Supplementary Information

A Zwitterionic Triphosphenium Compound as a Tunable Multifunctional Donor

*Stephanie C. Kosnik and Charles L. B. Macdonald**

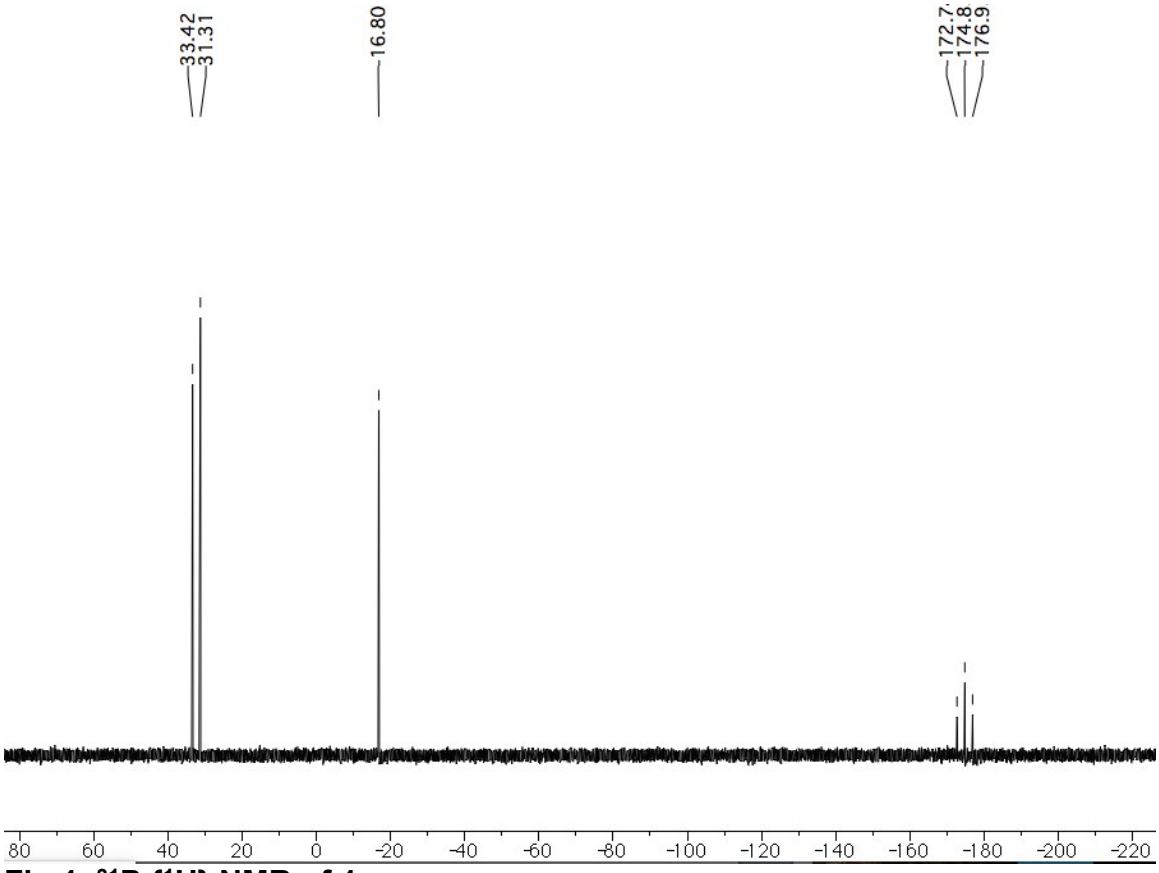


Fig 1. ^{31}P {^1H} NMR of 1

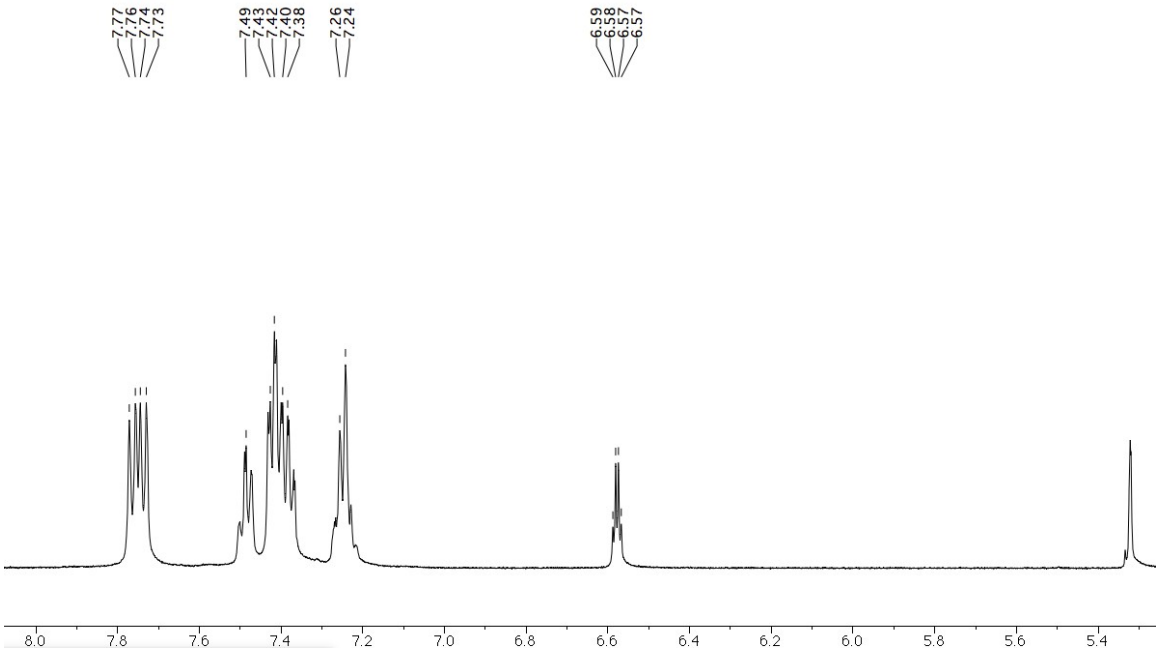


Fig. 2 ^{1}H NMR of 1

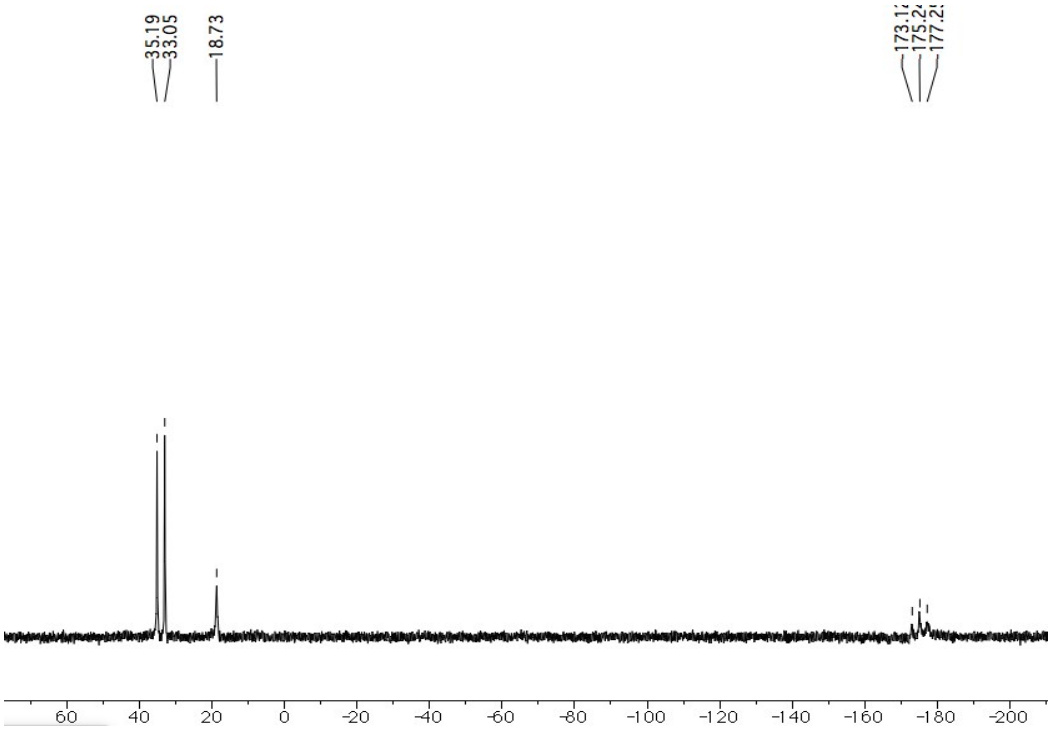


Fig. 3 ^{31}P {^{1}H} NMR of 2

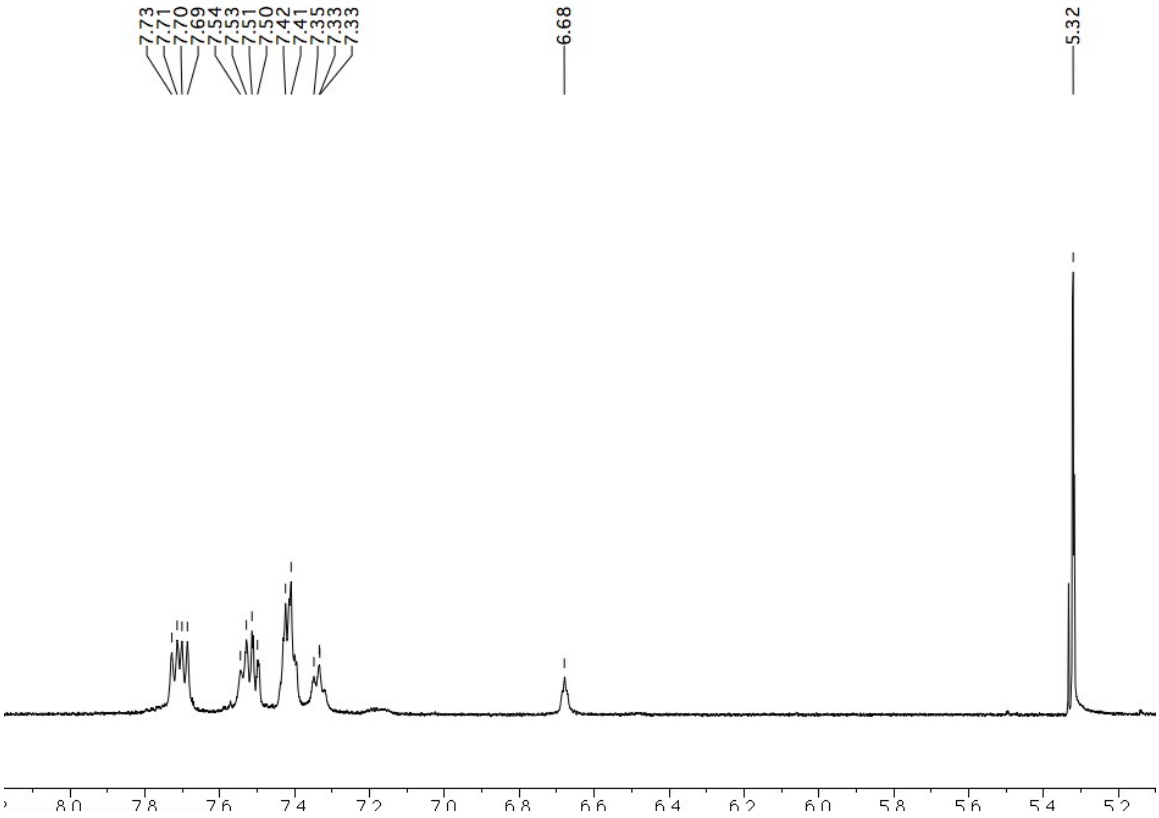


Fig. 4 ^{1}H NMR of 2

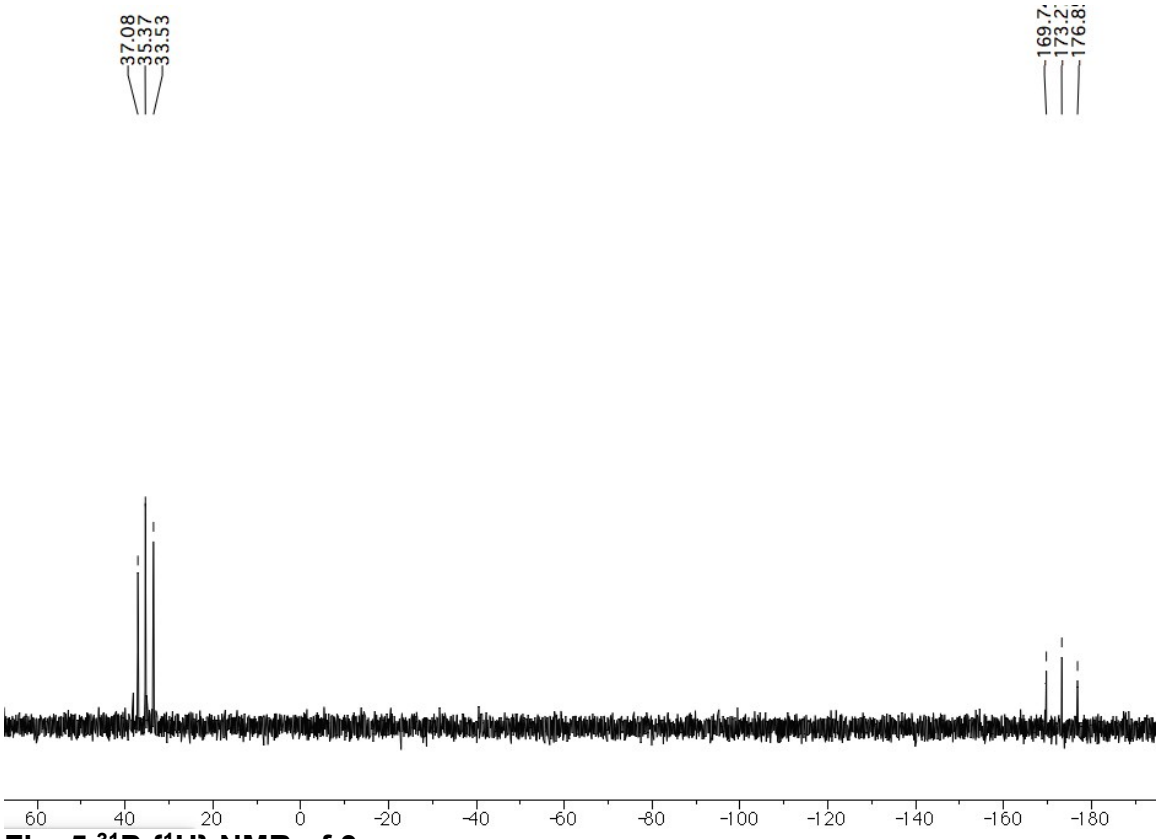


Fig. 5 ^{31}P {^{1}H} NMR of 3

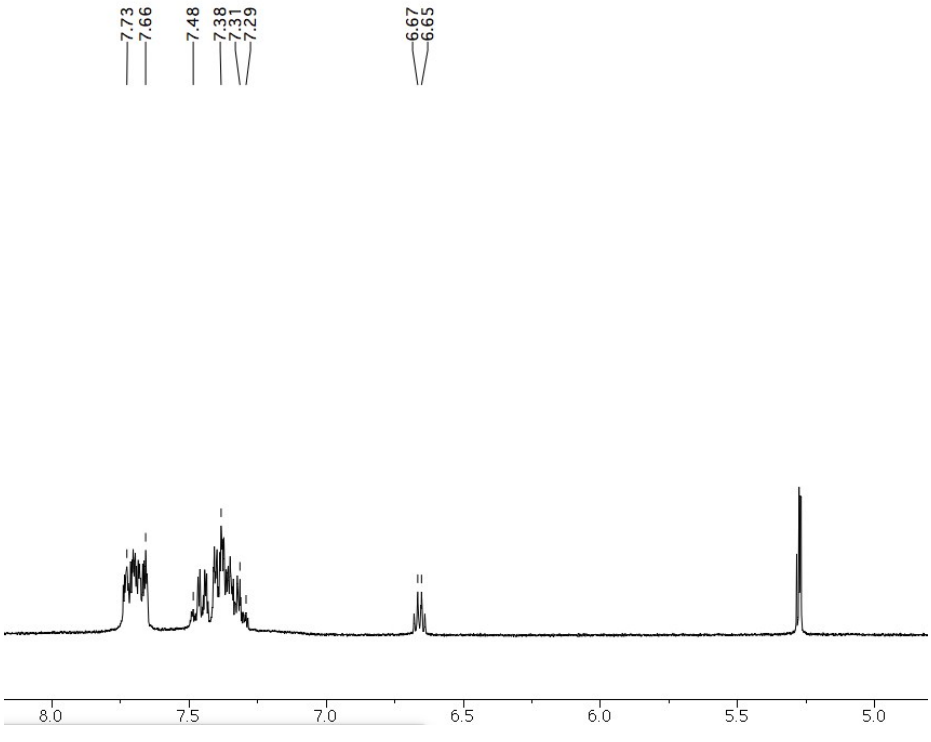


Fig. 6 ^{1}H NMR of 3

Experimental Procedure NMR Reactions with Triflic Acid

To a Schlenk flask containing **1** (0.200g, 0.39 mmol) in dichloromethane, was added 1 stoichometric equivalent of triflic acid via syringe (0.058g, 0.39 mmol). There is no colour change upon addition, however the reaction can be tracked by ^{31}P NMR; after stirring for five minutes the reaction is complete. $^{31}P\{^{1}H\}$ NMR: δ 35.17 (d, $^{1}J_{P\text{-}P}$= 443 Hz), -4.2 (s), -178.0 (t, $^{1}J_{P\text{-}P}$= 437 Hz). ^{31}P NMR: δ 35.2 (d, $^{1}J_{P\text{-}P}$= 445 Hz), -4.15 (d, $^{1}J_{P\text{-}H}$= 500 Hz), -178.0 (t, $^{1}J_{P\text{-}P}$= 445 Hz). ^{1}H NMR: δ 8.60 (d, $^{1}J_{P\text{-}H}$= 498 Hz, 1H, P-*H*), 7.8-7.4 (m, 30H, *Ph*), 6.82 (*pseudo*-q, $^{2}J_{P\text{-}H}$= 3.5 Hz, $^{3}J_{P\text{-}H\text{-}}$=3.5 Hz, 2H, C_5H_2).

To an NMR tube containing **1** in CD_2Cl_2, was added one drop of triflic acid syringe There is no colour change upon addition, and due to the instability of this molecule, however the NMR spectra were collected immediately upon addition. $^{31}P\{^{1}H\}$ NMR: δ 35.17 (d, $^{1}J_{P\text{-}P}$= 443 Hz), -4.2 (s), -178.0 (t, $^{1}J_{P\text{-}P}$= 437 Hz). ^{31}P NMR: δ 35.2 (d, $^{1}J_{P\text{-}P}$= 445 Hz), -4.15 (d, $^{1}J_{P\text{-}H}$= 500 Hz), -178.0 (t, $^{1}J_{P\text{-}P}$= 445 Hz). ^{1}H NMR: δ 11.2 (b, $^{1}J_{P\text{-}H}$ unresolved, 1H, P^{I}-*H*), 8.60 (d, $^{1}J_{P\text{-}H}$= 500 Hz, 1H, P-*H*), 8.8-7.1 (m, 30H, *Ph*), 6.82 (*pseudo*-q, $^{2}J_{P\text{-}H}$= 3.5 Hz, $^{3}J_{P\text{-}H\text{-}}$=3.5 Hz, 2H, C_5H_2). Excess triflic acid is visible in the spectrum.

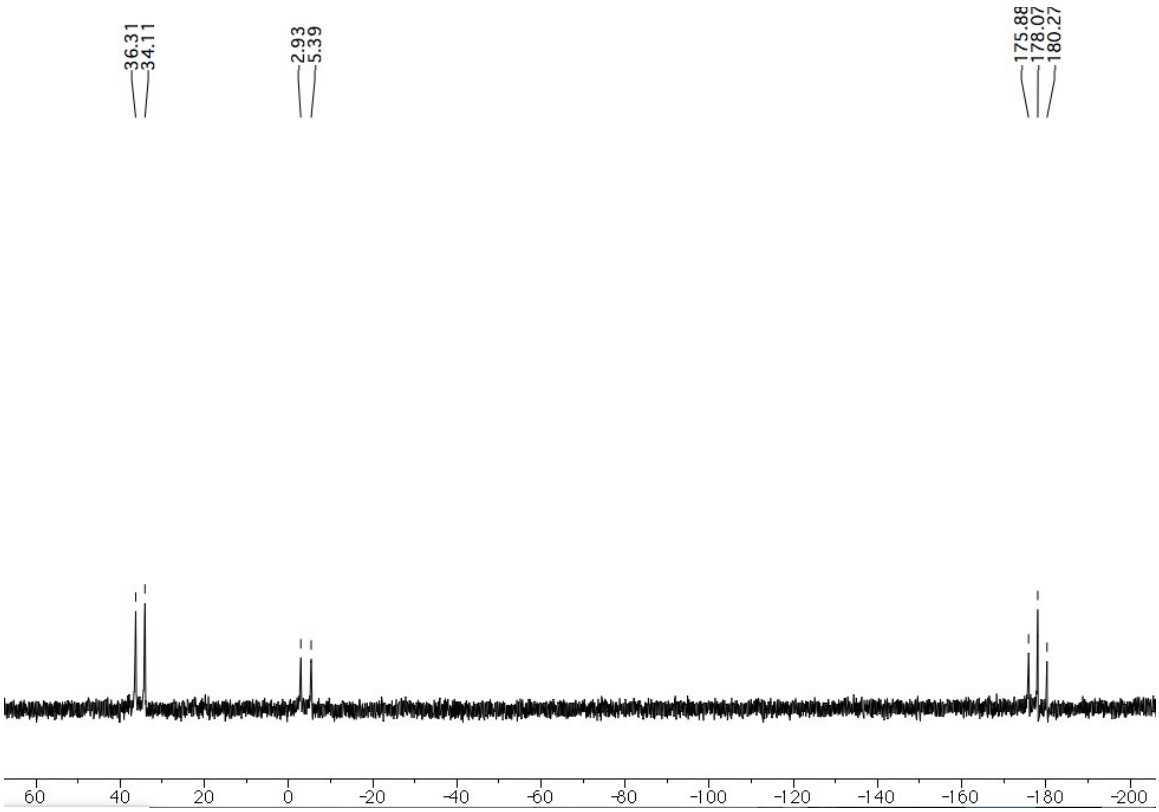


Fig. 7 ^{31}P NMR of the reaction with 1 eq. HOTf

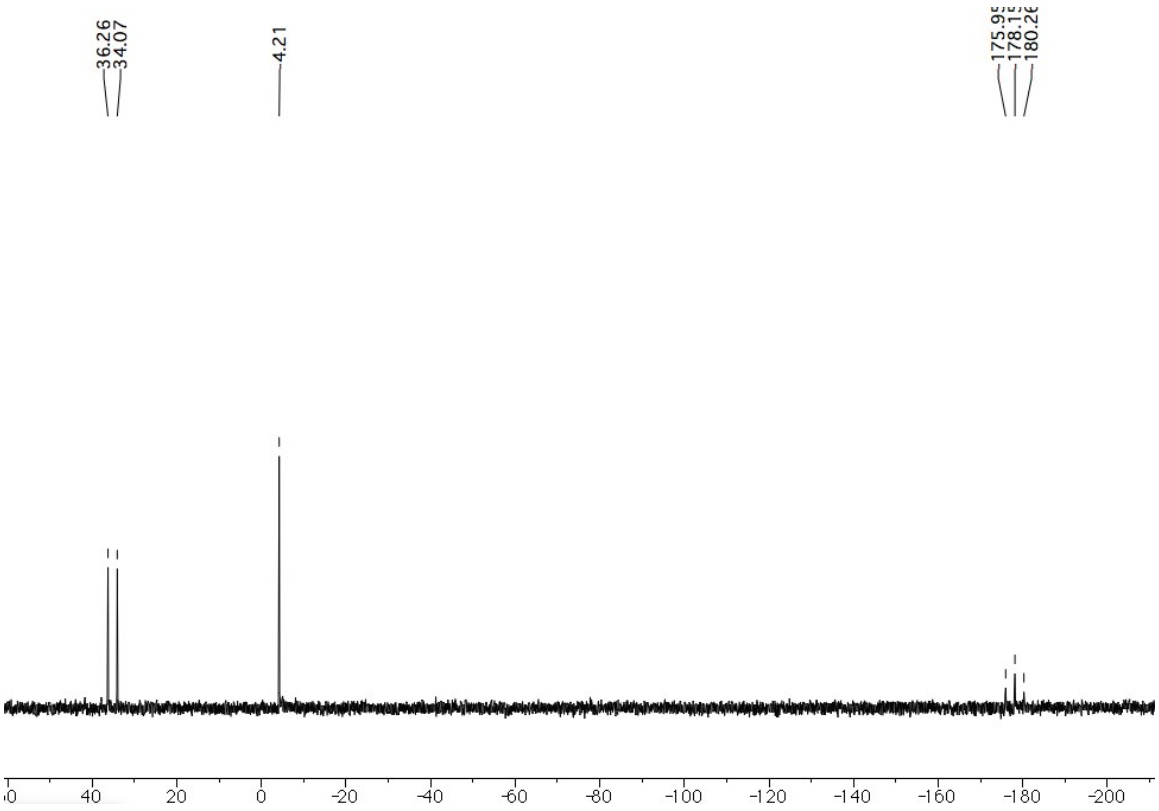


Fig. 8 ^{31}P {^{1}H} NMR of the reaction with 1 eq. HOTf

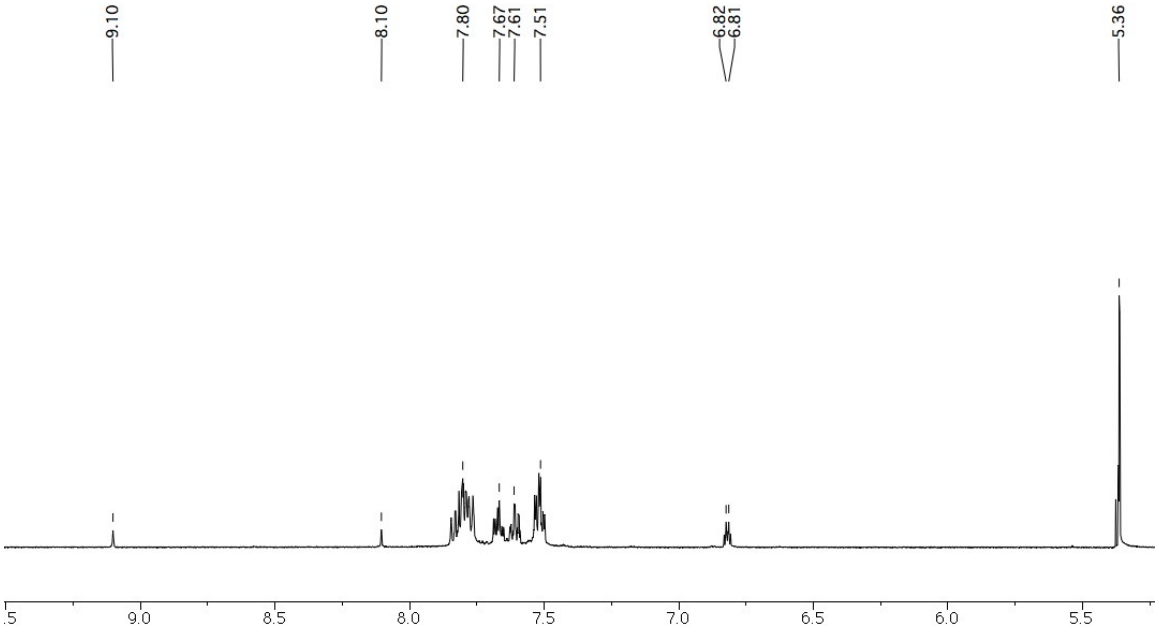


Fig. 9 ^{1}H NMR of the reaction with 1 eq. HOTf

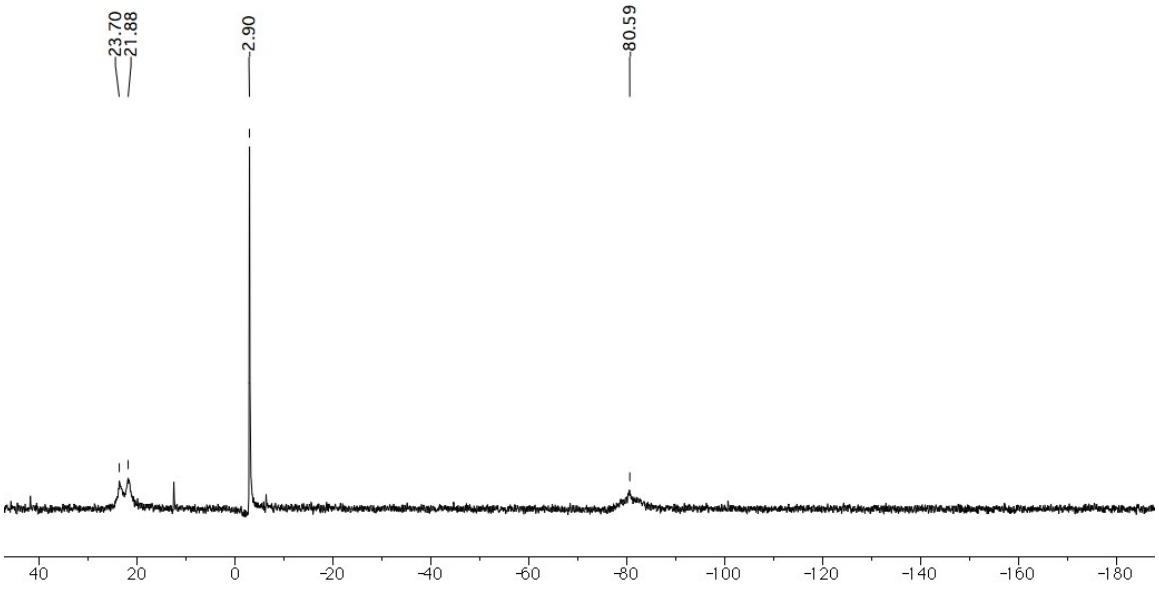


Fig. 10 ^{31}P {^{1}H} NMR of the reaction with 2 eq, HOTf

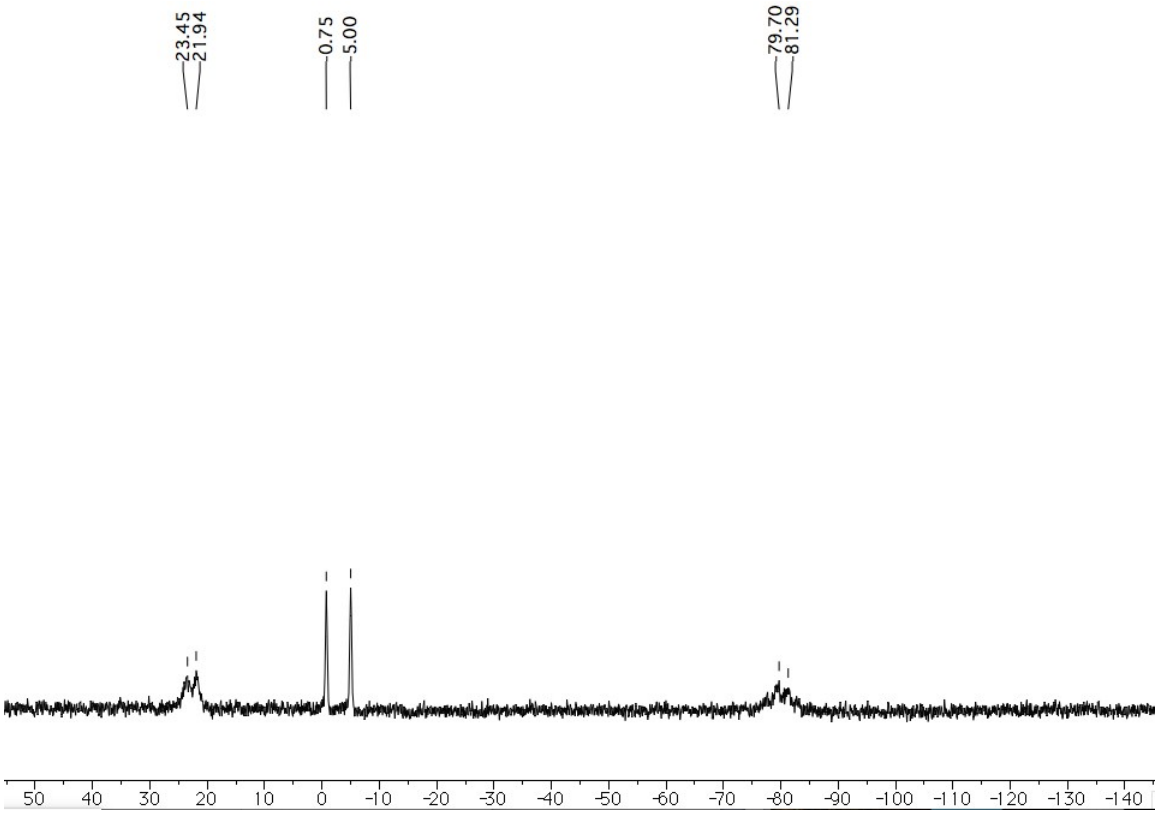


Fig. 11 ^{31}P NMR of the reaction with 2 eq. HOTf

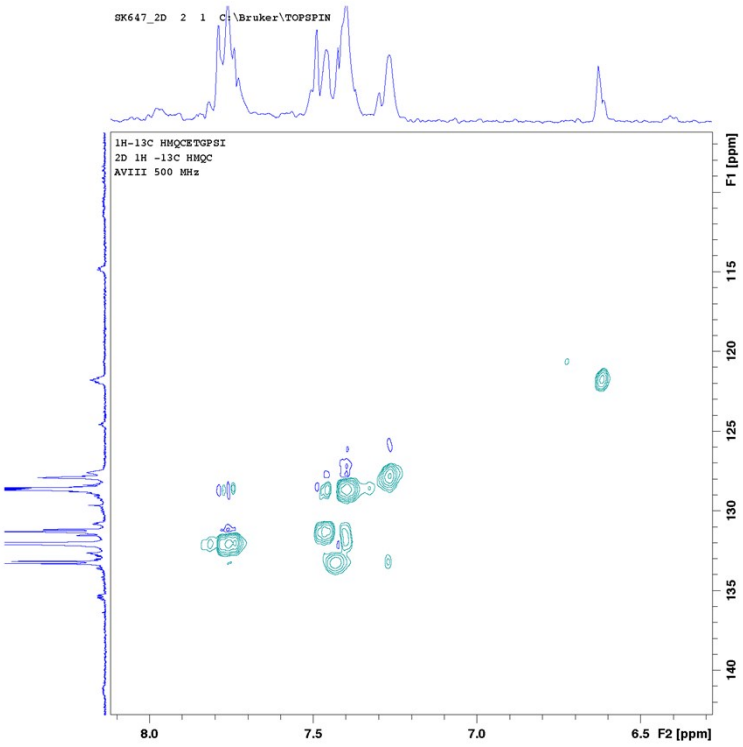


Fig. 12. HMQC of 1.

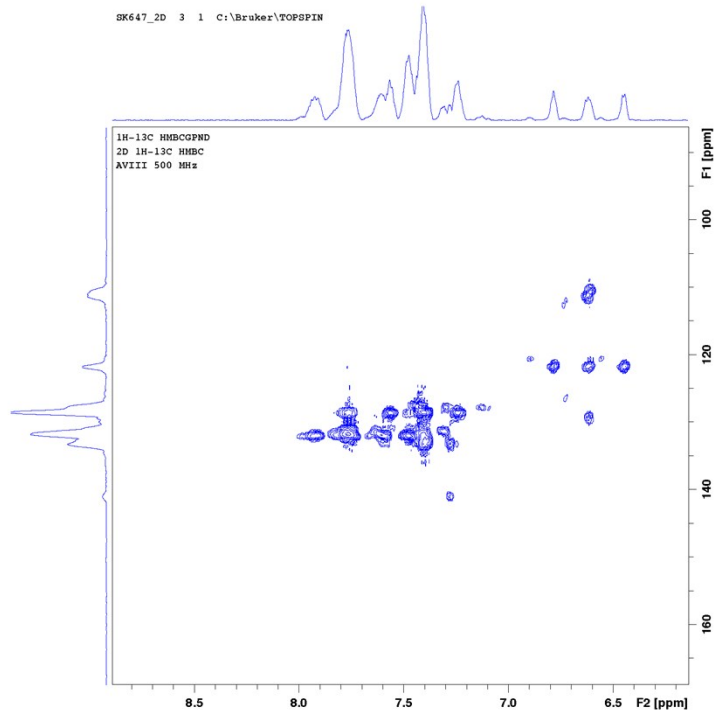


Fig. 13. HMBC of 1.

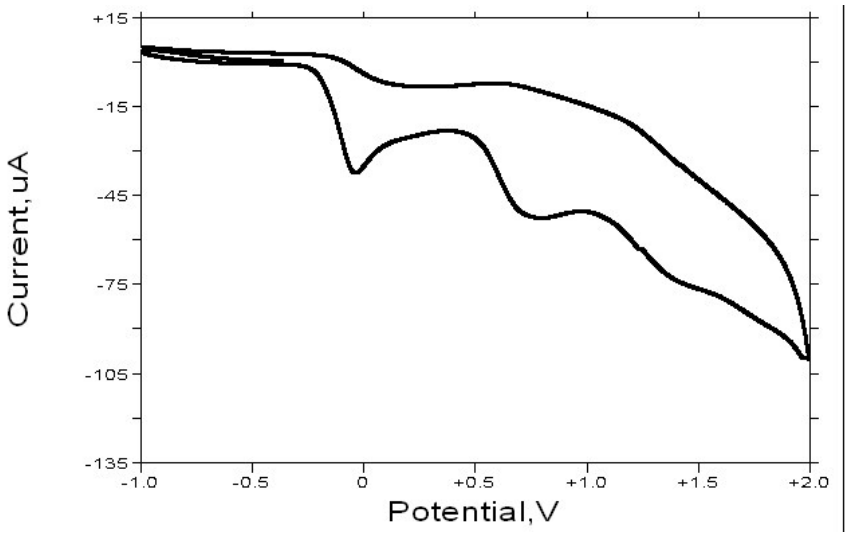


Fig. 14 Cyclic Voltammogram of K^+ $(Ph_2P)_3(C_5H_2)$

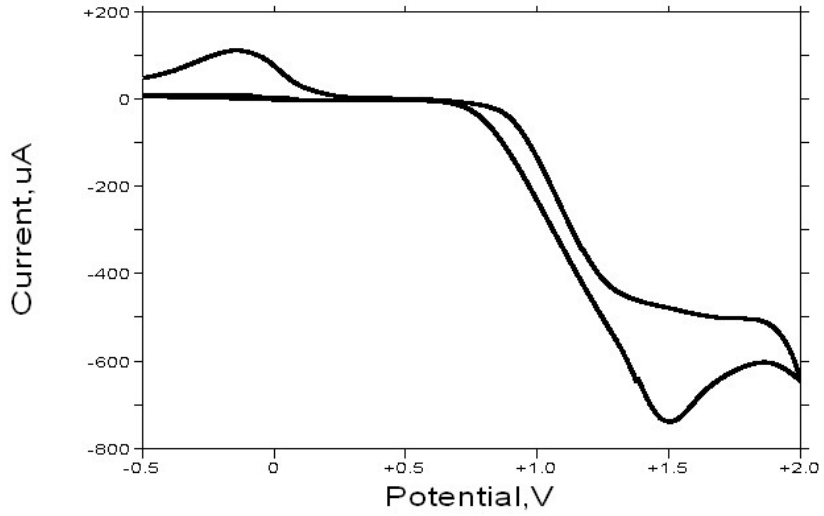
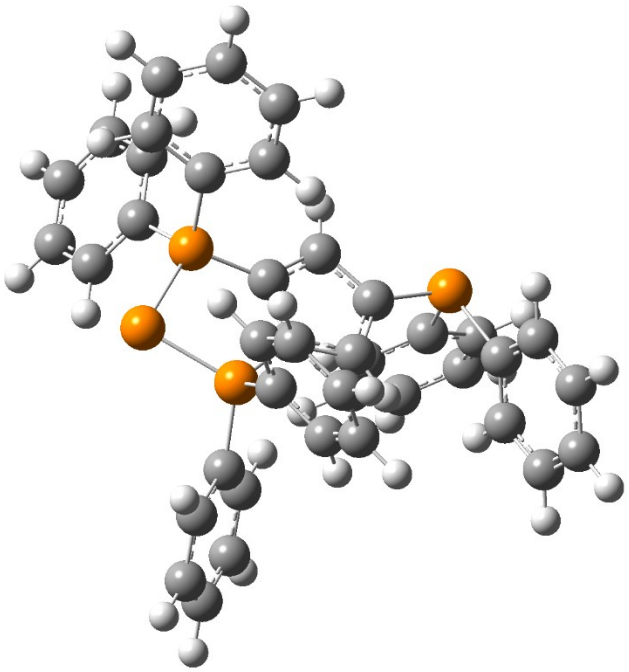


Fig. 15 Cyclic Voltammogram of [dppeP][Br]

Computational Investigations

All of the computational investigations were performed using the **Compute Canada** *Shared Hierarchical Academic Research Computing Network* (SHARCNET) facilities (www.sharcnet.ca) with the Gaussian09[1] program suites. Geometry optimizations have been calculated using density functional theory (DFT), specifically implementing the M062X method[2] _ENREF_60 in conjunction with the TZVP basis set[3] for all atoms. The geometry optimizations were not subjected to any symmetry restrictions and each stationary point was confirmed to be a minimum having zero imaginary vibrational frequencies. Pictures of the optimized structures were prepared using Gaussview 3.0.[4] Population analyses were conducted using the Natural Bond Orbital (NBO)[5] implementation included with the Gaussian package. Plots of molecular orbitals and electrostatic potentials were generated at the M062X/TZVP level of theory and examined using ADF2014.[6-8] Summaries of the optimized structures, including electronic energies and Cartesian components for each of the atoms, are detailed in the sections below.

$P(Ph_2P)_2C_5H_2PPh_2$ model



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Thermal correction to Gibbs Free Energy= 0.530634

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Sum of electronic and thermal Energies= -2946.164010

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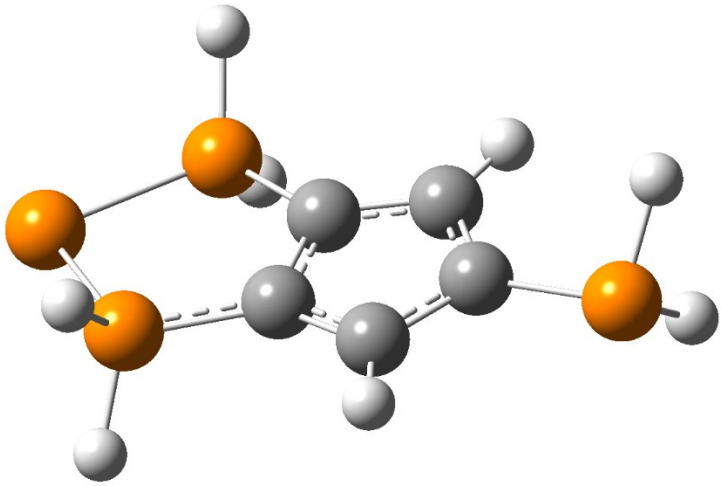
Sum of electronic and thermal Free Energies= -2946.281672

$P(H_2P)_2C_5H_2PH_2$ model



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Sum of electronic and zero-point Energies= -1560.468351

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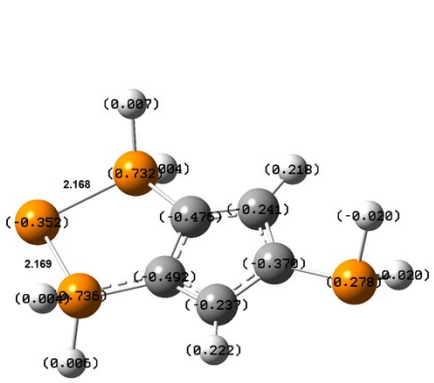
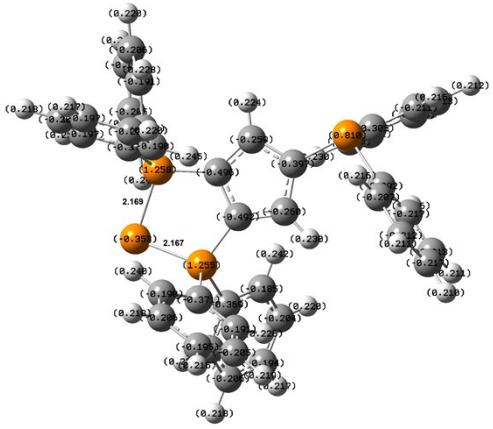
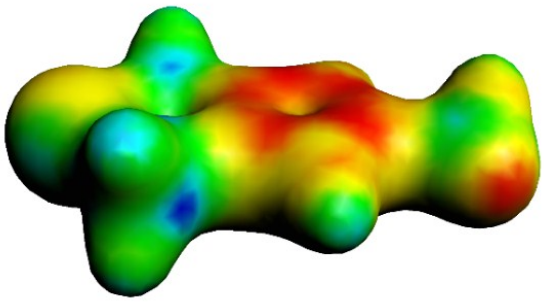


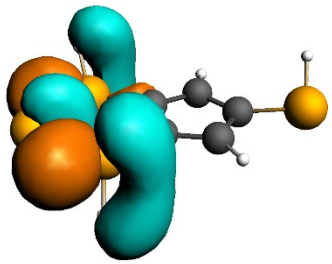


Electrostatic Potential

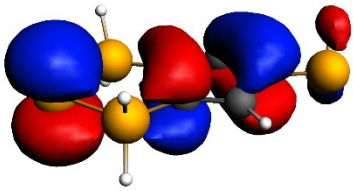


Kohn-Sham Orbitals

LUMO



HOMO



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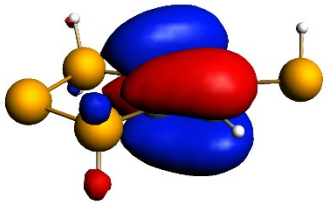

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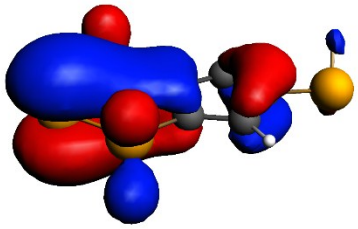

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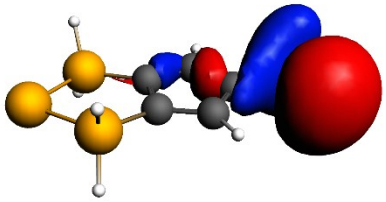

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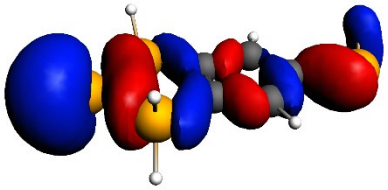
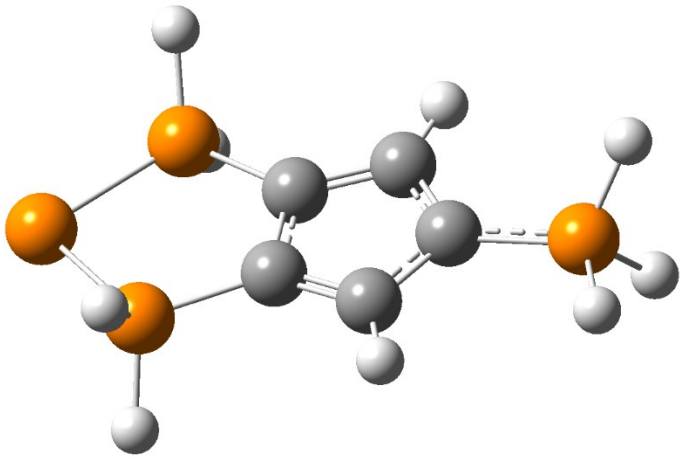


$[P(H_2P)_2C_5H_2PH_3]$ cation model



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256358\P,-3.121587693,0.011415822,-0.0259080124\P,-1.5830488364,-1.512

7250459,-0.0135027377\C,0.0216226326,0.6999370936,-0.0001743816\C,0.01

09748342,-0.7215542511,-0.0111075927\C,1.3327578286,1.1437373135,0.014

3688908\C,1.317511136,-1.1798908434,-0.0032994787\C,2.1354724572,-0.02

28365052,0.0141249713\H,1.6756841979,2.1671454847,0.0263490255\H,1.652

336091,-2.2061713532,-0.0065410549\P,3.8790145956,-0.0763297965,-0.005

5576163\H,-1.6643498393,-2.3949794713,1.0798673745\H,-1.6626676225,-2.

3988175181,-1.1034795348\H,-1.6292526435,2.3818405911,1.1131385951\H,-

1.6265571119,2.4155721535,-1.0699818281\H,4.5070888368,0.6216300765,1.

0380940164\H,4.4953490156,0.4220429705,-1.1649136501\H,4.3158695204,-1

.400726227,0.1064949879\\Version=EM64L-G09RevD.01\State=1-A\HF=-1560.9

414515\RMSD=5.846e-09\RMSF=3.722e-06\Dipole=3.1925595,-0.0579575,0.008

7366\Quadrupole=22.1261559,-2.2623484,-19.8638075,-0.6352519,-0.020189

8,0.1244438\PG=C01 [X(C5H9P4)]\\@

Zero-point correction= 0.121741 (Hartree/Particle)

Thermal correction to Energy= 0.131775

Thermal correction to Enthalpy= 0.132719

Thermal correction to Gibbs Free Energy= 0.084400

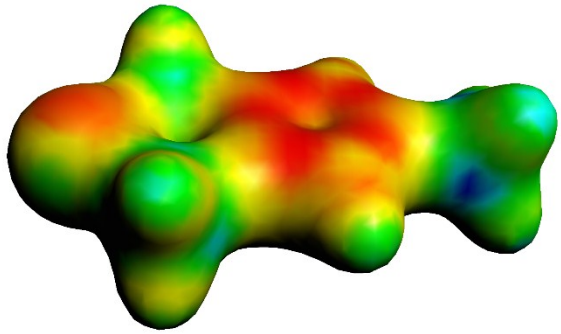
Sum of electronic and zero-point Energies= -1560.819710

Sum of electronic and thermal Energies= -1560.809677

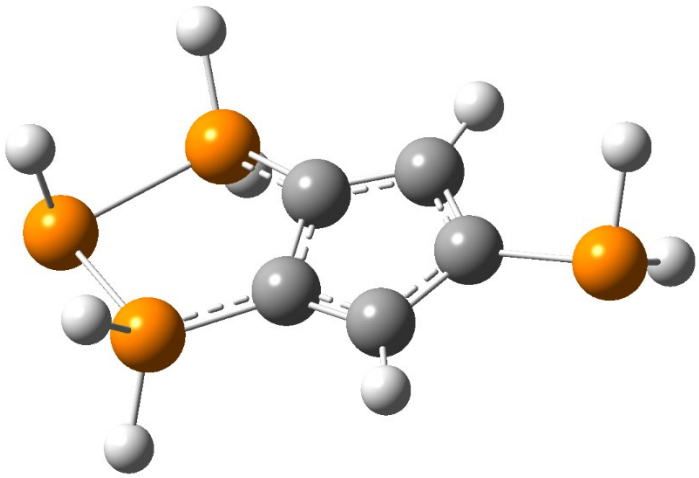
Sum of electronic and thermal Enthalpies= -1560.808733

Sum of electronic and thermal Free Energies= -1560.857052

Electrostatic Potential



[axial-HP(H_2P)$_2C_5H_2PH_2$] cation model



1\1\GINC-SAW130\FOpt\RM062X\TZVP\C5H9P4(1+)\CMACD\28-Sep-2015\0\\# M06

2x/TZVP scf=tight opt=tight freq pop=(full,nbo6read) test\\Optimizatio

n of H[P(Cp(PH2)3)] axial H-P(I) cation\\1,1\P,-1.5146539311,1.5669269

826,-0.0333562831\P,-3.1069997374,0.0022614781,0.0616882689\P,-1.52047

45672,-1.57350062,0.0424785341\C,-0.0119643481,0.7166530924,0.13437640

13\C,-0.0167190719,-0.7162065652,-0.0322123297\C,1.3183207464,1.138392

771,0.1326838228\C,1.3161347935,-1.1370116746,-0.0651912109\C,2.134701

8875,-0.001536079,0.0269993723\H,1.6671855318,2.1582605904,0.199566755

1\H,1.6675381829,-2.1560340696,-0.1371430151\P,3.9757958638,-0.1084302

865,0.009721685\H,-1.768506602,-2.3885154246,1.1661892276\H,-1.8017084

473,-2.4246600111,-1.0397503816\H,-1.8115558562,2.5240452657,0.9535929

177\H,-1.7336410859,2.2598342139,-1.2390459225\H,4.2073515837,0.799504

2412,1.072750458\H,4.1922455112,0.8664220615,-0.997256647\H,-3.1297664

537,0.0411250337,1.4788483473\\Version=EM64L-G09RevD.01\State=1-A\HF=-

1560.9264077\RMSD=5.380e-09\RMSF=1.095e-05\Dipole=-3.6300402,0.3059787

,0.1992868\Quadrupole=6.1550404,5.0750513,-11.2300917,2.8912412,-1.954
2039,-0.1425096\PG=C01 [X(C5H9P4)]\\@

Zero-point correction= 0.119568 (Hartree/Particle)

Thermal correction to Energy= 0.130569

Thermal correction to Enthalpy= 0.131514

Thermal correction to Gibbs Free Energy= 0.079551

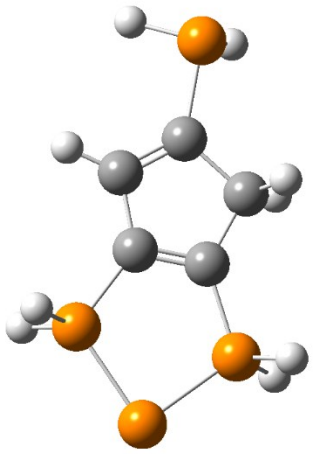
Sum of electronic and zero-point Energies= -1560.806840

Sum of electronic and thermal Energies= -1560.795838

Sum of electronic and thermal Enthalpies= -1560.794894

Sum of electronic and thermal Free Energies= -1560.846856

[$P(H_2P)_2C_5H_3PH_2$] cation model (isomer 1)



1\1\GINC-SAW298\FOpt\RM062X\TZVP\C5H9P4(1+)\CMACD\05-Oct-2015\0\\#M06

2x/TZVP scf=tight opt=tight freq pop=(full,nbo6read) test\\Optimizatio

n of H[P(Cp(PH2)3)] axial H-Cp 1 cation\\1,1\P,-1.6573767634,1.4964453

423,0.0826449333\P,-3.1963932504,-0.012038042,-0.0854294412\P,-1.61487

75328,-1.4911837593,-0.1446451613\C,-0.0418629671,0.6829551371,0.10433

66645\C,-0.0357583888,-0.6608403619,0.011124922\C,1.3155357884,1.19970

82333,0.1912295297\C,1.3871309557,-1.1343844416,0.0371747532\C,2.16999

33962,0.1540032175,0.1424048273\H,1.5782739816,2.2442141558,0.27503378

33\H,1.6529966931,-1.6982419399,-0.8630935111\P,3.9870403022,0.1613416

336,0.3922898022\H,-1.6936712611,-2.4694233193,0.8634701338\H,-1.57431

0623,-2.2727346498,-1.3148615593\H,-1.7248901712,2.3015035693,1.234275

9465\H,-1.6148793866,2.4488646072,-0.9524899108\H,4.1874502519,1.49608

78269,-0.0316028514\H,4.3119686938,-0.4230914997,-0.8571139358\H,1.586

3890414,-1.7860895693,0.894298415\\Version=EM64L-G09RevD.01\State=1-A\

HF=-1560.9508734\RMSD=4.873e-09\RMSF=4.770e-06\Dipole=-0.3932632,-0.08

8672,-0.3122051\Quadrupole=4.0761962,7.4207321,-11.4969283,0.3395187,-

1.8775741,1.7538689\PG=C01 [X(C5H9P4)]\\@

Zero-point correction= 0.122695 (Hartree/Particle)

Thermal correction to Energy= 0.133552

Thermal correction to Enthalpy= 0.134497

Thermal correction to Gibbs Free Energy= 0.083735

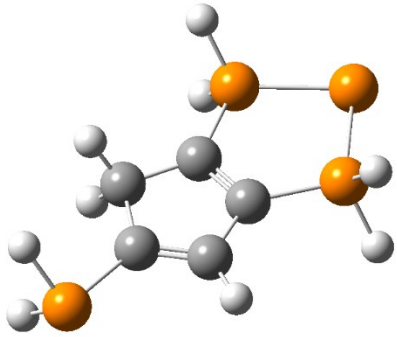
Sum of electronic and zero-point Energies= -1560.828178

Sum of electronic and thermal Energies= -1560.817321

Sum of electronic and thermal Enthalpies= -1560.816377

Sum of electronic and thermal Free Energies= -1560.867139

[$P(H_2P)_2C_5H_3PH_2$] cation model (isomer 2)



1\1\GINC-SAW125\FOpt\RM062X\TZVP\C5H9P4(1+)\CMACD\05-Oct-2015\0\\#M06

2x/TZVP scf=tight opt=tight freq pop=(full,nbo6read) test\\Optimizatio

n of H[P(Cp(PH2)3)] axial H-Cp 2 cation\\1,1\P,-1.6570074937,1.4941585

307,0.00099662\P,-3.1975829368,-0.0276299867,-0.0160552714\P,-1.616929

5979,-1.5030626743,-0.0037773246\C,-0.0484931906,0.6966021164,0.000201

9572\C,-0.0227919317,-0.6493252539,-0.0006559181\C,1.3617962983,1.2064

084297,0.0079674713\C,1.3555312493,-1.1304640877,0.0071636609\C,2.1780

165092,-0.0624572162,0.0118611488\H,1.5758518137,1.8208606092,0.888903

9561\H,1.6550865111,-2.1689990719,0.009743349\P,4.0218827755,-0.189836

9816,0.0229888283\H,-1.6085268561,-2.3799562481,1.0966480876\H,-1.6040

987332,-2.3864634878,-1.0986011947\H,-1.6956726498,2.3690925604,1.1027

322026\H,-1.6928407511,2.3838540544,-1.0885285003\H,4.2165457295,0.805

2480461,1.0164175336\H,4.2236637915,0.7185445484,-1.0480172262\H,1.585

7500728,1.821047163,-0.8703415401\\Version=EM64L-G09RevD.01\State=1-A\

HF=-1560.9501681\RMSD=8.025e-09\RMSF=4.721e-06\Dipole=-0.6536597,0.465

3677,-0.0076242\Quadrupole=2.7243097,6.9712329,-9.6955426,3.4817233,-0

.0855672,0.0880039\PG=C01 [X(C5H9P4)]\\@

Zero-point correction= 0.122571 (Hartree/Particle)

Thermal correction to Energy= 0.132571

Thermal correction to Enthalpy= 0.133516

Thermal correction to Gibbs Free Energy= 0.086432

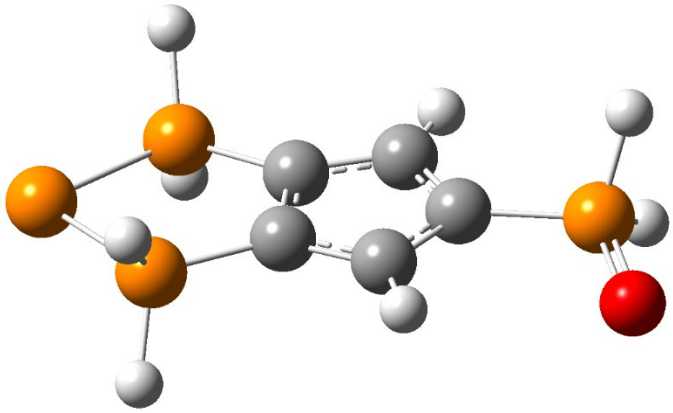
Sum of electronic and zero-point Energies= -1560.827597

Sum of electronic and thermal Energies= -1560.817597

Sum of electronic and thermal Enthalpies= -1560.816652

Sum of electronic and thermal Free Energies= -1560.863736

$P(H_2P)_2C_5H_2P(O)H_2$ model



1\1\GINC-SAW38\FOpt\RM062X\TZVP\C5H8O1P4\CMACD\30-Sep-2015\0\\#M062x/

TZVP scf=tight opt freq pop=(full,nbo6read) test\\Optimization of [P(C

p(PH2)3)O] oxide zwitterion\\0,1\P,1.5720136101,-1.5047476679,0.103060

528\P,3.1317816474,-0.0065309858,-0.0499954657\P,1.5762892135,1.500368

8889,-0.1054719111\C,0.0022106159,-0.7092817966,0.0531139729\C,0.00292

66588,0.7095650747,-0.0874680846\C,-1.3204513485,-1.1413393489,0.12583

38262\C,-1.3195864067,1.149742013,-0.08344668\C,-2.1289210931,0.004410

8995,0.0401119461\H,-1.686207871,-2.1504952751,0.2405345903\H,-1.65786

86266,2.1729317904,-0.158336008\P,-3.9148003993,-0.093450795,0.0645168

973\H,1.6827302546,2.4332720273,0.945775461\H,1.7100764991,2.351730036

1,-1.2207462352\H,1.694610671,-2.3028324272,1.257354524\H,1.6860018958

,-2.483180993,-0.9045503797\H,-4.33042071,0.2666507784,-1.2399262146\H

,-4.3114878385,1.0612254417,0.7851694933\O,-4.4694475226,-1.4004853306

,0.5509437199\\Version=EM64L-G09RevD.01\State=1-A\HF=-1635.8169409\RMS

D=4.185e-09\RMSF=9.538e-06\Dipole=2.2067803,1.2804909,-0.4572542\Quadr upole=-12.567451,11.939073,0.628378,-11.048655,4.2320712,0.5000082\PG= C01 [X(C5H8O1P4)]\\@

Zero-point correction= 0.116179 (Hartree/Particle)

Thermal correction to Energy= 0.127604

Thermal correction to Enthalpy= 0.128549

Thermal correction to Gibbs Free Energy= 0.076062

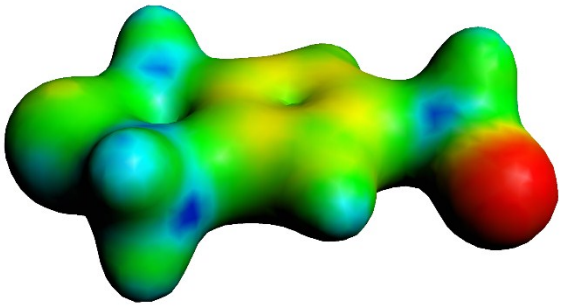
Sum of electronic and zero-point Energies= -1635.700762

Sum of electronic and thermal Energies= -1635.689337

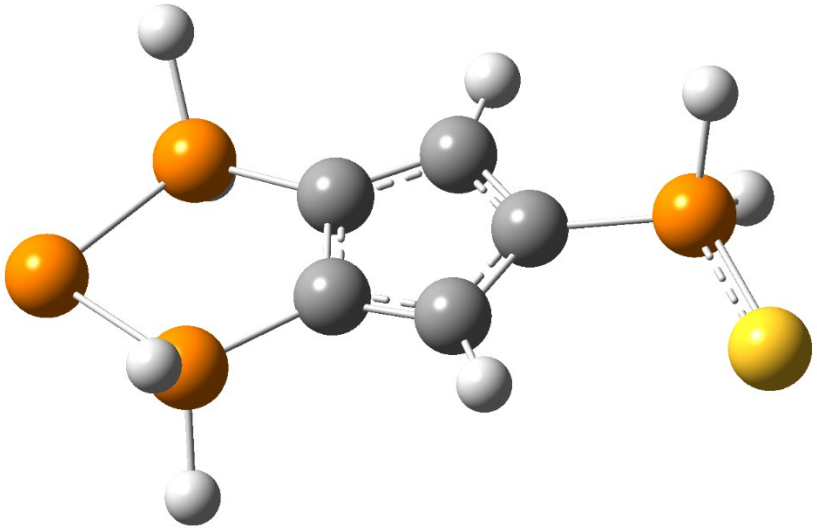
Sum of electronic and thermal Enthalpies= -1635.688392

Sum of electronic and thermal Free Energies= -1635.740879

Electrostatic Potential



$P(H_2P)_2C_5H_2P(S)H_2$ model



1\1\GINC-SAW52\FOpt\RM062X\TZVP\C5H8P4S1\CMACD\30-Sep-2015\0\\#
M062x/

TZVP scf=tight opt freq pop=(full,nbo6read) test\\Optimization of [P(C

p(PH2)3)S] sulfide zwitterion\\0,1\P,1.5764938673,-1.5020115536,0.1316

096122\P,3.1324709796,-0.0114940303,-0.1004414587\P,1.5784696998,1.495

6349919,-0.1624992807\C,0.0063158026,-0.7091279407,0.0668513195\C,0.00

45823378,0.7047759739,-0.1108887661\C,-1.3144740919,-1.141255903,0.167

0157396\C,-1.3172322476,1.1444205685,-0.1058608492\C,-2.1228016975,0.0

007889146,0.0590120512\H,-1.6800331925,-2.1475152259,0.3073561126\H,-1

.659412196,2.1636358432,-0.2085464594\P,-3.9164738804,-0.0502483411,0.

1048271364\H,1.6929408171,2.4491228402,0.8690824953\H,1.6991658592,2.3

238493521,-1.2953455365\H,1.7107169696,-2.2532645535,1.3157200683\H,1.

6817100549,-2.5188429131,-0.8380555896\H,-4.3227595396,0.4368176413,-1

.1576896988\H,-4.2594625138,1.05839169,0.9124212715\S,-4.7255017386,-1

.7641574243,0.6204824224\\Version=EM64L-G09RevD.01\State=1-A\HF=-1958.

7800991\RMSD=5.164e-09\RMSF=2.314e-06\Dipole=2.400365,1.396644,-0.3982

164\Quadrupole=-12.3586199,12.3594267,-0.0008068,-10.3448633,3.4019045

,-0.478375\PG=C01 [X(C5H8P4S1)]\\@

Zero-point correction= 0.114515 (Hartree/Particle)

Thermal correction to Energy= 0.126205

Thermal correction to Enthalpy= 0.127149

Thermal correction to Gibbs Free Energy= 0.073787

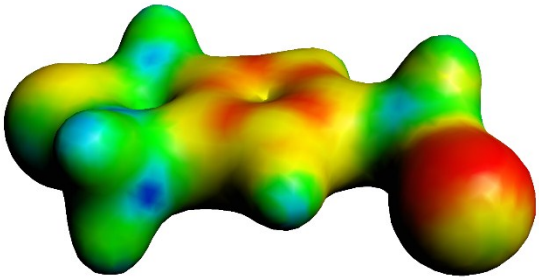
Sum of electronic and zero-point Energies= -1958.665584

Sum of electronic and thermal Energies= -1958.653894

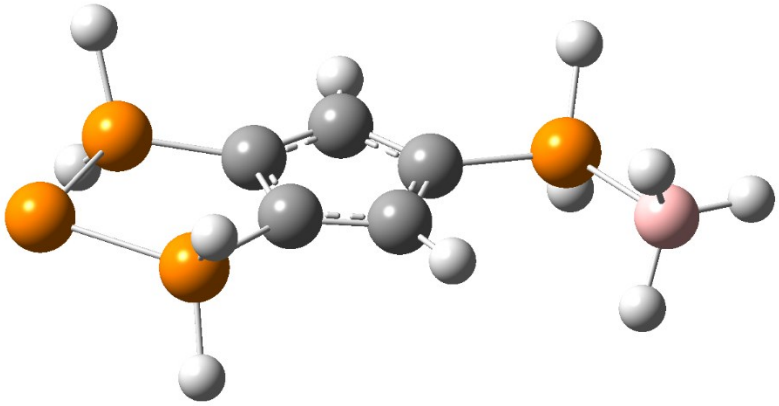
Sum of electronic and thermal Enthalpies= -1958.652950

Sum of electronic and thermal Free Energies= -1958.706312

Electrostatic Potential



$P(H_2P)_2C_5H_2P(BH_3)H_2$ model



1\1\GINC-SAW76\FOpt\RM062X\TZVP\C5H11B1P4\CMACD\30-Sep-2015\0\\#M062x

/TZVP scf=tight opt freq pop=(full,nbo6read) test\\Optimization of [P(

Cp(PH2)3)BH3] borane adduct zwitterion\\0,1\P,-0.0211255995,0.12430273

87,0.4347055102\P,2.0702603814,-0.0380793259,-0.1122550652\P,2.0650764

141,2.0966615462,-0.4808350585\C,-0.530370996,1.8008101381,0.269931576

6\C,0.4678846058,2.7432503936,-0.1142284433\C,-1.7251060657,2.48809483

41,0.4724690705\C,-0.118436908,4.0052449421,-0.1668561758\C,-1.4687266

254,3.8436419943,0.2000435927\H,-2.678809156,2.0828192119,0.7760568946

\H,0.3655841599,4.9323729669,-0.4355964379\P,-2.7464902002,5.098909739

9,0.3315368994\H,3.0641773204,2.7672371613,0.25203319\H,2.4517080017,2

.4171162464,-1.7973922662\H,-0.2703647977,-0.3612128791,1.7342941172\H

,-0.8414315942,-0.7309140211,-0.3262561327\H,-2.674939242,5.8086795438

,-0.8835869426\H,-2.2064258421,6.0759135192,1.193186138\B,-4.512184159

1,4.4428114144,0.8158443096\H,-4.7863990062,3.673357371,-0.0713462881\

H,-5.2058769383,5.4260820304,0.8521159943\H,-4.3393857028,3.9188452539

,1.8885709372\\Version=EM64L-G09RevD.01\State=1-A\HF=-1587.2218363\RMS

D=8.775e-09\RMSF=4.610e-06\Dipole=2.6297648,-0.6822138,-0.5201269\Quad

rupole=-13.0313784,10.6719963,2.359382,12.3324354,1.2010692,-4.5052192

\PG=C01 [X(C5H11B1P4)]\\@

Zero-point correction= 0.142949 (Hartree/Particle)

Thermal correction to Energy= 0.155733

Thermal correction to Enthalpy= 0.156678

Thermal correction to Gibbs Free Energy= 0.101559

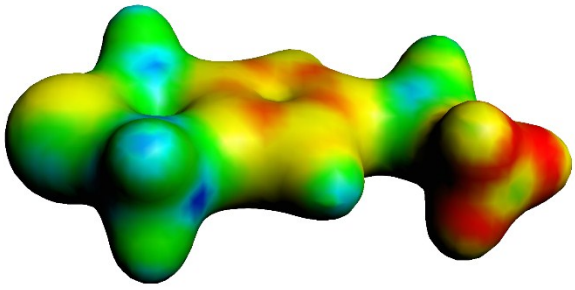
Sum of electronic and zero-point Energies= -1587.078887

Sum of electronic and thermal Energies= -1587.066103

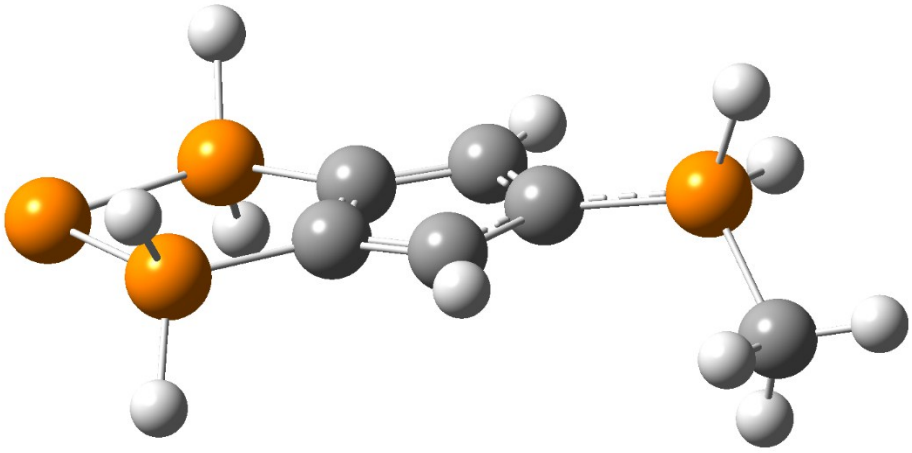
Sum of electronic and thermal Enthalpies= -1587.065159

Sum of electronic and thermal Free Energies= -1587.120277

Electrostatic Potential



$P(H_2P)_2C_5H_2P(CH_3)H_2$ model



1\1\GINC-SAW215\FOpt\RM062X\TZVP\C6H11P4(1+)\CMACD\01-Oct-2015\0\\# M0

62x/TZVP scf=tight opt freq pop=(full,nbo6read) test\\Optimization of

[P(Cp(PH2)3)CH3] methylated cation\\1,1\P,-0.01099758,0.0292929103,0.0

880868764\P,2.1487051881,0.0235622883,-0.0553030857\P,2.1001565343,2.1

877296921,-0.0654592066\C,-0.5884300879,1.7128545837,0.0417863298\C,0.

405201168,2.726724817,-0.0352484907\C,-1.8386535938,2.3096255362,0.078

9630601\C,-0.218377563,3.9642974018,-0.0462433502\C,-1.6077217749,3.70

52986701,0.0261019359\H,-2.7948416795,1.8112959057,0.1332698907\H,0.25

37406718,4.9339377646,-0.0962993542\P,-2.8429198941,4.9421547655,-0.00

68760705\H,2.7959242928,2.7812479117,1.0050693195\H,2.7543797222,2.749

9434526,-1.1782817118\H,-0.5116106568,-0.5998592542,1.2429037083\H,-0.

6365101888,-0.7099043002,-0.9330517734\H,-3.50012133,5.0679713626,-1.2

430847931\H,-2.2274614008,6.186572351,0.1798666135\C,-4.1390556854,4.7

352127724,1.2387497866\H,-4.6250649249,3.7726961205,1.0829103538\H,-4.

8751211034,5.5328631972,1.1476958046\H,-3.6826020638,4.7524268709,2.22

68795767\\Version=EM64L-G09RevD.01\State=1-A\HF=-1600.2700727\RMSD=5.4

34e-09\RMSF=6.047e-06\Dipole=-2.186539,2.0032121,0.1910243\Quadrupole=

11.7375502,7.5869848,-19.324535,-12.0985067,-2.7982975,0.525314\PG=C01

[X(C6H11P4)]\\@

Zero-point correction= 0.150971 (Hartree/Particle)

Thermal correction to Energy= 0.162374

Thermal correction to Enthalpy= 0.163318

Thermal correction to Gibbs Free Energy= 0.112023

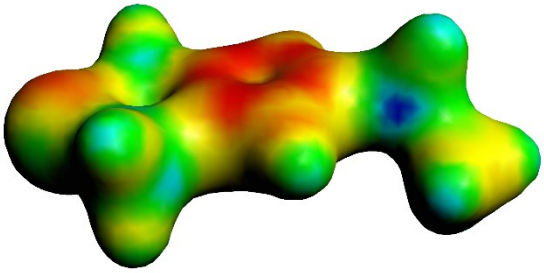
Sum of electronic and zero-point Energies= -1600.119102

Sum of electronic and thermal Energies= -1600.107699

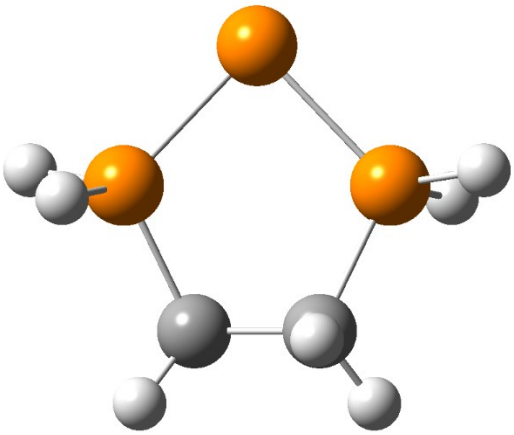
Sum of electronic and thermal Enthalpies= -1600.106754

Sum of electronic and thermal Free Energies= -1600.158049

Electrostatic Potential



[P($H_2PCH_2CH_2PH_2$)] cation model



1\1\GINC-SAW79\FOpt\RM062X\TZVP\C2H8P3(1+)\CMACD\02-Jun-2015\0\\#M062

x/TZVP scf=tight opt freq pop=(full,nbo6read) test\\Optimization of [P

(dHpe)] cation\\1,1\P,0.0000417394,-2.6793916749,-0.0001176252\P,1.398

1617574,-1.1226426049,-0.5163736556\P,-1.3980511753,-1.122671065,0.516

3085372\C,0.5308135091,0.5020920684,-0.5486435446\C,-0.530715773,0.502

0731751,0.5486045091\H,-1.2494406531,1.3100975502,0.4108666387\H,-0.08

26574128,0.6001755001,1.538378314\H,0.0827546957,0.6002057584,-1.53841

58681\H,1.2495276798,1.3101230931,-0.4108878402\H,-2.0044590682,-1.291

6926864,1.7724753102\H,-2.5052707011,-0.9807451649,-0.3423063083\H,2.5

053339555,-0.9807338347,0.3423073979\H,2.0046369368,-1.2916171942,-1.7

725127252\\Version=EM64L-G09RevD.01\State=1-A\HF=-1104.7489336\RMSD=3.

672e-09\RMSF=2.864e-05\Dipole=0.0000085,1.3694838,0.0000623\Quadrupole

=5.7988971,-2.434916,-3.3639811,0.0001105,-4.5007131,0.0000522\PG=C01

[X(C2H8P3)]\\@

Zero-point correction= 0.098120 (Hartree/Particle)

Thermal correction to Energy= 0.103877

Thermal correction to Enthalpy= 0.104822

Thermal correction to Gibbs Free Energy= 0.068202

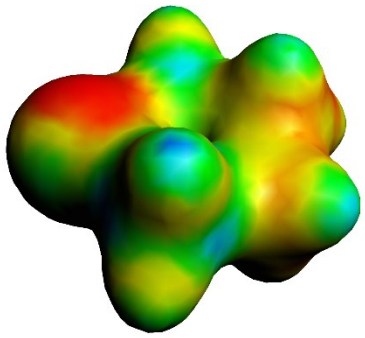
Sum of electronic and zero-point Energies= -1104.650813

Sum of electronic and thermal Energies= -1104.645056

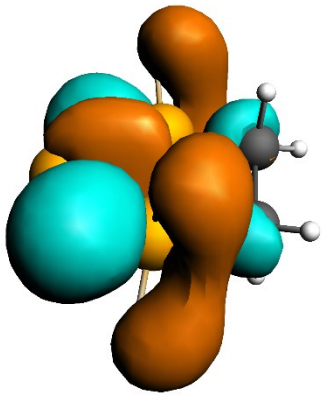
Sum of electronic and thermal Enthalpies= -1104.644112

Sum of electronic and thermal Free Energies= -1104.680731

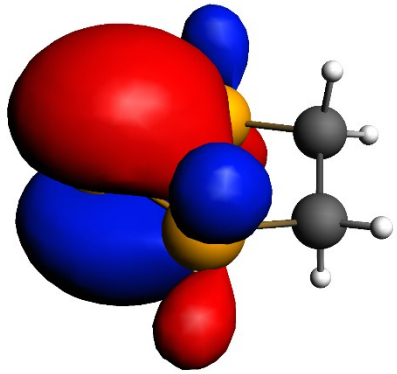
Electrostatic Potential



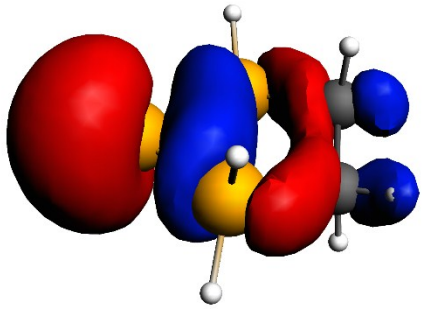
LUMO



HOMO



HOMO-1



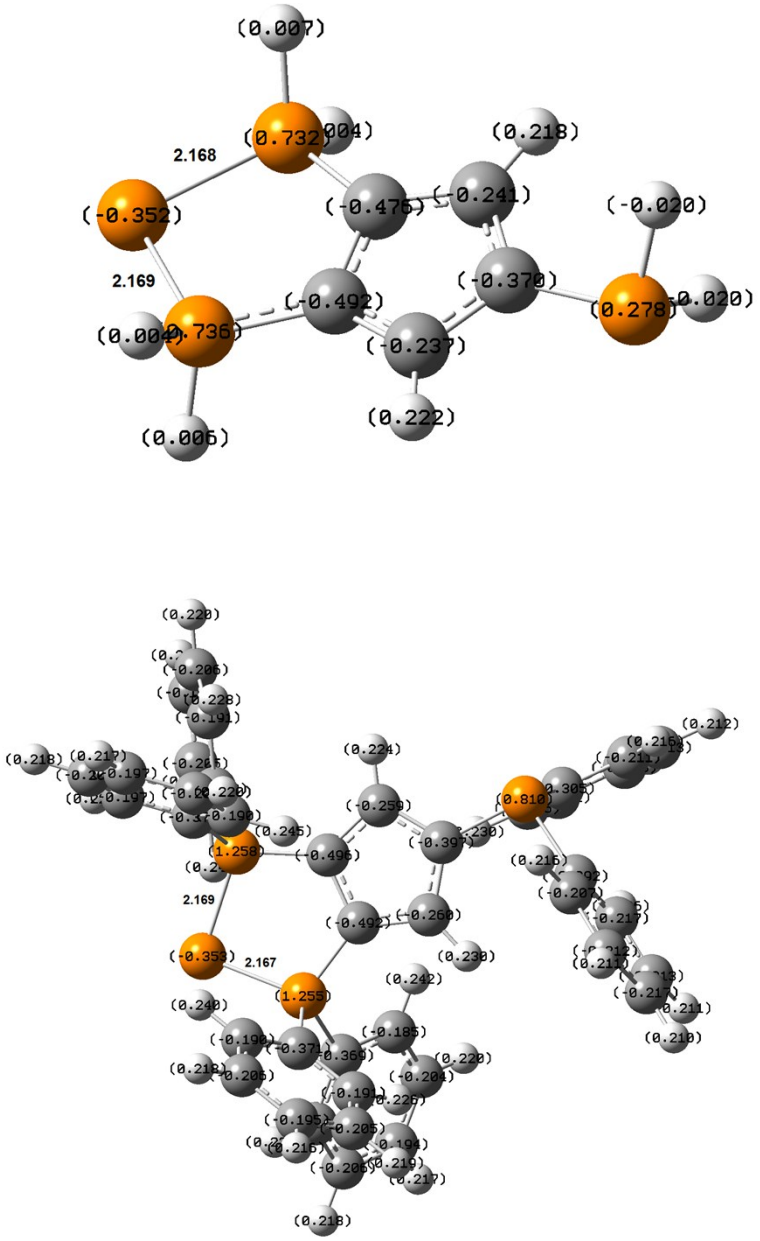


Fig. 16 NBO Charges and selected bond lengths of 1' (above) and 1 (below)

References

1. M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. Montgomery, J. A., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S.

S. Iyengar, J. Tomasi, M. Cossi, N. Rega, N. J. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian09, Revision D01*, (2009) Gaussian, Inc., Wallingford CT.

2. Y. Zhao and D. G. Truhlar, *Theor. Chem. Acc.*, 2008, **120**, 215-241.
3. A. Schafer, C. Huber and R. Ahlrichs, *J. Chem. Phys.*, 1994, **100**, 5829-5835.
4. *Gaussview 3.0*, (2003) Gaussian Inc., Pittsburgh, PA.
5. A. E. Reed, L. A. Curtiss and F. Weinhold, *Chem. Rev.*, 1988, **88**, 899-926.
6. G. te Velde, F. M. Bickelhaupt, E. J. Baerends, C. F. Guerra, S. J. A. Van Gisbergen, J. G. Snijders and T. Ziegler, *J. Comput. Chem.*, 2001, **22**, 931-967.
7. C. F. Guerra, J. G. Snijders, G. te Velde and E. J. Baerends, *Theor. Chem. Acc.*, 1998, **99**, 391-403.
8. *ADF 2014*, (2014) SCM, Theoretical Chemistry, Vrije Universiteit, Amsterdam, The Netherlands.