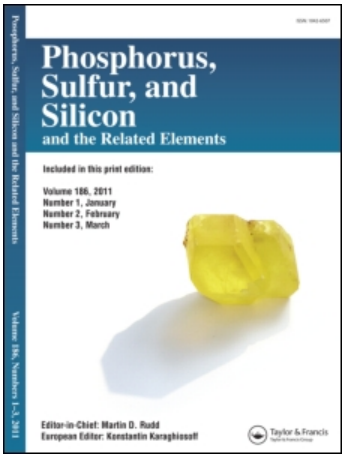


Phosphorus, Sulfur, and Silicon and the Related Elements
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713618290

STRUCTURES OF PHOSPHAETHYLENES AND A 1-PHOSPHAALLENE CONTAINING PHOSPHORUS IN LOWER COORDINATION STATE

Masaaki Yoshifuji[a]; Kozo Toyota[a]; Naoki Inamoto[a]; Ken Hirotsu[b]; Taiichi Higuchi[b]; Shigeru Nagase[c]
[a] Department of Chemistry, Faculty of Science, The University of Tokyo, Tokyo, Japan [b] Department of Chemistry, Faculty of Science, Osaka City University, Osaka, Japan [c] Department of Chemistry, Faculty of Education, Yokohama National University, Yokohama, Japan

To cite this Article Yoshifuji, Masaaki , Toyota, Kozo , Inamoto, Naoki , Hirotsu, Ken , Higuchi, Taiichi and Nagase, Shigeru(1985) 'STRUCTURES OF PHOSPHAETHYLENES AND A 1-PHOSPHAALLENE CONTAINING PHOSPHORUS IN LOWER COORDINATION STATE', Phosphorus, Sulfur, and Silicon and the Related Elements, 25: 3, 237 — 243
To link to this Article: DOI: 10.1080/03086648508072740
URL: http://dx.doi.org/10.1080/03086648508072740

Phosphorus and Sulfur, 1985, Vol. 25, pp. 237–243
0308-664X/85/2503–0237/$15.00/0

STRUCTURES OF PHOSPHAETHYLENES AND A 1-PHOSPHAALLENE CONTAINING PHOSPHORUS IN LOWER COORDINATION STATE

MASAAKI YOSHIFUJI,* KOZO TOYOTA and NAOKI INAMOTO

Department of Chemistry, Faculty of Science, The University of Tokyo, Hongo, Tokyo 113, Japan

KEN HIROTSU* and TAIICHI HIGUCHI

Department of Chemistry, Faculty of Science, Osaka City University, Sumiyoshi, Osaka 558, Japan

SHIGERU NAGASE*

Department of Chemistry, Faculty of Education, Yokohama National University, Hodogaya, Yokohama 240, Japan

(*Received June 3, 1985; in final form July 9, 1985*)

The X-ray analyses of sterically protected *Z*-2-*t*-butyldimethylsilyloxy-2-phenylphosphaethylene (*Z*-**2**) and 3,3-diphenyl-1-phosphaallene (**3**) were carried out and the structures of the parent compounds, $HP{=}CH_2$ and $HP{=}C{=}CH_2$, were optimized by *ab initio* methods.

INTRODUCTION

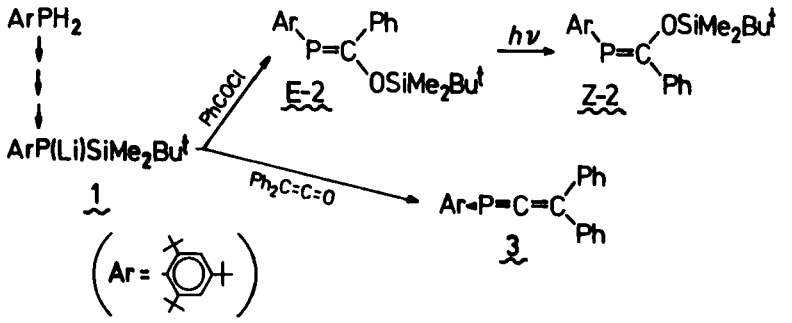
Organophosphorus compounds in lower coordination states are of current interest because of their unusual structure and reactivity.

Starting from lithium *t*-butyldimethylsilyl-2,4,6-tri-*t*-butylphenylphosphide (**1**) we have been successful in the preparation of such unusual organophosphorus compounds as sterically protected *E*- and *Z*-2-*t*-butyldimethylsilyloxy-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethylenes (**2**),[1] 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**3**),[2] *N*-phenyl-*P*-(2,4,6-tri-*t*-butylphenyl)iminomethylenephosphine (**4**),[2] and 1,3-bis(2,4,6-tri-*t*-butylphenyl)-1,3-diphosphaallene.[3]

We have been interested in the structures of P=C and P=C=C groups because of the expected unusual bonding nature involving $3p\pi$-$2p\pi$ contributions.[4] We now describe here the X-ray structures of *Z*-**2** and **3** and the calculational results for the parent compounds.

---

*Author to whom all correspondence should be addressed.



SCHEME 1

RESULTS AND DISCUSSION

The X-ray analyses of compounds *Z*-**2** (Figure 1) and **3** (Figure 2) were as follows.[5]

The P—C(1) bond distance of *Z*-**2** (1.687(5) Å) is longer by 0.02 Å than the sum of the covalent bond radii (1.667 Å). The double-bond system (P, C(1), C(2), C(14), and O) has a distorted planar conformation with deviation (0.05 Å) from the least-squares plane and the dihedral angles of C(14)—P—C(1)—O = −3.7(7)° and C(14)—P—C(1)—C(2) = −175.2(6)° because of the repulsion forces between bulky groups at the C(1) and P atoms. This plane makes angles of 54.8° and 80.3° with the trans-oriented benzene rings bonded to the C(1) and P atoms, respectively. Some selected bond distances and angles for *Z*-**2** are listed in Table I.

The P—C(1) bond distance of **3** is 1.625(4) Å, which is 0.062 Å shorter than that in *Z*-**2**. The P—C(1)—C(2) bond angle is 168.0(3)° and deviates by 12° from 180°. The C(1), (C2), (C3), and C(9) atoms are coplanar within 0.01 Å; the P atom deviates by 0.35 Å from this plane. The interplanar angle between this plane and the plane defined by the P, C(1), C(2), and C(15) atoms (deviation 0.02 Å) is 87.2°. The dihedral angle C(1)—P—C(15)—C(2) is −100.9(7)°. Some selected bond distances and angles for **3** are listed in Table II.

Furthermore, the benzene rings of the 2,4,6-tri-*t*-butyl-phenyl groups in both compounds (*Z*-**2** and **3**) are distorted to boat forms as have been observed in compounds containing the Ar—P group.[6]

Figure 3 shows the results of *ab initio* calculations on the parent compounds, $HP{=}CH_2$[7] and $HP{=}C{=}CH_2$, at the 6-31G* level.[8] The calculated structures are in good accord with those obtained by the X-ray analyses of the very bulky molecules (*Z*-**2** and **3**). It should be noted that the P=C parts of both compounds resemble each other and that the C=C in phosphaallene is almost the same as that of allene itself. The bent P=C=C bond appears to be caused not only by steric repulsion but also by electronic effects; however, the theoretical reason for this is not clear.

EXPERIMENTAL

Materials. Starting from lithium *t*-butyldimethylsilyl-2,4,6-tri-*t*-butylphenylphosphide (**1**) *Z*-2-*t*-butyldimethylsilyloxy-2-phenyl-1-(2,4,6-tri-*t*-butylphenyl)phosphaethylene (*Z*-**2**)[1] and 3,3-diphenyl-1-(2,4,6-tri-*t*-butylphenyl)-1-phosphaallene (**3**),[2,9] were prepared as described previously.

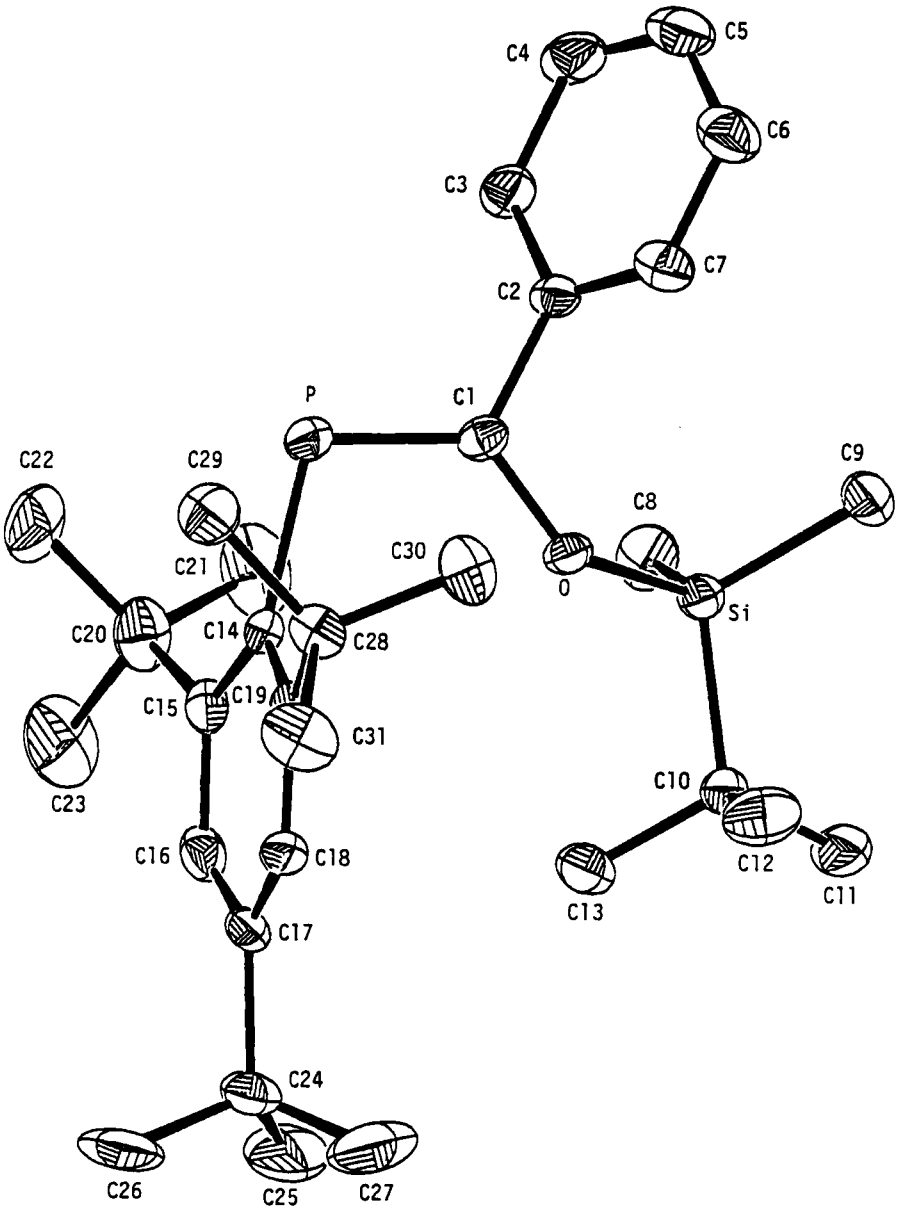


FIGURE 1 X-Ray structure of *Z*-**2** in the crystal.

X-Ray crystallographic and refinement data for Z-2. Crystallographic data of *Z*-**2** (recrystallized from pentane): $C_{31}H_{49}OSiP$, monoclinic, space group $P2_1/n$, $a = 27.832(8)$, $b = 11.298(2)$, $c = 10.257(2)$ Å, $\beta = 100.18(2)°$, $Z = 4$, $\rho_c = 1.039$ g · cm^{-3}, Mo Kα radiation, $\lambda = 0.7107$ Å. 4680 Reflections with $2\theta \leq 46°$ were recorded. The structure was solved by MULTAN.[10] Full-matrix least-squares refinement with anisotropic temperature factors for non-hydrogen atoms and isotropic hydrogens converged to R value ($= \Sigma(|F_0| - |F_c|)/\Sigma|F_0|$) of 0.04 for 2261 reflections with $I > 3\sigma(I)$.[11] Fractional coordinates of the non-hydrogen atoms for *Z*-**2** are listed in Table III.

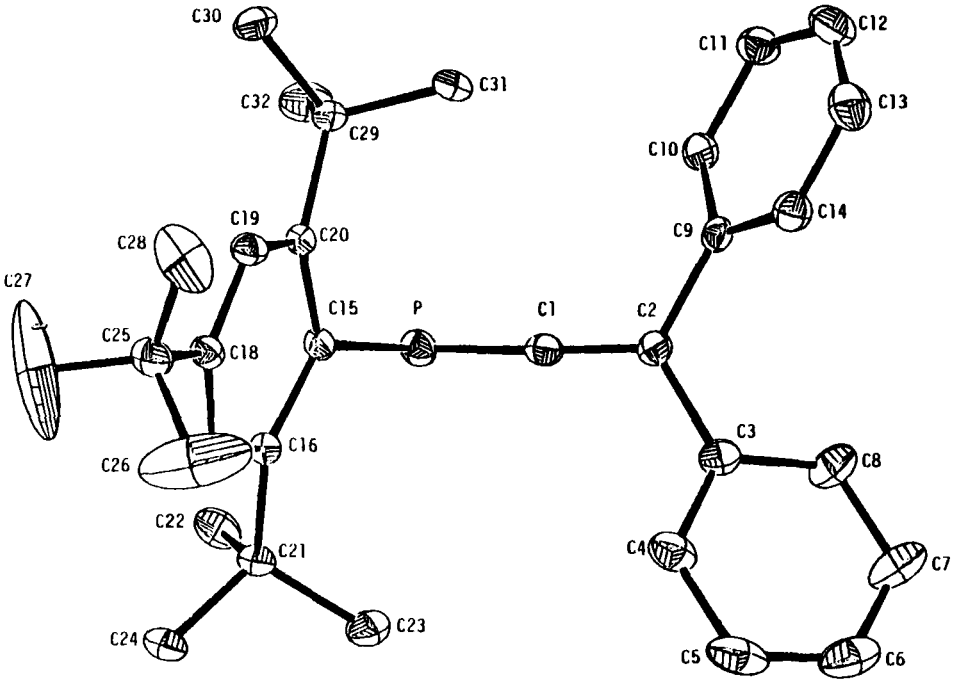


FIGURE 2 X-Ray structure of **3** in the crystal.

TABLE I

Some selected bond distances (Å) and angles (°) for *Z*-**2**

P—C(1)	1.687(5)
P—C(14)	1.861(5)
∠C(1)—P—C(14)	103.9(2)
∠P—C(1)—O	126.3(4)
∠P—C(1)—C(2)	117.3(4)
∠C(2)—C(1)—O	116.0(4)

TABLE II

Some selected bond distances (Å) and angles (°) for **3**

P—C(1)	1.625(4)
P—C(15)	1.864(3)
C(1)—C(2)	1.327(5)
C(2)—C(3)	1.494(5)
C(2)—C(9)	1.485(5)
∠C(1)—P—C(15)	103.6(2)
∠P—C(1)—C(2)	168.0(3)
∠C(1)—C(2)—C(3)	119.9(3)
∠C(1)—C(2)—C(9)	121.8(3)

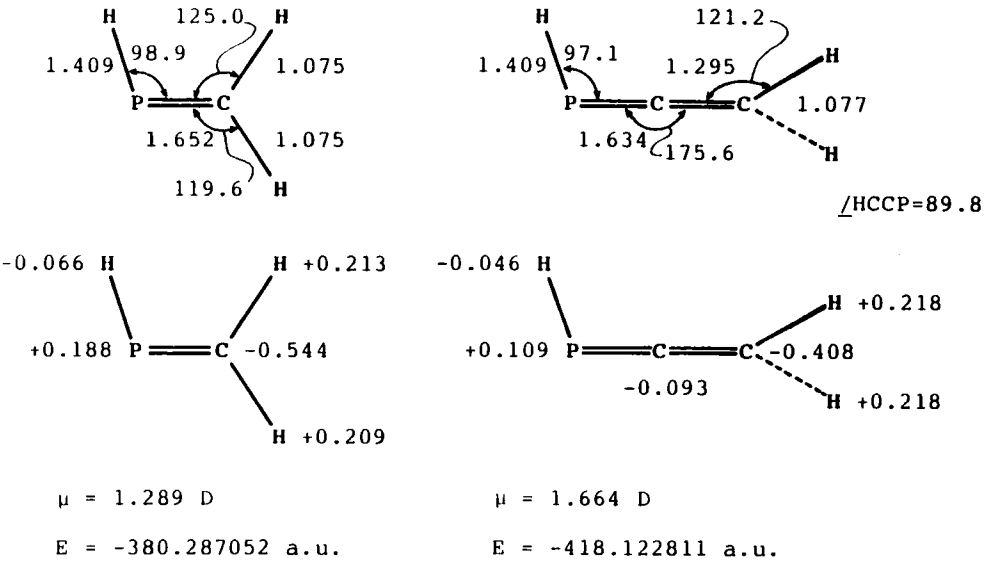


FIGURE 3 6-31G* Optimized structures (Å and degrees), charge densities, dipole moments (μ in D), and total energies (E in a.u.) of $HP{=}CH_2$ and $HP{=}C{=}CH_2$.

X-Ray crystallographic and refinement data for **3**. Crystallographic data of **3** (recrystallized from pentane): $C_{32}H_{39}P$, space group $P2_1/n$, a = 14.566(1), b = 17.295(1), c = 10.975(1) Å, β = 90.07(1)°, Z = 4, ρ_c = 1.092 g · cm^{-3}, Mo Kα radiation, λ = 0.7107 Å. 4042 Reflections with $2\theta \leq 46°$ were recorded. Structure determination and refinement by use of the same procedure as that for *Z*-**2**, R = 0.055 for 2583 reflections with $I > 3\sigma(I)$. Fractional coordinates of the non-hydrogen atoms for **3** are listed in Table IV.

ab initio Calculations. The structures of $HP{=}CH_2$ and $HP{=}C{=}CH_2$ were optimized by the *ab initio* method at the 6-31G* level using the GAUSSIAN 80 program.[12]

TABLE III

Fractional atomic coordinates of non-hydrogen atoms with standard deviations in parentheses for *Z*-**2**

Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
P	0.4139(1)	0.0978(1)	0.1766(1)	C15	0.3153(2)	0.1635(5)	0.0769(5)
Si	0.4314(1)	0.4683(1)	0.2424(1)	C16	0.2810(2)	0.2217(5)	−0.0154(6)
O	0.4324(1)	0.3341(3)	0.1717(3)	C17	0.2900(2)	0.2591(5)	−0.1368(5)
C1	0.4434(2)	0.2251(4)	0.2248(4)	C18	0.3337(2)	0.2249(5)	−0.1714(5)
C2	0.4899(2)	0.2162(4)	0.3231(5)	C19	0.3703(2)	0.1661(4)	−0.0849(5)
C3	0.4909(2)	0.1601(5)	0.4447(5)	C20	0.2985(2)	0.1183(6)	0.2053(6)
C4	0.5359(3)	0.1474(5)	0.5299(6)	C21	0.3211(3)	0.1918(8)	0.3255(7)
C5	0.5772(2)	0.1893(6)	0.4957(7)	C22	0.3100(3)	−0.0127(7)	0.2243(7)
C6	0.5769(2)	0.2452(6)	0.3763(6)	C23	0.2428(3)	0.1287(9)	0.1963(8)
C7	0.5329(2)	0.2573(5)	0.2905(5)	C24	0.2523(2)	0.3299(6)	−0.2350(7)
C8	0.4012(2)	0.4568(6)	0.3900(6)	C25	0.2226(3)	0.4123(8)	−0.162(1)
C9	0.4936(2)	0.5315(5)	0.2938(6)	C26	0.2212(4)	0.2513(8)	−0.323(1)
C10	0.3956(2)	0.5592(4)	0.1068(5)	C27	0.2784(3)	0.4162(8)	−0.3164(9)
C11	0.3898(3)	0.6860(5)	0.1549(7)	C28	0.4154(2)	0.1208(5)	−0.1404(5)
C12	0.4210(3)	0.5609(7)	−0.0124(6)	C29	0.4256(2)	−0.0099(6)	−0.1051(6)
C13	0.3447(2)	0.5048(5)	0.0662(6)	C30	0.4611(2)	0.1956(6)	−0.0919(6)
C14	0.3623(2)	0.1451(4)	0.0461(5)	C31	0.4060(2)	0.1255(7)	−0.2922(6)

TABLE IV

Fractional atomic coordinates of non-hydrogen atoms with standard deviations in parentheses for **3**

Atom	*X*	*Y*	*Z*	Atom	*X*	*Y*	*Z*
P	0.5372(1)	0.2469(1)	0.1598(1)	C17	0.7890(2)	0.1408(2)	0.1190(3)
C1	0.4775(2)	0.1718(2)	0.1192(3)	C18	0.8128(2).	0.1179(2)	0.2352(3)
C2	0.4154(2)	0.1213(2)	0.0805(3)	C19	0.7600(2)	0.1477(2)	0.3293(3)
C3	0.4000(2)	0.1104(2)	−0.0531(3)	C20	0.6823(2)	0.1925(2)	0.3114(3)
C4	0.3944(2)	0.1736(2)	−0.1300(3)	C21	0.7038(2)	0.2154(2)	−0.0411(3)
C5	0.3801(3)	0.1635(2)	−0.2538(3)	C22	0.6713(3)	0.2988(3)	−0.0468(4)
C6	0.3708(3)	0.0909(3)	−0.2993(3)	C23	0.6399(3)	0.1629(3)	−0.1123(3)
C7	0.3767(3)	0.0273(2)	−0.2245(4)	C24	0.7965(3)	0.2146(3)	−0.1076(3)
C8	0.3905(3)	0.0370(2)	−0.1011(3)	C25	0.8962(2)	0.0669(2)	0.2595(3)
C9	0.3583(2)	0.0758(2)	0.1666(3)	C26	0.9265(4)	0.0217(3)	0.1506(5)
C10	0.3912(3)	0.0503(2)	0.2764(3)	C27	0.9677(5)	0.1082(4)	0.311(1)
C11	0.3326(4)	0.0088(2)	0.3571(4)	C28	0.8721(5)	0.0025(5)	0.3477(7)
C12	0.2441(4)	−0.0062(3)	0.3207(4)	C29	0.6343(2)	0.2277(2)	0.4253(3)
C13	0.2114(3)	0.0172(3)	0.2144(4)	C30	0.6953(3)	0.2219(2)	0.5393(3)
C14	0.2680(3)	0.0584(2)	0.1370(4)	C31	0.5443(3)	0.1860(2)	0.4544(3)
C15	0.6539(2)	0.2067(2)	0.1890(3)	C32	0.6183(3)	0.3144(2)	0.4066(3)
C16	0.7138(2)	0.1871(2)	0.0923(3)				

Supplementary material available. Fractional coordinates and isotropic thermal parameters with standard deviations and interatomic distances and angles for *Z*-**2** and **3** are available on request from the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Road, Cambridge, CB2 1EW (Requests require full literature citation of this paper).

ACKNOWLEDGMENTS

This work was supported in part by Scientific Research Grant-in-Aids (5754027 and 58840023) from the Ministry of Education, Culture and Science of Japan and a Kurata Research Grant from the Kurata Foundation. We thank the Crystallographic Research Centre, Institute for Protein Research, Osaka University, for computer calculations. All *ab initio* calculations were carried out at the Institute for Molecular Science, Japan. We thank Shin-Etsu Chemical Co., Ltd. for donating silyl reagents used throughout this work.

REFERENCES AND NOTES

1. M. Yoshifuji, K. Toyota, K. Shibayama and N. Inamoto, *Chem. Lett.*, **1983**, 1653.
2. M. Yoshifuji, K. Toyota, K. Shibayama and N. Inamoto, *Tetrahedron Lett.*, **25**, 1809 (1984).
3. M. Yoshifuji, K. Toyota and N. Inamoto, *J. Chem. Soc., Chem. Commun.*, **1984**, 689; An X-ray structure was reported very recently: H. H. Karsch, H.-U. Reisacher and G. Müller, *Angew. Chem., Int. Ed. Engl.*, **23**, 618 (1984).
4. R. Appel, F. Knoll and I. Ruppert, *Angew. Chem., Int. Ed. Engl.*, **20**, 731 (1981).
5. The crystallographic results for *Z*-**2** and **3** were presented at the 12th Symposium on Organosulfur and Phosphorus Compounds, Osaka, January 25–26, 1984 and at the 49th National Meeting of the Chemical Society of Japan, Tokyo, April 1–4, 1984. In the meantime, the X-ray structure of **3** was reported: R. Appel, P. Fölling, B. Josten, M. Siray, V. Winkhaus and F. Knoch, *Angew. Chem., Int. Ed. Engl.*, **23**, 619 (1984). Very recently, X-ray data of the compounds with the P=C bond have been reported: G. Becker, W. Becker and O. Mundt, *Phosphorus and Sulfur*, **14**, 267 (1983); G. Becker and O. Mundt, *Z. Anorg. Allg. Chem.*, **443**, 53 (1978); T. A. van der Knaap, T. C. Klebach, F. Visser, F. Bickelhaupt, P. Ros, E. J. Baerends, C. H. Stam and M. Konijn, *Tetrahedron*, **40**, 765 (1984); 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.*, **106**, 7015 (1984); R. Appel, F. Knoch, B. Laubach and R. Sievers, *Chem. Ber.*, **116**, 1873 (1983).

6. M. Yoshifuji, I. Shima, N. Inamoto, K. Hirotsu and T. Higuchi, *Angew. Chem., Int. Ed. Engl.*, **19**, 399 (1980); M. Yoshifuji, N. Inamoto, K. Hirotsu and T. Higuchi, *J. Chem. Soc., Chem. Commun.*, **1985**, in press.
7. M. J. Hopkinson, H. W. Kroto, J. F. Nixon and N. P. C. Simmons, *J. Chem. Soc., Chem. Commun.*, **1976**, 513. Very recently MO calculation of $HP{=}CH_2$ has also been reported at the STO-3G level. W. W. Schoeller, *J. Chem. Soc., Chem. Commun.*, **1985**, 334.
8. M. M. Francl, W. J. Hehre, J. S. Binkley, M. S. Gordon, D. J. DeFrees and J. A. Pople, *J. Chem. Phys.*, **77**, 3654 (1982).
9. Compound **3** reacted with excess elemental sulfur in benzene in the presence of DBU (diazabicyclo[5.4.0]undec-7-ene) gave 3-methylene-1-(2,4,6-tri-*t*-butylphenyl)thiaphosphirane 2-sulfide in 77% yield; mp, 143–145°C; δP ($CDCl_3$) −18.9; MS *m/z* 518 (M^+). Monitoring the ^{31}P NMR during the reaction indicated the initial formation of the *P*-sulfide at δP 79. On the other hand, **4**, a reaction product of **1** with phenyl isocyanate, reacted with sulfur to give 2,4,6-tri-*t*-butylphenyldithioxophosphorane, $ArPS_2$, δP (PhH) 295.6.[13] The above results were consistent with the stability toward air.[2] Indeed, when **4** was allowed to stand at room temperature for a few days in air **4** decomposed to give 2,4,6-tri-*t*-butylphenylphosphine oxide.[14]
10. G. Germain, P. Main and M. M. Woolfson, *Acta Crystallogr.*, **B24**, 274 (1970).
11. W. R. Busing, K. O. Martin and H. S. Levy, "A Fortran Crystallographic Least Square Program," USAEC Report ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.
12. J. S. Binkley, R. A. Whiteside, R. Krishnan, R. Seeger, D. J. DeFrees, H. B. Schlegel, S. Topiol, L. R. Kahn and J. A. Pople, QCPE, **13**, 406 (1981).
13. R. Appel, F. Knoch and H. Kunze, *Angew. Chem., Int. Ed. Engl.*, **22**, 1004 (1983); J. Navech, M. Revel and R. Kraemer, *Phosphorus and Sulfur*, **21**, 105 (1984); M. Yoshifuji, K. Toyota, K. Ando and N. Inamoto, *Chem. Lett.*, **1984**, 317.
14. M. Yoshifuji, K. Shibayama, K. Toyota and N. Inamoto, *Tetrahedron Lett*, **24**, 4227 (1983).