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Triimidosulfonic Acid and Organometallic Triimidosulfonates: $S^{+}{-}N^{-}$ versus $S{=}N$ Bonding

Bernhard Walfort,[†] Angela P. Leedham,[‡] Christopher A. Russell,[‡] and Dietmar Stalke*,[†]

Institut für Anorganische Chemie der Universität Würzburg, Am Hubland, D-97074 Würzburg,
Germany, and School of Chemistry, University of Bristol, Cantock's Close, Bristol BS8 1TS, U.K.

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Sulfonic acids RSO_2OH and their metal salts MO_3SR are versatile catalysts in large-scale industrial cyclization and polymerization processes. Isoelectronic replacement of the oxygen atoms by NR imido groups gives triimidosulfonic acid and triimidosulfonates. The salts form nonaggregated soluble molecules rather than infinite solid-state lattices such as their oxo analogues. In this paper, we present the synthesis and structure of the basic starting material $MeS(N^tBu)_3H$ (**1**), the metal complexes $[Me_2Al(N^tBu)_3SMe]$ (**2**) and $[Zn\{(N^tBu)_3SMe\}_2]$ (**3**), and the mixed metal adduct $[(thf)Li\{(N^tBu)_3SMe\}{\cdot}ZnMe_2]$ (**4**). The chelating coordination, rather than the tripodal coordination, cannot be attributed to steric effects of the S-bonded methyl group, as the less demanding Ph−C≡C−alkynyl substituent at sulfur in $[(thf)_2Li\{(N^tBu)_3SCCPh\}]$ (**5**) causes the same conformation. S−N bond shortening to the pendant imido group has to be attributed to closed-shell electrostatic attraction rather than to S−N double bonding by valence expansion at the central sulfur atom. Coordination to an additional N→Zn dative bond in **4** widens the bond length to values normally interpreted as S−N single bonds. We take this fact as experimental evidence that S−N bonding is predominantly governed by electrostatic interaction rather than by valence expansion employing d-orbitals. This was predicted by theoreticians more than a decade ago.

Introduction

Isoelectronic replacement of the oxygen atoms in the omnipresent p-block element oxoanions SiO_4^{4-}, PO_3^{-}, AsO_3^{3-}, SbO_3^{3-}, PO_4^{3-}, SO_3^{2-}, SeO_3^{2-}, TeO_3^{2-}, or SO_4^{2-} by a NR imido group gives the polyimido anions $Si(NR)_4^{4-}$, $P(NR)_3^{-}$, $As(NR)_3^{3-}$, $Sb(NR)_3^{3-}$, $P(NR)_4^{3-}$, $S(NR)_3^{2-}$, $Se(NR)_3^{2-}$, $Te(NR)_3^{2-}$, or $S(NR)_4^{2-}$.[1] These species are soluble because, contrary to the simple oxoanions, they form contact ion pairs in cage complexes surrounded with a lipophilic layer rather than infinite solid-state lattices by multiple oxygen/cation contacts. Furthermore, their redox potential and coordination behavior is tunable by variation of the organic substituents. An organic substituent might be bonded to the central element in polyimido sulfur anions further broadening the scope of target materials. Sulfonic acids[2] (e.g., triflic acid[3]) or metal sulfonates[4] are outstanding catalysts in large-scale industrial cyclization or polymerization processes, as well as in pharmaceutical production. To date, the *S*-alkyl-,[5] *S*-aryldiimidosulfinates[6] $[RS(NR)_2]^{-}$, and *S*-alkyltriimidosulfonates[7] $[RS(NR)_3]^{-}$ are known in detail. The organic substituent at the sulfur atom in the first species can be deprotonated to give dianionic sulfur ylide imides in which the CR_2 group replaces the oxygen or NR group isoelectronically.[8]

Until recently, the direct reaction of thiols with chloroamines or better bromoamines was the only known synthetic access to *S*-alkyltriimidosulfonates.[9] We present herein a new straightforward synthetic route which involves the nucleophilic addition of lithium alkyls to the S═N formal double bond of sulfurtriimides.[7] Due to the steric crowding in the products from the few known sulfurtriimides ($S(NR)_3$, R = ^tBu, $SiMe_3$), only sterically less demanding alkyls can be added (e.g., MeLi).

[†] Universität Würzburg.

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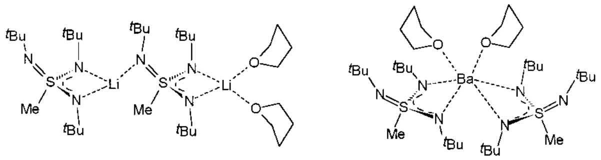
Scheme 1. The Only Known Structures of Metal *S*-Alkyltriimidosulfonates



Addition reactions with ^{n}BuLi and ^{t}BuLi failed. In principle, the resulting $[\mathrm{MeS(NR)_3}]^-$ anion possesses C_{3v} symmetry prompting feasible tripodal cap-shaped metal coordination. While the triimidosulfite $\mathrm{S(NR)_3}^{2-}$ and triimidosulfate $\mathrm{OS(NR)_3}^{2-}$ dianions show this anticipated tripodal behavior even in mixed metal complexes,[10] only $\mathrm{SN_2}$ chelation has been observed for the $[\mathrm{MeS(NR)_3}]^-$ anion.[1j,7]

This paper deals with various strategies to synthesize metal complexes containing the *S*-alkyltriimidosulfonate $[\mathrm{RS(NR)_3}]^-$, even in mixed metal species. The reactivity and structural features of the molecular contact ion pairs clearly favor the closed-shell electrostatic S−N bonding model over S−N double bonding involving valence expansion at the sulfur atom.

Results and Discussion

[M{(N*t*Bu)₃SMe}] Metal Complexes. To date, there are three different routes to *S*-alkyltriimidosulfonate metal complexes. The first involves deprotonation of the *S*-methyl-tri(*tert*-butylimido)-sulfonic acid $\mathrm{MeS(N^tBu)_2NH^tBu}$ (**1**). The deprotonation reagent could be an alkali metal organic compound, but equally it may be a metal amide (eq 1).[7] Second, lithium-*S*-methyl-tri(*tert*-butylimido)sulfonate, $[\mathrm{(thf)Li\{(N^tBu)_3SMe\}}]_2$, is a suitable starting material for transmetalation reactions with metal amides such as $[\mathrm{M\{N(SiMe_3)_2\}_2}]$ (M = Ba, Zn, Sn, Fe) (eq 2).[10] In this paper, we describe for the first time the insertion reaction of sulfurtriimide into the metal−carbon bond of dimethylzinc and trimethylaluminum to give the aluminum- and zinc-*S*-methyl-tri(*tert*-butylimido)sulfonates (eq 3).

Deprotonation:

$$\underset{\mathbf{1}}{\mathrm{MeS(N^tBu)_2NH^tBu}} + \mathrm{RM} \rightarrow [\mathrm{M\{(N^tBu)_3SMe\}}] + \mathrm{RH}\uparrow \qquad (1)$$

Transmetalation:

$$[\mathrm{(thf)Li\{(N^tBu)_3SMe\}}]_2 + [\mathrm{M(NR_2)_2}] \rightarrow [\mathrm{M\{(N^tBu)_3SMe\}_2}] + 2[\mathrm{LiNR_2}] \qquad (2)$$

Insertion:

$$\mathrm{S(N^tBu)_3} + \mathrm{MMe} \rightarrow [\mathrm{M\{(N^tBu)_3SMe\}}] \qquad (3)$$

Synthesis and Structure of the *S*-Methyl-tri(*tert*-butylimido)-sulfonic Acid MeS(N*t*Bu)₂NH*t*Bu (1). Isoelectronic replacement of the oxygen atoms in the sulfonic acid $\mathrm{MeSO_2OH}$ by NR groups gives **1** by protonation of lithium-*S*-methyl-tri(*tert*-butylimido)sulfonate with *tert*-butylammonium chloride in THF at −5 °C (eq 4).

$$[\mathrm{(thf)Li\{(N^tBu)_3SMe\}}]_2 + 2\,{}^t\mathrm{BuNH_3Cl} \rightarrow 2\underset{\mathbf{1}}{\mathrm{MeS(N^tBu)_2NH^tBu}} + 2\mathrm{LiCl} + 2\,{}^t\mathrm{BuNH_2} \qquad (4)$$

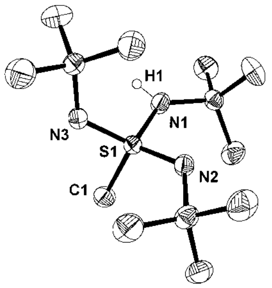


Figure 1. Solid-state structure of $\mathrm{MeS(N^tBu)_2NH^tBu}$ (**1**); anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (pm) and angles (deg) are presented in Table 1.

Recently, we found that two molecules of the triimidosulfonic acid **1** rearrange into one di(*tert*-butyl)diimine and two *S*-methyl-di(*tert*-butyl)diimidosulfinic acid molecules, $\mathrm{MeS(N^tBu)NH^tBu}$, at room temperature.[7] However, performing the preparation at −5 °C gave crystalline **1** in 76% yield. Colorless crystals of the pure *S*-methyl-tri(*tert*-butylimido)sulfonic acid with a decomposition point of ca. 80 °C could be obtained. Surprisingly, the crystal structure shows separated molecules (Figure 1), whereas a N−H···N hydrogen-bonded network was anticipated. The central sulfur atom is tetrahedrally coordinated and slightly displaced from the center of the tetrahedron toward the $\mathrm{N_3}$ face (av N−S−N 112.9°; av C−S−N 105.4°). The C2−N1(H1)−S1−N3 −C6 moiety is almost ideally planar (mean esd from best plane 9.17 pm) and arranged in an E/Z type of orientation to minimize steric strain between the N3 lone pair and the N1-bonded hydrogen atom. The third ^{t}Bu group points away from the methyl group down toward the N3 plane. The S1−N1 bond of 164.77(11) pm is significantly longer than the two others (S1−N2 152.24(12) and S1−N3 151.57(11) pm). Both S−N distances match the range normally defined as a S−N single and S═N double bond, respectively. The position of the N(H1) hydrogen atom was taken from the difference Fourier map and refined freely with no evidence of any disorder. The S1−C1 distance of 179.04(13) pm is also typical for a S−C single bond.

Insertion of Sulfurtriimide into the Metal−Carbon Bond of Trimethylaluminum and Dimethylzinc. Addition of ionic methyllithium across the formal S═N double bond in sulfurtriimides, $\mathrm{S(NR)_3}$, yields the lithium-*S*-methyl-triimidosulfonate. This reactivity is not surprising in view of the $\mathrm{S}^{\delta+}$ charge. Addition of other lithium organics such as ^{n}BuLi, ^{t}BuLi, or PhLi failed presumably because of steric crowding in the sulfonates. In our quest to introduce metals other than lithium, we expected the electrophilicity of the central sulfur atom to be high enough to be substituted by even more covalent-bonded metal organics such as $\mathrm{AlMe_3}$ or $\mathrm{ZnMe_2}$. Formally, this would be an insertion into a metal−carbon bond rather than an addition of ionic MeLi across the formal S═N double bond. In fact, $\mathrm{AlMe_3}$ reacted with $\mathrm{S(N^tBu)_3}$ in a 1:1 ratio (eq 5), while 1 equiv of $\mathrm{ZnMe_2}$ reacted with 2 equiv of sulfurtriimide (eq 6). The triimide is inserted into only one of the three present Al−C bonds, while it is inserted into both of the Zn−C bonds. With $\mathrm{AlMe_3}$, other stoichiometries always result in the same product $[\mathrm{Me_2Al(N^tBu)_3SMe}]$ (**2**). In $[\mathrm{Zn\{(N^tBu)_3SMe\}_2}]$ (**3**), the central zinc atom is exclusively coordinated by four nitrogen atoms. In the reaction sequence of initially adding MeLi and then $\mathrm{ZnMe_2}$, the lithium organic first adds across the formal S═N double bond to give the lithium-*S*-methyl-triimidosulfonate. The third available ^{t}BuN group coordinates to the $\mathrm{ZnMe_2}$ to afford the mixed metal

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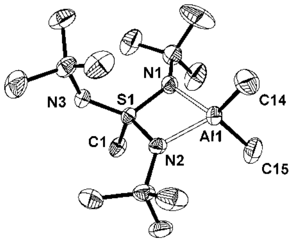
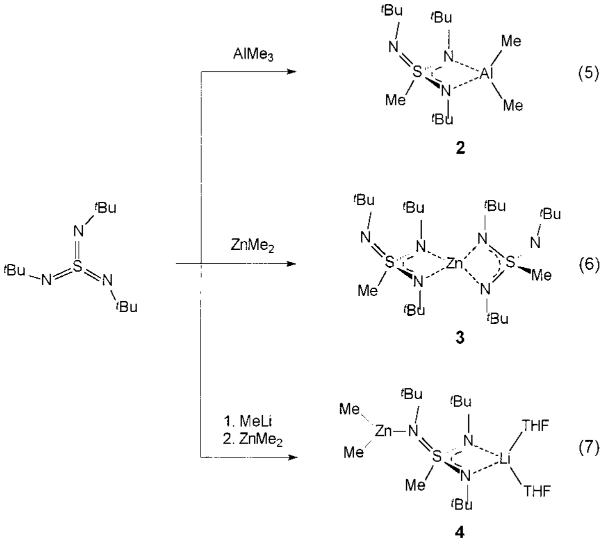


Figure 2. Solid-state structure of $[Me_2Al\{(N^tBu)_3SMe\}]$ (**2**); anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (pm) and angles (deg) are presented in Table 1.

triimidosulfonate $[(thf)_2Li\{(N^tBu)_3SMe\}\cdot ZnMe_2]$ (**4**) according to eq 7.



Structures of $[Me_2Al(N^tBu)_3SMe]$ (2), $[Zn\{(N^tBu)_3SMe\}_2]$ (3), and $[(thf)_2Li\{(N^tBu)_3SMe\}\cdot ZnMe_2]$ (4). The crystal structure of **2**, depicted in Figure 2, shows the *S*-methyl-tri(*tert*-butylimido)sulfonate chelating the cationic dimethylaluminum moiety with two nitrogen atoms of the N^tBu groups. The negative charge is delocalized over the chelating SN_2 backbone, indicated by the almost ideal planar arrangement of the C2−N1−S1−N2−C6−Al1 part (mean deviation from the best plane is only 9 pm). Both S−N bond distances in the SN_2-Al four-membered ring are equal within esd's (160.3(2) pm) and are significantly longer than the S−N distances to the pendant N^tBu group of 150.8(2) pm. The latter is the shortest known S−N bond length in triimidosulfonates and is even shorter than the S−N distances in sulfurdiimides ($S({=}N^tBu)_2$[11a] av 153.8 pm; $S({=}NSiMe_3)_2$[11b] av 152.0 pm) and is comparable with sulfurtriimides ($S({=}N^tBu)_3$[11c] av 150.4 pm; $S({=}NSiMe_3)_3$[11c] av 151.5 pm). In the lithium[1j] and barium[4] triimidosulfonates, the S−N(M) and S═N distances are on average 157.3 and 153.7 pm, respectively. The average Al−N bond lengths in **2** of 191.0(2) pm are significantly longer than in aluminum amides such as $[Al\{N(SiMe_3)_2\}_3]$[12] (178.0 pm) or $[(Et_2O)_2LiAlH_3\{N(SiMe_3)_2\}]$[13] (185.8 pm), but they fit the distances where the Me_2Al^+ cationic moiety is additionally chelated by two nitrogen atoms.[14] In the dimeric metallacycle $[Me_2AlN\{(CF_3)_2C_6H_3\}S(O)^tBu]_2$, the dimethyl-substituted aluminum atoms are coordinated by a nitrogen atom next to a sulfur atom and an oxygen atom with S−N and Al−N bond lengths of 161.5(2) and 193.2(2) pm, respectively.[15] Further bond lengths and angles are presented in Table 1 in direct comparison to structures **2**−**5**.

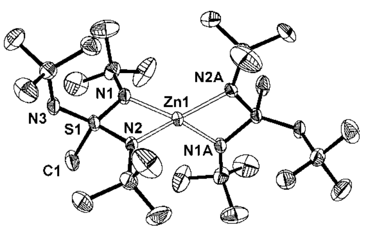


Figure 3. Solid-state structure of $[Zn\{(N^tBu)_3SMe\}_2]$ (**3**); anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (pm) and angles (deg) are presented in Table 1.

Table 1. Selected Bond Lengths (pm) and Angles (deg) of **1**−**5**

	1 M = H	**2** M = Al	**3** M = Zn	**4** M = Li, Zn	**5** M = Li
S1−C1	179.04(13)	178.1(2)	178.3(4)	180.0(2)	171.8(3)
C1−C2					116.9(4)
C2−C3					140.7(4)
S1−N1	164.77(11)	160.52(19)	160.2(3)	156.07(17)	151.3(2)
S1−N2	151.57(11)	160.12(18)	159.3(3)	156.22(17)	167.0(3)
S1−N3	152.24(13)	150.72(18)	151.9(3)	158.06(18)	154.4(3)
M−N1	84.4(19)	190.95(19)	201.9(3)	201.4(4)	214.6(7)
M−N2		191.0(2)	200.4(3)	200.0(4)	196.7(6)
M−N3				213.74(17)	
M−C		195.8(3)		199.1(3)	
M−C		196.8(3)		198.6(3)	
N1−S1−N2	101.87(6)	91.38(9)	94.35(14)	98.23(9)	96.97(14)
N2−S1−N3	127.43(6)	122.76(10)	122.69(17)	119.70(9)	127.98(13)
N1−S1−N3	109.41(6)	122.68(10)	123.21(17)	119.92(9)	117.99(14)
C1−S1−N1	104.05(6)	110.32(10)	108.59(18)	110.45(10)	113.34(13)
C1−S1−N2	112.92(6)	108.89(10)	108.53(18)	109.70(10)	109.20(15)
C1−S1−N3	99.28(6)	100.55(10)	98.94(16)	98.89(10)	91.75(13)
N1−M−N2		73.83(8)	71.27(11)	72.05(14)	70.8(2)
C−M−C		115.21(13)		131.64(13)	

The aluminum atom in $[Me_2Al(N^tBu)_3SMe]$ (**2**) shows a distorted tetrahedral geometry coordinating two methyl groups and two nitrogen atoms of the *S*-methyltriimidosulfonate. The methyl groups at the aluminum atom are neither chemically nor magnetically equivalent; this is reflected in the marginally different aluminum−carbon bond lengths (196.8(3) and 195.8(3) pm) and two single resonances in the ^1H NMR spectrum at $\delta = -0.921$ and -0.915. There are considerable steric interactions between the pendant ^tBuN group and the aluminum-bonded methyl group (C14, Figure 2) on the same side of the N_3 plane, resulting in different S1···Al1−C angles of 127.3° (C14) and 117.8° (C15), respectively.

The structure of $[Zn\{(N^tBu)_3SMe\}_2]$ (**3**) is shown in Figure 3, and selected bond lengths and angles are compiled in Table 1. The zinc atom is coordinated tetrahedrally by four nitrogen atoms of two chelating sulfonate anions, while both methyl groups of the $ZnMe_2$ starting material are transferred to the electrophilic sulfur atom. As in **2**, the C2−N1−S1−N2−C6−Zn1 group of **3** is almost ideally planar with a mean deviation from the best plane of only 3.4 pm. Both symmetry-independent

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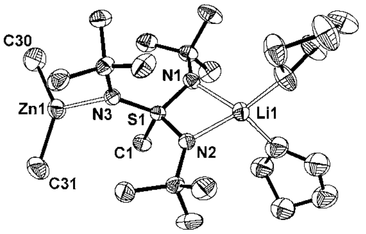

Figure 4. Solid-state structure of $[(thf)_2Li\{(N^tBu)_3SMe\}\cdot ZnMe_2]$ (**4**); anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (pm) and angles (deg) are presented in Table 1.

S−N bond distances in the SN_2Zn four-membered rings are equal within esd's (av 159.2(3) pm). The S1−N3 bond is 7.9 pm shorter and is closer to the distance defined as a S═N double bond. The two symmetry-independent Zn−N bond distances in the two orthogonal SN_2Zn four-membered rings are only marginally different (Zn1−N1 201.86(18) and Zn1−N2 200.38(18) pm). These values are between those in zinc amides such as $[Zn\{N(SiMe_3)_2\}_2]$[16] (182 pm in the gas phase) and Zn←N dative bonds[17] (212−216 pm) and are similar to the values found in $[MeZnPy_2CH]_2$[18] (204 pm). In $[EtZnN(Me)S(O)PhCH_2O]_2$,[19] the Zn−N bond distance is 210.0 pm, while the S−N bond is 152.8 pm long. It is important to mention that each single molecule of **3** is chiral along the S1···Zn1···S1*A* axis. According to the Cahn−Ingold−Prelog rules, it adopts *P* chirality. However, the compound crystallizes in a centrosymmetric space group as a racemate.

The structure of $[(thf)_2Li\{(N^tBu)_3SMe\}\cdot ZnMe_2]$ (**4**) is shown in Figure 4, and selected bond lengths and angles are listed in Table 1. In common with the metals in **2** and **3**, the triimidosulfonate chelates the lithium cation via two nitrogen atoms of the imido groups. The C2−N1−S1−N2−C6−Li1 moiety is planar (mean deviation from the best plane is only 8.13 pm). Both S−N bond distances of the chelating SN_2 backbone in the SN_2Li four-membered ring are equal within esd's (156.1(2) pm) and are almost identical to those found in the dimeric $[(thf)Li\{(N^tBu)_3SMe\}]_2$.[1j] The third imido group in **4** is no longer a pendant spectator ligand but is involved in donation to the neutral $ZnMe_2$ organometallic group. Like the lithium cation, the zinc atom is located at the N1−S1−N2 bisection. The bridging of the N3 nitrogen atom between the electropositive Zn metal and sulfur atoms causes charge density to shift from the sulfur to the metal and results in a substantial S1−N3 bond lengthening. If the short S−N bond to the pendant imido nitrogen atom N3 in **2** and **3** (av 151 pm) was suggesting some double bond character, the related bond in **4** now is 158.06(18) pm long and is almost as long as the S−N(M) bonds in **2** and **3**.

The Zn1←N3 dative bond of 213.74(17) pm is about 13 pm longer than the Zn−N contacts in **3**, although the coordination number decreases to three. In the known structures of $ZnMe_2$ with bidentate nitrogen donor bases, the Zn atom is tetrahedrally coordinated and the Zn←N bond length spans the range from 220 pm in $[Me_2Zn\{N(^tBu)CH\}_2]$[20a] to 228 pm in $[Me_2Zn\{N(Me_2)CH_2\}_2]$.[20b] $[(thf)_2Li\{(N^tBu)_3SMe\}\cdot ZnMe_2]$ (**4**) is the first structural example containing a tricoordinate zinc atom in a dimethylzinc adduct with only one Zn←N bond.[21]

Lithium-*S*-phenylalkynyl-*N*,*N′*,*N″*-tri(*tert*-butylimido)sulfonate $[(thf)_2Li\{(N^tBu)_3SCCPh\}]$ (5). In all known metal complexes, the methyltriimidosulfonate chelates as a bidentate ligand, although tripodal coordination occurs with the triimidosulfite[1j,22] $[S(N^tBu)_3]^{2-}$ and the triimidosulfate[22,23] $OS(N^tBu)_3{}^{2-}$. In these dianions, tripodal coordination is facilitated by all *tert*-butyl groups pointing toward the lone pair of the sulfur atom, leaving all lone pairs of the nitrogen atoms pointing in the opposite direction. This is also valid for the $MeSi(N^tBu)_3{}^{3-}$ trianion. All *tert*-butyl groups are oriented toward the methyl group at the silicon atom. Hence, all nitrogen atoms are exposed to lithium coordination in the dimeric cage structure of $[Li_6\{(N^tBu)_3SiMe\}_2]$.[24] This arrangement is possible because the Si−N bonds are considerably longer (174 pm) than the S−N bonds in the systems reported here (160 pm). Furthermore, the Si−N−C angles are wider (av 130°) than the S−N−C angles in $MeS(N^tBu)_3{}^-$ (120−125°), allowing the methyl group at the central silicon atom to be sterically unrestrained. Similar orientation of the *tert*-butyl groups in $MeS(N^tBu)_3{}^-$ is not possible due to steric crowding. The anion minimizes steric strain by turning one *tert*-butyl group away from the methyl group down to the N_3 face and by blocking one nitrogen atom from tripodal metal coordination.

To achieve tripodal coordination, we aimed to minimize the steric demands of the sulfur-bonded organic group. An alkynyl group R−C≡C− seemed a good choice since an sp-hybridized carbon atom is smaller in radius than an sp^3 carbon atom,[25] and the linear C_2 chain should shift the substituent R out of reach of the ^tBuN groups. To synthesize the target molecule, in the first step phenylacetylene is lithiated in situ with butyllithium. To this solution, tri(*tert*-butyl)sulfurtriimide $S(N^tBu)_3$ is added slowly at −78 °C. The reaction temperature must be kept below −20 °C. At a slightly higher temperature, the product decomposes and mainly polymerization occurs. In addition, the product $[(thf)_2Li\{(N^tBu)_3SCCPh\}]$ (**5**) is extremely air sensitive (eq 8).

$$PhCCLi + S(N^tBu)_3 \rightarrow \underset{\mathbf{5}}{[(thf)_2Li\{(N^tBu)_3SCCPh\}]} \quad (8)$$

Storage of the cold filtered reaction solution at −36 °C for 3 days yields green-yellow crystals. They were transferred to the diffractometer at −80 °C. The solid-state structure (Figure 5) of the lithium-*S*-phenylalkynyl-tri(*tert*-butylimido)sulfonate (**5**) shows that tripodal coordination does not occur to the lithium cation. Like the methyl derivatives, this anion coordinates in a bidentate fashion with only two nitrogen atoms to the metal. Comparison with the tripodal $OS(N^tBu)_3{}^{2-}$ dianion suggests that

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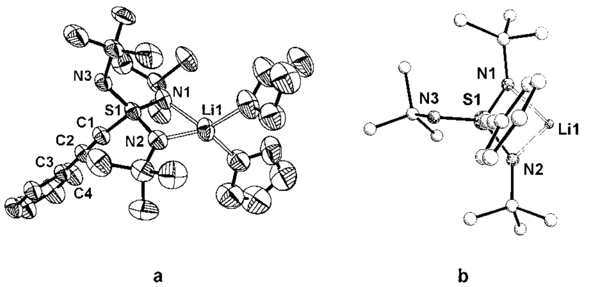

Figure 5. Solid-state structure of $[(thf)_2Li\{(N^tBu)_3SCCPh\}]$ (**5**); (a) shows the molecule similar to the projections of **1**−**4**, (b) shows the N_3 face in the paper plane and the orientation of the phenylalkynyl substituent in conjugation to the S1−N1 bond. Anisotropic displacement parameters are depicted at the 50% probability level. Selected bond lengths (pm) and angles (deg) are presented in Table 1.

tripodal coordination is primarily caused by the higher negative charge rather than by steric effects. Hence, for a single negative charge in the triimidosulfonates, it is sufficient to be delocalized in two S−N bonds, while for a double negative charge in the triimidosulfites and -sulfates, three S−N bonds are required.

The intriguing structure of $[(thf)_2Li\{(N^tBu)_3SCCPh\}]$ (**5**) sheds light upon the charge density distribution in the SN_2Li kite-shaped four-membered ring. While the four S−N(Li) bonds in the lithium-*S*-methyl-tri(*tert*-butylimido)sulfonate dimer $[(thf)Li\{(N^tBu)_3SMe\}]_2$ are equal and on average 157.2 pm long, the two related distances in **5** differ by 15.7 pm (S1−N1 151.3(2) and S1−N2 167.0(3) pm). Although N1 is coordinated to a lithium cation, the S1−N1 distance in **5** is as short as the S−N3 bonds in the pendant noncoordinated ^{t}BuN groups in **2** and **3** and as in sulfurdiimides.[11] The S1−N2 bond in the metallacycle of **5** is even longer than the S−N(H)^{t}Bu single bond in **1** (164.77(11) pm). This asymmetry is reflected in the Li−N bond distances. In the methyl derivative, they were approximately equal and on average 199.3 pm long. In **5**, however, they differ by 17.9 pm (Li1−N1 214.6(7) and Li1−N2 196.7(6) pm). The lithium cation is considerably shifted toward N2 which is remote from the sulfur. The orientation of the phenylalkynyl substituent relative to the SN_2Li four-membered ring explains the asymmetry. The phenyl group is in plane with the short N1−S1 bond (see Figure 5b) and, consequently, couples electronically via the C1≡C2 triple bond to the negative charge at the N1 nitrogen atom. Conjugation to the phenylalkynyl substituent results in S−N bond shortening. While the short S−C1 bond in **5** (171.8(3) pm) can be attributed to the ca. 8 pm smaller radius of the sp carbon atom compared to the sp^3 carbon atom in **1**−**4** (av $S-CH_3$ 179.2 pm), the C1≡C2 bond of 116.9(4) pm is significantly shorter than a standard C≡C triple bond (120.2 pm). The same is valid for the C2−C3 distance of 140.7(4) pm (standard C(sp^2)−C(sp) single bond: 143.2 pm). The $C_{ipso}-C_{ortho}$ bond above the S1−N1 bond is 8.4 pm shorter than the other. All of this indicates that the electron density is shifted from the N1 nitrogen atom toward the phenylalkynyl substituent. This leaves N1 unattractive to the lithium cation resulting in a long Li−N bond. To get electronically saturated, the lithium cation needs closer contact to N2, but this obviously causes elongation of the S1−N2 bond. As the negative charge density of N2 is required by the metal, it cannot result in electrostatic $S^{\delta+}-N^{\delta-}$ bond shortening. Electronic deficiency at sulfur is substituted by N3 of the pendant ^{t}BuN group, and, hence, the S1−N3 distance is as short as the related distance in $[(thf)Li\{(N^tBu)_3SMe\}]_2$.

Conclusions from the Structural Comparisons. To date, all known complexes of the triimidosulfonate monoanion chelate the metal in a bidentate rather than a tripodal fashion. The two adjacent ^{t}Bu substituents are in plane with the SN_2M four-membered ring, while the third is twisted toward the open N_3 face. From these studies, the possibility that this is caused by steric crowding about the S-bound substituent can be excluded. The phenylalkynyl group in **5** would give enough room for the third ^{t}BuN group to flip toward the S-bonded substituent and release the N3 plane for tripodal metal coordination. It is obvious now that two S−N bonds are sufficient to delocalize a single negative charge. The two chelating S−N bonds are elongated relative to that of the pendant ^{t}BuN− group as the metal and the electropositive sulfur atom compete for the negative charge of the imido nitrogen atom. Consequently, the nonchelating S−N arm is shortened by electrostatic attraction. However, the Lewis basicity of the lone pair at the pendant imido nitrogen atom is high enough to be employed in N→M dative bonding in mixed metal complexes as shown in **4**. The sulfur/metal competition lengthens the bond to a distance similar to the S−N(H)^{t}Bu amido bond found in **1**. It is interesting to note that the sum of all three S−N bonds in all known metal complexes (M = Li, Ba, Al, Zn) and in the triimidosulfonic acid **1** is constant at 470(2) pm. The SN_3 unit responds flexibly to different electronic requirements induced by either different metal cations (**2**−**4**) or conjugated S-substituents (**5**) in terms of the sulfur atom being shifted relative to an otherwise fixed N_3 environment. This experimentally emphasizes the predominantly ionic S−N bonding rather than valence expansion and d-orbital participation in bonding.[26] Assuming a classical S═N double bond in polyimido sulfur species would not explain the facile NR transfer in transimidation reactions with this class of compounds.[8b,10,27] If there is much ionic contribution and negative hyperconjugation as anticipated from the computational chemistry,[26] then polyimido sulfur compounds would indeed act as NR transfer reagents. From this knowledge, the differentiation of the mechanisms of reaction in nucleophilic addition of organometallics and the insertion in the metal−carbon bond seems arbitrary. In the course of the reaction, most likely the metal center will be coordinated by the negatively charged imido nitrogen atom, followed by a 1,3 migration of the methanide anion to the electropositive sulfur atom.

Experimental Section

All manipulations were performed under an inert-gas atmosphere of dry N_2 with Schlenk techniques or were performed in an argon glovebox. All solvents were dried over Na/K alloy and were distilled prior to use.

NMR data were obtained from a Bruker AMX 400 and a Bruker AMX 300 instrument in the FT mode in C_6D_6 solvent. Elemental analyses were performed by the Microanalytisches Labor der Universität Würzburg.

Syntheses. $S(N^tBu)_3$ and $[(thf)_2Li_2\{(N^tBu)_3SMe\}_2]$ were obtained as described previously in ref 23.

$H(N^tBu)_3SMe$ (1). A suspension of *tert*-butylammonium chloride (8 mmol, 0.88 g) in THF (10 mL) was added at −5 °C to a solution of $[(thf)_2Li_2\{(N^tBu)_3SMe\}_2]$ (4 mmol, 2.72 g) in THF (10 mL) and was stirred for 1 h. All of the volatile material was removed under vacuum, and pentane was added to the residue. After filtration of lithium chloride, most of the pentane was removed in vacuo. After storage of the oily solution at −36 °C for 2 d, colorless crystals were obtained and used for structure determination. Total isolation yielded 0.8 g (76%) of $H(N^t$-

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Table 2. Crystal Data and Structure Refinement for Complexes **1**−**5** at $T = 173(2)$ K

	1	**2**	**3**	**4**	**5**
empirical formula	$C_{13}H_{31}N_3S$	$C_{15}H_{36}AlN_3S$	$C_{26}H_{60}N_6S_2Zn$	$C_{23}H_{52}LiN_3O_2SZn$	$C_{56}H_{96}Li_2N_6O_4S_2$
fw	261.47	317.51	586.29	507.05	995.39
CCDC no.	163257	163258	163259	163260	163261
space group	*Cc* (No. 9)	$P2_1/c$ (No. 14)	*I*2/*a* (No. 15)	$P2_1/c$ (No. 14)	$P2_1/n$ (No. 14)
a [pm]	914.20(18)	1064.2(2)	1790.4(4)	1076.50(7)	1002.4(2)
b [pm]	2236.7(5)	1644.7(3)	878.48(18)	1763.96(12)	1808.5(4)
c [pm]	904.06(18)	2344.1(5)	2120.4(4)	1534.56(11)	1694.6(3)
β [°]	117.08(3)	92.39(3)	98.40(3)	93.3720(10)	94.53(3)
V [nm^3], *Z*	1.6459(6), 4	4.099.1(14), 8	3.2993(12), 4	2.9089(3), 4	3.0624(11), 2
D_c [Mg m^{-3}]	1.055	1.029	1.180	1.158	1.079
μ [mm^{-1}]	0.185	0.198	0.894	0.937	0.132
θ range [°]	2.66−28.08	2.41−24.73	2.51−26.38	1.76−26.42	2.33−24.72
data/restraints/parameter	3789/92/169	7001/30/416	3347/150/200	5891/140/384	5192/384/443
R1^a [$I > 2\sigma(I)$]	0.0260	0.0357	0.0322	0.0410	0.0587
wR2^b (all data)	0.0687	0.0910	0.0711	0.1074	0.1674
largest diff. peak and hole [e nm^{-3}]	173, −206	199, −263	319, −415	425, −194	429, −444

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$ with $w = 1/\sigma^2(F_o^2) + (g_1P)^2 + g_2P$; $P = (\max(F_o^2,0) + 2F_c^2)/3$.

Bu)$_3$SMe (**1**). $M = 261.5$ g/mol; mp 18 °C. Elemental analyses $C_{13}H_{31}N_3S$ (261.5). Calcd: C, 59.71; H, 11.95; N, 16.07; S, 12.26. Found: C, 58.63; H, 11.42; N, 15.74; S, 12.44. ^{1}H NMR (400 MHz, C_6D_6): δ 1.37 [s, 27H, ^{t}Bu], 2.79 [s, 3H, CH_3], 2.80 [s, 1H, NH]. ^{13}C (C_6D_6): δ 32.21 [C(CH$_3$)$_3$], 52.12 [NC(CH$_3$)$_3$], 53.33 [SCH$_3$]. IR (Nujol) [cm^{-1}]: 3395.1 N(H), 3070−2860 (Nujol), 1465.6, 1408.8, 1379.3, 1356.6, 1300.3, 1247.5, 1129.4, 1024.0, 966.3, 941.9, 848.2, 829.8, 818.1, 745.5.

[Me$_2$Al{(N^{t}Bu)$_3$SMe}] (2). To a solution of 0.98 g (4.00 mmol) of tri(*tert*-butyl)sulfurtriimide in 20 mL of tetrahydrofuran was added dropwise 2 mL of a 2 M Me$_3$Al solution in diethyl ether. The color of the solution changed instantaneously from yellow to colorless. After 3 h of stirring, 80% of the THF was removed in vacuo. After storage of the clear solution at −26 °C for 3 d, colorless crystals were obtained and used for the structure determination. After filtration, 0.84 g (66%) of dimethylaluminum-methyl(tri-*tert*-butylimido)sulfonate was isolated. $M = 317.4$ g/mol; mp 133 °C. Elemental analyses. Calcd: C, 56.74; H, 11.43; N, 13.24; S, 10.10. Found: C, 57.92; H, 12.18; N, 12.93; S, 10.19. ^{1}H NMR (400 MHz, C_6D_6): δ −0.921, −0.915 [s, 6H, Al(CH_3)$_2$], 1.26 [s, 18H, −NC(CH_3)$_3$], 1.27 [s, 9H, =NC(CH_3)$_3$], 3.11 [s, 3H, SCH_3]. ^{13}C (C_6D_6): δ 30.07, 30.89 [−NC(CH$_3$)$_3$], 31.11 [=NC(CH$_3$)$_3$], 49.14, 50.24 [−NC(CH$_3$)$_3$], 51.51 [SCH$_3$], 53.39 [=NC(CH$_3$)$_3$].

[Zn{(N^{t}Bu)$_3$SMe}$_2$] (3). To a solution of 2.50 g (10.20 mmol) of tri-(*tert*-butyl)sulfurtriimide in 20 mL of tetrahydrofuran was added dropwise 2.55 mL of a 2 M Me$_2$Zn solution in diethyl ether. After 3 h of stirring, the volume of the solution was reduced by one-half, and 10 mL of hexane was added. Colorless crystals were grown by storage of the solution at −26 °C for 3 days and were used for structure determination. After filtration, 1.93 g (64%) of zinc-di-*S*-methyl-tri-(*tert*-butylimido)sulfonate was isolated. $M = 586.3$ g/mol; mp 186 °C. Elemental analyses. Calcd: C, 53.26; H, 10.32; N, 14.34; S, 10.94. Found: C, 52.24; H, 10.16; N, 13.25; S, 11.13. ^{1}H NMR (400 MHz, C_6D_6): δ 1.41 [s, 18H, −NC(CH_3)$_3$], 1.50 [s, 18H, −NC(CH_3)$_3$], 1.61 [s, 18H, =NC(CH_3)$_3$], 2.96 [s, 3H, SCH_3]. ^{13}C (C_6D_6): δ 31.91, 32.05 [−NC(CH$_3$)$_3$], 32.31 [=NC(CH$_3$)$_3$], 50.65, 51.34 [−NC(CH$_3$)$_3$], 51.04 [SCH$_3$], 52.55 [=NC(CH$_3$)$_3$].

[(thf)$_2$Li{(N^{t}Bu)$_3$SMe}·ZnMe$_2$] (4). To a solution of 2.00 g (8.16 mmol) of tri-(*tert*-butyl)sulfurtriimide in 20 mL of tetrahydrofuran was added dropwise 5.10 mL of a 1.6 M MeLi solution in diethyl ether. Subsequently, after the solution was stirred for 1 h, 4.08 mL of a 2 M Me$_2$Zn solution in diethyl ether was added. After 3 h of stirring, 50% of the THF was removed, and 10 mL of hexane was added. While the solution was stored at −26 °C for 3 d, colorless crystals were obtained and were used for structure determination. After filtration, 3.2 g (77%) of lithium-*S*-methyl-tri(*tert*-butylimido)sulfonate-dimethylzinc adduct was isolated. $M = 507.3$ g/mol; mp 86 °C dec. Elemental analyses. Calcd: C, 54.48; H, 10.34; N, 8.29; S, 6.32. Found: C, 52.12; H, 9.22; N, 9.07; S, 6.89. ^{1}H NMR(400 MHz, C_6D_6): δ −0.39 [s, 6H, ZnMe$_2$], 1.39 [s, 27H, NC(CH_3)$_3$], 1.34 [q, 8H, THF], 3.53 [t, 8H, THF], 3.16 [s, 3H, SCH_3]. ^{13}C (C_6D_6): δ −9.57 [ZnMe$_2$], 32.09 [NC(CH$_3$)$_3$], 51.75 [NC(CH$_3$)$_3$], 24.21 [THF], 66.64 [t, 8H, THF], 47.23 [SCH$_3$]. ^{7}Li (155 MHz, C_6D_6): δ 0.56.

[(thf)$_2$Li{(N^{t}Bu)$_3$SCCPh}] (5). To a solution of (22.76 mmol, 2.32 g) phenylacetylene in 20 mL of THF was slowly added 11.40 mL of a 2 M solution of ^{n}butyllithium (22.76 mmol) at −78 °C, and the reaction mixture was stirred for 1 h. To this solution was slowly added tri-(*tert*-butyl)sulfurtriimide (22.76 mmol, 5.8 g). The temperature must be held below −20 °C. At slightly higher temperatures, the product decomposes as indicated by a change of color from yellow to orange, to brown, and then finally to a green solution. Next, 50% of the THF was removed in vacuo. After storage of the concentrated solution at −36 °C for 3 days, yellow crystals were obtained and used for structure determination. Because of the air sensitivity and thermolability at temperatures higher than −20 °C, no further analytical data could be obtained.

Crystal Structure Determinations. Crystal data for the structures **1**−**5** are presented in Table 2. Data for structures **1**−**3**, **5** were collected on a Stoe IPDS and for **4** were collected on a Bruker Smart Apex with a D8 goniometer at low temperature using oil-coated shock-cooled crystals[28] and Mo−Kα radiation ($\lambda = 0.71073$ Å). The structures were solved by direct methods using SHELXS 97.[29] The structures were refined by full-matrix least-squares procedures on F^2 using SHELXL 97.[30] All non-hydrogen atoms were refined anisotropically, and a riding model was employed in the refinement of the hydrogen atom positions. The position of the N-bound atom H1 in **1** was taken from the difference Fourier map and was refined freely. Refinement of the Flack *x* parameter[31] in **1** to 0.00(1) confirms the right absolute structure. In complex **3**, one disordered *tert*-butyl moiety (C2−C5) was refined to a split-site occupation factor of 0.20/0.80. In complex **4**, both disordered thf molecules were refined to split occupancies of 0.45/0.55 and 0.30/0.70. Similarly, in compound **5**, one *tert*-butyl group (0.55/0.45) and both thf molecules (0.55/0.45 and 0.50/0.50) are disordered. In all these refinements, bond length and similarity restraints were applied. Other crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Center as supplementary publication (CCDC numbers see Table 2). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. [fax (internat.) + 44(1223)336−033; E-mail deposit@ccdc.cam.ac.uk].

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Supporting Information Available: Five X-ray crystallographic files, in CIF format, are available. This material is available free of charge via the Internet at http://pubs.acs.org.

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