π-Spacer-coupled Diimidosulfinates

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Z. Naturforsch. **2010**, *65b,* 711 – 718; received February 9, 2010

To synthesize ligands that are capable of coordinating two metals, 1,4-dilithiumbenzene and 4,4′-dilithiumbiphenyl were reacted with different sulfurdiimides to give coupled diimidosulfinates. $[(THF)_4Li_2\{(NSiMe_3)_2S\}_2$biphenyl] (**1**) and $[(THF)_{1.5}Li_2\{(NSiMe_3)_2S\}_2$biphenyl$]_\infty$ (**2**) could be isolated and structurally characterized. While **1** forms distinct molecules in the solid state, **2** crystallizes in infinite chains. The lithium complex with a benzene group as spacer could not be isolated due to co-complexed lithium bromide. Subsequent metal exchange reactions with dimethylaluminum chloride afforded $[\{Me_2Al(N^tBu)_2S\}_2$biphenyl] (**3**) and $[\{Me_2Al(NSiMe_3)_2S\}_2(C_6H_4)]$ (**4**).

Key words: Sulfur, Imide, Aromatic Spacers, Lithium, Aluminum

Introduction

Heterobimetallic complexes are known to be excellent catalysts for a variety of reactions [1 – 7]. The main areas of application are the polymerization of various alkenes [8 – 10] and the catalytic enhancement of organic reactions [11 – 13]. Furthermore, oxidation reactions can be facilitated by the use of heterobimetallic catalysts [14, 15]. To combine two metals in one molecule it is often feasible to use Janus-Head ligands [16 – 20]. These ligands provide the option to coordinate hard and soft metals [21] by employing two different coordination sites. Since diimidosulfinates are known to coordinate hard metals like lithium [22 – 24] but also soft metals like cesium [25] and barium [26] they are an obvious choice for the design of Janus-Head ligands. In addition to their flexibility in metal coordination it is their solubility in nearly all organic solvents that makes coupled diimidosulfinates a worthwhile synthetic target.

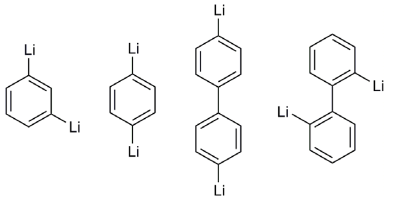

Fig. 1. Spacers for the synthesis of coupled diimidosulfinates.

Previous investigations in our group showed that it is possible to connect two sulfurdiimides through an organic spacer. Two sulfurdiimides and also two sulfurtriimides were coupled with a methylene bridge [27, 28] or with a thiophene, dithiophene or selenophene bridge [29]. Fueled by these promising results, in the work presented in this paper we embarked to broaden the field of organic spacers (Fig. 1) and investigated the metal exchange of the coupled lithium diimidosulfinates.

Since aryl groups are more rigid and therefore tend to give less intramolecular side reactions when doubly metalated [30] our choice was to employ dibromobenzene and dibromobiphenyl as synthons for organic spacers. Another advantage of those aryl groups is the possibility to exploit different regio isomers. By the use of either 1,4-dibromobenzene and 1,3-dibromobenzene or 2,2′-biphenyl and 4,4′-dibromobiphenyl the distance of the coordination sites and hence the distance between the two metal atoms can be varied. With this in mind we synthesized, isolated and characterized $[(THF)_4Li_2\{(NSiMe_3)_2S\}_2$biphenyl] (**1**), $[(THF)_{1.5}Li_2\{(NSiMe_3)_2S\}_2$biphenyl$]_\infty$ (**2**) and $[\{Me_2Al(N^tBu)_2S\}_2$biphenyl] (**3**) with biphenyl as a longer spacer and $[\{Me_2Al(NSiMe_3)_2S\}_2(C_6H_4)]$ (**4**) with benzene for a shorter bridge.

Results and Discussion

Synthesis of coupled lithium diimidosulfinates

For the synthesis of the coupled lithium diimidosulfinates, 1,4-dibromobenzene, 1,3-dibromobenzene,

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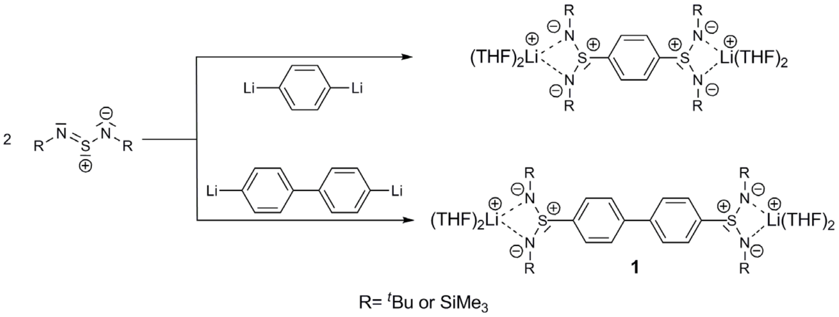

Scheme 1. Synthesis of coupled lithium diimidosulfinates.

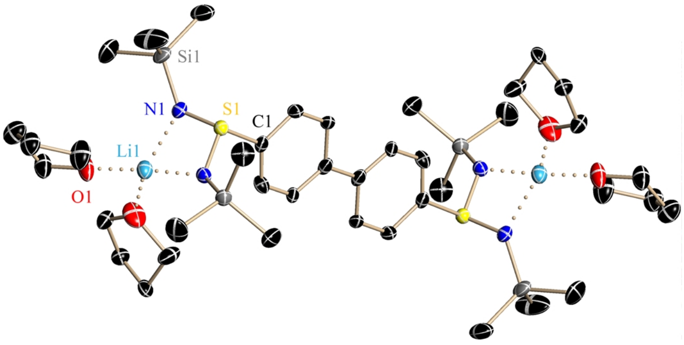

Fig. 2 (color online). Crystal structure of $[(THF)_4Li_2\{(NSiMe_3)_2S\}_2$biphenyl] (**1**). Anisotropic displacement parameters are depicted at the 50 % probability level, and all hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 1.

2,2′-dibromobiphenyl and 4,4′-dibromobiphenyl were lithiated twice with ^{n}BuLi, or with ^{t}BuLi in the case of the dibromobenzene compounds. The reactions of 2,2′-dilithiumbiphenyl and 1,3-dilithiumphenyl with the sulfurdiimides did not afford the desired products. The reason for this is probably the insufficient distance between the lithiated positions. Apparently there is not enough room for the simultaneous addition of both sulfurdiimides. The other spacers reacted readily with the sulfurdiimides (Scheme 1) and yielded the coupled diimidosulfinates.

Unfortunately, $[\{(THF)_2Li(NR)_2S\}_2(C_6H_4)]$ could not be isolated and characterized due to the co-complexation with the lithium bromide side product generated in the synthesis of 1,4-dilithiumbenzene from 1,4-dibromobenzene. Several attempts to separate the lithium bromide or prevent its formation in the course of the synthesis failed. It seems that the twofold lithiated benzene is highly reactive and attacks the formed RBr (R= *n*-butyl, *t*-butyl) to give lithium bromide. The LiBr co-complexation hampers further experiments since the molecular weight of the dimetalated species remains unknown, and the amount of employed 1,4-dilithiumbenzene is difficult to determine. In addition it makes it nearly impossible to get reliable evidence of the formation of $[\{(THF)_2Li(NR)_2S\}_2(C_6H_4)]$ in the NMR experiment since the spectra are not free of signals of side products due to the uncertain stoichiometry. The crystal structure could also not be determined because the lithium bromide tends to crystallize more readily than the lithium diimidosulfinate. In spite of these purification problems the metal exchange from lithium to aluminum (*vide infra*) worked and proved *a posteriori* that the reaction of the lithiated benzene with the sulfurdiimide was successful.

Structural characterization of $[(THF)_4Li_2\{(NSiMe_3)_2S\}_2$*biphenyl*] (**1**) *and* $[(THF)_{1.5}Li_2\{(NSiMe_3)_2S\}_2$*biphenyl*]$_\infty$ (**2**)

1 crystallizes at −30° in the triclinic space group $P\bar{1}$ (Fig. 2) with half of the molecule in the asymmetric unit. In contrast to the diimidosulfinates described in the literature, the molecule does not dimerize but accomplishes the favored fourfold coordination of the lithium atom by coordination of two THF molecules. Up to now monomeric diimidosulfinates have only been known with a chelating donor base like TMEDA [31]. Otherwise only triimidosulfinates or the $S(N^tBu)_4{}^{2-}$ anion have been known to crystallize as monomers when THF is the only donor base present [32, 33].

When the reaction of 4,4′-dilithiumbiphenyl with bis(trimethylsilyl)sulfurdiimide is performed in a

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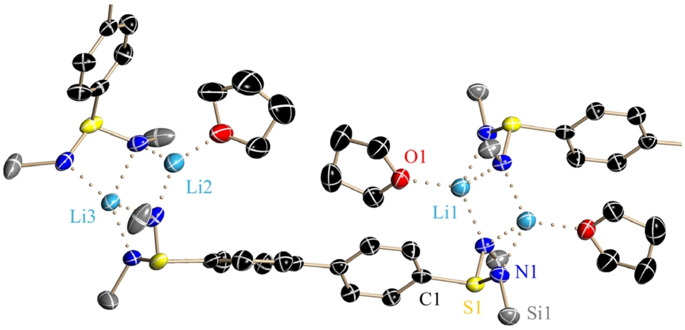

Fig. 3 (color online). Part of the crystal structure of $[(THF)_{1.5}Li_2\{(NSiMe_3)_2S\}_2biphenyl]_\infty$ (**2**). All hydrogen atoms and the carbon atoms of the trimethylsilyl groups have been omitted for clarity. Anisotropic displacement parameters are depicted at the 50 % probability level. Selected bond lengths and angles are presented in Table 1.

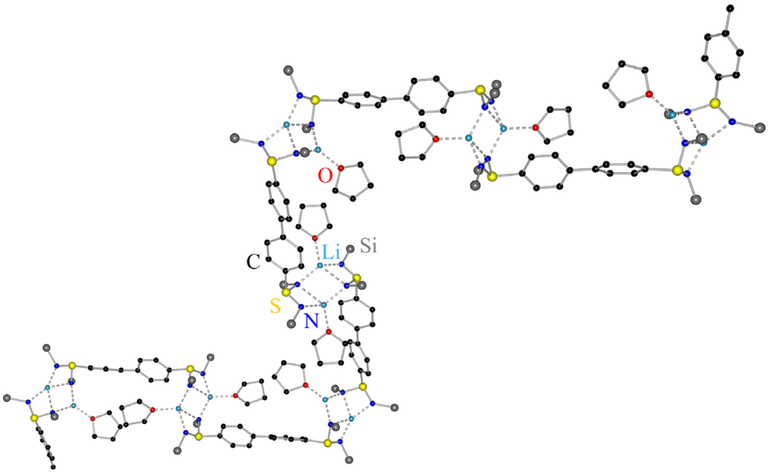

Fig. 4 (color online). Part of the packing plot of $[(THF)_{1.5}Li_2\{(NSiMe_3)_2S\}_2biphenyl]_\infty$ (**2**). All hydrogen atoms and the carbon atoms of the trimethylsilyl groups have been omitted for clarity.

Table 1. Selected bond lengths (Å) and angles (deg) for **1**, **2**, **3** and **4**.

	1	**2**		**3**	**4**
S-N (av.)	1.601(1)	1.560(4)	S-N1	1.644(2)	1.622(2)
S-C (av.)	1.810(2)	1.793(4)	S-N2	1.648(2)	1.625(2)
Li1-N	2.040(3)	1.989(8)	Al-C	1.957(3)	1.958(3)
	2.082(3)	2.426(8)		1.980(3)	1.959(3)
		2.055(8)			
Li2-N		2.019(8)	Al-N1	1.908(2)	1.929(2)
Li3-N		2.199(8)	Al-N2	1.915(2)	1.936(2)
		1.984(5)			
Li1-O	1.941(3)	1.973(8)	S-C	1.796(2)	1.801(3)
	1.947(4)				
Li2-O		1.89(1)			
			N-S1-N	91.17(9)	94.94(12)
N-S-N (av.)	104.02(7)	105.89(18)	C-S-N	105.71(9)	105.05(11)
				106.30(9)	105.36(11)
C-S-N (av.)	102.99(8)	103.22(20)	N-Al-N	75.90(7)	76.49(10)

THF/hexane mixture, and the saturated solution is afterwards stored at r. t., the compound $[(THF)_{1.5}Li_2\{(NSiMe_3)_2S\}_2biphenyl]_\infty$ (**2**) is obtained. In contrast to **1**, it is a coordination polymer (Figs. 3 and 4) as already expected from known lithium diimidosulfinate structures [24, 26, 34]. Interestingly, **2** shows different coordination geometries at the metal atoms depending on the conformation at the Li_2N_2 four-membered rings. While the mode of connectivity in the first of these units provides a co-linear orientation of the biphenyl substituents, the second one induces an almost perpendicular twisted kink (99.4°) in the polymeric chain. This kink is caused by a donor base-free four-fold N-coordinated lithium atom (Li3) which leads to an overall stair-like arrangement. The corresponding lithium atom at the hollow of the knee is only in a trigonal planar coordination by two nitrogen atoms of different diimidosulfinate ligands and a single THF molecule. In the unit leading to a co-linear arrangement both lithium atoms (Li1 and Li2) exhibit a distorted tetrahedral coordination by three nitrogen atoms and an oxygen atom of a THF donor base each. Alternating Li–N contacts provide the linkages along the chain.

Both structural motifs are known for lithium diimidosulfinates, and the bond lengths and angles are in the normal range expected for S–N and Li–N distances [25, 34, 35]. Comparing those in **2** and in the com-

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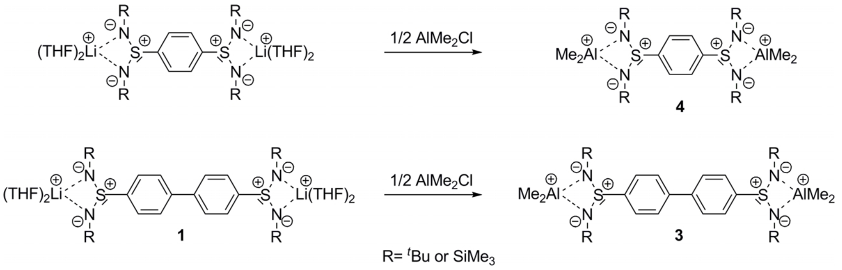

Scheme 2. Synthesis of **3** and **4**.

plex [(THF)Li(NSiMe$_3$)$_2$SPh]$_2$ [35], which also exhibits a tetrahedrally LiN$_3$(THF) coordinated lithium atom, shows the N–S–N backbone to be very similar. The Li–N distances show only slight differences (±0.03 Å see Table 1).

One of the two Li$_2$N$_2$ motifs exhibited by **2** can also be observed in [(Et$_2$O){Li(NSiMe$_3$)$_2$SPh}$_2$] [35]. Li2 shows the same Li–N and Li–O distances although [(Et$_2$O){Li(NSiMe$_3$)$_2$SPh}$_2$] crystallizes with Et$_2$O as the donor base instead of THF. The comparison of the Li3–N distances in **2** (2.20 Å / 1.98 Å) and in [(Et$_2$O){Li(NSiMe$_3$)$_2$SPh}$_2$] (2.24 Å / 1.99 Å) shows more distinct differences [35]. The change of the donating solvent from Et$_2$O to THF seems not to be the reason for the differences since the bond lengths around Li2 are similar in both structures. So they must be induced by the packing of the coordination polymer **2**.

The inspection of the three different lithium atom environments present in **2** shows the Li–N and Li–O distances around Li2 to be the shortest. Since Li2 exhibits only three instead of four coordinative bonds, it needs to compensate for the lack in charge density by closer contacts to the electron-rich neighbors. Especially the Li–O distance is 0.06 Å shorter than in **1** and even 0.09 Å shorter than the Li1–O bond in **2**. Finally the fact that both compounds can be crystallized at only slightly different conditions shows that **1** and **2** must be rather close in energy. From the comparison of known dimeric diimidosulfinates it seems clear that **2** exhibits the most favorable coordination of the lithium atoms. The different coordination in **1** may be due to the formation of hydrogen bonds. While in **2** only intramolecular hydrogen bonds can be found, in **1** the stability of the solid-state structure is enhanced by one intermolecular hydrogen bond per molecule.

Synthesis of the dimethylaluminum diimidosulfinates

For the metal exchange the lithium diimidosulfinates were treated with half an equivalent of Me$_2$AlCl at −78° (Scheme 2). The reactions proceeded smoothly and afforded [{Me$_2$Al(N^{t}Bu)$_2$S}$_2$biphenyl] (**3**) and [{Me$_2$Al(NSiMe$_3$)$_2$S}$_2$(C$_6$H$_4$)] (**4**). Both compounds could be crystallized and structurally characterized. Although only half an equivalent of Me$_2$AlCl was employed to get mixed metal complexes, both lithium atoms got replaced by the dimethylaluminum moiety. In **4** the amount of the used lithium diimidosulfinate could not be determined unequivocally due to the LiBr co-complexation discussed earlier, but obviously the exchange reaction with dimethylaluminum chloride is not selective enough to substitute only one lithium atom.

The addition of the dilithiated spacers and the following metal exchange with Me$_2$AlCl were performed with the di-*tert*-butyl-sulfurdiimide as well as with the bis(trimethylsilyl)sulfurdiimide. Regarding the lithium compounds, only the trimethylsilyl derivates had been crystallized and characterized. The reactions with the bis(*tert*-butyl)sulfurdiimide only afforded powders that gave no satisfactory NMR spectra. Nevertheless, the subsequent metal exchange with Me$_2$AlCl afforded **3**.

Structural characterization of [{Me$_2$Al(N^{t}Bu)$_2$S}$_2$biphenyl] (3) and [{Me$_2$Al(NSiMe$_3$)$_2$S}$_2$(C$_6$H$_4$)] (4)

[{Me$_2$Al(N^{t}Bu)$_2$S}$_2$biphenyl] (**3**) and [{Me$_2$Al(NSiMe$_3$)$_2$S}$_2$(C$_6$H$_4$)] (**4**) show almost the same structural motif (Figs. 5 and 6). The N–S–N planes exhibit a similar arrangement relative to the aromatic spacer planes (120.0° for **3** and 125.1° for **4**), and in both structures the two sulfurdiimido moieties are arranged *trans* relative to each other. Both aluminum atoms show a tetrahedral coordination geometry with the N–Al–N angle clearly smaller than the ideal tetrahedral angle. All the other angles around the metal atom are slightly larger.

All bond lengths and angles are similar and in the same range as in other known aluminum di- and tri-

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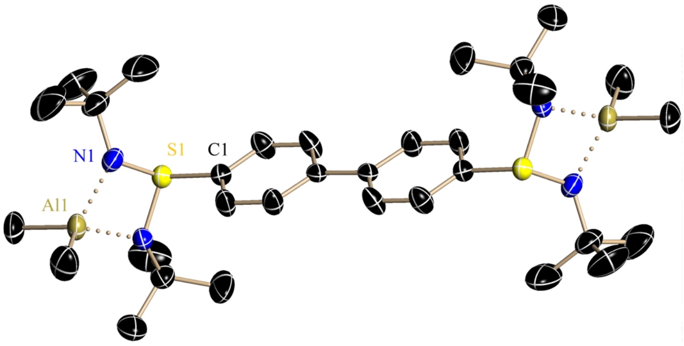

Fig. 5 (color online). Crystal structure of [$\{Me_2Al(N^tBu)_2S\}_2$biphenyl] (**3**). Anisotropic displacement parameters are depicted at the 50 % probability level, and all hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 1.

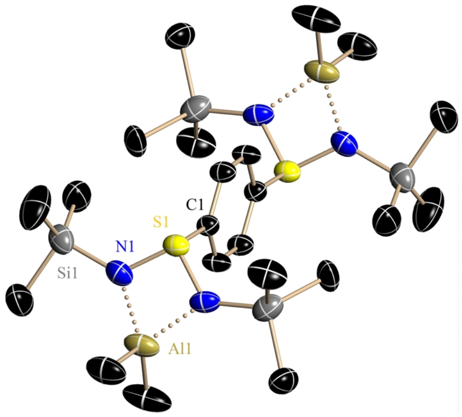

Fig. 6 (color online). Crystal structure of [$\{Me_2Al(NSiMe_3)_2S\}_2$Ph] (**4**). Anisotropic displacement parameters are depicted at the 50 % probability level, and all hydrogen atoms have been omitted for clarity. Selected bond lengths and angles are presented in Table 1.

imido sulfinates [32, 36]. Only marginal differences can be detected in the S–N and Al–N bond lengths (Table 1). In **3** the S–N bond lengths are elongated by 0.02 Å while the Al–N bond lengths are shortened by the same amount.

When comparing **3** and **4** with the lithium diimidosulfinates the only noticeable differences that can be spotted are in the M–N bond lengths (av. Li: 2.04 Å *vs.* av. Al: 1.92 Å), and the N–S–N angles are also different (av. Li: 103° *vs.* av. Al: 93°). As the metal-nitrogen bonds are shortened the sulfur-metal distances get smaller, too. To prevent both electropositive atoms from getting too close, the N–S–N angle is widened. The S–N bond lengths are slightly elongated in **3** and **4** (av. 1.64 and 1.62 Å) compared to **1** and **2** (av. 1.60 Å) probably because the aluminum atom acquires more from the negative charge at the nitrogen atom resulting in smaller electrostatic interactions between the sulfur and the nitrogen atom.

Conclusion

In this paper we report the syntheses and structures of four bis(sulfurdiimides) linked by arene spacers. Our experiments showed that the starting materials 1,4-dibromobenzene, 1,3-dibromobenzene, 2,2′-biphenyl and 4,4′-dibromobiphenyl can easily be twofold lithiated. Presumably due to steric hindrance only 1,4-dilithiumbenzene and 4,4′-dilithiumbiphenyl react cleanly with sulfurdiimides to give the coupled diimidosulfinates **1** – **4**. The reactions show aryl groups to be perfect candidates for the connection of two chelating ligands. The twofold lithiation proceeds almost quantitatively and without side products. Although the addition reactions worked well and yielded **1** and **2**, the following metal exchange reactions where not selective enough to allow substitution of only one of the two lithium sites. Therefore, better suited metal fragments have to be found with reduced reactivity and increased selectivity to accomplish the intended synthesis of heterobimetallic complexes. Further metal exchange reactions are currently under investigation. A promising candidate for further studies is 9,10-dibromo-anthracene.

Experimental Section

All experiments were carried out either in an atmosphere of purified dry nitrogen or argon by using modified Schlenk techniques or in an argon drybox. The glassware was dried for several hours at 120 °C, assembled hot, and cooled under vacuum. The solvents were freshly distilled from potassium prior to use and degassed. The reactants were commercially available or synthesized according to published procedures $S(N^tBu)_2$ [37].

All NMR spectra were recorded on Bruker Avance 500 spectrometers. The chemical shifts δ are given in ppm with positive values for low-field shifts relative to tetramethylsilane as external standard.

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Elemental analyses were performed by the Mikroanalytisches Labor des Instituts für Anorganische Chemie der Universität Göttingen with an Elementar Vario EL3 apparatus. The determined values deviate more than usual from the calculated ones, as the substances are highly sensitive to oxygen and moisture.

Mass spectra were recorded with the electron ionization method (EI-MS: 70 eV) on a Finnigan MAT 95 spectrometer. The mass-to-charge ratios (*m/z*) of the fragment ions are based on the molecular mass of the isotopes with the highest natural abundance. The molecular ion peak M is defined as the compound without coordinated solvent. Some spectra were unspecific as the ionic character and the reactivity of the synthesized compounds made the measurement difficult. Due to the reactivity and solubility of the compounds, no electron spray ionization (ESI-MS) or fast atom bombardment (FAB-MS) mass spectra could be recorded.

*Synthesis of the dilithium-biphenyl-4,4′-bis-trimethylsilyl-diimidosulfinates (**1**) and (**2**)*

A suspension of 3.1 g (10 mmol) 4,4′-dibromobiphenyl in 15 mL Et_2O was treated with 11.2 mL (20 mmol) of a 1.79 M solution of ^{n}BuLi at −78 °C. After stirring for 2 h the resulting colorless solid was filtered and washed with cold hexane.

4.0 g (8.7 mmol) 4,4′-dilithiumbiphenyl was suspended in THF (for **2** a THF/hexane mixture was used), and 3.6 g (17.4 mmol) of $S(NSiMe_3)_2$ was added at −78 °C. After stirring over night, part of the solvent was removed under reduced pressure. After 2 d storage at 4° colorless crystals suitable for X-ray diffraction were obtained. For **2** the highest peaks in the mass spectrum and the signals of the NMR spectrum where the same as for **1**. The elemental analysis for **2** gave poor results. Yield (%): 6.16 g, 7.1 mmol, 71 % (referring to 4,4′-dibromobiphenyl). – Elemental analysis in % found (calcd.): C 55.47 (55.38), H 9.47 (8.72), N 6.69 (6.50), S 7.79 (7.39). – ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 7.77$ (d, $^3J_{HH} = 8.0$ Hz, 4 H, *ortho*), 7.50 (d, $^3J_{HH} = 8.0$ Hz, 4 H, *meta*), 3.62 ppm (m, 8 H, OCH_2CH_2), 1.77 (m, 8 H, OCH_2CH_2), 0.11 (s, 36 H, $Si(CH_3)_3$). – $^{13}C\{^1H\}$ NMR (125 MHz, [D$_8$]THF): $\delta = 150.81$ (s, *ipso*), 143.54 (s, *para*), 127.81 (s, *ortho*), 126.99 (s, *meta*), 67.4 (OCH_2CH_2), 25.3 (OCH_2CH_2), 1.11 (s, $Si(CH_3)_3$). – EI-MS: *m/z* (%) = 565 (12) $[M–2 Li+H]^+$, 464 (21) $[M–2 Li–NSiMe_3–CH_3+H]^+$, 392 (100) $[M–2 Li–2 NSiMe_3+H]^+$, 287 (25) $[M–2 Li–S(NSiMe_3)_2–SiMe_3+H]^+$, 73 (26) $[SiMe_3]^+$.

*Synthesis of bis-dimethylaluminum-biphenyl-4,4′-bis-di^{t}butyl-diimidosulfinate (**3**)*

A solution of 5.3 g (6.6 mmol) **1** in 15 mL THF was reacted with 0.6 mL (6.5 mmol) Me_2AlCl at −78 °C. After stirring over night, part of the solvent was removed under reduced pressure. After 2 d storage at 4° colorless crystals suitable for X-ray diffraction were obtained. Yield (%): 3.79 g, 5.0 mmol, 76 %. – Elemental analysis in % found (calcd.): C 61.85 (62.50), H 9.61 (9.18), N 8.90 (9.11), S 10.20 (10.43). – ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 7.98$ (d, $^3J_{HH} = 8.2$ Hz, 4 H, *meta*), 7.80 (d, $^3J_{HH} = 8.4$ Hz, 4 H, *ortho*), 1.36 (s, 36 H, $C(CH_3)_3$), −0.58 – −0.68 (br, 12 H, $Al(CH_3)_2$). – $^{13}C\{^1H\}$ NMR (125 MHz, [D$_8$]THF): $\delta = 150.92$ (s, *ipso*), 144.09 (s, *para*), 128.96 (s, *ortho*), 127.50 (s, *meta*), 53.29 (s, $C(CH_3)_3$), 31.95 (s, $C(CH_3)_3$), −4.79 (s, $Al(CH_3)_2$).

EI-MS: *m/z* (%) = 502 (11) $[M–2 AlMe_2+H]^+$, 429 (13) $[M–2 AlMe_2–N^tBu]^+$, 360 (30) $[M–2 AlMe_2–2 N^tBu+H]^+$, 289 (10) $[M–2 AlMe_2–3 N^tBu+2 H]^+$, 57 (100) $[AlMe_2/^tBu]^+$, 41 (50) $[C_3H_5]^+$.

*Synthesis of bis-dimethylaluminum-benzene-1,4-bis-trimethylsilyldiimidosulfinate (**4**)*

To a solution of 4.7 g (20 mmol) 1,4-dibromobenzene in 30 mL toluene 24 mL of a 1.67 M solution of ^{t}BuLi (40 mmol) was added. After stirring for 2 h the resulting light-yellow solid was filtered and washed with cold Et_2O.

4.2 g (16 mmol) 1,4-dilithiumbenzene was suspended in 20 mL of Et_2O, and 6.6 g (32 mmol) of $S(NSiMe_3)_2$ was added at −78 °C. After stirring over night the light-orange precipitate was filtered and washed with cold Et_2O.

A solution of 9.0 g (12.3 mmol) dilithium-benzene-1,4-bis-trimethylsilyldiimido-sulfinate in 15 mL THF was reacted with 1.2 mL (12.3 mmol) Me_2AlCl at −78 °C. After stirring over night, part of the solvent was removed under reduced pressure. The remaining solid was filtered and the solution stored in the refrigerator at 4 °C. After 2 d storage colorless crystals suitable for X-ray diffraction were obtained. Yield (%): 5.67 g, 9.4 mmol, 47 % (referring to 1,4-dibromobenzene). – Elemental analysis in % found (calcd.): C 43.33 (43.81), H 9.01 (8.69), N 9.45 (9.29), S 10.09 (10.63). – ^{1}H NMR (500 MHz, [D$_8$]THF): $\delta = 8.16–7.98$ (m, 4 H), −0.03 (br, 36 H, $Si(CH_3)_3$), −0.61 – −0.72 (br, 12 H, $Al(CH_3)_2$). – $^{13}C\{^1H\}$ NMR (125 MHz, [D$_8$]THF): $\delta = 155.78$ (s, *ipso*), 127.16 (br, *meta*, *ortho*), 3.20 (s, $Si(CH_3)_3$), −4.71 (s, $Al(CH_3)_2$). – EI-MS: *m/z* (%) = 588 (61) $[M–Me]^+$, 574 (22) $[M–2 Me+H]^+$, 530 (19) $[M–SiMe_3]^+$, 73 (18) $[SiMe_3]^+$, 57 (100) $[AlMe_2]^+$.

X-Ray structure determination

The data for **1**–**4** (Table 2) were collected from shock-cooled crystals at 100 K (**1**, **2** and **4**) or 170 K (**3**) [38, 39] on Bruker SMART-APEX II diffractometers with D8 goniometers. For **1**–**3** a Bruker TXS-Mo rotating anode was used as X-ray source, for **4** an Incoatec microfocus source was utilized [40]. All diffractometers were equipped with a low-temperature device and used monochromated MoK_α

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Table 2. Crystal structure data for **1** – **4**.

	1	**2**	**3**	**4**
Formula	$C_{40}H_{76}Li_2N_4O_4S_2Si_4$	$C_{60}H_{112}Li_4N_8O_3S_4Si_8$	$C_{40}H_{72}Al_2N_4O_2S_2$	$C_{22}H_{52}Al_2N_4S_2Si_4$
M_r	867.41	1374.30	759.10	603.12
CCDC no.	764284	764287	764286	764285
Crystal size, mm^3	0.35 × 0.2 × 0.1	0.2 × 0.1 × 0.1	0.4 × 0.2 × 0.2	0.15 × 0.15 × 0.1
Crystal system	triclinic	orthorhombic	monoclinic	orthorhombic
Space group	$P\bar{1}$	*Pbcn*	$P2_1/c$	*Pccn*
a, Å	10.1713(16)	13.4045(13)	9.0151(13)	15.7678(11)
b, Å	10.426(3)	18.8417(16)	15.890(2)	16.5892(11)
c, Å	13.924(3)	33.228(3)	16.808(3)	14.3223(9)
α, deg	80.687(4)	90	90	90
β, deg	68.710(6)	90	102.658(3)	90
γ, deg	68.492(5)	90	90	90
V, Å^3	1279.4(5)	8392.3(13)	2349.3(6)	3746.4(4)
Z	1	4	2	4
D_{calcd}, g cm^{-3}	1.13	1.09	1.07	1.07
μ(MoK_α), cm^{-1}	0.2 mm^{-1}	0.3	0.2	0.3
F(000), e	470	2960	828	1304
hkl range	$-11 \leq h \leq +12$	$-16 \leq h \leq +16$	$-11 \leq h \leq +10$	$-18 \leq h \leq +18$
	$-12 \leq k \leq +12$	$-22 \leq k \leq +22$	$0 \leq k \leq +19$	$-19 \leq k \leq +19$
	$0 \leq l \leq +16$	$-36 \leq l \leq +40$	$0 \leq l \leq +20$	$-16 \leq l \leq +17$
$((\sin\theta)/\lambda)_{max}$, Å^{-1}	25.35	25.46	26.04	25.34
Refl. measured	31830	56409	53732	21854
Refl. unique	4687	7750	4630	3431
R_{int}	0.0221	0.1079	0.0327	0.0503
Param. refined	349	455	241	224
$R(F) / wR(F^2)$[a] (all refl.)	0.0417 / 0.0946	0.0990 / 0.1959	0.0561 / 0.1465	0.0671 / 0.1084
GoF (F^2)[b]	1.043	1.167	1.049	1.023
$\Delta\rho_{fin}$ (max / min), e Å^{-3}	0.46 / 0.30	0.58 / −0.34	0.49 / −0.46	0.38 / −0.38

[a] $R1 = \Sigma||F_o| - |F_c|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o{}^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2)+(AP)^2+BP]^{-1}$, where $P = (\mathrm{Max}(F_o{}^2, 0)+2F_c{}^2)/3$ and A and B are constants adjusted by the program; [b] GoF = $S = [\Sigma w(F_o{}^2 - F_c{}^2)^2/(n_{obs} - n_{param})]^{1/2}$, where n_{obs} is the number of data and n_{param} the number of refined parameters.

radiation, λ = 0.71073 Å, with mirror optics as monochromator. The data of **1** – **4** were integrated with SAINT [41], and an empirical absorption correction (SADABS) was applied [42]. All structures were solved by Direct Methods (SHELXS-97) [43] and refined by full-matrix least-squares methods against F^2 (SHELXL-97) [44]. All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were refined isotropically on calculated positions using a riding model with their U_{iso} values constrained to 1.5 times the U_{eq} of their pivot atoms for terminal sp^3 carbon atoms and 1.2 times for all other carbon atoms. Disordered moieties were refined using bond lengths restraints and isotropic displacement parameter restraints [44].

CCDC 764284–764287 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgement

The authors like to thank the DFG priority programme 1178, the Georg-August Universität Göttingen, the Land Niedersachsen and the Volkswagenstiftung for providing superb X-ray facilities.

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