

## Electronic supplementary information

Can HN=NH, FN=NH, or HN=CHOH Bridge the  $\sigma$ -Hole and the Lone Pair at P in Binary Complexes with H<sub>2</sub>XP, for X = F, Cl, NC, OH, CN, CCH, CH<sub>3</sub>, and H?

Janet E. Del Bene, Ibon Alkorta, and José Elguero

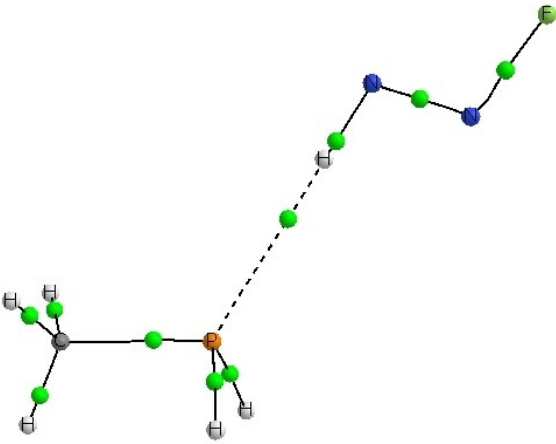
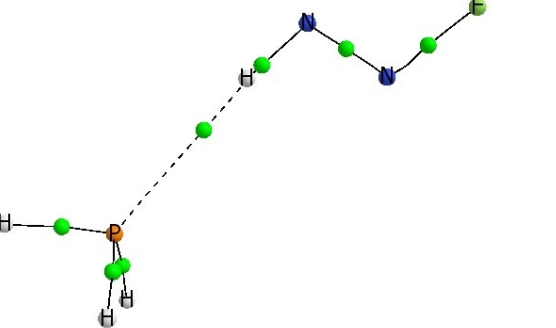
Pg. S2 – S7	Table S1. Structures, total energies, and molecular graphs of complexes of HN=NH, FN=NH, and NH=CHOH with H <sub>2</sub> XP, for X = F, Cl, NC, OH, CN, CCH, CH <sub>3</sub> , and H
Pg. S8-S9	Table S2. Electron density properties at the intermolecular BCPs
Pg. S10	Figure S1. Energy densities at bond critical points (au) vs. the P-N distance (Å) for P...N pnictogen bonds (Å) in H <sub>2</sub> XP:NH=CHOH complexes
Pg. S10	Figure S2. Energy densities at bond critical points (au) vs the P-H <sub>2</sub> distance (Å) for hydrogen bonds in H <sub>2</sub> XP:NH=CHOH complexes
Pg. S11	Table S3. Components of spin-spin coupling constants <sup>1</sup> pJ(P-N <sub>1</sub> ) (Hz) for complexes of H <sub>2</sub> XP with HN=NH, FN=NH, and NH=CHOH
Pg. S12	Table S4. Components of spin-spin coupling constants J(N <sub>2</sub> -P) (Hz) for complexes of H <sub>2</sub> XP with HN=NH and FN=NH, and <sup>2</sup> hJ(O-P) for complexes with NH=CHOH
Pg. S13	Figure S3. <sup>2</sup> hJ(O-P) versus the O-P distance for complexes H <sub>2</sub> XP:NH=CHOH

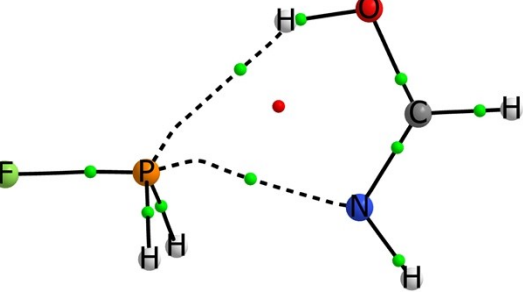
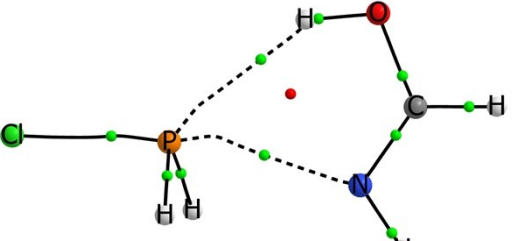
Table S1. Structures, total energies, and molecular graphs of complexes of HN=NH, FN=NH, and NHCHOH with H<sub>2</sub>XP, for X = F, Cl, NC, OH, CN, CCH, CH<sub>3</sub>, and H

	<p>H<sub>2</sub>FP:HNNH MP2= -552.29335375 NIMAG= 0  P,-0.7075959708,0.0505089122,0.  F,-2.3273279387,0.3011845003,0.  H,-0.688098141,-0.9121877708,1.0323793257  H,-0.688098141,-0.9121877708,-1.0323793257  N,1.7122993586,-0.623935582,0.  N,2.4805822327,0.3634579486,0.  H,1.859943778,1.1902307451,0.  H,2.2989590567,-1.4699796358,0.</p>
	<p>H<sub>2</sub>ClP:HNNH MP2= -912.26849542 NIMAG= 0  P,-0.7017347424,0.0511871117,0.  Cl,-2.7734246091,0.387702706,0.  H,-0.7070821535,-0.9095843996,1.0307157817  H,-0.7070821535,-0.9095843996,-1.0307157817  N,1.8459622565,-0.6616478043,0.  N,2.5808366313,0.3523711666,0.  H,1.9365637575,1.1600019186,0.  H,2.4666252482,-1.4833549525,0.</p>
	<p>H<sub>2</sub>(NC)P:HNNH MP2= -545.18434164 NIMAG= 0  P,-0.37523138,-0.04063612,0.  N,-2.12032188,0.02092393,0.  H,-0.28446673,-0.98522254,1.03875265  H,-0.28446673,-0.98522254,-1.03875265  N,2.23962692,-0.47716957,0.  N,2.85778944,0.61203627,0.  H,2.13064407,1.34586345,0.  H,2.94821008,-1.22402663,0.  C,-3.28687666,0.22821058,0.</p>
	<p>H<sub>2</sub>(OH)P:HNNH MP2= -528.27171709 NIMAG= 0  P,-0.7970474145,-0.0169243332,0.  O,-2.47178047,0.1243391569,0.  H,-0.6782959167,-0.9723656362,1.0306367398  H,-0.6782959167,-0.9723656362,-1.0306367398  N,1.9069431213,-0.5464433761,0.  N,2.4788780597,0.5689191959,0.  H,1.7142179865,1.2634586227,0.  H,2.6502558122,-1.2591887603,0.  H,-2.7041730018,1.0576137466,0.</p>
	<p>H<sub>2</sub>(CN)P:HNNH MP2= -545.21191931 NIMAG= 0  P,-0.39587837,-0.04802252,0.  C,-2.19292837,0.02539502,0.  H,-0.3118776,-0.99177536,1.04105009  H,-0.3118776,-0.99177536,-1.04105009  N,2.45041955,-0.49853889,0.  N,2.9522764,0.65041838,0.  H,2.15398556,1.3050913,0.</p>

	<p>H,3.23870779,-1.1608139,0. N,-3.35597855,0.19205228,0.</p>
	<p>H<sub>2</sub>(CCH)P:HNNH MP2= -529.11405377 NIMAG= 0 P,-0.3978265573,-0.1137093417,0. C,-2.172127883,0.0094275063,0. H,-0.2853278257,-1.059488078,1.0391948482 H,-0.2853278257,-1.059488078,-1.0391948482 N,2.5841173022,-0.5190006164,0. N,2.9401458982,0.6838859712,0. H,2.063358146,1.2291648263,0. H,3.4503910117,-1.0759470316,0. C,-3.3725699061,0.2333163281,0. H,-4.4216497703,0.4077963637,0.</p>
	<p>H<sub>2</sub>(CH<sub>3</sub>)P:HNNH MP2= -492.34969280 NIMAG= 0 P,-0.7920302298,-0.0724030464,0. C,-2.6243349036,0.2206999429,0. H,-0.7370773115,-1.0297219705,1.0348375497 H,-0.7370773115,-1.0297219705,-1.0348375497 N,2.3664923745,-0.6465013221,0. N,2.6187838587,0.5829647703,0. H,1.6963911692,1.0468519226,0. H,3.2784350408,-1.1257175128,0. H,-2.8841848856,0.8074220799,-0.8791831992 H,-3.2048921256,-0.6974731635,0. H,-2.8841848856,0.8074220799,0.8791831992</p>
	<p>H<sub>3</sub>P:HNNH MP2= -453.12120386 NIMAG= 0 P,-0.9469862941,0.1044569286,0. H,-2.3296027645,0.3958066703,0. H,-1.0339803893,-0.8476744791,1.0358812415 H,-1.0339803893,-0.8476744791,-1.0358812415 N,2.1131766582,-0.792800885,0. N,2.5335130852,0.3895335184,0. H,1.6870862604,0.9800691194,0. H,2.9497545824,-1.3936239971,0.</p>
	<p>H<sub>2</sub>FP:HNNF MP2= -651.39209724 NIMAG= 0 P,-0.8827721519,0.0890600794,0. F,-2.4939831322,0.2890673092,0. H,-0.8024880766,-0.8777335601,1.0272170187 H,-0.8024880766,-0.8777335601,-1.0272170187 N,1.8189647517,-0.5386961615,0. N,2.5769767444,0.4105482837,0. H,1.9391562525,1.2194516431,0. F,2.588726132,-1.7271997641,0.</p>

	<p>H<sub>2</sub>(OH)P:HNNF MP2= -627.37335818 NIMAG= 0  P,-0.9288368228,-0.027535284,0.  O,-2.5794631059,0.2187887369,0.  H,-0.8493745324,-0.9892637272,1.0298788137  H,-0.8493745324,-0.9892637272,-1.0298788137  N,2.0845791737,-0.525489887,0.  N,2.4827063678,0.6215424639,0.  H,1.6041610208,1.162780225,0.  F,3.2148286025,-1.3887115878,0.  H,-2.7585239082,1.1641957673,0.</p>
	<p>H<sub>2</sub>CIP:HNNF MP2= -1011.36835154 NIMAG= 0  P,-0.8670583859,0.0804362356,0.  Cl,-2.9072673444,0.4566248149,0.  H,-0.8619569855,-0.8853039166,1.0283020641  H,-0.8619569855,-0.8853039166,-1.0283020641  N,1.9885695287,-0.6160144566,0.  N,2.6435309383,0.4071577092,0.  H,1.9250241124,1.1454653097,0.  F,2.883086617,-1.7163394756,0.</p>
	<p>H<sub>2</sub>(CN)P:HNNF MP2= -644.28332042 NIMAG= 0  P,-0.5381725717,0.0002842733,0.  N,-2.2676718298,-0.0042027595,0.  H,-0.3846673639,-0.9437569596,1.0342813694  H,-0.3846673639,-0.9437569596,-1.0342813694  N,2.333349776,-0.3609755147,0.  N,3.0011761904,0.6541161107,0.  H,2.2976790681,1.405757574,0.  F,3.211212344,-1.4711672978,0.  C,-3.441530495,0.1580229822,0.</p>
	<p>H<sub>2</sub>(NC)P:HNNF MP2= -644.31249690 NIMAG= 0  P,-0.517032112,-0.0533465211,0.  C,-2.3052397242,0.0322704228,0.  H,-0.4257411057,-1.0001573864,1.0398200334  H,-0.4257411057,-1.0001573864,-1.0398200334  N,2.533865787,-0.3976948185,0.  N,3.0336652842,0.7098321891,0.  H,2.2190231123,1.3396105977,0.  F,3.5800022442,-1.3540988627,0.  N,-3.4670482147,0.2063365119,0.</p>
	<p>H<sub>2</sub>(CCH)P:HNNF MP2= -628.21687331  NIMAG= 0  P,-1.07331507,-0.2122254,0.  C,-2.83552506,-0.03724057,0.  H,-0.97206859,-1.15954727,1.04017745  H,-0.97206859,-1.15954727,-1.04017745  N,2.217211,-0.08877856,0.  N,2.19762577,1.12443618,0.  H,1.18689513,1.33490662,0.  F,3.57920983,-0.50951685,0.  C,-4.02889584,0.21793079,0.</p>

	<p>H,-5.07334861,0.41933356,0.  H<sub>2</sub>(CH<sub>3</sub>)P:HNNF MP2= -591.45563867 NIMAG= 0  P,-0.627589143,1.5524418434,0.  C,0.3370098042,3.1314671934,0.  H,-1.5349428762,1.844926707,1.0391329882  H,-1.5349428762,1.844926707,-1.0391329882  N,-0.0262772685,-2.4154794794,0.  N,0.9133801788,-1.6552779413,0.  H,0.4713798037,-0.7157932017,0.  F,0.4904259529,-3.7611867337,0.  H,0.9766301592,3.1481006168,-0.8800021808  H,-0.2977258899,4.0125086755,0.  H,0.9766301592,3.1481006168,0.8800021808</p>
	<p>H<sub>3</sub>P:HNNF MP2= -552.22575945 NIMAG= 0  P,-1.1585455985,-0.068994455,0.  H,-2.1270120872,0.9547908494,0.  H,-1.7566086895,-0.808458267,1.0398830505  H,-1.7566086895,-0.808458267,-1.0398830505  N,2.7319537426,-0.8804172306,0.  N,2.4384585765,0.2941904661,0.  H,1.4036607519,0.2836481188,0.  F,4.1636827472,-0.978208818,0.</p>

	<p>H<sub>2</sub>FP:NHCHOH MP2= -611.44318650 NIMAG= 0  P,-1.0974052509,-0.058928926,0.  F,-2.6899974887,0.3352648426,0.  H,-1.1513378361,-0.9975072412,1.0458013564  H,-1.1513378361,-0.9975072412,-1.0458013564  N,1.1953039681,-1.0721899065,0.  C,2.1373239741,-0.208613757,0.  O,1.9038802705,1.1007322279,0.  H,3.2009842083,-0.430757073,0.  H,0.9260432854,1.2055559589,0.  H,1.5660097521,-2.0173587415,0.</p>
	<p>H<sub>2</sub>ClP:NHCHOH MP2= -971.41763344  NIMAG= 0  P,-1.0965666508,-0.0572623552,0.  Cl,-3.1446648969,0.4252504902,0.  H,-1.1568198736,-0.9970508858,1.0423501352  H,-1.1568198736,-0.9970508858,-1.0423501352  N,1.3006692101,-1.1024027682,0.  C,2.2303530697,-0.2274732598,0.</p>

	<p>O,1.9816202727,1.0818620178,0.  H,3.2979907076,-0.4307595025,0.  H,1.0068122815,1.1827594866,0.  H,1.6887087199,-2.0410326877,0.</p>
	<p>H<sub>2</sub>(OH)P:NHCHOH MP2= -587.42098059 NIMAG= 0  P,-1.1496936988,-0.0860815499,0.  O,-2.7973260638,0.2328602314,0.  H,-1.1129747082,-1.0316360429,1.0402779193  H,-1.1129747082,-1.0316360429,-1.0402779193  N,1.4284800142,-1.1206479577,0.  C,2.2685789254,-0.1599811774,0.  O,1.890586012,1.1200524755,0.  H,3.3517944512,-0.2546359717,0.  H,0.907123677,1.1163422789,0.  H,-2.9357073231,1.1846714683,0.  H,1.9137555991,-2.0129349961,0.</p>
	<p>H<sub>2</sub>(CN)P:NHCHOH MP2= -604.33320818 NIMAG= 0  P,-0.7669014056,-0.159415007,0.  N,-2.5027714712,0.0770327495,0.  H,-0.7621918278,-1.0914244897,1.0485394303  H,-0.7621918278,-1.0914244897,-1.0485394303  N,1.7027385855,-1.0345885175,0.  C,2.5908764325,-0.1176749939,0.  O,2.2840581916,1.1796399985,0.  H,3.6665295576,-0.2714558823,0.  H,1.3089632723,1.2447855223,0.  C,-3.6437114214,0.3969765237,0.  H,2.1367748266,-1.9528718101,0.</p>
	<p>H<sub>2</sub>(CCH)P:NHCHOH MP2= -588.26202844 NIMAG= 0  P,-0.8217269431,-0.1892753693,0.  C,-2.5870189777,0.023981948,0.  H,-0.733088045,-1.1251294875,1.0465756747  H,-0.733088045,-1.1251294875,-1.0465756747  N,2.0665076537,-1.0738853572,0.  C,2.7737734188,-0.0133922425,0.  O,2.2368113661,1.2118202388,0.  H,3.8600610465,0.0378738527,0.  H,1.2643693273,1.0978091208,0.  C,-3.7751940228,0.3058652262,0.  H,-4.8146594294,0.5310171745,0.  H,2.6712479521,-1.8903388723,0.</p>

	<p>H<sub>2</sub>(NC)P:NHCHOH MP2= -604.35962171 NIMAG= 0  P,-0.8270561244,-0.129158908,0.  C,-2.6159023724,0.0785581829,0.  H,-0.7964795794,-1.0635169129,1.0486862264  H,-0.7964795794,-1.0635169129,-1.0486862264  N,1.8876842264,-1.0705614452,0.  C,2.7249167631,-0.1096360119,0.  O,2.3481194873,1.1736633407,0.  H,3.8081992496,-0.1978471046,0.  H,1.3728986711,1.1871714439,0.  N,-3.7636979115,0.3301320489,0.  H,2.3786597773,-1.9599623503,0.</p>
	<p>H<sub>2</sub>(CH<sub>3</sub>)P:NHCHOH MP2= -551.49813525 NIMAG= 0  P,-1.1525449873,-0.0930447648,0.  C,-2.959729222,0.3132772233,0.  H,-1.1288481308,-1.0402884546,1.0415460113  H,-1.1288481308,-1.0402884546,-1.0415460113  N,1.8445884219,-1.2463223226,0.  C,2.5283934857,-0.1701952443,0.  O,1.9681249868,1.0440325697,0.  H,3.6140239587,-0.0970919903,0.  H,0.9936204939,0.9140764491,0.  H,-3.1846181607,0.9134768334,-0.8796433267  H,-3.5920405437,-0.5703073774,0.  H,-3.1846181607,0.9134768334,0.8796433267  H,2.4715524745,-2.0460338057,0.</p>
	<p>H<sub>3</sub>P:NHCHOH MP2= -512.26874042 NIMAG= 0  P,-1.3556025557,0.038314336,0.  H,-2.7352295586,0.3417275494,0.  H,-1.4201068652,-0.9042641688,1.0426047589  H,-1.4201068652,-0.9042641688,-1.0426047589  N,1.5875622569,-1.245021778,0.  C,2.3465068128,-0.221607264,0.  O,1.8720686802,1.0302397718,0.  H,3.4342317033,-0.2232004736,0.  H,0.8947723601,0.9683729515,0.  H,2.1536735629,-2.088811653,0.</p>

Table S2. Electron density properties at intermolecular BCPs (au)  
 $P \cdots N_1$  pnictogen bonds in  $H_2XP:HN=NH$  complexes

HN=NH with	$\rho_{BCP}$	$\nabla^2\rho_{BCP}$	$H_{BCP}$
$H_2FP$	0.035	0.069	-0.005
$H_2CIP$	0.027	0.063	-0.002
$H_2(NC)P$	0.027	0.062	-0.002
$H_2(OH)P$	0.022	0.057	-0.001
$H_2(CN)P$	0.017	0.048	0.000
$H_2(CCH)P$	0.014	0.041	0.001
$H_2(CH_3)P$	0.009	0.031	0.001
$H_3P$	0.010	0.032	0.001

$N_2-H_2 \cdots P$  hydrogen bonds in  $H_2XP:HN=NH$  complexes

HN=NH with	$\rho_{BCP}$	$\nabla^2\rho_{BCP}$	$H_{BCP}$
$H_2(CH_3)P$	0.012	0.030	0.001
$H_3P$	0.011	0.028	0.001

$P \cdots N$  pnictogen bonds in  $H_2XP:HN=NF$  complexes

HN=NF with	$\rho_{BCP}$	$\nabla^2\rho_{BCP}$	$H_{BCP}$
$H_2FP$	0.019	0.055	0.000
$H_2CIP$	0.014	0.044	0.001
$H_2(NC)P$	0.016	0.047	0.001
$H_2(OH)P$	0.012	0.038	0.001
$H_2(CN)P$	0.011	0.036	0.001

$N_2-H_2 \cdots P$  hydrogen bonds in  $H_2XP:HN=NF$  complexes

HN=NF with	$\rho_{BCP}$	$\nabla^2\rho_{BCP}$	$H_{BCP}$
$H_2(OH)P$	0.011	0.029	0.001
$H_2(CCH)P$	0.012	0.028	0.001
$H_2(CH_3)P$	0.018	0.034	-0.001
$H_3P$	0.016	0.032	-0.0002



P $\cdots$ N pnicoen bonds in H<sub>2</sub>XP:NH=CHOH complexes

NH=CHOH with	$\rho_{\text{BCP}}$	$\nabla^2\rho_{\text{BCP}}$	$H_{\text{BCP}}$
H <sub>2</sub> FP	0.034	0.068	-0.005
H <sub>2</sub> CIP	0.029	0.063	-0.002
H <sub>2</sub> (NC)P	0.028	0.063	-0.002
H <sub>2</sub> (OH)P	0.021	0.054	-0.0004
H <sub>2</sub> (CN)P	0.018	0.048	0.000
H <sub>2</sub> (CCH)P	0.014	0.039	0.001
H <sub>2</sub> (CH <sub>3</sub> )P	0.010	0.030	0.001
H <sub>3</sub> P	0.010	0.030	0.001

O-H<sub>2</sub> $\cdots$ P hydrogen bonds in H<sub>2</sub>XP:NH=CHOH complexes

NH=CHOH with	$\rho_{\text{BCP}}$	$\nabla^2\rho_{\text{BCP}}$	$H_{\text{BCP}}$
H <sub>2</sub> FP	0.023	0.041	-0.002
H <sub>2</sub> CIP	0.020	0.039	-0.001
H <sub>2</sub> (NC)P	0.017	0.037	0.000
H <sub>2</sub> (OH)P	0.023	0.038	-0.002
H <sub>2</sub> (CN)P	0.015	0.033	0.000
H <sub>2</sub> (CCH)P	0.019	0.036	-0.001
H <sub>2</sub> (CH <sub>3</sub> )P	0.023	0.036	-0.002
H <sub>3</sub> P	0.019	0.036	-0.001

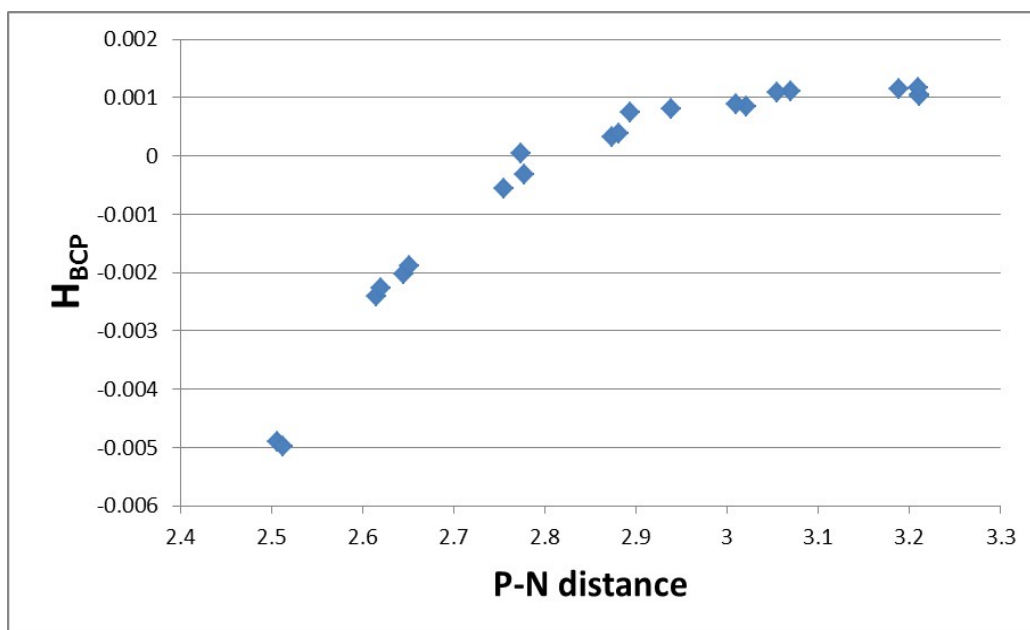


Figure S1. Energy densities at bond critical points (au) vs. the P-N distance (Å) for P...N pnictogen bonds in  $H_2XP:NH=CHOH$  complexes

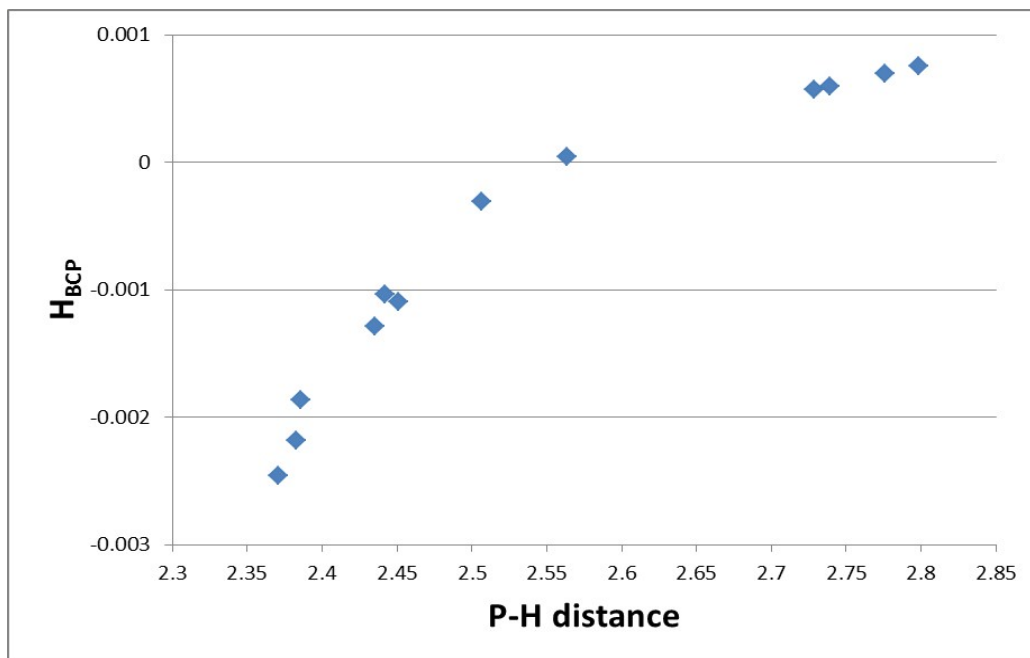


Fig. S2. Energy densities at bond critical points (au) vs the P- $H_2$  distance (Å) for hydrogen bonds in  $H_2XP:NH=CHOH$  complexes

Table S3. Components of  ${}^1\text{P}(\text{P}-\text{N}_1)$  (Hz) for complexes of  $\text{H}_2\text{XP}$  with  $\text{HN}=\text{NH}$ ,  $\text{FN}=\text{NH}$ , and  $\text{NH}=\text{CHOH}$

	PSO	DSO	FC	SD	${}^1\text{P}(\text{P}-\text{N}_1)$
<b>HNNH w.</b>					
$\text{H}_2\text{FP}$	-0.2	-0.1	-55.5	0.0	-55.8
$\text{H}_2\text{CIP}$	-0.3	-0.1	-55.7	0.1	-55.9
$\text{H}_2(\text{NC})\text{P}$	-0.2	0.0	-49.6	0.0	-49.8
$\text{H}_2(\text{OH})\text{P}$	-0.2	0.0	-37.0	0.0	-37.1
$\text{H}_2(\text{CN})\text{P}$	-0.1	0.0	-30.8	0.0	-30.9
$\text{H}_2(\text{CCH})\text{P}$	0.0	0.0	-20.9	0.0	-21.0
$\text{H}_2(\text{CH}_3)\text{P}$	0.0	0.0	-8.4	0.0	-8.3
$\text{H}_3\text{P}$	0.0	0.0	-10.2	0.0	-10.2
<b>FNNH w</b>					
$\text{H}_2\text{FP}$	-0.2	-0.1	-57.7	0	-57.9
$\text{H}_2\text{CIP}$	-0.2	-0.1	-41.7	0	-41.9
$\text{H}_2(\text{NC})\text{P}$	-0.1	-0.1	-47.1	0	-47.3
$\text{H}_2(\text{OH})\text{P}$	-0.1	-0.1	-21.5	0	-21.6
$\text{H}_2(\text{CN})\text{P}$	0	-0.1	-27.9	0	-28
$\text{H}_2(\text{CCH})\text{P}$	0	0	-8.7	0	-8.7
$\text{H}_2(\text{CH}_3)\text{P}$	0.1	0	1.1	0	1.2
$\text{H}_3\text{P}$	0.1	0	1.6	0	1.6
<b>NHCHOH w</b>					
$\text{H}_2\text{FP}$	-0.8	-0.1	-51.3	-0.1	-52.3
$\text{H}_2\text{CIP}$	-0.7	-0.1	-57.8	0.1	-58.5
$\text{H}_2(\text{NC})\text{P}$	-0.5	-0.1	-51.8	0.0	-52.4
$\text{H}_2(\text{OH})\text{P}$	-0.3	-0.1	-39.0	0.1	-39.3
$\text{H}_2(\text{CN})\text{P}$	-0.1	0.0	-36.6	0.1	-36.7
$\text{H}_2(\text{CCH})\text{P}$	0.0	0.0	-27.5	0.1	-27.5
$\text{H}_2(\text{CH}_3)\text{P}$	0.0	0.0	-16.0	0.1	-15.9
$\text{H}_3\text{P}$	0.0	0.0	-16.9	0.1	-16.8

Table S4. Components of spin-spin coupling constants J(N-P) (Hz) for complexes of H<sub>2</sub>XP with HN=NH and FN=NH, and <sup>2h</sup>J(O-P) for complexes with NH=CHOH

HNNH w	PSO	DSO	FC	SD	J(N <sub>2</sub> -P)
H <sub>2</sub> FP	0.7	0.0	-6.3	0.0	-5.6
H <sub>2</sub> CIP	0.5	0.0	-5.0	0.0	-4.5
H <sub>2</sub> (NC)P	0.4	0.0	-4.4	0.0	-4.0
H <sub>2</sub> (OH)P	0.3	0.0	-5.4	0.0	-5.0
H <sub>2</sub> (CN)P	0.1	0.0	-3.3	0.0	-3.1
H <sub>2</sub> (CCH)P	0.1	0.0	-4.5	0.1	-4.3
H <sub>2</sub> (CH <sub>3</sub> )P	0.1	0.0	-5.6	0.1	-5.3
H <sub>3</sub> P	0.1	0.0	-4.2	0.1	-4.1
FNNH w					
H <sub>2</sub> FP	0.2	0	0.2	0	0.4
H <sub>2</sub> CIP	0.1	0	-0.2	0	-0.1
H <sub>2</sub> (NC)P	0.1	0	0.4	0	0.4
H <sub>2</sub> (OH)P	0.1	0	-2.7	0.1	-2.5
H <sub>2</sub> (CN)P	0	0	0	0	0.1
H <sub>2</sub> (CCH)P	0.1	0	-4.1	0.1	-3.9
H <sub>2</sub> (CH <sub>3</sub> )P	0	0	-17.8	-0.3	-18 <sup>a</sup>
H <sub>3</sub> P	0.1	0	-12	-0.2	-12.1 <sup>a</sup>
NHCHOH w					<sup>2h</sup> J(O-P)
H <sub>2</sub> FP	0.4	0.0	-18.5	0.2	-17.9
H <sub>2</sub> CIP	0.4	0.0	-11.8	0.2	-11.2
H <sub>2</sub> (NC)P	0.3	0.0	-7.3	0.2	-6.9
H <sub>2</sub> (OH)P	0.0	0.0	-19.2	0.2	-19.1
H <sub>2</sub> (CN)P	0.0	0.0	-5.0	0.1	-4.8
H <sub>2</sub> (CCH)P	-0.1	0.0	-14.0	0.1	-14.0
H <sub>2</sub> (CH <sub>3</sub> )P	-0.2	0.0	-23.5	0.0	-23.8
H <sub>3</sub> P	-0.2	0.0	-16.1	0.1	-16.2

a) <sup>2h</sup>J(N-P)

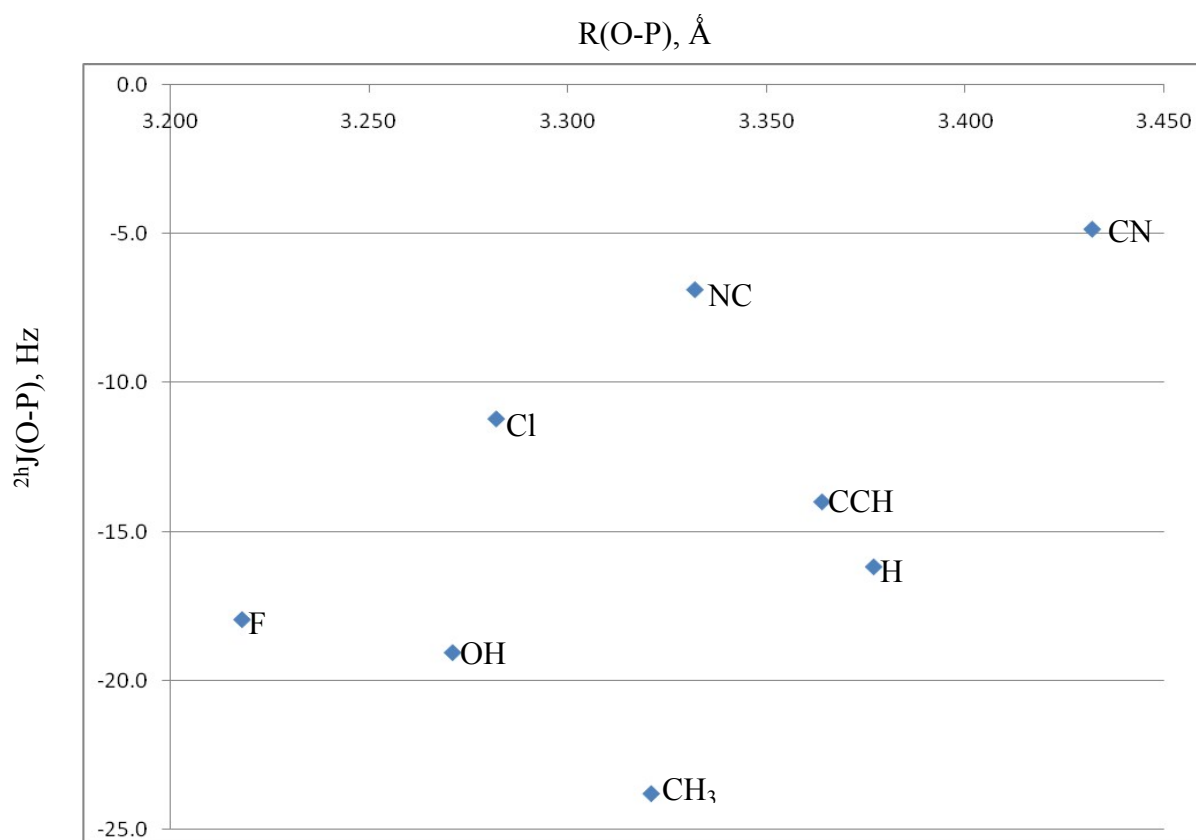


Figure S3.  ${}^2hJ(\text{O-P})$  versus the O-P distance for complexes  $\text{H}_2\text{XP}:\text{NH}=\text{CHOH}$