Synthesis and Characterization of Four- and Five-Coordinate Organoaluminum Complexes Incorporating the Amido Diphosphine Ligand System $N(SiMe_2CH_2PPr^i_2)_2$

Michael D. Fryzuk,* Garth R. Giesbrecht, Gunnar Olovsson,[†] and Steven J. Rettig[†]

Department of Chemistry, University of British Columbia, 2036 Main Mall,
Vancouver, British Columbia, Canada V6T 1Z1

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The preparation of new four- and five-coordinate aluminum amido diphosphine complexes is reported. The reaction of the potentially tridentate ligand precursor $LiN(SiMe_2CH_2PPr^i_2)_2$ with $AlCl_3$ in toluene at 25 °C leads to the formation of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$. The X-ray crystal structure shows it to be monomeric with a distorted-trigonal-bipyramidal geometry having the tridentate ligand meridionally bound. The solution NMR spectra are also consistent with this geometry. Addition of the alkyllithium reagents RLi (where R = Me, Et) or dialkyl magnesium reagents R_2Mg (R = Me, CH_2Ph) leads to the formation of bis(hydrocarbyl) derivatives of the formula $AlR_2[N(SiMe_2CH_2PPr^i_2)_2]$. The X-ray structure of $Al(CH_2Ph)_2[N(SiMe_2CH_2PPr^i_2)_2]$ shows that it is mononuclear in the solid state with a distorted-tetrahedral geometry in which coordination to only one phosphine is observed. Variable-temperature NMR studies are consistent with a rapidly fluxional molecule at ambient temperature. In solution, the NMR spectroscopic parameters of $AlMe_2[N(SiMe_2CH_2PPr^i_2)_2]$ and $AlEt_2[N(SiMe_2CH_2PPr^i_2)_2]$ are consistent with overall C_{2v} symmetry. These observations are supported by ^{27}Al NMR studies. Attempts to generate the monoalkyls $Al(R)X[N(SiMe_2CH_2PPr^i_2)_2]$ (R = Me, Et; X = Cl) by the addition of 1 equiv of the appropriate alkylating reagent results in equimolar mixtures of the corresponding dialkyl and dichloride; however, the reaction of the lithium salt $LiN(SiMe_2CH_2PPr^i_2)_2$ with $RAlCl_2$ (R = Me, Et) produces mixtures containing predominantly $Al(R)X[N(SiMe_2CH_2PPr^i_2)_2]$ (R = Me, Et). Treatment of the monoethyl derivative with excess $AlCl_3$ affords $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]\cdot AlCl_3$. The X-ray crystal structure of this compound shows it to be monomeric, with each phosphine bound to a tetrahedral Al center. Solution NMR studies are consistent with this geometry. This species is likely formed as the result of the coordination of an $AlCl_3$ molecule to the aluminum center, followed by coordination of a second molecule to a free phosphine and subsequent elimination of $EtAlCl_2$. This species is also generated by the addition of 3 equiv $AlCl_3$ to the starting lithium salt $LiN(SiMe_2CH_2PPr^i_2)_2$.

Introduction

Our previous studies on the coordination properties of the potentially tridentate, mixed-donor ligand $^{-}N(SiMe_2CH_2PR_2)_2$ have centered on the transition metals and the lanthanoids.[1−3] In an effort to expand the territory to which this ligand can be applied, we have initiated a study of the coordination chemistry of certain main-group elements. As a starting point we began looking at complexes of aluminum using this ligand, since both amide and phosphine type donors have been used previously with this metal, although never before at the same time. Our primary goal was to try to use this ancillary ligand system to stabilize cationic Al(III) alkyl systems[4−14] of the formula $\{AlR[N(SiMe_2CH_2PR_2)_2]\}^+$. While this has not yet been achieved, along the way we did uncover some intriguing results that are reported here.

Typically, Al(III) tends to form complexes that are four- or five-coordinate. Simple adducts of $AlCl_3$ or AlR_3

[†] UBC Structural Chemistry Laboratory.

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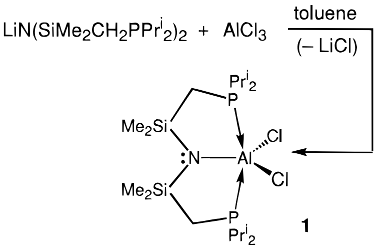
with phosphines[15−24] or amines[10,14,25−35] tend to generate four-coordinate species; chelating ligands can enforce higher coordination numbers by virtue of the chelate effect. With amido or imido type ligands, dimers, trimers or cage structures can be obtained.[26,36] Because our mixed-donor system is potentially tridentate, we anticipated that five-coordinate complexes of the general formula $AlX_2[N(SiMe_2CH_2PR_2)_2]$ would result. While this was generally found to be true, four-coordinate derivatives were also found to form under certain conditions.

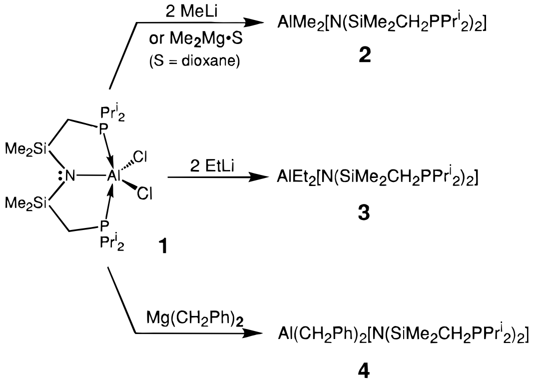
Results and Discussion

The reaction of the lithium salt of the ancillary ligand that contains isopropyl substituents, $LiN(SiMe_2CH_2PPr^i_2)_2$,[37] with $AlCl_3$ in toluene at 25 °C for 24 h generates the monomeric starting dichloride $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**) in good yield (eq 1). The ^1H NMR spectrum of the product is indicative of a C_{2v} symmetric complex: one observes resonances due to equivalent silylmethyl protons ($SiCH_3$), methylene (PCH_2Si), isopropyl methyls ($CH(CH_3)_2$) and methines ($CH(CH_3)_2$) at typical chemical shifts. The $^{31}P\{^1H\}$ NMR spectrum of **1** consists of a single broad resonance at −10.5 ppm, which is upfield as compared to the starting lithium derivative. The broadness of the peak is undoubtedly the result of coordination to the quadrupolar ^{27}Al nucleus (^{27}Al, $I = {}^5/_2$, 100% natural abundance),[38,39] while the upfield shift upon coordination is in contrast to that found for other complexes of this ligand system, for which a downfield shift is typical.[40] Small upfield or negative shifts upon coordination have been previously reported for the phosphorus-31 resonances of phenyl- and benzylphosphines coordinated to trimethylaluminum.[17] Elemental analyses on **1** are indicative of some LiCl incorporation that can be removed by successive recrystallizations. This type of behavior has been observed previously in aluminum complexes[29,32,36,41] and also during our investigations of this ligand system with early transition metals.[40,42]



(1)

Scheme 1



In typical metathesis fashion, the starting dichloride **1** reacts with lithium or magnesium alkyls to yield monomeric aluminum hydrocarbyl complexes of the general formula $AlR_2[N(SiMe_2CH_2PPr^i_2)_2]$ (R = Me (**2**), Et (**3**), CH_2Ph (**4**)) with concomitant formation of the appropriate metal-halide salt as a byproduct in each case (Scheme 1). The reactions to form **2** and **3** were carried out at 25 °C in toluene, whereas the metathesis reaction to form the dibenzyl **4** proved to be more successful at −60 °C using THF as the solvent. The dimethyl complex **2** may also be generated via the reaction of the starting lithium salt $LiN(SiMe_2CH_2PPr^i_2)_2$ with Me_2AlCl at room temperature in hexanes. All three dialkylaluminum compounds are isolated in good yields either as colorless oils, as in the case of **2** and **3**, or as pale yellow crystals, as found for **4**. These thermally stable derivatives are soluble in aromatic solvents as well as THF; however, their solubility is more limited in hydrocarbon solvents. As is the case with **1**, the elemental analysis of **4** is valid only if one allows for the inclusion of salt, in this case $MgCl_2$. All three of these air- and moisture-sensitive hydrocarbyl derivatives exhibit room-temperature ^1H NMR spectra indicative of highly symmetric environments. Interestingly, and in contrast to that found for **1**, the solution $^{31}P\{^1H\}$ NMR spectra of the dialkyl complexes **2**−**4** all consist of sharp singlets in the range of −3.6 to −4.9 ppm, consistent with very weak phosphine coordination

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Table 1. Crystallographic Data for 1, 4, and 7[a]

	1	4	7
formula	$C_{18}H_{44}AlCl_2NP_2Si_2$	$C_{32}H_{58}AlNP_2Si_2$	$C_{18}H_{44}Al_2Cl_5NP_2Si_2$
fw	490.56	601.92	623.90
color, habit	colorless, prism	colorless, needle	colorless, prism
cryst syst	monoclinic	triclinic	monoclinic
space group	$P2_1/n$	$P\bar{1}$	$P2_1/c$
a, Å	10.015(3)	11.724(3)	12.227(2)
b, Å	16.132(5)	18.649(4)	17.388(2)
c, Å	17.951(7)	9.047(3)	15.935(2)
α, deg	90	98.38(2)	90
β, deg	101.41(3)	98.06(2)	102.987(8)
γ, deg	90	73.92(2)	90
V, $Å^3$	2842(1)	1870.0(9)	3301.0(6)
Z	4	2	4
ρ_{calcd}, g/cm^3	1.146	1.069	1.255
F(000)	1056	656	1312
radiation	Mo	Mo	Cu
μ, cm^{-1}	4.61	2.18	62.01
cryst size, mm	0.45 × 0.45 × 0.40	0.12 × 0.20 × 0.40	0.20 × 0.45 × 0.50
transmissn factors		0.94−1.00	0.36−1.00
scan type	$\omega-2\theta$	$\omega-2\theta$	$\omega-2\theta$
scan range, ω, deg	$1.52 + 0.35 \tan \theta$	$1.15 + 0.35 \tan \theta$	$0.89 + 0.20 \tan \theta$
scan speed, deg min^{-1}	8 (up to 9 scans)	16 (up to 9 scans)	16 (up to 9 scans)
data collected	$+h,+k,\pm l$	$+h,\pm k,\pm l$	$+h,+k,\pm l$
$2\theta_{max}$, deg	55	50	155
cryst decay, %	negligible	6.3	7.4
total no. of rflns	6048	6933	7300
no. of unique rflns	5781	6574	6992
R_{merge}	0.077	0.045	0.073
no. of rflns with $I \geq 3\sigma(I)$	1405	2569	3611
no. of variables	245	343	272
R	0.081	0.056	0.046
R_w	0.076	0.050	0.046
GOF	3.88	2.43	2.00
Max Δ/σ (final cycle)	0.07	0.002	0.0003
residual density, e/$Å^3$	−0.47 to +0.47	−0.28 to +0.28	−0.28 to +0.30

[a] Conditions: temperature 294 K, Rigaku AFC6S diffractometer, Mo Kα (λ = 0.710 69 Å) or Cu Kα (λ = 1.541 78 Å) radiation, graphite monochromator, takeoff angle 6.0°, aperture 6.0 × 6.0 mm at a distance of 285 mm from the crystal, stationary background counts at each end of the scan (scan/background time ratio 2:1), $\sigma^2(F^2) = [S^2(C + 4B)]/Lp^2$ (S = scan rate, C = scan count, B = normalized background count), function minimized $\sum w(|F_o| - |F_c|)^2$, where $w = 4F_o^2/\sigma^2(F_o^2)$, $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$, and GOF $= [\sum w(|F_o| - |F_c|)^2/(m - n)]^{1/2}$ (where m = number of observations, n = number of variables). Values given for R, R_w, and GOF are based on those reflections with $I \geq 3\sigma(I)$.

and/or rapid exchange. In an effort to probe these aspects of phosphine ligation, we undertook some solid-state structural analyses where possible.

Solid-State Structures of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (1) and $Al(CH_2Ph)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (4). Slow evaporation of a saturated toluene solution of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**) resulted in colorless needles that were suitable for single-crystal X-ray diffraction. The molecular structure and numbering scheme are illustrated in Figure 1. Complete details of the structural analyses of **1** and **4**, as well as **7** (see later) are presented in Table 1. The structural analysis confirms the monomeric nature of **1** and illustrates the coordination geometry of the complex that is best described as trigonal bipyramidal. The ancillary amido diphosphine ligand is bound in a meridional fashion with the phosphine donors occupying axial positions. The greatest deviation from ideal trigonal-bipyramidal geometry is evident in the P(1)−Al(1)−P(2) bond angle of 171.8(3)°. The Cl(1)−Al(1)−Cl(2) bond angle of 118.2(3)° is close to that expected (120°) and is complemented by Cl(1)−Al(1)−N(1) and Cl(2)−Al(1)−N(1) bond angles of 121.3(5) and 120.5(4)°, respectively. Presumably, the twist in the backbone of the tridentate ligand is due to the relatively small Al(III) radius; the dihedral angle between the $AlNSi_2$ and $AlNP_2$ planes is 37.8°. In addition, this twist may be necessary in order to maintain a trigonal bipyramidal environment for the Al center, the preferred geometry for five-coordinate aluminum.[43,44] This has been observed previously in early-metal complexes that contain this same ancillary ligand system[40,45] and compares to values ranging from 34.4

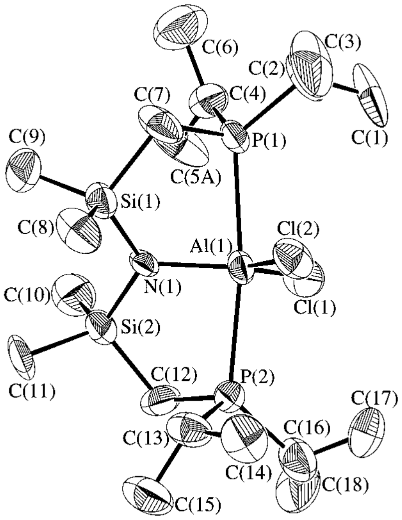

Figure 1. Molecular structure of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**), with 33% probability thermal ellipsoids. Hydrogen atoms and disorder are not shown for clarity.

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Table 2. Selected Bond Angles (deg) for 1, 4, and 7 with Estimated Standard Deviations in Parentheses

	Compound **1**		
Al(1)−P(1)−C(2)	124.5(8)	N(1)−Si(2)−C(12)	107.9(7)
Al(1)−P(1)−C(4)	116.7(7)	C(10)−Si(2)−C(11)	107.4(9)
Al(1)−P(1)−C(7)	97.4(6)	C(10)−Si(2)−C(12)	109.1(9)
C(2)−P(1)−C(4)	102(1)	C(11)−Si(2)−C(12)	109.3(8)
C(2)−P(1)−C(7)	109.1(9)	Cl(1)−Al(1)−Cl(2)	118.2(3)
C(4)−P(1)−C(7)	106(1)	Cl(1)−Al(1)−P(1)	93.5(2)
Al(1)−P(2)−C(12)	95.3(5)	Cl(1)−Al(1)−P(2)	89.3(2)
Al(1)−P(2)−C(13)	113.4(6)	Cl(1)−Al(1)−N(1)	121.3(5)
Al(1)−P(2)−C(16)	125.9(6)	Cl(2)−Al(1)−P(1)	89.8(2)
C(12)−P(2)−C(13)	104.7(9)	Cl(2)−Al(1)−P(2)	95.7(3)
C(12)−P(2)−C(16)	110.0(9)	Cl(2)−Al(1)−N(1)	120.5(4)
C(13)−P(2)−C(16)	105.4(9)	P(1)−Al(1)−P(2)	171.8(3)
N(1)−Si(1)−C(7)	107.9(7)	P(1)−Al(1)−N(1)	84.6(4)
N(1)−Si(1)−C(8)	111.3(8)	P(2)−Al(1)−N(1)	87.4(4)
N(1)−Si(1)−C(9)	114.5(8)	Si(1)−N(1)−Si(2)	121.8(6)
C(7)−Si(1)−C(8)	107.3(9)	Si(1)−N(1)−Al(1)	119.3(6)
C(7)−Si(1)−C(9)	108(1)	Si(2)−N(1)−Al(1)	118.7(6)
C(8)−Si(1)−C(9)	108.0(9)	P(1)−C(7)−Si(1)	108.3(7)
N(1)−Si(2)−C(10)	110.4(7)	P(2)−C(12)−Si(2)	110.6(9)
N(1)−Si(2)−C(11)	112.7(7)		
	Compound **4**		
Al(1)−P(1)−C(1)	97.2(2)	N(1)−Si(2)−C(6)	112.1(3)
Al(1)−P(1)−C(7)	123.6(2)	C(2)−Si(2)−C(5)	108.8(3)
Al(1)−P(1)−C(8)	114.9(2)	C(2)−Si(2)−C(6)	108.5(3)
C(1)−P(1)−C(7)	106.9(3)	C(5)−Si(2)−C(6)	106.5(3)
C(1)−P(1)−C(8)	107.4(3)	P(1)−Al(1)−N(1)	92.1(2)
C(7)−P(1)−C(8)	105.4(3)	P(1)−Al(1)−C(19)	106.3(2)
C(2)−P(2)−C(13)	105.3(3)	P(1)−Al(1)−C(26)	110.4(2)
C(2)−P(2)−C(14)	102.5(4)	N(1)−Al(1)−C(19)	113.6(2)
C(13)−P(2)−C(14)	100.6(5)	N(1)−Al(1)−C(26)	117.5(3)
N(1)−Si(1)−C(1)	108.1(3)	C(19)−Al(1)−C(26)	114.1(3)
N(1)−Si(1)−C(3)	113.5(3)	Si(1)−N(1)−Si(2)	121.7(3)
N(1)−Si(1)−C(4)	115.6(3)	Si(1)−N(1)−Al(1)	117.4(3)
C(1)−Si(1)−C(3)	105.3(3)	Si(2)−N(1)−Al(1)	120.9(3)
C(1)−Si(1)−C(4)	106.5(3)	P(1)−C(1)−Si(1)	112.7(3)
C(3)−Si(1)−C(4)	107.1(3)	P(2)−C(2)−Si(2)	117.2(3)
N(1)−Si(2)−C(2)	109.4(3)	Al(1)−C(19)−C(20)	110.4(4)
N(1)−Si(2)−C(5)	111.3(3)	Al(1)−C(26)−C(27)	116.2(4)
	Compound **7**		
Al(1)−P(1)−C(1)	98.6(2)	C(2)−Si(2)−C(5)	110.0(2)
Al(1)−P(1)−C(7)	113.1(2)	C(2)−Si(2)−C(6)	111.5(2)
Al(1)−P(1)−C(10)	120.8(2)	C(5)−Si(2)−C(6)	106.8(2)
C(1)−P(1)−C(7)	107.3(3)	Cl(1)−Al(1)−Cl(2)	108.90(8)
C(1)−P(1)−C(10)	109.1(2)	Cl(1)−Al(1)−P(1)	110.02(7)
C(7)−P(1)−C(10)	107.0(3)	Cl(1)−Al(1)−N(1)	115.4(1)
Al(2)−P(2)−C(2)	115.0(2)	Cl(2)−Al(1)−P(1)	110.29(8)
Al(2)−P(2)−C(13)	109.2(2)	Cl(2)−Al(1)−N(1)	115.9(1)
Al(2)−P(2)−C(16)	106.3(2)	P(1)−Al(1)−N(1)	95.5(1)
C(2)−P(2)−C(13)	108.3(2)	Cl(3)−Al(2)−Cl(4)	111.7(1)
C(2)−P(2)−C(16)	107.6(2)	Cl(3)−Al(2)−Cl(5)	110.30(9)
C(13)−P(2)−C(16)	110.4(3)	Cl(3)−Al(2)−P(2)	105.79(8)
N(1)−Si(1)−C(1)	107.9(2)	Cl(4)−Al(2)−Cl(5)	112.1(1)
N(1)−Si(1)−C(3)	113.4(2)	Cl(4)−Al(2)−P(2)	108.32(8)
N(1)−Si(1)−C(4)	112.0(2)	Cl(5)−Al(2)−P(2)	108.42(9)
C(1)−Si(1)−C(3)	107.3(2)	Si(1)−N(1)−Si(2)	124.1(2)
C(1)−Si(1)−C(4)	106.3(3)	Si(1)−N(1)−Al(1)	116.7(2)
C(3)−Si(1)−C(4)	109.6(3)	Si(2)−N(1)−Al(1)	118.9(2)
N(1)−Si(2)−C(2)	105.6(2)	P(1)−C(1)−Si(1)	113.8(2)
N(1)−Si(2)−C(5)	110.9(2)	P(2)−C(2)−Si(2)	125.3(3)
N(1)−Si(2)−C(6)	112.1(2)		

Table 3. Selected Bond Lengths (Å) for 1, 4, and 7 with Estimated Standard Deviations in Parentheses

	Compound **1**		
Cl(1)−Al(1)	2.183(6)	Si(1)−N(1)	1.72(1)
Cl(2)−Al(1)	2.164(7)	Si(1)−C(7)	1.89(2)
P(1)−Al(1)	2.542(7)	Si(1)−C(8)	1.86(2)
P(1)−C(2)	1.88(2)	Si(1)−C(9)	1.80(2)
P(1)−C(4)	1.81(2)	Si(2)−N(1)	1.72(1)
P(1)−C(7)	1.85(2)	Si(2)−C(10)	1.90(2)
P(2)−Al(1)	2.509(7)	Si(2)−C(11)	1.88(2)
P(2)−C(12)	1.82(2)	Si(2)−C(12)	1.84(2)
P(2)−C(13)	1.90(2)	Al(1)−N(1)	1.89(1)
P(2)−C(16)	1.86(2)		
	Compound **4**		
P(1)−Al(1)	2.453(3)	Si(1)−C(3)	1.862(7)
P(1)−C(1)	1.835(6)	Si(1)−C(4)	1.867(7)
P(1)−C(7)	1.843(6)	Si(2)−N(1)	1.745(5)
P(1)−C(8)	1.846(7)	Si(2)−C(2)	1.881(7)
P(2)−C(2)	1.848(6)	Si(2)−C(5)	1.862(7)
P(2)−C(13)	1.846(8)	Si(2)−C(6)	1.876(7)
P(2)−C(14)	1.84(1)	Al(1)−N(1)	1.853(5)
Si(1)−N(1)	1.716(5)	Al(1)−C(19)	1.991(7)
Si(1)−C(1)	1.882(7)	Al(1)−C(26)	1.987(6)
	Compound **7**		
Cl(1)−Al(1)	2.132(2)	P(2)−C(13)	1.833(5)
Cl(2)−Al(1)	2.124(2)	P(2)−C(16)	1.843(5)
Cl(3)−Al(2)	2.115(2)	Si(1)−N(1)	1.727(3)
Cl(4)−Al(2)	2.106(2)	Si(1)−C(1)	1.892(5)
Cl(5)−Al(2)	2.112(2)	Si(1)−C(3)	1.860(6)
P(1)−Al(1)	2.403(2)	Si(1)−C(4)	1.856(6)
P(1)−C(1)	1.807(5)	Si(2)−N(1)	1.729(3)
P(1)−C(7)	1.815(6)	Si(2)−C(2)	1.908(5)
P(1)−C(10)	1.832(5)	Si(2)−C(5)	1.854(5)
P(2)−Al(2)	2.412(2)	Si(2)−C(6)	1.858(5)
P(2)−C(2)	1.808(4)	Al(1)−N(1)	1.828(3)

to 40.8° for similar compounds of scandium.[40] Selected bond angles for **1** can be found in Table 2.

The aluminum−chloride distances of 2.183(6) and 2.164(7) Å compare well with those previously reported for terminal Al−Cl bonds,[11,16,20,21,33,46] falling just outside the cited range of the longer bridging chlorides.[47,48] The aluminum−phosphorus bond lengths of 2.509(7) and 2.542(7) Å are also common in terms of Al−P bond distances for phosphine adducts of aluminum, which usually span the range from ~2.4 to 2.8 Å.[17,22,49] The intermediary solvation of the aluminum center by the phosphine donors is further illustrated by comparison to the bond lengths of 2.53 and 2.535 Å in Me$_3$AlPMe$_3$ and Me$_3$AlPPh$_3$, respectively.[19] The aluminum−nitrogen bond distance of 1.89(1) Å falls well within the usual range for aluminum−amide bonds.[25,26,28−30,36,50] As is expected, the amide bond present is slightly shorter than for the N-donor amine adducts of aluminum (~2.0−2.2 Å)[30,33,35] but is similar to the bond lengths cited in structures retaining an Al$_2$N$_2$ or bridging nitrogen core,[12,26,32,36] in which a lower degree of dative bonding is usually invoked. The Al−N bond distance in **1** compares well with that in the similar amido diamine compound Al(CH$_3$)$_2$[(NCH$_2$CH$_2$NEt$_2$)$_2$] (Al−N(amido) = 1.84(1) Å), which also exhibits a trigonal-bipyramidal Al coordination geometry.[29] It is unclear to what extent this bond length, approximately 0.1 Å shorter than the sum of the covalent radii, is indicative of some degree of p−p π bonding.[25] A partial list of bond lengths for **1**, **4**, and **7** is presented in Table 3.

Evaporation of a saturated toluene solution of Al(CH$_2$Ph)$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] (**4**) resulted in the deposition of pale yellow needles that were suitable for X-ray diffraction. The molecular structure and numbering

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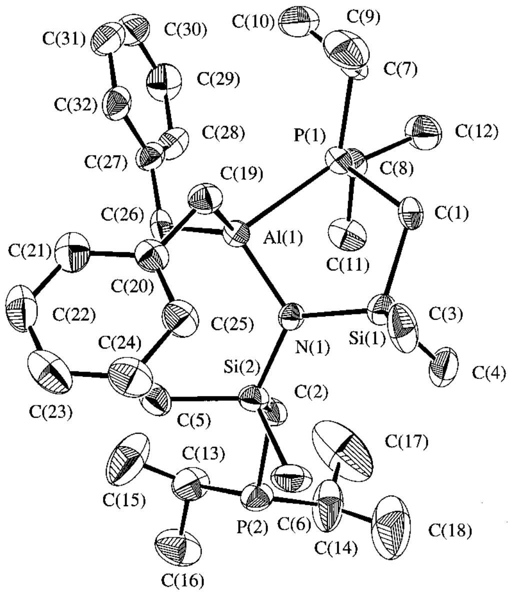

Figure 2. Molecular structure of $Al(CH_2C_6H_5)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**4**), with 33% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

scheme of this compound can be seen in Figure 2. The structural study reveals **4** to be four-coordinate via coordination to only one phosphine arm of the ancillary $^-N(SiMe_2CH_2PPr^i_2)_2$ ligand. Presumably, the steric repulsion between the aryl rings of the benzyl groups and the isopropyl substituents on the phosphorus donors is great enough to force one of the weakly bound phosphines to dissociate, allowing the Al center to adopt a distorted-tetrahedral geometry. This is the most prevalent and preferred mode of coordination for Al(III).[51] The six tetrahedral angles, varying from 92.1(2) to 117.5(3)°, do indicate the extent of the distortion from a pure tetrahedron with the most acute angle, defined by the P(1), Al(1), and N(1) atoms, being the result of the bidentate ligand "pinching back".

The single aluminum–phosphorus bond measures 2.453(3) Å and is slightly shorter than the Al–P bond lengths of **1**. The aluminum–nitrogen bond is also similar to that ascertained for **1**, although the slightly longer silicon–amide bond (1.745(5) vs 1.72(1) Å) coupled with the marginally shorter Al–N bond (1.853(5) vs 1.89(1) Å) may point to a slightly higher degree of π-donation from the amide lone pair to the metal. Compound **4** also possesses unremarkable aluminum–carbon bond lengths of 1.991(7) and 1.987(6) Å, which are akin to those previously reported for terminal Al–C bonds.[10,25,48,52–54] The strongest similarity is with the Al–C distances found in $Al(CH_2C_6H_5)_3$, for which average values of 1.989(6) Å were found.[55]

The recent X-ray structure of $Cr(CH_2C_6H_5)[N(SiMe_2CH_2PPh_2)_2]$,[45] which possesses an η^2-bound benzyl fragment, prompted us to further examine the structure of **4.** The Al–C_{ipso} lengths of 2.883 and 2.974 Å, coupled with Al–$C_{benzylic}$–C_{ipso} bond angles of 110.4(4) and 116.2(4)°, were outside of the range normally found for an η^2 interaction. Furthermore, the Al–C_{ortho} distances of 3.589–3.924 Å were convincing evidence against an η^3 formulation of any type. The $C_{benzylic}$–C_{ipso} bond lengths of 1.505(8) Å also fall within the desired range for σ-bound benzyl groups devoid of any additional interactions and are longer than that found in the related chromium derivative.

^{31}P and ^{27}Al NMR Studies and Coordination Number. While the X-ray structure of dichloride **1** is compatible with the solution ^1H and $^{31}P\{^1H\}$ NMR studies, the simple ^1H NMR spectrum and single sharp resonance in the $^{31}P\{^1H\}$ NMR spectrum of the dibenzyl **4** was at odds with the bidentate mode of coordination of the ancillary ligand found in the solid state. Even though we were unable to isolate either the dimethyl **2** or the diethyl **3** as solids, we were curious about their solution structures. In the past, ^{27}Al NMR spectroscopy has proved helpful in correlating chemical shift with coordination number,[38,39] even at temperatures where highly dynamic molecules show only averaged ^1H and $^{31}P\{^1H\}$ signals.[17]

As already mentioned, the solution spectroscopic data for dichloride **1** reinforces the results of the solid-state X-ray analysis. The ^1H NMR spectrum is indicative of a molecule with overall C_{2v} symmetry, and the single broad resonance in the $^{31}P\{^1H\}$ NMR spectrum at −10.5 ppm suggests some aluminum–phosphorus interaction. The $^{31}P\{^1H\}$ NMR spectrum is temperature invariant down to the solvent limit (−90 °C, d_8-toluene). The ^{31}P and ^{27}Al MAS NMR spectrum of a solid sample of dichloride **1** is consistent with the same sort of Al–P coupling that is present in solution. The solution ^{27}Al NMR spectrum contains a very broad peak at 65 ppm, which is well within the typical range for five-coordinate aluminum derivatives.[38,39] Large peak widths appear to be common when quadrupolar nuclei are observed in heteroleptic environments.[23,56] The dichloride **1** does not form adducts with THF, pyridine, or acetonitrile in solution. Presumably, the steric constraints of the ancillary ligand system prevent the aluminum center from attaining a higher coordination number, even in the presence of excess donor molecules. Interestingly, the addition of a strongly Lewis acidic moiety such as $AlCl_3$ to **1** results in the reduction of the aluminum coordination number to 4, with a further $AlCl_3$ interaction being observed with a free phosphine (see later).

The $^{31}P\{^1H\}$ NMR spectrum of dimethyl **2** features a much narrower peak than would be expected for a compound harboring an Al–P interaction. The position of this peak, −4.9 ppm, is also close to that of the starting lithium salt $LiN(SiMe_2CH_2PPr^i_2)_2$, which resonates at −4.7 ppm and most likely does not experience any sort of quadrupolar interaction. As the temperature is lowered, the peak broadens slightly, but no evidence of decoalescence behavior is observed even down to −90 °C. It is unclear whether this indicates a three-coordinate structure or a rapidly fluxional process that could not be frozen out. The solution ^{27}Al NMR spectrum of **2**, however, consists of a peak at 70 ppm, indicating a geometry similar to that found in **1**. In addition, the equivalent methyl groups ($AlMe_2$) appear as a triplet in the ^1H NMR spectrum, the result of coupling to two equivalent phosphorus-31 nuclei. All

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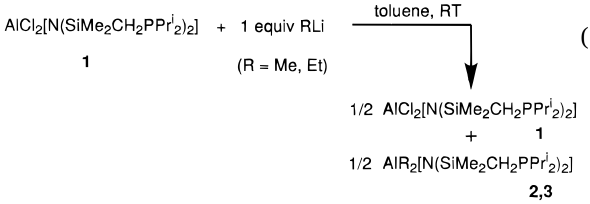
the spectroscopic data taken together point to a highly fluxional structure for **2**, presumably a result of rapid phosphine-arm dissociation and reassociation on the NMR time scale.

Examination of the ^{1}H and ^{31}P{^{1}H} NMR spectra of diethyl **3** reveals properties similar to those found for **2**. The ^{1}H NMR spectrum is characteristic of a highly symmetric molecule in which the methylene protons of the ethyl groups ($\mathrm{AlC}H_2\mathrm{CH_3}$) appear as a quartet of triplets due to coupling to two equivalent phosphines as well as the terminal $-\mathrm{CH_3}$ protons of the ethyl group. As in **2**, the ^{31}P{^{1}H} NMR spectrum of **3** exhibits only a single sharp resonance at −4.2 ppm, which broadens but does not decoalesce as the temperature is lowered. However, the ^{27}Al NMR spectrum is shifted downfield from that of **1** or **2** to 140 ppm, well within the range normally associated with four-coordinate species.[38,39] Again, the data point toward a rapidly fluxional structure; however, to account for the ^{27}Al NMR spectral result, one can suggest that diethyl **3** spends a comparatively greater amount of time in the dissociated state as compared to dimethyl **2**. That this is the case can be rationalized on the similarity in size between the $-\mathrm{Cl}$ and $-\mathrm{CH_3}$ groups in **1** and **2**; the larger $-\mathrm{CH_2CH_3}$ groups in **3** undoubtedly destabilize coordination by both of the bulky isopropyl-substituted phosphine donors.

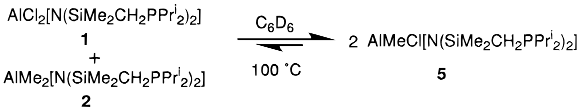
The crystal structure of $\mathrm{Al(CH_2Ph)_2[N(SiMe_2CH_2PPr^i{}_2)_2]}$ (**4**) illustrates that, with large enough alkyl groups, aluminum will reside in its preferred tetrahedral geometry. Once again, the ^{1}H NMR spectrum displays resonances indicative of a C_{2v}-symmetric complex, although instead of a triplet for the benzylic protons, a broad peak at 3.50 ppm is observed. No useful information could be garnered from variable-temperature ^{1}H NMR due to a systematic broadening of all resonances with no obvious low-temperature limit. However, the sharp singlet at −3.6 ppm in the ^{31}P{^{1}H} NMR spectrum does display typical coalescence behavior; the singlet broadened and shifted slightly upfield as the temperature was lowered, and at −74 °C, two singlets of equal intensity at −5.4 and −6.8 ppm were evident. Unfortunately, the kinetic parameters, $\Delta G^‡$, $\Delta H^‡$, and $\Delta S^‡$, could not be derived due to the error associated with a fluxional process such as this occurring over such a limited temperature range (−63 to −74 °C). The solution ^{27}Al NMR spectrum consists of a broad peak at 54 ppm, both at room temperature and at −74 °C. These data suggest that, at room temperature in solution, **4** is rapidly fluxional through a five-coordinate intermediate (associative pathway). That dibenzyl **4** would be five-coordinate in solution, while diethyl **3** would remain four-coordinate, is counterintuitive, on the basis of the relative sizes of the ethyl and benzyl groups. In other words, one would expect the solution ^{27}Al NMR shift for dibenzyl **4** to be similar to that for the diethyl **3** on the basis of the solid-state structure of **4**. It may be that, in the case of **4**, the correlation of ^{27}Al NMR chemical shift and solution coordination number breaks down.

Synthesis of the Monoalkyl Derivatives $\mathbf{Al(R)Cl[N(SiMe_2CH_2PPr^i{}_2)_2]}$ (R = Me, Et). The difference in structure between dichloride **1** and the dialkyls, **2**−**4** prompted us to examine the preparation of the monoalkyl derivatives $\mathrm{Al(R)Cl[N(SiMe_2CH_2PPr^i{}_2)_2]}$. It would stand to reason that intermediate behavior should obtain for these latter species; in addition, these derivatives might be useful starting materials for cationic derivatives by halide abstraction.[8,9,11−14] Crown ether ligands have been the most successful in this regard, although nitrogen-based ancillary ligands have also been of some use.[7,10] Unfortunately, our attempts to selectively remove one alkyl group from the dialkyls **2** and **4** with the strong Lewis acid $\mathrm{B(C_6F_5)_3}$[57,58] or with Brookhart's acid, $\mathrm{HB(3,5\text{-}CF_3(C_6H_3))_4}$,[59] resulted in a mixture of intractable products.

When dichloride **1** was subjected to the slow addition of 1 equiv of methyllithium or equivalent Grignard reagent (i.e., MeMgBr, MeMgCl, or $^1/_2$ equiv of $\mathrm{Me_2Mg}$), equimolar mixtures of starting dichloride **1** and dimethyl **2** were obtained. Similarly, addition of just 1 equiv of EtLi to **1** also produced a mixture of starting dichloride **1** and diethyl **3** (eq 2). To account for this behavior,[41] we suggest that the monoalkyl intermediate reacts faster than dichloro **1**, because in the former species, phosphine dissociation becomes more likely, thus opening the coordination sphere to attack by nucleophiles. However, we did find that the mixture of dichloride **1** and dimethyl **2** could be induced to equilibrate to a mixture that contained the monomethyl derivative $\mathrm{Al(Me)Cl[N(SiMe_2CH_2PPr^i{}_2)_2]}$ (**5**) upon heating; it was found that after 1 week at 100 °C, the exchange was approximately 85% complete, as monitored by ^{1}H NMR spectroscopy (eq 3). When the equilibrium shown in eq 3 was monitored at temperatures between 20 and 100 °C by ^{1}H NMR spectroscopy, the following thermodynamic data were calculated using the van't Hoff equation: $\Delta H° = 106 \pm 8$ kJ mol^{-1} and $\Delta S° = 311 \pm 24$ J mol^{-1} K^{-1}.



$$\underset{\mathbf{1}}{\mathrm{AlCl_2[N(SiMe_2CH_2PPr^i{}_2)_2]}} + \underset{(\mathrm{R = Me, Et})}{\text{1 equiv RLi}} \xrightarrow{\text{toluene, RT}} 1/2\ \underset{\mathbf{1}}{\mathrm{AlCl_2[N(SiMe_2CH_2PPr^i{}_2)_2]}} + 1/2\ \underset{\mathbf{2,3}}{\mathrm{AlR_2[N(SiMe_2CH_2PPr^i{}_2)_2]}} \qquad (2)$$



$$\underset{\mathbf{1}}{\mathrm{AlCl_2[N(SiMe_2CH_2PPr^i{}_2)_2]}} + \underset{\mathbf{2}}{\mathrm{AlMe_2[N(SiMe_2CH_2PPr^i{}_2)_2]}} \underset{100\ °\mathrm{C}}{\overset{\mathrm{C_6D_6}}{\rightleftharpoons}} 2\ \underset{\mathbf{5}}{\mathrm{AlMeCl[N(SiMe_2CH_2PPr^i{}_2)_2]}} \qquad (3)$$

In an effort to obtain pure $\mathrm{Al(Me)Cl[N(SiMe_2CH_2PPr^i{}_2)_2]}$ (**5**), we studied the reaction of the starting lithium salt $\mathrm{LiN(SiMe_2CH_2PPr^i{}_2)_2}$ with $\mathrm{MeAlCl_2}$. Although in this reaction we were able to prepare more pure $\mathrm{Al(Me)Cl[N(SiMe_2CH_2PPr^i{}_2)_2]}$ (**5**), small quantities of **1** and **2** were present, and these impurities persisted even if the reaction was done under dilute conditions at −78 °C. Given the equilibrium between **5** and dichloro **1** and dimethyl **2**, this last result is not surprising.

As mentioned above, the reaction of **1** with 1 equiv of EtLi produced an equimolar mixture of **1** and diethyl **3**; however, in this case prolonged heating (2 weeks, 100

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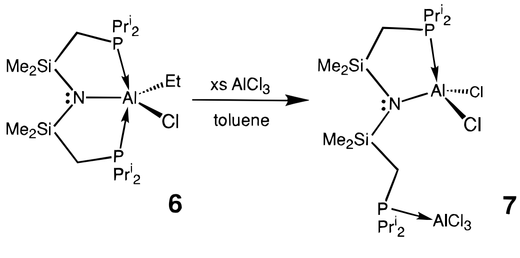
°C) did not result in any observable exchange to produce the monoethyl derivative, as monitored by ^{1}H NMR spectroscopy. As a result, we examined the reaction of the lithium salt LiN(SiMe$_2$CH$_2$PPr$^i_2$)$_2$ with EtAlCl$_2$, in hopes of producing Al(Et)Cl[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$] (**6**). The ^{1}H NMR spectrum of this reaction mixture indeed did show predominantly **6**, but small amounts (<5%) of **1** were invariably present, presumably due to contamination by AlCl$_3$ in the starting AlEtCl$_2$. The complete absence of diethyl **3** is consistent with the lack of an exchange equilibrium being present. In other words, once the monoethyl complex **6** forms, it does not disproportionate into **1** and **3**, as was observed for the monomethyl derivative **5**.

Synthesis of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]·AlCl$_3$ (7). Although we were unable to isolate pure monoalkyl derivatives Al(R)Cl[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$], we decided to attempt the formation of the cation {AlR[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]}$^+$ by reaction of the slightly impure monoethyl complex **6** with AlCl$_3$. Upon addition of the solution of **6** to a slurry of AlCl$_3$ in toluene (approximately 2.5 equiv), the solution turned slightly amber and most of the AlCl$_3$ was taken up into solution. Upon workup, colorless crystals were isolated that displayed the following spectroscopic characteristics: the ^{31}P{^{1}H} NMR spectrum consisted of two broad peaks at 0.0 and −11.8 ppm of roughly equal intensity, and the ^{1}H NMR spectrum indicated a single clean but unsymmetrical product, with no resonances due to ethyl groups present. The elemental analysis, coupled with the ^{31}P{^{1}H} and ^{1}H NMR data, pointed toward an AlCl$_3$ adduct of dichloro **1**, in which the $^-$N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$ ligand is bound to an AlCl$_2$ unit in a bidentate fashion via the amide function and one phosphine donor, with the remaining phosphine arm of the ancillary ligand coordinated to an AlCl$_3$ molecule (eq 4).



(4)

Structure of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]·AlCl$_3$ (7). X-ray quality crystals of **7** were grown by slow evaporation of a saturated toluene solution. The molecular structure and numbering scheme are depicted in Figure 3. The most important feature of this molecule is that two four-coordinate aluminum centers are present. One Al is bound in a bidentate fashion to the tridentate ligand, with the remaining phosphine arm coordinated to the AlCl$_3$ unit. We presume that the presence of this coordinated AlCl$_3$ unit in **7** serves the same function as the large benzyl groups in **4**, in that they both allow for the central aluminum to retain a tetrahedral geometry. The bond angles involving this aluminum range from 115.9(1) to 95.5(1)°. The smallest angle, as in **4**, involves chelation of the ligand to the metal (P(1)−Al(1)−N(1)). The second aluminum also exhibits a four-coordinate, tetrahedral geometry. The angles involving the phosphine in this case are slightly smaller (105.79(8)−108.42(9)°) than those between the chlorides (110.30(9)−112.1(1)°) and are the result of the donation of the lone pair from the phosphine to the metal center. The aluminum−chlorine bond lengths are all similar (2.106(2)−2.132(2) Å) and unexceptional. The aluminum−phosphorus bond lengths of 2.403(2) Å (P(1)−Al(1)) and 2.412(2) Å (P(2)−Al(2)) are both smaller than those found in **1** and **4**.

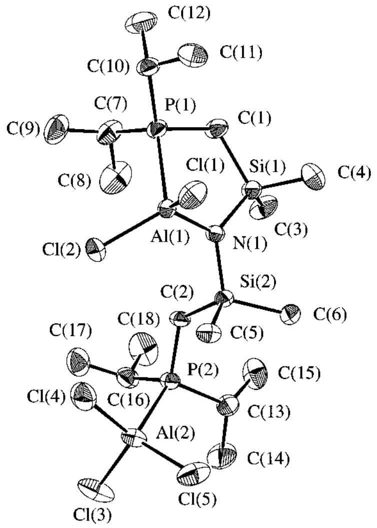


Figure 3. Molecular structure of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]·AlCl$_3$ (**7**), with 33% probability thermal ellipsoids. Hydrogen atoms are omitted for clarity.

The ^{1}H NMR spectrum of **7** is consistent with its structure, in that a doubling of all ligand resonances is seen as a result of the lack of symmetry. The ^{31}P{^{1}H} NMR spectrum consists of two broad singlets, due to the coordination of each phosphorus nucleus to a quadrupolar Al center. Also, the methylene protons associated with the "free" arm (C(2)) appear as a broad doublet. Examination of the crystal structure reveals a short intramolecular C(2)−H(3)···Cl(2) distance of 3.082 Å. It appears this interaction slows the rotation of the free arm on the NMR time scale, resulting in a broadening of these protons. The molecule also has three other short intramolecular contacts of note: two protons on a silyl methyl group on the free side of the ligand interact with chlorides on Al(1) and Al(2) (C(5)−H(12)···Cl(2) = 3.623(5) Å, C(5)−H(13)···Cl(5) = 3.755(5) Å), and a proton on an isopropyl group (C(11)−H(25)) interacts with a chloride (Cl(1)) associated with Al(1) (3.750(7) Å). Finally, there is also an intermolecular contact measuring 3.739(6) Å between C(12)−H(28) and Cl(4) of an adjacent molecule of **7**. No broadening of the resonances associated with these further intramolecular contacts was observed.

Polynuclear aluminum compounds are numerous in the literature, although those incorporating amido ligands are more rare. Complex **7** is one of only three known polynuclear aluminum complexes with a tridentate amido ligand.[29,60] Its asymmetric nature is similar to that of Al$_3$(CH$_3$)$_8$(Et$_2$NCH$_2$CH$_2$NCH$_2$CH$_2$NEt$_2$), although ligation to the amide lone pair is not observed in our case. Exposure of **7** to additional AlCl$_3$ did not result in any further rearrangement.

Mechanism of Formation of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^i_2$)$_2$]·AlCl$_3$ (7). The most striking feature of the structure of **7** is the absence of an ethyl group bound to

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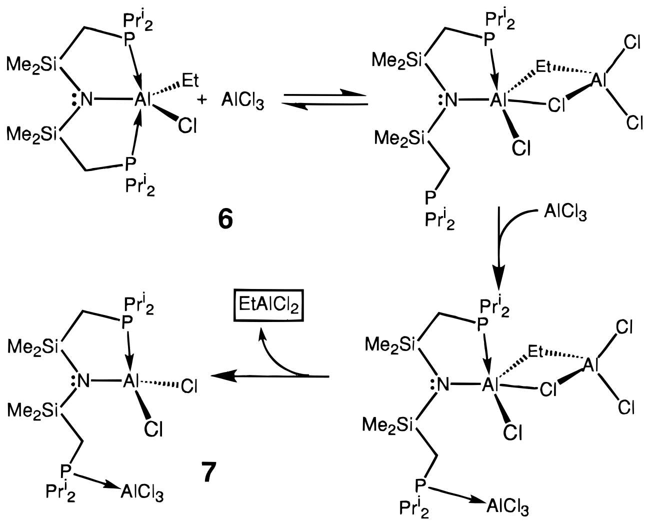
(60) Wannagat, U.; Blumenthal, T.; Brauer, D. J.; Burger, H. *J. Organomet. Chem.* **1983**, *249*, 33.

Scheme 2



the central aluminum. It appears that monoethyl **6** undergoes two separate reactions with $AlCl_3$ to form **7**: first, a ligand redistribution reaction at the central aluminum to eliminate an ethyl group, and second, ligation of a second $AlCl_3$ molecule by a dissociated phosphine arm. The ligand redistribution behavior of mixed alkyl−halo aluminum compounds is well-documented and is most often called upon to explain a deficiency of alkyl groups in organoaluminum compounds.[61] For example, redistribution of Et_2AlCl to generate $EtAlCl_2$ and Et_3Al has been suggested to occur through the formation of the unsymmetrical dimer $Et_2Al(\mu\text{-}Cl)(\mu\text{-}Et)AlEtCl$. Such a process accounts for the shortage of ethyl groups (relative to that expected) for a number of organoaluminum compounds found when Et_2AlCl is added to ligand systems as varied as crown ethers,[12] macrocyclic and open-chain multidentate amines,[33,34] and aluminum−phosphorus dimers.[16,20] A similar explanation has been invoked to account for analogous results using Me_2AlCl.[21] As well, asymmetric bridge cleavage has been implicated in the formation of cationic species of crown ethers.[12]

It is possible that a similar type of process operates in our system. As shown in Scheme 2, exposure of monoethyl **6** to $AlCl_3$ could result in the equilibrium formation of a mixed ethyl−chloro-bridged species. For this intermediate to form, dissociation of one phosphine arm alleviates steric crowding that would otherwise occur in a six-coordinate species. The dangling Lewis basic phosphine then coordinates to a second equivalent of $AlCl_3$, effectively negating any further chance for aluminum coordination. The transient alkyl−halo-bridged dimer then eliminates $EtAlCl_2$ to yield **7** (Scheme 2).

Some support for this mechanism comes from the following observations. (i) The number of equivalents of $AlCl_3$ required for this reaction to ensue is 2. The addition of **6** to a toluene slurry of 1 equiv of $AlCl_3$ does not result in the formation of **7**. (ii) The trace amount of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (**1**) present in starting samples of $AlEtCl[N(SiMe_2CH_2PPr^i_2)_2]$ (**6**) reacts in a manner similar to that for **6**, as no $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ can be found after the reaction with $AlCl_3$. Thus, the addition of 2 equiv of $AlCl_3$ to $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ also forms the $AlCl_3$ adduct **7**, although 1 equiv does not. This suggests that if the phosphine arms of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ were rapidly fluxional, and an $AlCl_3$ molecule simply trapped a transiently dangling phosphine arm, the addition of 1 equiv of $AlCl_3$ should be sufficient to form **7**. The need for 2 equiv of $AlCl_3$ supports our contention that the formation of a bridged species is necessary to dissociate one phosphine arm, which is then trapped by the excess $AlCl_3$.

In an effort to track down the $EtAlCl_2$ postulated to be generated, we collected the volatiles from the reaction and examined them by ^1H NMR spectroscopy. Although peaks at 0.93 (t) and 0.22 (q) ppm, corresponding to the methyl and methylene protons of the Et group, respectively, could be seen, the spectrum was further complicated by additional resonances in the range 0−2 ppm. In light of the ^1H NMR results, it is difficult to conclusively determine the presence or absence of the desired aluminum alkyl halide. That $EtAlCl_2$ is produced and then forms other products as the result of exchange cannot be ruled out.

The analogous reaction of the methyl derivative $Al(Me)Cl[N(SiMe_2CH_2PPr^i_2)_2]$ (**5**) with $AlCl_3$ provides a mixture of products, among them a small amount of **7** (as observed by ^1H NMR spectroscopy). The smaller $-CH_3$ group likely experiences a more facile exchange and quickly forms other products as well. No attempt to further characterize the products of this addition was made.

Conclusions

Bis(hydrocarbyl)aluminum derivatives of the ancillary, potentially tridentate ligand $^-N(SiMe_2CH_2PPr^i_2)_2$ were synthesized via metathesis of the starting dichloride $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ with various alkylating reagents. The solution structures of these compounds are postulated to be highly fluxional on the basis of their variable-temperature NMR spectroscopic properties. In all cases, these compounds resisted attempts at chemical transformation. The aluminum alkyl halides could be synthesized, upon addition of $RAlCl_2$ ($R = Me, Et$) to the lithium salt $LiN(SiMe_2CH_2PPr^i_2)_2$, but attempts to abstract a chloride resulted in the formation of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]\cdot AlCl_3$, a compound retaining two four-coordinate tetrahedral aluminum centers rather than a cationic structure. It is postulated that an exchange process is responsible for the lack of an alkyl group in the final product. It appears that, even in the presence of a tridentate anionic ligand, the aluminum center will still tend to reside in a four-coordinate environment if at all possible.

Experimental Section

Procedures. Unless otherwise stated, all manipulations were performed under an atmosphere of dry, oxygen-free dinitrogen or argon by means of standard Schlenk or glovebox techniques. The glovebox used was a Vacuum Atmospheres HE-553-2 model equipped with an MO-40-2H purification system and a −40 °C freezer. ^1H and $^{31}P\{^1H\}$ NMR spectroscopy was performed on a Bruker AMX-500 instrument operating at 500.1 and 202.5 MHz, respectively. ^{27}Al NMR spectroscopy was performed on a Varian XL-300 instrument operating at 75.48 MHz. ^{27}Al MAS and ^{31}P MAS NMR

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[61] Ziegler, K. *Organometallic Chemistry*; Reinhold: New York, 1960.

spectroscopy was performed on a Bruker MSL 400 instrument. ^{1}H NMR spectra were referenced to internal $C_6D_5\mathit{H}$ (7.15 ppm) or $C_6D_5CD_2\mathit{H}$ (2.09 ppm). ^{31}P{^{1}H} NMR spectra were referenced to external *P*(OMe)$_3$ (141.0 ppm with respect to 85% H_3PO_4 at 0.0 ppm). ^{27}Al spectra were referenced to external *Al*Cl$_3$ in D_2O (0.0 ppm). Mass spectral studies were carried out on a Kratos MS 50 using an EI source. Microanalyses (C, H, N) were performed by Mr. P. Borda of this department.

Materials. LiN(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$ was prepared by a published procedure.[37] MeLi (1.4 M solution in ether) and Me$_2$AlCl (1.0 M solution in hexanes) were purchased from Aldrich and used as received. AlCl$_3$ was purchased from Aldrich and sublimed prior to use. MeAlCl$_2$ (1.0 M solution in hexanes) and EtAlCl$_2$ (1.0 M solution in hexanes) were purchased from Aldrich, crystallized, and used in the solid form. EtLi, Mg(CH$_2$Ph)$_2$·2THF and MgMe$_2$·dioxane were prepared according to published procedures.[62,63]

Hexanes, toluene, THF, and Et$_2$O were refluxed over CaH$_2$ prior to a final distillation from either sodium metal or sodium benzophenone ketyl under an Ar atmosphere. Deuterated solvents were dried by distillation from sodium benzophenone ketyl; oxygen was removed by three freeze−pump−thaw cycles.

AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (1). To a slurry of AlCl$_3$ (650 mg; 4.88 mmol) in toluene (10 mL) was added a toluene solution (10 mL) of LiN(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$ (1.78 g; 4.47 mmol). The mixture was then stirred for 12 h. The reaction mixture was then passed through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield a white waxy solid. The residue was taken up in a minimum amount of toluene (approx 4 mL). Slow evaporation of the solvent afforded large colorless needles (1.84 g; 84% yield). ^{1}H NMR (C$_6$D$_6$): δ 1.91 (d of sept, 4H, C*H*Me$_2$, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz, $^{2}J_{\mathrm{H-P}} = 1.0$ Hz), 1.21 and 1.11 (dd, 24H, CH*Me*$_2$, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz, $^{3}J_{\mathrm{H-P}} = 7.0$ Hz), 0.65 (d, 4H, C*H*$_2$P, $^{2}J_{\mathrm{H-P}} = 9.0$ Hz), 0.27 (s, 12H, Si*Me*$_2$). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −10.5 (400 Hz peak width at half-height). ^{27}Al NMR (C$_6$D$_6$): δ 65 (900 Hz peak width at half-height). MS: *m/e* 490 (M$^+$). Anal. Calcd for $C_{18}H_{44}Cl_2NP_2Si_2\cdot0.34LiCl$: C, 42.81; H, 8.78; N, 2.77. Found: C, 42.84; H, 8.34; N, 2.48. Calcd after an additional recrystallization for $C_{18}H_{44}Cl_2NP_2Si_2$: C, 44.07; H, 9.04; N, 2.86. Found: C, 44.08; H, 9.02; N, 2.66.

Al(CH$_3$)$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (2). Method 1. To a toluene solution (5 mL) of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (500 mg; 1.02 mmol) was added MeLi (1.50 mL of a 1.4 M Et$_2$O solution, diluted with 5 mL of ether; 2.08 mmol) dropwise. The reaction mixture was then stirred for 3 h, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield **2** as a clear colorless oil (398 mg; 87% yield). Purification by recrystallization was not possible either due to the compound's extreme solubility in hydrocarbon solvents or because it was low melting; as a result, characterization by either mass spectrometry or elemental analysis was not possible.

Method 2. To Me$_2$AlCl (0.60 mL of a 1.0 M hexanes solution, diluted with 10 mL of hexanes; 0.60 mmol) was added LiN(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$ (200 mg; 0.502 mmol) in 10 mL of toluene. The reaction mixture was stirred overnight, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield **2** as a clear colorless oil (174 mg; 72% yield).

Method 3. AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (250 mg; 0.51 mmol) was dissolved in 10 mL of THF. The solution was then cooled to −60 °C and Me$_2$Mg·dioxane (3.7 mL of a 0.14 M THF/Et$_2$O solution; 0.52 mmol) added. The reaction mixture was then warmed to room temperature and stirred overnight. The THF/Et$_2$O was removed under vacuum and toluene added to the solution, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield **2** as a clear colorless oil (140 mg; 58% yield). ^{1}H NMR (C$_6$D$_6$): δ 1.63 (d of sept, 4H, C*H*Me$_2$, $^{3}J_{\mathrm{H-H}} = 7.5$ Hz, $^{2}J_{\mathrm{H-P}} = 5.0$ Hz), 0.99 and 0.97 (dd, 24H, CH*MeMe'*, $^{3}J_{\mathrm{H-H}} = 7.5$ Hz, $^{3}J_{\mathrm{H-P}} = 10.0$ Hz), 0.60 (d, 4H, C*H*$_2$P, $^{2}J_{\mathrm{H-P}} = 10.0$ Hz), 0.44 (s, 12H, Si*Me*$_2$), −0.24 (t, 6H, Al*Me*$_2$, $^{3}J_{\mathrm{H-P}} = 2.4$ Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −4.9. ^{27}Al NMR (C$_6$D$_6$): δ 70 (4.3 kHz peak width at half-height).

Al(CH$_2$CH$_3$)$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (3). To a toluene solution (5 mL) of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (200 mg; 0.408 mmol) was added EtLi (30 mg; 0.83 mmol) in toluene (5 mL). The reaction mixture was stirred overnight and then filtered through a frit lined with Celite to remove LiCl, followed by solvent removal *in vacuo* to yield a clear, colorless oil (144 mg; 74% yield). Purification by recrystallization was not possible either due to the compound's extreme solubility in hydrocarbon solvents or because it was low melting; as a result, characterization by mass spectrometry or elemental analysis was not possible. ^{1}H NMR (C$_6$D$_6$): δ 1.64 (d of sept, 4H, C*H*Me$_2$, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, $^{2}J_{\mathrm{H-P}} = 3.5$ Hz), 1.42 (t, 6H, AlCH$_2$*Me*, $^{3}J_{\mathrm{H-H}} = 7.7$ Hz), 0.99 and 0.98 (dd, 24H, CH*MeMe'*, $^{3}J_{\mathrm{H-H}} = 6.9$ Hz, $^{3}J_{\mathrm{H-P}} = 6.3$ Hz), 0.60 (d, 4H, C*H*$_2$P, $^{2}J_{\mathrm{H-P}} = 7.7$ Hz), 0.43 (s, 12H, Si*Me$_2$*), 0.34 (t of q, 4H, AlC*H$_2$*Me, $^{3}J_{\mathrm{H-H}} = 8.4$ Hz, $^{3}J_{\mathrm{H-P}} = 2.5$ Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −4.2. ^{27}Al NMR (C$_6$D$_6$): δ 140 (5.8 kHz peak width at half height).

Al(CH$_2$Ph)$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (4). A solution of Mg(CH$_2$Ph)$_2$·2THF (150 mg; 0.431 mmol) in THF (10 mL) was added to a THF solution (15 mL) of AlCl$_2$[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (198 mg; 0.404 mmol) at −60 °C. The reaction mixture was warmed to room temperature and stirred overnight, after which the solvent was removed *in vacuo*. Toluene was then added to the reaction vessel and the mixture filtered through a frit lined with Celite to remove LiCl. The solvent was then reduced in volume to approx 5 mL. Slow evaporation of the solvent resulted in the formation of pale yellow needles (197 mg; 81% yield). ^{1}H NMR (C$_6$D$_6$): δ 7.28 (d, 4H, *o*-Ph, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz), 7.20 (t, 2H, *p*-Ph, $^{3}J_{\mathrm{H-H}} = 3.5$ Hz), 6.96 (t, 4H, *m*-Ph, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz), 3.50 (br s, 4H, AlC*H$_2$*C$_6$H$_5$), 1.52 (d of sept, 4H, C*H*Me$_2$, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz, $^{2}J_{\mathrm{H-P}} = 3.8$ Hz), 0.89 and 0.85 (dd, 24H, CH*MeMe'*, $^{3}J_{\mathrm{H-H}} = 7.0$ Hz, $^{3}J_{\mathrm{H-P}} = 5.6$), 0.39 (d, 4H, C*H*$_2$P, $^{2}J_{\mathrm{H-P}} = 7.8$ Hz), 0.33 (s, 12H, Si*Me$_2$*). ^{31}P{^{1}H} NMR (C$_6$D$_6$): δ −3.6. ^{27}Al NMR (C$_6$D$_6$): δ 54 (5.6 kHz peak width at half-height). MS: *m/e* 510 (M$^+$ − Bz). Anal. Calcd for $C_{32}H_{58}AlNP_2Si_2\cdot0.39MgCl_2$: C, 60.14; H, 9.15; N, 2.19. Found: C, 60.11; H, 9.56; N, 1.94.

Al(CH$_3$)Cl[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (5). To a hexanes solution (5 mL) of LiN(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$ (204 mg; 0.511 mmol) was added MeAlCl$_2$ (69 mg; 0.61 mmol) in hexanes (5 mL) dropwise. The reaction mixture was then stirred overnight, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield a clear colorless oil (144 mg; 59% yield). Purification by crystallization was hampered by contamination of small amounts of **1** and **2**. ^{1}H NMR (C$_6$D$_6$): δ 1.71 and 1.62 (d of sept, 4H, C*H*Me$_2$, $^{3}J_{\mathrm{H-H}} = 6.6$ Hz, $^{2}J_{\mathrm{H-P}} = 4.8$ Hz), 1.05, 1.02, 0.95, and 0.92 (dd, 24H, CH*MeMe'*, $^{3}J_{\mathrm{H-H}} = 6.6$ Hz, $^{3}J_{\mathrm{H-P}} = 10.0$ Hz), 0.68 and 0.61 (d, 4H, C*H*$_2$P, $^{2}J_{\mathrm{H-P}} = 12.0$ Hz), 0.48 and 0.40 (s, 12H, Si*Me*$_2$), −0.05 (t, 3H, Al*Me*$_2$, $^{3}J_{\mathrm{H-P}} = 2.8$ Hz). ^{31}P{^{1}H} NMR (C$_6$D$_6$)SPCLN δ −6.6.

Al(CH$_2$CH$_3$)Cl[N(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$] (6). To a hexanes solution (5 mL) of LiN(SiMe$_2$CH$_2$PPr$^{i}_2$)$_2$ (198 mg; 0.495 mmol) was added EtAlCl$_2$ (70 mg; 0.55 mmol) in hexanes (5 mL) dropwise. The reaction mixture was then stirred overnight, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* to yield a clear colorless oil (208 mg; 87% yield). Purification by recrystallization was not possible, due to the persistence of small amounts of **1** (<5%) in the reaction mixture. ^{1}H NMR (C$_6$D$_6$): δ 1.70 and 1.64 (d of sept, 4H, C*H*Me$_2$, $^{3}J_{\mathrm{H-H}} = 7.5$ Hz, $^{2}J_{\mathrm{H-P}} = 3.4$ Hz), 1.41 (t, 3H, AlCH$_2$*Me*, $^{3}J_{\mathrm{H-H}} = 8.7$ Hz), 1.05, 1.02, 0.96, and 0.94 (dd, 24H, CH*MeMe'*, $^{3}J_{\mathrm{H-H}} = 7.5$ Hz, $^{3}J_{\mathrm{H-P}} = 7.3$ Hz), 0.67 and 0.65 (d, 4H, C*H*$_2$P, $^{2}J_{\mathrm{H-P}} = 8.6$ Hz),

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[62] Brookhart, M.; Green, M. L. H. *J. Organomet. Chem.* **1983**, *250*, 395.

[63] Dryden, N. H.; Legzdins, P.; Trotter, J.; Yee, V. C. *Organometallics* **1991**, *10*, 2857.

0.48 and 0.40 (s, 12H, Si*Me*$_2$), 0.46 (t of q, 4H, AlC*H*$_2$Me, $^3J_{H-H}$ = 8.0 Hz, $^3J_{H-P}$ = 1.6 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ −2.0.

$AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]\cdot AlCl_3$ (7). Method 1. To a slurry of $AlCl_3$ (88 mg; 0.66 mmol) in toluene (5 mL) was added a 5 mL toluene solution of $Al(Et)Cl[N(SiMe_2CH_2PPr^i_2)_2]$ (150 mg; 0.310 mmol) dropwise. The reaction mixture turned slightly amber and was then stirred overnight, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* and the residue taken up in a minimum amount of toluene (approx 5 mL). Slow evaporation of the solvent resulted in the formation of colorless plates (157 mg; 81% yield).

Method 2. To a slurry of $AlCl_3$ (500 mg; 3.75 mmol) in toluene (10 mL) was added a 10 mL toluene solution of $LiN(SiMe_2CH_2PPr^i_2)_2$ (498 mg; 1.25 mmol) dropwise. The reaction mixture was then stirred overnight, after which time it was filtered through a frit lined with Celite to remove LiCl. The solvent was then removed *in vacuo* and the residue taken up in a minimum amount of toluene (approx 5 mL). Slow evaporation of the solvent resulted in the formation of colorless plates (615 mg; 78% yield). ^{1}H NMR (C_6D_6): δ 2.11 and 1.48 (d of sept, 4H, C*H*Me$_2$, $^3J_{H-H}$ = 7.3 Hz, $^2J_{H-P}$ = 2.0 Hz), 1.56 (br d, 2H, C*H*$_2$P, $^2J_{H-P}$ = 14.1 Hz), 1.09, 1.08, 0.86, and 0.81 (dd, 24H, CH*MeMe′*, $^3J_{H-H}$ = 7.3 Hz, $^3J_{H-P}$ = 7.5 Hz), 0.69 and 0.24 (s, 12H, Si*Me*$_2$), 0.26 (d, 2H, C*H*$_2$P, $^2J_{H-P}$ = 13.5 Hz). ^{31}P{^{1}H} NMR (C_6D_6): δ 0.0 (800 Hz peak width at half-height) and −11.8 (500 Hz peak width at half-height). MS: *m*/*e* 490 ($M^+ - AlCl_3$). Anal. Calcd for $C_{14}H_{36}Al_2Cl_5NP_2Si_2$: C, 34.65; H, 7.11; N, 2.25. Found: C, 34.32; H, 7.26; N, 2.07.

X-ray Crystallographic Analyses of $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]$ (1), $Al(CH_2C_6H_5)_2[N(SiMe_2CH_2PPr^i_2)_2]$ (4), and $AlCl_2[N(SiMe_2CH_2PPr^i_2)_2]\cdot AlCl_3$ (7). Crystallographic data appear in Table 1. The final unit-cell parameters were obtained by least squares using the setting angles for 25 reflections with 2θ = 23.2−31.0° for **1**, 9.9−18.3° for **4**, and 45.9−57.9° for **7**. The intensities of 3 standard reflections, measured every 200 reflections throughout the data collections, decayed linearly by 6.3% for **4** and by 7.4% for **7** and showed only small random fluctuations for **1**. The data were processed[64] and corrected for Lorentz and polarization effects, decay (where appropriate), and absorption (empirical, based on azimuthal scans for **4** and **7**).

The structures were solved by direct methods. The structure analysis of **4** was initiated in the centrosymmetric space group $P\bar{1}$ on the basis of the *E* statistics. This choice was confirmed by subsequent calculations. The isopropyl carbon atom C(5) in **1** was modeled as disordered over two sites, C(5A) and C(5B). The occupancy factors of the disordered carbon atoms were adjusted as the refinement progressed to give approximately equal thermal parameters. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were fixed in calculated positions (C−H = 0.99 Å for **1**, 0.98 Å for **4** and **7**; $B_H = 1.2B_{\text{bonded atom}}$). Secondary extinction corrections were applied for **1** and **7**, the final values of the extinction coefficients being $[1.9(8)] \times 10^{-7}$ and $[3.75(13)] \times 10^{-6}$, respectively. Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from ref 65. Crystals of **1** were of poor quality, resulting in relatively high residuals and large standard deviations for the derived geometric parameters. The structure analysis of **1** is, however, sufficient to establish the identity and geometry of this complex. Selected bond angles and bond lengths appear in Tables 2 and 3, respectively. Atomic parameters, anisotropic thermal parameters, bond lengths, bond angles, torsion angles, intermolecular contacts, and least-squares planes are included as Supporting Information.

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Supporting Information Available: Complete tables of bond lengths and bond angles, final atomic coordinates, hydrogen atom parameters, anisotropic thermal parameters, torsion angles, intermolecular contacts, and least-squares planes for **1**, **4**, and **7** (59 pages). Ordering information is given on any masthead page.

OM9604583

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(64) teXsan: Crystal Structure Analysis Package; Molecular Structure Corp., The Woodlands, TX, 1985 and 1992.

(65) (a) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, U.K., 1974; Vol. IV, pp 99−102 (present distributor Kluwer Academic: Boston, MA). (b) *International Tables for Crystallography*; Kluwer Academic: Boston, MA, 1992; Vol. C, pp 200−206.