

Radical Ring-Opening Polymerization of Phosphorus Heterocycles: Computational Design of Suitable Phosphetane Monomers

**Michelle L. Coote,¹ Jennifer L. Hodgson, Elizabeth H. Krenske, Mansoor
Namazian, and S. Bruce Wild**

*Research School of Chemistry, Australian National University, Canberra, ACT 0200,
Australia*

SUPPLEMENTARY DATA

¹ To whom correspondence should be addressed. Email mcoote@rsc.anu.edu.au

Table S1. B3-LYP/6-31G(d) Optimized Geometries

CH₃CH₂CH₂•

1\1\GINC-AC45\FOpt\UB3LYP\6-31G(d)\C3H7(2)\JOH501\08-May-2007\0\#\ UB3
LYP/6-31G* OPT FREQ=noraman maxdisk=134217728\ch2ch2ch3_1\0,2\C,0.00
615,0.00178,-0.00216\C,1.49813,-0.00764,0.01039\C,-0.59908,1.41317,0.0
0014\H,-1.69402,1.3762,0.02192\H,2.0521,0.78072,0.51282\H,2.05655,-0.8
7417,-0.33031\H,-0.38351,-0.54891,0.87554\H,-0.36213,-0.56007,-0.87284
\H,-0.29535,1.9723,-0.89192\H,-0.26592,1.9805,0.8777\Version=IA64L-G0
3RevD.01\State=2-A\HF=-118.4713715\S2=0.753881\S2-1=0.\S2A=0.75001\RMS
D=3.444e-09\RMSF=2.554e-06\Thermal=0.\Dipole=0.0489268,0.0715637,0.047
5383\PG=C01 [X(C3H7)]\@

CH₃CH(CH₃)•

1\1\GINC-AC14\FOpt\UB3LYP\6-31G(d)\C3H7(2)\EXK501\02-Apr-2007\0\#\ B3L
YP/6-31G(D) OPT FREQ=NORAMAN MAXDISK=134217728\midchaintri-betaCl-SM
a1b1_B3LYP_alphacore_2\0,2\C,-0.0004167261,0.5344863575,0.\H,0.277354
0653,1.5861958564,0.\C,-0.015699752,-0.1971297645,1.3010857006\C,-0.01
5699752,-0.1971297645,-1.3010857006\H,-0.2479791894,0.4667304682,2.141
6436582\H,-0.2479791894,0.4667304682,-2.1416436582\H,0.9587646647,-0.6
688558619,1.5275654021\H,0.9587646647,-0.6688558619,-1.5275654021\H,-0
.7540138179,-1.0116530199,1.297162033\H,-0.7540138179,-1.0116530199,-1
.297162033\Version=IA64L-G03RevC.02\State=2-A'\HF=-118.4781544\S2=0.7
54003\S2-1=0.\S2A=0.750011\RMSD=4.197e-09\RMSF=3.357e-06\Dipole=0.0669
559,-0.0433416,0.\PG=CS [SG(C1H1),X(C2H6)]\@

CH₃CHCl•

1\1\GINC-AC55\FOpt\UB3LYP\6-31G(d)\C2H4Cl1(2)\MXN501\30-Aug-2006\0\#\
UB3LYP/6-31G* OPT INT=ULTRAFINE MAXDISK=134217728\rad-8\0,2\C,-0.060
2316193,0.6321151825,0.4080532218\C,-0.0259308697,-0.1479485279,1.6719
354264\H,0.2116841013,1.6789651368,0.3452023804\C1,0.0209144392,-0.207
5199464,-1.109485472\H,-0.7673850355,-0.9561850242,1.6657424924\H,-0.2
40564768,0.5132447153,2.5188843335\H,0.957695169,-0.6131856667,1.85149
19287\Version=IA64L-G03RevC.02\State=2-A'\HF=-538.7611965\S2=0.753953\
S2-1=0.\S2A=0.750011\RMSD=3.324e-09\RMSF=1.461e-05\Dipole=0.0920494,0.
1900201,0.6149136\PG=C01 [X(C2H4Cl1)]\@

CH₃CHF•

1\1\GINC-AC22\FOpt\UB3LYP\6-31G(d)\C2H4F1(2)\MXN501\31-Aug-2006\0\#\ U
B3LYP/6-31G* OPT INT=ULTRAFINE MAXDISK=134217728\title\0,2\C,-0.0962
260581,0.5223929361,-0.0844720512\C,-0.0223708132,-0.245919653,1.18233
12638\H,0.2782854737,1.538437345,-0.1890698534\F,0.0496272819,-0.20518
80953,-1.2177920491\H,-0.7393348765,-1.0763739721,1.1792185758\H,-0.25
17755635,0.4068893636,2.0307589638\H,0.9777606567,-0.6810995769,1.3520
654799\Version=IA64L-G03RevC.02\State=2-A'\HF=-178.3909891\S2=0.753092
\S2-1=0.\S2A=0.750007\RMSD=3.488e-09\RMSF=3.341e-05\Dipole=0.1027791,0
.1777116,0.5326005\PG=C01 [X(C2H4F1)]\@

CH₃OCH₂•

1\1\GINC-AC35\FOpt\UB3LYP\6-31G(d)\C2H5O1(2)\MXN501\06-Sep-2006\0\#\ U
B3LYP/6-31G* OPT INT=ULTRAFINE MAXDISK=134217728\title\0,2\O,-0.5479
495177,-0.0407875876,0.0411106385\C,0.1176982134,-1.2178184377,-0.1005
013138\C,0.2815560191,1.1092313093,0.1166086894\H,0.9170398242,1.19505
41392,-0.7766296357\H,0.9209244358,1.0754031373,1.0082443924\H,-0.3805
395219,1.9756681249,0.1741113034\H,1.0778939561,-1.2016573556,-0.61703

88445\H,-0.5472479473,-2.0666445747,-0.2142165767\\Version=IA64L-G03RevC.02\State=2-A\HF=-154.3618181\S2=0.752857\S2-1=0.\S2A=0.750006\RMSD=3.088e-09\RMSF=1.880e-05\Dipole=0.3976869,0.3154862,-0.147946\PG=C01 [X(C2H5O1)]\@

1-Phenylphosphetane (1)

1\1\GINC-AC49\Freq\RB3LYP\6-31G(d)\C9H11P1\EXK501\16-Mar-2007\0\#\ B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=134217728\\PhPhosphetane\\0,1\P,0.8639792,-1.26213895,0.\C,0.3224682,0.50990905,0.\C,-1.0179408,0.92958805,0.\C,1.3260872,1.49125105,0.\C,-1.3444648,2.28493905,0.\C,1.0036732,2.85048105,0.\C,-0.3327718,3.24934305,0.\H,-1.8187078,0.19396605,0.\H,-2.3877908,2.59072105,0.\H,-0.5877808,4.30591505,0.\H,1.7956542,3.59496905,0.\H,2.3693372,1.18451105,0.\C,-0.6947278,-3.14052695,0.\H,-1.7238258,-3.51900595,0.\H,-0.0252118,-4.00788295,0.\C,-0.3327718,-2.17645795,1.159546\C,-0.3327718,-2.17645795,-1.159546\H,0.1011792,-2.62223195,2.058903\H,0.1011792,-2.62223195,-2.058903\H,-1.1821998,-1.54952795,1.449999\H,-1.1821998,-1.54952795,-1.449999\\Version=IA64L-G03RevC.02\State=1-A\HF=-690.9091432\RMSD=9.665e-09\RMSF=1.929e-05\Dipole=-0.532715,0.2136813,0.\PG=CS [SG(C7H7P1),X(C2H4)]\@

1-Phenylphosphetane oxide (2)

1\1\GINC-AC44\Freq\RB3LYP\6-31G(d)\C9H11O1P1\EXK501\16-Mar-2007\0\#\ B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=134217728\\oxide\\0,1\P,-0.8731828409,-1.0074738295,0.\O,-2.3638578409,-0.8460348295,0.\C,0.8164691591,-2.7416928295,0.\C,-0.0067858409,0.6063421705,0.\C,1.3891741591,0.7454181705,0.\C,1.9701431591,2.0132921705,0.\C,1.1619751591,3.1529931705,0.\C,-0.2273658409,3.0219781705,0.\C,-0.8109148409,1.7540431705,0.\H,1.8450431591,-2.3690468295,0.\H,0.8626721591,-3.8346408295,0.\H,2.0331091591,-0.1302708295,0.\H,3.0524251591,2.1121991705,0.\H,1.6162631591,4.1403011705,0.\H,-0.8584898409,3.9066481705,0.\H,-1.8904408409,1.6361901705,0.\C,-0.0067858409,-2.1478788295,1.186048\C,-0.0067858409,-2.1478788295,-1.186048\H,0.5601511591,-1.6972898295,2.004668\H,0.5601511591,-1.6972898295,-2.004668\H,-0.7235098409,-2.8630568295,1.601621\H,-0.7235098409,-2.8630568295,-1.601621\\Version=IA64L-G03RevC.02\State=1-A\HF=-766.1627109\RMSD=7.704e-09\RMSF=1.882e-06\Dipole=1.6180901,-0.0037462,0.\PG=CS [SG(C7H7O1P1),X(C2H4)]\@

1-Phenylphosphetane-borane adduct (3)

1\1\GINC-AC53\Freq\RB3LYP\6-31G(d)\C9H14B1P1\EXK501\16-Mar-2007\0\#\ B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=134217728\\boraneadduct\\0,1\P,-0.5170529659,-1.0893810227,0.\B,-2.4177819659,-1.4697510227,0.\C,0.9285210341,-3.0223480227,0.\C,-0.0601769659,0.6802379773,0.\C,1.2769020341,1.1101309773,0.\C,1.5809020341,2.4700609773,0.\C,0.5519180341,3.4158879773,0.\C,-0.7792109659,2.9985039773,0.\C,-1.0867219659,1.6367839773,0.\H,1.9694940341,-3.3614200227,0.\H,0.2843470341,-3.9057550227,0.\H,-2.4717239659,-2.6811460227,0.\H,2.0873500341,0.3850509773,0.\H,2.6184550341,2.7930069773,0.\H,0.7900750341,4.4762009773,0.\H,-1.5812519659,3.7314459773,0.\H,-2.1216629659,1.3092799773,0.\H,-2.8527719659,-0.9698660227,1.015492\H,-2.8527719659,-0.9698660227,-1.015492\C,0.5519180341,-2.0699920227,1.17486\C,0.5519180341,-2.0699920227,-1.17486\H,1.4058010341,-1.4898800227,1.537801\H,1.4058010341,-1.4898800227,-1.537801\H,0.0338740341,-2.5166720227,2.026432\H,0.0338740341,-2.5166720227,-2.026432\\Version=IA64L-G03RevC.02\State=1-A\HF=-717.57264\RMSD=6.558e-09\RMSF=3.799e-05\Dipole=1.9576244,0.6458541,0.\PG=CS [SG(C7H8B1P1),X(C2H6)]\@

1-Methylphosphetane (4)

1\1\GINC-AC46\FOpt\RB3LYP\6-31G(d)\C4H9P1\EXK501\10-Apr-2007\0\#\ B3LYP/6-31G(D) OPT FREQ=NORAMAN MAXDISK=134217728\4ring-PMe_a\0,1\C,-0.421075,-1.707384,0.\C,-0.244867,-0.695116,1.161988\H,-1.198941,-0.24489,1.458719\P,0.736411,0.441255,0.\C,-0.244867,2.029597,0.\H,0.020911,2.620835,0.883714\H,-1.328516,1.862966,0.\H,0.020911,2.620835,-0.883714\C,-0.244867,-0.695116,-1.161988\H,0.266872,-1.059549,-2.056954\H,-1.198941,-0.24489,-1.458719\H,0.266872,-1.059549,2.056954\H,-1.360593,-2.272897,0.\H,0.399314,-2.433575,0.\Version=IA64L-G03RevC.02\State=1-A'\HF=-499.1753407\RMSD=3.509e-09\RMSF=5.282e-05\Dipole=-0.5448702,0.0136267,0.\PG=CS [SG(C2H3P1),X(C2H6)]\@\@

1-t-Butylphosphetane (5)

1\1\GINC-SC36\FOpt\RB3LYP\6-31G(d)\C7H15P1\JOH501\18-May-2005\0\#\ B3LYP/6-31G* OPT FREQ=NORAMAN MAXDISK=671088640\4ring-ptb_2_6db3\0,1\P,-0.7880704994,-0.5188501166,0.\C,1.1200534219,-0.5238857468,0.\C,-2.2064921866,1.453560631,0.\H,-3.2161200166,1.028629351,0.\H,-2.3082121273,2.5454576889,0.\C,-1.368224022,0.8609856861,-1.164333135\C,-1.368224022,0.8609856861,1.164333135\H,-1.9184830287,0.5516112348,-2.0572092567\H,-1.9184830287,0.5516112348,2.0572092567\H,-0.562970982,1.5389701427,-1.464108926\H,-0.562970982,1.5389701427,1.464108926\C,1.7917488037,0.8572420836,0.\C,1.5470424311,-1.3036858544,1.2600339889\C,1.5470424311,-1.3036858544,-1.2600339889\H,2.6391557086,-1.420414399,-1.2828172818\H,1.102064041,-2.3050369196,-1.2849591914\H,1.2522655472,-0.7806239134,-2.178050323\H,2.8844400009,0.7404633614,0.\H,1.5296029588,1.4450446345,-0.8866383929\H,1.5296029588,1.4450446345,0.8866383929\H,2.6391557086,-1.420414399,1.2828172818\H,1.2522655472,-0.7806239134,2.178050323\H,1.102064041,-2.3050369196,1.2849591914\Version=Al64T-G03RevC.02\State=1-A'\HF=-617.1112934\RMSD=4.392e-09\RMSF=2.358e-05\Dipole=0.3039384,0.4226839,0.\PG=CS [SG(C3H3P1),X(C4H12)]\@\@

cis,cis-2,4-Dimethyl-1-phenylphosphetane (6)

1\1\GINC-AC9\FOpt\RB3LYP\6-31G(d)\C11H15P1\EXK501\15-Apr-2007\0\#\ B3LYP/6-31G(D) OPT FREQ=NORAMAN MAXDISK=134217728 MAXDISK=134217728\allcis-diMe4ringPPH\0,1\P,-1.0317261706,1.098957761,0.\C,-2.335034045,-1.0375302567,0.\H,-3.3528578067,-1.4544733947,0.\H,-1.6425952492,-1.888108952,0.\C,-2.0104949354,-0.0724938529,1.1670788032\C,-2.0104949354,-0.0724938529,-1.1670788032\C,-1.3985394241,-0.6370404325,2.4412652711\C,-1.3985394241,-0.6370404325,-2.4412652711\H,-2.909578978,0.5018553077,1.4279960462\H,-2.909578978,0.5018553077,-1.4279960462\H,-1.1899537993,0.1576401354,3.1672958395\H,-2.0862464485,-1.3495077232,2.917011278\H,-0.4571888862,-1.1606727845,2.2452430926\H,-1.1899537993,0.1576401354,-3.1672958395\H,-0.4571888862,-1.1606727845,-2.2452430926\H,-2.0862464485,-1.3495077232,-2.917011278\C,0.7176487227,0.4688916685,0.\C,1.151421861,-0.8707341371,0.\C,2.5097748605,-1.1894925121,0.\C,3.4709328072,-0.1764639922,0.\C,1.7034634446,1.4720198748,0.\C,3.0638555469,1.1572548048,0.\H,0.4291144961,-1.6791797155,0.\H,2.817415122,-2.2322504016,0.\H,4.5285442285,-0.4270307017,0.\H,1.3952371212,2.5145560422,0.\H,3.8030039977,1.9542295633,0.\Version=IA64L-G03RevC.02\State=1-A'\HF=-769.5358786\RMSD=7.144e-09\RMSF=1.746e-05\Dipole=0.1186288,-0.5255212,0.\PG=CS [SG(C7H7P1),X(C4H8)]\@\@

cis,cis-2,4-Dichloro-1-phenylphosphetane (7)

1\1\GINC-AC33\FOpt\RB3LYP\6-31G(d)\C9H9Cl2P1\MXN501\30-Aug-2006\0\#\ B3LYP/6-31G* OPT INT=ULTRAFINE MAXDISK=134217728\d\0,1\P,-1.1551920688,-0.7391606693,-0.6743764378\C,0.6743381751,-0.7734359916,-0.6736251435\C,-1.7840505204,1.0601816982,-0.6671174914\C,-1.8144871222,-0.50422

22518,1.0985710846\C,-2.5991777761,0.7384087717,0.6099632467\C1,-0.666
2005168,-0.1295381055,2.4488044533\H,-2.3752737238,1.328702916,-1.5418
239587\C1,-0.6165276087,2.4258618678,-0.43549472\H,-2.4268864785,-1.32
99674377,1.4589408096\H,-2.6469115947,1.5557708808,1.3333544019\H,-3.6
25286742,0.457573624,0.3434380365\C,1.3947457453,-0.048266968,-1.63603
11387\C,2.7798890979,-0.1825969323,-1.7276811945\C,3.4614138197,-1.047
0948033,-0.8695602185\C,1.3646603212,-1.6519881521,0.1764212277\C,2.74
9903025,-1.782114845,0.0799943138\H,0.8797181195,0.6300601908,-2.30963
40692\H,3.3260902635,0.3921960184,-2.4707702622\H,4.5406538151,-1.1498
37362,-0.9425781161\H,0.8261141278,-2.2293069713,0.921921164\H,3.27263
27851,-2.4585089341,0.7509249777\Version=IA64L-G03RevC.02\State=1-A\HF=
-1610.0906583\RMSD=4.769e-09\RMSF=9.914e-06\Dipole=-0.4107242,-0.4162
742,-0.376049\PG=C01 [X(C9H9C12P1)]\@

***cis,cis*-2,4-Difluoro-1-phenylphosphetane (8)**

1\1\GINC-AC11\FOpt\RB3LYP\6-31G(d)\C9H9F2P1\MXN501\31-Aug-2006\0\#\# B3
LYP/6-31G* FOPT INT=ULTRAFINE MAXDISK=134217728\title\0,1\P,-1.312566814
, -0.5723434167, -0.5287872215\C,0.521769328, -0.5572448452, -0.4846500388
\C,-1.811333188,1.2766182085, -0.4675447035\C,-1.8408107743, -0.27914906
22,1.289497822\C,-2.5169820198,1.0445202934,0.8826521539\F,-0.79551525
61,-0.0669006477,2.1765967677\H,-2.444008075,1.6281529404,-1.287732115
7\F,-0.7531776102,2.1654569506, -0.3445199845\H,-2.494580679,-1.0400292
958,1.725625091\H,-2.3456950173,1.8530469099,1.6014285804\H,-3.5980471
307,0.9180320591,0.7525294814\C,1.2480726376,0.2077238859,-1.410537161
4\C,2.6403780403,0.1345554937,-1.4483190204\C,3.3256864697,-0.70220366
52,-0.5659522879\C,1.2176907957,-1.3955167579,0.4001963186\C,2.6100645
653,-1.4650701105,0.3583340759\H,0.729829099,0.8732261194,-2.094184700
6\H,3.1899500222,0.7370465243,-2.1668873517\H,4.4104894706,-0.75769136
96,-0.5968802305\H,0.6756700054,-1.9847029633,1.1336246175\H,3.1359151
832,-2.1143370433,1.0535309508\Version=IA64L-G03RevC.02\State=1-A\HF=
-889.3597159\RMSD=8.707e-09\RMSF=9.143e-06\Dipole=-0.5119899,-0.060434
, -0.0619476\PG=C01 [X(C9H9F2P1)]\@

1-Phenyl-3-oxaphosphetane (9)

1\1\GINC-AC23\FOpt\RB3LYP\6-31G(d)\C8H9O1P1\MXN501\06-Sep-2006\0\#\# B3
LYP/6-31G* OPT INT=ULTRAFINE MAXDISK=134217728\title\0,1\P,0.9684735
18,-1.3600041247,-0.002546015\C,0.4047320632,0.4029448257,0.0014102398
\C,-0.9452359406,0.7978847884,0.0011600811\C,1.3966076084,1.3952328798
,0.0047556857\C,-1.2868204555,2.149336532,0.0042557751\C,1.0538946209,
2.7495738469,0.0078414703\C,-0.2883556831,3.1279129242,0.0075865178\H,
-1.7270073507,0.0426508355,-0.0014434029\H,-2.3340169307,2.4410394968,
0.004059687\H,-0.5582589523,4.1807337774,0.009960413\H,1.8347490434,3.
5055479332,0.0104046977\H,2.4444482113,1.1045011423,0.0049472902\O,-1.
2643319885,-2.4241159736,-0.0072216838\C,-0.3661439684,-2.1675727959,1
.0874196477\C,-0.3642200902,-2.1619685221,-1.0989572402\H,-0.828698510
5,-1.5283958098,1.8474028259\H,-0.8254405418,-1.5189190036,-1.85648713
07\H,-0.0210994543,-3.0931079157,-1.5715228238\H,-0.0238713042,-3.1011
276711,1.5558090743\Version=IA64L-G03RevC.02\State=1-A\HF=-726.794325
4\RMSD=7.544e-09\RMSF=9.987e-06\Dipole=0.0869917,0.524905,0.0013865\PG
=C01 [X(C8H9O1P1)]\@

TS: CH₃ + 1-Phenylphosphetane

1\1\GINC-AC57\Freq\UB3LYP\6-31G(d)\C10H14P1(2)\EXK501\01-Apr-2007\0\#\#
B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=1342177280\TS_PhPhosphetane_IRC_
pt5\0,2\P,-1.1769498876,0.4902808989,-0.4183788764\C,0.6015201124,0.0
484308989,-0.1411088764\C,-2.1940798876,-0.2519591011,0.9880911236\C,-
1.9269498876,-1.1707291011,-1.1396588764\C,-2.9672898876,-1.1648291011

,0.0018911236\C,-0.9455898876,2.6736608989,0.6938611236\H,-1.2052398876,-1.9900291011,-1.0563488764\H,-2.7880598876,0.4681308989,1.5591411236\H,-1.5806198876,-0.8228591011,1.6931111236\H,-2.3119698876,-1.1318491011,-2.1618688764\H,-3.2364198876,-2.1527191011,0.3949311236\H,-3.8936098876,-0.6778891011,-0.3226288764\H,-1.9805598876,2.9977108989,0.7785411236\H,-0.4729298876,2.3752108989,1.6277211236\H,-0.3300298876,3.2866608989,0.0403311236\C,1.0315501124,-1.0884791011,0.5612211236\C,2.3910801124,-1.3652891011,0.7137611236\C,3.3476001124,-0.5152491011,0.1549911236\C,-1.5760501124,0.8888608989,-0.7015788764\C,2.9361401124,0.6107508989,-0.5589888764\H,0.3057501124,-1.7689791011,0.9992211236\H,2.7033401124,-2.2463591011,1.2689011236\H,4.4061501124,-0.7309791011,0.2740511236\H,1.2652401124,1.7727508989,-1.2525288764\H,3.6730201124,1.2759708989,-1.0017788764\\Version=IA64L-G03RevC.02\State=2-A\HF=-730.7461319\S2=0.763026\S2-1=0.\S2A=0.750062\RMSD=7.027e-09\RMSF=9.548e-04\Dipole=0.1780894,-0.3373415,0.215483\ PG=C01 [X(C10H14P1)]\@

Product: CH₃• + 1-Phenylphosphetane

1\1\GINC-AC34\Freq\UB3LYP\6-31G(d)\C10H14P1(2)\EXK501\24-Feb-2007\0\#\B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=134217728\\PhPhosphetane_product\0,2\C,-3.307283,-2.1825209775,0.2412439101\C,-2.291897,-1.3232319775,-0.4350480899\C,-2.104718,0.0470450225,0.2685829101\P,-0.875208,1.1589340225,-0.6190960899\C,-0.860155,2.5912730225,0.5818679101\H,-0.075034,3.2974910225,0.2935509101\H,-0.693576,2.2888360225,1.6219869101\H,-1.821322,3.1137010225,0.5209739101\C,0.73394,0.3283880225,-0.2024360899\H,-1.812964,-0.1056109775,1.3159039101\H,-3.061032,0.5864210225,0.2802259101\H,-1.321874,-1.8360939775,-0.4639040899\H,-2.583407,-1.1383129775,-1.4782110899\H,-3.027284,-2.8425779775,1.0569219101\H,-4.368275,-2.0351869775,0.0604569101\C,1.134833,0.0061650225,1.1049019101\C,2.359911,-0.6148599775,1.3464629101\C,3.209699,-0.9266089775,0.2816789101\C,1.598683,0.0078840225,-1.2597830899\C,2.826989,-0.6142429775,-1.0225370899\H,0.487912,0.2401590225,1.9473309101\H,2.653245,-0.8559329775,2.3652519101\H,4.164722,-1.4100949775,0.4702929101\H,1.304489,0.2508960225,-2.2779640899\H,3.482508,-0.8534449775,-1.8559800899\\Version=IA64L-G03RevC.02\State=2-A\HF=-730.7847\S2=0.753894\S2-1=0.\S2A=0.75001\RMSD=5.417e-09\RMSF=2.499e-06\Dipole=0.1927198,-0.0377321,0.5130217\PG=C01 [X(C10H14P1)]\@

TS: CH₃CH₂CH₂• + 1-Phenylphosphetane

1\1\GINC-AC57\Freq\UB3LYP\6-31G(d)\C12H18P1(2)\EXK501\08-Apr-2007\0\#\B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=671088640\\TS_Ph+Pr_IRC_pt3\0,2\P,0.5411801905,1.09078,-0.3955299048\C,-0.8602098095,-0.07441,-0.0893599048\C,0.6440101905,2.21091,1.1206300952\C,-0.4139998095,2.72266,-0.9003999048\C,0.2930501905,3.45386,0.2625700952\C,2.2726301905,-0.4949,0.3964600952\H,-1.4918598095,2.61212,-0.7419699048\H,1.6079201905,2.22706,1.6377900952\H,-0.1412898095,1.98291,1.8492400952\H,-0.2296398095,3.10806,-1.9062899048\H,-0.3130998095,4.21231,0.7728400952\H,1.2069901905,3.94603,-0.0897399048\H,3.1253901905,0.18474,0.4323700952\H,1.8508601905,-0.70771,1.3812300952\C,2.3771401905,-1.65241,-0.5584399048\C,-1.1362598095,-0.6217,1.1723500952\C,-2.1761998095,-1.53753,1.3443700952\C,-2.9610098095,-1.92209,0.2566000952\C,-1.6553998095,-0.47397,-1.1764599048\C,-2.6976598095,-1.38533,-1.0055299048\H,-0.5386998095,-0.33152,2.0327600952\H,-2.3740498095,-1.94804,2.3314600952\H,-3.7710898095,-2.63399,0.3904500952\H,-1.4588898095,-0.06783,-2.1665799048\H,-3.3029498095,-1.6784,-1.8596899048\C,3.4180001905,-2.70957,-0.1310699048\H,1.3980401905,-2.13989,-0.6566299048\H,2.6387001905,-1.27887,-1.5575399048\H,3.4607301905,-3.53191,-0.8563199048\H,4.4210001905,-2.27257,-0.0582399048\H,3.1696801905,-3.13732,0.8474800952\\Version=IA64L-G03RevC.02\State=2-A\HF=-809.3775084\S2=0.762126\S2-1=0.\S2A=0.750057\RMSD=6.810

e-09\RMSF=3.118e-04\Dipole=-0.2623795,0.0774,0.2231298\ PG=C01 [X(C12H18P1)]\@

Product: CH₃CH₂CH₂• + 1-Phenylphosphetane

1\1\GINC-AC44\FOpt\UB3LYP\6-31G(d)\C12H18P1(2)\EXK501\07-Apr-2007\0\#\#
B3LYP/6-31G* OPT FREQ=NORAMAN MAXDISK=134217728\prod Prod_Pr+4ringPh_a1\0,2\C,-3.3770518615,-2.8060378007,0.1423936907\C,-2.3430753485,-1.969350152,-0.5340184793\C,-2.13732381,-0.5977507833,0.1622339931\P,-0.893576194,0.4948595201,-0.7311705903\C,-0.8666829927,1.9374006145,0.4719241577\C,0.152977349,3.0219907936,0.0948341975\H,-0.6842133328,1.5866195192,1.4973623676\H,-1.8800059419,2.3630074397,0.4614795916\C,0.7047320424,-0.3589540426,-0.3159372886\H,-1.850835534,-0.7493575775,1.2112615868\H,-3.0864204159,-0.0458337682,0.1691220745\H,-1.3820441684,-2.4990813592,-0.5538516272\H,-2.6256478713,-1.7865907198,-1.5800152589\H,-3.1133561947,-3.4654802288,0.9639842995\H,-4.4342740727,-2.64045995,-0.0446779257\C,1.0934984169,-0.7046186376,0.9892775516\C,2.3086283592,-1.3453826577,1.2300273262\C,3.1609693655,-1.6539923036,0.1663958527\C,1.5723956649,-0.6767046641,-1.3719646735\C,2.7906014855,-1.3186384119,-1.1357229813\H,0.4440465479,-0.4732137536,1.8303498632\H,2.5918268849,-1.604574808,2.2472402178\H,4.1079534546,-2.1533886169,0.3541001337\H,1.2875049514,-0.416870238,-2.3885813318\H,3.4479706721,-1.5555923928,-1.968368462\C,0.1255970985,4.2188403456,1.0524020473\H,1.1603204665,2.5859786787,0.083343374\H,-0.0445229604,3.3656358693,-0.9291788447\H,0.8593402552,4.97872729,0.759370933\H,-0.8623725795,4.6955954829,1.0638705186\H,0.356778134,3.911172531,2.0796749807\Version=IA64L-G03RevC.02\State=2-A\HF=-809.4108053\S2=0.753895\S2-1=0.\S2A=0.75001\RMSD=6.138e-09\RMSF=1.914e-06\Dipole=0.2136078,-0.0227406,0.4978841\PG=C01 [X(C12H18P1)]\@

TS: CH₃• + 1-Phenylphosphetane oxide

1\1\GINC-AC53\Freq\UB3LYP\6-31G(d)\C10H14O1P1(2)\EXK501\29-Mar-2007\0\#\#
B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=1342177280 MAXDISK=1342177280\TS_oxide_IRC_pt0\0,2\P,1.1721890309,-0.391088134,0.0507969278\C,-0.6451079691,-0.106961134,0.0374129278\C,2.0013860309,1.169184866,0.7244719278\C,1.6506660309,0.648858866,-1.5293260722\C,1.7891550309,1.892752866,-0.6226390722\C,1.2496780309,-1.437745134,1.7155829278\H,0.9342740309,0.713149866,-2.3530920722\H,3.0610340309,0.938906866,0.8947279278\H,1.6048060309,1.630686866,1.6355289278\H,2.6201990309,0.327728866,-1.9269180722\H,0.8613300309,2.473301866,-0.6067530722\H,2.6086180309,2.564202866,-0.9016840722\H,2.2913800309,-1.634444134,1.9837769278\H,0.7874280309,-0.797717134,2.4769669278\H,0.7038370309,-2.381851134,1.6604019278\C,-1.2914389691,0.740408866,0.9476529278\C,-2.6761789691,0.910334866,0.8984769278\C,-3.4314989691,0.226604866,-0.0556480722\C,-1.4131359691,-0.790110134,-0.9171180722\C,-2.7976189691,-0.626781134,-0.9613650722\H,-0.7181599691,1.272559866,1.7022809278\H,-3.1640249691,1.574964866,1.6067149278\H,-4.5097529691,0.357225866,-0.0924380722\H,-0.9218609691,-1.455917134,-1.6218740722\H,-3.3814949691,-1.164377134,-1.7038320722\O,1.6280150309,-1.788923134,-0.6175960722\Version=IA64L-G03RevC.02\State=2-A\HF=-805.9644245\S2=0.754035\S2-1=0.\S2A=0.750012\RMSD=7.302e-09\RMSF=5.472e-06\Dipole=-0.4834228,0.7418592,0.3835855\PG=C01 [X(C10H14O1P1)]\@

Product: CH₃• + 1-Phenylphosphetane oxide

1\1\GINC-AC53\Freq\UB3LYP\6-31G(d)\C10H14O1P1(2)\EXK501\24-Feb-2007\0\#\#
B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=134217728\oxide_product\0,2\C,-3.2120670103,-2.428289134,0.0129591031\C,-2.1936580103,-1.445698134,-0.4591628969\C,-2.0053430103,-0.264380134,0.5316031031\P,-0.824517010

3,1.004353866,-0.1000198969\C,-0.8300890103,2.310112866,1.1896001031\H,-0.0984570103,3.077360866,0.9196881031\H,-0.5827740103,1.914825866,2.1802501031\H,-1.8216240103,2.772384866,1.2259471031\C,0.8348679897,0.235499866,0.0036611031\H,-1.6690500103,-0.630080134,1.5103461031\H,-2.9643900103,0.245216866,0.6897761031\H,-1.2239650103,-1.940036134,-0.6001948969\H,-2.4809390103,-1.024179134,-1.4301018969\H,-2.9349770103,-3.255373134,0.6597261031\H,-4.2714490103,-2.246539134,-0.1423968969\C,1.3653499897,-0.289050134,1.1921791031\C,2.6370529897,-0.861391134,1.2039991031\C,3.3896749897,-0.914444134,0.0277591031\C,1.5959129897,0.178462866,-1.1714368969\C,2.8688679897,-0.394595134,-1.1581798969\H,0.7906389897,-0.254642134,2.1153121031\H,3.0410999897,-1.265309134,2.1285301031\H,4.3806189897,-1.360702134,0.0379181031\H,1.1755929897,0.588459866,-2.0851748969\H,3.4532019897,-0.434964134,-2.0735738969\O,-1.1411490103,1.498862866,-1.4842048969\Version=IA64L-G03RevC.02\State=2-A\HF=-806.0402015\S2=0.753882\S2-1=0.\S2A=0.75001\RMSD=6.120e-09\RMSF=5.516e-06\Dipole=0.5308397,-0.5280237,1.4103426\PG=C01 [X(C10H14O1P1)]\@

TS: CH₃• + 1-Phenylphosphetane–borane adduct

1\1\GINC-AC43\Freq\UB3LYP\6-31G(d)\C10H17B1P1(2)\EXK501\23-Mar-2007\0\ \# B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=671088640\TS_boraneadduct_IRC_pt0\0,2\P,-1.0647558557,0.3346119381,-0.0445709175\C,0.7529041443,0.0258179381,-0.0325159175\C,-2.0459848557,-0.8973880619,0.9998880825\C,-1.6925738557,-1.0431500619,-1.3006059175\C,-2.6869288557,-1.5595060619,-0.2431409175\C,-0.8104178557,1.6386799381,1.7671260825\H,-0.8761308557,-1.7377630619,-1.5176099175\H,-2.7305108557,-0.4284120619,1.7120820825\H,-1.3776008557,-1.5638220619,1.5546200825\H,-2.1067538557,-0.6370140619,-2.2240569175\H,-2.7720178557,-2.6502980619,-0.1846309175\H,-3.6874798557,-1.1544450619,-0.4200259175\H,-1.8354208557,1.8210729381,2.0823650825\H,-0.2301508557,1.0018499381,2.4340750825\H,-0.2936518557,2.5281829381,1.4219900825\C,1.3122101443,-1.1941770619,0.3737330825\C,2.6943631443,-1.3844370619,0.3462880825\C,3.5341831443,-0.3617710619,-0.0982249175\C,1.6042541443,1.0489429381,-0.4759999175\C,2.9856011443,0.8526409381,-0.5133579175\H,0.6752661443,-2.0071840619,0.7126570825\H,3.1134661443,-2.3338880619,0.6690880825\H,4.6100901443,-0.5119820619,-0.1220539175\H,1.1837861443,1.9970899381,-0.7998089175\H,3.6325831443,1.6518829381,-0.8647699175\B,-1.8552438557,1.9627409381,-1.0306179175\H,-3.0213618557,1.6306719381,-1.0188169175\H,-1.3118098557,1.8216129381,-2.1032469175\H,-1.6104078557,2.9856469381,-0.4493429175\Version=IA64L-G03RevC.02\State=2-A\HF=-757.3912994\S2=0.75985\S2-1=0.\S2A=0.750043\RMSD=9.807e-09\RMSF=1.442e-04\Dipole=0.8302377,-1.291445,0.9349431\PG=C01 [X(C10H17B1P1)]\@

Product: CH₃• + 1-Phenylphosphetane–borane adduct

1\1\GINC-AC53\Freq\UB3LYP\6-31G(d)\C10H17B1P1(2)\EXK501\24-Feb-2007\0\ \# B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=134217728\boraneadduct_product\0,2\C,3.074634,2.5558039794,-0.2560880722\C,2.117928,1.4684239794,-0.6160460722\C,1.985974,0.4083409794,0.5115129278\P,0.839599,-0.9853750206,0.0849039278\C,0.849167,-2.0270990206,1.6043059278\H,0.139746,-2.8492680206,1.4743339278\H,0.579754,-1.4585360206,2.4995879278\H,1.849136,-2.4524350206,1.7337609278\C,-0.834968,-0.2398410206,0.0376099278\H,1.655673,0.8824409794,1.4440399278\H,2.963171,-0.0487530206,0.7096479278\H,1.124043,1.8882969794,-0.8178540722\H,2.440818,0.9583299794,-1.5311850722\H,2.749428,3.4198729794,0.3156089278\H,4.140883,2.4358879794,-0.4222860722\C,-1.350453,0.5014299794,1.1134239278\C,-2.629713,1.0510559794,1.0455489278\C,-3.409869,0.8652849794,-0.0987920722\C,-1.624938,-0.4199190206,-1.1071630722\C,-2.906742,0.1304139794,-1.1724590722\H,-0.755308,0.6535439794,2.0108559278\H,-3.018137,1.6229509794,1.8840089278\H,-4.407374,1.2933719794,-0.1509200722\H,-1.232196,-0.9919240206,-

1.9421200722\H,-3.510384,-0.0161160206,-2.0639340722\B,1.347447,-1.9756320206,-1.5021910722\H,0.548791,-2.8842300206,-1.5910410722\H,1.301426,-1.2025560206,-2.4343520722\H,2.47319,-2.3554610206,-1.2518750722\Version=IA64L-G03RevC.02\State=2-A\HF=-757.4514674\S2=0.753886\S2-1=0.\S2A=0.75001\RMSD=7.403e-09\RMSF=2.144e-06\Dipole=-0.7523347,1.0564753,1.5493788\PG=C01 [X(C10H17B1P1)]\@

TS: CH₃CH₂CH₂• + 1-Methylphosphetane

1\1\GINC-AC16\Freq\UB3LYP\6-31G(d)\C7H16P1(2)\EXK501\20-Apr-2007\0\#\B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=1342177280\TS_Pr+4ringPMe_a3_pt7\0,2\P,0.73542,0.3707486301,-0.381369726\C,1.21344,2.0363686301,0.315570274\C,1.08791,-0.8579513699,1.012300274\C,2.49238,-0.3610113699,-0.788109726\C,2.20335,-1.5357513699,0.175650274\C,-1.67434,0.6841386301,0.184070274\H,3.29228,0.2958786301,-0.426999726\H,0.25378,-1.4963613699,1.319150274\H,1.48345,-0.3541313699,1.901940274\H,2.69103,-0.6229613699,-1.830629726\H,3.06568,-1.8948313699,0.750400274\H,1.79843,-2.3924613699,-0.374669726\H,-1.54997,0.7319786301,1.268340274\H,-1.8599,1.6564386301,-0.273429726\C,-2.46652,-0.4739813699,-0.358069726\H,1.47481,2.7052286301,-0.512689726\H,0.37756,2.4848586301,0.860310274\H,2.07709,1.9663286301,0.986350274\C,-3.96765,-0.4122013699,-0.004459726\H,-2.35744,-0.5111713699,-1.449879726\H,-2.0544,-1.4188813699,0.023400274\H,-4.50531,-1.2733013699,-0.421229726\H,-4.1195,-0.4139413699,1.081460274\H,-4.43031,0.4984386301,-0.402989726\Version=IA64L-G03RevC.02\State=2-A\HF=-617.6434504\S2=0.761234\S2-1=0.\S2A=0.750052\RMSD=6.096e-09\RMSF=2.887e-04\Dipole=0.2270243,0.0938794,0.2850799\PG=C01 [X(C7H16P1)]\@

Product: CH₃CH₂CH₂• + 1-Methylphosphetane

1\1\GINC-AC58\FOpt\UB3LYP\6-31G(d)\C7H16P1(2)\EXK501\07-Apr-2007\0\#\B3LYP/6-31G* OPT FREQ=NORAMAN MAXDISK=134217728\prod_Pr+4ringMe_a1\0,2\C,-2.4128776251,-3.2965668217,0.1435225881\C,-1.3658331219,-2.4832848518,-0.5419379522\C,-1.1065421798,-1.1250335383,0.1645982007\P,0.1328439112,-0.0408976999,-0.7415782423\C,0.1896923157,1.387742805,0.4747377961\C,1.1901206634,2.4883594733,0.0894389811\H,0.4052119806,1.0168011586,1.4877933889\H,-0.8234000525,1.8130488069,0.5037523869\C,1.7201489382,-0.9173050568,-0.2847386862\H,-0.7849322759,-1.295957355,1.2014664155\H,-2.0471308953,-0.5608472523,0.2118326531\H,-0.4254116811,-3.0484484962,-0.5861814742\H,-1.6608065275,-2.2806354677,-1.5807369627\H,-2.1557943333,-3.971832641,0.9542514844\H,-3.4671652856,-3.0912676002,-0.0190177556\C,1.1513377274,3.6859281771,1.0461861251\H,2.2076073024,2.0751031749,0.0714730194\H,0.9802257089,2.8284264389,-0.9332358608\H,1.8765415756,4.4536960466,0.7523860879\H,0.1580544268,4.151262765,1.0565387518\H,1.3850286309,3.3815105036,2.0738091618\H,2.5787916795,-0.3197609369,-0.6083578195\H,1.8061406899,-1.0988282131,0.7943630039\H,1.778100082,-1.8778465527,-0.8073051625\Version=IA64L-G03RevC.02\State=2-A\HF=-617.6766144\S2=0.753886\S2-1=0.\S2A=0.75001\RMSD=7.801e-09\RMSF=8.322e-06\Dipole=0.1377393,0.0169677,0.5072796\PG=C01 [X(C7H16P1)]\@

TS: CH₃CH₂CH₂• + 1-t-Butylphosphetane

1\1\GINC-AC42\Freq\UB3LYP\6-31G(d)\C10H22P1(2)\EXK501\08-Apr-2007\0\#\B3LYP/6-31G(D) FREQ=NORAMAN MAXDISK=671088640\TS_tBu_IRC_pt0\0,2\P,-0.2344990515,0.3605909691,-0.3723009381\C,-1.5255240515,-1.0106760309,0.0119070619\C,-0.1752020515,1.5168279691,1.1184520619\C,-1.2232450515,1.9447409691,-0.9218669381\C,-0.5223720515,2.7273369691,0.2145020619\C,1.8997929485,-0.8441250309,0.2009570619\H,-2.3031240515,1.8726829691,-0.7673659381\H,0.7739619485,1.5609779691,1.6609820619\H,-0.9762810515,1.3085339691,1.8372700619\H,-1.0322100515,2.2887029691,-1.941783938

1\H,-1.1329040515,3.5044989691,0.6899730619\H,0.3927809485,3.206350969
1,-0.1506629381\C,2.9984739485,0.0353189691,-0.3332259381\H,1.81194294
85,-0.9054390309,1.2871290619\H,1.7742009485,-1.8063600309,-0.29672893
81\C,4.4112049485,-0.5037510309,-0.0333099381\H,2.8807649485,0.1514029
691,-1.4187049381\H,2.9093629485,1.0453899691,0.0921920619\H,5.1838199
485,0.1619189691,-0.4391159381\H,4.5795439485,-0.5948420309,1.04647406
19\H,4.5567339485,-1.4964420309,-0.4758029381\C,-1.5520400515,-1.94401
90309,-1.2156649381\C,-1.0868900515,-1.8076230309,1.2562600619\C,-2.94
09280515,-0.4614460309,0.2584440619\H,-1.8289870515,-2.5889600309,1.47
08280619\H,-0.1214630515,-2.2992530309,1.1137830619\H,-1.0157880515,-1
.1698690309,2.1452270619\H,-2.2646570515,-2.7649380309,-1.0557229381\H
, -1.8620480515,-1.4091930309,-2.1216259381\H,-0.5680640515,-2.38600703
09,-1.4073669381\H,-3.6128410515,-1.2854270309,0.5352410619\H,-2.96678
70515,0.2686989691,1.0759120619\H,-3.3600950515,0.0131989691,-0.634343
9381\\Version=IA64L-G03RevC.02\State=2-A\HF=-735.5741143\S2=0.76181\S2
-1=0.\S2A=0.750054\RMSD=3.734e-09\RMSF=3.636e-06\Dipole=-0.3803883,0.0
130727,0.2040598\PG=C01 [X(C10H22P1)]\@

Product: $\text{CH}_3\text{CH}_2\text{CH}_2\cdot + 1\text{-}t\text{-Butylphosphetane}$

1\1\GINC-AC41\FOpt\UB3LYP\6-31G(d)\C10H22P1(2)\EXK501\05-Apr-2007\0\#\n
B3LYP/6-31G(D) OPT FREQ=NORAMAN MAXDISK=134217728\@tBu-product_a1\0,
2\C,-2.7939235892,-2.9354384986,0.0803208295\C,-1.8352491113,-2.053003
8264,-0.6476606452\C,-1.1553379544,-1.0095004842,0.2820763279\@P,-0.002
1667021,0.1706064257,-0.6358165014\C,-0.1168290753,1.6576719716,0.5119
329305\H,0.7848759343,2.2650692527,0.3583617458\H,-0.1101708569,1.3447
892739,1.5649461845\C,-1.3554074771,2.5238960718,0.2311991485\C,1.7451
708474,-0.5051713563,-0.2336647434\H,-0.6396243257,-1.519131294,1.1056
551901\H,-1.9351652521,-0.3915287583,0.7441655892\H,-1.0618758493,-2.6
596618641,-1.1354650284\H,-2.3511465268,-1.5078474205,-1.4497101658\H,
-2.4646936828,-3.8606171406,0.5443096274\H,-3.7946504074,-2.5874672021
,0.3209223048\C,2.7537640311,0.4012934416,-0.9689165798\C,2.0911236663
, -0.5433106866,1.2646613611\C,1.8422487908,-1.9271412705,-0.820036523\
H,3.7752121557,0.023655946,-0.824294393\H,2.5551040807,0.4316977993,-2
.0460052463\H,2.7318272192,1.4312251364,-0.5937913054\H,3.0891125228,-
0.980489088,1.4091871815\H,2.1075772218,0.458181687,1.7071216603\H,1.3
845819378,-1.1544379688,1.837738918\H,2.8692702784,-2.304797424,-0.723
2383054\H,1.18521331,-2.63130092,-0.297333816\H,1.5800355581,-1.943778
5802,-1.8845302284\C,-1.4506853887,3.7391399667,1.161415489\H,-1.33431
07801,2.8574897719,-0.8142370834\H,-2.2664145436,1.9185390652,0.336982
3284\H,-2.3389336011,4.3420241192,0.9394589078\H,-1.5103073743,3.43088
35453,2.2125313172\H,-0.5722649234,4.3877937041,1.0565065672\\Version=
IA64L-G03RevC.02\State=2-A\HF=-735.6092831\S2=0.753888\S2-1=0.\S2A=0.7
5001\RMSD=6.725e-09\RMSF=8.218e-06\Dipole=0.1860718,0.0319496,0.483491
4\PG=C01 [X(C10H22P1)]\@

TS: $\text{CH}_3\text{CH}(\text{CH}_3)\cdot + \text{cis,cis-2,4-Dimethyl-1-phenylphosphetane}$

1\1\GINC-AC25\FTS\UB3LYP\6-31G(d)\C14H22P1(2)\MXN501\11-Aug-2006\0\#\n
UB3LYP/6-31G* OPT=(TS,CALCF,NOEIGENTEST,MAXCYC=200) MAXDISK=134217728
\@tsa2\0,2\@P,-0.7853137231,-0.0333520503,-0.5937897136\C,0.9081431082
, -0.3261104744,0.0836015284\C,-2.045315169,0.3383187956,0.7908657515\C
, -1.7222478851,-1.7521784256,-0.3246123437\C,-2.8157352285,-0.96946841
25,0.4471055231\C,-0.3408722761,2.3201549603,-1.174340481\C,-1.0623766
868,-2.8724933667,0.4739416264\H,-2.6140808299,1.2400596426,0.53825610
96\C,-1.6112054231,0.4401965388,2.2538668851\H,-2.0734477431,-2.147528
0489,-1.283378648\H,-3.1863396231,-1.4998869161,1.3348419387\H,-3.6817
663864,-0.7589810193,-0.1904892006\C,-1.6121896727,2.8291559962,-1.801
9134558\H,-0.162943901,2.6789914262,-0.1568548861\C,0.8771396337,2.311
2881933,-2.0587917279\C,1.508483259,0.4518555933,1.087403528\C,2.83246

12692,0.2316859171,1.473657967\C,3.5899350148,-0.7664005136,0.86033696
67\C,1.6932320718,-1.3152288246,-0.5371843356\C,3.0147784026,-1.537455
413,-0.1518186225\H,0.9451610924,1.2413428282,1.5725470252\H,3.2714533
656,0.8454935625,2.2563744083\H,4.6199604422,-0.9368540524,1.161826103
6\H,1.2687428284,-1.9128755141,-1.3403857555\H,3.5970803082,-2.3104334
921,-0.6470493636\H,-1.7972178298,-3.6631109368,0.6864895458\H,-0.2324
112103,-3.3339732786,-0.0710485529\H,-0.6669207641,-2.5216999328,1.433
1130367\H,-2.4988830076,0.4162656631,2.9008223717\H,-0.9580471038,-0.3
84880765,2.552705299\H,-1.0847259154,1.3781223166,2.4622836365\H,-1.5
116269215,3.8861380382,-2.1026191816\H,-1.8610814539,2.2624218014,-2.7
082437906\H,-2.4697327693,2.7709593906,-1.1221365013\H,1.1414164365,3.
3333877339,-2.3807259056\H,1.7519004685,1.8903546373,-1.5538942371\H,0
.6978338568,1.727044285,-2.9708658364\\Version=IA64L-G03RevC.02\State=
2-A\HF=-888.003727\S2=0.762018\S2-1=0.\S2A=0.750056\RMSD=9.985e-09\RMS
F=4.492e-06\Dipole=-0.0072537,-0.0593801,0.3262405\PG=C01 [X(C14H22P1)
J]\@

TS: CH₃CHCl• + *cis,cis*-2,4-Dichloro-1-phenylphosphetane

1\1\GINC-AC57\SP\UB3LYP\6-31G(d)\C11H13Cl3P1(2)\MXN501\29-Jun-2007\0\#\nub3lyp/6-31G* maxdisk=134217728\\title\\0,2\P,0,0.446993,0.247589,-0.671895\C,0,-0.933611,-0.814718,-0.098623\C,0,0.989197,1.520674,0.628528\C,0,-0.346484,1.930608,-1.280777\C,0,0.603548,2.678559,-0.320863\C,0,2.201528,-1.439683,-0.158251\Cl,0,-2.098057,2.275359,-0.969876\H,0,2.048182,1.450886,0.873377\Cl,0,0.128991,1.603536,2.225405\H,0,-0.191956,2.127921,-2.340715\H,0,0.148907,3.536239,0.179879\H,0,1.491673,3.029296,-0.860671\Cl,0,3.775801,-0.622036,-0.114223\H,0,1.891929,-1.690439,0.854711\C,0,2.080392,-2.507981,-1.201299\C,0,-0.958914,-1.423927,1.165735\C,0,-1.976174,-2.319941,1.497658\C,0,-2.976732,-2.624494,0.574223\C,0,-1.943251,-1.13156,-1.023548\C,0,-2.957485,-2.027254,-0.687453\H,0,-0.200294,-1.186809,1.903375\H,0,-1.986174,-2.776258,2.48386\H,0,-3.767273,-3.322498,0.835852\H,0,-1.94332,-0.67334,-2.008706\H,0,-3.733461,-2.256279,-1.412786\H,0,2.784706,-3.332348,-1.016971\H,0,1.06482,-2.918909,-1.185901\H,0,2.280795,-2.109609,-2.201063\\Version=IA64L-G03RevD.01\State=2-A\HF=-2148.8493897\S2=0.762344\S2-1=0.\S2A=0.750058\RMSD=1.182e-05\Thermal=0.\Dipole=0.0353541,-0.7281951,-0.5129492\PG=C01 [X(C11H13Cl3P1)J]\@

TS: CH₃CHF• + *cis,cis*-2,4-Difluoro-1-phenylphosphetane

1\1\GINC-AC57\SP\UB3LYP\6-31G(d)\C11H13F3P1(2)\MXN501\29-Jun-2007\0\#\nub3lyp/6-31G* maxdisk=134217728\\title\\0,2\C,0,1.962533,-0.044422,-1.114483\C,0,3.295939,0.254901,-0.838161\C,0,3.658169,0.752139,0.415396\C,0,2.679383,0.937953,1.392074\C,0,1.343889,0.636301,1.120133\C,0,0.96804,0.148263,-0.141031\P,0,-0.779833,-0.158232,-0.623484\C,0,-1.658056,-0.986956,0.850955\F,0,-0.895748,-1.101223,2.011844\C,0,-0.724353,-2.101165,-1.006724\F,0,0.486835,-2.714105,-0.729766\C,0,-1.75567,-2.331381,0.108237\C,0,-1.603836,2.051854,0.002262\F,0,-2.935905,1.823298,0.239914\C,0,-1.378098,3.031088,-1.102914\H,0,-2.603738,-0.512199,1.124364\H,0,-1.024533,-2.392046,-2.017365\H,0,-1.506006,-3.18559,0.746224\H,0,-2.760865,-2.485848,-0.301286\H,0,-1.075725,2.211665,0.944877\H,0,0.600223,0.754704,1.899505\H,0,2.954053,1.312246,2.374928\H,0,4.696973,0.987963,0.630343\H,0,1.695042,-0.433287,-2.093714\H,0,4.05216,0.09838,-1.602962\H,0,-1.807298,4.014419,-0.857324\H,0,-0.304712,3.158305,-1.276382\H,0,-1.842346,2.681587,-2.031338\\Version=IA64L-G03RevD.01\State=2-A\HF=-1067.7519787\S2=0.762311\S2-1=0.\S2A=0.75005\RMSD=2.016e-05\

Thermal=0.\Dipole=-0.0374156,0.3868862,-0.3775383\PG=C01 [X(C11H13F3P1)]\@

TS: CH₃OCH₂• + 1-Phenyl-3-oxaphosphetane

1\1\GINC-AC57\SP\UB3LYP\6-31G(d)\C10H14O2P1(2)\MXN501\29-Jun-2007\0\#\ub3lyp/6-31G* maxdisk=134217728\title\0,2\P,0,0.7608,0.758505,-0.411315\C,0,-0.837714,-0.146201,-0.171692\C,0,0.696622,2.071719,0.954698\C,0,0.066047,2.446555,-1.119016\O,0,-0.037354,3.035713,0.185205\C,0,2.001414,-0.767931,1.046712\H,0,1.696047,2.445399,1.226152\H,0,0.796841,2.974312,-1.747733\O,0,2.430791,-1.863059,0.351401\H,0,2.792907,-0.105306,1.412256\C,0,-2.02284,0.489728,0.236849\C,0,-3.206601,-0.235929,0.373543\C,0,-3.228117,-1.605588,0.100397\C,0,-0.871484,-1.523789,-0.440363\C,0,-2.057946,-2.247702,-0.306335\H,0,-2.016899,1.555422,0.449932\H,0,-4.11412,0.269901,0.693694\H,0,-4.152056,-2.168435,0.205189\H,0,0.039775,-2.034362,-0.739111\H,0,-2.065695,-3.313849,-0.518193\C,0,3.542072,-1.620386,-0.501191\H,0,3.800603,-2.575034,-0.963906\H,0,3.279558,-0.887198,-1.273915\H,0,4.401731,-1.247387,0.074228\H,0,1.240136,-1.04604,1.772756\H,0,-0.904756,2.412274,-1.626013\H,0,0.157729,1.798632,1.869928\Version=IA64L-G03RevD.01\State=2-A\HF=-881.1567441\S2=0.760294\S2-1=0.\S2A=0.750039\RMSD=2.651e-05\Thermal=0.\Dipole=0.4832181,-0.5084449,0.005031\PG=C01 [X(C10H14O2P1)]\@

Product: CH₃CH(CH₃)• + *cis,cis*-2,4-Dimethyl-1-phenylphosphetane

1\1\GINC-AC42\FOpt\UB3LYP\6-31G(d)\C14H22P1(2)\MXN501\23-Jun-2007\0\#\ub3lyp/6-31G(d) Opt=(maxcyc=200) maxdisk=268435456\title\0,2\C,-0.1169622686,0.0261087029,-0.0152454848\C,-0.2056171439,0.2165102902,1.3745479735\C,0.938356493,0.3725021901,2.1593919271\C,2.2017206945,0.3231440782,1.5693205607\C,2.3113644664,0.1210108662,0.192174688\C,1.1646756253,-0.0220622957,-0.5909720794\P,-1.7198916175,-0.1606500272,-0.9370271739\C,-1.9239971636,1.5446769227,-1.7519655532\C,-0.789685042,2.020252567,-2.6684633895\C,-1.244603321,-1.2720066997,-2.388883714\C,-0.9131829564,-2.6801388522,-1.8675460386\C,-2.3986520313,-1.3277713782,-3.4037147289\C,-2.2466491817,2.5914699183,-0.6587205753\C,-2.7639317905,3.8883542546,-1.1980869391\C,-2.6703599059,5.158512554,-0.4191803177\H,-2.8348363049,1.4210312363,-2.3564864804\H,-3.458859321,3.8470285707,-2.0365558245\H,-1.3483407404,2.7751286506,-0.0507067958\H,-2.9857043379,2.1533379033,0.040177603\H,-0.3589656527,-0.8729787465,-2.9003116967\H,1.2773118606,-0.177926124,-1.6598398962\H,3.2920638646,0.0762923255,-0.2750888913\H,3.0952234684,0.4346642324,2.1780443678\H,-1.185471226,0.232850117,1.8457664708\H,0.8419366688,0.5208895405,3.2319510644\H,-1.6849820242,5.2704174868,0.0535548262\H,-2.8466862503,6.0375195004,-1.0501087851\H,-3.4117629403,5.2035729926,0.4002626482\H,-1.0329754163,3.00205915,-3.092395791\H,0.1491707358,2.1255288509,-2.1132805395\H,-0.6152404449,1.3324524073,-3.5031541383\H,-2.5942328287,-0.3544753251,-3.8662633361\H,-2.1609532162,-2.0332965419,-4.2099954896\H,-3.3275622996,-1.6675246374,-2.9292538934\H,-0.072133551,-2.6696670817,-1.1668348592\H,-1.7746214873,-3.120490206,-1.3512061625\H,-0.64842569,-3.3431060276,-2.7012912655\Version=IA64L-G03RevD.01\State=2-A\HF=-888.0389698\S2=0.753966\S2-1=0.\S2A=0.750011\RMSD=5.861e-09\RMSF=4.340e-06\Thermal=0.\Dipole=0.3534773,0.1880765,-0.1824503\PG=C01 [X(C14H22P1)]\@

Product: CH₃CHCl• + *cis,cis*-2,4-Dichloro-1-phenylphosphetane

1\1\GINC-AC42\FOpt\UB3LYP\6-31G(d)\C11H13Cl3P1(2)\MXN501\23-Jun-2007\0\#\ub3lyp/6-31G(d) Opt=(maxcyc=200) maxdisk=268435456\title\0,2\C,-

0.0814300473,0.0050586363,0.0096659012\C,-0.1219080105,0.0119347235,1.4146112618\C,1.0525854338,0.0815132088,2.1658616928\C,2.2887252214,0.1316134528,1.5216456834\C,2.3459254372,0.1147442017,0.1259642549\C,1.1725333294,0.0545011441,-0.6255343599\P,-1.716248357,-0.0958607937,-0.8496494183\C,-1.8690719023,1.5621118385,-1.7355937928\C1,-0.5353085024,1.9742306648,-2.9422686081\C,-1.3375410456,-1.2482237562,-2.2916067012\C1,-2.8206231056,-1.2726778417,-3.3713943571\C,-1.0180836051,-2.6648181859,-1.8293384219\C,-2.0240097158,2.708523117,-0.7263632536\C,-2.455597935,3.9886984048,-1.360167385\C1,-3.0081101149,5.2719775244,-0.3351485939\H,-2.7655147976,1.4809700208,-2.3544644604\H,-2.1175707155,4.3068102178,-2.3383786537\H,-1.0781988969,2.8345769774,-0.1741512511\H,-2.7740649273,2.4047050453,0.0177491804\H,-0.5449786135,-0.8505115824,-2.9283610387\H,1.2379612148,0.0572261013,-1.7080037345\H,3.3069387219,0.1530475715,-0.3800058947\H,3.2053677886,0.1803560793,2.1033021075\H,-1.0819648208,-0.0423109816,1.921883301\H,1.0004642014,0.0898299875,3.2511852105\H,-1.8318380077,-3.0785428834,-1.2261183164\H,-0.8583124498,-3.3193313431,-2.6916862743\H,-0.1040551299,-2.6589506903,-1.2253009484\\Version=IA64L-G03RevD.01\State=2-A\HF=-2148.8856308\S2=0.753876\S2-1=0.\S2A=0.750011\RMSD=8.762e-09\RMSF=1.508e-06\Thermal=0.\Dipole=1.0936171,-0.646458,0.7803705\PG=C01 [X(C11H13Cl3P1)]\@

Product: CH₃CHF• + *cis,cis*-2,4-Difluoro-1-phenylphosphetane

1\1\GINC-AC42\FOpt\UB3LYP\6-31G(d)\C11H13F3P1(2)\MXN501\23-Jun-2007\0\ \# ub3lyp/6-31G(d) Opt=(maxcyc=200) maxdisk=268435456\title\0,2\C,-0.1191646242,0.053376947,0.1106833732\C,-0.0177389578,-0.4177797178,1.4307480239\C,1.1976455595,-0.3766295811,2.1161778534\C,2.3311146129,0.1456262461,1.4926932359\C,2.2442373127,0.6249418754,0.1834172165\C,1.0323984378,0.5778028544,-0.5059797329\P,-1.7782933861,-0.1007443013,-0.6929939857\C,-1.9396649966,1.4772216592,-1.7067730371\F,-0.8814691588,1.6447873621,-2.6313298408\C,-1.3900602204,-1.245495091,-2.1473287472\F,-2.5373846278,-1.1941567409,-2.9585785676\C,-1.1405715245,-2.6842506201,-1.7385118718\C,-2.0321505092,2.7432885467,-0.8610816672\C,-2.2389367574,3.953461303,-1.7051820402\F,-2.5405539488,5.08353813,-1.0259289171\H,-2.8457283754,1.3504150936,-2.3097266674\H,-1.6750191052,4.1369380138,-2.6156136922\H,-1.1188864202,2.8387405381,-0.2482024577\H,-2.868302906,2.64563676,-0.1555877323\H,-0.5610959004,-0.8472379585,-2.7417168302\H,0.9732018594,0.9642068383,-1.51663921\H,3.1240710825,1.0368084853,-0.3042318455\H,3.2781540179,0.1822192618,2.0246067543\H,-0.9004154059,-0.8172772908,1.9240560879\H,1.2563355973,-0.7472154354,3.13612022\H,-1.9883334019,-3.0783940196,-1.1689466866\H,-1.00283706,-3.305268912,-2.6304359459\H,-0.2389098415,-2.7596444567,-1.1218440222\\Version=IA64L-G03RevD.01\State=2-A\HF=-1067.7873883\S2=0.753035\S2-1=0.\S2A=0.750006\RMSD=5.308e-09\RMSF=3.614e-06\Thermal=0.\Dipole=0.9297484,-0.5145055,0.5073329\PG=C01 [X(C11H13F3P1)]\@

Product: CH₃OCH₂• + 1-Phenyl-3-oxaphosphetane

1\1\GINC-AC57\FOpt\UB3LYP\6-31G(d)\C10H14O2P1(2)\MXN501\23-Jun-2007\0\ \# ub3lyp/6-31G(d) Opt=(maxcyc=200) maxdisk=268435456\title\0,2\C,0.0479294728,-0.0160426408,0.08372887\C,0.0371352137,-0.1246278665,1.4842535273\C,1.2282053354,-0.1314321972,2.2129463421\C,2.4512936047,-0.0360063707,1.5487926335\C,2.4780356173,0.0661984613,0.1554841627\C,1.2884573431,0.0787485017,-0.5731735294\P,-1.5981167361,-0.0090883853,-0.7650315948\C,-1.5897804007,1.6250443456,-1.7298898924\H,-0.5764096223,1.9275290272,-2.01807608\C,-1.308393268,-1.1410604042,-2.2309129908\H,-2.2855186136,-1.2883378247,-2.7224618812\O,-0.3674357658,-0.6297625519,

-3.1623217364\O,-2.2419864754,2.6702234197,-1.0201960443\C,-1.48942437
71,3.3295606254,-0.0964205139\H,-2.0726720435,3.9916059227,0.532169907
9\H,-2.1727455039,1.4652317921,-2.6411288799\H,-0.5807982367,2.8602965
931,0.2695732953\H,-0.9897229756,-2.1230701098,-1.8441597451\H,1.31605
32384,0.145334155,-1.6556648666\H,3.4296188061,0.1367637291,-0.3656759
803\H,3.3804685669,-0.0425356298,2.1127930574\H,-0.9139789049,-0.20317
11099,2.005149027\H,1.1995187256,-0.2136525046,3.2963789133\C,-0.17865
20181,-1.4899907384,-4.2715578173\H,0.5458120333,-1.0079170215,-4.9330
29708\H,0.2134784993,-2.4707982316,-3.9604192497\H,-1.1187695939,-1.64
95388128,-4.8226569719\\Version=IA64L-G03RevD.01\State=2-A\HF=-881.183
9409\S2=0.753263\S2-1=0.\S2A=0.750008\RMSD=9.275e-09\RMSF=2.530e-06\Th
ermal=0.\Dipole=0.6699558,-0.8181579,-0.4251345\PG=C01 [X(C10H14O2P1)]
\\@

Table S2. Absolute Energies for the Species Listed in Table S1

Species	E (B3LYP/ 6-31G(d)) (Hartrees)	ZPE (kJ mol ⁻¹)	$\Delta\Delta H$ (kJ mol ⁻¹)	S (J K ⁻¹ mol ⁻¹)	E (CCSD(T)/ 6-31G(d)) (Hartrees)	E (R(O)MP2/ 6-31G(d)) (Hartrees)	E (R(O)MP2/ G3MP2large) (Hartrees)	E (G3(MP2)- RAD) (Hartrees)	Imag. freq. (cm ⁻¹)
CH ₃ CH ₂ CH ₂ •	-118.47137	228.5	15.4	286.5	-118.05588	-118.00038	-118.16543	-118.30962	
CH ₃ CH(CH ₃)•	-118.47815	228.2	15.9	292.3	-118.06103	-118.00532	-118.16947	-118.31386	
CH ₃ CHCl•	-538.76120	134.7	14.0	286.0	-537.92182	-537.87089	-538.06715	-538.20823	
CH ₃ CHF•	-178.39099	139.0	13.1	271.3	-177.89439	-177.85458	-178.07552	-178.20549	
CH ₃ OCH ₂ •	-154.36182	170.9	14.0	275.1	-153.89707	-153.85216	-154.04917	-154.18424	
1	-690.90914	452.5	26.5	398.2	-689.30112	-689.17024	-689.63856	-690.01418	
2	-766.16271	463.9	28.9	418.8	-764.37725	-764.24794	-764.81367	-765.27244	
3	-717.57264	533.5	32.5	438.0	-715.83837	-715.68929	-716.20838	-716.67751	
4	-499.17534	314.0	18.8	322.8	-498.11891	-498.03492	-498.31977	-498.54495	
5	-617.10645	533.8	29.1	403.8	-615.66568	-615.53517	-615.97699	-616.33341	
6	-769.53588	598.0	34.3	453.0	-767.66695	-767.50510	-768.07826	-768.54132	
7	-1610.09066	405.3	32.4	452.1	-1607.3755	-1607.22303	-1607.86278	-1608.31647	
8	-889.35972	411.9	30.8	436.2	-887.32694	-887.19349	-887.87656	-888.31123	
9	-726.79433	391.0	25.7	390.2	-725.13886	-725.01735	-725.51521	-725.88145	
<i>trans</i> - 10	-538.49105	386.4	22.7	353.1	-537.30370	-537.20411	-537.54097	-537.81000	
<i>cis</i> - 10	-538.48770	386.5	22.7	353.8	-537.30069	-537.20105	-537.53858	-537.80765	
TS: CH ₃ • + 1	-730.74613	539.1	33.1	450.4	-728.98592	-728.83079	-729.36677	-729.79884	-253 <i>i</i>

Product: CH ₃ • + 1	-730.78470	539.5	36.1	479.9	-729.02830	-728.87494	-729.40805	-729.83836	
TS: CH ₃ CH ₂ CH ₂ • + 1	-809.37751	687.9	40.2	515.7	-807.35377	-807.16703	-807.80630	-808.32646	-189 <i>i</i>
Product: CH ₃ CH ₂ CH ₂ • + 1	-809.41081	687.7	43.2	540.5	-807.39222	-807.20710	-807.84388	-808.36242	
TS: CH ₃ • + 2	-805.96442	552.1	34.2	460.0	-804.02832	-803.86551	-804.49380	-804.96179	-656 <i>i</i>
Product: CH ₃ • + 2	-806.04020	551.5	38.5	497.2	-804.10794	-803.95603	-804.58550	-805.09907	
TS: CH ₃ • + 3	-757.39130	621.6	38.7	486.2	-755.50719	-755.33475	-755.92132	-756.39894	-352 <i>i</i>
Product: CH ₃ • + 3	-757.45147	621.6	41.9	516.0	-755.57113	-755.39970	-755.98256	-756.50624	
TS: CH ₃ CH ₂ CH ₂ • + 4	-617.64345	549.4	32.4	445.3	-616.17021	-616.02957	-616.48439	-616.85492	-185 <i>i</i>
Product: CH ₃ CH ₂ CH ₂ • + 4	-617.67661	549.2	35.4	467.1	-616.20840	-616.06960	-616.52257	-616.89126	
TS: CH ₃ CH ₂ CH ₂ • + 5	-735.57411	769.7	42.4	521.2	-733.71304	-733.52584	-734.13865	-734.64044	-168 <i>i</i>
Product: CH ₃ CH ₂ CH ₂ • + 5	-735.60928	769.0	45.6	539.5	-733.75293	-733.56737	-734.17764	-734.67779	

TS: CH ₃ CH(CH ₃)• + 6	-888.00373	833.0	48.1	566.1	-885.72193	-885.50520	-886.25057	-886.85720	-190 <i>i</i>
Product: CH ₃ CH(CH ₃)• + 6	-888.03897	833.7	50.3	587.1	-	-885.54467	-886.28600	-	
TS: CH ₃ CHCl• + 7	-2148.84928	545.4	45.3	565.9	-2145.2972	-2145.09433	-2145.93715	-2146.53140	-162 <i>i</i>
Product: CH ₃ CHCl• + 7	-2148.88563	546.9	47.3	585.0	-	-2145.13556	-2145.97591	-	
TS: CH ₃ CHF• + 8	-1067.75159	555.2	43.1	544.5	-1065.22266	-1065.04900	-1065.95713	-1066.52217	-146 <i>i</i>
Product: CH ₃ CHF• + 8	-1067.78739	558.8	44.5	554.0	-1065.26437	-1065.09213	-1065.99630	-1066.55992	
TS: CH ₃ OCH ₂ • + 9	-881.15675	566.9	38.2	497.0	-879.036	-878.86910	-879.56786	-879.58911	-161 <i>i</i>
Product: CH ₃ OCH ₂ • + 9	-881.18394	566.3	41.2	528.8	-879.06666	-878.90118	-879.59867	-880.09905	
TS: CH ₃ CH(CH ₃)• + <i>trans</i> - 10 (<i>anti attack</i>)	-656.96330	621.4	36.4	468.9	-655.36053	-655.20499	-655.71279	-656.12645	-194 <i>i</i>
TS: CH ₃ CH(CH ₃)• + <i>trans</i> - 10 (<i>syn attack</i>)	-656.96009	622.5	35.8	463.0	-655.35804	-655.20249	-655.71071	-656.12438	-174 <i>i</i>
TS: CH ₃ CH(CH ₃)•	-656.95953	621.4	36.6	473.7	-655.35668	-655.20095	-655.70936	-656.12321	-194 <i>i</i>

+ <i>cis</i> - 10 (<i>anti</i> attack)									
TS: CH ₃ CH(CH ₃)• + <i>cis</i> - 10 (<i>syn</i> attack)	-656.95945	621.9	36.3	470.7	-655.35710	-655.20146	-655.71020	-656.12396	-191 <i>i</i>
H ₄ P•	-343.65600	77.5	10.4	225.3	-343.07525	-343.04227	-343.15557	-343.23018	
H ₄ P(BH ₃)•	-370.28386	159.3	16.8	297.5	-369.31512	-369.52135	-369.68364	-369.54726	
Me ₃ ^t BuP• (^t Bu equatorial)	-618.86500	604.6	36.4	451.4	-617.36959	-617.22904	-617.71482	-618.09466	
Me ₂ PhP	-652.83127	430.4	27.9	404.2	-651.32480	-651.20273	-651.64185	-651.98984	
TS: CH ₃ • + Me ₂ PhP	-692.66336	516.8	34.8	467.0	-691.00526	-690.85986	-691.36763	-691.77116	-191 <i>i</i>
Me ₂ ^t BuP	-579.03297	512.0	30.4	410.5	-577.68893	-577.56705	-577.98012	-578.30909	
TS: CH ₃ • + Me ₂ ^t BuP	-618.86194	600.7	36.1	452.4	-617.36591	-617.22085	-617.70357	-618.08792	-191 <i>i</i>

Tables S3(a-l). Details of IRC Calculations on the Ring-Opening Transition States at 298.15 K. The variational transition states are indicated by shading.

Table S3a. CH₃• + 1

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	Rel. G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.669	-730.74503	537.1	34.1	461.4	-729.37924	7.8
2.582	-730.74519	538.0	33.6	455.5	-729.37858	11.8
2.552	-730.74533	538.1	33.7	457.4	-729.37842	11.8
2.524	-730.74551	538.1	33.7	457.4	-729.37840	11.8
2.495	-730.74576	538.7	33.4	453.4	-729.37854	13.0
2.461	-730.74613	539.1	33.1	450.4	-729.37887	13.1
2.428	-730.74659	539.3	33.1	450.2	-729.37955	11.6
2.394	-730.74716	539.6	32.9	448.3	-729.38064	9.4
2.360	-730.74784	539.8	32.8	447.6	-729.38235	5.3
2.326	-730.74863	540.1	32.7	446.1	-729.38481	-0.6

Table S3b. CH₃CH₂CH₂• + 1

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	Rel. G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.623	-809.37735	686.7	40.9	530.5	-807.82158	0.0
2.575	-809.37727	686.8	40.8	526.6	-807.82133	1.8
2.525	-809.37730	687.2	40.6	524.2	-807.82126	2.9
2.498	-809.37740	687.6	40.3	517.9	-807.82127	4.9
2.478	-809.37751	687.9	40.2	515.7	-807.82142	5.3
2.458	-809.37763	687.9	40.3	517.9	-807.82159	4.3
2.439	-809.37776	687.9	40.0	513.4	-807.82182	4.7
2.425	-809.37787	687.8	40.4	521.3	-807.82215	1.8

Table S3c. CH₃CH₂CH₂• + 4

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	<i>S</i>	E (ROMP2/ 6-311+G(3df,2p))	Rel. <i>G</i>
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.380	-617.64432	550.0	32.0	440.9	-616.49520	3.0
2.410	-617.64401	549.8	32.1	442.6	-616.49424	5.0
2.439	-617.64376	549.7	32.2	442.7	-616.49361	6.5
2.466	-617.64358	549.5	32.3	445.1	-616.49323	6.7
2.495	-617.64345	549.4	32.4	445.3	-616.49311	6.9
2.568	-617.64331	548.9	32.6	449.3	-616.49317	5.4
2.641	-617.64342	548.5	32.8	452.3	-616.49371	2.9
2.662	-617.64349	548.4	32.9	453.3	-616.49383	2.2
2.685	-617.64357	548.2	33.1	456.2	-616.49411	0.6

Table S3d. CH₃CH₂CH₂• + 5

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	Rel. G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.517	-735.57422	769.2	42.7	526.8	-734.15241	0.0
2.449	-735.57411	769.7	42.4	521.2	-734.15232	2.1
2.422	-735.57425	770.2	42.2	516.4	-734.15312	1.6
2.394	-735.57439	770.3	42.1	515.5	-734.15378	0.3
2.372	-735.57459	770.5	42.0	513.8	-734.15482	-1.9
2.346	-735.57479	770.6	41.9	512.7	-734.15591	-4.3

Table S3e. CH₃CH(CH₃)• + 6

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	Rel. G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.436	-888.00372	833.1	48.0	564.9	-886.26960	0.0
2.444	-888.00371	833.1	48.1	565.3	-886.26947	0.2
2.451	-888.00370	833.1	48.1	565.5	-886.26937	0.4
2.464	-888.00369	833.0	48.1	566.1	-886.26919	0.7
2.479	-888.00370	832.9	48.2	566.9	-886.26907	0.7
2.486	-888.00371	832.9	48.2	567.4	-886.26902	0.7
2.494	-888.00372	832.8	48.2	567.7	-886.26897	0.7
2.501	-888.00373	832.8	48.3	568.2	-886.26894	0.6
2.509	-888.00375	832.7	48.3	568.5	-886.26891	0.6
2.517	-888.00377	832.7	48.3	569.1	-886.26889	0.4
2.541	-888.00385	832.5	48.4	570.9	-886.26888	-0.1
2.571	-888.00398	832.4	48.5	572.1	-886.26894	-0.7
2.593	-888.00410	832.2	48.6	572.7	-886.26901	-1.1
2.615	-888.00423	832.1	48.7	573.8	-886.26911	-1.8

Table S3f. CH₃CHCl• + 7

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.541	-2148.84924	545.1	45.5	568.3	-2145.94323	0.0
2.530	-2148.84924	545.2	45.4	568.0	-2145.94323	0.1
2.521	-2148.84925	545.2	45.4	567.5	-2145.94324	0.2
2.511	-2148.84926	545.3	45.4	567.1	-2145.94326	0.3
2.488	-2148.84931	545.4	45.3	565.9	-2145.94338	0.4
2.480	-2148.84933	545.4	45.3	565.6	-2145.94343	0.4
2.473	-2148.84935	545.4	45.3	565.2	-2145.94350	0.3
2.465	-2148.84938	545.4	45.3	564.9	-2145.94359	0.2

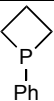
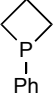



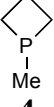

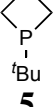

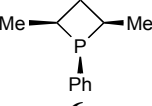

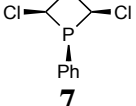

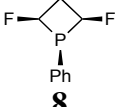

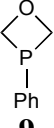
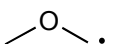
Table S3g. CH₃CHF• + 8

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.557	-1067.75159	554.7	43.5	550.3	-1065.98699	0.0
2.533	-1067.75161	554.7	43.5	550.0	-1065.98681	0.6
2.529	-1067.75161	554.8	43.4	549.8	-1065.98679	0.7
2.525	-1067.75162	554.8	43.4	549.6	-1065.98677	0.8
2.520	-1067.75162	554.8	43.4	549.3	-1065.98675	0.9
2.478	-1067.75173	555.0	43.3	546.8	-1065.98668	1.9
2.463	-1067.75179	555.1	43.2	545.9	-1065.98672	2.2
2.455	-1067.75183	555.1	43.2	545.3	-1065.98674	2.3
2.448	-1067.75187	555.2	43.2	545.0	-1065.98679	2.3
2.440	-1067.75191	555.2	43.1	544.5	-1065.98684	2.3
2.433	-1067.75196	555.3	43.1	544.1	-1065.9869	2.3
2.403	-1067.75218	555.4	43.0	542.6	-1065.98732	1.7

Table S3h. CH₃OCH₂• + 9

P...C	E (B3LYP/ 6-31G(d))	ZPE	$\Delta\Delta H$	S	E (ROMP2/ 6-311+G(3df,2p))	G
(Å)	(Hartrees)	(kJ mol ⁻¹)	(kJ mol ⁻¹)	(J K ⁻¹ mol ⁻¹)	(Hartrees)	(kJ mol ⁻¹)
2.478	-881.15676	566.8	38.3	497.9	-879.58911	0.0
2.469	-881.15676	566.8	38.3	497.8	-879.58910	0.1
2.461	-881.15676	566.8	38.3	497.5	-879.58911	0.1
2.456	-881.15677	566.8	38.2	497.3	-879.58911	0.2
2.452	-881.15677	566.9	38.2	497.2	-879.58913	0.2
2.449	-881.15678	566.9	38.2	497.1	-879.58914	0.2
2.427	-881.15681	566.9	38.2	496.2	-879.58926	0.1
2.419	-881.15683	566.9	38.2	495.9	-879.58932	0.0
2.412	-881.15685	567.0	38.1	495.6	-879.58940	-0.1
2.396	-881.15691	567.0	38.1	495	-879.58961	-0.4
2.373	-881.15701	567.1	38.0	494.2	-879.59005	-1.4
2.357	-881.15710	567.1	38.0	493.7	-879.59046	-2.3

Table S4. ΔS^\ddagger and its components.

Phosphetane	Attacking radical	ΔS^\ddagger sum	ΔS^\ddagger elec.	ΔS^\ddagger trans.	ΔS^\ddagger rot.	ΔS^\ddagger vib.
 1	Me•	-143.1	0.0	-141.3	-40.4	38.6
 1		-172.7	0.0	-152.5	-85.2	65.0
 2	Me•	-154.2	0.0	-141.5	-41.7	29.0
 3	Me•	-147.1	0.0	-141.4	-41.5	35.8
 4		-167.8	0.0	-150.7	-78.8	61.9
 5		-172.7	0.0	-152.1	-83.9	63.3
 6		-183.2	0.0	-153.0	-89.2	58.9
 7		-172.1	0.0	-157.3	-89.7	74.8
 8		-163.0	0.0	-154.0	-85.3	76.3
 9		-168.2	0.0	-153.0	-82.5	67.3