

Synthesis and Characterization of Magnesium and Aluminum Bis(phosphoranyl)methanediide Complexes

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The reaction of $[CH_2(PPh_2=NSiMe_3)(PPh_2=E)]$ (E = S (1), NSiMe_3 (2)) with Mg(Buⁿ)₂ in refluxing toluene afforded the magnesium bis(phosphoranyl)methanediide complexes [{(PPh_2=NSiMe_3)-(PPh_2=E)}CMg]₂ (E = S (3), NSiMe_3 (4)), respectively. The X-ray structures and DFT calculations of **3** and **4** show that they are bimetallic methanediide complexes of magnesium containing a strong Mg-C_{methanediide} electrostatic bonding. Treatment of **4** with water in toluene gave **2** and the magnesium hydroxide complex [HC(PPh_2=NSiMe_3)_2Mg(μ -OH)]₂ (**5**), confirmed by X-ray crystallography. The reaction of **1** with AlMe₃ in refluxing toluene afforded the aluminum bis(phosphoranyl)methanediide complex [{(PPh_2=NSiMe_3)(PPh_2=S)}CAIMe]₂ (**6**). The X-ray structure of **6** shows that a methanediide carbon is bonded to one aluminum atom. DFT calculations of **6** demonstrate that Al-C_{methanediide} is highly polar with weak covalent bonding, consistent with the topological analysis of electron densities of **6**.

Introduction

The chemistry of metal bis(phosphoranyl)methanediide complexes has attracted attention over the past few decades.¹ Main-group,² transition-metal,³ and lanthanide-metal⁴ bis-(phosphoranyl)methanediide complexes were obtained by

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In this paper, we report the synthesis and characterization of magnesium and aluminum bis(phosphoranyl)methanediide complexes derived from [CH₂(PPh₂=NSiMe₃)(PPh₂=S)] or [CH₂(PPh₂=NSiMe₃)₂].

Results and Discussion

Synthesis and Characterization of Magnesium Bis(phosphoranyl)methanediide Complexes. The reaction of $[CH_2(PPh_2=NSiMe_3)(PPh_2=E)]$ (E = S (1), NSiMe_3 (2)) with Mg(Buⁿ)₂ in

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Figure 1. Molecular structure of 3 with thermal ellipsoids at the 50% probability level.



Scheme 1. Synthesis of 3 and 4

refluxing toluene afforded the magnesium bis(phosphoranyl)methanediide complexes [{(PPh₂=NSiMe₃)(PPh₂=E)}CMg]₂ (E = S (3), NSiMe₃ (4)), respectively (Scheme 1). The intermediate [H₂C=Mg] can be synthesized by the α -elimination of methane from Me₂Mg or by the disproportionation of [CH₂(MgBr)₂].⁸ The heavier congeners [(PPh₂=NSiMe₃)₂-CM]₂ (M = Ca, Ba) have been synthesized by the reaction of [CH₂(PPh₂=NSiMe₃)₂] with [{(C₆H₄-4-Bu^t)CH₂}₂Ca(THF)₄] and [(PhCH₂)₂Ba], respectively.^{2f,g}

Compounds **3** and **4** were isolated as highly moisturesensitive colorless crystalline solids which are soluble in Et₂O and toluene. They have been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **3** displays resonances for the SiMe₃ and phenyl protons. The ¹³C{¹H} NMR spectrum of **3** shows one doublet of doublets for the carbenic carbon at δ 34.35 ppm ($J_{P-C} = 32.6, 33.5$ Hz), which is shifted upfield compared with that of [(PPh₂=NSi-Me₃)₂CM]₂ (M = Ca 44.9 ppm; M = Ba, 53.9 ppm).^{2f,g} The ³¹P{¹H} NMR displays two doublets at δ 19.9 and 29.9 ppm ($^{2}J_{P-P'} = 52.0, 26.0$ Hz) due to two nonequivalent phosphorus nuclei. The ¹³C{¹H} NMR spectrum of **4** displays one triplet at 36.87 ppm ($J_{P-C} = 83.3$ Hz) for the carbenic carbon, which is comparable with that of **3**. The ³¹P{¹H} NMR spectrum of **4** displays one signal at δ 18.6 ppm.

The molecular structures of **3** and **4** are shown in Figures 1 and 2, respectively. Selected bond distances (Å) and angles



Figure 2. Molecular structure of **4** with thermal ellipsoids at the 50% probability level.

(deg) are given in Table 1. The magnesium centers in compounds 3 and 4 adopt a distorted-tetrahedral geometry, being bound to the methanediide carbon atoms and coordinated to two imino nitrogen atoms or two sulfur atoms of the ligand. With the Mg(1)C(1)Mg(2)C(2) ring as the base, compounds 3 and 4 show an "open-box"-like structure framework. The structures of 3 and 4 are similar to that of $[(PPh_2=NSiMe_3)_2CCa]_2$.^{2f} The Mg-C bonds (3, average 2.241 Å; 4, average 2.235 Å) are significantly shorter than that of the magnesium methanide complexes [HC(PPh₂= NSiMe₃)₂Mg(µ-Cl)]₂ (2.460(8) Å) and [HC(PPh₂=NSiMe₃)₂-MgI(THF)] (2.573(6) Å).⁹ The Mg–N bonds (3, average 2.035) Å; 4, average 2.046 Å) are shorter than those of $[HC(PPh_2=$ $NSiMe_{3}_{2}Mg(\mu$ -Cl)]₂ (average 2.134 Å) and [HC(PPh₂=NSi-Me_{3})₂MgI(THF)] (average 2.110 Å),⁹ but they are slightly longer than the Mg-N_{amide} σ bonds in the magnesium amide complexes $[(Et_2O)Mg(Cl){N(SiMe_3)_2}]_2$ (1.970(3) A) and $[Mg{N(SiMePh_2)_2}_2]$ (1.963(6), 1.969(6) Å).¹⁰ The Mg-S bond lengths in 3 (2.433(1), 2.429(1) Å) are within the range of terminal Mg–S σ bond lengths (2.33–2.66 Å), while they are slightly shorter than bridging Mg-S bond lengths (2.46-2.61 Å).¹¹ The P–C bonds are shortened and the P–N bonds are lengthened in compounds 3 and 4 compared with those of 1 and 2.

In order to understand the binding situation in **3** and **4**, compound **4** was investigated by means of quantum-chemical calculations. The molecule was fully optimized with the DFT-variant B3LYP¹² as implemented in the Gaussian 03 program¹³ using the 6-31G(d) basis set.¹⁴ The calculated

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Table 1. Selected Bond Distan	nces (A) and A	angles (deg) for	Compounds 3–6
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	Comp	pound 3	
$\begin{array}{l} Mg(1)-C(1) \\ Mg(1)-N(1) \\ Mg(2)-C(1) \\ Mg(2)-S(1) \\ C(1)-P(1) \\ P(1)-N(1) \\ C(2)-P(3) \\ P(3)-N(2) \end{array}$	$\begin{array}{c} 2.277(3) \\ 2.036(3) \\ 2.219(3) \\ 2.433(1) \\ 1.724(3) \\ 1.611(3) \\ 1.720(3) \\ 1.619(3) \end{array}$	$\begin{array}{c} Mg(1)-C(2)\\ Mg(1)-N(2)\\ Mg(2)-C(2)\\ Mg(2)-S(2)\\ C(1)-P(2)\\ P(2)-S(1)\\ C(2)-P(4)\\ P(4)-S(2) \end{array}$	2.257(3) 2.033(3) 2.212(3) 2.429(1) 1.706(3) 2.045(1) 1.702(3) 2.038(1)
$\begin{array}{l} C(1)-Mg(1)-C(2)\\ C(2)-Mg(1)-N(2)\\ C(1)-Mg(2)-S(1)\\ Mg(1)-C(1)-Mg(2)\\ P(1)-C(1)-P(2) \end{array}$	100.4(1) 75.7(1) 81.7(8) 77.7(1) 129.0(2)	C(1)-Mg(1)-N(1) C(1)-Mg(2)-C(2) C(2)-Mg(2)-S(2) Mg(1)-C(2)-Mg(2) P(3)-C(2)-P(4)	75.2(1) 103.6(1) 81.4(8) 78.3(9) 130.4(2)
	Comp	pound 4	
$ \begin{array}{l} Mg(1)-C(1) \\ Mg(1)-N(1) \\ Mg(2)-C(1) \\ Mg(2)-N(2) \\ C(1)-P(1) \\ P(1)-N(1) \\ C(2)-P(3) \\ P(3)-N(3) \end{array} $	2.219(2) 2.046(2) 2.250(2) 2.045(2) 1.701(2) 1.624(2) 1.707(2) 1.618(2)	Mg(1)-C(2) Mg(1)-N(3) Mg(2)-C(2) Mg(2)-N(4) C(1)-P(2) P(2)-N(2) C(2)-P(4) P(4)-N(4)	2.229(2) 2.051(2) 2.242(2) 2.043(2) 1.706(2) 1.611(2) 1.705(2) 1.614(2)
C(1)-Mg(1)-C(2) C(2)-Mg(1)-N(3) C(1)-Mg(2)-N(2) Mg(1)-C(1)-Mg(2) P(3)-C(2)-P(4)	100.6(8) 76.4(8) 76.0(8) 80.0(8) 132.3(1)	C(1)-Mg(1)-N(1) C(1)-Mg(2)-C(2) C(2)-Mg(2)-N(4) Mg(1)-C(2)-Mg(2) P(1)-C(1)-P(2)	76.2(8) 99.3(8) 75.7(8) 79.9(7) 131.5(1)
	Comp	pound 5	
$ \begin{array}{l} Mg(1) - N(1) \\ Mg(1) - O(1) \\ C(1) - P(1) \\ P(1) - N(1) \end{array} $	2.084(3) 1.961(2) 1.731(3) 1.599(3)	Mg(1)-N(2) Mg(1)-O(1A) C(1)-P(2) P(2)-N(2)	2.112(3) 1.951(2) 1.706(3) 1.598(3)
$\begin{array}{l} N(1)-Mg(1)-N(2) \\ N(2)-Mg(1)-O(1) \\ Mg(1)-N(1)-P(1) \\ P(1)-C(1)-P(2) \\ P(2)-N(2)-Mg(1) \end{array}$	101.3(1) 120.8(1) 105.6(1) 127.7(2) 103.8(1)	$ \begin{array}{l} N(1)-Mg(1)-O(1) \\ Mg(1)-O(1)-Mg(1A) \\ N(1)-P(1)-C(1) \\ C(1)-P(2)-N(2) \end{array} $	118.0(1) 98.6(1) 113.6(1) 110.8(1)
	Comp	bound 6	
Al(1)-C(2) Al(1)-N(1) P(1)-C(2) P(1)-N(1)	1.976(1) 1.915(1) 1.710(1) 1.634(1)	AI(1)-C(1)AI(1)-S(1)P(2A)-C(2)P(2)-S(1)	1.949(1) 2.316(5) 1.686(1) 2.044(5)
C(2)-Al(1)-N(1) C(2)-Al(1)-S(1) P(1)-C(2)-P(2A) C(2)-P(1)-N(1)	81.5(5) 111.3(4) 129.7(8) 98.8(6)	C(2)-Al(1)-C(1) N(1)-Al(1)-S(1) Al(1)-C(2)-P(1) P(1)-N(1)-Al(1)	125.2(6) 99.6(4) 87.7(6) 92.0(5)

structural parameters $(Mg(1)-C(1) = 2.251 \text{ Å}, Mg(1)-C(2) = 2.251 \text{ Å}, Mg(1)-N(1) = 2.074 \text{ Å}, Mg(1)-N(3) = 2.074 \text{ Å}, C(1)-P(1) = 1.732 \text{ Å}, P(1)-N(1) = 1.647 \text{ Å}; Mg(1)-C(1)-Mg(2) = 78.0^{\circ}, C(1)-Mg(1)-C(2) = 103.1^{\circ})$ are in good agreement with the crystallographic data. The calculated charges of compound 4 by natural population analysis $(NPA)^{15}$ show that the bonding between the ligand and magnesium centers is highly ionic (Table 2). The charge distributions on the ligand backbone are consistent with the resonance structure A (Figure 3), which is an extreme case. A similar calculation result is found in $[(PPh_2=NSiMe_3)_2CCa]_2$ (NPA charges: N,

-1.665; P, +1.706; C, -1.778).^{2f} Therefore, it is suggested that compounds **3** and **4** are bimetallic methanediide complexes containing a strong Mg–C electrostatic bonding.

The reaction of 4 with water in toluene for 3 h gave 2, the magnesium hydroxide complex [HC(PPh₂=NSiMe₃)₂Mg- $(\mu$ -OH)]₂ (5), and unreacted 4, confirmed by ³¹P{¹H} NMR spectroscopy (Scheme 2). When the reaction proceeded overnight, compound 2 and a trace amount of 5 were afforded. An attempt to isolate pure compound 5 by recrystallization failed. A mixture of compounds 2 and 5 was isolated as colorless crystalline solids in toluene. The ³¹P{¹H} NMR spectrum of the mixture shows one singlet for 5 at δ 24.5 ppm. The resonances for 5 in the ¹H NMR spectrum of the mixture compound 5. Other examples of magnesium hydroxide complexes,

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 Table 2. Calculated Charges of Compounds 4 and 6A by Natural

 Population Analysis (NPA)



Figure 3. Charge distributions on the ligand backbone A or B.

 $[\{Tp^{Ar,Me}\}Mg(\mu-OH)]_2$ (Tp = tris(pyrazolyl)hydroborate, Ar = 4-Bu^tC_6H_4),¹⁶ [{HC(CMeNAr)_2}Mg(\mu-OH)(THF)]_2 (Ar = 2,6-Prⁱ_2C_6H_3),¹⁷ and [Mg_2(OMes)(\mu-OMes)_2(OH)-(THF)_2]_2 \cdot 2THF (Mes = 2,4,6-Me_3C_6H_2), have been reported and structurally characterized.¹⁸

Compound **5** has been characterized by X-ray crystallography (Figure 4). Selected bond distances (Å) and angles (deg) are given in Table 1. Compound **5** is a dimeric complex with two hydroxide groups μ_2 -bonded to the magnesium centers. The ligand backbone adopts a twist-boat conformation with the Mg(1) atom displaced from the P(2)–N(2)– N(1)–P(1) least-squares plane by 1.171 Å. The Mg(1) atom is coordinated with two nitrogen atoms of the ligand and two oxygen atoms of the hydroxide. The Mg(1) atom displays a tetrahedral geometry. The Mg(1)–C(1) bond (2.889 Å) is significantly longer than that of [HC(PPh₂=NSiMe₃)₂Mg-(μ -Cl)]₂ (2.460(8) Å),⁹ showing that the negative charge is delocalized throughout the ligand. The Mg–O bond lengths (1.951(2), 1.961(2) Å) are comparable to those of [{Tp^{Ar,Me}}-Mg(μ -OH)]₂ (1.955(5), 1.951(6) Å).¹⁶

Harder and co-workers have reported that $[(PPh_2=NSiMe_3)_2-CM]_2$ (M = Ca, Ba) underwent [2 + 2] cycloaddition with



Figure 4. Molecular structure of 5 with thermal ellipsoids at the 50% probability level.

cyclohexyl isocyanate at room temperature.^{2f,g} However, there was no reaction between compound **4** with adamantyl isocyanate, azobenzene, or N,N'-di-*tert*-butylcarbodiimide in toluene at room temperature.

Synthesis and Characterization of Aluminum Bis(phosphoranyl)methanediide Complex. The reaction of 1 with a stoichiometric amount of AlMe₃ in refluxing toluene afforded the aluminum bis(phosphoranyl)methanediide complex [{(PPh₂=NSiMe₃)(PPh₂=S)}CAlMe]₂ (**6**) (Scheme 3). Cavell and his co-workers have reported that the reaction of $[CH_2(PPh_2=NSiMe_3)_2]$ with 2 equiv of AlMe₃ gave the bimetallic methanediide complex [(AlMe₂)₂{ μ_2 -C(Ph₂=NSiMe₃)₂] with 2 equiv of AlMe₃ gave the bimetallic methanediide complex [(AlMe₂)₂{ μ_2 -C(Ph₂=NSiMe₃)₂- κ^4 C,C',N,N'}] (**7**) (Scheme 4).^{2h} A similar bimetallic methanediide complex of aluminum, [(AlMe₂)₂{C(PPh₂=NBu¹)-(8-C₉H₆N)}], has been reported and structurally characterized.¹⁹ The reaction of [CH₂(PPh₂=O)₂] with excess AlMe₃ afforded [{AlMe}{C(PPh₂=O)₂}{AlMe₂}] (**8**).²⁰ To the best of our knowledge, compound **6** is the first example of a methanediide carbon bonded to one aluminum center.

Compound **6** was isolated as a highly air- and moisturesensitive colorless crystalline solid which is soluble in Et₂O and toluene. It has been characterized by NMR spectroscopy and X-ray crystallography. The ¹H NMR spectrum of **6** displays resonances for the SiMe₃ and phenyl protons. It is noteworthy that the ¹³C{¹H} NMR signal for the carbenic carbon in **6** is not observed. Similarly, there is no ¹³C{¹H} NMR resonance for the carbenic carbon in **7**.^{2h} The ³¹P{¹H} NMR spectrum of **6** displays two doublets at δ 22.8 and 25.9

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Scheme 4. Aluminum Bis(phosphoranyl)methanediide Complexes 7 and 8



ppm (${}^{2}J_{P-P'} = 13.0 \text{ Hz}$) due to two nonequivalent phosphorus nuclei. The ${}^{27}\text{Al}$ NMR spectrum shows one broad signal at δ 54.6 ppm.

The molecular structure of 6 is shown in Figure 5. Selected bond distances (Å) and angles (deg) are given in Table 1. It is symmetric and is comprised of two "{(PPh₂=NSiMe₃)- $(PPh_2 = S)$ CAlMe" moieties bonded together in a head-tohead manner. The aluminum atom Al(1) is bonded to the methanediide carbon atom C(2), one nitrogen, and one sulfur atom of each ligand. Therefore, the geometry around the aluminum atom is tetrahedral. The Al(1)-C(2) bond (1.976(1) Å) is shorter than that of 7 (2.121(3), 2.117(3) Å).^{2h} Similar to the case for 7, the Al(1)-C(2) bond in 6 is longer than the terminal Al- C_{methyl} bond (1.949(1) Å). The Al-(1)-N(1) bond (1.915(1) Å) is shorter than these of 7 (1.926(3), 1.933(3) Å),^{2h} but it is longer than the Al-N_{amide} σ bond in the aluminum amide complexes [(2,6-Prⁱ₂C₆H₃)N- $(SiMe_3)AIMe_2]_2$ (average 1.821 Å)²¹ and $[(Me_3Si)N\{CH_2CH_2-(Me_3Si)N\}_2AICI]$ (average 1.807 Å).²² The Al(1)–S(1) bond (2.316(5) Å) in 6 is longer than the Al-S σ bond in $[(Bu^{t})_{2}Al(SCH_{2}CH_{2}NEt_{2})]$ (2.272(4) Å).²³ Similar to the case for compounds 3 and 4, the P-C bonds are shortened and the P-N/P-S bonds are lengthened in 6 compared with those of 1.

In order to understand the binding situation in **6**, the simple derivative [{(PH₂=NH)(PH₂=S)}CAIH]₂ (**6A**) (Figure S1; see the Supporting Information) is applied as a model for the theoretical calculation of compound **6**. The molecule was first fully optimized by the density functional theory (DFT) B3LYP¹² functional with 6-311+G(d,p) basis set²⁴ using the Gaussian 03 program.¹³ The calculated structural parameters (Al(1)-C(2) = 2.000 Å, Al(1)-N(1) = 1.920 Å, Al(1)-S(1) = 2.348 Å, P(1)-C(2) = 1.705 Å, P(2A)-C(2) = 1.689 Å, P-(2A)-S(1A)=2.064 Å; C(2)-Al(1)-N(1) = 79.4°) are in good



Figure 5. Molecular structure of **6** with thermal ellipsoids at the 50% probability level.

agreement with the crystallographic data. Each " ${PH_2=}$ NH)(PH₂=S)}CAl" moiety in compound 6A is almost located at the same plane, which is slightly different from the X-ray structure of 6. The natural bond orbital (NBO)²⁵ analysis (Table S1; see the Supporting Information) shows that the aluminum atom adopts a sp³d hybridization. The Al(1)–C(2) σ bond is formed by sp^{2.25}d^{0.03} hybrids on the aluminum atom and sp^{1.66} hybrids on the carbon atom. The Al(1)–C(2) π bond is formed by $s^{0.06}p^{3.00}d^{1.19}$ hybrids on the aluminum atom and the p orbital on the carbon atom. The electron density of the Al-(1)–C(2) σ and π bonds are mostly contributed by the C(2) atom (85.7% electron density of the σ bond and 98.2% electron density of the π bond). Therefore, the NBO bond order by the natural resonance theory (NRT)²⁶ analysis shows that the Al(1)–C(2) bond is highly polar (16.2% covalent character, 83.8% ionic character). Moreover, the Natural Hybrid Orbitals (NHOs) on the aluminum and carbon atoms for forming the Al(1)–C(2) σ bond deviate at angles of 9.0 and 19.7° from the bond axis, respectively. The hybrids on the aluminum and carbon atoms for forming the Al(1)–C(2) π bond deviate at angles of 60.3 and 32.2° from the bond axis, respectively. These result in weak covalent bonding between the Al(1) and C(2)atoms. The Wiberg bond index (WBI)²⁷ indicates that the Al(1)-C(2) bond (WBI order 0.474) has weak covalent binding. The calculated charges of compound 6A by natural population analysis (NPA)¹⁵ also show that the bonding between the ligand and aluminum center is highly ionic (Table 2). The WBI bond orders of the P-C (1.117, 1.121), P-N (0.985), and P-S bonds (1.078) in **6A** show that the charge distributions on the ligand backbone are consistent with the resonance structure B with little or no π -electron delocalization (Figure 3). Thus, it is suggested that compound 6 is an aluminum methanediide complex. Weak metal-Cmethanediide bonding is also found

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Table 3. Theoretical Topological Features at the BCP of 6, $[H_3C-Al(CH_3)-SH]$, and $[H_2C=Al(CH_3)]^a$

bond	ρ	$ abla^2 ho$	G	Н	V
		Compound	d 6		
Al(1)-C(2)	0.47	7.08	0.59	-0.10	0.69
Al(1)-C(1)	0.55	7.58	0.67	-0.14	0.80
Al(1) - S(1)	0.33	3.09	0.30	-0.08	0.38
Al(1) - N(1)	0.44	8.86	0.64	-0.02	0.66
C(2) - P(1)	1.22	0.72	1.28	-1.23	2.51
C(2) - P(2A)	1.25	2.17	1.39	-1.24	2.64
P(1) - N(1)	1.21	12.64	1.87	-0.99	2.86
P(2) - S(2)	0.95	-5.45	0.24	-0.62	0.85
	[H	I ₃ C-Al(CH ₃	s)-SH]		
Al-C	0.55	7.66	0.67	-0.14	0.81
		$[H_2C=Al(C$	H ₃)]		
Al-C	0.55	7.37	0.66	-0.14	0.80
Al=C	0.66	11.98	1.01	-0.17	1.17
^{<i>a</i>} Units: <i>ρ</i> , e	$Å^{-3}$: $\nabla^2 \rho$, e	$Å^{-5}$: H, G,	VI. hartree	$Å^{-3}$.	

in the metal bis(thiophosphoranyl)methanediide complexes $[(PPh_2=S)_2C=Pd(PPh_3)]$,⁶ $[(PPh_2=S)_2C=Ru(PPh_3)_2]$,²⁸ and $[(PPh_2=S)_2C=ZrCp_2]$.²⁹

The topological analysis of the electron densities of compound **6** according to Bader's quantum theory of atoms in molecules (QTAIM) was performed (Table 3).³⁰ The Laplacian of electron density $\nabla^2 \rho$ and the total energy density *H* at the (3,-1) bond critical point (BCP) show that the Al(1)– C(2) bond in **6** is polar and covalent. The bond nature of the Al(1)–C(2) bond in **6** is very similar to that of Al–C bonds in [H₃C–Al(CH₃)–SH] and [H₂C=Al–CH₃].

Experimental Section

General Procedures. All manipulations were carried out under an inert atmosphere of dinitrogen gas using standard Schlenk techniques. Solvents were dried over and distilled over Na/K alloy prior to use. **1** and **2** were prepared as described in the literature.^{7,32} The ¹H, ¹³C, ³¹P, and ²⁷Al NMR spectra were recorded on a JEOL ECA 400 spectrometer. The NMR spectra were recorded in C₆D₆. The chemical shifts δ are relative to SiMe₄ for ¹H and ¹³C, 85% H₃PO₄ for ³¹P, and 0.5 M AlCl₃/ MeOH for ²⁷Al. Elemental analyses were performed by the Division of Chemistry and Biological Chemistry, Nanyang Technological University. Melting points were measured in sealed glass tubes and were not corrected.

[(**PPh₂=NSiMe₃**)(**PPh₂=S**)**CMg**]₂ (**3**). Mg(Buⁿ)₂ (1.20 mL, 1.0 M in heptane, 1.20 mmol) was added to a solution of **1** (0.50 g, 0.99 mmol) in toluene (20 mL) at room temperature. The reaction mixture was refluxed at 140 °C for 15 h. The resulting yellow solution was filtered and concentrated in vacuo to yield colorless crystals of **3**. Yield: 0.34 g (65.4%). Mp: 234.3 °C. Anal. Found: C, 63.47; H, 5.34; N, 2.28. Calcd for C₅₆H₅₈-N₂Mg₂P₄S₂Si₂: C, 63.99; H, 5.57; N, 2.67. ¹H NMR (399.5 MHz): δ -0.15 (s, 18 H, SiMe₃), 6.68-6.95 (m, 8H, Ph), 6.97-7.14 (m, 13H, Ph), 7.18-7.43 (m, 5H, Ph), 7.57-7.74 (m, 8H, Ph), 7.92-7.98 (m, 2H, Ph), 8.13-8.19 ppm (m, 4H, Ph). ¹³C{¹H} NMR (100.4 MHz): δ 3.52 (SiMe₃), 34.35 (dd, PCP, $J_{P-C} = 32.6, 33.5$ Hz), 129.68–130.70 (m), 131.92–133.12 (m), 137.12, 138.24, 138.68, 138.80, 139.41–140.13 (m), 140.60, 141.37 ppm (Ph). ³¹P{¹H} NMR (161.7 MHz): δ 19.9 (d, ² $J_{P-P'} = 52.0$ Hz), 29.9 ppm (d, ² $J_{P-P'} = 26.0$ Hz).

[(**PPh₂=NSiMe₃)₂CMg]₂ (4).** Mg(Buⁿ)₂ (2.20 mL, 1.0 M in heptane, 2.20 mmol) was added to a solution of **2** (1.18 g, 2.11 mmol) in toluene (20 mL) at room temperature. The reaction mixture was refluxed at 140 °C for 15 h. The resulting yellow solution was filtered and concentrated in vacuo to yield colorless crystals of **4**. Yield: 0.55 g (44.9%). Mp: 329 °C dec. Anal. Found: C, 63.83; H, 6.31; N, 4.55. Calcd for C₆₂H₇₆Mg₂N₄P₄Si₄: C, 64.12; H, 6.60; N, 4.83. ¹H NMR (399.5 MHz): δ 0.30 (s, 36 H, SiMe₃), 6.92–6.96 (m, 8H, Ph), 7.01–7.04 (m, 4H, Ph), 7.12–7.26 (m, 12H, Ph), 7.51–7.56 (m, 8H, Ph), 7.66–7.71 ppm (m, 8H, Ph). ¹³C{¹H} NMR (100.4 MHz): δ 4.09 (SiMe₃), 36.87 (t, PCP, $J_{P-C} = 83.3$ Hz), 129.68, 129.91, 130.22, 131.88, 131.93, 132.71, 132.76, 132.81, 138.41, 138.56, 139.37, 139.50, 140.33, 140.46, 141.37, 141.50 ppm (Ph). ³¹P{¹H} NMR (161.7 MHz): δ 18.6 ppm.

[HC(PPh₂=NSiMe₃)₂Mg(μ -OH)]₂ (5). H₂O (24.0 mL, 0.03% weight in toluene, 0.40 mmol) was added to 4 (0.23 g, 0.20 mmol) at room temperature and the mixture stirred overnight. The insoluble precipitate was filtered off, and the colorless filtrate was concentrated to yield 2 and a trace amount of colorless crystals of 5. ³¹P{¹H} NMR (161.7 MHz) for 5: δ 24.5 ppm. The resonances for 5 in the ¹H and ¹³C NMR spectra of the mixture cannot be identified, due to trace amounts of 5.

[(**PPh₂=NSiMe₃**)(**PPh₂=S**)**CAIMe**]₂ (6). AlMe₃ (0.72 mL, 2.0 M in toluene, 1.44 mmol) was added to a solution of **1** (0.53 g, 1.05 mmol) in toluene (20 mL) at room temperature. The reaction mixture was refluxed at 140 °C for 15 h. Volatiles were removed under reduced pressure, and the residue was extracted with Et₂O. After filtration and concentration of the filtrate, **6** was obtained as colorless crystals. Yield: 0.12 g (21.0%). Mp: 266 °C. Anal. Found: C, 63.82; H, 5.67; N, 2.35. Calcd for C₅₈H₆₄N₂Al₂P₄S₂Si₂: C, 64.07; H, 5.94; N, 2.58. ¹H NMR (395.9 MHz): δ 0.057 (s, 18H, SiMe₃), 0.17 (s, 6H, AlMe), 6.65–6.70 (m, 8H, Ph), 6.78–6.79 (m, 4H, Ph), 7.15–7.17 (m, 8H, Ph), 7.40–7.43 (m, 12H, Ph), 7.88–7.94 (m, 4H, Ph), 8.19–8.22 ppm (m, 4H, Ph). ¹³C{¹H} NMR (100.5 MHz): 2.87 (SiMe₃), 2.90 (AlMe), 129.39, 130.22, 130.74, 130.80, 131.19, 131.29, 131.62, 131.73, 132.83, 133.54, 133.66, 137.24, 137.47, 138.09, 138.34, 138.71, 139.54 ppm (Ph). ³¹P{¹H} NMR (160.3 MHz): δ 22.8, 25.9 ppm (d, $^{2}J_{P-P'} = 13.0$ Hz). ²⁷Al{¹H} NMR (104.1 MHz) δ 54.6 ppm.

X-ray Data Collection and Structural Refinement. Intensity data for compounds 3-6 were collected using a Bruker APEX II diffractometer. The crystals of 3-5 were measured at 173(2) K, and that of 6 was measured at 103(2) K. The structures were solved by direct phase determination (SHELXS-97) and refined for all data by full-matrix least-squares methods on $F^{2,31}$ All non-hydrogen atoms were subjected to anisotropic refinement. The hydrogen atoms were generated geometrically and allowed to ride in their respective parent atoms; they were assigned appropriate isotopic thermal parameters and included in the structure-factor calculations. A summary of X-ray data is given in Table S2 (see the Supporting Information).

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Supporting Information Available: Figures and tables giving selected calculation results of 4 and 6A and CIF files giving X-ray data for 3–6. This material is available free of charge via the Internet at http://pubs.acs.org.

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