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Infrared, UV/Vis, and W-band EPR Spectroscopic Characterization and Photochemistry of Triplet Mesitylphosphinidene**

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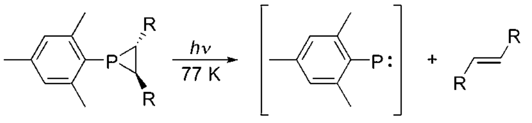
Although many simple carbenes (R_2C)[1] and nitrenes (RN)[2–4] have been detected by various spectroscopic techniques, analogous phosphinidenes (RP) have not.[5–7] In sharp contrast to the abundant examples of transition-metal complexed phosphinidenes,[8–10] evidence of noncomplexed phosphinidines has remained elusive except for a recent matrix-IR study by Glatthaar and Maier[11] on H_3SiP, which was generated by the reaction of atomic silicon with phosphine, and an earlier electron paramagnetic resonance (EPR) study by Gaspar and co-workers[12] on mesitylphosphinidene (2,4,6-$Me_3C_6H_2P$; MesP; **3**), which was obtained by photolysis of *trans*-1-mesityl-2,3-dimethylphosphirane (**1**) in methylcyclohexane at $T = 77$ K (Scheme 1). No other direct experimental confirmation has been obtained for the existence of **3**.

Theoretical studies concur with the spectroscopic observation that a strongly preferred triplet ground state is predicted for aryl phosphinidene.[13,14] From the X-band



1 R = Me
2 R = H

3

Scheme 1. Photochemical formation of triplet MesP (**3**).

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EPR spectrum, a zero-field-splitting (ZFS) parameter, D, of $|D/hc| = 3.521\ \text{cm}^{-1}$ was determined,[12] which is much larger than that for triplet phenylnitrenes ($\approx 1\ \text{cm}^{-1}$) and triplet phenylcarbenes ($\approx 0.5\ \text{cm}^{-1}$). The unusually large value of D was attributed to second-order spin–orbit contributions. Recent calculations on spin–orbit coupling in alkyl nitrenes, phosphinidenes, and arsinidenes yielded a D value of $|D/hc| = 3.46\ \text{cm}^{-1}$ for triplet methyl phosphinidene,[15] in line with the results of Gaspar and co-workers.[12] However, it should also be noted that on photolysis of more congested phosphiranes, Yoshifuji and co-workers[16] were unable to obtain an EPR signal in the reported region other than a weak signal at 5 K that was believed to be due to triplet oxygen.

We have investigated the photochemistry of **1** and **2** by using matrix-isolation spectroscopy and laser flash photolysis; herein we report EPR, infrared, and UV/Vis data that unequivocally support the formation of mesitylphosphinidene **3**.

Initially, using an X-band EPR spectrometer, we tried in vain to reproduce the EPR spectrum reported by Gaspar and co-workers.[12] Photolysis (248 nm, KrF-excimer, or 254 nm) of **2**, which was matrix-isolated in glassy methylcyclohexane ($T = 5$ K), resulted in the formation of yellow matrices but the corresponding spectra only showed strong doublet signals around $g = 2$ (g is the g factor) without EPR transitions attributable to triplet **3**. However, employing a W-band (95 GHz) EPR spectrometer, we detected a very weak signal exactly at the place predicted (4926 mT, Figure 1) for a triplet species with the ZFS parameters reported by Gaspar and co-workers; a background scan without sample showed no transitions in this spectral region.

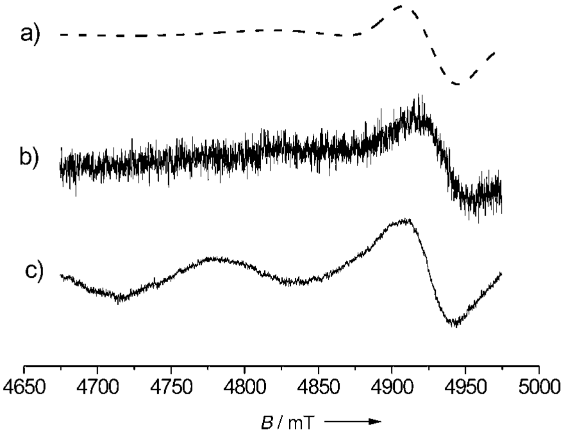


Figure 1. W-band EPR spectra of a sample of **2** in polycrystalline cyclohexane ($T = 5$ K), irradiated for 60 min with $\lambda = 254$ nm. a) Simulated spectrum. Simulation parameters: line width = 10 mT, $D = -3770.6$ mT ($|D/hc| = 3.521\ \text{cm}^{-1}$). b) Experimental spectrum obtained by sweeping the magnetic field from lower to higher values and c) from higher to lower values.

Monitoring by IR spectroscopy of the photolysis ($\lambda_{exc} = 254$ nm, 48 h) of **1** or **2**, which were matrix-isolated in Ar at 10 K, showed slow disappearance of the phosphirane IR bands and formation of very weak new bands. Some of these bands are attributable to *trans*-2-butene (from **1**) or ethylene (from **2**), whose IR spectra were also recorded independently by matrix isolation of these alkenes. The remaining bands are assigned to triplet **3** based on a comparison with the IR spectrum calculated at the B3LYP/6-31G(d) level (Table 1).

Table 1: Calculated and experimental IR data of **3** (range 1700 to 500 cm^{-1}).

No.	$\tilde{\nu}_{calcd}$ [cm^{-1}]	$\tilde{\nu}_{calcd}$ (×0.97) [cm^{-1}]	Calcd intensity [km mol^{-1}]	$\tilde{\nu}_{exp.}$ [cm^{-1}]	Exp. intensity	Description[a]
46	1644.7	1595.0	50.2			8A
45	1575.9	1528.6	4.7	1532.4	vw	8B+τ *p*-CH$_3$
44	1527.6	1481.8	8.3	–	–	δ_{as} *o*-CH$_3$
43	1523.0	1477.3	33.0			δ_{as} *o*-CH$_3$
42	1516.5	1471.0	5.6	–	–	δ_{as} *p*-CH$_3$
41	1515.9	1470.4	9.3	–	–	δ_{as} *p*-CH$_3$
40	1512.6	1467.2	0.2	–	–	τ *o*-CH$_3$
39	1511.5	1466.2	15.9	1431.1	w	τ *o*-CH$_3$
38	1457.6	1413.9	1.6	1407.3	vw	19B+τ *p*-CH$_3$
37	1445.8	1402.4	3.1	1398.9	w	δ_s CH$_3$
36	1443.3	1400.0	1.4			δ_s CH$_3$
35	1443.3	1400.0	1.0	–	–	19A+δ_s CH$_3$
34	1439.2	1396.0	1.2	–	–	δ_s CH$_3$
33	1319.2	1279.6	1.6	1296.0	vw	14
32	1309.9	1270.6	9.4	1286.2	w	13
31	1271.5	1233.4	0.8	1237.8	vw	3
30	1206.5	1170.3	0.3	1170.5	vw	9A
29	1074.9	1042.7	2.2	–	-	17B+ρ CH$_3$
28	1070.8	1038.7	0.0	–	–	17A+ρ CH$_3$
27	1068.3	1036.3	5.0	1033.3	w	ρ CH$_3$
26	1065.3	1033.3	19.2			ρ CH$_3$
25	1059.7	1027.9	0.7	–	–	ρ CH$_3$
24	1041.9	1010.6	0.0	–	–	ρ CH$_3$
23	1026.8	996.0	1.9	993.0	vw	ρ CH$_3$
22	973.9	944.7	1.1	–	–	ρ CH$_3$
21	941.1	912.9	0.3	–	–	ρ CH$_3$
20	898.0	871.1	0.0	–	–	10A
19	874.0	847.8	12.5	849.8	m	5
18	725.5	703.7	0.9	709.7	w	4
17	630.5	611.6	4.8	625.8	w	6A
16	572.8	555.6	0.03	542.9	vw	12

[a] Descriptions are analogous to those of the vibrations of benzene as proposed by Pitzer and Scott.[17]

When the sample was subjected to further irradiation ($\lambda_{exc} = 385$–420 nm or $\lambda_{exc} > 455$ nm, 90 min), the IR bands associated with both triplet **3** and *trans*-2-butene or ethylene disappeared, while those of the starting materials **1** or **2** partially re-emerged, together with a new set of IR bands.[18a] The new photoproduct showed a broad IR band at $\tilde{\nu} = 2261.2\ \text{cm}^{-1}$, thus indicating the presence of a P–H bond. By comparison with a calculated IR spectrum (B3LYP/6-31G(d)), the product could be identified as 1*H*,2*H*-dihydrobenzophosphete **4** (Figure 2; see also the Supporting Information).[18b] Intramolecular C–H insertion of the phosphorus center of supermesitylphosphinidene (2,4,6-*t*Bu$_3$(C$_6$H$_2$)P; Mes*P) into the *ortho*-*t*Bu group to give a phosphaindane is common[6–7] and λ^5-benzophosphetes have been reported previously.[19] The new dihydro-λ^3-benzophosphete **4**, which is energetically favored over triplet **3**, may be formed similarly or via phosphaquinone methide **5** (Scheme 2).

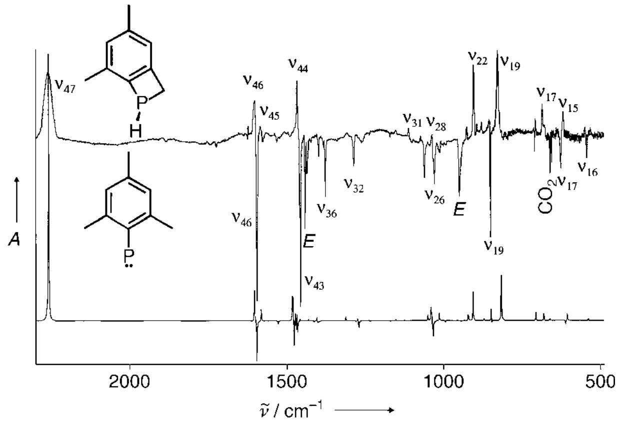
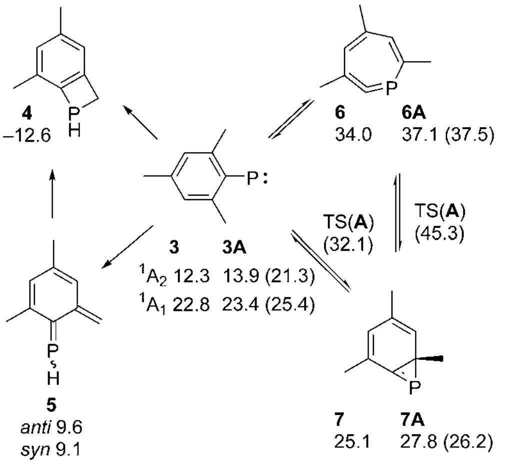


Figure 2. Top: Difference IR spectrum (Ar, 10 K) of the spectra obtained after photolysis of **2** at $\lambda_{exc} = 254$ nm (48 h) and subsequently at $\lambda_{exc} > 385$ nm (90 min). Bands pointing down disappear on photolysis at $\lambda_{exc} > 385$ nm and are attributed to a mixture of ethylene (E) and triplet **3**. The splitting of phosphinidene bands at $\tilde{\nu} = 1028.6$ and 1061.3 cm^{-1} (ν_{26}) is likely due to Fermi resonance.[18b] Several very weak bands remain unassigned. Bands pointing up are attributed to the secondary photoproduct **4** and traces of **2**. The highest intensity of the difference spectrum amounts to ca. 0.1. The assignment of a number of selected bands has been indicated by giving the transition numbers (see Tables 1 and S1). Bottom: calculated IR difference spectrum (0.97×scaling, (U)B3LYP/6-31G(d)) of **4** minus triplet **3**.



Scheme 2. B3LYP/6-31G(d) energies [kcal mol^{-1}] for the $C_9H_{11}P$ and unsubstituted C_6H_5P (**A**) isomers relative to triplet **3** and **3A**. CASPT2-(8/8)/6-31G(d) energies for **A** are given in parentheses.

The UV/Vis spectrum further supports the photochemical formation of **3** from matrix-isolated phosphiranes **1** (and **2**). Photolysis ($\lambda_{exc} = 254$ nm, 80 min, Ar, 10 K) gave rise to two new strong absorptions at $\lambda = 278$ and 292 nm, three weaker absorptions around 350, 370, and 390 nm, and a weak, broad absorption with fine structure between 420 and 470 nm. Subsequent long-wavelength photolysis ($\lambda_{exc} > 455$ nm) resulted in depletion of the absorptions at $\lambda = 278$, 292, 350, and >420 nm, while those at $\lambda = 370$ and 390 nm initially increased in intensity (Figure 3). Extended near-UV photolysis ($\lambda_{exc} = 360$–400 nm, 2 h) resulted in bleaching of all absorptions with $\lambda > 300$ nm.

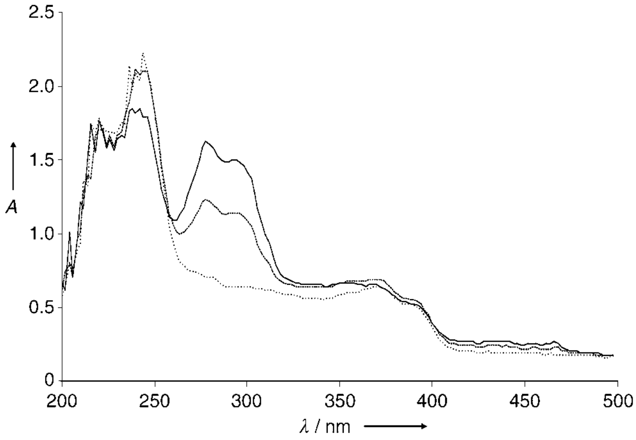


Figure 3. UV/Vis spectra (Ar, 10 K) obtained after photolysis of **1** after photolysis at $\lambda_{exc} = 254$ nm for 80 min (——), after subsequent photolysis at $\lambda_{exc} > 455$ nm for 10 min (-----), and after extended photolysis at $\lambda_{exc} > 455$ nm for 100 min (•••••).

These observations are rationalized by assigning the absorptions $\lambda = 278$, 292, 350, and 420–470 nm to triplet mesitylphosphinidene **3**, and those at $\lambda = 370$ and 390 nm to a secondary photoproduct other than **4**. The UV/Vis spectrum of **3**, with a weak, structured broad band extending to $\lambda = 470$ nm, strongly resembles the UV/Vis spectra of known triplet aryl nitrenes.[4a] The intense excitations at $\lambda = 285$, 310, 340, 415, and 440 nm calculated with time-dependent B3LYP/6-311+G(d,p)[20] for triplet mesitylphosphinidene provide convincing evidence that triplet **3** is indeed formed upon photolysis of matrix-isolated mesitylphosphiranes **1** and **2**,[21] albeit in small yield.[22] The origin of the absorptions at 370 and 390 nm cannot be attributed to secondary photoproduct **4** because its calculated UV/Vis spectrum (TD-B3LYP/6-311+G(d,p)) gives a longest-wavelength absorption at $\lambda_{max} = 255$ nm. Among the compounds considered, the calculated spectrum of didehydrophosphepine **6** ($\lambda_{max} = 360$ and 385 nm) matches best the experimental data.[23,24] Formation of **6** from **3** may occur by ring enlargement, either directly,[25] or via bicyclic phosphirene **7**.[26] Borden and co-workers showed by using multiconfigurational second-order perturbation theory (CASPT2) that the ring expansion of singlet phenylphosphinidene **3A** to **6A** (via **7A**) is endothermic with sizeable barriers (Scheme 2);[27] our calculations at the B3LYP/6-31G(d) level give similar results, except for the state $^1A_2$ of the parent molecule.[28] The tentative assignment of didehydrophosphepine **6** as a minor photoproduct may appear surprising as it is the least-stable isomer of those considered, though bulky linear phospha-allenes are known.[29] However, steady-state irradiation under conditions of matrix-isolation spectroscopy frequently allows for the observation of processes that are thermodynamically unfavorable and whose outcome mostly depends on the concentration of photostationary equilibriums.

Finally, we explored the laser flash photolysis (LFP) of an argon-purged cyclohexane solution of **1** at ambient temperature with an excitation of 266 nm and nanosecond time resolution. The resulting transient spectrum (Figure 4) contained a single species with absorptions at $\lambda_{max} = 285$ nm (vs)

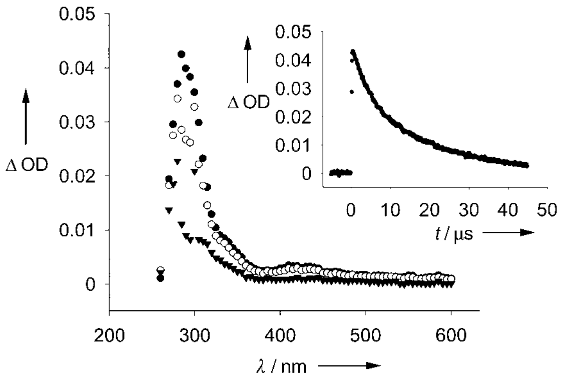


Figure 4. Transient spectra, recorded after LFP ($\lambda_{exc} = 266$ nm) of phosphirane **1** in cyclohexane under Ar atmosphere. Black circles: 470 ns after LFP, white circles: 1.7 µs after LFP, black triangles: 75 µs after LFP. Inset: transient trace, monitored at $\lambda = 285$ nm.

and 400–475 nm (broad, weak) and a lifetime $\tau = 13$ µs, which we assign to phosphinidene **3** based on the similarity with the UV/Vis spectrum of the matrix-isolated species at 10 K (Figure 3). The transient species could be quenched with oxygen,[30] and it reacted with the π-systems ethyl propiolate HC≡CCOOEt ($k_{ETP} = (7.7 \pm 1.1) \times 10^6$ L mol^{-1} s^{-1}) and tetramethylallene ($k_{TMA} = (5.0 \pm 0.8) \times 10^6$ L mol^{-1} s^{-1}, see the Supporting Information) but not with 1-hexene. This reactivity supports the formation of triplet **3**, which is expected to give an allylic triplet diradical with tetramethylallene, whereas such stabilization cannot occur with hexene as a reaction partner.

In conclusion, we have unequivocally identified triplet mesitylphosphinidene **3** as the primary reaction product in the photolytic cleavage of phosphiranes **1** and **2** by using a variety of low-temperature and time-resolved spectroscopic techniques. Under conditions of matrix isolation, **3** is formed in very low yield only, which is likely to be due to the efficient photoinduced addition of **3** to the alkene still present in the matrix cage. Upon further irradiation, **3** rearranges into 1*H*,2*H*-dihydrobenzophosphete **4**. Results obtained by using laser flash photolysis provide further support for the formation of **3**, and show that **3** will readily be quenched by reactive π-systems. Further studies on the photochemistry of **1**, **2**, and related compounds are in progress.

Experimental Section

The matrix isolation setup used in this work has been described before.[31] As light sources, a Hg low-pressure lamp ($\lambda = 254$ nm; Gräntzel, Germany) and Hg high-pressure lamps (Osram, 500 W, Oriel housing) in combination with cut-off filters were used. Argon (Messer-Griesheim, 99.999 %) was used as the matrix material. Compounds **1** and **2** were synthesized according to reported procedures.[32] Deposition was performed by using the slow-spray-on technique at a sample temperature of 20 °C. *Trans*-2-butene (99 %) was supplied by Matheson and deposited as 0.1 %/99.9 % mixture with Ar. X-band EPR-spectroscopic measurements were performed by using a Bruker Elexsys E500 EPR spectrometer with an ER077R magnet (75 mm pole cap distance) and an ER047 XG-T microwave bridge. Frozen solutions of **2** in methylcyclohexane were irradiated both within the resonator cavity ($T = 5$ K) by using a Lambda-Physik Compex 110 excimer laser operated with Kr/F$_2$ (248 nm, 200 mJ per pulse) or externally ($T = 77$ K) by using $\lambda = 254$ nm (Hg low-pressure lamp). W-band EPR-spectroscopic measurements employed a Bruker Elexsys E680 spectrometer. Prior to measurement, a degassed solution of **2** in cyclohexane was irradiated ($\lambda = 254$ nm, 60 min, $T = 77$ K) in a quartz capillary cooled to 77 K in a quartz dewar and transferred frozen into the precooled cryostat. Experimental parameters: frequency = 94.185061 GHz, microwave power = 15 dB, modulation amplitude = 0.1 mT, modulation frequency = 100 kHz. Simulations were performed by using the Easyspin routine[33] and all the parameters entering the simulation are given in the figure caption.

The setup used for laser flash photolysis has been described before.[34] Solutions (ca. 0.1 mM) of **1** in cyclohexane (Baker, spectroscopic grade) were purged with Ar for 20 min prior to the experiment. Tetramethylallene (Aldrich) and ethyl propiolate (Fluka) were of the highest purity commercially available and were used as received. 1-Hexene (Aldrich) was freshly distilled immediately prior to use.

All calculations were performed with Gaussian 98.[35] All geometry optimizations and frequency calculations (scaled by 0.97)[36] were performed at the (U)B3LYP/6-31G(d) level of theory. UV spectra were calculated using time-dependent density functional theory (TDDFT; B3LYP/6-311+G(d,p)).

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irradiation times. b) The observed spectrum of **3** has two medium intensity bands at $\tilde{\nu} = 1040–1070\,\text{cm}^{-1}$ but only one is calculated. This may be due to Fermi resonance between the bands at $\tilde{\nu}_{\text{calcd}} = 1065.3\,\text{cm}^{-1}$ (A′) and $\tilde{\nu}_{\text{calcd}} = 572.8\,\text{cm}^{-1}$ (A′, $\tilde{\nu}_{\text{exp.}} = 542.9\,\text{cm}^{-1}$), which would split the band at $\tilde{\nu}_{\text{calcd}} = 1065.3\,\text{cm}^{-1}$ into the two components observed at 1028.6 and $1061.3\,\text{cm}^{-1}$.

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[22] The reversibility of the phosphirane cleavage indicates that the low yield of **3** is due to an unfavorable photostationary equilibrium rather than a very low quantum yield or pronounced filter effects.

[23] The observation of an extremely weak IR band at $\tilde{\nu} = 1723.7\,\text{cm}^{-1}$ supports the formation of **6** (C=C=P stretching mode: $\tilde{\nu}_{\text{calcd}} = 1712.9\,\text{cm}^{-1}$ (scaled by 0.97, weak).

[24] Phosphaquinone methide **5** (*anti*-**5**: $\lambda_{\text{max, calcd}} = 482$ nm; *syn*-**5**: $\lambda_{\text{max, calcd}} = 495$ nm) and bicyclic phosphirene **7** ($\lambda_{\text{max, calcd}} = 334$ and 494 nm) are less likely candidates.

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