Supporting Information

An N-Heterocyclic Carbene Ligand Promotes Highly Selective Alkyne Hydrogenation on Copper Nanoparticles Supported on Passivated Silica

Nicolas Kaeffer,[a] Hsueh-Ju Liu,[a,b] Hung-Kun Lo,[a] Alexey Fedorov,[a,*] Christophe Copéret[a,*]

a. ETH Zürich, Department of Chemistry and Applied Biosciences, Vladimir-Prelog-Weg 1-5, CH-8093, Zürich, Switzerland.

b. Present address: Department of Applied Chemistry, National Chiao Tung University, 1001 University Road, Hsinchu, 30010, Taiwan.

E-mail:

*fedoroal@ethz.ch
*ccoperet@ethz.ch

***Abstract**:*

We report a surface organometallic route that generates copper nanoparticles (NPs) on a silica support while simultaneously passivating the silica surface with trimethylsiloxy groups. The material is active for the catalytic semihydrogenation of phenylalkyl-, dialkyl- and diaryl-alkynes and displays high chemo- and stereoselectivity at full alkyne conversion to corresponding (Z)-olefins in the presence of a N-heterocyclic carbene (NHC) ligand. Solid-state NMR spectroscopy using the NHC ligand ^{13}C-labeled at the carbenic carbon reveals a genuine coordination of the carbene to Cu NPs. The presence of distinct Cu surface environments and the coordination of the NHC to specific Cu sites likely accounts for the increased selectivity.

DOI: 10.1039/c8sc01924j

Table of Contents

Experimental Procedures

General Experimental Methods

Unless otherwise noted, all experiments were conducted with dry, oxygen-free solvents using standard Schlenk techniques or in N_2 or Ar-filled gloveboxes. Toluene and pentane were purified by passage through double solvent purification alumina columns (MBraun) and degassed prior to utilization. THF was distilled from purple Na/benzophenone and stored over 3 Å sieves. Benzene-d_6 was vacuum distilled from purple Na/benzophenone and stored over 3 Å sieves. Unless otherwise noted, reagents were obtained from commercial suppliers and used as received. 1-phenyl-propyne (**S1**), 1-phenyl-1-hexyne (**S2**), 1-phenyl-4-hexyne (**S3**) were dried under CaH_2, vacuum-distilled, degassed by freeze-pump-thaw cycles and filtered over activated alumina pad before use. Diphenylacetylene (**S4**), 4-methoxydiphenylacetylene (**S5**), 4-chlorodiphenylacetylene (**S6**), 4-bromodiphenylacetylene (**S7**) were dried and degassed at 60 ºC under high-vacuum (10^{-5} mbar).

Synthetic procedures for 1,3-bis(2,4,6-trimethylphenyl)imidazol-2-ylidene (IMes) and its analogue ^{13}C-labeled at the carbenic carbon (IMes*) were adapted from literature.[1] Passivated silica ($SiO_{2\text{-}TMS}$) was prepared according to the literature procedure.[2]

Characterization methods

Elemental analysis of the supported material was performed by the Mikroanalytisches Labor Pascher, Remagen, Germany. Liquid-state NMR spectra were recorded on a Bruker DPX-300 instrument operating at the denoted spectrometer frequency given in MHz for the specified nucleus. The ^{1}H and ^{13}C chemical shifts are calibrated with the residual solvent peak. Solid-state NMR spectra were recorded under MAS conditions on Bruker Advance III 400 spectrometer with conventional triple resonance 4 mm CP-MAS probe. Samples were introduced in zirconia rotors inside a glovebox. Spinning rate was set to 10 kHz, ^{13}C CP-MAS spectra were recorded using a contact time of 2 ms unless otherwise noted and ^{13}C HP-DEC spectra were recorded using a baseline-subtraction sequence to subtract residual signals from the probe. Electron microscopy was performed at the ScopeM facilities, ETH Zürich. Infrared (IR) spectra were recorded using a Bruker FT-IR Alpha spectrometer placed in the glovebox, equipped with OPUS software, and using 275-7500 spectral range, resolution < 2 cm^{-1}, RockSolid interferometer, DTGS (triglycine sulphate) detector and SiC globar source. IR spectra with added gases were recorded on a Nicolet 550-FT spectrometer by using an infrared *in situ* cell equipped with CaF_2 windows. Typically, 32 scans were accumulated for each spectrum (resolution < 2 cm^{-1}). Gas chromatography (GC) analysis were performed on Shimadzu-QP 2010 Ultra equipped with FID and MS detectors using an HP-5 column, N_2 as a carrier gas (30 mL·min^{-1}) and the following temperature programs: ramp of 10 ºC·min^{-1} from 60 ºC to 110 ºC, plateau at 110 ºC for 1 min, ramp of 40 ºC·min^{-1} from 110 ºC to 250 ºC, plateau at 250 ºC for 11 min or ramp of 20 ºC·min^{-1} from 70 ºC to 100 ºC, plateau at 100 ºC for 1 min, ramp of 40 ºC·min^{-1} from 100 ºC to 200 ºC, ramp of 10 ºC·min^{-1} from 200 ºC to 260 ºC, plateau at 260 ºC for 8 min. Concentrations in substrates and products were determined assuming the same response factors for an alkyne and its respective alkenes and alkane. H_2 chemisorption was performed using a Belsorp-Max (BEL Japan, Inc.) instrument. Approximately 100 mg the sample were loaded into cells in an Ar-filled glovebox. H_2 adsorption experiments were recorded 25 °C under isothermal conditions using a bath regulated by a Julabo GF40 circulating thermostat.

Quick X-ray absorption spectroscopy at the Cu K-edge was measured at the SuperXAS beamline at the Swiss Light Source (SLS; Paul Scherrer Institute, Villigen, Switzerland). The SLS is a third-generation synchrotron operating at a 2.4 GeV electron energy and a current of 400 mA. The incident beam was collimated by a Si-coated mirror at 2.8 mrad, monochromatized using a double crystal Si(111) monochromator, and focused with an Rh-coated toroidal mirror (at 2.8 mrad) down to 100 × 100 µm with a beam intensity of 4-5 x 10^{11} ph·s^{-1}. Samples were pressed into wafers in a glovebox and sealed in Kapton tape. XAS spectra were collected in the transmission mode using ion chambers filled with He-N_2 gas mixtures. Multiple X-ray adsorption scans (8820 - 10000 eV) were averaged with a scan time of 5 min. All spectra were calibrated with respect to the spectrum of a Cu reference foil recorded simultaneously by setting the first inflexion point to 8979 eV (Cu K-edge).

Catalytic Tests

Procedure #1. Hydrogenation reactions with monitoring of the H_2 uptake.

Kinetic studies were performed on an Endeavour 8-reactor autoclave (Biotage) operated inside a glovebox. The pressure is referenced to atmospheric pressure. The H_2 feed was passed through activated Cu/Al_2O_3 sorbent (BASF) and activated 4-Å molecular sieves. Stock

solutions of substrate **S1** in toluene (1 M) and of ligands in toluene (10 and 100 mM) were prepared using volumetric flasks. In a typical experiment, 20.0 mg of material **1** (7.3 μmol Cu_{total}) were loaded in glass liners, appropriate volumes of 1 M **S1** solution (400 μL, 400 μmol) and optionally of ligand solution added using a micropipette and toluene added to make the total volume of 4 mL. The liners were then placed in the 8-port autoclave and purged 5 times with H_2 (25 bars). The reaction media were stirred at 500 rpm and set to a pressure of 20 bars H_2 and a temperature of 60 ºC. Reactions were performed under *quasi*-isobaric conditions. H_2 consumption data were recorded using the Endeavour Advanced software.
At the end of the catalytic run, 200 μL aliquots were sampled from all reactors into GC vials, 200 μL of GC standard solution (tridecane 10 mM) added into each vials and the mixtures analyzed by GC. Areas of GC peaks were normalized against the area of the tridecane peak. Final concentrations in substrates and products were determined from normalized areas using a GC calibration. H_2 consumption profiles were normalized using final concentrations in substrates.

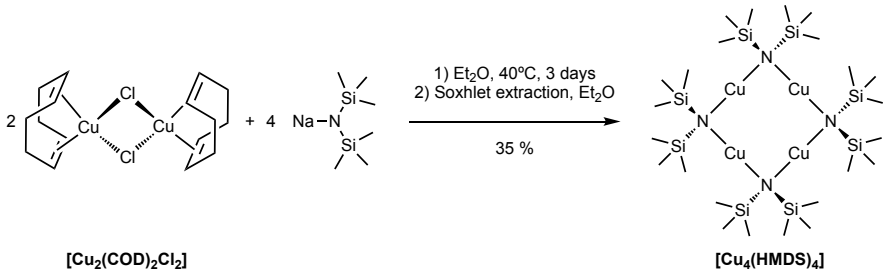
Procedure #2. Hydrogenation reactions for substrate screening.
The procedure is identical to procedure #1, with the following alteration:
Stock solutions of substrates in toluene (100 mM) were prepared. 10.0 mg of material **1** (3.6 μmol Cu_{total}) were loaded in glass liners, 420 μL of substrate solution (42 μmol) and optionally 84 μL of 10 mM IMes solution (0.84 μmol) were added using a micropipette. Toluene was then added to make the total volume of 4.2 mL. The reaction media were stirred at 500 rpm and set to a pressure of 20 bars H_2 and a temperature of 60 ºC for 24h. At the beginning and the end of the hydrogenation runs, 200 μL aliquots were drawn from all reactors into GC vials, 200 μL of GC standard solution (tridecane 50 mM) added into each vial, and the mixtures analyzed by GC. Areas of GC peaks normalized against the area of the tridecane peak provide conversion and selectivities in hydrogenation and side products. At the end of the hydrogenation runs, 400 μL aliquots were sampled from all reactors into NMR tubes, mixed with 200 μL C_6D_6 and analyzed by ^1H NMR spectroscopy to identify the isomeric nature of the formed alkenes.

Procedure #3. Hydrogenation reactions including internal standard.
The procedure is identical to procedure #1, with the following alterations:
In addition to solutions of a ligand and 1-phenyl-1-propyne, 1 mL of internal GC standard solution (10 mM tridecane) was introduced to the liners. At the beginning and the end of the hydrogenation runs, 400 μL aliquots were sampled from all reactors into GC vials and analyzed by GC. Areas of GC peaks normalized against the area of the tridecane peak provide conversion and selectivities in hydrogenation and side products.

Procedure #4. Hydrogenation of (*Z*)-**S1**$_{2H}$**.**
The procedure is identical to procedure #1, with the following alterations:
5 mg of material **1** (1.8 μmol Cu_{total}) were loaded in glass liners and 2 mL of a 200 mM toluene solution of (*Z*)-**S1**$_{2H}$ (400 μmol) containing GC standard tridecane (200 μmol) and optionally a ligand (8 μmol) was added. The reaction media were stirred at 500 rpm and set to desired pressures and temperatures. At the beginning and the end of the hydrogenation runs, 400 μL aliquots were sampled from all reactors into GC vials and analyzed by GC. Areas of GC peaks normalized against the area of the tridecane peak provide conversion and selectivities in hydrogenation and side products.

Synthetic procedures

$[Cu_4(HMDS)_4]$



$[Cu_2(COD)_2Cl_2]$ $[Cu_4(HMDS)_4]$

Scheme S1. Synthesis of $[Cu_4(HMDS)_4]$.

2.5 g $[Cu_2(COD)_2Cl_2]$ (5.3 mmol, 1.0 equiv.) were suspended in 80 mL Et_2O. 2.1 g NaHMDS (11.5 mmol, 2.2 equiv.) were added to the suspension and the mixture stirred at room temperature for 3 days. The greyish suspension was filtered and the precipitate extracted in Et_2O using a Soxhlet apparatus to yield the desired complex (yield: 39%, 910 mg).
^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 0.35 (s). **^{13}C NMR** ($CDCl_3$, 75 MHz): δ (ppm) 7.96.
E.A.: calcd for $C_6H_{18}NSi_2Cu$: C, 32.18; H, 8.10; N, 6.25; found: C, 31.99; H, 7.93; N, 6.06.

$SiO_{2\text{-}700}$
$SiO_{2\text{-}700}$ was prepared by calcination of compacted Aerosil Degussa (206 $m^2 \cdot g^{-1}$) in a flow reactor under a stream of synthetic air (80 $mL \cdot min^{-1}$) with the following temperature program: from R.T. to 700 ºC at 300 ºC·h^{-1}; 700 ºC for 12 h.
Titration with $[Mg(Bn)_2(THF)_2]$: 0.34 $mmol_{SiOH} \cdot g^{-1}$; 0.99 $OH \cdot nm^{-1}$.

$[Cu_{HMDS}]/SiO_{2\text{-}TMS}$
$[Cu_4(HMDS)_4]$ (160 mg, 0.72 $mmol_{Cu}$, 2.1 Cu equiv.) was dissolved in 10 mL of warm THF (60 ºC). 1.0 g $SiO_{2\text{-}700}$ (0.34 $mmol_{SiOH}$, 1 equiv.) was added and the reaction medium stirred at 60 ºC and 120 rpm for 24 h. The supernatant was removed, the material washed 3 times with warm THF (5 ml) and dried under high vacuum to afford a white solid (815 mg).
E.A. (wt%): Cu, 2.12; C, 1.81; H, 0.29; N, 0.26.

$Cu/SiO_{2\text{-}TMS}$ (1)
$[Cu_{HMDS}]/SiO_{2\text{-}TMS}$ was charged into a flow glass reactor and submitted to the following treatment: under H_2 flow from R.T. to 300 ºC at 30 ºC·h^{-1} then at 300 ºC for 12 h and under high-vacuum at 300 ºC for 4 h. A dark red solid is obtained (720 mg).
E.A. (wt%): Cu, 2.31; C, 0.89; H, 0.17; N < 0.4.

IMes*-$Cu/SiO_{2\text{-}TMS}$ (2*)
$Cu/SiO_{2\text{-}TMS}$ (120 mg, 2.8 mg Cu, 44 µmol Cu) was suspended in 5 mL toluene and 15 mg of IMes* (49 µmol) were added to the suspension. The reaction mixture was stirred at room temperature and 120 rpm for 2 days. The mixture was allowed to decant, the supernatant removed. The material was washed twice with toluene, once with pentane (5 ml and 5 ml, respectively) and then dried under vacuum.
E.A. (wt%): Cu, 1.82 ; C, 3.37; H, 0.48; N, 0.44.

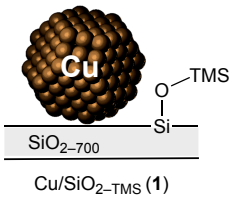
IMes-$Cu/SiO_{2\text{-}TMS}$ (2)
Non-labeled IMes was coordinated to $Cu/SiO_{2\text{-}TMS}$ according to the same procedure as for IMes*-$Cu/SiO_{2\text{-}TMS}$.

IMes*/$SiO_{2\text{-}TMS}$
$SiO_{2\text{-}TMS}$ (120 mg) was suspended in 5 mL of toluene and 15 mg IMes* (49 µmol) were added to the suspension. The reaction mixture was stirred at room temperature and 120 rpm for 1 day. The mixture was allowed to decant, the supernatant removed. The material was washed twice with toluene and once with pentane (5 mL and 5 mL, respectively), then dried under vacuum.

IMes*/$SiO_{2\text{-}700}$
$SiO_{2\text{-}700}$ (180 mg) was suspended in 5 mL of toluene and 15 mg IMes* (49 µmol) were added to the suspension. The reaction mixture was stirred at room temperature and 120 rpm for 1 day. The mixture was allowed to decant, the supernatant removed. The material was washed twice with toluene and once with pentane (5 mL and 5 mL, respectively), then dried under vacuum.

Results and Discussion

Characterization of 1



Scheme S2. Material **1**.

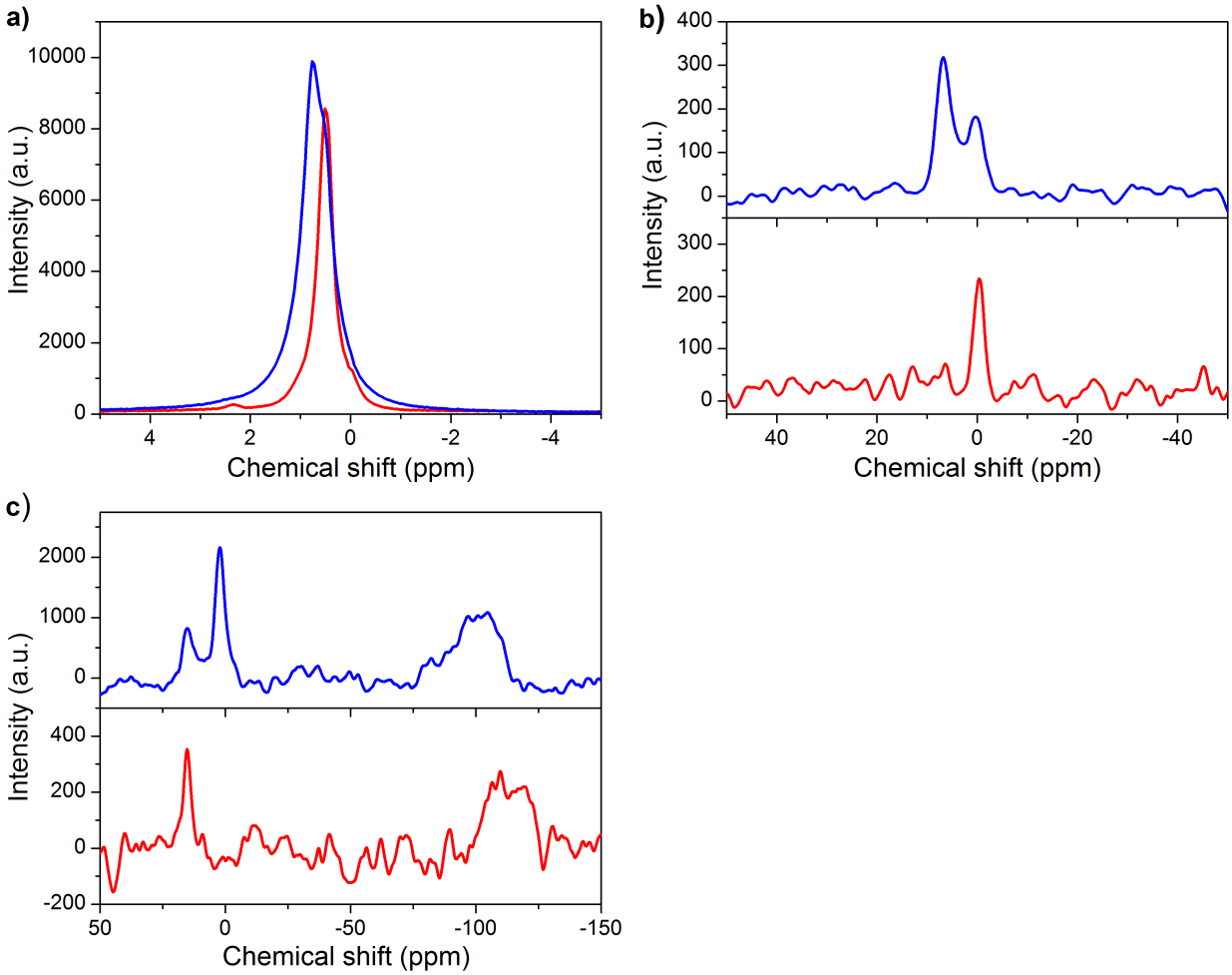


Figure S1. MAS ^{1}H (16 scans) (a), CP-MAS ^{13}C (16000 scans) (b) and CP-MAS ^{29}Si (40000 scans) (c) solid-state NMR spectra of $[Cu_{HMDS}]/SiO_{2\text{-}TMS}$ (blue) and **1** (red).

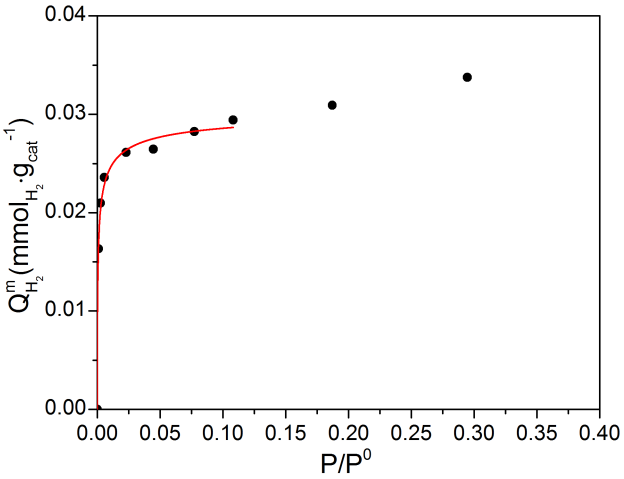


Figure S2. H_2 adsorption isotherm of **1** at 25 °C (dots) with the respective Langmuir dissociative adsorption isotherm fit (line).

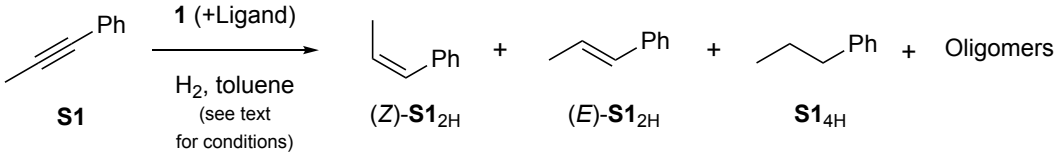
H_2 chemisorption curve was fitted with the following Langmuir dissociative adsorption isotherm:

$$Q_{H_2}(P) = Q_{H_2}^{max} \cdot \frac{\sqrt{K_{H_2}\frac{P}{P^0}}}{1+\sqrt{K_{H_2}\frac{P}{P^0}}} \qquad \textbf{Equation S1}$$

where Q_{H_2}, $Q_{H_2}^{max}$ are coverage and maximal coverage in H_2, respectively, *P* and P^0 are partial and standard (1 bar) pressure in H_2 and K_{H_2} the adsorption equilibrium constant for H_2.

The adsorption equilibrium constant was found at $K_{H_2} = 1430 \pm 285$. The maximal surface coverage in H_2 was found at $Q_{H_2}^{max} = 0.03\ mmol_{H_2} \cdot g_{cat}^{-1}$, giving a coverage in Cu surface sites of ca $0.07\ mmol_{Cu_{surface}} \cdot g_{cat}^{-1}$.[3]

Catalytic Results



Scheme S3. Hydrogenation of **S1** over catalyst **1** in the presence or absence of ligand.

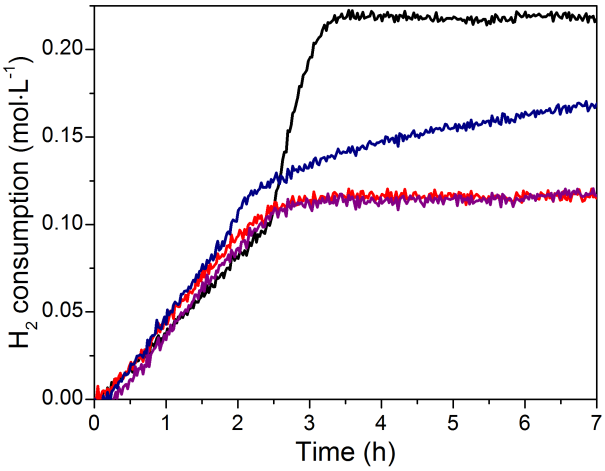
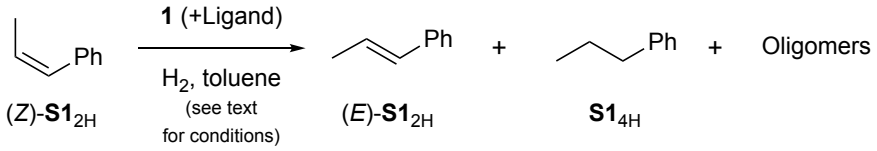


Figure S3. H_2 consumption profile for hydrogenation of **S1** at 20 bar and 60 °C over catalyst **1** in the absence of ligand (black) or in the presence of IMes/**S1** ratios of 1:50 (red), 1:100 (purple) and 1:500 (navy) according to procedure #1.

Table S1. Hydrogenation of **S1** according to procedure #3.

Entry	Catalyst	Ligand	Ligand/**S1**	P (bar)	T (°C)	Time (h)	Conversion (%)	Selectivity $\mathbf{S1}_{2H}$ (%) (*Z*/*E*)	Selectivity $\mathbf{S1}_{4H}$ (%)	Selectivity others (%)
1	**1**	None	–	20	60	8	>99	**<1**	98	2
2	**1**	IMes	1:50	20	60	8	98	**97 (99:1)**	2	1
3	**1**	PCy_3	1:50	20	60	8	99	**92 (99:1)**	2	4
4	None	None	–	20	60	8	1	**<1**	<1	>99



(*Z*)-**S1**$_{2H}$ (*E*)-**S1**$_{2H}$ **S1**$_{4H}$

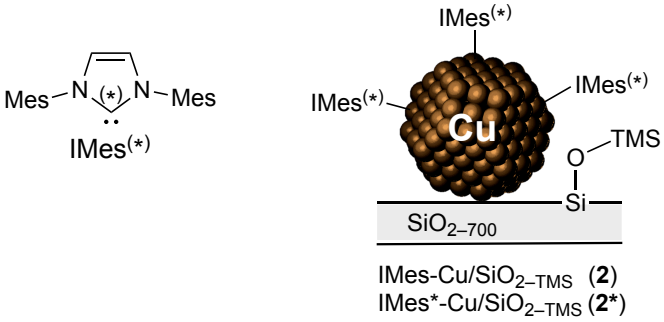
Scheme S4. Hydrogenation of (*Z*)-**S1**$_{2H}$ over catalyst **1** in the presence or absence of ligand.

Table S2. Hydrogenation of (*Z*)-**S1**$_{2H}$ over catalyst **1** according to procedure #4.

Entry	Ligand	P (bar)	T (°C)	Time (h)	Conversion (%)	Selectivity (*E*)-**S1**$_{2H}$ (%)	Selectivity **S1**$_{4H}$ (%)
1	None	5	60	2	**100**	<1	99
2	PCy_3	5	60	2	**15**	32	39
3*	PCy_3	5	100	2	**33**	27	44
4	IMes	5	60	2	**1**	<1	99
5*	IMes	5	100	2	**17**	23	64
6	None	10	60	2	**100**	<1	99
7	PCy_3	10	60	2	**18**	32	47
8	IMes	10	60	2	**1**	<1	99

* After collecting an aliquot for GC analysis, runs from entries 2 and 4 were continued for additional 2 h at 60 °C followed by 2 h at 100 °C.

Characterization of 2 and 2*



Scheme S5. Ligand IMes$^{(*)}$, materials **2** and **2***.

Table S3. Elemental analyses.

Compound	**1**		**2***		Difference (**2*–1**)		IMes*
Element	Mass/mass loading ($g_{element}{\cdot}g_{cat}^{-1}$)	Molar/mass loading ($mol_{element}{\cdot}g_{cat}^{-1}$)	Mass/mass loading ($g_{element}{\cdot}g_{cat}^{-1}$)	Molar/mass loading ($mol_{element}{\cdot}g_{cat}^{-1}$)	Molar/mass loading ($mol_{element}{\cdot}g_{cat}^{-1}$)	Molar ratios (C, H, N)	Molar ratios (C, H, N)
C	$0.89\ 10^{-2}$	$7.4\ 10^{-4}$	$3.37\ 10^{-2}$	$2.80\ 10^{-3}$	$2.06\ 10^{-3}$	**0.38**	**0.44**
H	$0.17\ 10^{-2}$	$1.7\ 10^{-3}$	$0.48\ 10^{-2}$	$4.8\ 10^{-3}$	$3.1\ 10^{-3}$	**0.57**	**0.51**
N	n.d. (<0.4)	n.d.	$0.44\ 10^{-2}$	$3.1\ 10^{-4}$	$3.1\ 10^{-4}$*	**0.05**	**0.04**

* N loading in **1** taken as 0.

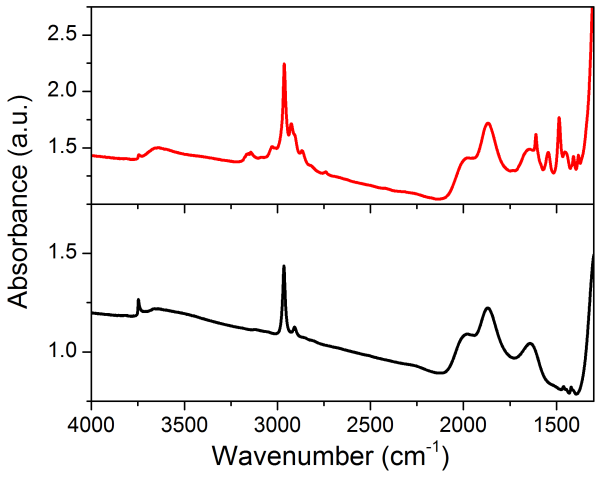


Figure S4. FTIR spectra of **1** (black) and **2** (red).

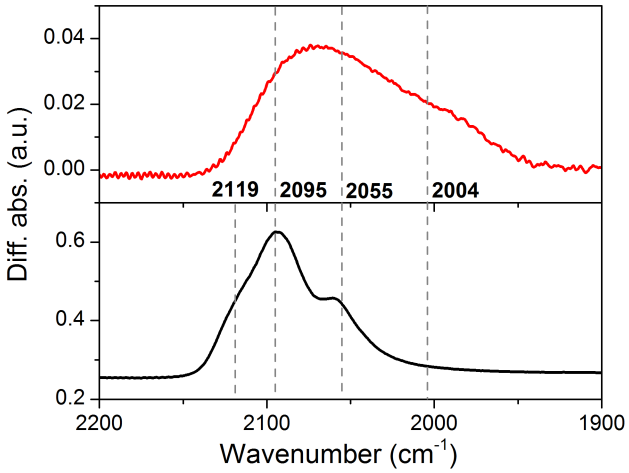


Figure S5. FTIR differential spectra after contacting CO with **1** at 33 mbar (black) and **2** at 28 mbar (red).

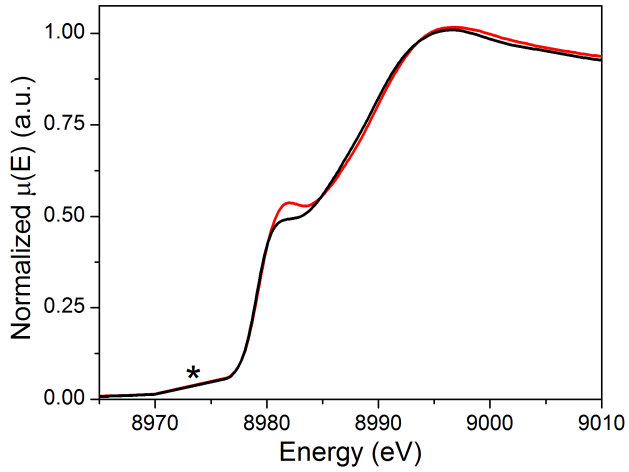


Figure S6. XANES spectra of **1** (black) and **2** (red). *Region between 8970 and 8977 was deglitched.

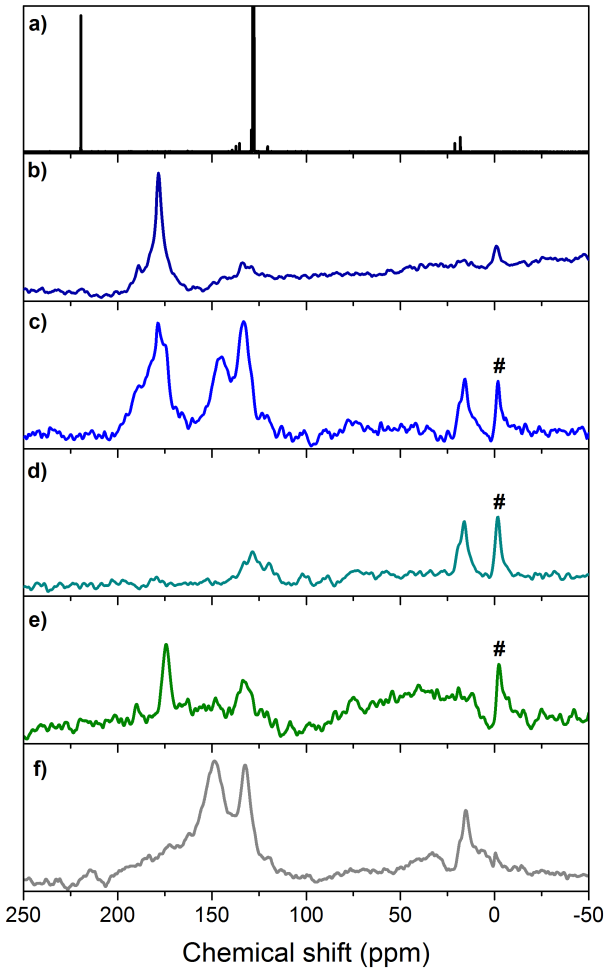


Figure S7. (a) ^{13}C NMR solution-state spectrum of free IMes* (C_6D_6, 75 MHz); (b) ^{13}C NMR solid-state HPDEC spectrum of **2*** (30000 scans); ^{13}C NMR solid-state CP-MAS spectra of (c) **2*** (90000 scans), (d) **2** (90000 scans), (e) IMes*/$SiO_{2\text{-}TMS}$ (27513 scans), (f) IMes*/$SiO_{2\text{-}700}$ (64000 scans). ^{13}C NMR solid-state CP-MAS spectra of **2***, **2** and IMes*/$SiO_{2\text{-}TMS}$ are normalized versus signals of the TMS groups of the support (**#**).

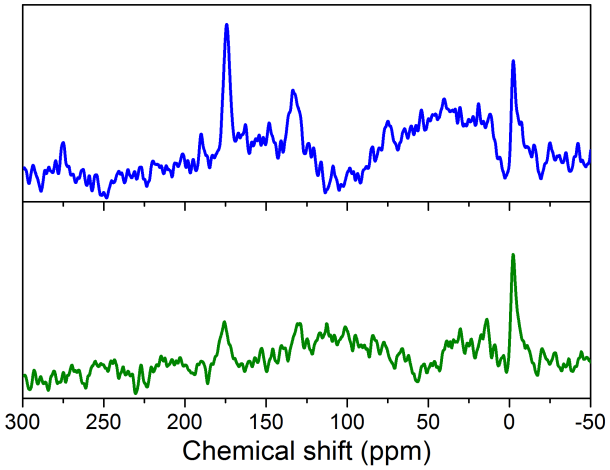


Figure S8. ^{13}C solid-state MAS spectra of IMes*/$SiO_{2\text{-}TMS}$ in CP-MAS (27513 scans) (blue) and HPDEC (64788 scans) (green) modes.

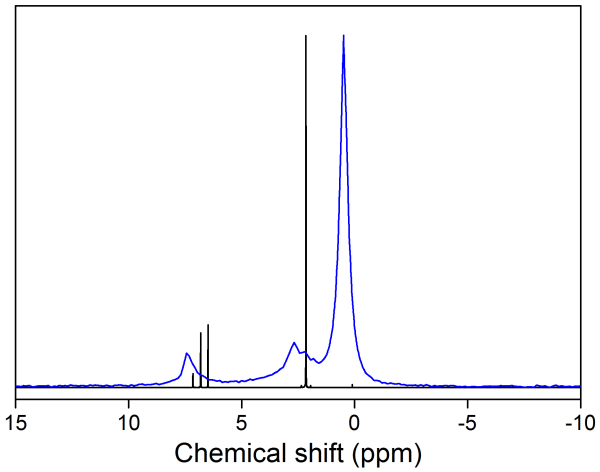


Figure S9. ^{1}H NMR solution-state spectrum of free IMes* (C_6D_6, 300 MHz) (black) and ^{1}H NMR solid-state MAS spectra of **2*** (32 scans) (blue).

References

1. L. Jafarpour, E. D. Stevens and S. P. Nolan, *J. Organomet. Chem.*, 2000, 606, 49-54.
2. D. P. Estes, G. Siddiqi, F. Allouche, K. V. Kovtunov, O. V. Safonova, A. L. Trigub, I. V. Koptyug and C. Coperet, *J. Am. Chem. Soc.*, 2016, 138, 14987-14997.
3. K. Larmier, S. Tada, A. Comas-Vives and C. Coperet, *J. Phys. Chem. Lett.*, 2016, 7, 3259-3263.

Author Contributions

N. K., A.F., and C.C. designed research; N. K., H.-J.L., and H-K. L. performed research; all authors analysed the data; N. K., A.F., and C.C. wrote the paper.