Supporting Information for

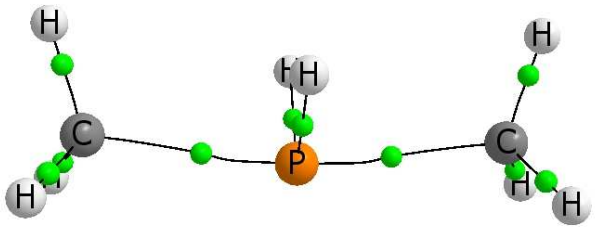
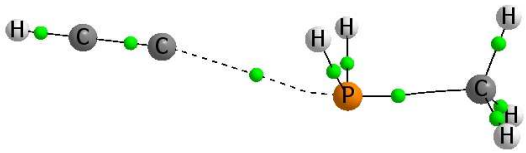
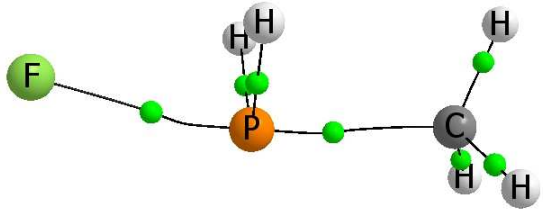
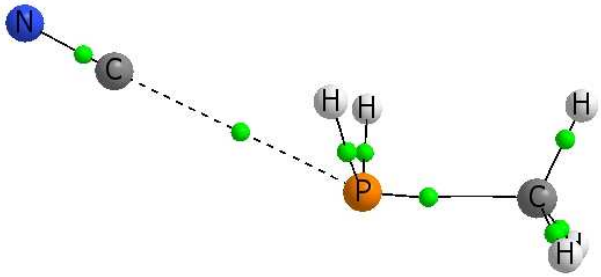
Pnicogen-Bonded Anionic Complexes

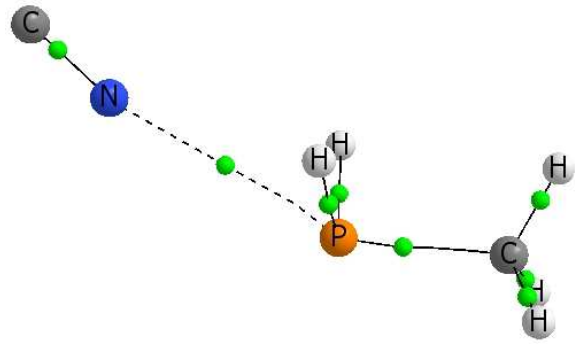
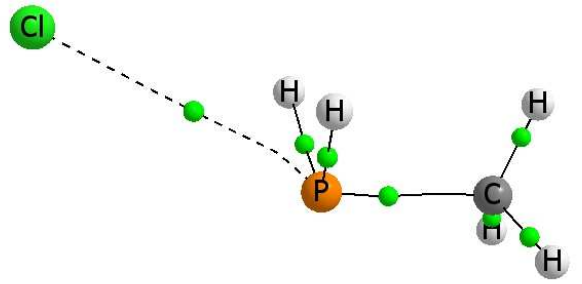
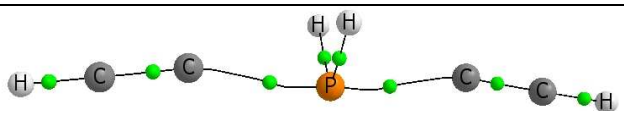
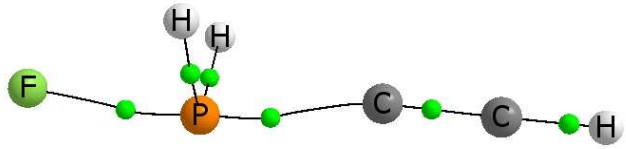
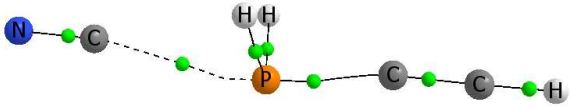
Janet E. Del Bene,[*,†] Ibon Alkorta,[*,‡] and José Elguero[‡]

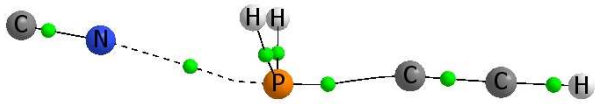
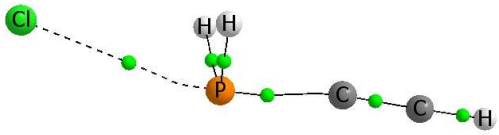
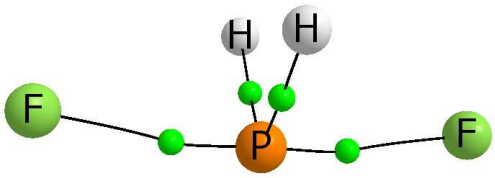
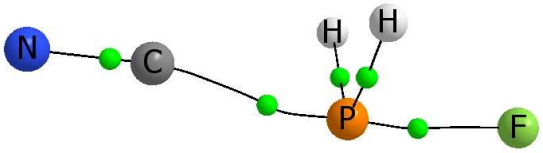
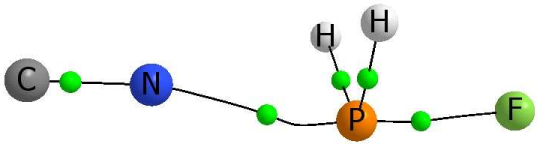
[†] Department of Chemistry, Youngstown State University, Youngstown, Ohio 44555 USA

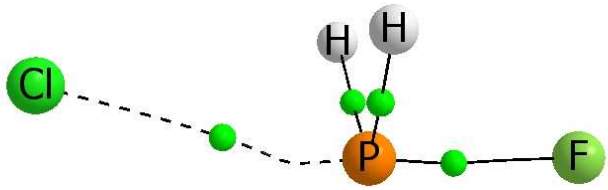
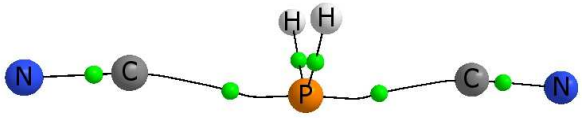
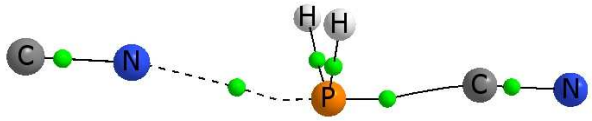
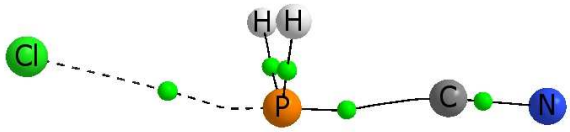
[‡] Instituto de Química Médica (IQM–CSIC), Juan de la Cierva, 3, E-28006 Madrid, Spain

Table S1. Structures (Å), total energies (au), and molecular graphs of complexes $H_2YP:X^-$

	$H_2(CH_3)P:CH_3$ MP2= -421.65324189 NIMAG= 0 P,0.,0.,0.17511391 C,-2.04914627,0.,-0.06290892 C,2.04914627,0.,-0.06290892 H,0.,1.12551038,-0.69834116 H,0.,-1.12551038,-0.69834116 H,-2.37034062,0.,-1.11385135 H,-2.44494104,0.89082122,0.43800953 H,-2.44494104,-0.89082122,0.43800953 H,2.37034062,0.,-1.11385135 H,2.44494104,-0.89082122,0.43800953 H,2.44494104,0.89082122,0.43800953
	$H_2(CH_3)P:CCH$ MP2= -458.45014070 NIMAG= 0 P,0.0684959441,0.,-0.3780798359 C,0.0532495235,0.,2.4974217348 C,-0.5115903609,0.,-2.1904929762 H,-0.773421361,-1.0453366152,0.0367659821 H,-0.773421361,1.0453366152,0.0367659821 C,0.222790153,0.,3.7393518026 H,0.3726298294,0.,4.798447948 H,-1.5951385534,0.,-2.313328808 H,-0.1065025696,-0.8790942957,-2.695104187 H,-0.1065025696,0.8790942957,-2.695104187
	$H_2(CH_3)P:F$ MP2= -481.65553567 NIMAG= 0 P,0.0129956167,0.,0.0350195859 F,-0.0352617988,0.,2.0866204687 C,-0.4127077349,0.,-1.8786334339 H,-0.8775531502,-1.0741648841,0.2352694765 H,-0.8775531502,1.0741648841,0.2352694765 H,-1.4806874274,0.,-2.1201901957 H,0.0412170834,-0.8806300445,-2.3436303236 H,0.0412170834,0.8806300445,-2.3436303236
	$H_2(CH_3)P:CN$ MP2= -474.58760637 NIMAG= 0 P,0.1960375431,0.,-0.3296039294 C,0.0745294418,0.,2.7833085978 C,-0.4925850893,0.,-2.0828970937 H,-0.6094217897,-1.0383178022,0.1682071167 H,-0.6094217897,1.0383178022,0.1682071167 N,-0.0146661472,0.,3.9698737921 H,-1.5806431686,0.,-2.1291268121 H,-0.1217596254,-0.879157208,-2.6113608613 H,-0.1217596254,0.879157208,-2.6113608613

	$H_2(CH_3)P:NC$ MP2= -474.58840493 NIMAG= 0 P,0.248908162,0.,-0.2228199994 N,0.107326099,0.,2.7492078736 C,-0.4910746314,0.,-1.9512567351 H,-0.5395100195,-1.0387466744,0.3016100683 H,-0.5395100195,1.0387466744,0.3016100683 C,-0.1928031913,0.,3.9014847136 H,-1.579867164,0.,-1.9629628255 H,-0.1370973306,-0.878676339,-2.4913319695 H,-0.1370973306,0.878676339,-2.4913319695
	$H_2(CH_3)P:Cl$ MP2= -841.67596515 NIMAG= 0 P,0.2430612941,0.,-0.0580338962 Cl,-0.2709337877,0.,3.2035831748 C,-0.3602083143,0.,-1.8394619272 H,-0.5845781385,-1.0375556443,0.4053870102 H,-0.5845781385,1.0375556443,0.4053870102 H,-1.4449104599,0.,-1.934164968 H,0.0344585827,-0.8789544913,-2.3500839379 H,0.0344585827,0.8789544913,-2.3500839379
	$H_2(CCH)P:CCH$ MP2= -495.23221372 NIMAG= 0 P,0.,0.,0.09856884 C,-2.06929066,0.,-0.09687925 C,2.06929066,0.,-0.09687925 H,0.,-1.07635645,-0.80008112 H,0.,1.07635645,-0.80008112 C,-3.29728779,0.,0.07273239 H,-4.35456631,0.,0.20590087 C,3.29728779,0.,0.07273239 H,4.35456631,0.,0.20590087
	$H_2(CCH)P:F$ MP2= -518.44269145 NIMAG= 0 P,-0.0157200073,0.,0.045251202 F,0.0797786414,0.,1.9576700087 C,-0.5229032214,0.,-1.831113698 H,-0.9085692209,-1.0749421474,0.2091639557 H,-0.9085692209,1.0749421474,0.2091639557 C,-0.6317694305,0.,-3.0615012198 H,-0.739027718,0.,-4.1200377435
	$H_2(CCH)P:CN$ MP2= -511.36331410 NIMAG= 0 P,0.0051798418,0.,-0.1880002808 C,0.0572380212,0.,2.4734944994 C,-0.5088227442,0.,-1.9634194307 H,-0.8588489964,-1.0513603011,0.1512132048 H,-0.8588489964,1.0513603011,0.1512132048 N,0.2256400486,0.,3.6495158867 C,-0.6808168919,0.,-3.1792439871 H,-0.8512650056,0.,-4.228463231

	$H_2(CCH)P:NC$ MP2= -511.36342433 NIMAG= 0 P,0.1951728306,-0.2598020736,0. N,-2.3996722731,0.0522116665,0. C,1.9934175614,0.0740248715,0. H,-0.0757614859,0.6303750422,-1.0500052219 H,-0.0757614859,0.6303750422,1.0500052219 C,-3.5873600609,0.1256931817,0. C,3.2184616609,0.1370478656,0. H,4.278452786,0.2138891996,0.
	$H_2(CCH)P:Cl$ MP2= -878.45108009 NIMAG= 0 P,0.3678874622,-0.2737829216,0. Cl,-2.5547492437,0.0594925738,0. C,2.1638217931,0.0629581519,0. H,0.0950756449,0.6204485154,-1.0474702761 H,0.0950756449,0.6204485154,1.0474702761 C,3.3889555074,0.1279506642,0. H,4.4486858855,0.2067345868,0.
	$H_2FP:F$ MP2= -541.63963116 NIMAG= 0 P,0.,0.,-0.15256031 F,0.,1.8263726,0.04071421 F,0.,-1.8263726,0.04071421 H,1.0600529,0.,0.77782834 H,-1.0600529,0.,0.77782834
	$H_2FP:CN$ MP2= -534.56629141 NIMAG= 0 P C,1,PCL X,1,1.,2,90. F,1,PHA,3,ANGA,2,180.,0 X,1,2.,2,ANGB,3,180.,0 H,1,PHB,5,ANGC,3,90.,0 H,1,PHB,5,ANGC,3,-90.,0 N,1,PN,3,APN,4,180.,0 PCL=2.02149252 PHA=1.8362855 ANGA=102.46290586 ANGB=80.85953187 PHB=1.40678956 ANGC=49.40695691 PN=3.19343416 APN=86.50479492
	$H_2FP:NC$ MP2= -534.55574842 NIMAG= 0 P N,1,PCL X,1,1.,2,90. F,1,PHA,3,ANGA,2,180.,0 X,1,2.,2,ANGB,3,180.,0 H,1,PHB,5,ANGC,3,90.,0 H,1,PHB,5,ANGC,3,-90.,0

	C,1,PN,3,APN,4,180.,0 PCL=2.13136084 PHA=1.75615735 ANGA=103.11436945 ANGB=75.7972221 PHB=1.40621338 ANGC=48.3420437 PN=3.31094805 APN=87.14185924
	H_2FP:Cl MP2= -901.63834574 NIMAG= 0 P Cl,1,PCL X,1,1.,2,90. F,1,PHA,3,ANGA,2,180.,0 X,1,2.,2,ANGB,3,180.,0 H,1,PHB,5,ANGC,3,90.,0 H,1,PHB,5,ANGC,3,-90.,0 PCL=2.59523376 PHA=1.73291113 ANGA=102.18717114 ANGB=74.5022337 PHB=1.40744846 ANGC=47.59269865
	$H_2(CN)P$:CN MP2= -527.48002786 NIMAG= 0 P,0.,0.,0.1565327 C,-2.0822674,0.,-0.07411822 C,2.0822674,0.,-0.07411822 H,0.,-1.06718339,-0.75080198 H,0.,1.06718339,-0.75080198 N,-3.26217537,0.,0.00313459 N,3.26217537,0.,0.00313459
	$H_2(CN)P$:NC MP2= -527.47674507 NIMAG= 0 P,0.0165856368,0.,-0.0326501616 N,0.0116170009,0.,2.3244182995 C,-0.4732933659,0.,-1.854346051 H,-0.8703889853,-1.0553583324,0.2193438638 H,-0.8703889853,1.0553583324,0.2193438638 C,0.1613971021,0.,3.5039496946 N,-0.6269525709,0.,-3.0225732656
	$H_2(CN)P$:Cl MP2= -894.56452691 NIMAG= 0 P,0.0185092007,0.,0.0644451607 Cl,-0.0060742962,0.,2.7860708145 C,-0.4348286767,0.,-1.7538320623 H,-0.8788277402,-1.0509107717,0.306803037 H,-0.8788277402,1.0509107717,0.306803037 N,-0.5649149481,0.,-2.9249366931

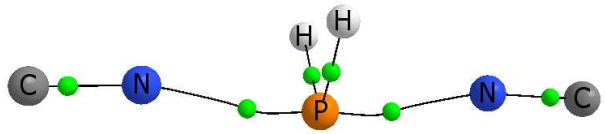
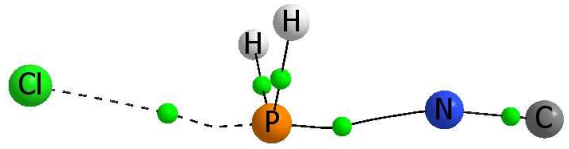
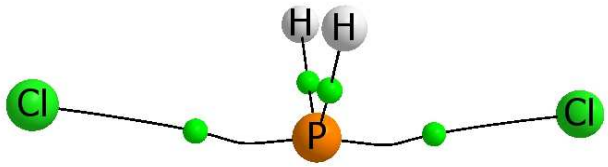
	$H_2(NC)P:NC$ MP2= -527.46096201 NIMAG= 0 P,0.,0.,0.18166083 N,-1.99002366,0.,-0.06685512 N,1.99002366,0.,-0.06685512 H,0.,-1.05617682,-0.73806845 H,0.,1.05617682,-0.73806845 C,-3.17564623,0.,-0.0262081 C,3.17564623,0.,-0.0262081
	$H_2(NC)P:Cl$ MP2= -894.54452983 NIMAG= 0 P,0.0096321282,0.,0.1538505379 Cl,0.0275645219,0.,2.630660378 N,-0.4371711282,0.,-1.7166449562 H,-0.9105362601,-1.0466238218,0.3091548085 H,-0.9105362601,1.0466238219,0.3091548085 C,-0.5244121962,0.,-2.8987175491
	$H_2ClP:Cl$ MP2= -1261.62632250 NIMAG= 0 P,0.,0.,0.19524272 Cl,-2.3757579,0.,-0.04188275 Cl,2.3757579,0.,-0.04188275 H,0.,-1.03661405,-0.75193748 H,0.,1.03661405,-0.75193748

Table S2. Binding energies (kJ/mol) of complexes $H_2YP:X^-$ relative to $H_2YP + X^-$ and $H_2XP + Y^-$ [a]

$H_2YP:X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	-70.0	-158.0	-240.8	-264.7	-346.4	-353.7
CCH	-24.0	-73.1	-242.9	-163.0	-242.9	-250.5
F	-57.4	-119.8	-180.5	-190.1	-242.0	-236.3
CN	-17.7	-50.0	-126.5	-102.2	-173.2	-181.1
NC	-19.8	-50.3	-98.5	-93.6	-131.8	-128.6
Cl	-19.4	-50.2	-85.4	-93.8	-120.9	-113.1

a) The diagonal elements are the binding energies of the symmetric C_{2v} complexes $(H_2XPX)^-$. The energies below the diagonal are the binding energies relative to the more stable monomers $H_2YP + X^-$. The energies above the diagonal are the binding energies relative to $Y^- + H_2XP$.

Table S3. P-A' distances (Å) in complexes $H_2YP:X^-$ [a,b]

$H_2YP:X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
	$P\text{-}CH_3$	P-CCH	P-F	P-CN	P-NC	P-Cl
X = CH3	*2.063*					
CCH	1.903	*2.079*				
F	*1.960*	*1.944*	*1.837*			
CN	1.884	1.848	*1.836*	*2.095*		
NC	1.880	1.829	*1.756*	1.886	*2.005*	
Cl	1.881	1.827	*1.733*	1.874	*1.924*	*2.388*

a) A' is the atom of Y directly bonded to P.
b) P-A' covalent bonds with some ion-molecule character are indicated in italics.

Table S4. Properties of the P-A BCPs (au) in complexes $H_2YP{:}X^{-}$[a]

ρ_{BCP}

$H_2YP{:}X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	0.108					
CCH	0.021	0.093				
F	0.069	0.087	0.098			
CN	0.013	0.031	0.099	0.089		
NC	0.014	0.027	0.068	0.045	0.087	
Cl	0.012	0.022	0.044	0.035	0.056	0.067

$\nabla^2\rho_{BCP}$

$H_2YP{:}X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	-0.145					
CCH	0.042	-0.086				
F	0.070	0.045	0.139			
CN	0.036	0.046	-0.087	-0.067		
NC	0.045	0.065	0.027	0.066	-0.013	
Cl	0.035	0.048	0.043	0.050	0.028	0.008

H_{BCP}

$H_2YP{:}X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	-0.070					
CCH	-0.001	-0.060				
F	-0.028	-0.055	-0.068			
CN	0.001	-0.004	-0.074	-0.054		
NC	0.001	-0.002	-0.032	-0.010	-0.059	
Cl	0.001	-0.001	-0.011	-0.006	-0.019	-0.027

a) A is the atom of X directly bonded to P.

Table S5. Properties of the P-A' BCPs (au) in Complexes $H_2YP{:}X^-$

ρ_{BCP}

$H_2YP{:}X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	0.108					
CCH	0.139	0.093				
F	0.126	0.115	0.098			
CN	0.143	0.135	0.099	0.089		
NC	0.144	0.140	0.113	0.125	0.087	
Cl	0.144	0.140	0.118	0.127	0.100	0.067

$\nabla^2\rho_{BCP}$

$H_2YP{:}X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	-0.145					
CCH	-0.147	-0.086				
F	-0.191	-0.064	0.139			
CN	-0.130	0.060	0.121	-0.067		
NC	-0.125	0.095	0.318	0.020	-0.013	
Cl	-0.125	0.098	0.386	0.038	0.033	0.008

H_{BCP}

$H_2YP{:}X^-$	$H_2(CH_3)P$	$H_2(CCH)P$	H_2FP	$H_2(CN)P$	$H_2(NC)P$	H_2ClP
$X = CH_3$	-0.070					
CCH	-0.133	-0.060				
F	-0.116	-0.100	-0.068			
CN	-0.139	-0.121	-0.070	-0.054		
NC	-0.140	-0.126	-0.078	-0.109	-0.059	
Cl	-0.139	-0.125	-0.079	-0.111	-0.076	-0.027

Table S6. ^{1p}J(P-A) and components (Hz) for complexes $H_2YP{:}X^-$

H2YP:Cl-	PSO	DSO	FC	SD	^{1p}J(P-Cl)
Y = CH3	2.3	0	18.1	0.5	21
CCH	5.9	0	43.7	1.8	51.5
F	18.2	0	59.9	7.1	85.2
CN	9.7	0	57.5	3.5	70.6
NC	18	0	61.7	8.5	88.3
Cl	25.6	0	47	12.9	85.5
H2YP:NC-					^{1p}J(P-N)
Y = CH3	-0.3	0	-25.6	0	-26
CCH	-0.7	0	-42.5	-0.1	-43.4
F	-1.8	-0.1	-1	-0.9	-3.8
CN	-1.2	-0.1	-34.5	-0.4	-36.2
NC	-1.5	-0.1	16.6	-1.2	13.7
H2YP:CN-					^{1p}J(P-C)
Y = CH3	0.3	0.1	73	-0.1	73.3
CCH	0.4	0.1	98.7	-0.1	99.1
F	-2.1	0.2	-79.3	0.2	-81
CN	-0.9	0.2	-36.6	0.5	-36.9
H2YP:F-					^{1p}J(P-F)
Y = CH3	101.9	0.3	132.3	39.2	273.7
CCH	86.4	0.3	94.7	49	230.4
F	126.3	0.4	-37.1	74.4	164.1
H2YP:CCH-					^{1p}J(P-C)
Y = CH3	0.6	0.1	95.3	-0.2	95.8
CCH	-1	0.1	-57.4	0.4	-57.8
H2YP:CH3-					^{1p}J(P-C)
Y = CH3	2.8	0.1	-39.5	3.7	-32.9

Table S7. ^{1}J(P-A') and components (Hz) for complexes $H_2YP{:}X^-$

H2(CH3)P:X-	PSO	DSO	FC	SD	^{1}J(P-C)
X = CH3	2.8	0.1	-39.5	3.7	-32.9
CCH	2.4	0.1	2.6	6.3	11.5
F	2.8	0.1	11.2	5.3	19.4
CN	2.3	0.1	-3.6	6.5	5.3
NC	2.3	0.1	-3.3	6.5	5.6
Cl	2.5	0.1	-5.4	6.5	3.6
H2(CCH)P:X-					^{1}J(P-C)
X = CCH	-1	0.1	-57.4	0.4	-57.8
F	-2.9	0.2	-85	0.5	-87.2
CN	-3.5	0.2	-44.9	1.8	-46.5
NC	-3.8	0.2	-36.1	1.8	-38
Cl	-3.9	0.2	-39.6	1.8	-41.5
H2FP:X-					^{1}J(P-F)
X = F	126.3	0.4	-37.1	74.4	164.1
CN	76.4	0.3	3.2	57.3	137.2
NC	88.4	0.3	-157.3	78	9.4
Cl	112.9	0.4	-305.9	91.7	-100.8
H2(CN)P:X-					^{1}J(P-C)
X = CN	-0.9	0.2	-36.6	0.5	-36.9
NC	-3.3	0.2	-60.7	1.3	-62.5
Cl	-3.5	0.2	-65.3	1.3	-67.2
H2(NC)P:X-					^{1}J(P-N)
X = NC	-1.5	-0.1	16.6	-1.2	13.7
Cl	-1.6	-0.1	34.3	-1.7	30.9
H2ClP:X-					^{1}J(P-Cl)
X = Cl	25.6	0	47	12.9	85.5

Full references (27) and (37)

(27) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T.; Montgomery, J., J. A.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, N. J.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, Ö.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. Gaussian 09, Gaussian, Inc., 2009.

(37) Stanton, J. F.; Gauss, J.; Watts, J. D.; Nooijen, M.; Oliphant, N.; Perera, S. A.; Szalay, P. G.; Lauderdale, W. J.; Gwaltney, S. R.; Beck, S.; Balkova, A.; Bernholdt, D. E.; Baeck, K.-K.; Tozyczko, P.; Sekino, H.; Huber, C.; Bartlett, R. J. ACES II is a program product of the Quantum Theorey Project, University of Florida. Integral packages included are VMOL (J. Almlöf and Taylor PR); VPROPS (P. R. Taylor); ABACUS (T Helgaker, H. J. Aa. Jensen, P. Jørgensen, J. Olsen, and P. R. Taylor). Brillouin-Wigner perturbation theory was implement by J. Pittner.