**Supporting Information**

# Selectivity for $HCO_2^-$ over $H_2$ in the electrochemical catalytic reduction of $CO_2$ by (POCOP)$IrH_2$

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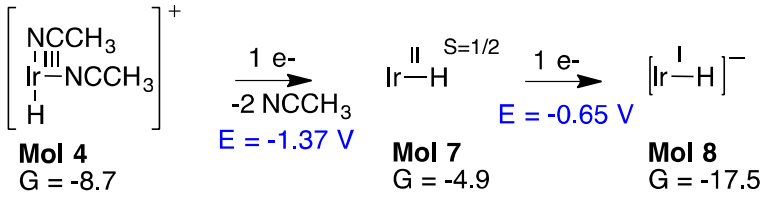
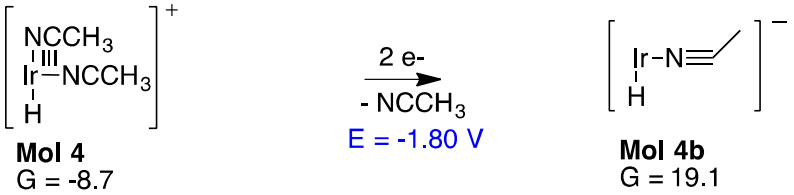
## Appendix 1: Calculation of the doubly reduced acetonitrile complex

**Currently Proposed Reduction**




**Previously Proposed Reduction**




**Scheme S1: Free energies calculated in acetonitrile at -1.2V vs SHE. Reduction with loss of solvent is preferred to a two-electron reduction of the solvento complex as previously proposed,[1] which leads to a reduced acetonitrile adduct.**

In previous work[1] a doubly reduced cationic solvento complex was calculated, as shown below. However, the geometry showed a bent acetonitrile, suggesting that the acetonitrile had been reduced, not the metal center. When this complex is recalculated with our methods, we compute a reduction potential of -1.8, which is inconsistent with the experimentally observed reduction potential.

**Appendix 2**

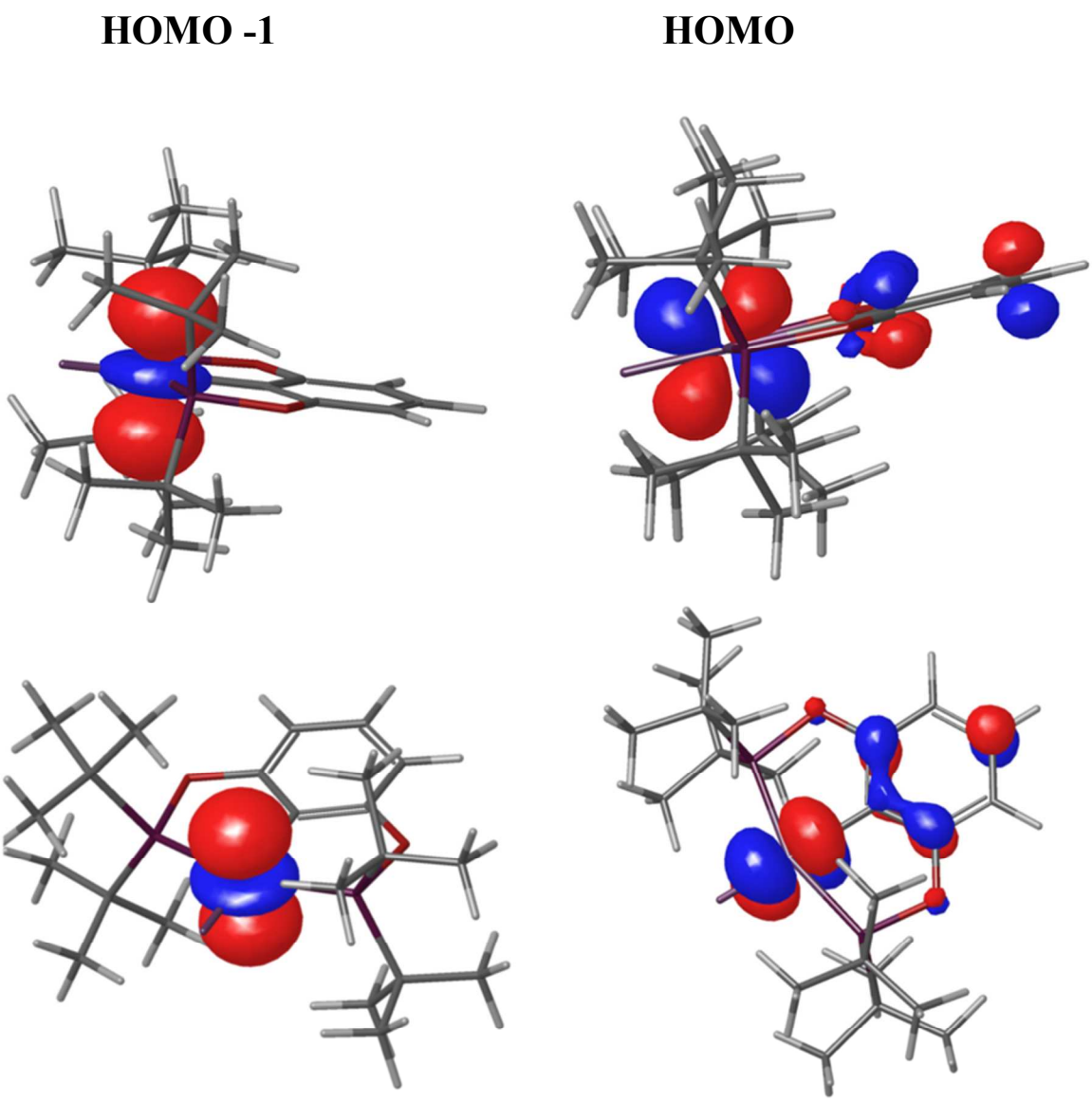



**Figure S1: HOMO of $Ir^{I}$ complex**

The HOMO -1 and HOMO of POCOP-$Ir^{I}$ hydride anion (**Mol 7**) is shown. The high electron density in axial positions explains why oxygen cannot coordinate simultaneously in a transition state analogous to **TS 4**.

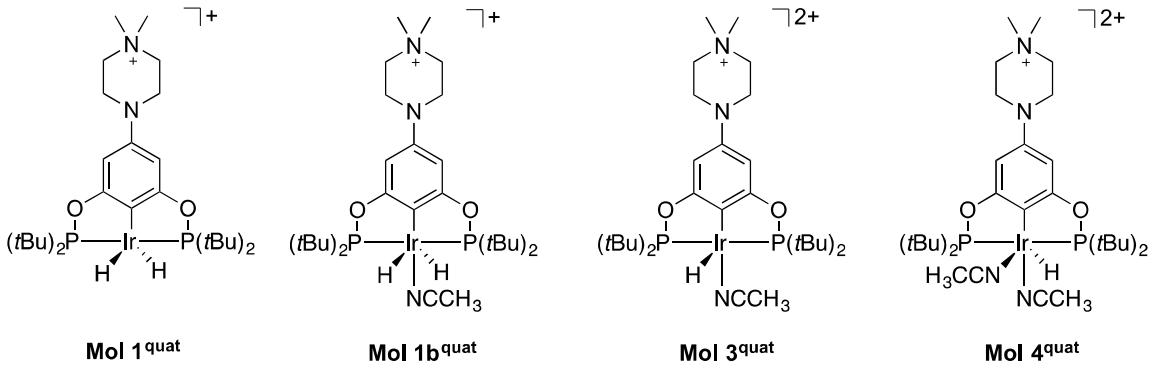
## Appendix 3: Justification for Calculations with Water Clusters

The calculated free energy and pKa for the auto-dissociation of water is used to justify our use of an explicit four-water cluster (plus continuum solvation) in transition state calculations. A neutral $4H_2O$ and anionic $OH^- \bullet 3H_2O$ cluster were used.

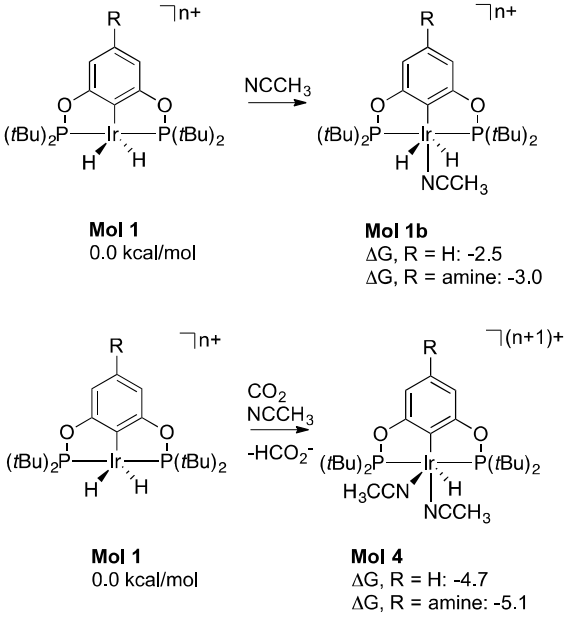
$4\ H_2O\ (liq) \rightarrow H^+\ (1M) + OH^- \bullet 3H_2O\ (1\ M)$ $\quad \Delta G_{calc} = 20.2$ kcal/mol

$\Delta G_{exp} = 19.05$ kcal/mol

# Appendix 4




**(a)**



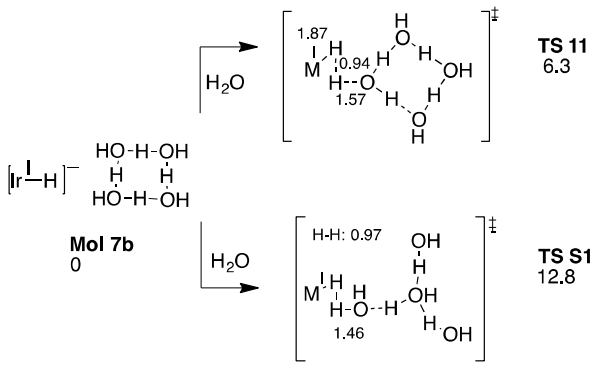

**(b)**

**Scheme S2: (a) Structures of quaternary amine POCOP complexes, (b) Free energies of reactions featuring the full ligand versus the truncated ligand.**

Experimentally a quaternary amine solvation handle (1,1-piperazinium) was added to the standard (POCOP) ligand in order to aid with solvation. In our calculations, for simplicity, we eliminated this handle, but validated two calculations to ensure that our free energies would be similar. The first is the loss of acetonitrile in water and the second is the free energy of reaction with $CO_2$ to form formate, involving a change in overall charge. These can be seen in Scheme S2b.

The difference in free energies of these reactions does not exceeds 0.5 kcal/mol, which is well within the error of DFT. Thus we feel comfortable in using the simplified ligand scaffold.

# Appendix 5




**Scheme S3 – Free energies for protonation via the Y-shaped cluster**

Protonation via the Y-shaped cluster used previously for protonation has a higher barrier than the square shaped cluster, showing that water orientation is significant.

## Appendix 6

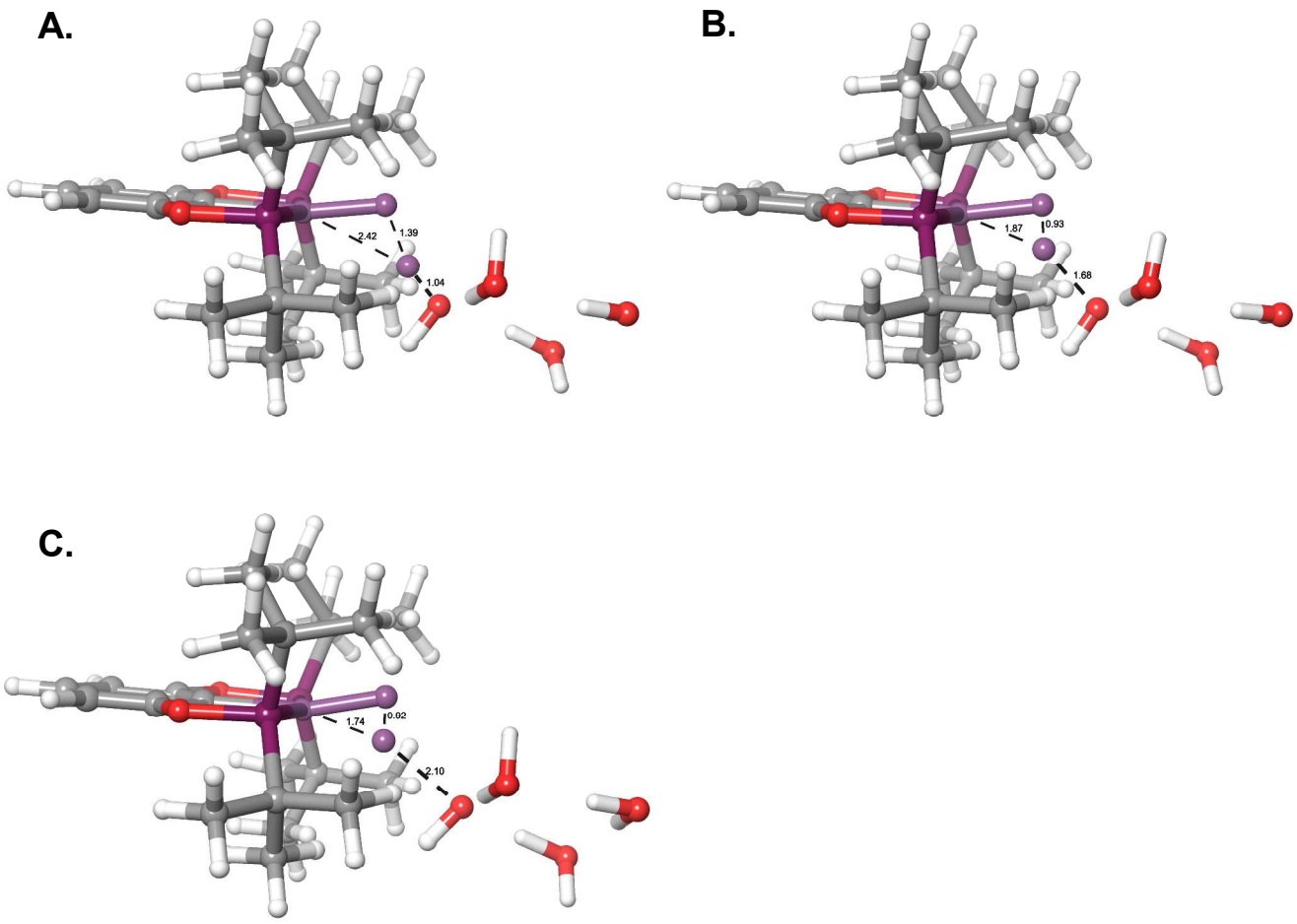



**Figure S2 –** Figures of images along the intrinsic reaction coordinate calculation. A. Point on the reverse path; B. The transition state; C. Point on the forward path. All bond lengths in Angstroms. For reference, the spectator Ir-H bond length is 1.70 Å.

**Appendix 7**

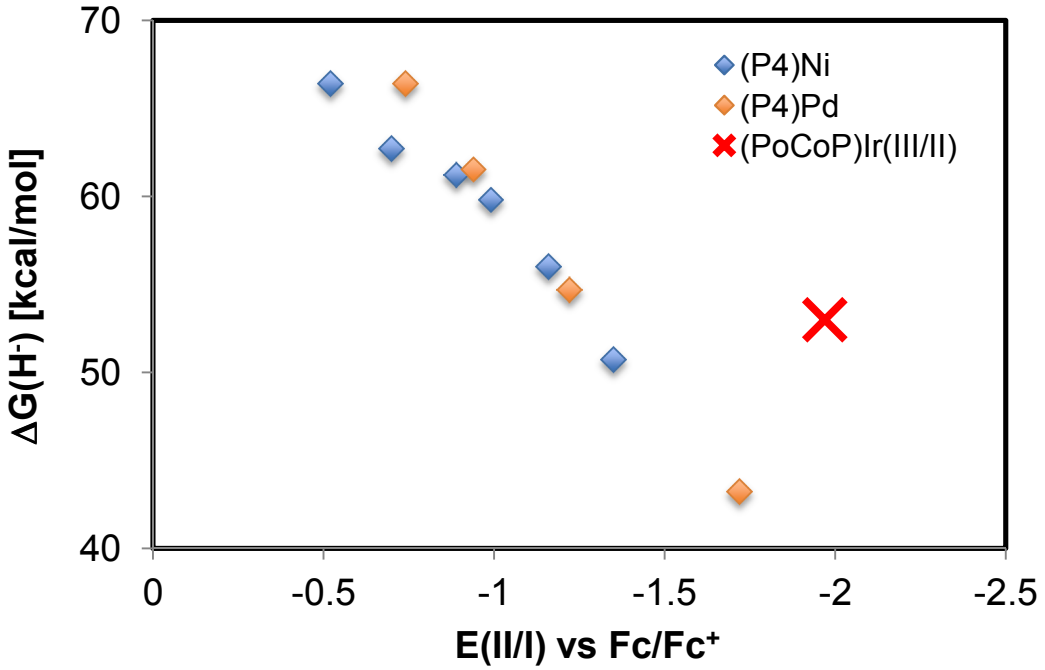



**Figure S3 – Hydricities of (POCOP) Ir compared to other hydridic compounds**

In Figure S3, the first reduction potential vs ferrocene of several $P_4$ Ni[2] and Pd[3] compounds are plotted against their measured hydricites in acetonitrile, denoted by the blue and yellow diamonds. Dubois and coworkers noted that the first half-wave one electron reduction potential correlated linearly with the resulting measured hydricity. The point marked by the red "X" is that calculated for (POCOP)Ir$(H)_2(NCCH_3)$ for the (III/II) couple vs ferrocene. The value for this does not lie on the line established by the Pd and Ni compounds, which means that while the Ir complex has a calculated hydricity near some of the more reactive Pd and Ni compounds, more energy is required to gain the same return in hydricity. This indicates an interesting relationship between hydricity and structure.

**References**


1. Cao, L.; Sun, C.; Sun, N.; Meng, L.; Chen, D. *Dalton Trans.* **2013**, *42*, 5755.
2. Berning, D. E.; Miedaner, A.; Curtis, C. J.; Noll, B. C.; Rakowski DuBois, M. C.; DuBois, D. L., *Organometallics* **2001**, *20*, 1832-1839.
3. Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; Anderson, O. P.; DuBois, D. L., *J. Am. Chem. Soc.* **2004**, *126*, 5502-5514.

## Appendix 8: Geometries of Molecules

Optimized molecular geometries can be found in the supplemental file SI_POCOP_Ir.xyz In order to open these files for viewing and analysis, the authors suggest a program as Mercury, which can be found at http://www.ccdc.cam.ac.uk/pages/Home.aspx free of charge.

# Appendix 9: Calculation Details

| | ZPE | Hvib | Svib | 6kT | 1/2 (Strans+Srot) | Selec | Htot | Stot | G(Solv) H20 | E(SCF, large basis M06) | Water | # basis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| **Iridium** | | | | | | | | | | | | |
| Mol 1b | 399.59 | 22.31 | 141.52 | 3.5528 | 40.81 | 0.00 | 24.68 | 224.74 | -0.01256 | -1933.20098 | -1212739.99 | 1022 |
| TS 1 | 407.24 | 23.76 | 156.05 | 3.5528 | 41.08 | 0.00 | 26.13 | 234.40 | -0.01872 | -2121.74772 | -1331054.06 | 1088 |
| TS 3 | 377.19 | 21.66 | 136.94 | 3.5528 | 40.77 | 0.00 | 24.03 | 220.32 | -0.00766 | -1989.03209 | -1247793.14 | 1001 |
| TS 1 wat | 393.809 | 22.62 | 140.91 | 3.5528 | 40.91 | 0.00 | 24.99 | 223.71 | -0.01259 | -2065.46577 | -1295742.75 | |
| Mol 2 | 408.64 | 24.30 | 153.01 | 3.5528 | 41.08 | 0.00 | 26.67 | 237.08 | -0.02298 | -2121.75015 | -1331055.42 | 1088 |
| TS 2 | 409.46 | 24.28 | 155.34 | 3.5528 | 41.07 | 0.00 | 26.65 | 239.70 | -0.03552 | -2121.72765 | -1331049.05 | 1088 |
| Mol 3b | 410.88 | 24.38 | 155.57 | 3.5528 | 41.04 | 0.00 | 26.75 | 240.27 | -0.02502 | -2121.76261 | -1331062.94 | 1088 |
| Mol 3 | 394.78 | 22.53 | 145.70 | 3.5528 | 40.80 | 0.00 | 24.90 | 228.76 | -0.05674 | -1932.42918 | -1212289.23 | 1015 |
| Mol 4 | 425.84 | 25.36 | 165.45 | 3.5528 | 41.08 | 0.00 | 27.73 | 250.77 | -0.05958 | -2065.14991 | -1295546.63 | 1102 |
| Mol 3 | 394.78 | 22.53 | 145.70 | 3.5528 | 40.80 | 0.00 | 24.90 | 228.76 | -0.05674 | -1932.42918 | -1212289.23 | 1015 |
| Mol 4b | 393.28 | 22.43 | 143.35 | 3.5528 | 42.18 | 1.38 | 24.80 | 227.68 | -0.01274 | -1932.58575 | -1212361.19 | 1015 |
| Mol 1 | 368.95 | 19.85 | 124.68 | 3.5528 | 40.49 | 0.00 | 22.22 | 206.18 | -0.00526 | -1800.49114 | -1129486.70 | 935 |
| TS 4 | 377.31 | 21.35 | 134.05 | 3.5528 | 40.77 | 0.00 | 23.72 | 216.21 | -0.00662 | -1989.02359 | -1247786.50 | 1001 |
| Mol 5 | 380.84 | 21.50 | 133.90 | 3.5528 | 40.73 | 0.00 | 23.87 | 218.68 | -0.01035 | -1989.06614 | -1247811.80 | 1001 |
| Mol 6 | 363.56 | 19.56 | 123.09 | 3.5528 | 41.86 | 1.38 | 21.93 | 206.03 | -0.00462 | -1799.87224 | -1129103.53 | 928 |
| Mol 7 | 361.83 | 19.57 | 122.60 | 3.5528 | 40.47 | 0.00 | 21.94 | 204.54 | -0.07053 | -1799.94434 | -1129191.30 | 928 |
| TS 5 | 369.19 | 21.79 | 141.61 | 3.5528 | 40.81 | 0.00 | 24.16 | 224.88 | -0.06127 | -1988.50825 | -1247507.36 | 994 |
| Mol 8 | 370.71 | 20.79 | 142.11 | 3.5528 | 40.78 | 0.00 | 23.16 | 213.41 | -0.07378 | -1988.51208 | -1247517.22 | 994 |
| Mol 9 | 406.04 | 22.90 | 145.43 | 3.5528 | 40.83 | 0.00 | 25.27 | 229.05 | -0.05862 | -1933.60785 | -1213018.35 | 1029 |
| TSHER Cluster 2 | 459.34 | 27.98 | 180.84 | 3.5528 | 41.54 | 0.00 | 30.35 | 266.30 | -0.04477 | -2238.87669 | -1404521.18 | 1166 |
| TS 6 | 383.27 | 20.59 | 127.79 | 3.5528 | 40.60 | 0.00 | 22.96 | 209.96 | -0.01176 | -1876.87981 | -1177411.30 | 971 |
| TS 7 | 398.39 | 21.63 | 133.96 | 3.5528 | 40.72 | 0.00 | 24.00 | 216.16 | -0.01501 | -1953.32014 | -1225366.09 | 1007 |
| TS 8 | 412.79 | 23.17 | 144.76 | 3.5528 | 40.86 | 0.00 | 25.54 | 227.57 | -0.01855 | -2029.74777 | -1273314.72 | 1043 |
| Mol 14 | 383.68 | 20.90 | 134.00 | 3.5528 | 40.60 | 0.00 | 23.27 | 210.24 | -0.01520 | -1876.89017 | -1177421.09 | 971 |
| Mol 7b | 427.51 | 25.67 | 165.17 | 3.5528 | 41.09 | 0.00 | 28.04 | 249.11 | -0.06997 | -2105.69896 | -1320996.01 | 1072 |
| TS 11 | 423.12 | 25.14 | 167.84 | 3.5528 | 41.21 | 0.00 | 27.51 | 246.68 | -0.07858 | -2105.67114 | -1320989.72 | 1072 |
| TS 12 | 420.88 | 25.88 | 169.41 | 3.5528 | 41.16 | 0.00 | 28.25 | 256.50 | -0.07754 | -2105.65875 | -1320983.25 | 1072 |
| TS 5b | 434.52 | 27.78 | 180.39 | 3.5528 | 41.39 | 0.00 | 30.15 | 266.18 | -0.06640 | -2294.25691 | -1439311.21 | 1138 |
| Mol 10 | 385.48 | 21.10 | 130.67 | 3.5528 | 40.60 | 0.00 | 23.47 | 213.12 | -0.01580 | -1876.90628 | -1177428.58 | 971 |
| TS 9 Carbonic Acid | 393.62 | 22.01 | 138.09 | 3.5528 | 40.90 | 0.00 | 24.38 | 221.23 | -0.01428 | -2065.47240 | -1295747.94 | 1037 |
| TS 10 Carbonic Acid | 393.17 | 22.72 | 141.94 | 3.5528 | 40.89 | 0.00 | 25.09 | 224.88 | -0.01784 | -2065.47418 | -1295752.17 | 1037 |
| Mol 14 Carbonic Acid | 395.70 | 22.15 | 138.89 | 3.5528 | 40.91 | 0.00 | 24.52 | 222.05 | -0.01413 | -2065.47436 | -1295747.10 | 1037 |
| Mol 15 Carbonic acid | 395.21 | 21.80 | 141.27 | 3.5528 | 40.90 | 0.00 | 24.17 | 217.82 | -0.01782 | -2065.48631 | -1295758.45 | 1037 |
| TS 9 Formate | 390.27 | 21.41 | 133.41 | 3.5528 | 40.77 | 0.00 | 23.78 | 216.07 | -0.00891 | -1990.23128 | -1248532.56 | 1015 |
| TS 10 Formate | 389.78 | 22.14 | 138.48 | 3.5528 | 40.76 | 0.00 | 24.51 | 220.00 | -0.01192 | -1990.23117 | -1248535.64 | 1015 |
| Mol 14 Formate | 392.36 | 21.55 | 134.16 | 3.5528 | 40.78 | 0.00 | 23.92 | 216.86 | -0.00926 | -1990.23268 | -1248531.65 | 1015 |
| Mol 15 Formate | 391.93 | 21.72 | 135.69 | 3.5528 | 40.77 | 0.00 | 24.09 | 218.44 | -0.01160 | -1990.24372 | -1248540.75 | 1015 |
| TS 9 Bicarbonate | | | | | | | | | | | | |
| TS 10 Bicarbonate | 385.43 | 21.93 | 136.57 | 3.5528 | 40.86 | 0.00 | 24.30 | 218.67 | -0.10187 | -2064.90695 | -1295455.88 | 1030 |
| Mol 14 Bicarbonate | 387.83 | 21.98 | 138.37 | 3.5528 | 40.89 | 0.00 | 24.35 | 221.46 | -0.08187 | -2064.96181 | -1295475.85 | 1030 |

| | ZPE | Hvib | Svib | 6kT | 1/2 (Strans+Srot) | Selec | Htot | Stot | G(Solv) H20 | E(SCF, large basis M06) | Water | # basis |
|---|---|---|---|---|---|---|---|---|---|---|---|---|
| Mol 15 Bicarbonate | | | | | | | | | | | | |
| Mol 17 | 388.59 | 22.33 | 144.81 | 3.5528 | 40.78 | 0.00 | 24.70 | 227.78 | -0.01109 | -1932.02271 | -1212011.65 | 1008 |
| Mol 18 | 374.476 | 21.13 | 134.52 | 3.5528 | 40.57 | 0.00 | 23.50 | 215.65 | -0.01506 | -1875.721586021 | -1176696.82 | |
| TS 12 | 419.464 | 25.81 | 167.63 | 3.5528 | 41.03 | 0.00 | 28.18 | 249.70 | -0.02394 | -2104.9958299874 | -1320534.53 | 1065 |
| Mol 16 | 372.773 | 21.75 | 139.41 | 3.5528 | 40.74 | 0.00 | 24.12 | 224.74 | -0.06927 | -1988.5334083546 | -1247523.93 | 994 |
| Mol 1 – Quart Amine | 493.056 | 25.36 | 161.75 | 3.5528 | 41.85 | 0.00 | 27.725 | 246.71 | -0.08158 | -2146.06056 | -1346264.59 | 1202 |
| Mol 1b – Quart Amine | 523.78 | 27.73 | 177.96 | 3.5528 | 42.06 | 0.00 | 30.102 | 264.87 | -0.08151 | -2278.77740 | -1429517.43 | 1289 |
| Mol 4 – Quart Amine | 550.133 | 30.70 | 200.25 | 3.5528 | 42.25 | 0.00 | 33.068 | 287.04 | -0.18942 | -2410.66765 | -1512324.92 | 1369 |
| Mol 4b – Quart Amine | 519.019 | 27.94 | 181.59 | 3.5528 | 42.05 | 0.00 | 30.305 | 267.30 | -0.19048 | -2277.94302 | -1429067.86 | 1282 |
| | | | | | | | | | 67.70966 | | | |
| **Cobalt** | | | | | | | | | 68.37620 | | | |
| Mol 1b | 399.11 | 22.18 | 140.24 | 3.55 | 40.39 | 0.00 | 24.55 | 222.65 | -0.01076 | -1973.57 | -1238068.8 | 1026 |
| TS 1 | 406.62 | 24.24 | 153.33 | 3.55 | 40.71 | 0.00 | 26.61 | 238.12 | -0.01509 | -2162.11 | -1356381.0 | 1092 |
| Mol 4 | 425.39 | 25.20 | 162.75 | 3.55 | 40.70 | 0.00 | 27.57 | 245.82 | -0.06031 | -2105.52 | -1320878.5 | 1106 |
| Mol 1 | 368.76 | 19.89 | 125.14 | 3.55 | 40.04 | 0.00 | 22.26 | 206.23 | -0.00397 | -1840.87 | -1154825.7 | 939 |
| TS 4 | 376.75 | 21.30 | 132.69 | 3.55 | 40.36 | 0.00 | 23.67 | 214.92 | -0.00533 | -2029.40 | -1273120.6 | 1005 |
| Mol 6 | 363.34 | 19.46 | 122.50 | 3.55 | 41.41 | 1.38 | 21.83 | 204.39 | -0.00825 | -1840.28 | -1154464.1 | 932 |
| Mol 7 | 361.22 | 19.55 | 122.53 | 3.55 | 38.52 | 0.00 | 21.92 | 203.34 | -0.06724 | -1840.32 | -1154524.7 | 932 |
| Mol 3 | 394.59 | 22.38 | 143.74 | 3.55 | 40.38 | 0.00 | 24.75 | 225.48 | -0.05806 | -1972.80 | -1237623.3 | 1019 |
| | 388.40 | 22.29 | 144.27 | 3.55 | 40.36 | 0.00 | 24.66 | 226.60 | -0.01079 | -1972.41 | -1237354.9 | 1012 |
| | | | | | | | | | | | | |
| **Small Molecules** | | | | | | | | | | | G (Water) | |
| Acetonitrile | 28.512 | 0.48 | 2.32 | 3.552756 | 28.8895 | 0 | 2.85 | 60.102 | | -132.6941011102 | -83255.820706 | 87 |
| CO2 | 7.282 | 0.178 | 0.78 | 3.552756 | 25.1875 | 0 | 2.252 | 51.157 | | -188.5592316715 | -118328.438828 | 66 |
| Formate | 12.67 | 0.085 | 0.35 | 3.552756 | 28.9915 | 0 | 2.455 | 58.336 | | -189.1736055058 | -118784.81265 | 73 |
| Carbonic Acid | 25.019 | 0.551 | 2.46 | 3.552756 | 30.9195 | 0 | 2.921 | 64.301 | -0.01705 | -264.9702066404 | | |
| Bicarbonate | 16.533 | 0.438 | 1.95 | 3.552756 | 30.866 | 0 | 2.808 | 63.684 | | -264.4235014483 | -166002.222456 | |
| H2 | 6.384 | 0 | 0.00 | 3.552756 | 20.566 | 0 | 2.074 | 31.132 | | -1.1706233064 | -735.3966987686 | 14 |
| Water | 13.413 | 0.002 | 0.01 | 3.552756 | 23.2415 | 0 | 2.372 | 46.49 | | -76.418225434 | -47953.2890948 | 36 |
| Electron | -71.0248 | -71.0248 | | Potential | -1.2 | V | | | | | -279.4820529839 | |
| H+ (pH = 7) | -279.82 | -279.82 | 7.00 | | | | H+ (1M) | -270.3 | | | | |
| H+ (pH = 0) | -270.3 | | | | | | | | | | | |
| H+ (1 M Acn) | -256.2 | | | | | | | | | | | |
| | -6.3 | kcal/mol | -0.01 | | | | | | | | | |