Synthesis and *X*-Ray Crystal Structure of 1,2,3-Triphenylphosphirene

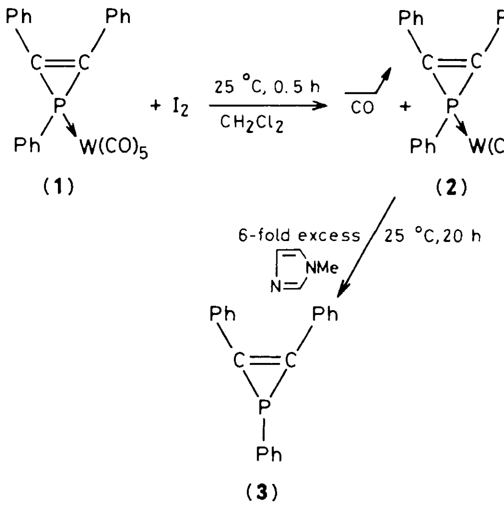
Angela Marinetti,[a] François Mathey,*[a] Jean Fischer,[b] and André Mitschler[b]

[a] *Laboratoire CNRS-SNPE, 2—8 rue Henry Dunant, Boite Postale 28, 94320 Thiais, France*
[b] *Laboratoire de Cristallochimie, ERA 08, Institut Le Bel, Université Louis Pasteur, 67070 Strasbourg Cedex, France*

1,2,3-Triphenylphosphirene is prepared from its P→W(CO)$_5$ complex by a two step decomplexation procedure involving iodine and 1-methylimidazole; its *X*-ray crystal structure analysis shows a very strained ring (< CPC = 41.8°) with no electronic delocalization.

The heterocyclic analogues of cyclopropene $\overline{-C=C-X}$ have been shown to be highly unstable whenever the heteroatom bears a lone pair which can interact efficiently with the carbon–carbon double bond. Such is the case with 1*H*-azirines (X = NR) which rearrange to 2*H*-azirines, and with thiirenes (X = S)[1] and oxirenes (X = O)[2] which can be studied only in matrices at very low temperatures. In contrast, whenever the heteroatom is electron deficient (electronic sextet, positive charge, low lying empty d orbitals[3]), these species acquire some stability. Such is the case with borirenes (X = Br),[4] thiirenium salts (X = $\overset{+}{S}$R),[5] silirenes (X = SiR$_2$),[6,7] and germirenes (X = GeR$_2$).[8] In this context, the phosphirene case (X = PR) is especially interesting since here two types of interaction can be envisaged: firstly, a destabilizing interaction between the lone pair at phosphorus and the carbon–carbon double bond; secondly, a stabilizing interaction between the empty 3d orbitals of appropriate symmetry at phosphorus and the carbon–carbon double bond. Thus, it was difficult to predict whether tervalent phosphirenes would be stable or not.

Up to now, only two reliable approaches for building the phosphirene ring have been described in the literature. The first allows the synthesis of phosphirene P→M(CO)$_5$ complexes (M = Cr, W)[9] and the second the synthesis of 1-chlorophosphirenium salts [X = $\overset{+}{P}$(R)Cl].[10] Since the phosphirene complexes are very stable and easy to handle, we selected them as starting materials for the synthesis of free tervalent phosphirenes. Our preliminary attempts were carried out on the 1,2,3-triphenylphosphirene P→W(CO)$_5$ complex (**1**). The decomplexation procedure followed the same general pattern as for the decomplexation of R$_3$P→Fe(CO)$_4$ complexes.[11] In the first step, the P-metal bond was weakened by increasing the oxidation state of the metal using iodine, which caused the transformation of (**1**) to (**2**), with the release of CO (1 equiv.).[12]



Complex (**2**) was precipitated by adding hexane and cooling the reaction mixture. Its formula was established by C, H, I, P, and W elemental analysis and i.r. spectroscopy [ν(CO) : 2080s, 2025vs, 1997s,br, and 1962s,br cm^{-1} in CH$_2$Cl$_2$]. That the phosphirene ring and the P–W bond are both preserved in this complex is obvious from the ^{31}P n.m.r. data [δ(^{31}P) −175.3 p.p.m. in CH$_2$Cl$_2$, ^1J(^{31}P–^{183}W) 180.7 Hz]. 1,2,3-Triphenylphosphirene (**3**) was then displaced from (**2**) by reaction with 1-methylimidazole. When both steps were carried out *in situ*, the overall yield of (**3**) from (**1**) was *ca.* 60%. The phosphirene† was purified by chromatography on silica gel with hexane–ether (97.5 : 2.5); it is stable at room temperature. Its half-life at 90 °C in toluene is greater than 17 h. It shares many n.m.r. spectroscopic characteristics with phosphiranes[13] including a ^{31}P chemical shift at very high field and large ^1J(P–C) coupling constants. It reacts cleanly at room temperature with sulphur in the presence of 1-methylimidazole as a catalyst[14] to give (**4**) [δ(^{31}P)(C$_6$D$_6$ −79 p.p.m.] and with Fe$_2$(CO)$_9$ at 50 °C to give (**5**) [δ(^{31}P) (toluene) −92 p.p.m.]. The sulphide (**4**) appears to have low stability in solution and all attempts at preparing the corresponding oxide have failed so far.

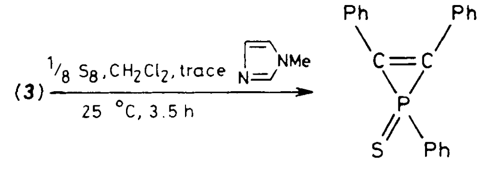
In order to understand the reasons underlying the relative stability of (**3**), we carried out its *X*-ray crystal structure analysis.‡ Principal geometrical data are given in the caption of Figure 1. The heteroatomic ring can be compared to that described in the complexed form.[9] The intracyclic P–C bonds are about 0.03 Å longer in the uncomplexed ring and become almost as long as a normal P–C σ bond. The C=C double bond remains well localized, whereas the C–P–C intracyclic bond

---

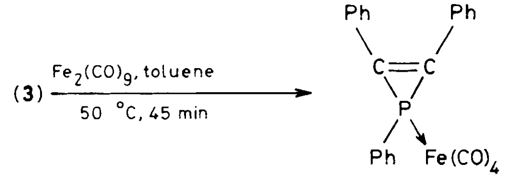
† (**3**): m.p. 73 °C (hexane); δ (^{31}P) n.m.r. (C$_6$D$_6$) − 190.3 p.p.m.; δ (^{13}C) n.m.r. (CDCl$_3$) 122.65 [d, ^1J(C–P) 43.9 Hz, ring C–P] and 141.96 p.p.m. [d, ^1J(C–P) 64.4 Hz, phenyl C–P]; mass spectrum (electron impact, 70 eV) *m/z* 286 (*M*, 100%), 209 (*M*−Ph, 26), 178 (Ph$_2$C$_2$, 24), 108 (PhP, 16), and 107 (25).

‡ *Crystal data for* (**3**): C$_{20}$H$_{15}$P, M = 286.32, triclinic, a = 10.015(3), b = 10.144(3), c = 9.155(3) Å, α = 110.94(2), β = 114.65(2), γ = 84.71(2)°, U = 787.7 Å^3, Z = 2, D_c = 1.207 g cm^{-3}, space group $P\bar{1}$ (No. 2), Cu-K_α (1.5418 Å) radiation, μ = 14.39 cm^{-1}, $F(000)$ = 300. Intensity data were collected with a Philips PW 1100/16 diffractometer using the θ/2θ flying step-scan technique. The intensities of 2078 reflections were measured within 0.056 <sin θ/λ <0.544. The structure was solved using direct methods and refined by full matrix least-squares techniques using the 1637 unique reflections having $F^2 > 3\sigma(F^2)$. The final values of $R_1(F)$ and $R_2(F)$ are 0.056 and 0.073 respectively. The estimated standard deviation of a unit weight observation is 1.67.

The atomic co-ordinates of this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication. The structure factor table is available as Supplementary Publication No. SUP 23821 (8 pp.) from the British Library Lending Division. For details, see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1983, issue 3, p. xvii.



(4)



(5)

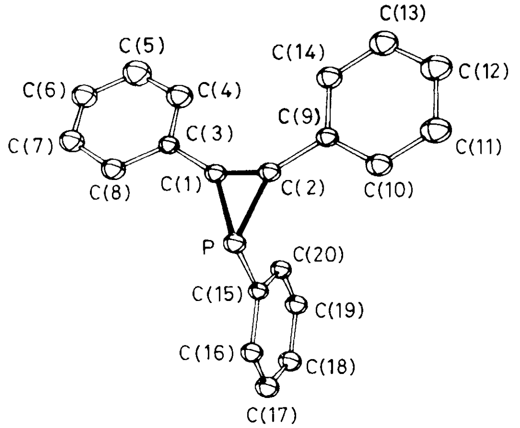


Figure 1. Structure of compound (**3**). Ellipsoids are scaled to enclose 30% of the electronic density; hydrogen atoms are omitted. Principal distances (Å): C(1)–C(2) 1.299(3), P–C(1) 1.820(2), P–C(2) 1.821(3), P–C(15) 1.842(2), C(1)–C(3) 1.456(3), C(2)–C(9) 1.456(3). Selected bond angles (°): C(1)–P–C(2) 41.8(1), P–C(1)–C(2) 69.1(1), P–C(2)–C(1) 69.1(1), C(1)–P–C(15) 104.4(1), C(2)–P–C(15) 104.0(1), P–C(1)–C(3) 142.7(2), P–C(2)–C(9) 141.8(2).

angle decreases to 41.8° and P–C–C intracyclic angles increase by about half a degree. The pyramidal character of the phosphorus atom is more pronounced in the uncomplexed form (Figure 1 caption). All these data indicate that the electron density over the ring is very poorly delocalized, in contrast to the situation found in the only other heterocyclopropene ring which has been structurally characterized.[7] In this structure, a silacyclopropene ring, the intra- and exocyclic Si–C bond lengths differ by up to 0.07 Å and the C=C bond is lengthened suggesting some aromatic character for that ring. In contrast, the structure of (**3**) suggests no unusual stabilization mechanism for the phosphirene ring. All that can be said is that the destabilizing (2p–3p)π interaction between phosphorus and carbon atoms is probably very weak owing to the high pyramidal character of phosphorus.

Received, 11th October 1983; Com. 1348

References

1 A. Krantz and J. Laureni, *J. Am. Chem. Soc.*, 1981, **103**, 486.

2 M. Torres, J. L. Bourdelande, A. Clement, and O. P. Strausz, *J. Am. Chem. Soc.*, 1983, **105**, 1698.

3 The stability of silirenes has been partly ascribed to some favourable p_π–d_π overlap between carbon and silicon atoms, see: P. R. Jones and D. D. White, *J. Organomet. Chem.*, 1978, **154**, C33; J. C. Barthelat, G. Trinquier, and G. Bertrand, *J. Am. Chem. Soc.*, 1979, **101**, 3785. However, more recent SCF calculations suggest only a weak aromatic character and a weak overlap for these species.

4 S. M. van der Kerk, P. H. M. Budzelaar, A. van der Kerk-van Hoof, G. J. M. van der Kerk, and P. v. R. Schleyer, *Angew. Chem., Int. Ed. Engl.*, 1983, **22**, 48.

5 G. Capozzi, V. Lucchini, G. Modena, and P. Scrimin, *Tetrahedron Lett.*, 1977, 911.

6 R. T. Conlin and P. P. Gaspar, *J. Am. Chem. Soc.*, 1976, **98**, 3715.

7 K. Hirotsu, T. Higuchi, M. Ishikawa, H. Sugisawa, and M. Kumada, *J. Chem. Soc., Chem. Commun.*, 1982, 726.

8 A. Krebs and J. Berndt, *Tetrahedron Lett.*, 1983, **24**, 4083.

9 A. Marinetti, F. Mathey, J. Fischer, and A. Mitschler, *J. Am. Chem. Soc.*, 1982, **104**, 4484.

10 K. S. Fongers, H. Hogeveen, and R. F. Kingma, *Tetrahedron Lett.*, 1983, **24**, 643.

11 F. Mercier, F. Mathey, J. Angenault, J. C. Couturier, and Y. Mary, *J. Organomet. Chem.*, 1982, **231**, 237.

12 Similar oxidations with iodine have been carried out on more classical phosphine-molybdenum and tungsten carbonyl complexes, see: J. Lewis and R. Whyman, *J. Chem. Soc.*, 1965, 5486; J. A. Connor, G. K. McEwen, and C. J. Rix, *J. Chem. Soc., Dalton Trans.*, 1974, 589.

13 H. Goldwhite, D. Rowsell, L. E. Vertal, M. T. Bowers, M. Ashley Cooper, and S. L. Manatt, *Org. Magn. Res.*, 1983, **21**, 494 and references cited therein.

14 Tertiary amines are known to catalyse the reaction of crude S_8 with tertiary phosphines: P. D. Bartlett, E. F. Cox, and R. E. Davis, *J. Am. Chem. Soc.*, 1961, **83**, 103. Without 1-methylimidazole, the reaction of S_8 with (**3**) is too slow and (**4**) is accompanied by various decomposition products.