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Novel Dialkyl Aluminum Bis(iminophosphorano) Methanide and Methanediide Complexes

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Summary: Reaction of bis{trimethylsilyliminodi(phenyl)phosphorano}methane, $H_2C(Ph_2P{=}NSiMe_3)_2$ *(**1**) with 1 equiv of trimethylaluminum in toluene gave a four-coordinated alkyl aluminum complex of the formula* $[AlMe_2\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^2N,N'\}]$ *(**2**) via the elimination of methane. The crystal structure confirms the monomeric nature of the complex and the bidentate coordination of the bisiminophosphoranomethanide ligand to aluminum. Reaction of **1** with 2 equiv of trimethylaluminum yielded the novel bimetallic complex* $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}]$ *(**3**), in which the methylene backbone carbon has been doubly deprotonated.*

Intense recent interest in nitrogen donor ligands as alternatives to cyclopentadienyl groups on metals[1−8] has yielded a new "organometallic" chemistry with impact on homogeneous catalysis. Many chelate structures have been used to stabilize low-valent metal species or unusual coordination geometries.[4,5,9] In the specific case of aluminum, recent interest has focused on the development of nitrogen donor complexes.[10−18] Aluminum alkyls are employed as activators of group 4 complexes in Zeigler−Natta and related systems and are known to act themselves as ethylene oligomerization and polymerization catalysts. In particular the potential of cationic aluminum alkyls as stand-alone catalysts is just emerging.[19−22] Our study[23−26] of bis(iminophosphorano)methane chemistry has provided novel group 4 metal carbene complexes derived either directly or via the initial process of forming doubly lithiated ligand.[26] We have also described alkyl zinc complexes[25] containing the singly deprotonated ligand. Here we report novel aluminum derivatives. In the case of aluminum we have observed both a single and the rare double deprotonation of the methylene backbone of the ligand to a monometallic alkyl methanide and to a bimetallic bridging methanediide. These species are also the first examples of group 13 bis(iminophosphorano)methane complexes of aluminum. There is extensive chemistry of this ligand system with the group 9 and 10 metals.[27,28]

The monomeric aluminum bis(iminophosphorano)methanide complex $[AlMe_2\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^2N,N'\}]$ (**2**) resulted when 1 equiv of trimethylaluminum was added to a toluene solution of $H_2C(Ph_2P{=}NSiMe_3)_2$ (**1**)[29] (Scheme 1) under an argon atmosphere at room temperature.[30] The reaction proceeds rapidly via elimination of methane. Using 2 equiv of trimethylaluminum under reflux conditions gave the novel bimetallic bridged carbene complex $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C,C',N,N'\}]$ (**3**)[31] (Scheme 1). Complex **2** has been identified (^{31}P NMR evidence) as an intermediate that is formed at room temperature during the preparation of **3**, and the transformation is induced by facile C−H thermolytic bond cleavage of the second proton on the methylene backbone. In both cases, the ^{31}P NMR of the final reaction mixtures showed that quantitative conversion of the ligand **1** to either **2** or **3** had occurred as determined by the stoichiometry and conditions. Also,

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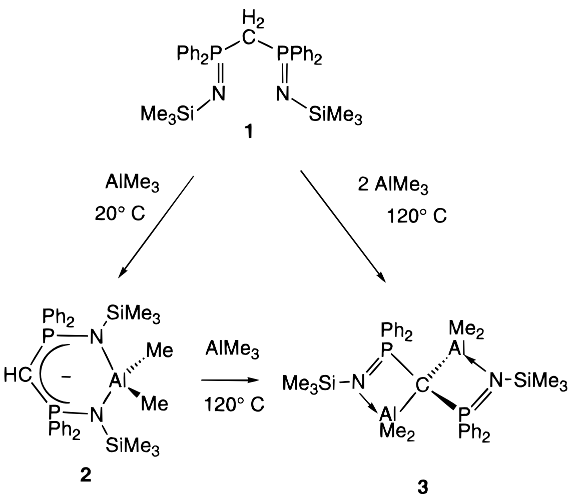
Scheme 1



reaction of **2** with 1 equiv of $AlMe_3$ in toluene under reflux conditions gave **3** (Scheme 1). The complexes were isolated as colorless air-sensitive crystalline solids in high yield. A related double deprotonation of the methylene backbone of analogous ligands was found in the aluminum complexes of $H_2C(Ph_2P{=}X)_2$ (X = O, S). The products in those cases, $[Al(R)][C\{P(O)(C_6H_5)_2\}_2]_2[AlR_2]_2$ (R = Me,[32] Et[33]) and $[Al(C_4H_9)]_2[(C_6H_5)_2P(S)CP(C_6H_5)_2(S)_2][Al(C_4H_9)_2]_2$,[34] were bridging tri- and tetrametallic complexes, respectively. Our reactions are unique in the sense that stepwise synthesis and isolation of well-defined mono- and bimetallic methanide and methanediide complexes have been achieved perhaps because the bulky substituent on the imine nitrogen centers provides a better control and protection of the reaction site. It is also noteworthy that only an adduct was obtained from the reaction of $Ph_2PCH_2PPh_2$ (dppm) with $AlMe_3$[35] in contrast to the double deprotonation effected by all doubly oxidized systems $R_2P(X)CH_2R_2P(X)$ (X = NR, O, S) presumably because these protons are more acidic when the phosphorus centers are oxidized.

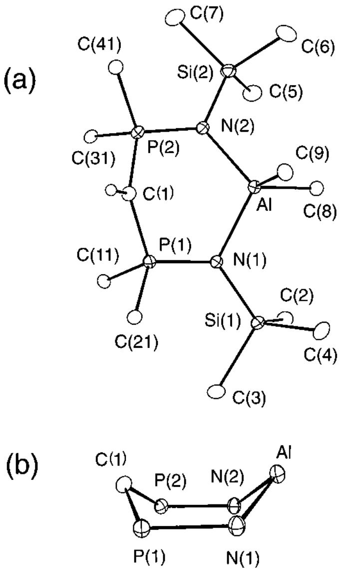


Figure 1. (a) ORTEP[38] view of $[AlMe_2\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^2N,N'\}]$ (**2**) showing the atom-labeling scheme. All hydrogen atoms except that on the methine carbon and all but *ipso* carbon atoms of the phenyl groups have been removed for clarity. Remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances [Å] and angles [deg]: Al−N(1) = 1.954(2), Al−N(2) = 1.943(2), Al−C(8) = 1.984(3), Al−C(9) = 1.986(3), N(1)−P(1) = 1.628(2), P(1)−C(1) = 1.716(2), P(2)−C(1) = 1.709(2), P(2)−N(2) = 1.625(2), N(1)−Al−N(2) = 108.96(8), C(8)−Al−C(9) = 111.5(1), C(9)−Al−N(2) = 112.2(1), P(1)−C(1)−P(2) = 121.8(1), N(1)−P(1)−C(1) = 111.8(1). (b) View of the core of **2** showing the boat conformation of the six-membered AlN_2P_2C ring.

The ^{31}P NMR spectra of **2** and **3** consisted of one sharp singlet at 29.5 and 27.6 ppm, respectively, both substantially shifted downfield (ca. 33 ppm) relative to the free ligand. The $^{13}C\{^1H\}$ APT spectrum gave a negative triplet signal at 25.2 ppm ($^1J_{PC} \approx 113.9$ Hz) for the methanide unit in complex **2** due to coupling with two equivalent phosphorus nuclei. Proton NMR of **3** showed no signal for the backbone methylene unit, indicating that the ligand has been doubly deprotonated. The quaternary P−C−P carbon atom was silent in the $^{13}C\{^1H\}$ NMR despite trials with long acquisition periods, possibly because the signal is broad due to coupling with two aluminum nuclei and, in addition, there are no nearby protons to facilitate magnetization transfer. Both the ^1H and ^{13}C NMR of **3** show two distinct methyl and phenyl resonances because the spirocyclic nature of the complex (vide infra) creates magnetic inequivalence. Only a single methyl resonance was observed in **2** possibly because of a dynamic conformational interchange process which averages the environments.

The molecular structures of both $[AlMe_2\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^2N,N'\}]$ (**2**)[36] and $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}$

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(30) Preparation of $[AlMe_2\{HC(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^2N,N'\}]$ (**2**). All experimental manipulations were performed under rigorously anaerobic conditions using , Schlenk techniques for refluxing steps and an argon-filled glovebox for manipulations. To a toluene (5 mL) solution of $H_2C(Ph_2P{=}NSiMe_3)_2$ (0.20 g, 0.36 mmol) was added $AlMe_3$ (2.0 M solution in toluene, 0.18 mL, 0.36 mmol) with stirring at room temperature. Immediately evolution of gas was observed. The reaction mixture was stirred at room temperature for a day. Colorless crystals were obtained upon concentration to half of the original volume and leaving the flask at room temperature for 3 days. The product was filtered and dried under vacuum. Yield: 0.15 g, 68.2%. ^1H NMR (C_6D_6): δ 7.70 (m, phenyl), 6.95 (m, phenyl), 1.90 (s, P−CH−P), 0.18 (s, CH_3Si methyl), −0.49 (br, s, CH_3−Al). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 135.6 (m, *ipso* phenyl), 132.2 (m, *ortho* phenyl), 130.6 (s, *para* phenyl), 128.1 (m, *meta* phenyl), 25.2 (t, P−CH−P, $^1J_{PC} = 113.9$ Hz), 4.6 (s, CH_3Si), 2.4 (br, s, CH_3−Al). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 29.5 (s). Anal. Calcd for $C_{33}H_{45}AlN_2P_2Si_2$: C, 64.47; H, 7.38; N, 4.56. Found: C, 64.23; H, 7.69; N, 4.49.

(31) Preparation of $[(AlMe_2)_2\{\mu_2\text{-}C(Ph_2P{=}NSiMe_3)_2\text{-}\kappa^4C, C',N,N'\}]$, **3**: Anaerobic techniques were used. To a toluene (5 mL) solution of $H_2C(Ph_2P{=}NSiMe_3)_2$ (0.20 g, 0.36 mmol) was added $AlMe_3$ (2.0 M solution in toluene, 0.36 mL, 0.72 mmol) with stirring at room temperature. Immediately evolution of gas was observed. The reaction mixture was stirred at room temperature for a day and refluxed for 3 h. Colorless crystals were obtained upon concentration to half of the original volume and leaving the flask at room temperature for 2 days. The product was filtered and dried under vacuum. Yield: 0.16 g, 66.6%. ^1H NMR (C_6D_6): δ 7.70 (m, phenyl), 7.35 (m, phenyl), 7.10 (m, toluene), 6.90 (m, toluene), 6.65 (m, phenyl), 2.10 (s, toluene), 0.27 (s, CH_3−Al), 0.11 (s, CH_3Si), −0.75 (s, CH_3−Al). $^{13}C\{^1H\}$ NMR (C_6D_6): δ 137.0 (m, *ipso* phenyl), 132.7 (m, *ortho* phenyl), 131.4 (s, *ortho* phenyl), 131.0 (s, *meta* phenyl), 129.9 (m, *ipso* phenyl), 129.3 (s, *para* phenyl), 128.8 (s, *meta* phenyl), 125.6 (s, *para* phenyl), 2.3 (s, CH_3Si), −2.5 (br, s, CH_3−Al), −4.1 (br, s, CH_3−Al). $^{31}P\{^1H\}$ NMR (C_6D_6): δ 27.6 (s). Anal. Calcd for desolvated crystals of $C_{35}H_{50}Al_2N_2P_2Si_2$: C, 62.66; H, 7.51; N, 4.18. Found: C, 62.98; H, 7.72; N, 3.99.

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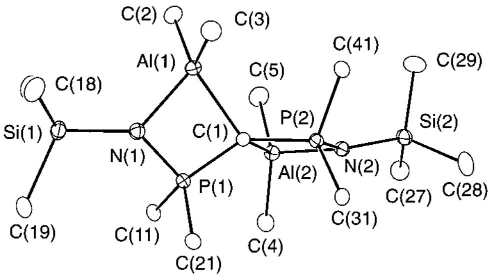

Figure 2. ORTEP[38] view of [(AlMe$_2$)$_2${μ_2-C(Ph$_2$P=NSiMe$_3$)$_2$-κ^4C,C',N,N'}] (**3**) showing the atom-labeling scheme. All hydrogen atoms and all but *ipso* carbon atoms of the phenyl groups have been removed for clarity. Remaining atoms are represented by Gaussian ellipsoids at the 20% probability level. Selected interatomic distances [Å] and angles [deg]: Al(1)−N(1) = 1.926(3), Al(2)−N(2) = 1.933(3), Al(1)−C(1) = 2.121(3), Al(2)−C(1) = 2.117(3), Al(1)−C(2) = 1.959(4), N(1)−P(1) = 1.612(3), P(1)−C(1) = 1.751(3), P(2)−C(1) = 1.746(3), P(2)−N(2) = 1.615(3), N(1)−Al(1)−C(1) = 79.8(1), N(2)−Al(2)−C(1) = 80.2(1), C(2)−Al(1)−C(3) = 115.3(2), N(1)−P(1)−C(1) = 101.2(1).

NSiMe$_3$)$_2$-κ^4C,C',N,N'}] (**3**)[37] are illustrated in Figures 1 and 2.[38] Complex **2** (Figure 1) is a four-coordinated monomeric aluminum complex in which the two phosphinimine units of the ligand chelate to a dimethyl aluminum center with a distorted tetrahedral geometry. The core structure consists of a six-membered metallacyclic ring with Al, N(1), P(1), C(1), P(2), and N(2) atoms adopting a distorted boat conformation (Figure 1b). Complex **3** has a more unusual spirocyclic dimetallic structure (Figure 2); the framework consists of two nearly planar four-membered rings{C(1), Al(1), N(1), P(1) and C(1), Al(2), N(2), P(2)} fused at the corner; thus a bridging carbene unit connecting two dimethyl aluminum centers is formed. The dihedral angle between these two planes is 75.28(5)°. Intramolecular coordination of the nitrogen centers of the iminophosphorane units subtended from the bridging carbene center in a μ_2-κ^4 fashion completes the structure. Each aluminum has a distorted tetrahedral geometry, and the carbene carbon atom has a "squashed" tetrahedral environment {Al(1)−C(1)−Al(2) = 129.8(2), Al(1)−C(1)−P(1) = 84.2(1), P(1)−C(1)−P(2) = 133.1(2), Al(2)−C(1)−P(2) = 84.0(1)°}. The Al−C bond length in the bridging carbene center (Al(1)−C(1) = 2.121(3), A(2)−C(1) = 2.117(3) Å) is slightly longer than the terminal Al−C(methyl) distances (average 1.985(3) Å in **2** and average 1.963(4) Å in **3**) in **2** and **3**; however all these distances fall within the usual range observed for the aluminum−carbon distances. The Al−N bond distances are slightly longer than the distances observed for aluminum amide complexes.[22]

The bond distances within the ligand framework in both the complexes **2** and **3** are considerably affected in comparison with the related values in free bis(iminophosphorano) ligands.[27,39] The P=N bond distances are elongated and the endocyclic P−C bond distances are shorter; however, the exocyclic P−C distances are unaffected. The P−C−P bond angles (121.8(1)° in **2**, 133.1(2)° in **3**) are considerably expanded compared to the corresponding values in CH$_3$CH{Ph$_2$P=N(Tol)}$_2$, 112.4(2°),[27] as well as in H$_2$C{Cy$_2$P=NSiMe$_3$}$_2$, 117.4(1)°.[39] These factors suggest that there is a delocalization of π electron density within the metallocyclic rings.

Thus two novel dialkyl aluminum complexes, **2** and **3**, with bisiminophosphoranomethanide ligand systems have been prepared in which the ligand has been either singly or doubly deprotonated. Reactivity studies of these new species are being pursued.

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Supporting Information Available: This material is available free of charge via the Internet at http://pubs.acs.org.

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(36) Crystal Data for [AlMe$_2${HC(Ph$_2$P=NSiMe$_3$)$_2$-κ^2N,N'], **2**: Monoclinic, $P2_1/c$ (No. 14), a = 12.1522(6) Å, b = 20.9210(11) Å, c = 14.8491(8) Å, β = 112.4820(10)°, V (Å^3) = 3488.3(3), Z = 4. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 0.0440 (wR2 = 0.1081) for 4523 reflections with $F_o^2 \geq \sigma(F_o^2)$.

(37) Crystal data for [(AlMe$_2$)$_2${μ_2-C(Ph$_2$P=NSiMe$_3$)$_2$-κ^4C,C',N,N'}]·toluene, **3**: Triclinic, $P\bar{1}$ (No. 2), a = 11.7414(8) Å, b = 14.1321(9) Å, c = 14.2319(10) Å, α = 83.4900(10)°, β = 72.5960(10)°, γ = 79.471(2)°, V (Å^3) = 2211.1(3), Z = 2. The structure was solved by direct methods and refined by full-matrix least-squares procedures: R1 = 0.0607 (wR2 = 0.1879) for 5702 reflections with $F_o^2 \geq 2\sigma(F_o^2)$.

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