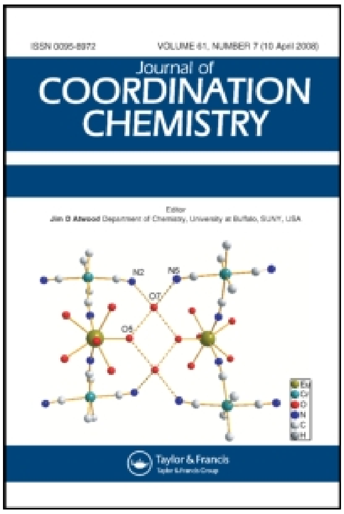

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THIA AND AZA BASED ALANES: SYNTHESIS AND MOLECULAR STRUCTURE OF $[Np_2Al\text{-}N(H)Ph]_2$, $[Np_2Al\text{-}SNp]_2$, AND $[Ph_2Al\text{-}N(H)Ph']_2$ ($Np = Me_3CCH_2\text{-}$; Ph = Biphenyl)

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Reaction of trineopentylaluminum, Np_3Al ($Np = Me_3CCH_2\text{-}$), with 1,2-diphenylhydrazine, Ph(H)N-N(H)Ph, or elemental sulfur in toluene affords the dimeric crystalline products $[Np_2Al\text{-}N(H)Ph]_2$, **I**, and $[Np_2Al\text{-}SNp]_2$, **II**, respectively. The etherate of triphenylalumium, $Ph_3Al \cdot OEt_2$, when allowed to react with 2-aminobiphenyl, yields the dimer $[Ph_2AL\text{-}N(H[Ph']_2$, (Ph' = Biphenyl) **III**. Each compound has been characterized by ^1H NMR, elemental analysis, and single crystal X-ray diffraction. **I** and **II** crystallize in the monoclinic space group $P2_1/n$ (No. 14); **I**: $a = 9.801$ (3), $b = 20.490$ (9), $c = 17.569$ (8) Å, $\beta = 97.81$ (3)°, $V = 3496$ (3) Å^3 for $Z = 4$; **II**: $a = 10.191$ (5) Å, $b = 10.907$ (5) Å, $c = 16.779$ (6) Å, $\beta = 97.18$ (3)°, $V = 1851$ (1) Å^8 for $Z = 2$. Refinement of **I** converged at $R = 0.051$, $R_w = 0.049$, while refinement of **II** converged at $R = 0.051$, $R_w = 0.066$. **III** crystallizes in the tetragonal space group $I4_1/a$ (No. 88); $a = 26.628$ (5) Å, $c = 11.017$ (4) Å, $V = 7812$ (4) Å^3, for $Z = 8$. Refinement of **III** converged at $R = 0.065$, $R_w = 0.058$. All compounds reside about planar Al_2Z_2 (Z = N, S) four-membered rings with Al-N bond distances ranging from 1.978 (8) to 1.992 (8) Å for **I**, Al-S distances ranging from 2.353 (2) to 2.364 (2) Å for **II**, and Al-N distances of 1.983 (7) and 1.946 (6) Å for **III**. Further pyrolysis of these products did not yield higher oligomers.

KEYWORDS: aluminum alkyl, aminoalane, hydrazine, sulfur, X-ray structure

INTRODUCTION

While initial studies were conducted decades ago,[1] reaction of R_3Al with ammonia continues to be a fertile area of study. Moreover, this chemistry has gradually progressed to encompass a wide variety of organoaluminum moieties as well as diverse amine systems. Interest has recently shifted from simple aluminum alkyls to investigations of their sterically demanding congeners, and the effects of steric bulk on subsequent reactivity in a variety of systems.[2] Trineopentylaluminum, Np_3Al ($Np = Me_3CCH_2\text{-}$), and triphenylaluminum, Ph_3Al, are sterically demanding R_3Al species under investigation in our laboratory.

An important class of amines is conspicuously absent from contemporary aminoalane chemistry: the simplest diamines, namely hydrazines, $R_2N\text{-}NR_2$

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(R = H, alkyl, aryl). Clearly hydrazine, or its substituted congeners such as 1,2-diphenylhydrazine, represent an interesting facet of organoaluminum chemistry. The insertion of Group 16 elements (S, Se, Te) into organoaluminum complexes has been reported for decades.[3] While the literature abounds with studies of the organoaluminum chemistry of amines,[4] considerably less is known about the organoaluminum chemistry of the diamines and their derivatives. Relative to aluminum aryls, triphenylaluminum presents an interesting contrast to the well-documented reactivity of simple aluminum alkyls. To this end, and in an effort to assess the feasibility of these substances as potential synthetic templates towards novel amino- and thio-alanes, we examined the organoaluminum chemistry of hydrazines, elemental sulfur, and a bulky amine with the sterically demanding aluminum alkyls trineopentylaluminum, Np_3Al and Ph_3Al. The crystalline dimers $[Np_2Al\text{-}N(H)Ph]_2$, **I**, and $[Np_2Al\text{-}SNp]_2$, **II**, were isolated from reaction of Np_3Al with 1,2-diphenylhydrazine, Ph(H)N-N(H)Ph, or elemental sulfur, respectively, in toluene. **III** was prepared by reaction of Ph_3Al with 2-aminobiphenyl, H_2NPh' (Ph' = Biphenyl). **I** and **II** represent rare structural characterizations of a hydrazine-based aminolane and of a bulky dialkylaluminum fragment with elemental sulfur, respectively, while **III** is an interesting triphenylaluminum-based aminoalane dimer.

EXPERIMENTAL

General

Standard Schlenk techniques were employed in conjunction with an inert atmosphere dry box (Vacuum Atmospheres HE-43 Dri-Lab). Toluene was distilled over sodium-benzophenone under an atmosphere of argon prior to use. Trineopentylaluminum and triphenylaluminum were prepared as described by literature methods.[5] Sulfur (Humco Laboratory), 1,2-diphenylhydrazine (Aldrich Chemical Co.), and 2-aminobiphenyl (Aldrich Chemical Co.) were used without further purification. Elemental Analyses were performed by E + R Microanalytical Laboratory, Inc. (Corona, NY). ^1H NMR data were recorded on a Bruker AC-300-P NMR spectrometer.

Synthesis of $[Np_2Al\text{-}N(H)Ph]_2$, I

Inside the dry box a reaction vessel was charged with Np_3Al (0.50 g, 2.1 mmol) and toluene (20 cm^3). To this solution was added 1,2-diphenylhydrazine (0.38 g, 2.1 mmol). Reaction was immediate resulting in a homogeneous solution with a slight brownish tint. The system was removed from the dry box and placed in an oil bath at 80°C for 4 h. After cooling to room temperature, the reaction mixture was concentrated and cooled in the freezer at -10°C. After several days, a modest yield (0.49 g, 60%) of X-ray quality crystals of $[Np_2Al\text{-}N(H)Ph]_2$, **I**, was isolated. m.p. 137–139°C. ^1H NMR (C_6D_6): δ 0.86 (s, 8H, Al-$CH_2C(CH_3)_3$), 1.13 (s, 36H, Al-$CH_2C(CH_3)_3$), 2.70 (bs, 2H, N-*H*), 7.04–7.12 (mult., 4H, arom. H), 8.0 (d, 6H, arom. H). *Anal.* Calcd. for $C_{32}H_{56}N_2Al_2$: C, 73.52; H, 10.8. Found: C, 71.54; H, 8.60.

Synthesis of [Np_2Al-SNp]$_2$, II

To a reaction vessel containing a 20 cm^3 toluene solution of Np_3Al (0.80 g, 3.3 mmol) was added sulfur (0.105 g, 3.3 mmol) in the drybox. The reaction vessel was heated in an oil bath (100°C) for 24 h, during which time the sulfur completely dissolved forming a clear solution. Upon cooling to −10°C in the freezer, a crop of clear, air-sensitive, X-ray quality crystals formed in 92% yield. m.p. 245–247°C. ^1H NMR (C_6D_6): δ 0.77 (s, 8H, $AlCH_2$), 0.87 (s, 18H, $SCH_2C(CH_3)_3$), 1.31 (s, 36H, $AlCH_2C(CH_3)_3$), 2.79 (s, 4H, SCH_2). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 28.5 ($SCH_2C(CH_3)_3$), 30.3 ($AlCH_2$), 32.0 ($AlCH_2C$), 32.3 (SCH_2C), 35.2 $AlCH_2C(CH_3)_3$), 42.9 (SCH_2). *Anal.* Calcd for $C_{30}H_{66}Al_2S_2$: C, 66.12; H, 12.21. Found: C, 66.14; H, 12.03.

Synthesis of [Ph_2Al-N(H)Ph′]$_2$, III

A reaction vessel containing a hexane (15 cm^3) solution of H_2NPh' (0.18 g, 1.10 mmol) was introduced to the dry box where $Ph_3Al \cdot OEt_2$ (0.40 g, 1.10 mmol) was added. The system was removed from the dry box and heated in an oil bath (100°C) for 12 h. Cooling afforded a substantial amount of solid. Recrystallization after the addition of toluene (15 cm^3) with gradual warming (until all solids dissolved) yielded a quantitative yield of slightly beige, X-ray quality, rectangular crystals of [Ph_2Al-N(H)Ph′]$_2$. m.p. 239–241°C. ^1H NMR (C_6D_6): δ 5.32 (s, 1H, NH), 5.61 (s, 1H, NH), 6.74–7.67 (mult., 38H, arom.). *Anal.* Calcd. for $C_{48}H_{40}Al_2N_2$: C, 82.50, H, 5.77. Found: C, 81.61; H, 6.16.

X-ray Structural Determinations

Single, colorless parallelepiped crystals of each compound were mounted in glass capillaries under an atmosphere of argon. X-ray intensity data were collected on a Nicolet R3m/V diffractometer using an $\omega/2\theta$ scan technique with Mo-Kα radiation (λ = 0.71073 Å) at 21°C. Both **I** and **II** crystallize in the monoclinic space group $P2_1/n$ (No. 14), while **III** crystallizes in the tetragonal space group $I4_1/a$ (No. 88). The structures were solved by direct methods with the use of SHELXTL.[6] Relevant crystallographic data are given in Table 1. Atomic coordinates are given in Tables 2, 3 and 4 for compounds **I**, **II**, and **III**, respectively. Bond distances and angles are given in Tables 5, 6 and 7. Molecular structures for **I**, **II**, and **III** are given in Figures 1, 2 and 3, respectively.

[Np_2Al-N(H)Ph]$_2$, I

Cell parameters and an orientation matrix for data collection were obtained from a least-squares refinement of the setting angles of 24 carefully centered reflections in the range $14.75 < 2\theta < 25.65°$ with intensities $I > 3\sigma(I)$. Anisotropic thermal parameters were used for the non-hydrogen atoms. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at idealized positions (d_{C-H} = 0.96 Å; d_{N-H} = 0.90 Å), and were allowed to ride upon the atom to which they were bonded. Isotropic group thermal parameters were refined for the amine, methylene, and phenyl hydrogen atoms (U_{iso} = 0.069(8) $Å^2$) and for the methyl hydrogen atoms (U_{iso} = 0.17(1) $Å^2$). The

Table 1 Crystallographic data for $[Np_2Al\text{-}N(H)Ph]_2$, **I**, $[Np_2Al\text{-}SNp]_2$, **II**, and $[Ph_2Al\text{-}N(H)Ph']_2$ **III**

	I	II	III
Chemical formula	$C_{32}H_{56}N_2Al_2$	$C_{30}H_{66}S_2Al_2$	$C_{48}H_{40}N_2Al_2$
Formula weight	522.75	544.93	698.82
Crystal system	Monoclinic, $P2_1/n$ (No. 14)		Tetragonal, $I4_1/a$ (No. 88)
a(Å)	9.801(3)	10.191(5)	26.628(5)
b(Å)	20.490(9)	10.907(5)	
c(Å)	17.569(8)	16.779(6)	11.017(4)
β(°)	97.81(3)	97.18(3)	
V(Å^3)	3496(3)	1851(1)	7812(4)
Z	4	2	8
D_{calc}(g/cm^3)	0.993	0.978	1.19
Diffractometer		Nicolet R3m/V	
Radiation		Mo-Kα(γ = 0.71073 Å)	
Temperature (°C)		21	
2θ range (°)	3.5–40.0	3.5–45.0	3.5–45.0
Reflections collected	4095	5665	2828
Reflections observed	1160 ($I > 3\sigma(I)$)	1646 ($I > 3\sigma(I)$)	1054 ($I > 3\sigma(I)$)
GOF	0.93	1.65	1.30
R	0.051	0.051	0.064
R_W	0.049	0.066	0.058

weighting scheme was based on counting statistics and included a factor (p = 0.0005) to downweight the intense reflections. Peaks on the final difference map ranged from −0.16 to 0.16 e$^-$/Å^3. The final cycle of full-matrix least-squares refinement, based on 1160 observed reflections, converged at $R = 0.051$, $R_w = 0.049$.

$[Np_2Al\text{-}SNp]_2$, II

The setting angles of 49 carefully centered reflections in the range $25.51 < 2\theta < 33.44$°C afforded cell parameters and an orientation matrix for data collection. The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were located by standard difference Fourier techniques, were included in the structure factor calculation at idealized positions (d_{C-H} = 0.96 Å), and were allowed to ride onthe atom to which they were bonded. An isotropic thermal parameter (U_{iso} = 0.159 (5) Å^2) was refined for all of the hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on 1646 observed reflections ($I > 3\sigma(I)$) and 155 variable parameters and converged (largest parameter shift was 0.01 times its estimated standard deviation) with final residual values of $R = 0.051$, $R_w = 0.066$. The weighting scheme was based on counting statistics and included a factor (p = 0.0005) to downweight the intense reflections. Peaks on the final difference map ranged from −0.14 to 0.27 e$^-$/Å^3.

$[Ph_2Al\text{-}N(H)Ph']_2$, III

Cell parameters and an orientation matrix for data collection were obtained from a least-squares analysis of the setting angles of 41 carefully centered reflections in the range 18.39 < 20 < 26.38°. The non-hydrogen atoms were refined anisotropi-

Table 2 Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2$ × 10^3) for $[Np_2Al\text{-}N(H)Ph]_2$, **I**

Atom	*x*	y	z	U(eq)*
Al(1)	4356(3)	4215(2)	2540(2)	48(1)
Al(2)	6789(3)	3390(2)	2723(2)	47(1)
N(1)	4859(7)	3338(4)	2961(4)	46(4)
N(2)	6322(7)	4294(4)	2376(4)	46(4)
C(1)	3300(9)	4123(5)	1515(5)	53(5)
C(2)	2765(11)	4708(5)	991(6)	57(5)
C(3)	1587(10)	5071(5)	1319(6)	87(6)
C(4)	3971(10)	5196(5)	971(6)	87(6)
C(5)	2226(12)	4486(5)	171(6)	103(6)
C(6)	3897(10)	4828(5)	3335(5)	60(5)
C(7)	2812(12)	4665(6)	3872(7)	62(6)
C(8)	3483(13)	4204(6)	4494(6)	140(8)
C(9)	1561(12)	4359(6)	3431(7)	130(8)
C(10)	2413(11)	5284(5)	4271(6)	99(6)
C(11)	7046(10)	2835(5)	1831(5)	59(5)
C(12)	8238(12)	2962(6)	1347(7)	62(6)
C(13)	8520(12)	2358(6)	902(8)	143(8)
C(14)	7829(13)	3499(6)	775(7)	146(9)
C(15)	9542(12)	3159(7)	1833(7)	133(8)
C(16)	8029(10)	3409(5)	3702(6)	71(5)
C(17)	8338(13)	2794(6)	4229(7)	71(6)
C(18)	8977(14)	2269(6)	3829(7)	166(9)
C(19)	9348(12)	2973(6)	4931(7)	137(8)
C(20)	7040(14)	2544(6)	4497(7)	144(8)
C(21)	3986(11)	2778(5)	2829(8)	45(5)
C(22)	3576(11)	2537(6)	2095(7)	51(5)
C(23)	2710(13)	2005(7)	1967(8)	73(7)
C(24)	2231(14)	1692(6)	2582(11)	96(8)
C(25)	2637(15)	1934(7)	3307(9)	93(8)
C(26)	3489(13)	2460(6)	3433(7)	68(6)
C(27)	7202(11)	4858(6)	2590(9)	54(6)
C(28)	7722(12)	5208(7)	2028(7)	64(6)
C(29)	8539(15)	5725(8)	2213(9)	93(8)
C(30)	8875(13)	9550(7)	2948(7)	101(9)
C(31)	8331(13)	5594(8)	3524(8)	80(7)
C(32)	7520(12)	5064(6)	3350(8)	63(6)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

cally. Hydrogen atoms were located by standard difference Fourier techniques and were included in the structure factor calculation at idealized positions (d_{C-H} = 0.96 Å; d_{N-H} = 0.90 Å), and were allowed to ride on the atoms to which they were bonded. An isotropic group thermal parameter (U_{iso} = 0.079(7) $Å^2$) was refined for all hydrogen atoms. The final cycle of full-matrix least-squares refinement was based on 1054 observed reflections and 236 variable parameters and converged (largest parameter shift was 0.01 times its estimated standard deviation) with final residual values of R = 0.064, R_w = 0.058. The weighting scheme was based on counting statistics and included a factor (p = 0.0005) to downweight the intense reflections. Peaks on the final difference map ranged from −0.21 to 0.29 $e^-/Å^3$. Relevant crystallographic data are given in Table 1, while atomic coordinates are given in Table 4. Bond distances and angles are given in Table 7.

Table 3 Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for $[Np_2Al\text{-}SNp]_2$, **II**

Atom	*x*	y	z	U(eq)*
Al (1)	1350 (1)	9191 (1)	5162 (1)	57 (1)
S (1)	-834 (1)	8879 (1)	5438 (1)	58 (1)
C (1)	2465 (5)	9553 (4)	6184 (3)	77 (2)
C (2)	2777 (5)	8630 (4)	6858 (3)	69 (2)
C (3)	3143 (9)	7425 (6)	6544 (4)	157 (4)
C (4)	3860 (6)	9110 (6)	7476 (3)	124 (3)
C (5)	1584 (6)	8413 (7)	7284 (3)	126 (3)
C (6)	1716 (5)	7999 (4)	4334 (3)	85 (2)
C (7)	2668 (5)	8220 (4)	3728 (3)	67 (2)
C (8)	2993 (7)	7046 (5)	3320 (4)	124 (3)
C (9)	3887 (7)	8820 (9)	4138 (5)	185 (5)
C (10)	2131 (10)	9090 (6)	3109 (4)	177 (5)
C (11)	-1662 (5)	7664 (4)	4804 (3)	71 (2)
C (12)	-2157 (5)	6617 (4)	5275 (3)	65 (2)
C (13)	-3155 (6)	7056 (6)	5794 (4)	111 (3)
C (14)	-1021 (6)	6019 (5)	5805 (4)	116 (3)
C (15)	-2801 (6)	5694 (4)	4667 (3)	92 (2)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 4 Atomic coordinates (× 10^4) and equivalent isotropic thermal parameters ($Å^2 \times 10^3$) for $[Ph_2Al\text{-}N(H)Ph']_2$, **III**

Atom	*x*	y	z	U(eq)*
Al (1)	5637 (1)	5212 (1)	792 (2)	43 (1)
N (1)	4721 (2)	4847 (2)	956 (5)	38 (3)
C (1)	5301 (3)	5871 (3)	1558 (7)	46 (3)
C (2)	4864 (4)	6166 (4)	1551 (8)	58 (4)
C (3)	4839 (4)	6617 (4)	2225 (9)	69 (5)
C (4)	5238 (5)	6765 (4)	2923 (9)	78 (5)
C (5)	5663 (4)	6478 (4)	2983 (9)	70 (5)
C (6)	5690 (3)	6041 (3)	2304 (8)	54 (4)
C (7)	5956 (3)	4812 (3)	1262 (8)	39 (3)
C (8)	6028 (3)	4627 (3)	2424 (9)	57 (4)
C (9)	6472 (4)	4395 (3)	2780 (9)	62 (4)
C (10)	6846 (4)	4331 (3)	1957 (10)	66 (5)
C (11)	6797 (3)	4495 (3)	796 (9)	58 (4)
C (12)	6351 (3)	4725 (3)	455 (8)	51 (4)
C (13)	4693 (3)	4455 (3)	1877 (8)	38 (3)
C (14)	4907 (3)	3990 (3)	1652 (8)	51 (4)
C (15)	4893 (3)	3613 (3)	2514 (10)	62 (4)
C (16)	4671 (4)	3698 (4)	3614 (9)	67 (5)
C (17)	4465 (3)	4163 (4)	3879 (8)	57 (4)
C (18)	4463 (3)	4536 (3)	2990 (9)	41 (4)
C (19)	4215 (4)	5022 (4)	3298 (9)	51 (4)
C (20)	3734 (4)	5123 (4)	2899 (8)	64 (5)
C (21)	3500 (5)	5582 (5)	3149 (11)	99 (6)
C (22)	3751 (6)	5939 (5)	3807 (12)	103 (7)
C (23)	4220 (6)	5838 (5)	4239 (11)	100 (6)
C (24)	4452 (4)	5392 (4)	3962 (9)	70 (5)

* Equivalent isotropic U defined as one third of the trace of the orthogonalized U_{ij} tensor

Table 5 Selected bond distances (Å) and angles (°) for $[Np_2Al\text{-}N(H)Ph]_2$, **I**

Atoms	Distance	Atoms	Distance
Al(1)-Al(2)	2.904 (4)	Al(1)-N(1)	1.978 (8)
Al(1)-N(2)	1.992 (8)	Al(1)-C(1)	1.961 (9)
Al(1)-C(6)	1.977 (10)	Al(2)-N(1)	1.994 (8)
Al(2)-N(2)	1.985 (8)	Al(2)-C(11)	1.981 (10)
Al(2)-C(16)	1.966 (9)	N(1)-C(21)	1.432 (13)
N(2)-C(27)	1.460 (13)		

Atoms	Angle	Atoms	Angles
N(1)-Al(1)-N(2)	86.1 (3)	N(1)-Al(1)-C(1)	109.3 (4)
N(2)-Al(1)-C(1)	106.0 (4)	N(1)-Al(1)-C(6)	112.5 (4)
N(2)-Al(1)-C(6)	111.6 (4)	C(1)-Al(1)-C(6)	124.6 (4)
N(1)-Al(2)-N(2)	85.9 (3)	N(1)-Al(2)-C(11)	111.2 (4)
N(2)-Al(2)-C(11)	110.0 (4)	N(1)-Al(2)-C(16)	108.0(4)
N(2)-Al(2)-C(16)	109.9 (4)	C(11)-Al(2)-C(16)	125.0(4)
Al(1)-N(1)-Al(2)	94.0 (3)	Al(1)-N(1)-C(21)	123.7 (6)
Al(2)-N(1)-C(21)	124.9 (7)	Al(1)-N(2)-Al(2)	93.8 (3)
Al(1)-N(2)-C(27)	125.2 (7)	Al(2)-N(2)-C(27)	123.8 (6)
Al(1)-C(1)-C(2)	124.2 (7)	C(1)-C(2)-C(3)	110.9 (9)

Table 6 Selected bond distances (Å) and angles (°) for $[Np_2Al\text{-}SNp]_2$, **II**

Atoms	Distance	Atoms	Distance
Al(1)-Al(2)	2.752 (4)	Al(1)-S(1)	2.353 (2)
Al(1)-S(1A)	2.364 (8)	Al(1)-C(1)	1.976 (4)
Al(1)-C(6)	1.972 (5)	S(1)-C(11)	1.837 (4)
C(1)-C(2)	1.517 (8)	C(2)-C(3)	1.481 (8)
C(2)-C(4)	1.510 (9)		

Atoms	Angle	Atoms	Angles
S(1)-Al(1)-S(1A)	92.7 (1)	S(1)-Al(1)-C(1)	108.2 (2)
S(1)-Al(1)-C(6)	108.1 (2)	S(1)-C(11)-C(12)	113.7 (3)
S(1)-C(11)-C(12)	113.7 (3)	Al(1)-S(1)-C(11)	111.5 (2)
Al(1)-C(1)-C(2)	123.9 (3)	C(1)-C(2)-C(3)	111.3 (4)
Al(1)-C(6)-C(7)	124.3 (3)	C(11)-C(12)-C(13)	111.0 (4)
S(1)-C(11)-C(12)	113.7 (3)	C(1)-Al(1)-C(6)	127.2 (2)

Table 7 Selected bond distances (Å) and angles (°) for $[Ph_2Al\text{-}N(H)Ph]_2$, **III**

Atoms	Distance	Atoms	Distance
Al(1)-Al(1A)	2.854 (4)	Al(1)-N(1)	1.983 (7)
Al(1)-N(1A)	1.946 (6)	Al(1)-C(1)	1.956 (8)
Al(1)-C(7)	1.964 (9)	Al(1A)-N(1)	1.946 (6)
N(1)-C(13)	1.459 (11)	C(1)-C(6)	1.384 (13)
C(18)-C(19)	1.493 (13)	C(2)-C(3)	1.414 (14)

Atoms	Angle	Atoms	Angles
N(1)-Al(1)-N(1A)	86.9 (3)	N(1)-Al(1)-C(1)	108.8 (3)
N(1A)-Al(1)-C(1)	119.2 (3)	N(1)-Al(1)-C(7)	113.7 (3)
N(1A)-Al(1)-C(7)	108.3 (3)	C(1)-Al(1)-C(7)	116.4 (4)
Al(1)-N(1)-Al(1A)	93.1 (3)	Al(1)-C(1)-C(2)	125.0 (7)
Al(1)-C(1)-C(6)	118.6 (6)	N(1)-C(13)-C(18)	121.7 (8)
C(2)-C(1)-C(6)	115.8 (8)	C(13)-C(18)-C(19)	122.1 (8)

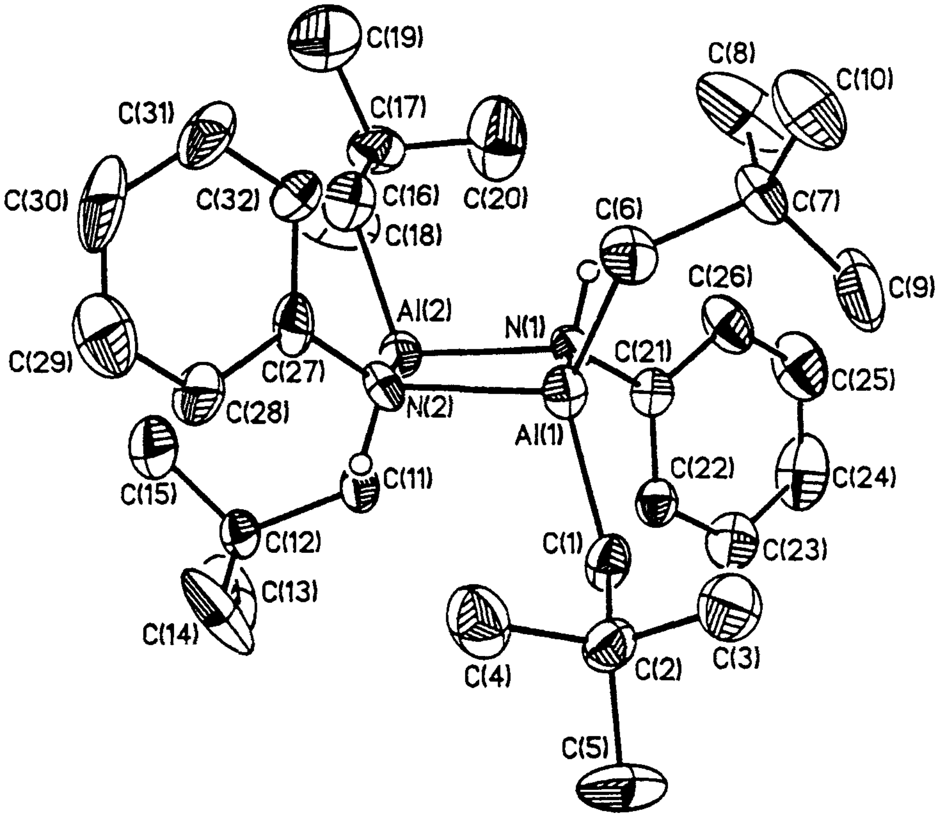


Figure 1 X-ray structure of $[Np_2Al\text{-}N(H)Ph]_2$, I.

RESULTS AND DISCUSSION

Studies of a variety of nitrogen-based crown ethers[7] and sterically demanding amines[8] have been conducted in our exploration of organoaminoalane chemistry. Previous studies in this laboratory have also involved the coordination chemistry of alkylaluminum compounds with sulfur-based crown ethers.[9] Only sterically unremarkable and readily available organoaluminum moieties such as Me_3Al have been reported with hydrazine derivatives or elemental Group 16 derivatives.

Hydrazines have substantial reactivity. The moderate reactivity of Np_3Al makes it an ideal probe for such reactive systems. The isolation of $[Np_2Al\text{-}N(H)Ph]_2$, **I**, is noteworthy as it was produced *via* an interesting reaction between hydrazine and a bulky alkyl aluminum moiety. **I** consists of two *aniline-based* moieties bridged by a pair of dineopentylaluminum units constituting a planar Al_2N_2 four-membered ring. Indeed, the planarity of the Al_2N_2 ring may well be predicted from the sum of the internal ring angles of 359.8°.[10] The core Al-N bond distances ranged from 1.978 (8) to 1.985 (8) Å. The phenyl rings are approximately orthogonal to the Al_2N_2 ring. The Al(1)-N(1)-Al(2) bond angle for **I** is 94.0 (3)°, while the

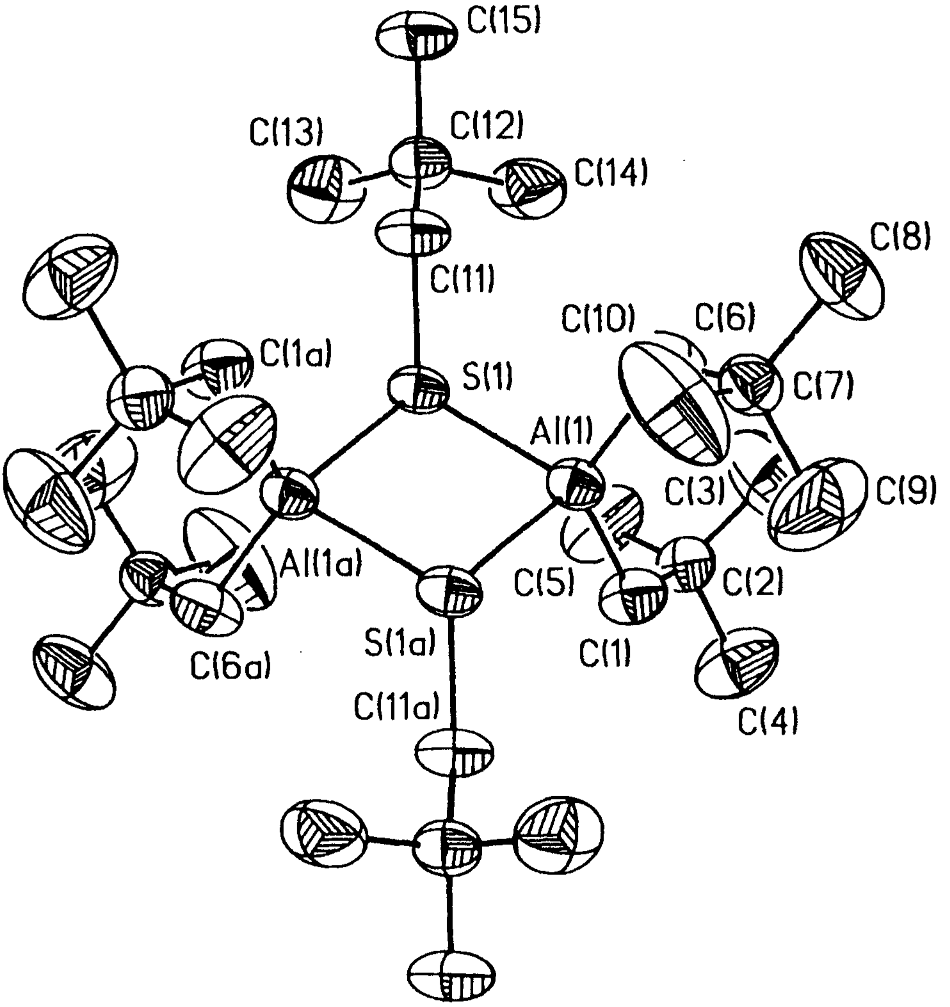


Figure 2 X-ray structure of $[Np_2Al\text{-}S(Np)]_2$, **II**.

N(1)-Al(1)-N(2) angle is 86.1 (3)°. The mean Al-C bond distance of 1.97 (1) Å is well within the range normally found in $[R_2Al\text{-}N(H)R']_2$ complexes. The coordination about the aluminum and nitrogen atoms may be described as distorted tetrahedral.

It is interesting to consider the hydrazine behaving as a primary amine in the presence of R_3Al. Indeed, Krannich[11] observed similar, albeit hetero-bimetallic, Group 15 bond cleavage in the reaction of Me_3Al with aminoarsines. While one may envisage the preparation of **I** more direct methods (such as reaction of Np_3Al with H_2NPh) the compound was isolated from a hydrazine system. Indeed, reaction of Me_3Al with H_2NPh affords the novel Al_6N_6 hexamer

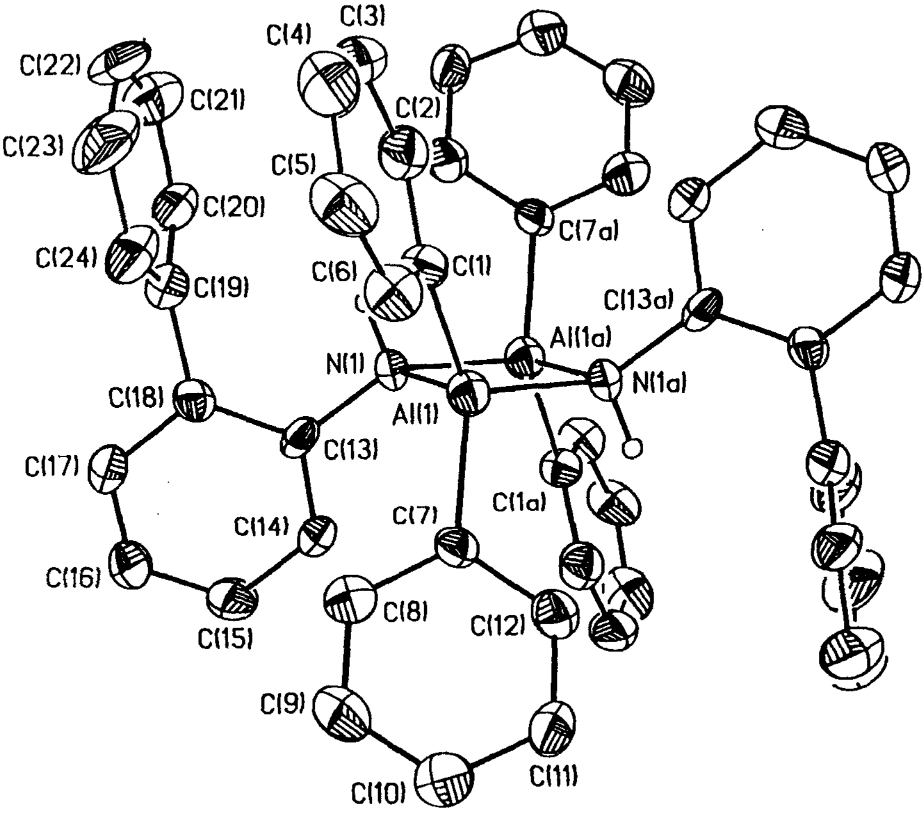
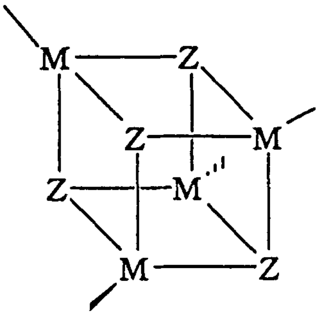


Figure 3 X-ray structure of $[Ph_2Al\text{-}N(H)Ph']_2$, **III**.

hexakis(methyl-μ_3-phenylimidoaluminum), $[MeAl\text{-}NPh]_6$.[12] Thus, it is reasonable to consider that **I** resulted from direct cleavage of the N—N bond in 1,2-diphenylhydrazine.

Organoaluminum chemistry of chalcogens may be traced to more than fifty years ago with the preparation of $[Me_2Al\text{-}SMe]$ by Davidson and Brown.[13] This product was reported to be dimeric in the vapor phase by electron diffraction,[14] but polymeric in the solid state by X-ray diffraction techniques.[15] Aluminum and group 16 complexes are presently popular as shown by the preparation of $[(t\text{-}Bu)_2Al(Se\text{-}t\text{-}Bu)]_2$, isolated from reaction of $t\text{-}Bu_3Al$ with elemental selenium.[16] Indeed, a number of novel aluminum-chalcogen cubane derivatives $[RM(\mu_3\text{-}Z)]_4$ (M = Al, Ga; Z = S, Se, Te), below, have been reported.[17]

The central core of **II** contains a four-membered Al_2S_2 ring, and represents a structural characterization of a thioalane resulting from R_3Al interacting with elemental sulfur. The Al(1)-S(1) distance of 2.353(2) Å and the Al(1)-S(1A) distance of 2.364(2) compare to the Al-S distances of 2.413(2) and 2.397(2) Å in $[Me_2Al(\mu\text{-}SC_6F_5]_2$[18] and 2.328(2) Å in $[(CH_3)_2AlS(CH_3)]_n$, respectively.[19] Indeed, the observed Al-S distances are within the range of reported Al-S distances of



2.304–2.489 Å.[20] While the Al-S distances in **II** may be regarded as reasonably short when one considers the reported Al-S distance of 2.718 Å,[9b] an Al-S distance of 2.18 Å has also been reported,[21] revealing a wide range of bond distances for Al-S compounds. Similar to **I**, the dimer **II** consists of two *neopentathiol-based* moieties bridged by two dineopentylaluminum units constituting the Al_2S_2 core. The Al-S bond distances, as well as the Al(1)-S-Al(1A) angle of 87.3(1)° and the S(1)-Al(1)-S(1A) angle of 92.7(1)°, support an asymmetric Al_2S_2 core. Further heating of **II** did not afford higher Al-S oligomers. The literature reveals few structurally characterized Al-S compounds, particularly discrete Al-S dimers.

While aryl ligands have clearly been gaining popularity in Group 13 chemistry.[22] there are few reported structural characterizations of Ph_3Al derivatives. Aside from the solid-state structure of Ph_3Al, which confirmed a dimeric structure,[23] only the triphenyl(η^5-cyclopentadienyl)dicarbonyliron)aluminate anion, $[Ph_3Al\text{-}Fe(CO)_2Cp^-]$,[24] and the Ph_3Al-amine monomer, $[Ph_3Al\text{-}N(H)_2t\text{-}Bu]$[2a] have been structurally characterized. The $[Ph_3Al\text{-}N(H)_2t\text{-}Bu]$ monomer was particularly interesting as it demonstrated unusual thermal stability, resisting condensation even in boiling benzene. As evidenced by the isolation of **III**, the Ph_3Al ligand is sufficiently reactive to undergo condensation with 2-aminobiphenyl. We also reported reactions wherein the $H_2Nt\text{-}Bu$ reacts with Np_3Al,[25] also affording a dimeric product $[Np_2Al\text{-}N(H)t\text{-}Bu]_2$. The difference in reactivity of the phenyl ligand makes it a useful probe for exploring the effects of steric bulk in Group 13–15 systems. **III** possesses crystallographic inversion symmetry and resides in a *trans* conformation about a planar Al_2N_2 four-membered ring. The Al_2N_2 core in **III** is asymmetric with Al-N bond distances of 1.983(7) and 1.946(6) Å. The Al(1)-N(1)-Al(1A) angle of 93.1(3)° compares to 86.9(3)° for the N(1)-Al(1)-N(1A) angle. The Al-C bond distances in **III**, 1.956(8) and 1.964(9) Å, are somewhat shorter than the Al-C distances found in the $Ph_3Al\text{-}N(H)_2t\text{-}Bu$ monomeric adduct. The Al-N distances (mean 1.96 Å) in **III** are very similar to the Al-N distance of 1.98(2) Å found in the adduct, and are well within the 1.95 to 2.00 Å range typical of Al-N bonds in Al_2N_2 fragments.

Sterically demanding and less often employed aluminum alkyls such as Np_3Al and Ph_3Al offer insight into important aspects of the coordination chemistry of aluminum — particularly in cases where the Lewis base is quite reactive. Indeed, it is interesting that further pyrolysis of these products did not afford higher oligomers.

Acknowledgment

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Supplementary material

Summaries of data collection and refinement, plots of the molecules, and tables of crystal data, bond distances and angles, atomic coordinates, and thermal parameters and a listing of observed and calculated structure factors are available from the authors upon request.

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