Electronic Supplementary Material (ESI) for Catalysis Science & Technology.

Supplementary Information

Solvent-Free Iridium-Catalyzed Hydrosilylation of CO_2: Experiments and Kinetic Modeling

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General Procedure for the Catalytic Reactions of Hydrosilylation of CO_2 with 1,1,1,3,5,5,5-heptamethyltrisiloxane (HMTS) using the complex [IrH(CF_3SO_3)(NSiN)(coe)] (3) as catalysts precursor.

A 25 mL batch reactor with Teflon lining inside was charged with dry HMTS (3 mL, 11.04 mmol). Then the reactor was closed, purged with CO_2 gas few times and heated to the corresponding temperature. After stabilization to the particular temperature, the reactor was opened under argon atmosphere and the iridium catalyst **3** (75 mg, 0.11 mmol), which was weighed in a glove box, was added. After closing the reactor, the mixture was again purged few times using vacuum and CO_2 gas. Then the pressure of CO_2 gas was adjusted to 3 bars. Liquid samples were taken periodically after releasing the CO_2 pressure, without opening the reactor, using a long needle through sample withdrawal valve. The reactor was purged with vacuum and CO_2 several times after each sample withdrawal and the CO_2 pressure was returned back to 3 bars using CO_2. The samples were diluted using 0.5 ml of anhydrous tetrahydrofuran and analyzed by quantifiable GC-MS. The product yield was obtained by comparison of the integral of the area corresponding to the peaks assigned to the reaction products with the integral of the peak corresponding to the starting material HMTS.

Examples of GC-MS spectra from reaction samples:

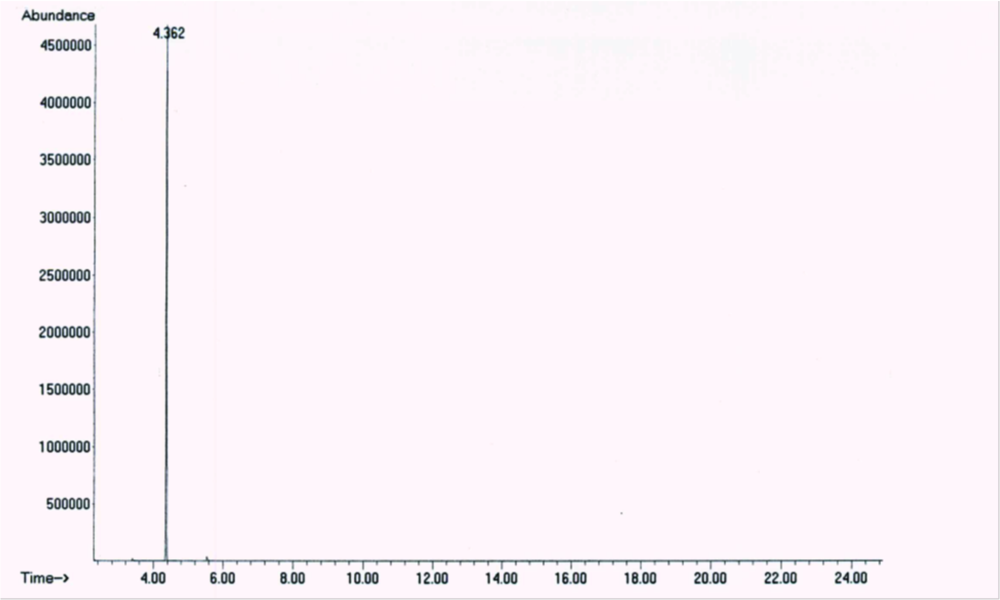


Figure S1. GC spectrum of a sample of the catalytic hydrosilylation of CO_2 with HMTS at 25°C at the beginnig of the reactions. A major peak of HMTS (at 4.36 min) and traces of cyclooctane (at 5.70 min) were observed.

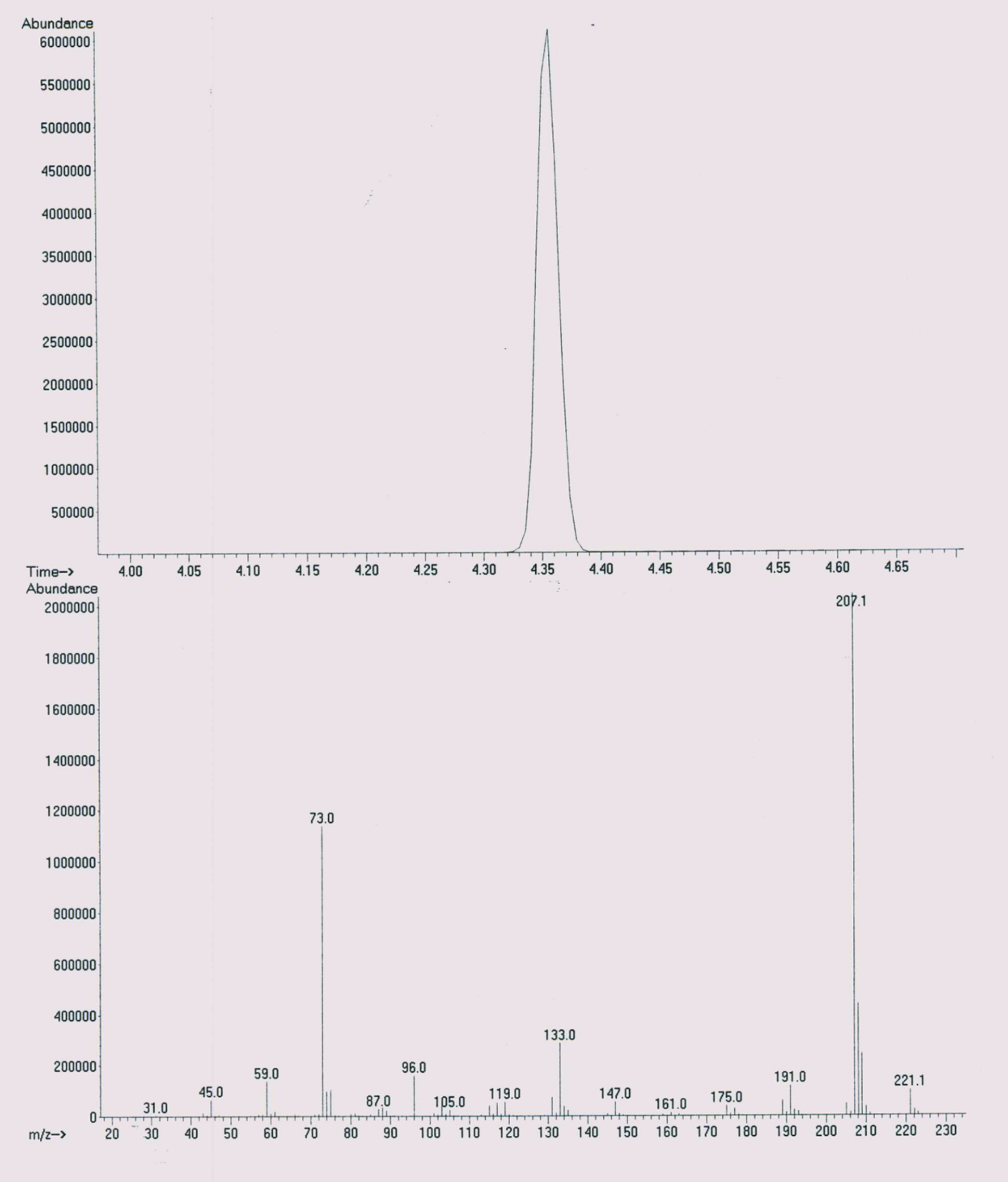


Figure S2. Peak corresponding to the starting HTMS in the GC-MS spectrum of a sample of the catalytic hydrosilylation of CO_2 with HMTS at 25°C at the beginning of the reaction.

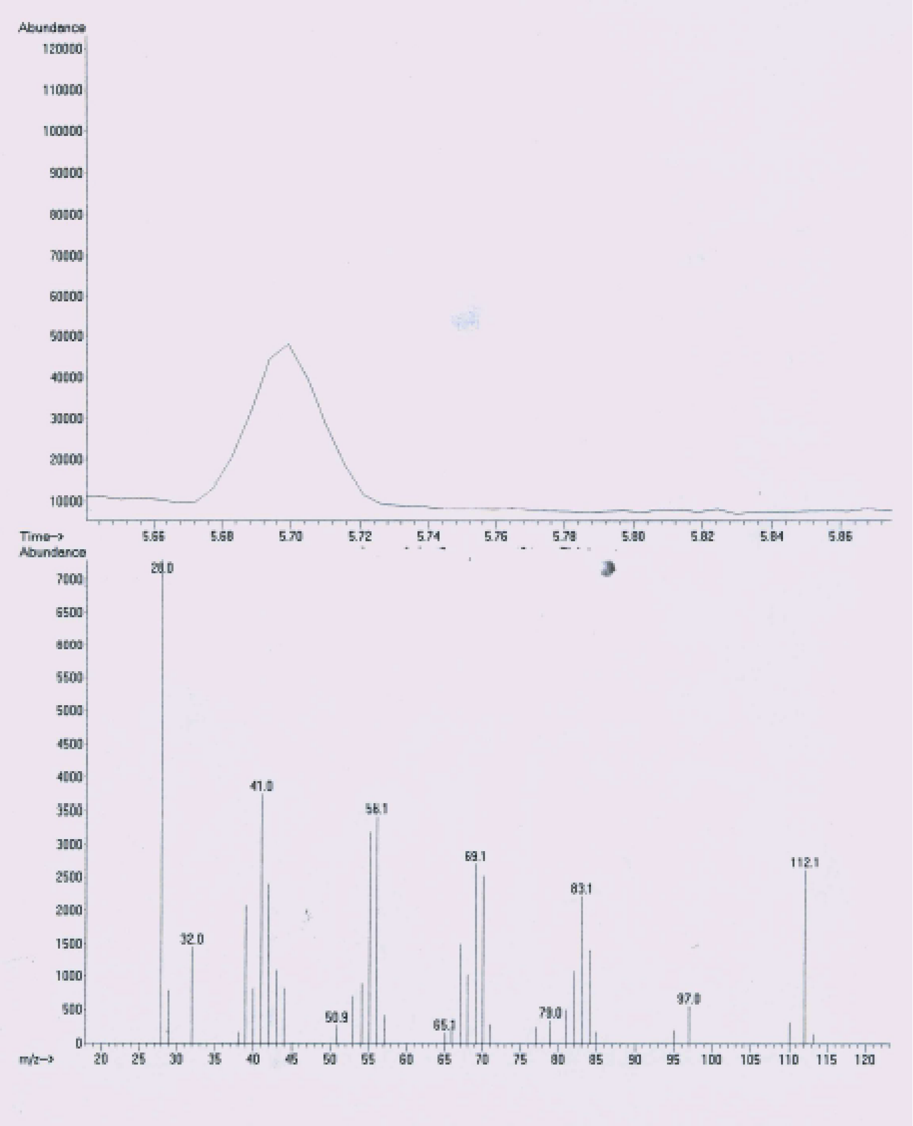
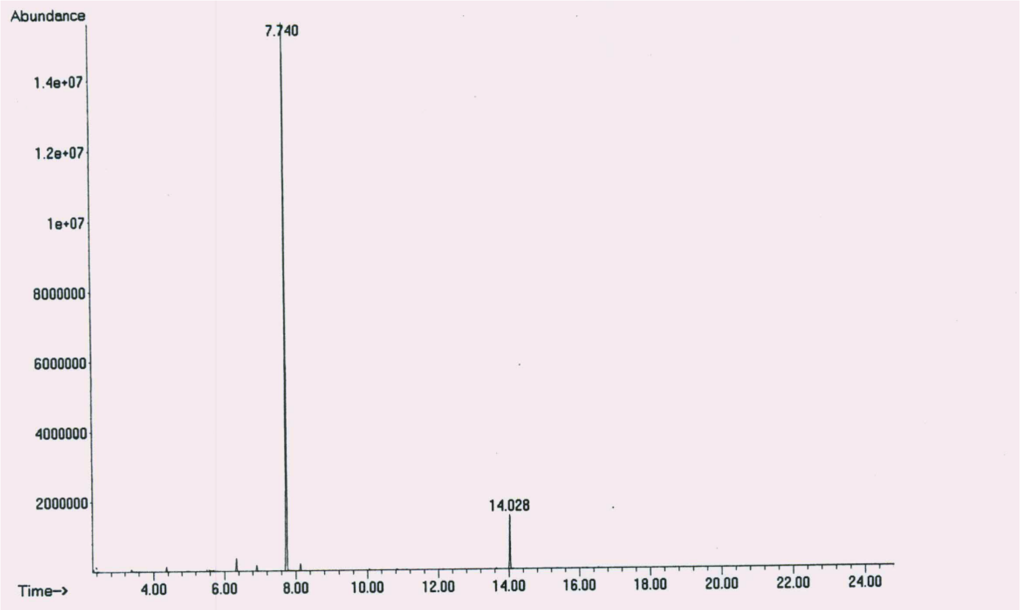
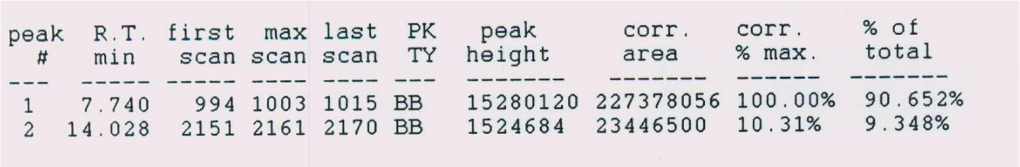


Figure S3. Peak corresponding to cyclooctane in the GC-MS spectrum of a sample of the catalytic hydrosilylation of CO_2 with HMTS at 25°C at the beginning of the reaction.





```
peak  R.T.  first  max  last  PK   peak       corr.     corr.     % of
 #    min    scan  scan  scan  TY   height      area     % max.    total
---  -----  -----  ----  ----  ---  -------   -------   ------   -------
 1    7.740   994  1003  1015  BB   15280120 227378056 100.00%   90.652%
 2   14.028  2151  2161  2170  BB   1524684  23446500  10.31%     9.348%
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Figure S4. GC-MS spectrum of a sample of the catalytic hydrosilylation of CO_2 with HMTS at 25°C at the end of the reaction. The main peak at 7.74 min corresponds to silyl formate and the minor peak at 14.02 min is due to $\{(Me_3SiO)_2MeSi\}_2O$.

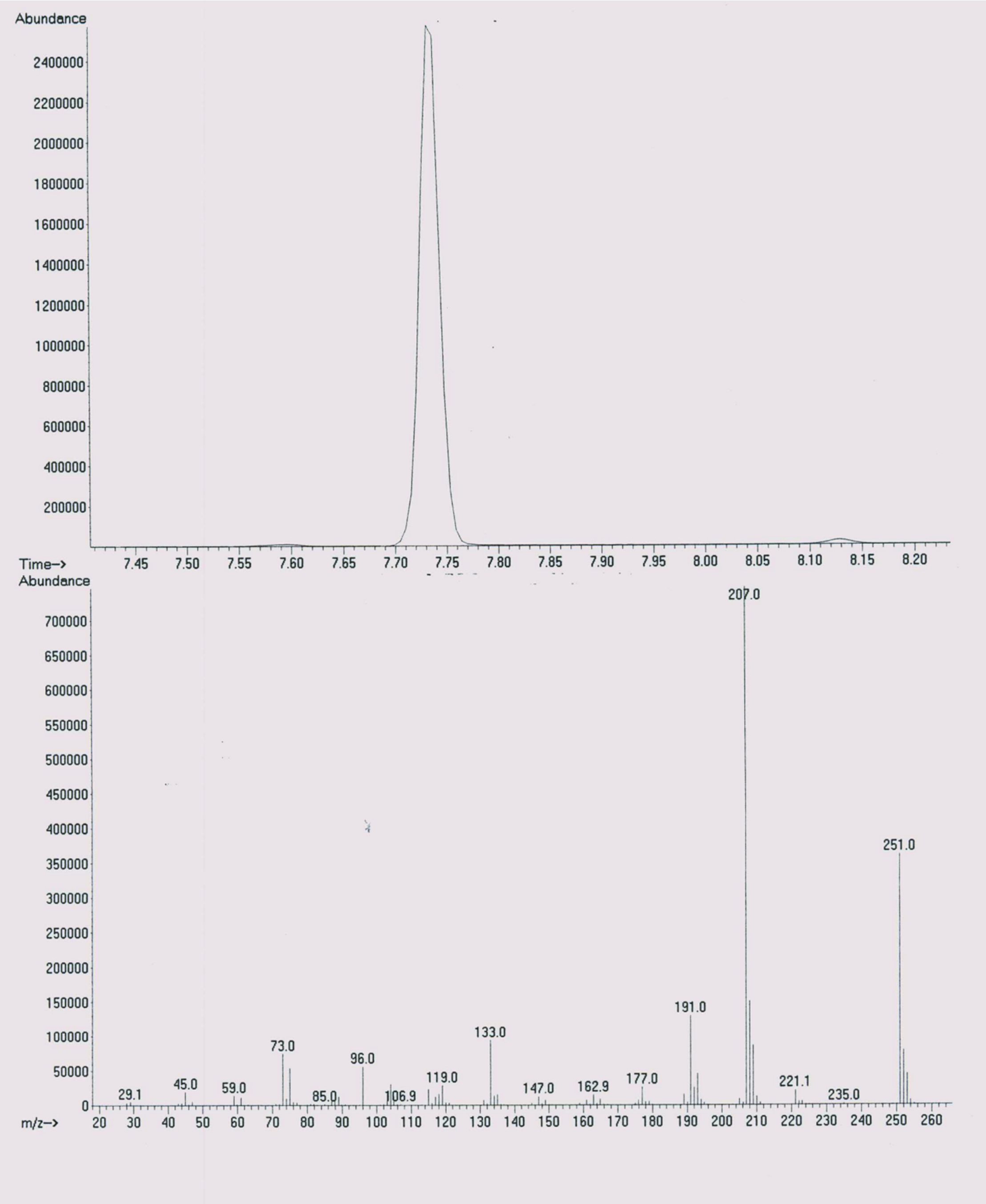


Figure S5. Peak corresponding to silyl formate in the GC-MS spectrum of a sample of the catalytic hydrosilylation of CO_2 with HMTS at 25°C at the end of the reaction.

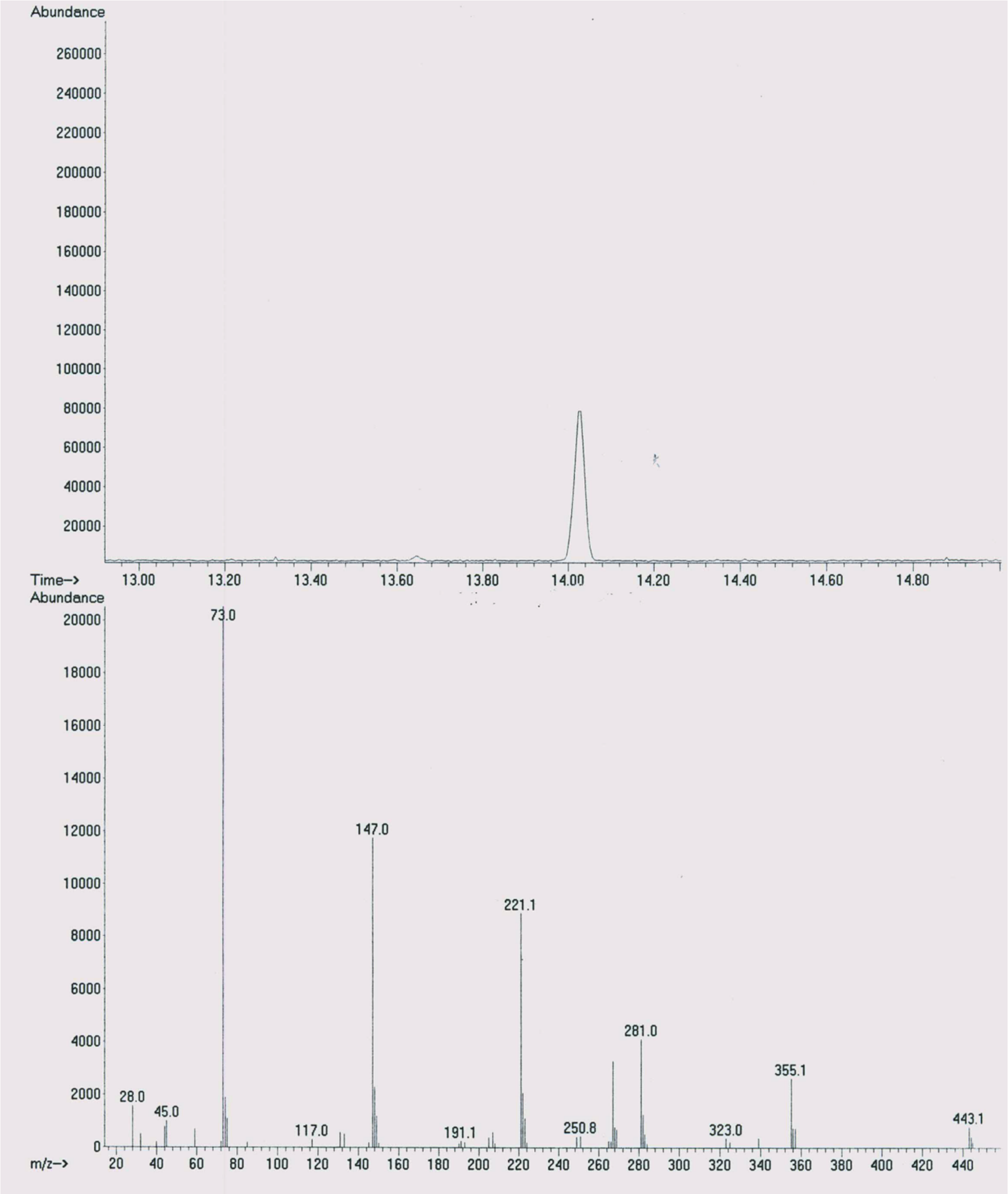


Figure S6. Peak corresponding to $\{(Me_3SiO)_2MeSi\}_2O$ in the GC-MS spectrum of a sample of the catalytic hydrosilylation of CO_2 with HMTS at 25°C at the end of the reaction.

Figure S7: ^{1}H NMR (300 MHz, CD_2Cl_2) of the product of the reaction of CO_2 (3 bar) with HTMS after 3 days at 25 ºC using **3** (1.0 mol %) as catalyst precursor.

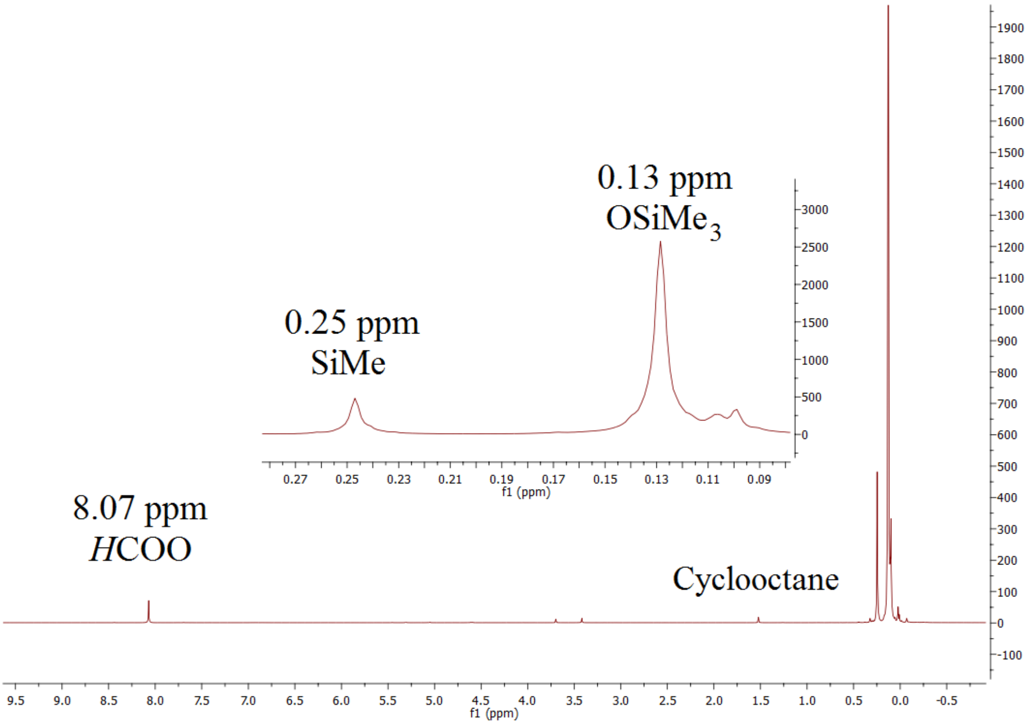
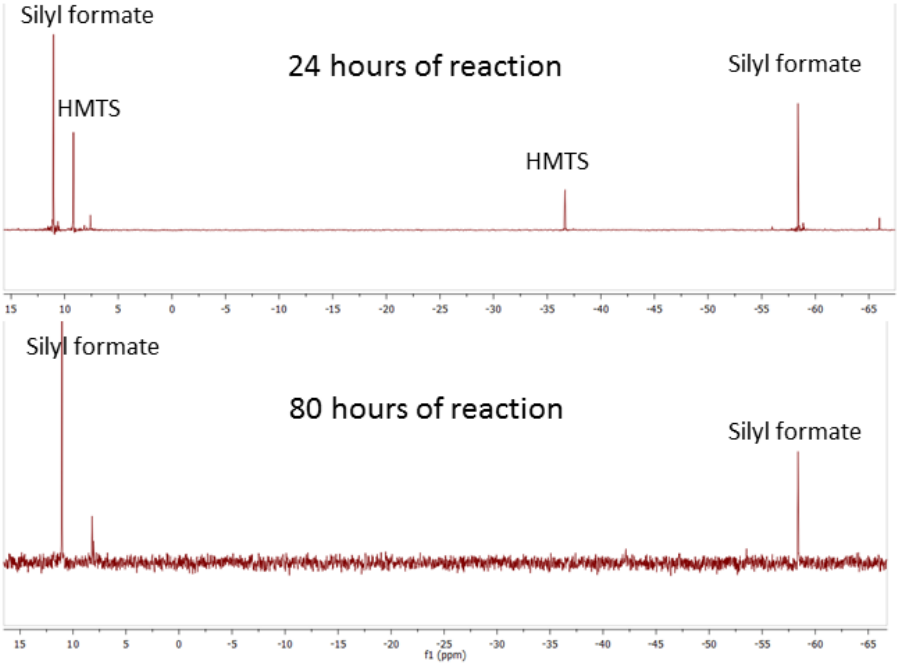


Figure S8: $^{29}Si\{^1H\}$ NMR (79.5 MHz, CD_2Cl_2) spectra of samples taken from the reaction of CO_2 (3 bar) at 25 ºC using **3** (1.0 mol %) as catalyst precursor.



Reactions in a Young NMR tube.

A Young NMR tube was charged with $(Me_3SiO)_2MeSiH$ (79 µL, 0.30 mmol), complex **3** (23 mg, 0.03 mmol), CD_2Cl_2 (0.35 mL) and CD_3CN (0.15 mL). The reaction was monitored by ^{1}H NMR at 295 K.

Figure S9: ^{1}H NMR (300 MHz, CD_2Cl_2) of the reation of complex **3** with 10 equivalents of HMTS in a mixture of CD_2Cl_2 and CD_3CN after 4 hours of reaction at r.t.

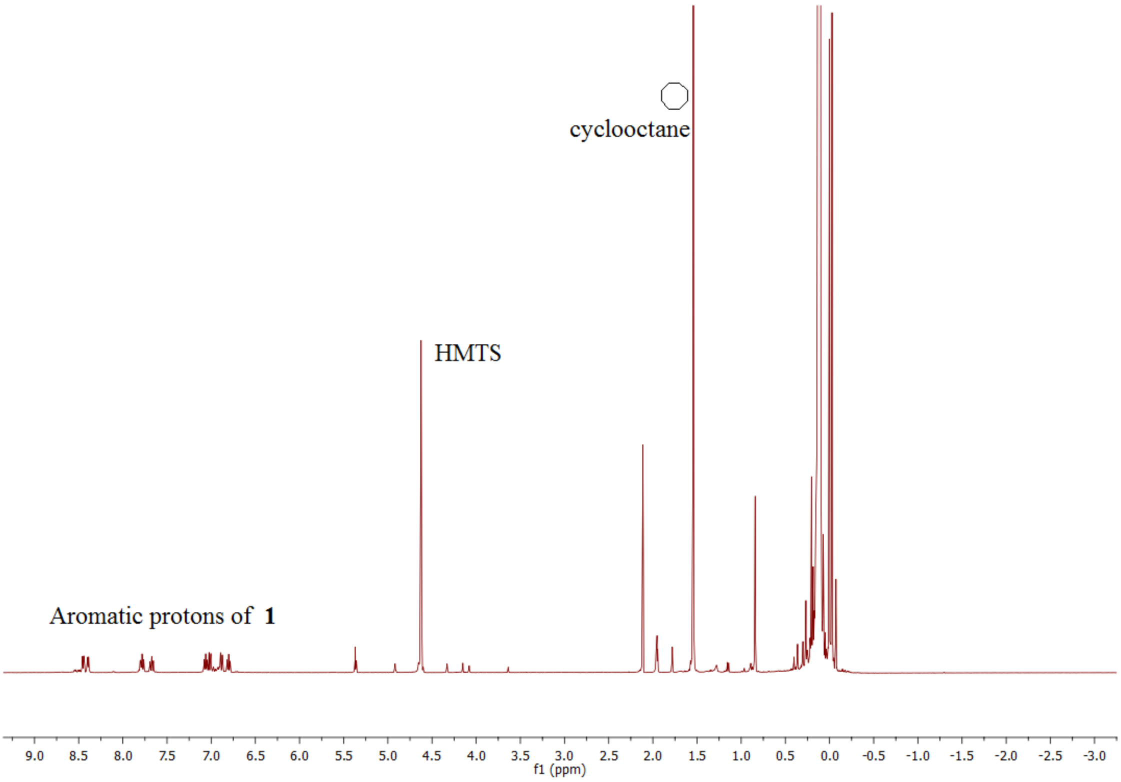
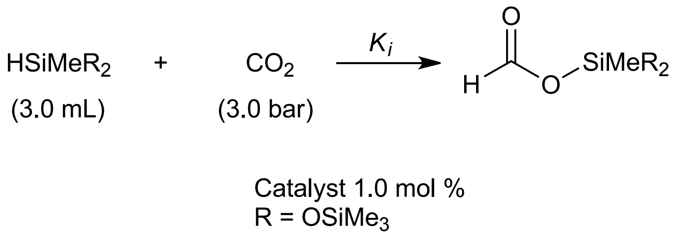


Table S1: Data obtained from the GC-MS studies of the reaction of CO_2 with HTMS using **3** (1.0 mol %) as catalyst precursor at different temperatures. Time is expressed in hours and concentration of HMTS, silylformate and $(R_2MeSi)_2O$ (R = $(OSiMe_3)$) are expressed in %.

Room Temperature: 25 C			
Time	**HMTS**	**Silylformate**	**$(R_2MeSi)_2O$**
12	99,4	0,6	0,0
24	97,7	1,5	0,8
36	88,2	9,9	1,9
48	56,9	37,8	5,3
60	23,2	70,4	6,4
72	6,8	83,8	9,4
80	1,8	88,8	9,4
Temperature: 35 C			
8	98,9	0,8	0,3
17	89,2	9,1	1,8
24	55,8	40,0	4,2
32	11,8	82,4	5,8
41	1,4	91,1	7,5
Temperature: 45 C			
3	99,5	0,5	0,0
7	95,4	3,4	1,2
11	56,9	39,3	3,8
14	22,3	71,5	6,2
23	0,9	91,1	8,0
Temperature: 55 C			
2	96,8	2,1	1,0
4	50,3	44,8	4,9
6	13,5	79,5	6,9
8	3,2	89,7	7,1
9	1,5	87,2	11,3
Temperature: 65 C			
1	71,4	25,8	2,9
2	32,2	60,7	7,2
3	17,7	78,0	4,3
4	9,2	85,8	5,1
5	4,9	85,8	9,3
Temperature: 75 C			
0,5	58,7	39,9	1,4
1	27,5	69,4	3,1
1,5	17,8	79,3	2,9
2	10,4	83,1	6,5
2,5	4,6	90,2	5,2
3	2,3	87,1	10,5

Reaction kinetic model for the CO_2 hydrosilation shown in Scheme S1:



Scheme S1. Catalytic CO_2 hydrosilylation with HMTS using **3** as catalyst precursor.

The following first order differential equations represent the model equations that were derived based on the above scheme.

The rate of the disapperance of HMTS is

$$-\frac{\mathrm{V}}{\mathrm{W_c}}\frac{\mathrm{d}C_{SX}}{\mathrm{dt}} = (k_i C_{SX}) \qquad (1)$$

The rate of formation of formate:

$$\frac{\mathrm{V}}{\mathrm{W_c}}\frac{\mathrm{d}C_{F}}{\mathrm{dt}} = (k_i C_{SX}) \qquad (2)$$

Where C_{Sx}, C_F are the molar concentration of HMTS and silyl formate in the system, V is the volume of the reactor, W_c is the weight of the catalyst, t is the time in hours and k_i is the rate constant at the temperature T_i.

The molar concentration C_x can be expressed in term of weight fraction y_i, of every species in the system, which is the measurable variable from the chromatographic analysis, hence:

$$C_x = \frac{y_x W_f}{MW_x V} \qquad (3)$$

Where W_f is the weight of feed used in the reactor, MW_i is the molecular weight of the corresponding species *i*.

The reaction rate constants are related to temperature through Arrhenius equation:

$$k_i = k_o \exp\left[-\frac{E_a}{R}\left(\frac{1}{T_i}-\frac{1}{T_0}\right)\right] \tag{4}$$

Were k_i is the rate constant at the average temperature T_i and E_a the apparent activation energy of the reaction.

The model equations (equations 1-4) were evaluated by a least square fitting of the kinetic parameters using the experimental data for the reaction of HMTS with CO_2. The experimental conversion data points were taken at various reaction times and at different temperature levels ranging from 23 ºC to 75 ºC. The differential equation was solved by Runge-Kutta method (MATLAB ODE 45 subroutine).[1] The activation energy and the Arrhenius pre-exponential factor were estimated using the Modified Marquad method technique (MATLAB LSQCURVEFIT subroutine). The optimization criteria for the model evaluation are that all the activation energy and the rate constant had to be positive, all consistent with physical principles.[2]

References:

1. D. Marquardt, *J. Appl. Math.* 1963, **11**, 431-441.

2. Details about the regression analysis are described in S. Waziri, A. M. Aitani, S. Al-Khattaf, *Ing. Eng. Chem. Res.*, 2010, **49**, 6376-6387.