Homoatomic cations: From \([\text{P}_5]^+\) to \([\text{P}_9]^+\)

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Recent synthetic approaches to a series of \([\text{P}_9]\)X salts \((X = \text{[F[Al(OR)]_3]}\)₂, \([\text{Al(OR)}^5]_4\), and \((R^5 = \text{C}(\text{CF}_3)_3); \text{Ga}_2\text{Cl}_7\)) overcome limitations in classical synthesis methods that proved unfavorable for phosphorus cations. These salts contain the homopolyatomic cation \([\text{P}_9]^+\) via \((I)\) oxidation of \(\text{P}_4\) with NO[Al(OR)]₃, \((\text{II})\) the arene-stabilized Co(I) sandwich complex \([\text{Co(arene)}_3][\text{Al(OR)}^5]_4\) \((\text{arene} = \text{ortho-diﬂuorobenzene (o-DFB) and ﬂuorobenzene (FB))}, \) or \((\text{III})\) the reduction of \([\text{P}_5\text{Cl}_2][\text{GaCl}_4]\) with Ga[Ga₂Cl₇] as Ga(I) source in the presence of \(\text{P}_4\). Quantum chemical CCSD(T) calculations suggest that \([\text{P}_9]^+\) formation from \([\text{Co(arene)}_3]^+\) occurs via the nido-type cluster \([\text{o-DFB-CoP}_4]^+\), which resembles the iso-electronic, elusive \([\text{P}_5]^+\). Apparently, the nido-cation \([\text{P}_5]^+\) forms immediately in all reactions, particularly during the Ga(I)-induced reduction of \([\text{P}_5\text{Cl}_2]^+\) and the subsequent pick up of \(\text{P}_4\) to yield the final salt \([\text{P}_9][\text{Ga}_2\text{Cl}_7]\). The solid-state structure of \([\text{P}_9][\text{Ga}_2\text{Cl}_7]\) reveals the anticipated \(D_{2d}\)-symmetric Zintl-type cage for the \([\text{P}_9]^+\) cation. Our approaches show great potential to bring other \([\text{P}_n]^+\) cations from the gas to the condensed phase.

INTRODUCTION

Intensely colored oleum solutions of nonmetallic homopolyatomic cations of sulfur, selenium, and tellurium were likely the first examples for this elusive cation class and were observed as early as around 1800 (1). However, the first real evidence for representatives began with the synthesis and characterization of \([\text{O}_2][\text{PtF}_6]\) in 1962 (2, 3), and many more examples of homopolyatomic cations of most nonmetallic elements have been isolated and characterized in the solid state in the past 60 years excluding examples of crystal structures of homopolyatomic phosphorus cations. For the latter element, experimental and theoretical work showed that it is possible to generate pure polyphosphorus cations in the gas phase (4). Moreover, Martin et al. (5) observed larger \([\text{P}_n]^+\) cations \((n = 2 \text{ to } 24)\) in the gas phase by mass spectrometric studies as early as 1986, with cation \([\text{P}_9]^+\) being the largest to date (6). More recent calculations suggest the smaller, odd-numbered cluster cations \([\text{P}_n]^+\) with \(n \leq 15\) to be the most approachable in the condensed phase (7). The first evidence for the existence of \([\text{P}_9]^+\) in the condensed phase was published only in 2012: The oxidant \([\text{NO}][\text{Al(OR)}^5]_4\) \((R^5 = \text{C}(\text{CF}_3)_3)\) reacts with an excess of \(\text{P}_4\) (8) to the \(C_{3v}\)-symmetric \([\text{P}_9\text{NO}]^+\) cation, which acts toward \(\text{P}_4\) as a "P⁺" donor. Very likely, the elusive \([\text{P}_5]^+\) cation is formed and acts as an intermediate, which subsequently adds a second molecule \(\text{P}_4\) to yield \([\text{P}_9]^+\) (Fig. 1, I).

RESULTS AND DISCUSSION

The aforementioned reaction has been studied in quite some detail, and despite the use of the larger and more robust weakly coordinating anion \([\text{F[Al(OR)]_3]}_2\) in route I (Fig. 1) (9), it was not possible so far to crystallize any \([\text{P}_9]^+\) cation salt \([\text{P}_9][\text{X} = [\text{F[Al(OR)}^5]_3)]_2, [\text{Al(OR)}^5]_4]; \) cf. table S5 and figs. S7 to S11. Nevertheless, the amorphous salt \([\text{P}_9][\text{F[Al(OR)}^5]_3)]_2\) obtained in 1,2,3,4-tetraﬂuorobenzene (4FB) as reaction medium in 69% yield reversibly dissolves in this solvent and shows a superior long-time stability of over 40 days, which is fundamentally different to the corresponding \([\text{Al(OR)}^5]_4\) salt and allows stoichiometric reactions in the future.

From a retrosynthetic point of view and realizing that \([\text{P}_5]^+\) plays a pivotal role in the synthesis of \([\text{P}_9]^+\), we developed two new approaches. This includes the new reaction pathway II toward \([\text{P}_9][\text{Al(OR)}^5]_4\) via oxidation of white phosphorus with the "naked" Co(I) sandwich cations \([\text{Co(arene)}_3][\text{Al(OR)}^5]_4\) \((\text{arene} = \text{ortho-diﬂuorobenzene (o-DFB) and ﬂuorobenzene (FB))}, \) which was confirmed by nuclear magnetic resonance (NMR) spectroscopy (Fig. 1, II). Quantum chemical calculations suggest occurrence of a nido-cluster intermediate \([\text{o-DFB-CoP}_4]^+\) that resembles the iso-electronic \([\text{P}_5]^+\) (cf. figs. S36 and S37). The crude nonmagnetic black by-product was analyzed by powder diffraction [powder x-ray diffraction (pXRD)] and energy-dispersive x-ray (EDX) measurements. The analysis agrees with its tentative assignment as the well-known cobalt phosphide \([\text{CoP}_3]\) (cf. fig. S22). (11–13)

Recent years gave access to cationic polyphosphorus compounds such as \([\text{P}_n\text{X}_n]^+\) \((\text{X} = \text{Br, I})\) (14) and \([\text{P}_n\text{R}_n]^+\) \((\text{R} = \text{alkyl, aryl})\) (15–17). Hence, for the most successful route III, particularly cation \([\text{P}_5\text{Cl}_2]^+\) in combination with an adequate reducing agent that turned out to be the best \([\text{P}_5]^+\) synthon (Fig. 1, III). However, the synthesis of a \([\text{Al(OR)}^5]_4\) salt containing the cation \([\text{P}_5\text{Cl}_2]^+\) following the reported procedure for the Br and I analogs only led to mixtures. By contrast, it succeeds as the salt \([\text{P}_5\text{Cl}_2][\text{GaCl}_4]\), when \(\text{P}_4\) is reacted in \(\text{PCl}_3\) as the reaction medium with the required stoichiometric amount of \(\text{GaCl}_3\) at room temperature. \([\text{P}_5\text{Cl}_2][\text{GaCl}_4]\) can be isolated as colorless solid in excellent yields (86%) and starts to decompose in solution \((\text{CH}_2\text{Cl}_2, \text{FB}, \text{and } \text{o-DFB})\) and in the solid state at room temperature in the course of a few hours (solution) up to a few days (solid material) to \(\text{P}_4, \text{GaCl}_3, \text{PCl}_3, \) and an insoluble orange solid of unknown constitution, likely Schenck-type phosphorus (18). However, when stored in the dark and at −30°C, the salt is stable for several weeks. The molecular structure of \([\text{P}_5\text{Cl}_2]^+\) was confirmed by single-crystal x-ray structure determination of the more stable \([\text{P}_5\text{Cl}_2][\text{Ga}_2\text{Cl}_7]\) salt (cf. table S12 and fig. S23). The optimized synthesis of \([\text{P}_9][\text{Ga}_2\text{Cl}_7]\) requires the slow treatment of \([\text{P}_5\text{Cl}_2][\text{GaCl}_4]\) with \(\text{GaCl}_3\) and \(\text{Ga[Ga}_2\text{Cl}_7]\) as reducing agent, in the presence of a huge excess of \(\text{P}_4\) (10.0 equivalents), and a 5:1 solvent mixture of FB and CS₂ as reaction medium (Fig. 1, III).
Typically, the dissolved Ga(I) source Ga[Ga₂Cl₇] in FB is added dropwise to the FB/CS₂ solution of [P₅Cl₂][GaCl₄], GaCl₃, and P₄ over the course of 30 min, leading to the precipitation of [P₉][Ga₂Cl₇] as an orange microcrystalline material in 77% yield. Salt [P₉][Ga₂Cl₇] is stable when stored at low temperature (−35°C) for a long period of time (several month) but starts to decompose when heated above 60°C. The excess of P₄ can be conveniently and quantitatively recovered from the reaction medium. The purity of solid [P₉][Ga₂Cl₇] was confirmed by ³¹P MAS (magic angle spinning) NMR spectroscopy and Raman spectroscopy (Fig. 2, I and II), elemental analysis [inductively coupled plasma (ICP)], and pXRD (f.g. S5 and S26). The salt is poorly soluble in common solvents such as CH₂Cl₂, FB, and o-DFB, but sufficiently concentrated solutions for liquid NMR studies and crystal preparations can be obtained by addition of small amounts of GaCl₃. Note that if the reduction is performed without CS₂ and only stoichiometric amounts of P₄ are present, then the formation of a much smaller amount of [P₉]⁺ is observed in the reaction mixture that is, however, sufficiently concentrated for NMR studies in solution. The solution of ³¹P NMR spectrum of dissolved...
crystalline \([P_9][Ga_3Cl_7]\) reveals the expected \(A_2A'_2B_{C_2}C_2\) spin system with signals at \(\delta_{A} = 111.31 \text{ ppm} \) and \(\delta_{A'} = 60.91 \text{ ppm}, \) and \(\delta_C = -247.49 \text{ ppm}. \) The chemical shifts and coupling constants retrieved from the iteration of the \(^{31}\text{P}\left\{^1\text{H}\right\}\text{NMR}\) spectrum compare well to all the aforementioned \([P_5]^+\) salts (Fig. 2, I; fig. S5; and tables S1 and S2).

Suitable crystals for XRD were obtained by overlaying either reaction solutions without CS\(_2\) (polymorph 1, space group \(P2_1/n\)) or concentrated solutions of \([P_9][Ga_2Cl_7]\) with additional GaCl\(_3\) in o-DFB (polymorph 2, space group \(I2/a\)) with \(n\)-pentane at \(-30^\circ\text{C}\) (Fig. 2, III, and cf. the Supplementary Materials). The second polymorph shows half of the salt composition in the asymmetric unit, and the \(P−P\) bond lengths of \([P_9]\) + compare well to those observed in morph shows half of the salt composition in the asymmetric unit, \((\text{Fig. }2, \text{III}, \text{and cf. the Supplementary Materials}).\) The second poly-o

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**Fig. 3. Calculated mechanism toward the formation of \([P_9]^+\) starting from \([P_5Cl_2][Ga_{11}Cl_{22}]\), \(P_4,\) and in situ formed \([FB][Ga_{11}III\text{Cl}_4]\) \((\text{Fig. }3, \text{2}), \text{liberates the FB molecule, and forms \([ClP_5(Ga_{11}\text{III})_2\text{Cl}_5]\) + with Ga(I) and Ga(III) centers. Excess Ga(III)Cl\(_3\) leads to the formation of the observed counter anion \([Ga_{11}\text{III}\text{Cl}_6]^-\), which, however, is known to equilibrate readily in arene solution with \([Ga_{11}\text{III}\text{Cl}_4]^-\) and Ga(III)Cl\(_3\) (22). The ion pair \((FB)Ga_{11}\text{III}\text{Cl}_3\) then oxidatively adds via the Ga(I) ion into one of the two identical \(P−\text{Cl}\) bonds of \([P_5Cl_2]^+\) \((\text{Fig. }3, \text{2})\), liberates the FB molecule, and forms \([ClP_5(Ga_{11}\text{III})_2\text{Cl}_5]^+\) \((\Delta G_{\text{solv}} = -75.0 \text{ kJ mol}^{-1})\). This \(P\)-coordinated P_3 Cl adduct to the very strong chloride acceptor \([(Ga_{11}\text{III})_2\text{Cl}_3]^+\) reacts by a rearrangement reaction \((\text{Fig. }3, \text{3})\) via intermediate CI coordination to give \([P_3]^+\) under separation of neutral \((Ga_{11}\text{III})_2\text{Cl}_6\) \((\Delta G_{\text{solv}} = -19.7 \text{ kJ mol}^{-1})\).

The \([P_3]^+\) intermediate generated picks up free \(P_4\), which is present in a huge excess, to give the final product \([P_9]^+\) \((\Delta G_{\text{solv}} = -43.8 \text{ kJ mol}^{-1})\) in an oxidative addition \((\text{Fig. }3, \text{4})\). With excess \((Ga_{11}\text{III})_2\text{Cl}_6\) in the solution, it crystallizes as salt \([P_9][(Ga_{11}\text{III})_2\text{Cl}_7]\), facilitated by the rather low solubility of the formed salt. The suggested entire reaction path is highly exergonic by \(-197.9 \text{ kJ mol}^{-1}\), and although we evaluated alternative reaction pathways as well, the one described here appears most likely to us (cf. the Supplementary Materials). However, all likely reaction pathways include the elusive \([P_3]^+\) as intermediate \((\text{Fig. }1, \text{retrosynthesis}).\)

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With the crystal structure of \([P_9][Ga_3Cl_7]\), the present work provides the first structural confirmation of a homopolyatomic phosphorus cation. The successful implementation of new synthetic strategies and a detailed elucidation of the possible reaction pathways showcase the elusive \([P_3]^+\) as an intermediate, isoelectronic to the putative cyclopentadienyl cation \((C_5H_5)^+\) (23). The transition from the planar cyclic organic cation toward the Wadeian nido type (24) was calculated to occur even by the substitution of only one CH group for the entire series \([(HC)_{x}P_5-x]\)+, with \(x = 0 \text{ to } 4\) by Green and
colleagues (25). However, only the synthesis of [3,5-trBu3-1,2,4-C6P3][AlCl4] was reported by Russell and colleagues (26, 27) so far. Now, the elusive [P5]+ has also strong evidence to be present in condensed phases, and our synthetic strategies pave the way for the discovery of further novel molecules.

MATERIALS AND METHODS

General remarks for [P5][Ga2Cl7]
Manipulations were performed in a Glovebox MB UNIlab or using Schlenk techniques under an atmosphere of purified nitrogen or argon, respectively. Dry, oxygen-free solvents (CH2Cl2, FB, o-DPB, and CS2; distilled from CaH2), and n-hexane and n-pentane (distilled from potassium) were used. Deuterated benzene (CD6) was distilled from potassium. Deuterated dichloromethane (CD2Cl2) was dried over molecular sieves. All distilled and deuterated solvents were stored over molecular sieves (4 Å: CH2Cl2, CD2Cl2, FB, o-DPB, CD6, n-hexane, n-pentane, and CS2). All glassware were oven-dried at 160°C before use. Ga[Ga2Cl7] was purchased from Shanghai Richem International. All NMR measurements were performed with the Bruker AVANCE III HD Nanobay, 400-MHz UltraSield [1H (400.13 MHz), 13C (100.61 MHz), 31P (161.98 MHz), and 71Ga (152.52 MHz)] equipped with a BBO Prodigy CryoProbe. Chemical shifts were referenced to δTMS = 0.00 ppm ([1H and 13C, externally) and δ31PO4(85%) = 0.00 ppm ([31P, externally). Chemical shifts (δ) are reported in parts per million. Coupling constants (J) are reported in hertz. 31P solid-state NMR spectra were recorded on a BRUKER Avance 300-MHz spectrometer using a commercial 2.5-mm MAS NMR probe and operating at a resonance frequency of 121.5 MHz. The MAS frequency was 15 and 23 kHz. NaH2PO4 · H2O was used as an external standard. Melting points were recorded on an electrothermometer melting point apparatus ( Büchi, Switzerland, Melting Point M-560) in sealed capillaries under argon atmosphere and are uncorrected. Infrared (IR) and Raman spectra were recorded at ambient temperature using a Bruker Vertex 70 instrument equipped with a RAM II module (Nd-YAG laser, 1064 nm). The Raman intensities are reported in percent relative to the most intense peak and are given in parenthesis. An attenuated total reflection (ATR) unit (diamond) was used for recording IR spectra. The intensities are reported relative to the most intense peak and are given in parenthesis. The abbreviations: ≥0.8 = very strong (vs), ≥0.6 = strong (s), ≥0.4 = medium (m), ≥0.2 = weak (w), and ≤0.2 = very weak (vw). Elemental analysis and the Ga, P content were determined, which was filtered, washed with n-hexane (5 ml), and dried in vacuo to yield [P5Cl2][GaCl4] as pale yellow, light sensitive, and pyrophoric solid in 86% yield (1.5 g). [P5Cl2][GaCl4] decomposes in solution and slowly in the solid state when stored at room temperature to P4, GaCl3, PCl3, and an insoluble orange solid material of unknown constitution. Figure S2 shows the 31P NMR spectrum of dissolved [P5Cl2][GaCl4] in CD2Cl2 after 4 hours, indicating its decomposition. When stored at −30°C under the exclusion of light, solid [P5Cl2][GaCl4] is stable for at least 3 months. 31P NMR (202.45 MHz, CD2Cl2, 300 K): δ = 148.7 ppm [2P, dt, J(P5P4) = −341 Hz, J(P5P4) = −143 Hz, P4, [P5Cl2]+, 56.2 ppm [1P, tt, J(P5P4) = −341 Hz, J(P5P4) = −143 Hz, P4, [P5Cl2]+], and −269.2 ppm [2P, td, J(P5P4) = −142 Hz, J(P5P4) = 27 Hz, P4, [P5Cl2]+]. Raman (100 mW, 298 K): ν = 594 cm−1 (10), 562 cm−1 (13), 537 cm−1 (100), 435 cm−1 (33), 415 cm−1 (69), 392 cm−1 (26), 382 cm−1 (20), 357 cm−1 (38), 339 cm−1 (59), 262 cm−1 (23), 227 cm−1 (18), 182 cm−1 (51), 151 cm−1 (24), 132 cm−1 (18), and 118 cm−1 (14). IR (ATR, 298 K): v = 1211 cm−1 (w), 630 cm−1 (w), 585 cm−1 (vs), 564 cm−1 (s), 552 cm−1 (vs), 536 cm−1 (vs), and 412 cm−1 (vs). Elemental analysis (solvent free): GaP5Cl2 calculated: N: 0.00, C: 0.00, H: 0.00; found: N: 0.03, C: 0.32; H: 0.01. Melting point: 62−64°C (decomposition).

Synthesis of [P5Cl2][Ga2Cl7]
GaCl3 (528 mg, 3.0 mmol) in PCl3 (3 ml) was added to P4 (124 mg, 1.0 mmol). The mixture was stirred for 1 hour at ambient temperature under the exclusion of light. A colorless precipitate formed within 5 min. Converted to a colorless oil. The supernatant was decanted from the oil and washed with n-hexane (3 × 5 ml), and all volatiles were removed in vacuo leaving pure [P5Cl2][GaCl4] as colorless microcrystalline material in 92% yield (599 mg). Dissolved and solid [P5Cl2][Ga2Cl7] also decomposes to P4, GaCl3, PCl3, and an insoluble orange solid. It is also much longer stable in the dark at −30°C at least for several month. Crystals suitable for x-ray analysis can be grown from concentrated CH2Cl2 solution layered with n-pentane at −30°C. 31P NMR (202.45 MHz, CD2Cl2, 300 K): δ = 149.1 ppm [2P, dt, J(P5P4) = −340 Hz, J(P5P4) = −143 Hz, P4, and [P5Cl2]+], 56.2 ppm [1P, td, J(P5P4) = −340 Hz, J(P5P4) = 27 Hz, P4, [P5Cl2]+], and −269.3 ppm [2P, td, J(P5P4) = −143 Hz, J(P5P4) = 27 Hz, P4, and [P5Cl2]+]. Raman (100 mW, 298 K): ν = 595 cm−1 (15), 564 cm−1 (14), 540 cm−1 (100), 437 cm−1 (37), 420 cm−1 (59), 393 cm−1 (42), 363 cm−1 (80), 339 cm−1 (30), 276 cm−1 (12), 264 cm−1 (29), 227 cm−1 (22), 181 cm−1 (54), 152 cm−1 (20), 135 cm−1 (43), and 102 cm−1 (31). IR (ATR, 298 K): v = 1189 cm−1 (m), 637 cm−1 (w), 590 cm−1 (vs), 562 cm−1 (vs), and 539 cm−1 (vs). Elemental analysis (solvent free): Ga3P5Cl6 calculated: N: 0.00, C: 0.00, and H: 0.00; found: N: 0.03, C: 0.40, and H: 0.144. Melting point: 52° to 55°C (decomposition).

Synthesis of [P9][Ga2Cl7]
P4 (140 mg, 1.2 mmol, 10 equivalents) dissolved in 1 ml of CS2 was added to a solution of [P5Cl2][GaCl4] (50 mg, 0.12 mmol, 1 equivalents) and GaCl3 (21 mg, 0.12 mmol, 1 equivalents) in 2 ml of FB. Ga[Ga3Cl6] (54 mg, 0.12 mmol, 1 equivalents) dissolved in 1.5 ml of FB was added dropwise over a period of 30 min accompanied with the formation of a pale orange powder. The suspension was filtered, and the precipitate washed with 1 ml of CS2 and 2 ml of n-pentane. After drying in vacuo, [P9][Ga2Cl7] was obtained as orange microcrystalline powder in 77% yield (61 mg), which was characterized by 31P MAS spectroscopy, pXRD, IR, Raman, and ICP (vide infra). Note
that, from the filtrate, the excess of P₄ can be quantitatively recovered by sublimation. The filtrate contains [P₉][GaCl₃], P₄, and Cl₃POGaCl₃ (fig. S3), of which the latter was identified by single-crystal x-ray analysis. We believe that the formation of Cl₃POGaCl₃ is a result of the presence of either very low amounts of moisture or the reaction of PCl₃ with the glass surface of the reaction vessels in the presence of the strong Lewis acid GaCl₃. This was independently confirmed by the diffusion of n-pentane in a solution of GaCl₃ in PCl₃ at −30°C, which leads to the deposition of colorless crystalline Cl₃POGaCl₃. The ³¹P NMR spectrum of the GaCl₃/PCl₃ solution is depicted in fig. S4 and the molecular structure is depicted in fig. S19.

Note that [P₉][Ga₂Cl₇] is also obtained without additional GaCl₃, however, with a slightly decreased yield of 70%. ³¹P{¹H} NMR (202.45 MHz, CD₂Cl₂ + GaCl₃, 300 K): δ = 111.5 ppm (4P, m, P₄, [P₉]), 61.0 ppm (1P, m, P₄, [P₉]) and −247.4 ppm (4P, m, P₄, [P₉]). IR (ATR, 298 K): ν = 554 cm⁻¹ (m), 523 cm⁻¹ (vs), and 501 cm⁻¹ (s). Raman (100 mW, 298 K): v = 555 cm⁻¹ (11), 542 cm⁻¹ (100), 525 cm⁻¹ (32), 513 cm⁻¹ (12), 498 cm⁻¹ (62), 446 cm⁻¹ (30), 429 cm⁻¹ (5), 412 cm⁻¹ (74), 401 cm⁻¹ (12), 391 cm⁻¹ (32), 361 cm⁻¹ (48), 347 cm⁻¹ (10), 309 cm⁻¹ (6), 272 cm⁻¹ (5), 198 cm⁻¹ (96), 157 cm⁻¹ (80), 143 cm⁻¹ (16), 126 cm⁻¹ (9), 106 cm⁻¹ (15) (assignment; see table S3).

Melting point: Compound starts to decompose at temperature above 60°C. Elemental analysis with ICP-OES: calculated: P 41.83 and Ga 20.93; found: P 41.92 and Ga 20.41.

Experimental details for [P₉][Al(OR₃)₄] via [Co(arene)][Al(OR₃)₄]

The following synthesis in 4FB typify for all other used solvents (CH₂Cl₂, o-DFB, and m-DFB).

Experimental details for [P₉][Al(OR₃)₄]

The following synthesis in 4FB typify for all other used solvents (CH₂Cl₂, o-DFB, and m-DFB). Inside, a glovebox P₄ (81 mg, 0.7 mmol, 2.5 equivalents) and [NO][Al(OR₃)₃] (399 mg, 0.26 mmol, 1.0 eq.) were weighed in one side of a double Schlenk tube. Under reverse flow of argon, 4FB (4 ml) was added to the solids. Immediately, a dark red color of the solution was observed. The solution itself was stirred for at least 3 days in the dark. During this period, the color of the solution changed to yellow or orange, depending on the amount of solvent used for the reaction. The solution was filtered through the frit to the other side of the double Schlenk tube, and the solvent was slowly removed under reduced pressure. The desired product (320 mg, 0.18 mmol, 69%) was obtained as a yellowish powder and was characterized solely by NMR, because [P₉]⁺ and [F{Al(OR₃)₃}]⁻ are already known from literature (8, 9).

¹H NMR (400.17 MHz, 4FB, 298 K): only solvent signal at 6.97 ppm. ¹³F NMR (376.54 MHz, 4FB, 298 K): δ = −76.1 ppm (s, 54F, [F{Al(OC(FC₃)₂)₃}]⁻) and −184.8 ppm (br. s, 1F, [F{Al(OC(FC₃)₂)₃}]⁻). ³¹Al NMR (104.27 MHz, 4FB, 298 K): δ = −32 ppm (br. s, 1Al, [F{Al(OC(FC₃)₂)₃}]⁻). ³¹P NMR (161.99 MHz, 4FB, 298 K): δ = 123.2 ppm (m, 4P, P₄, [P₉]⁺), 69.2 ppm (m, 1P, P₄, [P₉]⁺), and −263.2 ppm (m, 4P, P₄, [P₉]⁺). Note the small impurities of unknown compounds at 50.5 and −236.2.

SUPPLEMENTARY MATERIALS

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