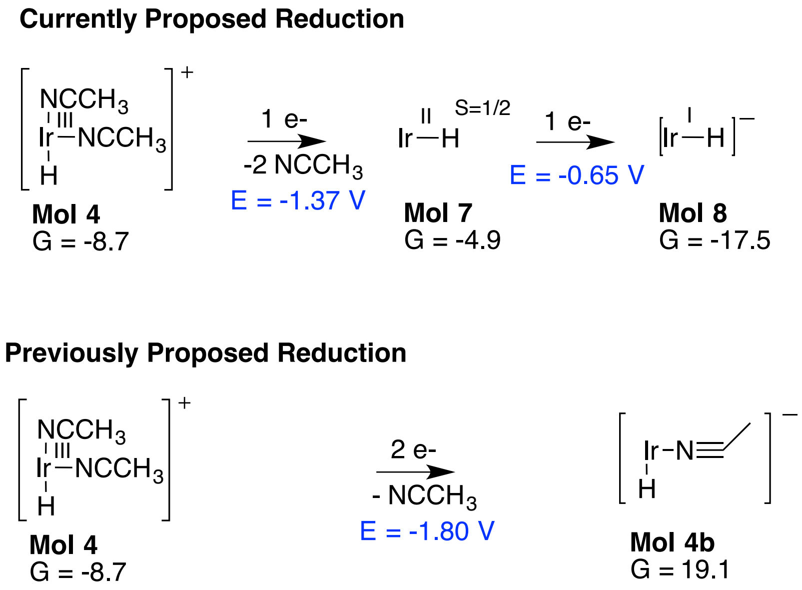
Appendix A

Appendix A: Supplementary Calculations Supporting CO_2 Reduction

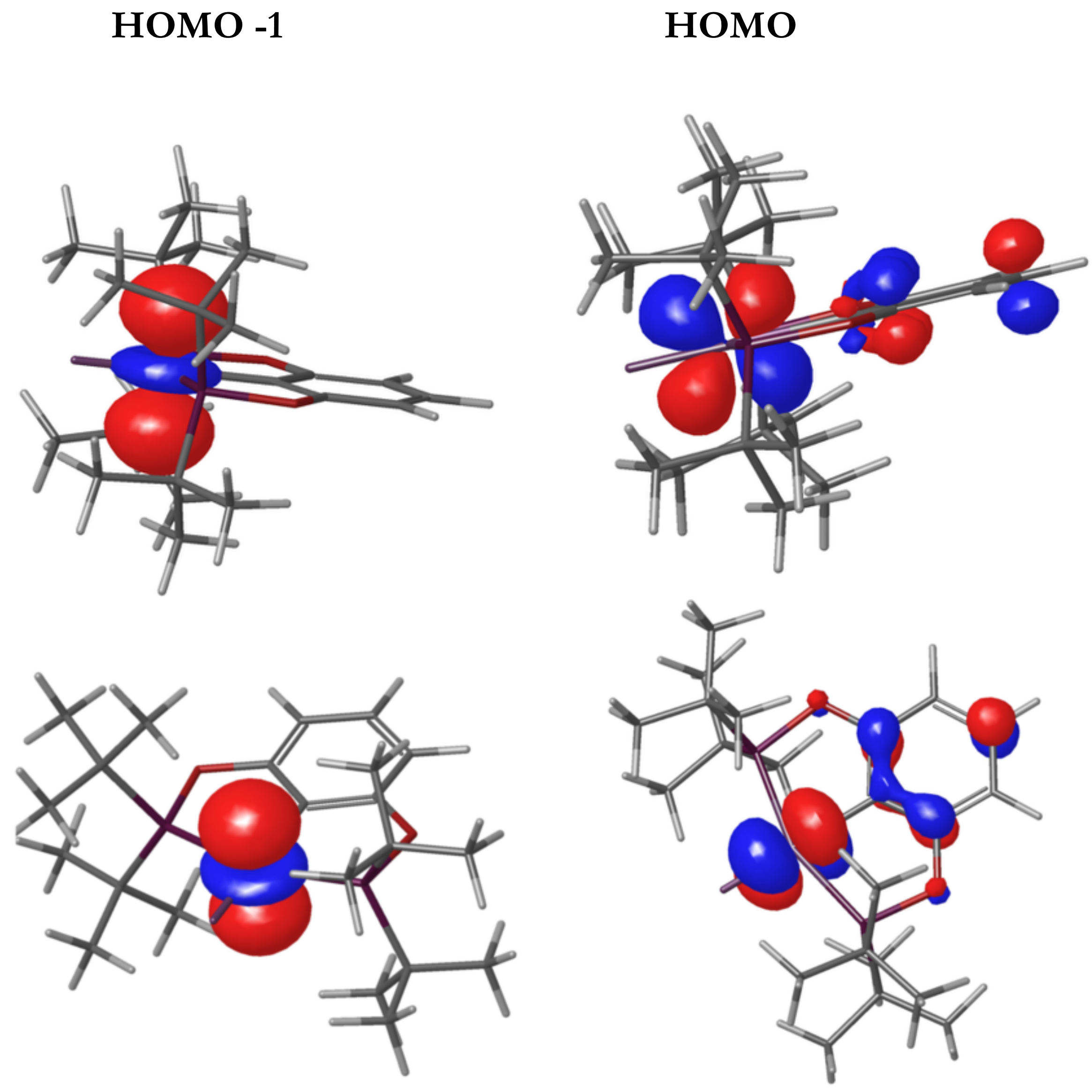
Appendix A.1: Calculation of the doubly reduced acetonitrile complex

In work by Cao et al., (Cao, L.; Sun, C.; Sun, N.; Meng, L.; Chen, D. *Dalton Trans.* **2013**, 42, 5755.) 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 see a reduction potential of -1.8 vs SHE, which is too negative for the experimentally observed reduction potential.



Scheme A.1: 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. Energies in kcal/mol.

Appendix A.2



HOMO -1

HOMO

Figure S1: HOMO of Ir^{I} complex

The HOMO -1 and HOMO of POCOP-Ir^{I} hydride anion (**Mol 8**) is shown. The high electron density in axial positions explains why oxygen cannot coordinate simultaneously in a transition state analogous to **TS 2**.

Appendix A.3: Justification for Calculations with Water Clusters

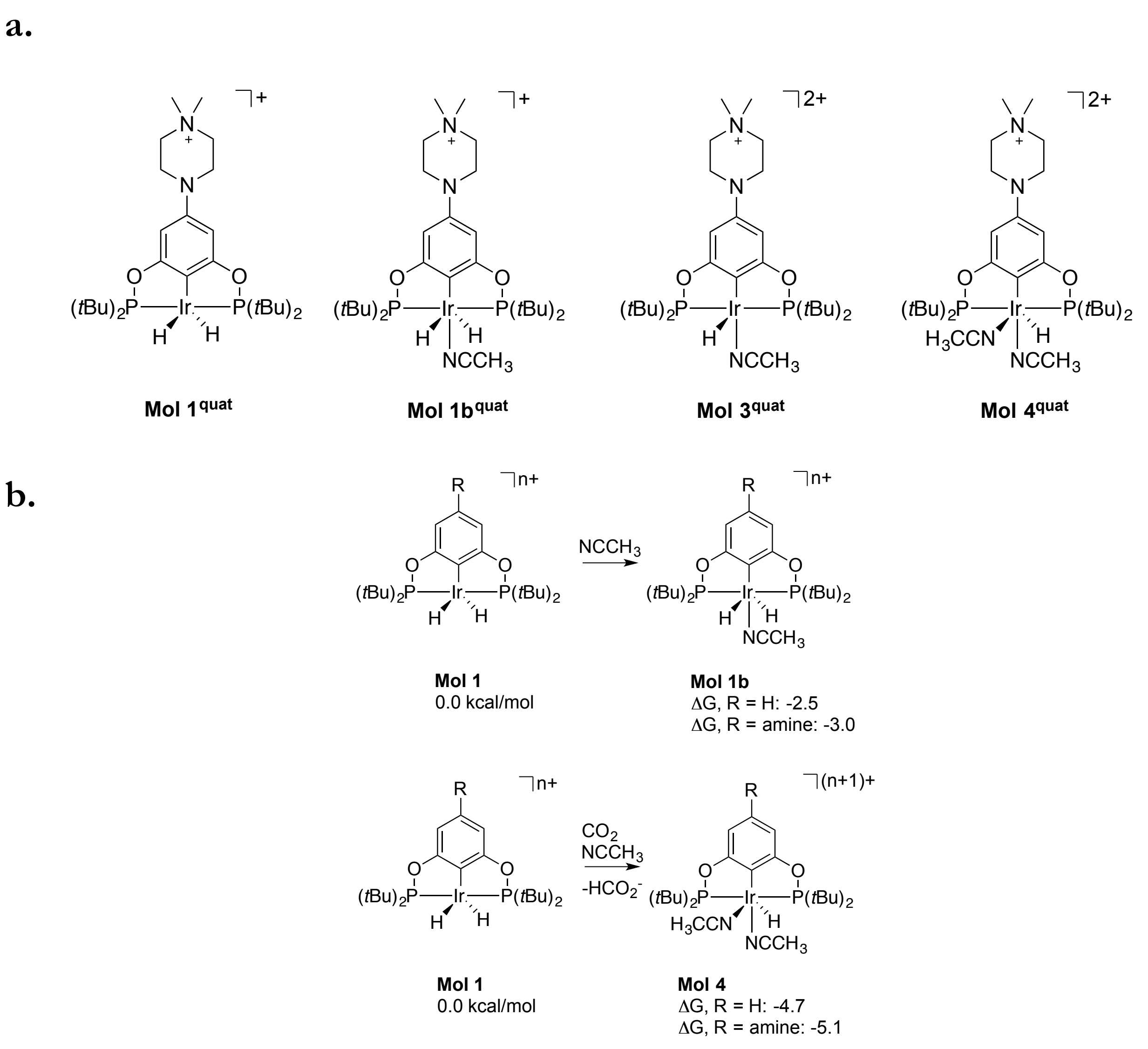
The calculated free energy and pKa for the auto-dissociation of water is used to justify our use of an explicit four-water cluster (plus continuum solvation) in transition state calculations. A neutral $4H_2O$ and anionic $OH^- \bullet 3H_2O$ cluster were used.

$$4\,H_2O\ (liq) \rightarrow H^+\ (1M) + OH^- \bullet 3H_2O\ (1\ M)$$

$$\Delta G_{calc} = 20.2\ kcal/mol$$

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

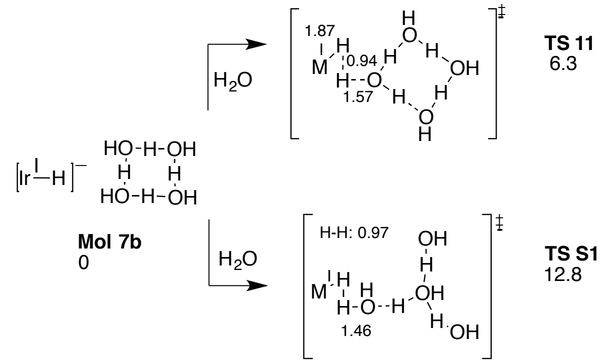
Appendix A.4



Scheme A.4: a) Structures of quaternary amine POCOP; 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, shown in Scheme 2a. 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 2b. The difference in free energies of these reactions does not exceed 0.5 kcal/mol, which is well within the error of DFT. Thus, we feel comfortable in using the simplified ligand scaffold.

Appendix A.5



Scheme A.5: 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 A.6

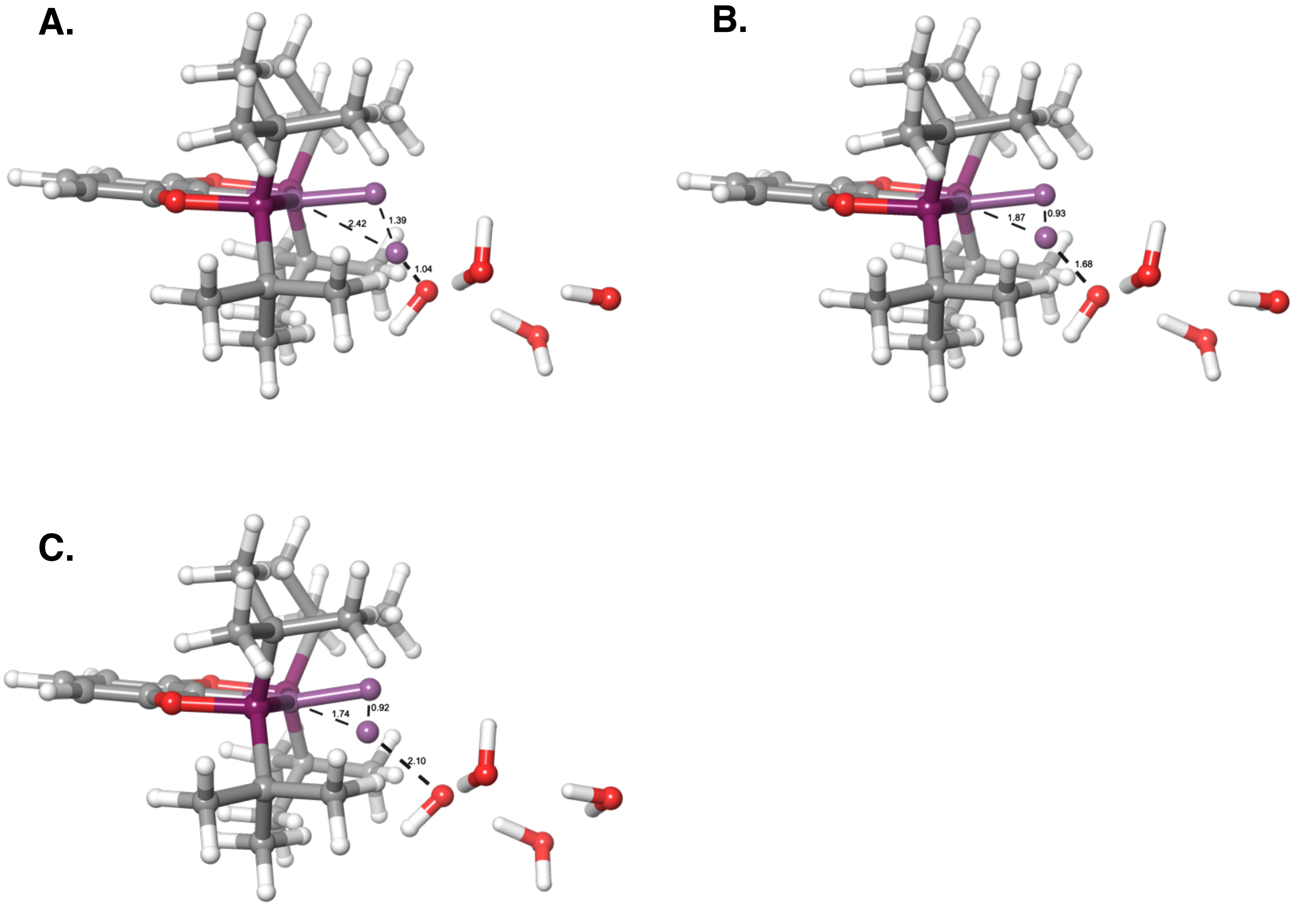


Figure A.6: Figures of points along the intrinsic reaction coordinate calculation. A. Point on the reverse path; B. The transition state; C. Point on the forward path. All bond lengths in Angstroms. For reference, the spectator Ir-H bond length is 1.70 Å.

Appendix A.7

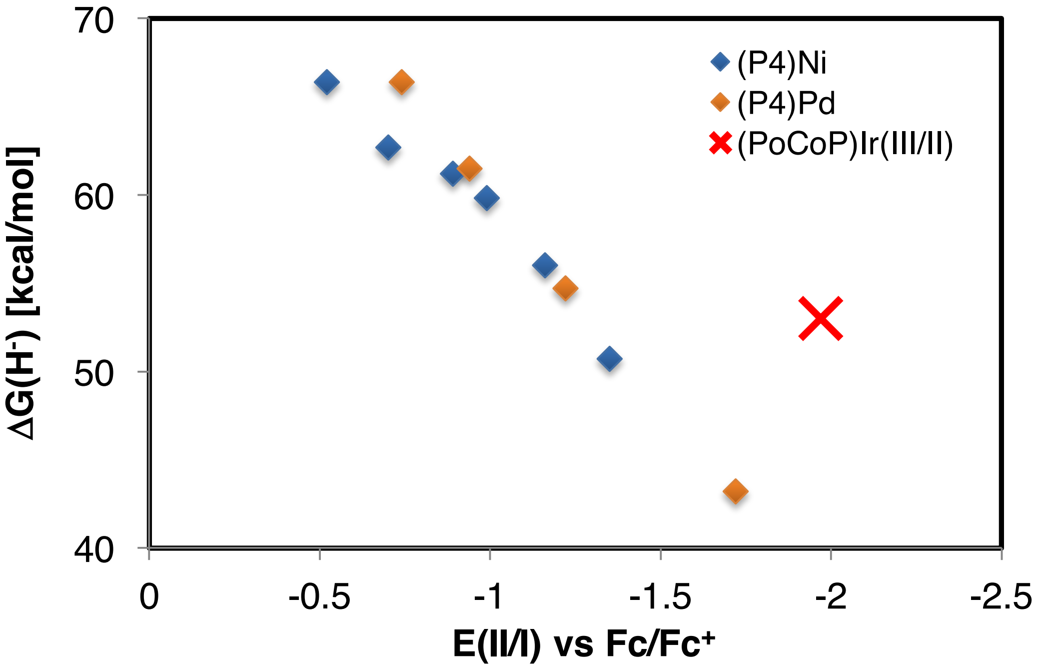


Figure A.7: Hydricities of (POCOP) Ir compared to other hydridic compounds

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., Free-Energy Relationships between the Proton and Hydride Donor

Abilities of [HNi(diphosphine)2]+ Complexes and the Half-Wave Potentials of Their Conjugate Bases. *Organometallics* **2001**, *20* (9), 1832-1839.

3. Raebiger, J. W.; Miedaner, A.; Curtis, C. J.; Miller, S. M.; Anderson, O. P.; DuBois, D. L., Using Ligand Bite Angles To Control the Hydricity of Palladium Diphosphine Complexes. *J. Am. Chem. Soc.* **2004**, *126* (17), 5502-5514.

APPENDIX B: FULL RESULTS ON MODIFICATION OF POCOP PINCERS

Appendix B.1: Results of simulations involving substitutions of (R-POCOP)Ir

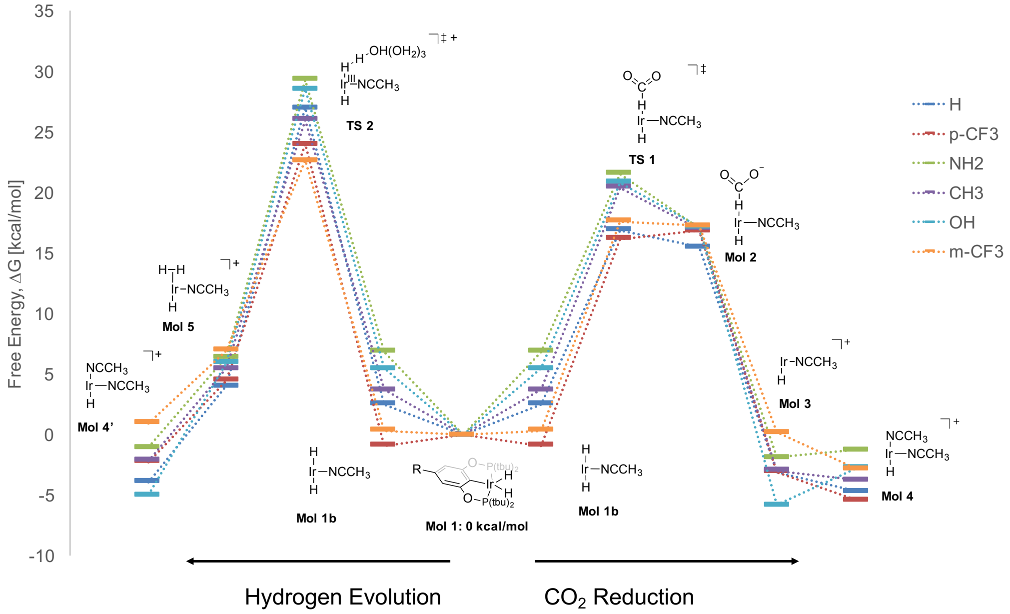


Figure B.1: Full results of modifications of the *para* position of pincers. Trends here largely scale with electron withdrawing ability of the catalysts. Numerical results can be seen in the table below.

***Table B.1:** All free energies (ΔG) of para substitutions on barriers and kinetics of CO_2RR and HER*

Energies in kcal/mol		Functional group (R)					
		H	***p*-CF_3**	**NH2**	**CH3**	**OH**	**m-CF3**
Intermediate Name	**Mol 4'**	-3.9	-4.6	-0.5	-3.0	-2.0	-2.0
	Mol 9	4.0	4.5	6.4	5.5	5.9	7.0
	TS 2	27.0	24.0	29.3	26.0	28.5	22.6
	Mol 1b	2.5	-0.9	6.8	3.7	5.5	0.4
	Mol 1	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*	*0.0*
	Mol 1b	2.5	-0.9	6.8	3.7	5.5	0.4
	TS 1	16.9	16.2	21.5	20.4	20.8	17.6
	Mol 2	15.5	16.8	17.1	17.0	17.1	17.2
	Mol 3	-3.1	-3.1	-1.9	-3.0	-5.8	0.2
	Mol 4	-4.7	-5.4	-1.3	-3.8	-2.8	-2.8

Appendix C

APPENDIX C: MOLECULAR COORDINATES

The molecular coordinates for many of the complexes found in this thesis can be found online as supplementary material. These coordinates are in .xyz format and are titled in the coordinates as they are in the figures of this document. They can be viewed using several free programs available online including Mercury (www.ccdc.cam.ac.uk/mercury) and MacmolPLT (brettbode.github.io/wxmacmolplt).