Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Diazaphospholenes as Reducing Agents: A Thermodynamic and Electrochemical DFT Study

Mohammed F. Alkhater,[1,2] Abdulaziz W. Alherz,[2] Charles B. Musgrave* [2,3,4,5]

[1]Chemical Engineering Department, King Fahd University of Petroleum and Minerals, Dhahran 31261, Saudi Arabia

[2]Department of Chemical and Biological Engineering, University of Colorado Boulder, Boulder, Colorado, United States

[3]Materials Science and Engineering Program, University of Colorado Boulder, Boulder, Colorado, United States

[4]Renewable and Sustainable Energy Institute, University of Colorado Boulder, Boulder, Colorado, United States

[5]Department of Chemistry, University of Colorado Boulder, Boulder, Colorado, United States

Contents

1. Reduction Potential Calculations:

Reduction potentials are calculated using the following equation:

$$E^0 = G_{X+} - G_{X^\bullet} - E^0_{ref} \quad (1)$$

where E^0_{ref} is the absolute redox potential of the reference electrode (4.988 V for Fc^+/Fc in acetonitrile)[1] and both G_{X+} and $G_{X^\bullet}$ are in eV. In the main article, we report vertical reduction potentials where $G_{X^\bullet}$ is calculated using a single-point energy calculation at the geometry of X^+. Reduction potentials can also be calculated adiabatically where $G_{X^\bullet}$ is calculated at the relaxed structure. **Figure S1** shows the discrepancy between the two methods, which corresponds to the reorganization energy associated with the electron transfer.

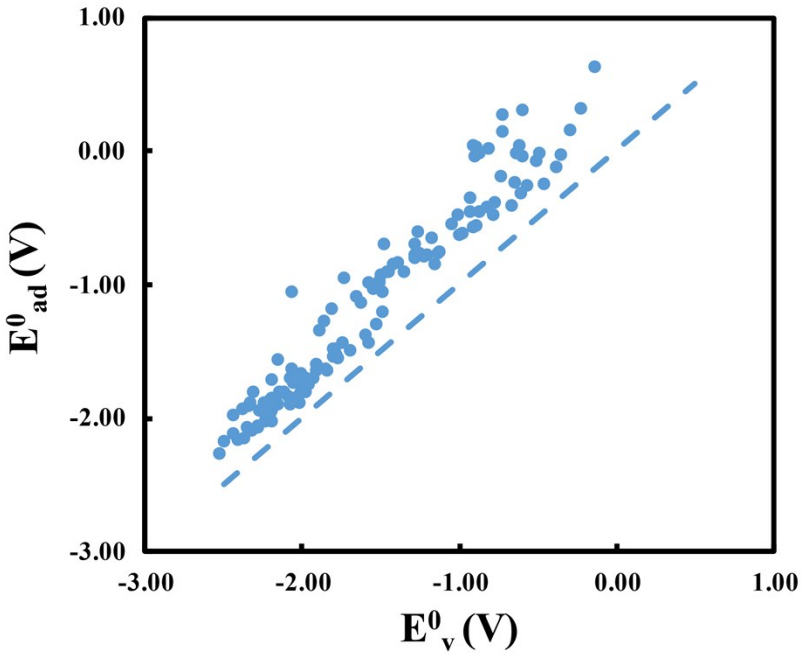


Figure S1: Adiabatic vs. vertical reduction potentials for diazaphospholenes in acetonitrile. The dashed line indicates perfect agreement between adiabatic and vertical reduction potentials where the reorganization energy associated with the reduction step is zero.

2. Solvation Model:

In this work, we report thermodynamic and electrochemical properties based on computed free energies in acetonitrile using the SMD solvation model.[2] This choice is based on examining several solvation models and benchmarking them against available experimental data.[3] We observe a significant deviation in hydricities, pK_a values and reduction potentials due to changing the solvation model. **Figure S2** compares SMD and CPCM models and demonstrates a deviation of up to 10 kcal/mol in hydricity, 7 in pK_a and 0.4 V in reduction potential. These deviations are significant and far beyond the DFT error limit. Although the CPCM model is commonly used in calculating solvation effects, the more advanced SMD model performed better in our comparison study as it has a more accurate cavity parametrization that can significantly shift solvation energies, especially for charged species.[4]

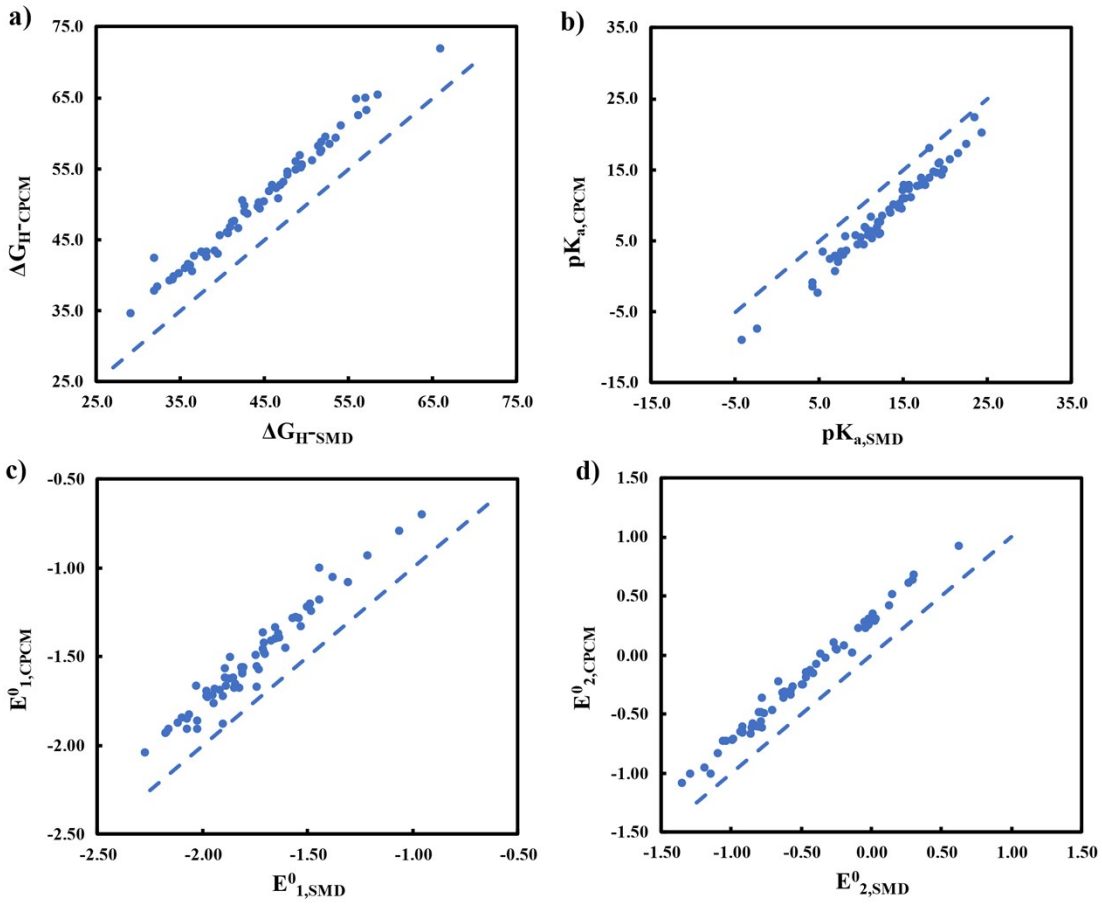


Figure S2: Comparison of CPCM vs. SMD solvation models for calculating: a) hydricities [kcal/mol], b) pKa values, c) 1st reduction potentials E_1^0 [V] (vs. Fc^+/Fc), and d) 2nd reduction potentials E_2^0 [V] (vs. Fc^+/Fc) of PBHs in acetonitrile. The dashed lines corresponds to perfect agreement between the two models.[5-6]

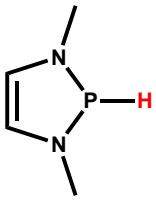
3. Level of Theory:

In this study, the M06 exchange correlation functional is implemented in combination with the 6-31+G(d,p) basis set. This level of theory is found to accurately describe organic molecular hydrides. **Table S1** compares the properties calculated with the M06 functional to the B3LYP and range-separated functionals, CAM-B3LYP and wB97XD and shows the effect of basis set choice in describing the thermodynamics of PBHs. We note that deviations from M06/6-31+G(d,p) are almost within DFT error. While adding diffuse functions to hydrogen atoms did not change the results, expanding to triple-zeta basis sets led to a slight overestimation of hydricities, BDFEs and reduction potentials. These benchmarking results show that the M06/6-31+G(d,p) level of theory provides an accurate description of PBHs with a reasonable computation cost. Furthermore, the M06/6-31+G(d,p) computed properties agree closely with the experimental data available for molecule **8**.

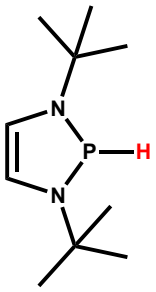
Table S1: Benchmarking of theory level in calculating hydricities [kcal/mol], BDFEs [kcal/mol], pK_a values and reduction potentials [V] of PBHs in acetonitrile. Comparison is based on molecules 1, 2, 7 and 8. Results show that most deviations are within DFT error.

Molecule	Functional	Basis Set	ΔG_{H^-}	BDFE	pK_a	E^0_1
1	M06	6-31+G(d,p)	36.4	61.8	17.2	-2.23
	B3LYP	6-31+G(d,p)	35.6	59.6	17.8	-2.17
	CAM-B3LYP	6-31+G(d,p)	36.1	59.1	16.4	-2.13
	wB97XD	6-31+G(d,p)	37.9	62.1	18.3	-2.18
	M06	6-31++G(d,p)	36.5	61.8	17.2	-2.23
	M06	6-311+G(d,p)	38.6	62.9	16.9	-2.18
	M06	6-311++G(d,p)	38.7	62.9	16.9	-2.18
2	M06	6-31+G(d,p)	34.1	62.3	17.4	-2.35
	B3LYP	6-31+G(d,p)	31.5	59.5	18.8	-2.34
	CAM-B3LYP	6-31+G(d,p)	32.3	59.3	17.4	-2.30
	wB97XD	6-31+G(d,p)	34.5	62.3	19.3	-2.33
	M06	6-31++G(d,p)	34.2	62.4	17.5	-2.35
	M06	6-311+G(d,p)	36.3	63.6	17.0	-2.31
	M06	6-311++G(d,p)	36.3	63.6	17.0	-2.31
7	M06	6-31+G(d,p)	47.3	70.7	8.1	-2.14
	B3LYP	6-31+G(d,p)	45.3	68.7	9.6	-2.14
	CAM-B3LYP	6-31+G(d,p)	45.5	68.6	7.1	-2.13
	wB97XD	6-31+G(d,p)	48.8	72.3	9.3	-2.15
	M06	6-31++G(d,p)	47.6	71.3	8.1	-2.16
	M06	6-311+G(d,p)	49.0	71.4	7.7	-2.10
	M06	6-311++G(d,p)	49.3	72.4	7.7	-2.13
8	M06	6-31+G(d,p)	48.8	79.0	10.6	-2.44
	B3LYP	6-31+G(d,p)	47.7	76.9	12.7	-2.39
	CAM-B3LYP	6-31+G(d,p)	48.0	76.6	10.6	-2.37
	wB97XD	6-31+G(d,p)	50.3	78.8	13.3	-2.36
	M06	6-31++G(d,p)	48.9	78.9	10.7	-2.43
	M06	6-311+G(d,p)	50.3	79.9	10.6	-2.41
	M06	6-311++G(d,p)	50.5	79.9	9.6	-2.40

4. SMD-M06/6-31+G(d,p) optimized structures (Cartesian coordinates):

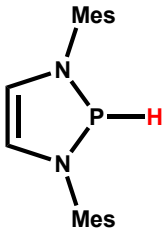


P	0.000001	-1.110077	-0.093688
N	1.228849	0.103098	-0.322322
N	-1.228849	0.103098	-0.322318
C	0.672577	1.350875	0.029751
C	-0.672577	1.350875	0.029752
H	1.328549	2.207199	0.154939
H	-1.328550	2.207198	0.154942
C	2.557847	-0.213008	0.173663
H	2.570966	-0.324496	1.272455
H	3.254705	0.585470	-0.102857
H	2.912278	-1.146528	-0.276431
C	-2.557849	-0.213008	0.173662
H	-2.912280	-1.146527	-0.276436
H	-2.570972	-0.324499	1.272453
H	-3.254704	0.585471	-0.102860
H	0.000003	-1.089910	1.380624



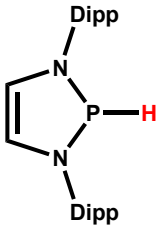
P	0.000000	0.995869	-0.036531
N	-1.228476	-0.211884	-0.310797
N	1.228476	-0.211884	-0.310796
C	-2.659330	0.055660	-0.021987
C	2.659330	0.055659	-0.021987
C	-0.672512	-1.471069	-0.003472
C	0.672512	-1.471070	-0.003471
C	-2.985922	1.482232	-0.447185
C	-2.956009	-0.116634	1.467031
C	-3.511063	-0.907449	-0.842959

C	2.985924	1.482228	-0.447195
C	3.511062	-0.907456	-0.842952
C	2.956008	-0.116622	1.467032
H	-0.000001	0.963675	1.436974
H	2.338805	0.557474	2.075593
H	2.764046	-1.145976	1.795595
H	4.009707	0.112355	1.671456
H	4.062123	1.659404	-0.334065
H	2.717409	1.653048	-1.497607
H	2.466889	2.227103	0.171793
H	3.335680	-1.954100	-0.567324
H	3.301242	-0.791094	-1.913851
H	4.574421	-0.696785	-0.673574
H	1.306861	-2.345529	0.094493
H	-1.306862	-2.345528	0.094491
H	-2.338804	0.557455	2.075598
H	-4.009707	0.112345	1.671456
H	-2.764051	-1.145991	1.795583
H	-3.301237	-0.791084	-1.913857
H	-3.335686	-1.954095	-0.567335
H	-4.574421	-0.696774	-0.673585
H	-2.717398	1.653062	-1.497593
H	-4.062123	1.659405	-0.334063
H	-2.466894	2.227102	0.171815



C	0.677058	0.335461	1.723531
C	-0.667919	0.400541	1.744821
H	1.346704	0.224410	2.571066
H	-1.317338	0.338881	2.612279
N	-1.232799	0.529648	0.457701
N	1.207857	0.396862	0.420575
P	-0.001065	0.947377	-0.691520
H	0.071808	2.369861	-0.374174
C	-2.570789	0.157274	0.155583
C	-3.484868	1.153652	-0.226358
C	-2.969630	-1.187800	0.245188
C	-4.801477	0.785958	-0.508168
C	-4.299734	-1.509849	-0.033576

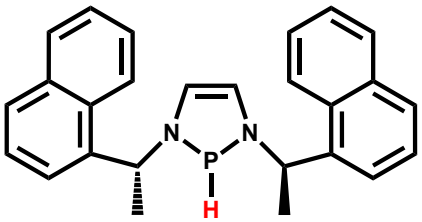
C	-5.229227	-0.540214	-0.415023
H	-5.515207	1.559210	-0.796941
H	-4.614174	-2.552539	0.035914
C	2.562595	0.084812	0.116405
C	3.509104	1.118522	0.037944
C	2.937561	-1.253536	-0.085323
C	4.837263	0.791437	-0.242531
C	4.276148	-1.538156	-0.362636
C	5.239043	-0.529885	-0.448799
H	5.578105	1.590736	-0.296625
H	4.574422	-2.576252	-0.517775
C	-1.987006	-2.260286	0.601035
H	-1.066371	-2.158782	0.011096
H	-1.689896	-2.218165	1.657102
H	-2.410436	-3.252446	0.413358
C	-6.642330	-0.916618	-0.745713
H	-6.751531	-1.138284	-1.815859
H	-6.958993	-1.810162	-0.196074
H	-7.338504	-0.102900	-0.512567
C	-3.054111	2.585990	-0.317027
H	-2.497072	2.893933	0.576914
H	-2.392734	2.759973	-1.177599
H	-3.919383	3.247001	-0.432956
C	1.918206	-2.348213	-0.017618
H	1.425413	-2.386302	0.962696
H	1.125704	-2.195554	-0.762925
H	2.378636	-3.323670	-0.205364
C	6.664417	-0.856359	-0.779024
H	6.943107	-1.851563	-0.414606
H	6.827792	-0.852105	-1.865056
H	7.354267	-0.123475	-0.345645
C	3.098926	2.543228	0.253728
H	2.484447	2.914480	-0.578057
H	2.496990	2.657166	1.164384
H	3.975442	3.194581	0.333640



C	-0.668453	-0.432549	1.585233
C	0.670426	-0.574736	1.616319
H	-1.348896	-0.416277	2.431749

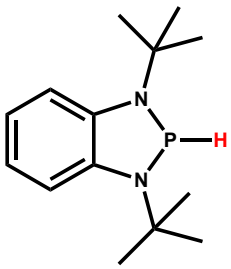
H	1.304911	-0.671510	2.491773
N	1.256973	-0.525572	0.329808
N	-1.168991	-0.239724	0.285818
P	0.038397	-0.683175	-0.885107
H	-0.138459	-2.130230	-0.793310
C	2.586402	-0.053158	0.125235
C	3.597638	-0.996580	-0.148166
C	2.869118	1.322633	0.212553
C	4.902422	-0.535526	-0.334106
C	4.191968	1.738767	0.029566
C	5.199641	0.821328	-0.241579
H	5.700145	-1.243901	-0.551440
H	4.433523	2.799257	0.095989
C	-2.546284	-0.032798	-0.013557
C	-3.454775	-1.101835	0.098988
C	-2.968418	1.249389	-0.427383
C	-4.804566	-0.858882	-0.175611
C	-4.323239	1.441278	-0.703608
C	-5.237481	0.399337	-0.573084
H	-5.522566	-1.673726	-0.088989
H	-4.675442	2.421944	-1.018158
H	6.222843	1.163762	-0.384084
H	-6.290426	0.570783	-0.788256
C	-3.008508	-2.499000	0.475763
C	-3.213220	-3.466916	-0.688511
C	-3.712696	-3.003077	1.733048
H	-1.932222	-2.466537	0.688586
H	-2.701658	-3.117655	-1.595229
H	-2.817468	-4.459145	-0.436159
H	-4.279264	-3.582620	-0.927527
H	-3.558274	-2.323027	2.580829
H	-4.794800	-3.103222	1.574089
H	-3.327489	-3.990771	2.016366
C	-1.990382	2.403076	-0.503487
C	-1.880012	3.081801	0.863129
C	-2.333305	3.431663	-1.574376
H	-1.001641	1.988057	-0.746244
H	-1.564458	2.378818	1.645349
H	-1.153217	3.905247	0.828948
H	-2.851530	3.502842	1.159355
H	-2.486900	2.966006	-2.555863
H	-3.238052	4.001143	-1.322794
H	-1.514156	4.155776	-1.668821
C	1.790891	2.349395	0.484719
C	1.680970	3.361639	-0.653631
C	2.018910	3.055461	1.819943

H	0.830047	1.820940	0.544426
H	1.484942	2.865820	-1.614155
H	0.858687	4.063916	-0.459135
H	2.601180	3.951904	-0.759123
H	2.071318	2.339129	2.650215
H	2.955569	3.629675	1.810866
H	1.201346	3.757843	2.029062
C	3.258019	-2.464751	-0.291724
C	4.342440	-3.399013	0.232271
C	2.950248	-2.785646	-1.755820
H	2.343547	-2.646875	0.291664
H	4.626102	-3.157080	1.264060
H	3.981763	-4.434869	0.214634
H	5.248782	-3.362429	-0.386587
H	2.157999	-2.141787	-2.163302
H	3.845461	-2.634743	-2.375799
H	2.630377	-3.829568	-1.868500



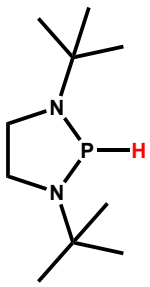
C	0.648845	-0.095851	-0.544670
C	-0.609183	0.377944	-0.583955
H	1.284104	-0.300954	-1.400758
H	-1.171637	0.651620	-1.472037
N	1.173516	-0.210714	0.763363
N	-1.161047	0.582105	0.689487
P	-0.178816	-0.187284	1.881116
H	-0.578258	-1.581421	1.628191
C	2.201021	-1.231831	0.995820
H	1.736378	-2.224725	0.821194
C	-2.276125	1.508377	0.890317
H	-1.925919	2.523878	0.637990
C	2.677611	-1.214367	2.444480
H	1.873173	-1.501522	3.134316
H	3.485931	-1.942912	2.571964
H	3.050096	-0.228431	2.745021
C	-2.726142	1.542926	2.344280
H	-1.917520	1.889558	2.997850
H	-3.561417	2.244658	2.444907
H	-3.063832	0.560977	2.698688
C	3.356219	-1.129958	0.017474

C	4.129818	0.061085	-0.172514
C	3.697124	-2.268631	-0.681799
C	3.849664	1.292818	0.480069
C	5.242222	0.020970	-1.072102
C	4.795982	-2.304833	-1.567374
H	3.100023	-3.169464	-0.542703
C	4.628121	2.406406	0.267133
H	2.991735	1.355721	1.143117
C	6.024464	1.187450	-1.270520
C	5.555889	-1.179757	-1.757660
H	5.029863	-3.226211	-2.096020
C	5.730050	2.357201	-0.614568
H	4.389282	3.335939	0.779695
H	6.866935	1.132495	-1.959086
H	6.407674	-1.185497	-2.436593
H	6.337395	3.245292	-0.774988
C	-3.435529	1.229548	-0.054432
C	-4.068514	-0.049201	-0.185459
C	-3.916106	2.292235	-0.790335
C	-3.644442	-1.215171	0.508846
C	-5.188703	-0.173461	-1.068193
C	-5.024278	2.167633	-1.656017
H	-3.424131	3.260343	-0.697554
C	-4.289857	-2.418905	0.348409
H	-2.788725	-1.161625	1.174338
C	-5.832519	-1.429155	-1.212194
C	-5.649597	0.955420	-1.791882
H	-5.370401	3.034504	-2.214461
C	-5.397595	-2.531928	-0.519539
H	-3.940358	-3.292906	0.893894
H	-6.683094	-1.497602	-1.889515
H	-6.504008	0.835828	-2.456715
H	-5.898968	-3.489798	-0.639117



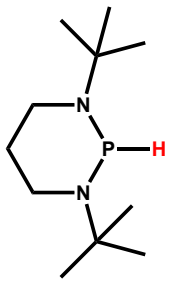
C	-0.711701	0.900771	-0.053686
C	0.711701	0.900771	-0.053686
C	1.399711	2.111487	0.007747
C	0.693372	3.318525	0.066314

C	-0.693373	3.318525	0.066315
C	-1.399712	2.111487	0.007748
H	2.483455	2.140548	0.017409
H	1.245865	4.254086	0.120932
H	-1.245865	4.254085	0.120933
H	-2.483455	2.140547	0.017411
H	0.000000	-1.325071	1.715322
C	2.672772	-0.747008	-0.077025
C	3.431340	-0.138324	-1.255506
C	3.256604	-0.305397	1.265559
C	2.819625	-2.263627	-0.180047
H	3.021051	-0.513793	-2.201419
H	3.395459	0.954262	-1.280052
H	4.487026	-0.432022	-1.199278
H	2.686505	-0.747923	2.093406
H	4.295809	-0.648027	1.348074
H	3.254532	0.781513	1.394550
H	3.887137	-2.513349	-0.187684
H	2.372455	-2.786432	0.676738
H	2.373588	-2.651792	-1.104119
C	-2.672772	-0.747009	-0.077025
C	-3.256603	-0.305403	1.265561
C	-3.431341	-0.138319	-1.255503
C	-2.819625	-2.263627	-0.180053
H	-2.686507	-0.747936	2.093406
H	-3.254525	0.781507	1.394558
H	-4.295810	-0.648027	1.348073
H	-3.021047	-0.513777	-2.201418
H	-4.487026	-0.432027	-1.199280
H	-3.395469	0.954267	-1.280039
H	-3.887136	-2.513349	-0.187688
H	-2.373589	-2.651789	-1.104127
H	-2.372453	-2.786435	0.676729
P	0.000000	-1.551822	0.268445
N	1.228520	-0.399203	-0.169957
N	-1.228520	-0.399203	-0.169957



P	-0.008709	-0.952438	0.163561

N	1.222068	0.174971	-0.276596
N	-1.219945	0.213939	-0.261729
C	2.654995	-0.118869	-0.064997
C	-2.656900	-0.111939	-0.082248
C	0.762611	1.554960	-0.059059
C	-0.736011	1.499014	0.246772
C	2.961630	-1.513489	-0.602639
C	3.037302	-0.055637	1.416201
C	3.481482	0.894267	-0.853951
C	-2.966016	-1.373311	-0.883150
C	-3.494560	1.032686	-0.646936
C	-3.028681	-0.335439	1.385600
H	-2.517943	-1.214931	1.800033
H	-2.775195	0.533951	2.005684
H	-4.109349	-0.504952	1.479160
H	-4.038196	-1.598313	-0.824416
H	-2.697843	-1.237134	-1.938859
H	-2.423773	-2.247532	-0.501198
H	-3.418302	1.943012	-0.040277
H	-3.188733	1.270889	-1.674168
H	-4.551016	0.738011	-0.663055
H	-1.259750	2.334253	-0.232511
H	0.958644	2.153802	-0.960576
H	2.510303	-0.827652	1.992670
H	4.115527	-0.221745	1.540809
H	2.799195	0.921530	1.855680
H	3.198151	0.884555	-1.914753
H	3.358952	1.914955	-0.472037
H	4.546232	0.640279	-0.780035
H	2.661221	-1.600847	-1.654904
H	4.038933	-1.708859	-0.532599
H	2.448244	-2.298258	-0.031625
H	1.290477	2.038128	0.778663
H	-0.898737	1.580460	1.338168
H	-0.026365	-0.762867	1.611456



C	1.269830	1.648123	0.216624
C	-1.269833	1.648116	0.216631

C	-0.000006	2.293702	-0.312324
H	1.321719	1.794959	1.314474
H	-2.134794	2.164283	-0.214649
H	-0.000007	3.355337	-0.030488
N	-1.322354	0.224149	-0.121684
N	1.322356	0.224156	-0.121688
P	0.000003	-0.684743	0.535587
H	-1.321712	1.794946	1.314482
H	-0.000008	2.242642	-1.410846
H	2.134780	2.164296	-0.214668
C	-2.677306	-0.401435	-0.124290
C	-2.572523	-1.880917	-0.487204
C	-3.357045	-0.267947	1.239954
C	-3.536048	0.267725	-1.198753
H	-2.004348	-2.020622	-1.416516
H	-2.097171	-2.477393	0.299725
H	-3.581656	-2.282616	-0.639971
H	-3.520953	0.782317	1.512015
H	-4.336774	-0.763820	1.229574
H	-2.749865	-0.736473	2.027178
H	-4.506448	-0.240571	-1.260938
H	-3.740496	1.323237	-0.988139
H	-3.048087	0.197433	-2.179633
C	2.677306	-0.401436	-0.124289
C	3.356989	-0.268087	1.239998
C	2.572518	-1.880881	-0.487356
C	3.536111	0.267820	-1.198641
H	3.520847	0.782152	1.512187
H	2.749801	-0.736729	2.027148
H	4.336736	-0.763923	1.229595
H	2.004414	-2.020477	-1.416728
H	3.581652	-2.282593	-0.640080
H	2.097084	-2.477421	0.299474
H	4.506470	-0.240547	-1.260893
H	3.048158	0.197722	-2.179540
H	3.740649	1.323282	-0.987861
H	0.000005	-0.095105	1.862794

5. References:

1. Namazian, M.; Lin, C. Y.; Coote, M. L., Benchmark calculations of absolute reduction potential of ferricinium/ferrocene couple in nonaqueous solutions. *Journal of chemical theory and computation* **2010,** *6* (9), 2721-2725.
2. Marenich, A. V.; Cramer, C. J.; Truhlar, D. G., Universal solvation model based on solute electron density and on a continuum model of the solvent defined by the bulk dielectric constant and atomic surface tensions. *The Journal of Physical Chemistry B* **2009,** *113* (18), 6378-6396.
3. Zhang, J.; Yang, J.-D.; Cheng, J.-P., Diazaphosphinanes as hydride, hydrogen atom, proton or electron donors under transition-metal-free conditions: thermodynamics, kinetics, and synthetic applications. *Chemical Science* **2020,** *11* (14), 3672-3679.
4. Mirzaei, S.; Ivanov, M. V.; Timerghazin, Q. K., Improving Performance of the SMD Solvation Model: Bondi Radii Improve Predicted Aqueous Solvation Free Energies of Ions and p K a Values of Thiols. *The Journal of Physical Chemistry A* **2019,** *123* (44), 9498-9504.
5. Li, H.; Jensen, J. H., Improving the efficiency and convergence of geometry optimization with the polarizable continuum model: New energy gradients and molecular surface tessellation. *Journal of computational chemistry* **2004,** *25* (12), 1449-1462.
6. Li, H.; Pomelli, C. S.; Jensen, J. H., Continuum solvation of large molecules described by QM/MM: a semi-iterative implementation of the PCM/EFP interface. *Theoretical Chemistry Accounts* **2003,** *109* (2), 71-84.