Phosphane-Catalyzed Reactions of $LAlH_2$ with Elemental Chalcogens; Preparation of $[LAl(\mu\text{-}E)_2AlL]$ [E = S, Se, Te, L = $HC\{C(Me)N(Ar)\}_2$, Ar = $2,6\text{-}i Pr_2C_6H_3$]

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Dedicated to Professor Raymundo Cea Olivares

Keywords: Aluminum / Catalysis / Chalcogens / Phosphanes / Reaction mechanisms

Addition of catalytic amounts of a phosphane to a reaction mixture containing $LAlH_2$ [**2**; L = $HC\{C(Me)N(Ar)\}_2$, Ar = $2,6\text{-}i Pr_2C_6H_3$] and elemental Se or Te resulted in the formation of poorly soluble $[LAl(\mu\text{-}Se)_2AlL]$ (**3**) and $[LAl(\mu\text{-}Te)_2AlL]$ (**4**), respectively. The sulfur analogue $[LAl(\mu\text{-}S)_2AlL]$ (**5**) could not be obtained from the direct reaction of **2** with elemental sulfur; consequently, its synthesis was successfully achieved from the reaction of $[LAlH_2]$ and $[LAl(SH)_2]$. A possible mechanism for the formation of $[LAl(\mu\text{-}Se)_2AlL]$ and $[LAl(\mu\text{-}Te)_2AlL]$ is discussed. The molecular structures of compounds **3**–**5** were determined by X-ray structure analyses.

Introduction

Aluminum compounds containing heavier Group 16 elements have been comparatively less-well studied than those containing Al−O bonds, mainly due to the thermodynamic stability of the latter species. Recently, we have reported the preparation of unusual species of composition $[LAl(EH)_2]$ [L = $HC\{C(Me)N(Ar)\}_2$, Ar = $2,6\text{-}i Pr_2C_6H_3$, E = O, S, Se],[1−3] as well as the catalytic role of $P(NMe_2)_3$ in the synthesis of $[LAl(SH)_2]$ (**1**).[2] As an extension of our interest in this type of compounds, we explored the influence of phosphanes on the $LAlH_2$/Se(Te) system. So far, there are only a few examples of compounds containing Al−E moieties in which the chalcogen atom is not directly bonded to any alkyl, aryl or trialkylsilyl group.[4−25] Three different aggregation modes have been observed for species containing Al and chalcogen atoms in a 1:1 molar ratio, mainly depending on the hapticity of the chalcogen atom. In these systems, the chalcogens can act either as a μ- or μ_3-bridging ligand as a consequence of the steric hindrance of the substituents present on the aluminum. Thus, the $[AlE]_n$ core can be either square planar (n = 2),[4−13,17] cubic (n = 4)[13−17] or adopt a hexagonal drum structure (n = 6).[14] Other examples containing Al and E in a ratio that deviates from 1:1 have also been reported to exhibit a bent Al−E−Al moiety, adamantane-like Al_4E_6 or more complex structures.[3,20−24] We have recently shown that $[LAlH_2]$ (**2**), prepared from LH and $AlH_3{\cdot}NMe_3$, reacts with elemental selenium[3] and, in the presence of a phosphane as catalyst, also with elemental sulfur,[2] to give species of the general formula $[LAl(EH)_2]$ (E = Se, S). The selenium derivative is thermodynamically unstable and decomposes to yield $[\{LAl(SeH)\}_2Se]$ with elimination of H_2Se.[3] Nevertheless, no product formation was observed from the reaction of $LAlH_2$ with elemental Te, although extreme reaction conditions were used. Herein, we report on the significant influence of catalytic amounts of phosphane in the reaction of **2** and Se and Te leading to $[LAl(\mu\text{-}Se)_2AlL]$ (**3**) and $[LAl(\mu\text{-}Te)_2AlL]$ (**4**), respectively. $[LAl(\mu\text{-}S)_2AlL]$ (**5**) could not be obtained using this protocol, therefore **5** was synthesized by the direct reaction of $[LAl(SH)_2]$ with $[LAlH_2]$.

Results and Discussion

Addition of catalytic amounts of $P(NMe_2)_3$ or PMe_3 to a suspension of **2** and Se or Te resulted in the formation of $[LAl(\mu\text{-}E)_2AlL]$ (**3** E = Se; **4** E = Te) in high yields at ambi-

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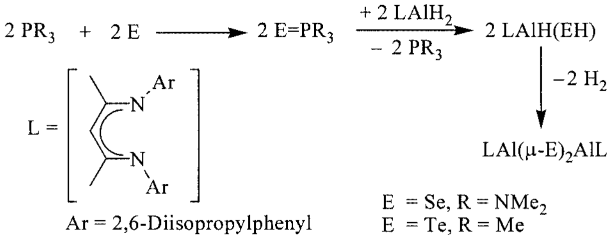
DOI: 10.1002/ejic.200400062

ent temperature. Compounds **3** and **4** are sparingly soluble in common organic solvents such as toluene, dichloromethane and tetrahydrofuran. In order to gain further insight regarding the role of the phosphane in this system, we investigated the reaction mechanism and possible by-products involved in this reaction. All attempts to follow the kinetics of these reactions by means of ^1H NMR spectroscopy failed due to the poor solubility of the elemental chalcogens and resulting products. However, previous experimental data revealed that the formation of **1** proceeds via the reactive intermediate [LAlH(SH)].[2] In order to obtain further insight into the reaction mechanism, we carried out several experiments varying the stoichiometry of the starting materials. The most striking finding was that, in the presence of phosphane, [LAl(μ-E)$_2$AlL]. analogous to the [LGa(μ-E)$_2$GaL] (E = O, S) derivatives prepared recently by Power et al.,[26] was the only product formed, regardless of the stoichiometry of the reagents employed; the direct reaction of **2** with elemental Se (in absence of the phosphane) led entirely to the formation of [LAl(SeH)$_2$].[3] In the latter case, another type of reaction mechanism involving a higher coordinated aluminum center formed by complexation of Se_2 to the aluminum has been suggested.[3,27−29] Finally, due to the fact that $TePR_3$ compounds are known to be good sources of soluble and reactive Te,[30−32] we carried out the direct reaction of **2** with $TePEt_3$ in an equimolar ratio. The reaction leads to pure **4** and free PEt_3 in almost quantitative yield, indicating that the gas evolved during the reaction is H_2 instead of H_2Te. All the experimental results outlined here are highly supportive of the proposed reaction mechanism. Therefore, we assume that Se and Te initially react with the corresponding phosphanes to yield $SeP(NMe_2)_3$ and $TePMe_3$, respectively. These compounds are unstable[30−32] and react in the following steps with **2** to yield [LAlH(EH)] (E = Se, Te), with elimination of phosphane. The last step corresponds to the formation of [LAl(μ-E)$_2$AlL] (E = Se, Te) by an elimination of two molecules of H_2. The splitting of the species into monomer units LAlE in the gas phase can indicate an intramolecular elimination followed by dimerisation, but we were not able to isolate such intermediates. Scheme 1 shows the steps involved in this reaction.

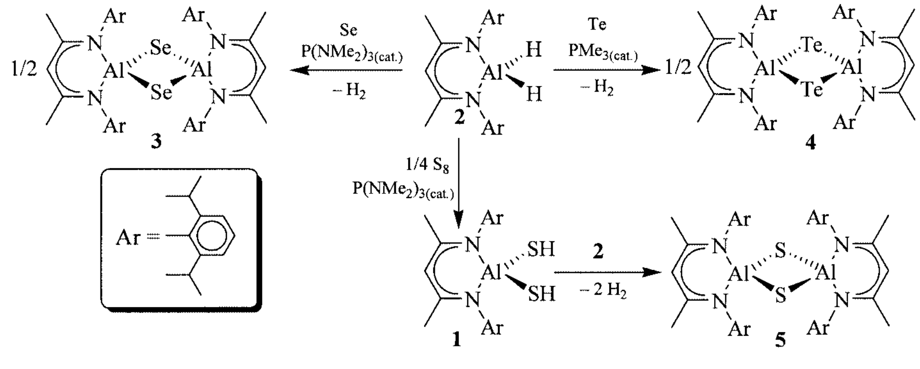


Scheme 1

As mentioned above, the reaction between [LAlH$_2$] (**2**) and elemental sulfur catalyzed by phosphane leads to [LAl(SH)$_2$] (**1**) and not to the desired [LAl(μ-S)$_2$AlL] (**5**).[2] Therefore we used the latent protic character of the hydrogen atoms from the SH groups of **1** and reacted the latter species in refluxing toluene with **2**. After 15 h we obtained **5** as a white insoluble microcrystalline solid in 92% yield. Scheme 2 summarizes the preparation of the three compounds.

Compounds **3**−**5** are insoluble in common organic solvents, and the powders obtained after the syntheses yielded nicely shaped monocrystals from a mixture of toluene/trichloromethane (10:1). The crystallization was achieved by solvation of [LAl(μ-E)$_2$AlL] with 2.32 equivalents of trichloromethane and 0.68 equivalents of toluene (**5**; E = S), two molecules of trichloromethane and one molecule of toluene (**3**; E = Se), or 2.73 molecules of trichloromethane and 0.27 molecules of toluene (**4**; E = Te) sharing the same spatial position in the crystal lattice, as shown by single-crystal X-ray structural analysis (Figures 1−3).[19]

The three isostructural compounds crystallize in the monoclinic space group *C*2/*m* and possess almost identical cell parameters (see Table 1). Taking into account the covalent radii (1.02 S, 1.17 Se and 1.35 Å Te),[33] the Al−S (2.237, 2.245 Å), Al−Se (2.359, 2.370 Å) and Al−Te bonds (2.575, 2.581 Å) are similar to one another. Furthermore, the E(1)−Al−E(1A) angles vary from 96.5° in **5** to 97.9° in



Scheme 2

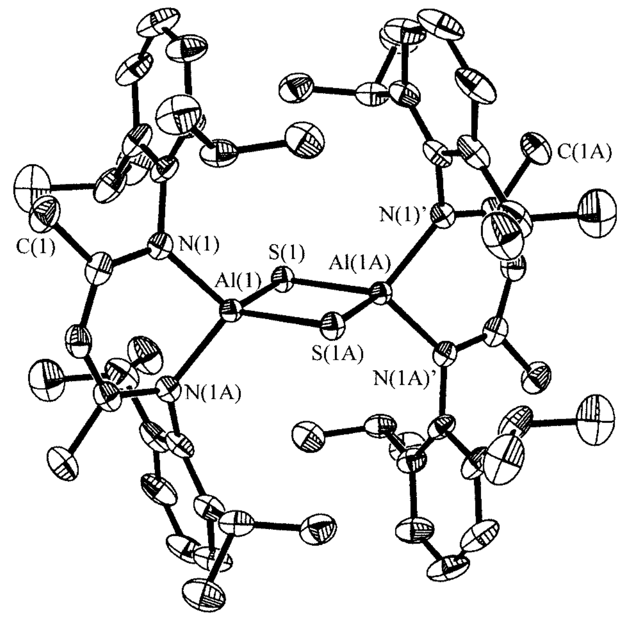


Figure 1. Molecular structure of LAl(μ-S)$_2$AlL (**5**) with 50% thermal ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: Al(1)−N(1)[N(1A)] 1.928(2), Al(1)−S(1) 2.237(1), Al(1)−S(1A) 2.245(1), S(1)−Al(1)−S(1A) 96.5(1), Al(1)−S(1)−Al(1A) 83.5(1), N(1)−Al(1)−N(1A) 94.9(1)

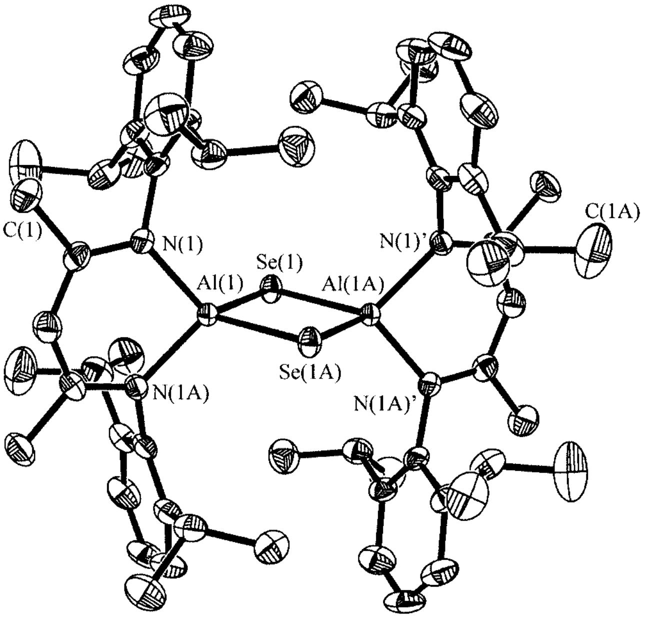


Figure 2. Molecular structure of LAl(μ-Se)$_2$AlL (**3**) with 50% thermal ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: Al(1)−N(1)[N(1A)] 1.924(3), Al(1)−Se(1) 2.359(1), Al(1)−Se(1A) 2.370(1), Se(1)−Al(1)−Se(1A) 97.5(1), Al(1)−Se(1)−Al(1A) 82.5(1), N(1)−Al(1)−N(1A) 95.2(2)

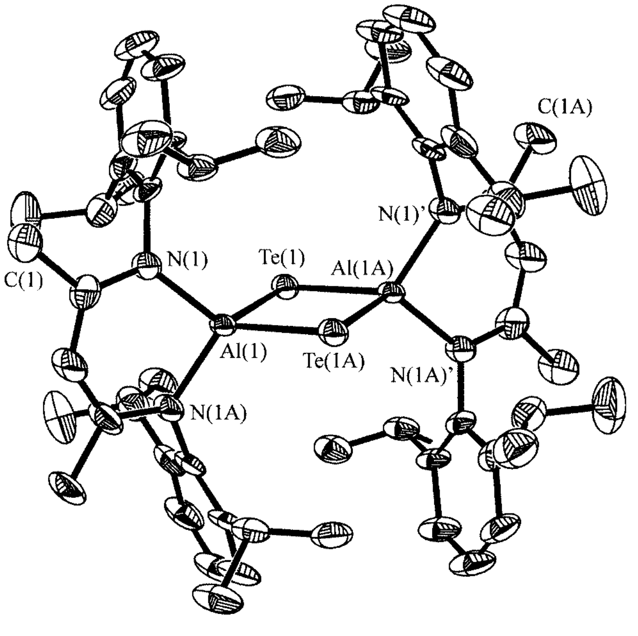


Figure 3. Molecular structure of LAl(μ-Te)$_2$AlL (**4**) with 50% thermal ellipsoids; hydrogen atoms and solvent molecules are omitted for clarity; selected bond lengths [Å] and angles [°]: Al(1)−N(1)[N(1A)] 1.908(5), Al(1)−Te(1) 2.575(3), Al(1)−Te(1A) 2.581(2), Te(1)−Al(1)−Te(1A) 97.9(1), Al(1)−Te(1)−Al(1A) 82.1(1), N(1)−Al(1)−N(1A) 96.0(3)

4 due to the larger radii of the chalcogen atom. All Al_2E_2 rings are, due to their symmetry, essentially planar, and the Al−E bond lengths are analogous to those of similar Al_2E_2 species (2.208−2.248 Å for S, 2.221−2.381 Å for Se, and 2.562−2.588 Å for Te), but the E(1)−Al−E(1A) (E = Se, Te) angle is significantly more obtuse than those reported in the literature (99.9−103.6° for Se and 102.8−103.8° for Te)[4−12] due to the steric bulk of the β-diketiminato ligand. The latter values are similar to those of Al_4E_4 clusters (94.2−99.2° for Se and 94.1−96.3° for Te),[14,15] where the chalcogen atoms are always coordinated to three aluminum atoms. The S(1)−Al−S(1A) angle fits within the range of similar compounds (95.9−101.9°).[9−11] Selected bond lengths and angles for **3**−**5** are listed in Table 2.

All three compounds decompose without melting at temperatures above 200 °C, indicating their high thermal stability. The high stability of compounds **3**−**5** is further supported by the EI-mass spectra, which exhibit [M^+] ions for all three molecules: *m/z* = 952 (100%) for S, 1048 (48%) for Se and 1144 (25%) for Te. Unfortunately, due to the low solubility of **3**−**5** we were not able to record NMR spectra.

Conclusion

In summary, we have prepared and structurally characterized three new thermally stable aluminum chalcogenides [LAl(μ-E)AlL] (E = S, Se, Te). Furthermore, the significant influence of the phosphane on the product formation has been demonstrated and a possible mechanism for the conversion of aluminum hydrides to aluminum selenides and tellurides outlined.

Experimental Section

General: All the reactions and handling of reagents were performed under an atmosphere of dry nitrogen using Schlenk techniques or a

Table 1. X-ray crystallographic data for **3**−**5**

	3·C_7H_8·2$CHCl_3$	**4**·0.27C_7H_8·2.73$CHCl_3$	**5**·0.68C_7H_8·2.32$CHCl_3$
Empirical formula	$C_{67}H_{92}Al_2Cl_6N_4Se_2$	$C_{62.63}H_{86.9}Al_2Cl_{8.18}N_4Te_2$	$C_{65.08}H_{89.78}Al_2Cl_{6.97}N_4S_2$
Molecular mass	1378.03	1495.14	1293.08
Temperature (K)	200(2)	100 (2)	100 (2)
Crystal system	monoclinic	monoclinic	monoclinic
Space group	*C*2/*m*	*C*2/*m*	*C*2/*m*
a (Å)	18.329 (4)	17.972 (2)	18.021 (3)
b (Å)	19.161 (5)	19.125 (2)	19.107 (3)
c (Å)	11.984 (3)	11.923 (2)	11.920 (2)
β (°)	125.54 (2)	124.84 (2)	125.22 (2)
V (Å^3)	3424.7(14)	3363.5 (8)	3353.0 (10)
Z	2	2	2
$D_{calcd.}$ (Mg·m^{-3})	1.336	1.476	1.281
Wavelength (Å)	0.71073	1.54178	1.54178
Absorption coefficient (mm^{-1})	1.38	10.40	3.84
F(000)	1436	1520	1369
θ range (°)	3.51−24.99	3.78−58.10	3.79−57.76
	$-21 \leq h \leq 21$	$-19 \leq h \leq 19$	$-19 \leq h \leq 19$
	$-4 \leq k \leq 22$	$-18 \leq k \leq 20$	$-20 \leq k \leq 15$
	$-14 \leq l \leq 14$	$-12 \leq l \leq 12$	$-13 \leq l \leq 13$
Reflections collected	4065	6352	7081
Independent reflections	3111 (R_{int} = 0.0307)	2314 (R_{int} = 0.0356)	2370 (R_{int} = 0.0224)
Data/restraints/parameters	3111/111/258	2314/405/332	2370/285/295
Goodness-on-fit on F^2	1.076	1.126	1.146
Final R_{int} [$I > 2\sigma(I)$]	R_1 = 0.0435	R_1 = 0.0510	R_1 = 0.0398
	wR_2 = 0.1083	wR_2 = 0.1174	wR_2 = 0.0989
R_{int} (all data)	R_1 = 0.0546	R_1 = 0.0535	R_1 = 0.0451
	wR_2 = 0.1171	wR_2 = 0.1187	wR_2 = 0.1017
Largest different peak and hole (e·Å^{-3})	0.881, −0.614	1.661, −0.878	0.436, −0.416

Table 2. Selected bond lengths (Å) and angles (°) for **3**−**5**

	3·1 C_7H_8·2 $CHCl_3$ (E = Se)	**4**·0.27 C_7H_8·2.73 $CHCl_3$ (E = Te)	**5**·0.68 C_7H_8·2.32 $CHCl_3$ (E = S)
Al−N	1.924 (3)	1.908 (5)	1.928 (2)
Al−E(1)	2.359 (2)	2.575 (3)	2.237 (1)
Al−E(1A)	2.370 (2)	2.581 (2)	2.245 (1)
E(1)−Al−E(1A)	97.5 (1)	97.9 (1)	96.5 (1)
Al(1)−E−Al(1A)	82.5 (1)	82.1 (1)	83.5 (1)

glovebox. Toluene was dried (Na/benzophenone ketyl) and distilled prior to use. Tellurium (99.5%; Aldrich) and PMe_3 (1 M solution in toluene; Fluka) were used as received. $P(NMe_2)_3$ (97%; Aldrich) was freshly distilled prior to use. Elemental red selenium,[34] [$LAlH_2$],[3] [$LAl(SH)_2$][2] and $TePEt_3$ [35] were prepared by literature procedures.

Infrared spectra were recorded as KBr pellets on a Bio-Rad Digilab FTS-7 spectrometer in the range 4000−350 cm^{-1}. Mass spectra were obtained with a Finnigan MAT 8230 or a Varian MAT CH5 instrument (70 eV). Elemental analyses were performed by the Analytical Laboratory, Institute of Inorganic Chemistry, University of Goettingen. Melting points were measured in sealed glass tubes and are uncorrected.

[LAl(μ-Se)$_2$AlL] (3): Toluene (20 mL) was added to a mixture of **2** (1.000 g, 2.239 mmol) and red selenium (0.176 g, 2.239 mmol) and after dissolution of **2**, freshly distilled $P(NMe_2)_3$ (0.03 mL, 0.055 mmol) was added. The reaction mixture was stirred for an additional 16 h and the white insoluble product was filtered off, washed with toluene (5 mL) and dried in vacuo. Yield: 1.07 g (91%). Decomp. without melting above 260 °C. IR (KBr pellet): $\tilde{\nu}$ = 3061 vw, 2959 st, 2927 w, 2868 w, 1588 vw, 1544 vst, 1462 w, 1438 m, 1392 vst, 1317 m, 1291 vw, 1249 w, 1177 w, 1101 w, 1058 vw, 1024 w, 937 vw, 867 w, 801 m, 775 vw, 763 w, 539 vw, 463 vw, 435 w, 411 vw cm^{-1}. EI-MS: *m*/*z* (%) = 1048 (48) [M]$^+$, 523 (28) [M/2]$^+$. $C_{58}H_{82}Al_2N_4Se_2$ (1047.2): calcd. C 66.52, H 7.89, N 5.35; found C 67.10, H 8.03, N 5.33.

[LAl(μ-Te)$_2$AlL] (4). Method 1: Toluene (20 mL) was added to a mixture of **2** (1.000 g, 2.239 mmol) and tellurium (0.285 g, 2.230 mmol) and after complete dissolution of **2**, PMe_3 (0.03 mL, 1 M solution in toluene, 0.030 mmol) was added. The reaction mixture was stirred for an additional 15 h, the pale yellow insoluble product was filtered off, washed with toluene (5 mL) and dried in vacuo. Yield: 1.15 g (90% based on Te). Decomp. without melting above 260 °C. IR (KBr pellet): $\tilde{\nu}$ = 3061 w, 3024 vw, 2990 w, 2968 vs, 2956 vs, 2930 st, 2866 m, 1587 w, 1543 vs, 1462 vs, 1440 vs, 1394 vs, 1365 sh, 1300 m, 1251 s, 1176 m, 1100 m, 1057 m, 1024 m, 937 m, 942 w, 868 st, 798 vs, 780 m, 761 st, 708 vw, 648 w, 595 vw, 537 w, 447 vw, 417 vst cm^{-1}. EI-MS: *m*/*z* (%) = 1144 (25) [M]$^+$, 574 (60) [M/2]$^+$, 443 (100) [M/2 − Te − H]$^+$. $C_{58}H_{82}Al_2N_4Te_2$ (1144.5): calcd. C 60.87, H 7.22, N 4.90; found C 60.50, H 7.15, N 4.82.

Method 2: Toluene (20 mL) was added to a mixture of **2** (1.000 g, 2.239 mmol) and $TePEt_3$ (0.550 g, 2.239 mmol) and the reaction mixture was stirred for an additional 2 h. The pale-yellow insoluble product was filtered off, washed with toluene (5 mL) and dried in vacuo. Yield: 1.22 g (95%).

[LAl(μ-S)$_2$AlL] (5): Toluene (20 mL) was added to a mixture of **1** (1.144 g, 2.239 mmol) and **2** (1.000 g, 2.239 mmol) and the reaction mixture was refluxed over a period of 15 h. After this time, the mixture was cooled to ambient temperature and a white insoluble product was filtered off, washed with toluene (5 mL) and dried in vacuo. Yield: 1.96 g (92%). Decomp. without melting above 200 °C. IR (KBr pellet): $\tilde{\nu}$ = 3062 vw, 2959 st, 2924 m, 2866 w, 1589 vw, 1547 vst, 1529 sh, 1462 m, 1437 m, 1390 vst, 1317 st, 1291 vw, 1249 m, 1176 w, 1100 vw, 1058 vw, 1024 w, 937 vw, 868 w, 801 m, 775 w, 763 w, 652 vw, 541 w, 516 m, 472 w, 454 m cm^{-1}. EI-MS: *m/z* (%) = 952 (100) $[M]^+$, 937 (64) $[M - CH_3]^+$, 909 (21) $[M - C_3H_7]^+$, 477 (58) $[M/2]^+$. $C_{58}H_{82}Al_2N_4S_2$ (953.40): calcd. C 73.07, H 8.67, N 5.88; found C 72.63, H 8.53, N 5.88.

X-ray Crystallographic Study: Data for the X-ray structures of [LAl(μ-S)$_2$AlL] and [LAl(μ-Te)$_2$AlL] were collected on a Bruker three-circle diffractometer equipped with a SMART 6000 CCD area-detector, whereas data for the X-ray structural analysis of [LAl(μ-Se)$_2$AlL] were collected on a Stoe-AED 2 four-circle diffractometer. Structures were solved by direct methods (SHELXS-97)[36] and refined by full-matrix least-squares methods on F^2 with SHELXL-97.[37] The non-hydrogen atoms were refined anisotropically; hydrogen atoms were included at geometrically idealized positions and refined with the riding model.

CCDC-228825 (for **5**), -228826 (for **3**), -228827 (for **4**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html [or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; Fax: + 44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk].

Acknowledgments

We thank the Deutsche Forschungsgemeinschaft, the Göttinger Akademie der Wissenschaften and the Fonds der Chemischen Industrie (predoctoral fellowship to V. J.) for funding.

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Received January 23, 2004