

Electric Supplementary Information

Highly Efficient Catalytic Hydrosilylation of Carbon Dioxide by an *N*-Heterocyclic Carbene Copper Catalyst

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General Information

Unless otherwise noted, all manipulations were performed under a dry nitrogen atmosphere using Schlenk-line techniques or under a nitrogen atmosphere in an Mbraun glovebox. Nitrogen gas was purified by being passed through a Dryclean column (4Å molecular sieves, Nikka Seiko Co.) and a Gasclean GC-RX column (Nikka Seiko Co.).

The NMR spectra were recorded on a JEOL AL-400 or JEOL ECS-400 spectrometer. Elemental analyses were conducted by a MICRO CORDER JM10 instrument.

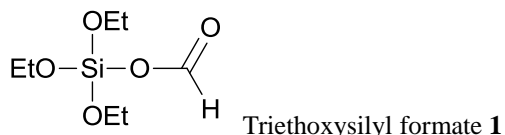
Carbon dioxide and commercially available reagents were used without further purification unless otherwise stated. [(IPr)Cu(O*t*Bu)] and [(IMes)Cu(O*t*Bu)]¹ were prepared according to literature method.

NHC-Cu Catalyzed Hydrosilylation of CO₂ in NMR Tube (Table 1 and Scheme 3)

In an NMR tube equipped with a J. Young valve, copper catalyst (0.0025 mmol) and (EtO)₃SiH (0.15 mmol) were mixed up in C₆D₆ (0.7 mL) under 1 atm of CO₂. The reaction mixture was heated in an oil bath and monitored by ¹H NMR spectroscopy. Conversion of (EtO)₃SiH (Si-H: δ 4.6 ppm in C₆D₆) was determined by internal standard technique. Toluene was used as an internal standard.

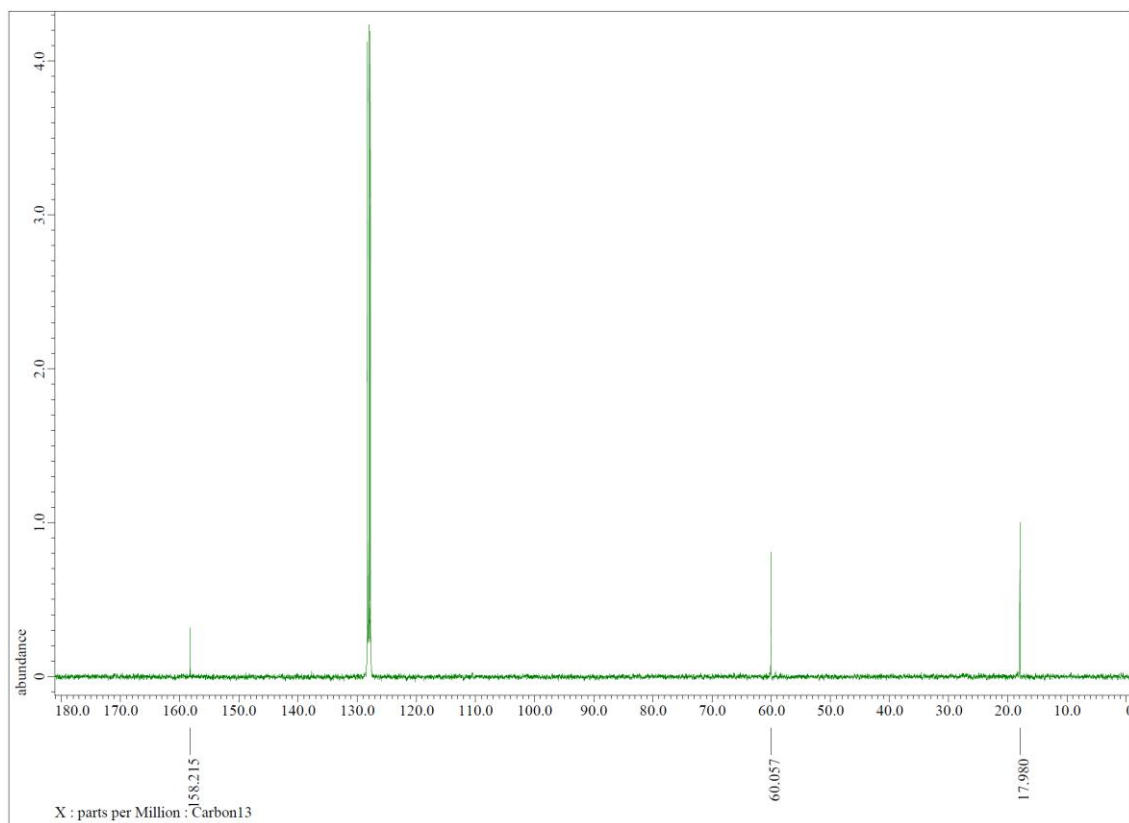
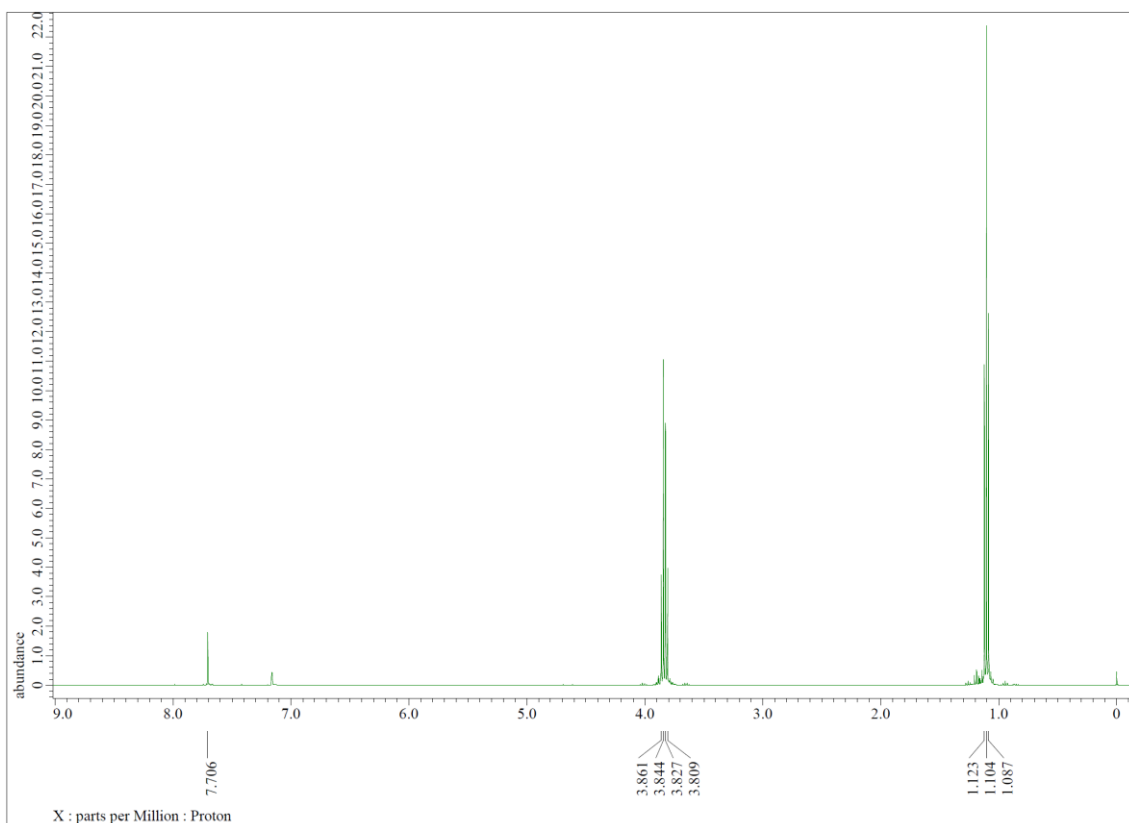
Synthesis of Triethoxysilyl Formate on Large Scale (Scheme 1)

To (EtO)₃SiH (8.47 g, 50 mmol) was added [(IPr)Cu(O*t*Bu)] (2.6 mg, 0.005 mmol) while stirring under 1 atm of CO₂. The system was kept under a CO₂ flow (1 atm) and the reaction mixture was stirred at 60 °C for 6 h. ¹H NMR analysis of the resulting mixture showed 75% yield of **1**. The TON based on this result is 7489 while TOF is 1248 h⁻¹. The product² was isolated by distillation of the mixture *in vacuo* as a colorless liquid (7.4 g, 71%).



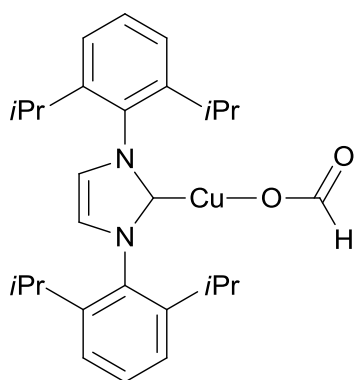
¹H NMR (400 MHz, C₆D₆) δ 1.10 (t, *J* = 6.9 Hz, 9H), 3.84 (q, *J* = 6.9 Hz, 6H), 7.71 (s, 1H).

¹³C NMR (100 MHz, C₆D₆) δ 158.2, 60.1, 18.0.



Synthesis of [(IPr)CuO₂CH] from [(IPr)Cu(O*t*Bu)] and Triethoxysilane (Scheme 2)

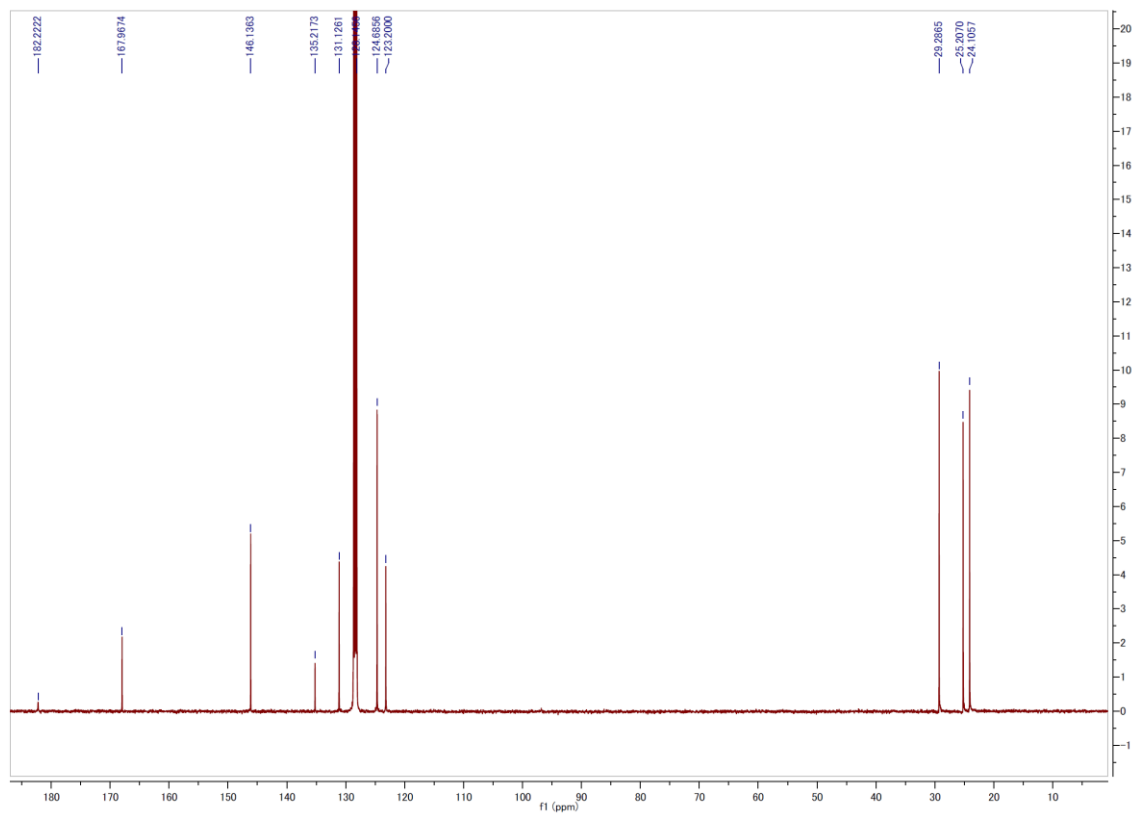
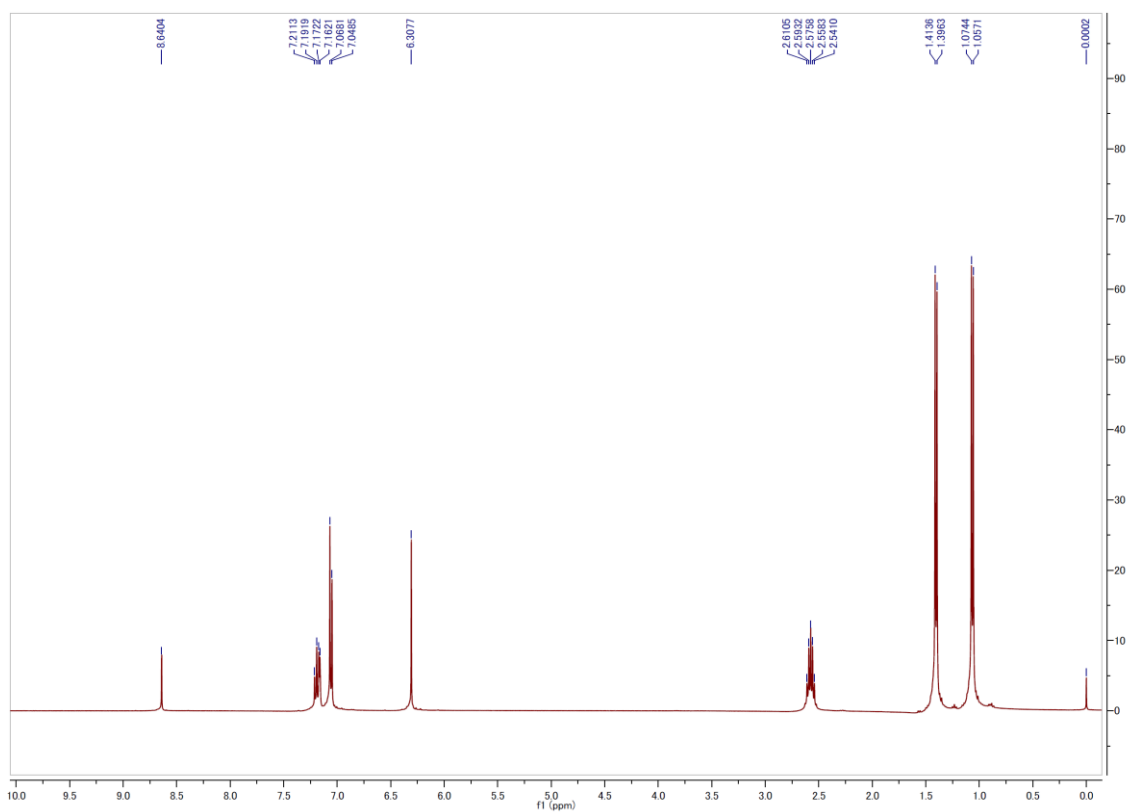
Under 1 atm of CO₂, (EtO)₃SiH (80 μL, 1.0 equiv) was added into a solution of [(IPr)Cu(O*t*Bu)] (227 mg, 0.432 mmol) in benzene (3 mL). The reaction mixture was stirred at room temperature for 4h. The solution was filtrated and the solvent was removed under vacuum. The resulting solid was washed with hexane to give the product as a white solid (174 mg, 81%). Colorless single crystals suitable for X-ray analysis was obtained from recrystallization of a benzene/hexane solution at room temperature.



¹H NMR (400 MHz, C₆D₆) δ 1.07 (d, *J* = 6.9 Hz, 12H), 1.40 (d, *J* = 6.9 Hz, 12H), 2.52-2.63 (m, 4H), 6.31 (s, 2H), 7.06 (d, *J* = 7.8 Hz, 4H), 7.19 (t, *J* = 7.8 Hz, 2H), 8.64 (s, 1H).

¹³C NMR (100 MHz, C₆D₆) δ 182.2, 168.0, 146.1, 135.2, 131.1, 124.7, 123.2, 29.3, 25.2, 24.1.

Anal. Calcd. for C₂₈H₃₇CuN₂O₂: C, 67.65; H, 7.50; N, 5.63. Found: C, 67.61; H, 7.50, N, 4.89.

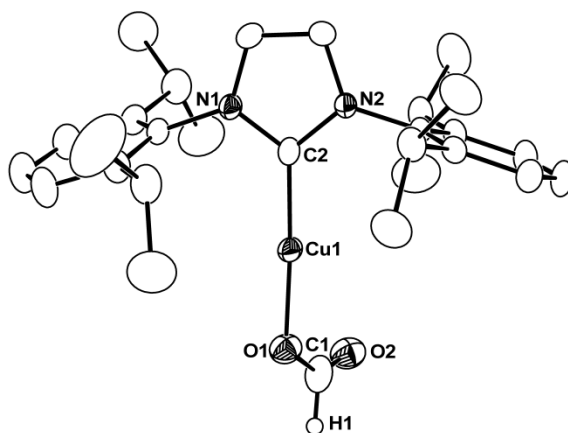


The reaction of [(IPr)CuO₂CH] with Triethoxysilane

In an NMR tube, triethoxysilane (9.2 μ L, 0.05 mmol) was added into a solution of [(IPr)CuO₂CH] (10 mg, 0.02 mmol) in C₆D₆ (0.7 mL). The solution immediately became yellow in color. The NMR tube was soon cooled in an ice-bath. ¹H NMR spectrum show that facile decomposition occurred even within 5 min. A new singlet at 2.6 ppm was designated to [(IPr)CuH].

X-ray Data for Crystallographic Analysis of Complex 2

A crystal was sealed in a thin-walled glass capillary under a microscope in the glove box. Data collections were performed at -100 °C on a Bruker SMART APEX diffractometer with a CCD area detector using graphite-monochromated Mo K α radiation ($\lambda = 0.71069$ Å). The determination of crystal class and unit cell was carried out by SMART program package. The raw frame data were processed using SAINT and SADABS to yield the reflection data file. The structures were solved by using SHELXTL program. Refinements were performed on F^2 anisotropically for non-hydrogen atoms by the full-matrix least-squares method. The SQUEEZE routine of the program PLATON was implemented to remove the contributions of the disordered solvents (benzene) to the observed structure factors. The analytical scattering factors for neutral atoms were used throughout the analysis. The hydrogen atom in the formate moiety was located by difference Fourier syntheses, only the coordinates were refined while the displacement parameter was constrained. Other hydrogen atoms were placed at the calculated positions and were included in the structure calculation without further refinement of the parameters. The residual electron densities were of no chemical significance. CCDC 912051 (2) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.



ORTEP drawing of **2**. Thermal ellipsoids set at 30% probability. Hydrogen atoms have been omitted for clarity.

Crystal data and structure refinement for **2**.

Identification code	2
Empirical formula	C ₂₈ H ₃₇ Cu N ₂ O ₂
Formula weight	497.14
Temperature	163(2) K
Wavelength	0.71073 Å
Crystal system, space group	Triclinic, P-1
Unit cell dimensions	a = 9.798(3) Å alpha = 70.744(5) deg. b = 10.814(3) Å beta = 86.134(7) deg. c = 16.337(6) Å gamma = 85.896(5) deg.
Volume	1628.1(9) Å ³
Z, Calculated density	2, 1.014 Mg/m ³
Absorption coefficient	0.691 mm ⁻¹
F(000)	528
Crystal size	0.30 x 0.25 x 0.23 mm
Theta range for data collection	1.32 to 25.00 deg.
Limiting indices	-10<=h<=11, -9<=k<=12, -19<=l<=19
Reflections collected / unique	8138 / 5523 [R(int) = 0.0252]
Completeness to theta = 25.00	96.4 %
Absorption correction	Empirical
Max. and min. transmission	0.8572 and 0.8194
Refinement method	Full-matrix least-squares on F ²
Data / restraints / parameters	5523 / 2 / 301
Goodness-of-fit on F ²	1.045
Final R indices [I>2sigma(I)]	R1 = 0.0558, wR2 = 0.1296
R indices (all data)	R1 = 0.0741, wR2 = 0.1370
Largest diff. peak and hole	1.054 and -0.383 e.Å ⁻³

Reference:

- 1 N. P. Mankad, D. S. Laitar and J. P. Sadighi, *Organometallics*, 2004, **23**, 3369.
- 2 W. Sattler and G. Parkin, *J. Am. Chem. Soc.*, 2012, **134**, 17462.