# *X*-Ray Crystal Structure of a Phosphirenium Ion

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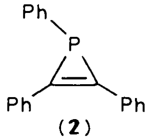
The first *X*-ray crystal structure of a phosphirenium ion is reported and comparison with the structures of neutral phosphirenes indicates cyclic delocalisation in the phosphirenium ion.

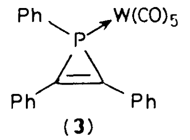
Hogeveen and co-workers reported the first synthesis of phosphirenium ions *via* the addition of $RPCl_2$–$AlCl_3$ complexes to a series of alkynes in 1983.[1] Subsequently, Breslow and Deuring extended this type of reaction to include $R_2PCl$–$AlCl_3$ complexes.[2] The interest in phosphirenium ions stems from the possibility of 'Hückel-type three-orbital two-electron delocalization characteristic of cyclopropenyl cations.'[2] However, on the basis of chemical and thermal instability, low propensity to formation *via* quaternisation,[3] and theoretical calculations,[4] Mathey *et al.* have questioned the aromaticity of this ring system.[5] To address, at least in part, the question of delocalisation, we sought to characterise the structure of a phosphirenium ion. We now report a single-crystal *X*-ray study of 1-di-isopropylamino-2,3-diphenyl-1-(2-chloro-1,2-diphenylvinyl)phosphirenium tetrachloroaluminate (**1**), and present the first structural data for a phosphirenium ion.



(**2**)

av. P–C = 1.820(2) Å

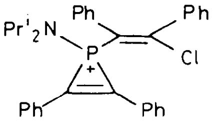
C–C = 1.299(3) Å



(**3**)

av. P–C = 1.788(4) Å

C–C = 1.307(6) Å



(**1**)

av. P–C = 1.731(12) Å

C–C = 1.36(2) Å

Compound (**1**) was prepared by the addition of diphenylacetylene to chloro(di-isopropylamino)phosphenium tetrachloroaluminate in dry $CH_2Cl_2$, and suitable crystals were grown by allowing hexane to diffuse into a $CH_2Cl_2$ solution of (**1**) at −35 °C.[†] The ORTEP diagram for (**1**) is presented in Figure 1.

It is of interest to compare the structural parameters for the $C_2P$ ring of (**1**) with those of 1,2,3-triphenylphosphirene (**2**)[6]

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[†] *Crystal data* for (**1**): $C_{34}H_{34}AlCl_5NP$, monoclinic, space group $P2_1/n$ (No. 14), $a$ = 15.286(3), $b$ = 8.851(3), $c$ = 27.001(4) Å, $\beta$ = 104.24(1)°, $U$ = 3540.6 Å$^3$, $Z$ = 4, $D_c$ = 1.298 g cm$^{-3}$, $\mu$(Mo-$K_\alpha$) = 5.04 cm$^{-1}$. Data were collected on an Enraf-Nonius CAD-4 diffractometer over the range $3.0 \leqslant 2\theta \leqslant 46.0°$ at 298 K. From a total of 4928 unique reflections, 1901 [$I > 3\sigma(I)$] were considered observed and used to solve (direct methods) and refine (full-matrix, least-squares) the structure of (**1**). The least-squares refinement converged smoothly to give residuals $R$ = 0.0677 and $R_w$ = 0.0751. Atomic co-ordinates, bond lengths and angles, and thermal parameters have been deposited at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

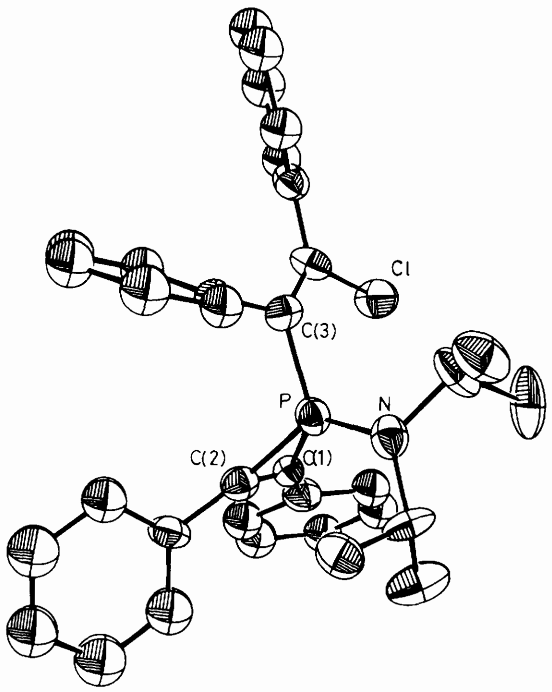

**Figure 1.** ORTEP diagram of the *X*-ray crystal structure of (**1**). Selected bond lengths and angles: P–C(1) 1.732 (11); P–C(2) 1.730 (12), P–C(3) 1.799 (10), P–N 1.640 (10), C(1)–C(2) 1.36 (2) Å; P–C(1)–C(2) 66.9 (7), P–C(2)–C(1) 67.0 (7), C(1)–P–C(2) 46.1 (5)°. The angle between the C(1)–P–C(2) and N–P–C(3) planes is 91.3°.

and its $W(CO)_5$ complex (**3**).[7] In (**2**), the presence of a phosphorus lone pair confers anti-aromatic character[8] on the ring resulting in relatively long P–C bonds and an olefinic carbon–carbon bond length. In (**3**), the phosphorus lone pair is co-ordinated to a $W(CO)_5$ fragment. However, the P(3d) orbital is involved in π-acceptance from the W; consequently, the aromatic character of the $C_2P$ ring is slight as reflected by only modest changes in the P–C and C–C bond lengths. In (**1**), the presence of a formal positive charge at phosphorus renders the P(3d) orbitals more effective for Hückel-type interaction with the C(2p) orbitals. In fact, the average P–C distance of 1.731(12) Å corresponds roughly to a bond order of 1.5.

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