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Ligand-Stabilized $[P_4]^{2+}$ Cations**

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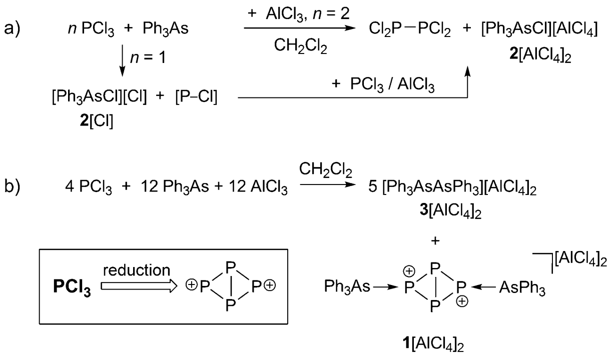
Ligand stabilization has been exploited to access novel, soluble allotropes of main-group elements.[1] A series of neutral, homoatomic units (Si_2, C_1, P_2, P_4, P_{12}) in an oxidation state of zero have been recently isolated using carbenes as supporting ligands.[2–8] Homoatomic cages and clusters of Group 15 elements are known, and derivatives of P_4, polyphosphorus anions (for example Zintl anions), and polyphosphanes have been extensively developed;[9,10] however, examples of polyphosphorus cations have not been reported.[11] Cations based on silicon[12] or germanium[13,14] have been reported, including complexes such as $[Cp^*Si][B(C_6F_5)_4]$ (Cp^* = pentamethylcyclopentadienyl),[15–17] which mimic the coordination chemistry of transition metals. Furthermore, the triflate salt of a cryptand-encapsulated germanium(II) dication $[Ge(cryptand[2.2.2])]^{2+}$ was recently reported.[18] The coordination chemistry of electron-rich (lone-pair-bearing) phosphorus centers as Lewis acceptors has been extensively utilized in recent years to realize a facile synthetic method to form bonds between phosphorus and a variety of donor atoms (for example C, N, O, P, S, Se, Ga).[19–21]

The first examples of cationic polyphosphorus cages $[P_5X_2]^+$ were obtained by Krossing et al.[22,23] from the reaction of $Ag[Al\{OC(CF_3)_3\}_4]$ with PX_3 (X = Cl, Br, I) in the presence of P_4. We obtained analogous results by applying a stoichiometric melt at elevated temperatures (60 to 100 °C) and extended this chemistry to the more stable diorganophosphenium cation $[Ph_2P]^+$ with P_4. This approach resulted in the formation of the cationic cages $[Ph_2P_5]^+$, $[Ph_4P_6]^{2+}$, and $[Ph_6P_7]^{3+}$ by the consecutive insertion of $[Ph_2P]^+$ into the P–P bonds of the P_4 tetrahedron[24] and is a general method for the formation of $[R_2P_5]^+$ cations, which are polyphosphorus cationic frameworks involving organic substituents.[25,26]

Recognizing the isolobal relationship between the organic substituent and a Group 15 ligand, we have now utilized the Lewis acceptor behavior of phosphorus centers as a means to stabilize the bicyclo[1.1.0]-tetraphosphane-1,4-diium dication ($[P_4]^{2+}$), analogues of neutral and anionic derivatives.[27]

Our experience with reductive coupling reactions of monocationic chlorophosphanylphosphonium cations $[R_3PP(R)Cl]^+$ with Ph_3P or Ph_3Sb to give dications $[R_3PP(R)P(R)PR_3]^{2+}$ reveals a powerful method for P–P bond formation[28,29] that we have applied to PCl_3 to give the ligand-stabilized dication $\mathbf{1}^{2+}$. Moreover, the redox system $PCl_3/SnCl_2$ has been used as a source for the in situ generation of chlorophosphandiyl [P–Cl], which, in the presence of the cyclophosphane *cyclo*-tBu_3P_3, gives the cyclotetraphosphane *cyclo*-tBu_3P_4Cl.[30] On this basis, we anticipated that the appropriate combination of PCl_3, Lewis basic reducing agent, and halide abstracting agent should result in the formation of phosphorus cations with the potential for ligand stabilization. In this context we examined reaction mixtures of PCl_3, Ph_3As, and $AlCl_3$ in CH_2Cl_2 and observed the formation of the highly reactive $Cl_2P\text{-}PCl_2$ ($\delta = 155.1$ ppm)[31] and $[Ph_3AsCl]^+$ (**2**) (Scheme 1 a), indicating the in situ formation of **2**-Cl resulting from oxidation of the arsane and reduction of PCl_3.[32] When PCl_3, Ph_3As, and $AlCl_3$ are combined in a 4:12:12 stoichiometry in CH_2Cl_2 (RT, dark, 12 h; Scheme 1 b), quantitative formation of $\mathbf{1}[AlCl_4]_2$ and $\mathbf{3}[AlCl_4]_2$ is observed, where $\mathbf{1}^{2+}$ is the reduction product and



Scheme 1. a) Idealized reaction of PCl_3, Ph_3As, and $AlCl_3$ showing the in situ formation of $Cl_2P\text{–}PCl_2$ and $\mathbf{2}^{2+}$; b) formation of the bicyclo-[1.1.0]-tetraphosphane-1,4-diium dication $\mathbf{1}^{2+}$ and hexaphenyldiarsane-1,2-diium dication $\mathbf{3}^{2+}$ as tetrachloroaluminate salts $\mathbf{1}[AlCl_4]_2$ and $\mathbf{3}[AlCl_4]_2$, respectively.

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the hexaphenyldiarsane-1,2-diium dication $\mathbf{3}^{2+}$ (Supporting Information, Figure S4)[33,35] is the oxidation product. The ^{31}P{^{1}H} NMR spectrum of $\mathbf{1}^{2+}$ reveals an A_2X_2 spin system ($\delta_A = -325.9$ ppm, $\delta_X = -174.9$ ppm; $^1J_{AX} = -160$ Hz; Supporting Information, Figure S1),[33] which is significantly upfield-shifted with respect to that reported for $(\text{Mes}^*)_2\text{P}_4$ ($\text{Mes}^* = 2,4,6\text{-}t\text{Bu}_3\text{C}_6\text{H}_4$, $\delta_A = -272$ and $\delta_X = -130$ ppm).[34]

Compound $\mathbf{1}[\text{AlCl}_4]_2$ was isolated by fractional crystallization as a CH_2Cl_2 solvate ($\mathbf{1}[\text{AlCl}_4]_2\cdot 3\,CH_2Cl_2$) in good yield (84%). The dichloromethane molecules can be completely removed from $\mathbf{1}[\text{AlCl}_4]_2\cdot 3\,CH_2Cl_2$ in vacuo to give analytically pure $\mathbf{1}[\text{AlCl}_4]_2$ as an amorphous, colorless powder, which is stable for longer periods when stored in the dark at −35 °C.[36] Decomposition associated with melting was observed at temperatures higher than 40 °C. The geometrical parameters for the $[P_4]^{2+}$ core of the molecular structure of cation $\mathbf{1}^{2+}$ (Figure 1) are typical of butterfly structures showing a distinctly shorter P–P bond between the bridgehead phosphorus atoms (P2–P4 2.184(2) Å). In comparison to P_4 (P–P distance of 2.21 Å),[37] the remaining P–P bonds are typical P–P single bonds. The Ph_3As ligands are arranged in an *exo*,*exo* fashion and the P–As bonds (2.332(2); P4–As2 2.335(2) Å) are in the same range as found in phosphanylarsonium cations.[38] To gain further insights into the bonding in $\mathbf{1}^{2+}$, we optimized the geometry of the molecule using density functional theory (DFT) at the BP86/TZVPP level of theory.[39]

Figure 1 shows that the calculated bond lengths of $\mathbf{1}^{2+}$ agree well with the experiment, except for the P–As interatomic distances, which are about 0.07 Å longer than the observed values. We think that the difference probably comes from interatomic interactions in the solid state, which are known to shorten donor–acceptor bonds.[40] Analysis of the electronic structure using the atoms-in-molecules (AIM) method[41] suggests that the P←As donor–acceptor bond is polarized toward the phosphorus acceptor end. The Laplacian distribution (Figure 2) exhibits an area of charge concentration ($\nabla^2\rho(r) < 0$, solid lines) along the P–As axis, which is strongly localized at P. This result is in agreement with the NBO atomic partial charges, which give a value of +1.31 e at As and −0.01 e at P1/P3. Note that there is no P1–P3 bond path in $\mathbf{1}^{2+}$, which has a rather long distance of 2.725 Å (Expt. 2.719 Å). The P_4^{2+} moiety in $\mathbf{1}^{2+}$ is significantly deformed from its equilibrium structure as the result of the P←As donor–acceptor interactions. The optimized geometry of free P_4^{2+} has D_{2d} symmetry with four short (2.168 Å) and two long (2.692 Å) P–P bonds (Figure 1). NBO[42] calculations agree with the description of the bonding situation in $\mathbf{1}^{2+}$. According to the NBO results, there are five P–P single bonds and four electron lone pairs at the P atoms of the P_4^{2+} moiety and two P–As bonds. The NBO partial charges suggest that the P_4 fragment carries a positive charge of only +0.12 e while the $AsPh_3$ ligands have a total charge of +1.88 e.

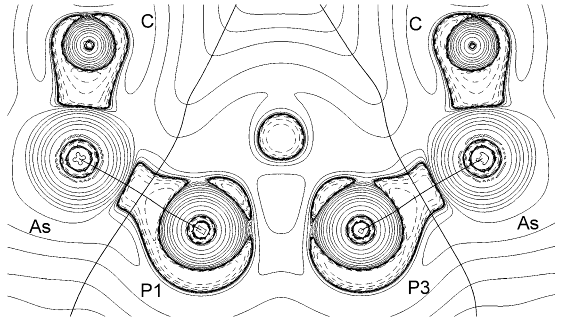

Figure 2. Laplacian contour diagram $\nabla^2\rho(r)$ of $\mathbf{1}^{2+}$ in the As-P1-P3-As′ plane. Solid lines indicate areas of charge concentration ($\nabla^2\rho(r) < 0$); dashed lines show areas of charge depletion ($\nabla^2\rho(r) > 0$). The thick solid straight lines connecting the atomic nuclei are the bond paths. The thick solid lines separating the atomic basins indicate the zero-flux surfaces crossing the molecular plane.

We have calculated the bond strength of the P←As bonds in $\mathbf{1}^{2+}$ according to reaction (1):

$$\mathbf{1}^{2+} \rightarrow P_4^{2+} + 2\,AsPh_3 \qquad (1)$$

The free energy of reaction (1) is $\Delta G_R^{298} = 185.5$ kcal mol^{-1}, which gives a very high average bond strength of 92.75 kcal mol^{-1} for the $Ph_3As \rightarrow P_4^{2+}$ donor–acceptor bond. This can be explained with the very large acceptor strength of the doubly charged P_4^{2+} cation.[43] We have also calculated the geometry and bond energy of the related triphenylphosphane complex $[P_4(Ph_3P)_2]^{2+}$ ($\mathbf{4}^{2+}$). Figure 1 shows that the equilib-

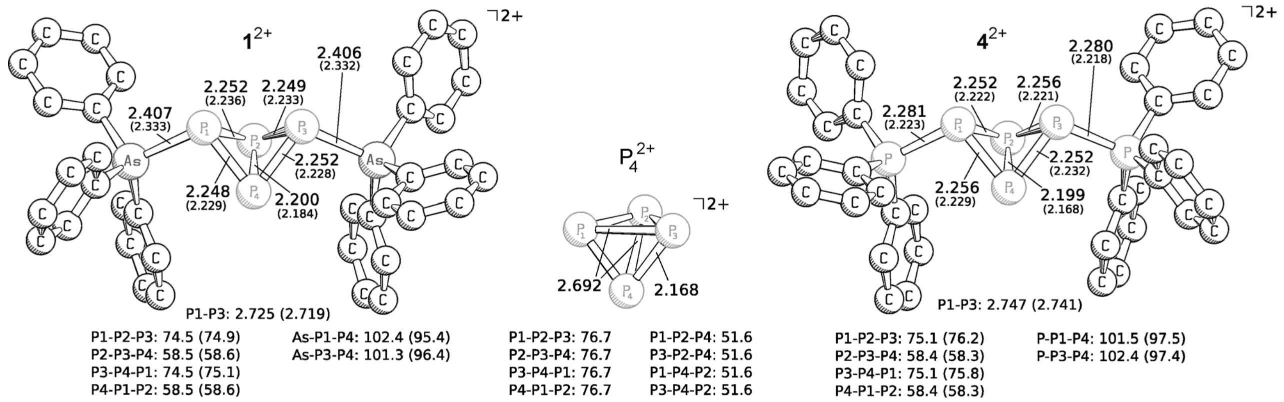

Figure 1. Molecular view of cations $\mathbf{1}^{2+}$ and $\mathbf{4}^{2+}$ in $\mathbf{1}[\text{AlCl}_4]_2\cdot 3\,CH_2Cl_2$ and $\mathbf{4}[\text{AlCl}_4]_2\cdot 3\,CH_2Cl_2$ in the solid state (X-ray crystallography) together with the calculated structure of free P_4^{2+}. Tetrachloroaluminate anions, solvate molecules, and hydrogen atoms have been omitted for clarity. Selected calculated bond lengths [Å] and angles [°] are compared with the experimental values (in parentheses).

rium geometry of **4**$^{2+}$ resembles that of **1**$^{2+}$. The P–P bond lengths of the P_4 core are in good agreement with experiment while the calculated exocyclic P←PPh_3 donor bonds are again about 0.07 Å too long. The analysis of the bonding in **4**$^{2+}$ gave very similar results as for **1**$^{2+}$ and thus it is not reported here (Supporting Information, Figure S3).[39] The calculation of the P←P donor strength according to reaction (2):

$$\mathbf{4}^{2+} \rightarrow P_4{}^{2+} + 2\,PPh_3 \qquad (2)$$

gives a value of $\Delta G_R{}^{298} = 201.2$ kcal mol^{-1}. The bond strength of one $Ph_3P{\rightarrow}P_4{}^{2+}$ donor–acceptor bond is thus 100.6 kcal mol^{-1}.

On the basis of our calculations, the Ph_3As ligands in **1**$^{2+}$ should be easily displaced by a stronger ligand, such as Ph_3P. Consistently, the addition of 2 equiv of Ph_3P to a solution of **1**[OTf]$_2$ in CH_2Cl_2 resulted in the formation of a pale yellow solution. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture shows a new set of resonances, which was fitted as a $A_2MM'XX'$ spin system ($\delta_A = -317.7$ ppm, $\delta_M = -180.2$ ppm, $\delta_X = 29.8$ ppm; $^1J_{AM} = {}^1J_{AM'} = -157$ Hz, $^1J_{MX} = {}^1J_{M'X'} = -377$ Hz, $^2J_{MM'} = 339$ Hz, $^2J_{AX} = {}^2J_{AX'} = 19$ Hz, $^3J_{MX'} = {}^3J_{M'X'} = -139$ Hz, $^4J_{XX'} = 39$ Hz) in a ratio of 2:2:2, indicating the formation of a new species (Supporting Information, Figure S2).[33] The resonances for the $A_2MM'XX'$ spin system are consistent with the displacement of the Ph_3As ligands in **1**$^{2+}$ by Ph_3P, suggesting the formation of dication **4**$^{2+}$ and proving the coordinative nature of the P–As bond in **1**$^{2+}$. The postulated structure was confirmed by X-ray diffraction (Figure 1) and the bond lengths and angles in the [P_4] core of **4**$^{2+}$ are reminiscent of that of cation **1**$^{2+}$, including the exocyclic P1–P5 and P3–P6 bonds (2.223(3) and 2.218(3) Å).

In summary, cation **1**$^{2+}$ results from the one-pot reduction of PCl_3 in the presence of Ph_3As and $AlCl_3$ and can be considered as ligand-stabilized $[P_4]^{2+}$. The ease of this reaction, together with the facile accessibility of **1**[AlCl$_4$]$_2$ from cheap, commercially available starting materials, makes this compound a potential precursor for a plethora of interesting subsequent transformation reactions and may give access to many new, hitherto-unknown polyphosphorus moieties.

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