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VIP Cationic Phosphorus

$[P_9]^+[Al(OR^F)_4]^-$, the Salt of a Homopolyatomic Phosphorus Cation**

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Dedicated to Professor Dieter Naumann on the Occasion of his 70th Birthday

Since its first discovery by Hennig Brand in 1669, elemental phosphorus has continued to fascinate scientists all over the world.[1–4] Metastable white phosphorus is currently produced on a million-ton scale per year, and its compounds have wide-ranging applications in basic and materials chemistry as well as the life sciences. Currently six modifications of elemental phosphorus are known; the last three were discovered as late as 2004 and 2005.[5,6] Pure phosphorus anions $[P_n]^{x-}$ are known in hundreds of structural variations since 1955[7] and cover almost all combinations of n and x.[8] They reversibly intercalate lithium ions, for example, as electrode materials for lithium-ion batteries.[9] Elemental and anionic phosphorus has a strong tendency to catenate and forms isolated molecular, 1D, 2D, and 3D structures in the solid state. Despite this structural diversity of neutral or anionic (poly)phosphorus compounds and the relative strengths of a P–P single bond (about 200 kJ mol^{-1}), currently no homopolyatomic phosphorus cation is known in the condensed phase. However, some examples of cationic phosphorus-containing clusters, such as $[P_5X_2]^+$ (X = Cl,[10] Br, I[11]), the series $[P_5Ph_2]^+$, $[P_6Ph_4]^+$, and $[P_7Ph_6]^+$,[12] or the recently reported $[P_4R_2]^{2+}$ (R = PPh$_3$, AsPh$_3$) have been reported.[13] In the gas phase, mass spectrometric (MS) investigations[14] and quantum-chemical calculations[15,16] suggest that the diamagnetic cluster cations $[P_n]^+$ with uneven values of n are more stable than the paramagnetic even-value radical cations. Smaller $[P_n]^+$ cations with $n = 5$ and 7 should be electron-deficient Wade clusters, while the larger clusters starting with $n = 9$ are expected to have electron-precise Zintl-type structures with four-coordinate, formally positively charged phosphonium atoms. Herein, we close this gap between the extensive gas-phase knowledge and the absence in condensed phases by using the pseudo gasphase conditions provided by the very weakly coordinating $[Al(OR^F)_4]^-$ anion ($R^F = C(CF_3)_3$).[17]

The optimized synthesis of the first pure phosphorus cation $[P_9]^+[Al(OR^F)_4]^-$ proceeds by oxidation of excess P_4 (> 2.5 equivalents) in CH_2Cl_2 solution with $[NO]^+[Al(OR^F)_4]^-$[18] and intermediate formation of the known yellow species $[P_4NO]^+[Al(OR^F)_4]^-$[19] according to Figure 1.Previous gas-phase collision-induced dissociation (CID) experiments suggested that the NO moiety is excluded from the $[P_4NO]^+$ cluster as PNO, as $[P_3]^+$ was formed by direct exclusion of PNO upon collisional activation. With separation of monomeric (SiO_2-analogous) PNO, the reaction to $[P_9]^+$ is slightly endergonic according to our conservative estimate. However, starting with the dimer $(PNO)_2$ this reaction is already highly exergonic (Figure 1c, Supporting Information). As expected from the calculated frontier orbitals (Supporting Information; Ref. [19]) and the yellow color of the intermediate, the progress of the reaction is facilitated by broad band UV/Vis irradiation that additionally transforms most of the excess P_4 to insoluble red phosphorus, destroys the intermediate $[P_4NO]^+$, but, according to repeated investigation by NMR spectroscopy, leaves the $[P_9]^+$ cation intact. Without irradiation we were never able to prepare pure $[P_9]^+$ by this route. After irradiation and filtration from insoluble materials, a clear yellow-orange solution is obtained that only shows signals in the NMR spectrum for the intact anion and the $[P_9]^+$ cation together with a small amount of white phosphorus (< 10 mol %). In agreement with earlier calculations,[15,16] $[P_9]^+$ is a D_{2d}-symmetric Zintl cation that contains three symmetry-independent atom groups A, B, and C (Figure 1a). As the atoms in each subgroup A and C are chemically equivalent but magnetically inequivalent, the NMR spectrum is of higher order (Figure 1b).

To gain deeper insight into the ^{31}P NMR signals and the spin system of the $[P_9]^+$ cation, the structure was optimized at the PBE0/aug-cc-pVTZ level. The different contributions to the nuclear spin–spin coupling were calculated as a single point with PBE0 theory using the aug-cc-pVTZ-J basis set that was especially designed for such purposes.[20] By this analysis, we assigned the spin system as $A_2A'_2BC_2C'_2$. The calculated spin–spin coupling constants served as a very reasonable starting point for the iteration[21] of the experimental coupling constants. Together with the over 160 observed lines in the measured spectrum, the iteration converged to an adjusted RMS of 0.1887, confirming the assigned spin system and being in good agreement with the calculated coupling constants (Table 1).

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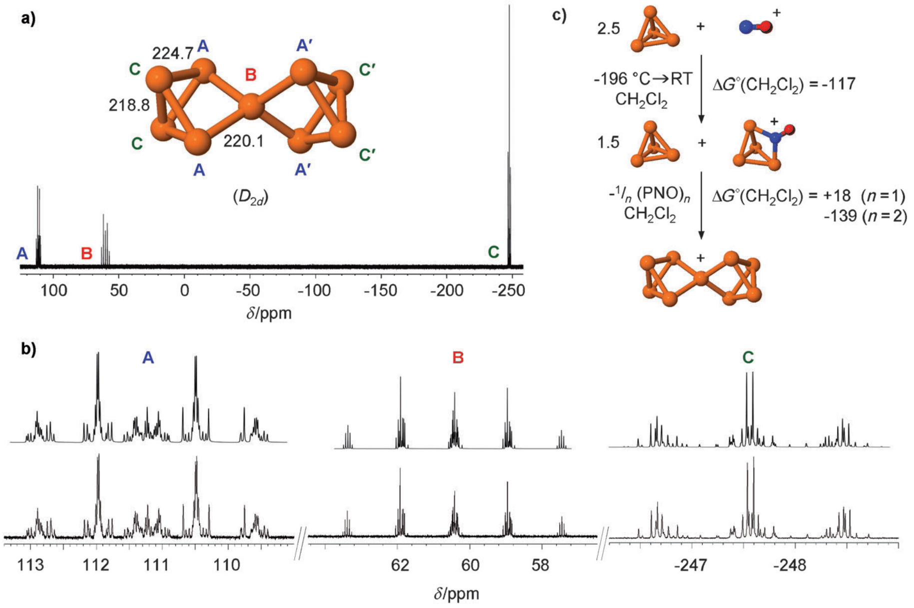

Figure 1. a) ^{31}P NMR spectrum (161.99 MHz) of $[P_9]^+[Al(OC(CF_3)_3)_4]^-$ in CH_2Cl_2/CD_2Cl_2 at 298 K (20000 scans, standard: aqueous H_3PO_4 (85 %)). No further signal, except traces of white phosphorus at −522 ppm, was visible between +630 and −630 ppm. The atom labeling is shown with the assigned spin system $A_2A'_2BC_2C'_2$. The bond lengths [pm] given were taken from the PBE0/aug-cc-pVTZ calculations. b) Enlargements the three signal sets A, B, and C of $[P_9]^+$ (lower trace: experimental spectrum, upper trace: calculated spectrum). c) Observed reaction pathway to $[P_9]^+$, including the calculated thermodynamics at the PBE0/aug-cc-pVTZ level. $\Delta_r G^\circ(CH_2Cl_2)$ includes solvation effects at $\varepsilon_r = 8.93$ (CH_2Cl_2 at room temperature, COSMO model).

Table 1: Calculated (PBE0/aug-cc-pVTZ-J) and experimental J(PP) coupling constants in Hz.

	Calculated	Experimental
$^1J(A_2B) = {}^1J(A_2'B)$	−312.5	−240.8
$^1J(A_2C_2) = {}^1J(A_2'C_2')$	−163.9	−143.5
$^2J(BC_2) = {}^2J(BC_2')$	15.6	9.8
$^3J(A_2C_2') = {}^3J(A_2'C_2)$	−11.1	−7.3
$^2J(A_2A_2')$	24.8	26.8
$^4J(C_2C_2')$	−0.6	−0.1

These NMR spectroscopic investigations unambiguously confirmed the nature and structure of the polyphosphorus cation as being D_{2d}-$[P_9]^+$. The ESI-MS spectrum recorded from a CH_2Cl_2 spray (Supporting Information) also shows the presence of $[P_9]^+$ ($m/z = 278.8$) as the major signal. $[P_5]^+\cdot CH_2Cl_2$, $[P_7]^+\cdot CH_2Cl_2$, $[P_9]^+\cdot CH_2Cl_2$, and $[P_{11}]^+\cdot CH_2Cl_2$ were also present in the spray in lower concentrations and suggest that it might also be possible to stabilize those either as pure cations or as solvent adducts.

Upon removal of all volatiles from the yellow-orange CH_2Cl_2 solution of $[P_9]^+[Al(OR^F)_4]^-$, a yellow-orange powder is obtained. Despite many attempts, it was impossible for us to crystallize the salt under all conditions tested. However, solid-state ^{31}P-MAS-NMR of the isolated solid material (Supporting Information) confirmed that $[P_9]^+[Al(OR^F)_4]^-$ is also present in the solid state, as almost unchanged chemical shifts and incompletely resolved fine structure arising from J coupling were observed, which supports the unchanged composition of the cation relative to that in solution. Moreover, when the powder is redissolved in CD_2Cl_2, the original $[P_9]^+[Al(OR^F)_4]^-$ NMR spectra can be obtained. To further confirm the nature of the solid as $[P_9]^+[Al(OR^F)_4]^-$, the compound was characterized by Raman and IR spectroscopy (Figure 2; for the less-informative IR data, see the Supporting Information).

The Raman bands of $[P_9]^+$ were assigned using ab initio calculations (RI-MP2/def2-TZVPP). Those of the anion $[Al(OR^F)_4]^-$ were assigned by comparison with $[NMe_4]^+[Al(OR^F)_4]^-$, which has no bands belonging to the cation $[NMe_4]^+$ in the P−P stretching range below 600 cm^{-1} and serves as an excellent comparison for the undistorted anion bands (Figure 2). A very small amount of unreacted starting material (white phosphorus) is visible in the spectrum (breathing mode at about 600 cm^{-1}), which was also found in the ^{31}P MAS NMR spectrum (Supporting Information). All bands of cation and anion were fully assigned and are in excellent agreement with the calculations (see the Table in the Supporting Information).

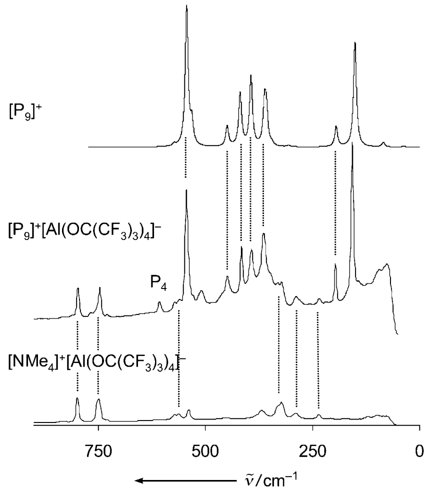

Figure 2. Sections of the experimental Raman spectra of $[P_9]^+[Al(OR^F)_4]^-$ (central trace), $[NMe_4]^+[Al(OR^F)_4]^-$ (lower trace), and the RI-MP2/def2-TZVPP calculated simulation of $[P_9]^+$ (upper trace).

PBE0/aug-cc-pVTZ and MP2/TZVPP calculations suggest bond lengths d_{PP} in $[P_9]^+$ to range from 218.8/219.7 (C−C) and 220.1/218.0 (A−B) to 224.7/225.1 pm (A−C) (Figure 1 a). A natural bond order (NBO) analysis assigns those as single bonds, with Wiberg bond orders of between 0.91 and 1.00. The natural charges are almost evenly distributed over all nine atoms and range at various levels of theory from +0.06 to +0.13, which contradicts the seemingly simple electron-precise Lewis formula with eight three-coordinate neutral and one four-coordinate phosphonium atom. A MO diagram of $[P_9]^+$ (Supporting Information) suggests that the bonding in $[P_9]^+$ is strongly delocalized, and thus more related to the P_4 cluster, which is in agreement with the completely delocalized charges.

Is the $[Al(OR^F)_4]^-$ counterion necessary? Preliminary investigations show that there is a definite need for using the large and weakly coordinating $[Al(OR^F)_4]^-$ anion[17,23] to stabilize the pure phosphorus cation: In our reactions of P_4 with $[NO]^+[BF_4]^-$ or $[NO_2]^+[SbF_6]^-$ and without ultrasonic enhancement, no reaction occurred in CH_2Cl_2 (owing to insolubility). With ultrasonic enhancement, we only detected PF_3 (^{31}F NMR spectrum) as the main resulting oxidation/decomposition product, thus the $[P_4NO]^+$ intermediate is not compatible with classical, more nucleophilic fluorinated anions such as $[BF_4]^-/[SbF_6]^-$. This result is in agreement with a thermodynamic investigation that suggested that solid $[P_5]^+[SbF_6]^-$ is unstable towards decomposition to $PF_{3(g)}$, $SbF_{3(s)}$, and $P_{4(s)}$ by at least $-208\,kJ\,mol^{-1}$ (in contrast to $[N_5]^+[SbF_6]^-_{(s)}$, which is stable by more than $+108\,kJ\,mol^{-1}$).[22] The driving force for this decomposition is the formation of the very strong P–F bond in PF_3 (maximal bond energy mBE = 490 kJ mol^{-1}). The stability of solid and dissolved $[P_9^+][Al(OR^F)_4]^-$ suggests that the more stable C–F bonds in the $[Al(OR^F)_4]^-$ anion (mBE ≈ 525 kJ mol^{-1}) are sufficiently compatible with the phosphorus cations.

In conclusion, we have shown that a pure phosphorus cation may be prepared in condensed phases in good yield. Owing to the chemically robust and weakly coordinating nature[17] of the $[Al(OR^F)_4]^-$ counterion,[23] the salt is stable at room temperature in CH_2Cl_2 for weeks. As the salt is readily available, we expect many uses in future fundamental and applied work, for example, the currentless deposition of semiconducting metal particles on metal surfaces (M = Al, Ga, In).

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