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Article

A New Type of Asymmetric Tridentate Pyrrolyl-Linked Pincer Ligand and Its Aluminum Dihydride Complexes

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The new pyrrolyl-linked pincer-type ligand, $[C_4H_2NH(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]$ (**1**), that has been employed conveniently in high yield by treatment of (2-*t*-butylaminomethyl)pyrrole with 1 equiv of formaldehyde and dimethylamine hydrochloride each in diethylether and its corresponding aluminum derivative, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]AlH_2$ (**2**), that has been generated from $Me_3N\cdot AlH_3$ using diethylether as a solvent are described. Furthermore, reactions of **2** with 2 equiv of either 1,3-diphenylpropane-1,3-dione in diethylether or phenyl thioisocyanate in dichloromethane interestingly formed $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(PhCOCHCOPh)_2$ (**3**) and $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(SCHNPh)_2$ (**4**), respectively, following deprotonation or hydroalumination reaction kinetics under a dry nitrogen environment. All of the compounds have been subjected to the X-ray diffraction technique in the solid state as well as characterized by NMR spectra.

Introduction

Organometallic pincer complexes containing tridentate monoanionic ligands composed of an anionic aryl carbon atom and two mutually trans-chelating donor sites at the 2,6 positions of the aromatic ring have been attracting widespread interest in catalysis and material science.[1] Pincer compounds are a group of species showing high thermal stability and unusual characteristics of robustness that attract the continuous attention of the chemistry community for multiple applications, this being particularly true in the case of homogeneous catalysis.[2]

Transition metal complexes of bulky pincer-type ligands[3] have found significant applications in synthesis, bond activation, and catalysis. Among those, complexes of the pyridine-based bulky ligand ^{tBu}PNP (^{tBu}PNP = 2,6-(di-*tert*-butylphosphinomethyl) pyridine) have been explored in recent years.[4] The different electronic properties of the phosphine and amine ligands and the more labile coordination of the latter in the case of late transition metal complexes[5] can play important roles in catalytic and stochiometric reactions, as shown for complexes based on PNN-type ligands.[6] The field of aluminum hydride chemistry could be said to have been inaugurated because of its diverse range of applications in the solid state regarding some alane amine adducts showing dimeric connectivities $[(H_3Al\cdot L)_2]$[7] with five-coordinated aluminum atoms and somewhat counterintuitive unsymmetrical Al−H−Al bridges, while, on the other hand, others seem to favor a monomeric mode with four-coordinated Al in $H_3Al\cdot L$.[8] In this regard, hydroalumination reactions using complex aluminum hydrides work extremely well for terminal alkenes and internal alkynes that result in an interesting observation of the regeoselectivity involved in bis(dialkylamino)alane.[9] This group reported earlier the details of the $HAl(NR_2)_2$ hydroalumination of alkenes[10] and catalytic

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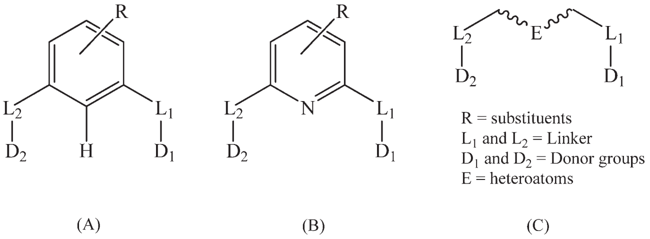
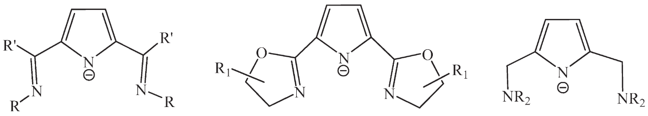
Scheme 1



activities of bis(dialkylamino)alanes to olefins and alkynes. Furthermore, it is a convenient phenomenon related to aluminum hydrogen bonds because of its well-known modulations, and the topics relating to their applications have been reviewed periodically.[11] However, the tendency for the hydride to bridge two metal atoms allows the aluminum hydride compounds to aggregate as dimers[12] or oligomers.[13] The aggregated aluminum compounds may show less reactivity in comparison to those of monomeric[14] ones presumably because of the modulation for breaking the Al−H−M (where M = Al, Li, etc.) bond.[15] Organic ligands containing bulky groups bound to an aluminum center not only take part in increasing the solubility of organoaluminum hydride compounds in organic solvents but also are very consistent in preventing the aggregation of aluminum hydride.[16] Therefore, ligand design participates in a well-known criterion in organometallic chemistry and activates not only an increase in the stability of these compounds but also the reactivity as well, both sterically and electronically.[17] Multidentate pincer-type ligands containing rigid and nonrigid linker have raised much attention in the past decade because of their multiple-bonding modes and versatility of coordinating groups.[18]

Scheme 2



A schematic drawing of the pincer-type ligands is shown in Scheme 1 where types A and B are formed from aromatic rings of phenyl or pyridine and type C represents donor atom linkages.[19−21] The D_1 and D_2 of the pincer-type ligands are donating atoms such as N, P, As, O, S, and so forth.

In addition to the aromatic-linked tridentate pincer ligands, pyrrolyl-linked anionic tridentate pincer ligands are also used in many groups as supporting ligands to bind metals.[22,23] Some of the pyrrolyl ligand systems are shown in Scheme 2, where all of these ligands exhibit symmetrical manners. To be concise about the chemistry of the pyrrolyl-based system, reactions of aluminum hydride complexes with ketones generating aluminum alkoxide complexes via hydride insertion have been reported previosuly,[24] and we also showed the reactivity of monomeric aluminum hydride compounds with pyrrolyl ligands[25] reflecting insertion and a C−C coupling mechanistic pathway. In the present contribution, we have developed a new type of asymmetrical pyrrolyl-linked anionic tridentate pincer ligand, $[C_4H_2NH(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]$ (**1**), and its corresponding aluminum derivative, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]AlH_2$ (**2**), that moderately undergoes further reaction to $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(PhCOCHCOPh)_2$ (**3**) and $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(SCHNPh)_2$ (**4**), to explore the reactivity via deprotonation or hydroalumination reactions. All of the compounds are well characterized by single-crystal X-ray diffraction analysis and NMR spectra.

Results and Discussion

Preparation of Asymmetrical Ligand 1 and Aluminum Dihydride Compound 2. A rational design and synthetic

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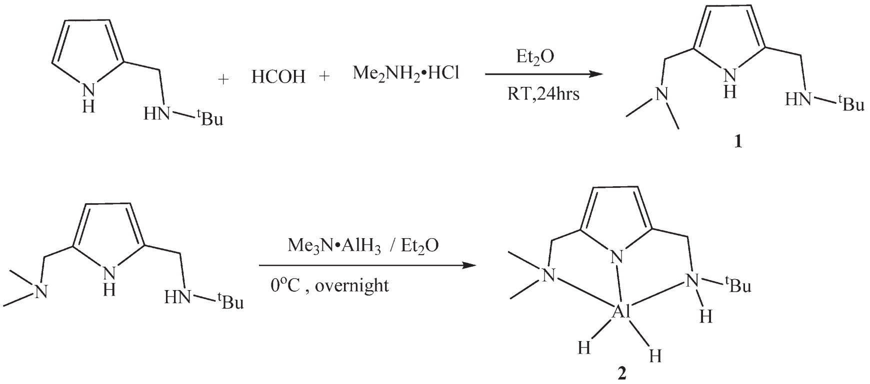
Scheme 3



procedure of the pyrrolyl-linked tridentate ligand **1** and its aluminum dihydride compound **2** is shown in Scheme 3.

Ligand **1** was obtained from the reaction of $[C_4H_3NH(2\text{-}CH_2NH^tBu)]$[26] with 1 equiv each of formaldehyde and $Me_2NH\cdot HCl$ in a diethyl ether/water biphase solution. The ^1H NMR spectrum of **1** shows two singlets at δ 1.11 and 2.18 for the methyl protons of ^tBuNH and Me_2N with a ratio of 3:2. A broad triplet for the amino proton of ^tBuNH was observed at ca. δ 2.14, which partly overlapped with the methyl protons of NMe_2. We have tried to employ an alternative method to synthesize **1** from $[C_4H_3NH(2\text{-}CH_2NMe_2)]$, formaldehyde, and $^tBuNH\cdot HCl$, and several compounds along with **1** have been retrieved from the reaction mixture. However, we were unable to separate **1** from other unidentified products using simple trap-to-trap distillation. Ligand **1**, obtained after appropriate workup of the reaction, appears as a sticky liquid at room temperature and is difficult to solidify. However, a few colorless crystals were obtained suitable for X-ray diffraction from a trap-to-trap distillation following a purification procedure. The molecular structure of **1** and selected bond lengths and angles are represented in Figure 1 and Table 1, respectively. The asymmetrical ligand **1** exhibits a dimeric form where two units of molecules bind together through intermolecular hydrogen bonding. The distances of N(3)−N(5) and N(2)−N(6) are 3.142 and 3.168 Å, respectively, confirming the existence of hydrogen bonding of $^tBuNH\cdots NMe_2$.[27]

During an overnight reaction between **1** and $AlH_3\cdot NMe_3$,[28] obtained from the reaction of $LiAlH_4$ with $Me_3N\cdot HCl$, in diethyl ether at 0 °C, an aluminum dihydride compound **2**, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]AlH_2$, was moderately yielded. A similar isotopic compound **2-D**, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]AlD_2$, was obtained using $AlD_3\cdot NMe_3$, following the same synthetic route mentioned above for **2**. Compound **2** is soluble in most of the organic solvents such as toluene, diethyl ether, methylene chloride, and tetrahydrofuran but only slightly soluble in hydrocarbon-like solvents such as heptane. The ^1H NMR spectra of **2** show one singlet at δ 2.18 for the Me_2N and one broad triplet at δ 2.14 for the amino proton of ^tBuNH. A homonuclear decoupling of the amino proton of ^tBuNH results in the methylene protons of $^tBuNHCH_2$ changing from doublet to singlet, which further confirms the existence of the amino proton of ^tBuNH. Basically, the ^1H NMR spectra of **2-D** and **2** are the same except for a broad signal observed at δ 4.29 for **2**, but which is absent in **2-D**, that corresponds to the AlH_2 protons. The evidence for the existence of hydride for **2** can also be established by means of correlating the IR stretching frequency of Al−H appearing at 1813 cm^{-1}, which is not observed for **2-D**. Compound **2** is highly moisture-sensitive and decomposes to form unidentified products while being exposed to the air for a short period. Considering the coordinating nature of **1**, it can be treated either as a mono anionic ligand system by removing the pyrrolyl NH proton or as a dianionic form executed by removal of an additional amino proton of ^tBuNH. In this regard, **2** has been heated in C_6D_6 at 90 °C in a J. Young NMR tube over 24 h in an attempt to eliminate 1 equiv of hydrogen molecules, however, resulting in unidentified products.

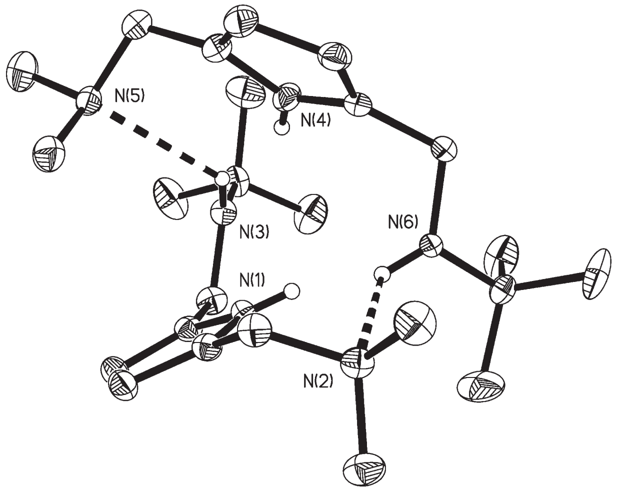


Figure 1. Molecular structure of **1**. The thermal ellipsoids are shown at the 30% probability level. All of the hydrogen atoms (except N*H*) are omitted for clarity.

A colorless crystal of **2** suitable for X-ray crystallography was obtained at −20 °C from a diethyl ether solution. Figure 2 shows a perspective drawing of the molecule **2** and the selective atomic labeling, and the necessary bond lengths and angles are presented in Table 2. The molecular structure of **2** is quite similar to that of $[C_4H_2N(CH_2NMe_2)_2\text{-}2,5]AlH_2$,[23d] considering the Al−N (pyrrolyl-N and N-Me_2 fragments) bond distances, 1.8487(10) and

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Table 1

	1	**2**	**3**	**4**
formula	$C_{24}H_{46}N_6$	$C_{12}H_{24}AlN_3$	$C_{45.5}H_{47.5}AlN_3O_4$	$C_{56}H_{78}Al_2N_{10}S_4$
fw	418.67	237.32	727.34	1089.48
T, K	150(2)	150(2)	150(2)	150(2)
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	$C_{2/c}$	$C_{2/c}$	$P_{\bar{1}}$	$P_{2(1)/n}$
a, Å	27.1751(8)	22.9553(16)	9.426(3)	9.2065(3)
b, Å	16.7898(7)	6.5478(4)	12.260(4)	23.2457(8)
c, Å	12.3090(4)	19.3734(12)	18.019(5)	14.1390(6)
α, deg	90	90	75.317(6)	90
β, deg	105.747(2)	103.110(2)	82.890(6)	108.7240(10)
γ, deg	90	90	83.565(6)	90
V, Å^3	5405.4(3)	2836.1(3)	1991.9(10)	2865.76(18)
Z	8	8	2	2
d_{calcd}, Mg/m^3	1.029	1.112	1.213	1.263
μ, mm^{-1}	0.063	0.124	0.097	0.245
F(000)	1856	1040	773	1164
cryst size	0.31 × 0.22 × 0.15	0.28 × 0.17 × 0.12	0.28 × 0.19 × 0.18	0.25 × 0.17 × 0.16
λ, Å	0.71073	0.71073	0.71073	0.71073
no. of reflns collected	21796	18114	29794	23122
ind reflns	6529 (R_{int} = 0.0272)	3422 (R_{int} = 0.0282)	9529 (R_{int} = 0.0926)	6784 (R_{int} = 0.0263)
data/restraints/params	6529/0/297	3422/0/162	9592/0/497	6784/0/346
goodness-of-fit on F^2	1.067	1.078	0.994	1.074
R_1, wR_2 ($I > 2\sigma(I)$)	$R_1 = 0.0543$ $wR_2 = 0.1469$	$R_1 = 0.0327$ $wR_2 = 0.0907$	$R_1 = 0.0674$ $wR_2 = 0.1689$	$R_1 = 0.0377$ $wR_2 = 0.0956$
R_1, wR_2 (all data)	$R_1 = 0.0823$ $wR_2 = 0.1620$	$R_1 = 0.0428$ $wR_2 = 0.0949$	$R_1 = 0.1508$ $wR_2 = 0.2164$	$R_1 = 0.0517$ $wR_2 = 0.1046$
largest diff peak, hole (e/Å^3)	0.616 and −0.224	0.248 and −0.196	0.390 and −0.423	0.507 and −0.491

2.2543(10) Å, respectively, well comparable to those of the previously reported structure, 1.8381(14), 2.2264(15), and 2.2461(16) Å. It can be described as a distorted trigonal bipyramidal where the nitrogen atoms of ^{t}BuNH and Me_2N fragments occupy the axial positions with a corresponding bond angle of N(1)−Al(1)−N(3) at 155.61(4)°. The bond length of Al(1)−N(1) (2.203(1) Å) is slightly shorter than that of Al(1)−N(3) (2.254(1) Å); presumably, the Al atom has less congestion with the smaller ^{t}BuNH than with Me_2N. The pyrrolyl nitrogen atom in combining with two hydride atoms forms a trigonal plane where the entire angle for the three individual plane angles (N(2)−Al(1)−H(13), N(2)−Al(1)−H(15), and H(15)−Al(1)−H(13)) is close to 360°. The bond length of Al(1)−N(2), 1.8487(9) Å, belongs in the normal range of the pyrrolyl nitrogen linked aluminum atom, as reported in the literature.[23b−d] Again, the Al−H bond lengths (1.51 Å) are well comparable, belonging in the range of previously published Al−H bond lengths in neutral and anionic aluminum hydride compounds.[16,23d]

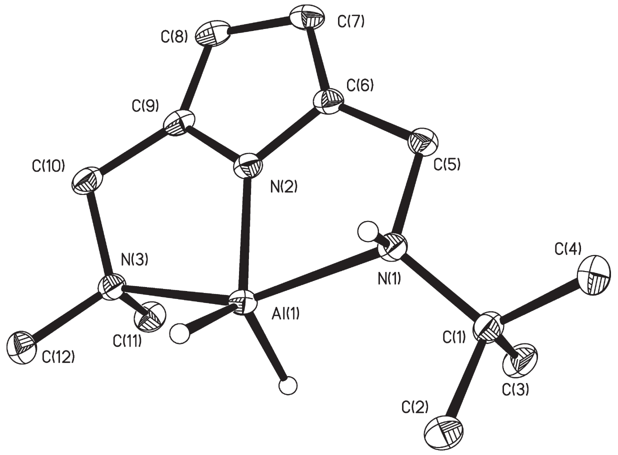


Figure 2. Molecular structure of **2**. The thermal ellipsoids are shown at the 30% probability level. All of the hydrogen atoms are omitted for clarity.

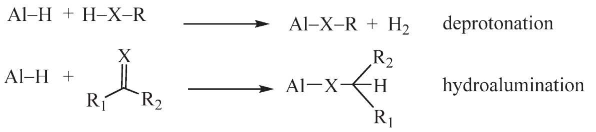
Deprotonation and Insertion Reactions of 2. The aluminum hydride of compound **2** may react with organic compounds via hydroalumination or deprotonation, as shown in Scheme 4, depending on the relative acidity of organic molecules and the hydrides. The reactions of **2** with 1,3-diphenylpropane-1,3-dione and phenyl thioisocyanate are shown in Scheme 5. Reacting **2** with 2 equiv of 1,3-diphenylpropane-1,3-dione in diethyl ether results in a deprotonation of the methylene proton of the propane backbone to generate diphenylacetonate aluminum compound **3**, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(PhCOCHCOPh)_2$, in 64% yield. The compound can be further purified via recrystallization from a toluene solution at −20 °C to yield yellowish orange crystals. The presence of a small amount of toluene is observed in the ^{1}H and ^{13}C NMR spectra. Compound **3** shows two doublets at δ 3.58 and 4.64 for the methylene protons of the Me_2NCH_2, representing the diasterotopic geometry of the two methylene protons. The methylene protons of ^{t}BuNHCH$_2$, however, show two more complicated multiplets at δ 3.64 and 4.03. Presumably, the strong steric congestion of the bulky *t*-butyl amino group with the phenyl ring of the acetylacetonate ligands blocks the C−N bond rotation to resolve the slow limit of methylene protons in the NMR spectroscopy. Two singlets appearing at δ6.88 and 7.07 were assigned due to the methine protons of the two acetylacetonate backbone, which further confirms the asymmetrical manner of **3**.

Reacting **2** with 2 equiv of PhNCS in a diethyl ether solution results in a double hydroaluminumation generating compound **4**, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(SCHNPh)_2$, in 57% yield. A similar reaction of **2-D** with PhNCS affords deuterium-inserted compound **4-D**, $[C_4H_2N(2\text{-}CH_2NH^tBu)(5\text{-}CH_2NMe_2)]Al(SCDNPh)_2$. The ^{1}H NMR

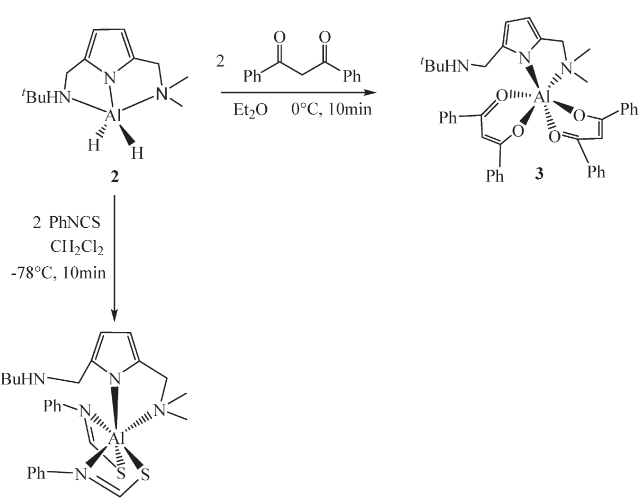
Table 2. Selected Bond Lengths (Å) and Angles (deg) for Compounds **1**−**4**

	1		
C(1)−N(1)	1.376(2)	C(1)−C(2)	1.365(3)
C(4)−N(1)	1.370(2)	C(3)−C(4)	1.365(2)
N(1)−C(1)−C(5)	122.43(16)	N(2)−C(5)−C(1)	114.24(14)
N(1)−C(4)−C(8)	121.53(15)		
	2		
Al(1)−N(1)	2.2030(10)	Al(1)−N(2)	1.8487(10)
Al(1)−N(3)	2.2543(10)	C(1)−N(1)	1.5108(14)
N(2)−Al(1)−N(1)	78.04(4)	N(2)−Al(1)−N(3)	77.68(4)
N(1)−Al(1)−N(3)	155.62(4)	C(1)−N(1)−Al(1)	119.87(7)
C(5)−N(1)−Al(1)	110.50(7)	C(10)−N(3)−Al(1)	106.79(7)
	3		
Al(1)−O(4)	1.859(2)	Al(1)−O(1)	1.881(2)
Al(1)−O(2)	1.883(2)	Al(1)−O(3)	1.891(2)
Al(1)−N(1)	1.931(2)	Al(1)−N(3)	2.111(3)
O(4)−Al(1)−O(1)	92.50(10)	O(4)−Al(1)−O(2)	87.40(9)
O(1)−Al(1)−O(2)	88.32(9)	O(4)−Al(1)−O(3)	89.74(9)
O(1)−Al(1)−O(3)	85.52(9)	O(2)−Al(1)−O(3)	173.09(10)
O(4)−Al(1)−N(1)	97.36(10)	O(1)−Al(1)−N(1)	170.11(10)
O(2)−Al(1)−N(1)	92.87(9)	O(3)−Al(1)−N(1)	93.74(10)
O(4)−Al(1)−N(3)	175.32(10)	O(1)−Al(1)−N(3)	89.25(10)
O(2)−Al(1)−N(3)	96.99(9)	O(3)−Al(1)−N(3)	86.07(9)
N(1)−Al(1)−N(3)	80.86(10)		
	4		
Al(1)−N(1)	1.9021(13)	Al(1)−N(4)	1.9837(14)
Al(1)−N(5)	2.0207(14)	Al(1)−N(2)	2.1206(14)
Al(1)−S(2)	2.4822(6)	Al(1)−S(1)	2.5184(6)
N(1)−Al(1)−N(4)	97.79(6)	N(1)−Al(1)−N(5)	100.24(6)
N(4)−Al(1)−N(5)	99.74(6)	N(1)−Al(1)−N(2)	85.07(6)
N(4)−Al(1)−N(2)	99.31(6)	N(5)−Al(1)−N(2)	159.31(6)
N(1)−Al(1)−S(2)	97.15(4)	N(4)−Al(1)−S(2)	162.49(5)
N(5)−Al(1)−S(2)	68.56(4)	N(2)−Al(1)−S(2)	91.02(4)
N(1)−Al(1)−S(1)	164.11(5)	N(4)−Al(1)−S(1)	68.18(4)
N(5)−Al(1)−S(1)	89.84(4)	N(2)−Al(1)−S(1)	89.79(4)
S(2)−Al(1)−S(1)	97.97(2)		

Scheme 4



Scheme 5



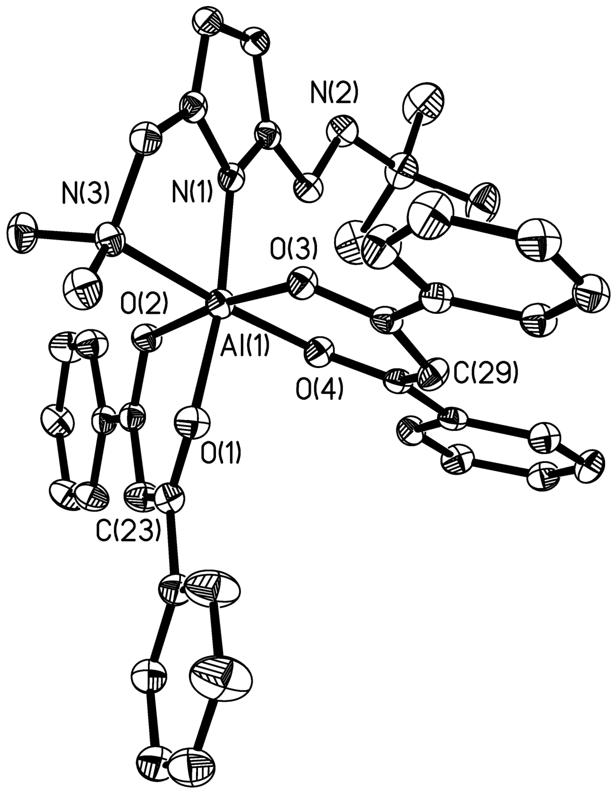


Figure 3. Molecular structure of **3**. The thermal ellipsoids are shown at the 30% probability level. All of the toluene and hydrogen atoms are omitted for clarity.

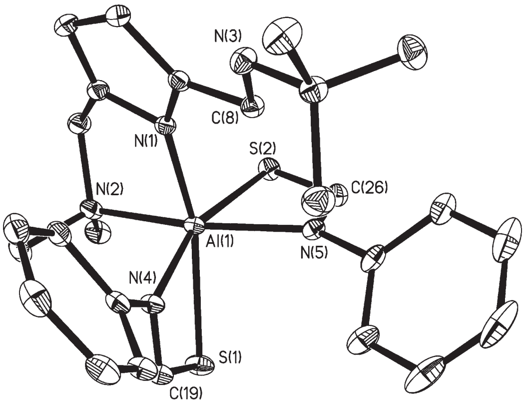


Figure 4. Molecular structure of **4**. The thermal ellipsoids are shown at the 30% probability level. All of the diethyl ether and hydrogen atoms are omitted for clarity.

spectra of **4** showed two singlets at δ 9.09 and 9.48 for the methine protons of the two SCHNPh fragments. In addition, the ^{13}C NMR spectra of **4-D** show two triplets at δ 184.7 and 188.9 with the $^1J_{C-D}$ of both at 26 Hz, further confirming the existence of the two SCDNPh fragments.[29] The methylene protons of **4** for the two asymmetric side arms, ^{t}BuNHCH$_2$ and Me$_2$NCH$_2$, are all exhibiting stereospecific differentiation where four doublets are observed. Presumably, the bulky ^{t}BuNH and Me$_2$N fragments block the C−N bond rotation of the methylene carbon and amino nitrogen atom.

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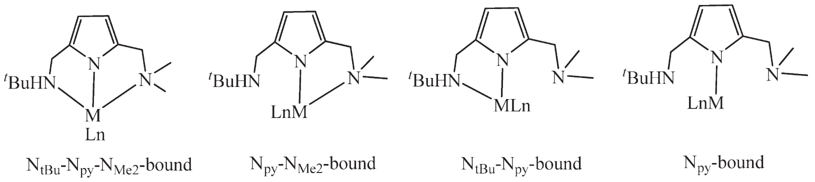
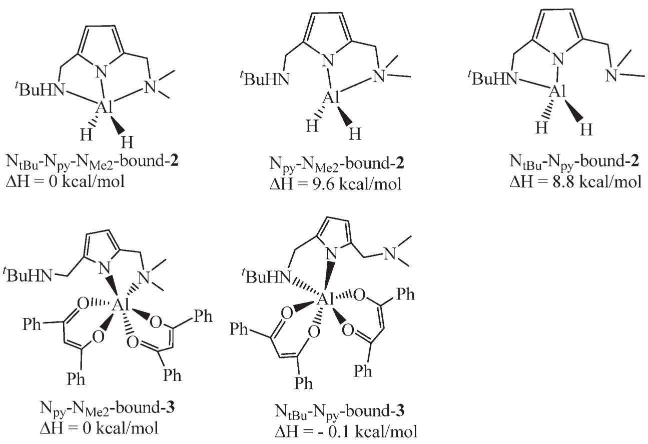
(29) (a) Monsted, L.; Monsted, O. *Inorg. Chem.* **2005**, *44*, 1950. (b) Casey, C. P.; Strotman, N. A. *J. Am. Chem. Soc.* **2004**, *126*, 1699.

Scheme 6



Scheme 7



X-ray-quality crystals of **3** and **4** were obtained from saturated solutions of toluene and methylene chloride, respectively, at −20 °C. The data collections and selected bond lengths and angles of **3** and **4** are listed in Tables 1 and 2, respectively. The molecular structure of **3** (Figure 3) contains a toluene molecule and exhibits a distorted octahedral geometry where the bond angles of the three axes are close to linearity [O(2)−Al(1)−O(3), 173.09(10)°; O(4)−Al(1)−N(3), 175.32(10)°; and O(1)−Al(1)−N(1), 170.11(10)°]. The corresponding bond lengths between aluminum and oxygen of diphenylactetylacetonate are relatively shorter and smaller in biting angles in comparison to those of the oxygen atoms of the acetylacetonate. The pincer-type pyrrolyl ligand binds to the aluminum atom only through the nitrogen atoms of pyrrole and Me_2N groups, leaving the ^{t}BuNH fragment outside the coordinating sphere. The bond lengths of Al−N are rather similar to those of earlier reported aluminum pyrrolyl compounds.[23d,e]

The crystal of **4** contains one unit each of the aluminum molecule and diethyl ether. One of the carbon atoms of the diethyl ether is disordered and splits into two parts with a 50:50 ratio. The molecular structure of **4** (Figure 4) can be described as a distorted octahedral considering the bond angles of the three axes being close to linearity [N(1)−Al(1)−S(1), 164.11(5)°; N(4)−Al(1)−S(2), 162.49(5)°; and N(2)−Al(1)−N(5), 159.31(6)°]. The bonding mode of the phenyl thioisocyanates to the aluminum atom is relatively similar to that described in the literature[30] by Jordan et al., where the thioisocyanate exhibits a N=C double bond [N(4)−C(19), 1.309(2) Å; N(5)−C(26), 1.303(2) Å] and a C−S single bond [C(19)−S(1), 1.7006(17) Å; C(26)−S(2), 1.6983(17) Å]. The bond angles of N(4)−C(19)−S(1) and N(5)−C(26)−S(2) are 116.07(12) and 116.78(12)°, respectively, showing sp^2 hybridization for the carbon atom of the NCS.

Geometry Optimization of the Bonding Modes of the Pincer Ligand. As we mentioned earlier, the pincer ligands can bind metal atoms in various modes such as tridentate N_{tBu}−N_{py}−N_{Me2}-bound, bidentate N_{tBu}−N_{py}-bound. and N_{py}−N_{Me2}-bound, and monodentate N_{py}-bound, as shown in Scheme 6. The molecular structures of **2**, **3**, and **4**, adopted directly from X-ray crystal data, show the aforementioned bound nature that has been represented as N_{tBu}−N_{py}−N_{Me2}-bound **2**, N_{py}−N_{Me2}-bound **3**, and N_{py}−N_{Me2}-bound **4**, shown in Scheme 7. The factor influencing the molecular geometries of these compounds is mainly the steric congestion. This is further verified and established by density functional theory, that is, B3LYP/6-31G*.[31] The relative energies of species with respect to that of the X-ray resolved isomers of **2** and **3** (enthalpy at 298 K) are shown in Scheme 7. The enthalpies in regard to N_{py}−N_{Me2}-bound **2** and N_{tBu}−N_{py}-bound **2** are 9.6 and 8.8 kcal/mol, respectively, higher than N_{tBu}−N_{py}−N_{Me2}-bound **2**. Similarly, N_{tBu}−N_{py}-bound **3** is 0.2 kcal/mol, higher in energy than N_{py}−N_{Me2}-bound **3**. Even the energy difference is small from our (gas-phase) computations; only the crystals of N_{py}−N_{Me2}-bound **3** can be generated. Variable-temperature ^{1}H NMR spectra of **3** show that the activation energy ($\Delta G^{\ddagger}$) of fast exchange between N_{py}−N_{Me2}-bound **3** and N_{tBu}−N_{py}-bound **3** is estimated at ca. 62.8 kJ/mol (15.0 kcal/mol).

Again, the relative energy profiles concerning the possible geometries of **4** were investigated. The corresponding geometric isomers of **4** and their relative energy are presented in Scheme 8. The theoretical computation indicates that the crystal geometry of **4**, that is, the N_{py}−N_{Me2}-bound **4**, is the lowest-energy isomer. In contrast, isomers consisting of rotation of one or two phenyl thiocyanate fragments are higher in energy.

Conclusion

In summary, we are able to synthesize a new type of asymmetrical pyrrolyl-linked anionic tridentate pincer ligand that further reacts with alane to form an asymmetrical aluminum dihydride compound. The aluminum dihydride compound shows high reactivity toward small organic molecules such as diphenyl acetylacetone and phenyl thioisocyanate undergoing deprotonating or insertion reactions. Future work will explore the mechanistic pathway and modification that corresponds to several applications in organic synthesis of the highly reactive asymmetrical aluminum dihydride compound, **2**. In addition, the development of an asymmetrical pyrrolyl-linked anionic tridentate pincer

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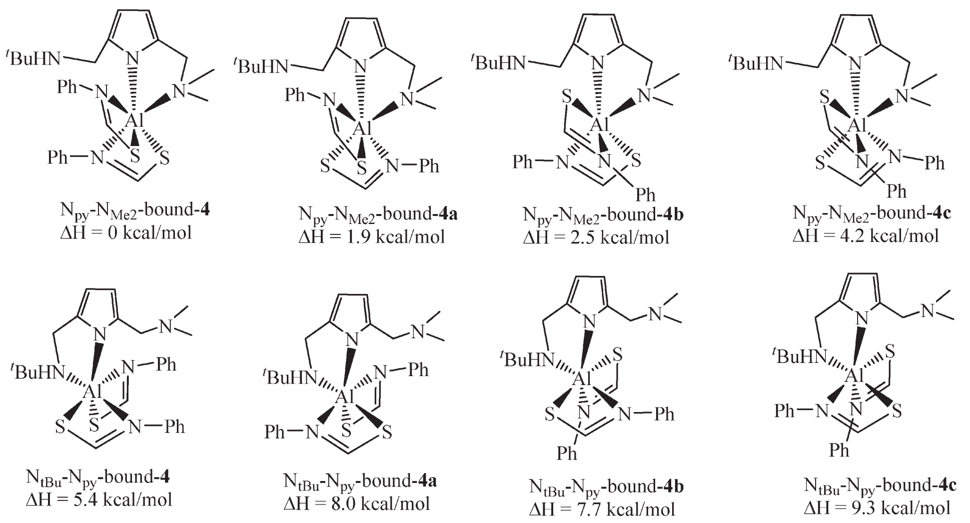
(30) Coles, M. P.; Swenson, D. C.; Jordan, R. F. *Organometallics* **1998**, *17*, 4042.

(31) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785.

Scheme 8



N_{py}-N_{Me2}-bound-**4** ΔH = 0 kcal/mol

N_{py}-N_{Me2}-bound-**4a** ΔH = 1.9 kcal/mol

N_{py}-N_{Me2}-bound-**4b** ΔH = 2.5 kcal/mol

N_{py}-N_{Me2}-bound-**4c** ΔH = 4.2 kcal/mol

N_{tBu}-N_{py}-bound-**4** ΔH = 5.4 kcal/mol

N_{tBu}-N_{py}-bound-**4a** ΔH = 8.0 kcal/mol

N_{tBu}-N_{py}-bound-**4b** ΔH = 7.7 kcal/mol

N_{tBu}-N_{py}-bound-**4c** ΔH = 9.3 kcal/mol

ligand with a late transition metal is under progress in response to growing interest as well.

Experimental Section

General Procedure. All of the reactions were performed using standard Schlenk techniques in an atmosphere of high-purity nitrogen or in a glovebox. Diethyl ether was dried by refluxing over sodium benzophenone ketyl. CH_2Cl_2 was dried over P_2O_5. All solvents were distilled and stored in solvent reservoirs which contained 4 Å molecular sieves and were purged with nitrogen. $CDCl_3$ and C_6D_6 were degassed by using freeze-and-thaw cycles and dried over 4 Å molecular sieves. ^{1}H and ^{13}C NMR spectra were measured on a Bruker avance 300 MHz NMR spectrometer at room temperature. Chemical shifts for ^{1}H and ^{13}C spectra were recorded in parts per million relative to the residual proton and ^{13}C of $CDCl_3$ (δ 7.24, 77.0) and C_6D_6 (δ 7.15, 128.0). IR spectra were obtained as KBr pellets using a Shimadzu FTIR-8100 spectrophotometer. Elemental analysis was performed on a Perkin-Elmer CHN-2400 or Heraeus CHN-OS Rapid.

[C_4H_2NH(2-CH_2NH^tBu)(5-CH_2NMe_2)] (1). A round-bottom flask charged with $Me_2NH\cdot HCl$ (5.410 g, 65.70 mmol) was cooled to 0 °C and 37% formaldehyde (5.330 g, 65.70 mmol) was added. The mixture was stirred for 30 min and a diethyl ether solution of [C_4H_3NH(2-CH_2NH^tBu)] (10.000 g, 65.70 mmol) was added slowly. The biphase solution was stirred for 24 h and then was neutralized with a 20% NaOH solution. The solution was extracted three times with diethyl ether in 20 mL portions. The diethyl ether extraction was dried over $MgSO_4$, and the volatiles were removed in vacuo to yield a yellowish final product in 74.5% yield (10.250 g). ^{1}H NMR ($CDCl_3$): 1.11 (s, 9H, NCMe_3), 2.14 (br, 7H, NMe_2, N*H*CMe$_3$), 3.31 (s, 2H, CH_2NMe$_2$), 3.67 (s, 2H, CH_2NHCMe$_3$), 5.85 (s, 2H, pyrrolyl C*H*), 9.07 (s, 1H, pyrrolyl N*H*). ^{13}C ($CDCl_3$): 28.9 (q, J_{CH} = 124 Hz, NCMe_3), 40.0 (t, J_{CH} = 134 Hz, *C*H$_2$NHCMe$_3$), 45.0 (q, J_{CH} = 132 Hz, NMe_2), 50.4 (s, N*C*Me$_3$), 56.6 (t, J_{CH} = 135 Hz, *C*H$_2$NMe$_2$), 105.0 (d, J_{CH} = 170 Hz, pyrrolyl *C*H), 107.3 (d, J_{CH} = 171 Hz, pyrrolyl *C*H), 128.4 (s, pyrrolyl C_{ipso}), 131.3 (s, pyrrolyl C_{ipso}). Anal. Calcd for $C_{12}H_{23}N_3$: C, 68.85; H, 11.07; N, 20.07. Found: C, 69.07; H, 11.19; N, 20.23%.

[C_4H_2N(2-CH_2NH^tBu)(5-CH_2NMe_2)]AlH_2 (2). A flask charged with a diethyl ether (20 mL) solution of $Me_3N\cdot HCl$ (2.000 g, 20.90 mmol) was cooled to 0 °C and a diethyl ether (20 mL) suspension of $LiAlH_4$ (0.950 g, 25.10 mmol) was added slowly. The mixture was stirred at room temperature for 2 h and filtered through Celite. To this filtrate was added dropwise a diethyl ether (15 mL) solution of **1** (4.380 g, 20.90 mmol). The solution was stirred at room temperature for 12 h, and the volatiles were removed in vacuo to generate 3.770 g of a white solid (76% yield). Colorless crystals suitable for X-ray analysis were obtained from a diethyl ether solution at −20 °C. ^{1}H NMR (C_6D_6): 1.02 (s, 9H, NCMe_3), 2.14 (t, 1H, N*H*CMe$_3$), 2.18 (s, 6H, NMe$_2$), 3.37 (s, 2H, CH_2NMe$_2$), 3.46 (d, J_{HH} = 8.4 Hz, 2H, CH_2NHCMe$_3$), 4.29 (br, 2H, Al-*H*), 6.27 (s, 1H, pyrrolyl C*H*), 6.33 (s, 1H, pyrrolyl C*H*). ^{13}C (C_6D_6): 27.7 (q, J_{CH} = 124 Hz, NCMe_3), 41.9 (t, J_{CH} = 138 Hz, *C*H$_2$NHCMe$_3$), 46.9 (q, J_{CH} = 135 Hz, NMe_2), 53.5 (s, N*C*Me$_3$), 59.8 (t, J_{CH} = 138 Hz, *C*H$_2$NMe$_2$), 104.0 (d, J_{CH} = 164 Hz, pyrrolyl *C*H), 105.5 (d, J_{CH} = 164 Hz, pyrrolyl *C*H), 130.0 (s, pyrrolyl C_{ipso}), 131.9 (s, pyrrolyl C_{ipso}). IR (KBr): 1813 cm^{-1} (υ_{Al-H}). Anal. Calcd for $C_{12}H_{24}AlN_3$: C, 60.73; H, 10.19; N, 17.71. Found: C, 60.38; H, 10.37; N, 17.70.

[C_4H_2N(2-CH_2NH^tBu)(5-CH_2NMe_2)]Al(PhCOCHCOPh)$_2$ (3). A 100 mL Schlenk flask charged with **2** (0.5 g, 2.107 mmol) and 30 mL of diethyl ether was cooled to 0 °C and a diethyl ether (30 mL) solution of 1,3-diphenyl-1,3-propanedione (0.9642 g, 4.214 mmol) was added. The mixture was stirred at 0 °C for 10 min, and volatiles were removed under a vacuum. The residue was purified from a toluene solution at −20 °C to generate 0.925 g of orange crystals in 64% yield. ^{1}H NMR ($CDCl_3$): 0.81 (s, 9H, NCMe_3), 1.17 (s, 1H, N*H*CMe_3), 2.33 (s, 3H, NMe_2), 2.38 (s, toluene *Me*), 2.72 (s, 3H, NMe_2), 3.58 (d, 1H, CH_2NMe$_2$), 3.64 (m, 1H, CH_2NHCMe$_3$), 4.03 (m, 1H, CH_2NHCMe$_3$), 4.64 (d, 1H, CH_2NMe$_2$), 5.99 (s, 1H, pyrrolyl C*H*), 6.10 (s, 1H, pyrrolyl C*H*), 6.88 (s, 1H, PhCOC*H*COPh), 7.07 (s, 1H, PhCOC*H*COPh), 7.19−7.59 (m, 17H, phenyl C*H* and toluene C*H*), 7.92−8.16 (m, 8H, phenyl C*H*). ^{13}C ($CDCl_3$): 21.4 (q, J_{CH} = 126 Hz, toluene *Me*), 28.9 (q, J_{CH} = 125 Hz, NCMe_3), 42.1 (t, J_{CH} = 133 Hz, *C*H$_2$NHCMe$_3$), 46.6 (q, J_{CH} = 140 Hz, NMe_2), 47.5 (q, J_{CH} = 137 Hz, NMe_2), 49.7 (s, N*C*Me$_3$), 60.7 (t, J_{CH} = 135 Hz, *C*H$_2$NMe$_2$), 93.7 (d, J_{CH} = 160 Hz, PhCO*C*HCOPh), 94.3 (d, J_{CH} = 160 Hz, PhCO*C*HCOPh), 101.4 (d, J_{CH} = 164 Hz, pyrrolyl *C*H), 103.3 (d, J_{CH} = 162 Hz, pyrrolyl *C*H), 125.2, 127.5, 127.6, 127.7, 127.8, 127.9, 128.1, 128.2, 128.4, 128.5, 128.9, 131.5, 131.7, 131.8, 132.0, 132.2, 137.3, 137.5, 137.6, 138.4, 138.5 (phenyl and pyrrolyl), 184.1 (s, Ph*C*OCH), 184.2 (s, Ph*C*OCH), 185.6 (s, Ph*C*OCH), 185.7 (s, Ph*C*OCH). Anal. Calcd for $C_{42}H_{44}AlN_3O_4\cdot 0.25C_6H_5CH_3$: C, 74.55; H, 6.58; N, 5.96. Found: C, 74.47; H, 6.91; N, 5.83.

[C_4H_2N(2-CH_2NH^tBu)(5-CH_2NMe_2)]Al(SCHNPh)$_2$ (4). A methylene chloride (30 mL) solution of **2** (0.50 g, 2.107 mmol) was treated dropwise with a methylene chloride (30 mL) solution of PhNCS (0.581 g, 4.214 mmol) at −78 °C. The solution was then allowed to warm to room temperature and was stirred for another 10 min. The solvent was removed under reduced pressure to yield pale orange powder. The powder was redissolved in a mixed diethyl ether and methylene chloride solution and stored at −20 °C. Colorless crystals of **4** were obtained in 57.1% yield (0.61 g). ^{1}H NMR ($CDCl_3$): 0.38 (s, 9H, NC*Me*$_3$), 0.51 (s, 1H, N*H*CMe$_3$), 1.19 (t, OCH_2CH_3), 2.52 (s, 3H, N*Me*$_2$), 2.66 (d, 1H, C*H*$_2$NMe$_2$), 2.81 (s, 3H, N*Me*$_2$), 3.14 (d, 1H, C*H*$_2$NMe$_2$), 3.46 (q, OC*H*$_2$CH$_3$), 3.57 (d, 1H, C*H*$_2$NHCMe$_3$), 4.14 (d, 1H, C*H*$_2$NHCMe$_3$), 6.01 (s, 1H, pyrrolyl C*H*), 6.06 (s, 1H, pyrrolyl C*H*), 6.37−7.27 (phenyl C*H*), 9.09 (s, 1H, NC*H*S), 9.48 (s, 1H, NC*H*S). ^{13}C ($CDCl_3$): 15.2 (q, J_{CH} = 126 Hz, NC*Me*$_3$), 28.3 (q, OCH$_2$*C*H$_3$), 43.6 (t, J_{CH} = 131 Hz, *C*H$_2$NHCMe$_3$), 46.5 (q, J_{CH} = 137 Hz, N*Me*$_2$), 49.1 (s, CH$_2$NH*C*Me$_3$), 49.8 (q, J_{CH} = 137 Hz, N*Me*$_2$), 60.6 (t, J_{CH} = 140 Hz, *C*H$_2$NMe$_2$), 65.8 (t, OCH$_2$*C*H$_3$), 104.6 (d, J_{CH} = 165 Hz, pyrrolyl *C*H), 106.1 (d, J_{CH} = 165 Hz, pyrrolyl *C*H), 120.9, 121.4, 126.1, 129.2, 130.8, 138.3, 144.9, 146.2 (phenyl and pyrrolyl), 185.1 (d, J_{CH} = 181 Hz, N*C*HS), 189.2 (d, J_{CH} = 178 Hz, N*C*HS). Anal. Calcd for $C_{26}H_{34}AlN_5S_2$: C, 61.51; H, 6.75; N, 13.79. Found: C, 60.98; H, 7.06; N, 13.50.

Crystallographic Structure Determination of 1−4. All of the crystals were mounted on a glass fiber using epoxy resin and transferred to a goniostat. Data collections were performed at 150 K under liquid nitrogen vapor for complexes **1**−**4**. Data were collected on a Bruker SMART CCD diffractometer with graphite monochromated Mo Kα radiation. Crystal data were collected at 150 K with an Oxford Cryosystems Cryostream. No significant crystal decay was found. Data were corrected for absorption empirically by means of ψ scans. All non-hydrogen atoms were refined with anisotropic displacement parameters. For all of the structures, the hydrogen atom positions were calculated, and they were constrained to idealized geometries and treated as riding where the H atom displacement parameter was calculated from the equivalent isotropic displacement parameter of the bound atom. The structures of both complexes were determined by direct methods procedures in SHELXS[32] and refined by full-matrix least-squares methods, on F^2's, in SHELXL.[33] All of the relevant crystallographic data and structure refinement parameters for **1** and **2** are summarized in Table 1. For all of the structures, the hydrogen atoms on Al(1) and N(1) in compound **2** and N(1), N(3), N(4), and N(6) in compound **1** were found on the difference Fourier maps and refined isotropically. The other hydrogen atom positions were calculated, and they were constrained to idealized geometries and treated as riding where the H atom displacement parameter was calculated from the equivalent isotropic displacement parameter of the bound atom.

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Supporting Information Available: Crystallographic data in CIF file format for compounds **1**−**4** and Cartesian coordinates of stationary points for all compounds **1**−**4** and their possible geometries. This material is available free of charge via the Internet at http://pubs.acs.org.

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