Supporting information

Photoswitching a Molecular Catalyst to Regulate CO_2 Hydrogenation

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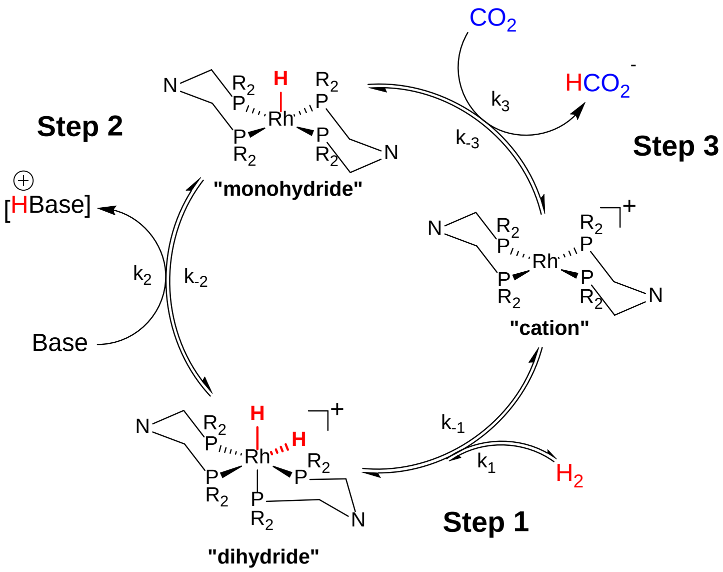
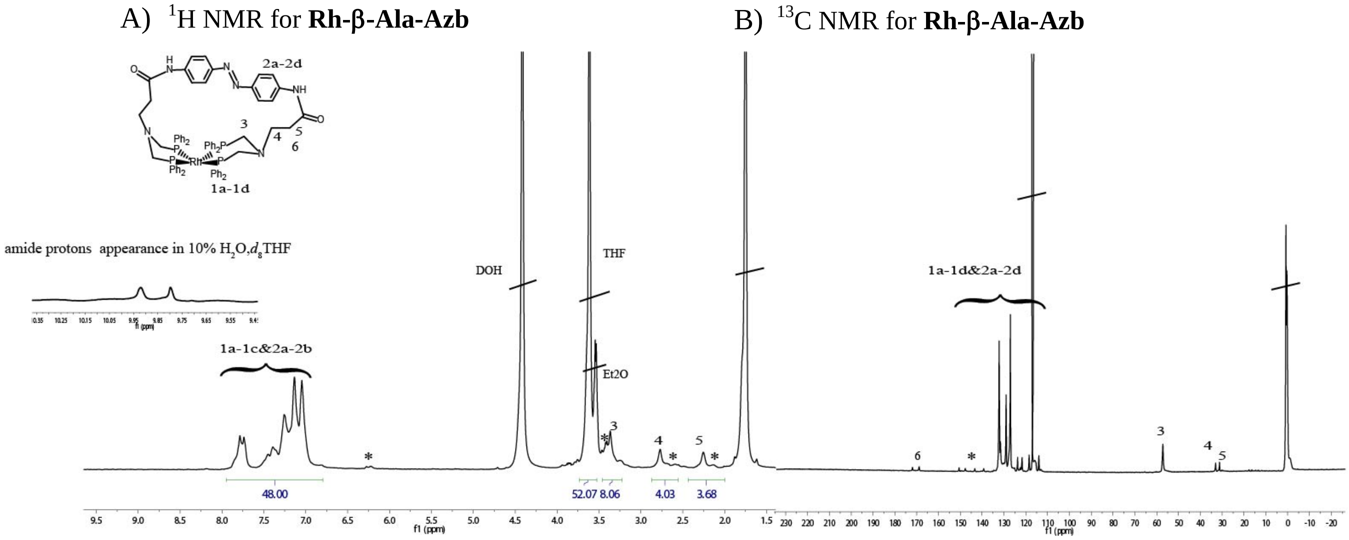


Figure S1. Proposed catalytic cycle for CO_2 hydrogenation by $[Rh(PN^RP)_2]^+$.[1] R-groups on N are not shown.



A) ^{1}H NMR for **Rh-β-Ala-Azb**

B) ^{13}C NMR for **Rh-β-Ala-Azb**

Figure S2. Characterization data for **Rh-β-Ala-Azb.** A) ^{1}H NMR (500 MHz, 10% D_2O and d_8-THF): δ 2.30 (br, 4H, NCH_2CH_2CONH), 2.83 (br 4H, NCH_2CH_2CONH), 3.43 (s, 8H, PCH_2N), 6.74-7.91 (m, 48H, PPh*H* & Azb-Ph*H*); A-inset ^{1}H NMR showing the appearance of a new amide proton resulting from the coupling of the azobenzene to the complex. B) $^{13}C\{^1H\}$ NMR (125 MHz, 10% D_2O and d_8-THF)): δ 31.22, (NCH_2CH_2-), 33.37, (NCH_2CH_2-), 57.18 (br, P-CH_2-N), 119.3, 123.3, 128.2, 130.1, 131.0, 132.2, 132.8, 133.3,(*C*-Ph) 169.9 (-*C*ONH). * indicates peaks relevant to the *cis* conformation confirmed by the increase in those peaks under UV light irradiation. Slashes indicate solvent peaks

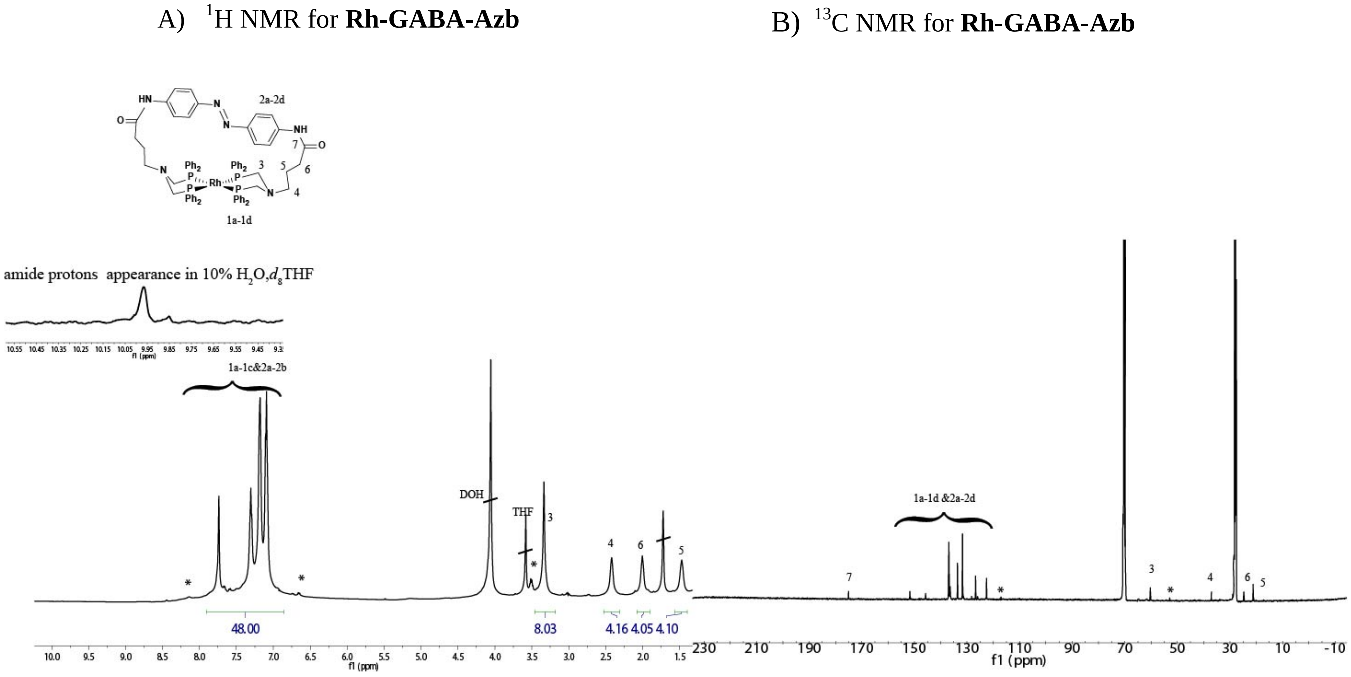


Figure S3. Characterization data for **Rh-GABA-Azb.** A) ^{1}H NMR (500 MHz, 10% D_2O and d_8-THF)): δ 1.52 (br 4H, $NCH_2CH_2CH_2CONH$), 2.06 (br 4H, $NCH_2CH_2CH_2CONH$), 2.47 (br 4H, $NCH_2CH_2CH_2CONH$), 3.38 (s, 8H, PCH_2N), 6.72 -7.79 (m, 48 H, PPh*H* & AzbPh*H*); A-inset) ^{1}H NMR showing the appearance of a new amide proton resulting from the coupling of the azobenzene to the complex d_8-THF and H_2O.B) $^{13}C\{^1H\}$ NMR (125 MHz, CD_3CN): δ 25.7, 27.3, 33.9 (-$CH_2CH_2CH_2$-), 60.9 (PCH_2N-), 119.0, 119.3, 123.2, 123.4, 141.9, 147.4, 157.4 (*C*Ph), 171.5 (*C*ONH). * indicates peaks relevant to the *cis* conformation confirmed by the increase in those peaks under UV light irradiation.

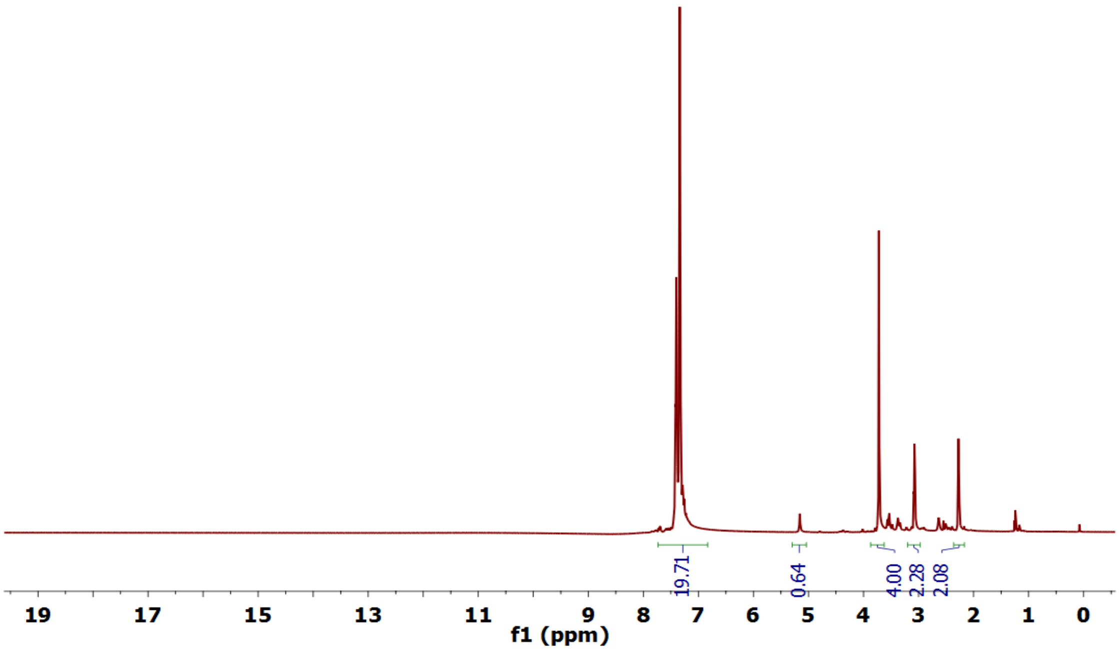


Figure S4. ^{1}H NMR **PN$^{\beta\text{-Ala-OH}}$P** showing lack of formaldehyde peak beyond 9 ppm, where it is observed.

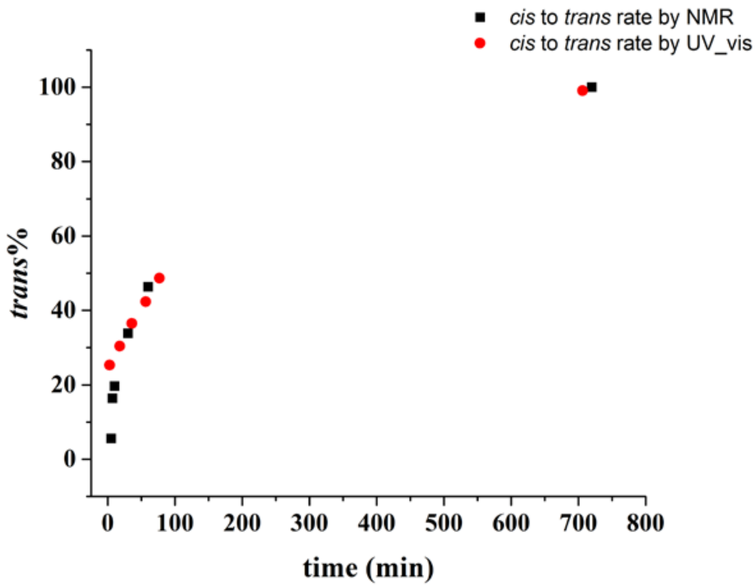


Figure S5. The rate of *cis-trans* isomerization observed from ^{1}H NMR spectroscopy and UV/Vis absorption methods shows similar relaxation.

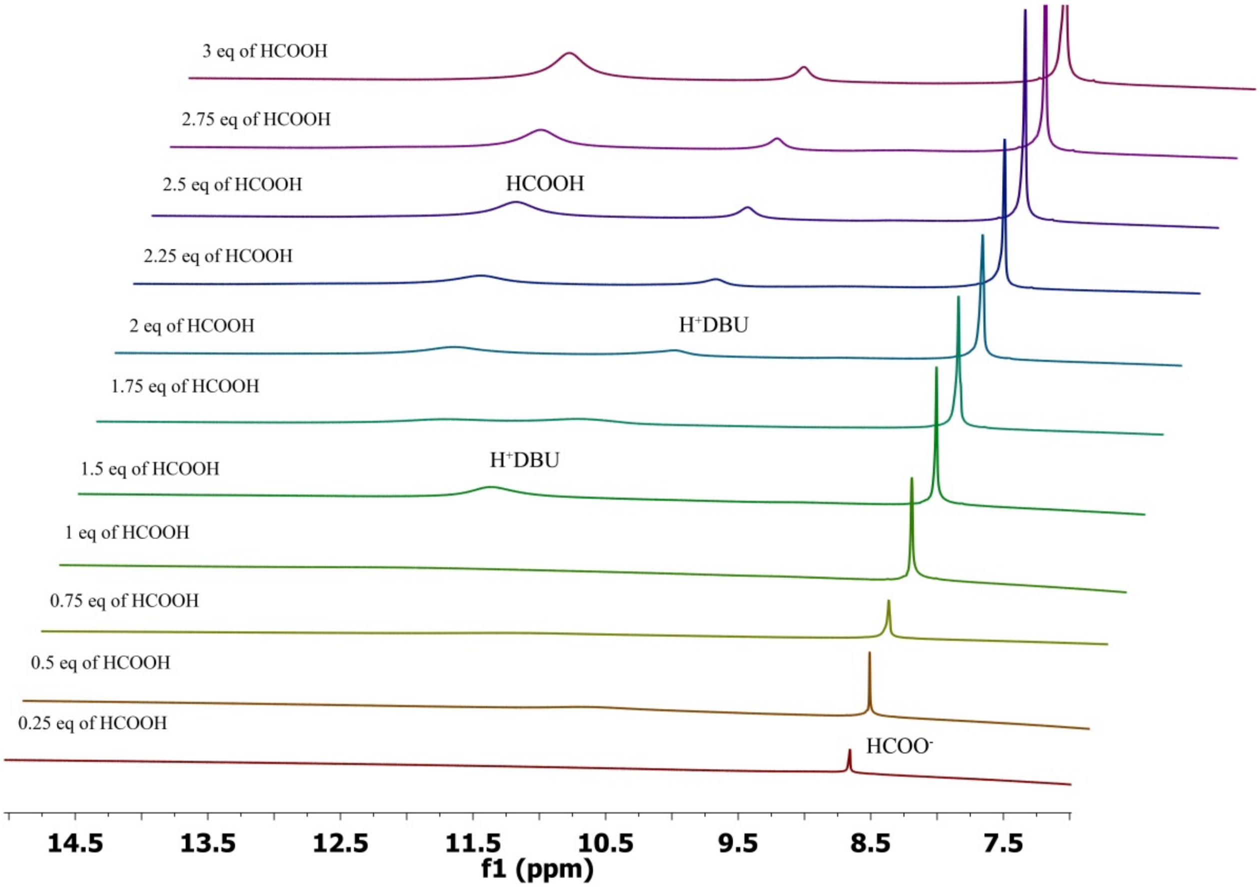


Figure S6. Data used to determine the extent of homoassociation of formate and DBU in NMP, achieved by adding formic acid to DBU in NMP.

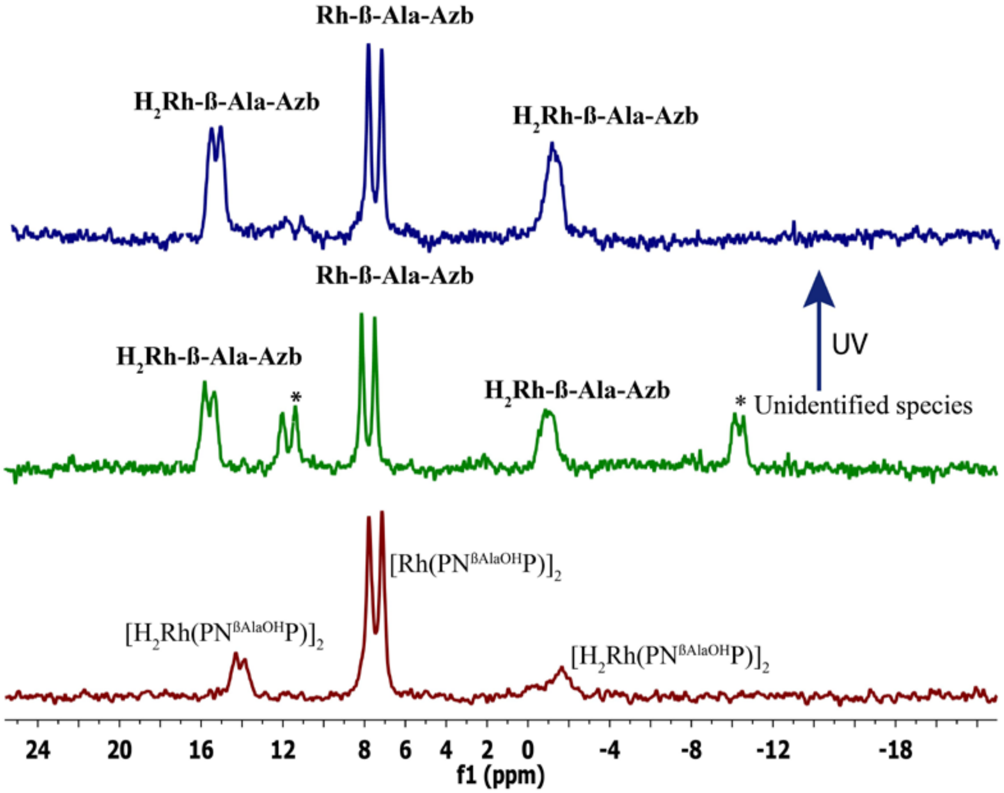


Figure S7. The $^{31}P\{^{1}H\}$ NMR spectra of **$[H_2Rh(PN^{\beta\text{-Ala-OH}}P)_2]^+$** (bottom) and **$H_2$Rh-ß-Ala-Azb** (middle *trans* and top *cis*). The unidentified species is not observed after irradiation.

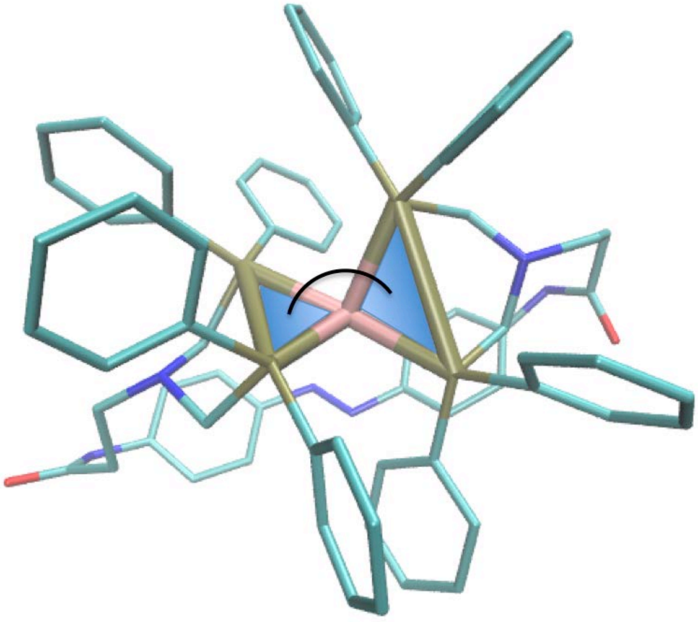


Figure S8. Measured dihedral angle

Table S1. Additional geometrical parameters for **Rh-β-Ala-Azb and Rh-GABA-Azb**.resulting from the computational analysis.

Complex	r(Rh-N*) (Å)	∠C-N-C (°)	∠C-N=N-C (°)
Rh-β-Ala-(*cis*)-Azb	3.6±0.1	96±5	0.16±7.7
Rh-β-Ala-(*trans*)-Azb	3.7±0.1	143±6	163±6
Rh-GABA-(*cis*)-Azb	3.6±0.1	98±5	0.2±8.1
Rh-GABA-(*trans*)-Azb	3.7±0.1	152±8	167±6

N* = pendant amine

Synthesis and catalysis for $[Rh(PN^{Gly\text{-}Azb}P)_2]^+$: A 250 mL Schlenk flask containing 0.32 g (0.27 mmol) $[Rh(PN^{Gly\text{-}OH}P)_2](OTf)$[2] and 2.2 equivalent of HATU (0.223 g, 0.589 mmol) in 100 mL of THF was stirred and diisopropylethyl amine (DIPEA) (0.154 g, 1.2 mmol) was added to the flask. This solution was stirred for 15 minutes and diaminoazobenzene (0.057 g, 0.27 mmol) dissolved in 5 mL of THF was added drop wise in the dark to the above reaction solution and stirred for 24 hours under ambient light. Removal of solvent resulted in a yellow powder which was redissolved in 2-3 mL of THF and precipitated into 15 mL of diethyl ether. This precipitate was filtered through a medium frit, the yellow solid was washed thoroughly washed with diethyl ether followed by washing with acetonitrile to obtain a bright yellow solid in 30% yield, which has a PF6 as the counter anion after exchanging with HATU.. ^{1}H NMR in CD_3CN): δ 2.30 (br, 4H, NCH_2CH_2CONH), 3.18 (br 4H, NCH_2CONH), 3.69 (s, 8H, PCH_2N), 6.74-7.91 (m, 56H, PPh*H* & AzbPh*H*); $^{31}P\{^1H\}$ NMR (202 MHz, CD_3CN): δ 6.22 (d, J_{RhP} = 131.3 Hz). ESI MS: Observed (MH^+- *OTf*) m/z = 1433.38; calculated (MH^+- *OTf*) m/z = 1433.40. Rates obtained in light and dark conditions are shown in Table S1.

Table S2. Rates for $[Rh(PN^{Gly}P)_2]^+$ under light (*cis*) and dark (*trans*) conditions.

Catalyst	**[M+]/mM**	**[DBU]/mM**	**Azobenzene conformation**	**TOF/h^{-1}**
$[Rh(PN^{Gly\text{-}AZB}P)_2]^+$	0.8	438	*Trans*	11
	0.8	439	*Cis*	12

Table S3. Rate comparison with PF_6 as the only counter anion for the Rh complexes or a mixture of counter anions (PF_6 & OTf)

Catalyst	**TOF/h^{-1}**
[Rh-β-Ala-(trans)Azb]PF6:OTf	**13**
[Rh-β-Ala-(trans)Azb] PF6	**12**
[Rh-β-Ala-(cis)Azb]PF6:OTf	**17**
[Rh-β-Ala-(cis)Azb]PF6	**16**

REFERENCES:

1. Jeletic, M. S.; Mock, M. T.; Appel, A. M.; Linehan, J. C., A Cobalt-Based Catalyst for the Hydrogenation of CO2 under Ambient Conditions. *Journal of the American Chemical Society* **2013,** *135* (31), 11533-11536.
2. Bays, J. T.; Priyadarshani, N.; Jeletic, M. S.; Hulley, E. B.; Miller, D. L.; Linehan, J. C.; Shaw, W. J., The influence of the second and outer coordination spheres on Rh(diphosphine)$_2$ CO_2 hydrogenation catalysts. *ACS Catalysis* **2014,** *4* (10), 3663-3670.