Reaction of a Halogenophosphenium Ion with Cyclo-octa-1,5-diene; Direct Synthesis and *X*-Ray Crystal Structure of a Phosphetane Moiety

Steven A. Weissman,[a] S. G. Baxter,*[a] Atta M. Arif,[b] and Alan H. Cowley*[b]

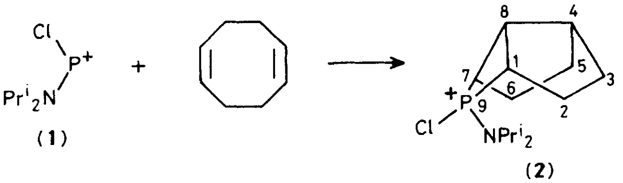
[a] *Fred Stark Pearson Memorial Laboratory, Department of Chemistry, Tufts University, Medford, Massachusetts 02155, U.S.A.*

[b] *Department of Chemistry, The University of Texas at Austin, Austin, Texas 78712, U.S.A.*

Chloro(di-isopropylamino)phosphenium tetrachloroaluminate reacts with cyclo-octa-1,5-diene to afford the phosphetanium salt, 9-chloro-9-di-isopropylamino-9-phosphoniatricyclo[5.1.1.0^{4,8}]nonane tetrachloroaluminate, as confirmed by *X*-ray crystallography.

It has been noted by Quin[1] that 'there is a clear need for new approaches to phosphetanes.' We have observed that phosphenium ions (R_2P^+)[2] can be utilised to synthesise a number of interesting phosphorus-containing heterocycles.[3] We now report the addition of chloro(di-isopropylamino)phosphenium ion (**1**) to cyclo-octa-1,5-diene (COD) to yield 9-chloro-9-di-isopropylamino-9-phosphoniatricyclo[5.1.1.0^{4,8}]nonane tetrachloroaluminate (**2**), a structure which contains the phosphetane ring system (Scheme 1).

Dropwise addition of COD (12.5 mmol, ~3.6 M in CH_2Cl_2) to a stirred solution of (**1**) (12.5 mmol, ~0.4 M in CH_2Cl_2) cooled in an ice–water bath produced a cloudy yellow mixture. On warming to room temperature, the mixture became clear, and, after stirring for 2 h, ^{31}P n.m.r. spectroscopy indicated that the reaction was complete, with one major absorption being present at δ 79.4 p.p.m. Removal of solvent yielded crude (**2**), and pure crystals were obtained by allowing pentane to diffuse into a CH_2Cl_2 solution of (**2**) at −35 °C.†



Scheme 1

---

† Satisfactory elemental analyses were obtained. ^{13}C N.m.r. δ(CD_2Cl_2, room temp., *J* in Hz): 22.99 (d, $J_{Me,P}$ 7.0, CH*Me*$_2$), 30.31 (d, J_{CP} 7.7, 2-, 6-, or 3-, 5-C), 35.13 (d, J_{CP} 11.2, 3-, 5- or 2-, 6-C), 47.46 (d, J_{CP} 16.5, 4- or 8-C), 49.91 (d, J_{CP} 14.9, 8- or 4-C), 51.01 (s, *C*HMe$_2$), and 58.67 (d, J_{CP} 58.3, 1-, 7-C).

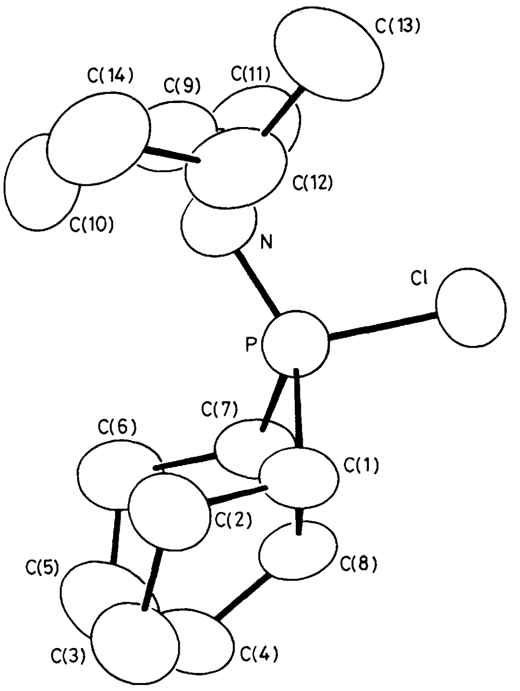


Figure 1. ORTEP drawing of the *X*-ray crystal structure of (**2**). Selected bond lengths (Å) and angles (°): P–Cl, 2.017(5); P–N, 1.606(11); P–C(1), 1.821(11); P–C(7), 1.820(15); C(1)–C(8), 1.57(2); C(7)–C(8), 1.61(2); P–C(1)–C(8), 85.2(7); P–C(7)–C(8), 84.0(8); C(1)–P–C(7), 85.2(6); C(1)–C(8)–C(7), 101.(1).

Since unambiguous assignment of the orientation of the substituents on P is impossible by n.m.r. spectroscopy alone, and the pucker of the phosphetane moiety is of interest, the *X*-ray crystallographic structure determination of (**2**) was undertaken (see Figure 1).‡ At first glance the orientation of the bulky $\mathrm{Pr^i{}_2N}$ group *cis* to the three carbon substituents on the phosphetane ring may seem somewhat surprising. However, examination of a large number of phosphetane crystal structures reveals that a major consideration in the direction of their pucker is the minimization of 1,3-diaxial interactions.[1] Thus, a possible explanation for the observed orientation of the $\mathrm{Pr^i{}_2N}$ group is that the polycyclic skeleton constrains the phosphetane ring to be puckered [dihedral angle between C(1)C(7)C(8) and C(1)PC(7) 22.4°] such that the P is bent away from C-3, C-4, and C-5 and that only in the *cis*-orientation can the $\mathrm{Pr^i{}_2N}$ group occupy a pseudoequatorial position. Support for this notion is found in the pronounced ring pucker in the same direction in 1-isopropyl-4,6-dimethyl-6λ^5-phosphabicyclo[3.1.1]-hept-3-ene 6-oxide (41°),[4a] 4-methyl-4-*p*-nitrobenzyl-4-phosphoniatetracyclo[3.3.0.0.^{2,8}.0^{3,6}]octane bromide (46.6°),[4b] and {3,4-bis(methoxycarbonyl)-1,5-dimethyl-7-phenyl-7-phosphatricyclo[3.2.0.0^{4,6}]hept-2-ene}pentacarbonyl-chromium (26.3°).[4c]

Since singlet phosphenium ions feature a lone pair and a formally vacant p-orbital at phosphorus,[2d] these species behave like electrophilic carbenes in their reactions with 1,3- and 1,4-dienes.[3a—c] However, the present result implies that phosphenium ions can also exhibit a carbocation-like behaviour.§ We have no experimental evidence bearing on the mechanism; however, the intermediacy of the bicyclo[3.3.0]octan-1-yl carbenium ion[5] is regarded as highly probable. Further support for the carbocation-like behaviour stems from the fact that only halogenophosphenium ions will react with cyclo-octa-1,5-diene. Thus, $\mathrm{(R_2N)_2P^+}$ ions, which feature a smaller positive charge at phosphorus, are unreactive towards this substrate.¶

We are grateful to the National Science Foundation, the Robert A. Welch Foundation, and the donors of the Petroleum Research Fund, administered by the American Chemical Society, for financial support.

Received, 6th March 1986; Com. 301

References

1 L. D. Quin, 'The Heterocyclic Chemistry of Phosphorus,' Wiley-Interscience, New York, 1981.

2 (a) B. E. Maryanoff and R. O. Hutchins, *J. Org. Chem.*, 1972, **37**, 3475; (b) S. Fleming, M. K. Lupton, and K. Jekot, *Inorg. Chem.*, 1972, **11**, 2534; (c) M. G. Thomas, C. W. Schultz, and R. W. Parry, *ibid.*, 1977, **16**, 994; (d) For a review see: A. H. Cowley and R. A. Kemp, *Chem. Rev.*, 1985, **85**, 367.

3 (a) C. K. SooHoo and S. G. Baxter, *J. Am. Chem. Soc.*, 1983, **105**, 7443; (b) A. H. Cowley, R. A. Kemp, J. G. Lasch, N. C. Norman, and C. A. Stewart, *ibid.*, 1983, **105**, 7444; (c) A. H. Cowley, C. A. Stewart, B. R. Whittlesey, and T. C. Wright, *Tetrahedron Lett.*, 1984, **25**, 815; (d) S. A. Weissman, S. G. Baxter, A. M. Arif, and A. H. Cowley, *J. Am. Chem. Soc.*, 1986, **108**, 529.

4 (a) E. Vilkas, M. Vilkas, D. Joniaux, and C. Pascard-Billy, *J. Chem. Soc., Chem. Commun.*, 1978, 125; (b) Mazhar-ul-Haque, M. Rashid, and S. E. Cremer, *J. Chem. Soc., Perkin Trans. 2*, 1978, 1115; (c) A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *Nouveau J. Chim.*, 1984, **8**, 453.

5 G. A. Olah, J. M. Bollinger, and D. P. Kelly, *J. Am. Chem. Soc.*, 1970, **92**, 1432; G. A. Olah and G. Liang, *ibid.*, 1971, **93**, 6873; G. A. Olah, G. Liang, and P. W. Westerman, *J. Org. Chem.*, 1974, **39**, 367.

---

‡ *Crystal data* for (**2**): $\mathrm{C_{14}H_{26}AlCl_5NP}$, a = 17.965(2), b = 8.342(2), c = 15.492(3) Å, β = 109.16(1)°, U = 2187.0 Å^3, monoclinic, space group $C2$ (No. 5), Z = 4, D_c = 1.347 g cm^{-3}, $\mu(\text{Mo-}K_\alpha)$ = 7.56 cm^{-1}. Data were collected on an Enraf–Nonius CAD-4 diffractometer over the range $3.0 < 2\theta < 48.0°$ at 293 K. From a total of 1855 unique reflections, 1197 [$I > 3\sigma(I)$] were considered observed and used to solve (direct methods) and refine (full-matrix, least-squares) the structure of (**2**). The least-squares refinement converged smoothly to give residuals R = 0.0555 and R_w = 0.0626. 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, 1986.

§ It is well known that $\mathrm{PCl_3/AlCl_3}$ mixtures will react with alkenes. However, there is no direct evidence to support the concept that $\mathrm{P^{III}}$ halides form $\mathrm{P^+}$ ions with $\mathrm{AlCl_3}$. For further discussion, see ref. 1.

¶ The relative charges at phosphorus can be inferred from, *e.g.*, ^{31}P n.m.r. chemical shifts. See ref. 2d.