Supporting Information for

S_N2 versus E2 Competition of F^- and PH_2^- Revisited

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Table of Contents

Table S1: Computed Gibbs free energies of the stationary points (in kcal mol^{-1}) for the S_N2 and E2 reactions between **1** and the Lewis bases F^- and PH_2^-. **S2**

Table S2: Cartesian coordinates (in Å), energies (in kcal mol^{-1}), and number of imaginary frequencies of all stationary points, computed at ZORA-OLYP/QZ4P. **S3**

Table S1: Computed Gibbs free energies of the stationary points (in kcal mol^{-1}) for the S_N2 and E2 reactions between **1** and the Lewis bases F^- and PH_2^-. [a]

Lewis base	Stationary point [b]	E2	S_N2
F^-	RC	–15.8	–15.8
	TS	–16.0	–8.6
	PC	–33.6	–38.8
	P	–35.6	–36.3
PH_2^-	RC	–0.8	–0.8
	TS	5.6	5.9
	PC	–22.2	–35.4
	P	–27.2	–34.5

[a] Computed at ZORA-OLYP/QZ4P. [b] RC = reactant complex, TS = transition state, PC = product complex, and P = products.

Table S2: Cartesian coordinates (in Å), energies (in kcal mol^{-1}), and number of imaginary frequencies of all stationary points, computed at ZORA-OLYP/QZ4P.

Chloroethane (C_2H_5Cl)

E = −870.21
H = −826.18
G = −845.81
N_{imag} = 0

C	-0.000000	0.001627	0.775044
C	-0.000000	-0.003125	-0.742534
H	-0.886952	0.501383	1.172974
H	0.886952	0.501384	1.172973
H	0.000001	-1.033995	1.136421
Cl	0.000001	1.663284	-1.436517
H	-0.887477	-0.494030	-1.147525
H	0.887477	-0.494031	-1.147524

F^-

E = −91.22
H = −90.33
G = −100.00
N_{imag} = 0

F	0.000000	0.000000	0.000000

PH_2^-

E = −265.73
H = −255.45
G = −270.21
N_{imag} = 0

P	0.000000	-0.000000	0.677420
H	0.000000	1.032048	-0.326034
H	0.000000	-1.032048	-0.326034

H^+

E = 291.47
H = 292.36
G = 284.61
N_{imag} = 0

H	0.000000	0.000000	0.000000

Ethylene (C_2H_4)

E = −716.50
H = −682.70
G = −698.32
N_{imag} = 0

C	-0.000000	-0.000000	0.665693
C	0.000000	-0.000000	-0.665693
H	0.000000	0.924392	-1.237324
H	-0.000000	0.924392	1.237324
H	-0.000000	-0.924392	1.237324
H	0.000000	-0.924392	-1.237325

Cl^-
E = −87.76
H = −86.87
G = −97.14
N_{imag} = 0

Cl	0.000000	0.000000	0.000000

Fluoroethane (C_2H_5F)
E = −910.82
H = −866.13
G = −884.97
N_{imag} = 0

C	0.727300	0.233845	-0.015963
C	-0.711266	-0.238683	0.015206
H	0.971112	0.804959	0.883856
H	0.914579	0.860525	-0.892012
H	1.395314	-0.632833	-0.064278
F	-1.588795	0.857134	0.078270
H	-0.913342	-0.861702	0.894746
H	-0.970585	-0.805052	-0.887316

Ethylphosphane ($C_2H_5PH_2$)
E = −1087.41
H = −1032.55
G = −1053.33
N_{imag} = 0

C	0.706450	0.242292	-0.036473
C	-0.780477	-0.113200	0.058334
H	1.049319	0.785726	0.850048
H	0.915614	0.868658	-0.910080
H	1.316090	-0.663362	-0.127972
H	-1.820605	1.900905	-1.003334
H	-0.953864	-0.765315	0.922774
H	-1.101925	-0.666733	-0.828803
P	-1.865195	1.392968	0.329410
H	-3.121140	0.752528	0.113412

HF
E = −181.66
H = −173.83
G = −186.20
N_{imag} = 0

F	0.000000	0.000000	0.821452
H	0.000000	0.000000	-0.103412

PH_3
E = −349.91
H = −332.82
G = −347.80
N_{imag} = 0

P	0.061656	0.282457	0.065020
H	-0.238695	-1.044387	0.489727
H	-0.238732	-0.013173	-1.296382

H	1.445313	-0.013151	-0.105595

S_N2_RC: F^- + C_2H_5Cl

E = −982.00

H = −938.02

G = −961.58

N_{imag} = 0

C	0.517152	-0.000050	-0.349996
Cl	2.439341	-0.000673	-0.259806
H	0.327646	-0.891452	-0.949145
H	0.328220	0.891463	-0.949160
F	-2.812454	0.001069	0.307990
C	-0.204009	0.000195	0.940710
H	0.010040	0.894042	1.537608
H	-1.360984	0.000555	0.673247
H	0.009489	-0.893761	1.537641

S_N2_TS: F^- + C_2H_5Cl

E = −976.33

H = −931.75

G = −954.56

N_{imag} = 1, −342.878 cm^{-1}

C	0.003829	0.000176	0.020199
Cl	2.166988	-0.000646	-0.427244
H	-0.169073	-0.916064	-0.515327
H	-0.168325	0.916443	-0.515524
F	-2.135012	0.000800	-0.132362
C	0.003566	0.000279	1.520610
H	0.506659	0.886618	1.919114
H	-1.042138	-0.000085	1.840763
H	0.507303	-0.885660	1.919194

S_N2_PC: F^- + C_2H_5Cl

E = −1006.11

H = −959.80

G = −984.65

N_{imag} = 0

C	-1.170719	-0.004669	-0.002716
Cl	2.987701	0.021842	-0.518598
H	-0.975241	-0.880335	-0.630709
H	-0.972686	0.898608	-0.589364
F	-2.572807	-0.009329	0.274680
C	-0.353067	-0.035124	1.262581
H	0.709335	-0.028203	0.979693
H	-0.559431	0.841622	1.886424
H	-0.559775	-0.940523	1.843975

E2_RC: F^- + C_2H_5Cl

E = −982.01

H = −938.02

G = −961.59

N_{imag} = 0

C	0.157999	-0.000246	-0.138530
C	0.069461	-0.000912	1.337347
Cl	1.928413	0.000255	-0.892446
H	-0.272740	-0.891526	-0.596341
H	-0.272885	0.891394	-0.595494
H	0.521655	0.892688	1.782396
H	0.521271	-0.895103	1.781601
H	-1.088715	-0.000579	1.599524
F	-2.554524	0.000428	1.902160

E2_TS: F^- + C_2H_5Cl

E = −981.20

H = −939.00

G = −961.76

N_{imag} = 1, −263.212 cm^{-1}

C	0.108084	0.000008	-0.118978
C	-0.003124	-0.000019	1.330669
Cl	1.965712	0.000009	-0.907249
H	-0.272308	-0.896991	-0.606628
H	-0.272293	0.897034	-0.606593
H	0.410048	0.898152	1.801850
H	0.410033	-0.898216	1.801814
H	-1.242162	-0.000013	1.588405
F	-2.525895	-0.000007	1.920894

E2_PC: F^- + C_2H_5Cl

E = −996.48

H = −952.17

G = −979.40

N_{imag} = 0

C	-0.020451	-0.714845	1.351259
C	-0.150439	0.130547	2.381659
Cl	1.973758	0.170034	-1.530293
H	-0.397160	-1.735833	1.425370
H	0.489940	-0.434028	0.422525
H	0.243054	1.143766	2.321614
H	-0.620776	-0.155883	3.322081
H	-2.190785	0.277144	1.367287
F	-3.116152	0.432194	1.325853

S_N2_RC: PH_2^- + C_2H_5Cl

E = −1143.79

H = −1089.03

G = −1116.81

N_{imag} = 0

C	0.174508	0.039614	0.514960
C	0.956260	-0.021697	1.804252
Cl	2.770326	0.004801	1.566595
H	0.392887	-0.817091	-0.130293
H	-0.898729	0.019715	0.771488
H	0.380983	0.960836	-0.038814
H	0.743605	0.830913	2.451415
H	0.757022	-0.940158	2.358972
P	-3.870086	-0.028915	1.748888
H	-3.855746	-1.433612	2.055773
H	-3.684774	0.316841	3.132173

S_N2_TS: PH_2^- + C_2H_5Cl

E = −1137.87

H = −1083.64

G = −1110.12

N_{imag} = 1, −286.616cm^{-1}

C	0.030610	-0.001530	-0.049843
C	0.048161	0.013318	1.455955
Cl	2.246632	-0.003891	1.878417
H	0.477732	-0.924773	-0.431065
H	-0.987087	0.074094	-0.441533
H	0.610625	0.838344	-0.445093
H	-0.130957	0.936914	1.980698
H	-0.147837	-0.890412	2.007470
P	-2.878142	0.002575	1.853428
H	-2.910039	-1.390974	1.513871
H	-2.866152	-0.298959	3.256256

S_N2_PC: PH_2^- + C_2H_5Cl

E = −1180.72

H = −1124.22

G = −1151.41

N_{imag} = 0

C	-0.020451	-0.714845	1.351259
C	-0.150439	0.130547	2.381659
Cl	1.973758	0.170034	-1.530293
H	-0.397160	-1.735833	1.425370
H	0.489940	-0.434028	0.422525
H	0.243054	1.143766	2.321614
H	-0.620776	-0.155883	3.322081
H	-2.190785	0.277144	1.367287
F	-3.116152	0.432194	1.325853

E2_RC: PH_2^- + C_2H_5Cl

E = −1143.77

H = −1089.01

G = −1116.80

N_{imag} = 0

C	0.615848	-0.044067	0.084036
C	0.484512	0.011568	1.586163
Cl	2.087949	0.003759	2.468527
H	-0.015725	0.922771	1.918144
H	-0.058588	-0.849003	1.980073
H	1.119049	-0.958923	-0.244274
H	1.163017	0.819717	-0.306346
H	-0.402918	-0.033661	-0.341100
P	-3.431238	0.005794	-1.158704
H	-3.076969	-0.938552	-2.183602
H	-3.128525	1.116110	-2.020820

E2_TS: PH_2^- + C_2H_5Cl

E = −1134.83

H = −1083.63

G = −1110.46

N_{imag} = 1, −604.369 cm^{-1}

C	-0.104963	-0.068880	0.103595
C	0.022834	0.056829	1.501969
Cl	2.232435	0.000619	2.405605
H	-0.129049	1.028953	1.959500
H	-0.246609	-0.783459	2.133267
H	0.169397	-1.038192	-0.318450
H	0.282242	0.760068	-0.491928
H	-1.404932	-0.034340	-0.265654
P	-3.058729	-0.021616	-1.076090
H	-2.546883	-0.491971	-2.327625
H	-2.906853	1.345286	-1.473238

E2_PC: PH_2^- + C_2H_5Cl

E = −1161.84

H = −1109.58

G = −1138.23

N_{imag} = 0

C	2.625328	-1.298971	-1.879513
C	1.668796	-1.587640	-0.994719
Cl	0.560698	0.415200	2.241671
H	1.509802	-1.006594	-0.086051
H	0.996155	-2.429341	-1.158094
H	2.774457	-1.880812	-2.788683
H	3.305018	-0.463181	-1.724747
H	-1.745749	0.670578	1.394750
P	-3.105060	0.706245	0.910266
H	-2.809495	1.570969	-0.186083
H	-3.491388	1.797220	1.745805