

Isolation and Chemistry of Aluminum Compounds Containing (S)-3,3'-Bis(triphenylsilyl)-1,1'-bi-2,2'-naphthoxide Ligands

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The reaction of the resolved, bulky binol (S)-3,3'-bis(triphenylsilyl)-2,2'-dihydroxy-1,1'-binaphthyl, (S)-H₂O₂C₂₀H₁₀{SiPh₃}₂-3,3' (**1**), with a variety of alkyl and amide compounds has been investigated. Reaction of **1** with [Al₂Me₆] initially proceeds only in a 1:1 ratio to produce dinuclear [Al₂(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)₄], (S)-**2**. Compound **2** contains a [Al(μ-C)(μ-O)] core, Al–Al = 2.739(2) Å, with the binaphthoxide ligand oxygen atoms occupying terminal and bridging positions. In the presence of pyridine, **2** reacts further with **1** to produce [Al(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)(py)], (S)-**4**. The ethyl analogue of **4**, [Al(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)(py)], (S)-**5**, was obtained from [Et₂AlCl]. Both **4** and **5** were shown to adopt tetrahedral geometries in the solid state with O–Al–O angles of ~107°. Reaction of [LiAl(NMe₂)₄] with **1** produced a dinuclear compound, [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NHMe₂)(NMe₂)₂], (S)-**6**, containing a terminal and bridging amido group. The lithium-bound HNMe₂ ligand could be substituted by pyridine to produce [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NC₆H₅)(NMe₂)₂], (S)-**7**. In the solid state the formally three-coordinated lithium atoms in **6** and **7** are pyramidalized. The sum of the three angles for the LiN₂O core is 305° and 322° for **6** and **7**, respectively. This is due to an interaction of the lithium with one arene ring of an SiPh₃ group. In **6** the carbon atoms involved are an *ipso*- and *ortho*-carbon, while for **7** the *ortho*- and *meta*-carbon atoms of a Ph–Si ring are in close contact.

Introduction

The application of aluminum reagents has made some significant contributions to organic synthesis. Besides their application as Lewis acids, aluminum compounds have also been important as reducing and alkylating agents.¹ In all three areas the reactivity of aluminum reagents can be modified by the addition of suitable oxygen donor (typically alkoxide or aryloxy) ligation into the metal coordination sphere. More recently the use of bulky aryloxy ligands attached to aluminum to generate monomeric, “designer” Lewis acid catalysts has been pioneered by Yamamoto and co-workers.^{2,3} Important examples include the compounds [Al(Me)(OC₆H₂-Bu^t-2,6-X-4)₂] (X = Me, acronym “MAD”,^{4,5} and X = Br, “MABR”⁶), [Al(Me)(OC₆H₃Ph₂-2,6)₂] (“MAPH”⁷), and [Al(OC₆H₃Ph₂-2,6)₃] (“ATPH”⁸). These compounds are all

easily obtained by adding the corresponding phenol to AlMe₃ and can be generated “in situ” for use. Significant structural and chemical studies have also been reported from the Barron group.⁹ A continuing challenge centers on the development of chiral analogues for the synthesis of optically pure compounds.¹⁰ A series of aluminum reagents containing C₂-symmetric, chiral aryloxides were also synthesized and have been applied to asymmetric Claisen rearrangements,² aldol reactions,¹¹ and aldehyde alkylations. Over the years many studies have also dealt with the utilization of 2,2'-dihydroxy-1,1'-binaphthyl ligands (BINOLS) in conjunction with aluminum reagents. Despite this extensive literature and demonstrated utility, there are still few structural studies of isolated binaphthoxide derivatives of aluminum.¹² An extensive study of “Noyori’s reagent” did lead to the structures of a number of LiAl binaphthoxide compounds.¹³ As an extension of our work with early transition metal aryloxy compounds, we have begun to study resolved 3,3'-disubstituted-1,1'-bi-2,2'-naphthoxide compounds of these metals. This work is being

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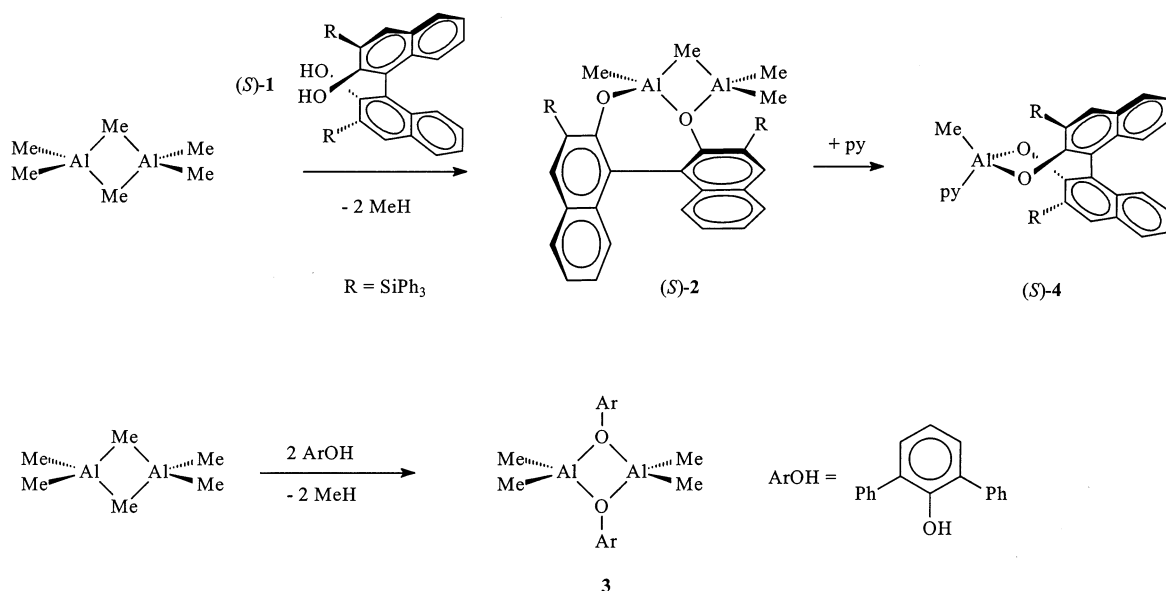
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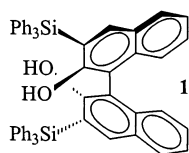
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Scheme 1



extended to cover a variety of chiral, main group derivatives of this ligand set. Recent publications have dealt with germanium compounds.¹⁴ In this paper we report on the synthesis and structures of a series of aluminum compounds containing the bulky (*S*)-3,3'-bis(triphenylsilyl)-1,1'-bi-2,2'-naphthoxide ligand, **1**.



Results and Discussion

Synthesis and Characterization of Methyl Compounds. Reaction of a toluene solution of [Al₂Me₆] with (*S*)-H₂O₂C₂₀H₁₀{SiPh₃}₂-3,3', **1** (1 binol per 2Al), leads to the formation of a single new organometallic product, **2** (Scheme 1). Compound **2** does not react further with **1** under ambient conditions. In fact when a solution of **2** and excess **1** is heated at 100 °C for several hours in C₆D₆, very little noticeable change (as determined by NMR) is observed. The solid state structure of **2** (Figure 1, Table 1) shows the presence of an edge-shared, bis-tetrahedral structure related to that of the [Al₂Me₆] substrate. The binol ligand has two protonated methyl groups and occupies one terminal and one bridging position. Hence the two tetrahedral aluminum atoms in **2** have different coordination environments. In contrast the addition of monophenols (1 HOAr per Al) to [Al₂Me₆] leads to the more symmetric structural motif with both oxygen atoms bridging and the four remaining methyl groups being terminal. This is highlighted by the reaction with 2,6-diphenylphenol, which leads to compound **3** (Scheme 1), which we have structurally characterized (Figure 2, Table 2). Compound **3** has been used as a Lewis acid catalyst/reagent in a number of organic synthesis applications.¹⁵ A ubiquitous stoichiometry, [R₂M(μ₂-OAr)]₂, is well known for all of the

Table 1. Selected Bond Distances (Å) and Angles (deg) for [Al₂(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)₄], (*S*)-2****

Al(1)–O(2)	1.748(3)	Al(1)–O(1)	1.857(3)
Al(2)–O(1)	1.854(3)	Al(1)–C(1)	1.926(4)
Al(1)–C(2)	2.064(5)	Al(2)–C(4)	1.940(5)
Al(2)–C(2)	2.175(5)	Al(2)–C(3)	1.986(5)
Al(1)–Al(2)	2.739(2)		
O(2)–Al(1)–C(1)	114.7(2)	O(2)–Al(1)–O(1)	105.8(1)
O(2)–Al(1)–C(2)	108.5(2)	O(1)–Al(1)–C(1)	118.3(2)
C(1)–Al(1)–C(2)	114.1(2)	O(1)–Al(1)–C(2)	93.2(2)
O(1)–Al(2)–C(3)	114.3(2)	O(1)–Al(2)–C(4)	112.8(2)
O(1)–Al(2)–C(2)	89.8(2)	C(4)–Al(2)–C(3)	123.6(2)
C(3)–Al(2)–C(2)	98.7(2)	C(4)–Al(2)–C(2)	110.7(2)
Al(1)–O(1)–C(11)	118.8(2)	Al(2)–O(1)–C(11)	135.6(2)
Al(1)–C(2)–Al(2)	80.5(2)	Al(2)–O(1)–Al(1)	95.1(1)

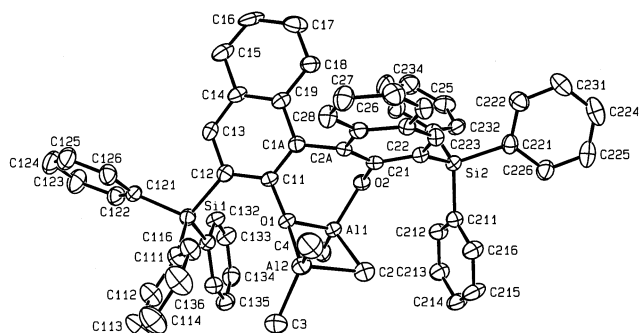


Figure 1. Molecular structure of [Al₂(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)₄], (*S*)-**2**.

group 13 (M = Al, Ga, In, Tl) metals,² although the metal coordination number varies from 4 with simple aryloxides¹⁶ to 5 for chelating ligands.¹⁷ The only other structurally characterized compound related to **2** containing a [Al(μ-R)(μ-OX)Al] core is that reported by Scott et al.¹⁸ This also contains a chelating bis(aryloxide) ligand, although a pair of such units are linked by an anthracene spacer, resulting in a 1,8-anthracene-methanediyl-tetraphenoxide ligand.

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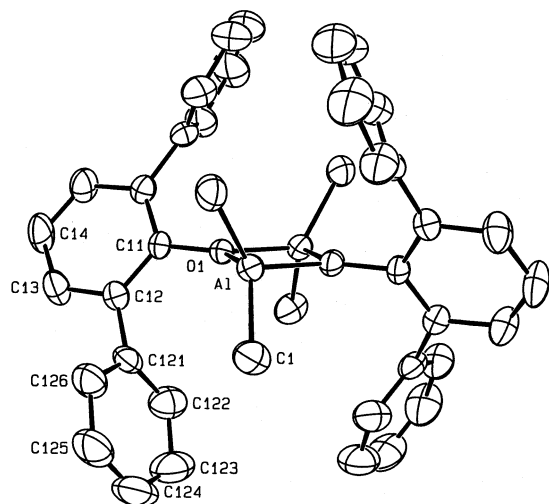


Figure 2. Molecular structure of $[\text{Al}_2(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{CH}_3)_4]$, **3**.

Table 2. Selected Bond Distances (Å) and Angles (deg) for $[\text{Al}_2(\mu\text{-OC}_6\text{H}_3\text{Ph}_2\text{-2,6})_2(\text{CH}_3)_4]$, **3**

Al–O(1)	1.879(1)	Al–C(1)	1.935(2)
Al–Al'	2.898(2)		
C(1)–Al–C(1)'	116.9(2)	O(1)–Al–O(1)'	79.10(8)
Al–O(1)–Al'	100.90(8)		

The Al–Al distances in $[\text{Al}_2\text{Me}_6]$ have been reported as 2.600(4)¹⁹ and 2.606(2) Å,²⁰ whereas a neutron study of $[\text{Al}_2(\text{CD}_3)_6]$ yielded 2.700(8) Å.²¹ This elongates to 2.739(2) Å in (*S*)-**2** and 2.898(2) Å in **3** as $\mu\text{-Me}$ groups are replaced by $\mu\text{-O}$. The value in **3** compares favorably to the distance of 2.757(2) Å found in the Scott compound.¹⁸

Although the molecular structure of **2** contains four nonequivalent methyl groups, only one signal is ob-

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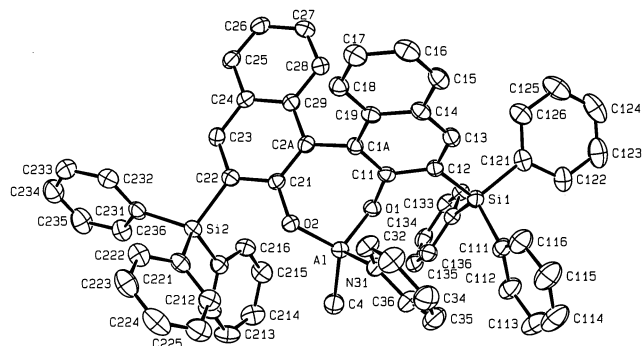
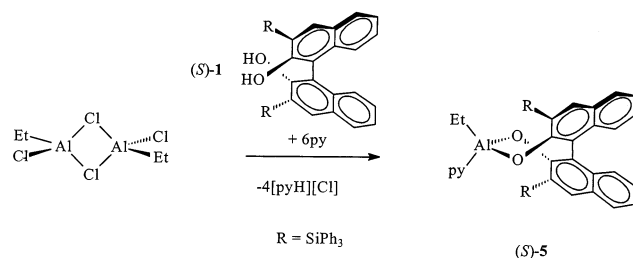


Figure 3. Molecular structure of $[\text{Al}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2\text{-3,3}')(\text{CH}_3)(\text{NC}_5\text{H}_5)]$, (*S*)-**4**.

Table 3. Selected Bond Distances (Å) and Angles (deg) for $[\text{Al}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2\text{-3,3}')(\text{CH}_3)(\text{py})]$, (*S*)-4****

Al–O(2)	1.75(2)	Al–O(1)	1.76(1)
Al–C(4)	1.94(2)	Al–N(31)	1.98(2)
O(2)–Al–O(1)	106.83(7)	O(2)–Al–C(4)	119.63(9)
O(1)–Al–C(4)	115.36(9)	O(2)–Al–N(31)	102.39(7)
O(1)–Al–N(31)	105.25(7)	C(4)–Al–N(31)	105.6(1)
C(11)–O(1)–Al	113.8(1)	C(21)–O(2)–Al	123.5(1)
C(36)–N(31)–Al	121.5(2)	C(32)–N(31)–Al	121.3(2)

Scheme 2



served in both the ¹H and ¹³C NMR spectra even at low temperatures (–60 °C, toluene-*d*₈). Hence the molecules are undergoing fast bridge/terminal exchange on the NMR time scale. Again a similar situation was reported for the 1,8-anthracenemethanediyl-tetraphenoxide compound.¹⁸

Addition of pyridine to **2** leads, as determined by NMR, to a mixture of products. We assume one of these is the adduct $[\text{AlMe}_3(\text{py})]$,²² while the other product was identified as $[\text{Al}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2\text{-3,3}')(\text{CH}_3)(\text{py})]$, (*S*)-**4**. Compound (*S*)-**4** was obtained in moderate yield by the reaction of $[\text{Al}_2\text{Me}_6]$ with 2 equiv of (*S*)-**1** in the presence of added pyridine (Scheme 1). The compound adopts a pseudo-tetrahedral geometry about the Al metal center in the solid state (Figure 3, Table 3). The ethyl analogue of (*S*)-**4**, (*S*)-**5**, was also obtained via reaction of a hydrocarbon solution of $[\text{EtAlCl}_2]$ with (*S*)-**1** in the presence of pyridine (Scheme 2). The solid state structures of (*S*)-**4** and (*S*)-**5** (Figure 4, Table 4) can be compared with previously reported $[\text{MeAl}(\text{OC}_6\text{H}_2\text{Me}_3\text{-2,4,6})_2(\text{pyMe}_2\text{-3,5})]$.²³ The Al–O, Al–C, and Al–N(py) distances are very similar in all three compounds. However, the chelate rings in (*S*)-**4** and (*S*)-**5** lead to

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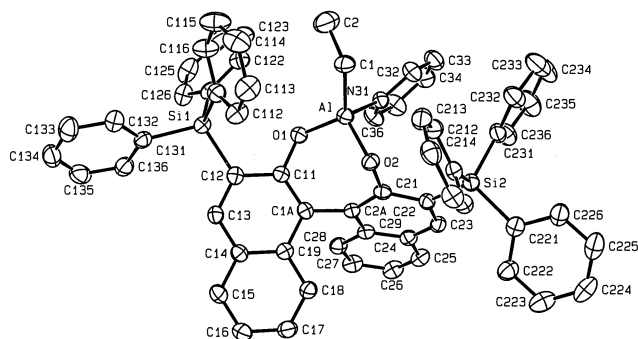


Figure 4. Molecular structure of $[\text{Al}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2-3,3')(\text{C}_2\text{H}_5)(\text{NC}_5\text{H}_5)]_2-$, (S)-5.

Table 4. Selected Bond Distances (Å) and Angles (deg) for $[\text{Al}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2-3,3')(\text{C}_2\text{H}_5)(\text{py})]$, (S)-5

Al–O(2)	1.762(1)	Al–O(1)	1.754(1)
Al–C(1)	1.944(2)	Al–N(31)	1.987(2)
O(1)–Al–O(2)	106.65(6)	O(2)–Al–C(1)	113.28(7)
O(1)–Al–C(1)	122.36(8)	O(2)–Al–N(31)	106.43(6)
O(1)–Al–N(31)	101.66(6)	C(1)–Al–N(31)	104.76(7)
Al–O(1)–C(11)	124.2(1)	Al–O(2)–C(21)	114.2(1)
Al–N(31)–C(36)	121.6(1)	Al–N(31)–C(32)	121.2(1)
Al–C(1)–C(2)	120.9(1)	C(36)–N(31)–C(32)	117.2(2)

O–Al–O angles of 107° compared to slightly larger angles, 111° , in the bis(aryloxide). The methyl signal in (S)-4 appears as a single resonance at $\delta -1.20$ ppm and -14.8 ppm in the ^1H and ^{13}C NMR spectra. The ethyl group in (S)-5 appears as an ABX₃ pattern due to the presence of the chiral binaphthoxide ligand.

Synthesis and Characterization of Dimethylamido Compounds. Metal dialkylamido compounds have proven extremely useful substrates for the synthesis of the corresponding alkoxides and aryloxides. In fact we have found that there are many synthetic advantages to the use of transition metal dimethylamides for the synthesis of binaphthoxide derivatives over the use of more traditional halide starting materials.²⁴ The reaction of the compound $[\text{LiAl}(\text{NMe}_2)_4]$ with (S)-1 leads to a new mixed metal product containing (as determined by ^1H NMR) both dimethylamido and dimethylamino groups. The product was identified as $[\text{LiAl}(\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2-3,3')(\text{NHMe}_2)(\text{NMe}_2)_2]$, (S)-6, by X-ray diffraction studies. A directly related pyridine compound (S)-7 was obtained by carrying out the reaction in the presence of pyridine (Scheme 3), and this was also structurally characterized.

The molecular structures of (S)-6 and (S)-7 (Figures/Tables 5 and 6) are of some interest. The aluminum atom in both compounds is pseudo-tetrahedral. The binaphthoxide ligand has one terminal oxygen atom, while the other is bridging between aluminum and lithium. In this respect the binding of the (S)-1 ligand resembles that seen in (S)-2 above (Figure 1). The aluminum atom is also bound to one terminal and one bridging dimethylamido ligand. There are numerous examples of dinuclear compounds of aluminum and the other group 13 metals that contain terminal and bridging NMe_2 groups.²⁵ The compound $[(\text{THF})_2\text{Li}(\mu-\text{NMe}_2)_2-\text{Al}(\text{NMe}_2)]$ has an Li–Al distance of 2.742 Å with tetrahedral Li and Al.²⁶ A simple adduct $[\text{Al}(\text{NMe}_2)_3-$

(OPPh₃)] has also been structurally characterized.²⁷ What makes compounds (S)-6 and (S)-7 interesting is the coordination environment about the lithium atoms. In each case they are bound to a bridging binaphthoxide oxygen, a bridging NMe_2 nitrogen, and the nitrogen of a terminal dimethylamine or pyridine ligand (Figures 5 and 6). The formally three-coordinate Li atom is severely pyramidalized. The sum of the three angles for the LiN_2O core is 305° and 322° for (S)-6 and (S)-7, respectively. The coordination environment about the electron-deficient Li atom is completed by an interaction with a phenyl ring of a Ph_2Si group. This type of interaction is absent in trigonal planar, three-coordinate amine and pyridine adducts of lithium. Examples include $[(\text{Pr}^i_2\text{HN})\text{Li}(\mu-\text{NPhCy})_2\text{Li}(\text{NHPr}^i_2)]$ (Cy = cyclohexenyl)²⁸ and $[(\text{py})\text{Li}(\mu-\text{X})_2\text{Li}(\text{py})]$ (X = NR_2 , OR).²⁹ Of particular relevance are the two mixed metal species $[(\text{py})\text{Li}\{\mu-\text{N}(\text{CH}_2\text{Ph})_2\}_2\text{AlMe}_2]$ ³⁰ and $[(\text{py}-4\text{NMe}_2)\text{Li}\{\mu-\text{NMe}(\text{SiMe}_3)\}_2\text{Al}\{\text{NMe}(\text{SiMe}_3)\}_2]$.³¹ In these last two cases the three angles about Li sum to 347° and 359° , respectively. There are many examples of π -arene interactions with alkali metals.³² In the case of (S)-6 and (S)-7 there are two close contacts, 2.66 – 2.74 Å, with an arene ring. In (S)-6 the carbon atoms involved are an *ipso*- and *ortho*-carbon, while for (S)-7 the *ortho*- and *meta*-carbon atoms of a $\text{Ph}-\text{Si}$ ring are in close contact.

Experimental Section

General Remarks. All manipulations were carried out using standard syringe, Schlenk line, and glovebox techniques.³³ Benzene, toluene, ether, THF, and hexane were dried over sodium benzophenone ketyl and were freshly distilled before use. Pentane was dried over sodium ribbon. The 3,3'-bis(triphenylsilyl)-2,2'-dihydroxy-1,1'-binaphthyl ligand (S)- $\text{H}_2\text{O}_2\text{C}_{20}\text{H}_{10}\{\text{SiPh}_3\}_2-3,3'$ (1) was prepared according to literature procedures or slight variations thereof.^{34,35} ^1H NMR spectra were recorded on a Varian INOVA-300 NMR spec-

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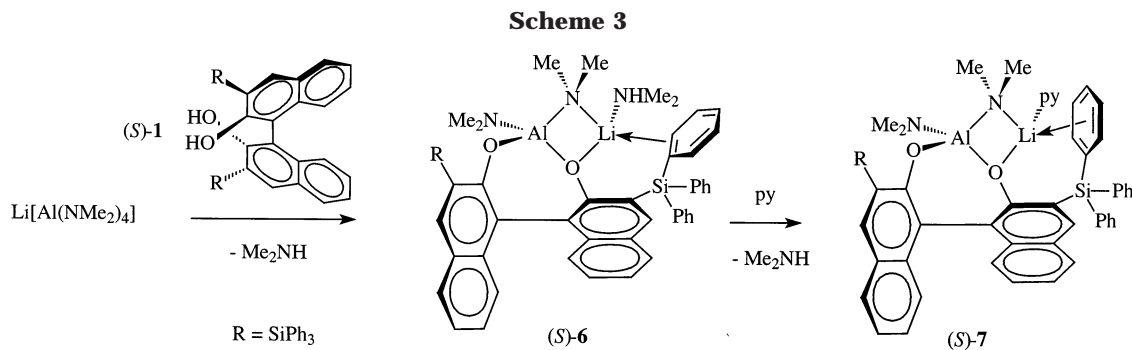


Table 5. Selected Bond Distances (Å) and Angles (deg) for [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NMe₂)₂(NHMe₂)], (S)-6

Al–O(2)	1.764(3)	Al–O(1)	1.802(3)
Al–N(3)	1.864(5)	Al–N(4)	1.790(5)
Al–Li	2.774(9)	Li–O(1)	1.893(9)
Li–N(3)	2.13(1)	Li–N(9)	2.11(1)
Li–C(111)	2.73(9)	Li–C(116)	2.66(1)
O(2)–Al–N(4)	106.9(2)	O(2)–Al–O(1)	103.8(1)
N(4)–Al–O(1)	118.6(2)	O(2)–Al–N(3)	116.5(2)
O(2)–Al–Li	122.8(2)	N(4)–Al–Li	129.0(2)
O(1)–Al–Li	42.6(2)	N(3)–Al–Li	50.0(2)
O(1)–Li–N(9)	105.0(4)	O(1)–Li–N(3)	82.1(4)
N(9)–Li–N(3)	118.0(5)	O(1)–Li–C(116)	89.2(4)
N(9)–Li–C(116)	137.9(4)	N(3)–Li–C(116)	102.9(4)
O(1)–Li–C(111)	81.8(3)	N(9)–Li–C(111)	111.8(4)
N(3)–Li–C(111)	130.1(4)	C(116)–Li–C(111)	30.3(2)
Al–Li–O(1)	40.1(2)	Al–Li–N(9)	122.0(4)
Al–Li–N(3)	42.2(2)	Al–Li–C(116)	94.5(3)
Al–Li–C(111)	106.2(3)		

Table 6. Selected Bond Distances (Å) and Angles (deg) for [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NMe₂)₂(py)], (S)-7

Al–O(2)	1.813(3)	Al–O(1)	1.766(3)
Al–N(3)	1.790(4)	Al–N(4)	1.849(4)
Al–Li	2.759(8)	Li–O(2)	1.923(8)
Li–N(4)	2.103(9)	Li–N(911)	2.016(9)
Li–C(232)	2.63(1)	Li–C(233)	2.738(9)
O(2)–Al–N(4)	92.5(2)	O(2)–Al–O(1)	102.9(1)
N(4)–Al–O(1)	118.3(2)	O(2)–Al–N(3)	117.2(2)
O(2)–Al–Li	43.97(2)	N(4)–Al–Li	49.6(2)
O(1)–Al–Li	127.4(2)	N(3)–Al–Li	123.1(2)
O(2)–Li–N(911)	116.2(4)	O(2)–Li–N(4)	82.1(4)
N(911)–Li–N(4)	124.2(4)	O(2)–Li–C(42)	93.0(3)
N(911)–Li–C(232)	125.2(4)	N(4)–Li–C(232)	107.0(4)
O(2)–Li–C(233)	115.0(4)	N(911)–Li–C(42)	90.3(4)
Li–N(911)–C(911)	128.5(4)	C(42)–Li–C(233)	123.9(3)
Al–Li–O(2)	40.9(2)	Al–Li–N(911)	138.2(4)
Al–Li–N(4)	42.1(2)	Al–Li–C(232)	92.4(3)
Al–N(4)–Li	88.3(3)	Al–O(2)–Li	95.2(3)

trometer or a Bruker DRX-500 NMR spectrometer and were referenced to residual protio solvent. ¹³C NMR spectra were recorded on a Bruker DRX-500 NMR spectrometer at 125.7 MHz and were internally referenced to the solvent signal.

Synthesis of [Al₂(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)₄], (S)-2. To a 50 mL solvent seal round-bottom flask containing benzene (30 mL) was added a toluene solution of AlMe₃ (2.0 M, 1.1 mL, 2.2 mmol). One equivalent of (S)-1 (1.798 g 2.24 mmol) dissolved in benzene (10 mL) was slowly added to the stirring reaction mixture. This mixture was stirred for 1 h and evaporated to dryness. The crude red solid was dissolved in a minimal amount of toluene and carefully layered with hexane to afford red crystals of product. Yield: 0.45 g (24%). Anal. Calcd for Al₂C₆₀H₅₂O₂Si₂: C, 78.74; H, 5.72. Found: C, 78.70; H, 5.62. ¹H NMR (C₆D₆): δ 8.31 (s, 2H, meta-H); 6.80–7.91 (aromatics); –1.21 (s, 12H, CH₃). ¹³C NMR (C₆D₆, 25 °C): 157.16 (ipso-C); –7.84 (CH₃).

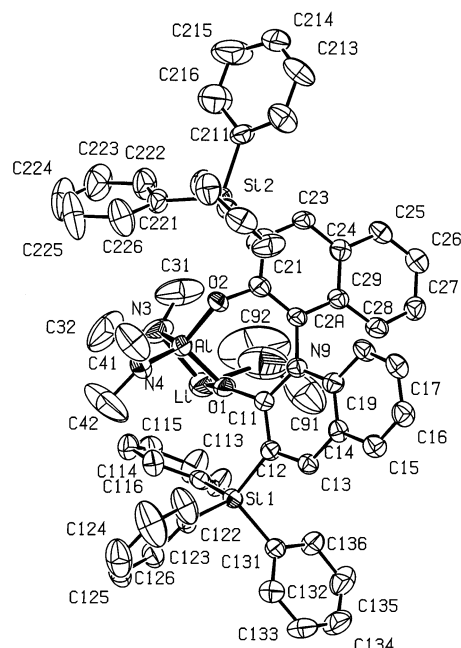


Figure 5. Molecular structure of [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NHMe₂)(NMe₂)₂], (S)-6.

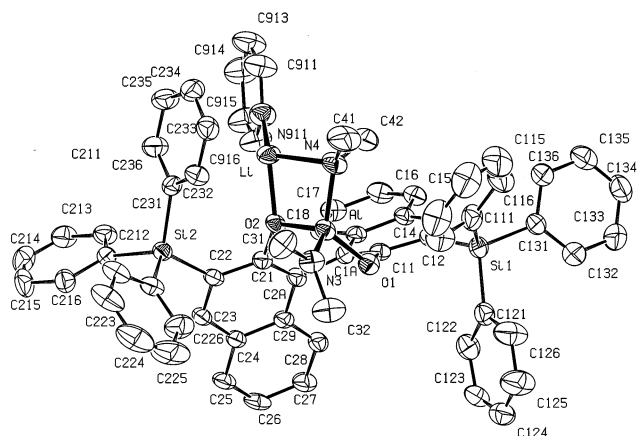


Figure 6. Molecular structure of [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NC₅H₅)(NMe₂)₂], (S)-7.

Synthesis of [Al(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(CH₃)(py)], (S)-4. To a 50 mL solvent seal round-bottom flask containing benzene (30 mL) was added a toluene solution of AlMe₃ (2.0 M, 0.48 mL, 0.96 mmol). Two equivalents of (S)-1 (1.55 g 1.93 mmol) dissolved in benzene (10 mL) was slowly added to the stirring reaction mixture. Pyridine (2.5 equiv, 0.195 mL, 2.4 mmol) was also added to the reaction mixture. This mixture was stirred for 17 h and then evaporated to dryness. The crude white solid was dissolved in a minimal amount of toluene and carefully layered with hexane to afford white crystals of

Table 7. Crystal Data and Data Collection Parameters

	(S)-2	3	(S)-4	(S)-5
formula	Al ₂ C ₆₆ H ₅₇ O ₂ Si ₂	Al ₂ C ₄₀ H ₃₈ O ₂	AlC ₆₉ H ₅₆ NO ₂ Si ₂	AlC ₇₀ H ₅₈ NO ₂ Si ₂
fw	992.32	604.71	1014.37	1028.40
space group	<i>P</i> 2 ₁ (No. 4)	<i>Ccca</i> (No. 68)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
<i>a</i> , Å	13.4646(3)	15.2476(9)	11.9573(2)	12.10690(10)
<i>b</i> , Å	14.6264(4)	19.486(2)	17.3102(2)	17.35720(10)
<i>c</i> , Å	14.1823(4)	11.4194(12)	26.4682(4)	26.2629(3)
α, deg	90	90	90	90
β, deg	98.5360(10)	90	90	90
γ, deg	90	90	90	90
<i>V</i> , Å ³	2762.1(2)	3392.8(10)	5478.5(2)	5518.94(8)
<i>Z</i>	2	4	4	4
ρ _{calc} , g cm ⁻³	1.193	1.184	1.230	1.238
temperature, K	150.	203	150.	150.
radiation (wavelength)	Mo Kα (0.71073Å)	Mo Kα (0.71073Å)	Mo Kα (0.71073Å)	Mo Kα (0.71073Å)
<i>R</i>	0.048	0.045	0.044	0.039
<i>R</i> _w	0.114	0.103	0.092	0.086

	(S)-6	(S)-7
formula	AlliC ₆₂ H ₅₉ N ₃ O ₂ Si ₂	AlliC ₆₅ H ₅₇ N ₃ O ₂ Si ₂
fw	968.27	1002.29
space group	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)	<i>P</i> 2 ₁ 2 ₁ 2 ₁ (No. 19)
<i>a</i> , Å	12.9970(3)	13.3931(4)
<i>b</i> , Å	18.2917(5)	18.2342(6)
<i>c</i> , Å	22.4617(7)	22.4204(9)
α, deg	90	90
β, deg	90	90
γ, deg	90	90
<i>V</i> , Å ³	5340.0(4)	5475.3(3)
<i>Z</i>	4	4
ρ _{calc} , g cm ⁻³	1.204	1.216
temperature, K		
radiation (wavelength)	Mo Kα (0.71073Å)	Mo Kα (0.71073Å)
<i>R</i>	0.053	0.055
<i>R</i> _w	0.131	0.124

product. Yield: 0.45 g (46%). Anal. Calcd for AlNC₆₉H₅₆O₂Si₂: C, 81.69; H, 5.56; N, 1.38. Found: C, 81.68; H, 5.66; N, 1.37. ¹H NMR (C₆D₆): δ 8.24 (s, 2H, meta-H); 6.91–7.79 (aromatics); 6.49 (t, meta H of coordinating pyridine); 5.92 (t, para-H of coordinating pyridine); –1.20 (s, 3H, CH₃). ¹³C NMR (C₆D₆, 25 °C): 161.69 (ipso-C); –14.75 (CH₃).

Synthesis of [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(C₂H₅)(py)], (S)-5. To a 50 mL solvent seal round-bottom flask containing benzene (30 mL) was added a toluene solution of AlEtCl₂ (1.8 M, 1.60 mL, 2.88 mmol). One equivalent of (S)-1 (1.55 g, 1.93 mmol) dissolved in benzene (10 mL) was slowly added to the stirred reaction mixture. Pyridine (3 equiv, 0.46 mL, 5.5 mmol) was also added to the reaction mixture. This mixture was stirred for 17 h and evaporated to dryness. The resulting crude product was dissolved in a minimum of toluene and carefully layered with hexane to afford transparent crystals of product. Yield: 1.12 g (42%). Anal. Calcd for AlNC₆₃H₅₀O₂Si₂: C, 81.82; H, 5.68; N, 1.36. Found: C, 81.17; H, 5.37; N, 1.58. ¹H NMR (C₆D₆): δ 8.22 (s, 2H, meta-H); 6.84–7.84 (aromatics); 6.61 (t, meta-H of coordinating pyridine); 6.03 (t, para-H of coordinating pyridine); –0.59 (m, 2H, CH₂); 0.67 (t, 3H, CH₃). ¹³C NMR (C₆D₆, 25 °C): 161.76 (ipso-C); 8.86 (CH₂); –3.68 (CH₃).

Preparation of [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(NHMe₂)(NMe₂)₂], (S)-6. To a 50 mL solvent seal round-bottom flask containing benzene (30 mL) was added LiAl(NMe₂)₄ (0.31 g, 1.43 mmol). One equivalent of (S)-1 (1.14 g, 1.43 mmol) dissolved in benzene (10 mL) was slowly added to the stirring reaction mixture. This mixture was stirred for 17 h and evaporated to dryness. The crude yellow solid was dissolved in a minimum of toluene and carefully layered with hexane to afford pale yellow crystals of product. Yield: 0.61 g (44%). Anal. Calcd for AlliC₆₂H₅₉O₂N₃Si₂: C, 76.90; H, 6.14; N, 4.34. Found: C, 76.83; H, 6.17; N, 3.96. ¹H NMR (C₆D₆): δ 8.32 (s, 2H, meta-H); 6.80–8.00 (aromatics); 2.066 (s, AlNMe₂); 1.213 (br, NMe₂); 1.070 (br, NHMe₂); –1.211 (t, H, NMe₂H). ¹³C NMR (C₆D₆, 25 °C): 162.1 (ipso-C); 41.49 (NMe₂); 37.24 (NHMe₂).

Preparation of [LiAl(O₂C₂₀H₁₀{SiPh₃}₂-3,3')(py)(NMe₂)₂], (S)-7. A 50 mL solvent seal round-bottom flask containing benzene (30 mL) was charged with LiAl(NMe₂)₄ (0.31 g, 1.43 mmol). One equivalent of (S)-1 (1.14 g, 1.43 mmol) dissolved in benzene (10 mL) was slowly added to the stirring reaction mixture. Then 2.5 equiv of pyridine (0.29 mL, 2.4 mmol) was also added to the reaction mixture. This mixture was stirred for 17 h and evaporated to dryness. The crude brown solid was dissolved in a minimal amount of hot toluene to afford pale brown crystals of product. Yield: 0.65 g (48%). Anal. Calcd for AlliC₆₂H₅₉O₂N₃Si₂: C, 77.88; H, 5.73; N, 4.19. Found: C, 75.22; H, 5.67; N, 3.20. ¹H NMR (C₆D₆): δ 8.27 (s, 2H, meta-H); 6.80–7.93 (aromatics); 6.68 (t, meta-H of coordinating pyridine); 6.26 (t, para-H of coordinating pyridine); 2.076 (s, NMe₂); 2.016 (s, NMe₂). ¹³C NMR (C₆D₆, 25 °C): 149.07 (ipso-C); 41.56 (NMe₂); 37.79 (NHMe₂).

X-ray Data Collection and Reduction. Crystal data and data collection parameters are contained in Table 7. A suitable crystal was mounted on a glass fiber in a random orientation under a cold stream of dry nitrogen. Preliminary examination and final data collection were performed with Mo Kα radiation (λ = 0.71073 Å) on a Nonius Kappa CCD. Lorentz and polarization corrections were applied to the data.³⁶ An empirical absorption correction using SCALEPACK was applied.³⁷ Intensities of equivalent reflections were averaged. The structure was solved using the structure solution program PATTY in DIRDIF92.³⁸ The remaining atoms were located in succeeding difference Fourier syntheses. Hydrogen atoms were included in the refinement but restrained to ride on the atom to which they are bonded. The structure was refined in full-

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matrix least-squares where the function minimized was $\sum w(|F_o|^2 - |F_c|^2)^2$ and the weight w is defined as $w = 1/[\sigma^2(F_o^2) + (0.0585P)^2 + 1.4064P]$ where $P = (F_o^2 + 2F_c^2)/3$. Scattering factors were taken from the *International Tables for Crystallography*.³⁹ Refinement was performed on a AlphaServer 2100

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using SHELX-97.⁴⁰ Crystallographic drawings were done using the programs ORTEP.⁴¹

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