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### Supporting Information.

### Hydrosilylation and electroreduction of CO<sub>2</sub> using a Zirconocene Hydride Catalyst Diego A.Roa and Juventino J. García\*

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Abundance



Figure 2S. MS for Methoxy(phenyl)silane





Figure 3S. MS for dimethoxy(phenyl)silane



Figure 4S. MS for trimethoxy(phenyl)silane

#### Abundance











Scan 1553 (10.962 min): DR-ZC01.D(151.9)a.ms (-1564) (-)



Figure 7S. Typical GC for crude mixture for CO2 hydrosilylation reaction. 100 °C, 24 h in THF.

$$CO_2 + PhSiH_3 \xrightarrow{3 \text{ mol}\%[Cp_2ZrHCI]}_{THF, 120 °C, 48h} RSi \left( \begin{array}{c} H \\ I \\ O \end{array} \right)_n + \begin{array}{c} 0 \\ H \\ H \end{array} \right)_n + \begin{array}{c} 0 \\ H \\ H \\ O \end{array} \right)_n + CH_3OH$$

| Entry | Promotor  | %SiOMe | % FM   | % MeOH | % Conv |
|-------|-----------|--------|--------|--------|--------|
| 1     | KF        | 31     | 5      | 4      | 40     |
| 2     | TBAF      | nd     | nd     | nd     | >99    |
| 3     | $B(Et)_3$ | 68     | 8      | 2      | 80     |
| 4     | $H_2O$    | nd     | traces | traces | <1     |

Table 1S. Promotors used for CO<sub>2</sub> hydrosilylation reaction<sup>a</sup>

<sup>a</sup> Reactions were performed using 0.012 mmol [Cp<sub>2</sub>ZrHCl] with 0.401 mmol PhSiH<sub>3</sub> at 120 °C under 100 psi CO<sub>2</sub>. Yields and conversion were determined by GC-MS

$$CO_2 + PhSiH_3 \xrightarrow{3 \text{ mol} \& [Cp_2 ZrHCI]}_{\text{Solvent, 120 °C, 72h}} RSi \left( \begin{array}{c} H \\ I \\ O \end{array} \right)_n + \begin{array}{c} 0 \\ H \\ H \end{array} \right)_n + \begin{array}{c} 0 \\ H \\ H \\ O \end{array} \right)_n + CH_3OH$$

| Entry | Solvent | %SiOMe | % FM | % MeOH | % Conv |
|-------|---------|--------|------|--------|--------|
| 1     | THF     | 92     | 5    | 3      | >99    |
| 2     | Dioxane | 4      | 1    | 0      | 5      |
| 3     | Toluene | nd     | nd   | nd     | 0      |
| 4     | ACN     | nd     | nd   | nd     | >99    |

Table 2S. Solvents used for CO<sub>2</sub> hydrosilylation reaction<sup>a</sup>

<sup>a</sup> Reactions were performed using 0.012 mmol [Cp<sub>2</sub>ZrHCl] with 0.401 mmol PhSiH<sub>3</sub> at 120 °C under 100 psi CO<sub>2</sub>. Yields and conversion were determined by GC-MS

$$CO_2 + PhSiH_3 \xrightarrow{3 \text{ mol}\%[Cp_2ZrHCI]}_{THF, 120 °C, 48h} RSi \left( \begin{array}{c} H \\ 0 \end{array} \right)_n + \begin{array}{c} 0 \\ H \end{array} \right)_n + \begin{array}{c} 0 \\ H \end{array} \right)_n + CH_3OH$$

Table 38. Different pressures of  $CO_2$  at the hydrosilylation reaction<sup>a</sup>

| Entry | CO <sub>2</sub> (psi) | %SiOMe | % FM | % MeOH | % Conv |
|-------|-----------------------|--------|------|--------|--------|
| 1     | 100                   | 87     | 8    | 2      | 97     |
| 2     | 80                    | 72     | 25   | 1      | 98     |
| 3     | 50                    | 27     | 65   | 4      | 96     |

<sup>a</sup> Reactions were performed using 0.012 mmol [Cp<sub>2</sub>ZrHCl] with 0.401 mmol PhSiH<sub>3</sub> at 120 °C for 48 h. Yields and conversion were determined by GC-MS

### Quantification of methanol at the optimized reaction

| Addition | mmol MeOH | Area     |  |
|----------|-----------|----------|--|
| 0        | 0         | 6417951  |  |
| 20 uL    | 0.494     | 8621609  |  |
| 60 uL    | 1.483     | 15539820 |  |

Table 5S. Addition of MeOH to the crude reaction



The negative intercept on the x-axis corresponds to the amount of the analyte in the test sample. This value is given by b/a, the ratio of the intercept and the slope of the regression line.

Moles of MeOH in the crude reaction: 0.031mmol

 $\% Yield_{MeOH} = \frac{0.9662 \ mmol}{1.203 \ mmol \ H^{-}} \times 100 = 80.31\% \approx 80\%$ 

# Hg drop test of the optimized reaction

$$CO_{2} + PhSiH_{3} \xrightarrow{3 \text{ mol} (Cp_{2}ZrHCI)}_{THF, 120 °C, 72h} RSi \left( \begin{array}{c} H \\ 0 \end{array} \right)_{n} + \begin{array}{c} 0 \\ H \end{array} \right)_{n} + \begin{array}{c} 0 \\ H \end{array} \right)_{n} + CH_{3}OH \\ H \end{array}$$

### Reaction of CO<sub>2</sub> with [Cp<sub>2</sub>ZrHCl]

| $CO_2$ | [Cp <sub>2</sub> ZrHCl]       | - MeOH |
|--------|-------------------------------|--------|
| 1 atm  | 1) THF, rt, 15h<br>2) 10% HCl | 28 %   |

Table 5S. Addition of MeOH to the crude reaction

| Addition | mmol MeOH | Area    |  |  |
|----------|-----------|---------|--|--|
| 0        | 0         | 159584  |  |  |
| 20 uL    | 0.494     | 695799  |  |  |
| 60 uL    | 1.483     | 2538090 |  |  |



Graphic 1S. Addition Standard (MeOH) to the crude reaction

The negative intercept on the x-axis corresponds to the amount of the analyte in the test sample. This value is given by b/a, the ratio of the intercept and the slope of the regression line.

Moles of MeOH in the crude reaction: 0.031mmol  $\% Yield_{MeOH} = \frac{0.030mmol}{0.1146mmol} \times 100 = 26.18\% \approx 26\%$ 



## Figure 9S. <sup>1</sup>H-NMR of the reaction of CO<sub>2</sub> with [Cp<sub>2</sub>ZrHCl]





Figure 11S. Cyclic voltammetry of [Cp<sub>2</sub>ZrHCl] in argon



Figure 128. Cyclic voltammetry of [Cp<sub>2</sub>ZrHCl] with PhB(OH)<sub>2</sub>







Figure 14S Cyclic voltammetry of [Cp<sub>2</sub>ZrHCl] with AcOH



Figure 15S. FTIR resulting from the reaction of Wilkinson's reagent with the outlet gas of the chronoamperometry.



### **Calculation of Faradic Efficiency**



An approximate calculation of the faradaic efficiency (FE) was made with the data obtained from chronoamperometry (equation 1).<sup>1</sup> The estimated proportion of Wilkinson's catalyst containing CO was 6.7%.

$$FE(\%) = \frac{(n_{pro} \times n_e^{CO} \times F)}{Q}$$
 Ec. 1

Where  $n_{pro}$  are the moles of product,  $n_e^{CO}$  is the number of electrons for CO, F is a constant (96485 C mol-1) and Q is the total charge that passes during electrolysis.

$$J(mA * cm^{-2}) = \frac{I}{A} = \frac{1}{2}$$
  

$$J = -2.13 mA * cm^{-2}$$

Where I = -0.064 mA, this was a value at the start of chronoamperometry, A = 0.03 cm<sup>2</sup> at - 2.8 V.

Being  $FE_{CO} = 8.3\%$ , with current density J = -2.13 mA cm<sub>2</sub> at -2.8 V. It is estimated that the calculated FE is below the real value of the process, due to the limitations of the CO

quantification method. Likewise, the amount of  $H_2$  generated is currently unknown, so selectivity data is not included.

### References

(1) N. Eliaz, E. Gileadi, Physical Electrochemistry – Fundamentals, Techniques, and Applications, 2nd Edition, Wiley-VCH, 2019

Figure 16S. GC for the reaction mixture of chronoamperometry with PhCO<sub>2</sub>H









## Figure 18S. Full spectrum of <sup>1</sup>H-NMR of the reaction of CO<sub>2</sub> with [Cp<sub>2</sub>ZrHCl]

Figure 198. Electrochemical control experiments in absence of [Cp<sub>2</sub>ZrHCl]



