Syntheses and Structures of Main Group Metal Complexes of the $S(N^tBu)_3^{2-}$ Dianion, an Inorganic Y-Conjugated Tripod

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The metal metathesis reactions of $[Li_4\{(N^tBu)_3S\}_2]$, **1**, with various main group metal compounds are investigated. The reactions of **1** with group 14 metal(II) halides result in decomposition of the $S(N^tBu)_3^{2-}$ dianion and subsequent formation of cubane-type structures of the metal *tert*-butylamides. In the reaction of $GeCl_2$ with **1** a Ge═S double bond is formed. While the use of **1**·thf initiates a complex redox reaction affording the mixed-valence Ge(II)/Ge(IV) complex $[Ge_4(S)(N^tBu)_4]$, **2**, partial metal metathesis is achieved by employing metal(II) bis[bis(trimethylsilyl)amides] in reactions with **1**. The mixed-metal complexes $[(thf)_2CaLi_2\{(N^tBu)_3S\}_2]$, **3**, $[(thf)_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2]$, **4**, and $[(thf)LiSn\{N(SiMe_3)_2\}\{(N^tBu)_3S\}]$, **5**, were synthesized and structurally investigated. A closer inspection of the structural parameters of the complexes **3**−**5** reveals some of the intriguing ligand properties of the $S(N^tBu)_3^{2-}$ dianion like the flexible electronic structure, the favorable cap-shaped geometry, and the Lewis base character of the central sulfur atom.

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Introduction

Our current interest lies in the synthesis of new nitrogen chelate ligands with main group elements of low oxidation states as central atoms.[1] These anionic ligands facilitate delocalization of the negative charge between the central atom E and the nitrogen atoms of the substituents. The nitrogen atoms can be directly bonded to the central atom or connected to it via a π electron system. The cations are generally coordinated to the peripheral atoms, although electron density is partly located at the central atom. The Lewis base character of the central atom is additionally induced by its lone pair. Some examples of these ligands are the aminosulfinimides $R'S(NR)_2^-$ (R, R′ = alkyl, aryl, etc.),[2,3] and the dipyridylamides, -phosphinates, and -arsenates $E(py)_2^-$ (py = pyridyl; E = N, P, As).[4,5] The triamidogermanates, -stannates, and -plumbates $E(NR)_3^-$ (*E* = Ge, Sn, Pb)[6] and the tris(pyrazolyl)germanates and -stannates $E(pz)_3^-$ (pz = pyrazolyl, dimethylpyrazolyl; E = Ge, Sn)[7] behave like the ligands described above, but their electronic structure is different. Formally they are Lewis acid/Lewis base adducts of an amide and a germylene, stannylene, or plumbylene. The use of these ligands allows the design of heterobimetallic complexes, which contain hard cations coordinated to the nitrogen atoms in the substituent periphery, while soft metal fragments (e.g., transition-metal carbonyls) are coordinated to the lone pair of the central atom.

There has been a recent growth in interest in tripodal ligands. Various mono- and trianionic systems have been designed and applied to numerous reactions. Like the widely used π ligands (e.g., Cp, Cp*), their steric and electronic properties promise access to catalytically active complexes in transition-metal chemistry. Numerous complexes of the monoanionic tris(pyrazolyl)borate $(HB(pz)_3^-)$ with transition and main group metals are reported, and several reviews have been published on this subject.[8] Recently, the trianionic triaminosilanes $(RSi(NR')_3^{3-})$[9] and trianionic compounds

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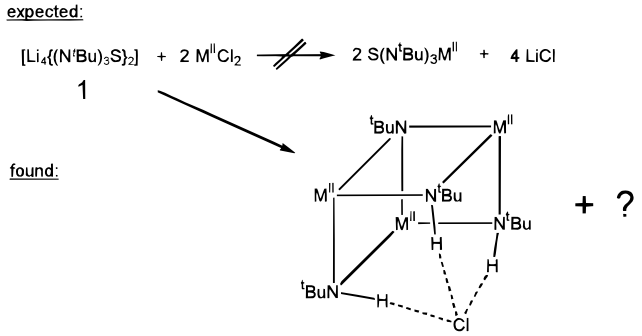
of the type $RE(E'R'_2NR'')_3^{3-}$ (R, R′ = H, alkyl; R″ = alkyl, aryl; E, E′ = C, Si)[10] have attracted much interest.

Our aim was to extend this range of mono- and trianionic ligands by synthesizing dianionic ligands. Recently, we reported the synthesis and structure of $[Li_4\{(N^tBu)_3S\}_2]$, a complex that contains the tripodal dianion $S(N^tBu)_3^{2-}$.[11] The dianionic character of this ligand should provide access to homoleptic complexes of group 2/12 metals. The tridentate tripodal character is expected to prevent (or at least reduce) aggregation of its complexes. The variation of the N-bonded substituents also permits electronical and sterical fine-tuning of the ligands. These properties provide the ligands a unique multitude of opportunities in organometallic chemistry. All tripodal dianionic nitrogen ligands reported up to now are of the type $E(N^tBu)_3^{2-}$ (with E = S,[11,12] Se,[13] Te,[14]). It is important to note that the dianionic guanidine derivatives $C(NR)_3^{2-}$ are planar;[15] hence tripodal coordination to one metal in these systems is hampered.

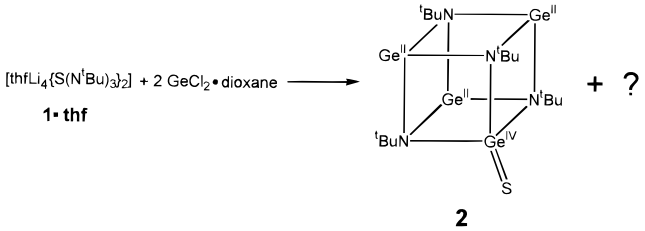
Results and Discussion

The intention of this work was the synthesis of iminosulfindiamide complexes with different main group metals in order to investigate the coordination properties of this tripodal dianionic ligand. A priori one can think of various different strategies to synthesize these compounds. First, direct synthesis of iminosulfindiamine complexes can be achieved by addition of metal amides to sulfur diimides ($S(N^tBu)_2$). Second, transmetalation of the lithium compound ($[Li_4\{(N^tBu)_3S\}_2]$, **1**) by metal halides, alkoxides, or amides should give metal iminosulfindiamide complexes. Third, reduction of $S(N^tBu)_3$ with active metals should give the $S(N^tBu)_3^{2-}$ dianion complexed to the metal. While the latter strategy is limited to alkali and the heavier alkaline-earth metals, the first is restricted by the limited availability of primary metal amides which provide sufficient nucleophilicity to facilitate addition to sulfur diimides. While it turned out that the syntheses of the *tert*-butylamides of the heavier alkali metals are difficult, reduction of $S(N^tBu)_3$ with sodium and potassium yielded the alkali-metal complexes of iminosulfindiamide.[16] As expected, only three metal cations are encapsulated between two anionic iminosulfindiamine ligands; hence the isolated complexes are radicals. Transmetalation reactions of $[Li_4\{(N^tBu)_3S\}_2]$, **1**, with alkali-metal alkoxides were also carried out, but in the resulting complexes 2 equiv of alkali-metal alkoxides were incorporated to expand the dimeric cage structure of **1** and no transmetalation could be observed so far.[17]

Scheme 1. Reaction of 1 with MCl_2 (M = Ge, Sn)



Scheme 2. Reaction of [1·thf] with $GeCl_2$·dioxane



Reactions with Metal Halides. Metal metathesis reactions with metal halides are widely used in organometallic chemistry. Usually alkali-metal compounds are employed as starting materials in this type of reaction, utilizing the high tendency to form alkali-metal halides. In order to obtain the complexes of group 14 metals in the oxidation state +II, their chlorides ($GeCl_2$, $SnCl_2$) were used in metal metathesis reactions with **1**. Unfortunately total decomposition of the starting material occurred. Surprisingly, the metal amides (Scheme 1) were isolated.

The metal amides obtained were reported by *Veith* and co-workers[18] in 1982 as the reaction product of $Me_2Si(N^tBu)_2M$ (M = Ge, Sn, Pb) with *tert*-butylamine. The presence of $^tBuNH_2$ in the synthesis presented here might therefore explain our results. In the synthesis of $[Li_4\{(N^tBu)_3S\}_2]$, **1**, *tert*-butylamine is formed as a byproduct. The amine was confirmed to coordinate one lithium atom. This complex has presumably a structure similar to **1**·thf where the thf molecule is replaced by an amine. The amine initiates decomposition of the $S(N^tBu)_3^{2-}$ ligand in the same way as was found for the $Me_2Si(N^tBu)_2^{2-}$ ligand. However, the reaction of the thf adduct **1**·thf and $GeCl_2$·dioxane leads to a similar hetero cubane structure (Scheme 2).

The structure[19] can also be rationalized as a $(^tBuN)_4$ tetrahedron penetrating a second Ge_4 tetrahedron. The three tricoordinated germanium atoms are in the oxida-

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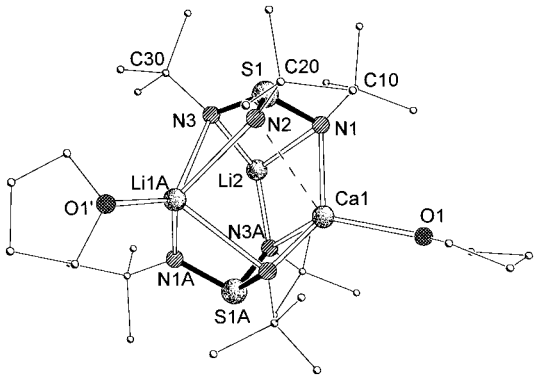

Figure 1. Solid-state structure of $[(thf)_2CaLi_2\{(N^tBu)_3S\}_2]$, **3**. Selected bond lengths (pm) and angles (deg): S1−N1 162.8(4), S1−N2 155.2(8), S1−N3 163.3(4), Li1A−N1A 219(6), Li1A−N2 203(5), Li1A−N3 250(6), Li1A−O1′ 217(5), Li2−N1 225(2), Li2−N3 200(2), Li2−N3A 193(2), Ca1−N1 222.7(8), Ca1···N2 305(1), Ca1−N2A 237(1), Ca1−N3A 259.3(7), Ca1−O1 234(2), N1−S1−N2 110.6(4), N2−S1−N3 108.6(4), N3−S1−N1 104.8(2), S1−N1−C10 115.9(3), S1−N2−C20 119.5(7), S1−N3−C30 116.6(3).

tion state +II while the single germanium atom substituted by an additional sulfur atom is a germanium(IV). The Ge−S distance of 204.9(3) pm is remarkably short and has to be considered as a Ge═S double bond.[20] The presence of sulfur and germanium in different oxidation states proves that redox chemistry is favored over transmetalation reactions when metal dihalides are employed.

Reactions with Metal Amides. Although metal amides are predominantly used in deprotonation reactions, we endeavored to transmetalate **1** with secondary amides of certain alkaline-earth metals (Mg, Ca, Ba) and tin. Different from the alkaline-earth metal halides, which are nearly inert and insoluble, and from $SnCl_2$, reaction with which leads to decomposition of the starting material, the related metal amides provide excellent solubility and sufficient reactivity. The alkali-metal alkoxides are not very soluble, either, and are incorporated in the resulting complexes.[17] The bis(trimethylsilyl)amides do not suffer from this disadvantage. Various soluble and reactive metal complexes of bis(trimethylsilyl)amide are known and easy to synthesize.[21]

Syntheses of $[(thf)_2CaLi_2\{(N^tBu)_3S\}_2]$, 3, $[(thf)_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2]$, 4, and $[(thf)LiSn\{N(SiMe_3)_2\}\{(N^tBu)_3S\}]$, 5. Different types of complexes are obtained in the reactions of **1** with $[(thf)_2M\{N(SiMe_3)_2\}_2]$ (M = Ca, Ba). While two lithium atoms are still present in the calcium derivative **3** (eq 1), only one remains in the barium complex **4** (eq 2). Hence, they exhibit different levels of transmetalation. In the calcium complex **3** only half the equivalent of the present lithium cations is replaced by calcium dications, while in the barium complex **4** three out of four lithium cations are exchanged by two barium dications. The bis(trimethylsilyl)amide group found in the barium complex provides charge balance. In both compounds the dimeric structure of two cap-shaped ligands facing each other with their concave sides is retained. The monomeric compound **5** is obtained in the analogous reaction of **1** with $[Sn\{N(SiMe_3)_2\}_2]$ (eq 3). In none of the reactions can complete transmetalation be achieved. Obviously the affinity of the $S(N^tBu)_3^{2-}$ dianion to lithium is quite high.

$$\mathbf{1} + [(thf)_2Ca\{N(SiMe_3)_2\}_2] \xrightarrow{thf} 2LiN(SiMe_3)_2 + \underset{\mathbf{3}}{[(thf)_2CaLi_2\{(N^tBu)_3S\}_2]} \quad (1)$$

$$\mathbf{1} + 2[(thf)_2Ba\{N(SiMe_3)_2\}_2] \xrightarrow{thf} 3LiN(SiMe_3)_2 + \underset{\mathbf{4}}{[(thf)_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2]} \quad (2)$$

$$\mathbf{1} + [Sn\{N(SiMe_3)_2\}_2] \xrightarrow{thf} \underset{\mathbf{5}}{[(thf)LiSn\{N(SiMe_3)_2\}\{(N^tBu)_3S\}]} \quad (3)$$

Structures of $[(thf)_2CaLi_2\{(N^tBu)_3S\}_2]$, 3, $[(thf)_2Ba_2Li\{N(SiMe_3)_2\}\{(N^tBu)_3S\}_2]$, 4, and $[(thf)LiSn\{N(SiMe_3)_2\}\{(N^tBu)_3S\}]$, 5. X-ray-suitable crystals of **3** (Figure 1) are obtained within a few days' storage of the thf/hexane solution at room temperature. The colorless blocks lose thf upon heating to about 176 °C and turn blue when exposed to traces of oxygen.

The single-crystal structure analysis of **3** reveals three metal atoms in the region between the triazasulfite dianions. Two of the four lithium atoms present in the starting material have been replaced by a single calcium atom. The structure solution and refinement of **3** was difficult since the space group symmetry emulates disorder of the three metal atoms. However, all crystallographic problems have been solved satisfactorily and the basic structural parameters have been determined reliably. The Ca−N distances range from 222.7(8) to 259.3(7) pm and cover the typical scope found in calcium amides.[22,23] The structural parameters affected most by transmetalation are the S−N distances. While these distances are almost identical in the starting material and average to 165.5 pm, the S1−N2 distance (155.2(8) pm) and the S1−N3 distance (163.3(4) pm) differ by about 8 pm (Table 1). Hence the S1−N2 distance displays a higher double-bond character than the other two. Accordingly, the S1−N2−C20 angle of 119.5(7)° is the widest among the S−N−C angles (115.9(3) and 116.6(3)°) and the adjacent N−S−N angles are considerably wider than the opposite (104.8(2)° in contrast to 110.6(4)° and 108.6(4)°), because a double bond requires more space than a single bond.[24] N2 is trigonal planar coordinated to its three closest neighboring atoms, S1, Li1a, and C20 (sum of angles: 357.8°), and shows an additional long-range interaction with Ca1 (305(1) pm).

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Table 1. Selected Bond Lengths (pm) and Angles (deg) for 3−5

	compound		
	3 (M = Ca)	**4** (M = Ba)	**5** (M = Sn)
S1−N1	162.8(4)	165.7(6)	158.9(3)
S1−N2	155.2(8)	167.2(6)	169.9(3)
S1−N3	163.3(4)	164.6(7)	169.8(3)
S2−N4		164.8(6)	
S2−N5		161.5(6)	
S2−N6		166.6(6)	
M−N av	**240(1)**	**277.2(6)**	**218.8(3)**
[min−max]	[222.7(8)−259.3(7)]	[263.8(6)−284.6(6)]	[218.2(3)−219.4(3)]
M−O	234(2)	291.7(6)	
		283.7(6)	
M−N(SiMe$_3$)$_2$		271.1(6)	227.6(3)
Li−N av	**215(6)**	**205(2)**	**220.5(7)**
[min−max]	[193(2)−250(6)]	[202(2)−208.6(14)]	[204.4(7)−236.6(7)]
Li−O	217(5)		197.7(7)
N−S−N av	**108.0(4)**	**102.7(3)**	**101.0(2)**
[min−max]	[104.8(2)−110.6(4)]	[97.5(3)−109.0(3)]	[91.8(2)−110.3(2)]
S−N−C av	**117.3(7)**	**116.0(6)**	**117.6(3)**
[min−max]	[115.9(3)−119.5(7)]	[112.2(5)−120.5(5)]	[114.9(2)−120.4(3)]

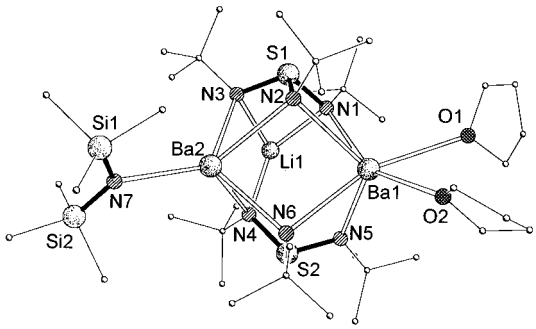

Figure 2. Solid-state structure of [(thf)$_2$Ba$_2$Li{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}$_2$], **4**. Selected bond lengths (pm) and angles (deg): S1−N1 165.7(6), S1−N2 167.2(6), S1−N3 164.6(7), S2−N4 164.8(6), S2−N5 161.5(6), S2−N6 166.6(6), Ba1−N1 266.9(6), Ba1−N2 284.5(6), Ba1−N5 263.8(6), Ba1−N6 283.8(6), Ba1−O1 291.7(6), Ba1−O2 283.7(6), Ba2−N2 284.6(6), Ba2−N3 283.9(6), Ba2−N4 279.5(6), Ba2−N6 270.7(6), Ba2−N7 271.1(6), Li1−N1 208.6(14), Li1−N3 204(2), Li1−N4 202(2), N1−S1−N2 100.0(3), N2−S1−N3 105.5(3), N3−S1−N1 101.5(3), N4−S2−N5 109.0(3), N5−S2−N6 102.8(3), N6−S2−N4 97.5(3), S1−N1−C10 116.9(5), S1−N2−C20 112.2(5), S1−N3−C30 116.1(6), S2−N4−C40 116.4(5), S2−N5−C50 120.5(5), S2−N6−C60 114.1(4).

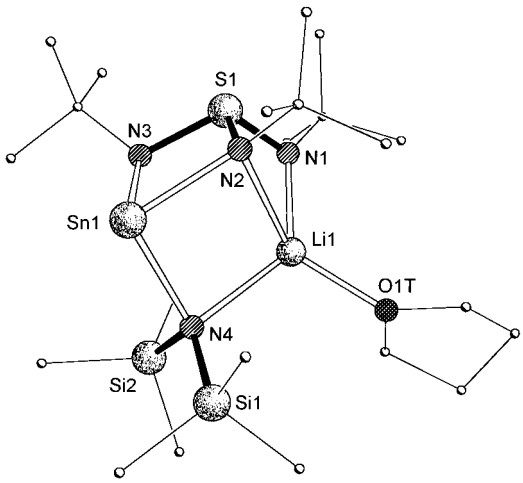

Figure 3. Solid-state structure of [(thf)LiSn{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}], **5**. Selected bond lengths (pm) and angles (deg): S1−N1 158.9(3), S1−N2 169.9(3), S1−N3 169.8(3), Sn1−N2 218.2(3), Sn1−N3 219.4(3), Sn1−N4 227.6(3), Li1−N1 204.4(7), Li1−N2 236.6(7), Li1−N4 220.6(7), Li1−O1t 197.7(7), N1−S1−N2 100.9(2), N2−S1−N3 91.8(2), N3−S1−N1 110.3(2), S1−N1−C10 120.4(3), S1−N2−C20 117.6(2), S1−N3−C30 114.9(2).

[(thf)$_2$Ba$_2$Li{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}$_2$], **4**, crystallizes from thf/hexane within 2 days' storage at −20 °C. The colorless blocks turn turquoise blue if not handled under strict absence of oxygen. On heating to about 173 °C decomposition is observed.

The solid-state structure of **4** shows that the dimeric structure of **1** in principle is retained (Figure 2). Between two dianionic $S(N^tBu)_3^{2-}$ ligands two barium dications are coordinated. However, one lithium cation remains in the coordination sphere of the two ligands. To balance the charges one barium atom is still coordinated to a $N(SiMe_3)_2^-$ monoanion. In this mixed-metal complex, the two barium dications are coordinated very differently. Both barium dications coordinate to four nitrogen atoms of the two $S(N^tBu)_3^{2-}$ ligands, but while the coordination sphere of Ba1 is completed by two thf donor molecules, Ba2 still coordinates to one $N(SiMe_3)_2^-$ ligand. Hence, Ba1 displays a distorted octahedral environment while Ba2 shows a distorted square pyramidal coordination polyhedron. The Ba−N distances range from 263.8(6) pm (Ba1−N5) to 284.6(6) pm (Ba2−N2) with an average of 276.4(6) pm. A similar range is found in the barium complex [(thf)$_2$Ba{(NSiMe$_3$)$_2$PPh$_2$}$_2$][23] (274.3(2)−282.3(2) pm). In the barium bis{bis(trimethylsilyl)amide}[21b] the Ba−N distances are much shorter (259 pm), but this is due to the smaller coordination number (4) in this compound.

The Li−N distances in **4** (average 205(2) pm) are slightly elongated compared to those in the lithium complex **1** (average 200.6(4) pm).[11] Unlike the negative charges in other metal-coordinated $S(N^tBu)_3^{2-}$ dianions, those in **4** are not completely delocalized. While the first dianionic cap (S1) shows one longer (S1−N2, 167.2(6) pm) and two shorter (S1−N1(3), 165.2(7) pm, average) S−N distances, the second (S2) shows two longer (S2−N4(6), 165.7(6) pm, average) and one shorter (S2−N5, 161.5(6) pm) S−N distance.

X-ray-suitable crystals of [(thf)LiSn{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}], **5**, are obtained from the thf/hexane solution after few hours' storage at −20 °C. The colorless blocks lose thf upon heating to about 161 °C.

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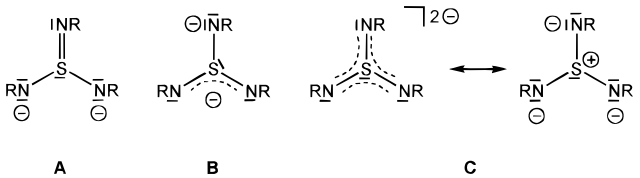
Scheme 3. Electronic Structure of Iminosulphindiamides



Unlike **4**, **5** has a monomeric structure in the solid state (Figure 3). Although one tin dication is coordinated to the $S(N^tBu)_3^{2-}$ ligand, one lithium cation remains in the coordination sphere of the ligand, accompanied by coordination of a $N(SiMe_3)_2^-$ anion. The $N(SiMe_3)_2^-$ anion μ_2 bridges the tin dication and the lithium cation. While the tin atom is three-coordinated, the coordination sphere of the lithium is completed to a distorted coordination tetrahedron by an additional thf donor molecule. This arrangement can be rationalized as an adduct of lithium bis(trimethylsilyl)amide and the target molecule $Sn(N^tBu)_3S$, but the M−N distances (Li1−N4, 220.6(7) pm, and Sn−N, 227.6(3) pm) do not distinguish between a $LiN(SiMe_3)_2$ (Li−N in $LiN(SiMe_3)_2$, 202.4 pm)[25] and a $SnN(SiMe_3)_2$ fragment (Sn−N in $Sn\{N(SiMe_3)_2\}_2$, 209.5 pm).[26] The $S(N^tBu)_3^{2-}$ backbone exhibits two S−N single bonds (S−N2,3, 169.9(3) pm, average) and one S=N double bond (S1=N1, 158.9(3) pm).

Structural Comparison of Iminosulfindiamines $S(NR)_3^{2-}$. A priori the Y-conjugated, pyramidal $S(NR)_3^{2-}$ residue emulates three mesomeric extremes (Scheme 3): **A** might be interpreted as a located double bond to one nitrogen atom, the two negative charges being accumulated at the two other nitrogen atoms. In **B** one negative charge is localized at a singly bound nitrogen atom while the other is delocalized over two nitrogen atom positions. The related S−N bond order for the latter is $1^1/_2$. **C** shows delocalization of both charges over the whole SN_3 skeleton. The associated bond order here would be $1^1/_3$. Obviously this resonance form is not distinguishable from the pure electrostatic model. In fact, it is very likely that this is the major contribution in the description of these anions, not displaying any covalent multiple bonding at all.

All three resonance forms are realized in different complexes, and sometimes two of them are present in the same dimer. The type **C** structure is the most frequent one and is found in the donor-free lithium complex **1** and in all lithium salt adducts.[27] The type **A** localized double bond is found in the mixed-metal complexes **3** and **5** and in the upper dianionic cap of **1**·thf. Pure type **B** structures have not been observed up to now. However, in some structures none of these resonance extremes can be assigned unambiguously. In the mixed-metal (Li, Ba) complex **4** one dianionic cap is more of a type **A** arrangement while the other is rather of type **B**. To assign electron distribution in the SN_3 skeleton unambiguously every complex needs to be calculated by high-level ab initio methods. Several theoretical studies on the bonding situation in sulfur diimides were reported several years ago.[28]

Scheme 4. Geometric Comparison of $S(NR)_3^{2-}$ and $C(NR)_3^{2-}$

Conclusion

Easy metal metatheses of $[Li_4\{(N^tBu)_3S\}_2]$ from reactions with metal(II) halides are hampered by complex redox reactions. These reactions lead to total decomposition of the ligand and to formation of metal(II) amides. The use of metal(II) bis(bis(trimethylsilyl)amides) in metal metathesis reactions with **1** does not result in decomposition, but yields the partially transmetalated complexes **3**−**5**. However, up until now, no complete metal metathesis was observed. Structural investigation of the mixed-metal complexes reveals some intriguing properties of the $S(NR)_3^{2-}$ ligand. The most important features are as follows.

Variable Electronic Structure. Depending on the electronic requirements, different resonance forms of the ligand can be utilized, by which the charges of the coordinated cations are stabilized (Scheme 3).

The electronic requirements of different cations can also be satisfied simultaneously. Therefore, mixed-metal complexes are quite common in the coordination chemistry of this ligand. The electronic flexibility also facilitates stabilization of unusual electronic states such as radicals.

Cap-Shaped Geometry. The coordination chemistry of the iminosulfindiamides is unique among the chelating nitrogen ligands due to the two negative charges and its cap-shaped geometry. In contrast to the $S(NR)_3^{2-}$ dianion the analogous carbon compounds (guanidines $C(NR)_3^{2-}$) are planar (Scheme 4).

While the iminosulfindiamides facilitate cage-type complexes, the corresponding guanidines form polymers,[15] due to their planar structure. The cap-shaped geometry together with the steric demand of the nitrogen bonded substituents should enable the formation of homoleptic metal(II) complexes. Up to now no such complexes of $S(NR)_3^{2-}$ are known. All attempts to obtain pure metal(II) complexes by transmetalation failed so far, because of the ability of the ligand to simultaneously stabilize different cations which are additionally coordinated by the anions of the starting material. Thus, adducts with metal salts are formed by coordination expansion rather than complete transmetalation occurring.

The Lewis Base Character of the Sulfur Atom. Due to its oxidation state the central sulfur atom occupies a stereochemically active lone pair. This lone pair not only causes the tetrahedral geometry, which

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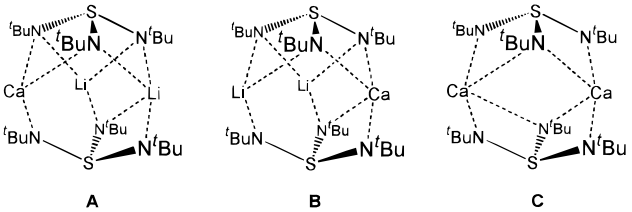
Table 2. Crystal Data and Structure Refinement for 3−5

	3	4	5
empirical formula	$C_{36}H_{78}CaLi_2N_6O_3S_2$	$C_{38}H_{88}Ba_2LiN_7O_2S_2Si_2$	$C_{24}H_{51}LiN_3O_3SSi_2Sn$
fw	761.12	1077.07	643.55
temp (K)	193(2)	153(2)	193(2)
cryst syst	orthorhombic	triclinic	triclinic
space group	*Pccn*	$P\bar{1}$	$P\bar{1}$
a (pm)	1517.00(2)	1178.3(3)	1141.3(2)
b (pm)	1577.24(2)	1281.0(3)	1186.1(2)
c (pm)	1923.09(3)	1974.6(5)	1221.5(2)
α (deg)	90	94.290(10)	93.815(7)
β (deg)	90	104.35(2)	95.791(8)
γ (deg)	90	93.84(2)	101.563(8)
vol (nm^3), *Z*	4.60133(11), 4	2.8681(12), 2	1.6053(5), 2
ρ_c (Mg/m^3)	1.099	1.247	1.331
μ (mm^{-1})	0.264	1.512	0.963
F(000)	1672	1112	674
cryst size (mm)	0.5 × 0.5 × 0.4	0.4 × 0.3 × 0.2	0.5 × 0.4 × 0.4
θ range (deg)	2.14−23.25	3.20−22.50	2.26−25.03
limiting indices	$0 \le h \le 17$	$-12 \le h \le 12$	$-15 \le h \le 15$
	$0 \le k \le 18$	$-13 \le k \le 13$	$-16 \le k \le 15$
	$0 \le l \le 22$	$-14 \le l \le 21$	$0 \le l \le 16$
no. of rflns collected	43 546	7661	14 213
no. of indep rflns	3308	7475	5629
R(int)	0.0642	0.0566	0.077
data/restns/params	3308/799/394	7475/1188/660	5629/105/324
abs corr	semiempirical	semiempirical	semiempirical
transm (max/min)	0.9361/0.9190	0.7851/0.7391	0.7861/0.7348
goodness of fit on F^2	1.095	1.070	1.090
R1 [$I > 2\sigma(I)$]	0.0847	0.0459	0.0466
wR2 (all data)	0.2233	0.1450	0.1264
g1/g2	0.101/8.24	0.084/9.48	0.061/2.51
extinction coeff			0.017(2)
largest diff peak and hole (e nm^{-3})	445 and −546	1788 and −933	2371 and −1252

results in the cap shape of the ligand, but also gives rise to the Lewis base character of the sulfur atom. Hence it should be possible to facilitate S-coordination as well as N-coordination. Some examples for S-coordination are known from the chemistry of sulfur diimides.[29]

Scheme 5. Possible Arrangements in 3



Experimental Section

All manipulations were performed under an inert gas atmosphere of dry N_2 with Schlenk techniques or in an argon glovebox. All solvents were dried over a Na/K alloy and distilled prior to use. NMR spectra were obtained on a Bruker AM 250, Bruker MS 400, or Bruker DMX 300 at 25 °C. Melting points and decomposition temperatures were measured by differential thermal analysis using a DuPont TA 9000 thermal analyzer. Due to the easy oxidizability no meaningful mass spectra could be recorded and no correct elemental analysis was obtained.

[(thf)$_2$Li$_2$Ca{(N^{t}Bu)$_3$S}$_2$], 3. A solution of **1**·thf (2 mmol, 1.18 g) in 5 mL of hexane is added to a solution of calcium bis(bis(trimethylsilyl)amide) (4 mmol, 2.02 g) in 5 mL of thf and stirred for 4 h. Crystals are obtained directly from the reaction mixture upon a few days' storage at room temperature. *M* = 689.00 g/mol. Yield: 0.41 g (30%). Mp: 176 °C. ^{1}H NMR (300 MHz, C_6D_6): δ = 1.39 (s, 27H, ^{t}Bu); 1.26 (m, 4H, thf); 3.63 ppm (m, 4H, thf).

[(thf)$_2$LiBa$_2${N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}$_2$], 4. A solution of **1**·thf (2 mmol, 1.18 g) in 5 mL of hexane is added to a solution of barium bis(bis(trimethylsilyl)amide) (4 mmol, 2.41 g) in 5 mL of thf and stirred for 12 h. Crystals are obtained directly from the reaction mixture upon 2 days' storage at −20 °C. *M* = 1077.00 g/mol. Yield: 1.87 g (87%). Mp: 173 °C dec. ^{1}H NMR (300 MHz, C_6D_6): δ = 0.55 (s, 18H, $SiMe_3$); 1.3−1.4 (m); 3.47 ppm (m, 4H, thf). ^{13}C NMR (75 MHz, C_6D_6): δ = 7.94 (s, Si*C*H$_3$); 25.90 (OCH$_2$*C*H$_2$, thf); 34.14 (C (*C*H$_3$)$_3$); 55.37 (*C*(CH$_3$)$_3$); 68.23 ppm (O*C*H$_2$, thf). ^{29}Si NMR (49 MHz, C_6D_6): δ = −17.79 ppm (s, *Si*(CH$_3$)$_3$).

[(thf)LiSn{N(SiMe$_3$)$_2$}{(N^{t}Bu)$_3$S}], 5. A solution of **1**·thf (2 mmol, 1.18 g) in 5 mL of thf is added to a solution of tin bis(bis(trimethylsilyl)amide) (4 mmol, 1.76 g) in 5 mL of hexane and stirred for 12 h. Crystals are obtained directly from the reaction mixture upon 2 days' storage at −20 °C. *M* = 612.52 g/mol. Yield: 1.81 g (74%). Mp: 161 °C. ^{1}HNMR (300 MHz, C_6D_6): δ = 0.37 (s, 18H, $SiMe_3$); 1.28 (m, 4H, thf); 1.38, 1.43, 1.47 (s, 9H, ^{t}Bu); 3.60 ppm (m, 4H, thf). ^{13}C NMR (75 MHz, C_6D_6): δ = 5.78 (s, Si*C*H$_3$); 24.88 (OCH$_2$*C*H$_2$, thf); 32.63, 32.78 (C(*C*H$_3$)$_3$); 55.26, 55.45 (*C*(CH$_3$)$_3$); 68.10 ppm (O*C*H$_2$, thf).[29] Si NMR (49 MHz, C_6D_6): δ = −11.41 ppm (s, *Si*(CH$_3$)$_3$).

X-ray Measurements of 3−5. Crystal data for the three structures are presented in Table 2. Data of all structures were collected at low temperatures using oil-coated shock-cooled crystals[30] on a Stoe-Siemens AED (**5**) or Stoe-Huber-Siemens-Eigenbau fitted with a Siemens CCD detector (**3** and **4**) using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). A semiempirical absorption correction was applied.[31,32] The structures were solved by Patterson or direct

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methods with SHELXS-96.[33] All structures were refined by full-matrix least-squares procedures against F^2, using SHELXL-96.[34] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The denoted R values are defined as follows:

$$\mathrm{R1} = \sum ||F_o| - |F_c||/\sum |F_o|$$

$$\mathrm{wR2} = \{\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2\}^{1/2}$$

$$w = 1/\{\sigma^2(F_o^2) + [(g1)P]^2 + (g2)P\}$$

$$P = (F_o^2 + 2F_c^2)/3$$

Refinement of **3** was convoluted by more than normal substituent disorder. The structure solution in the orthorhombic space group *Pccn* showed a dimer of two cap-shaped dianions. Refinement of a single calcium site revealed a residual electron density peak at an unoccupied site between the two $S(N^tBu)_3^{2-}$ ligands and severe disorder in the whole molecule. From the crystallographic symmetry it follows that there are three possible arrangements (Scheme 5), but these cannot be assigned unambiguously by X-ray structure analysis. The chemically most plausible explanation was that the lithium cations were not fully exchanged by the metal metathesis reaction with $[(thf)_2Ca\{N(SiMe_3)_2\}_2]$. Due to the necessity of charge balance, not only can the residual electron density be assigned to a lithium cation but the calcium site must be partly occupied by a lithium cation as well. The presence of an arrangement with two calcium dications and no lithium cations in the dimer (**C**) cannot be ruled out, but the best results were obtained by refinement of a 50/50 disorder of the arrangements **A** and **B**.

Therefore, refinement with constrained 50% occupancies was successful. The disorder could be modeled satisfactorily, using distance and similarity restraints. The uncoordinated thf molecule was refined, the space group symmetry being suppressed (2-fold axis). Due to the disorder in the whole molecule, the esd's for the structural parameters are high.

In the refinement of **4**, substituent disorder could be resolved. Three *tert*-butyl groups were refined to split occupancies (C40−C43, 0.73/0.27; C50−C53, 0.72/0.28; C60−C63, 0.56/0.44). Additionally, two coordinated thf molecules were disordered. They could be refined to split occupancies of 0.62/0.38 (O1 C1t−C4t) and 0.52/0.48 (O2 C5t−C8t). Bond length and similarity restraints were used in the refinement of the disorder.

The thf molecule in **5** exhibits a twist disorder. C2t and C3t were refined to a split occupany of 0.45/0.55, using bond length and similarity restraints. Further details on structure investigation can be obtained from the Director of the Cambridge Crystallographic Data Center, 12 Union Rd., GB-Cambridge CB2 1EZ, U.K., by quoting the full journal citation.

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Supporting Information Available: Tables containing details of crystal data and structure refinement, atomic coordinates and equivalent isotropic displacement parameters, bond lengths and angles, anisotropic displacement parameters, and hydrogen coordinates for **3**−**5** (18 pages). X-ray crystallographic files in CIF format for compounds **3**−**5** are available on the Internet only. Ordering and access information is given on any current masthead page.

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