Supplementary Material for article

Going beyond the routine consideration of solvent effects on ^{31}P NMR shielding constants: a meticulous basis set study and new aug-pecS-*n* (*n* = 1, 2) basis sets for phosphorus atom

by Yuriy Yu. Rusakov, Yuliya A. Nikurashina and Irina L. Rusakova

Contents

The **aug-pecS-1** basis sets for **phosphorus** atom in Gaussian format, [6s5p4d]

P 0

S 10 1.00

9.624103D+04	2.5050D-04
1.433680D+04	1.9880D-03
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4.193807D+01	4.1841D-01
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1.781925D+00	-2.4702D-03

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The **aug-pecS-2** basis sets for **phosphorus** atom in Gaussian format, [7s6p5d2f]

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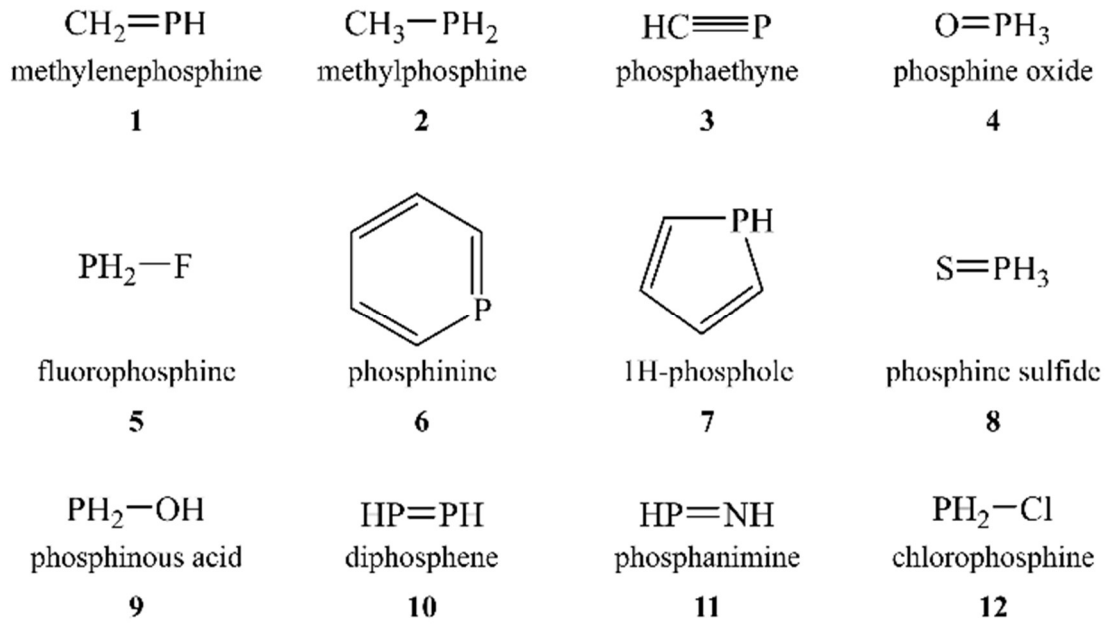
Molecules used in theoretical analysis:

Neutral molecules:



Anions: cyaphide anion $[P{\equiv}C]^-$ (**13**), hydrogen phosphite anion $[HPO_3]^{2-}$ (**14**), orthophosphate anion $[PO_4]^{3-}$ (**15**), methylenephosphine anion $[CH_2P]^-$ (**16**) and phosphine anion $[PH_2]^-$ (**17**)

Table S1. Equilibrium geometries for neutral molecules **1**-**12** and anions **13**-**17** calculated at the DFT(M06-2X)/cc-pVQZ level of theory.

#	Cartesian Coordinates, Å			
1	C	0.000000	0.000000	0.000000
	P	0.000000	0.000000	1.650001
	H	0.944541	0.000000	-0.530507
	H	-0.884965	0.000000	-0.621918
	H	-1.406919	0.000000	1.835076
2	C	0.000000	0.000000	0.000000
	P	0.000000	0.000000	1.845354
	H	1.395494	0.000000	2.035990
	H	-0.108199	-1.391294	2.035990
	H	-1.010665	-0.200586	-0.349099
	H	0.278343	0.992070	-0.349099
	H	0.676271	-0.730905	-0.432458
3	C	0.000000	0.000000	0.000000
	P	0.000000	0.000000	1.541463
	H	0.000000	0.000000	-1.086501
4	O	-0.000367	-0.000008	0.034520
	P	0.000146	-0.000004	1.504616
	H	1.260034	0.000031	2.141949
	H	-0.629493	1.090883	2.142605
	H	-0.629435	-1.090922	2.142611
5	P	-0.028385	0.002394	1.534141
	F	1.456627	-0.008599	2.145613
	H	-0.535160	1.110572	2.267621
	H	-0.620982	-0.920632	2.439529
6	C	-0.095493	-0.000383	-0.051544
	C	-0.010978	-0.000263	1.334201
	C	1.191024	0.000102	2.020862
	P	2.758407	0.000413	1.294605
	C	2.321985	0.000233	-0.376667
	C	1.027432	-0.000139	-0.867504
	H	-1.073140	-0.000658	-0.512557
	H	-0.933492	-0.000445	1.901739
	H	1.156535	0.000207	3.103216
	H	3.135118	0.000396	-1.091848
	H	0.878914	-0.000242	-1.940391
7	C	0.039539	-0.039290	0.088204
	C	0.007918	0.189970	1.413499
	P	1.649171	0.637665	2.000348
	C	2.358220	0.189973	0.408068
	C	1.377898	-0.039300	-0.484328
	H	-0.841974	-0.210665	-0.514168
	H	-0.888310	0.238343	2.010933
	H	1.980374	-0.494357	2.774575
	H	3.409245	0.238347	0.172492
	H	1.551033	-0.210680	-1.537864

8	S	0.000365	0.000257	0.046153
	P	0.000173	-0.000261	1.980913
	H	1.246019	-0.003463	2.630372
	H	-0.620936	1.080836	2.630999
	H	-0.625620	-1.077369	2.631015
9	P	-0.155475	0.510294	0.052790
	O	-0.320633	-0.358783	1.452496
	H	1.037864	-0.084885	-0.418441
	H	-0.962634	-0.293628	-0.785009
	H	-0.516150	0.227002	2.184497
10	P	-0.232578	0.000003	0.081851
	P	0.232578	0.000002	2.038349
	H	1.120791	-0.000002	-0.343836
	H	-1.120791	-0.000001	2.464036
11	P	-0.158597	0.000000	-0.008122
	N	0.110956	-0.000001	1.535267
	H	1.197549	0.000001	-0.456876
	H	-0.765122	0.000003	2.055598
12	P	0.003182	0.610184	-0.051561
	Cl	-0.006385	-0.160819	1.871241
	H	1.021879	-0.230238	-0.553711
	H	-1.018676	-0.220400	-0.563145
13	C	0.000000	0.000000	-1.134236
	P	0.000000	0.000000	0.453694
14	P	0.000019	0.000000	0.173829
	O	-0.746541	1.285022	-0.177271
	O	-0.739652	-1.288999	-0.177271
	O	1.486127	0.003977	-0.177318
	H	0.000253	0.000001	1.647448
15	P	0.000002	-0.000006	0.000008
	O	0.954406	-0.985443	0.772863
	O	0.261749	1.474284	0.487148
	O	0.282730	-0.099954	-1.545659
	O	-1.498888	-0.388876	0.285633
16	C	0.000003	-1.041662	0.000000
	P	0.000003	0.637232	-0.000000
	H	-0.000029	-1.654257	0.907039
	H	-0.000029	-1.654257	-0.907039
17	P	0.000000	0.000000	0.116959
	H	0.000000	1.023932	-0.877191
	H	-0.000000	-1.023932	-0.877191

Molecules used in experimental analysis:

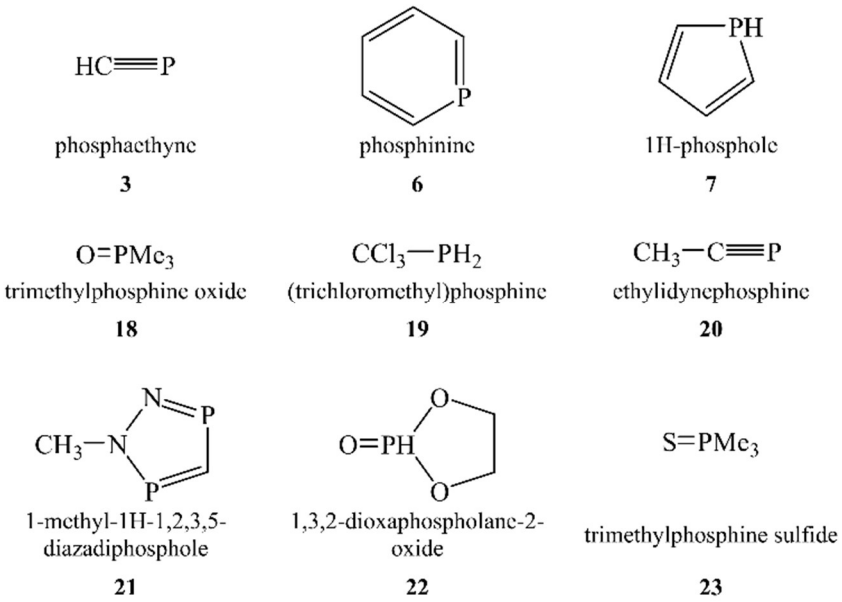


Table S2. Equilibrium geometries for molecules **3, 6, 7, 18-23** calculated at the DFT(M06-2X)/cc-pV5Z level of theory.

#	Cartesian Coordinates, Å			
3	P	0.000000	0.000000	0.534076
	C	0.000000	0.000000	-0.991396
	H	0.000000	0.000000	-2.062772
6	P	0.000000	0.000000	1.473854
	C	0.000000	1.326974	0.370561
	C	0.000000	1.218126	-1.010523
	C	0.000000	0.000000	-1.677925
	C	0.000000	-1.218126	-1.010523
	C	0.000000	-1.326974	0.370561
	H	0.000000	2.320367	0.801341
	H	0.000000	2.124947	-1.602372
	H	0.000000	0.000000	-2.758665
	H	0.000000	-2.124947	-1.602372
	H	0.000000	-2.320367	0.801341
7	P	0.167540	1.199679	0.000000
	C	-0.051850	-0.043090	-1.279255
	C	-0.051850	-1.272090	-0.728102
	C	-0.051850	-1.272090	0.728102
	C	-0.051850	-0.043090	1.279255
	H	-1.085251	1.844385	0.000000
	H	-0.040992	0.160644	-2.338119
	H	-0.050729	-2.189356	-1.300666
	H	-0.050729	-2.189356	1.300666
	H	-0.040992	0.160644	2.338119

18	P	0.000249	-0.000182	0.176265
	O	0.000777	-0.001875	1.659879
	C	1.645259	-0.182531	-0.545714
	C	-0.664344	1.516296	-0.543333
	C	-0.981752	-1.331954	-0.545818
	H	2.077294	-1.121060	-0.204582
	H	1.602543	-0.176662	-1.633143
	H	2.273050	0.637370	-0.203040
	H	-1.685952	1.652484	-0.194684
	H	-0.064559	2.359603	-0.207276
	H	-0.654165	1.474124	-1.630718
	H	-2.008224	-1.240497	-0.196783
	H	-0.963070	-1.291807	-1.633151
	H	-0.581851	-2.286686	-0.210446
19	P	1.855813	0.139149	0.000000
	C	-0.017185	-0.006367	0.000000
	H	2.037117	-0.800132	1.035109
	H	2.037117	-0.800132	-1.035109
	Cl	-0.623692	0.823631	-1.449925
	Cl	-0.623692	-1.673660	0.000000
	Cl	-0.623692	0.823631	1.449925
20	P	0.000003	0.000001	0.237963
	C	0.000003	0.000001	1.771380
	C	0.000003	0.000001	3.229747
	H	1.019440	-0.000054	3.613794
	H	-0.509668	0.882886	3.613794
	H	-0.509762	-0.882830	3.613794
21	C	-0.565223	-1.483137	0.000000
	P	1.161568	-1.304101	0.000000
	P	-1.410546	-0.013410	0.000000
	N	0.000000	0.909385	0.000000
	N	1.184440	0.331418	0.000000
	C	-0.010233	2.371284	0.000000
	H	-1.068439	-2.438369	0.000000
	H	0.501559	2.733380	0.887425
	H	0.501559	2.733380	-0.887425
	H	-1.038353	2.719775	0.000000
22	C	-1.569006	-0.718402	-0.011383
	C	-1.471235	0.776766	-0.303979
	O	-0.212504	1.177077	0.258502
	O	-0.217503	-1.192371	-0.065584
	P	0.825421	-0.036051	0.282517
	O	2.001511	0.041310	-0.568374
	H	-2.149468	-1.255366	-0.754305
	H	-1.974074	-0.907343	0.981724
	H	-2.258259	1.350909	0.173276
	H	-1.459337	0.977660	-1.373376
	H	1.129226	-0.183414	1.630752

23	P	0.182971	-0.000118	0.000173
	C	0.911232	0.821763	-1.436521
	C	0.903064	-1.658992	0.006135
	C	0.910349	0.832377	1.430674
	H	0.564164	1.851887	-1.463970
	H	1.997993	0.799741	-1.376147
	H	0.580548	0.311660	-2.338023
	H	0.561722	-2.185895	0.893889
	H	0.560311	-2.192107	-0.877429
	H	1.990220	-1.602588	0.005719
	H	0.573364	0.334891	2.336858
	H	1.997054	0.801141	1.374173
	H	0.570475	1.865046	1.445183
	S	-1.780518	0.002945	-0.000286

Table S3. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-pcS-4** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	70.36	64.11	6.24
2	CH_3PH_2	487.42	486.91	0.51
3	HCP	336.99	339.57	-2.59
4	OPH_3	354.83	367.21	-12.38
5	PH_2F	204.31	208.81	-4.50
6	Phosphinine	103.42	91.15	12.27
7	1H-phosphole	365.78	365.89	-0.11
8	SPH_3	385.39	392.07	-6.68
9	PH_2OH	278.15	276.63	1.52
10	P_2H_2	-243.93	-248.69	4.77
11	HP-NH	-280.42	-280.45	0.03
12	PH_2Cl	350.47	354.59	-4.12

Table S4. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**cc-pVDZ** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	165.56	158.15	7.40
2	CH_3PH_2	558.64	555.56	3.09
3	HCP	396.25	397.49	-1.24
4	OPH_3	453.32	461.40	-8.08
5	PH_2F	310.74	313.64	-2.90
6	Phosphinine	197.41	186.25	11.16
7	1H-phosphole	446.45	445.42	1.03
8	SPH_3	474.85	479.07	-4.22
9	PH_2OH	381.94	379.64	2.29

10	P_2H_2	-145.28	-151.67	6.39
11	HP-NH	-148.73	-151.90	3.17
12	PH_2Cl	426.80	430.81	-4.01

Table S5. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**cc-pVTZ** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	105.80	98.88	6.92
2	CH_3PH_2	514.68	512.38	2.30
3	HCP	349.44	352.48	-3.05
4	OPH_3	389.30	400.23	-10.93
5	PH_2F	242.12	245.70	-3.58
6	Phosphinine	139.94	127.71	12.23
7	1H-phosphole	396.21	395.64	0.57
8	SPH_3	418.41	425.12	-6.71
9	PH_2OH	313.92	311.39	2.52
10	P_2H_2	-205.08	-210.16	5.08
11	HP-NH	-231.44	-233.25	1.81
12	PH_2Cl	379.25	383.52	-4.27

Table S6. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**cc-pVQZ** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	127.78	121.66	6.12
2	CH_3PH_2	521.77	520.69	1.08
3	HCP	366.80	368.90	-2.10
4	OPH_3	395.12	406.05	-10.93
5	PH_2F	257.73	261.75	-4.02
6	Phosphinine	161.50	149.92	11.58
7	1H-phosphole	410.69	410.71	-0.01
8	SPH_3	424.97	431.07	-6.09
9	PH_2OH	327.08	325.15	1.93
10	P_2H_2	-171.32	-175.96	4.64
11	HP-NH	-200.99	-201.69	0.70
12	PH_2Cl	392.31	396.26	-3.95

Table S7. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**cc-pV5Z** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	65.64	59.18	6.45

2	CH_3PH_2	488.07	487.17	0.89
3	HCP	332.21	334.80	-2.58
4	OPH_3	356.59	369.10	-12.51
5	PH_2F	203.46	207.98	-4.52
6	Phosphinine	99.54	87.35	12.19
7	1H-phosphole	364.44	364.44	-0.01
8	SPH_3	386.08	392.79	-6.71
9	PH_2OH	277.54	275.93	1.61
10	P_2H_2	-253.27	-258.32	5.05
11	HP-NH	-286.76	-286.85	0.10
12	PH_2Cl	349.47	353.63	-4.16

Table S8. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-cc-pVDZ** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	163.79	156.71	7.09
2	CH_3PH_2	557.31	556.39	0.92
3	HCP	394.32	395.93	-1.61
4	OPH_3	451.51	461.82	-10.30
5	PH_2F	298.33	303.47	-5.13
6	Phosphinine	194.12	181.88	12.25
7	1H-phosphole	445.43	445.28	0.15
8	SPH_3	477.25	482.86	-5.62
9	PH_2OH	371.80	370.74	1.05
10	P_2H_2	-141.49	-145.31	3.83
11	HP-NH	-160.50	-160.08	-0.41
12	PH_2Cl	424.21	429.12	-4.91

Table S9. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-cc-pVTZ** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	101.88	95.43	6.45
2	CH_3PH_2	509.52	508.54	0.98
3	HCP	358.07	360.37	-2.30
4	OPH_3	389.12	401.24	-12.12
5	PH_2F	243.08	247.65	-4.57
6	Phosphinine	134.37	122.63	11.73
7	1H-phosphole	389.85	389.87	-0.02
8	SPH_3	418.75	425.31	-6.56
9	PH_2OH	312.46	311.06	1.40
10	P_2H_2	-201.22	-205.93	4.71

11	HP-NH	-233.77	-233.66	-0.11
12	PH_2Cl	379.14	383.47	-4.33

Table S10. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-cc-pVQZ** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	123.60	117.40	6.20
2	CH_3PH_2	517.31	516.58	0.73
3	HCP	366.99	369.15	-2.15
4	OPH_3	394.39	405.64	-11.25
5	PH_2F	254.21	258.51	-4.30
6	Phosphinine	144.18	132.58	11.60
7	1H-phosphole	403.38	403.36	0.03
8	SPH_3	427.85	434.00	-6.15
9	PH_2OH	323.62	322.26	1.36
10	P_2H_2	-172.10	-176.80	4.69
11	HP-NH	-206.61	-206.49	-0.13
12	PH_2Cl	389.73	393.70	-3.97

Table S11. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-cc-pV5Z** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	67.49	61.08	6.40
2	CH_3PH_2	487.77	487.07	0.71
3	HCP	332.58	335.18	-2.59
4	OPH_3	356.49	369.01	-12.52
5	PH_2F	203.39	207.94	-4.55
6	Phosphinine	98.24	86.07	12.17
7	1H-phosphole	361.81	361.87	-0.06
8	SPH_3	385.90	392.72	-6.81
9	PH_2OH	277.17	275.64	1.53
10	P_2H_2	-252.15	-257.03	4.88
11	HP-NH	-285.83	-285.85	0.01
12	PH_2Cl	349.37	353.55	-4.18

Table S12. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**pecS-1** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	70.49	66.56	3.93
2	CH_3PH_2	492.01	491.13	0.88

3	HCP	337.21	341.19	-3.98
4	OPH_3	361.67	374.12	-12.45
5	PH_2F	211.75	215.68	-3.92
6	Phosphinine	103.80	93.52	10.28
7	1H-phosphole	364.34	364.34	0.00
8	SPH_3	390.30	397.75	-7.44
9	PH_2OH	284.72	282.34	2.38
10	P_2H_2	-235.40	-236.84	1.43
11	HP-NH	-270.12	-272.69	2.56
12	PH_2Cl	353.22	357.45	-4.24

Table S13. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**pecS-2** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	70.50	64.72	5.78
2	CH_3PH_2	490.32	489.46	0.86
3	HCP	337.12	340.17	-3.05
4	OPH_3	356.82	369.01	-12.19
5	PH_2F	206.41	210.64	-4.23
6	Phosphinine	105.17	93.49	11.68
7	1H-phosphole	366.88	366.94	-0.06
8	SPH_3	387.50	393.96	-6.46
9	PH_2OH	280.61	278.76	1.85
10	P_2H_2	-247.16	-251.68	4.52
11	HP-NH	-283.71	-284.79	1.08
12	PH_2Cl	350.70	355.14	-4.44

Table S14. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-pecS-1-mixed** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	78.33	73.08	5.25
2	CH_3PH_2	491.91	491.43	0.47
3	HCP	342.02	344.91	-2.90
4	OPH_3	360.31	373.08	-12.77
5	PH_2F	207.60	212.49	-4.88
6	Phosphinine	112.61	101.15	11.46
7	1H-phosphole	371.76	372.10	-0.34
8	SPH_3	388.77	396.06	-7.29
9	PH_2OH	283.54	282.29	1.25
10	P_2H_2	-233.81	-235.77	1.96
11	HP-NH	-270.68	-269.21	-1.47

12	PH_2Cl	349.43	353.90	-4.48

Table S15. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**aug-pecS-2-mixed** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	69.99	63.86	6.14
2	CH_3PH_2	488.07	487.43	0.63
3	HCP	336.41	339.08	-2.67
4	OPH_3	356.25	368.65	-12.40
5	PH_2F	205.16	209.72	-4.56
6	Phosphinine	103.18	91.23	11.95
7	1H-phosphole	366.11	366.22	-0.11
8	SPH_3	385.75	392.52	-6.77
9	PH_2OH	279.11	277.64	1.47
10	P_2H_2	-244.45	-248.99	4.53
11	HP-NH	-280.09	-280.09	0.00
12	PH_2Cl	349.33	353.59	-4.26

Table S16. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**6-31G(d,p)** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	162.40	152.73	9.67
2	CH_3PH_2	540.32	536.58	3.74
3	HCP	404.17	404.16	0.00
4	OPH_3	418.61	429.46	-10.86
5	PH_2F	277.93	280.97	-3.04
6	Phosphinine	194.41	181.75	12.66
7	1H-phosphole	430.73	430.14	0.59
8	SPH_3	445.38	452.80	-7.42
9	PH_2OH	351.29	349.01	2.28
10	P_2H_2	-172.33	-181.17	8.84
11	HP-NH	-160.54	-163.08	2.54
12	PH_2Cl	400.67	406.06	-5.39

Table S17. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**6-311G(d,p)** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	78.90	71.90	7.00
2	CH_3PH_2	503.46	500.17	3.29
3	HCP	328.43	331.56	-3.14

4	OPH_3	380.27	392.17	-11.90
5	PH_2F	221.31	226.81	-5.50
6	Phosphinine	116.58	103.91	12.67
7	1H-phosphole	380.32	380.00	0.32
8	SPH_3	410.86	418.30	-7.44
9	PH_2OH	297.06	295.45	1.61
10	P_2H_2	-264.59	-275.89	11.30
11	HP-NH	-268.79	-269.81	1.02
12	PH_2Cl	354.99	362.54	-7.55

Table S18. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**6-31++G(d,p)** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	150.41	143.15	7.26
2	CH_3PH_2	537.26	533.46	3.79
3	HCP	396.52	398.21	-1.69
4	OPH_3	421.08	434.19	-13.11
5	PH_2F	263.81	269.07	-5.27
6	Phosphinine	190.31	178.29	12.02
7	1H-phosphole	433.12	432.83	0.29
8	SPH_3	451.05	459.39	-8.34
9	PH_2OH	339.40	338.26	1.14
10	P_2H_2	-174.96	-184.26	9.30
11	HP-NH	-180.40	-179.27	-1.13
12	PH_2Cl	403.09	409.77	-6.68

Table S19. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**6-311++G(d,p)** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	73.91	67.30	6.60
2	CH_3PH_2	502.80	499.78	3.03
3	HCP	327.22	330.39	-3.17
4	OPH_3	379.45	392.40	-12.95
5	PH_2F	217.13	223.08	-5.95
6	Phosphinine	107.94	95.83	12.11
7	1H-phosphole	377.15	377.52	-0.37
8	SPH_3	409.98	417.56	-7.58
9	PH_2OH	295.45	294.49	0.96
10	P_2H_2	-258.75	-268.56	9.81
11	HP-NH	-279.14	-277.85	-1.30
12	PH_2Cl	355.55	362.11	-6.56

Table S20. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**pcS-1** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	83.62	77.36	6.25
2	CH_3PH_2	512.51	509.23	3.28
3	HCP	337.66	341.24	-3.58
4	OPH_3	391.64	402.92	-11.28
5	PH_2F	239.44	244.06	-4.62
6	Phosphinine	122.72	112.09	10.63
7	1H-phosphole	390.37	390.08	0.29
8	SPH_3	418.37	425.77	-7.41
9	PH_2OH	311.25	309.62	1.63
10	P_2H_2	-256.97	-267.44	10.47
11	HP-NH	-267.85	-270.85	3.00
12	PH_2Cl	367.83	373.71	-5.88

Table S21. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**pcS-2** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	69.07	62.00	7.07
2	CH_3PH_2	492.41	490.05	2.36
3	HCP	331.79	334.82	-3.03
4	OPH_3	362.63	375.04	-12.41
5	PH_2F	210.72	215.46	-4.74
6	Phosphinine	104.98	92.85	12.13
7	1H-phosphole	369.63	369.49	0.14
8	SPH_3	392.87	399.56	-6.69
9	PH_2OH	284.03	282.52	1.51
10	P_2H_2	-260.22	-269.27	9.06
11	HP-NH	-287.02	-287.10	0.08
12	PH_2Cl	352.60	357.57	-4.97

Table S22. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**pcS-3** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	69.10	62.79	6.31
2	CH_3PH_2	487.66	486.78	0.89
3	HCP	335.92	338.60	-2.68
4	OPH_3	354.93	367.32	-12.40
5	PH_2F	203.93	208.40	-4.47

6	Phosphinine	102.55	90.50	12.04
7	1H-phosphole	365.24	365.32	-0.08
8	SPH_3	385.26	391.92	-6.66
9	PH_2OH	277.89	276.37	1.52
10	P_2H_2	-246.94	-252.12	5.19
11	HP-NH	-282.49	-282.37	-0.12
12	PH_2Cl	350.18	354.32	-4.14

Table S23. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**pcS-4** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	70.33	64.09	6.24
2	CH_3PH_2	487.73	487.05	0.68
3	HCP	336.99	339.57	-2.59
4	OPH_3	354.82	367.19	-12.37
5	PH_2F	204.34	208.82	-4.49
6	Phosphinine	103.18	91.19	11.99
7	1H-phosphole	365.75	365.86	-0.12
8	SPH_3	385.36	392.04	-6.68
9	PH_2OH	278.15	276.63	1.52
10	P_2H_2	-244.10	-248.90	4.80
11	HP-NH	-280.45	-280.44	-0.01
12	PH_2Cl	350.53	354.64	-4.11

Table S24. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**aug-pcS-1** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	89.85	83.93	5.92
2	CH_3PH_2	511.02	510.20	0.82
3	HCP	342.54	345.17	-2.64
4	OPH_3	390.44	402.78	-12.34
5	PH_2F	229.92	235.03	-5.12
6	Phosphinine	125.04	113.05	11.99
7	1H-phosphole	388.93	389.16	-0.23
8	SPH_3	417.31	424.32	-7.01
9	PH_2OH	307.10	305.91	1.20
10	P_2H_2	-233.04	-235.48	2.44
11	HP-NH	-259.11	-257.78	-1.33
12	PH_2Cl	367.63	372.50	-4.87

Table S25. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-pcS-2** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	69.79	63.31	6.48
2	CH_3PH_2	490.77	489.99	0.78
3	HCP	334.41	336.91	-2.50
4	OPH_3	361.52	374.02	-12.50
5	PH_2F	206.66	211.23	-4.57
6	Phosphinine	101.51	89.16	12.34
7	1H-phosphole	367.59	367.69	-0.10
8	SPH_3	391.12	398.02	-6.90
9	PH_2OH	280.87	279.36	1.51
10	P_2H_2	-249.39	-254.87	5.48
11	HP-NH	-283.64	-283.80	0.16
12	PH_2Cl	351.41	355.71	-4.30

Table S26. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**aug-pcS-3** level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	69.19	62.95	6.24
2	CH_3PH_2	487.42	486.76	0.67
3	HCP	336.14	338.73	-2.59
4	OPH_3	354.90	367.31	-12.41
5	PH_2F	203.69	208.19	-4.50
6	Phosphinine	102.44	90.41	12.03
7	1H-phosphole	365.09	365.19	-0.10
8	SPH_3	385.23	391.94	-6.71
9	PH_2OH	277.75	276.25	1.50
10	P_2H_2	-245.94	-250.68	4.74
11	HP-NH	-281.96	-282.00	0.04
12	PH_2Cl	349.99	354.10	-4.11

Table S27. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1**-**12** calculated at the GIAO-DFT(B97-2)/**cc-pVDZ-LDBS** (P = aug-cc-pVDZ; rest = cc-pVDZ) level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	168.70	161.46	7.24
2	CH_3PH_2	559.42	558.35	1.07
3	HCP	398.23	399.70	-1.47
4	OPH_3	457.28	467.42	-10.14

5	PH_2F	298.41	302.90	-4.49
6	Phosphinine	198.54	185.93	12.61
7	1H-phosphole	444.77	444.40	0.37
8	SPH_3	476.09	482.02	-5.93
9	PH_2OH	373.22	371.17	2.05
10	P_2H_2	-139.89	-143.42	3.53
11	HP-NH	-147.63	-150.09	2.46
12	PH_2Cl	423.15	428.11	-4.97

Table S28. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**cc-pVTZ-LDBS** (P = aug-cc-pVTZ; rest = cc-pVTZ) level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	108.46	101.86	6.60
2	CH_3PH_2	515.05	514.19	0.86
3	HCP	351.64	353.97	-2.33
4	OPH_3	391.98	404.04	-12.05
5	PH_2F	240.76	245.26	-4.49
6	Phosphinine	138.16	126.16	12.00
7	1H-phosphole	395.93	395.88	0.05
8	SPH_3	421.33	427.90	-6.57
9	PH_2OH	313.56	311.78	1.78
10	P_2H_2	-199.26	-203.98	4.72
11	HP-NH	-227.89	-228.78	0.90
12	PH_2Cl	379.67	384.05	-4.37

Table S29. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**pcS-1-LDBS** (P = aug-pcS-1; rest = pcS-1) level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	89.50	84.24	5.27
2	CH_3PH_2	512.08	511.50	0.58
3	HCP	342.76	345.88	-3.12
4	OPH_3	391.45	403.64	-12.19
5	PH_2F	229.62	234.98	-5.36
6	Phosphinine	126.01	114.70	11.31
7	1H-phosphole	389.82	390.30	-0.48
8	SPH_3	418.20	425.67	-7.47
9	PH_2OH	306.24	304.80	1.44
10	P_2H_2	-233.70	-236.42	2.72
11	HP-NH	-260.04	-261.60	1.55

12	PH_2Cl	366.57	372.52	-5.95

Table S30. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**pcS-2-LDBS** (P = aug-pcS-2; rest = pcS-2) level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	70.45	63.95	6.50
2	CH_3PH_2	491.51	490.43	1.08
3	HCP	334.89	337.54	-2.66
4	OPH_3	361.50	374.04	-12.54
5	PH_2F	207.48	212.29	-4.81
6	Phosphinine	104.02	91.82	12.20
7	1H-phosphole	369.35	369.43	-0.08
8	SPH_3	391.31	398.33	-7.02
9	PH_2OH	282.53	281.14	1.39
10	P_2H_2	-249.55	-255.12	5.57
11	HP-NH	-282.76	-282.82	0.07
12	PH_2Cl	351.86	356.48	-4.62

Table S31. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**pecS-1-LDBS-mixed** (P = aug-pecS-1, rest = pcS-1) level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol
1	CH_2PH	79.02	74.20	4.82
2	CH_3PH_2	491.81	491.61	0.20
3	HCP	342.86	346.01	-3.15
4	OPH_3	360.12	372.81	-12.69
5	PH_2F	207.30	212.40	-5.10
6	Phosphinine	115.21	104.33	10.88
7	1H-phosphole	372.82	373.26	-0.44
8	SPH_3	388.65	396.15	-7.50
9	PH_2OH	282.81	281.20	1.61
10	P_2H_2	-234.93	-236.97	2.04
11	HP-NH	-270.72	-271.66	0.95
12	PH_2Cl	348.05	353.24	-5.20

Table S32. ^{31}P NMR shielding constants (in ppm) and solvent corrections (Δsol) of molecules **1-12** calculated at the GIAO-DFT(B97-2)/**pecS-2-LDBS-mixed** (P = aug-pecS-2, rest = pcS-2) level of theory.

#	Molecule	Solvated phase	Gas phase	Δsol

1	CH_2PH	70.53	64.52	6.01
2	CH_3PH_2	488.48	487.88	0.60
3	HCP	336.68	339.44	-2.76
4	OPH_3	356.14	368.53	-12.39
5	PH_2F	205.07	209.73	-4.66
6	Phosphinine	104.07	92.39	11.68
7	1H-phosphole	366.66	366.87	-0.21
8	SPH_3	386.17	392.96	-6.79
9	PH_2OH	279.28	277.77	1.51
10	P_2H_2	-245.06	-249.62	4.56
11	HP-NH	-280.20	-280.41	0.21
12	PH_2Cl	349.15	353.77	-4.62

Table S33. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**pecS-1-mixed** (P = pecS-1, rest = pcS-1) level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	38.80
14	$[HPO_3]^{2-}$	312.52
15	$[PO_4]^{3-}$	294.46
16	$[CH_2P]^-$	-1180.30
17	$[PH_2]^-$	649.81

Table S34. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**aug-pecS-1-mixed** (P = aug-pecS-1, rest = aug-pcS-1) level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	105.92
14	$[HPO_3]^{2-}$	302.75
15	$[PO_4]^{3-}$	272.48
16	$[CH_2P]^-$	-1015.42
17	$[PH_2]^-$	701.45

Table S35. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**pecS-2-mixed** (P = pecS-2, rest = pcS-2) level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	67.46
14	$[HPO_3]^{2-}$	300.49
15	$[PO_4]^{3-}$	281.66
16	$[CH_2P]^-$	-1170.99
17	$[PH_2]^-$	677.24

Table S36. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**aug-pecS-2-mixed** (P = aug-pecS-2, rest = aug-pcS-2) level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	101.26
14	$[HPO_3]^{2-}$	297.26
15	$[PO_4]^{3-}$	274.90
16	$[CH_2P]^-$	-1020.32
17	$[PH_2]^-$	702.93

Table S37. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**pcS-1** level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	47.40
14	$[HPO_3]^{2-}$	328.08
15	$[PO_4]^{3-}$	312.96
16	$[CH_2P]^-$	-1190.83
17	$[PH_2]^-$	655.03

Table S38. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**aug-pcS-1** level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	109.90
14	$[HPO_3]^{2-}$	321.99
15	$[PO_4]^{3-}$	300.03
16	$[CH_2P]^-$	-1005.20
17	$[PH_2]^-$	715.81

Table S39. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**pcS-2** level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	54.31
14	$[HPO_3]^{2-}$	303.30
15	$[PO_4]^{3-}$	286.29
16	$[CH_2P]^-$	-1121.09
17	$[PH_2]^-$	677.34

Table S40. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**aug-pcS-2** level of theory in gas phase.

#	Molecule	σ_{GP}

13	$[P{\equiv}C]^-$	97.50
14	$[HPO_3]^{2-}$	301.01
15	$[PO_4]^{3-}$	293.47
16	$[CH_2P]^-$	-1027.19
17	$[PH_2]^-$	704.47

Table S41. ^{31}P NMR shielding constants (in ppm) of molecules **13**-**17** calculated at the GIAO-DFT(B97-2)/**aug-pcS-4** level of theory in gas phase.

#	Molecule	σ_{GP}
13	$[P{\equiv}C]^-$	101.31
14	$[HPO_3]^{2-}$	295.55
15	$[PO_4]^{3-}$	279.97
16	$[CH_2P]^-$	-1008.36
17	$[PH_2]^-$	702.26

Table S42. Experimental ^{31}P NMR chemical shifts (in ppm) of molecules **3**, **6**, **7**, **18**-**23**.[a]

#	Molecule	Solvent	Exp.
19	Cl_3CPH_2	$CHCl_3$	-12.0
3	HCP	$CHCl_3$	-32.0
20	MeCP	$CHCl_3$	-61.0
18	$OPMe_3$	C_6H_6	31.5
21	1-methyl-1H-1,2,3,5-diazadiphosphole	$CHCl_3$	265.1
			279.5
22	1,3,2-dioxaphospholane-2-oxide	CCl_4	21.3
6	phosphinine	$CHCl_3$	211.0
7	1H-phosphole	THF	-49.2
23	$SPMe_3$	$CHCl_3$	30.57

[a] References on experimental data are given main paper (see text).

Table S43. Basic values of ^{31}P NMR shielding constants (σ_B) of molecules **3**, **6**, **7**, **18**-**23** together with relativistic (Δ_{rel}) and vibrational (Δ_{vib}) corrections used within the combined computational approach, in ppm.

#	Molecule	σ_B[a]	Δ_{rel}[b]	Δ_{vib}[c]	$\sigma_B + \Delta_{rel} + \Delta_{vib}$
19	Cl_3CPH_2	375.42	11.92	-13.86	373.48
3	HCP	384.73	13.79	-10.57	387.95
20	MeCP	401.33	12.9	-8.02	406.21
18	$OPMe_3$	312.26	14.98	-3.27	323.97
21	1-methyl-1H-1,2,3,5-diazadiphosphole	78.38	10.43	-8.46	80.35
		65.02	10.16	-11.83	63.35
22	1,3,2-dioxaphospholane-2-oxide	321.52	14.82	-3.28	333.06

6	phosphinine	131.64	11.13	-13.64	129.13
7	1H-phosphole	401.65	13.82	-11.99	403.48
23	$SPMe_3$	303.52	21.13	-5.38	319.27

[a] GIAO-CCSD/pecS-2(pcS-2 for Cl and S), gas phase

[b] 4c-GIAO-DFT(SVWN5)/dyall.av3z, gas phase

[c] GIAO-DFT(B97-2)/pecG-2(P), rest - 6-311G(3df,3pd), VPT2, gas phase

Table S44. Solvent corrections to ^{31}P NMR shielding constants (in ppm) (Δ_{sol}) of molecules **3**, **6**, **7**, **18**-**23** calculated at the GIAO-DFT(B97-2) level of theory with different basis sets.

#	Molecule	pecS-1-mixed	aug-pecS-1-mixed	pcS-1	aug-pcS-1	cc-pVDZ	aug-cc-pVDZ	6-31G(d,p)	6-31++G(d,p)
19	Cl_3CPH_2	-2.13	-2.05	-1.67	-2.02	-1.07	-1.87	-1.21	-1.48
3	HCP	-2.37	-1.81	-2.25	-1.60	-0.66	-0.89	0.18	-0.98
20	MeCP	4.53	5.11	4.63	5.44	5.37	5.67	6.07	5.05
18	$OPMe_3$	-5.26	-5.35	-4.84	-5.18	-3.89	-4.52	-4.76	-5.39
21	1-methyl-1H-1,2,3,5-diazadiphosphole	3.37	3.48	3.58	3.76	3.88	4.20	3.45	3.60
		0.91	0.73	0.86	0.62	1.21	0.78	1.65	1.18
22	1,3,2-dioxaphospholane-2-oxide	-3.11	-3.25	-3.01	-3.18	-2.44	-2.70	-2.93	-3.06
6	phosphinine	7.23	7.92	7.48	8.32	7.80	8.51	8.82	8.41
7	1H-phosphole	0.09	-0.24	0.27	-0.15	0.84	0.13	0.48	0.23
23	$SPMe_3$	-5.62	-5.17	-5.40	-4.86	-4.46	-3.90	-5.78	-5.71

Table S45. Scaled (against experiment) ^{31}P NMR chemical shifts (in ppm) of molecules **3**, **6**, **7**, **18**-**23** calculated on the shielding constants obtained within a combined scheme $\sigma = \sigma_{basic} + \Delta_{vib} + \Delta_{rel} + \Delta_{sol}$ with $\sigma_{basic} + \Delta_{vib} + \Delta_{rel}$ taken from Table S43 and solvent corrections Δ_{sol} taken from Table S44 (the latter were calculated with different basis sets).

#	Molecule	pecS-1-mixed	aug-pecS-1-mixed	pcS-1	aug-pcS-1	cc-pVDZ	aug-cc-pVDZ	6-31G(d,p)	6-31++G(d,p)	Exp.
19	Cl_3CPH_2	-21.08	-20.99	-21.35	-20.84	-21.25	-20.56	-21.17	-21.32	-12.0
3	HCP	-35.32	-35.70	-35.23	-35.73	-36.13	-36.02	-37.03	-36.29	-32.0
20	MeCP	-60.47	-60.88	-60.37	-61.03	-60.42	-60.84	-61.18	-60.57	-61.0
18	$OPMe_3$	31.55	31.82	31.34	31.82	31.08	31.59	31.89	32.11	31.5
21	1-methyl-1H-1,2,3,5-diazadiphosphole	266.55	266.61	266.54	266.51	266.93	266.49	267.29	266.74	265.1
		286.00	286.36	286.25	286.65	286.60	286.92	286.10	286.15	279.5

22	1,3,2-dioxaphospholane-2-oxide	20.32	20.63	20.42	20.73	20.54	20.69	20.96	20.69	21.3
6	phosphinine	213.90	213.39	213.86	213.17	214.23	213.40	213.15	213.14	211.0
7	1H-phosphole	-53.31	-52.80	-53.28	-52.72	-53.16	-52.57	-52.86	-53.02	-49.2
23	$SPMe_3$	36.62	36.34	36.59	36.21	36.35	35.67	37.61	37.13	30.57