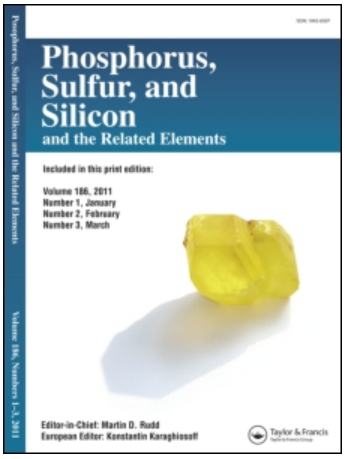


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# Phosphine and phosphinite complexes of P and $P_2$

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# PHOSPHINE AND PHOSPHINITE COMPLEXES OF $P^+$ AND $P_2$

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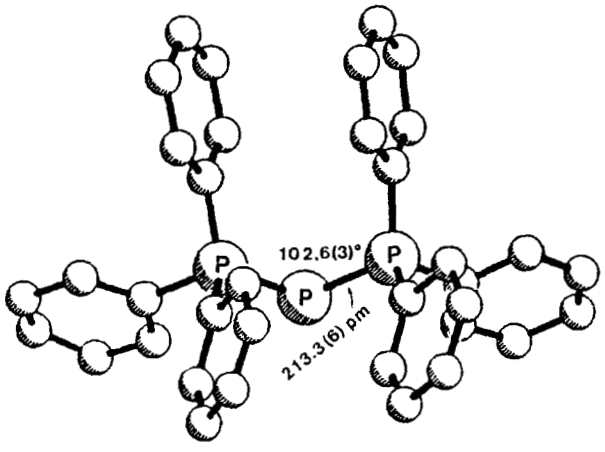
Reduction of $PCl_3$ e.g. with trialkyl phosphines produces the well-known but ill-defined insoluble, amorphous, orange material approximating a phosphorus subchloride. In repeating this reduction with $Ph_3P$ and with $AlCl_3$ as a third component we now obtained crystalline hexaphenyl triphosphenium tetrachloroaluminate. It may be thought to derive from the four electron cation $P^+$ being complexed by two $Ph_3P$.

$$PCl_3 \longrightarrow Ph_3P\text{-}P\text{-}PPh_3^+AlCl_4^- + Ph_3PCl^+AlCl_4^-$$

$$+ 3\ Ph_3P \qquad \delta\ ^{31}P\ +30\ -174 \qquad J_{PP}\ 502\ Hz$$

$$+ 2\ AlCl_3$$

The structure of the cation is in accord with such an interpretation. It shows a PPP angle much smaller than the PNP angle in the homologous $Ph_3P\text{-}N\text{-}PPh_3^+$ (ranging from 135 to 180°). dPP is



half way between the single bond distance (220 - 225 pm) and the distance found in diphosphenes (200 - 203 pm).

The central phosphorus may be protonated or alkylated to yield triphosphine dionium cations. It is also accessible to nucleophilic substitution. Thus triphenylphosphine can be replaced by other phosphines.

$$Ph_3P\text{-}P\text{-}PPh_3^+ \xrightarrow{+MePh_2P/-Ph_3P} MePh_2P\text{-}P\text{-}PPh_3^+ \xrightarrow{+MePh_2P/-Ph_3P} MePh_2P\text{-}P\text{-}PPh_2Me^+$$

| | | | |
|---|---|---|---|
| $\delta\,^{31}P$ | -174 30 | 28 -180 35 | 28 -169 |
| $^{1,2}J_{PP}$ | 502 Hz | 480 482 Hz, 25 Hz | 467 Hz |

$$Ph_3P\text{-}P\text{-}PPh_3^+ \xrightarrow{+(Me_2N)_3P/Ph_3P} (Me_2N)_3P\text{-}P\text{-}PPh_3^+ \xrightarrow{+(Me_2N)_3P/-Ph_3P} (Me_2N)_3P\text{-}P\text{-}P(NMe_2)_3^+$$

| | | | |
|---|---|---|---|
| $\delta\,^{31}P$ | -174 30 | 84 -180 29 | 85 -194 |
| $^{1,2}J_{PP}$ | 502 Hz | 493 523 Hz, 30 Hz | 518 Hz |

With diphos a fivemembered heterocyclic triphosphenium cation is obtained. It can also be prepared directly by reducing $PCl_3$ with $SnCl_2$ in the presence of diphos[2]. Its PPP angle is even below 90°.

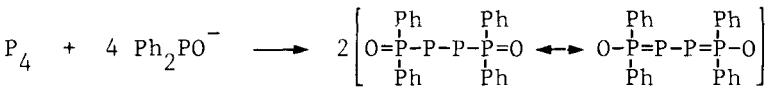
While $P(NMe_2)_3$ and $PCl_3$ otherwise just enter a ligand exchange, they give the hexakis(dimethylamino) triphosphenium ion when sodium tetraphenyloborate is added as a third component.

$$PCl_3 + 3\ P(NMe_2)_3 + 2\ NaBPh_4 \longrightarrow (Me_2N)_3P\text{-}P\text{-}P(NMe_2)_3^+\,BPh_4^- + (Me_2N)_3PCl^+\,BPh_4^- + 2\ NaCl$$

$\delta\,^{31}P$ 85 -194; $J_{PP}$ 518 Hz

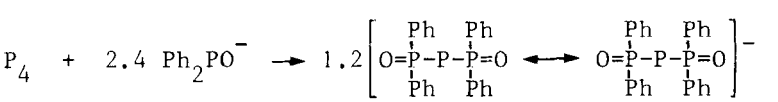
Its $P^+$ center can be transfered to and inserted into an electron-rich olefin to give novel phosphaallyl cations[3].

A second source of $P^+$ could be the oxidation or just disproportionation of $P_4$. To degrade $P_4$ it takes a stronger nucleophile and instead of a phosphine a phosphinite is used. Its action on $P_4$ gives a tetraphosphinate which may be understood as the ten electron $P_2$ unit stabilized by two phosphinite anions.



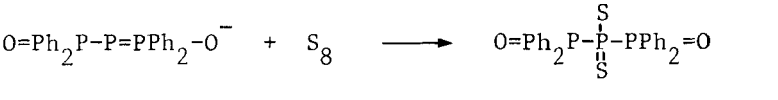
$\delta^{31}P$ +69 -183 $J_{PP}$ 573 268 Hz

If the relative amount of phosphinite is reduced, the $P_2$ unit enters a disproportionation to give a triphosphinate (i.e. $P^+$ complexed by two phosphinite ions), and $P_7^{3-}$ or higher polyphosphides up to $P_{16}^{2-}$; this corresponds to a range of 12/5 to 8/9 $Ph_2PO^-$ per $P_4$. If still less phosphinate is used, unreacted white phosphorus is left.

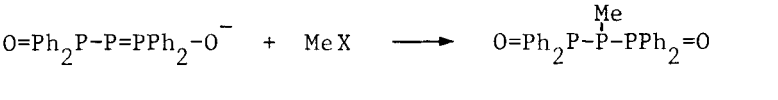


$\delta^{31}P$ +56 -116 $J_{PP}$ 398 Hz

The triphosphinate is a most stable representative of the dicoordinate phosphorus resisting the attack of water and oxygen. It may though be oxidized by sulfur and it may be alkylated to give triphosphine 1,3-dioxides.

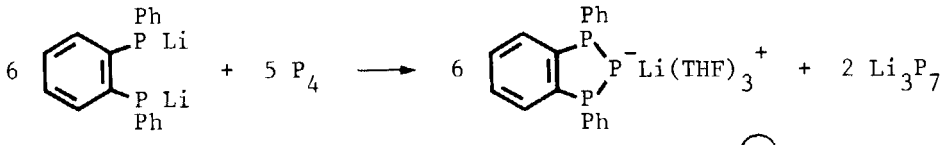


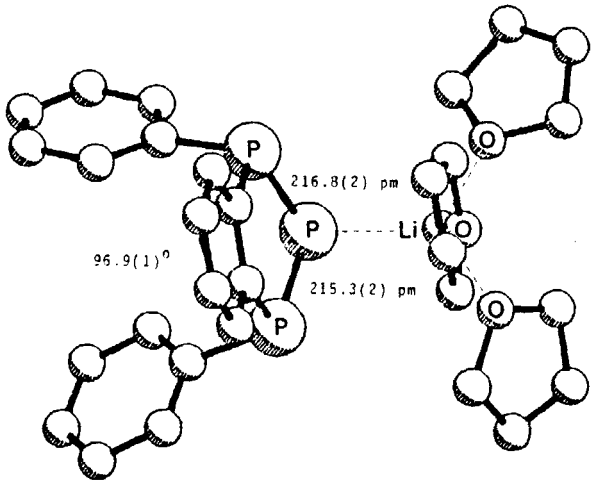
$\delta^{31}P$ +22 +58 $J_{PP}$ 33 Hz



$\delta^{31}P$ +42 -64 $J_{PP}$ 236 Hz

Similar $P_4$ disproportionations can be accomplished by phosphides instead of phosphinites. Diphenyl phenylenediphosphide[4] thus gives a cyclic triphosphide.




By ligand exchange cyanophosphinidene phosphates (i.e. $P^+$ complexed by $R_2PO^-$ and $CN^-$) may be obtained from dicyanophosphide[5].

$$P(CN)_2^- + Ph_2PO^- \longrightarrow O{=}Ph_2P{-}P{-}CN^- + CN^-$$

$\delta\,^{31}P$ +56 −161 $J_{PP}$ 362 Hz

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