

K[Al₄(PPh₂)₇PPh]: An Al^{II} Phosphanide / Phosphinidene Intermediate on the Path to AlP Formation

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Dedicated to Professor Werner Uhl on the Occasion of His 60th Birthday

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Abstract. The reaction of metastable AlCl·(Et₂O)_n with potassium diphenylphosphanide results in the formation of the aluminum(II) phosphanide / phosphinidene K[Al₄(PPh₂)₇PPh] compound, which is the

first reported aluminum(II) phosphinidene complex. The Al^{II} structure results from ligand decomposition and represents the first step in the conversion of AlPPh₂ to AlP and biphenyl.

Introduction

Low oxidation state aluminum compounds have drawn considerable interest due to their unprecedented structural chemistry,^[1] unusual chemical reactivity^[2–4] and their propensity for metal-metal bond formation.^[5–7] Solutions of Al^I halides have proven to be excellent precursors to low oxidation state Al^I complexes,^[7] such as Al₄Cp*₄,^[8] but can also undergo redox (disproportionation) reactions to give new classes of clusters and compounds containing Al oxidation states from 0.27 to 3.0.^[11,7] The most famous of these are the Al metalloid clusters that can be isolated during the disproportionation process: 3Al^{I+} → Al³⁺ + 2 Al⁰. These clusters, such as [Al₇₇{N(SiMe₃)₂]₂₀]²⁻, can be trapped due to the presence of various kinetic barriers on the way to forming aluminum metal and represent the transition from large metallic clusters to small metallic nanoparticles. Recently, we have shown that a completely different reaction pathway is viable with some ligand systems in which ligand redox chemistry can lead to salt-like aluminum binaries. In particular, dialkyl phosphanides

(R₂P⁻ where R = *t*Bu), react with Al^I halides to give Al₂(PR₂)₄, Al₄(PR₂)₆, Al₈Br₈(PR₂)₆ and the intriguing Al₃P(PR₂)₄Cl₂.^[9–11] The latter complex contains a naked P³⁻ ion that presumably results from a successive ligand-based decomposition process leading to the Al₃P moiety. DFT studies showed how the ligand redox vs. disproportionation pathways followed different routes from the Al^I precursors to give markedly different products.^[10] The propensity of the phosphanide ligands to bridge between two aluminum atoms seems to preclude the formation of metalloid clusters and propels the system into the ligand based redox pathway. We describe here a fortuitous isolation of an intermediate along this pathway that provides additional evidence for the ligand-based decomposition process. The intermediate complex, K[Al₄(PPh₂)₇PPh], is formed during the reaction of AlCl·(Et₂O)_n with potassium diphenylphosphanide and contains Al^{II} ions and a PhP²⁻ phosphinidene ligand in addition to the expected phosphanide ligands. The isolation and characterization of this complex represents the first step in the formation of AlP from phosphanide precursors.

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Results and Discussion

The title complex was prepared from the reaction of a cold (–78 °C) solution of AlCl·(Et₂O)_n with a solution of potassium diphenylphosphanide in diethyl ether. This reaction mixture was warmed to room temperature overnight, evaporated to dryness and extracted into toluene. Storage of the reaction mixture at –25 °C for six months resulted in the formation of a few yellow crystals of K[Al₄(PPh₂)₇PPh]·HPPH₂·4 C₇H₈ (**1**) on the vessel wall. For **1**, the inclusion of the non-coordinated phosphane solvate (HPPH₂) in the crystal lattice suggests incomplete deprotonation of HPPH₂ in the production of the KPPH₂ precursor used in the reaction.

The ESI-MS studies of the reaction mixtures showed the presence of the closely related [Al₄(PPh₂)₆(PPh)₂KCl]⁻, [Al₅(PPh₂)₇HKCl]⁻ and [Al₅(PPh₂)₆HKCl]⁻ clusters in solution (Figure S3) but **1** was not observed; presumably due to its insolubility.

The solid-state X-ray crystal structure of **1** contains polymeric chains of [Al₄(PPh₂)₇PPh]⁻ units (Figure 1 and Figure S1). Each [Al₄(PPh₂)₇PPh]⁻ unit contains two Al–Al pairs, three bridging diphenylphosphanide ligands, four terminal diphenylphosphanide ligands, and one terminal phenylphosphinidene ligand. The idealized (AIP)₄P₄ core comprises four fused cyclopentane-like rings with a bis-noradamantane structure^[12] and has virtual D_{2d} point symmetry (Figure 1). The ring structure is reminiscent of the P₄Al₆ adamantane-like core in P₄(AlCp*)₆ and the Ga₄P₁₀ core in Ga₁₆(PrBu)₂₁₀ that contains an inverse P₄O₁₀ structure.^[13,14] However, when the asymmetry of the lone phosphinidene ligand is considered, the (AIP)₄P₄ core has virtual C₂ symmetry with a C₂ axis of rotation passing through P1 and P5. The aluminum atoms are formally +2 and each achieves an 8-electron configuration through Al–P coordinate bonds and Al–Al interactions. The terminal phosphorus atoms are all distinctly pyramidalized as evidenced by the 106 ± 5 °C–P–C bond angles. Trigonal pyramidal geometries for the terminal phosphanide ligands are indicative of non-interacting lone pairs on phosphorus, consistent with aluminum atoms that are electronically saturated from the σ-bonding framework.

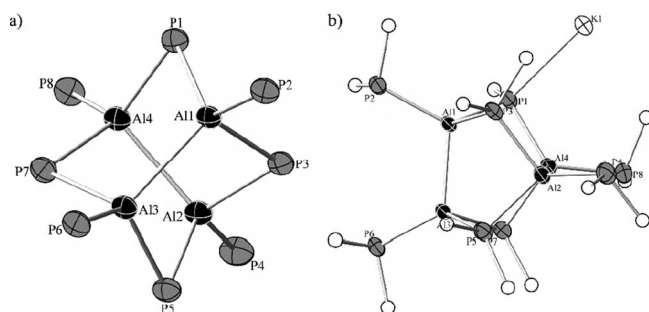


Figure 1. X-ray crystal structure of **1** a) without and b) with the potassium atom. Thermal ellipsoids drawn at the 50% probability level, hydrogen and carbon atoms omitted for clarity. The phosphinidene ligand contains the phosphorus atom P1. Selected bond lengths /Å and angles /°: Al1–Al3 2.643(2), Al2–Al4 2.655(2), Al1–P1 2.380(1), Al1–P2 2.428(2), Al1–P3 2.450(2), Al2–P3: 2.429(2), Al2–P4 2.402(2), Al2–P5 2.457(1), Al3–P5 2.436(1), Al3–P6 2.392(1), Al3–P7 2.424(1), Al4–P7 2.436(1), Al4–P8 2.395(2), Al4–P1 2.365(1), P1–K1 3.182(1), Al1–P1–Al4 91.12(5), Al2–P5–Al3 93.62(5).

The Al–Al bond lengths in **1**, 2.642(2) and 2.655(21) Å, are similar to those of other aluminum(II) compounds containing Al–Al bonds. For example, the Al–Al bond lengths in [(IPr)(H)₂Al]₂ (IPr = C{(Dip)NCH₂}, Dip = 2,6-diisopropylphenyl) and Al₂Br₄·2 anisole are 2.638(1) and 2.527(1) Å, respectively.^[6,15] The four non-bonding Al···Al separations in **1** are in the range 3.385(1) to 3.581(1) Å.

The Al–P bond lengths involving the terminal and bridging phosphanide ligands are in the ranges 2.425(8) to 2.459(8) [2.445(3) Å, av.], and 2.392(5) to 2.421(3) [2.412(4) Å, av.],

respectively. The distances are quite similar to those in Al^{III} phosphanide complexes^[16] and other low oxidation state Al–P complexes (i.e. Al–P bonds ranging from 2.308 to 2.422 Å in [P₄(AlCp*)₆]).^[13] The phosphorus atom of the phosphinidene ligand (P1) is tetracoordinate, with one P–C bond (1.767(1) Å), one P–K bond (3.182(1) Å), and two P–Al bonds (2.379(1) and 2.365(1) Å). The latter are slightly shorter than the average P–Al bonds of the phosphanide ligands in **1**, and longer than the Al–P bond lengths in the Al^{III} phosphinidene reported by Power (average Al–P 2.328(3) Å).^[17] The small distortion in phosphinidene Al–P bond lengths imparts a more acute Al1–P1–Al4 bond angle of 91.12(5)° relative to the others (Al–P–Al = 94.3°, av.) and results in a non-bonding Al1–Al4 distance of 3.387(2) Å. This separation is shorter than the others (3.577(3) Å, av.) and slightly distorts the Al₄P₈ core from the idealized bis-noradamantane structure.

The phosphinidene ligand forms a coordinate bond to the potassium ion, which is in turn intramolecularly bound to two phenyl rings through η⁶-interactions from two diphenylphosphanide moieties within the [Al₄(PPh₂)₇PPh]⁻ unit (Figure 2). The phenyl ring of the P6 diphenylphosphanide ligand in a neighboring [Al₄(PPh₂)₇PPh]⁻ unit is also coordinated to the K⁺ ion in an η⁶-fashion. The potassium ion has nineteen total bonding contacts in a 1+6+6+6 coordination pattern, with K–C bonding distances in the range of 3.018(4) to 3.424(4) Å (Figure 2). The chain can be viewed as a series of [Al₄(PPh₂)₇PPh]⁻ units held together by a K–P coordinate bond and cation–π interactions between the potassium ion and phenyl rings (Figure S2a). Similar alkali metal–π interactions are known in organometallic polymers prepared in arene solvents^[18] as well as sodium-containing ‘dialumyne’ species.^[5] The [Al₄(PPh₂)₇PPh]⁻ units are chiral and form homochiral chains that propagate along the 2₁ screw axis of the crystal lattice. Chains of alternating chirality pack in layers separated by the layers of solvate molecules (Figure S2b).

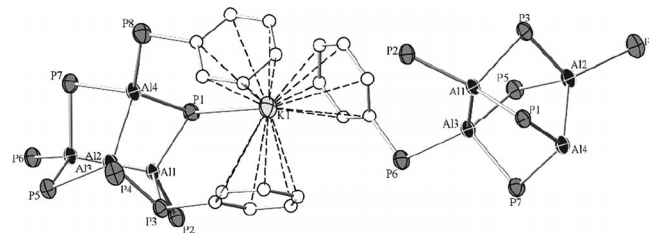


Figure 2. Drawing of the potassium ion coordination sphere in **1**. Carbon atoms (white) are isotropic whereas the K (light gray) and P (gray) atom thermal ellipsoids are drawn at the 50% probability level. Select atoms omitted for clarity. Average K–C(centroid) distance 2.925 Å.

Conclusions

The Al/P core of complex **1** is closely related to the previously-reported aluminum phosphanide clusters Al₂(PR₂)₄ (2) and Al₄(PR₂)₆ (3) where R = *t*Bu.^[9,11] Although the alkyl substituent of the phosphanides differs, the Al/P frameworks in all three compounds have notably similarities in Al–P coordination and metric parameters. These structures are shown in the SI.

The disproportionation reactions involving AIX precursors to give low oxidation state metalloids and other oxidized aluminum cluster compounds require ligand scrambling and multiple electron transfers. While the mechanistic details of formation are always difficult to discern, the products give clues about general reaction pathways. The formation of the phosphinidene ligand presumably results from a redox reaction of a coordinated Al–PPh₂, which is the first step on the pathway to AIP formation that can simplistically be viewed as: Al(PPh₂)₃ → AIP + Ph₂. The prior isolation of the Al₃P complex PAI₃(PR₂)₄Cl₂ (R = *t*-Bu) represents a subsequent step in oxidative decomposition of aluminum phosphanide complexes to give the thermodynamic end product AIP.^[10] In contrast, disproportionation of a metastable “GaPR₂” solution (formed during the reaction of GaX with LiPR₂) is favored, resulting in metalloid clusters such as Ga₁₆(GaPR₂)₁₀^[14] and Ga₅₁(PR₂)₁₄Br₆.^[19] These clusters contain cores of “naked” gallium atoms, such as a Ga₄ unit in the Ga₁₆ cluster and a cuboctahedral Ga₁₃ unit in the Ga₅₁ cluster, which are surrounded by bridging and terminal GaPR₂ moieties.^[14,19] These clusters have been discussed to be precursors for core-shell nanoparticles containing a metallic gallium core and a semi-conducting GaP shell.^[19] Therefore, the formation of **1** in small quantities may be a hint that the main product may be an intermediate metalloid Al_n(AlPR₂)_m (*n* > *m*) cluster on the way to an AIP particle, which is similar to the GaP shells described above.

Experimental Section

General Considerations: All reactions are performed under a dinitrogen atmosphere in a glovebox or under argon using standard Schlenk techniques. Toluene and diethyl ether were purified by distillation from sodium benzophenone ketyl under a dinitrogen atmosphere. All purified solvents were stored in modified Schlenk vessels over 3 Å molecular sieves under a dinitrogen atmosphere. Diphenylphosphane was purchased as a 10% (w/w) solution in hexane from Strem and the hexane was removed in vacuo immediately prior to use.

AlCl·(Et₂O)_n: Aluminum metal (0.950 g, 35.2 mmol) was reacted with gaseous HCl (36.5 mmol) over 3 h at approx. 1200 K in a modified Schnöckel-type metal halide co-condensation reactor.^[20,21] The resultant gas-phase AlCl was co-condensed with a mixture of toluene:diethyl ether (4:1 v/v) at approx. 77 K. The solvent matrix was thawed to –80 °C and the resultant yellow-brown solution stored at that temperature prior to use.^[20,21] Titration of the AlCl·(Et₂O)_n solution via Mohr’s method determined a chloride concentration of 220 mM and an Al:Cl ratio of 1:1.03.

K[Al₄(PPh₂)₇PPh]_n (1**):** Diphenylphosphane (500 mg, 2.68 mmol) was dissolved in diethyl ether (75 mL) and this solution added dropwise via cannula onto potassium metal (117 mg, 3.0 mmol) at room temperature. The resulting orange reaction mixture was stirred vigorously for 20 h, filtered via cannula, and concentrated to approximately 5 mL in vacuo. The reaction mixture was then cooled to –78 °C and AlCl·(Et₂O)_n (2.55 mmol, 11.6 mL of a 220 mM solution in toluene:diethyl ether 4:1) was added via syringe. The brown reaction mixture was warmed from –78 °C to room temperature over 2 h and stirred at for 16 h. The resulting dark brown reaction mixture was

evaporated to dryness in vacuo and extracted into toluene (approx. 25 mL). The brown solution was filtered via cannula, further concentrated to approx. 5 mL, and heated at 65 °C for 4 days. The reaction mixture was then placed in a –15 °C freezer, where a few small yellow crystals of **1** suitable for single crystal x-ray analysis formed on the glass wall after six months. X-ray crystal data: Bruker APEX-II CCD (Mo-K_α sealed tube, λ = 0.71073 Å); final *R* indices (all data): *R*₁ = 0.0663, ω*R*₂ = 0.1097.

Supporting Information (see footnote on the first page of this article): Additional drawings of the molecular structure and crystallographic data and ESI-MS data. See CCDC reference number 934411 for crystallographic .cif file.

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