Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Five-Membered N-Heterocyclic Beryllium(I) Compounds: Fluctuating Electronic Structure with Ambiphilic Reactivity

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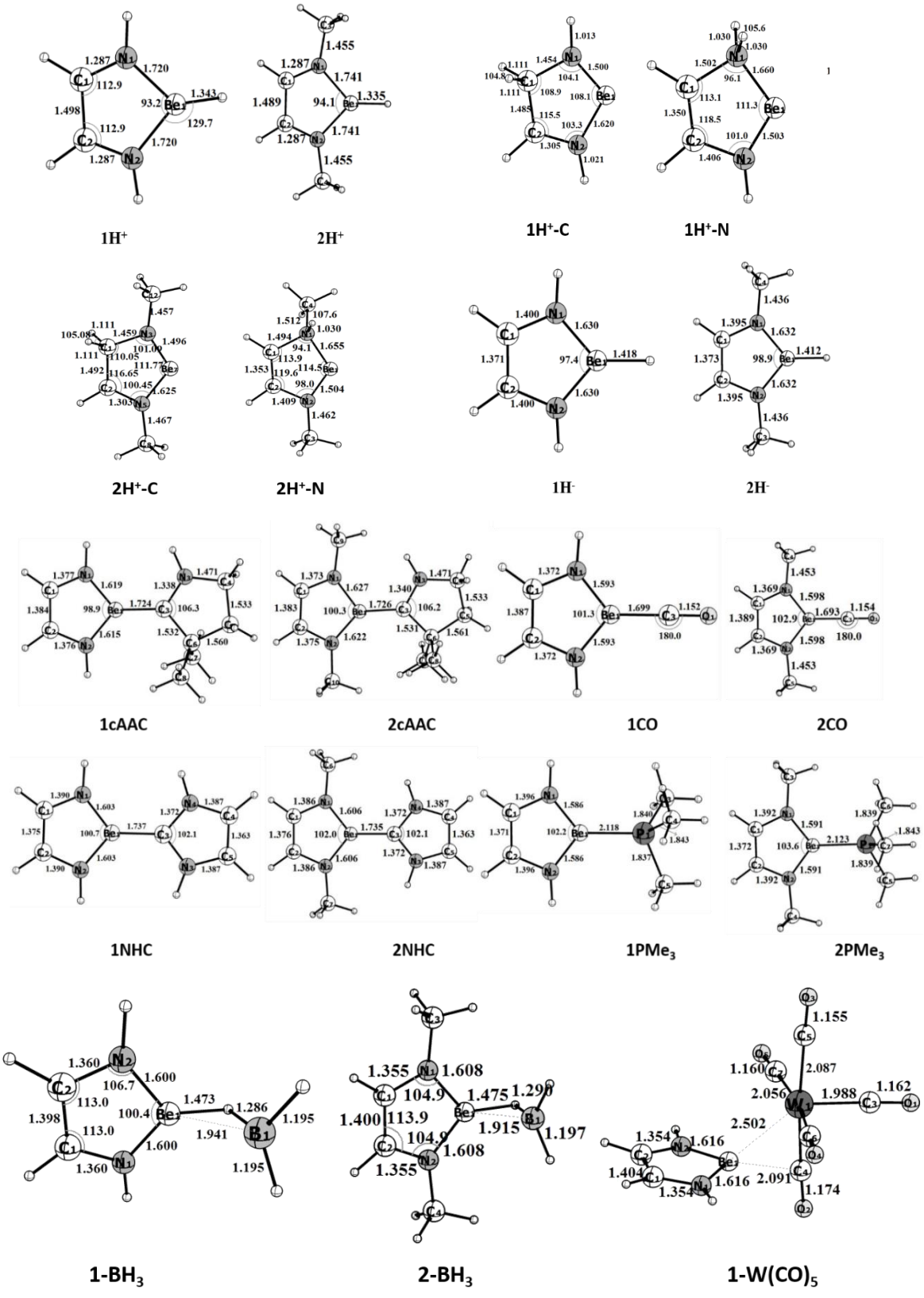


Figure S1. Equilibrium geometries and important geometric parameters of adducts of **1** and **2**, at the BP86/def2-TZVPP level of theory.

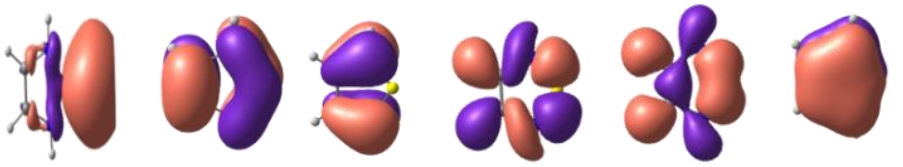


Figure S2: Important molecular orbitals of **1** at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. Eigenvalues are given in eV.

Table S1. Relative energy, charge distribution, and orbital occupancies on beryllium from NBO analysis of **1, 1′, 2,** and **2′** at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Molecule	Relative Energy (kcal/mol)	Charge					Occupancies on Be			
		q(Be)	*q*(N1)	*q*(N2)	*q*(C1)	*q*(C2)	2s	$2p_x$	$2p_y$	$2p_z$
1	0	1.21	-1.07	-1.07	-0.11	-0.11	0.24	0.26	0.26	0.03
1′	25.8	0.55	-0.87	-0.87	0.02	0.02	0.76	0.27	0.31	0.09
2	0	1.22	-0.86	-0.86	-0.11	-0.11	0.24	0.26	0.25	0.03
2′	23.03	0.57	-0.67	-0.67	0.02	0.02	0.75	0.15	0.43	0.08

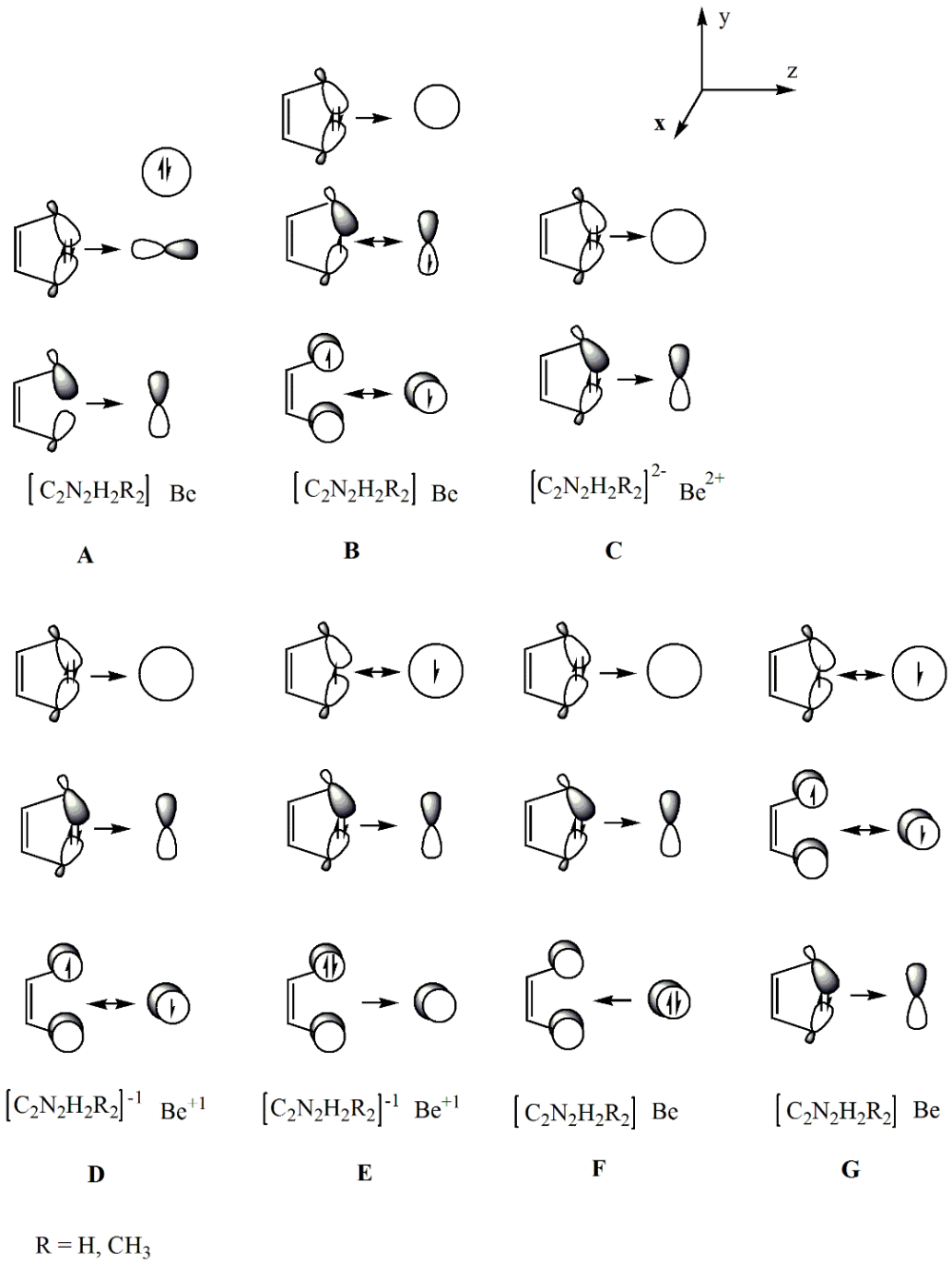
Table S2. Molecular electrostatic potential on selected atoms of **1** and **2** on the Van der Waals surface at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Atom	Electrostatic Potential (kcal/mol)	
	1	**2**
Be	30.4	31.37
N1	-16.51	-14.32
N2	-16.63	-14.26
C1	-25.91	-23.52
C2	-25.88	-23.49

Table S3. NICS values calculated for BeL and its adducts with proton, hydride and ligands calculated at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Molecules	NICS(0)[a] (NICS(0)zz)	NICS(1)[a] (NICS(1)zz)	NICS(-1)[a] (NICS(-1)zz)
1	-7.8 (5.1)	-4.1 (-11.2)	-4.1 (-10.8)
2	-7.8 (7.2)	-3.7 (-9.6)	-3.7 (-9.6)
NHC	-13.2 (-12.7)	-10.3 (-29.3)	-10.3 (-29.3)
$1H^+$	3.3 (19.7)	-1.7 (-0.14)	-0.83 (-0.14)
$2H^+$	4.7 (25.6)	-0.56 (3.9)	-0.57 (3.9)
$1H^+$-C	-3.9 (13.11)	-2.9 (-6.6)	-2.9 (-6.6)
$2H^+$-C	-4.1 (14.3)	-2.9 (-4.8)	-2.9 (-4.8)
$1H^+$-N	-2.17 (20.0)	-0.8 (-0.5)	-0.8 (-0.5)
$2H^+$-N	-2.4 (18.2)	-2.9 (1.0)	-0.88 (-0.51)
$1H^-$	-6.6 (3.4)	-3.6 (-14.1)	-3.6 -14.1
$2H^-$	-5.5 (8.6)	-3.3 (-9.9)	-3.3 (-9.9)
1cAAC	-6.7 (2.9)	-5.0 (-15.0)	-5.0 (-15.3)
2cAAC	-6.1 (5.7)	-4.7 (-12.5)	-4.7 (-12.4)
1CO	-8.0 (-0.21)	-5.8 (-17.8)	-5.9 (-17.9)
2CO	-7.2 (2.9)	-5.4 (-14.9)	-5.4 (-14.9)
1NHC	-6.7 (3.8)	-4.5 (-14.4)	-4.5 (-14.4)
2NHC	-6.0 (7.1)	-4.0 (-11.3)	-4.0 (-11.3)
$1PMe_3$	-7.2 (2.2)	-4.8 -15.8)	-4.8 (-15.8)
$2PMe_3$	-6.6 (5.4)	-4.4 (-12.6)	-4.4 (-12.6)

[a]NICS(0), NICS(1) and NICS(-1) represent NICS values at the center, 1 Å above the ring and 1 Å below the ring respectively. The dissected NICS(0)zz, NICS(1)zz and NICS(-1)zz are given in parentheses.



Scheme S1. Schematic representation of possible bonding possibilities for the interaction between beryllium and L (L = $N_2C_2H_4$ and $N_2C_2H_2(CH_3)_2$) chosen for EDA-NOCV analysis. Double-headed arrow (↔) indicates the electron-sharing interaction, and the single-headed arrow (→) indicates the donor-acceptor interaction between the fragments.

Table S4. EDA-NOCV results of different bonding situations for **Be-L** bonds of **1** and **2** in **Scheme S1** at the BP86/TZ2P level of theory. Energies are given in kcal/mol.

Compound	Bonding Possibilities	ΔE_{Int}	ΔE_{Pauli}	ΔE_{Elstat}	ΔE_{Orb}
1	**A**	-130.9	496.6	-277.9	-349.6
	B	-306.0	250.4	-205.0	-351.3
	C	-878.5	106.3	-688.1	-296.7
	D	-398.4	98.3	-274.2	-222.5
	E	-394.4	152.6	-275.7	-271.3
	F	-289.1	116.1	-105.9	-299.3
	G	-246.6	183.9	-123.6	-306.9
2	**A**	-119.7	510.2	-286.6	-343.3
	B	-319.2	287.7	-234.7	-372.2
	C	-841.8	104.2	-611.1	-334.9
	D	-388.2	99.1	-256.7	-230.6
	E	-380.2	165.3	-265.0	-280.5
	F	-277.9	122.0	-108.8	-291.1
	G	-233.2	201.2	-135.1	-299.2

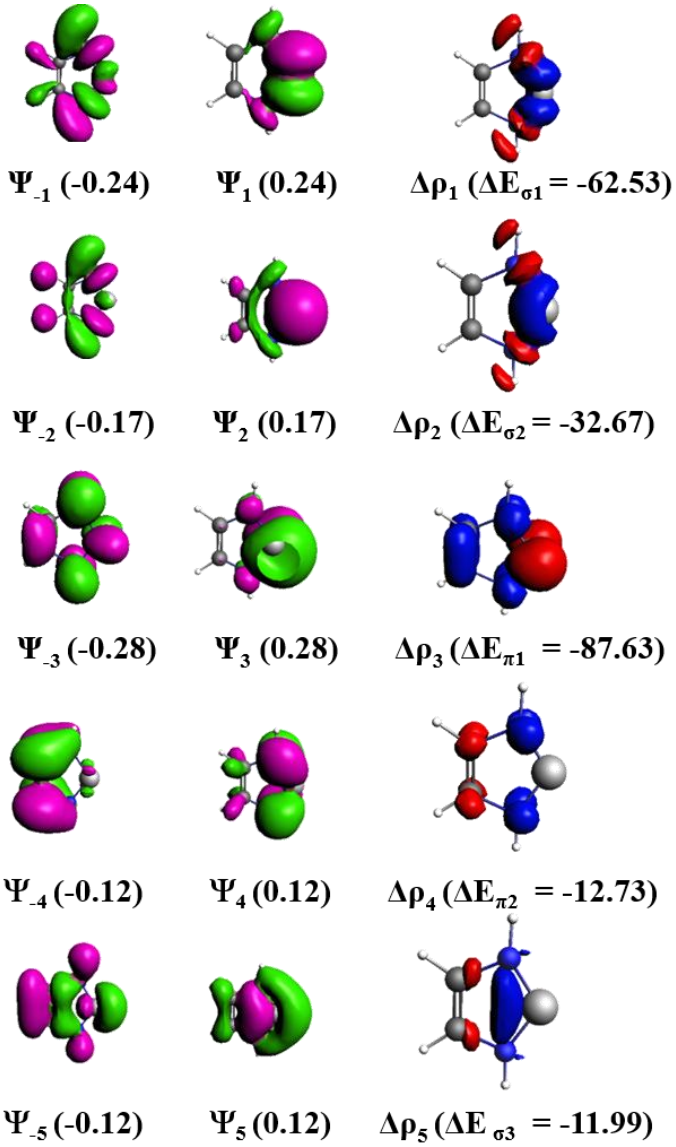


Figure S3: Plots of important alpha NOCV pair of orbitals Ψ_{-n}/ Ψ_n of best bonding possibility in **1** with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.003, respectively.

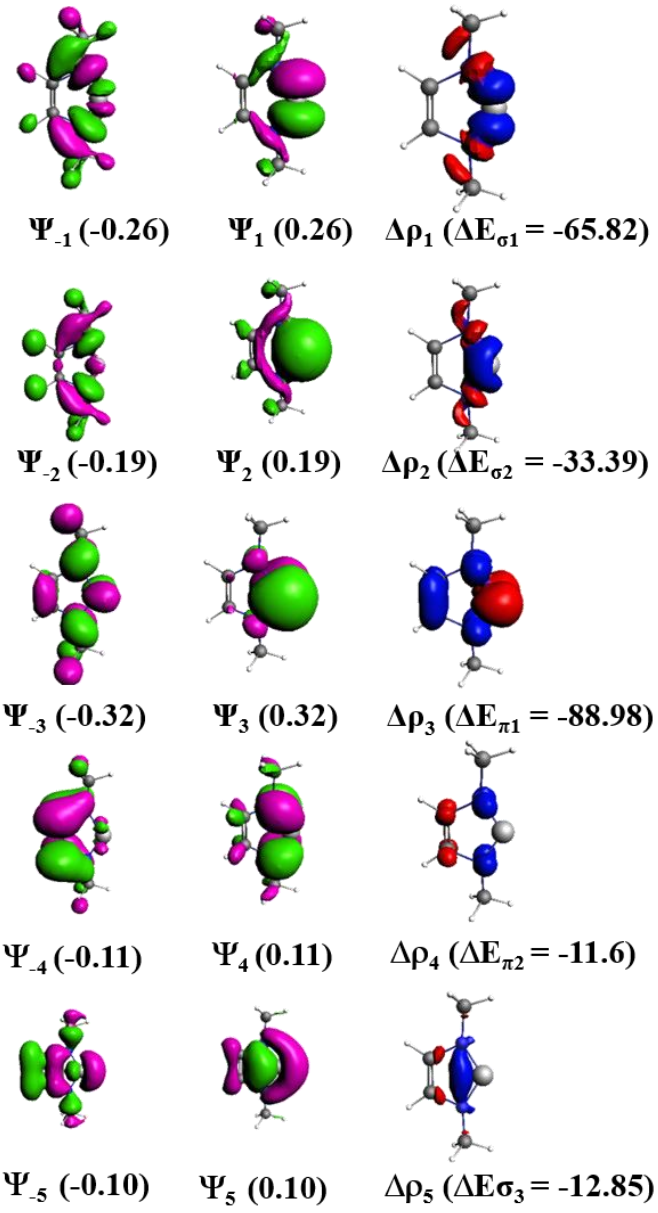


Figure S4. Plots of important alpha NOCV pair of orbitals Ψ_{-n}/ Ψ_n of best bonding possibility in **2** with their eigenvalues in the parenthesis, the associated deformation densities $\Delta\rho_n$ and the orbital stabilization energies ΔE (kcal/mol) at the BP86/TZ2P level of theory. The direction of the charge flow in the deformation density plot $\Delta\rho_n$ is from red→blue. The isosurface values for NOCV orbitals and deformation densities are 0.03 and 0.003, respectively.

Table S5. The vertical Electron Affinity **(EA),** and vertical Ionization Energy **(IE)** of **1** and **2** calculated at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. All values are given in kcal/mol.

Compounds	1	2
1st vertical EA	2.4	0.1
2nd vertical EA	106.1	98.8
1st vertical IE	155.4	148.9
2nd vertical IE	477.9	446.7

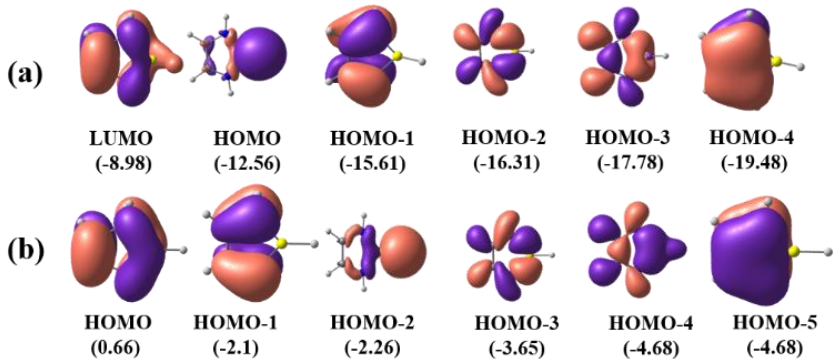


Figure S5. Important MOs of (a) **1H**$^{+}$ and (b) **1H**$^{-}$ calculated at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. Eigenvalues are given in eV.

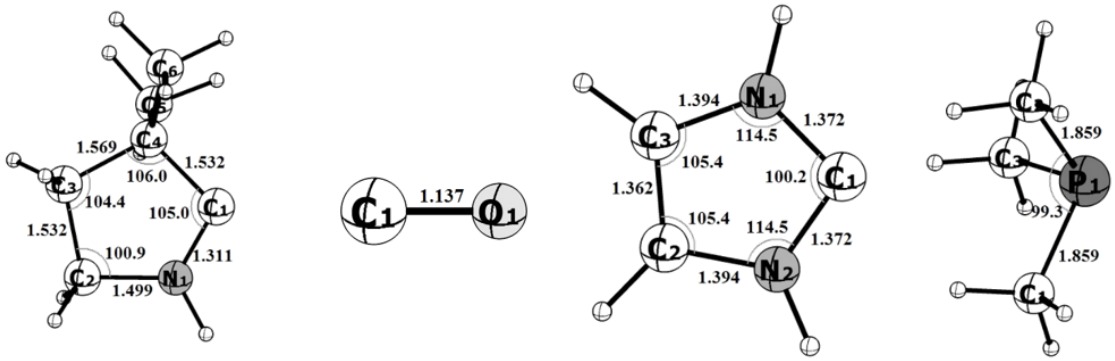


Figure S6. Optimized geometries of cAAC, CO, NHC, and PMe_3 at the BP86/def2-TZVPP level of theory.

Table S6. Wiberg bond index of important bonds of **1, 2, 1CO, 2CO, 1PMe$_3$, 2PMe$_3$, 1NHC, 2NHC, 1cAAC**, **2cAAC**,**1H$^+$, 2H$^+$, 1H$^-$** and **2H$^-$** of adducts at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. A = CO, PMe$_3$, NHC and cAAC.

Compounds	Wiberg Bond Index					
	Be-N1	**Be-N2**	**N1-C1**	**N2-C2**	**C1-C2**	**Be-A**
1	0.65	0.65	1.12	1.12	1.72	
2	0.61	0.61	1.1	1.1	1.72	
1CO	0.69	0.69	1.26	1.26	1.53	0.74
2CO	0.64	0.64	1.24	1.24	1.52	0.76
1PMe$_3$	0.69	0.69	1.17	1.17	1.66	0.62
2PMe$_3$	0.63	0.63	1.15	1.15	1.66	0.62
1NHC	0.67	0.67	1.19	1.19	1.63	0.6
2NHC	0.61	0.61	1.16	1.16	1.63	0.6
1cAAC	0.63	0.63	1.23	1.23	1.56	0.61
2cAAC	0.56	0.58	1.21	1.21	1.56	0.6
1H$^+$	0.35	0.35	1.85	1.85	1.02	0.84
2H$^+$	0.31	0.31	1.80	1.80	1.03	0.85
1H$^-$	0.59	0.59	1.16	1.16	1.65	0.78
2H$^-$	0.53	0.53	1.14	1.14	1.66	0.79

Table S7. The contribution of different configurational state of compounds **1** and **2** at the CASSCF [6,6]/ def2-TZVPP//BP86/def2-TZVPP level of theory.

1	96.04% ($1\pi^2 2\pi^2 3\pi^2 4\pi^0 1\sigma^0 5\pi^0$)	3.24% ($1\pi^0 2\pi^2 3\pi^2 4\pi^0 1\sigma^0 5\pi^2$)	0.36% ($1\pi^2 2\pi^{1\alpha} 3\pi^{1\beta} 4\pi^{1\alpha} 1\sigma^0 5\pi^{1\beta}$)	0.36% ($1\pi^2 2\pi^0 3\pi^2 4\pi^2 1\sigma^0 5\pi^0$)
2	96.04% ($1\pi^2 2\pi^2 3\pi^2 1\sigma^0 4\pi^0 5\pi^0$)	3.24% ($1\pi^2 2\pi^2 3\pi^0 1\sigma^0 4\pi^0 5\pi^2$)	0.36% ($1\pi^{1\alpha} 2\pi^{1\beta} 3\pi^2 1\sigma^0 4\pi^{1\alpha} 5\pi^{1\beta}$)	0.36% ($1\pi^2 2\pi^0 3\pi^2 1\sigma^0 4\pi^2 5\pi^0$)

Table S8. Hirshfeld charge analysis at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Compounds	Charge		
	Be	C1/C2	N1/N2
1	0.42	-0.02	-0.2
2	0.42	-0.01	-0.3

Table S9. Comparison of proton affinity (PA), hydride affinity (HA), and reaction energies of **1** using 'fine' grid and 'ultrafine' grid at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory.

Compounds	**Grid = fine**	**Grid = ultrafine**
PA[a]	215.7	215.7
HA[b]	92.9	93.0
ΔE_{cAAC}[c]	-56.3	-56.3
ΔE_{CO}[c]	-26.5	-26.6
ΔE_{NHC}[c]	-51.2	-51.2
ΔE_{PMe3}[c]	-32.6	-32.6

[a]PA is the proton affinity. [b]HA is the hydride affinity. ΔE_{CAAC}, ΔE_{CO}, ΔE_{NHC} and ΔE_{PMe3} are the reaction energies of 1 and 2 with cAAC, CO, NHC, and PMe_3.

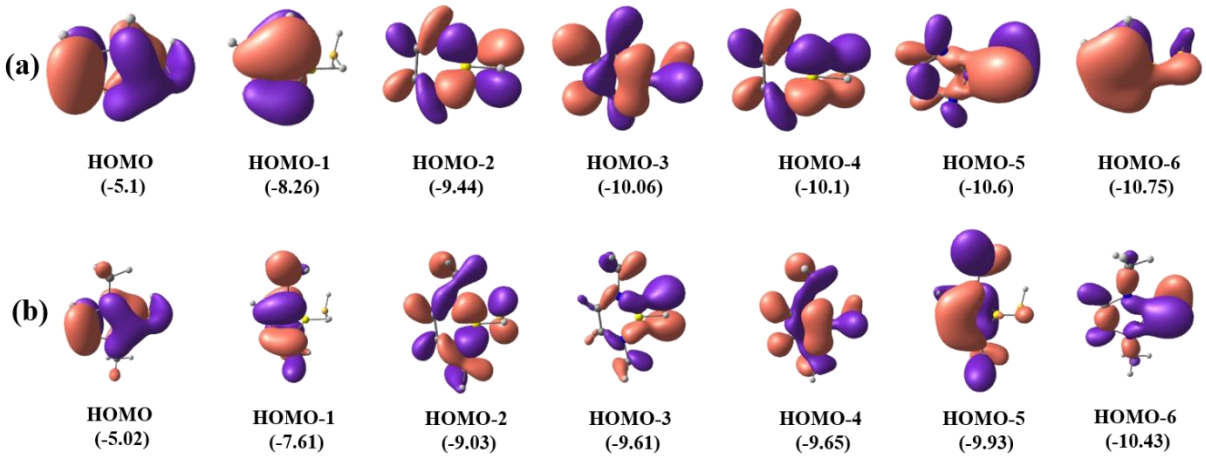


Figure S7. Important MOs of (a) **1BH$_3$** and (b) **2BH$_3$** calculated at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. Eigenvalues are given in eV.

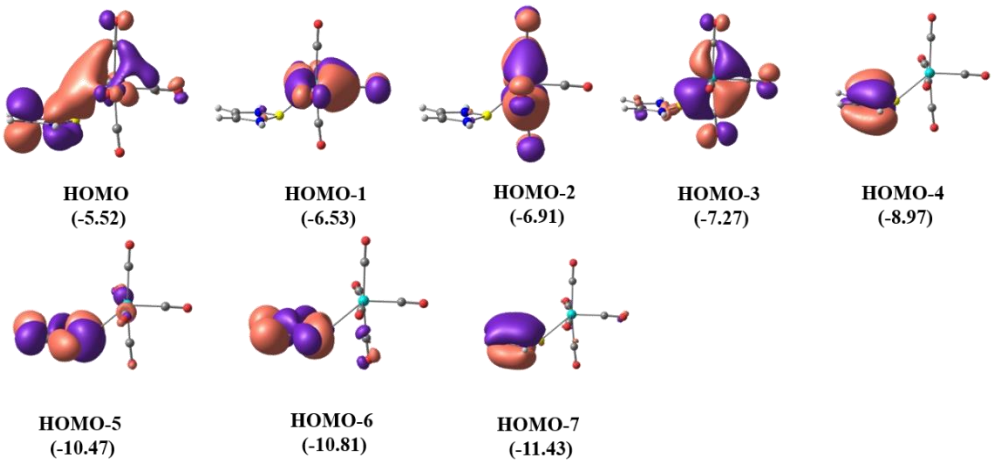


Figure S8. Important MOs of 1-$W(CO)_5$ calculated at the M06/def2-TZVPP//BP86/def2-TZVPP level of theory. Eigenvalues are given in eV.

Cartesian coordinates of molecules

1

Electronic energy (BP86) = -202.891294

Zero-point correction (BP86) = 0.064739

Thermal correction to Gibbs free energy (BP86) = 0.038488

Electronic energy (M06) = -202.825961

6	0.000000000	0.682810000	-0.808083000
6	0.000000000	-0.682810000	-0.808083000
7	0.000000000	1.274859000	0.480796000
1	0.000000000	1.302010000	-1.702779000
7	0.000000000	-1.274859000	0.480796000
1	0.000000000	-1.302010000	-1.702779000
4	0.000000000	0.000000000	1.330500000
1	0.000000000	2.283205000	0.524707000
1	0.000000000	-2.283205000	0.524707000

1'

Electronic energy (BP86) = -202.863222

Zero-point correction (BP86) = 0.065628

Thermal correction to Gibbs free energy (BP86) = 0.037938

Electronic energy (M06) = -202.7856256

6	0.000000000	1.076609000	0.000000000
6	-1.067647000	0.138897000	0.000000000
7	1.204165000	0.494364000	0.000000000
1	-0.152316000	2.157910000	0.000000000
7	-0.645624000	-1.130298000	0.000000000
1	-2.120273000	0.429465000	0.000000000
4	1.027007000	-1.169152000	0.000000000
1	2.016045000	1.104251000	0.000000000
1	-1.355392000	-1.856512000	0.000000000

2

Electronic energy (BP86) = -281.470513

Zero-point correction (BP86) = 0.118230

Thermal correction to Gibbs free energy (BP86) = 0.086779

Electronic energy (M06) = -281.3959718

6	0.000000000	0.684551000	-0.986475000
6	0.000000000	-0.684551000	-0.986475000
7	0.000000000	1.293382000	0.290735000
1	0.000000000	1.301940000	-1.884476000
7	0.000000000	-1.293382000	0.290735000
1	0.000000000	-1.301940000	-1.884476000
4	0.000000000	0.000000000	1.116532000
6	0.000000000	-2.735956000	0.382189000
1	0.000000000	-3.048853000	1.435235000

1 -0.891041000 -3.181341000 -0.096631000

1 0.891041000 -3.181341000 -0.096631000

6 0.000000000 2.735956000 0.382189000

1 -0.891041000 3.181341000 -0.096631000

1 0.000000000 3.048853000 1.435235000

1 0.891041000 3.181341000 -0.096631000

2'

Electronic energy (BP86) = -281.448552

Zero-point correction (BP86) = 0.118349

Thermal correction to Gibbs free energy (BP86) = 0.083748

Electronic energy (M06) = -281.3593804

6 -0.708501000 1.002007000 -0.000084000

6 0.708501000 1.002007000 0.000068000

7 -1.251647000 -0.220963000 -0.000257000

1 -1.310629000 1.914946000 -0.000165000

7 1.251648000 -0.220960000 0.000085000

1 1.310627000 1.914948000 0.000112000

4 -0.000001000 -1.330182000 -0.000166000

6 2.693454000 -0.393790000 0.000042000

1 3.009907000 -0.964833000 -0.886237000

1 3.216809000 0.574776000 0.001322000

1 3.009614000 -0.967102000 0.884939000

6 -2.693455000 -0.393789000 0.000138000

1 -3.216805000 0.574764000 -0.005316000

1 -3.009253000 -0.970780000 -0.882462000

1 -3.010269000 -0.961137000 0.888690000

1cAAC

Electronic energy (BP86) = -492.885250

Zero-point correction (BP86) = 0.224512

Thermal correction to Gibbs free energy (BP86) = 0.185020

Electronic energy (M06) = -492.7524355

6	3.611500000	0.652576000	0.025131000
6	3.464346000	-0.723032000	0.009956000
7	2.409068000	1.322857000	-0.006347000
1	4.570968000	1.169476000	0.057575000
7	2.147653000	-1.120492000	-0.035423000
1	4.292383000	-1.431949000	0.030208000
4	1.233286000	0.210454000	-0.050806000
6	-0.478680000	0.416628000	-0.066214000
7	-1.105154000	1.598356000	-0.065103000
6	-2.575264000	1.581081000	-0.007682000
6	-2.873707000	0.127136000	-0.392964000
1	-0.588939000	2.472924000	-0.020776000
1	-3.765762000	-0.268020000	0.110701000
1	-2.921642000	1.832160000	1.010274000
1	-3.038984000	0.057216000	-1.478365000
1	-3.003317000	2.320067000	-0.700395000
6	-1.576053000	-0.650341000	-0.011020000
1	2.480022000	2.334867000	0.002900000
1	1.994787000	-2.123075000	-0.048831000
6	-1.656508000	-1.172946000	1.444690000
1	-2.447259000	-1.935190000	1.528750000
1	-0.701071000	-1.622215000	1.746940000
1	-1.883086000	-0.364166000	2.155260000

6 -1.308637000 -1.819758000 -0.969488000

1 -0.381681000 -2.343332000 -0.701140000

1 -2.136045000 -2.545560000 -0.930403000

1 -1.206463000 -1.468129000 -2.005823000

2cAAC

Electronic energy (BP86) = -571.463811

Zero-point correction (BP86) = 0.277284

Thermal correction to Gibbs free energy (BP86) = 0.233856

Electronic energy (M06) = -571.3242011

6 3.265943000 0.582880000 0.053601000

6 3.159940000 -0.792743000 -0.046924000

7 2.054906000 1.229521000 0.074251000

1 4.210373000 1.126140000 0.130401000

7 1.864962000 -1.252563000 -0.083110000

1 4.012244000 -1.473825000 -0.092829000

4 0.922220000 0.065183000 -0.014321000

6 -0.780259000 0.350120000 -0.047986000

7 -1.290531000 1.562414000 -0.302770000

6 -2.756040000 1.689937000 -0.310553000

6 -3.175588000 0.389824000 0.384779000

1 -0.692747000 2.343726000 -0.560311000

1 -3.300808000 0.569460000 1.462812000

1 -3.074305000 2.598357000 0.221164000

1 -4.122333000 -0.009655000 -0.002369000

1 -3.127059000 1.759552000 -1.348159000

6 -1.977083000 -0.583415000 0.153785000

6 -1.785947000 -1.535104000 1.343634000

1	-2.674423000	-2.172620000	1.474465000
1	-0.915126000	-2.186667000	1.193369000
1	-1.624829000	-0.973699000	2.275001000
6	-2.177461000	-1.393841000	-1.150126000
1	-1.290605000	-2.001469000	-1.374265000
1	-3.043548000	-2.066730000	-1.048484000
1	-2.354321000	-0.734921000	-2.013115000
6	2.047155000	2.672793000	0.185054000
1	2.152638000	3.177149000	-0.795674000
1	1.104805000	3.020632000	0.639734000
1	2.865568000	3.042754000	0.828241000
6	1.670436000	-2.682259000	-0.224877000
1	0.598896000	-2.923502000	-0.242742000
1	2.110367000	-3.072800000	-1.161503000
1	2.124389000	-3.247377000	0.610638000

1CO

Electronic energy (BP86) = -316.304770

Zero-point correction (BP86) = 0.074186

Thermal correction to Gibbs free energy (BP86) = 0.043174

Electronic energy (M06) = -316.1738023

6	1.925458000	0.693650000	-0.000211000
6	1.925520000	-0.693586000	-0.000346000
7	0.663209000	1.232098000	0.000244000
1	2.823396000	1.310745000	-0.000432000
7	0.663303000	-1.232114000	0.000079000
1	2.823495000	-1.310626000	-0.000653000
4	-0.346505000	-0.000057000	0.000641000

1 0.599666000 2.243947000 0.000721000

1 0.599847000 -2.243964000 0.000525000

6 -2.045208000 0.000009000 -0.000268000

8 -3.197573000 -0.000025000 -0.000005000

2CO

Electronic energy (BP86) = -394.885641

Zero-point correction (BP86) = 0.127193

Thermal correction to Gibbs free energy (BP86) = 0.091190

Electronic energy (M06) = -394.745215

6 -1.787243000 -0.687231000 -0.000177000

6 -1.781660000 0.701463000 0.000192000

7 -0.538257000 -1.248287000 -0.000653000

1 -2.691133000 -1.298989000 -0.000305000

7 -0.528191000 1.252455000 0.000310000

1 -2.680592000 1.320486000 0.000139000

4 0.462358000 -0.001925000 -0.000521000

6 2.155612000 -0.008572000 0.000266000

8 3.309792000 -0.012995000 -0.000098000

6 -0.413910000 -2.695482000 0.000345000

1 0.645650000 -2.981076000 -0.004975000

1 -0.880303000 -3.144502000 0.894359000

1 -0.889885000 -3.146381000 -0.887606000

6 -0.392211000 2.698594000 0.000000000

1 -0.863746000 3.152830000 0.888637000

1 0.669616000 2.975667000 0.004615000

1 -0.855768000 3.151821000 -0.893349000

1NHC

Electronic energy (BP86) = -429.181694

Zero-point correction (BP86) = 0.137454

Thermal correction to Gibbs free energy (BP86) = 0.101618

Electronic energy (M06) = -429.0159452

6	-3.125697000	-0.685739000	0.049367000
6	-3.125963000	0.685385000	-0.049633000
7	-1.847588000	-1.230625000	0.083449000
1	-4.022586000	-1.303287000	0.100148000
7	-1.848073000	1.230791000	-0.083298000
1	-4.023091000	1.302561000	-0.100724000
4	-0.824682000	0.000314000	0.000276000
1	-1.811058000	-2.239003000	0.180106000
1	-1.811885000	2.239206000	-0.179681000
6	0.911875000	0.000305000	0.000164000
7	1.774766000	1.063076000	0.091506000
7	1.774248000	-1.062877000	-0.091412000
6	3.107153000	-0.679126000	-0.058420000
6	3.107491000	0.678700000	0.058141000
1	1.445462000	2.016113000	0.184744000
1	1.444443000	-2.015744000	-0.184620000
1	3.927747000	1.382714000	0.119250000
1	3.927066000	-1.383521000	-0.119758000

2NHC

Electronic energy (BP86) = -507.761771

Zero-point correction (BP86) = 0.190033

Thermal correction to Gibbs free energy (BP86) = 0.149686

Electronic energy (M06) = -507.5884233

6	2.790711000	0.688084000	-0.022969000
6	2.791081000	-0.687220000	0.024034000
7	1.522429000	1.247279000	-0.041205000
1	3.689115000	1.307942000	-0.048527000
7	1.523121000	-1.247135000	0.040611000
1	3.689819000	-1.306554000	0.050534000
4	0.511987000	-0.000259000	-0.000943000
6	-1.223400000	-0.000283000	-0.000490000
7	-2.086173000	-1.050668000	-0.189844000
7	-2.085876000	1.050209000	0.189546000
6	-3.418420000	0.670586000	0.120860000
6	-3.418614000	-0.670884000	-0.119966000
1	-1.756375000	-1.990636000	-0.373955000
1	-1.755782000	1.990098000	0.373546000
1	-4.238708000	-1.366457000	-0.245487000
1	-4.238311000	1.366266000	0.247110000
6	1.418530000	2.688255000	-0.091511000
1	0.376620000	2.993754000	-0.281487000
1	1.737108000	3.176132000	0.850907000
1	2.028683000	3.125669000	-0.904728000
6	1.419861000	-2.688160000	0.091265000
1	2.028453000	-3.124899000	0.906013000
1	0.377685000	-2.994102000	0.279012000
1	1.740751000	-3.176242000	-0.850251000

1PMe$_3$

Electronic energy (BP86) = -664.029896

Zero-point correction (BP86) = 0.176863

Thermal correction to Gibbs free energy (BP86) = 0.136836

Electronic energy (M06) = -663.9172583

6	3.098431000	-0.685454000	0.006057000
6	3.084901000	0.685375000	0.004865000
7	1.821116000	-1.247715000	0.010640000
1	3.999044000	-1.299014000	0.001457000
7	1.795754000	1.220850000	0.008428000
1	3.972707000	1.317204000	-0.000757000
4	0.813083000	-0.023527000	0.014368000
1	1.784569000	-2.259843000	0.010106000
1	1.738041000	2.232046000	0.005789000
15	-1.304544000	-0.006034000	0.003311000
6	-2.092227000	-1.123449000	-1.227939000
1	-1.763250000	-2.154151000	-1.039964000
1	-3.189740000	-1.079546000	-1.176959000
1	-1.759980000	-0.841588000	-2.235363000
6	-2.147081000	-0.480443000	1.571838000
1	-1.831782000	0.203631000	2.370520000
1	-3.242489000	-0.451725000	1.475518000
1	-1.833861000	-1.494475000	1.853882000
6	-2.016149000	1.643877000	-0.377737000
1	-1.663024000	2.369217000	0.366974000
1	-1.664878000	1.969223000	-1.365316000
1	-3.114868000	1.622263000	-0.369000000

2PMe$_3$

Electronic Energy (BP86) = -742.608516

Zero-point correction (BP86) = 0.229768

Thermal correction to Gibbs free energy (BP86) = 0.186238

Electronic energy (M06) = -742.4892622

6	2.787550000	-0.685850000	0.009379000
6	2.787214000	0.686500000	0.009299000
7	1.515377000	-1.250432000	-0.005015000
1	3.683868000	-1.308510000	0.014959000
7	1.514756000	1.250482000	-0.005222000
1	3.683224000	1.309604000	0.014874000
4	0.531372000	-0.000247000	-0.016898000
6	1.418349000	-2.694312000	0.001777000
1	1.866324000	-3.142976000	0.909263000
1	0.364194000	-3.007124000	-0.029482000
1	1.922252000	-3.154209000	-0.869897000
6	1.417205000	2.694324000	0.001901000
1	0.362963000	3.006785000	-0.029599000
1	1.864783000	3.142923000	0.909614000
1	1.921193000	3.154606000	-0.869524000
15	-1.591335000	-0.000200000	-0.002244000
6	-2.370989000	1.447851000	-0.824823000
1	-3.467985000	1.392735000	-0.776674000
1	-2.036484000	2.370400000	-0.332438000
1	-2.051763000	1.487138000	-1.874090000
6	-2.371901000	-1.442771000	-0.833633000
1	-2.053676000	-1.475072000	-1.883452000
1	-2.036803000	-2.368561000	-0.347765000
1	-3.468868000	-1.388066000	-0.784080000
6	-2.397728000	-0.005236000	1.655445000

1 -2.070748000 0.880041000 2.216663000

1 -3.495103000 -0.004271000 1.577964000

1 -2.071964000 -0.894841000 2.210500000

1H$^+$

Electronic Energy (BP86) = -203.233452

Zero-point correction (BP86) = 0.073589

Thermal correction to Gibbs free energy (BP86) = 0.046273

Electronic energy (M06) = -203.1785046

6 0.748489000 -0.859882000 0.053390000

6 -0.749162000 -0.859322000 0.053362000

7 1.249482000 0.314494000 -0.108135000

1 1.332598000 -1.774296000 0.194175000

7 -1.249333000 0.315465000 -0.107813000

1 -1.334009000 -1.773391000 0.193313000

4 0.000421000 1.490425000 0.014950000

1 2.269809000 0.405019000 -0.107418000

1 -2.269609000 0.406537000 -0.107650000

1 0.002521000 2.679936000 0.638898000

2H$^+$

Electronic energy (BP86) = -281.843028

Zero-point correction (BP86) = 0.126816

Thermal correction to Gibbs free energy (BP86) = 0.094774

Electronic energy (M06) = -281.777054

6 0.744357000 -1.046601000 0.000059000

6 -0.744361000 -1.046592000 0.000035000

7 1.274187000 0.125910000 0.000005000

1 1.323973000 -1.976499000 0.000088000

7	-1.274184000	0.125923000	0.000012000
1	-1.323988000	-1.976483000	-0.000089000
4	-0.000005000	1.312002000	0.000093000
1	0.000071000	2.646513000	0.000186000
6	2.711430000	0.350843000	-0.000057000
1	3.276540000	-0.589210000	0.000256000
1	2.969893000	0.955431000	-0.882242000
1	2.969884000	0.956108000	0.881650000
6	-2.711435000	0.350846000	-0.000076000
1	-2.969751000	0.956522000	-0.881538000
1	-3.276531000	-0.589215000	-0.000929000
1	-2.970046000	0.955008000	0.882360000

1H$^-$

Electronic energy (BP86) = -203.552279

Zero-point correction (BP86) = 0.069681

Thermal correction to Gibbs free energy (BP86) = 0.042524

Electronic energy (M06) = -203.4812337

6	0.000000000	1.148306000	0.000000000
6	-1.100031000	0.329548000	0.000000000
7	1.203978000	0.433659000	0.000000000
1	-0.038293000	2.241767000	0.000000000
7	-0.760924000	-1.028925000	0.000000000
1	-2.136465000	0.680133000	0.000000000
4	0.863874000	-1.160533000	0.000000000
1	2.048335000	0.995043000	0.000000000
1	-1.540953000	-1.676704000	0.000000000
1	1.710682000	-2.298372000	0.000000000

2H$^-$

Electronic energy (BP86) = -282.138338

Zero-point correction (BP86) = 0.122223

Thermal correction to Gibbs free energy (BP86) = 0.090397

Electronic energy (M06) = -282.058914

6	-0.686368000	-1.072778000	0.000007000
6	0.686368000	-1.072778000	-0.000007000
7	-1.239596000	0.207512000	0.000013000
1	-1.311915000	-1.971690000	0.000010000
7	1.239596000	0.207512000	-0.000013000
1	1.311915000	-1.971690000	-0.000010000
4	0.000000000	1.268850000	0.000000000
6	2.670401000	0.327376000	0.000003000
1	2.952882000	1.391974000	-0.000031000
1	3.155418000	-0.139377000	0.890406000
1	3.155438000	-0.139440000	-0.890356000
6	-2.670401000	0.327376000	-0.000003000
1	-3.155438000	-0.139440000	0.890357000
1	-2.952882000	1.391974000	0.000031000
1	-3.155418000	-0.139377000	-0.890406000
1	0.000000000	2.681322000	0.000000000

1BH_3

Electronic energy (BP86) = -229.523923

Zero-point correction (BP86) = 0.095681

Thermal correction to Gibbs free energy (BP86) = 0.065075

Electronic energy (M06) = -229.4584645

6	0.267792000	-1.379882000	0.698786000
6	0.267792000	-1.379882000	-0.698786000
7	0.267792000	-0.127953000	1.228982000
1	0.209028000	-2.279438000	1.311046000
7	0.267792000	-0.127953000	-1.228982000
1	0.209028000	-2.279438000	-1.311046000
4	0.162796000	0.890906000	0.000000000
1	0.226360000	-0.056808000	2.240538000
1	0.226360000	-0.056808000	-2.240538000
5	-1.101057000	2.363653000	0.000000000
1	-1.581892000	2.638480000	-1.059422000
1	-1.581892000	2.638480000	1.059422000
1	0.184525000	2.363564000	0.000000000

2BH_3

Electronic energy (BP86) = -308.107318

Zero-point correction (BP86) = 0.148545

Thermal correction to Gibbs free energy (BP86) = 0.113083

Electronic energy (M06) = -308.0326213

6	0.699903000	-1.371970000	-0.252015000
6	-0.700551000	-1.371713000	-0.251989000

7	1.248630000	-0.195632000	0.135645000
1	1.309795000	-2.206859000	-0.603201000
7	-1.248894000	-0.195180000	0.135599000
1	-1.310766000	-2.206453000	-0.602972000
4	0.000045000	0.796190000	0.339878000
5	0.001063000	2.572366000	-0.375686000
1	0.001378000	2.178831000	0.852299000
1	1.058642000	3.002716000	-0.736138000
1	-1.056988000	3.001812000	-0.735940000
6	2.693559000	-0.049572000	0.186952000
1	3.102039000	-0.484713000	1.114665000
1	3.182910000	-0.546581000	-0.666073000
1	2.957674000	1.014784000	0.165026000
6	-2.693762000	-0.048619000	0.186901000
1	-3.183367000	-0.546671000	-0.665387000
1	-3.102282000	-0.482329000	1.115287000
1	-2.957575000	1.015808000	0.163551000

1W(CO)$_5$

Electronic energy (BP86) = -837.152414

Zero-point correction (BP86) = 0.106868

Thermal correction to Gibbs free energy (BP86) = 0.054128

Electronic energy (M06) = -836.6437627

6	-1.514928000	-3.730016000	-0.701846000
6	-1.514938000	-3.730012000	0.701855000
7	-1.515597000	-2.484434000	-1.231728000

1	-1.447918000	-4.631125000	-1.311003000
7	-1.515612000	-2.484428000	1.231730000
1	-1.447937000	-4.631119000	1.311017000
4	-1.369257000	-1.449092000	0.000000000
1	-1.489159000	-2.411942000	-2.244238000
1	-1.489188000	-2.411931000	2.244240000
74	0.378788000	0.341294000	-0.000002000
6	0.445555000	2.328237000	0.000002000
8	0.440048000	3.490096000	0.000005000
6	-1.628959000	0.625304000	-0.000002000
8	-2.781947000	0.844532000	-0.000003000
6	2.463177000	0.244169000	-0.000006000
8	3.618016000	0.213648000	-0.000009000
6	0.387223000	0.157917000	-2.048013000
8	0.385619000	0.026900000	-3.200919000
6	0.387228000	0.157909000	2.048008000
8	0.385627000	0.026886000	3.200913000