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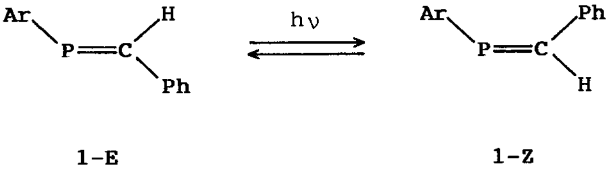
THE FIRST X-RAY STRUCTURE DETERMINATION OF A Z-PHOSPHAETHYLENE: Z-2-PHENYL-1-(2,4,6-TRI-t-BUTYLPHENYL)PHOSPHAETHYLENE

Masaaki Yoshifuji,* Kozo Toyota, and Naoki Inamoto,
Department of Chemistry, Faculty of Science,
The University of Tokyo, Hongo, Tokyo 113, Japan
and
Ken Hirotsu* and Taiichi Higuchi
Department of Chemistry, Faculty of Science,
Osaka City University, Sumiyoshi, Osaka 558, Japan

Abstract: The sterically protected Z-phosphaethylene, Z-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene (**1-Z**), was analyzed by X-ray crystallography.

Since Bickelhaupt et al. reported the isolation of a stable phosphaethylene, 1-mesityl-2,2-diphenyl-1-phosphaethylene,[1] compounds with multiple bond containing phosphorus atom in lower coordination state have been of current interest. We have been successful in preparing E-2-phenyl-1-(2,4,6-tri-t-butylphenyl)phosphaethylene (**1-E**) and found the E/Z photoisomerization to the corresponding Z-isomer (**1-Z**).[2] We now wish to report the X-ray analysis of the Z-phosphaethylene (**1-Z**).



(Ar=2,4,6-$Bu^t{}_3C_6H_2$)

The title Z-phosphaethylene (**1-Z**) was prepared and purified as reported previously (m.p. 95-97°C),[2] the structure of which was established unambiguously by a single crystal X-ray analysis as follows.[3]

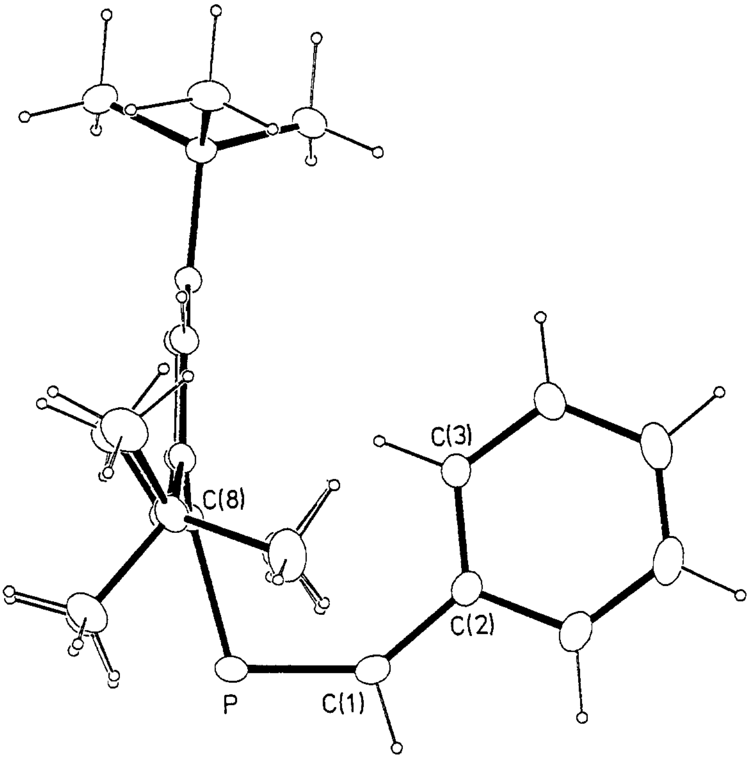


Figure 1. Molecular structure of Z-2-phenyl-1-(2,4,6-tri-t-butylphenyl)-1-phosphaethylene (**1-Z**). Some selected bond distances and bond angles: P-C(1) 1.674(2), P-C(8) 1.851(2), C(1)-C(2) 1.465(3) Å, ∠C(1)-P-C(8) 105.8(1), ∠P-C(1)-C(2) 139.1(2)°.

Crystal data (**1-Z**): $C_{25}H_{35}P$, M=366.532, monoclinic, space group $P2_1/c$, a=11.439(1), b=10.593(2), c=19.053(2) Å, β=96.99(1)°, U=2291.4(3) $Å^3$, Z=4, D_c=1.06 $g\cdot cm^{-3}$. 3405 Reflections with $2\theta \leq 120°$ were recorded on a four-circle diffractometer in the dark using graphite-monochromated Cu-Kα radiation. Of these 2866 (with $I > 3\sigma(I)$) were judged as observed. The structure was solved using MULTAN.[4] Full-matrix least squares refinement with anisotropic temperature factors for non-hydrogen atoms converged to R 0.040.[5]

Figure 1 is an ORTEP drawing[6] of **1-Z**. The C(8), P, C(1), and C(2) atoms are coplanar within 0.005 Å and the dihedral angle ∠C(8)-P-C(1)-C(2) is 1.0(3)°. The phenyl ring attached to C(1) makes an angle of 7.2° with this plane whereas the 2,4,6-tri-t-butylphenyl ring makes an angle of 88.3°. Therefore the latter bulky phenyl is almost perpendicular to the P=C π-system forming a striking contrast to the mesitylphosphaethylene,[1] where mesityl, Z-phenyl, and E-phenyl groups are arranged like a propeller around the P=C nodal plane making angles of 71°, 42.9°, and 36.6°, respectively. This conformation in **1-Z** may be attained owing to the steric hindrance caused by the ortho-t-butyl groups. The P-C(1) bond distance is 1.674(2) Å and is very close to that of $HP=CH_2$ determined by microwave spectroscopy.[7] The bulky aromatic ring is distorted to a boat form as has been observed in the compounds containing the 2,4,6-tri-t-butylphenylphosphorus group.[8] It should be noted that the hydrogen atom bonded to C(3) and the bulky aryl group are extraordinarily close to each other: the distance between H(C3) and the mean benzene plane = 2.33(2) Å and H(C3)···C(8) = 2.42(2) Å. Unusual up-field chemical shift upto δ 6.1 observed for the aromatic protons in the ^1H NMR of **1-Z** might account for this situation. The widening of the P-C(1)-C(2) angle in **1-Z** compared with the corresponding angle of 127.2° for the mesitylphosphaethylene might be due to this intramolecular repulsion.

This is the first X-ray analysis[9] of a very stable Z-phosphaethylene sterically protected by the extremely bulky 2,4,6-tri-t-butylphenyl group. Additionally **1** is the phosphaethylene with one hydrogen atom but without any hetero-atom substitution at C(1) in contrast to the hetherto known phosphaethylenes,[1,10] although the preparation of 1-(2,4,6-tri-t-butylphenyl)phosphaethylene has already been reported.[11] It is also important that an appropriate bulkiness is essential for stabilization of such unusual compounds in low coordination state. Indeed Bickelhaupt et al. have recently reported unsuccessful results on their attempts to prepare trimesitylphosphaethylene.[12]

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References and Notes

1. Th. C. Klebach, R. Lourens, and F. Bickelhaupt, J. Am. Chem. Soc., 1978, **100**, 4886; Th. A. van der Knaap, Th. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam, and M. Konijn, Tetrahedron, 1984, **40**, 765.
2. M. Yoshifuji, K. Toyota, and N. Inamoto, Tetrahedron Lett., 1985, **26**, 1727.
3. The compond **1-Z** was prepared from the corresponding **1-E** by photolysis, chromatographed (over silica gel eluted with hexane), and recrystallized (from pentane). A part of this work was presented at the 50th National Meeting of the Chemical Society of Japan: M. Yoshifuji, T. Hashida, K. Shibayama, K. Toyota, and N. Inamoto, Abstr., 2Q-16, Tokyo, April 1985.
4. G. Germain, P. Main, and M. M. Woolfson, Acta Crystallogr., Sec. B, 1970, **24**, 274.

5. W. R. Busing, K. O. Martin, and H. S. Levy, ORFLS, Oak Ridge National Laboratory Report, ORNL-TM-305, Oak Ridge, TN, 1965.

6. C. K. Johnson, ORTEP, Oak Ridge National Laboratory Report, ORNL-TM-3794, Oak Ridge, TN, 1965.

7. M. J. Hopkinson, H. W. Kroto, J. F. Nixon, and N. P. C. Simmons, J. Chem. Soc., Chem. Commun., **1976**, 513.

8. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu, and T. Higuchi, Angew. Chem., Int. Ed. Engl., 1980, **19**, 399; M. Yoshifuji, I. Shima, N. Inamoto, and T. Aoyama, Tetrahedron Lett., 1981, **22**, 3057; M. Yoshifuji, N. Inamoto, K. Hirotsu, and T. Higuchi, J. Chem. Soc., Chem. Commun., **1985**, 1109.

9. The X-ray crystallographic data of **1-Z**, fractional coordinates and temperature factors with standard deviations and bond distances and angles, are to be deposited at the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW. The X-ray data are available on request from the Director of CCDC by quoting the full literature citation of this paper.

10. B. Becker and O. Mundt, Z. Anorg. Allg. Chem., 1978, **443**, 53; G. Becker, W. Becker, and O. Mundt, Phosphorus and Sulfur, 1983, **14**, 267; R. Appel, F. Knoch, B. Laubach, and R. Sievers, Angew. Chem., Int. Ed. Engl., 1979, **18**, 872; A. H. Cowley, R. A. Jones, J. G. Lasch, N. C. Norman, C. A. Stewart, A. L. Stuart, J. L. Atwood, W. E. Hunter, and H.-M. Zhang, J. Am. Chem. Soc., 1984, **106**, 7015.

11. K. Issleib, H. Schmidt, and Chr. Wirkner, Z. Anorg. Allg. Chem., 1982, **488**, 75; R. Appel, C. Casser, M. Immenkeppel, and F. Knoch, Angew. Chem., Int. Ed. Engl., 1984, **23**, 896.

12. Th. A. van der Knaap and F. Bickelhaupt, Phosphorus and Sulfur, 1984, **21**, 227.

13. The Wittig type reaction of **1** is expected to occur, since the generation of phosphinidene oxides, "RP=O", has long been postulated.[14] However, either *E*- or *Z*-phosphaethylene (**1**) did not react with benzaldehyde in refluxing benzene overnight. Furthermore, photo-reaction did not proceed (medium-pressure mercury lamp, 2 h). Acetone did not react with **1** under similar conditions, either.

14. M. Yoshifuji, S. Nakayama, R. Okazaki, and N. Inamoto, J. Chem. Soc., Perkin I, **1973**, 2065; J. K. Stille, J. L. Eichelberger, J. Higgins, and M. E. Freeburger, J. Am. Chem. Soc., 1972, **94**, 4761; H. Quast and M. Heuschmann, Angew. Chem., Int. Ed. Engl., 1978, **17**, 867; E. Niecke, M. Engelmann, H. Zorn, B. Krebs, and G. Henkel, *ibid.*, 1980, **19**, 710; W. W. Schoeller and E. Niecke, J. Chem. Soc., Chem. Commun., **1982**, 569.

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