Electronic Supplementary Material (ESI) for Dalton Transactions.

Supporting Information

Electrochemical Reduction of CO_2 to CO and $HCOO^-$ on Metal-Cyclam Complex Catalysts: Selectivity and Limiting Potential from DFT

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Table S1. Computed reduction potentials of $[LM]^{3+}$

$[LCr]^{3+}$	$[LMn]^{3+}$	$[LFe]^{3+}$	$[LCo]^{3+}$	$[LRu]^{3+}$	$[LRh]^{3+}$	$[LOs]^{3+}$	$[LIr]^{3+}$	$[LCr]^{3+}$
1.19	-0.06	1.02	1.46	0.72	1.99	0.45	1.17	1.19

Table S2. AIM (Bader) charges of $[LM]^n$, $[LM]^{(n-1)}$ and $[LM\text{-}COO]^{(n-1)}$ in CO_2 adduct formation.

	$[LM]^n$		$[LM]^{(n-1)}$		$[LM\text{-}COO]^{(n-1)}$			
	L	M	L	M	L	M	L+M	CO_2
$[LNi]^{2+}$	1.23	0.77	0.44	0.56	0.66	1.00	1.66	C (1.78), O (-1.22), O (1.22)= -0.66
$[LPd]^{2+}$	1.31	0.69	0.68	0.32	0.90	0.66	1.56	C (1.91), O (-1.24), O (-1.23)= -0.55

Table S3. Reaction free energies (kJ/mol) of $[LM\text{-}H]^{(n-1)}$ with $CO_{2(g)}$, $HCO_3^-{}_{(aq)}$, and $CO_3^{2-}{}_{(aq)}$; and $[LM\text{-}H]^{(n-1)}$ with H^+ through HCO_3^- and H_2O.

Catalyst	$\Delta G^\circ_{rxn}(HCOO^-)$			$\Delta G^\circ_{rxn}(H_2)$	
	$CO_{2(g)}$	$HCO_3^-{}_{(aq)}$	$CO_3^{2-}{}_{(aq)}$	H_2O	$HCO_3^-{}_{(aq)}$
$[LCr]^{2+}$	-121.1	-116.74	-95.36	-86.22	-107.6
$[LCr]^{+}$	-139.84	-135.48	-114.1	-104.96	-126.34
$[LMn]^{2+}$	-106.19	-101.83	-80.45	-71.31	-92.69
$[LMn]^{+}$	-225.58	-221.22	-199.84	-190.7	-212.08
$[LFe]^{2+}$	-111.05	-106.69	-85.31	-76.17	-97.55
$[LFe]^{+}$	-94.42	-90.06	-68.68	-59.54	-80.92
$[LCo]^{2+}$	-101.5	-97.14	-75.76	-66.62	-88
$[LCo]^{+}$	-173.84	-169.48	-148.1	-138.96	-160.34
$[LMo]^{3+}$	125.4	129.76	151.14	160.28	138.9
$[LMo]^{2+}$	-16.8	-12.44	8.94	18.08	-3.3
$[LMo]^{+}$	-163.53	-159.17	-137.79	-128.65	-150.03
$[LTc]^{2+}$	-62.01	-57.65	-36.27	-27.13	-48.51
$[LTc]^{+}$	-126.92	-122.56	-101.18	-92.04	-113.42
$[LRu]^{2+}$	24.4	28.76	50.14	59.28	37.9

[LRu]$^{+}$	-116.15	-111.79	-90.41	-81.27	-102.65
[LRh]$^{2+}$	-74.48	-70.12	-48.74	-39.6	-60.98
[LRh]$^{+}$	-149.67	-145.31	-123.93	-114.79	-136.17
[LW]$^{3+}$	-20.67	-16.31	5.07	14.21	-7.17
[LW]$^{2+}$	-82.12	-77.76	-56.38	-47.24	-68.62
[LW]$^{+}$	-120.21	-115.85	-94.47	-85.33	-106.71
[LRe]$^{3+}$	83.4	87.76	109.14	118.28	96.9
[LRe]$^{2+}$	25.67	30.03	51.41	60.55	39.17
[LRe]$^{+}$	-130.8	-126.44	-105.06	-95.92	-117.3
[LOs]$^{2+}$	50.78	55.14	76.52	85.66	64.28
[LOs]$^{+}$	-106.7	-102.34	-80.96	-71.82	-93.2
[LIr]$^{2+}$	-66.73	-62.37	-40.99	-31.85	-53.23
[LIr]$^{+}$	-149.43	-145.07	-123.69	-114.55	-135.93
[LPt]$^{+}$	-132.66	-128.3	-106.92	-97.78	-119.16

Table S4. AIM (Bader) charges of $[LM\text{-}H]^{+}$ and $([LM]\text{-}H\text{-}COO)^{+}$ in $HCOO^{-}$ formation

M	$[LM\text{-}H]^{+}$			$([LM]\text{-}H\text{-}COO)^{+}$ **							
	M	L	H*	M	L	total	H	C	O	O	total
Mo	1.17	0.44	-0.62	1.38	0.55	1.94	-0.11	1.83	-1.33	-1.33	-0.94
Rh	0.63	0.90	-0.53	0.85	1.05	1.90	-0.05	1.81	-1.33	-1.32	-0.90
Co	0.98	0.72	-0.70	1.08	0.87	1.96	-0.06	1.80	-1.35	-1.35	-0.96

H* atom bound to the metal center (M-H); $([LM]\text{-}H\text{-}COO)^{+}$ ** final structure after constrained relaxation.

Table S5(a). Spin multiplicities of the ground state of the intermediates in the hydride cycle.

Metal center	$[LM]^{3+}$	$[LM]^{2+}$	$[LM]^{+}$	$[LM]^{0}$	$[LM\text{-}H]^{3+}$	$[LM\text{-}H]^{2+}$	$[LM\text{-}H]^{+}$	$[LM\text{-}H]^{0}$
Cr	--	4	5	4	--	4	5	4
Mn	--	4	5	4	--	7	4	3
Fe	--	3	2	3	--	2	3	4
Co	--	2	3	2	--	1	2	1
Mo	2	1	4	3	1	4	3	2
Tc	5	4	3	2	4	3	2	1
Ru	--	3	2	1	--	2	1	2
Rh	--	2	1	2	--	1	2	1
W	4	1	4	3	1	2	1	4
Re	1	2	3	2	4	2	2	1
Os	--	3	2	1	--	2	1	2
Ir	--	2	1	2	--	1	2	1
Pt	--	1	2	--	--	2	1	--

Table S5(b). Spin multiplicities of the ground state of the intermediates in the CO cycle

Metal center	$[LM]^{n}$	$[LM]^{(n-1)}$	$[LM\text{-}COO]^{(n-1)}$	$[LM\text{-}COO]^{(n-2)}$	$[LM\text{-}COOH]^{(n-1)}$	$[LM\text{-}CO]^{n}$
$[LNi]^{2+}$	3	2	2	3	3	3
$[LPd]^{2+}$	1	2	2	1	1	1
$[LTc]^{3+}$	5	4	--	--	--	--

Section S1. Determination of pK_a

Determining pK_a of carboxylate adducts: We use an isodesmic proton exchange (IPE) reaction scheme to determine pK_a of carboxylate adduct. This method has been used for different classes of acids and has an error of ± 0.40 pK_a unit[1]. In particular, this method has been successfully applied in determining pK_a of the porphyrin carboxylate adduct formed in CO_2 electrochemical reduction[2].

Following the IPE method, pK_a of an acid is calculated with reference to an acid of known pK_a, as shown in eqn. S.1. ΔG°_{PE} can be obtained from the frequency calculations of the DFT-optimized geometries of acid and its conjugate base. We used the carboxylic acids, including propanoic, succinic, 2-butynoic, oxalic, tartaric, 3-chloropropanoic, glycolic, flouroacetic, difluoroacetic and

formic acids, to determine ΔG°_{PE}. Formic acid was chosen as the reference acid. The computed ΔG°_{PE} of all acids were plotted against the experimental pK_a values[3] to construct the linear regression shown in Figure S1.

$$[R\text{-}COOH]^{n} + ref[R'\text{-}COO]_{(m-1)} \rightleftharpoons [R\text{-}COO]_{(n-1)} + ref[R'\text{-}COOH]_{m} \; ; \Delta G^{\circ}_{PE} \qquad (S.1)$$

$$\Delta G^{\circ}_{PE} = (G^{\circ}ref[R'\text{-}COOH]_{m} + G^{\circ}[R'\text{-}COO]_{(n-1)}) - (G^{\circ}[R\text{-}COOH]^{n} + G^{\circ}ref[R'\text{-}COO]_{(m-1)}) \qquad (S.2)$$

$$pK_a[R\text{-}COOH]^{n} = \frac{\Delta G^{\circ}_{PE}}{2.303RT} + pK_aref[R'\text{-}COOH]^{m} \qquad (S.3)$$

The linear regression of the experimental pK_a *vs*. $\Delta G^{\circ}_{PE,}$ in Figure S1 gives $pKa = 0.08\ \Delta G^{\circ}_{PE} + 3.64$. The intercept of 3.64 is close to the experimental pK_a (3.76) of formic acid. This equation was then used to determine the pK_a of a carboxylate adduct from the corresponding ΔG°_{PE} of optimized of $[LM\text{-}COOH]^{+}$ and $[LM\text{-}COO]^{0}$.

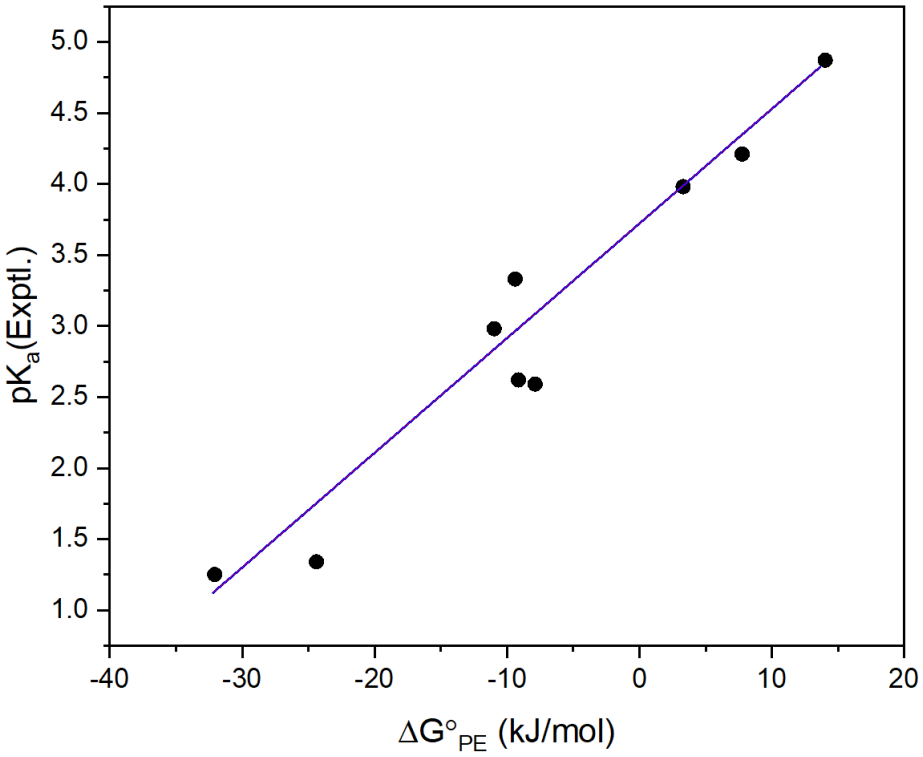


Figure S1. A plot of pK_a (experimental) values of different carboxylic acids versus ΔG°_{PE} eqn. S3 used to calculate pK_a values of carboxylate adduct for this study. (**R^2 = 0.94** and **Intercept = 3.64** and **slope = 0.08**).

Determining pK_a of proton adduct ($[LM\text{-}H]^n$): The pK_a values of $[LM\text{-}H]^n$ was calculated using the IPE scheme shown in equations S.4-S.6. IPE has been demonstrated to determine pK_a of metal-hydrides with an accuracy of 1.50 units for metal hydrides[4, 5].

The experimental pK_a=1.81[6] of $[LNi\text{-}H]^{2+}$ was used as a reference for the metal-cyclam hydride complexes reported in this study. $\Delta G^{\circ}_{PE(LM\text{-}H)}$ was computed using eqn. S.5 based on the DFT optimized geometries of $[LM\text{-}H]^n$, $[LNi]^+$, $[LNi\text{-}H]^{2+}$, and $[LM]^{(n-1)}$. pK_a of all proton adducts can then be computed using eqn. S.6.

$$[LM\text{-}H]^{n} + ref[LNi]_{+} \rightleftharpoons [LM]_{(n-1)} + ref[LNi\text{-}H]_{2+} \quad ; \Delta G^{\circ}_{PE(LM\text{-}H)} \qquad (S.4)$$

$$\Delta G^{\circ}_{PE(LM\text{-}H)} = (G^{\circ}[LM]_{(n-1)} + G^{\circ}ref[LNi\text{-}H]_{2+}) - (G^{\circ}[LM\text{-}H]^{n} + G^{\circ}ref[LNi]_{+}) \qquad (S.5)$$

$$pK_a[LM\text{-}H]^{n} = \frac{\Delta G^{\circ}_{PE(LM\text{-}H)}}{2.303RT} + 1.81 \qquad (S.6)$$

Section S2. Determination of Reduction Potentials.

The reduction potentials have been determined using the thermochemical cycle presented in Figure S2, where $(Ox)^{n}$ represents oxidized species and $(Red)^{(n-1)}$ the reduced species[7]. This cycle utilizes the computed free energies in gas phase and water as reactants and products and includes the SHE cycle that absorbs the computational errors in the reduction potential of hydrogen electrode and proton solvation energy. The reduction potential was then calculated from eqn S.8. We used a proton solvated with six water molecules (proton-water cluster approach) to compute G° for H^{+} as described in literature[8].

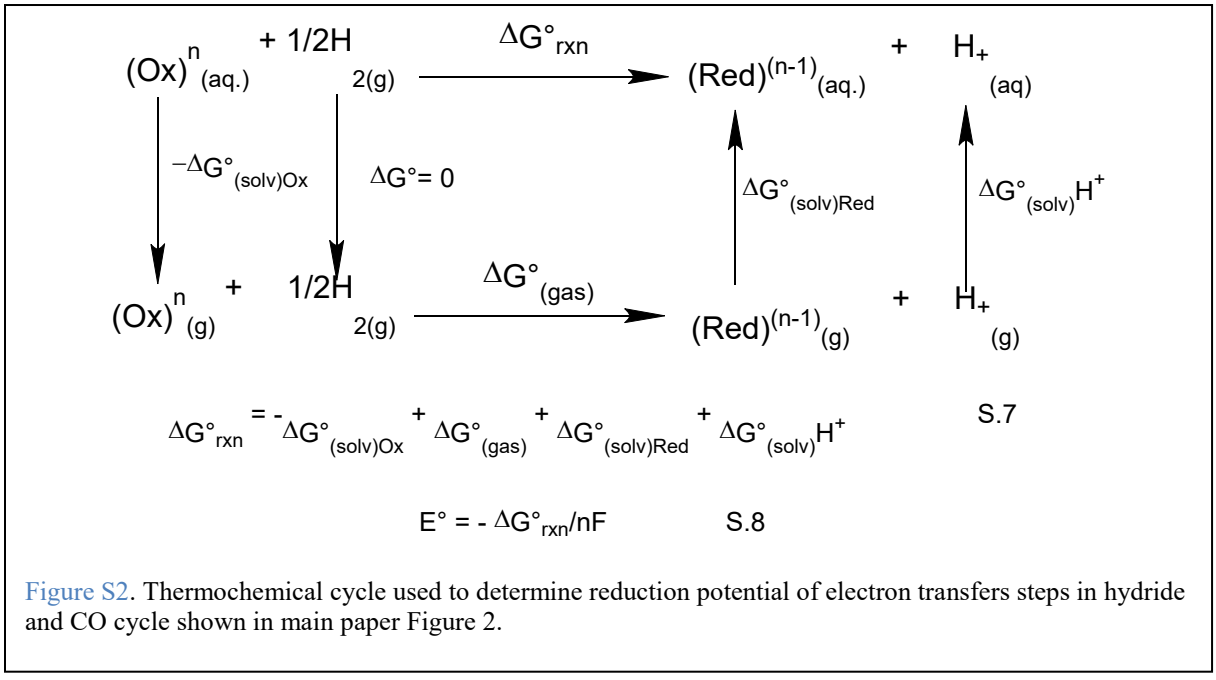
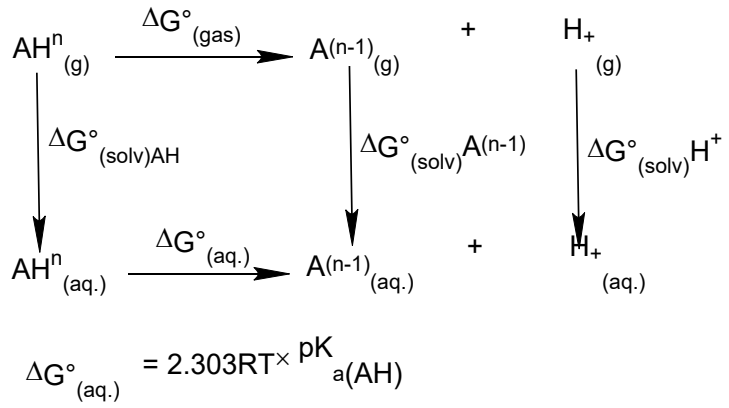


Figure S2. Thermochemical cycle used to determine reduction potential of electron transfers steps in hydride and CO cycle shown in main paper Figure 2.

A value of -1112.52 kJ/mol[9] for $G^{\circ}_{solv}(H^{+})$ can be reproduced using B3LYP/6-311++G(d,p) with the water cluster approach[8]. Using the optimized structure of proton-water cluster at B3LYP/6-311++G(d,p) level, we obtained $G^{\circ}_{solv}(H^{+})$ = -1125.96 kJ/mol at B3LYP-D3/6-31G(d,p) level. We point out that the difference in solvation energy of proton will not change the predicted trends and shifts the reduction potentials only by ~ 50 mV.

Section S3. Thermochemical cycle. The free energies of OH^{-}, HCO_3^{-}, CO_3^{2-} and $HCOO^{-}$ were determined through the thermochemical cycle shown in Figure S3.



$$\Delta G^{\circ}_{(solv)}A^{(n-1)} = \Delta G^{\circ}_{(aq.)} - \Delta G^{\circ}_{(solv)AH} - \Delta G^{\circ}_{(gas)} - \Delta G^{\circ}_{(solv)}H^{+} + RT \ln 24.46 \quad \text{(S.9)}$$

$$G^{\circ}(A^{(n-1)}_{(aq.)}) = \Delta G^{\circ}_{(aq.)} - \Delta G^{\circ}_{(solv)AH} - \Delta G^{\circ}_{(gas)} - \Delta G^{\circ}_{(solv)}H^{+} + RT \ln 24.46 + G^{\circ}(H_{+}{}_{(g)}) \quad \text{(S.10)}$$

Figure S3. Thermochemical cycle used to determine energy of OH^{-}, HCO_3^{-}, CO_3^{2-} and $HCOO^{-}$. These species are represented as $A^{(n-1)}_{(aq.)}$. AH is starting acid.

Section S4(a). Cartesian coordinates of intermediates of CO cycle

Ni (II)-cyclam

$[LNi]^{2+}$

```
Charge = 2 Multiplicity = 3
N  1.88513800  0.86465600  0.05018100
N -1.01232500  1.80944500  0.03693800
N -1.88513800 -0.86465600 -0.05018100
N  1.01232500 -1.80944500 -0.03693800
H  2.07117100  1.11485100  1.02463900
H -1.01969700  2.12158100  1.01132400
H -2.07117100 -1.11485100 -1.02463900
H  1.01969700 -2.12158100 -1.01132400
C  2.83620700 -0.21094700 -0.33185700
H  3.86533900  0.05318700 -0.06610800
H  2.78138800 -0.32856400 -1.41901200
C  2.03943200  2.09454100 -0.76763800
H  1.89026000  1.80851800 -1.81413500
H  3.06479900  2.47118600 -0.66679600
C  1.04059800  3.18358100 -0.37802500
H  1.34388400  4.10707500 -0.88182400
H  1.10130900  3.38051400  0.70091400
C -0.40589500  2.89348600 -0.77667500
H -1.01189300  3.80270800 -0.67878600
H -0.44790400  2.57523300 -1.82356000
C -2.41321500  1.50306800 -0.35012800
H -2.43533100  1.37614400 -1.43730800
H -3.08838100  2.32392000 -0.08578100
C -2.83620700  0.21094700  0.33185700
H -3.86533900 -0.05318700  0.06610800
H -2.78138800  0.32856400  1.41901200
C -2.03943200 -2.09454100  0.76763800
H -1.89026000 -1.80851800  1.81413500
H -3.06479900 -2.47118600  0.66679600
C -1.04059800 -3.18358100  0.37802500
H -1.34388400 -4.10707500  0.88182400
H -1.10130900 -3.38051400 -0.70091400
C  0.40589500 -2.89348600  0.77667500
H  1.01189300 -3.80270800  0.67878600
H  0.44790400 -2.57523300  1.82356000
C  2.41321500 -1.50306800  0.35012800
H  2.43533100 -1.37614400  1.43730800
H  3.08838100 -2.32392000  0.08578100
Ni 0.00000000  0.00000000  0.00000000
```

$[LNi]^{+}$

```
Charge = 1 Multiplicity = 2
N  1.90776200  0.87008200  0.05286900
N -1.02735300  1.82850400  0.04439000
N -1.90776200 -0.87008200 -0.05286900
```

```
N  1.02735300 -1.82850400 -0.04439000
H  2.11062600  1.12365100  1.02138300
H -1.04745900  2.15491000  1.01209500
H -2.11062600 -1.12365100 -1.02138300
H  1.04745900 -2.15491000 -1.01209500
C  2.84281900 -0.20954800 -0.33201200
H  3.88357500  0.03288700 -0.07822900
H  2.78303100 -0.33053000 -1.41928800
C  2.04812100  2.09448700 -0.76443500
H  1.89365800  1.81024900 -1.81139500
H  3.06901200  2.49646500 -0.68166300
C  1.03891000  3.17875600 -0.37371700
H  1.34366000  4.10840300 -0.86712800
H  1.09774800  3.36821500  0.70720900
C -0.41348400  2.89800800 -0.77160100
H -1.00089800  3.82517000 -0.69412900
H -0.45079600  2.57525300 -1.81810000
C -2.41680300  1.50761200 -0.34815600
H -2.43315500  1.37247400 -1.43528400
H -3.11552900  2.31796200 -0.10023900
C -2.84281900  0.20954800  0.33201200
H -3.88357500 -0.03288700  0.07822900
H -2.78303100  0.33053000  1.41928800
C -2.04812100 -2.09448700  0.76443500
H -1.89365800 -1.81024900  1.81139500
H -3.06901200 -2.49646500  0.68166300
C -1.03891000 -3.17875600  0.37371700
H -1.34366000 -4.10840300  0.86712800
H -1.09774800 -3.36821500 -0.70720900
C  0.41348400 -2.89800800  0.77160100
H  1.00089800 -3.82517000  0.69412900
H  0.45079600 -2.57525300  1.81810000
C  2.41680300 -1.50761200  0.34815600
H  2.43315500 -1.37247400  1.43528400
H  3.11552900 -2.31796200  0.10023900
Ni 0.00000000  0.00000000  0.00000000
```

[LNi-COO]$^{+}$

```
Charge = 1 Multiplicity = 2
N  1.43121400 -1.56969600 -0.01158200
N  1.43111000  1.56977100 -0.01167000
N -1.29968400  1.47758500 -0.70570800
N -1.29957600 -1.47765300 -0.70573600
H  1.48149100 -1.79506400  0.98259300
H  1.48153700  1.79515000  0.98249400
H -1.33563900  1.40949500 -1.72575700
H -1.33552300 -1.40954700 -1.72578500
C  0.80011000 -2.71880600 -0.70746600
H  1.29394600 -3.66400100 -0.45213000
H  0.91998400 -2.55595300 -1.78414000
C  2.80575200 -1.28716800 -0.48550300
H  2.76639900 -1.19793900 -1.57662100
H  3.45986000 -2.13699100 -0.24946100
C  3.37977000  0.00011900  0.11241300
```

```
H  4.45928200  0.00016700 -0.07201000
H  3.24714700  0.00023900  1.20278700
C  2.80556100  1.28719000 -0.48579900
H  3.45966900  2.13712400 -0.25015100
H  2.76597700  1.19762800 -1.57688200
C  0.79991600  2.71886900 -0.70748800
H  0.91975400  2.55606600 -1.78417200
H  1.29371200  3.66408100 -0.45213600
C -0.68488400  2.77901400 -0.36314100
H -1.16631900  3.60659600 -0.89793800
H -0.81781600  2.93683200  0.70887000
C -2.67977600  1.29780700 -0.19781100
H -2.62853300  1.29419500  0.89493000
H -3.30379400  2.14965300 -0.50041100
C -3.31224500 -0.00010100 -0.70783700
H -4.36360400 -0.00014300 -0.40161900
H -3.30780600 -0.00008100 -1.80693900
C -2.67968700 -1.29798100 -0.19785100
H -3.30364300 -2.14985900 -0.50048600
H -2.62845300 -1.29439700  0.89488900
C -0.68470000 -2.77905100 -0.36318500
H -0.81766700 -2.93691400  0.70881500
H -1.16605800 -3.60664900 -0.89802900
Ni 0.06142200  0.00001000 -0.13707300
C -0.32223200  0.00003400  1.90988100
O -0.39368700  1.14910800  2.33272000
O -0.39390100 -1.14905600  2.33264400
```

[LNi-COO]^{0}

```
Charge = 1 Multiplicity = 2
N -1.43121400  1.56969600 -0.01158200
N -1.43111000 -1.56977100 -0.01167000
N  1.29968400 -1.47758500 -0.70570800
N  1.29957600  1.47765300 -0.70573600
H -1.48149100  1.79506400  0.98259300
H -1.48153700 -1.79515000  0.98249400
H  1.33563900 -1.40949500 -1.72575700
H  1.33552300  1.40954700 -1.72578500
C -0.80011000  2.71880600 -0.70746600
H -1.29394600  3.66400100 -0.45213000
H -0.91998400  2.55595300 -1.78414000
C -2.80575200  1.28716800 -0.48550300
H -2.76639900  1.19793900 -1.57662100
H -3.45986000  2.13699100 -0.24946100
C -3.37977000 -0.00011900  0.11241300
H -4.45928200 -0.00016600 -0.07201000
H -3.24714700 -0.00023900  1.20278700
C -2.80556100 -1.28719000 -0.48579900
H -3.45966900 -2.13712400 -0.25015100
H -2.76597700 -1.19762800 -1.57688200
C -0.79991700 -2.71886900 -0.70748800
H -0.91975500 -2.55606600 -1.78417200
H -1.29371300 -3.66408100 -0.45213600
C  0.68488300 -2.77901400 -0.36314100
H  1.16631800 -3.60659600 -0.89793800
```

```
H  0.81781500 -2.93683200  0.70887000
C  2.67977600 -1.29780700 -0.19781100
H  2.62853300 -1.29419500  0.89493000
H  3.30379300 -2.14965400 -0.50041100
C  3.31224500  0.00010000 -0.70783700
H  4.36360400  0.00014200 -0.40161900
H  3.30780600  0.00008000 -1.80693900
C  2.67968700  1.29798100 -0.19785100
H  3.30364300  2.14985800 -0.50048600
H  2.62845300  1.29439700  0.89488900
C  0.68470000  2.77905100 -0.36318500
H  0.81766700  2.93691400  0.70881500
H  1.16605800  3.60664900 -0.89802900
Ni -0.0614220 -0.00001000 -0.13707300
C  0.32223200 -0.00003400  1.90988100
O  0.39368700 -1.14910800  2.33272000
O  0.39390100  1.14905600  2.33264400
```

[LNi-COOH]$^{+}$

```
Charge = 1, Multiplicity = 3
N -1.30805300 -1.48897000 -0.76548700
N -1.23276700  1.49365000 -0.83411500
N  1.49365100  1.52749900 -0.08018900
N  1.41667100 -1.62200000 -0.01228300
H -1.30086100 -1.48483900 -1.78745500
H -1.23031900  1.43905600 -1.85470300
H  1.56225800  1.75052200  0.91363300
H  1.48534600 -1.80805600  0.98918300
C -0.73419900 -2.77389500 -0.31074900
H -1.23788000 -3.63224300 -0.77288900
H -0.87621000 -2.83225900  0.77176500
C -2.69919600 -1.25068500 -0.32112700
H -2.68900200 -1.21055200  0.77205800
H -3.33962600 -2.09203400 -0.62025400
C -3.27022500  0.05046800 -0.89239700
H -4.33571800  0.08366300 -0.64122800
H -3.21042600  0.02656300 -1.98951100
C -2.63136300  1.34299800 -0.37565000
H -3.23068100  2.20305000 -0.70511700
H -2.61793500  1.34607700  0.71905500
C -0.59746100  2.77078800 -0.44361800
H -0.74155800  2.89608600  0.63270600
H -1.05631200  3.62685000 -0.95397800
C  0.89086900  2.69453500 -0.76884400
H  1.39356400  3.63041200 -0.49579500
H  1.02103100  2.54595400 -1.84644000
C  2.85214300  1.19941200 -0.56799100
H   2.79535300 1.09628200 -1.65730100
H  3.53559100  2.03242700 -0.35396900
C  3.40359500 -0.09422100  0.03833000
H  4.47799600 -0.12549700 -0.17223300
H  3.30035500 -0.07166800  1.13164600
C  2.78533500 -1.37921200 -0.52046900
H  3.42852700 -2.23728900 -0.28216500
```

```
H  2.72403300 -1.31063800 -1.61227400
C  0.75344700 -2.78742600 -0.64590800
H  0.88394700 -2.69295200 -1.72955800
H  1.21141600 -3.73367500 -0.33315100
Ni 0.04297400 -0.01249400 -0.10809600
C -0.38470200 -0.00815100  1.87206000
O -0.68009900 -0.97623200  2.58290100
O -0.25843000  1.21235300  2.52835700
H -0.44392000  1.05672500  3.47729800
```

[LNi-CO]$^{2+}$

```
Charge = 2 Multiplicity= 3
N -1.39076700 -1.18504100 -0.74428200
N -1.40327800  1.32039800 -0.52774900
N  1.43515200  1.29460600 -0.06531200
N  1.44766300 -1.21083300 -0.28184400
H -1.39208000 -1.09894300 -1.74056700
H -1.40459100  1.40649600 -1.52403500
H  1.43646500  1.20850900  0.93097400
H  1.44897600 -1.29693000  0.71444200
C -0.69119700 -2.41949300 -0.36005600
H -1.19171500 -3.26173800 -0.79017900
H -0.68979200 -2.51161700  0.70597000
C -2.77603500 -1.23425500 -0.25488300
H -2.77463000 -1.32637900  0.81114300
H -3.27655200 -2.07650000 -0.68500500
C -3.50891700  0.05898100 -0.65740400
H -4.51724200  0.02315900 -0.30117500
H -3.51032200  0.15110500 -1.72343000
C -2.78854600  1.27118400 -0.03835000
H -3.29775700  2.16973100 -0.31802400
H -2.78714100  1.17906000  1.02767600
C -0.71565100  2.47750100  0.06316700
H -0.71424600  2.38537700  1.12919300
H -1.22486200  3.37604800 -0.21650800
C  0.73558200  2.52905800 -0.44953700
H  1.23610000  3.37130300 -0.01941500
H  0.73417700  2.62118300 -1.51556300
C  2.82042000  1.34382000 -0.55471100
H  2.81901500  1.43594400 -1.62073700
H  3.32093800  2.18606500 -0.12458800
C  3.55330300  0.05058400 -0.15218900
H  4.56162700  0.08640700 -0.50841800
H  3.55470700 -0.04154000  0.91383700
C  2.83293100 -1.16161900 -0.77124300
H  3.34214200 -2.06016600 -0.49156900
H  2.83152600 -1.06949400 -1.83726900
C  0.76003600 -2.36793600 -0.87276000
H  0.75863100 -2.27581100 -1.93878600
H  1.26924700 -3.26648300 -0.59308600
Ni -0.15921300 0.07705300  0.26282700
C  0.06609300 -0.42552800  2.10213400
O  0.19698100 -0.71749500  3.17065700
```

Pd (II)-cyclam

$[LPd]^{2+}$

```
Charge = 2 Multiplicity = 1
N -1.37013700  1.53825600  0.29604600
N -1.37013200 -1.53825900  0.29604800
N  1.37017300 -1.53828900 -0.29600600
N  1.37016800  1.53829300 -0.29600600
H -1.46528300  1.62972700  1.31077900
H -1.46528000 -1.62973200  1.31078100
H  1.46543100 -1.62985700 -1.31071900
H  1.46543200  1.62986300 -1.31071800
C -0.72902400  2.78795300 -0.21264400
H -1.25169800  3.66925700  0.17260600
H -0.81020900  2.78433300 -1.30351500
C -2.72575200  1.29213200 -0.26249600
H -2.63197300  1.25442100 -1.35181100
H -3.36449600  2.14507200 -0.00502900
C -3.35080400 -0.00000400  0.26653300
H -4.40306600 -0.00000600 -0.03411500
H -3.33796300 -0.00000500  1.36465500
C -2.72574700 -1.29213800 -0.26249600
H -3.36449000 -2.14508000 -0.00503300
H -2.63196600 -1.25442500 -1.35181200
C -0.72901600 -2.78795500 -0.21264300
H -0.81020300 -2.78433500 -1.30351400
H -1.25168900 -3.66926000  0.17260800
C  0.72902000 -2.78795000  0.21273000
H  1.25168600 -3.66928600 -0.17246200
H  0.81019100 -2.78427200  1.30360200
C  2.72572900 -1.29212300  0.26266300
H  2.63184300 -1.25437700  1.35196800
H  3.36451400 -2.14506100  0.00528900
C  3.35081600  0.00000500 -0.26633400
H  4.40305700  0.00000600  0.03438900
H  3.33805100  0.00000700 -1.36445700
C  2.72572300  1.29212700  0.26266800
H  3.36450700  2.14506800  0.00530300
H  2.63183200  1.25437500  1.35197300
C  0.72901200  2.78795200  0.21273000
H  0.81018300  2.78427400  1.30360200
H  1.25167600  3.66928900 -0.17246200
Pd -0.00000700 0.00000000 -0.00014700
```

$[LPd]^{+}$

```
Charge = 1 Multiplicity = 2
N -1.43273100  1.66496100  0.34174600
N -1.43280800 -1.66495300  0.34177000
N  1.43288400 -1.66531000 -0.34195000
N  1.43296500  1.66530800 -0.34197900
H -1.58446300  1.81339300  1.33890500
H -1.58458300 -1.81342000  1.33891600
```

```
H  1.58555200 -1.81457800 -1.33883600
H  1.58570300  1.81463200 -1.33884600
C -0.74063000  2.85525700 -0.20612300
H -1.21299100  3.79032600  0.12471600
H -0.81464400  2.81551400 -1.29832600
C -2.73313000  1.32266400 -0.27622900
H -2.57919100  1.25314500 -1.35873400
H -3.46272100  2.12829900 -0.10310200
C -3.32590000  0.00004700  0.25123000
H -4.38623500  0.00006700 -0.02573000
H -3.29980900  0.00003900  1.34980700
C -2.73316700 -1.32258000 -0.27624700
H -3.46280300 -2.12818800 -0.10317600
H -2.57918200 -1.25303500 -1.35874400
C -0.74071700 -2.85524100 -0.20612700
H -0.81472800 -2.81547000 -1.29832900
H -1.21308600 -3.79031600  0.12468300
C  0.74043500 -2.85530900  0.20625700
H  1.21264300 -3.79056400 -0.12424400
H  0.81438500 -2.81523300  1.29845000
C  2.73283500 -1.32265400  0.27688800
H  2.57814000 -1.25295500  1.35927100
H  3.46266000 -2.12821800  0.10443400
C  3.32581600 -0.00004700 -0.25036200
H  4.38603200 -0.00006600  0.02706100
H  3.30020300 -0.00003300 -1.34894600
C  2.73286300  1.32255900  0.27692200
H  3.46273700  2.12809900  0.10455600
H  2.57810000  1.25281200  1.35929200
C  0.74052200  2.85529400  0.20626300
H  0.81446500  2.81518200  1.29845500
H  1.21273800  3.79055700 -0.12420200
Pd 0.00011600  0.00000100 -0.00041900
```

[LPd-COO]$^{+}$

```
Charge = 1 Multiplicity = 2
N -1.37013300 -1.61869300 -0.66155200
N -1.37053800  1.61840000 -0.66158900
N  1.46886000  1.68950000  0.01137200
N  1.46927300 -1.68921100  0.01138700
H -1.34749100 -1.67128300 -1.68106600
H -1.34792200  1.67100500 -1.68110200
H  1.68618600  1.84325900  0.99507800
H  1.68657100 -1.84286100  0.99511700
C -0.73743500 -2.84344600 -0.12213300
H -1.23119800 -3.75230800 -0.49075100
H -0.83590400 -2.82280100  0.96837500
C -2.75815600 -1.32559400 -0.24631100
H -2.77865100 -1.28890200  0.84502700
H -3.42340800 -2.13960500 -0.56769700
C -3.28168200 -0.00037500 -0.83618300
H -4.36756800 -0.00050000 -0.69147500
H -3.12009800 -0.00035100 -1.92358000
C -2.75846800  1.32496100 -0.24629900
```

```
H -3.42393600  2.13880500 -0.56765800
H -2.77892600  1.28825100  0.84504500
C -0.73809000  2.84327100 -0.12215500
H -0.83654500  2.82258500  0.96835500
H -1.23203400  3.75204600 -0.49075000
C  0.74474900  2.87010800 -0.52459500
H  1.20455100  3.80632800 -0.18661000
H  0.81963100  2.83795400 -1.61680600
C  2.71378900  1.31917600 -0.70254600
H  2.46957300  1.23432900 -1.76725500
H  3.45365800  2.12535200 -0.60056600
C  3.33987300  0.00036400 -0.20623800
H  4.37788700  0.00049500 -0.55587900
H  3.38552200  0.00038700  0.89013200
C  2.71413000 -1.31862800 -0.70249900
H  3.45419900 -2.12461600 -0.60046700
H  2.46992400 -1.23388500 -1.76721900
C  0.74541600 -2.86997400 -0.52455800
H  0.82029600 -2.83781000 -1.61677000
H  1.20541200 -3.80609900 -0.18656900
C -0.14751000  0.00002100  1.98698000
O -1.32574800  0.00036800  2.30686000
O  0.96070900 -0.00029600  2.50779000
Pd 0.04801400  0.00000800 -0.11848300
```

[LPd-COO]^{0}

```
Charge = 0 Multiplicity = 1
N  0.87064300  1.72010300 -0.51282900
N  1.90124700 -1.15252200 -0.63265800
N -0.71608800 -2.12143600  0.09304600
N -1.98026000  1.24364900 -0.76298900
H  0.85679700  1.32669700 -1.45484600
H  1.86944300 -1.24160800 -1.64828100
H -1.27243800 -2.49573200  0.85896200
H -2.43828700  1.43290800  0.12086500
C -0.10059900  2.83506400 -0.53017300
H  0.33927100  3.72452200 -1.00475000
H -0.35619300  3.09346400  0.50149400
C  2.28299500  2.05152200 -0.22989700
H  2.41535300  2.14181700  0.85369300
H  2.54476100  3.02228100 -0.67739700
C  3.22758200  0.98809300 -0.81377600
H  4.25273100  1.33806200 -0.65044800
H  3.08534500  0.95010800 -1.90345400
C  3.13811400 -0.43515500 -0.24577200
H  4.02385700 -1.00206300 -0.56970400
H  3.16154000 -0.39561300  0.84958400
C  1.78931600 -2.49298900 -0.01792900
H  1.97961000 -2.37480900  1.05380300
H  2.54077300 -3.19396600 -0.41180100
C  0.39484100 -3.08652900 -0.22929600
H  0.29159800 -3.98410700  0.38684400
H  0.29036700 -3.39520400 -1.27373100
```

```
C -1.62139500 -1.97648700 -1.10016000
H -0.99486900 -1.61511500 -1.92196000
H -1.95555500 -2.98542300 -1.37720600
C -2.86140600 -1.06939400 -0.94601800
H -3.69739000 -1.58562000 -1.43162700
H -3.13187000 -0.97358900  0.11094600
C -2.76532000  0.33635600 -1.58035800
H -3.79243300  0.69966100 -1.76971200
H -2.28363400  0.25448500 -2.56302900
C -1.35934900  2.42967900 -1.32245600
H -1.05950400  2.20309000 -2.35408300
H -2.02497200  3.30887900 -1.37620800
C -0.95822700  0.50243500  1.95554400
O -0.37170300  1.44259600  2.57575600
O -2.06333700 -0.02796200  2.25409700
Pd 0.15886800 -0.17161600  0.48006500
```

[LPd-COOH]$^{+}$

```
Charge = 1 Multiplicity = 1
N  1.53304100  1.57886800 -0.57162300
N  1.78958300 -1.48245700 -0.02166000
N -1.00068500 -1.69024600 -0.21224300
N -1.24507200  1.26024000 -0.72913000
H  1.87394200  1.60032800 -1.53570900
H  2.16614800 -1.77932600 -0.92510400
H -1.37631400 -1.48961500  0.73187100
H -1.60117700  1.32955700  0.26547500
C  0.64675400  2.76537100 -0.37113000
H  1.15430600  3.68186000 -0.69032600
H  0.43293800  2.83887700  0.69886400
C  2.71656800  1.56657900  0.32710100
H  2.35106400  1.66973000  1.35325000
H  3.33490200  2.44277600  0.09860400
C  3.55173900  0.29186500  0.18979300
H  4.49714100  0.46533900  0.71366700
H  3.80525300  0.11900200 -0.86448300
C  2.92155600 -0.96626200  0.79120100
H  3.67709900 -1.75625100  0.87716300
H  2.53771500 -0.75548400  1.79407500
C  1.09849000 -2.65469300  0.59456100
H  0.86471400 -2.39329300  1.63059600
H  1.75469600 -3.53141400  0.59635100
C -0.17961700 -2.93078000 -0.18140400
H -0.74168900 -3.75258000  0.27549000
H  0.05454100 -3.20729000 -1.21433400
C -2.12748800 -1.74161900 -1.17454800
H -1.70987300 -1.87495200 -2.17787200
H -2.74018100 -2.62253800 -0.94468600
C -3.00205900 -0.48772500 -1.11506100
H -3.87750000 -0.67047200 -1.74651000
H -3.37030300 -0.34632000 -0.09279300
C -2.34358900  0.80318400 -1.61038200
```

```
H -3.10080800  1.59644900 -1.65990500
H -1.94042600  0.66540200 -2.61969100
C -0.64071800  2.55003200 -1.15140000
H -0.43061000  2.49833600 -2.22512700
H -1.33945300  3.37686900 -0.97961700
C -1.87700200  0.74159500  2.11309300
O -1.99098300  1.47252600  3.29844000
O -1.73875600 -0.48952300  2.30035700
H -1.94387100  0.83264400  4.04376700
Pd 0.29086500 -0.08895200 -0.43308100
```

[LPd-CO]$^{2+}$

```
2 1
N -1.34738400 -1.40647800 -0.73074400
N -1.28592900  1.65820500 -0.45507500
N  1.43109000  1.53681700 0.23470600
N  1.36850900 -1.52161200 -0.03777200
H -1.39615300 -1.41309400 -1.75269500
H -1.33367900  1.84576900 -1.45999100
H  1.49059600  1.52080700  1.25626200
H  1.42484700 -1.68734600  0.97052500
C -0.75577700 -2.70627500 -0.29220000
H -1.28270300 -3.54269100 -0.76214800
H -0.88191900 -2.77894400  0.79168700
C -2.72231800 -1.17706300 -0.21294600
H -2.67939200 -1.24137300  0.87813500
H -3.36548400 -1.98718600 -0.57578100
C -3.29520600  0.17255500 -0.64877500
H -4.35993300  0.17142900 -0.39554600
H -3.23231000  0.27136100 -1.74047700
C -2.66812400  1.39490500  0.02350300
H -3.27717200  2.28349900 -0.17932300
H -2.61984700  1.25415100  1.10725800
C -0.64080800  2.83603100  0.19895500
H -0.76624800  2.72461100  1.27980200
H -1.13052400  3.76287500 -0.11617800
C  0.83297600  2.84464200 -0.16880700
H  1.35661000  3.67101200  0.32211100
H  0.95825900  2.94761200 -1.25072900
C  2.79711700  1.31141100 -0.30595000
H  2.73493300  1.37463700 -1.39641700
H  3.44515200  2.12277900  0.04552600
C  3.38011300 -0.03648900  0.12225800
H  4.44042800 -0.03399500 -0.14857800
H  3.33552700 -0.13265100  1.21514300
C  2.74489700 -1.26326200 -0.53415500
H  3.35658900 -2.15012800 -0.33109000
H  2.68530800 -1.13181300 -1.61860600
C  0.71797700 -2.71373400 -0.65948800
H  0.84351100 -2.63405900 -1.74320600
H  1.20376400 -3.63362400 -0.31894700
C -0.58943300 -0.14238400  2.61832000
O -0.34041300 -1.20999900  2.93071500
Pd 0.03914500  0.06751800 -0.24879500
```

Section S4(b). Cartesian coordinates of intermediates from hydride cycle

Mo(II)-cyclam

$[LMo]^{2+}$

```
Charge = 2 Multiplicity = 1
N  1.32325900 -1.42657000  0.44048000
N  1.32325900  1.42657000  0.44048000
N -1.39241200  1.56798800 -0.11033900
N -1.39241200 -1.56798800 -0.11033900
H  1.31513200 -1.21904000  1.44000600
H  1.31513200  1.21904000  1.44000600
H -1.55574900  1.91474200 -1.06713900
H -1.55575000 -1.91474200 -1.06713900
C  0.72878000 -2.77088300  0.25018900
H  1.24132300 -3.53147400  0.85273300
H  0.83952500 -3.04125400 -0.80562300
C  2.72418400 -1.29998000 -0.03732500
H  2.70729000 -1.33520100 -1.13362400
H  3.31653200 -2.15641700  0.31140500
C  3.37155900  0.00000000  0.45166300
H  4.41493600  0.00000000  0.12080500
H  3.38971900  0.00000000  1.55050100
C  2.72418400  1.29998000 -0.03732500
H  3.31653200  2.15641700  0.31140500
H  2.70729000  1.33520100 -1.13362400
C  0.72878000  2.77088300  0.25018900
H  0.83952600  3.04125400 -0.80562300
H  1.24132300  3.53147400  0.85273300
C -0.73618300  2.68606200  0.63819200
H -1.24902200  3.63668200  0.45361000
H -0.81850900  2.45720000  1.70521100
C -2.74217900  1.27656500  0.45246500
H -2.62669000  1.17667300  1.53643500
H -3.39891500  2.13589300  0.26709000
C -3.36170500  0.00000000 -0.10902100
H -4.42327400  0.00000000  0.16194100
H -3.31704600  0.00000000 -1.20649300
C -2.74217900 -1.27656500  0.45246500
H -3.39891500 -2.13589300  0.26709000
H -2.62669000 -1.17667300  1.53643500
C -0.73618300 -2.68606200  0.63819200
H -0.81850900 -2.45720000  1.70521100
H -1.24902200 -3.63668200  0.45361000
Mo 0.03827700  0.00000000 -0.71588200
```

[LMo]$^{+}$

```
Charge = 1 Multiplicity = 4
N  1.41756100  1.66805400 -0.31876400
N  1.41756000 -1.66805400 -0.31876400
N -1.41756000 -1.66805300  0.31876400
N -1.41756000  1.66805300  0.31876400
H  1.55165800  1.79677400 -1.32447600
H  1.55165700 -1.79677500 -1.32447600
H -1.55165500 -1.79677000  1.32447700
H -1.55165500  1.79677000  1.32447700
C  0.74272900  2.89453000  0.20167900
H  1.22638800  3.80442700 -0.17611600
H  0.83280000  2.89258400  1.29195900
C  2.74673000  1.33620800  0.27089100
H  2.63419500  1.30103700  1.35779600
H  3.46242000  2.13652800  0.03447800
C  3.32302300  0.00000000 -0.25266000
H  4.38491000 -0.00000100  0.01925300
H  3.29411000  0.00000000 -1.35049300
C  2.74672900 -1.33620900  0.27089100
H  3.46241900 -2.13652800  0.03447800
H  2.63419400 -1.30103800  1.35779600
C  0.74272800 -2.89453100  0.20167900
H  0.83279900 -2.89258400  1.29195900
H  1.22638700 -3.80442800 -0.17611500
C -0.74272900 -2.89453000 -0.20167600
H -1.22638900 -3.80442600  0.17612000
H -0.83280100 -2.89258600 -1.29195700
C -2.74673100 -1.33620800 -0.27088800
H -2.63419700 -1.30103800 -1.35779400
H -3.46242000 -2.13652800 -0.03447400
C -3.32302300  0.00000000  0.25266300
H -4.38491100  0.00000100 -0.01924900
H -3.29411000  0.00000000  1.35049600
C -2.74673000  1.33620800 -0.27088800
H -3.46241900  2.13652900 -0.03447500
H -2.63419700  1.30103800 -1.35779400
C -0.74272900  2.89453000 -0.20167600
H -0.83280000  2.89258600 -1.29195700
H -1.22638900  3.80442600  0.17611900
Mo 0.00000100  0.00000000 -0.00000300
```

[LMoH]$^{2+}$

```
Charge = 2 Multiplicity = 4
N  1.40608900  1.64075500 -0.35922900
N  1.40608500 -1.64075400 -0.35922800
N -1.42971700 -1.69959700  0.32057700
N -1.42971800  1.69960100  0.32056900
H  1.49882500  1.73873600 -1.37304400
H  1.49880100 -1.73871600 -1.37304700
H -1.62285900 -1.87092500  1.30794800
```

H -1.62287100 1.87092700 1.30793800
C 0.75508800 2.88210500 0.16117100
H 1.25375100 3.77762800 -0.22606800
H 0.85312800 2.88029000 1.25073000
C 2.75570500 1.32742300 0.19407300
H 2.66513800 1.29201200 1.28373600
H 3.44711700 2.14008500 -0.06007900
C 3.33043900 -0.00000200 -0.34157600
H 4.39424800 -0.00000300 -0.08148100
H 3.28600300 0.00000400 -1.43917900
C 2.75570800 -1.32743400 0.19405800
H 3.44711500 -2.14009400 -0.06011700
H 2.66515700 -1.29204100 1.28372300
C 0.75508500 -2.88210700 0.16116200
H 0.85313100 -2.88030200 1.25072100
H 1.25374500 -3.77762700 -0.22608800
C -0.72502000 -2.89498700 -0.24152600
H -1.19974700 -3.82166700 0.09684100
H -0.81082700 -2.84972600 -1.33195200
C -2.71165700 -1.32972600 -0.35515200
H -2.50899500 -1.26214000 -1.42944500
H -3.44226700 -2.13340000 -0.20604000
C -3.31491300 0.00000400 0.15295600
H -4.35994600 0.00000400 -0.17452700
H -3.34079900 0.00001400 1.25051300
C -2.71164500 1.32972000 -0.35517500
H -3.44225700 2.13339900 -0.20609400
H -2.50896500 1.26210900 -1.42946300
C -0.72501500 2.89499100 -0.24152600
H -0.81081600 2.84973500 -1.33195300
H -1.19974100 3.82167100 0.09684200
H 0.15547200 -0.00000100 1.83047500
Mo -0.0250800 0.00000200 0.10855900

[LMoH]$^{+}$

Charge = 1 Multiplicity = 3
N -1.40036900 1.62280100 0.36134300
N -1.39993600 -1.62314300 0.36139100
N 1.45090100 -1.71454600 -0.34154100
N 1.45048500 1.71496500 -0.34154300
H -1.48947500 1.71835800 1.37604500
H -1.48906000 -1.71871800 1.37608900
H 1.71885200 -1.94927100 -1.29694000
H 1.71881300 1.94988500 -1.29678600
C -0.76217700 2.87120100 -0.14016500
H -1.24919000 3.76339600 0.27790300
H -0.87800600 2.89840800 -1.22715000
C -2.76178000 1.33095500 -0.16112100
H -2.70033500 1.30665500 -1.25314500
H -3.45127000 2.14046500 0.11920800
C -3.33133300 -0.00042900 0.37437500
H -4.39989000 -0.00058000 0.13149900
H -3.27138300 -0.00041900 1.47204800
C -2.76140100 -1.33165300 -0.16111700
H -3.45068300 -2.14135100 0.11918700

```
H -2.69993200 -1.30733200 -1.25313800
C -0.76141400 -2.87138400 -0.14008000
H -0.87724600 -2.89865900 -1.22706300
H -1.24817300 -3.76370100  0.27802800
C  0.72556300 -2.88324700  0.24203700
H  1.18047400 -3.82978600 -0.07495000
H  0.81569000 -2.82164500  1.33178100
C  2.69211700 -1.32768400  0.38939000
H  2.43430600 -1.23895200  1.45132300
H  3.44250200 -2.12544400  0.30138300
C  3.31455900  0.00042700 -0.10185900
H  4.35067700  0.00060600  0.25532000
H  3.37279600  0.00063200 -1.19851700
C  2.69144700  1.32807500  0.38983000
H  3.44162600  2.12612100  0.30263500
H  2.43311100  1.23871600  1.45158400
C  0.72479600  2.88348400  0.24197200
H  0.81492300  2.82197900  1.33172000
H  1.17943800  3.83013500 -0.07506600
H -0.41204300 -0.00020300 -1.88591100
Mo 0.03294400  0.00004000 -0.15867200
```

W(III)-cyclam

$[LW]^{3+}$

```
Charge = 3 Multiplicity = 4
3 4
N  1.67480400 -1.22673300  0.33668200
N  0.99657700  1.56332800  0.67547500
N -1.79082700  1.43879600 -0.19663300
N -1.02464100 -1.80832500  0.13518900
H  1.61927600 -1.01857000  1.33892400
H  1.03880300  1.33216700  1.67127800
H -1.98359300  1.90397700 -1.08497600
H -1.22612800 -2.22554900 -0.78438400
C  1.29060100 -2.65864600  0.22678900
H  1.99053700 -3.29667600  0.77697100
H  1.30107600 -2.95007200 -0.82738700
C  3.03642100 -0.80248400 -0.08555700
H  3.07045600 -0.78188100 -1.17848900
H  3.77742000 -1.52718400  0.27128000
C  3.34269700  0.57484500  0.51819400
H  4.34596900  0.86858600  0.19426100
H  3.38329600  0.48329700  1.61196400
C  2.40120100  1.72632300  0.14692000
H  2.80175500  2.66352900  0.54630900
H  2.31980400  1.83360200 -0.94052200
C  0.17438500  2.80638000  0.50203100
H  0.32944200  3.16088500 -0.52177800
H  0.52146900  3.58171000  1.19123500
```

```
C -1.29199600  2.49141000  0.75136500
H -1.89069900  3.40275700  0.65912800
H -1.41390700  2.10496900  1.76642100
C -3.08169600  0.82421100  0.27496200
H -3.14466500  0.98217900  1.35445800
H -3.90771100  1.37428500 -0.18480100
C -3.25321000 -0.67066400 -0.01054100
H -4.29016100 -0.90949900  0.24903700
H -3.15392300 -0.87995900 -1.08404700
C -2.35511200 -1.62216200  0.79182700
H -2.82685600 -2.60698200  0.87122300
H -2.17757100 -1.24566400  1.80293200
C -0.10787500 -2.77157500  0.82847800
H -0.08639600 -2.50025700  1.88792200
H -0.50124600 -3.78716100  0.73498800
W  0.00242800  0.01192200 -0.54924000
```

$[LW]^{2+}$

```
Charge = 2 Multiplicity = 1
N  1.32864300 -1.44681100  0.53760000
N  1.32863500  1.44681500  0.53760300
N -1.38753100  1.57779300 -0.00370000
N -1.38752400 -1.57779800 -0.00369800
H  1.32486900 -1.23966600  1.53769600
H  1.32486000  1.23966900  1.53769800
H -1.55548800  1.92555100 -0.96379500
H -1.55548500 -1.92555900 -0.96379100
C  0.73231600 -2.79600000  0.35489100
H  1.24429900 -3.55153200  0.96274100
H  0.84233500 -3.06792300 -0.69994600
C  2.73198500 -1.30575300  0.05771400
H  2.71694000 -1.33918600 -1.03782500
H  3.32849900 -2.15755800  0.40875100
C  3.36647100  0.00000700  0.55480500
H  4.41468800  0.00001000  0.24010100
H  3.36914500  0.00000400  1.65392300
C  2.73197900  1.30576600  0.05772000
H  3.32848700  2.15757200  0.40876300
H  2.71693600  1.33920400 -1.03781900
C  0.73230300  2.79600200  0.35489300
H  0.84232400  3.06792600 -0.69994400
H  1.24428300  3.55153500  0.96274400
C -0.73391300  2.70697900  0.74352000
H -1.25249200  3.65129000  0.54824400
H -0.81895400  2.48036600  1.81000700
C -2.74130400  1.27960100  0.55946200
H -2.62320000  1.18005000  1.64236500
H -3.39852900  2.13696600  0.37042500
C -3.34871800 -0.00000800 -0.00986300
H -4.41587000 -0.00001100  0.23764200
H -3.27646800 -0.00001100 -1.10579900
C -2.74129400 -1.27960700  0.55947100
H -3.39851600 -2.13697700  0.37044800
H -2.62318200 -1.18004500  1.64237200
```

```
C -0.73390000 -2.70698200  0.74352200
H -0.81893900 -2.48036800  1.81000800
H -1.25247600 -3.65129500  0.54824700
W  0.01541700  0.00000000 -0.56101000
```

[LW-H]$^{3+}$

```
Charge = 3  Multiplicity = 1
N  1.28958000 -1.43843800  0.55450800
N  1.31971800  1.42057200  0.54632500
N -1.36805100  1.57433000  0.03410900
N -1.40486900 -1.55535600  0.02002200
H  1.25608300 -1.22044700  1.55690700
H  1.29472700  1.20742900  1.54979600
H -1.51273000  1.87922700 -0.94264100
H -1.53246400 -1.85945600 -0.95920400
C  0.69360200 -2.79483600  0.36942500
H  1.21338000 -3.52954400  0.99165100
H  0.81913100 -3.07109100 -0.68154200
C  2.71174800 -1.32223200  0.10656500
H  2.71413800 -1.37913500 -0.98715000
H  3.26568200 -2.18492500  0.49162100
C  3.35792500 -0.02550200  0.59607300
H  4.40389700 -0.03816100  0.27541300
H  3.36465800 -0.01208000  1.69404200
C  2.73162300  1.26938900  0.07781500
H  3.30637200  2.13245200  0.43018800
H  2.71729500  1.29619200 -1.01729900
C  0.74731600  2.78727100  0.36196600
H  0.86922100  3.05833600 -0.69078300
H  1.28372300  3.51474400  0.97836400
C -0.71335700  2.72099400  0.75520600
H -1.23417600  3.65271000  0.52023800
H -0.81136300  2.52717800  1.82654500
C -2.73032400  1.28869500  0.59077700
H -2.62004500  1.18557600  1.67378200
H -3.35570300  2.16561900  0.39632300
C -3.36228500  0.03331400  0.00281900
H -4.42430900  0.04668800  0.26856000
H -3.31403600  0.05031000 -1.09362300
C -2.77570700 -1.26079900  0.55052900
H -3.41544900 -2.11385800  0.30388200
H -2.69400700 -1.20455400  1.63935400
C -0.76877800 -2.70498500  0.75248300
H -0.86973800 -2.50253400  1.82199000
H -1.29919300 -3.63245300  0.52181400
H  0.18048000  0.00091400 -2.29101600
W  0.02958400  0.00101700 -0.55870100
```

$[LW\text{-}H]^{2+}$

```
Charge  = 2 Multiplicity = 2
N  1.39601300 -1.64373900  0.39274000
N  1.39601100  1.64374000  0.39274000
N -1.42354100  1.70858800 -0.29363800
N -1.42353900 -1.70859000 -0.29363800
H  1.49155600 -1.74323300  1.40722700
H  1.49155400  1.74323500  1.40722700
H -1.64237100  1.90171300 -1.27236000
H -1.64237000 -1.90171500 -1.27235900
C  0.75646600 -2.89588700 -0.12208000
H  1.25891300 -3.78425900  0.27560700
H  0.85879900 -2.89785500 -1.21089900
C  2.75048700 -1.32834900 -0.15586400
H  2.66050500 -1.29083600 -1.24530200
H  3.43995200 -2.14187700  0.10065200
C  3.31997700  0.00000200  0.38429500
H  4.38625800  0.00000300  0.13466200
H  3.26348200  0.00000200  1.48115300
C  2.75048600  1.32835300 -0.15586400
H  3.43994900  2.14188100  0.10065200
H  2.66050300  1.29083900 -1.24530200
C  0.75646200  2.89588800 -0.12208000
H  0.85879500  2.89785600 -1.21089800
H  1.25890800  3.78426100  0.27560800
C -0.72382900  2.90649200  0.27675200
H -1.20182800  3.83279800 -0.05628500
H -0.80927800  2.84942800  1.36623900
C -2.69549000  1.32840900  0.40064200
H -2.47125200  1.25092500  1.46972000
H -3.42939100  2.13249900  0.27074400
C -3.30119700 -0.00000200 -0.10758600
H -4.34628100 -0.00000300  0.21995000
H -3.32448200 -0.00000300 -1.20490000
C -2.69548700 -1.32841100  0.40064500
H -3.42938700 -2.13250300  0.27075000
H -2.47124600 -1.25092400  1.46972100
C -0.72382500 -2.90649300  0.27675100
H -0.80927400 -2.84943000  1.36623900
H -1.20182300 -3.83280000 -0.05628600
H  0.09220300  0.00000000 -1.85826200
W -0.01569300  0.00000000 -0.11924800
```

Co(II)-cyclam

$[LCo]^{2+}$

```
Charge = 2 Multiplicity = 2
N  1.33664900  1.46900800 -0.29097800
N  1.33671700 -1.46893700 -0.29103700
N -1.33663700 -1.46901200  0.29103200
N -1.33671000  1.46897100  0.29096100
H  1.43306900  1.56259600 -1.30637200
H  1.43298500 -1.56249800 -1.30645000
```

```
H -1.43290300 -1.56265900  1.30643600
H -1.43303100  1.56263700  1.30635900
C  0.72652900  2.73135900  0.20820800
H  1.25853900  3.60690300 -0.17764900
H  0.80738800  2.72876500  1.29967400
C  2.70473400  1.27270800  0.25697400
H  2.61460900  1.22886800  1.34714400
H  3.31606600  2.14708600  0.00433900
C  3.35939300  0.00009800 -0.26520700
H  4.40548900  0.00012100  0.05680000
H  3.36426600  0.00021900 -1.36352300
C  2.70489300 -1.27269600  0.25671300
H  3.31622900 -2.14696900  0.00372900
H  2.61496800 -1.22916300  1.34691100
C  0.72666700 -2.73130600  0.20819400
H  0.80758400 -2.72869300  1.29965600
H  1.25868700 -3.60683700 -0.17767900
C -0.72653900 -2.73131600 -0.20830300
H -1.25852700 -3.60689900  0.17749800
H -0.80745500 -2.72861800 -1.29976500
C -2.70481800 -1.27277500 -0.25670800
H -2.61488900 -1.22914000 -1.34690200
H -3.31612000 -2.14709700 -0.00380700
C -3.35937500 -0.00005600  0.26532700
H -4.40549400 -0.00009000 -0.05660600
H -3.36417200  0.00000300  1.36364300
C -2.70484900  1.27262700 -0.25683700
H -3.31619800  2.14695400 -0.00407000
H -2.61485700  1.22886600 -1.34702100
C -0.72665500  2.73129800 -0.20836900
H -0.80751200  2.72857400 -1.29983500
H -1.25871000  3.60686000  0.17738800
Co -0.00000100  0.00001300 0.00001100
```

[LCo]$^{+}$

```
Charge = 1 Multiplicity = 3
N -1.39993400  1.58244700  0.32153300
N -1.39993400 -1.58244700  0.32153300
N  1.39993400 -1.58244800 -0.32153300
N  1.39993400  1.58244800 -0.32153300
H -1.53186700  1.71439300  1.32587800
H -1.53186700 -1.71439300  1.32587800
H  1.53186700 -1.71439400 -1.32587800
H  1.53186700  1.71439400 -1.32587800
C -0.73671600  2.79304600 -0.20632600
H -1.22303700  3.71888000  0.13266600
H -0.80742700  2.76250800 -1.29955800
C -2.72656500  1.30486800 -0.26692000
H - 2.59722700 1.23900600 -1.35319800
H -3.42186300  2.13668300 -0.07198600
C -3.34441800  0.00000000  0.25578400
H -4.40117500  0.00000000 -0.03499500
H -3.32912900  0.00000000  1.35489400
C -2.72656500 -1.30486800 -0.26691900
```

```
H -3.42186300 -2.13668300 -0.07198500
H -2.59722700 -1.23900600 -1.35319700
C -0.73671600 -2.79304600 -0.20632600
H -0.80742800 -2.76250800 -1.29955800
H -1.22303700 -3.71888000  0.13266600
C  0.73671600 -2.79304600  0.20632700
H  1.22303700 -3.71888000 -0.13266500
H  0.80742800 -2.76250700  1.29955900
C  2.72656500 -1.30486800  0.26691900
H  2.59722700 -1.23900600  1.35319700
H  3.42186300 -2.13668300  0.07198500
C  3.34441800  0.00000000 -0.25578500
H  4.40117500  0.00000000  0.03499500
H  3.32912800  0.00000000 -1.35489400
C  2.72656500  1.30486800  0.26691900
H  3.42186300  2.13668300  0.07198600
H  2.59722700  1.23900600  1.35319700
C  0.73671600  2.79304600  0.20632700
H  0.80742700  2.76250700  1.29955900
H  1.22303700  3.71888000 -0.13266500
Co 0.00000000  0.00000000 -0.00000100
```

[LCo-H]$^{2+}$

```
Charge = 2 Multiplicity = 1
N  1.32014700  1.45565500 -0.29185100
N  1.32025600 -1.45558600 -0.29178200
N -1.33936700 -1.45438500  0.28755700
N -1.33948600  1.45428700  0.28768000
H  1.38209000  1.55455100 -1.31099300
H  1.38225000 -1.55455000 -1.31091400
H -1.45242200 -1.51622700  1.30232200
H -1.45230600  1.51614600  1.30247000
C  0.72473100  2.71312800  0.23657200
H  1.26246800  3.58762300 -0.14243500
H  0.81576900  2.68825000  1.32595500
C  2.70704100  1.26835300  0.21181800
H  2.65196900  1.23041800  1.30348100
H  3.29861300  2.14686200 -0.06972700
C  3.35073300  0.00010200 -0.32819800
H  4.40431600  0.00014800 -0.03225700
H  3.32744300  0.00004700 -1.42605400
C  2.70711200 -1.26813400  0.21193600
H  3.29875700 -2.14663400 -0.06948400
H  2.65198400 -1.23008100  1.30359300
C  0.72492200 -2.71307500  0.23670300
H  0.81588100 -2.68809700  1.32609100
H  1.26276900 -3.58755000 -0.14219300
C -0.72802200 -2.73054500 -0.17307100
H -1.25866100 -3.59071000  0.24599800
H -0.81521800 -2.76478600 -1.26326700
C -2.69448100 -1.26722800 -0.29702900
H -2.57778500 -1.22642900 -1.38468100
H -3.30048100 -2.14777700 -0.05490700
C -3.36895000 -0.00017100  0.20792100
H -4.40419100 -0.00020400 -0.14656300
```

```
H -3.40593700 -0.00038400  1.30539500
C -2.69475400  1.26719900 -0.29658900
H -3.30079100  2.14756800 -0.05391000
H -2.57836900  1.22690200 -1.38429100
C -0.72824200  2.73044400 -0.17310500
H -0.81550300  2.76456600 -1.26330100
H -1.25890900  3.59062300  0.24590200
H  0.31385100 -0.00002900  1.38416200
Co 0.00077900 -0.00001700  0.00172700
```

[LCo-H]$^{+}$

```
Charge = 1 Multiplicity = 2
N  1.33209600  1.45943300 -0.30733900
N  1.33210400 -1.45942900 -0.30733900
N -1.36580000 -1.49492500  0.26584100
N -1.36580800  1.49492000  0.26584200
H  1.38269900  1.50675300 -1.32868700
H  1.38270800 -1.50675200 -1.32868600
H -1.48585800 -1.61969700  1.27215500
H -1.48585800  1.61969000  1.27215700
C  0.72694900  2.73012700  0.16116000
H  1.25768900  3.59976000 -0.24320200
H  0.80660900  2.74999400  1.25222400
C  2.71766000  1.28066600  0.18749400
H  2.66910200  1.25247700  1.28018700
H  3.32185700  2.14916400 -0.10452500
C  3.35497100  0.00000700 -0.34414100
H  4.41034500  0.00001000 -0.05285800
H  3.33113500  0.00000700 -1.44272900
C  2.71766600 -1.28065400  0.18749600
H  3.32186800 -2.14914900 -0.10452100
H  2.66910700 -1.25246300  1.28018800
C  0.72696200 -2.73012500  0.16116300
H  0.80662100 -2.74998800  1.25222700
H  1.25770600 -3.59975700 -0.24319700
C -0.72897400 -2.72974600 -0.26091700
H -1.24800000 -3.62865900  0.08998900
H -0.79864500 -2.69925200 -1.35348400
C -2.71184700 -1.27691500 -0.31544200
H -2.59517400 -1.21952900 -1.40308700
H -3.34638700 -2.14448100 -0.09344600
C -3.36806900 -0.00000800  0.20164800
H -4.41260000 -0.00001100 -0.12640300
H -3.38112300 -0.00001300  1.29995400
C -2.71185900  1.27690900 -0.31543100
H -3.34640200  2.14446800 -0.09341800
H -2.59519700  1.21953700 -1.40307800
C -0.72898800  2.72974200 -0.26091900
H -0.79865900  2.69924500 -1.35348600
H -1.24801600  3.62865400  0.08998600
H  0.33707300 -0.00000200  1.91745500
Co 0.01083100 -0.00000100  0.14209500
```

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