Electronic Supplementary Material (ESI) for ChemComm.

Photochemical Reactions of Triplet Phenylphosphinidene with Carbon Monoxide and Nitric Oxide

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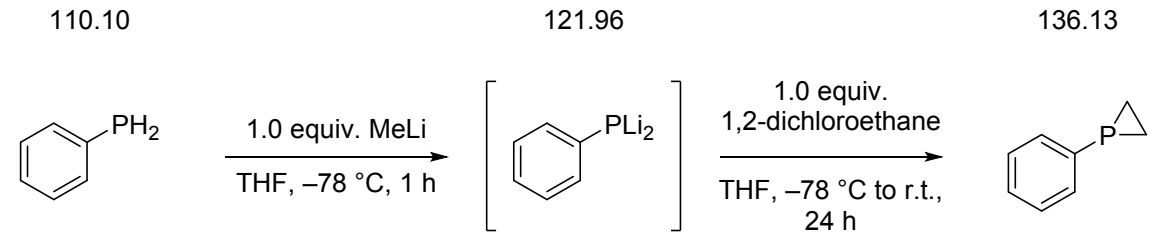
Synthesis of 1-Phenylphosphirane 3



In a flame dried 500 mL Schlenk flask 250 mL of dry and degassed THF was cannulated under complete exclusion of oxygen. Phenylphosphine **A** 2.00 g (2.00 mL, 18.2 mmol, 1.00 equiv.; 10 % m/v in *n*-hexane) was added under Schlenk conditions. The resulting clear solution was cooled to –78 °C using ^{i}PrOH dry ice bath. Then, MeLi 0.40 g (22.7 mL, 18.2 mmoL, 2.00 equiv.; 1.6 M in Et_2O) was added under complete exclusion of oxygen using a syringe. The reaction mixture directly changed color to pale yellow. After stirring at –78 °C for 1 h the mixture was intensive yellow colored (because of the formation of **B**). At this point 1.80 g (1.44 mL, 18.6 mmoL, 1.02 equiv.) of dry and degassed 1,2-dichloroethane was added under complete exclusion of oxygen using a syringe. The reaction mixture was allowed to warm to r.t. (very slowly) and was stirred for another 24 h. The reaction was quenched by adding 10 mL of degassed water. Then, ether was added (~20 mL) until phase separation occurred. The aqueous phase was cannulated off using a syringe. Degassed $MgSO_4$ was added and the resulting suspension was stirred for 1 h. Now the mixture was filtered under Ar using a Schlenk-frit. The solvents were removed via distillation under Ar. The resulting clear liquid was purified by fractional distillation under vacuum (1.7 mBar). The product **3** was obtained as a clear liquid (bp 45–46 °C, 1.7 mBar).

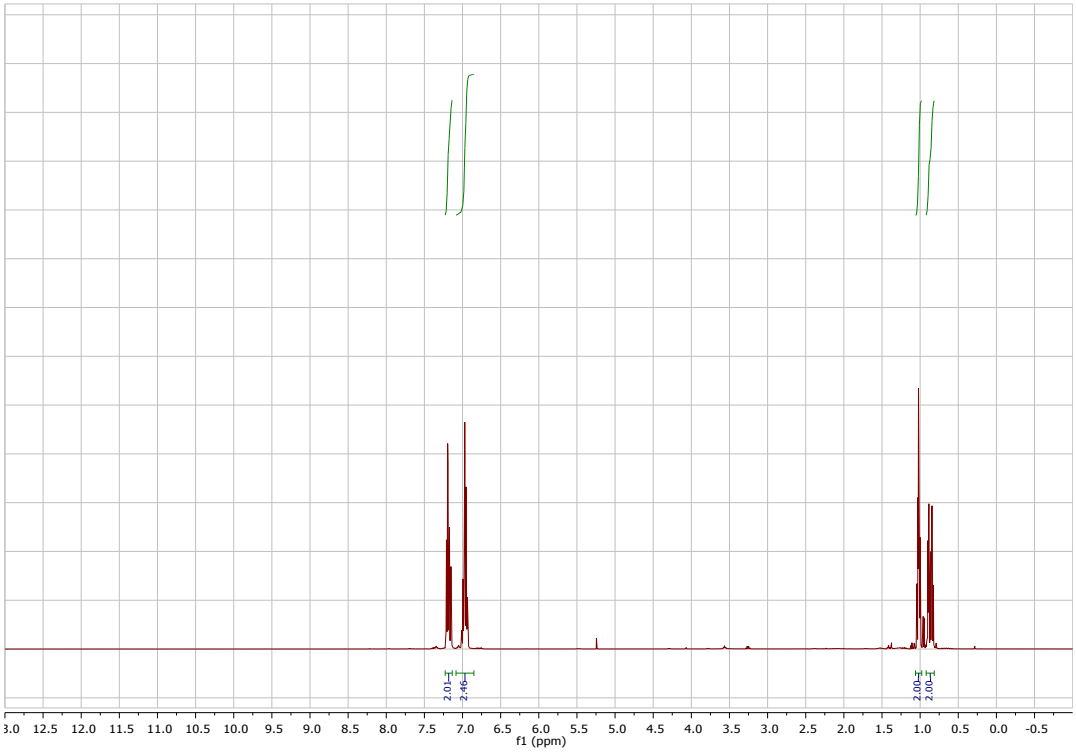
(The very oxygen sensitive product was stored under Ar at 4 °C due to the high tendency to oxidation and polymerization!!!)

NMR was measured under Ar in degassed and dry benzene-d_6.

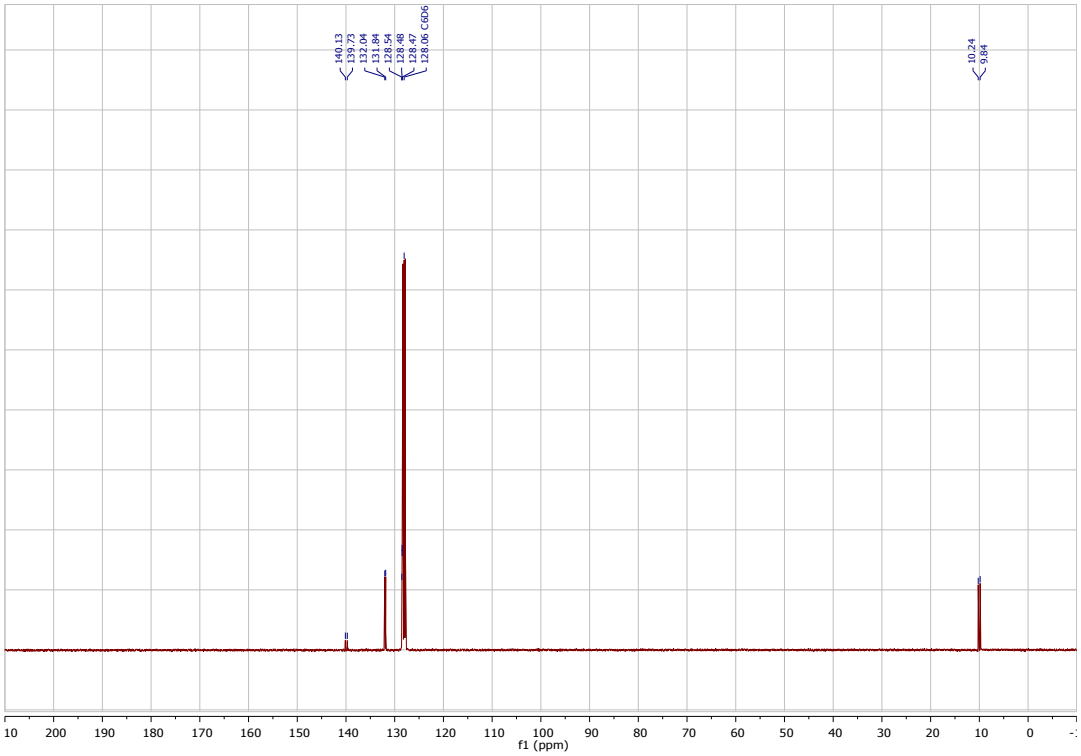
^{1}H NMR (400,25 MHz, C_6D_6): δ = 7.25 – 7.13 (m, 2 H, CH_{Ar}), 7.05 – 6.91 (m, 2 H, CH_{Ar}), 1.06 – 0.99 (m, 2 H, CH_2), 0.93 – 0.83 (m, 2 H, CH_2).

^{13}C NMR (100,65 MHz, C_6D_6): δ = 139.9 (d, $^{1}J_{C\text{-}P}$ = 40.4 Hz, Cq, C_{Ar}), 131.9 (d, $^{2}J_{C\text{-}P}$ = 19.5 Hz, Cq, C_{Ar}), 128.5 (d, $^{3}J_{C\text{-}P}$ = 6.3 Hz, Cq, C_{Ar}), 128.4 (CH_{Ar}), 10.4 (d, $^{1}J_{C\text{-}P}$ = 40.1 Hz, CH_2).

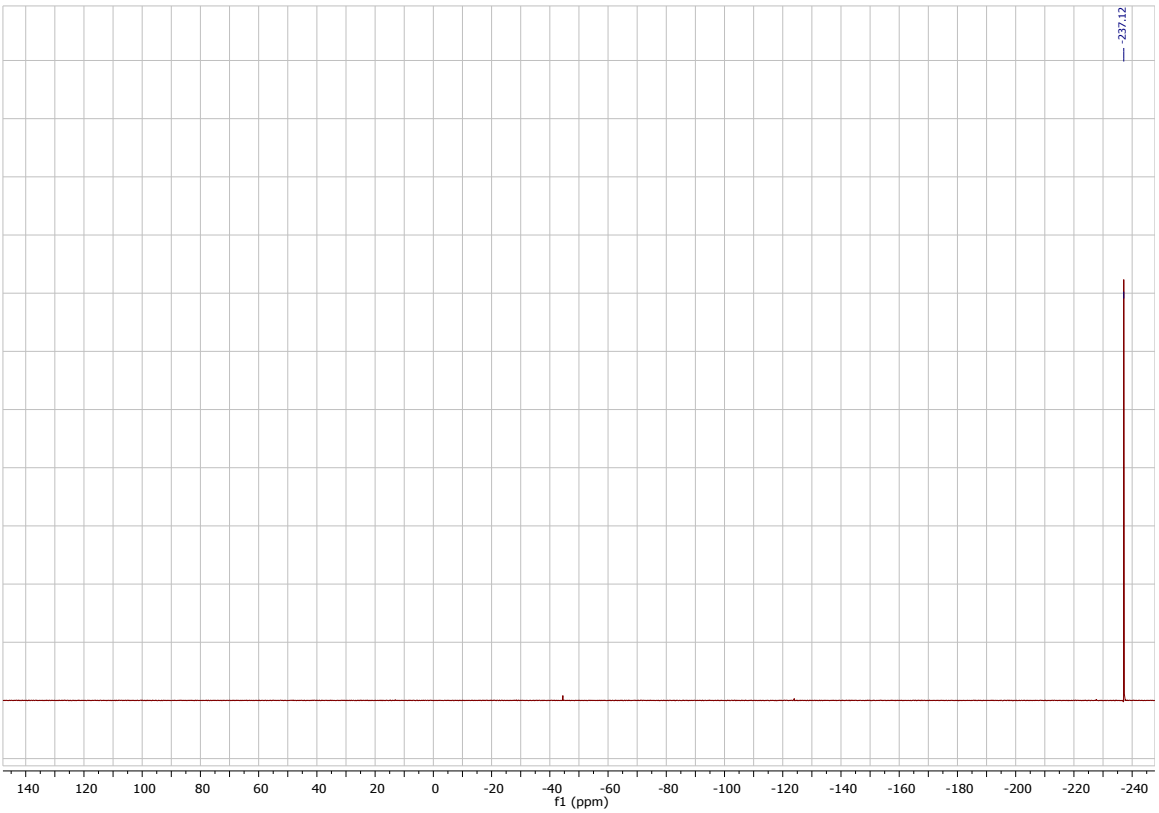
^{31}P NMR (162,02 MHz, C_6D_6): δ = –237.1 .



^{1}H NMR spectrum of 3 in benzene-d_6.



^{13}C NMR spectrum of 3 in benzene-d_6.



^{31}P NMR spectrum of 3 in benzene-d_6.

Matrix Apparatus Design. For the matrix isolation studies, we used an APD Cryogenics HC-2 cryostat with a closed-cycle refrigerator system, equipped with an inner CsI window for IR measurements. Spectra were recorded with a Bruker IFS 55 FT-IR spectrometer with a spectral range of 4500−400 cm^{-1} and a resolution of 0.7 cm^{-1} and UV/Vis spectra were recorded with a JASCO V-670 spectrophotometer. Matrices were generated by co-deposition of **3** (evaporated at 0 °C from a storage bulb) with a large excess of argon (typically 60−120 mbar from a 2000 mL storage bulb) on the surface of the matrix window at 10 K (20 K). A high-pressure mercury lamp (HBO 200, Osram) with a monochromator (Bausch & Lomb) was used for irradiation.

Computations. All geometries were optimized and characterized as minima or transition structures by means of analytical harmonic vibrational frequency computations at the M06-2X/6-311++G(2d,2p) level of theory.[1-4] All computations were performed with the Gaussian09 program.[5]

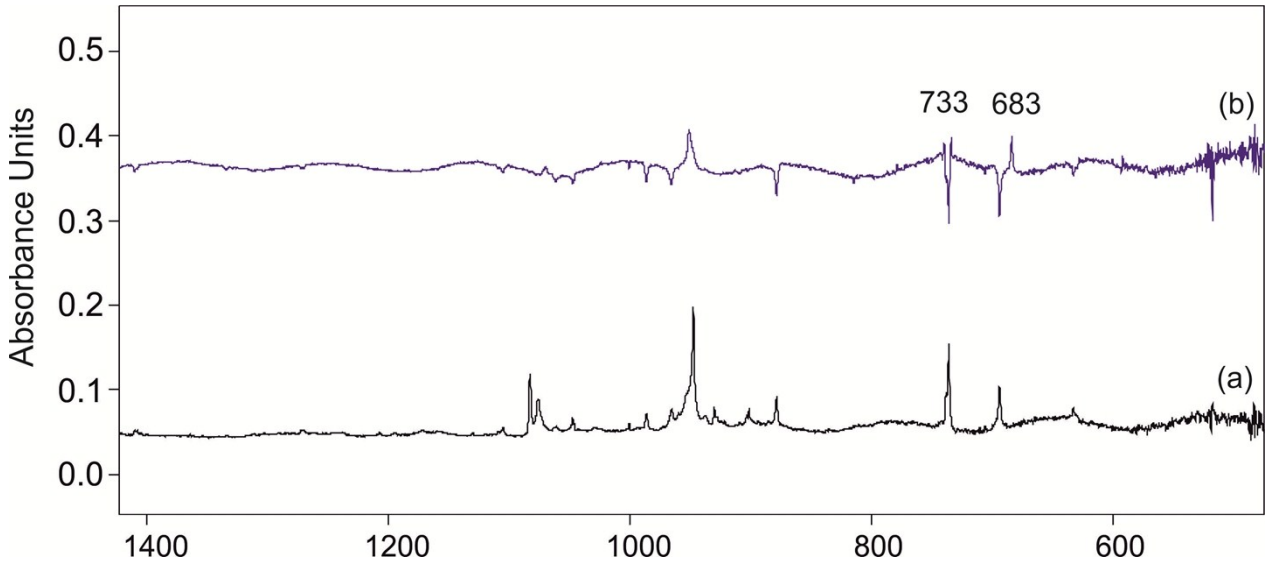


Figure S1. (a) IR spectrum of matrix isolated 3 in Ar at 10 K. (b) IR difference spectra showing the photochemistry of **1** after irradiation at λ=334 nm in argon at 10 K. (b) IR difference spectra showing the photochemistry of 3 after irradiation at λ = 254 nm in argon at 10 K. Downward bands assigned to 3 disappear while upward bands assigned to ^{3}2 appear after 15 min irradiation time.

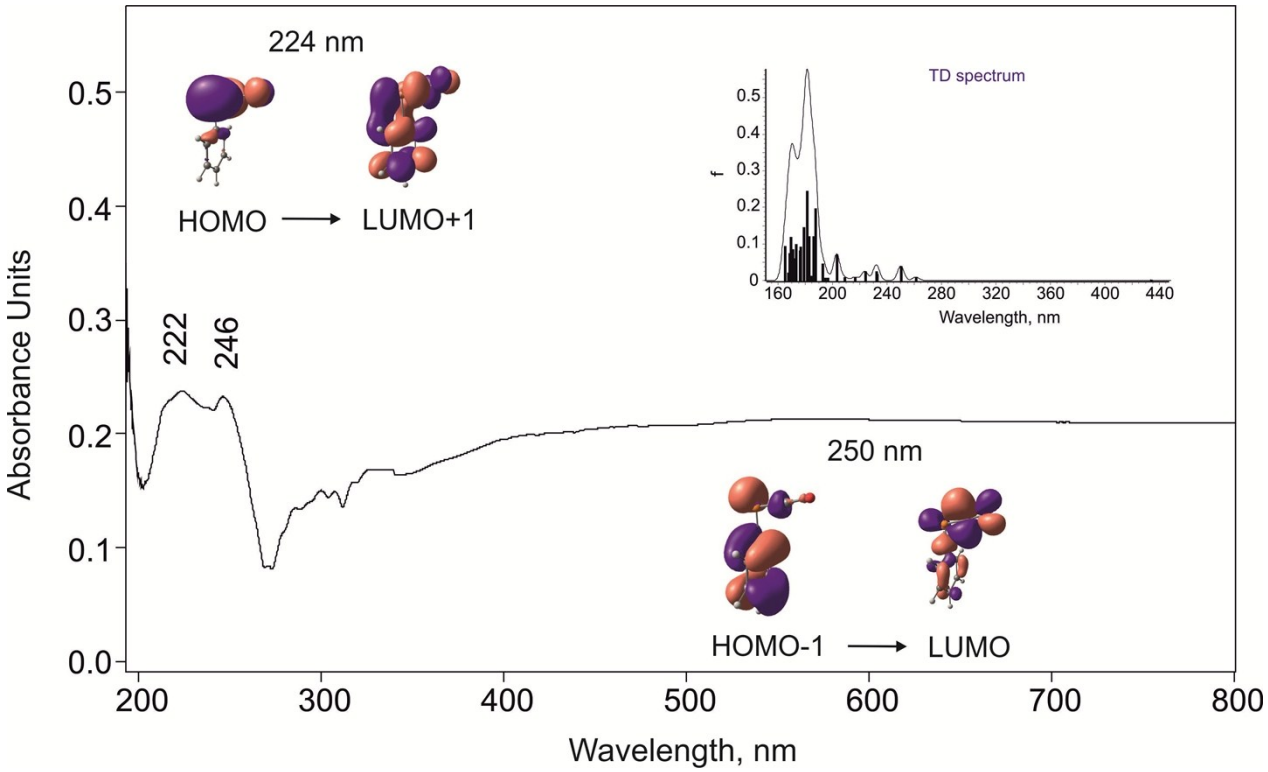


Figure S2. UV/vis difference spectrum of **1** at 10 K; the photochemistry of **3** in the presence of 2% CO after irradiation at λ = 254 nm in argon at 10 K. Inset: Computed [TD-M06-2X/6-311++G(2d,2p)] spectrum of **1**. Inset: the NBOs for the two electronic transitions computed at TD-M06-2X/6-311++G(2d,2p). HOMO = highest occupied molecular orbital; LUMO = lowest unoccupied molecular orbital.

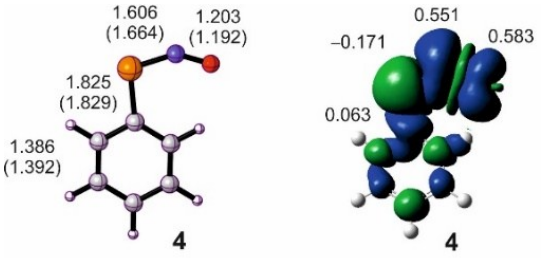
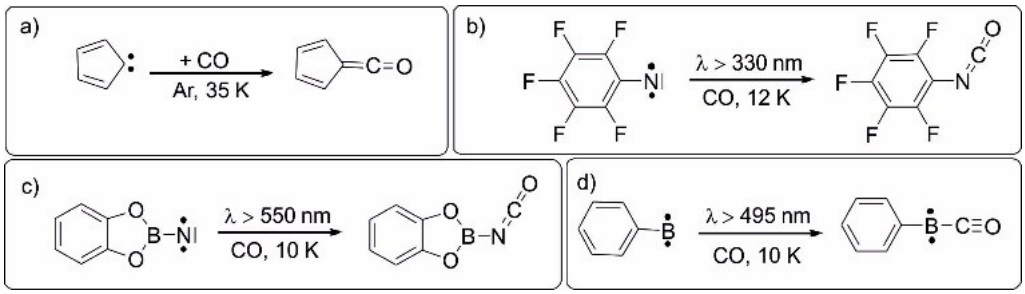


Figure S3. Selected bond lengths (Å) of **4** at the UM06-2X/6-311++G(2d,2p) level. The values in parentheses at UMP2/cc-pVTZ. Computed spin density of **4** at the UM06-2X/6-311++G(2d,2p) level.



Scheme S1. Reactions of carbene, nitrenes, and borylene with CO.

Table S1. Experimental (Ar matrix, 10 K) and computed IR frequencies of **1** and ^{13}CO-**1**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**1** M06-2X/6-311++G(2d, 2p) [a]	**1** B3LYP/cc-pVTZ [b]	**1** Ar, 10 K [c]	^{13}CO-**1** M06-2X/6-311++G(2d, 2p) [a]	^{13}CO-**1** B3LYP/cc-pVTZ [b]	^{13}CO-**1** Ar, 10 K [c]	Assignment
31	2104 (898)	2052 (765)	1978 (s)	2054 (850)	2002 (725)	1932 (s)	C=O str.
28	1524 (10.3)	1514 (12.5)	1482 (w)	1524 (10.4)	1514 (12.6)	1482 (w)	CH def.
27	1481 (9.8)	1471 (8.9)	1438 (w)	1481 (9.9)	1471 (8.9)	1438 (w)	CH def.
26	1351 (3)	1353 (2.8)	-	1351 (3)	1353 (2.8)	-	CH def.
21	1105 (4)	1094 (1.5)	-	1105 (3.6)	1094 (1.5)	-	CH def.
20	1055 (3.6)	1045 (6.7)	1027 (w)	1055 (3.6)	1045 (6.7)	-	ring distortion
18	1021 (5.5)	1020 (3.4)	998 (w)	1021 (5.5)	1020 (3.3)	-	ring distortion
14	777 (32.2)	766 (33.5)	746 (m)	776 (32.8)	765 (34.2)	746 (m)	CH o.o.p. def.
13	721 (39.7)	716 (22.7)	689 (m)	721 (39.5)	716 (33.4)	689 (m)	CH o.o.p. def.
12	715 (2)	714 (13.7)	-	705 (2)	710 (2.7)	-	P–C str.
9	561 (15.3)	558 (11)	-	549 (16.6)	546 (11.4)	-	PCO def.

[a]M06-2X/6-311++G(2d,2p), harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b]B3LYP/cc-pVTZ, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [c]Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: moderate, s: strong).

Table S2. Experimental (Ar matrix, 10 K) and computed IR frequencies of **4** and ^{15}NO-**4**, band origins in cm^{-1}, computed intensities (km mol^{-1}) in parentheses.

Mode	**4** M06-2X/6-311++G(2d, 2p) [a]	**4** B3LYP/cc-pVTZ [b]	**4** Ar, 10 K [c]	^{15}NO-**4** M06-2X/6-311++G(2d, 2p) [a]	^{15}NO-**4** B3LYP/cc-pVTZ [b]	^{15}NO-**4** Ar, 10 K [c]	Assignment
29	1613 (493)	1580 (411)	1545 (s)	1582 (481)	1549 (395)	1513 (s)	N=O str.
28	1527 (2.6)	1517 (3.1)	1439 (m)	1527 (3.3)	1516 (5.5)	1439 (m)	CH def.
27	1480 (15.2)	1470 (14.4)	1438 (w)	1480 (15.1)	1470 (14.4)	1438 (w)	CH def.
26	1363 (8.8)	1365 (8.2)	-	1363 (9.2)	1365 (8.6)	-	CH def.
22	1118 (8.8)	1107 (4.8)	-	1118 (8.8)	1107 (4.9)	-	ring distortion
21	1112 (8.8)	1094 (8.6)	1099 (m)	1112 (8.9)	1094 (8.7)	1099 (m)	ring distortion
18	1019 (1.9)	1016 (2.3)	998 (w)	1019 (1.9)	1016 (2.3)	-	ring distortion
14	763 (45)	758 (40.3)	744 (m)	763 (45)	758 (40.3)	744 (m)	CH o.o.p. def.
12	712 (37.3)	710 (32.5)	689 (m)	712 (37.2)	710 (32.5)	689 (m)	CH o.o.p. def.
11	706 (3.9)	700 (2.3)	-	706 (3.9)	700 (2.3)	-	P–C str.
9	485 (41.6)	480 (36)	463 (w)	479 (41.2)	473 (35.6)	461 (w)	PNO def.
8	473 (8.2)	471 (6.3)	-	472 (7.9)	470 (6.1)	-	ring breathing

[a]M06-2X/6-311++G(2d,2p), harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [b]B3LYP/cc-pVTZ, harmonic approximation, unscaled frequencies, intensities (in parentheses) in km mol^{-1}. [c]Experiment: argon matrix, 10 K.; approximate relative intensities (w: weak, m: moderate, s: strong).

References

1. Zhao, Y.; Truhlar, D. G. The M06 suite of density functionals for main group thermochemistry, thermochemical kinetics, noncovalent interactions, excited states, and transition elements: two new functionals and systematic testing of four M06-class functionals and 12 other functionals. *Theor. Chem. Acc.* **2008,** *120* (1), 215-241.
2. Becke, A. D. Density-functional exchange-energy approximation with correct asymptotic behavior. *Phys. Rev. A* **1988,** *38* (6), 3098-3100.
3. Lee, C.; Yang, W.; Parr, R. G. Development of the Colle-Salvetti correlation-energy formula into a functional of the electron density. *Phys. Rev. B* **1988,** *37* (2), 785-789.
4. Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. Results obtained with the correlation energy density functionals of becke and Lee, Yang and Parr. *Chem. Phys. Lett.* **1989,** *157* (3), 200-206.
5. M. J. Frisch et al. Gaussian 09, D.01, . *Wallingford CT,* **2013**.

Geometric Structures and Electronic energies

2: phenylphosphinidene - C_{2v} point group

0 3

15	0.000000000	0.000000000	2.387950000
6	0.000000000	0.000000000	0.594275000
6	0.000000000	1.205451000	-0.123883000
6	0.000000000	-1.205451000	-0.123883000
6	0.000000000	1.203503000	-1.509051000
6	0.000000000	-1.203503000	-1.509051000
6	0.000000000	0.000000000	-2.205634000
1	0.000000000	2.145464000	0.413215000
1	0.000000000	-2.145464000	0.413215000
1	0.000000000	2.140792000	-2.047886000
1	0.000000000	-2.140792000	-2.047886000
1	0.000000000	0.000000000	-3.286540000

E[M062X] = -572.89398323
ZPVE[M062X] = 0.091058

3: Phenyldioxophosphorane - (C_{2v} point group)

0 1

15	0.611207000	-1.715881000	0.000000000
6	-0.956661000	-2.360532000	0.747181000
6	-0.956661000	-2.360532000	-0.747181000
6	0.297503000	0.098779000	0.000000000
6	-0.956661000	0.709901000	0.000000000
6	1.431338000	0.910847000	0.000000000
6	1.319522000	2.295897000	0.000000000
6	-1.071779000	2.091978000	0.000000000
6	0.066486000	2.890214000	0.000000000
1	-1.577668000	-1.641573000	1.261261000
1	-1.577668000	-1.641573000	-1.261261000
1	-0.869254000	-3.313390000	1.248682000
1	-0.869254000	-3.313390000	-1.248682000
1	2.413305000	0.453837000	0.000000000
1	-1.859264000	0.112407000	0.000000000
1	-2.052272000	2.548080000	0.000000000
1	-0.025795000	3.967226000	0.000000000
1	2.211258000	2.907270000	0.000000000

E[M062X] = -651.54196666
ZPVE[M062X] = 0.147387

1: phenylphosphaketene -

0 1

15	-1.648173000	-0.660422000	-0.847176000
6	0.090812000	-0.241882000	-0.330113000
6	0.667897000	0.980578000	-0.669290000
6	0.858816000	-1.201487000	0.326791000
6	1.990441000	1.245329000	-0.339776000
6	2.184271000	-0.937909000	0.646627000
6	2.750233000	0.286531000	0.317446000
1	0.080769000	1.723172000	-1.191926000
1	0.417509000	-2.152796000	0.590757000
1	2.427083000	2.199345000	-0.600441000
1	2.771761000	-1.688221000	1.157147000
1	3.780951000	0.492309000	0.569977000
6	-2.294189000	0.260048000	0.412358000
8	-2.780645000	0.873159000	1.249735000

E[M062X] = -686.2552587
ZPVE[M062X] = 0.1004224

0 1

15	-1.633708000	-0.912127000	-0.624409000
6	0.089969000	-0.325454000	-0.252505000
6	0.551982000	0.932685000	-0.657244000
6	0.971705000	-1.210725000	0.378780000
6	1.870555000	1.307127000	-0.409894000
6	2.294899000	-0.837923000	0.606118000
6	2.745120000	0.422434000	0.218629000
1	-0.118621000	1.611259000	-1.167602000
1	0.619629000	-2.183094000	0.696563000
1	2.215834000	2.285024000	-0.717152000
1	2.969600000	-1.529285000	1.092588000
1	3.770617000	0.712004000	0.401746000
6	-2.285833000	0.317440000	0.329746000
8	-2.797727000	1.144061000	0.972275000

E[MP2] = -683.687117
ZPVE[MP2] = 0.099585

4: phosphinimine-N-oxyl radical

0 2

15	1.533549000	-1.112456000	-0.000009000
6	-0.123076000	-0.346279000	0.000002000
6	-0.401984000	1.021349000	0.000000000
6	-1.180089000	-1.261208000	0.000013000
6	-1.718306000	1.458485000	0.000008000
6	-2.494294000	-0.818670000	0.000021000
6	-2.764451000	0.543295000	0.000019000
1	0.401672000	1.742968000	-0.000009000
1	-0.973761000	-2.325152000	0.000014000
1	-1.928322000	2.518879000	0.000007000
1	-3.304051000	-1.534636000	0.000029000
1	-3.787643000	0.891872000	0.000026000
8	2.621105000	1.347319000	-0.000022000
7	2.530461000	0.147504000	-0.000019000

E[M062X] = -702.833538
ZPVE[M062X] = 0.0991585

0 2

15	1.520766000	-1.153624000	-0.000008000
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6	-0.384115000	1.018099000	0.000000000
6	-1.200563000	-1.264944000	0.000012000
6	-1.702223000	1.474658000	0.000009000
6	-2.513472000	-0.800147000	0.000021000
6	-2.765667000	0.572212000	0.000019000
1	0.434273000	1.723700000	-0.000008000
1	-1.008743000	-2.331907000	0.000014000
1	-1.896467000	2.538609000	0.000007000
1	-3.334029000	-1.504477000	0.000029000
1	-3.784161000	0.935250000	0.000026000
8	2.659377000	1.359094000	-0.000024000
7	2.523343000	0.174806000	-0.000019000

E[MP2] = -700.2034296
ZPVE[MP2] = 0.099039

12: phenyl isocyanate

0 1

6	0.091635000	-0.280442000	-0.000003000
6	-0.300715000	1.056231000	-0.000003000
6	-0.862971000	-1.290598000	-0.000001000
6	-1.649831000	1.373533000	0.000000000

6	-2.210281000	-0.961593000	0.000001000
6	-2.609094000	0.368367000	0.000002000
1	0.449773000	1.835080000	-0.000006000
1	-0.536437000	-2.320211000	-0.000002000
1	-1.951221000	2.411529000	-0.000001000
1	-2.949969000	-1.749619000	0.000003000
1	-3.659515000	0.621094000	0.000004000
6	2.509705000	-0.093058000	-0.000002000
8	3.590271000	0.337035000	0.000011000
7	1.444931000	-0.646970000	-0.000007000

E[M062X] = -399.6899612
ZPVE[M062X] = 0.1047234

0 1

6	-0.093259000	-0.283463000	-0.000049000
6	0.298236000	1.057954000	-0.000037000
6	0.867441000	-1.294458000	-0.000027000
6	1.651510000	1.379729000	0.000003000
6	2.218522000	-0.962434000	0.000010000
6	2.615658000	0.373167000	0.000026000
1	-0.454548000	1.835081000	-0.000059000
1	0.542754000	-2.325135000	-0.000041000
1	1.950507000	2.418804000	0.000013000
1	2.959994000	-1.749213000	0.000027000
1	3.665922000	0.628065000	0.000054000
6	-2.509770000	-0.084385000	0.000027000
8	-3.609244000	0.335394000	0.000122000
7	-1.440101000	-0.658201000	-0.000098000

E[MP2] = -397.440004
ZPVE[MP2] = 0.1039471

13: phenyl nitrene

0 3

6	0.000000000	0.000000000	1.056660000
6	0.000000000	1.224369000	0.336629000
6	0.000000000	-1.224369000	0.336629000
6	0.000000000	1.210225000	-1.040931000
6	0.000000000	-1.210225000	-1.040931000
6	0.000000000	0.000000000	-1.735881000
1	0.000000000	2.150831000	0.892742000
1	0.000000000	-2.150831000	0.892742000
1	0.000000000	2.143386000	-1.586435000
1	0.000000000	-2.143386000	-1.586435000
1	0.000000000	0.000000000	-2.816417000
7	0.000000000	0.000000000	2.390106000

E[M062X] = -286.2616536
ZPVE[M062X] = 0.09183

CO-carbon monoxide

0 1

6	0.000000000	0.000000000	-0.640469000
8	0.000000000	0.000000000	0.480352000

E[M062X] = -113.3127009
ZPVE[M062X] = 0.0051916