Supporting Information

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

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**Experimental**

**General** Compounds 1, 2, 5, 6, and Mes*P=PMes* 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-Trip2C6H3PCl2 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 ºC. Isolated yield: 0.71 g, 70%. 31P {1H} NMR (C6D6): δ -113.4 (JPP = 563 Hz), -1.6 (JPP = 564 Hz). 1H NMR (C6D6): δ 0.60 (dd, 9H, P(C3H3)3, JHP = 12 Hz, JHP = 3 Hz), 1.22 (d, 12H, CH(CH3)2, JHH = 6.9 Hz), 1.27 (d, 12H, CH(CH3)2, JHH = 6.9 Hz), 1.50 (d, 12H, CH(CH3)2, JHH = 6.8 Hz), 2.87 (m, 2H, CH(CH3)2), 3.2 (m, 6H, CH(CH3)2), 7.05 (t, 1H, JHH = 7.2 Hz), 7.14 (d, 2H, JHH = 7.9 Hz), 7.23 (s, 4H). 13C {1H} NMR (C6D6): δ 17.29 (dd, P(C3H3)3, JCP = 41.2 Hz, JCPP = 15.3 Hz), 24.36 (CH(CH3)2), 24.60 (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 ºC 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-Trip$_2$C$_6$H$_3$-P=PC$_6$H$_3$-2,6-Trip$_2$ and the cyclized phosphafluorene 6 in approximately a 1:9 ratio. Compound 6 is also photochemically active and produces two unidentified species ($^{31}$P $^1$H) NMR $\delta$ -35 and $\delta$ -69.8. This was confirmed by the independent synthesis$^3$ and subsequent photolysis of 6. No change is observed in the $^{31}$P NMR signal for the diphosphene 2,6-Trip$_2$C$_6$H$_3$-P=PC$_6$H$_3$-2,6-Trip$_2$, 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 $^{31}$P NMR spectroscopy indicating that the diphosphene is inert to photolysis.

Photolysis of 2 in presence of PMe$_3$  The photolysis of 2 was carried out in the presence of differing amounts of PMe$_3$ in order to gauge the effect of [PMe$_3$] on rate of conversion of 2 to 5. Four samples of 2 with 0, 1.3, 3.6, and 8.6 eq of PMe$_3$ were irradiated and monitored at time intervals of 0, 15, and 30 min. Plots of [5] versus [PMe$_3$] indicated that the rate of conversion of 2 to 5 is inhibited with increasing [PMe$_3$]. (See Figure 1, Supporting Information)

Photolysis of 1 and 3 in presence of PMe$_3$  The photolysis of 1 and 3 was carried out in the presence of 1, 3, 5, and 10 eq of PMe$_3$. Samples of 1 were monitored after 10 min whereas samples of 3 were monitored after 20 min. In both cases, the presence of excess PMe$_3$ 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=PC$_6$H$_3$-2,6-Mes$_2$ (7) is also observed on $^{31}$P 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 $^1$H NMR and the photochemistry of 7 itself (to be reported in full paper).
Photolysis of 2 in the presence of added PMe₃

Figure 1: Photolysis of 2 and added PMe₃ – Plot of conversion of 5 after 15 and 30 min

Equivalents of PMe₃
References