Supporting Information: Control of Reversible Oxidative Addition/Reductive Elimination of Surface-Attached Catalysts by External Electric Fields

Zhuoran Long,[1,2,†] H. Ray Kelly,[1,2†] Pablo E. Videla,[1,2] Jan Paul Menzel,[1,2] Tianquan Lian,[3] Clifford P. Kubiak,[4] and Victor S. Batista[1,2,]*

[1] Department of Chemistry, Yale University, P.O. Box 208107, New Haven, Connecticut 06520-8107, United States

[2] Energy Science Institute, Yale University, 810 West Campus Drive, West Haven, Connecticut 06516, United States

[3] Department of Chemistry, Emory University, 1515 Dickey Drive, Northeast, Atlanta, Georgia 30322, United States

[4] Department of Chemistry and Biochemistry, University of California, San Diego, 9500 Gilman Drive, MC 0358, La Jolla, California 92093, United States

1. Computational Structural Models

The gold cluster is constructed by taking one atom (top right corner) out of a 6*6 single layer. The odd number (35) of Au atoms is to make the total number of electrons even so that restricted density functional theory (DFT) calculation can be performed. The first Au atom at the lower left corner is placed at the origin of the coordinate system, and the complexes are placed at the positive region of the z axis.
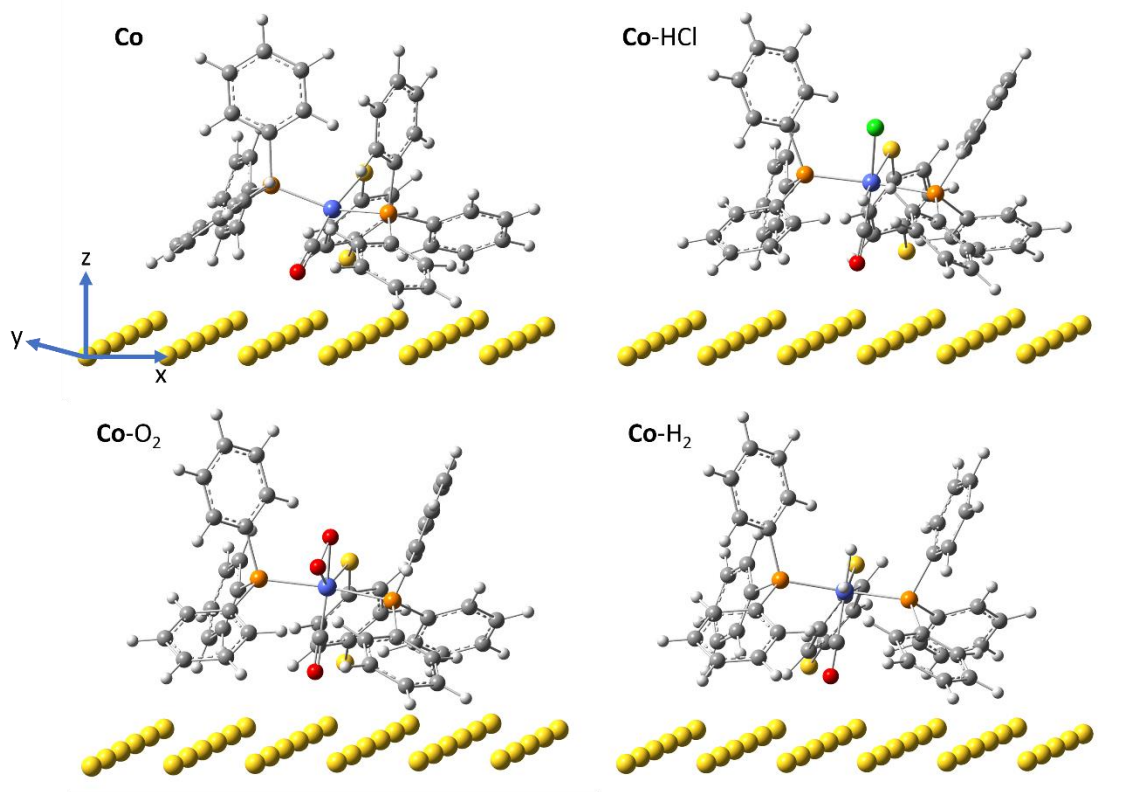
Figure S1 Vaska's complex analogue **Co** and its HCl/O_2/H_2 adduct. The cartesian axes are shown in the top left panel of **Co**. Color code: H-white, C-gray, O-red, P-orange, S-yellow, Cl-green, Co-blue, Au-yellow.
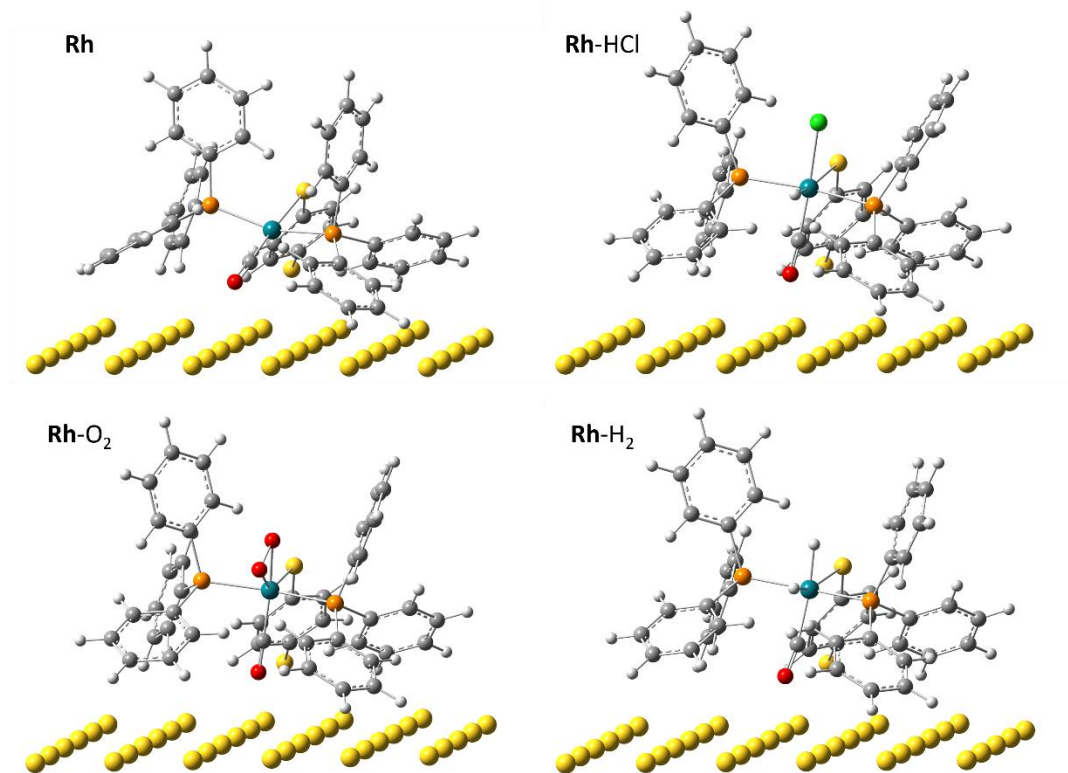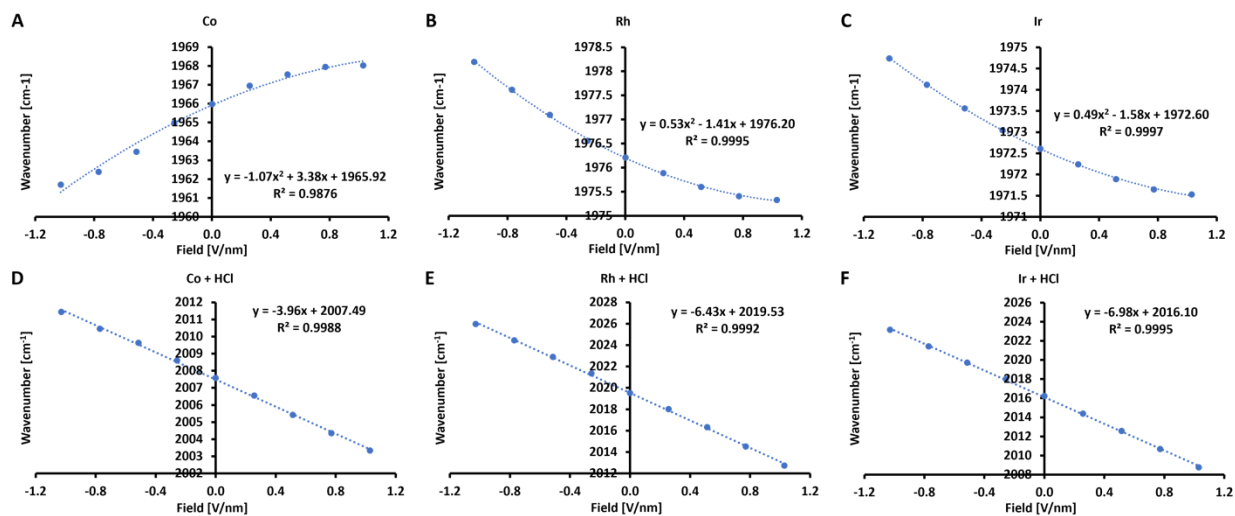
Figure S2 Vaska's complex analogue **Rh** and its HCl/O$_2$/H$_2$ adduct. Color code: H-white, C-gray, O-red, P-orange, S-yellow, Cl-green, Rh-blue, Au-yellow.
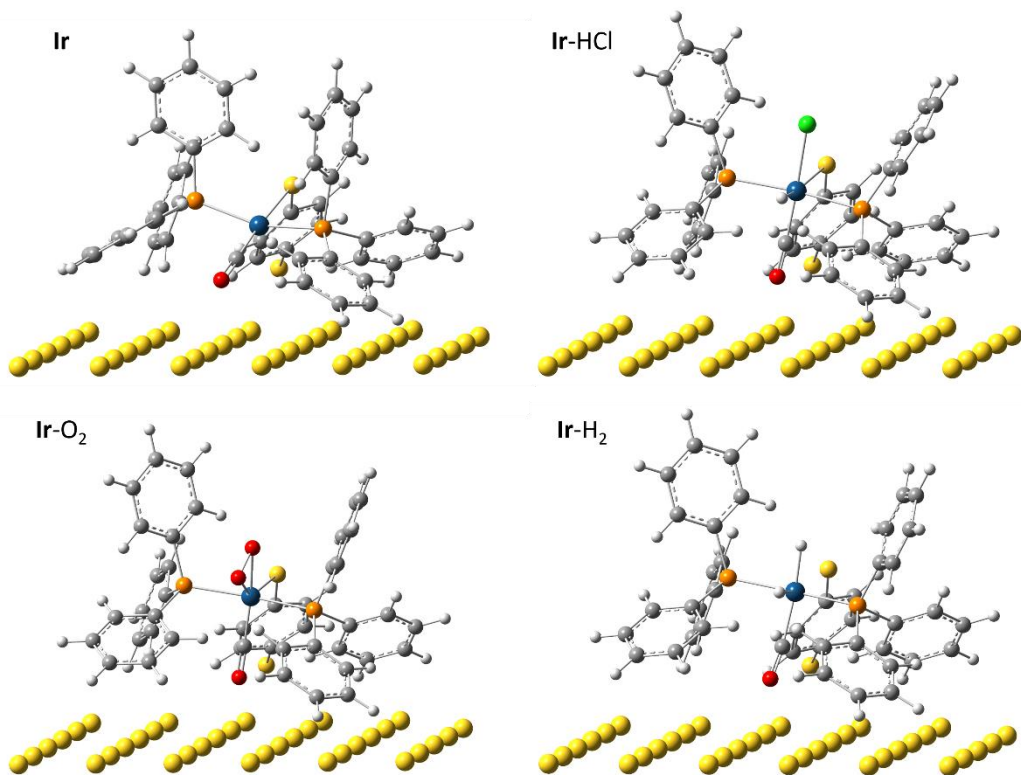
Figure S3 Vaska's complex analogue **Ir** and its HCl/O$_2$/H$_2$ adduct. Color code: H-white, C-gray, O-red, P-orange, S-yellow, Cl-green, Ir-blue, Au-yellow.

2. Stark Shift of the C-O Stretching Mode Frequency

Figure S4 DFT-computed CO vibrational frequency *vs* applied electric field strength for **Co** (**A**), **Rh** (**B**) and **Ir** (**C**) and their HCl adducts **Co**-HCl (**D**), **Rh**-HCl (**E**) and **Ir**-HCl (**F**). The best quadratic or linear fits are shown as dotted lines with corresponding equations and coefficients of determination (R^2) provided in each plot.

3. Isotropic Polarizability and Total Dipole moment

Table S1 Isotropic polarizability (α_{iso}) and total dipole moment z components ($|\boldsymbol{\mu}|$) of Vaska's complex analogues and their $HCl/O_2/H_2$ adducts.

Complex	α_{iso} [kcal$^2\cdot$mol^{-2}/ (V$^2\cdot$nm^{-2})]	$|\boldsymbol{\mu}|$ [kcal$\cdot$mol^{-1}/ (V$\cdot$nm^{-1})]
Co	23.0	9.0
Co-HCl	23.1	3.7
Co-O$_2$	23.2	5.3
Co-H$_2$	23.1	7.4
Rh	22.6	7.1
Rh-HCl	22.7	4.0
Rh-O$_2$	23.2	5.5
Rh-H$_2$	22.7	6.8
Ir	22.6	7.2
Ir-HCl	22.7	3.8
Ir-O$_2$	23.1	5.3
Ir-H$_2$	22.7	6.9

The isotropic polarizability is basically the same among the Vaska's complex analogues and their adducts. The difference in the zz-components α_{zz} in the main content **Table 2** is, therefore, mainly due to the different orientations of the complexes. **Co** and its adducts have slightly higher α_{iso} than complexes with Rh and Ir centers. As explained in the main text, the Co-ligand bond is more ionic in nature and the Co center is more positively charged. Therefore, the ligands of Co-centered complexes are more negatively charged. In other words, there are more charge densities on the ligands when bond to Co than Rh/Ir, which give rise to the higher polarizability. The total dipole moments follow the same trend as their z-components in **Table 2**.