Electronic Supplementary Material (ESI) for Physical Chemistry Chemical Physics.

Energetics and Kinetics of Various Cyano Radical Hydrogen Abstractions Supplementary Information:

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Contents

1 Reactants

1.1 CN ($^2\Sigma^+$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.044

D_1: 0.150

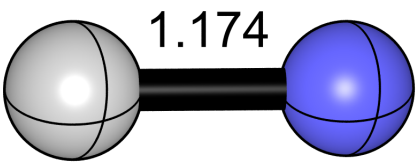

Figure S1: CN

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	-0.6319747809
N	0.0000000000	0.0000000000	0.5419298688

Rotational Constants (GHz): 56.7159810, 56.7159810

Harmonic Vibrational Frequencies (cm^{-1}):

a_1: 2071

1.2 H_2

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.005

D_1: 0.008

Figure S2: H_2

Cartesian Coordinates (Å):

H	0.0000000000	0.0000000000	-0.3709824635
H	0.0000000000	0.0000000000	0.3709824635

Rotational Constants (GHz): 1821.5695094,1821.5695094

Harmonic Vibrational Frequencies (cm^{-1}):

σ_g^+: 4401

1.3 CH_4

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.008

D_1: 0.014

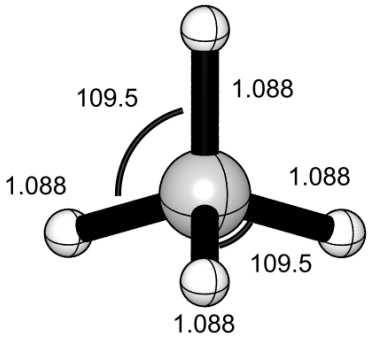

Figure S3: CH_4

Cartesian Coordinates (Å):

C	-0.0000000000	-0.0000000000	0.0000002049
H	-0.0002218767	0.0000000000	1.0878996099
H	0.5681112097	0.8540231244	-0.3625181658
H	0.4556610391	-0.9189462619	-0.3625411001
H	-1.0235503716	0.0649231378	-0.3628427853

Rotational Constants (GHz): 158.8678663, 158.8678664, 158.8680262

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:		3034
e:		1570
t_2:	3156	1346

1.4 NH_3

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.008

D_1: 0.017

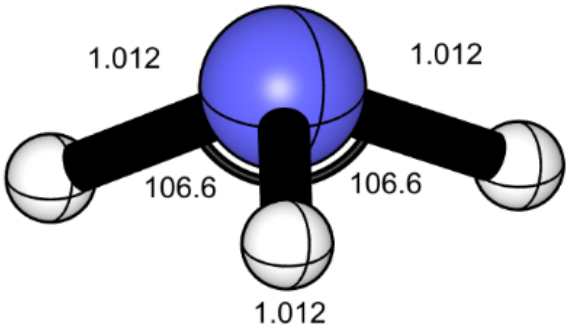

Figure S4: NH_3

Cartesian Coordinates (Å):

N	-0.0000004029	-0.0679223550	-0.0000000000
H	0.9373304824	0.3146230410	0.0000390111
H	-0.4686962260	0.3146253261	0.8117335062
H	-0.4686286573	0.3146253262	-0.8117725167

Rotational Constants (GHz): 298.5712125, 190.2256925, 298.5726454

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	3478	1056
e:	3609	1674

1.5 H_2O

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.009

D_1: 0.020

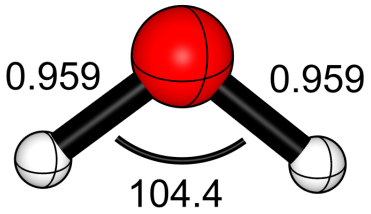

Figure S5: H_2O

Cartesian Coordinates (Å):

O	0.0000000000	-0.0657136648	0.0000000012
H	0.0000000000	0.5215485163	0.7576575163
H	0.0000000000	0.5215485019	-0.7576575348

Rotational Constants (GHz): 284.7781691, 436.7235659, 818.5133614

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	3834	1648
b_2:		3944

1.6 HF

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.009

D_1: 0.017

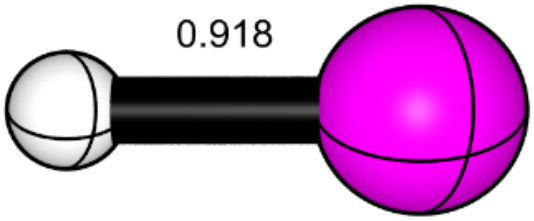

Figure S6: HF

Cartesian Coordinates (Å):

H	0.0000000000	0.0000000000	-0.8713491845
F	0.0000000000	0.0000000000	0.0462285013

Rotational Constants (GHz): 627.1153524, 627.1153524

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+: 4143

1.7 HCl

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.005

D_1: 0.013

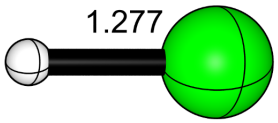

Figure S7: HCl

Cartesian Coordinates (Å):

H	0.0000000000	0.0000000000	-1.2414626581
Cl	0.0000000000	0.0000000000	0.0352951759

Rotational Constants (GHz): 316.3299504, 316.3299504

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+: 2994

1.8 C_2H_2

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.012

D_1: 0.030

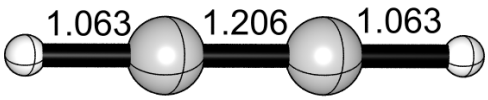

Figure S8: C_2H_2

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	-0.6029509599
C	0.0000000000	0.0000000000	0.6029509598
H	0.0000000000	0.0000000000	-1.6662535492
H	0.0000000000	0.0000000000	1.6662535502

Rotational Constants (GHz): 35.2669901, 35.2669901

Harmonic Vibrational Frequencies (cm^{-1}):

σ_g^+:	3503	3409	2008
σ_u^+:		753	615
π_u:			615

1.9 SiH_4

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1:	0.009
D_1:	0.019

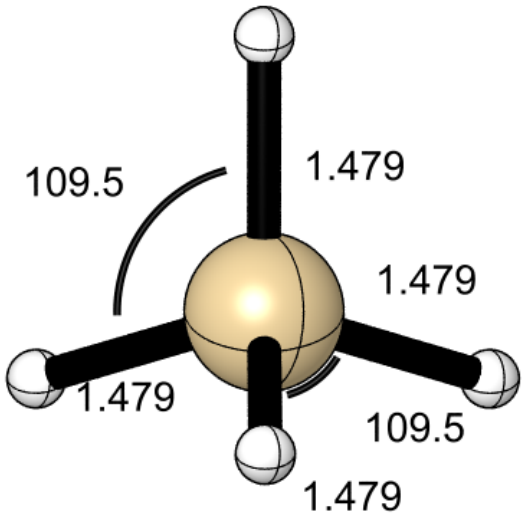

Figure S9: SiH_4

Cartesian Coordinates (Å):

Si	-0.0000009937	0.0000000027	0.0000000012
H	-1.4791576341	0.0023349088	-0.0000000000
H	0.4908623041	-1.3941102821	0.0584932404
H	0.4940815371	0.6452310537	-1.2359090023
H	0.4942414807	0.7465442442	1.1774157281

Rotational Constants (GHz): 85.9382004, 85.9375520, 85.9375533

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:		2260
e:		982
t_2:	2264	930

1.10 PH_3

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.010
D_1: 0.024

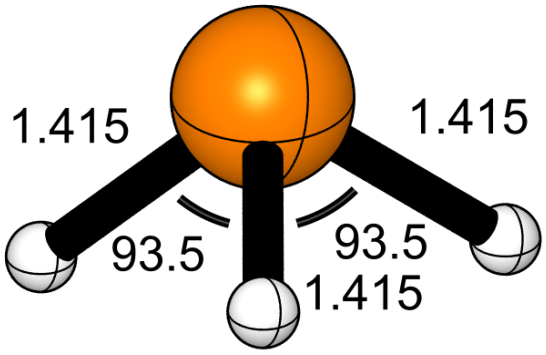

Figure S10: PH_3

Cartesian Coordinates (Å):

P	0.0000000411	-0.0680918703	-0.0000000155
H	1.1823453802	0.6974829675	-0.1383938055
H	-0.4713206072	0.6974820049	1.0931384206
H	-0.7110260354	0.6974822462	-0.9547441401

Rotational Constants (GHz): 134.5108534, 117.9403831, 134.5108205

Harmonic Vibrational Frequencies (cm^{-1}):

a_1: 2420 1013
e: 2428 1143

1.11 H_2S

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1:	0.008
D_1:	0.019

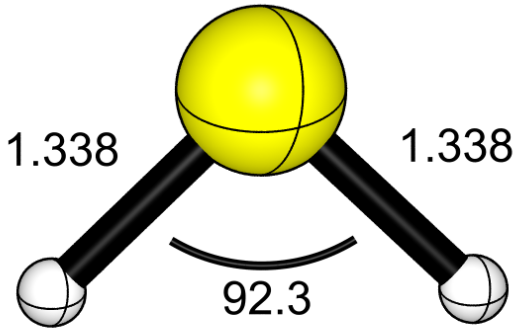

Figure S11: H_2S

Cartesian Coordinates (Å):

S	0.0000000000	-0.0548731756	-0.0000000001
H	0.0000000000	0.8726878618	0.9652217398
H	0.0000000000	0.8726878649	-0.9652217365

Rotational Constants (GHz): 143.9868205, 269.0904726, 309.7070385

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	2721	1213
b_2:		2737

1.12 HCN

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.013

D_1: 0.030

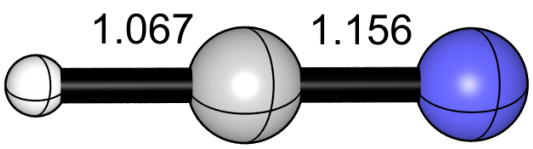

Figure S12: HCN

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	0.5591863743
H	0.0000000000	0.0000000000	1.6259526769
N	0.0000000000	0.0000000000	-0.5965181151

Rotational Constants (GHz): 44.3140612, 44.3140612

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	3437	2125
π:		729

1.13 HNC

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.014

D_1: 0.034

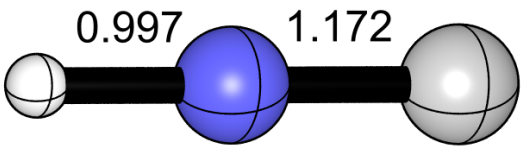

Figure S13: HNC

Cartesian Coordinates (Å):

N	0.0000000000	0.0000000000	0.4834305016
H	0.0000000000	0.0000000000	1.4800462604
C	0.0000000000	0.0000000000	-0.6879580247

Rotational Constants (GHz): 45.2604925, 45.2604925

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	3813	2053
π:		465

2 Products

2.1 CH_3 ($^2A_2''$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.006

D_1: 0.011

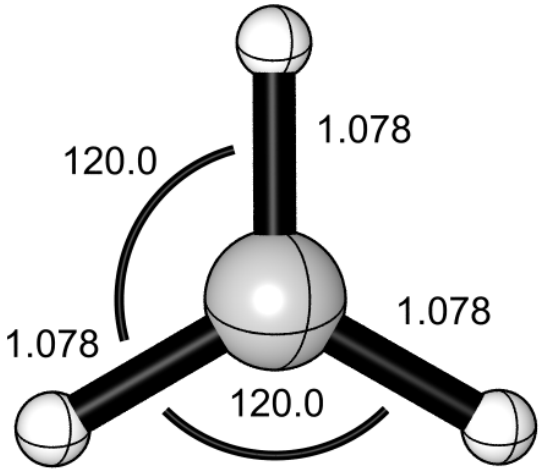

Figure S14: CH_3

Cartesian Coordinates (Å):

C	0.0000000000	-0.0000000000	-0.0000000000
H	0.0000000000	-1.0777093855	0.0000000000
H	0.0000000000	0.5388546928	0.9333237060
H	0.0000000000	0.5388546929	-0.9333237058

Rotational Constants (GHz): 143.8990480, 287.7980960, 287.7980959

Harmonic Vibrational Frequencies (cm^{-1}):

a_1':		3120
e:	3304	1421
a_2'':		518

2.2 NH_2 ($^2B_1$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.007

D_1: 0.014

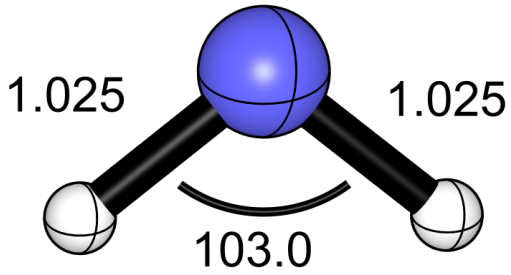

Figure S15: NH_2

Cartesian Coordinates (Å):

N	0.0000000000	-0.0802397172	-0.0000000000
H	0.0000000000	0.5575201136	0.8025151394
H	0.0000000000	0.5575201139	-0.8025151391

Rotational Constants (GHz): 250.8006512, 389.2656141, 705.0741749

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	3375	1541
b_2:		3470

2.3 OH ($^2\Pi$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.008

D_1: 0.017

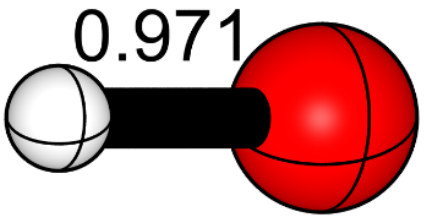

Figure S16: OH

Cartesian Coordinates (Å):

O	0.0000000000	0.0000000000	-0.0575165941
H	0.0000000000	0.0000000000	0.9129819196

Rotational Constants (GHz): 565.8814452, 565.8814452

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+: 3738

2.4 SiH_3 ($^2A_1$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.013

D_1: 0.035

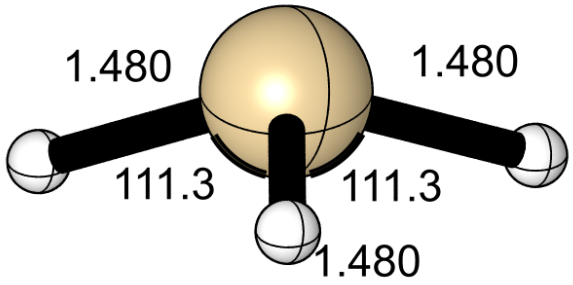

Figure S17: SiH_3

Cartesian Coordinates (Å):

Si	0.0000000003	-0.0435800318	0.0000001886
H	-0.0006845217	0.4047739671	-1.4106892395
H	1.2220361900	0.4047756383	0.7047491830
H	-1.2213516767	0.4047756361	0.7059348018

Rotational Constants (GHz): 142.0588464, 83.9843854, 142.0583091

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	2227	770
e:	2261	939

2.5 PH_2 ($^2B_1$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1:	0.009
D_1:	0.022

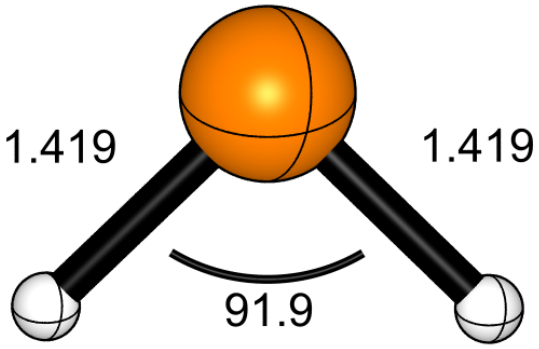

Figure S18: PH_2

Cartesian Coordinates (Å):

P	0.0000000000	-0.0603505120	-0.0000000001
H	0.0000000000	0.9272785444	1.0196157769
H	0.0000000000	0.9272785471	-1.0196157741

Rotational Constants (GHz): 128.2069785, 241.1456418, 273.7464142

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	2396	1128
b_2:		2404

2.6 SH ($^2\Pi$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.007

D_1: 0.018

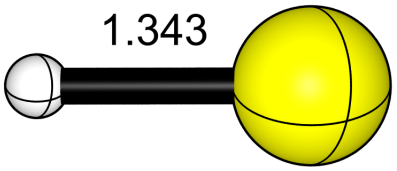

Figure S19: SH

Cartesian Coordinates (Å):

H	0.0000000000	0.0000000000	-1.3018375700
S	0.0000000000	0.0000000000	0.0409287010

Rotational Constants (GHz): 286.8305109, 286.8305109

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+: 2700

2.7 C_2H ($^2\Sigma^+$)

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.014

D_1: 0.032

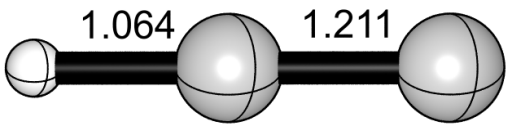

Figure S20: C_2H

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	-0.6725882558
C	0.0000000000	0.0000000000	0.5381060408
H	0.0000000000	0.0000000000	1.6025417027

Rotational Constants (GHz): 43.9464233, 43.9464233

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+: 3445 2020

π^+: 370

3 Pre-Reactive Complexes

3.1 $CN + H_2 \rightarrow HCN + H$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1:	0.041
D_1:	0.149

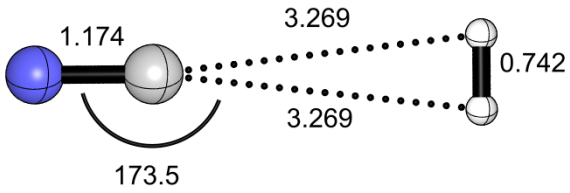

Figure S21: PRC ($CN + H_2 \rightarrow HCN + H$)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	-0.3529809957
N	0.0000000000	0.0000000000	0.8209492554
H	0.0000000000	0.3712222556	-3.6009758503
H	0.0000000000	-0.3712222556	-3.6009758503

Rotational Constants (GHz): 13.5293712, 13.6307420, 1819.2169740

Harmonic Vibrational Frequencies (cm^{-1}):

a_1:	4392	2071	85	$12i$
b_2:				160

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	-0.08	-0.28	+0.03	-0.04	-0.00	-0.00	[-0.37]
aug-cc-pVTZ	-0.05	-0.27	+0.04	-0.03	[-0.00]	[-0.00]	[-0.32]
aug-cc-pVQZ	-0.02	-0.26	+0.05	-0.03	[-0.00]	[-0.00]	[-0.27]
aug-cc-pV5Z	-0.01	-0.25	+0.04	-0.03	[-0.00]	[-0.00]	[-0.25]
CBS LIMIT	[-0.01]	[-0.23]	[+0.04]	[-0.03]	[-0.00]	[-0.00]	[-0.24]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= -0.23 + 0.34 - 0.01 + 0.00 - 0.07 + 0.19 = 0.22 \text{ kcal mol}^{-1}$$

3.2 $CN + H_2 \rightarrow HNC + H$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.041

D_1: 0.149

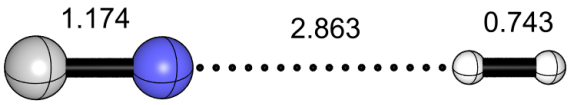

Figure S22: PRC ($CN + H_2$)

Cartesian Coordinates (Å):

N	0.0000000000	0.0000000000	-0.2702877289
C	0.0000000000	0.0000000000	0.9033919869
H	0.0000000000	0.0000000000	-3.1332849597
H	0.0000000000	0.0000000000	-3.8758644170

Rotational Constants (GHz): 14.0920604, 14.0920604

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	4391	2072	108
π:		181	22

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	-0.17	-0.40	+0.09	-0.05	-0.01	-0.00	[-0.55]
aug-cc-pVTZ	-0.15	-0.40	+0.09	-0.05	[-0.01]	[-0.00]	[-0.52]
aug-cc-pVQZ	-0.07	-0.37	+0.10	-0.04	[-0.01]	[-0.00]	[-0.40]
aug-cc-pV5Z	-0.06	-0.34	+0.10	-0.04	[-0.01]	[-0.00]	[-0.37]
CBS LIMIT	[-0.06]	[-0.31]	[+0.09]	[-0.04]	[-0.01]	[-0.00]	[-0.34]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= \text{-0.32 + 0.66 - 0.02 + 0.00 + 0.00 + 0.02} = 0.34 \text{ kcal mol}^{-1}$$

4 Transition States

4.1 $CN + H_2 \rightarrow HCN + H$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.028

D_1: 0.097

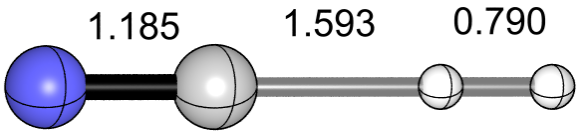

Figure S23: TS ($CN + H_2 \rightarrow HCN + H$)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	-0.4492016545
N	0.0000000000	0.0000000000	0.7358905242
H	0.0000000000	0.0000000000	-2.0417298808
H	0.0000000000	0.0000000000	-2.8316125133

Rotational Constants (GHz): 22.6706911, 22.6706911

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	3088	2001	$750i$
π :		431	132

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+12.50	-11.14	+2.87	-0.77	+0.21	-0.13	[+3.55]
aug-cc-pVTZ	+13.48	-11.60	+3.07	-0.84	[+0.21]	[-0.13]	[+4.20]
aug-cc-pVQZ	+13.71	-11.67	+3.11	-0.85	[+0.21]	[-0.13]	[+4.38]
aug-cc-pV5Z	+13.74	-11.65	+3.12	-0.85	[+0.21]	[-0.13]	[+4.44]
CBS LIMIT	[+13.74]	[-11.62]	[+3.12]	[-0.85]	[+0.21]	[-0.13]	[+4.48]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 4.40 - 0.37 + 0.08 - 0.02 + 0.03 + 0.11 = 4.24 \text{ kcal mol}^{-1}$$

4.2 $CN + H_2 \rightarrow HNC + H$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.059

D_1: 0.213

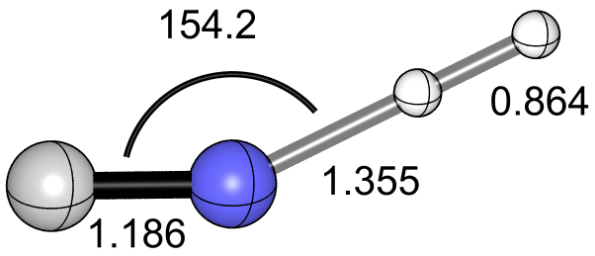

Figure S24: TS ($CN + H_2 \rightarrow HNC + H$)

Cartesian Coordinates (Å):

N	0.1272018683	0.0000000000	-0.3755122798
C	-0.0912393850	0.0000000000	0.7903786967
H	-0.2272181635	0.0000000000	-1.6832279975
H	-0.4531816168	0.0000000000	-2.5169730828

Rotational Constants (GHz): 26.9974073, 26.1783866, 862.9189757

Harmonic Vibrational Frequencies (cm^{-1}):

a':	$2337i$	2091	1845	779	103
a'':					782

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
cc-pVDZ	+26.03	-7.30	-0.46	-1.67	+0.06	-0.34	[+16.32]
cc-pVTZ	+26.92	-7.80	-0.05	-1.72	[+0.06]	[-0.34]	[+17.06]
cc-pVQZ	+27.19	-7.99	+0.06	-1.74	[+0.06]	[-0.34]	[+17.23]
cc-pV5Z	+27.23	-7.97	+0.10	-1.74	[+0.06]	[-0.34]	[+17.34]
CBS LIMIT	[+27.24]	[-7.95]	[+0.14]	[-1.74]	[+0.06]	[-0.34]	[+17.41]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 17.69 - 1.25 - 0.28 + 0.04 + 0.01 + 0.38 = 16.59 \text{ kcal mol}^{-1}$$

4.3 $CN + CH_4 \rightarrow HCN + CH_3$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.024

D_1: 0.097

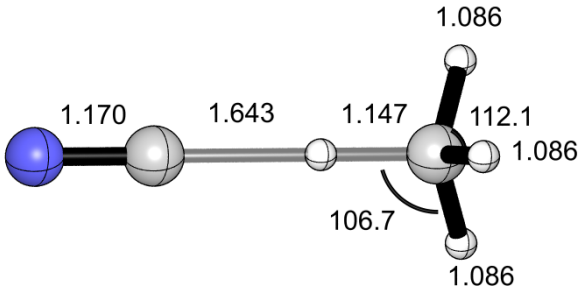

Figure S25: TS ($CN + CH_4 \rightarrow HCN + CH_3$)

Cartesian Coordinates (Å):

C	-0.0000000000	0.0000000000	0.6694214628
N	-0.0000000000	0.0000000000	1.8394835943
H	0.0000000000	0.0000000000	-0.9735927729
C	0.0000000000	0.0000000000	-2.1205017354
H	1.0407464759	0.0000000000	-2.4323030494
H	-0.5203732379	-0.9013128870	-2.4323030494
H	-0.5203732379	0.9013128870	-2.4323030494

Rotational Constants (GHz): 3.9710148, 3.9710148, 154.3019336

Harmonic Vibrational Frequencies (cm^{-1}):

a':	3189	3068	2115	1852	1481	1274	1214	$307.74i$	263	63
a'':						3189	1481	1274	262	63

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+9.57	-9.57	+2.92	-0.89	+0.28	-0.10	[+2.21]
aug-cc-pVTZ	+10.06	-10.13	+3.09	-0.90	[+0.28]	[-0.10]	[+2.29]
aug-cc-pVQZ	+10.24	-10.17	+3.12	-0.91	[+0.28]	[-0.10]	[+2.46]
aug-cc-pV5Z	+10.27	-10.12	+3.12	-0.90	[+0.28]	[-0.10]	[+2.54]
CBS LIMIT	[+10.27]	[-10.06]	[+3.11]	[-0.89]	[+0.28]	[-0.10]	[+2.60]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 2.43 - 1.37 - 0.17 - 0.06 - 0.08 + 0.10 = 1.19$ kcal mol^{-1}

4.4 $CN + CH_4 \rightarrow HNC + CH_3$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.045

D_1: 0.203

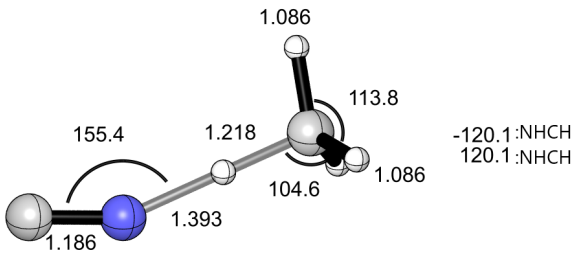

Figure S26: TS ($CN + CH_4 \rightarrow HNC + CH_3$)

Cartesian Coordinates (Å):

N	0.0000000000	-0.2099914824	0.6604948996
C	0.0000000000	0.1707590370	1.7838655116
H	0.0000000000	-0.0668530267	-0.7249558774
C	0.0000000000	0.0583250712	-1.9365666359
H	0.0000000000	1.1302368195	-2.1097668872
H	0.9094848134	-0.4375600668	-2.2620544093
H	-0.9094848134	-0.4375600668	-2.2620544093

Rotational Constants (GHz): 4.7058258, 4.7509181, 116.0661990

Harmonic Vibrational Frequencies (cm^{-1}):

a':	3066	$2040i$	2015	1448	1261	610	379	63	31
a'':						3205	1447	1196	376

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+24.36	-7.66	+0.35	-2.12	+0.18	-0.38	[+14.73]
aug-cc-pVTZ	+24.85	-8.14	+0.72	-2.08	[+0.18]	[-0.38]	[+15.14]
aug-cc-pVQZ	+25.16	-8.24	+0.85	-2.09	[+0.18]	[-0.38]	[+15.48]
aug-cc-pV5Z	+25.20	-8.14	+0.88	-2.08	[+0.18]	[-0.38]	[+15.67]
CBS LIMIT	[+25.21]	[-8.04]	[+0.91]	[-2.06]	[+0.18]	[-0.38]	[+15.82]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 16.02 - 3.26 - 0.20 + 0.13 + 0.04 + 0.06 = 12.79 \text{ kcal mol}^{-1}$$

4.5 $CN + NH_3 \rightarrow HCN + NH_2$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.045

D_1: 0.205

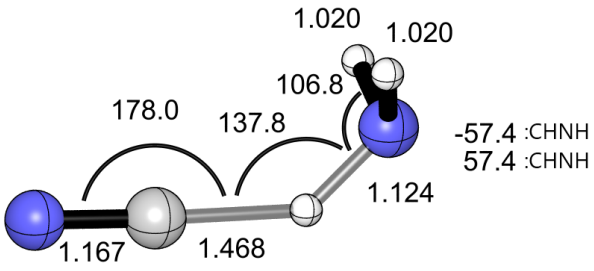

Figure S27: TS ($CN + NH_3 \rightarrow HCN + NH_2$)

Cartesian Coordinates (Å):

C	-0.1930371157	0.0000000000	0.5665903100
N	0.1240334970	0.0000000000	1.6899509343
H	-0.5417518488	0.0000000000	-0.8589157330
N	-0.0055362110	0.0000000000	-1.8470882501
H	0.5976874709	-0.8219316534	-1.8545773794
H	0.5976874709	0.8219316534	-1.8545773794

Rotational Constants (GHz): 5.0194476, 5.0036654, 166.1713330

Harmonic Vibrational Frequencies (cm^{-1}):

a':	3451	2160	1824	1580	1067i	862	380	127
a'':					3551	1453	562	152

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+5.39	-2.41	-2.08	-1.65	+0.28	-0.27	[-0.74]
aug-cc-pVTZ	+5.70	-3.21	-2.04	-1.57	[+0.28]	[-0.27]	[-1.13]
aug-cc-pVQZ	+5.97	-3.35	-1.98	-1.59	[+0.28]	[-0.27]	[-0.93]
aug-cc-pV5Z	+6.02	-3.32	-1.97	-1.58	[+0.28]	[-0.27]	[-0.84]
CBS LIMIT	[+6.02]	[-3.29]	[-1.96]	[-1.57]	[+0.28]	[-0.27]	[-0.79]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= -0.79 - 1.53 + 0.00 - 0.11 - 0.01 + 0.03 = -2.41$ kcal mol^{-1}

4.6 $CN + NH_3 \rightarrow HNC + NH_2$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.036

D_1: 0.163

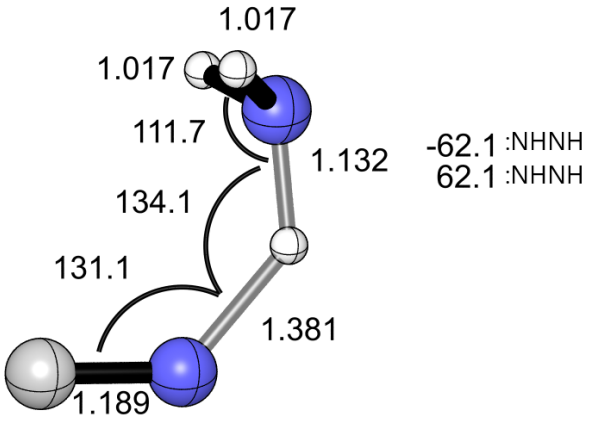

Figure S28: TS ($CN + NH_3 \rightarrow HNC + NH_2$)

Cartesian Coordinates (Å):

N	-0.5070289888	0.0000000000	-0.6798234275
C	0.4713907010	0.0000000000	-1.3559919725
H	-0.6617303346	0.0000000000	0.6923726031
N	0.0584015653	0.0000000000	1.5660884292
H	0.6393736215	0.8350936388	1.5751441262
H	0.6393736215	-0.8350936388	1.5751441262

Rotational Constants (GHz): 7.2401786, 6.6515466, 56.2229513

Harmonic Vibrational Frequencies (cm^{-1}):

a':	3476	1992	1903	1586	$902i$	794	409	132
a'':					3586	1450	513	154

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+4.91	+6.01	-1.44	-1.04	+0.01	-0.00	[+8.45]
aug-cc-pVTZ	+5.46	+5.31	-1.53	-0.78	[+0.01]	[-0.00]	[+8.47]
aug-cc-pVQZ	+5.76	+5.22	-1.51	-0.76	[+0.01]	[-0.00]	[+8.72]
aug-cc-pV5Z	+5.82	+5.28	-1.52	-0.74	[+0.01]	[-0.00]	[+8.84]
CBS LIMIT	[+5.83]	[+5.33]	[-1.53]	[-0.72]	[+0.01]	[-0.00]	[+8.91]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 8.91 - 1.68 + 0.00 + 0.04 - 0.01 + 0.01 = 7.27 \text{ kcal mol}^{-1}$$

4.7 $CN + H_2O \rightarrow HCN + OH$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)/aug-cc-pVTZ
Frequencies:	CCSD(T)/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.107

D_1: 0.503

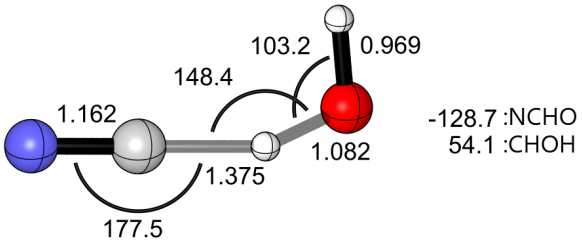

Figure S29: TS ($CN + H_2O \rightarrow HCN + OH$)

Cartesian Coordinates (Å):

C	0.5792365172	0.1057568987	0.0528501648
N	1.7251151012	-0.0677374396	-0.0349319533
H	-0.7706839662	0.3092592014	0.2160713101
O	-1.7829938575	0.0190036440	-0.0332787295
H	-1.7981330206	-0.9289223997	0.1681652006

Rotational Constants (GHz): 5.0247066, 4.9739375, 384.4788250

Harmonic Vibrational Frequencies (cm^{-1}):

a': 3767 2248 1563i 1514 1062 576 329 171 135

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+18.84	+6.47	-12.89	-2.20	+0.11	-0.67	[+9.66]
aug-cc-pVTZ	+18.47	+5.98	-12.81	-2.25	[+0.11]	[-0.67]	[+8.83]
aug-cc-pVQZ	+18.77	+6.16	-12.81	-2.32	[+0.11]	[-0.67]	[+9.25]
aug-cc-pV5Z	+18.81	+6.35	-12.85	-2.32	[+0.11]	[-0.67]	[+9.43]
CBS LIMIT	[+18.81]	[+6.54]	[-12.89]	[-2.31]	[+0.11]	[-0.67]	[+9.59]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 10.14 - 2.42 - 0.55 - 0.13 - 0.05 + 0.16 = 7.15$ kcal mol^{-1}

4.8 $CN + H_2O \rightarrow HNC + OH$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.095

D_1: 0.448

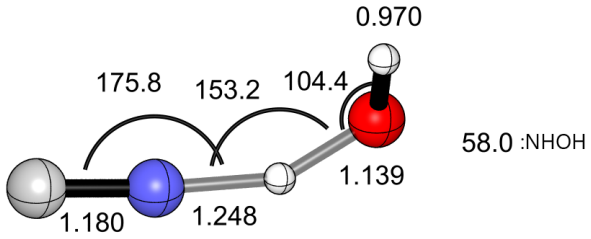

Figure S30: TS ($CN + H_2O \rightarrow HNC + OH$)

Cartesian Coordinates (Å):

N	0.0765387670	-0.1209349038	0.6115065409
C	-0.0635843563	0.1036718763	1.7613306402
H	0.1722998898	-0.2863148744	-0.6220040517
O	-0.0475444582	-0.0105527527	-1.7054502020
H	0.2764757917	0.8989840034	-1.7931704866

Rotational Constants (GHz): 5.3821932, 5.4377410, 335.4231434

Harmonic Vibrational Frequencies (cm^{-1}):

a: $3863i$ 3751 2123 1386 945 646 397 142 106

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+42.69	-14.59	-2.26	-4.66	-0.24	-1.45	[+19.50]
aug-cc-pVTZ	+42.93	-14.94	-1.83	-5.75	[-0.24]	[-1.45]	[+18.73]
aug-cc-pVQZ	+43.33	-14.85	-1.46	-5.92	[-0.24]	[-1.45]	[+19.41]
aug-cc-pV5Z	+43.38	-14.66	-1.38	-5.98	[-0.24]	[-1.45]	[+19.68]
CBS LIMIT	[+43.39]	[-14.46]	[-1.30]	[-6.04]	[-0.24]	[-1.45]	[+19.90]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 21.59 - 2.86 - 1.69 - 0.09 - 0.05 + 0.01 = 16.91$ kcal mol^{-1}

4.9 CN + HF → HCN + F

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.045

D_1: 0.198

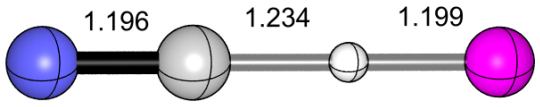

Figure S31: TS (CN + HF → HCN + F)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	0.6675335023
N	0.0000000000	0.0000000000	1.8631375133
H	0.0000000000	0.0000000000	-0.5665099344
F	0.0000000000	0.0000000000	-1.7655770898

Rotational Constants (GHz): 4.4519066, 4.4519066

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	7998i	2106	1136	
1101	566	164	49	

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+26.56	+5.48	-8.66	-2.09	-0.10	-0.54	[+20.65]
aug-cc-pVTZ	+27.00	+5.94	-8.59	-1.71	[-0.10]	[-0.54]	[+22.00]
aug-cc-pVQZ	+27.42	+6.66	-8.54	-1.69	[-0.10]	[-0.54]	[+23.20]
aug-cc-pV5Z	+27.48	+7.05	-8.58	-1.66	[-0.10]	[-0.54]	[+23.64]
CBS LIMIT	[+27.48]	[+7.46]	[-8.62]	[-1.64]	[-0.10]	[-0.54]	[+24.03]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 24.67 - 1.53 - 0.64 + 0.09 - 0.09 + 0.02 = 22.53 \text{ kcal mol}^{-1}$$

4.10 CN + HF → HNC + F

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.044

D_1: 0.203

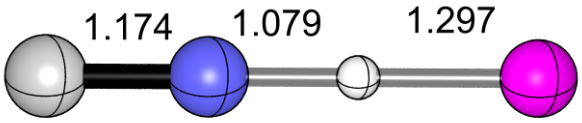

Figure S32: TS (CN + HF → HNC + F)

Cartesian Coordinates (Å):

N	0.0000000000	0.0000000000	0.6978316756
C	0.0000000000	0.0000000000	1.8719375340
H	0.0000000000	0.0000000000	-0.3807731160
F	0.0000000000	0.0000000000	-1.6777391342

Rotational Constants (GHz): 4.9289799, 4.9289799

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	2706i	2084	626
π:		366	197

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+59.29	-39.89	+16.09	-4.05	+0.40	-1.35	[+30.51]
aug-cc-pVTZ	+59.93	-40.58	+16.46	-4.45	[+0.40]	[-1.35]	[+30.41]
aug-cc-pVQZ	+60.45	-40.49	+16.81	-4.65	[+0.40]	[-1.35]	[+31.18]
aug-cc-pV5Z	+60.55	-40.29	+16.91	-4.72	[+0.40]	[-1.35]	[+31.51]
CBS LIMIT	[+60.57]	[-40.08]	[+17.02]	[-4.78]	[+0.40]	[-1.35]	[+31.78]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 32.72 - 3.40 - 0.94 - 0.03 - 0.08 - 0.01 = 28.25 \text{ kcal mol}^{-1}$$

4.11 CN + HCl → HCN + Cl

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.027

D_1: 0.137

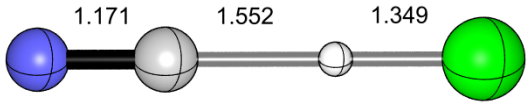

Figure S33: TS (CN + HCl → HCN + Cl)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	1.4085685018
N	0.0000000000	0.0000000000	2.5793511730
H	0.0000000000	0.0000000000	-0.1429663500
Cl	0.0000000000	0.0000000000	-1.4921843807

Rotational Constants (GHz): 2.5787448, 2.5787448

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	2114	1148	518i
π:		235	93

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+16.77	-13.47	+2.92	-1.59	+0.20	-0.21	[+4.62]
aug-cc-pV(T+d)Z	+16.96	-14.03	+3.30	-1.75	[+0.20]	[-0.21]	[+4.46]
aug-cc-pV(Q+d)Z	+17.15	-13.95	+3.46	-1.80	[+0.20]	[-0.21]	[+4.86]
aug-cc-pV(5+d)Z	+17.18	-13.89	+3.50	-1.80	[+0.20]	[-0.21]	[+4.98]
CBS LIMIT	[+17.18]	[-13.83]	[+3.55]	[-1.81]	[+0.20]	[-0.21]	[+5.08]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 5.09 - 1.64 - 0.01 - 0.09 + 0.06 + 0.06 = 3.47 \text{ kcal mol}^{-1}$$

4.12 CN + HCl → HNC + Cl

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.014

D_1: 0.044

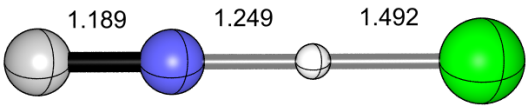

Figure S34: TS (CN + HCl → HNC + Cl)

Cartesian Coordinates (Å):

N	0.0000000000	0.0000000000	1.3470922075
C	0.0000000000	0.0000000000	2.5365431003
H	0.0000000000	0.0000000000	0.0980425130
Cl	0.0000000000	0.0000000000	-1.3943405797

Rotational Constants (GHz): 2.9445216, 2.9445216

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	2285i	1962	408
π:		537	207

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+34.69	-34.80	+14.94	-4.10	+0.87	-1.28	[+10.32]
aug-cc-pV(T+d)Z	+35.27	-35.85	+15.89	-4.49	[+0.87]	[-1.28]	[+10.41]
aug-cc-pV(Q+d)Z	+35.66	-36.00	+16.18	-4.61	[+0.87]	[-1.28]	[+10.82]
aug-cc-pV(5+d)Z	+35.74	-35.92	+16.27	-4.64	[+0.87]	[-1.28]	[+11.03]
CBS LIMIT	[+35.76]	[-35.84]	[+16.35]	[-4.67]	[+0.87]	[-1.28]	[+11.19]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 11.60 - 1.73 - 0.41 + 0.07 - 0.15 + 0.09 = 9.47$ kcal mol^{-1}

4.13 $CN + C_2H_2 \rightarrow HCN + C_2H$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.024

D_1: 0.083

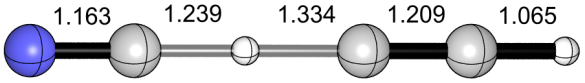

Figure S35: TS ($CN + C_2H_2 \rightarrow HCN + C_2H$)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	1.3015250371
C	0.0000000000	0.0000000000	2.5107935879
H	0.0000000000	0.0000000000	3.5761496032
H	0.0000000000	0.0000000000	-0.0321240518
C	0.0000000000	0.0000000000	-1.2710182629
N	0.0000000000	0.0000000000	-2.4342438807

Rotational Constants (GHz): 2.3911160, 2.3911160

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	3439	2210	2049	$1669i$	450
π:		705	594	184	66

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+29.45	-14.75	+3.34	-1.33	+0.39	-0.19	[+16.91]
aug-cc-pVTZ	+30.19	-14.90	+3.78	-1.34	[+0.39]	[-0.19]	[+17.94]
aug-cc-pVQZ	+30.48	-14.78	+3.90	-1.33	[+0.39]	[-0.19]	[+18.47]
aug-cc-pV5Z	+30.51	-14.62	+3.89	-1.32	[+0.39]	[-0.19]	[+18.67]
CBS LIMIT	[+30.51]	[-14.46]	[+3.89]	[-1.30]	[+0.39]	[-0.19]	[+18.84]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 18.64 - 3.55 + 0.20 - 0.11 + 0.05 + 0.02 = 15.25 \text{ kcal mol}^{-1}$$

4.14 $CN + C_2H_2 \rightarrow HNC + C_2H$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.059

D_1: 0.291

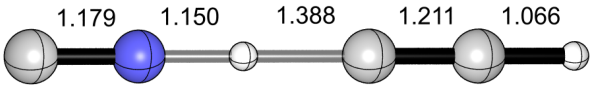

Figure S36: TS ($CN + C_2H_2 \rightarrow HNC + C_2H$)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	1.2436611786
C	0.0000000000	0.0000000000	2.4545628572
H	0.0000000000	0.0000000000	3.5201551011
H	0.0000000000	0.0000000000	-0.1443349062
N	0.0000000000	0.0000000000	-1.2939076582
C	0.0000000000	0.0000000000	-2.4726181587

Rotational Constants (GHz): 2.5226526, 2.5226526

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	3434	$2519i$	2106	2028	441
π:		712	359	140	$38i$

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+62.51	-37.68	+10.38	-4.71	+0.10	-0.27	[+30.33]
aug-cc-pVTZ	+63.64	-38.01	+11.17	-5.06	[+0.10]	[-0.27]	[+31.57]
aug-cc-pVQZ	+64.02	-37.97	+11.45	-5.15	[+0.10]	[-0.27]	[+32.17]
aug-cc-pV5Z	+64.19	-37.75	+11.33	-5.17	[+0.10]	[-0.27]	[+32.43]
CBS LIMIT	[+64.26]	[-37.51]	[+11.20]	[-5.19]	[+0.10]	[-0.27]	[+32.59]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 32.76 - 4.71 - 0.17 + 0.07 - 0.04 - 0.01 = 27.91$ kcal mol^{-1}

4.15 $CN + SiH_4 \rightarrow HCN + SiH_3$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.027

D_1: 0.135

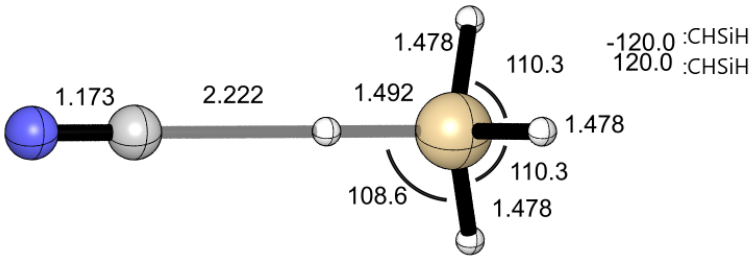

Figure S37: TS ($CN + SiH_4 \rightarrow HCN + SiH_3$)

Cartesian Coordinates (Å):

C	-0.0000002528	0.0000000000	1.7678150806
N	0.0000010680	0.0000000000	2.9411044838
H	-0.0000027540	0.0000000000	-0.4539749625
Si	-0.0000044339	0.0000000000	-1.9462478910
H	1.4007158027	0.0000000000	-2.4172983873
H	-0.7003006651	-1.2130971099	-2.4172960221
H	-0.7003006651	1.2130971099	-2.4172960221

Rotational Constants (GHz): 1.7675309, 1.7675332, 85.1840170

Harmonic Vibrational Frequencies (cm^{-1}):

a':	2274	2264	2113	2088	968	919	913	$844i$	750	66	19
a'':								2274	969	919	70

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+1.46	-2.74	+0.62	-0.35	+0.06	-0.03	[-0.97]
aug-cc-pV(T+d)Z	+1.60	-2.96	+0.70	-0.36	[+0.06]	[-0.03]	[-0.98]
aug-cc-pV(Q+d)Z	+1.77	-2.97	+0.74	-0.36	[+0.06]	[-0.03]	[-0.78]
aug-cc-pV(5+d)Z	+1.78	-2.90	+0.73	-0.35	[+0.06]	[-0.03]	[-0.71]
CBS LIMIT	[+1.78]	[-2.84]	[+0.71]	[-0.35]	[+0.06]	[-0.03]	[-0.66]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= -0.69 + 1.02 + 0.03 - 0.04 + 0.02 + 0.01 = 0.35$ kcal mol^{-1}

4.16 $CN + SiH_4 \rightarrow HNC + SiH_3$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.062

D_1: 0.333

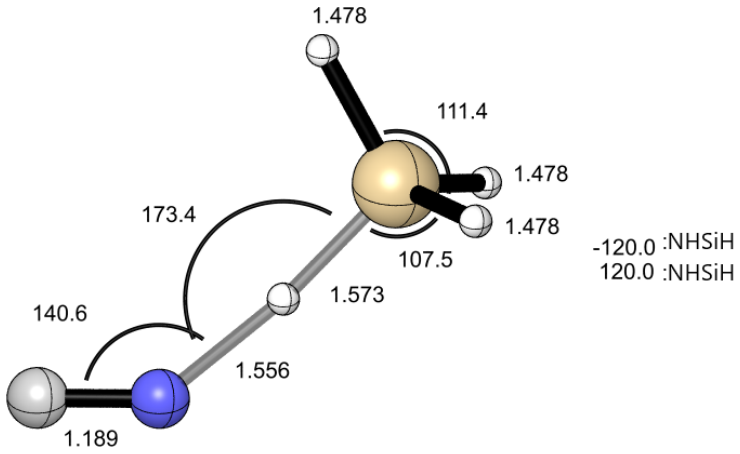

Figure S38: TS ($CN + SiH_4 \rightarrow HNC + SiH_3$)

Cartesian Coordinates (Å):

N	-0.0000000002	-0.3642314968	1.5069492427
C	0.0000000001	0.3236017559	2.4763922149
H	-0.0000000001	-0.2532467191	-0.0451714263
Si	0.0000000000	0.0391624289	-1.5907206166
H	0.0000000006	1.5067088210	-1.7636266496
H	1.2208278307	-0.5696819122	-2.1588532246
H	-1.2208278306	-0.5696819105	-2.1588532275

Rotational Constants (GHz): 2.5886166, 2.6312269, 55.1085223

Harmonic Vibrational Frequencies (cm^{-1}):

a: 2276 2254 1985 1455i 949 912 886 879 529 229 187 82 14

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+17.25	-1.83	-5.25	-1.70	+0.21	-0.44	[+8.23]
aug-cc-pV(T+d)Z	+17.34	-2.46	-4.91	-1.82	[+0.21]	[-0.44]	[+7.92]
aug-cc-pV(Q+d)Z	+17.61	-2.53	-4.84	-1.88	[+0.21]	[-0.44]	[+8.14]
aug-cc-pV(5+d)Z	+17.65	-2.44	-4.84	-1.88	[+0.21]	[-0.44]	[+8.26]
CBS LIMIT	[+17.65]	[-2.35]	[-4.85]	[-1.88]	[+0.21]	[-0.44]	[+8.35]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 8.57 - 2.09 - 0.22 - 0.01 - 0.04 + 0.15 = 6.36$ kcal mol^{-1}

4.17 $CN + PH_3 \rightarrow HCN + PH_2$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.026

D_1: 0.121

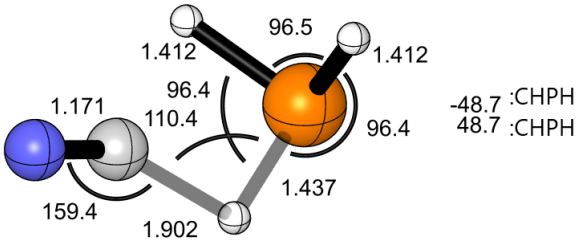

Figure S39: TS ($CN + PH_3 \rightarrow HCN + PH_2$)

Cartesian Coordinates (Å):

C	-0.0000000075	-0.0873996942	1.2534072381
N	0.0000000047	0.0573260226	2.4149894681
H	-0.0000000827	-0.9717416765	-0.4304532155
P	-0.0000000009	-0.0113581518	-1.4992755206
H	1.0532921202	0.7828199651	-0.9964066048
H	-1.0532919865	0.7828201520	-0.9964066140

Rotational Constants (GHz): 2.8928410, 2.8943724, 110.6984739

Harmonic Vibrational Frequencies (cm^{-1}):

a: 2458 2444 2234 2112 1113 1095 822 423i 307 187 67 55

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+6.38	-12.04	+3.69	-1.44	+0.28	-0.21	[-3.34]
aug-cc-pV(T+d)Z	+6.55	-13.07	+3.94	-1.53	[+0.28]	[-0.21]	[-4.03]
aug-cc-pV(Q+d)Z	+6.69	-13.25	+3.94	-1.56	[+0.28]	[-0.21]	[-4.11]
aug-cc-pV(5+d)Z	+6.71	-13.26	+3.92	-1.57	[+0.28]	[-0.21]	[-4.13]
CBS LIMIT	[+6.71]	[-13.28]	[+3.90]	[-1.57]	[+0.28]	[-0.21]	[-4.16]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
= -4.24 + 0.35 + 0.08 - 0.15 + 0.36 + 0.01 = -3.59 kcal mol^{-1}

4.18 $CN + PH_3 \rightarrow HNC + PH_2$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.076

D_1: 0.413

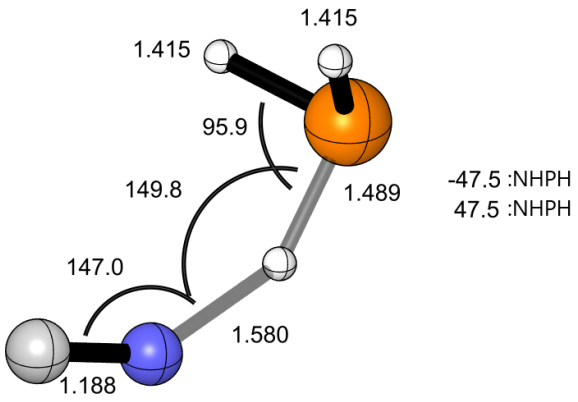

Figure S40: TS ($CN + PH_3 \rightarrow HNC + PH_2$)

Cartesian Coordinates (Å):

N	0.0000000001	-0.3995602301	1.4499044769
C	-0.0000000001	0.3634013428	2.3605469525
H	0.0000000001	-0.5894027024	-0.1187295886
P	-0.0000000000	-0.0014967831	-1.4862294390
H	1.0385583404	0.9287012664	-1.2436852534
H	-1.0385583397	0.9287012661	-1.2436852567

Rotational Constants (GHz): 2.9072600, 2.9711302, 62.5039513

Harmonic Vibrational Frequencies (cm^{-1}):

a: 2434 2424 2024 1240 1195*i* 1094 1048 774 295 246 81 51

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+16.93	-1.71	-8.05	-2.52	+0.79	-0.75	[+4.70]
aug-cc-pV(T+d)Z	+17.12	-1.47	-8.30	-2.75	[+0.79]	[-0.75]	[+4.65]
aug-cc-pV(Q+d)Z	+17.35	-1.44	-8.34	-2.84	[+0.79]	[-0.75]	[+4.77]
aug-cc-pV(5+d)Z	+17.39	-1.33	-8.38	-2.86	[+0.79]	[-0.75]	[+4.87]
CBS LIMIT	[+17.40]	[-1.20]	[-8.42]	[-2.87]	[+0.79]	[-0.75]	[+4.94]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 4.90 - 1.33 + 0.04 + 0.06 + 0.33 + 0.25 = 4.25$ kcal mol^{-1}

4.19 $CN + H_2S \rightarrow HCN + SH$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.025

D_1: 0.119

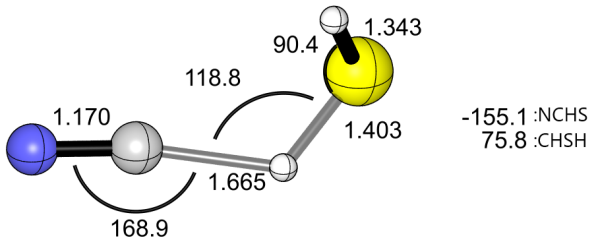

Figure S41: TS ($CN + H_2S \rightarrow HCN + SH$)

Cartesian Coordinates (Å):

C	-0.1359836200	-0.1005558394	1.2089899538
N	0.0873703345	0.0761492502	2.3434820405
H	-0.5004497750	-0.6596782401	-0.3163543654
S	-0.0096611295	0.0399881260	-1.4284198163
H	1.2140488054	-0.4721776587	-1.2219206511

Rotational Constants (GHz): 3.1116089, 3.0896794, 169.1724787

Harmonic Vibrational Frequencies (cm^{-1}):

a: 2705 2130 2005 1129 $987i$ 428 226 100 85

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+12.67	-16.58	+5.05	-1.93	+0.34	-0.29	[-0.73]
aug-cc-pV(T+d)Z	+12.84	-17.69	+5.59	-2.05	[+0.34]	[-0.29]	[-1.26]
aug-cc-pV(Q+d)Z	+13.02	-17.88	+5.74	-2.09	[+0.34]	[-0.29]	[-1.15]
aug-cc-pV(5+d)Z	+13.05	-17.88	+5.75	-2.09	[+0.34]	[-0.29]	[-1.11]
CBS LIMIT	[+13.06]	[-17.88]	[+5.77]	[-2.10]	[+0.34]	[-0.29]	[-1.10]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= -1.15 + 0.09 + 0.05 - 0.17 + 0.33 + 0.10 = -0.75$ kcal mol^{-1}

4.20 $CN + H_2S \rightarrow HNC + SH$

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.050

D_1: 0.268

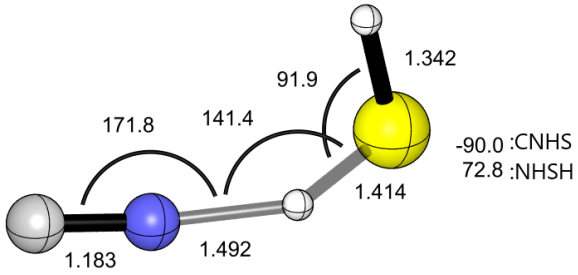

Figure S42: TS ($CN + H_2S \rightarrow HNC + SH$)

Cartesian Coordinates (Å):

N	-0.0866746370	0.1559174450	1.3010528157
C	0.0845121161	-0.1344158069	2.4350777736
H	-0.4243077877	0.3475393272	-0.1394762715
S	0.0309875258	0.0110286547	-1.4356594988
H	-0.3639429663	-1.2632677345	-1.2930813036

Rotational Constants (GHz): 3.0627876, 3.0957117, 178.6773960

Harmonic Vibrational Frequencies (cm^{-1}):

a: 2711 2481i 2035 1248 982 406 280 62 23

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pV(D+d)Z	+30.25	-23.28	+5.47	-3.90	+0.47	-1.22	[+7.79]
aug-cc-pV(T+d)Z	+30.61	-24.21	+6.37	-4.22	[+0.47]	[-1.22]	[+7.80]
aug-cc-pV(Q+d)Z	+30.88	-24.37	+6.59	-4.33	[+0.47]	[-1.22]	[+8.02]
aug-cc-pV(5+d)Z	+30.93	-24.29	+6.63	-4.35	[+0.47]	[-1.22]	[+8.16]
CBS LIMIT	[+30.94]	[-24.21]	[+6.67]	[-4.38]	[+0.47]	[-1.22]	[+8.27]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 9.03 - 1.45 - 0.76 - 0.04 + 0.67 + 0.03 = 7.47$ kcal mol^{-1}

4.21 CN + HCN → HCN + CN

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.026

D_1: 0.118

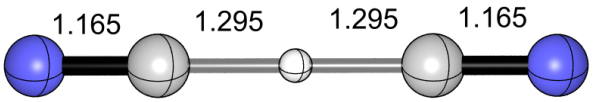

Figure S43: TS (CN + HCN → HCN + CN)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	1.2951575493
N	0.0000000000	0.0000000000	2.4604921202
H	0.0000000000	0.0000000000	0.0000000006
C	0.0000000000	0.0000000000	-1.2951575492
N	0.0000000000	0.0000000000	-2.4604921203

Rotational Constants (GHz): 2.4078391, 2.4078391

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	2198	2156	1895i	419
π:		829	224	102

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+36.50	-23.34	+5.79	-2.60	+0.32	-0.33	[+16.34]
aug-cc-pVTZ	+37.45	-23.58	+6.42	-2.79	[+0.32]	[-0.33]	[+17.50]
aug-cc-pVQZ	+37.71	-23.45	+6.61	-2.83	[+0.32]	[-0.33]	[+18.04]
aug-cc-pV5Z	+37.75	-23.28	+6.62	-2.83	[+0.32]	[-0.33]	[+18.26]
CBS LIMIT	[+37.75]	[-23.09]	[+6.64]	[-2.83]	[+0.32]	[-0.33]	[+18.47]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 18.47 - 2.87 - 0.00 + 0.02 - 0.00 + 0.15 = 15.77$ kcal mol^{-1}

4.22 CN + HCN → HNC + CN

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.033

D_1: 0.154

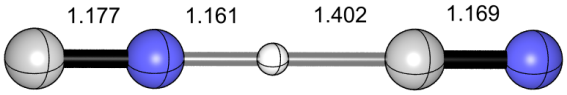

Figure S44: TS (CN + HCN → HNC + CN)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	1.2420848948
N	0.0000000000	0.0000000000	2.4106568533
H	0.0000000000	0.0000000000	-0.1603100495
N	0.0000000000	0.0000000000	-1.3214007314
C	0.0000000000	0.0000000000	-2.4988745718

Rotational Constants (GHz): 2.5343572, 2.5343572

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	2827i	2153	2064	431
π:		871	185	62

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+57.41	-40.72	+15.24	-5.37	+0.57	-0.26	[+26.86]
aug-cc-pVTZ	+58.41	-41.15	+16.25	-5.72	[+0.57]	[-0.26]	[+28.10]
aug-cc-pVQZ	+58.78	-41.06	+16.52	-5.82	[+0.57]	[-0.26]	[+28.73]
aug-cc-pV5Z	+58.85	-40.90	+16.57	-5.84	[+0.57]	[-0.26]	[+28.99]
CBS LIMIT	[+58.86]	[-40.72]	[+16.62]	[-5.86]	[+0.57]	[-0.26]	[+29.21]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 28.90 - 2.81 + 0.31 + 0.04 - 0.08 + 0.02 = 26.37$ kcal mol^{-1}

4.23 CN + HNC → HCN + CN

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	Molpro 2010.1

Wavefunction Diagnostics:

T_1: 0.033

D_1: 0.154

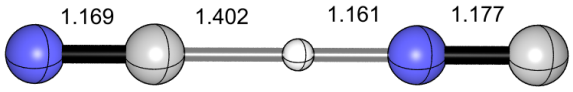

Figure S45: TS (CN + HNC → HCN + CN)

Cartesian Coordinates (Å):

C	0.0000000000	0.0000000000	1.2420848948
N	0.0000000000	0.0000000000	2.4106568533
H	0.0000000000	0.0000000000	-0.1603100495
N	0.0000000000	0.0000000000	-1.3214007314
C	0.0000000000	0.0000000000	-2.4988745718

Rotational Constants (GHz): 2.5343572, 2.5343572

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	2827i	2153	2064	431
π:		871	185	62

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+47.44	-48.31	+18.46	-5.57	+0.73	-0.59	[+12.16]
aug-cc-pVTZ	+48.66	-49.12	+19.47	-6.06	[+0.73]	[-0.59]	[+13.08]
aug-cc-pVQZ	+49.13	-49.08	+19.78	-6.19	[+0.73]	[-0.59]	[+13.78]
aug-cc-pV5Z	+49.19	-48.97	+19.84	-6.22	[+0.73]	[-0.59]	[+13.98]
CBS LIMIT	[+49.20]	[-48.85]	[+19.90]	[-6.26]	[+0.73]	[-0.59]	[+14.13]

$$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$$
$$= 13.99 - 2.83 + 0.14 + 0.04 - 0.08 + 0.02 = 11.27 \text{ kcal mol}^{-1}$$

4.24 CN + HNC → HNC + CN

Level of Theory:

Reference:	ROHF
Geometry:	CCSD(T)-F12a/aug-cc-pVTZ
Frequencies:	CCSD(T)-F12a/aug-cc-pVTZ
Program:	MOLPRO 2010.1

Wavefunction Diagnostics:

T_1: 0.016

D_1: 0.039

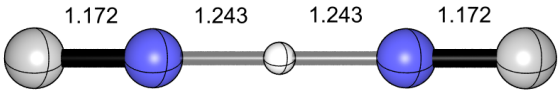

Figure S46: TS (CN + HNC → HNC + CN)

Cartesian Coordinates (Å):

N	0.0000000000	0.0000000000	1.2433472207
C	0.0000000000	0.0000000000	2.4156903194
H	0.0000000000	0.0000000000	-0.0000000002
N	0.0000000000	0.0000000000	-1.2433472207
C	0.0000000000	0.0000000000	-2.4156903194

Rotational Constants (GHz): 2.7542879, 2.7542879

Harmonic Vibrational Frequencies (cm^{-1}):

σ^+:	4232i	2131	2062	473
π:		1078	198	97

Incremental Focal Point Analysis Table (kcal mol^{-1}):

Basis	ROHF	+δMP2	+δCCSD	+δ(T)	+δT	+δ(Q)	Net
aug-cc-pVDZ	+51.07	-51.52	+21.84	-6.86	+1.12	-1.45	[+14.20]
aug-cc-pVTZ	+52.01	-52.62	+23.11	-7.35	[+1.12]	[-1.45]	[+14.83]
aug-cc-pVQZ	+52.53	-52.73	+23.41	-7.48	[+1.12]	[-1.45]	[+15.40]
aug-cc-pV5Z	+52.59	-52.58	+23.44	-7.50	[+1.12]	[-1.45]	[+15.63]
CBS LIMIT	[+52.59]	[-52.42]	[+23.48]	[-7.53]	[+1.12]	[-1.45]	[+15.80]

$\Delta H_{0K} = \Delta E_{CCSD(T)/CBS} + \delta_{ZPVE} + \delta_{T(Q)} + \delta_{CORE} + \delta_{REL} + \delta_{DBOC}$
$= 16.13 - 2.08 - 0.33 + 0.06 + 0.00 + 0.07 = 13.85$ kcal mol^{-1}