Supplementary Information

S1. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometries for the IR-detected isomers of 1-phosphabutyne (1)

S2. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of 1-methylphosph- -aallene (2a)

S3. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of 3-methylphosph- -aallene (2b)

S4. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of 1-propynylphosphine (3)

S5. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of P-methylethynylphosphine (4)

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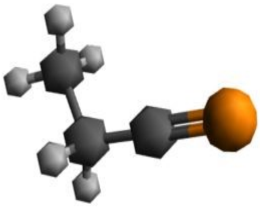
S1. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometries for the IR-detected isomers of 1-phosphabutyne (1)

S1.1. Optimized structure of 1-phosphabutyne (1)

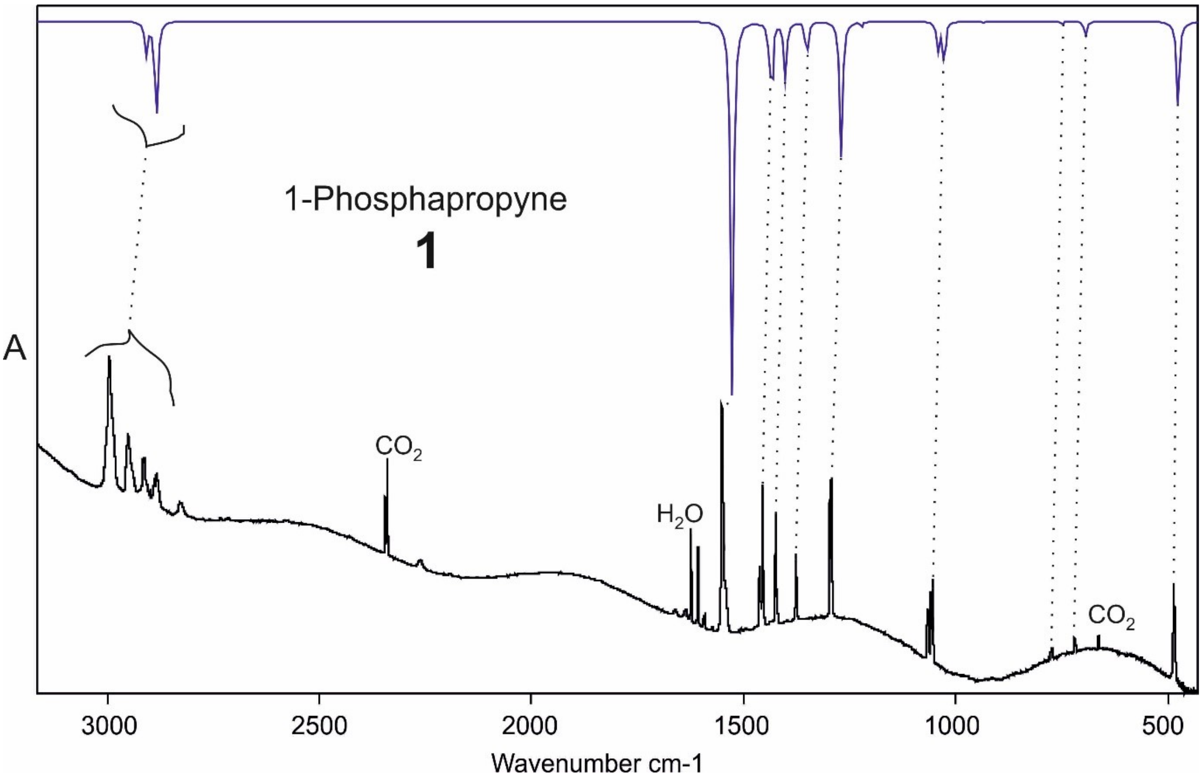
Cartesian coordinates / Å				Structure
C	2.06959	0.53578	0.00001	
C	1.10397	-0.66172	0.00005	
C	-0.30085	-0.27247	-0.00008	
P	-1.78417	0.16500	0.00002	
H	1.29699	-1.29091	0.87468	
H	1.29697	-1.29069	-0.87478	
H	1.91527	1.15602	0.88180	
H	1.91520	1.15589	-0.88186	
H	3.10180	0.18515	0.00001	

S1.2. Infrared vibrational bands of 1-phosphabutyne (1)

Mode	Theory		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
CCP bending	475.7	11.2	485.5
H_3C-C bending	695.3	1.4	719.8
CH_2 rocking (CH_3 and CH_2 unit)	749.5	0.3	774.5
H_3C-CH_2 bending	1027.8	4.6	1052.7, 1055.0, 1058.8
CH_2 twisting	1042.1	2.8	1064.7, 1065.6, 1067.9
CH_2 twisting (CH_3 and CH_2 unit)	1223.1	0.5	-
CH_2 wagging	1269.6	13.8	1292.2, 1296.6
H_3C sym. umberlla	1350.3	3.7	1376.4
CH_2 scissoring	1401.7	5.6	1421.1, 1425.5
H_3C twisting	1434.6	8.0	1455.6, 1462.9
	1441.4	1.6	-
C-P stretching	1527.3	38.7	1551.5
C-H stretching	2885.6, 2908.2, 2917.4 2980.6, 2987.8	10.7, 3.3, 31.0, 22.3, 19.6	2828.0, 2886.5, 2915.7, 2951.4, 2995.5

Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. * Scaling factor 0.96.

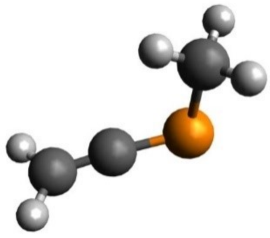
S1.3. IR spectrum of 1-phosphabutyne (1) in Ar matrix.



Top: B3LYP/aug-cc-pVTZ predictions (frequency scaled by 0.96) for the phosphapropyne **1**
Bottom: Deposition spectrum of **1** in argon matrix (1:1000).

S2. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of 1-methylphosphaallene (2a)

S2.1. Optimized structure of 1-methylphosphaallene (2a)

Cartesian coordinates / Å				
C	-0.94319	-0.06397	0.00011	
C	-2.16159	0.39973	-0.00005	
P	0.55591	-0.71997	-0.00000	
C	1.67738	0.78513	-0.00002	
H	-2.78525	0.33756	0.92403	
H	-2.78527	0.33718	-0.92417	
H	2.31744	0.73623	-0.88149	
H	2.31783	0.73595	0.88116	
H	1.12487	1.72280	0.00025	

S2.2. Infrared vibrational bands of 1-methylphosphaallene (2a)

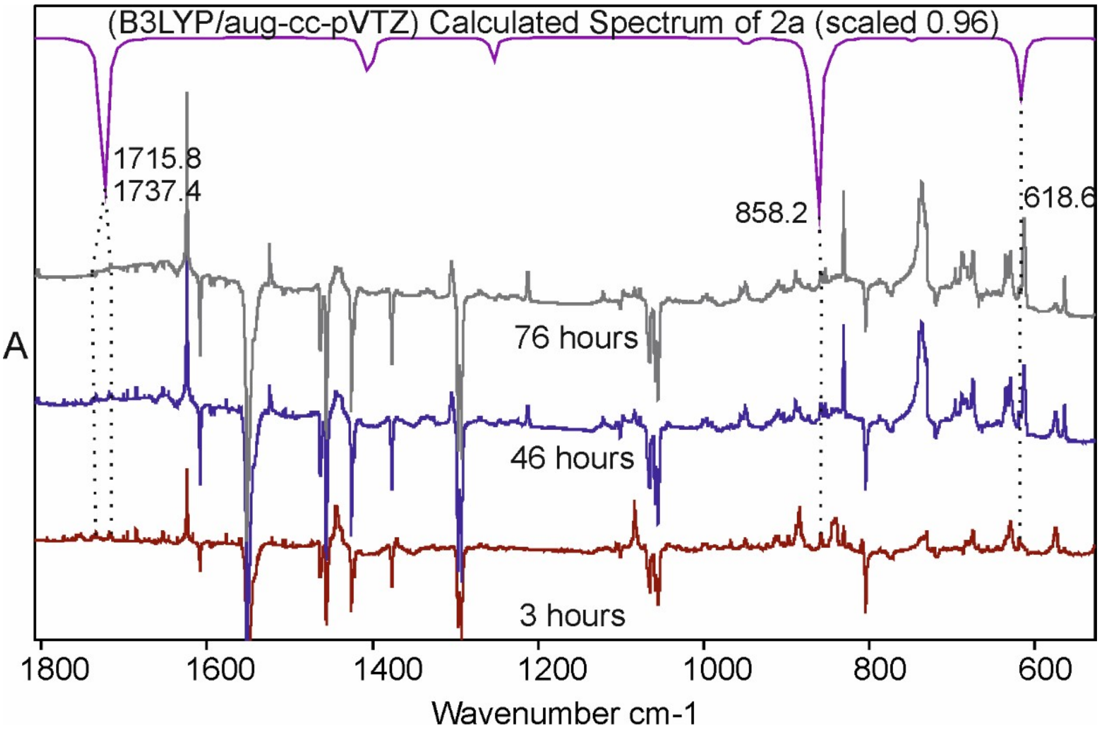
Mode	Theory		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
C-C-P bending	435.6	19.5	-
CH_2 twisting	518.4	1.5	-
P-CH_3 stretching	617.1	16.8	618.6

C-P stretching	748.0	1.0	-
CH_2 rocking (methyl group)	847.1	2.5	-
CH_2 wagging	861.4	44.1	858.2
H_3C-C bending	870.0	15.3	-
CH_2 rocking	948.3	2.7	-
H_3C umberlla	1253.8	6.7	-
CH_2 scissoring	1362.6	0.02	-
CH_2 scissoring (methyl group)	1401.9	6.5	-
	1409.1	8.1	-
CC stretching	1724.3	54.8	1715.8, 1737.4
CH stretching	2913.1	14.2	-
	2975.8	5.5	-
	2976.3	1.6	-
	3014.2	3.1	-
	3039.3	0.5	-

Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. * Scaling factor 0.96

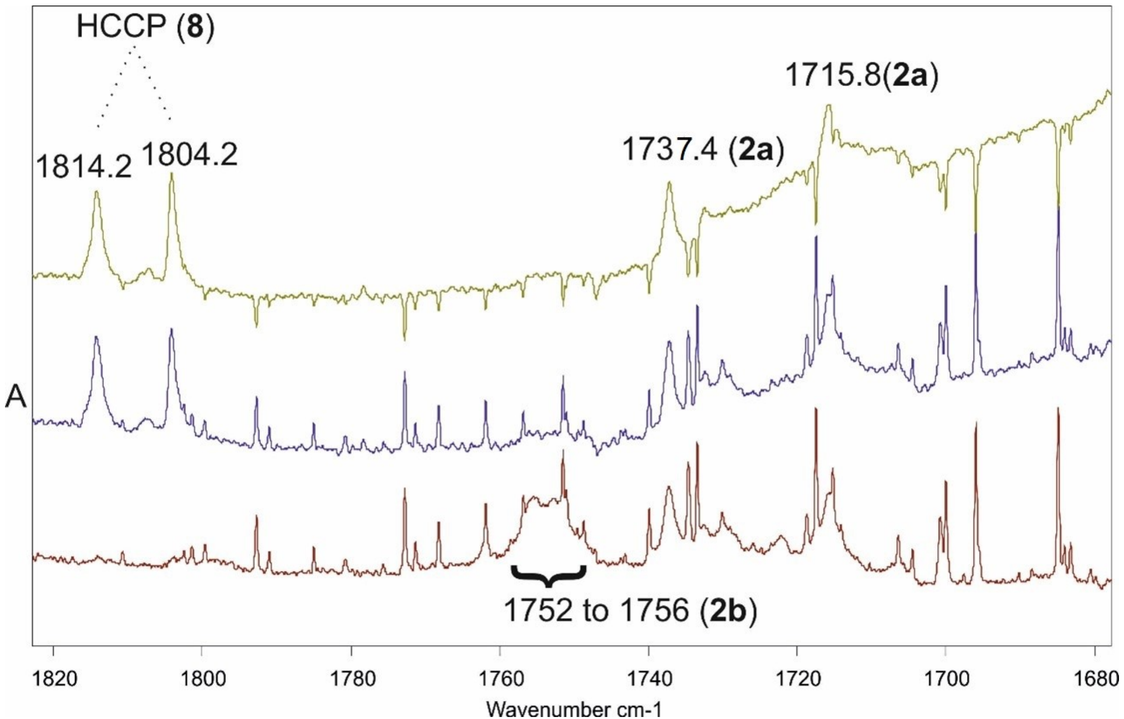
S2.3. Formation of 1-methylphosphaallene (2a) from photolyzed phosphabutyne (1)

a) **Difference spectra showing the effect of mercury lamp irradiation of 1 compared with the DFT-predicted spectrum of 2a:**



Topmost trace shows the B3LYP/aug-cc-pVTZ prediction for the IR spectrum of **2a** (frequency scaled by 0.96). The other three traces are difference spectra (after-minus-before photolysis) illustrating (top to bottom) the net effect of 76 h, 46 h, and 3 h of Hg-lamp irradiation of **1**. Numbers give the band wavenumbers assigned to **2a.** Species **2a** is formed as a product amidst other photoproducts and only the strong IR absorption bands are observed.

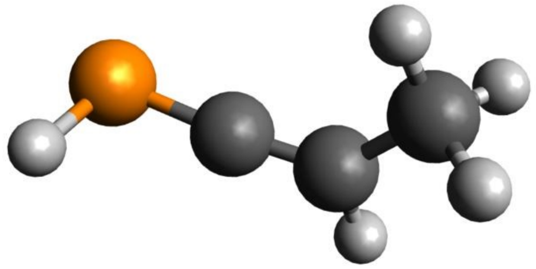
b) **The allenic C-C stretching region is focused on in the following image**



Difference spectra (after-minus-before photolysis) of **1** in argon matrix obtained after 3 h (bottom), 46 h (middle) and 76 h (top) of irradiation with Hg lamp (254 nm). Numbers give the band wavenumbers assigned to **2a, 2b** and **8**. Species **2b** is formed in the early stage of photolysis and is mostly destroyed by later stages of photolysis. The unassigned bands in this region are from atmospheric water.

S3. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of 3-methylphosphaallene (2b)

S3.1. Optimized structure of 3-methylphosphaallene (2b)

Cartesian coordinates / Å				
C	-2.24898	-0.40965	0.00031	
C	-1.10854	0.57279	0.00214	
C	0.15734	0.26254	0.03971	
P	1.74625	-0.13562	-0.10228	
H	2.02787	-0.19130	1.29944	
H	-1.37348	1.62839	-0.01634	
H	-1.88791	-1.43554	0.01176	
H	-2.87106	-0.26705	-0.88590	
H	-2.88808	-0.25424	0.87219	

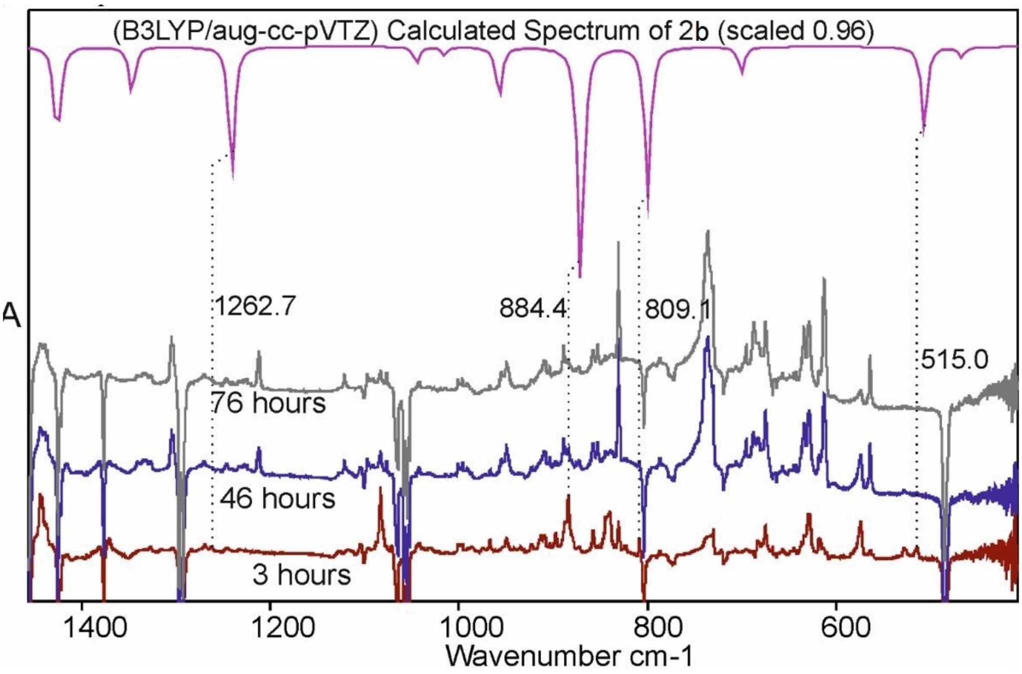
S3.2. Infrared vibrational bands of 3-methylphosphaallene (2b)

Mode	Theory		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
PH bending	467.2	1.4	-
CCCP bending	507.0	11.4	515.0
C-CH$_3$ bending	700.7	3.6	-
CH bending (CH unit)	800.3	20.2	809.1
PH bending (in CPH plane)	871.1	33.1	884.3
H$_3$C-C-H bending	957.4	6.9	-
CH$_2$ rocking (H$_3$C unit)	1015.8	1.1	-
H$_3$C-C-H bending	1045.1	2.3	-
CH bending (CH unit) (HCC plane)	1240.7	16.7	1262.7
H$_3$C umberlla	1346.7	6.5	-
CH$_2$ scissoring (methyl group)	1423.4	6.3	-
	1427.5	7.0	-
CC stretching	1745.7	25.1	1752-1756 (broad)
PH streching	2209.7	86.0	2182.0 or 2257.6#
CH stretching	2902.4	32.1	-
	2946.7	13.2	-
	2971.1	0.5	-
	2997.3	10.7	-

Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. * Scaling factor 0.96
Both 2182.0 and 2257.6 cm^{-1} share a common time evolution with the other peaks of **2b**. The peak at 2257.6 cm^{-1} is a closer match to what is observed for the P-H stretching of CH$_2$CPH although either could be a combination band, site splitting of the P-H stretching vibration, or a different species whose time evolution is similar to **2b**.

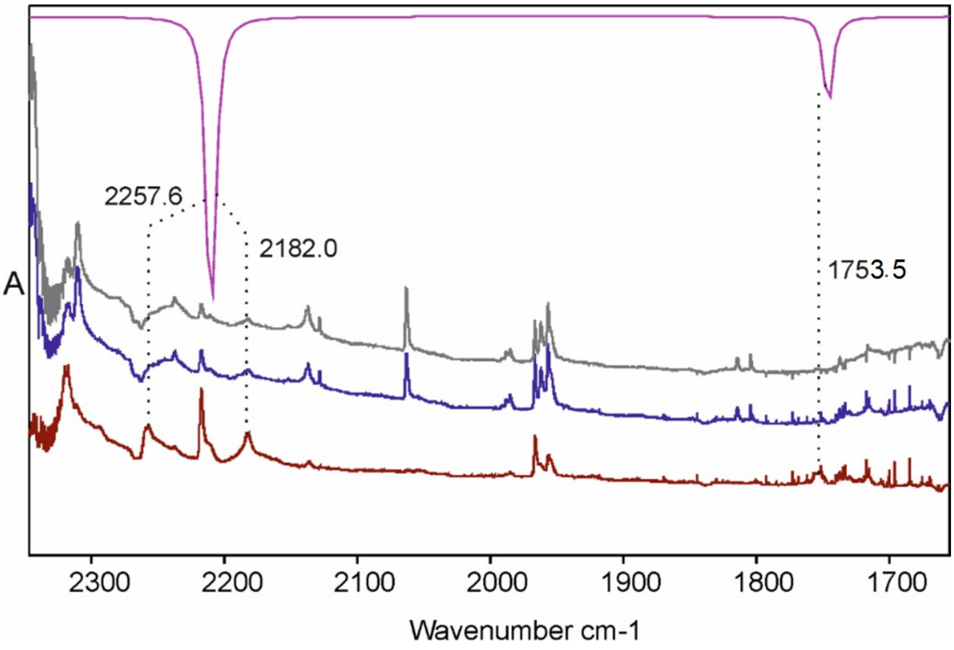
S3.3. Formation of 3-methylphosphaallene (2b) from photolyzed phosphabutyne (1)

a) **Fingerprint region:** Difference spectra showing the effect of Hg-lamp irradiation of **1** compared with the DFT-predicted spectrum of **2b**:



Topmost trace shows the B3LYP/aug-cc-pVTZ prediction for the IR spectrum of **2b** (frequency scaled by 0.96). The other three traces are difference spectra (after-minus-before photolysis) illustrating (bottom to top) the net effect of 3 hours, 46 h, and 76 h of Hg-lamp irradiation of **1**. Numbers give the band wavenumbers assigned to **2b**.Species **2b** is observed only in the early stages of photolysis and is mostly destroyed by later stages. Only a few strong bands of **2b** are observed and they are marked amidst the other photoproducts.

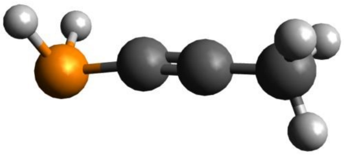
b) **The CC and PH stretching region is focused on below**



Topmost trace shows the B3LYP/aug-cc-pVTZ prediction for the IR spectrum of **2b** (frequency scaled by 0.96). The other three traces are difference spectra (after-minus-before photolysis) illustrating (top to bottom) the net effect of 76 h, 46 h, and 3 h of Hg-lamp irradiation of **1**. Numbers give the band wavenumbers assigned to **2b**. The broad band around 1754 cm^{-1} is also focused on in fig S2.3.b. The bands of **2b** are marked amidst the other photoproducts.

S4. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of 1-propynylphosphine (3)

S4.1. Optimized structure of 1-propynylphosphine (3)

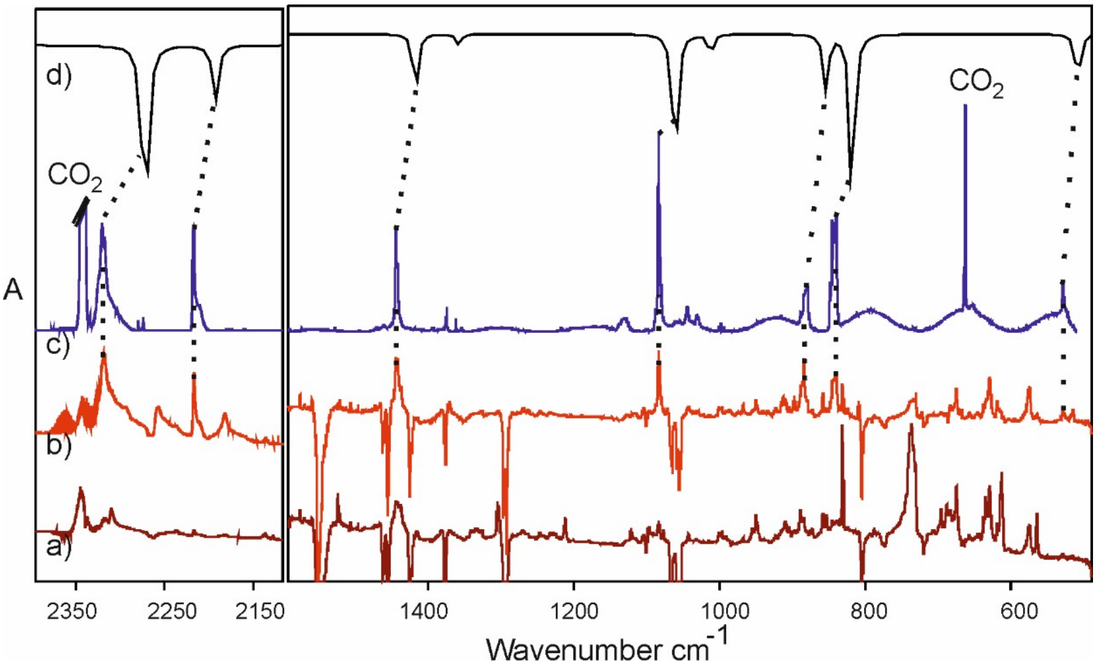
Cartesian coordinates / Å				
C	-2.61182	-0.00001	-0.00641	
C	-1.15854	0.00000	0.01273	
C	0.04739	0.00001	0.04904	
P	1.80968	-0.00000	-0.12730	
H	2.10084	-1.03653	0.80117	
H	2.10086	1.03652	0.80117	
H	-3.00690	0.88310	0.49883	
H	-3.00700	-0.87988	0.50437	
H	-2.99525	-0.00317	-1.02825	

S4.2. Infrared vibrational bands of 1-propynylphosphine (3)

Mode	Theory		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
C-P stretching	508.4	14.3	528.6 (528.5)
PH_2 wagging	817.8	49.6	840.4, 845.5, 847.6 (843.0 broad)
PH_2 twisting	854.6	16.1	880.8, 887.7 (882.7)
CH_3-C bending	1011.3	0.3	1030.5 (1030.5)
CH_3-C bending	1011.8	4.6	1032.0
H_3C-C bending	1014.8	0.7	1045.1(1043.6)
PH_2 scissoring	1061.1	40.9	1083.5, 1088.1 (1083.5)
H_3C-C-H bending	1357.6	2.9	1353.9, 1361.5, 1374.8
H_3C umberlla	1415.8	8.5	1442.1 (1443.7 broad)
CH_2 scissoring (methyl group)	1418.9	7.6	1444.0
CC stretching	2192.6	34.2	2217.6(2216.9)
PH_2 sym. and asym. stretching	2270.3	61.8	2319.0 (2320.0)
	2273.8	55.3	2320.2
CH stretching	2903.5	26.1	2867.1 (2865.9)
	2955.9	7.0	2939.9
	2957.5	5.9	2976.8

Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. Values in brackets were measured for **3** photochemically generated from Ar matrix-isolated **1**. * Scaling factor 0.96.

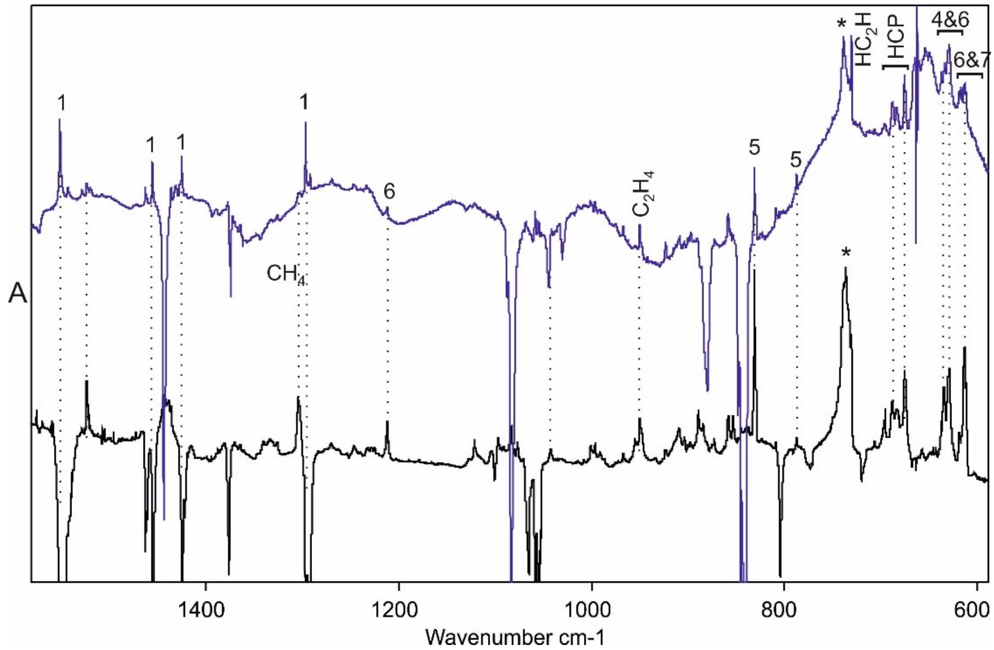
S4.3. Formation of 1-propynylphosphine (3) from photolyzed phosphabutyne (1)



Traces a) and b) are difference spectra (after-minus-before photolysis) showing the net effects of, respectively, 76 h and 3 h of Hg-lamp irradiation (concentration of **3** is highest at the beginning of photolysis); trace c) is the spectrum of authentic **3** isolated in solid Ar. d) B3LYP/aug-cc-pVTZ prediction for the IR spectrum of **3** (frequency scaled by 0.96). The bands of **3** are marked amidst the other photoproducts.

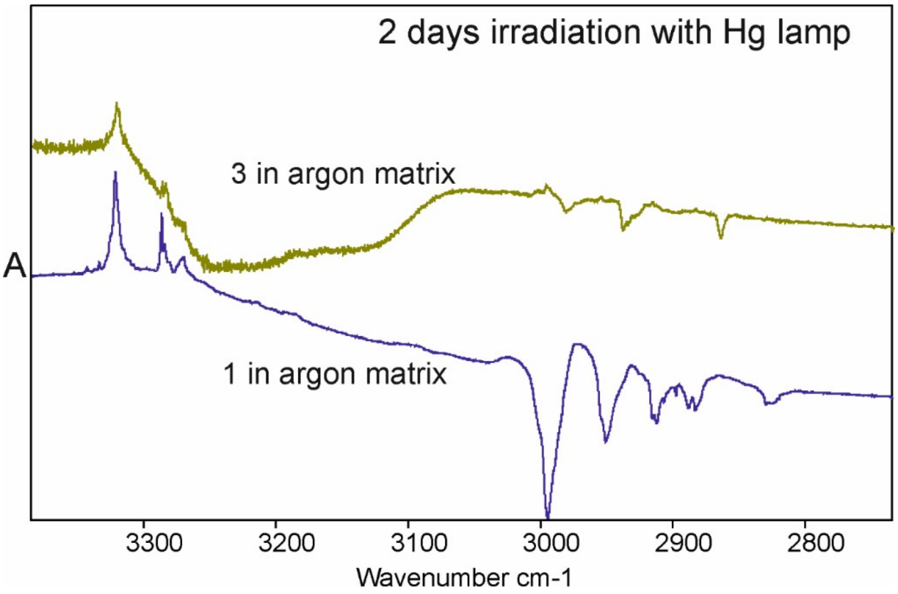
S4.4. Comparison of 1-propynylphosphine (3) and phosphabutyne (1) photolyses

a) Fingerprint region



Difference spectra (after-minus-before photolysis) in argon matrix obtained after 2 days irradiation of 1 (bottom) and 3 (top) in argon matrix. Species **1** and **3** are photoconvertible between each other and they both produce **5** along with other common photoproducts such as HCP, **6**, HCCP etc. Asterisk marks a spectral artifact originating from the substrate window.

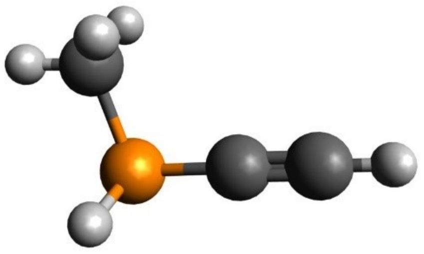
b) CH stretching region showing 3 and 5 producing common photoproducts (HCCCP, 6 and HCCP)



Difference spectra (after-minus-before photolysis) in argon matrix obtained after 2 days irradiation of **1** (bottom) and **3** (top in argon matrix.

S5. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of P-methylethynylphosphine (4)

S5.1. Optimized structure of P-methylethynylphosphine (4)

Cartesian coordinates / Å	
C 2.24257 0.37393 0.00588 C 1.10619 -0.02617 0.02917 P -0.53500 -0.69037 -0.11292 C -1.55663 0.86245 0.02528 H 3.24327 0.72940 -0.00207 H -0.65214 -1.12074 1.23617 H -1.44823 1.43130 -0.89648 H -1.26884 1.48436 0.86906 H -2.60187 0.56996 0.12512	

S5.2. Infrared vibrational bands of P-methylethynylphosphine (4)

Mode	Theory		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
C-P-C sym. stretching	597.1	14.6	-
CH bending	626.4	40.7	629.1
CH$_3$-P str. and PH bending	647.2	20.1	637.4, 645.7
CH$_3$-P bend. and PH bending	683.8	2.3	-
CH bending	696.4	34.7	695.8

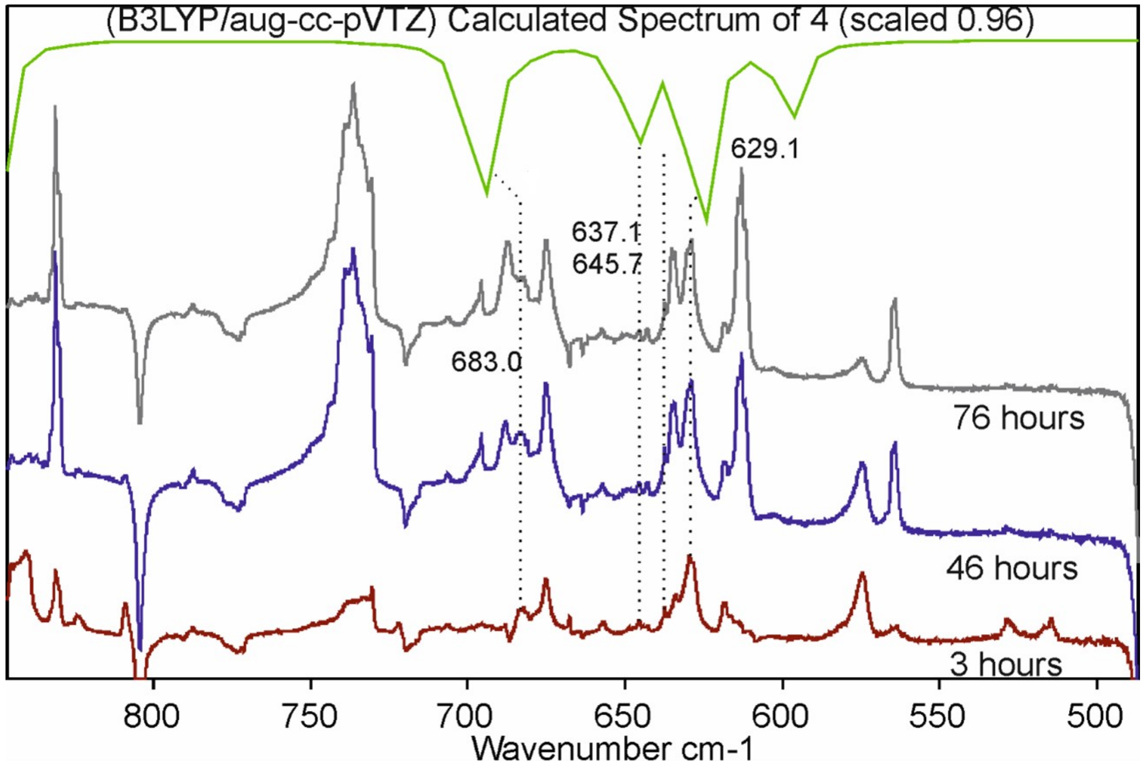
CH_3-P bend. and PH bending	848.8	22.4	844.8
CH_3-P bend. and PH bending	880.8	26.4	887.2
CH_3-P bend. and PH bending	978.5	33.1	997.9 (broad)
H_3C umberlla	1268.4	0.9	
CH_2 scissoring (methyl group)	1407.2	6.7	
	1416.3	5.5	
C-C stretching	2052.6	0.2	
PH stretching	2270.2	61.1	2237.2
CH stretching (methyl group)	2920.5	12.7	-
	2991.8	5.5	-
	3007.4	5.3	-
CH stretching	3322.9	67.9	3320.2, 3321.7

Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. * Scaling factor 0.96.

S5.3. Formation of P-methylethynylphosphine (4) from photolyzed phosphabutyne (1)

a)

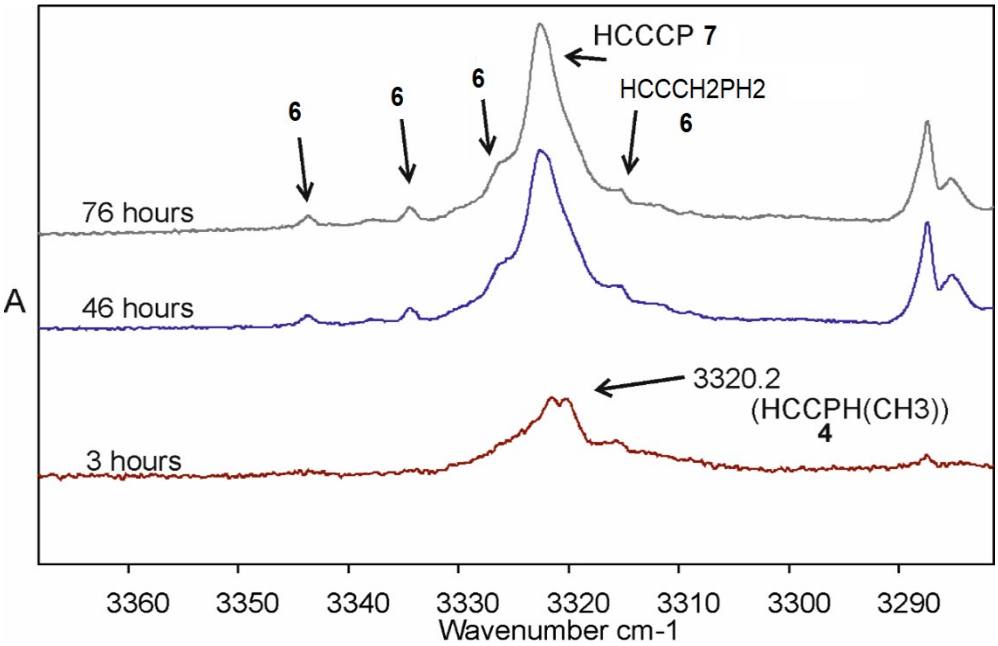
Difference spectra showing the net effect of Hg-lamp irradiation of **1** compared with the DFT-predicted spectrum of **4**.



Topmost trace shows the B3LYP/aug-cc-pVTZ prediction for the IR spectrum of **4** (frequency scaled by 0.96). The other three traces are difference spectra (after-minus-before photolysis) illustrating (bottom to top) the net effect of 3 hours, 46 h, and 76 hours of Hg-lamp irradiation of **1**. Many bands of **4** are overlapped with the bands of other photoproducts, therefore our interpretation is tentative for this species. The acetylenic CH stretching region is shown in the next image

b)

Upon longer irradiation, the C-H stretching band of **4** is overlapped with the analogous band of HCCCP:

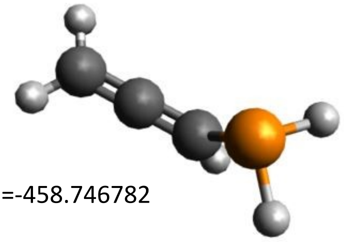


Difference spectra (after-minus-before photolysis) of **1** in argon matrix obtained after 3 h (bottom), 46 h (middle) and 76 h (top) of irradiation with Hg lamp (254 nm).

S6. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of propadienylphosphine (5)

S6.1. Optimized structure of propadienylphosphine (5)

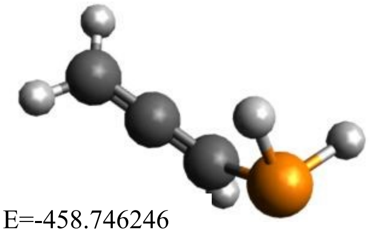
Optimized structure of the anti-conformer of **5**

<table>
<tr><th colspan="4">Cartesian coordinates / Å</th><th></th></tr>
<tr><td>C</td><td>2.37373</td><td>-0.31571</td><td>-0.00000</td><td rowspan="9">
E=-458.746782
ZPVE=0.063649</td></tr>
<tr><td>C</td><td>1.18810</td><td>0.21819</td><td>-0.00001</td></tr>
<tr><td>C</td><td>-0.00683</td><td>0.73300</td><td>0.00004</td></tr>
<tr><td>P</td><td>-1.50353</td><td>-0.34721</td><td>-0.00003</td></tr>
<tr><td>H</td><td>-0.12252</td><td>1.81182</td><td>0.00008</td></tr>
<tr><td>H</td><td>-2.21359</td><td>0.33657</td><td>1.02717</td></tr>
<tr><td>H</td><td>-2.21368</td><td>0.33696</td><td>-1.02691</td></tr>
<tr><td>H</td><td>2.88632</td><td>-0.54515</td><td>0.92597</td></tr>
<tr><td>H</td><td>2.88640</td><td>-0.54499</td><td>-0.92597</td></tr>
</table>

Optimisized structure of the gauche conformer of **5** (0.34 kcal/mole less stable than anti)

Cartesian coordinates / Å	

C	-2.36343	-0.32179	0.01031
C	-1.18081	0.22209	0.00860
C	0.00912	0.74413	0.00092
P	1.58330	-0.20930	-0.10225
H	0.11782	1.82349	-0.04673
H	1.04587	-1.48184	0.21937
H	2.05060	0.04097	1.21904
H	-2.86486	-0.58538	-0.91322
H	-2.88821	-0.52429	0.93636



E=-458.746246

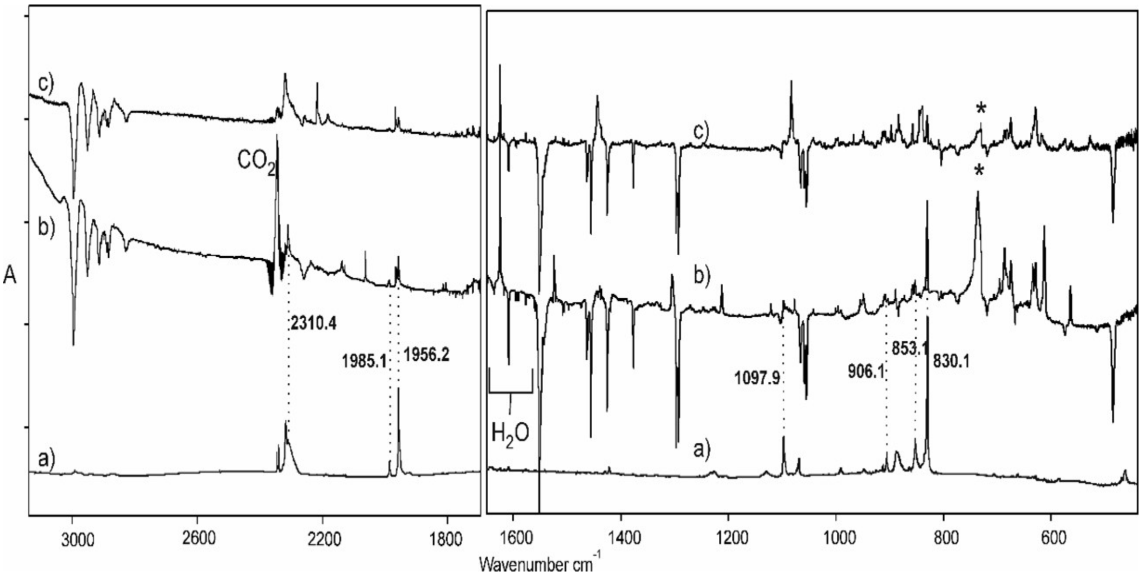
ZPVE=0.063662

S6.2. Infrared vibrational bands of propadienylphosphine (5)

Mode	Theory (anti)		Theory (gauche)		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
C-C-C bending	455.6	19.5	-	-	-
Allene twist	464.1	0.8	446.3	7.0	462.9
Allene twist	-	-	481.9	10.9	-
CP stetching	667.4	0.3	634.5	3.2	-
PH_2 wagging	825.4	31.9	806.8	23.4	829.8, 831.0 (787.7, 829.8, 831.0)
PH_2 twisting	825.8	0.03	-	-	-
CH_2 wagging	832.9	60.9	833.5	52.6	-
PH_2 wagging and CH_2 twist	-	-	851.2	27.3	-
PH_2 twist and CH bend	866.8	38.9	856.3	13.6	853.1, 859.8, 885.0, 887.1, 905.9 (853.1, 889.3, 909.4)
CH_2 rocking	973.7	0.9	976.5	0.9	-
PH_2 scissoring, allene str. and CH bend	1057.9	14.3	1052.5	16.5	1069.1
PH_2 scissor. and CH bend.	1077.6	12.8	1067.6	4.9	1084.1, 1097.7
CH_2 scissor., allene str. and CH bend.	1212.2	15.1	1229.8	3.0	1205.1, 1225.6, 1232.7
CH_2 scissor.	1401.9	2.0	1406.3	0.7	1421.6, 1429.3
CC stretching	1945.5	121.7	1945.5	105.0	1956.2, 1961.9, 1985.1 (1956.2, 1961.9, 1966.6)
PH_2 symmetric stretching	2264.4	74.0	2258.6	73.2	2310.4 (2310.4 & 2258.8)
PH_2 assymmetric stretching	2264.5	66.1	2301.6	39.9	2317.5 (2317.5)
CH stretching	2999.9	0.2	2994.2	1.7	2992.1
	3003.2	1.4	3000.0	0.8	-
	3070.1	0.2	3062.5	0.9	

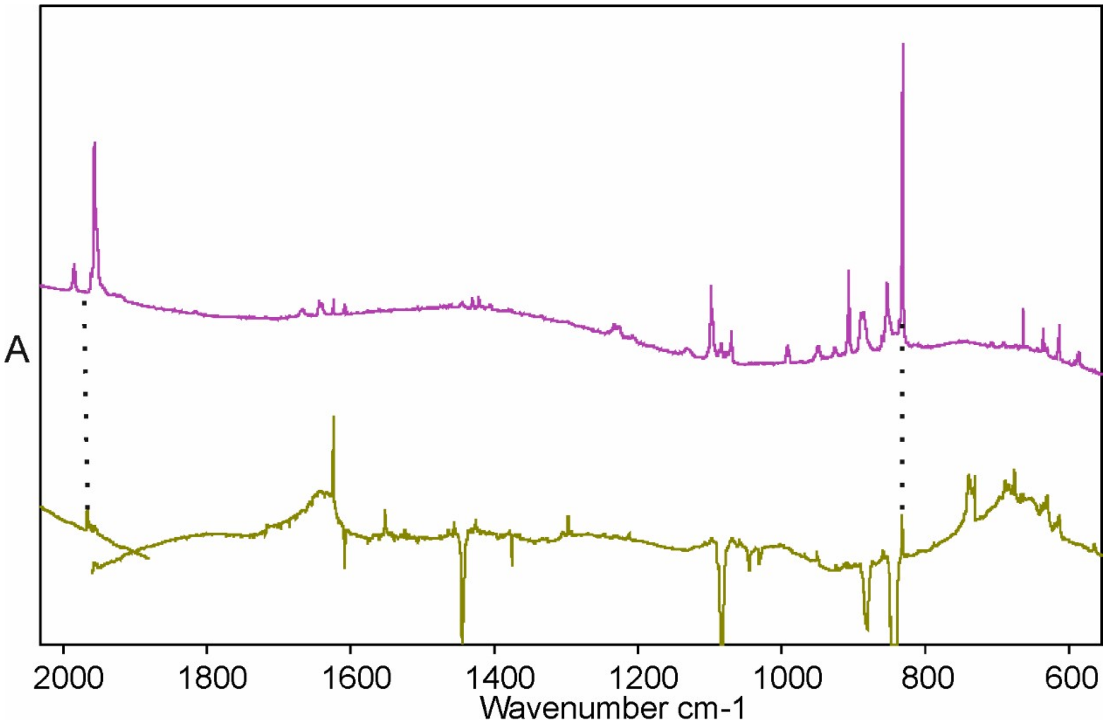
Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. Values in brackets were measured for **5** photochemically generated from Ar matrix-isolated **1**. * Scaling factor 0.96.

S6.3. Formation of propadienylphosphine (5) from photolyzed phosphabutyne (1)



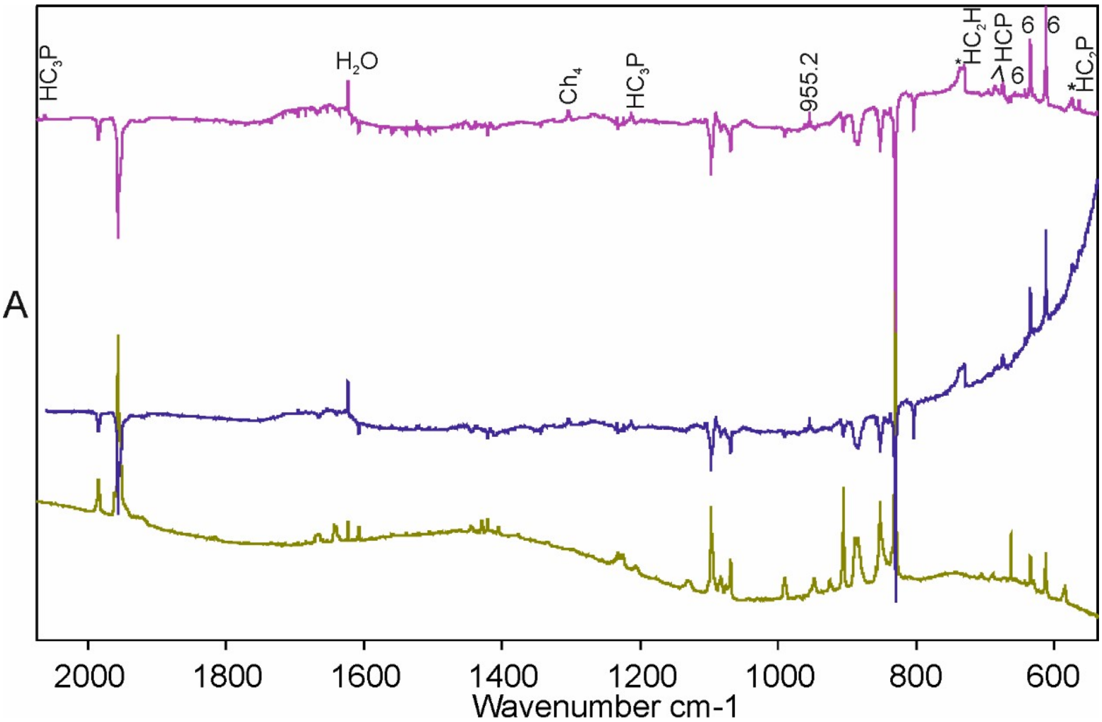
Trace (a) represents the spectrum of an authentic (synthesized) sample of **5** isolated in solid Ar. Trace (b) is the difference spectrum (after-minus-before photolysis) showing the net effects of 46 h of Hg-lamp irradiation. Trace (c) is the difference spectrum (after-minus-before photolysis) showing the net effects of 76 h of Hg-lamp irradiation

S6.4. Formation of propadienylphosphine (5) from photolyzed propynylphosphine (3)

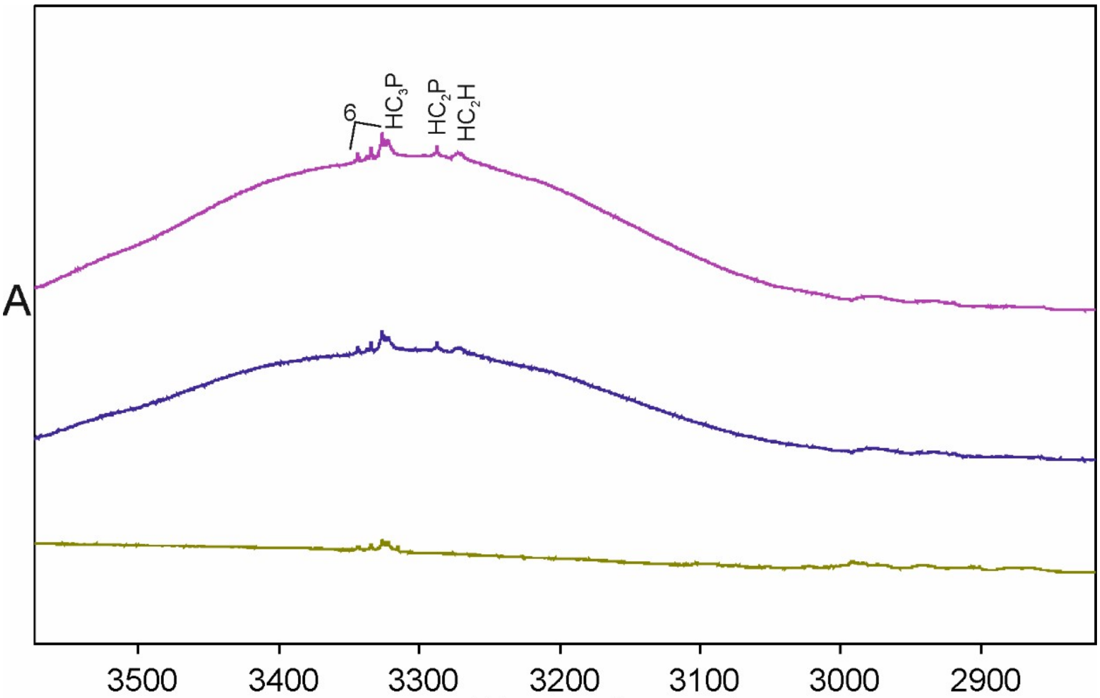


Spectra of Ar matrix-isolated **5**. Bottom: compound **5** photochemically formed from species **1** (after-minus-before photolysis; the net effect of 3 days of Hg-lamp irradiation of **3** in solid argon). Top: the compound obtained by preparative synthesis.

S6.5. Photolysis of 5 in argon matrix (254 nm)



Bottom: spectrum of **5** (obtained by preparative synthesis) isolated in Ar matrix (**6** is present as a contaminant). In the middle: difference spectrum (after-minus-before photolysis) showing the net effect of 1-day Hg-lamp irradiation of **5**. Top: difference spectrum showing the net effect of 3 days of irradiation.

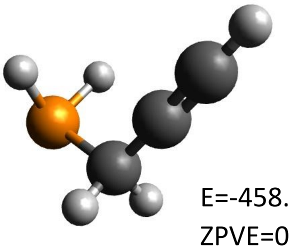


Bottom: spectrum of **5** (obtained by preparative synthesis) isolated in Ar matrix (**6** is present as a contaminant). In the middle: difference spectrum (after-minus-before photolysis) showing the net effect of 1-day Hg-lamp irradiation of **5**. Top: difference spectrum showing the net effect of 3 days of irradiation.

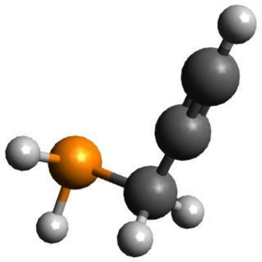
S7. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of propargylphosphine (6)

S7.1. Optimized structure of propargylphosphine (6)

Optimized structure of the anti-conformer of propargylphosphine (**6**):

Cartesian coordinates / Å				
C	-2.33383	-0.42359	0.00002	 E=-458.738625 ZPVE=0.064156
C	-1.29048	0.17001	0.00000	
C	-0.01986	0.86364	-0.00004	
P	1.51930	-0.23411	-0.00012	
H	0.06467	1.51192	0.87446	
H	0.06449	1.51220	-0.87433	
H	1.10235	-1.11256	1.03443	
H	-3.25732	-0.94596	0.00003	
H	1.10124	-1.11432	-1.03272	

Optimized structure of the gauche conformer of propargylphosphine (**6**) (2.85 kcal/mole less stable than anti):

Cartesian coordinates / Å				
C	-2.33642	-0.41646	-0.01039	 E=-458.743171 ZPVE=0.0640866
C	-1.29547	0.18015	0.00526	
C	-0.01761	0.86414	0.03032	
P	1.41854	-0.36529	-0.11340	
H	0.07828	1.46131	0.93634	
H	0.06335	1.54145	-0.82211	
H	1.30055	-0.90658	1.19442	
H	2.43889	0.55090	0.26725	
H	-3.26215	-0.93480	-0.02606	

S7.2 Infrared vibrational bands of propargylphosphine (6)

Mode	Theory (anti)		Theory (gauche)		Gas phase§	Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})	Frequencies (cm^{-1})
C-C-C bending	432.4	14.4	422.6	14.1	432	-
CPstretching	608.5	6.7	618.6	4.5		-
CH bending	629.9	43.1	642.2	40.7	628	612.4, 614.2 (612.8, 614.2)
CH_2 and PH_2 twist	633.3	1.1	-	-	-	-
CH bending	652.2	45.4	650.0	43.5	-	635.4 (635.4)
CH_2 rock PH_2 wag.	-	-	679.0	2.7	-	-
PH_2 twist	-	-	811.1	7.8	-	-
PH_2 wagging	822.2	16.1	-	-	833, 846, 863	-
CH_2 rock. PH_2 twist	-	-	914.3	19.3	-	-
CH_2 wag. PH_2 twist.	930.4	8.8	946.7	1.1	-	-
CC stretching	937.4	3.4	-	-	943	-
PH_2 scissoring	1069.8	12.9	1064.6	15.3	1083, 1095	-

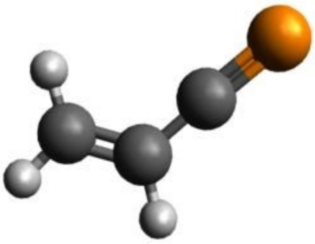
CH_2 twisting	1160.1	2.5	1138.5	6.8	-	-
CH_2 wagging	1193.9	0.7	1179.6	3.4	1230, 1243, 1257	-
CH_2 scissoring	1394.7	4.9	1401.6	4.8	1418	-
CC stretching	2123.3	15.7	2126.6	11.9	2129	2124.7, 2128.1, 2138.5 (2128.0, 2136.7, 2138.5)
PH_2 symmetric stretching	2290.4	37.0	2269.2	79.4	2301	-
PH_2 assymmetric stretching	2297.9	55.2	2291.2	54.8		-
CH_2 Sym and asym. stretching	2914.5	6.8	2919.3	6.5	2933	-
	2945.9	0.7	2961.2	0.9		-
CH stretching	3331.3	75.3	3331.3	73.5	3335	3322.3, 3326.3, 3334.3, 3343.7 (3322.3, 3326.3, 3334.3, 3343.7)

Some vibrational modes appear as multiple IR absorption bands in solid Ar due to the matrix site effect. Values in brackets were measured for **6** photochemically generated from Ar matrix-isolated **1**. * Scaling factor 0.96.

§ R. H. Shay, B. N. Diel, D. M. Schubert, A. D. Norman, *Inorg. Chem.* 1988, **27**, 2378-2382.

S8. Spectral data and B3LYP/aug-cc-pVTZ-predicted equilibrium geometry of vinylphosphaethyne 9

S8.1. Optimized structure of vinylphosphaethyne 9

Cartesian coordinates / Å				
C	2.17565	-0.40554	0.00000	
C	1.18928	0.50004	0.00000	
H	1.96812	-1.46647	-0.00000	
H	3.21119	-0.09640	-0.00000	
C	-0.19003	0.18838	-0.00000	
H	1.43940	1.55733	-0.00000	
P	-1.71121	-0.11278	0.00000	

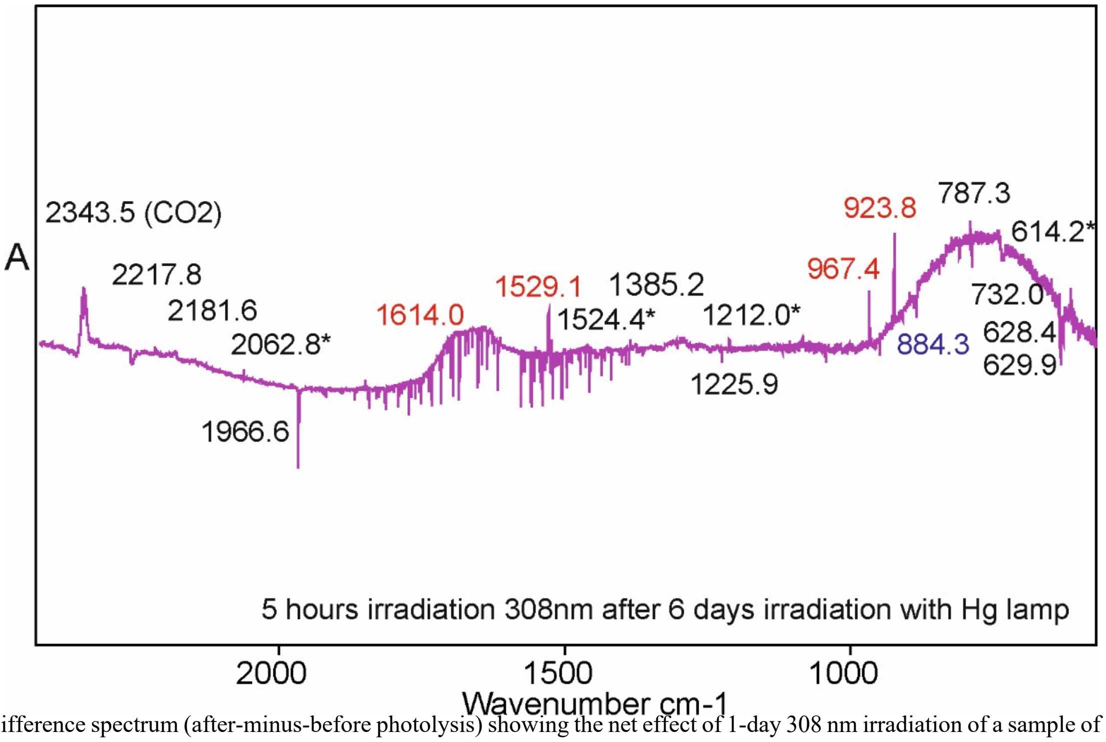
S8.2 Infrared vibrational bands of vinylphosphaethyne 9

Mode	Theory		Experiment (Argon matrix)
	Frequencies* (cm^{-1})	Intensities (km/mol)	Frequencies (cm^{-1})
CCP bending	505.5	9.6	-
CH bending (out of plane)	660.5	0.8	-
CH bending (in plane)	720.2	1.4	-
CH_2 wagging	924.3	44.8	923.8
CH_2 and CH twisting	961.7	8.9	967.4
CH_2 rocking	1032.5	2.4	-
CH bending (in plane)	1261.5	2.1	-
CH_2 scissoring	1366.4	2.2	-
CP stretching	1516.1	23.9	1529.1
CC stretching	1596.9	7.3	1614.0
CH stretching	2995.9	3.4	-
CH_2 sym. and asym. stretching	3022.8	3.3	-
	3108.4	3.5	-

* Scaling factor 0.96.

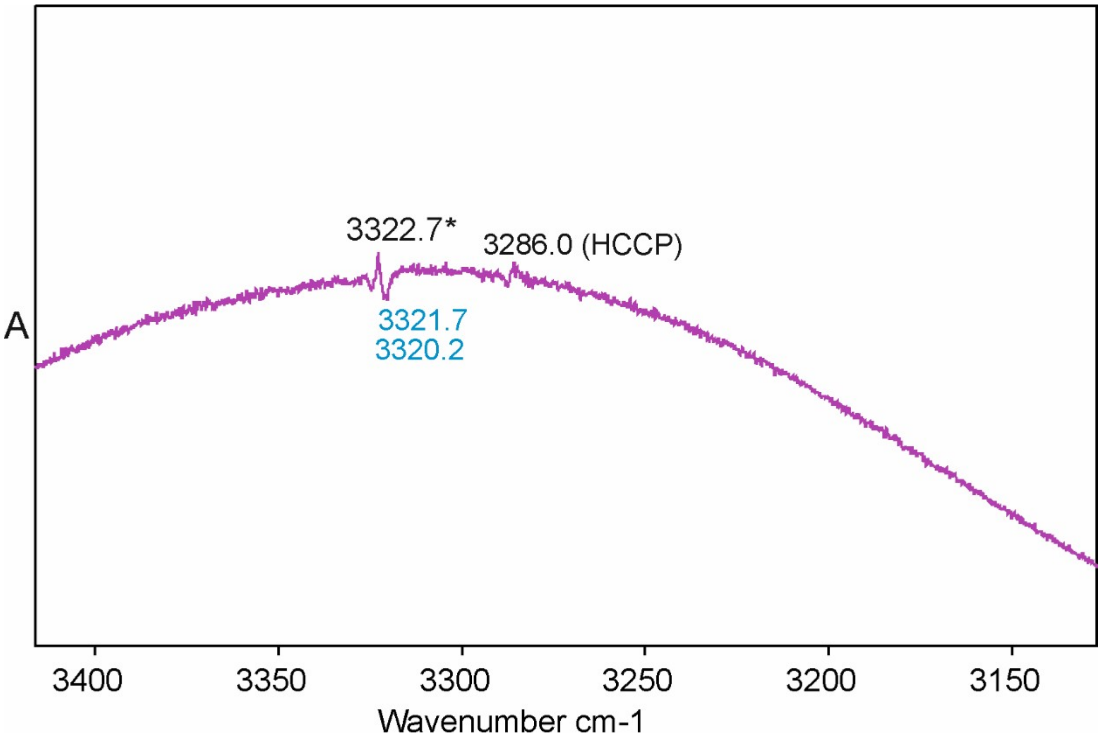
S8.3. Irradiation at 308 nm of a sample of 1 previously photolysed at 254 nm

a)



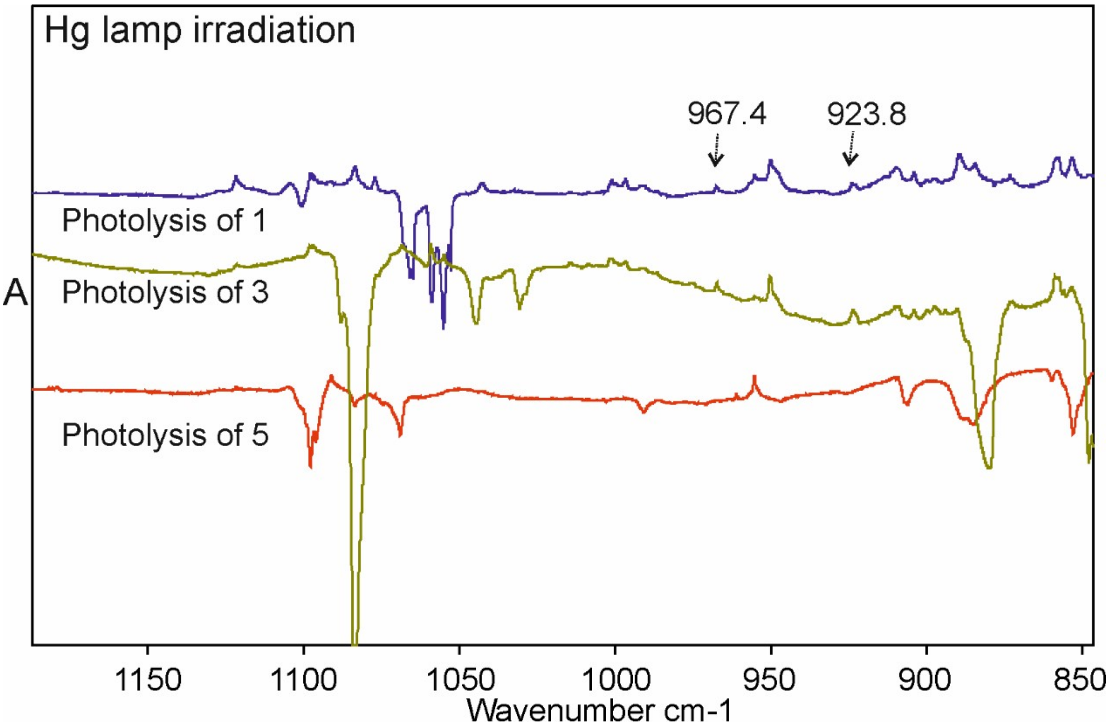
Difference spectrum (after-minus-before photolysis) showing the net effect of 1-day 308 nm irradiation of a sample of **1** in solid Ar previously photolyzed for six-days with a mercury lamp. Values marked in red correspond to **9**, the asterisks to **7**. Downward pointing bands 628, 629, 1966, and 884 cm^{-1} indicate the decomposition of species **4** and **5** upon 308 nm irradiation.

b)



Difference spectrum (after-minus-before photolysis) showing the net effect of 1-day 308 nm irradiation on a sample of **1** in solid Ar previously photolyzed for six-days with a mercury lamp.

S8.4. Vinylphosphaethyne appearing upon Hg-lamp photolyses of 1 and 3, and not in 5



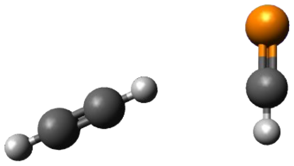
Difference spectrum (after-minus-before photolysis) showing the net effect of 76 h irradiation with Hg lamp (254 nm)

S9. Complexes of HCP with ethylene and acetylene

S9.1: IR frequencies of the acetylene ethylene complex

Optimized structure of complex *a*

Cartesian coordinates / Å	

`P 15.0 -2.1347590000 -0.4327770000 -0.0000490000`
`C 6.0 -1.4875740000 0.9623810000 -0.0000130000`
`C 6.0 3.5973390000 -0.0613400000 -0.0002010000`
`C 6.0 2.4018170000 -0.1130820000 0.0003120000`
`H 1.0 -1.0458290000 1.9377560000 0.0000010000`
`H 1.0 4.6579760000 -0.0166900000 -0.0006110000`
`H 1.0 1.3397450000 -0.1571680000 0.0007570000`
	a 

IR frequencies of Complex *a*

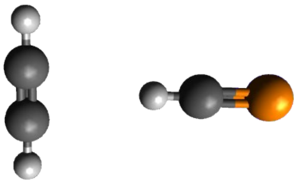
Modes of vibrations	bent-complex of acetylene-HCP		Uncomplexed acetylene and HCP (blue)		IR Shifts of the complexes	
	Infrared frequencies (Intensities)*		Infrared frequencies (Intensities)*			
	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz
	21.7(0.28)	12.0(0.76)	-	-	-	-
	37.8(0.04)	48.2(0.28)	-	-	-	-
	47.3(0.23)	57.2(0.17)	-	-	-	-
	73.3(0.59)	103.9(0.68)	-	-	-	-
C-H bend	646.1(4.17)	585.4(3.35)	638.2(0.00)	577.3(0.0)	7.9	8.1
	647.9(3.58)	587.2(3.68)			9.7	9.9
	685.1(61.07)	652.1(55.19)	683.8(159.0)	650.1(139.3)	1.3	2.0
	691.7(97.75)	662.6(95.1)			7.9	12.5
	749.2(90.49)	736.5(79.1)	737.4(98.06)	723.8(89.7)	11.8	12.7
	752.4(68.28)	739.6(62.5)			15.0	15.8
CP str.	1283.5(0.13)	1192.6(0.0)	1284.8(0.0)	1195.5(0.0)	-1.3	-2.9
CC str.	1982.4(2.03)	1883.5(1.9)	1986.6(0.00)	1889.2(0.0)	4.2	5.7
CH stretching	3211.9(17.09)	3214.2(17.7)	3215.9(15.8)	3221.1(16.1)	-4.0	-6.9
	3263.4(161.06)	3279.2(182.7)	3277.8(89.93)	3294.3(95.6)	-14.4	-15.1
	3366.8(1.85)	3379.7(3.3)	3378.3(0.00)	3392.3(0.0)	-11.5	-12.6

Number highlighted in blue are for uncomplexed HCP. * Scaling factor 0.96

T- complex between acetylene and phosphaethyne

Optimized structure of complex *b*

Cartesian coordinates / Å	

`P 15.0 2.4636040000 0.0012430000 -0.0002270000`
`C 6.0 0.9252250000 -0.0084920000 -0.0000680000`
`C 6.0 -3.0162890000 0.6016270000 0.0002200000`
`C 6.0 -3.0337150000 -0.5948060000 0.0003040000`
`H 1.0 -0.1471500000 -0.0155570000 0.0002360000`
`H 1.0 -3.0046620000 1.6634650000 0.0002380000`
`H 1.0 -3.0535750000 -1.6565290000 0.0002000000`
	b 

IR frequencies of Complex *b*

Modes of vibrations	T-complex of acetylene-HCP		Uncomplexed acetylene and HCP (blue)		IR Shifts of the complexes	
	Infrared frequencies (Intensities)*		Infrared frequencies (Intensities)*			
	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz
	24.6(0.06)	22.5(0.12)	-	-	-	-
	45.4 (0.23)	49.4(0.01)	-	-	-	-
	47.1(0.0)	73.1(0.30)	-	-	-	-
	79.4(0.14)	87.4(9.18)	-	-	-	-
C-H bend.	640.3(0.00)	577.4(0.00)	638.2(0.00)	577.3(0.0)	2.1	0.1
	645.0(0.61)	581.4(0.40)			6.8	4.1
	710.3(38.8)	685.5(37.50)	683.8(159.0)	650.1(139.3)	**26.5**	**35.4**
	719.2(56.89)	699.2(48.53)			**35.4**	**49.1**
	740.5(116.14)	723.1(101.72)	737.4(98.06)	723.8(89.7)	3.1	-0.7
	744.5(2.18)	729.5(109.01)			7.1	5.7
CP str.	1281.8(2.18)	1193.7(2.39)	1284.8(0.0)	1195.5(0.0)	3	1.8
CC str.	1984.3(0.68)	1885.9(0.48)	1986.6(0.00)	1889.2(0.0)	2.3	3.3
CH stretching	3192.5(79.91)	3190.9(114.19)	3215.9(15.8)	3221.1(16.1)	-23.4	-30.2
	3272.0(93.94)	3288.5(102.1)	3277.8(89.93)	3294.3(95.6)	-5.8	-5.8
	3372.0(0.19)	3382.5(0.31)	3378.3(0.00)	3392.3(0.0)	-6.3	-9.8

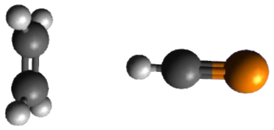
Number highlighted in blue are for uncomplexed HCP. * Scaling factor 0.96

Complexes between ethylene and phosphaethyne

Optimized structure of complex *c*

Cartesian coordinates / Å				
P	15.0	2.6601670000	-0.0000710000	0.0004540000
C	6.0	-2.9153770000	0.6632290000	0.0003790000
C	6.0	-2.9187900000	-0.6623330000	0.0003770000
C	6.0	1.1218950000	-0.0008070000	-0.0016360000
H	1.0	-2.9257730000	-1.2315520000	-0.9203680000
H	1.0	-2.9199050000	-1.2315670000	0.9211390000
H	1.0	-2.9194070000	1.2324770000	-0.9203650000
H	1.0	-2.9135160000	1.2324490000	0.9211490000
H	1.0	0.0497180000	-0.0012700000	-0.0030890000

c



IR frequencies of Complex *c*

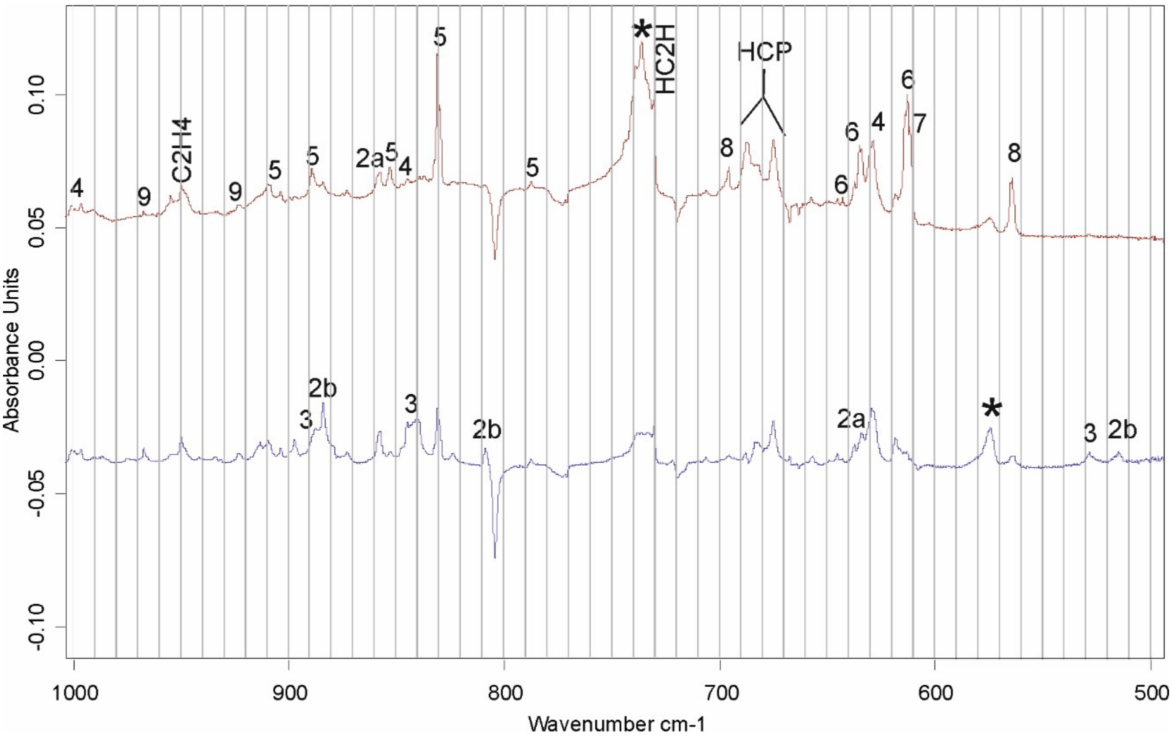
	T-complex of ethylene-HCP		Uncomplexed ethylene and HCP(blue)		IR Shifts of the complexes	
	Infrared frequencies (Intensities)*		Infrared frequencies (Intensities)*			
	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz	B3LYP/aug-cc-pvtz	MP2/aug-cc-pvtz
	24.9(0.03)	23.6(0.06)	-	-	-	-
	2.5(0.04)	24.97(0.11)	-	-	-	-
	41.5(0.19)	70.59(0.23)	-	-	-	-

	59.3(0.05)	70.6(0.07)	-	-	-	-
	84.0(0.06)	86.3(0.09)	-	-	-	-
C-H bend	712.6(55.7)	694.2(47.2)	683.8(159.0)	650.1(139.3)	**28.8**	**44.1**
	714.4(62.4)	695.1(53.94)			**30.6**	**45.0**
CH2 rock.	801.4(0.07)	789.4(0.00)	801.1(0.04)	790.3(0.00)	0.3	-0.9
CH2 wag.	946.5(118.9)	913.4(0.05)	939.7(97.15)	907.9(0.00)	6.8	5.5
CH2 wag.	950.7(0.07)	943.6(112.8)	945.4(0.05)	936.5(91.77)	5.3	7.1
CH2 twist.	1023.6(0.0)	1026.5(0.00)	1017.9(0.00)	1005.2(0.00)	5.7	21.3
CH2 rock.	1196.4(0.0)	1192.9(2.47)	1195.8(0.00)	1195.1(0.00)	0.6	2.2
CP str.	1281.7(2.0)	1195.2(0.00)	1284.8(0.0)	1195.5(0.0)	-3.1	-0.3
CH2 scissor.	1325.3(0.2)	1323.5(0.21)	1325.1(0.00)	1324.4(0.00)	0.2	-0.9
CH2 scissor.	1420.8(9.7)	1419.9(9.07)	1419.8(9.6)	1419.8(8.83)	1.0	0.1
CC str.	1619.9(0.5)	1606.9(0.35)	1620.9(0.00)	1610.7(0.00)	1.0	0.2
CH stretching	3001.1(12.5)	3044.0(6.0)	3000.9(16.49)	3045.9(9.54)	0.2	-1.9
	3013.7(0.0)	3060.9(0.051)	3014.1(0.00)	3064.2(0.00)	-0.4	-3.3
	3067.8(0.0)	3130.5(0.00)	3066.9(0.00)	3130.5(0.00)	1.1	0
	3094.5(15.3)	3155.8(8.2)	3094.1(20.36)	3157.1(13.08)	-0.4	-1.3
	3191.7(79.9)	3184.9(121.81)	3215.9(15.8)	3221.1(16.1)	-24.2	-36.2

Number highlighted in blue are for uncomplexed HCP. *Scaling factor 0.96

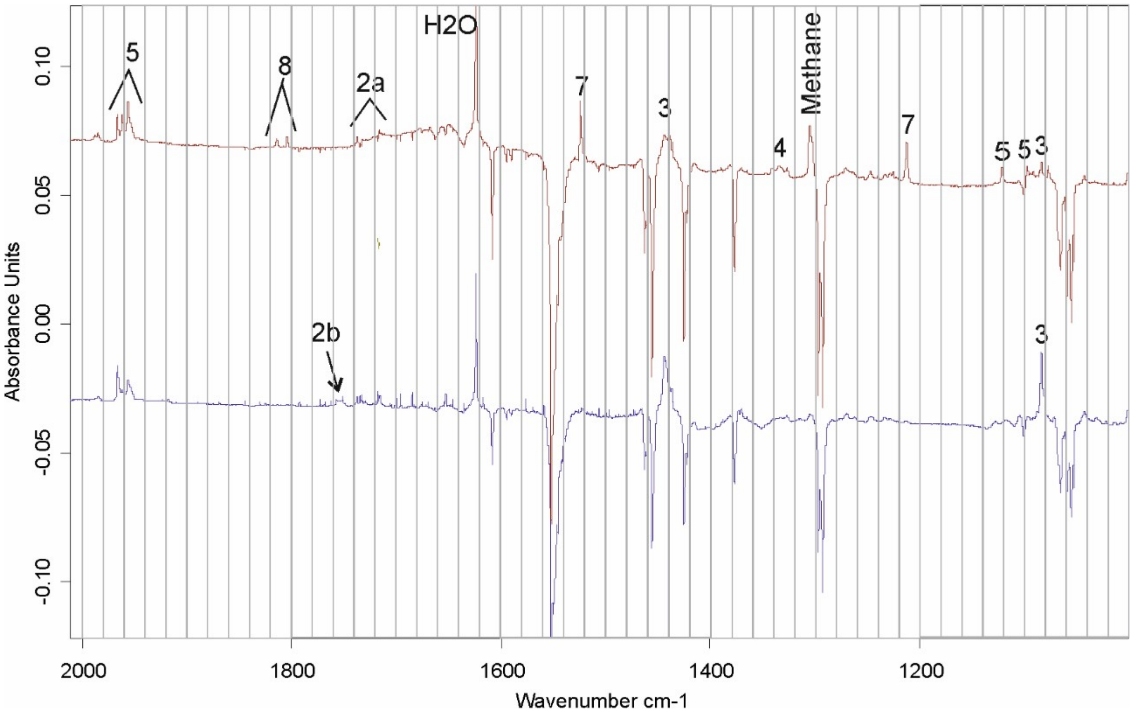
S10. Photoproducts generated from species 1. A collective picture of IR band assignments

Region 1:



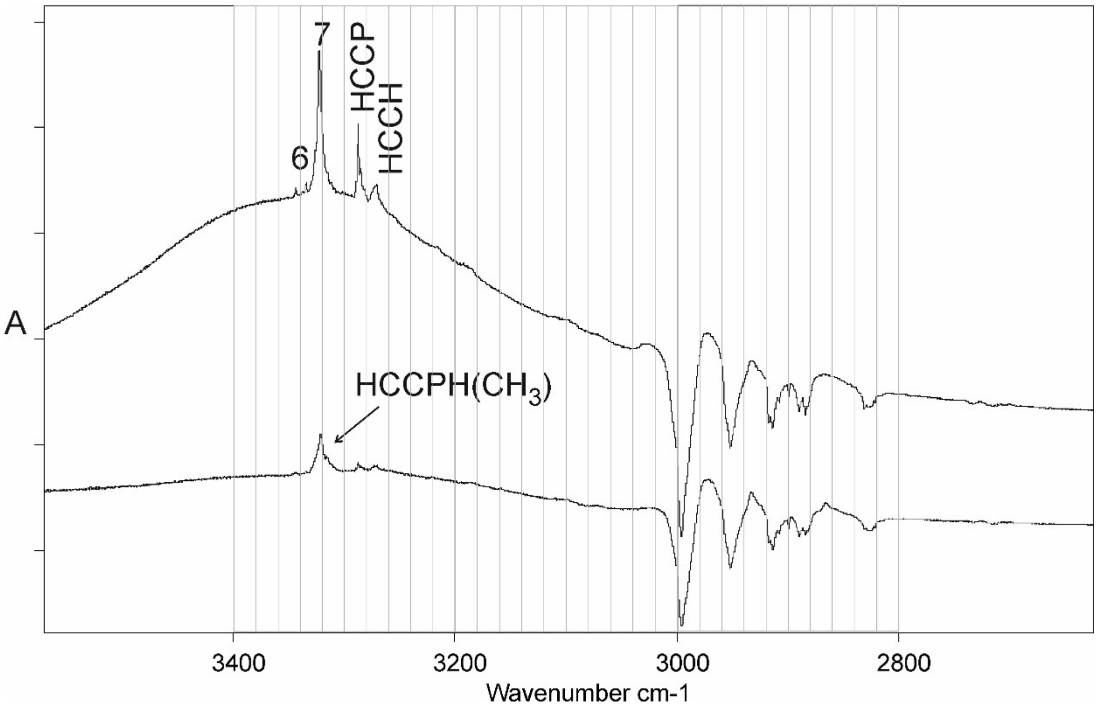
Photolysis of **1**: 3 h (bottom) and 76 h (top) of mercury lamp (254 nm) irradiation. Asterisk marks a spectral artifact originating from the substrate window.

Region 2:



Photolysis of **1**: 3 h (bottom) and 76 h (top) of mercury lamp (254 nm) irradiation.

Region 3:



Photolysis of **1**: 3 h (bottom) and 76 h (top) of mercury lamp (254 nm) irradiation.

S11. DFT predctions (VPT2//B3LYP/aug-cc-pVTZ) for anharmonic vibrational frequencies of HCCCP

```
Fundamental Bands
 -----------------
   Mode(n,l)                E(harm)   E(anharm)   Intensities(harm)
Intensities(anharm)
      1(1,+0)               3463.249   3337.719    117.76089573
113.59161086
      2(1,+0)               2162.501   2119.541     16.00217771
12.08337275
      3(1,+0)               1583.110   1563.178     90.12470279
91.29019297
      4(1,+0)                708.723    702.338      0.88716803
0.81822660
      5(1,-1)                648.101    635.038    247.84351167
256.90729679
      5(1,+1)                648.101    635.038    247.84351167
256.90729679
      6(1,-1)                517.133    514.034      5.62523450
5.41744435
      6(1,+1)                517.133    514.034      5.62523450
5.41744435
      7(1,-1)                204.832    205.385    154.97334292
152.14562050
      7(1,+1)                204.832    205.385    154.97334292
152.14562050

 Overtones
 ---------
   Mode(n,l)                E(harm)   E(anharm)
Intensities(anharm)
      1(2,+0)               6926.497   6574.454
1.44758203
      2(2,+0)               4325.003   4224.093
0.00133500
      3(2,+0)               3166.221   3117.297
0.00013215
      4(2,+0)               1417.447   1402.679
0.05701399
      5(2,-2)               1296.202   1276.591
46.94614978
      5(2,+0)               1296.202   1255.470
46.94614978
      5(2,+2)               1296.202   1276.591
46.94614978
      6(2,-2)               1034.267   1028.604
0.44493075
      6(2,+0)               1034.267   1032.144
0.44493075
      6(2,+2)               1034.267   1028.604
0.44493075
      7(2,-2)                409.664    412.173
0.01175933
      7(2,+0)                409.664    409.699
0.01175933
```

```
      7(2,+2)                 409.664    412.173
0.01175933

 Combination Bands
 -----------------
   Mode(n,l)   Mode(n,l)    E(harm)    E(anharm)
Intensities(anharm)
      2(1,+0)     1(1,+0)   5625.750   5450.530
0.04974663
      3(1,+0)     1(1,+0)   5046.359   4899.990
0.06587871
      3(1,+0)     2(1,+0)   3745.612   3672.433
0.03572999
      4(1,+0)     1(1,+0)   4171.972   4039.934
0.01679338
      4(1,+0)     2(1,+0)   2871.225   2814.933
0.14077028
      4(1,+0)     3(1,+0)   2291.834   2265.448
2.98627086
      5(1,-1)     1(1,+0)   4111.350   3953.869
0.79311713
      5(1,+1)     1(1,+0)   4111.350   3953.869
0.79311713
      5(1,-1)     2(1,+0)   2810.602   2746.038
0.07282705
      5(1,+1)     2(1,+0)   2810.602   2746.038
0.07282705
      5(1,-1)     3(1,+0)   2231.211   2197.687
0.00988286
      5(1,+1)     3(1,+0)   2231.211   2197.687
0.00988286
      5(1,-1)     4(1,+0)   1356.825   1337.626
0.00278731
      5(1,+1)     4(1,+0)   1356.825   1337.626
0.00278731
      6(1,-1)     1(1,+0)   3980.382   3851.210
0.02181514
      6(1,+1)     1(1,+0)   3980.382   3851.210
0.02181514
      6(1,-1)     2(1,+0)   2679.635   2627.979
0.02188849
      6(1,+1)     2(1,+0)   2679.635   2627.979
0.02188849
      6(1,-1)     3(1,+0)   2100.244   2074.319
0.04264883
      6(1,+1)     3(1,+0)   2100.244   2074.319
0.04264883
      6(1,-1)     4(1,+0)   1225.857   1211.414
0.00250294
      6(1,+1)     4(1,+0)   1225.857   1211.414
0.00250294
      6(1,-1)     5(1,-1)   1165.235   1150.865
0.02003548
      6(1,-1)     5(1,+1)   1165.235   1149.985
0.02003548
      6(1,+1)     5(1,-1)   1165.235   1149.985
0.02003548
```

```
     6(1,+1)      5(1,+1)   1165.235   1150.865
0.02003548
     7(1,-1)      1(1,+0)   3668.080   3541.871
0.15050675
     7(1,+1)      1(1,+0)   3668.080   3541.871
0.15050675
     7(1,-1)      2(1,+0)   2367.333   2323.073
0.01309481
     7(1,+1)      2(1,+0)   2367.333   2323.073
0.01309481
     7(1,-1)      3(1,+0)   1787.942   1766.740
0.00002316
     7(1,+1)      3(1,+0)   1787.942   1766.740
0.00002316
     7(1,-1)      4(1,+0)    913.555    911.610
0.17757482
     7(1,+1)      4(1,+0)    913.555    911.610
0.17757482
     7(1,-1)      5(1,-1)    852.933    841.439
0.41165672
     7(1,-1)      5(1,+1)    852.933    839.862
0.41165672
     7(1,+1)      5(1,-1)    852.933    839.862
0.41165672
     7(1,+1)      5(1,+1)    852.933    841.439
0.41165672
     7(1,-1)      6(1,-1)    721.965    719.978
2.42391807
     7(1,-1)      6(1,+1)    721.965    718.804
2.42391807
     7(1,+1)      6(1,-1)    721.965    718.804
2.42391807
     7(1,+1)      6(1,+1)    721.965    719.978
2.42391807
```