Notes

The First Structurally Characterized Monolithio Aluminum Amide Dimer

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Summary: Herein is reported the first synthesis and structural characterization of a monolithio aluminum amide dimer: $[Me_2AlNLi(THF)_2Ph]_2$*. It is prepared by deprotonation of the corresponding neutral dimeric species* $[Me_2AlNHPh]_2$ *with tBuLi in THF in 78% yield. Characterization data include* ^1H *and* ^{13}C *NMR, elemental analysis, and a single crystal X-ray analysis. The crystal structure demonstrates that the lithium atoms are still associated with the molecule. The spectroscopic and structural data indicate that there is not a significant degree of* π *bonding between the Al and N atoms.*

Introduction

Compared to the neutral species, very little, in general, has been reported for charged group 13−15 systems. We have been actively seeking to advance the chemistry of both anionic[1] and cationic[2] group 13 complexes and, potentially, discover complexes which possess π-bonding. In searching for π-bonded systems the anionic species would intuitively be the best complexes to examine. Indeed, a previously reported anionic complex $[Mes_2B{=}AsLi(THF)_3Ph]Li$ and the same complex with the lithium atom displaced, $[Mes_2B{=}AsPh]Li(TMEDA)_2$, have been shown to possess multiple bond character.[3] However, no analogous efforts have, as yet, been reported for the heavier group 13 elements. In this Note we report the first monolithio aluminum amide dimer of formula $[Me_2AlNLi(THF)_2Ph]_2$. It also represents the next step in the progression from monomeric to dimeric group 13 lithium complexes.

Results and Discussion

The dialkyl aluminum−primary amido dimer, $[Me_2AlNHPh]_2$ (**1**), was prepared by the reaction of $AlMe_3$ with H_2NPh.[4] Deprotonation of **1** with tBuLi in THF leads to the monolithio derivative $[Me_2AlNLi(THF)_2Ph]_2$ (**2**) which can be isolated as pale yellow crystals by recrystallization from a 50/50 toluene/THF mixture at −30 °C in 78% yield.

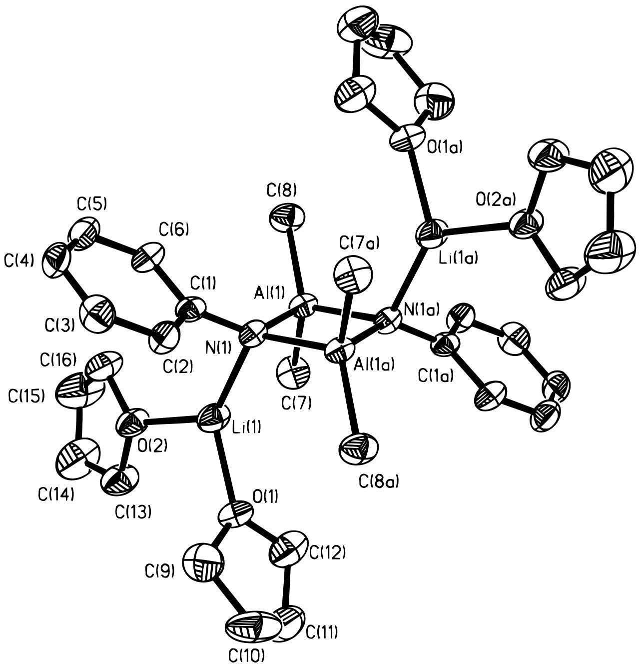

Figure 1. ORTEP drawing of $[Me_2AlNLi(THF)_2Ph]_2$ (**2**). Selected bond distances (Å) and angles (deg): Al(1)−N(1) 1.888(5), Al(1)−Li(1) 2.868(9), Al(1)−C(7) 1.994(8), Al(1)−C(8) 1.981(5), Al(1)−N(1A) 1.904(5), O(1)−Li(1) 1.918(9), O(2)−Li(1) 1.940(12), N(1)−Li(1) 2.023(12), N(1)−C(1) 1.400(8); N(1)−Al(1)−C(7) 109.8(2), N(1)−Al(1)−C(8) 120.8(3), C(7)−Al(1)−C(8) 107.3(3), N(1)−Al(1)−N(1A) 88.3(2), C(7)−Al(1)−N(1A) 110.4(3), C(8)−Al(1)−N(1A) 119.1(2), Al(1)−N(1)−Li(1) 94.3(5), Al(1)−N(1)−C(1) 134.0(3), Li(1)−N(1)−C(1) 98.6(5), Al(1)−N(1)−Al(1A) 91.7(2), Li(1)−N(1)−Al(1A) 115.5(3), C(1)−N(1)−Al(1A) 120.9(4).

The spectroscopic data for neutral **1** indicates that there is a dimer−trimer equilibrium present.[4] After lithiation, however, the resulting compound **2** does not show evidence of fluxional behavior. There is one singlet for the MeAl resonances (δ −0.22 ppm (C_6D_6)) which is shifted downfield from the multiplet seen for the neutral species (centered at δ −0.45 ppm (C_6D_6)). Additionally, there are two peaks (δ 1.73 and 3.58 ppm) for the two THF molecules. In the ^{13}C NMR, the carbon bonded to nitrogen appears as a resonace at δ 163.6 ppm. In **1** there are two carbons of this type located at δ 142.0 and 143.4.

In order to examine the possiblity of π bonding from a structural perspective, an X-ray crystallographic study was undertaken for **2**. A molecular structure of this complex is shown in Figure 1, with the important bond distances and angles making up the figure caption. Due

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[1] (a) Atwood, D. A.; Rutherford, D. *Inorg. Chem.* **1995**, *34*, 4008.

[2] (a) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *J. Am. Chem. Soc.* **1995**, *117*, 6779. (b) Atwood, D. A.; Jegier, J. A.; Rutherford, D. *Inorg. Chem.* **1995**, in press.

[3] Petrie, M. A.; Shoner, S. C.; Rasika Dias, H. V.; Power, P. P. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 1033.

[4] Al-Wassil, A.-A. I.; Hitchcock, P. B.; Sarisaban, S.; Smith, J. D.; Wilson, C. L. *J. Chem. Soc., Dalton Trans.* **1985**, 1929.

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Table 1. Summary of Structural Parameters for Selected Compounds Possessing an Al−N Bond

compound[a]	Al−N	C−N−Al	N−Al−N′	Al−N−Al′	ref
$[Me_2AlNLi(THF)_2Ph]_2$ (**2**)	1.888(5)	134.0(3)	88.3(2)	92.7(2)	this work
$[Me_2AlNH(Ad)]_2$	1.99(ave)	132.9(9)	82.6(4)	94.7(5)	5
$[iBu_2AlNHPh]_2$	1.978(2)	123.0(2)	86.5(1)	93.5(1)	6
$[iBu_2AlNHDipp]_2$	1.99(ave)	141.8(5)	84.4(3)	93.2(3)	6
$[MeAlNDipp]_3$	1.782(4)	not reported	115.3(5)	124.7(5)	5

[a] Ad = 1-adamantyl; Dipp = 2,6-diisopropylphenyl.

to the equilibrium inherent to solutions of **1**, crystals suitable for X-ray diffraction were not available. Thus, a direct comparison between the neutral **1** and anionic **2** systems was not possible. However, the structural parameters for **2** may be compared to known aluminum−amide structures, some important bond lengths and angles for which can be found in Table 1.

The structure of **2** consists of a nitrogen-bridged dimer with the aluminum atoms adopting a distorted tetrahedral geometry. The Al_2N_2 four-membered ring is planar with Al−N bond distances of 1.888(5). This is shorter than that found for the neutral, dimeric derivatives listed in Table 1. However it is also longer than that demonstrated for $[MeAlNDipp]_3$ (1.782(4) Å) which possesses a three-coordinate aluminum. The geometry around N(1) closely approximates trigonal pyramidal with C(1), Al(1), and Al(1A) forming the basal plane and Li(1) at its apex. The angles that Li makes with the constituents of the plane falls in the range 94.3(5)−115.5(3)°. The most significant deviation from planarity for the atoms in the basal plane is found for C1 (0.675 Å). Additionally, the phenyl ring forms a dihedral angle of 36° with the Al_2N_2 ring. In the absence of steric forces this angle would be expected to be 0° if there were a significant degree of π delocalization present. Thus, based upon the spectroscopic and structural data there is not a significant degree of π bonding within **2**.

Conclusion

Attempts to dissociate the lithium atom with 12-crown-4 and TMEDA (tetramethylethylenediamine) in order to prepare discrete dianionic complexes, and explore the possibility of Al═N bonding for the free dianionic species ($[Me_2AlNPh]_2^{2-}$) have, thus far, not been successful. Moreover, attempts to isolate clean, crystalline samples of other monolithio derivatives such as $[R_2AlNLi(THF)_2R']_2$ (with R(R′) = Me(tBu); Me(2,6-iPrPh); iBu(Ph); iBu(2,6-iPrPh)), have also not been successful. In fact, although the synthesis of **2** can be repeated consistently, to date no other derivatives have been fully characterizable. Thus, the isolation of this type of unique monolithio dimeric species may be dependant on a subtle combination of steric and electronic factors.

Table 2. Crystal Data for $[Me_2AlNLi(THF)_2Ph]_2$ (2)

compound	**2**
formula	$C_{16}H_{27}AlLiNO_2$
formula weight	299.3
crystal system	triclinic
space group	$P\bar{1}$
a (Å)	9.957(5)
b (Å)	10.074(5)
c (Å)	10.579(5)
α (deg)	115.66(4)
β (deg)	97.31(4)
γ (deg)	103.50(4)
V (Å^3)	897.9(8)
Z	2
D_{calc} (mg/cm^3)	1.107
crystal size (mm)	1.0 × 0.6 × 0.4
temperature (K)	298
2θ range (deg)	3.5−45
scan type	$2\theta-\theta$
scan speed (deg/min)	12−60
scan range (deg)	0.74
no. of reflections collected	2397
no. of indp reflections	2237
no. of obsd reflections ($F > x\sigma(F)$)	1483 (x = 6)
no. of parameters	187
R	0.0696
R_w	0.0693
GOF	0.91
largest diff peak (e/Å^3)	0.36

Table 3. Atomic Coordinates (×10^5) and Equivalent Isotropic Displacement Coefficients (×10^4 Å^2) for $[Me_2AlNLi(THF)_2Ph]_2$ (2)

atom	x	y	z	U
Al(1)	10589(16)	49770(18)	59309(18)	430(8)
O(1)	−13853(40)	4816(45)	22368(46)	647(23)
O(2)	17982(40)	11331(44)	28750(47)	645(24)
N(1)	6409(42)	44701(48)	39533(45)	437(22)
Li(1)	3735(101)	21835(115)	32193(123)	655(58)
C(1)	14638(55)	47227(58)	30503(60)	462(28)
C(2)	8367(62)	43587(69)	16401(64)	584(32)
C(3)	16198(76)	45728(74)	7127(69)	696(38)
C(4)	30983(77)	51542(74)	11862(81)	728(41)
C(5)	37427(68)	55240(75)	25494(80)	699(39)
C(6)	29716(57)	53143(66)	34921(66)	573(33)
C(7)	8343(68)	30446(69)	60987(66)	672(36)
C(8)	29027(60)	65250(71)	72958(69)	702(35)
C(9)	−20103(82)	−3027(92)	7278(86)	970(49)
C(10)	−35485(58)	−11677(69)	5437(86)	1220(58)
C(11)	−34696	−14716	17564	1139(61)
C(12)	−23055(73)	−1317(89)	29268(88)	892(49)
C(13)	14671(72)	−4576(74)	25522(88)	833(44)
C(14)	27936(88)	−7137(104)	28914(124)	1309(77)
C(15)	38453(87)	7772(103)	37777(122)	1311(70)
C(16)	33076(65)	19025(79)	35763(86)	837(45)

Experimental Section

General Considerations. All manipulations were conducted using Schlenk techniques in conjunction to an inert atmosphere glove box. All solvents were rigorously dried prior to use. NMR data were obtained on JEOL-GSX-400 and −270 instruments at 270.17 (^1H) and 62.5 (^{13}C) MHz. Chemical shifts are reported relative to $SiMe_4$ and are in ppm. Elemental analyses were obtained on a Perkin-Elmer 2400 Analyzer. Infrared data were recorded as KBr pellets on a Matheson Instruments 2020 Galaxy Series spectrometer and are reported in cm^{-1}.

Synthesis and Characterization of $[Me_2AlNLi(THF)_2Ph]_2$ (2). $[Me_2AlNHPh]_2$ (1.04 g, 3.49 mmol) was dissolved in 30 mL of freshly distilled, dry THF and stirred at 25 °C. tBuLi (4.1 mL, 1.72 M in pentane, 7.0 mmol) was added, and the

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(6) Unpublished Results: $[iBu_2AlNHPh]_2$, space group, triclinic *P*-1, with a = 9.393(1) Å, b = 9.479(1) Å, c = 10.891(1) Å, α = 67.22(1)°, β = 68.10(1)°, γ = 61.57(1)°, V = 764.66(13) Å^3, Z = 2, 1602 obs ($F > 4.0\sigma F$) and R = 0.046; $[iBu_2AlNHDipp]_2$, space group, Monoclinic $P2_1/n$, with a = 10.798(2) Å, b = 19.375(2) Å, c = 20.119(2) Å, β = 92.93(1)°, V = 4203.6(10) Å^3, Z = 4, 2316 obs ($F > 4.0\sigma F$) and R = 0.072.

solution momentarily turned deep red, but changed to a light orange upon complete addition. The exothermic reaction was stirred until it reached 25 °C (20 min), and then it was concentrated to 10 mL and 10 mL of toluene was added. Small diamond-shaped crystals grew after storage at −30 °C for 1 week (1.63 g, 78%): ^{1}H NMR (270 MHz, THF-d_8) δ −0.97 (s, 6H, AlCH_3)(in C_6D_6 = −0.22 ppm), 1.73 (m, 8H, THF), 3.58 (m, 8H, THF), 5.82−7.12 (m, 5H, Ph-*H*); ^{13}C NMR (100 MHz, THF-d_8) δ −7.1 (AlCH$_3$), 26.3 (THF), 68.2 (THF), 121.8 (Ph), 128.2, 128.6, 128.8, 129.5, 163.6; IR (neat) 2940, 1603, 1499, 1400, 1263, 1044, 802, 692 cm^{-1}. Anal. Calcd (Found): C, 64.21 (64.31); H, 9.03 (9.22).

X-ray Experimental Details. Crystals suitable for X-ray analysis were grown from a 50/50 toluene/THF mixture over the course of 1 week at −30 °C. There were two molecules in the unit cell and no molecules of solvent. Details of the crystal data and a summary of data collection parameters for the complexes are given in Table 2. Positional parameters are given in Table 3. Data were collected on a Siemens P4 diffractometer using graphite monochromated Mo K_α (0.71073 Å) radiation. The check reflections, measured every 100 reflections, indicated a less than 5% decrease in intensity over the course of data collection for each compound and hence, no correction was applied. All calculations were performed on a personal computer using the Siemens software package, SHELXTL-Plus. The structures were solved by direct methods and successive interpretation of difference Fourier maps, followed by least-squares refinement. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were included in the refinement in calculated positions using fixed isotropic parameters.

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Supporting Information Available: Tables of bond lengths and angles, positional parameters, anisotropic thermal parameters, and unit cell views are available upon request (10 pages). Ordering information is given on any current masthead page.

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