Supplementary Information

Evaluating the impacts of amino acids in the secondary and outer-coordination sphere of Rh-bis(diphosphine) complexes for CO_2 hydrogenation

Aaron P. Walsh[a†], Joseph A. Laureanti[a†], Sriram Katipamula[b], Geoffrey M. Chambers, Nilusha Priyadarshani[c], Sheri Lense[d], J. Timothy Bays, John C. Linehan, Wendy J. Shaw*

[†] Authors contributed equally to this work.

[a] Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, Richland, WA 99352, USA.

[a] Current address: Ferro Corporation, Penn Yan, NY 14527

[b] Current address: Rutgers University, Piscataway, NJ 08854

[c] Current address: Curium, Maryland Heights, MO

[d] Current address: University of Wisconsin-Oshkosh, Oshkosh, WI

Table of Contents

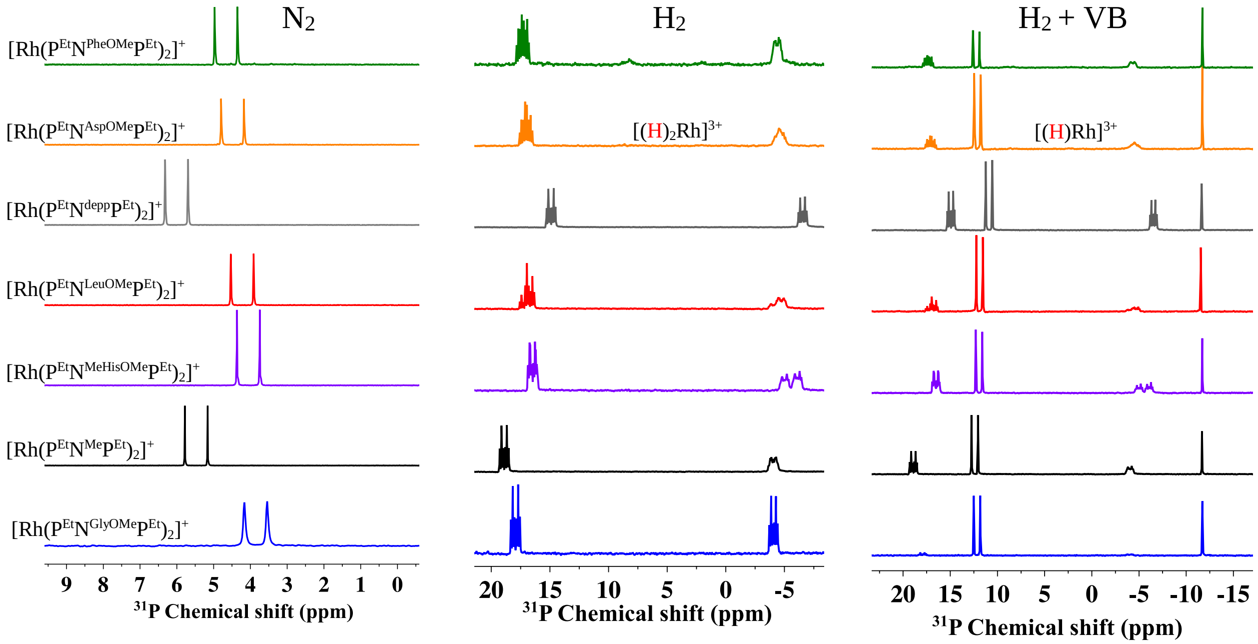

Figure S1. $^{31}P\{^{1}H\}$ NMR of the $[Rh[P^{Et}N^{R}P^{Et})_2]^+$ complexes under 1.0 atm of nitrogen (left), hydrogen (middle), and hydrogen + 1.1 equivalents of Verkade's base (VB, right). Black, red, green, purple, grey, blue, and orange represent the NMe, LeuOMe, PheOMe, MeHisOMe, depp, GlyOMe, and AspOMe complexes, respectively.

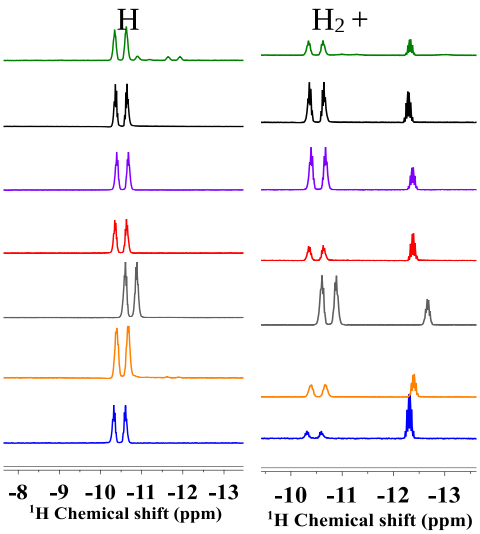

Figure S2. ^{1}H NMR of the $[Rh[P^{Et}N^{R}P^{Et})_2]^+$ complexes under 1.0 atm of hydrogen (left) and hydrogen + 1.1 equivalents of Verkade's base (VB, right). Black, red, green, purple, grey, blue, and orange represent the NMe, LeuOMe, PheOMe, MeHisOMe, depp, GlyOMe, and AspOMe complexes, respectively.

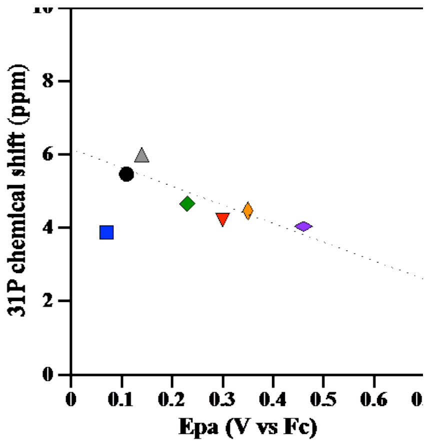

Figure S3. Plotting the E_{pa} from the cyclic voltammetry, Figure 7, vs. the ^{31}P NMR chemical shifts, Table 1 and Figure S1, shows an expected correlation for ^{31}P chemical shifts reporting on the electron density at the Rh metal. The glycine analog displays anomalous behavior. The black circle=NMe, red triangle=LeuOMe, green diamond=PheOMe, purple diamond=MeHisOMe, grey triangle=depp, blue square=GlyOMe, and orange diamond=AspOMe.

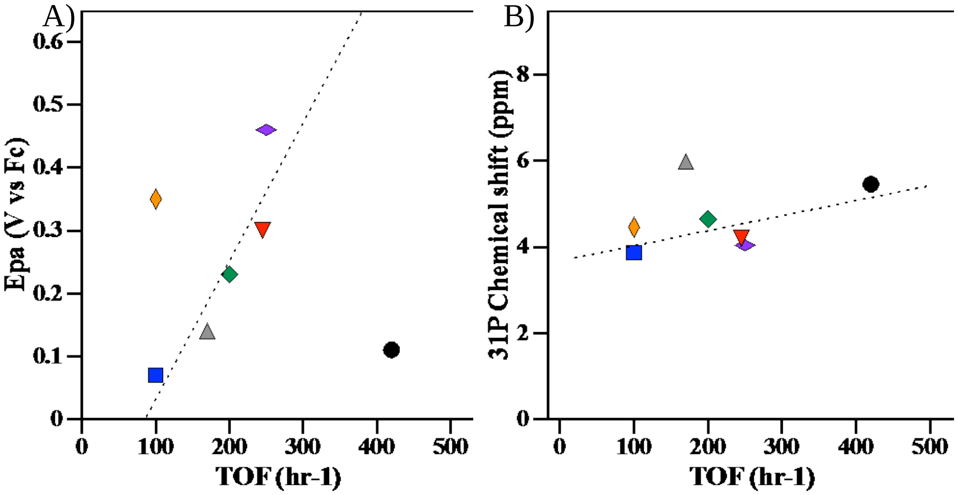

Figure S4. A) E_{pa} vs TOF for the complexes in this study. B) ^{31}P chemical shift vs. TOF for the complexes in this study. No correlation is observed between the electron density at the metal and the catalytic activity. Black=NMe, red=LeuOMe, green=PheOMe, purple=MeHisOMe, grey=depp, blue=GlyOMe, and orange=AspOMe.

Table S1. Selected bond distances (Å) and angles (°) for $(H)_2Rh(P^{Et}N^{Me}P^{Et})_2$

Atoms	Distance	Atoms	Angle
Rh-P(1)	2.2874(4)	P(1)-Rh-P(2)	92.908(16)
Rh-P(2)	2.3464(4)	P(2)-Rh-P(3)	98.720(16)
Rh-P(3)	2.2906(4)	P(3)-Rh-P(4)	91.790(15)
Rh-P(4)	2.3533(4)	P(1)-Rh-P(3)	162.526(17)
Rh-H(1)	1.57(2)		
Rh-H(2)	1.55(2)	P(1)-Rh-H(2)	83.0(8)
		P(3)-Rh-H(2)	84.1(8)
		P(4)-Rh-H(2)	87.1(8)
		H(1)-Rh-H(2)	85.5(12)
		H(1)-Rh-P(2)	88.4(8)