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Supporting Information

CO Assisted N_2 Functionalization Activated by Dinuclear Hafnium Complex: A DFT Mechanisitic Exploration

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Table S1. Calculated imaginary frequencies of transition states at B3LYP/BSI level.

The simplified model*

TS4-5	**TS6-7**	**TS7-I_a**	**TSI_a-I_{bA}**	**TS5-I_c**	**TSI_c- I_d**	**TSI_{dA}-I_{bA}**	**TSI_{bA}-12_A**
342.93 *i*	408.15 *i*	311.29 *i*	194.44 *i*	122.04 *i*	116.51 *i*	199.84 *i*	135.47 *i*

$TS12_A$-2_A	**TS8-12_A**	**TSI_{dB}-I_{eB}**	**TSI_{eB}-I_{bB}**	**TSI_{bB}-12_B**	**$TS12_B$-2_B**
115.55 *i*	318.44 *i*	221.23 *i*	36.58 *i*	207.68 *i*	248.51 *i*

* Simplified model: all tertiary butyl and methyl groups on the ring of cyclopentadienyl ligand are simplified to hydrogen atoms.

The full model

TS1-4_{A1}	**TS1-4_{A3}**	**TS4_{A2}-5_{A2}**	**TS4_{A1}-5_{A1}**	**TS5_{A1}-I_c**	**TSI_c-Id_{A1}**	**TSIda_A-Ib_A**	**TSIb_A -12_A**
53.54 *i*	83.19*i*	148.52 *i*	302.97 *i*	351.38 *i*	148.52 *i*	346.54 *i*	110.61 *i*

$TS12_A$ -2_A	**TS5_{A1}-6**	**TS6-7**	**TS7-Ia**	**TSIa-Ib**	**TS4_{A3}-5_{A3}**	**TS5_{A3}-Ic**	**TSIc-Id_C**	**TSIda_C-Ib_C**
140.55 *i*	54.37*i*	235.59 *i*	360.03 *i*	172.63 *i*	306.47 *i*	327.52 *i*	71.44 *i*	40.94 *i*

TSIb_C-12_C	**$TS12_C$ -2_C**	**TSId_B-I_{eB}**	**TSI_{eB}-Ib_B**	**TSIb_B-12_B**	**TSIb_B-12_B**	**TS8-12_A**	**TSId_A-Ida_A**
91.55 *i*	150.72 *i*	54.21 *i*	212.58 *i*	190.42 *i*	196.50 *i*	313.90 *i*	66.87*i*

TSId_C-Ida_C
346.54 *i*

Table S2. Relative energies of stationary points calculated at B3LYP/BSI level including potential energies with zero-point correction, free energies and potential energy with solvent effect. (unit: kcal/mol)

The simplified model*

	Relative free energy	Relative potential energy with zero-point correction	Relative potential energy with solvent effect
1	0.0	0.0	0.0
2_A	-83.2	-105.1	-108.1
4	1.8	-8.4	-8.3
5	0.7	-10.0	-12.0
6	0.8	-20.3	-21.9
7	0.0	-21.6	-24.7
I_a	-74.8	-97.3	-99.5
8	-61.1	-81.6	-81.4
12_A	-68.8	-90.4	-91.3
I_{bA}	-61.5	-83.4	-85.3
TSI_a-Ib_A	-46.6	-69.3	-71.4
TS4-5	9.3	-1.5	-2.1
TS6-7	5.8	-14.8	-16.9
TS7-I_a	5.4	-16.3	-19.6
TS8-12_A	-54.5	-77.2	-77.8
$TS2_A$-12_A	-61.6	-83.6	-85.2
TSI_{bA}-12_A	-54.0	-76.1	-79.2
I_c	-67.5	-78.5	-79.4
I_d	-64.8	-76.1	-76.6
TS5-I_c	0.9	-9.7	-11.5
TSI_c-I_{dA}	-50.9	-61.3	-62.1
TSI_{dA}-I_{bA}	-49.5	-71.0	-71.1
I_{dA}	-51.1	-72.3	-72.1
I_{dB}	-63.8	-82.8	-83.2
TSI_{dB}-I_{eB}	-61.8	-80.7	-81.6
I_{eB}	-66.2	-85.8	-88.6
TSI_{eB} -I_{bB}	-63.2	-84.7	-86.2
I_{bB}	-66.6	-88.5	-90.0
TSI_{bB}-12_B	-49.6	-71.6	-73.5
12_B	-70.8	-92.2	-93.3
$TS12_B$-2_B	-57.0	-79.9	-82.4
2_B	-79.9	-101.5	-104.8

* Simplified model: all tertiary butyl and methyl groups on the ring of cyclopentadienyl ligand are simplified to hydrogen atoms.

The full model

	Relative potential energy	Relative potential energy with zero-point correction	Relative free energy	Relative potential energy with solvent effect	Relative free energy with solvent effect
1	0.0	0.0	0.0	0.0	0.0
4_{A1}	-7.1	-5.3	5.2	-4.3	6.9
$TS4_{A1}$-5_{A1}	-2.6	-0.7	11.3	-0.2	12.3
5_{A1}	-12.8	-10.2	0.1	-11.5	1.6
$TS5_{A1}$-Ic	-8.4	-6.1	5.8	-6.5	4.2
Ic	-63.9	-61.3	-52.0	-62.3	-52.5
TSIc-Id_A	-49.0	-46.3	-35.9	-46.5	-36.0
Id_A	-64.8	-61.4	-50.7	-60.3	-51.0
Id_{aA}	-65.4	-60.5	-39.6	-58.4	-38.0
$TSIda_A$-Ib_A	-46.4	-40.9	-17.8	-39.0	-17.4
Ib_A	-86.3	-79.6	-56.6	-78.3	-55.7
TSIb$_A$ -12$_A$	-82.3	-76.1	-53.3	-75.3	-52.8
12_A	-100.1	-93.9	-72.4	-92.4	-71.7
$TS12_A$ -2_A	-94.5	-88.9	-67.0	-88.0	-66.5
2_A	-121.2	-114.6	-94.4	-115.1	-92.6
6	-23.6	-18.9	2.6	-18.2	2.8
TS6-7	-19.8	-14.9	7.5	-14.1	9.7
7	-34.9	-28.7	-6.4	-29.4	-5.5
TS7-Ia	-25.2	-20.3	2.5	-20.1	1.3
Ia	-83.5	-76.8	-54.9	-76.4	-54.6
TSIa-Ib	-67.4	-60.9	-38.8	-60.1	-37.4
4_{A3}	-0.3	1.3	11.4	2.2	11.3
$TS4_{A3}$-5_{A3}	8.0	9.5	20.7	9.6	20.1
5_{A3}	-11.7	-9.0	2.0	-10.2	0.5
$TS5_{A3}$-Ic	-7.2	-4.4	7.5	-5.0	7.4
TSIc-Id_C	-57.2	-55.2	-45.9	-57.3	-48.4
Id_C	-65.3	-62.1	-52.4	-61.2	-49.9
Ida_C	-64.3	-60.4	-40.6	-59.5	-41.3
$TSIda_C$-Ib_C	-61.0	-56.1	-33.8	-54.7	-32.9
Ib_C	-84.4	-78.0	-56.7	-77.5	-56.1
$TSIb_C$-12_C	-83.9	-77.4	-55.6	-77.0	-54.0
12_C	-99.4	-93.2	-71.5	-91.9	-70.7
$TS12_C$ -2_C	-94.7	-89.2	-71.5	-88.1	-66.7
2_C	-121.3	-114.3	-93.1	-114.5	-93.9
Id_B	-88.1	-80.7	-57.3	-82.7	-63.4
$TSId_B$-I_{eB}	-83.1	-78.1	-56.6	-77.5	-56.7
I_{eB}	-91.7	-85.3	-63.3	-85.8	-64.0
TS I_{eB} -Ib_B	-85.6	-79.0	-55.8	-79.1	-56.2
Ib_B	-90.6	-83.9	-60.8	-82.4	-59.7
$TSIb_B$-12_B	-78.1	-72.2	-50.1	-71.5	-48.1
12_B	-102.2	-96.0	-74.6	-94.1	-73.0
$TS12_B$ -2_B	-93.5	-87.8	-66.5	-86.9	-65.7

2_B	-117.8	-111.0	-90.1	-111.7	-93.0
8	-91.4	-86.1	-66.9	-84.0	-65.5
TS8-12_A	-86.6	-80.9	-58.0	-78.8	-56.2
TS1-4_{A1}	4.2	4.7	14.4	5.5	14.3
TS1-4_{A3}	8.4	9.1	19.4	9.9	19.7
TS5_{A1}-6	-10.6	-7.2	13.9	-7.6	12.3
TSId_A-Id_{aA}	-60.2	-56.9	-34.3	-53.7	-32.6
TSId_C-Id_{aC}	-60.5	-57.3	-37.3	-56.3	-36.8

Table S3. Energies of stationary points calculated at B3LYP/BSI level including potential energies with zero-point correction, free energies and potential energies with solvent effect. (unit: a.u.)

The simplified model*

	Free energy	Potential energy with zero-point correction	Potential energy with solvent effect
1	-1560.2912	-1560.2339	-1560.2380
2_A	-1787.0709	-1787.0103	-1787.0201
4	-1673.6119	-1673.5517	-1673.5561
5	-1673.6136	-1673.5543	-1673.5620
6	-1786.9370	-1786.8751	-1786.8828
7	-1786.9382	-1786.8772	-1786.8872
I_a	-1787.0575	-1786.9978	-1787.0064
8	-1787.0356	-1786.9727	-1786.9776
12_A	-1787.0480	-1786.9868	-1786.9934
I_{bA}	-1787.0364	-1786.9757	-1786.9837
TSI_a-Ib_A	-1787.0125	-1786.9532	-1786.9617
TS4-5	-1673.6000	-1673.5407	-1673.5462
TS6-7	-1786.9291	-1786.8664	-1786.8748
TS7-I_a	-1786.9297	-1786.8688	-1786.8791
TS8-12_A	-1787.0252	-1786.9659	-1786.9718
$TS2_A$-12_A	-1787.0364	-1786.9759	-1786.9836
TSI_{bA}-12_A	-1787.0244	-1786.9640	-1786.9740
I_c	-1673.7223	-1673.6635	-1673.6695
I_d	-1673.7180	-1673.6597	-1673.6650
TS5-I_c	-1673.6132	-1673.5538	-1673.5612
TSI_c-I_{dA}	-1673.6959	-1673.6360	-1673.6420
TSI_{dA}-I_{bA}	-1787.0172	-1786.9559	-1786.9612
I_{dA}	-1787.0197	-1786.9747	-1786.9628
I_{dB}	-1787.0399	-1786.9713	-1786.9804
TSI_{dB}-I_{eB}	-1787.0368	-1786.9794	-1786.9778
I_{eB}	-1787.0438	-1786.9778	-1786.9890
TSI_{eB} -I_{bB}	-1787.0389	-1786.9838	-1786.9852
I_{bB}	-1787.0444	-1786.9569	-1786.9912
TSI_{bB}-12_B	-1787.0173	-1786.9896	-1786.9650
12_B	-1787.0512	-1786.9700	-1786.9966
$TS12_B$-2_B	-1787.0291	-1787.0045	-1786.9791
2_B	-1787.0657	-1786.9747	-1787.0148

* Simplified model: all tertiary butyl and methyl groups on the ring of cyclopentadienyl ligand are simplified to hydrogen atoms.

The full model

	Potential energy	Potential energy with zero-point correction	Free energy	Potential energy with solvent effect	Free energy with solvent effect
1	-2346.8947	-2345.9926	-2346.0814	-2345.9992	-2346.0876
4_{A1}	-2460.2155	-2459.3055	-2459.3966	-2459.3110	-2459.4006
$TS4_{A1}$-5_{A1}	-2460.2083	-2459.2981	-2459.3870	-2459.3044	-2459.3920
5_{A1}	-2460.2246	-2459.3132	-2459.4047	-2459.3224	-2459.4091
$TS5_{A1}$-Ic	-2460.2176	-2459.3066	-2459.3957	-2459.3145	-2459.4050
Ic	-2460.3061	-2459.3946	-2459.4878	-2459.4034	-2459.4953
TSIc-Id_A	-2460.2823	-2459.3708	-2459.4621	-2459.3782	-2459.4689
Id_A	-2460.3074	-2459.3948	-2459.4858	-2459.4003	-2459.4928
Id_{aA}	-2573.6179	-2572.6978	-2572.7917	-2572.7021	-2572.7963
$TSIda_A$-Ib_A	-2573.5875	-2572.6666	-2572.7568	-2572.6712	-2572.7634
Ib_A	-2573.6512	-2572.7283	-2572.8187	-2572.7339	-2572.8244
$TSIb_A$ -12_A	-2573.6448	-2572.7227	-2572.8135	-2572.7290	-2572.8198
12_A	-2573.6732	-2572.7511	-2572.8439	-2572.7563	-2572.8500
$TS12_A$ -2_A	-2573.6642	-2572.7430	-2572.8352	-2572.7493	-2572.8416
2_A	-2573.7068	-2572.7840	-2572.8790	-2572.7925	-2572.8832
6	-2573.5513	-2572.6316	-2572.7244	-2572.6380	-2572.7312
TS6-7	-2573.5451	-2572.6251	-2572.7165	-2572.6315	-2572.7203
7	-2573.5693	-2572.6471	-2572.7387	-2572.6559	-2572.7445
TS7-Ia	-2573.5537	-2572.6337	-2572.7245	-2572.6411	-2572.7336
Ia	-2573.6468	-2572.7237	-2572.8160	-2572.7307	-2572.8228
TSIa-Ib	-2573.6211	-2572.6985	-2572.7904	-2572.7048	-2572.7953
4_{A3}	-2460.2046	-2459.2949	-2459.3868	-2459.3006	-2459.3936
$TS4_{A3}$-5_{A3}	-2460.1914	-2459.2818	-2459.3720	-2459.2887	-2459.3796
5_{A3}	-2460.2229	-2459.3113	-2459.4017	-2459.3204	-2459.4108
$TS5_{A3}$-Ic	-2460.2156	-2459.3041	-2459.3930	-2459.3121	-2459.3999
TSIc-Id_C	-2460.2952	-2459.3849	-2459.4782	-2459.3953	-2459.4888
Id_C	-2460.3082	-2459.3959	-2459.4885	-2459.4015	-2459.4911
Ida_C	-2573.6161	-2572.6977	-2572.7931	-2572.7039	-2572.8014
$TSIda_C$ -Ib_C	-2573.6108	-2572.6908	-2572.7824	-2572.6961	-2572.7882
Ib_C	-2573.6482	-2572.7257	-2572.8188	-2572.7326	-2572.8250
$TSIb_C$-12_C	-2573.6473	-2572.7247	-2572.8172	-2572.7318	-2572.8217
12_C	-2573.6721	-2572.7499	-2572.8424	-2572.7554	-2572.8483
$TS12_C$ -2_C	-2573.6646	-2572.7435	-2572.8358	-2572.7493	-2572.8420
2_C	-2573.7069	-2572.7835	-2572.8769	-2572.7915	-2572.8853
Id_B	-2573.6541	-2572.7300	-2572.8199	-2572.7408	-2572.8367
$TSId_B$-I_{eB}	-2573.6460	-2572.7258	-2572.8187	-2572.7325	-2572.8260
I_{eB}	-2573.6598	-2572.7373	-2572.8294	-2572.7458	-2572.8376
TS I_{eB} -Ib_B	-2573.6500	-2572.7274	-2572.8174	-2572.7350	-2572.8252
Ib_B	-2573.6581	-2572.7350	-2572.8255	-2572.7403	-2572.8308
$TSIb_B$-12_B	-2573.6381	-2572.7165	-2572.8083	-2572.7229	-2572.8123
12_B	-2573.6765	-2572.7543	-2572.8475	-2572.7590	-2572.8520

$TS12_B$ -2_B	-2573.6626	-2572.7413	-2572.8345	-2572.7475	-2572.8404
2_B	-2573.7013	-2572.7783	-2572.8720	-2572.7870	-2572.8839
8	-2573.6593	-2572.7386	-2572.8352	-2572.7429	-2572.8401
TS8-12_A	-2573.6516	-2572.7303	-2572.8209	-2572.7346	-2572.8252
TS1-4_{A1}	-2460.1975	-2459.2894	-2459.3820	-2459.2954	-2459.3889
TS1-4_{A3}	-2460.1907	-2459.2825	-2459.3740	-2459.2884	-2459.3803
$TS5_{A1}$-6	-2573.5305	-2572.6129	-2572.7063	-2572.6211	-2572.7161
$TSId_A$-Id_{aA}	-2573.6096	-2572.6905	-2572.7831	-2572.6946	-2572.7876
$TSId_C$-Id_{aC}	-2573.6100	-2572.6926	-2572.7879	-2572.6987	-2572.7943

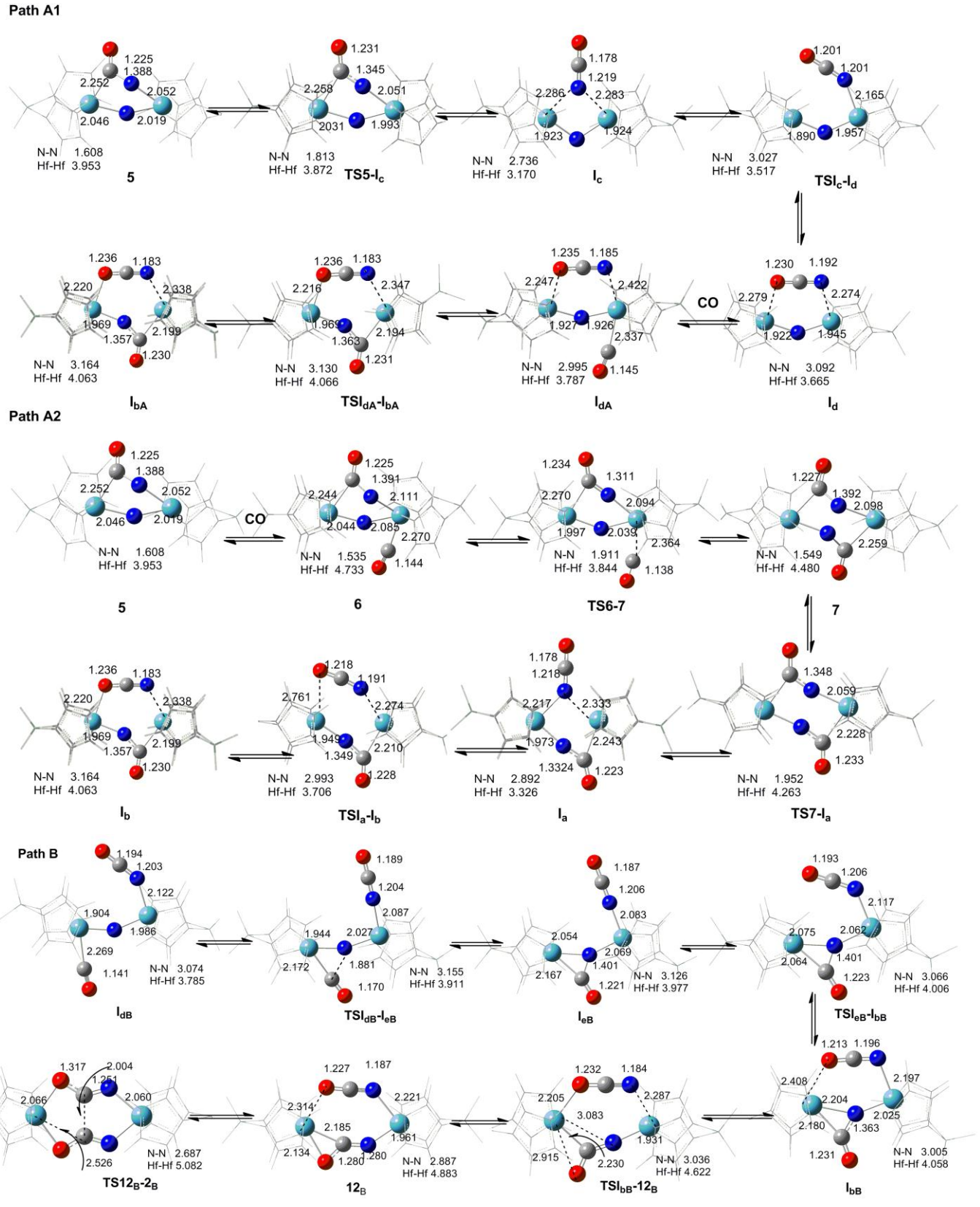
Table S4. Selected Structural Parameters of the optimized Structures of Path A (Path A_1 and Path A_2) using simplified model* (unit: Å).

	N^3-N^4	N^4-Hf^1	N^3-Hf^1	N^4-Hf^2	N^3-Hf^2	C^7-Hf^1	C^5-Hf^2	C^7-O^8	C^5-O^6	C^5-C^7	C^5-N^3	C^7-N^4	O^6-Hf^2	O^8-Hf^1
4	1.413	2.071	2.055	2.106	2.089	---	2.250	---	1.148	---	2.467	---	3.391	---
TS4-5	1.481	2.032	2.066	2.085	2.210	---	2.164	---	1.183	---	1.731	---	3.345	---
5	1.608	2.019	2.052	2.046	2.518	---	2.252	---	1.225	---	1.388	---	3.374	---
6	1.535	2.085	2.111	2.044	2.495	2.270	2.244	1.144	1.225	---	1.391	2.453	3.372	3.405
TS6-7	1.911	2.033	2.094	1.997	2.529	2.364	2.270	1.138	1.234	---	1.311	2.526	3.324	3.490
7	1.549	2.632	2.098	2.098	2.632	2.259	2.259	1.227	1.227	3.487	1.392	1.392	3.364	3.364
TS7-I_a	1.952	2.599	2.059	2.059	2.599	2.228	2.228	1.233	1.233	3.842	1.348	1.348	3.311	3.311
I_a	2.892	2.305	2.333	1.973	2.217	2.243	3.220	1.223	1.178	4.947	1.218	1.324	4.299	3.344
TSI_a-I_{bA}	2.993	2.274	2.310	3.025	1.949	2.210	2.703	1.228	1.218	4.509	1.191	1.349	2.761	3.344
I_{bA}	3.164	2.350	2.338	1.969	3.808	2.199	2.906	1.230	1.236	3.968	1.183	1.357	2.200	3.333
TS5-I_c	1.813	1.993	2.051	2.031	2.571	---	2.258	---	1.231	---	1.345	---	3.337	---
I_c	2.736	1.924	2.283	1.923	2.286	---	3.270	---	1.178	---	1.219	---	4.335	---
TSI_c- I_d	3.027	1.957	2.165	1.890	3.475	---	3.269	---	1.201	---	1.201	---	3.461	---
I_d	3.092	1.946	2.274	1.922	3.794	---	2.900	---	1.230	---	1.192	---	2.279	---
I_{dA}	2.995	1.976	2.422	1.977	3.790	2.337	2.910	1.145	1.235	---	1.185	2.404	2.247	---
TSI_{dA}-I_{bA}	3.130	2.331	2.347	1.969	3.803	2.194	2.902	1.231	1.236	3.960	1.183	1.363	2.216	3.337
TSI_{bA}-12_A	3.330	3.126	2.186	1.912	3.985	2.258	3.024	1.251	1.218	3.386	1.190	1.328	2.303	2.961
12_A	3.356	3.342	22.86	1.945	3.998	2.163	3.033	1.296	1.232	2.961	1.184	1.285	2.276	2.200
$TS12_A$-2_A	4.046	3.714	2.142	2.050	4.271	2.578	3.088	1.253	1.32	2.443	1.245	1.230	2.004	2.208
2_A	3.577	4.153	2.042	2.042	4.153	2.892	2.892	1.339	1.339	1.554	1.276	1.276	2.060	2.060

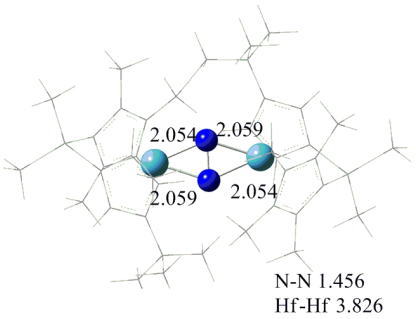
* Simplified model: all tertiary butyl and methyl groups on the ring of cyclopentadienyl ligand are simplified to hydrogen atoms.

The simplified model*

* Simplified model: all tertiary butyl and methyl groups on the ring of cyclopentadienyl ligand are simplified to hydrogen atoms.



The full model



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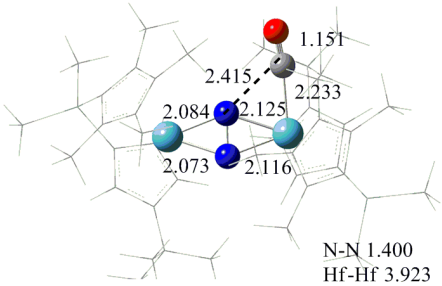
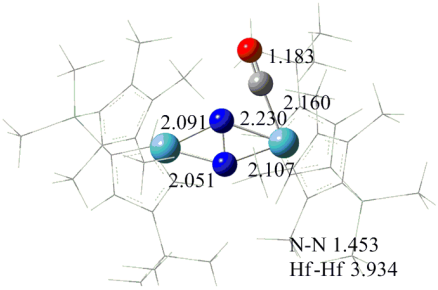
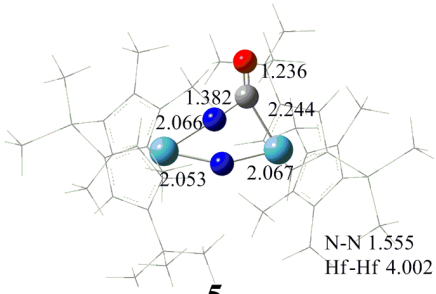


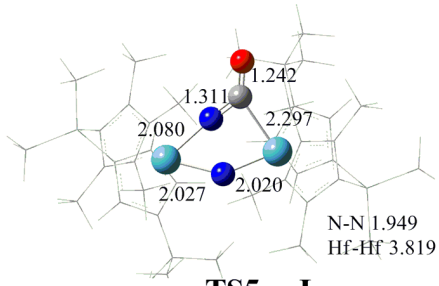
4_{A1}



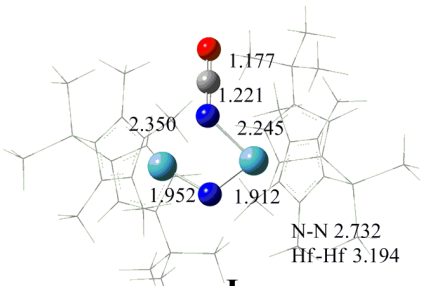
$TS4_{A1}$-5_{A1}



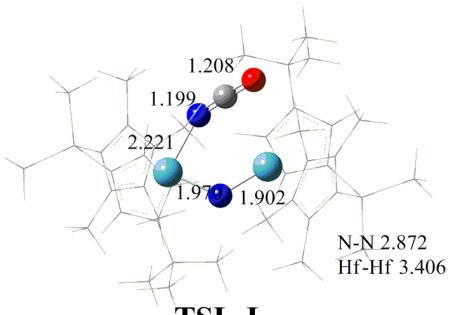
5_{A1}



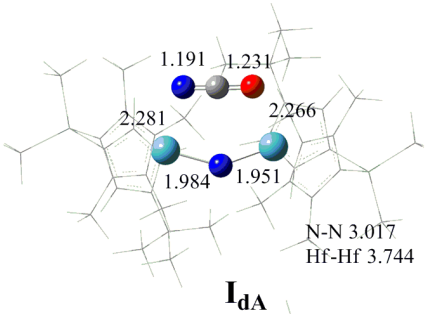
$TS5_{A1}$-I_c



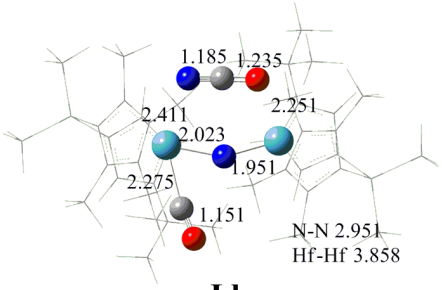
I_c



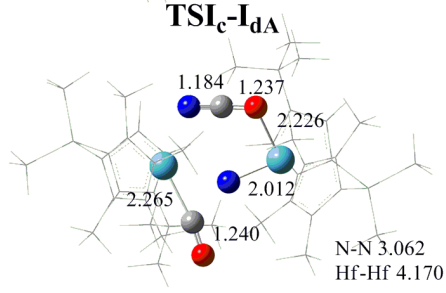
TSI_c-I_{dA}



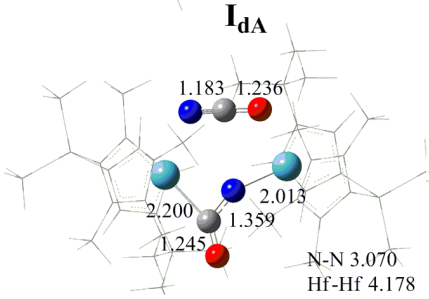
I_{dA}



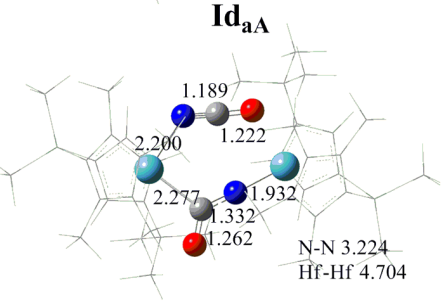
Id_{aA}



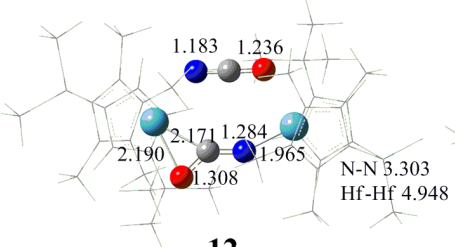
$TSId_{aA}$-Ib_A



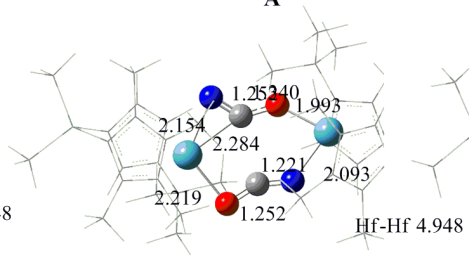
Ib_A



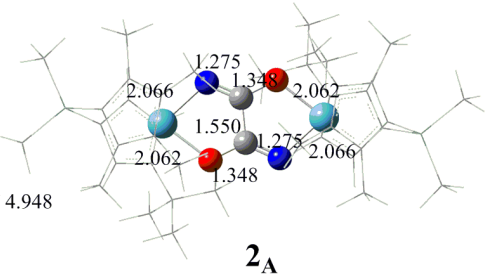
$TSIb_A$-12_A



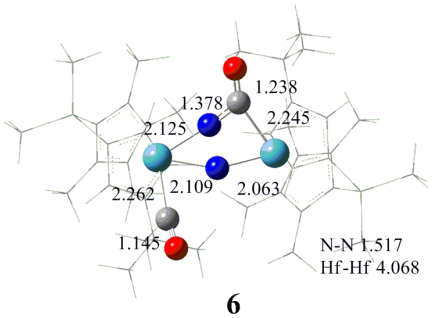
12_A



$TS12_A$-2_A



2_A



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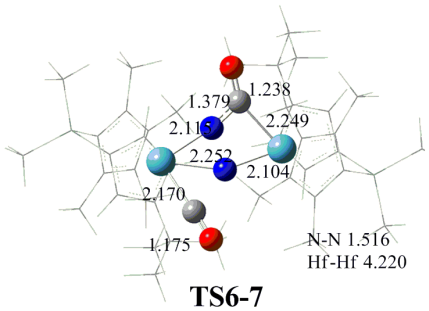
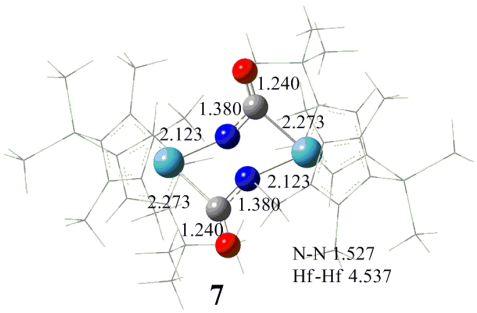


TS6-7



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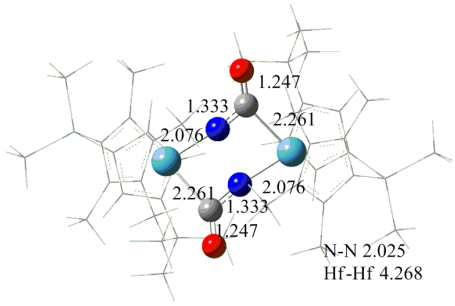
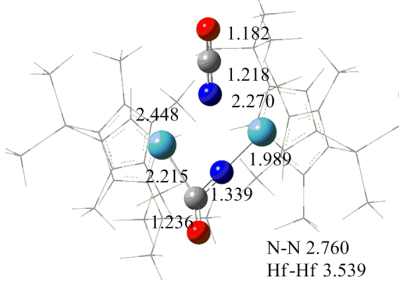
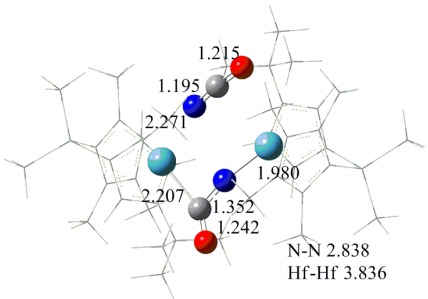


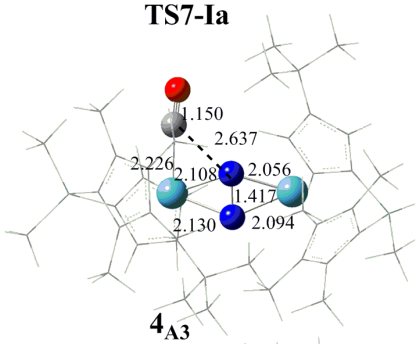
TS7-Ia



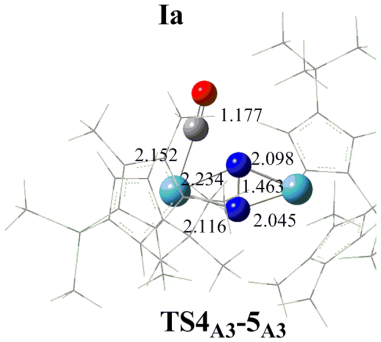
Ia



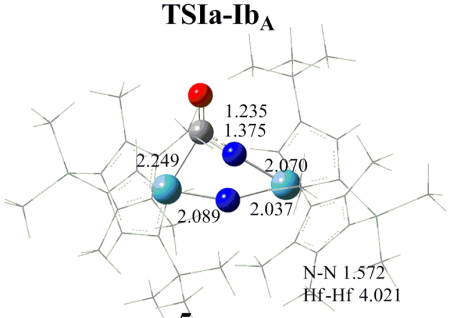
TSIa-Ib$_A$



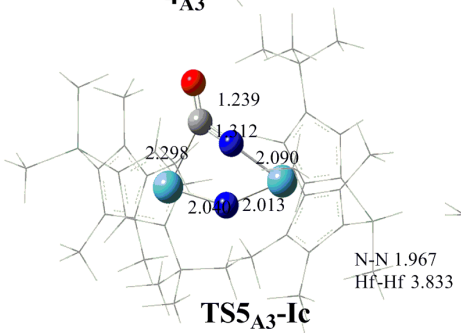
4$_{A3}$



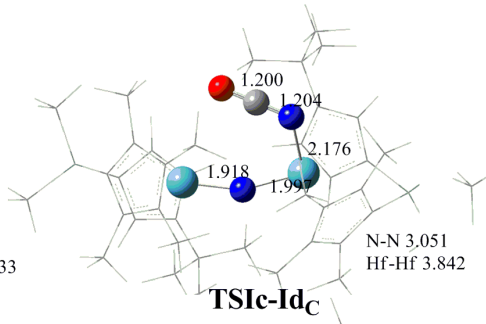
TS4$_{A3}$-5$_{A3}$



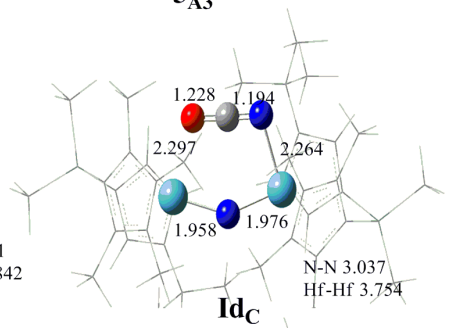
5$_{A3}$



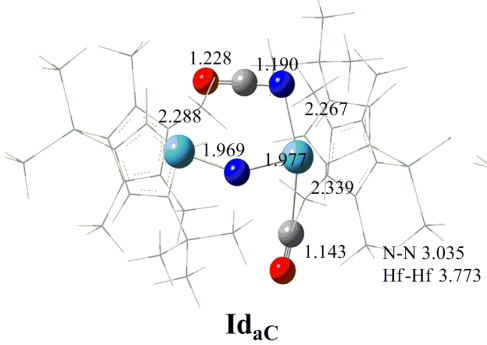
TS5$_{A3}$-Ic



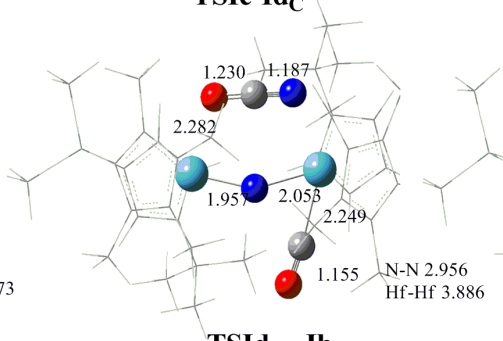
TSIc-Id$_C$



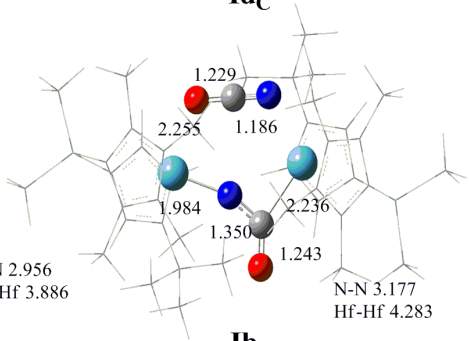
Id$_C$



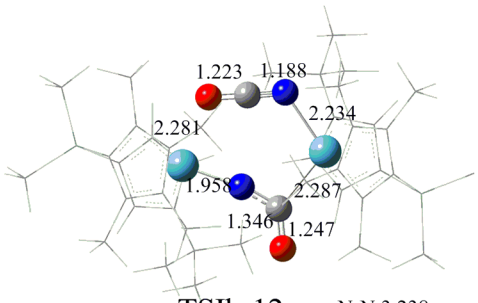
Id$_{aC}$



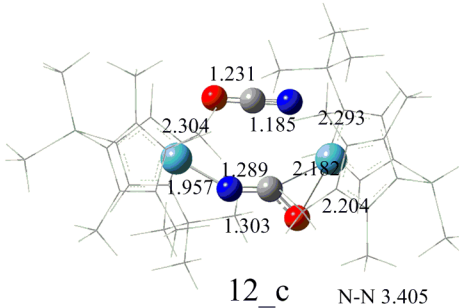
TSId$_{aC}$-Ib$_C$



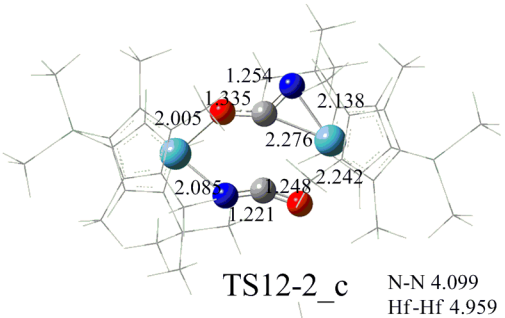
Ib$_C$



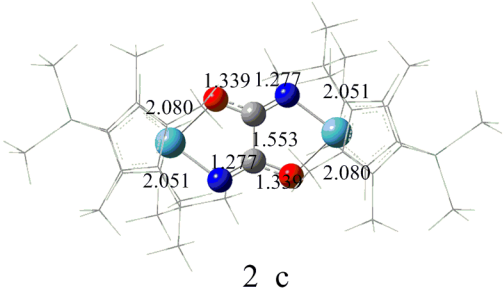
TSIb-12_c N-N 3.238 Hf-Hf 4.45730



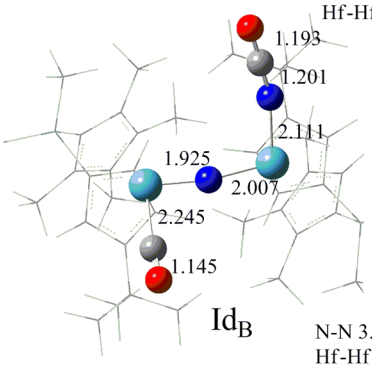
12_c N-N 3.405 Hf-Hf 4.941



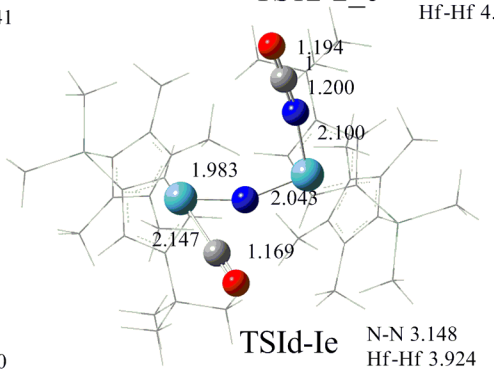
TS12-2_c N-N 4.099 Hf-Hf 4.959



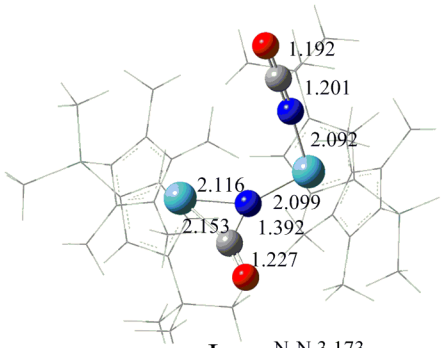
2_c



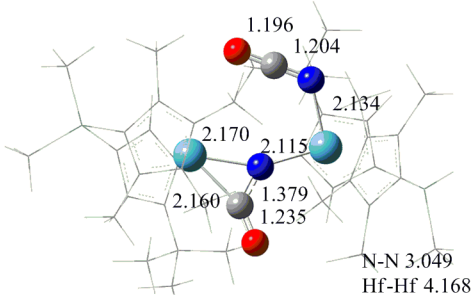
Id_B N-N 3.156 Hf-Hf 3.900



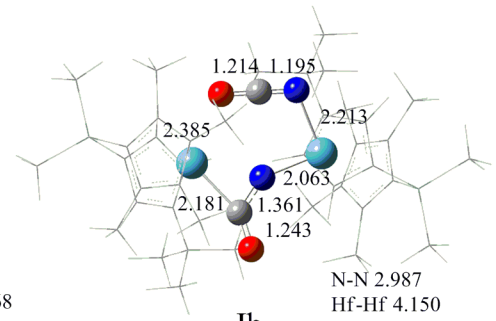
TSId-Ie N-N 3.148 Hf-Hf 3.924



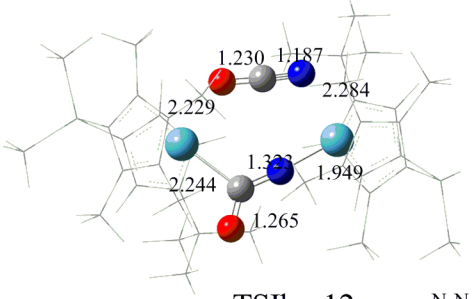
Ie N-N 3.173 Hf-Hf 4.021



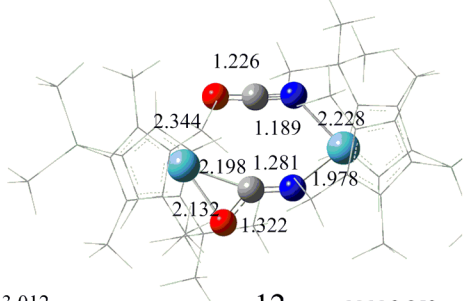
TSIe-Ib_B N-N 3.049 Hf-Hf 4.168



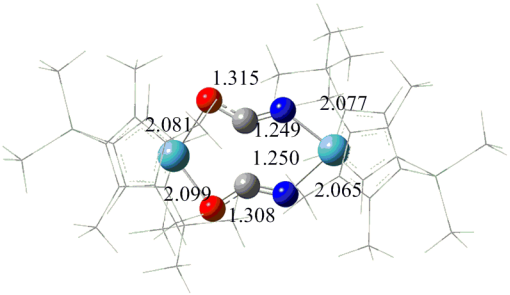
Ib_B N-N 2.987 Hf-Hf 4.150



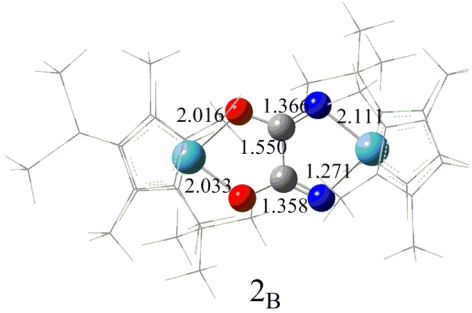
$TSIb_B$-12_B N-N 3.012 Hf-Hf 4.668



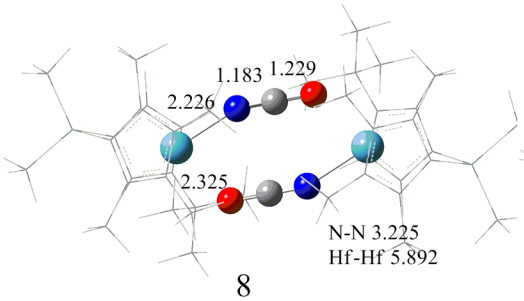
12_B N-N 2.853 Hf-Hf 4.936



$TS12_B$-2_B N-N 2.683 Hf-Hf 5.085

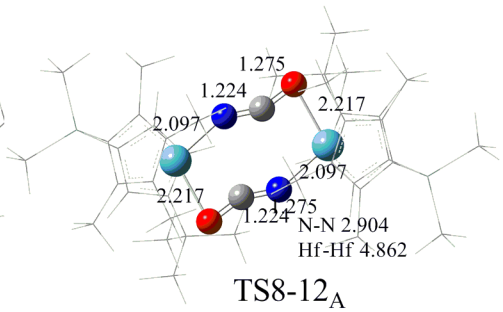


2_B



N-N 3.225 Hf-Hf 5.892

8



N-N 2.904 Hf-Hf 4.862

$TS8-12_A$

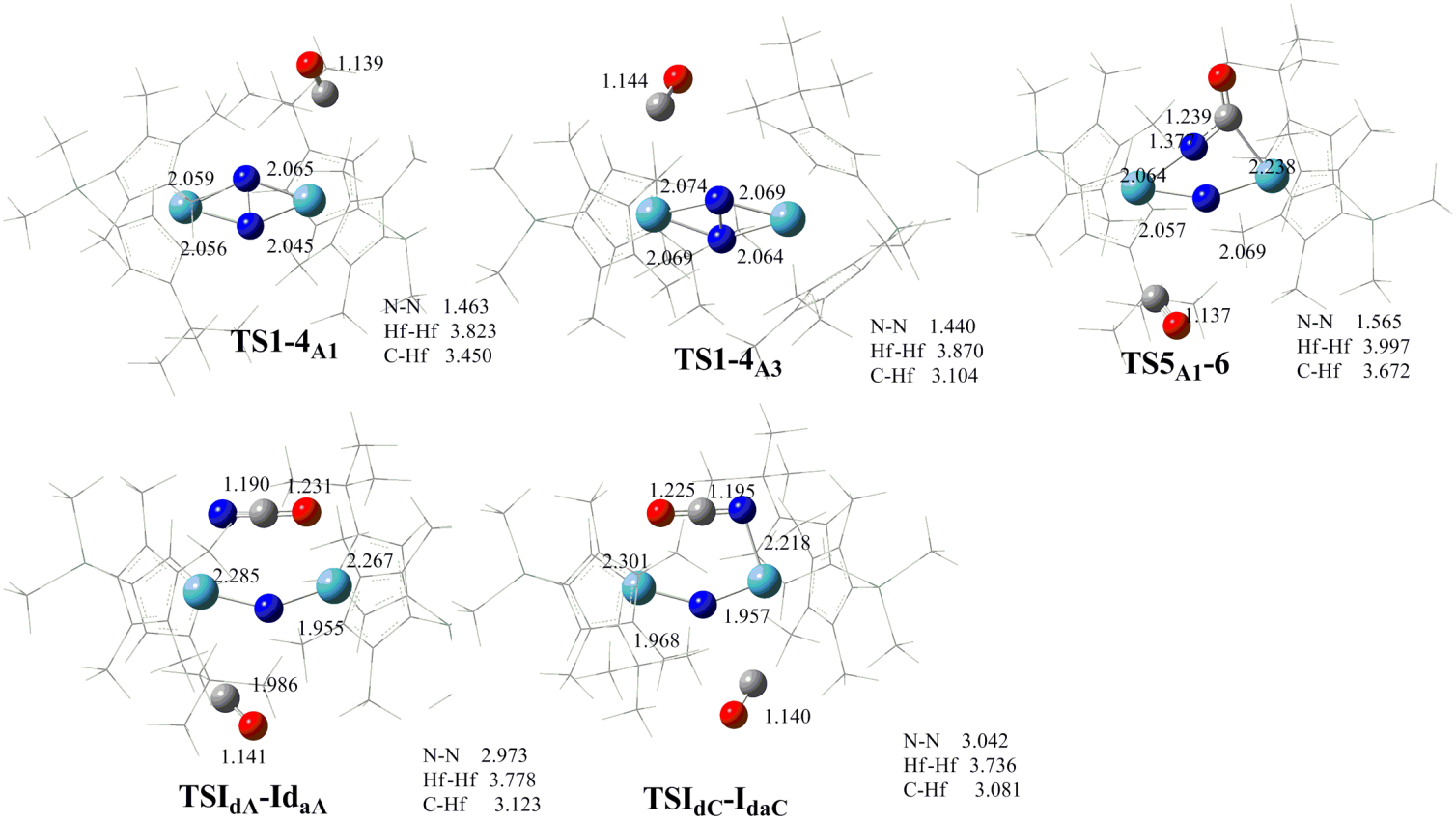
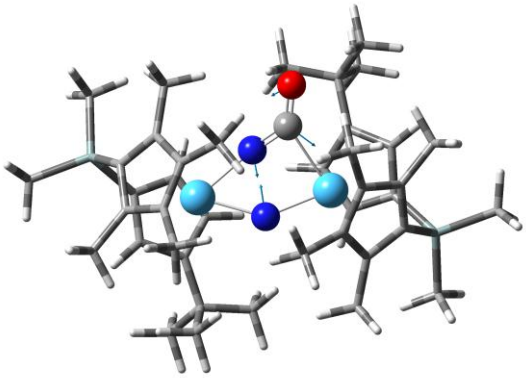
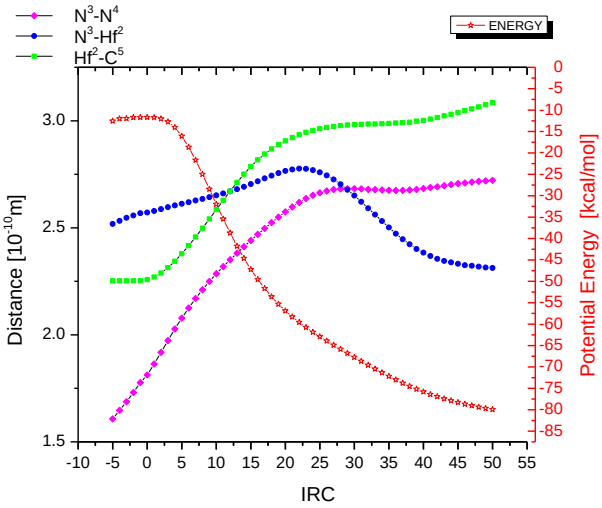


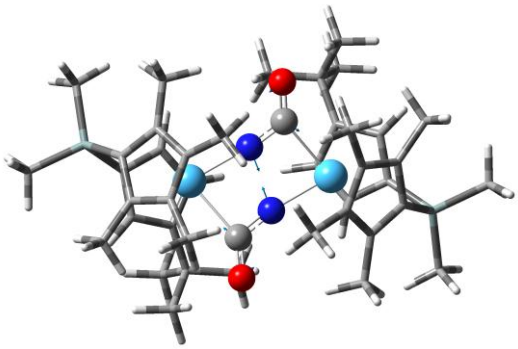
Figure S1. The geometrical parameters of optimized structures using simplified and full models (unit: Å).

TS5-I_c





TS7-I_a



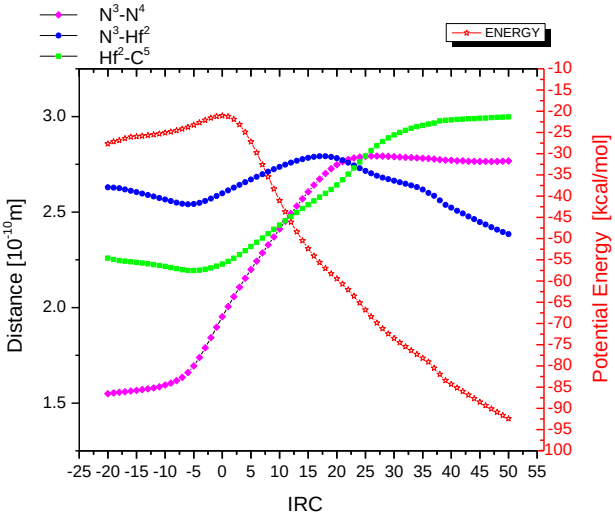


Figure S2. The vibration modes of imaginary frequencies of **TS5-I_c** and **TS7-I_a**, and the IRC analysis along **TS5-I_c** and **TS7-I_a**.

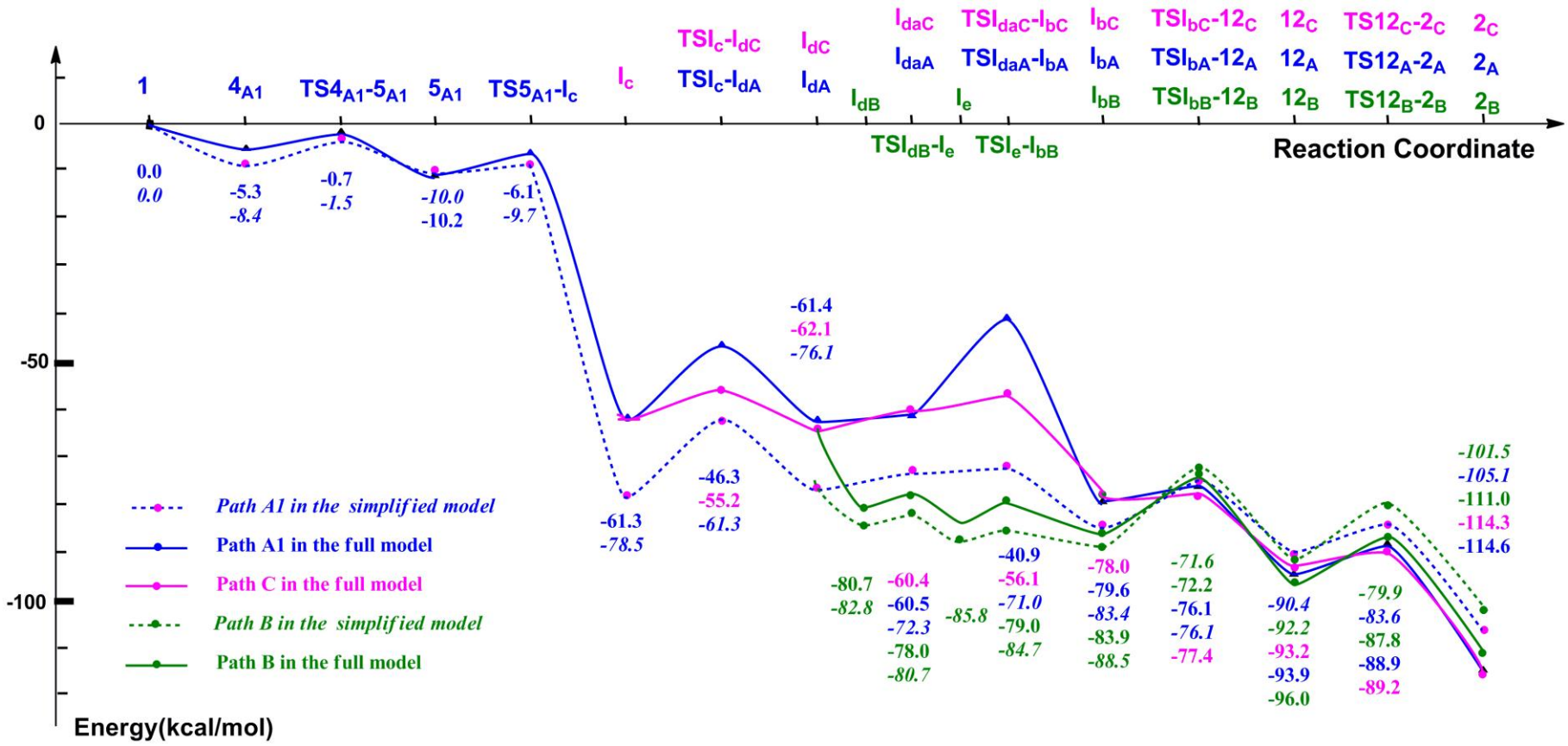


Figure S3. The comparison between full model and simplified model in the energy profiles of CO-assisted N_2 cleavage and functionalization. *

* Simplified model: all tertiary butyl and methyl groups on the ring of cyclopentadienyl ligand are simplified to hydrogen atoms. In the simplified model, **A** and **C** come to the same structure which is named by $\mathbf{2_A}$. Similarly, **B** and **D** are named by $\mathbf{2_B}$.