Supplementary Materials: $H_2XP{:}OH_2$ Complexes: Hydrogen *vs*. Pnicogen Bonds

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Table S1. Structures, total energies (au), and molecular graphs of hydrogen-bonded and pnicogen-bonded equilibrium complexes $H_2XP{:}HOH$.

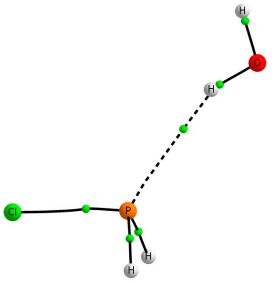
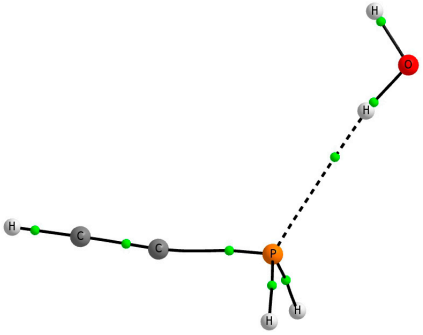
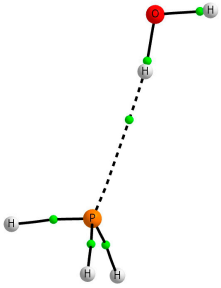
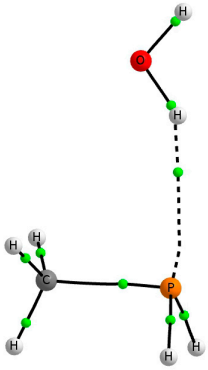
	$H_2ClP{:}OH_2$ HB MP2 = −878.13409463 NIMAG = 0 P, −0.0757664337, 0.6186129707, 0. H, −0.4324213182, 1.5148217923, 1.0294584093 H, −0.4324213182, 1.5148217923, −1.0294584093 Cl, −1.8194995272, −0.4959832257, 0. O, 3.3574545359, −0.296824191, 0. H, 2.3946436654, −0.3570061351, 0. H, 3.6552272761, −1.2108849235, 0.
	$H_2(CCH)P{:}OH_2$ HB MP2 = −494.98334508 NIMAG = 0 P, −0.1039827082, 0.8117147986, 0. H, −0.4694873808, 1.6910090832, 1.0407184128 H, −0.4694873808, 1.6910090832, −1.0407184128 C, −1.5723436874, −0.1795696538, 0. O, 3.2290606841, −0.5077352986, 0. H, 2.2946263578, −0.2638512499, 0. H, 3.2217660272, −1.4689787424, 0. C, −2.500012593, −0.9724094196, 0. H, −3.3224685386, −1.6467320523, 0.
	$H_3P{:}OH_2$ HB MP2 = −418.99207419 NIMAG = 0 P, −0.0081326406, 1.2638467598, 0. H, 0.910777613, 1.0022805441, 1.0371820207 H, 0.910777613, 1.0022805441, −1.0371820207 H, 0.2090561759, 2.6567857986, 0. O, −3.4985018585, 0.4908168281, 0. H, −2.5364274912, 0.5767830257, 0. H, −3.6507028216, −0.4581946103, 0.
	$H_2(CH_3)P{:}OH_2$ HB MP2 = −458.22171747 NIMAG = 0 P, 0.84087316, 0.65356573, 0. H, 1.76038168, 0.91501721, −1.038011 H, 1.76038168, 0.91501721, 1.038011 C, 0.92166228, −1.19591603, 0. O, −2.43484667, −0.09359193, 0. H, −3.21573871, 0.46726471, 0. H, −1.6919184, 0.5256794, 0. H, 0.39050281, −1.56088857, −0.8767117 H, 1.93719887, −1.58055334, 0. H, 0.39050281, −1.56088857, 0.8767117

Table S1. *Cont.*

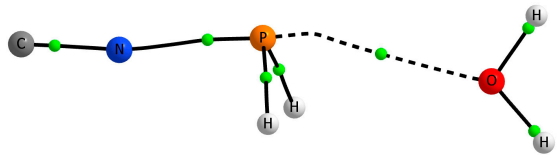
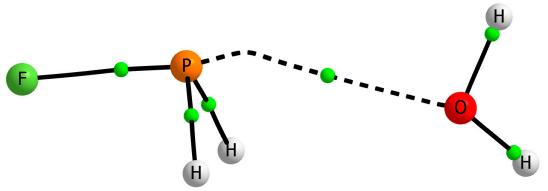
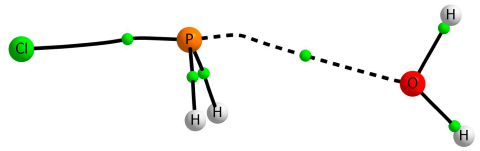
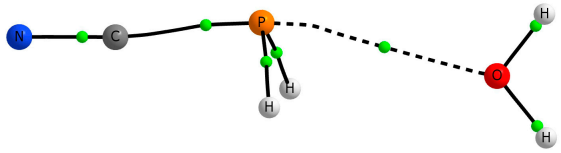
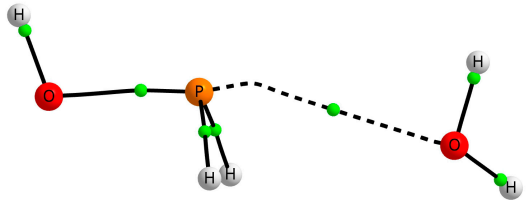
	$H_2(NC)P:OH_2$ ZB MP2 = −511.05378411 NIMAG = 0 P, −0.2025449056, −0.3182774709, 0. H, 0.1361142538, 0.5737906667, 1.0344014279 H, 0.1361142538, 0.5737906667, −1.0344014279 N, −1.8985836621, 0.0705728759, 0. O, 2.5953964792, −0.2009388375, 0. H, 3.0299941615, −1.0594070675, 0. H, 3.3147662454, 0.4380486446, 0. C, −3.0785832942, 0.1737749645, 0.
	$H_2FP:OH_2$ ZB MP2 = −518.16050717 NIMAG = 0 P, 0.0412998764, 0.4402312167, −0.1341303739 H, 0.3360749075, −0.0267082869, 1.1665665169 H, 1.0198324782, −0.3793408201, −0.7366075242 F, 0.9299122482, 1.8090086233, −0.0647952484 O, −0.9231072112, −2.1364628316, −0.0938290447 H, −0.8789396685, −2.7956104972, 0.6058156477 H, −1.8625296305, −2.0382224042, −0.2780199734
	$H_2ClP:OH_2$ ZB MP2 = −878.13710333 NIMAG = 0 P, 0.0283087811, 0.4620947505, −0.1424659357 H, 0.312655198, 0.0271691611, 1.1683006957 H, 1.0065703758, −0.3692627165, −0.7235208291 Cl, 1.207836693, 2.1873309509, −0.0676625691 O, −0.9765521576, −2.1857520608, −0.0501025204 H, −0.8939422937, −2.927725133, 0.557024769 H, −1.9132086766, −2.1528689823, −0.2680589804
	$H_2(CN)P:OH_2$ ZB MP2 = −511.08250292 NIMAG = 0 P, −0.2526492867, −0.374318383, 0. H, 0.10169491, 0.5077621956, 1.0389001444 H, 0.10169491, 0.5077621956, −1.0389001444 C, −1.9897323547, 0.0882336334, 0. O, 2.6854014668, −0.1882154039, 0. H, 3.1445796189, −1.0336576554, 0. H, 3.3892393191, 0.4677619024, 0. N, −3.1496444969, 0.2751656103, 0.
	$H_2(OH)P:OH_2$ ZB MP2 = −494.14006820 NIMAG = 0 P, 0.0235460579, 0.4529696488, −0.1186338515 H, 0.3490793975, −0.0396132105, 1.1633932365 H, 0.9747434776, −0.3610478528, −0.7671395588 O, 0.9217169174, 1.8726919032, −0.0613531753 O, −0.9265046998, −2.3141904626, −0.0842667997 H, −1.0120485444, −2.9365101635, 0.6443812371 H, −1.8316787849, −2.0659027402, −0.2964104581 H, 0.3651267286, 2.5986128976, −0.3582202402

Table S1. *Cont.*

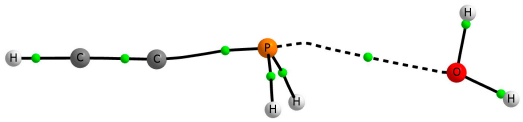
	$H_2(CCH)P:OH_2$ ZB MP2 = −494.98351807 NIMAG = 0 P, 0.01718031, −0.1851920829, 0. H, 0.3117889891, 0.7223718029, 1.0374539982 H, 0.3117889891, 0.7223718029, −1.0374539982 C, -1.7469622282, 0.0499304841, 0. O, 3.039583312, 0.1048877442, 0. H, 3.1973324894, −0.8442494659, 0. H, 3.9188324432, 0.495171272, 0. C, −2.9680851812, 0.0689212697, 0. H, −4.0306976007, 0.1075921463, 0.

Table S2. Components of spin-spin coupling constants ^{2h}J(O-P), ^{1h}J(H-P), and ^{1}J(O-H) (Hz) for hydrogen-bonded complexes H_2XP:HOH.

H_2XP					
X =	**PSO**	**DSO**	**FC**	**SD**	**^{2h}J(O-O)**
Cl	−0.2	0.0	−17.9	−0.1	−18.2
CCH	0.0	0.0	−14.1	−0.3	−14.4
H	0.0	0.0	−13.7	−0.3	−14.0
CH_3	−0.1	0.0	−24.2	0.1	−24.1
X =					**^{1}J(O-H)**
Cl	−10.2	-0.1	−66.9	−0.7	−78.0
CCH	−10.0	-0.1	−67.2	−0.6	−77.9
H	−9.9	-0.1	−67.5	−0.6	−78.1
CH_3	−9.8	-0.2	−67.8	−0.6	−78.4
X =					**^{1h}J(H-O)**
Cl	−0.6	0.9	−14.1	0.9	−12.9
CCH	−0.8	0.9	−14.4	1.3	−13.0
H	−0.8	0.8	−14.6	1.2	−13.5
CH_3	−1.0	0.9	−15.0	0.1	−15.0

Table S3. Structures, total energies (au), and molecular graphs of pnicogen-bonded complexes $H_2XP:OH_2$ with C_s symmetry and NIMAG = 1, with in-plane and out-of-plane H_2O molecules.

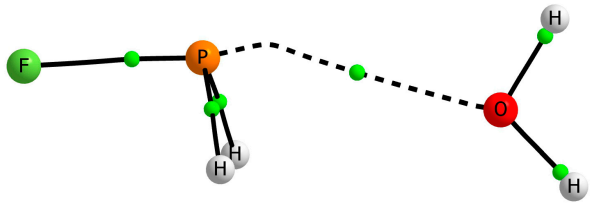
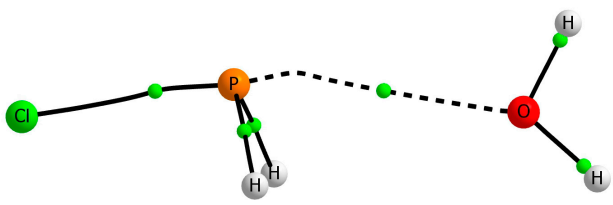
Complexes with in-plane H_2O molecules	
	$H_2FP:OH_2$ MP2 = −518.16036586 NIMAG = 1 P, 0.0658126594, 0.1268710934, 0. H, 0.3663350939, −0.7955105004, 1.0263262442 H, 0.3663350939, −0.7955105004, −1.0263262442 F, −1.5538304111, −0.0840832214, 0. O, 2.8096105425, −0.1192154894, 0. H, 3.5291603666, −0.7574405526,0. H, 3.2391730618, 0.741270354, 0.
	$H_2ClP:OH_2$ MP2 = −878.13706990 NIMAG = 1 P, 0.098561093, 0.1541636975, 0. H, 0.3892637987, −0.7667517155, 1.0268547952 H, 0.3892637987, −0.7667517155, −1.0268547952 Cl, −1.9700961818, −0.1498680194, 0. O, 2.9199196598, −0.120953969, 0. H, 3.6331923741, −0.7665681739, 0. H, 3.3619134237, 0.7334639266, 0.

Table S3. *Cont.*

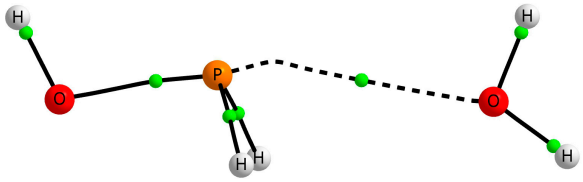
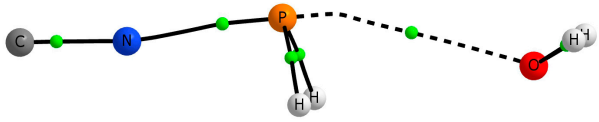
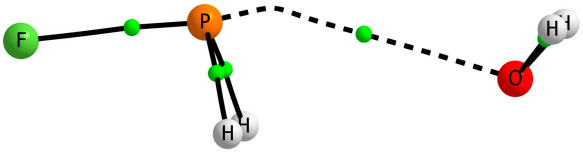
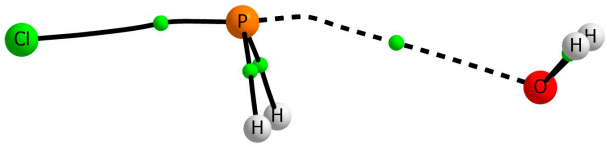
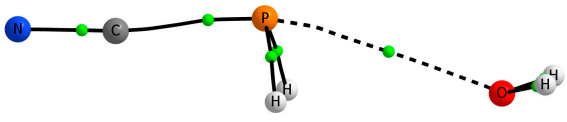
	$H_2(OH)P:OH_2$ MP2 = −494.13992251 NIMAG = 1 P, −0.4761782187, 0.0767268148, 0. H, −0.098030973, −0.8130261038, 1.027430512 H, −0.098030973, −0.8130261038, −1.027430512 O, −2.1262997519, −0.2484630397, 0. O, 2.4394195479, −0.073582608, 0. H, 3.2361815463, −0.6124320709, 0. H, 2.7576838908, 0.8339635203, 0. H, −2.6013502867, 0.5876840124, 0.
Complexes with out-of-plane H_2O molecules	
	$H_2(NC)P:OH_2$ MP2 = −511.05332378 NIMAG = 1 P, −0.1598326811, 1.5470132914, 0. H, 0.638919517, 1.0163025674, 1.0308515818 H, 0.638919517, 1.0163025674, −1.0308515818 N, 0.6036549285, 3.1109815307, 0. O, −0.493505822, −1.262210472, 0. H, −0.9396330802, −1.6504458457, 0.75940756 H, −0.9396330802, −1.6504458457, −0.75940756 C, 0.9728343931, 4.23649403, 0.
	$H_2FP:OH_2$ MP2 = −518.16012438 NIMAG = 1 P, −0.1011887454, 1.5067313611, 0. H, 0.7142828247, 0.9747877431, 1.0234703968 H, 0.7142828247, 0.9747877431, −1.0234703968 F, 0.5265340828, 3.0145772816, 0. O, −0.4312678133, −1.2582360846, 0. H, −0.9747863668, −1.4931530486, 0.7590266931 H, −0.9747863668, −1.4931530486, −0.7590266931
	$H_2ClP:OH_2$ MP2 = −878.13672612 NIMAG = 1 P, −0.1380165403, 1.4855256157, 0. H, 0.6808687086, 0.9671446866, 1.0240757515 H, 0.6808687086, 0.9671446866, −1.0240757515 Cl, 0.6863086327, 3.4069383308, 0. O, −0.4543918842, −1.3674889124, 0. H, −0.9912835927, −1.6164612301, 0.7592176206 H, −0.9912835927, −1.6164612301, −0.7592176206
	$H_2(CN)P:OH_2$ MP2 = −511.08205007 NIMAG = 1 P, −0.2114379737, 1.6309181796, 0. H, 0.5653359439, 1.0762725643, 1.0357918698 H, 0.5653359439, 1.0762725643, −1.0357918698 C, 0.6523495566, 3.2075504096, 0. O, −0.5362447453, −1.3326881028, 0. H, −0.9118459975, −1.7893436823, 0.7591480411 H, −0.9118459975, −1.7893436823, −0.7591480411 N, 1.1088837761, 4.2901192451, 0.

Table S3. *Cont.*

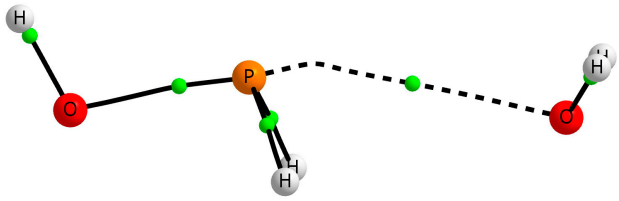
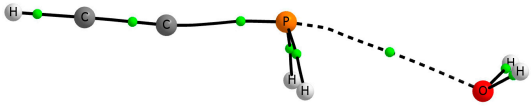
	$H_2(OH)P:OH_2$ MP2 = −494.13977471 NIMAG = 1 P, −0.0855999592, 1.5771190326, 0. H, 0.6989048614, 1.0068680709, 1.0249970943 H, 0.6989048614, 1.0068680709, −1.0249970943 O, 0.604753865, 3.1100827242, 0. O, −0.4311559495, −1.357373567, 0. H, −0.9960497577, −1.5355638749, 0.7583850979 H, −0.9960497577, −1.5355638749, −0.7583850979 H, −0.101449328, 3.7629203217, 0.
	$H_2(CCH)P:OH_2$ MP2 = −494.98306824 NIMAG = 1 P, −0.2818736, −0.00371665, 0. H, 0.61056921, −0.35111095, 1.03497371 H, 0.61056921, −0.35111095, −1.03497371 C, 0.06497721, 1.74302844, 0. O, 0.22482623, −3.06542477, 0. H, −0.19806405, −3.4800955, 0.75830046 H, −0.19806405, −3.4800955, −0.75830046 C, 0.15846222, 2.96079798, 0. H, 0.26258363, 4.0189868, 0.

Table S4. Components of spin-spin coupling constants ^{1p}J(P-O) for pnicogen-bonded complexes $H_2XP:OH_2$ with C_s symmetry and in-plane H_2O molecules.

H_2XP					
X =	**PSO**	**DSO**	**FC**	**SD**	**^{1p}J(P-O)**
NC	−0.8	0.0	−61.5	−0.2	−62.5
F	−1.2	0.0	−68.2	−0.2	−69.8
Cl	−0.9	0.0	−60.0	−0.1	−61.2
CN	−0.3	0.0	−41.5	0.0	−41.9
OH	−0.6	0.0	−45.9	−0.1	−46.7
CCH	−0.2	0.0	−36.4	0.0	−36.7

Table S5. Components of spin-$_{spin}$ coupling constants ^{1p}J(P-O) for pnicogen-bonded complexes $H_2XP:OH_2$ with C_s symmetry and out-of-plane H_2O molecules.

H_2XP					
X =	**PSO**	**DSO**	**FC**	**SD**	**^{1p}J(P-O)**
NC	−1.0	0.0	−44.6	−0.3	−46.0
F	−1.7	0.0	−41.9	−0.5	−44.2
Cl	−1.2	0.0	−37.2	−0.3	−38.8
CN	−0.3	0.0	−31.7	−0.1	−32.2
OH	−0.8	0.0	−26.9	−0.2	−28.0
CCH	−0.2	0.0	−20.9	−0.1	−21.1

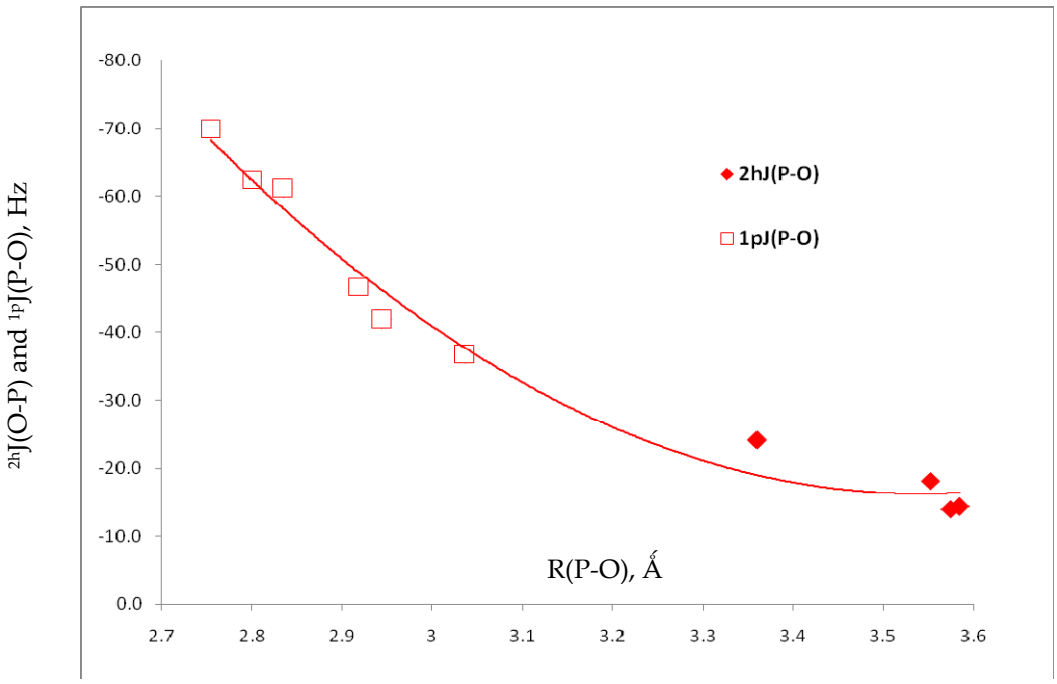


Figure S1. ^{2h}J(O-P) and ^{1p}J(P-O) versus the P-O distance for $H_2XP{:}OH_2$ complexes with C_s symmetry and in-plane H_2O molecules. The second-order trendline has a correlation coefficient of 0.981.