

Supporting Information

Three Different Fates for Phosphinidenes Generated by Photocleavage of Phospha-Wittig Reagents ArP=PMe₃

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Experimental

General Compounds **1**,¹ **2**,¹ **5**,² **6**,³ and Mes*P=PMe₃*⁴ were synthesized as per reported literature methods. PMe₃ was purchased from Aldrich and dried under Na and then filtered through alumina. THF and pentane were purified by distillation from purple Na-benzophenone solutions under N₂. ¹H and ³¹P NMR spectra were recorded using a 300 MHz Varian Gemini spectrometer. ³¹P NMR are referenced to external 85% H₃PO₄, while ¹H NMR are referenced to residual proton solvent signals of C₆D₆.

Synthesis of 2,6-Trip₂C₆H₃P=PMe₃ (3) To 1.00 g (1.71 mmol) of 2,6-Trip₂C₆H₃PCl₂³ was added 1.10 eq (123 mg) of Zn dust and 6.00 eq (1.06 mL) of PMe₃. The reaction mixture was stirred vigorously for 20 h and progressively changed from a clear to yellow solution. After filtration to remove excess Zn powder and removal of all volatiles under reduced pressure, a white-yellow solid was obtained which was extracted with 20 mL hexanes. The resultant bright-yellow solution was again stripped of all volatiles under reduced pressure to give a yellow solid. Pure yellow crystals of 2,6-Trip₂C₆H₃P=PMe₃ were obtained after recrystallization from hot pentane at -35 °C. Isolated yield: 0.71 g, 70%. ³¹P {¹H} NMR (C₆D₆): δ -113.4 (*J*_{PP} = 563 Hz), -1.6 (*J*_{PP} = 564 Hz). ¹H NMR (C₆D₆): δ 0.60 (dd, 9H, P(CH₃)₃, ²*J*_{HP} = 12 Hz, ³*J*_{HPP} = 3 Hz), 1.22 (d, 12H, CH(CH₃)₂, ³*J*_{HH} = 6.9 Hz), 1.27 (d, 12H, CH(CH₃)₂, ³*J*_{HH} = 6.9 Hz), 1.50 (d, 12H, CH(CH₃)₂, ³*J*_{HH} = 6.8 Hz), 2.87 (m, 2H, CH(CH₃)₂), 3.2 (m, 6H, CH(CH₃)₂), 7.05 (t, 1H, *J*_{HH} = 7.2 Hz), 7.14 (d, 2H, *J*_{HH} = 7.9 Hz), 7.23 (s, 4H). ¹³C {¹H} NMR (C₆D₆): δ 17.29 (dd, P(CH₃)₃, *J*_{CP} = 41.2 Hz, ³*J*_{CPP} = 15.3 Hz), 24.36 (CH(CH₃)₂), 24.60 (CH(CH₃)₂), 26.19 (CH(CH₃)₂), 31.28 (CH(CH₃)₂), 34.92 (CH(CH₃)₂), 121.55, 123.62, 130.30, 140.90, 146.34, 147.26, 148.11.

Photochemistry Irradiation of samples was performed using the 3rd harmonic (355 nm) of an Nd:YAG laser (Surelite, Continuum). The pulsewidth and repetition rate were ~10 ns and 20 Hz, respectively. The beam was passed through a quartz cylindrical lens to form an oblong spot of approximately 3.5 cm in length and 1.0 cm at the mid-point. All samples were irradiated at 22.2 °C at a wavelength of 355 nm and power of 200-220 mW. Sample concentrations of about 0.04 M in 0.4 mL C₆D₆ were employed in all instances unless otherwise stated. NMR yields were calculated by employing known concentrations of 1,4-dimethoxybenzene as an internal standard. Quartz 5 mM NMR tubes (Wilmad) were employed for all studies.

Photolysis of 1 Photolysis of **1** is accompanied by rapid fading of initial bright yellow color to a clear solution. The reaction is complete in 10 min as ascertained by ³¹P NMR to produce quantitative formation of the cyclometallated species **4** and PMe₃.

Photolysis of 2 Photolysis of **2** is accompanied by a gradual change of solution from an initial bright yellow to an orange solution characteristic of the diphosphene **5**. Monitoring of the reaction by ³¹P NMR indicates qualitatively that rate of formation of **5** is decreased over time. After 2.5 h, the reaction is > 95% complete with respect to starting **2**, and produces **5** (90-95 %), PMe₃. An unidentified species is also produced (³¹P NMR δ -27 ppm). Efforts are currently underway to characterize this compound.

Photolysis of 3 Photolysis of **3** is accompanied by a rapid color change from an initial bright yellow to orange. Monitoring of the reaction by NMR indicates that all **3** is consumed within 20 min to produce the diphosphene 2,6-Trip₂C₆H₃-P=PC₆H₃-2,6-Trip₂ and the cyclized phosphafluorene **6** in approximately a 1:9 ratio. Compound **6** is also photochemically active and produces two unidentified species (³¹P {¹H} NMR δ -35 and δ -69.8.). This was confirmed by the independent synthesis³ and subsequent photolysis of **6**. No change is observed in the ³¹P NMR signal for the diphosphene 2,6-Trip₂C₆H₃-P=PC₆H₃-2,6-Trip₂, indicating it to be inert to photolysis.

Photolysis of Mes*P=PMes* Photolysis of Mes*P=PMes* is accompanied by gradual fading of initial characteristic orange color of diphosphene to a pale yellow solution. After 2 h, reaction is complete with respect to starting Mes*P=PMes* to produce the cyclometallated species **4** (> 95%).

Photolysis of 5 No change in initial orange color was observed as the diphosphene was irradiated. After 2 h, only signals for **5** were observed on ³¹P NMR spectroscopy indicating that the diphosphene is inert to photolysis.

Photolysis of 2 in presence of PMe₃ The photolysis of **2** was carried out in the presence of differing amounts of PMe₃ in order to gauge the effect of [PMe₃] on rate of conversion of **2** to **5**. Four samples of **2** with 0, 1.3, 3.6, and 8.6 eq of PMe₃ were irradiated and monitored at time intervals of 0, 15, and 30 min. Plots of [**5**] versus [PMe₃] indicated that the rate of conversion of **2** to **5** is inhibited with increasing [PMe₃]. (See Figure 1, Supporting Information)

Photolysis of 1 and 3 in presence of PMe₃ The photolysis of **1** and **3** was carried out in the presence of 1, 3, 5, and 10 eq of PMe₃. Samples of **1** were monitored after 10 min whereas samples of **3** were monitored after 20 min. In both cases, the presence of excess PMe₃ has no influence on the rate of decomposition of **1** and **3** to the products of photolysis.

Photolysis of 2 with added 1 The photolysis of **2** was carried out in the presence of 1, 5, and 10 eq of **1**. In the case of **2** with 1 eq of **1**, monitoring the samples by NMR spectroscopy after 20 and 40 min shows that the predominant products are the respective decomposition products **5** and **4**. However, trace asymmetric diphosphene Mes*P=PC₆H₃-2,6-Mes₂ (**7**) is also observed on ³¹P NMR spectroscopy. In the presence of more **1** (5 and 10 eq), it can be observed (qualitatively) that more **7** is formed. Quantification of [**7**] with respect to [**1**] is difficult due to overlap of resonances in ¹H NMR and the photochemistry of **7** itself (to be reported in full paper).

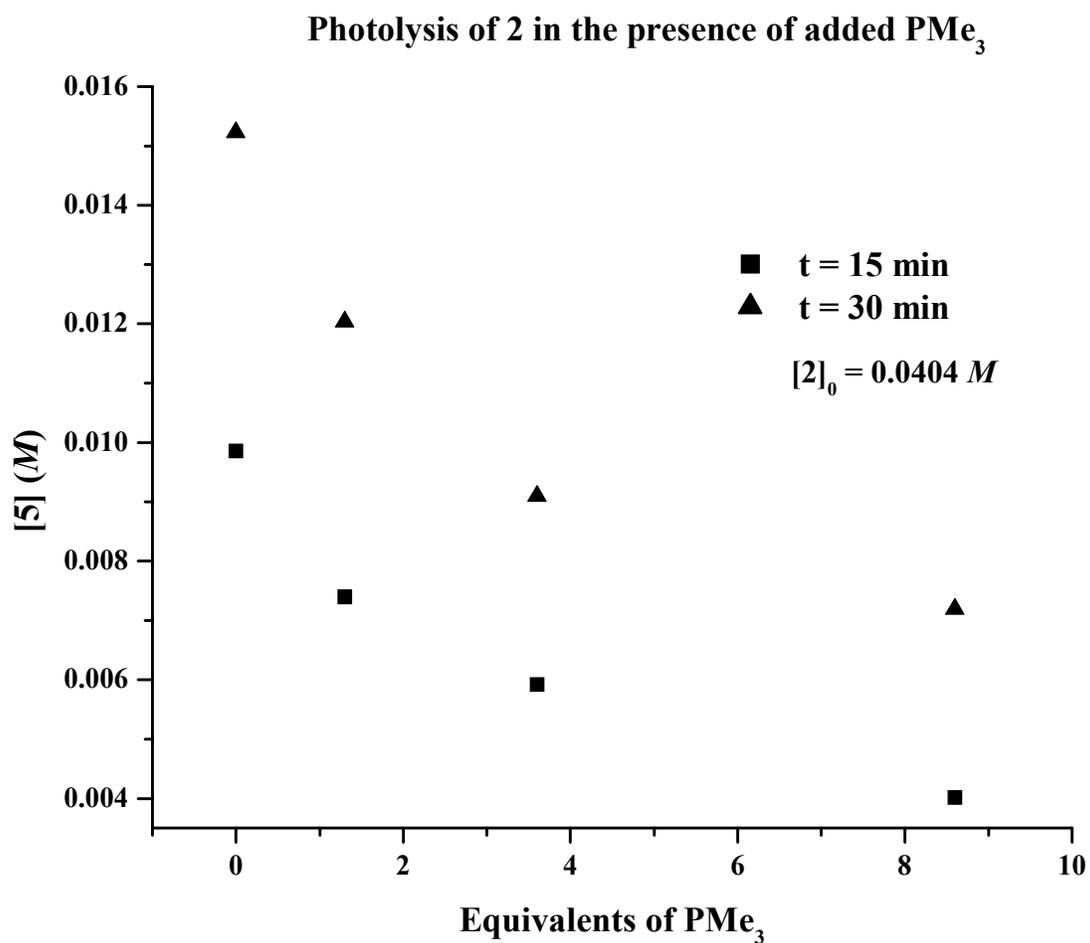


Figure 1: Photolysis of 2 and added PMe_3 – Plot of conversion of 5 after 15 and 30 min

References

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