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Observation of a Triplet Phosphinidene by ESR Spectroscopy

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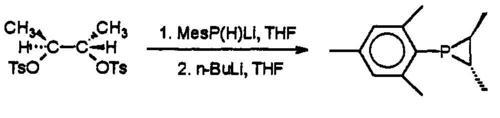
Phosphinidenes have been proposed as short-lived intermediates in several reaction systems.[1] We have reported products from the photodecomposition of 1-mesitylphosphirane that are in accord with the formation of free mesitylphosphinidene (**2**) as a reactive intermediate.[2] Product structures suggest that mesitylphosphinidene adds to π-bonds in a fashion similar to that for carbenes and silylenes.[2,3] But, heeding Mathey's warning regarding the invocation of phosphinidene intermediates without physical evidence,[4] it was recognized that spectroscopic studies were needed in order to fully establish the formation of phosphinidenes.

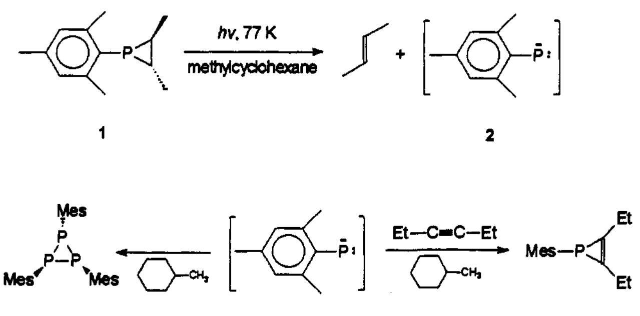
Theoretical studies predict that many phosphinidenes have triplet ground electronic states[5] and that the ground triplet state of arylphosphinidenes is lower in energy by more than 40 kcal/mol than the lowest excited (singlet) state.[6] It thus seemed likely that a triplet arylphosphinidene could be detected by ESR spectroscopy, as in the case of carbenes and nitrenes.[7] While ESR experiments on the photolysis of proposed phosphinidene precursors in frozen matrices have been reported previously,[8] the detection by ESR of a triplet phosphinidene was not achieved. We report here the observation of triplet mesitylphosphinidene.

Scheme 1



1

Scheme 2



1 **2**

3 **2** **4**

trans-2,3-Dimethyl-1-mesitylphosphirane (**1**) was synthesized from $MesPH_2$[9] and (±)-2,3-butanediol ditosylate[10] in 52% yield as shown in Scheme 1.[11]

Compound **1** was found to decompose more easily and cleanly than the previously reported 1-mesitylphosphirane.[2] Room temperature photolysis of compound **1** in the presence of 3-hexyne gave a 64% yield of 2,3-diethyl-1-mesitylphosphirene (**4**)[12] (Scheme 2).

When frozen solutions of compound **1** (0.01–0.1 M) in methylcyclohexane were irradiated at 77 K with a 254 nm light source, the methylcyclohexane glass became yellow. After thawing, trimesitylcyclotriphosphine (**3**) was observed in 30% yield in the absence of trapping agent;[13] in the presence of 3-hexyne, 2,3-dimethyl-1-mesitylphosphirene (**4**) was formed in yields of 22–80% based on the initial amount of compound **1**. The formation of these products strongly suggests that mesitylphosphinidene (**2**) was formed in the matrix.

A methylcyclohexane solution of compound **1** (0.1 M, 0.6 mL) was placed in a quartz ESR tube, degassed, and sealed. This mixture was cooled to 77 K, and the resulting organic glass was irradiated for 25 min at 254 nm (88 W). Upon irradiation, the matrix became yellow. The frozen tube was quickly transferred to the ESR cavity in a liquid helium cryostat. A Varian E-112 high-field ESR spectrometer (X-band, 9.045 85 GHz)[14] was employed in the measurements. With the sample at a temperature of 4 K, the magnetic field was scanned over the range of 600–

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(4) Reference 1c; p 34: "The effective generation of these transient phosphinidenes from appropriate precursors is deduced from the isolation of products whose formation can be explained by a mechanism involving such intermediates. However, in almost every case as will be demonstrated later, it is possible to conceive alternate mechanisms which do not involve phosphinidenes. Thus, only a thorough physicochemical study of the generating systems can provide a firm basis for the actual formation of phosphinidenes."

(5) For HP: (a) Nguyen, M. T. *Mol. Phys.* **1986,** *59,* 547. (b) Droege, A.T.; Engelking, P. C. *J. Chem. Phys.* **1984,** *80,* 5926. (c) Onashi, N.; Kawaguchi, K.; Hirota, E. *J. Mol. Spectrosc.* **1984,** *103,* 337. For CH_3P: Nguyen, M. T.; Mc Ginn, M. A.; Hegarty, A. F. *Inorg. Chem.* **1986,** *25,* 2185.

(6) See ref 1g.

(7) (a) Platz, M. S. In *Handbook of Organic Photochemistry*; Scaiano, J.C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. II, p 279. (b) Schuster, G.B.; Platz, M. S. In *Advances in Photochemistry*; Volmann, D. H., Hammond, G. S., Neckers, D. C., Eds.; John Wiley & Sons: New York, 1992; Vol. 17, p 69. (c) Wasserman, E. In *Prog. Phys. Org. Chem.* **1971,** *8,* 319.

(8) Schmidt, U.; Boie, I.; Osterroht, Ch.; Schroer, R.; Grutzmacher, H. F. *Chem. Ber.* **1968,** *101,* 1381.

(9) For the synthesis of $MesPH_2$, see ref 2 and the following: Oshikawa, T.; Yamashita, M. *Chem. Ind.* **1985,** 126.

(10) For the synthesis of 2,3-butanediol ditosylate, see: Corey, E. J.; Mitra, R.B., *J. Am. Chem. Soc.* **1962,** *84,* 2938.

(11) Spectroscopic data of compound **1**: ^{31}P NMR (121.4 MHz, C_6D_6) δ −186.20; ^1H NMR (300 MHz, C_6D_6) δ 1.01 (dd, J_{P-H} = 5.0 Hz, J_{H-H} = 6.2 Hz, 3 H, ring CH_3, *syn* to mesityl), 1.10–1.35 (m, 2 H, ring CHCH), 1.27 (dd, J_{P-H} = 13.8 Hz, J_{H-H} = 6.3 Hz, 3 H, ring CH_3, *anti* to mesityl), 2.08 (s, 3 H, *p*-CH_3), 2.42 (bs, 6 H, *o*-CH_3), 6.69 (s, 2 H, *m*-H); ^{13}C NMR (75.4 MHz, C_6D_6) δ 15.62 (s, ring CH_3, *syn* to mesityl), 18.74 (d, J_{P-C} = 17.7 Hz, ring CH_3, *anti* to mesityl), 21.02 (s, *p*-CH_3), 22.54 (bd, J_{P-C} = 37.6 Hz, *o*-CH_3), 29.08 (d, J_{P-C} = 34.3 Hz, ring C), 29.52 (d, J_{P-C} = 43.0 Hz, ring C), 129.33 (bs, *m*-ArC), 132.12 (d, J_{P-C} = 43.7 Hz, *ipso*-ArC), 136.89 (s, *p*-ArC), 143.21 (s, *o*-ArC); UV (cyclohexane) λ_{max} 284 nm ($\epsilon = 1.564 \times 10^3$), 275 nm ($\epsilon = 1.631 \times 10^3$), shoulder 246 nm ($\epsilon = 8.985 \times 10^3$); GC-MS(EI) *m/e* (relative intensity) 206 (M^+, 37), 150 (100), 135 (61), 105 (44), 91 (18); exact mass determination (EI) for $C_{13}H_{19}P$ (M^+) calcd 206.1244, found 206.1220. Anal. Calcd: C, 75.70; H, 9.28. Found: C, 74.77; H, 9.39.

(12) For spectroscopic data of compound **4**, see ref 2.

(13) For spectroscopic data of compound **3**, see ref 2.

(14) The spectrometer is housed in the Illinois EPR Research Center, Urbana, IL 61801. Irradiation was carried out at 77 K, and the ESR spectrum was recorded at 4 K.

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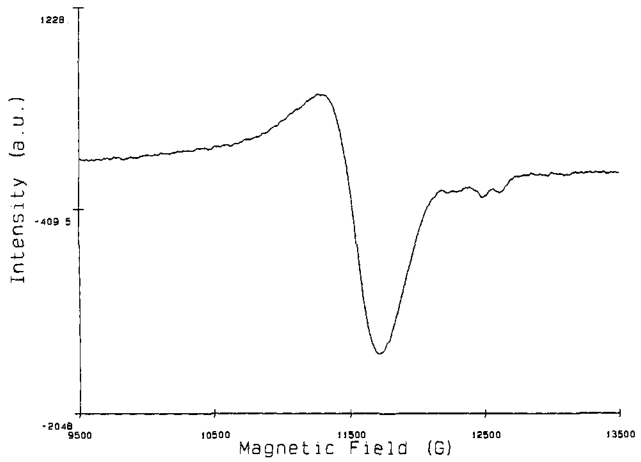

Figure 1. ESR spectrum of mesitylphosphinidene.

15 000 G to search for signals. We observed a signal at 3251 G (free radical) and another very strong and broad signal at 11 492 G (Figure 1). We assign the ultrahigh resonance field to the triplet state of mesitylphosphinidene.

The spin Hamiltonian for a triplet state is given as

$$H_{\mathrm{spin}} = \beta \mathbf{B}_0 g S + D[S_z^2 - S(S + 1)/3] + E[S_x^2 - S_y^2]$$

where the first term is the electronic Zeeman interaction and D and E are the zero-field splittings (ZFS) of the triplet state. The 11 492 G signal must arise from the (x,y) canonical orientation (perpendicular to the P–C bond). This is a prominent absorption peak. The observed ultrahigh resonance field (about 4 times greater than the resonance field for a free electron) implies a very large D value.

Assuming that the free electron g-value and E both equal 0 (similar to phenylnitrene), the D value can be evaluated from the resonance field of the perpendicular (x,y) orientation by the following equation,

$$\hbar\omega = -D' \pm [D'^2 + \sigma^2]^{1/2}$$

where ω is the microwave frequency, $D' = {}^1/_2|D|$, $\sigma = g\beta\mathbf{B}_0$, and $\mathbf{B}_0$ is the observed resonance field. We obtain 3.521 cm^{-1} for the $|D/hc|$ value. The signal due to the canonical z orientation would be much weaker and would lie around 35 000 G, which is beyond the limit of the available magnetic field of an X-band spectrometer.

It should be noted that the $|D/hc|$ value for mesitylphosphinidene is much larger than those for phenylnitrenes ($\approx$1 cm^{-1}) and phenylcarbenes ($\approx$0.5 cm^{-1}).[7] Two factors could contribute to the observed large ZFS: spin dipolar interaction between the two unpaired electrons and second-order spin–orbit coupling. The smaller the spatial separation of the two unpaired electrons, the greater the ZFS. To account for the observed value of $|D/hc|$ in this case, however, the unpaired electrons would have to be unreasonably close. The second-order spin–orbit contribution is likely to be dominant,[15] especially when the heavy atom effect is recognized: the spin–orbit coupling constant of a phosphorus atom is about 16 times that of nitrogen. Even for a singlet–triplet splitting of 40 kcal/mol, a spin–orbit coupling constant of 230 cm^{-1}, a reasonable value,[16] would give rise to the observed $|D/hc|$.

The observed triplet mesitylphosphinidene is believed to be in its ground state. In a phosphinidene R–P, a lone pair of electrons on phosphorus can occupy an orbital that is almost pure 3s, and it should be energetically favorable for the other two nonbonding electrons to occupy different 3p orbitals. The lowest energy state arising from this configuration should be a triplet.

Further work is needed to detect ESR signals from other transitions using a higher frequency spectrometer, such as a Q- or K-band instrument, and to determine by other means the singlet–triplet energy gap for phosphinidenes.

Acknowledgment. Because François Mathey's wise skepticism spurred us on, we dedicate this paper to him. Matthew Platz and Robert Conlin gave helpful advice and criticism. Financial support from the National Science Foundation under Grant No. CHE-9108130 is gratefully acknowledged.

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