

## Supplementary Information

### **Integrated electrochemical CO<sub>2</sub> reduction and hydroformylation**

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## 1. Chemicals and methods

*1.1 Chemicals.* All reagents were purchased from Sigma Aldrich and were used as received unless specified. *N,N*-dimethylformamide (DMF) was dried over 3 Å molecular sieves for at least 24 h prior to use. Styrene was distilled over MgSO<sub>4</sub> under an N<sub>2</sub> environment and stored in the glove box until use, purity was checked via NMR (Bruker, AV400 MHz) and GCMS (Agilent).

*1.2 Synthesis of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>.* In an Ar glovebox, 78 mg of diphenylphosphinoethyl-functionalized onto silica gel (PPh<sub>2</sub>/SiO<sub>2</sub>, 0.7 mmol g<sup>-1</sup> of PPh<sub>2</sub> groups, 200 - 400 mesh) was added to 10 mL of anhydrous toluene in a Schlenk flask, then brought out of the glovebox to sonicate for 15 min, then brought back in. 50 mg of HRh(CO)(PPh<sub>3</sub>)<sub>3</sub> ([Rh]) was then added and the mixture was allowed to stir overnight at ambient temperature. The [Rh] immobilized onto silica material ([Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>) was isolated via vacuum filtration and washed with two volumes of toluene and one of dichloromethane (10 mL per wash). [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> was then dried overnight in a Schlenk flask, yielding a yellow/gold material. 0.4 ± 0.02 wt% Rh was determined for the [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> species via inductively coupled plasma - mass spectrometry (ICP-MS, Agilent QQQ).

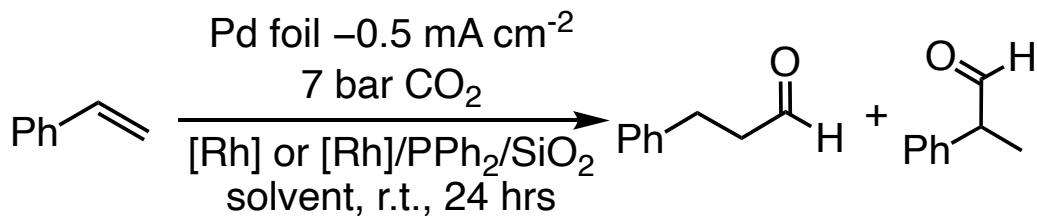
*1.2 Integrated CO<sub>2</sub>RR and hydroformylation.* Experiments in integrating CO<sub>2</sub>RR and hydroformylation were carried out in a high pressure electrochemical reactor equipped with an additional glass vial housing the hydroformylation catalysts. Electrochemistry was performed using a Gamry Instruments Interface 1000-E potentiostat. The electrolyte solution consisted of 0.25 M TBAPF<sub>6</sub> dissolved in DMF. A custom-designed high-pressure electrochemical reactor (Parr Instruments) was used equipped with electrical leads.<sup>1</sup> The solution volume was 200 mL and the gas headspace volume was ca. 750 mL (the value used for Faradaic efficiency calculations<sup>1</sup>). The reactor was purged three times, then pressurized using CO<sub>2</sub> (Airgas, 99.999%). A two-electrode configuration was utilized under constant applied current (*i*<sub>appl</sub>) and the headspace was sampled after electrolysis using a gas chromatograph (GC). Electrodes were cleaned post electrolysis via sequential rinsing and sonication in acetone, DI water, and dilute nitric acid. Unless noted otherwise, the average surface area of the Pd foil working electrodes was ~130 cm<sup>2</sup>.

Hydroformylation catalysts, both the homogeneous [Rh] and its heterogeneous analogue [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>, were handled and prepared in an Ar glovebox until ready for use in integrated experiments. Catalyst concentrations were kept at 15 mM of [Rh] or 40 mg mL<sup>-1</sup> of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>, both in a 1 mL DMF solution. [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> solutions were first prepared in a Schlenk flask, taken outside of the glovebox and sonicated for 30 min to disperse [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>,

then brought back into the glovebox. Lastly, once the electrolyte and catalyst solutions were added to the high pressure reactor, styrene was then added to the hydroformylation compartment, with a fixed  $[\text{styrene}] = 0.5 \text{ M}$ . The reactor was then sealed and pressurized with  $\text{CO}_2$  as described above.

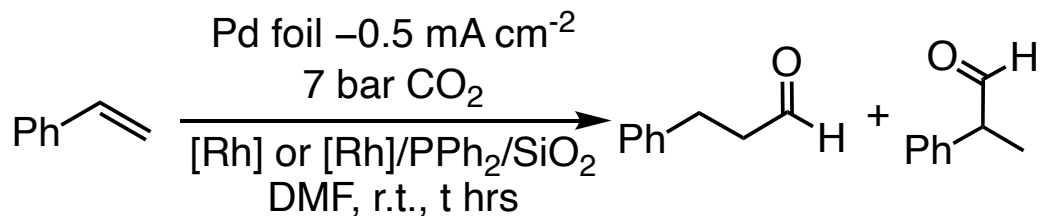
*1.3 Gas product quantification.* Gaseous products from  $\text{CO}_2$  reduction electrolysis ( $\text{CO}_2\text{RR}$ ) were quantified via online detection with a GC (SRI 8610C) equipped with both a flame ionization detector with a methanizer (FIDm), and a thermal conductivity detector (TCD). The concentration of  $\text{CO}$  and  $\text{H}_2$  in the headspace were often too high and lead to detector saturation. Thus, headspace samples were diluted by 5/83 with air. The valve oven was set to  $175 \text{ }^\circ\text{C}$ . Argon was used as a carrier gas at 15 psi and  $40 \text{ mL min}^{-1}$ . The GC method was as follows:  $50 \text{ }^\circ\text{C}$  for 1 min,  $20 \text{ }^\circ\text{C min}^{-1}$  ramp rate up to  $90 \text{ }^\circ\text{C}$ , hold at  $90 \text{ }^\circ\text{C}$  for 3.75 min, then a  $30 \text{ }^\circ\text{C min}^{-1}$  ramp rate to a final temperature of  $210 \text{ }^\circ\text{C}$ . Three columns employed: 0.5 m Haysep-D pre-column, 2 m MoleSieve5A column, and 2 m Haysep-D column in that order.  $\text{H}_2$  was supplied to the FID via a  $\text{H}_2$ -100 Hydrogen Generator at 20 psi and a  $30 \text{ mL min}^{-1}$  flow rate, air was also supplied at 5 psi and a  $250 \text{ mL min}^{-1}$  flow rate. The retention times of  $\text{CO}$  was 5.45 min (FIDm), and  $\text{H}_2$  was 1.25 min (TCD). A standard calibration gas mixture of consisting of 0.5% of  $\text{CO}_2$ ,  $\text{CO}$ ,  $\text{H}_2$ , and  $\text{O}_2$  each in  $\text{N}_2$ .

*1.4 Liquid product quantification.* Products from the hydroformylation vial were detected and quantified via GCMS analysis and using a naphthalene internal standard. The temperature profile method for the GC was as follows:  $100 \text{ }^\circ\text{C}$  for 5 min followed by a  $4 \text{ }^\circ\text{C min}^{-1}$  ramp up to  $160 \text{ }^\circ\text{C}$ . For experiments using the  $[\text{Rh}]/\text{PPh}_2/\text{SiO}_2$  catalyst, the hydroformylation solution was first centrifuged and decanted prior to sample preparation. 0.5 mL of the hydroformylation solution was diluted to 1 mL using 50  $\mu\text{L}$  of a  $20 \text{ mg mL}^{-1}$  naphthalene in acetone solution and 450  $\mu\text{L}$  of acetone. Additionally, product quantification by GCMS was corroborated by conducting an integrated experiment using  $d_7$ -DMF. This was achieved by taking advantage of the diagnostic benzylic  $^1\text{H-NMR}$  shifts between styrene and 2-/3-phenylpropionadelhyde, and using residual styrene as a pseudo internal standard.<sup>2</sup> Linear:branched ratios were assessed using the area under the curve or integral of their NMR of the respective isomer's.



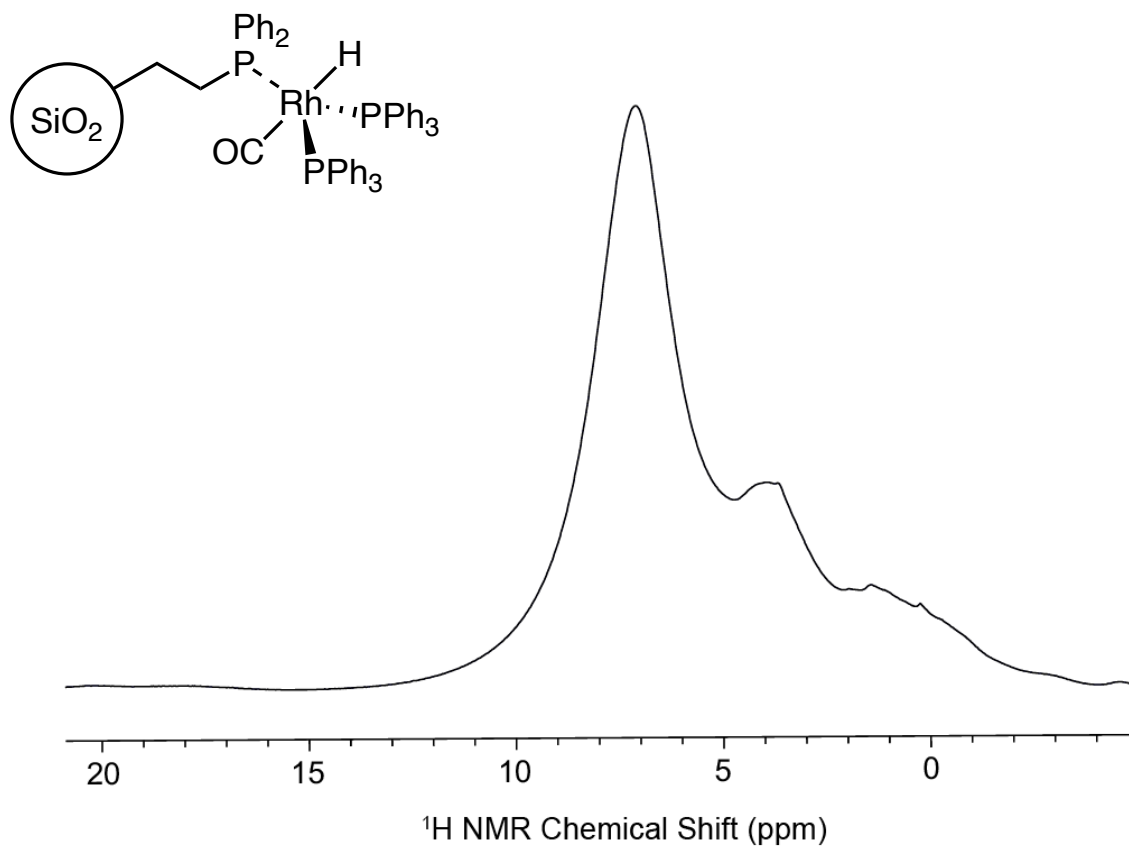
Entry	Catalyst	Solvent composition <sup>a</sup>	CO/H <sub>2</sub>	Aldehyde yield (%) <sup>b</sup>	l:b <sup>c</sup>
1	[Rh]	Toluene	0.2	76	0.7:1
2	[Rh]	DMF	0.2	53±21	0.8:1
3	No [Rh]	DMF	0.1	0	–
4	[Rh]	0.25 M TBAPF <sub>6</sub> , DMF	0.1	48	1:1
5	[Rh]	<i>d</i> <sub>7</sub> -DMF	0.04	31 (25) <sup>d</sup>	0.9:1
6	[Rh]	DMF	0.4	97 <sup>e</sup>	0.6:1
7	[Rh]/PPh <sub>2</sub> /SiO <sub>2</sub>	DMF	0.7	3±2	0.07:1
8	[Rh]/PPh <sub>2</sub> /SiO <sub>2</sub>	DMF	0.3	43 <sup>f</sup>	0.2:1
9	Bare PPh <sub>2</sub> /SiO <sub>2</sub>	DMF	0.6	0	–
10	[Rh]/PPh <sub>2</sub> /SiO <sub>2</sub> /Pd <sup>g</sup>	0.25 M TBAPF <sub>6</sub> , DMF	0.6	0	–

**Table S1.** Experiments and controls in integrated CO<sub>2</sub>RR - hydroformylation. [Rh] = HRh(CO)(PPh<sub>3</sub>), kept at 15 mM, [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> loading was kept at 40 mg mL<sup>-1</sup>, styrene concentration was kept at 0.5 M. CO<sub>2</sub> pressure was 7 bar. Applied current density (*i*) was  $\pm 0.5$  mA cm<sup>-2</sup> for 24 hours, resulting in an average of 0.21 bar CO and 0.44 bar H<sub>2</sub>. Pd foils were used as the working and counter electrode. Electrolyte solution consisted of 0.25 M TBAPF<sub>6</sub> in DMF. <sup>a</sup>Solvent composition for hydroformylation compartment. <sup>b</sup>Yield for both phenylpropionaldehyde species was determined from GCMS using a naphthalene internal standard. <sup>c</sup>Linear:branched ratio of phenylpropionaldehyde isomers. <sup>d</sup>Yield determined from NMR. <sup>e</sup>48 hours total reaction time, 24 hours electrolysis. <sup>f</sup>72 hours total reaction time, 24 hours electrolysis. <sup>g</sup>See section S2 for further details on [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> coated onto Pd ([Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>/Pd).

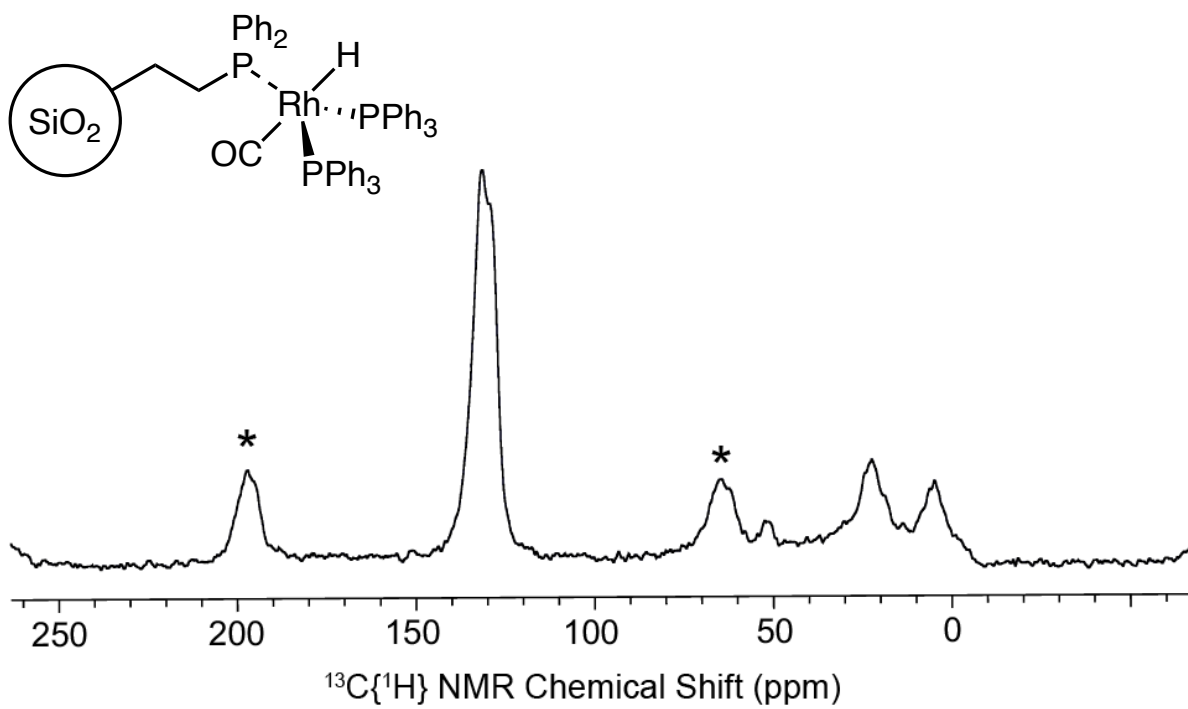


Catalyst	Electrolysis time (h)	Total time (h)	CO/H <sub>2</sub>	Aldehyde yield (%) <sup>a</sup>	l:b <sup>b</sup>
[Rh]	4	4	0.2	0.5	0.6:1
	8	8	0.3	9	0.9:1
	16	16	0.2	40	0.6:1
	24	24	0.2	64	0.8:1
	24	48	0.2	97	0.6:1
[Rh]/PPh <sub>2</sub> /SiO <sub>2</sub>	24	24	0.9	5	0.07:1
	24	36	0.5	11	0.05:1
	24	48	0.7	15	0.05:1
	24	60	0.4	37	0.13:1
	24	72	0.4	43	0.22:1

**Table S2.** Integrated CO<sub>2</sub>RR - hydroformylation time course study for both [Rh] and [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>. [Rh] = HRh(CO)(PPh<sub>3</sub>), kept at 15 mM, [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> loading was kept at 40 mg mL<sup>-1</sup>, styrene concentration was kept at 0.5 M. CO<sub>2</sub> pressure was 7 bar. Applied current density (*i*) was  $-0.5 \text{ mA cm}^{-2}$  for 24 hours, resulting in an average of 0.21 bar CO and 0.44 bar H<sub>2</sub>. Pd foils were used as the working and counter electrode. Electrolyte solution consisted of 0.25 M TBAPF<sub>6</sub> in DMF. <sup>a</sup>Yield for both phenylpropionaldehyde species was determined from GCMS using a naphthalene internal standard. <sup>b</sup>Linear:branched ratio of phenylpropionaldehyde isomers.

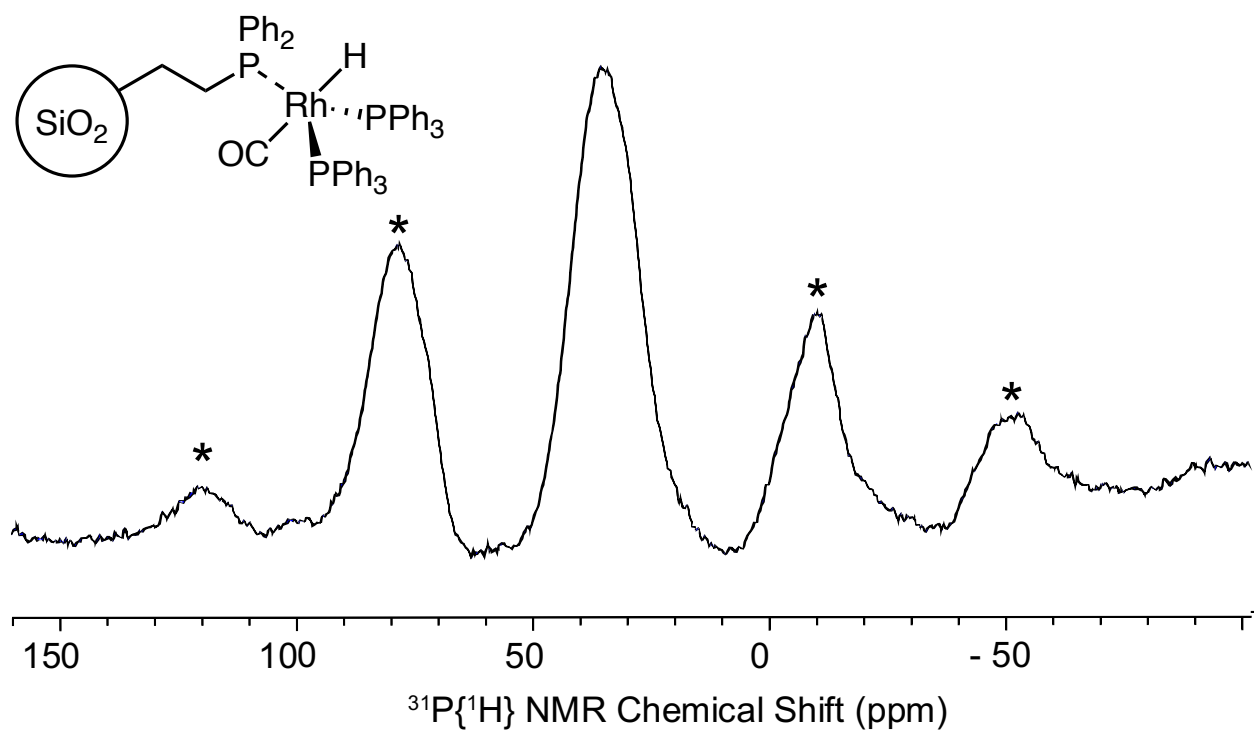


**Figure S1.** <sup>1</sup>H NMR (600 MHz, 10 kHz) of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>,  $\delta$  (ppm): 7.03 (Ph), 3.76, 1.35.

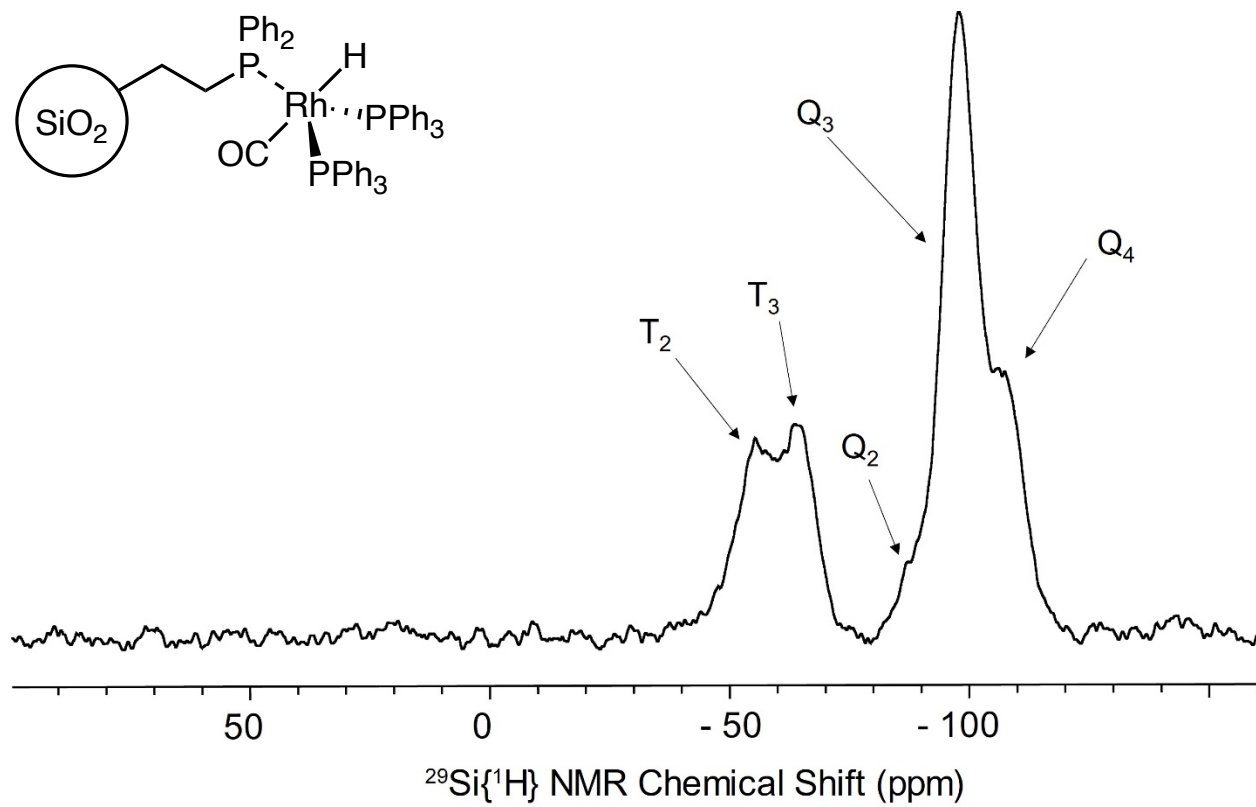


**Figure S2.** <sup>13</sup>C NMR of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> (151 MHz, 10 kHz),  $\delta$  (ppm): 131.1 (PPh), 128.9 (PPh), 52.0, 22.6, 5.0.

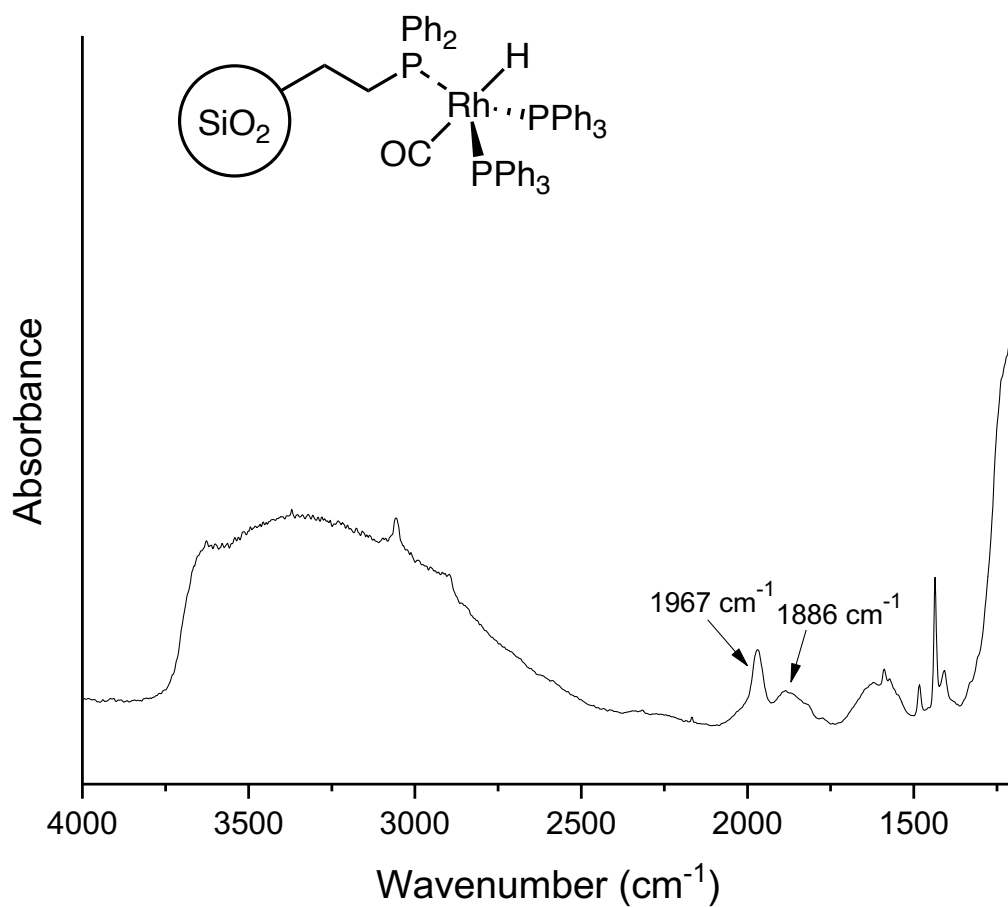




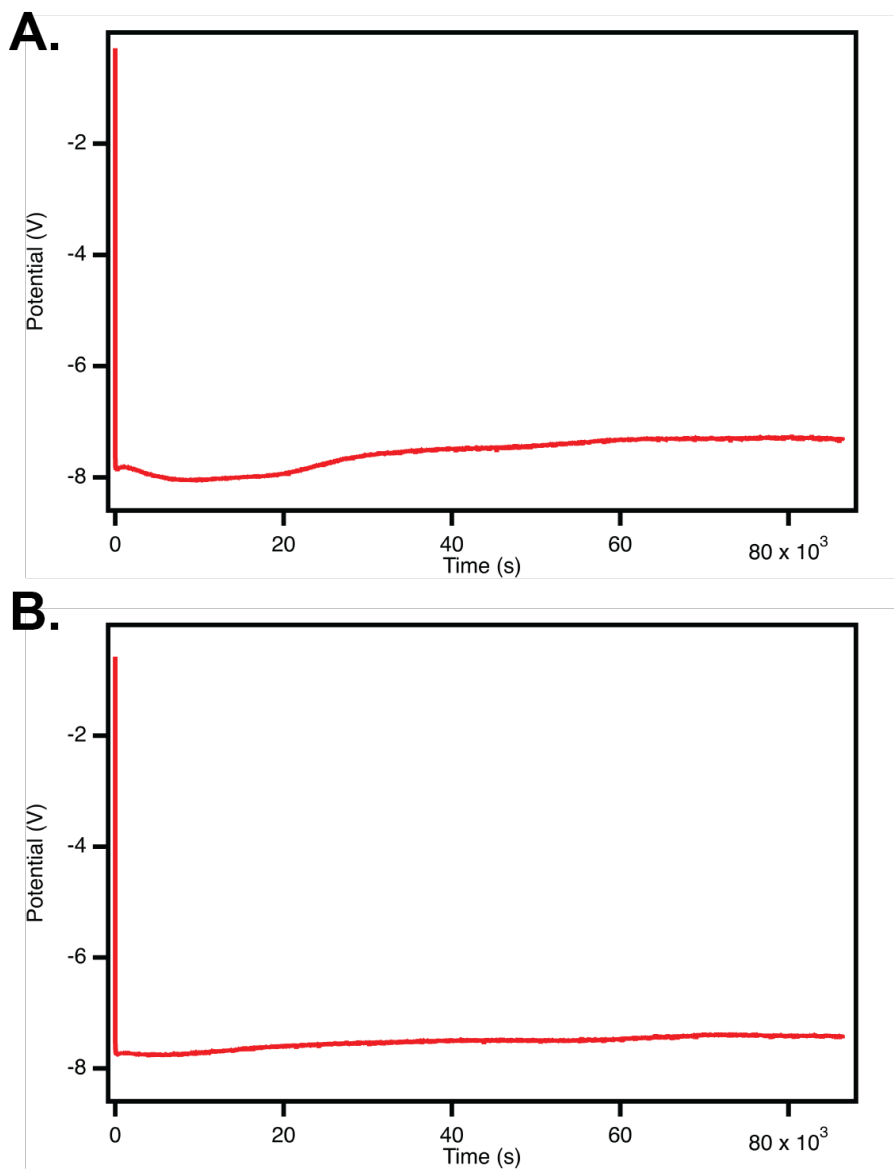
**Figure S3.**  $^{31}\text{P}$  NMR of  $[\text{Rh}]/\text{PPh}_2/\text{SiO}_2$  (243 MHz, 10 kHz),  $\delta$  (ppm): 34.8 (PPh)



**Figure S4.** <sup>29</sup>Si NMR of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> (119 MHz, 10 kHz).



**Figure S5.** ATR-IR of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>, Rh-H (1967 cm<sup>-1</sup>), Rh-CO (1886 cm<sup>-1</sup>).



**Figure S6.** Chronopotentiometry traces from two separate experiments conducted at  $-0.5 \text{ mA cm}^{-2}$  for 24 hours. Pd foils were used as the working and counter electrode. Electrolyte solution consisted of 0.25 M TBAPF<sub>6</sub> in DMF.

## 2. Coating of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> onto Pd foil

Spin coating, drop casting, and doctor blading were explored as methods of preparing a layer of [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> onto Pd foil with an insulating layer of SiO<sub>2</sub> in between. Solutions of 1 - 5 wt% of either SiO<sub>2</sub> or [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> in DMF, both with and without 2.5 wt% polyvinylidene fluoride (PVDF) as a binder, were tested. DMF was chosen on the basis of a prior report demonstrating superior dispersity and coating of SiO<sub>2</sub> compared to typical solvents such as H<sub>2</sub>O. In a typical coating attempt, 50 - 600 μL of a particular wt% of SiO<sub>2</sub> first, then [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> afterwards, were dispensed onto a sectioned 1 - 6 cm<sup>2</sup> area of a 5 x 5 cm<sup>2</sup> Pd foil, unless otherwise noted. For spin coating, Pd foil was taped down to a Si wafer, and spin rates between 200 - 800 rpm and 5 - 60 s were tested. For drop casting, the Pd foil was gently heated to 30 °C until all DMF had evaporated. For doctor blade, 500 μL of a 10 wt% [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> solution was dispensed onto a Pd foil, with thickness controlled by the amount of layers of ~20 μm thick tape around the area designated for coating. The excess [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> dispersed in DMF was then scraped off, and the Pd foil was gently heated at 30 °C until all DMF had evaporated. Thicknesses of Pd foil samples coated with [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub> (denoted as [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>/Pd) were measured via optical microscopy and SEM. Thicknesses varied from 40 - 200 μm. Unfortunately, no [Rh]/PPh<sub>2</sub>/SiO<sub>2</sub>/Pd demonstrated any hydroformylation activity in our integrated catalytic reactor.

### **Additional references**

1. H. M. Dodge, B. S. Natinsky, B. J. Jolly, H. C. Zhang, Y. Mu, S. M. Chapp, T. V. Tran, P. L. Diaconescu, L. H. Do, D. W. Wang, C. Liu and A. J. M. Miller, *ACS Catal.*, 2023, **13**, 4053-4059.
2. I. A. Tonks, R. D. Froese and C. R. Landis, *ACS Catal.*, 2013, **3**, 2905-2909.