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Cage Compounds

Phosphacycles as Building Blocks for Main Group Cages**

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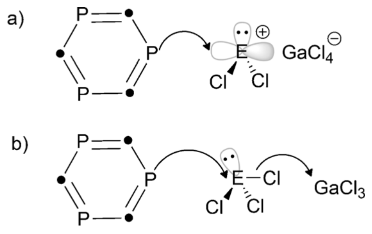
As part of an ongoing interest in phosphorus/carbon compounds[1] we have focused on the reactivity and synthetic utility of possible sources of electrophilic PX_2^+ and AsX_2^+ fragments with a view to accessing novel main group architectures. It has been suggested[2] that there is an analogy between these reactive pnictenium species and carbenes. For example, Krossing and co-workers reported[3] that PX_3 (X = Br, I) reacts in CH_2Cl_2 at −78 °C with $Ag[Al(OR^F)_4]$ ($R^F = C(CF_3)_3$) and P_4 to give the novel phosphorus rich molecules $[P_5X_2][Al(OR^F)_4]$ through a process thought to involve the insertion of the electrophilic carbenoid species $[PX_2][Al(OR^F)_4]$ into a P−P bond of P_4. Allied to this interesting observation is the report by Weigand and co-workers[4] that P_4 reacts, possibly by a similar reaction pathway, in a melt of Ph_2PCl and $GaCl_3$ (1:1 at 60 °C) to form a structurally related molecule $[P_5Ph_2][GaCl_4]$. Similarly, Burford and co-workers have used related methodology to prepare an extensive series of *catena*-phosphorus cations.[5]

In our initial studies we focused on the reaction of 2,4,6-tri-*tert*-butyl-1,3,5-triphosphabenzene (**1**) with latent sources of PX_2^+ and AsX_2^+ cations. It is interesting to note that **1** reacts with the Arduengo-type carbene 1,3,4,5-tetramethylimidazol-2-ylidene to give a ring-contracted 1,2,4-triphosphole,[6] whereas the silicon analogues, stable bis(amine)silylenes, afford (4+1) cycloaddition products.[7] It has also been found experimentally that in the case of the reaction of **1** with sources of H^+, CH_3^+, Me_3Si^+[8] and $[LAu]^+$ [L = P(*t*Bu)$_2$(*o*-biphenyl)],[9] η^1-P-bonded cationic adducts are formed.

As a first step we used density functional theory (see Supporting Information) to compare the relative thermodynamic stabilities of possible products which might result from the reaction of **1** with EX_3 (E = P, As; X = Cl, Br) and the Lewis acid $GaCl_3$. These calculations indicated that under thermodynamic control, a PX_2^+ electrophile could react with **1** to give a η^1-P-bonded adduct. For the phosphenium reagents, alternative products arising from electrophilic attack at carbon, ring contraction (analogous to the product from the reaction with an Arduengo carbene[6]) or 1,2-addition are less favorable. In contrast, for the arsenium systems, although η^1-As coordination is preferred, the energy difference between the alternative products is small. We can in fact envisage a possible reaction pathway to such a η^1-P/As-bonded cation where the reaction of ECl_3 (E = P or As) with $GaCl_3$ leads to the direct formation of the ion-separated electrophilic species $[ECl_2]^+[GaCl_4]^-$, which can then be captured by **1** (Scheme 1 a). However, there is an alternative and perhaps more plausible pathway not involving a free ECl_2^+ cation and that is through a synchronous S_N2 (P/As) push-pull ($GaCl_3$) process as illustrated in Scheme 1 b.[10] This alternative route can be related to the proposal by Wild, Radom, and co-workers that phosphenium cations can be readily transferred between unsaturated moieties with no evidence for the intermediacy of a free cation.[11] Although it might be argued that such processes (Scheme 1 a,b) would involve a loss of aromaticity, it has been shown computationally that **1** acting as a P-donor nucleophile does not significantly attenuate aromaticity.[9]



Scheme 1. E = P, As. ● = C(*t*Bu).

In view of the apparent subtle nature of these reactions we expected that PX_2^+ and AsX_2^+, or latent sources of these electrophiles, might react with **1** in ways which could provide valuable new insights. Reflecting on these ideas, we chose to initially explore experimentally the reaction of **1** in CH_2Cl_2 with $AsCl_3/GaCl_3$ and $AsBr_3/GaCl_3$, which led surprisingly to the formation of novel open-book-shaped cations (Figures 1 and 2). Workup by crystallization from CH_2Cl_2/*n*-hexane afforded colorless crystals of **2** (35 % yield) and **3** (40 % yield) suitable for X-ray diffraction studies[17] (Figure 1). The $^{31}P\{^1H\}$ NMR spectra[12] display three resonances, each a doublet of doublets with those substituted by halogens appearing downfield. In addition, an extra set of three doublet of doublets was observed for **3** as a result of variable halogen (X = Cl or Br) occupancy of the different P1−X sites.

In the $^{31}P\{^1H\}$ (C_6D_6) spectra[12] of the reaction mixture from which **2** and **3** were isolated there were matching doublet and triplet signals attributed to a minor unidentified product, possibly an intermediate. Although there have been a number of studies relating to the reactivity of the **1** with a variety of substrates[6,7,13] the formation of **2** and **3** is without precedent.

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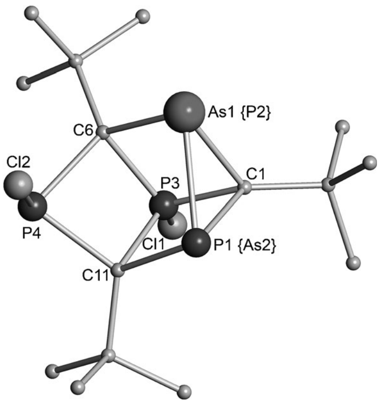


Figure 1. Molecular structure of the cation of **2**. All hydrogen atoms and the anion have been omitted for clarity. There is disorder between the As1 and P1 positions; only the major component of the disordered cation is shown. This disorder makes an analysis of bond dimensions within the P_3C_3As core of limited value and thus this information is not presented here but is available in the Supporting Information.

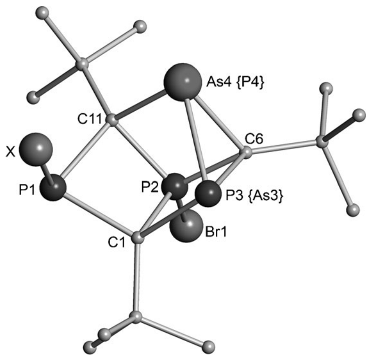


Figure 2. Molecular structure of the cation of **3**. All hydrogen atoms and the anion have been omitted for clarity. There is disorder between the As4 and P3 positions and between halogen atoms (Cl/Br) in the X site and in the GaX_4^- anion; only the major component of the disordered cation is shown. This disorder makes an analysis of bond dimensions within the P_3C_3As core of limited value and thus this information is not presented here but is available in the Supporting Information.

Remarkably, these structures show a trivalent arsenic atom lying above the rearranged $P_3C_3(t\text{Bu})_3$ fragments from the 1,3,5-triphosphabenzene ring, the halogen atoms having migrated from the arsenic to the ring phosphorus atoms, possibly because oxidative addition of AsX_2^+ to **1** would lead to As^V which is known to be is a relatively unstable oxidation state.

In the light of these unexpected findings we next explored whether reaction of **1** with $PCl_3/GaCl_3$ in CH_2Cl_2 would give a tetraphosphorus analogue of **2**. Reaction of **1** at room temperature with a solution of $GaCl_3$ and PCl_3 in CH_2Cl_2 gave, after 6 h and addition of *n*-hexane, a yellow precipitate, assigned to $[P_4Cl_2C_3(t\text{Bu})_3][GaCl_4]$ **4a**. Following anion exchange by reaction with $Na[BAr^F_4]$ ($Ar^F = 3,5$-bis(trifluoromethyl)phenyl) and layering a CH_2Cl_2 solution with *n*-hexane, crystals of the product $[P_4Cl_2C_3(t\text{Bu})_3][BAr^F_4]$ **4b** were obtained. Examination of the $^{31}P\{^1H\}$ and ^1H NMR spectra[12] clearly showed that **4b** (53% yield) was not a tetraphosphorus analogue of **2** and a single crystal X-ray diffraction study[17] showed the product **4b** was in fact a novel apparent (4+1) cheletropic addition product (Figure 3). A similar reaction between $PMeCl_2/GaCl_3$ and **1** afforded **5**, which was also identified by NMR spectroscopy and X-ray crystallography[17] (Figure 4). This new synthetic methodology is illustrated in Scheme 2.

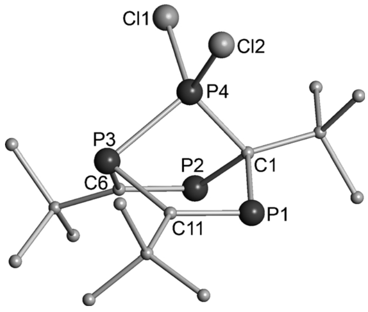


Figure 3. Molecular structure of the cation of **4b**. The anion and hydrogen atoms have been omitted for clarity. Selected bond lengths [Å]: P1–C1 1.885(3), C1–P2 1.900(3), P2–C6 1.681(3), C6–P3 1.849(3), P3–C11 1.845(3), C11–P1 1.685(2), P4–P3 2.1813(8), P4–C1 1.805(2).

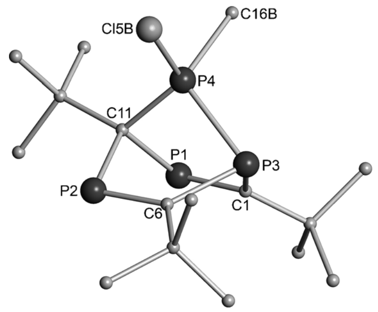
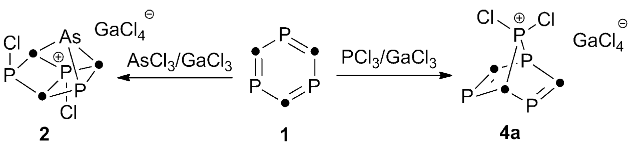


Figure 4. Molecular structure of the cation of **5**. The anion and hydrogen atoms have been omitted for clarity. There is site disorder over Cl5B/C16B in **5**. Selected bond lengths [Å]: C1–P3 1.865(4), P3–C6 1.862(4), P3–P4 2.1767(15), C6–P2 1.680(4), P2–C11 1.905(4), C11–P1 1.899(4), C11–P4 1.816(4), P1–C1 1.676(4).



Scheme 2. ● = C(*t*Bu).

The topology and bond dimensions of the tetraphosphanorbornadiene cations of **4** and **5** are very similar to the products derived from the addition of stable bis(amino)silylenes to **1**.[7] It is also interesting to note that addition of a transient phosphinidene complex to **1** results in a tetraphosphanorbornadiene cage which is in equilibrium with the tetraphosphaquadricyclane isomer.[13c] No corresponding tetraphosphaquadricyclane form was identified for either **4** or **5** under either thermal or photolytic conditions.

In the case of the formation of **4a/b** and **5** it is interesting that **1** does not react with PCl_3 or $PMeCl_2$ in the absence of $GaCl_3$. This contrasts with the formally related (4+1) McCormack reaction;[14] $({}_{\pi}4_s + {}_{\omega}2_s)$ reactions between 1,3-dienes and PCl_3, which do not require the presence of a Lewis acid and which probably involve a linear approach of PCl_3 in a process involving six electrons, that is, a $4n+2$ number. In contrast, the presence of $AlCl_3$ is required for alkynes to react with $RPCl_2$ to give a three-membered phosphirene ring in order to set-up a two-electron ($4n+2$ number) $({}_{\pi}2_s + {}_{\omega}0_s)$ process.[15] These considerations suggest that the formation of **4a** and **5** might involve a ${}_{\pi}6_s + {}_{\omega}0_s$ process requiring the interaction of a latent source of PCl_2^+ or $PMeCl^+$ with an aromatic six-electron 1,3,5-triphosphabenzene. However, there is also the possibility that a η^1-P cationic species is formed initially.

Finally, in the initial exploration of the reaction chemistry of the P_4C_3 cation in **4a**, it is interesting that when this compound is dissolved in tetrahydrofuran at room temperature, PCl_3 and **1** are readily formed.[16] As in the case for the formation of products resulting from the reaction of **1** with bis(amine)silylene, the mechanism of formation of **2–5** remains to be elucidated.

In summary, we have used carbene analogues, latent pnictenium ions, to access unprecedented phosphacyclic structures, which demonstrate differences in reactivity between arsenic and phosphorus systems.

Experimental Section

Typical procedure: $GaCl_3$ (0.03 mmol) and EX_3 (1 equiv) were stirred in CH_2Cl_2 (1 mL) for 5 min prior to the addition of **1** (1 equiv). After the reaction was complete ($^{31}P\{^1H\}$ NMR spectroscopy), the reaction mixture was filtered (porosity 3 sinter with Celite), concentrated in vacuo, and layered with *n*-hexane. Storage for short periods yielded pure crystalline samples of the appropriate product.

2: $^{31}P\{^1H\}$ NMR (C_6D_6, 122 MHz): $\delta = 155.4$ (dd, $J = 148$ Hz and 27 Hz, P3), 85.7 (dd, $J = 148$ Hz and 8 Hz, P4), 80.0 (d, $J = 23$ Hz, intermediate), −68.5 (dd, $J = 27$ Hz and 8 Hz, P1), −80.0 ppm (t, $J = 23$ Hz, intermediate). ^1H NMR (C_6D_6, 500 MHz): $\delta = 1.36$–1.34 (m, 18H, *t*Bu), 1.19–1.17 ppm (m, 9H, *t*Bu).

3: $^{31}P\{^1H\}$ NMR (C_6D_6, 122 MHz): $\delta = 386.0$ (d, $J = 35$ Hz, intermediate), 156.3 (dd, $J = 154$ Hz and 8 Hz, P2′), 153.3 (dd, $J = 162$ Hz and 11 Hz, P2), 74.8 (dd, $J = 154$ Hz and 25 Hz, P1′), 71.7 (dd, $J = 162$ Hz and 24 Hz, P1), 53.4 (t, $J = 35$ Hz, intermediate), −49.8 (dd, $J = 24$ Hz and 11 Hz, P3), −57.7 ppm (dd, $J = 25$ Hz and 8 Hz, P3′). ^1H NMR (C_6D_6, 500 MHz): $\delta = 1.39$–1.34 (2 × m, 18H, *t*Bu), 1.16–1.12 (m, 9H, *t*Bu).

4b: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 122 MHz): $\delta = 305.3$ (dd, $J = 12$ Hz, 6 Hz, P3), 89.1 (dt, $J = 313$ Hz and 6 Hz, P1), −9.4 ppm (dt, $J = 313$ Hz and 12 Hz, P2). ^1H NMR (CD_2Cl_2, 500 MHz): $\delta = 7.72$ (m, 8H, $BAr^F{}_4$), 7.56 (s, 4H, $BAr^F{}_4$), 1.78 (s, 9H, bridgehead *t*Bu), 1.51 ppm (s, 18H, ring *t*Bu).

5: $^{31}P\{^1H\}$ NMR (CD_2Cl_2, 122 MHz): $\delta = 312.0$ (pseudo t, P4), 308 (pseudo t, P3), 110.0 (d, $J = 243$ Hz, P1), −17.0 ppm (dt, $J = 243$ and 17 Hz, P2). ^1H NMR (CD_2Cl_2, 500 MHz): $\delta = 1.76$ (s, 3H, CH_3), 1.56–1.27 ppm (m, 27H, *t*Bu).

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[16] It is of interest that the (4+1) cycloaddition products (see Ref. [6]) obtained on reaction of **1** with bis(amine)silylenes can only be thermally reversed by refluxing (days) in toluene.

[17] Crystal data for **2**: $C_{15}H_{27}AsCl_6GaP_3$, $M = 657.62$, monoclinic, $a = 9.0699(8)$, $b = 25.866(2)$, $c = 11.0925(9)$ Å, $T = 100(2)$ K, space group $P21/n$, $Z = 4$, reflections measured 22468, 5878 unique ($R_{int} = 0.0189$) which were used in all calculations. The final $R1$ $[I > 2\sigma(I)]$ was 0.0215; the final wR_2 was 0.0642 (all data). Crystal data for **3**: $C_{15}H_{27}AsBr_3Cl_3GaP_3$, $M = 791.00$, monoclinic, $a = 9.0574(17)$, $b = 25.620(5)$, $c = 11.665(2)$ Å, $T = 100(2)$ K, space group $P21/n$, $Z = 4$, reflections measured 24082, 6114 unique ($R_{int} = 0.0687$) which were used in all calculations. The final $R1$ $[I > 2\sigma(I)]$ was 0.0410; the final wR_2 was 0.1046 (all data). Crystal data for **4b**: $C_{47}H_{39}BCl_2F_{24}P_4$, $M = 1265.37$, triclinic, $a = 9.9830(4)$, $b = 10.1990(4)$, $c = 13.3878(5)$ Å, $T = 100(2)$ K, space group $P1$, $Z = 1$, reflections measured 23415, 11020 unique ($R_{int} = 0.0302$) which were used in all calculations. The final $R1$ $[I > 2\sigma(I)]$ was 0.0349; the final wR_2 was 0.0997 (all data). Crystal data for **5**: $C_{16}H_{30}Cl_5GaP_4$, $M = 593.25$, monoclinic, $a = 10.092(4)$, $b = 16.196(6)$, $c = 16.948(6)$ Å, $T = 100(2)$ K, space group $P21/n$, reflections measured 24492, 6227 unique ($R_{int} = 0.0920$) which were used in all calculations. The final $R1$ $[I > 2\sigma(I)]$ was 0.0469; the final wR_2 was 0.1038 (all data). CCDC 916855 (**2**), 916856 (**3**), 916857 (**4b**), and 916858 (**5**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.