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FIRST SYNTHESIS OF PENTACOORDINATED PHOSPHIRENES[1]

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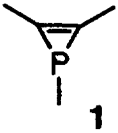
Abstract: 1-Halo- and 1-cyano-1*H*-phosphirenes **8a**-**d** react with tetrachloro-*o*-quinone (**9**) by oxidative addition at phosphorus to furnish the previously unknown title compounds **10a**-**d**. The chlorine atom in the pentacoordinated phosphirene **10a** undergoes nucleophilic exchange reactions yielding **10c**-**e**.

1*H*-Phosphirenes were first prepared in 1982 as the chromium or tungsten carbonyl complexes (**1**; P→Cr(or W)(CO)$_5$ in place of P) by Mathey and coworkers[2]. Since then, the complexes as well as the metal-free compounds **1** themselves have found many uses in the syntheses of organophosphorus compounds[3]. On the other hand, there was previously no conclusive evidence for the existence of the pentacoordinated phosphirenes **2**.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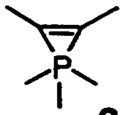
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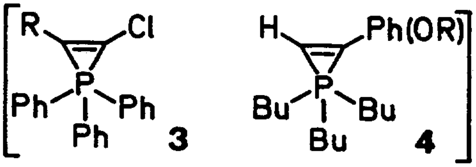
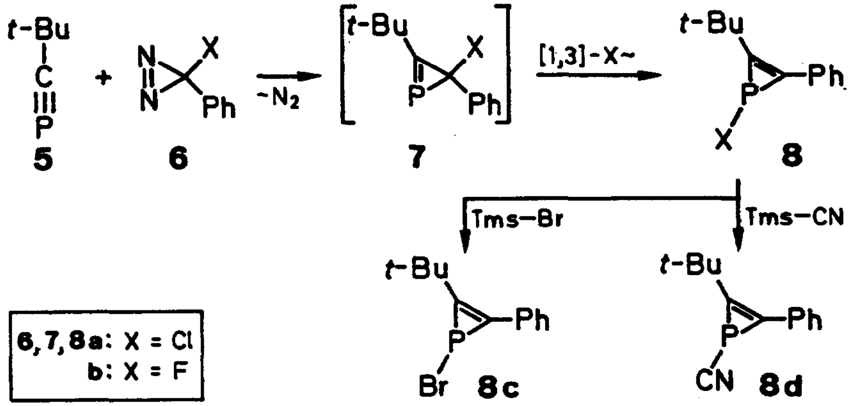


3 **4**

The products from the reactions of Ph$_3$P with CHCl$_3$/*t*-BuOK and aldehydes were assigned the structure **3**[4], but are almost certainly the isomeric alkynyl(triphenyl)phosphonium chlorides $(Ph_3P\text{-}C\equiv C\text{-}R)^+\ Cl^-$ (Ref.[5]). The existence of λ^5-phosphirenes of the type **4**, which were claimed to be formed by [2+1]-cycloaddition reactions of tributylphosphine with phenyl- or alkoxyacetylenes[6] is equally uncertain. The assumption of a λ^5-phosphirene structure from the *in situ* reactions of the products with electrophiles RX to furnish open-chain vinylphosphonium salts like $(Bu_3P\text{-}CPh(\text{or } OR)\text{=}CHR)^+\ Cl^-$ is premature in the absence of spectroscopic evidence[5]. We now report the first synthesis of an unambiguously characterized, pentacoordinated phosphirene.

Starting materials for the synthesis of **10** are the 1*H*-phosphirenes **8a**-**d**; **8a** had previously been prepared by us from **5** and chlorophenylcarbene (generated thermally from the diazirine **6a**). The 2*H*-phosphirene **7a** is certainly formed initially and then undergoes a 1,3-chlorine shift to yield **8a**[7].

The 1-fluoro-1*H*-phosphirene **8b** was prepared from **5**[8] and **6b**[9] analogously (160 °C, under pressure, Schlenk tube, bulb-to-bulb distillation)[10]. The 1*H*-phosphirenes **8c** and **8d** were obtained directly by nucleophilic exchange of the chlorine in **8a** using bromo- and cyanotrimethylsilane (excess, 20 °C, separation by distillation), respectively[10].



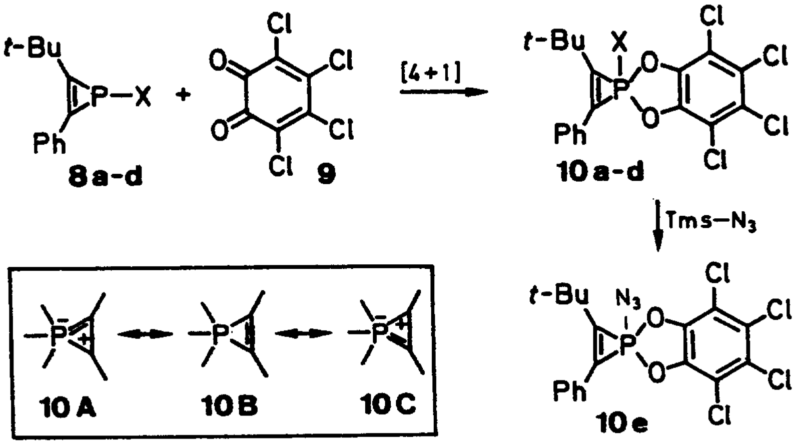
The increase in the coordination at phosphorus was realized by reaction of 8a–d with tetrachloro-*o*-quinone (9) in ether (if necessary in a gas pressure vessel, Table 1). Products 10a, c, d were obtained as colourless crystals while 10b separated as a colourless oil. Similar to the 1*H*-phosphirene 8a, the chlorine atom in the pentacoordinated phosphirene 10a can also be exchanged nucleophilically at room temperature (albeit more slowly) by treatment with bromo- and cyanotrimethylsilane to furnish 10c, d; the azide group in 10e can be introduced in an analogous manner.

The carbon atoms of the three-membered ring (Ph-C: δ = 163.4-171.3; *t*-Bu-C: δ = 171.6-180.0), which can be recognized readily on account of the small ${}^3J$(C,H) couplings in the proton-coupled spectra, appear at rather low field and can thus be compared with those of cyclopropenylium salts. Electron

Table 1. Reaction conditions, purification, yields, and NMR data for the λ^5-phosphirenes 10a–e.

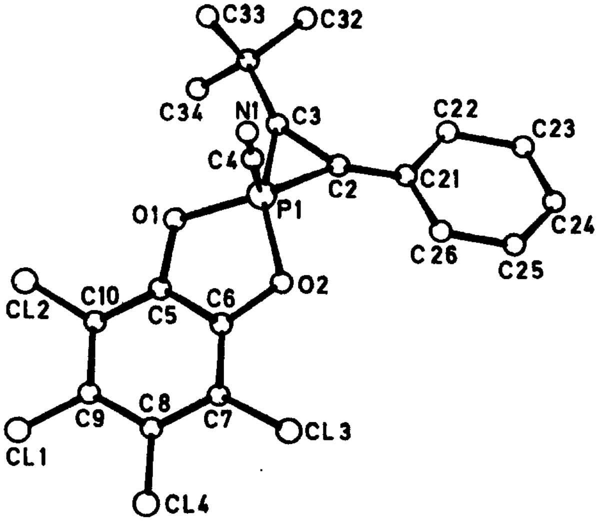
Product	Reaction conditions (purification)	Yield [%]	^{31}P-NMR[a] δ [ppm]	^{13}C-NMR[b] *t*-Bu-C	δ [ppm] Ph-C
10a	ether, 7 h, 40-45 °C	31	-82.2	178.8	169.2
(X = Cl)	(from CH_2Cl_2 at -78 °C)			(21.7)	(11.7)
10b	ether, 10 h, 40-45 °C	25	-69.8[c]	176.3	166.6
(X = F)	(MPLC, ether/hexane)			(35.6)[d]	(25.2)[d]
10c	ether, 0.5 h, 25 °C	27	-106.3	180.0	171.3
(X = Br)	(from ether at 25 °C)			(16.8)	(4.9)
10d	ether, 7 h, 35-40 °C	72	-126.6	171.6	163.4
(X = CN)	(from hexane at +7 °C)			(26.0)	(14.6)
10e	excess Tms-N_3, 25 °C[e]	100[f]	-85.4	175.9	165.4
(X = N_3)	(no purification)[f]			(25.1)	(15.1)

[a] $CDCl_3$, 85% phosphoric acid as external standard.
[b] $CDCl_3$, TMS as internal standard, ${}^1J$(P,C) coupling [Hz] in brackets.
[c] ${}^1J$(P,F) = 1108 Hz.
[d] ${}^2J$(C,F) = 8.5 (*t*-Bu-C) or 10.3 Hz (Ph-C).
[e] Transformation of 10b to 10e.
[f] Removal of volatiles under vacuum ($1 \cdot 10^{-2}$ mbar) furnishes 10e.



transfers according to **10A** ⟷ **10B** ⟷ **10C** could explain this phenomenon. The ^1J(P,C) couplings of the respective carbon atoms are markedly smaller than those of the 1H-phosphirenes **1**[7,11]. An increase of the coordination at phosphorus by one only through complex formation has the same result.

A crystal structure analysis performed on **10d** confirmed the constitution of the pentacoordinated phosphirene. A highly distorted, square pyramidal arrangement at phosphorus was found; the two carbon atoms of the three-membered ring and the oxygen atoms of the o-quinone form the base while the cyanide carbon atom occupies the apex (Fig. 1).



Selected bond lengths [Å] and angles [°]: P1-O1 1.668(3), P1-O2 1.700(3), P1-C2 1.709(4), P1-C3 1.715(4), P1-C4 1.784(4), O1-C5 1.371(5), O2-C6 1.351(5), N1-C4 1.126(6), C2-C3 1.360(6), C5-C6 1.374(6). O1-P1-O2 90.3(1), O1-P1-C2 140.4(2), O1-P1-C3 104.4(2), O1-P1-C4 102.0(2), O2-P1-C2 104.1(2), O2-P1-C3 146.8(2), O2-P1-C3 146.8(2), O2-P1-C4 97.3(2), C2-P1-C3 46.8(2), C2-P1-C4 112.3(2), C3-P1-C4 108.2(2).

Fig.1. Crystal structure and selected structural parameters of the λ^5-phosphirene **10d**[13].

The intracyclic distances in the three-membered ring unit are worthy of note: the markedly lengthened C/C double bond [1.360(6) Å] as well as the comparatively short P/C bonds [1.790(4) and 1.715(4) Å] as compared to the corresponding bonds in e.g. **8a** [1.303(5) Å, 1.784(4) and 1.781(4) Å][14] or in triphenyl-1H-phosphirene[11b] again emphasize the importance of the ylide structures **10A**, **10C** for the description of the pentacoordinated phosphirene.

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10. **8b**: ^{31}P-NMR ($CDCl_3$): $\delta = -48.4$ (d, $^{1}J(P,F) = 993$ Hz); ^{19}F-NMR ($CDCl_3$, C_6F_6 int. std.): $\delta = 17.0$ (d, $^{1}J(F,P) = 993$ Hz). **8c**: ^{31}P-NMR ($CDCl_3$): $\delta = -61.4$. **8d**: ^{31}P-NMR ($CDCl_3$): $\delta = -232.4$; IR (KBr): $\nu = 2145$ cm^{-1} (C≡N).
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13. $C_{19}H_{14}Cl_4NO_2P$, monoclinic, space group: $P2_1/n$, $a = 8.812(2)$, $b = 17.511(5)$, $c = 14.146(4)$ Å, $\beta = 108.02(2)^\circ$, $T = 20$ °C, $Z = 4$, $d_{calc} = 1.48$ g·cm^{-1}, Enraf-Nonius CAD 4 diffractometer, monochromatic MoK_α irradiation, 3591 independent reflections with $4.0 \leq 2\theta \leq 50.0^\circ$, absorption correction ($\mu = 6.623$ cm^{-1}), complete matrix refinement with 2705 reflections [$I > 2\sigma(I)$] and 244 variables, $R = 0.047$, $R_W = 0.044$. Atomic coordinates, tables of bond lengths and angles, and structural data are available on demand from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW, U.K. Each request should be accompanied by the complete citation of this publication.
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