delocalization of the negative charges over the nitrogen atoms in the ligand backbone. The partially transmetallated compounds discussed above can be rationalized in a similar fashion, however, the difference in polarizability of the cations only permits partial delocalization of the negative charges on the ligand.

Depending upon the electronic requirements, different resonance forms of the ligand can be utilized, by which the charges of the coordinated cations are stabilized. Table 3 summarizes the corresponding S–N bond lengths. In this context it must be denoted, that bonding in sulfurimides could be described as electrostatic rather than covalent, thus the depicted double bonds are just a useful formalism to describe the reactivity and to explain the structural features and not an expression



monomer

dimer

polymer

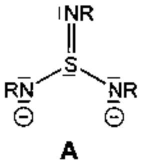
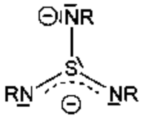
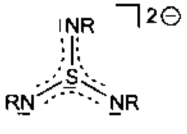
Fig. 7. Coordination patterns of lithium salt adducts.

of the real electronic situation. Currently we are investigating the $S(NR)_3^{2-}$ electronic situation by high level ab-initio calculations.

The electronic flexibility also facilitates stabilization of unusual electronic states for example radicals (Fleischer and Stalke, unpublished results).

(3) The *Lewis base character* of the sulfur atom: Owing to its oxidation state the central sulfur atom possesses a stereochemically active lone pair. This lone pair not

Table 3
Structural features of $S(NR)_3^{2-}$

	 **A**	 **B**	 **C**
S-N$_{av}$ [pm]	169.9	167.2	–
S=N$_{av}$ [pm]	158.9	–	–
S$\overset{\cdots}{-}$N$_{av}$ [pm]	–	165.2	165.5

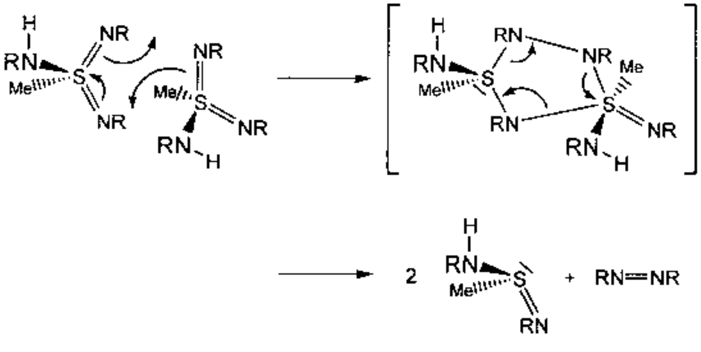
only causes the pyramidal geometry, which results in the cap shape of the ligand, but also gives rise to Lewis base character of the sulfur atom. It should therefore be possible to facilitate S-coordination as well as N-coordination, unless steric requirements prevent this. Some examples for S-coordination are already known from the chemistry of sulfurdiimides [5].

3. Sulfur(VI) nitrogen compounds

By analogy to the reactions of sulfurdiimides, addition of nucleophiles to the double bond of sulfurtriimides provides access to anionic S^{VI}–N species. However, although most reactions of sulfurdiimides are applicable to sulfurtriimides as well, only little is known of the anionic S^{VI}–N species. This is due to the lack of easy synthetic access to sulfurtriimides. Until recently, only two methods were known to build up the $S^{VI}N_3$ backbone, using either NSF_3 [40–43] or OSF_4 [44]. While the first synthesis is quite hazardous the second is limited to $S(NS{:}Me_3)_3$. Both methods give unsatisfactory yields. An easier synthesis is the oxidation of iminosulfindiamides with halogens, as mentioned above [33]. This route will provide access to a great variety of even unsymmetrically substituted sulfurtriimides.

3.1. Diiminosulfonamides ($RS(NR)_3^-$)

Unlike the S-alkyl iminosulfinamides $RS(NR')_2^-$, S-alkyl diiminosulfonamides $RS(NR')_3^-$ are relatively rare and only little structural information on these species is available. They can be obtained by oxidation of thiols with halogen amines in the presence of a base [45–47] or by the addition of lithium organyls to the S=N double bond of sulfurtriimide [48,49]. Like the lithium complexes of S-alkyl iminosulfinamides, the lithium complexes of S-alkyl diiminosulfonamides undergo easy hydrolysis to give the ‘free acid’. This hydrolysis reaction is accompanied by an interesting side reaction. $H(N_tBu)_2SMe$ was found to be a byproduct after workup of the hydrolysis of $[Li(N^tBu)_3SMe]$ with equimolar amounts of water. Since



Scheme 4. Rearrangement of $H(N^tBu)_3SMe$ to give $H(N^tBu)_2SMe$.

$H(N^tBu)_2SMe$ is a $S^{(IV)}$ compound, it cannot be formed in the hydrolysis reaction itself, but must be obtained in a subsequent redox reaction. Presumably, two $H(N^tBu)_3SMe$ molecules undergo a [2 + 4] cyclo addition reaction, followed by a [2 + 4] retro Diels–Alder reaction accompanied by abstraction of di(*tert*.butyl)diimide (Scheme 4).

The reaction of $H(N^tBu)_3SMe$ with alkaline earth bis[bis(trimethylsilyl)amides] give the alkaline earth metal complexes [50].

$$RSH + 3XHNR \longrightarrow RS(NR')_3H + 3HX \quad R,R' = \text{alkyl}; \quad X = Cl,Br \qquad [45\text{–}47]$$

$$S(N^tBu)_3 + LiMe \longrightarrow [Li(N^tBu)_3SMe] \qquad [48,49]$$

$$[Li(N^tBu)_3SMe] + H_2O \longrightarrow H(N^tBu)_3SMe + LiOH \qquad [50]$$

$$2H(N^tBu)_3SMe + BaX_2 \longrightarrow [Ba\{(N^tBu)_3SMe\}_2] + 2HX \quad X = N(SiMe_3)_2 \qquad [50]$$

Some organo tin compounds of the type $Sn(Me)_n\{MeS(NMe)_3\}_{4-n}$ have also been reported [51]. There is a strong relationship to the trianionic $RSi(NR)_3^{3-}$ system [52], which is isoelectronic with $RS(NR)_3^-$, but in contrast to the tripodal coordination behavior of the former, in the metal complexes of the latter only a chelating dipodal coordination mode of the anion is observed. This effect is obviously due to steric strain of the N-bounded ^{t}Bu groups in the few known S-methyldiiminosulfonamides [50]. The Si–N bond lengths in the $MeSi(N^tBu)_3^{3-}$ ligand (174 pm) are about 17 pm longer than the S–N bond lengths in the system reported here (157 pm), resulting in a remarkable overlap of the Van-der-Waals radii of the *tert*.-butyl groups with the sulfur bound methyl group (Fig. 8).

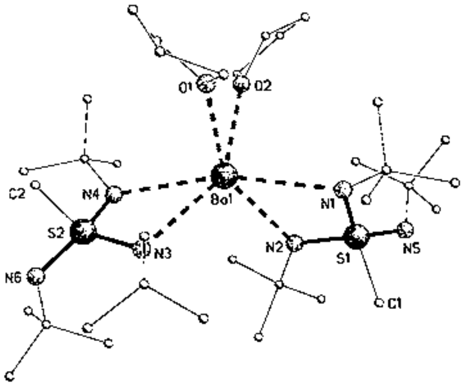


Fig. 8. Solid state structure of $[thf_2Ba\{(N^tBu)_3SMe\}_2]$.

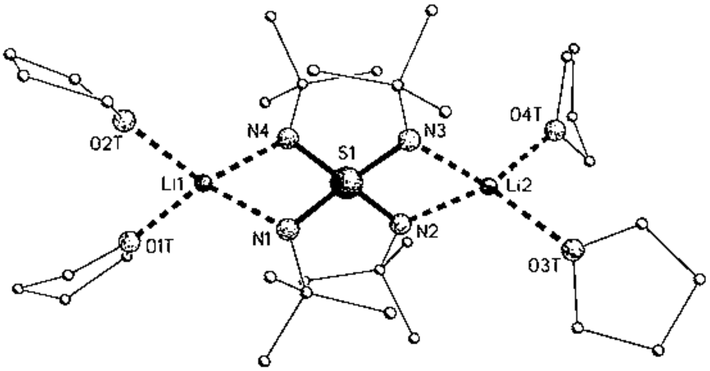


Fig. 9. Solid state structure of $[thf_4Li_2(N^tBu)_4S]$.

3.2. *Tetrakis(tert.-butyl)diiminosulfurdiamides* $(S(N^tBu)_4^{2-})$

The coordination number 4 is the most common of $S^{(VI)}$ and many compounds of the type $SO_x(NR)_{4-x}^{2-}$ are known [53–55]. In 1968 Appel and Ross [56–58] reported on the synthesis of $[K_3(NH)_3SN{\bullet}NH_3]$ from the reaction of *S,S*-dimethyl sulfur diimine with KNH_2 in liquid ammonia. Unfortunately it is only characterized by elemental analysis and no structural information is available. Rewriting the formula as $[K_2(NH)_4S{\bullet}KNH_2]$, the compound can be rationalized as the first member of the class of diiminosulfurdiamides $(S(NR)_4^{2-}$; R=H). The first fully structurally characterized example of this species is $[thf_4Li_2(N^tBu)_4S]$ (Fig. 9) which can easily be synthesized by addition of the lithium *tert.*-butylamide to the double bond of sulfurtriimide [48,49]. The resulting lithium complex $[thf_4Li_2(N^tBu)_4S]$ is sensitive to oxygen. Like the $[thfLi_4\{(N^tBu)_4S\}_2]$ the hexane solution turns blue immediately, when exposed to traces of oxygen and a turquoise precipitate is formed. Unfortunately, the nature of the product has not been fully examined up to now.

$$S(N^tBu)_3 + 2LiHN^tBu \xrightarrow{thf/hexane} \left[thf_4Li_2(N^tBu)_4S\right] + H_2N^tBu \qquad [48,49]$$

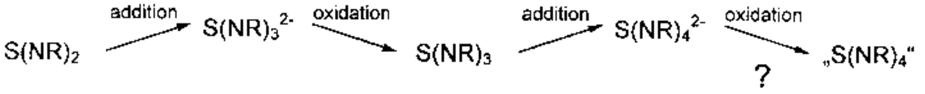
$$H_2O + \left[thf_4Li_2(N^tBu)_4S\right] \longrightarrow H_2(N^tBu)_4S + LiOH \qquad [50]$$

$$H_2(N^tBu)_4S + 2BaX_2 \xrightarrow{thf/hexane} \left[thf_2Ba_2X_2\{(N^tBu)_4S\}\right] + 2HX \quad X = N(SiMe_3)_2 \qquad [50]$$

The ‘free acid’ is available after hydrolysis of the lithium complex, or after reaction with $^tBuNH_3Cl$. Although it has not been characterized or even isolated up until now, subsequent reaction with barium bis(bis(trimethylsilyl)amide yields the barium complex $[thf_4Ba_2\{N(SiMe_3)_2\}_2(N^tBu)_4S]$ [50]. The S–N bond lengths in the $S(N^tBu)_4^{2-}$ dianion (159.9 pm) are not affected by the nature of the coordinated metal. There are investigations currently underway on other metal complexes of this ligand (Fig. 9).

4. Opportunities

The $RS(NR)_3^-$, $S(NR)_3^{2-}$ and $S(NR)_4^{2-}$ anions provide a vast variety of chemical opportunities in many fields of chemistry. In a sequence of an amide addition reaction followed by a halogen oxidation all $S(NR)_n^{m-}$ species (i.e. $S(NR)_3^{2-}$, $S(NR)_3$ and $S(NR)_4^{2-}$) can be synthesized. Due to the easy radicalic oxidizability of even the $S(NR)_4^{2-}$ containing species the syntheses of the SO_4 analogue $S(NR)_4$ seems feasible.



Scheme 5.

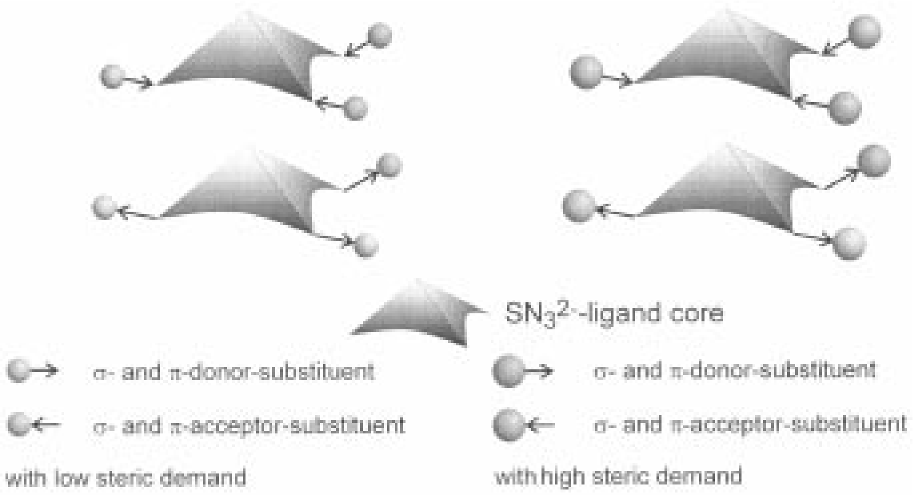


Fig. 10. Electronic and steric fine tuning of the S(NR)3 cap.

The dianions are tripodal ligands with tunable electronic and steric properties via the organic substituent periphery. Electron releasing substituents like Me_3Si-groups at the three nitrogen atoms at the basal plane of the SN_3 trigonal pyramid will increase the Lewis basicity of the central sulfur atom, whereas electron withdrawing groups like (substituted) aryls will couple to the nitrogen atom and decrease the electron density at sulfur (Figs. 10 and 11).

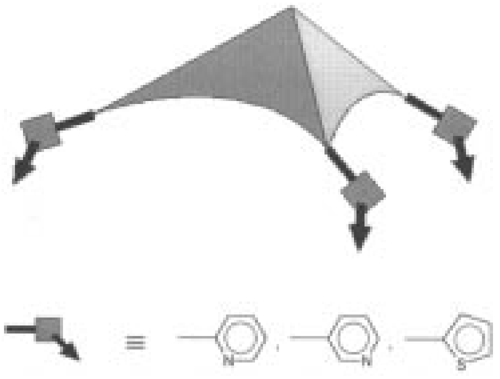
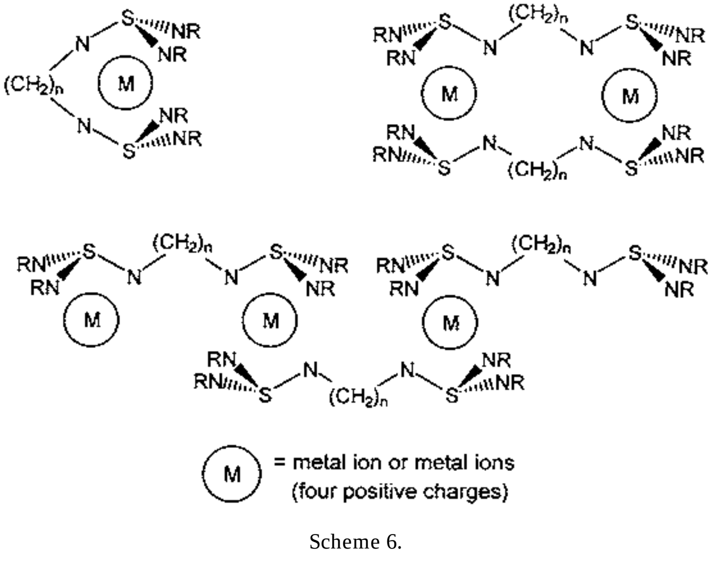
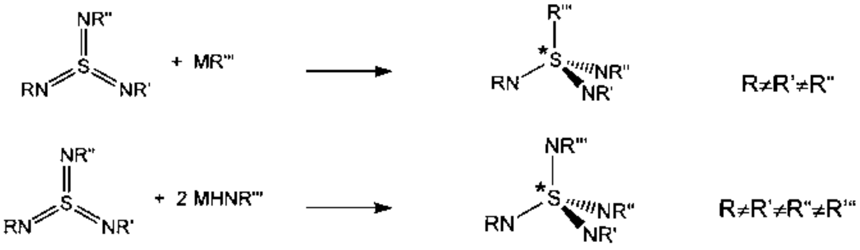


Fig. 11. Side arm donating S(NR)3 cap.

This allows one to tune the coordination site selectivity of the dianion. The 'hard' N_3 site is adjustable to the requirements of even 'soft' metals by employing electron withdrawing substituents and the S-Lewis base center can be made more attractive to 'hard' centers (e.g. early transition metal) by employing electron releasing substituents. The organic substituents need not only provide the appropriate steric bulk but could also participate in metal coordination ('side arm donation'; pioneered by Klumpp, van Koten, Corriu and others). By choice of the suitable primary amide the passive protecting hydrocarbon layer of the dianion can easily be converted into an active donating ligand periphery. Connection of two dianions will give rise to $(RN)_2SN(CH_2)_nNS(NR)_2^{4-}$ ions which make *ansa*-



Scheme 6.



Scheme 7.

metalocene-like residues feasible. This possibly provides access to macromolecular architectures consisting of metal cation layers separated by connected SN_3 moieties. Linkage of all six nitrogen atoms in two dianions facing each other by their concave side gives rise to structural motifs known from cryptands.

Simple access to asymmetrically substituted sulfur triimides $S(NR^{1,2,3})_3$ opens the door to chiral $RS(NR^{1,2,3})_3^-$ and $S(NR^{1,2,3,4})_4^{2-}$ species. Like the well known chiral phosphanes (DIPAMP, BINAP, CHIRAPHOS, etc.) in transition metal-based catalytic processes they might find an application as chiral auxiliaries in asymmetric synthesis and catalysis.

These opportunities might indicate that we only recently entered a field where still plenty is to be discovered.

Acknowledgements

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