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

SUPPORTING INFORMATION

for

Surprisingly high sensitivity of copper nanoparticles toward coordinating ligands: consequences for the hydride reduction of benzaldehyde

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Outline

1. General details

All syntheses and procedures were carried under inert gas (N_2 or Ar) using an inert glovebox (H_2O: ≤ 0.5 ppm, O_2: ≤ 0.5 ppm) and Schlenk techniques.

Powder X-ray reflection measurements (XRD) were performed with a Bruker D8 X-ray diffractometer operating in reflection mode with Cu Kα radiation (40 kV, 40 mA). The data were collected in the 15-80° range (2θ) with steps of 0.05° and a counting time of 2 s using Si-sample holders. The Scherrer equation was applied with a form factor K of 0.94, to a maximum number of reflections for each diffractogram.

For transmission electron microscopy (TEM) observations, the powders were dispersed in anhydrous THF. A few drops of the resulting dispersions were deposited on a carbon-coated copper grid. After solvent evaporation, TEM was performed with a FEI TECMAI G2 Spirit Twin electron microscope operating at 120 kV.

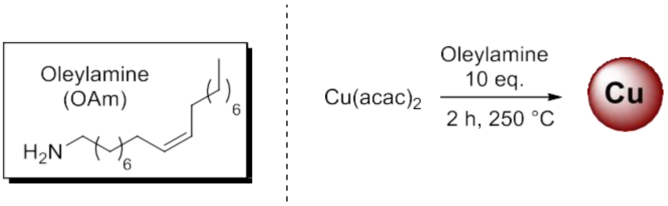
Nuclear Magnetic resonance (NMR) spectroscopy: ^{1}H NMR, and ^{31}P{^{1}H} NMR spectra were recorded at room temperature on a Bruker Avance 300 spectrometer. Shifts (δ) are given in parts per million (ppm) using the resonance of the solvent peak as a secondary reference (δ(^{1}H) = 7.26 ppm for the residual signal of $CDCl_3$). Multiplicities are reported using the following abbreviations: s (singlet), bs (broad signal), d (doublet), t (triplet), q (quartet), quint. (quintet), m (multiplet).

GC/MS of the supernatant was acquired on a simple quadripole mass spectrometer DSQII.

THF (99.8+%, anhydrous, unstab.) was purchased from Alfa-Aesar, toluene (99.8%, anhydrous) and acetonitrile (99.93%, anhydrous) were purchased from Aldrich and used as received in a glovebox. Benzaldehyde, tri(*n*-butyl)phosphine (99%, Strem Chemicals), tri-*tert*-butylphosphine (99%, Strem Chemicals), triphenylphosphine (99%, Strem Chemicals), tricyclohexylphosphine (97%, Strem Chemicals), 1,2-bis(diphenylphosphino)benzene (97%, Aldrich), 1,1,1-tris(diphenylphosphinomethyl)ethane (97%, Strem Chemicals), oleylamine (>98%, Aldrich), [$Cu(acac)_2$] (>99.9% Aldrich), copper foil (thickness 0.25 mm, 99.98%), phenylsilane (97+%, Acros), diphenysilane (97%, Aldrich), triphenylsilane (97%, Aldrich), triethoxysilane (95%, Aldrich), triethylsilane (99%, Acros), TMDS (1,1,3,3-tetramethyldisiloxane) (97%, Acros), PMHS (polymethylhydrosiloxane) (Fluka), $(9\text{-BBN-H})_2$ (Aldrich), sodium borohydride ($NaBH_4$) (98%, Alfa-Aesar), sodium hydride (NaH) (95%, Aldrich).

2. Nanoparticles synthesis and characterizations

Preparation of copper nanoparticles with oleylamine:[1]



In a round-bottom flask, 25 mL of oleylamine (73.8 mmol, 7.9 eq.) were added. The flask was put under vacuum and purged with N_2 three times. Under N_2, [$Cu(acac)_2$] (2.5 g, 9.55 mmol) was dissolved in oleylamine by heating the medium gently, under agitation. Once the solution was homogeneous, the temperature was increased to 250 °C for 2 h. The color changed from sky-blue to brown to black. After cooling at RT under N_2, *n*-hexane (5 mL), acetone (25 mL) and methanol (2 mL) were successively added to the crude solution. Then the nanoparticles were isolated by centrifugation (3,000 rpm, 20 min, 20 °C). The supernatant was removed and the particles were redispersed in *n*-hexane and washed with acetone/methanol (25 mL/2 mL) and centrifugated. This operation was repeated three times. The nanoparticles were then dried under a N_2 flow and stored in a glovebox (H_2O: ≤ 0.5 ppm, O_2: ≤ 0.5 ppm). 510 mg of powder were obtained (yield = 85%).

These nanoparticles will be referred as Cu NPs in the following.

The nanoparticles were confirmed to be Cu(0) nanoparticles by XRD. Scherrer equation indicated a size of crystallites of approx. 13 nm.

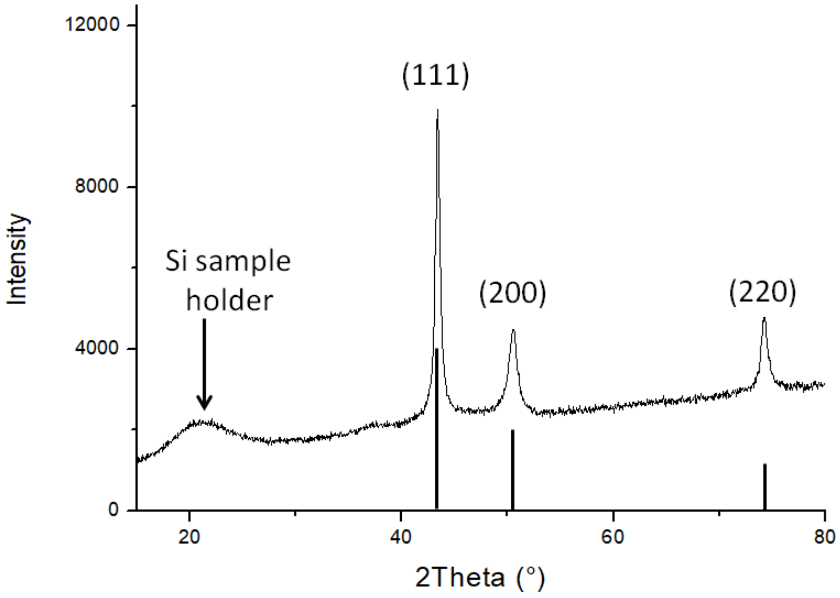


Figure S1 - XRD on the powder of the isolated Cu NPs.

^{1}H NMR Analysis of the supernatant of the Cu NPs synthesis:

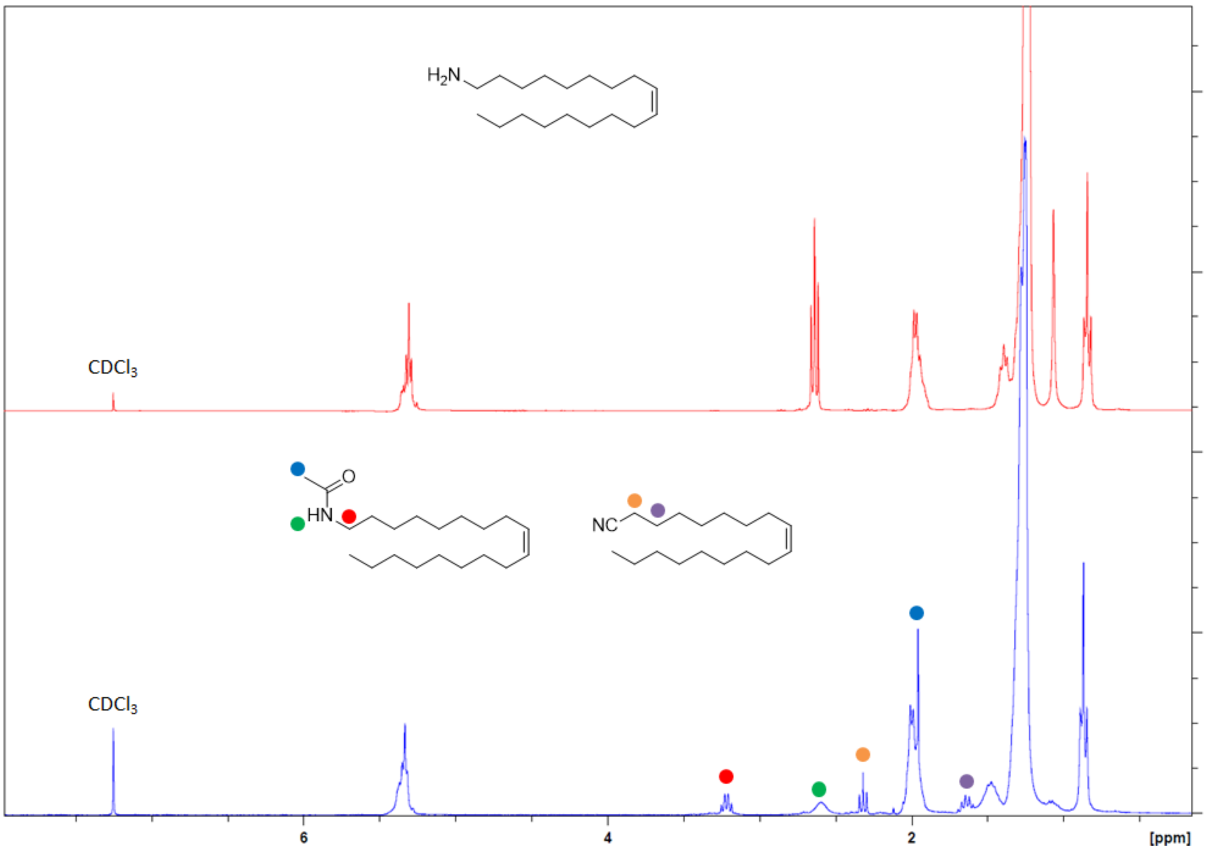


Figure S2 - Comparison of pure OAm (top) and the synthesis crude (bottom) by ^{1}H NMR. Colored dots indicate the attribution of characteristic NMR peaks.

Two side-products could be identified in the crude after elimination of the Cu NPs and concentration under vacuum, by ^{1}H NMR and GC/MS. Comparison with the spectrum of pure OAm shows the complete conversion of OAm into various products. Among them, *N*-oleylacetamide (mass 309 $g.mol^{-1}$) and oleanitrile (mass 263 $g.mol^{-1}$) can be identified with signature chemical shifts at 3.22 ppm (q, *J* = 7 Hz, N-C$\mathbf{H_2}$, red dot), 1.96 ppm (s, COC$\mathbf{H_3}$, blue dot) and 2.60 ppm (bs, N**H**, green dot) for *N*-oleylacetamide[2] and 2.32 ppm (t, *J* = 7 Hz, NC-C$\mathbf{H_2}$, orange dot), 1.65 ppm (quint., *J* = 7 Hz, NC-CH_2-C$\mathbf{H_2}$-CH_2, purple dot) for oleanitrile.[3]

ATR FT-IR cell at SMIS beamline (SOLEIL)

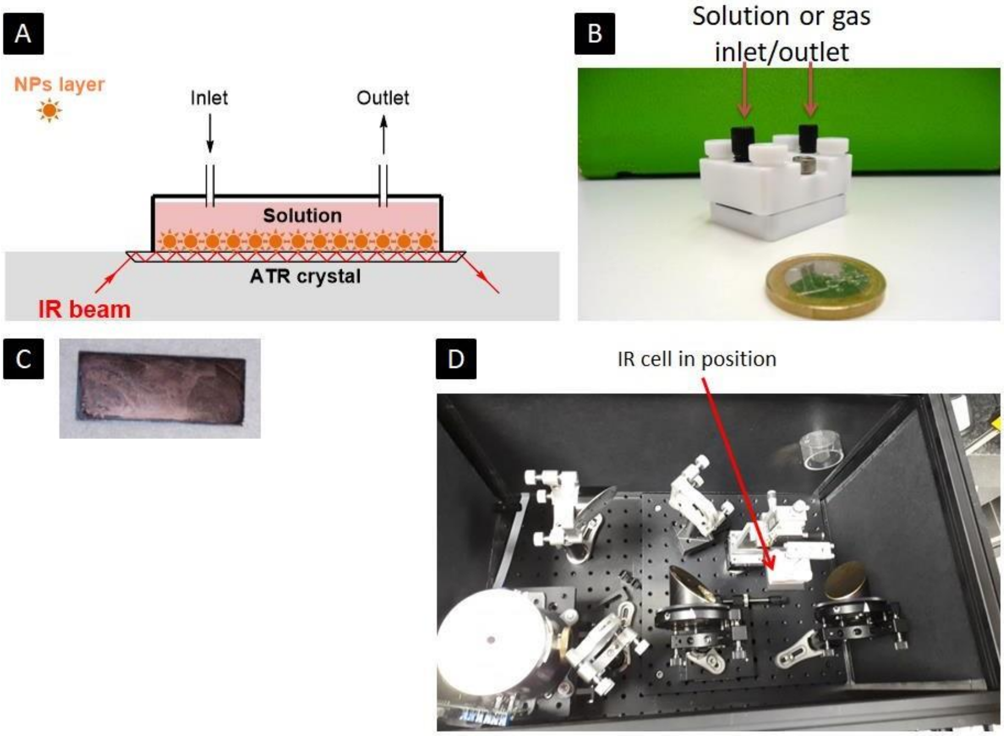


Figure S3 – FTIR cell used for the IR study (A) Simplified scheme of the ATR-FTIR cell; (B) view of the cell, 1 € coin for scale; (C) Cu NPs layered ATR crystal; (D) Top view of the experimental set-up.

The suspension of Cu NPs was drop-casted on an ATR Si-crystal (dimension: 1 cm x 2 cm) to get a thin layer of NPs, which was then analyzed by FT-IR. Frequencies below 1200 cm^{-1} could not be detected due to the absorption of the crystal.

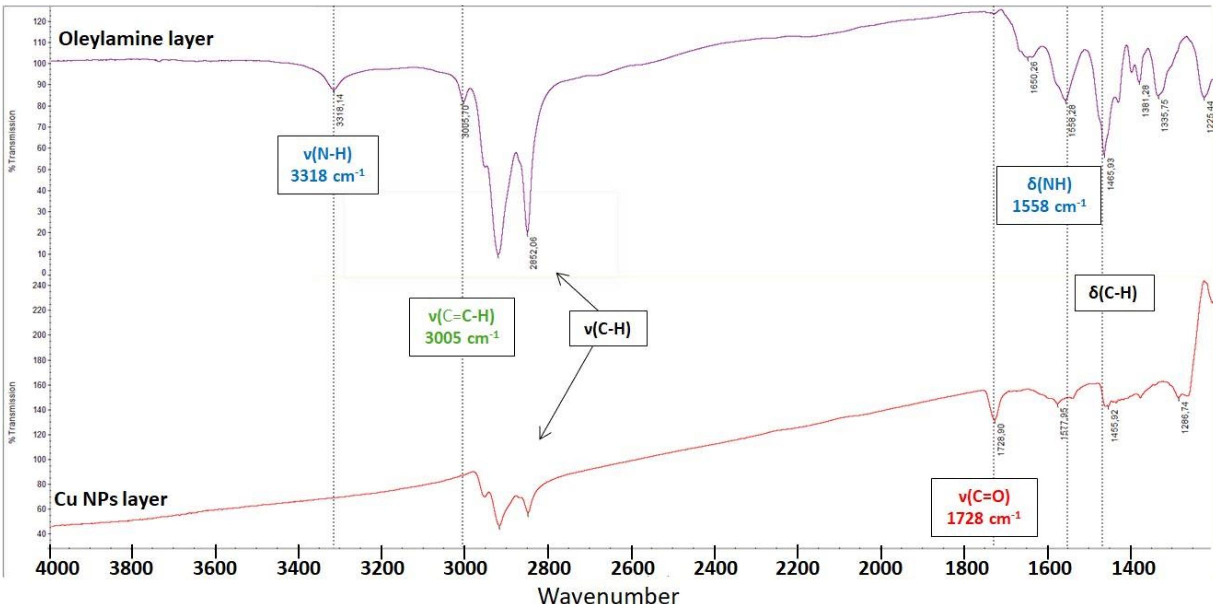


Figure S4 – FTIR spectra comparison between oleylamine and Cu NPs measured under inert atmosphere

3. Reaction profiles using the ATR FTIR cell

In a glovebox, a layer of Cu NPs was prepared by dropcasting a suspension of Cu NPs in THF on the ATR crystal. The crystal was then placed in the IR-cell and sealed. The FTIR analysis takes place under a nitrogen flushed box. In the FTIR cell, a THF solution (5 mL) containing PhCHO (0.5 mL), $PhSiH_3$ (0.24 mL) and $P(n\text{-}Bu)_3$ (0.02 mL) is added with a syringe on the layer of Cu NPs and the spectra are recorded every 80 s.

In a glovebox, a layer of Cu NPs was prepared by dropcasting a suspension of Cu NPs in THF on the ATR crystal. The crystal was then placed in the IR-cell and sealed. The FTIR analysis takes place under a nitrogen flushed box. In the FTIR cell, a THF solution (5 mL) containing PhCHO (0.5 mL) and $PhSiH_3$ (0.24 mL) is added with a syringe on the layer of Cu NPs and the spectra are recorded every 80 s.

without $P(n\text{-}Bu)_3$: Overlay of spectra (over 30 min) from light grey to dark:[4]

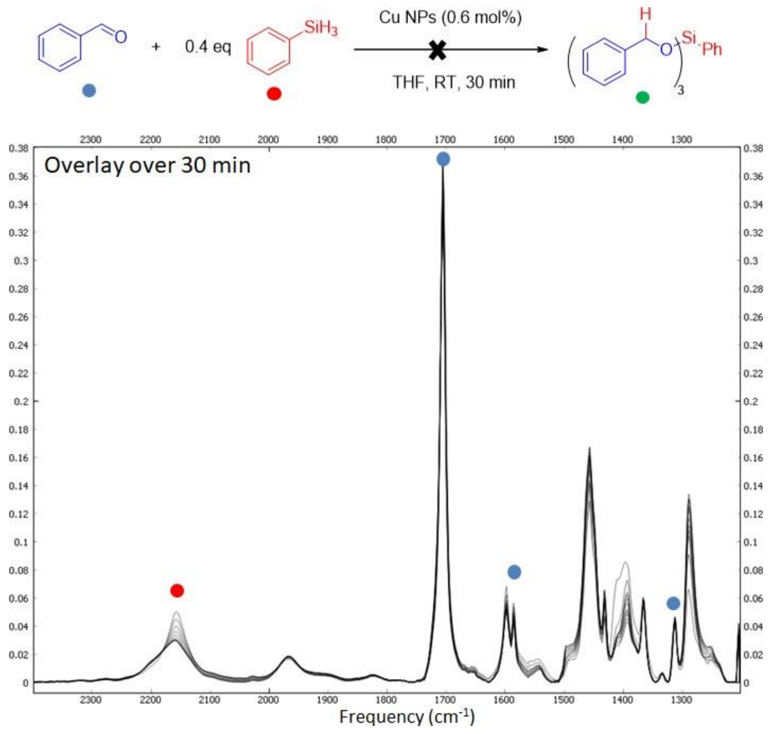


Figure S5 - Overlay of FTIR evolution of the reaction medium in the absence of $P(n\text{-}Bu)_3$. Light-gray spectra as the first ones in the series. The last spectrum is the black one.

Observations: no change of the signal of benzaldehyde (green dots), the v(Si-H) signal slightly shifts to the left (2 cm^{-1}) and broadens over time. No detection of new signals.

Without benzaldehyde:

In a glovebox, a solution of $PhSiH_3$ (0.240 mL) in THF (5 mL) is prepared. Under a flow of N_2, 0.1 mL of this solution is added to the FI-IR cell. Then, 0.1 mL of a well-dispersed THF solution (5 mL) containing 2 mg of Cu NPs and 0.02 mL of P(*n*-Bu)$_3$, is added to the cell through the inlet. The spectra are recorded every 80 s.

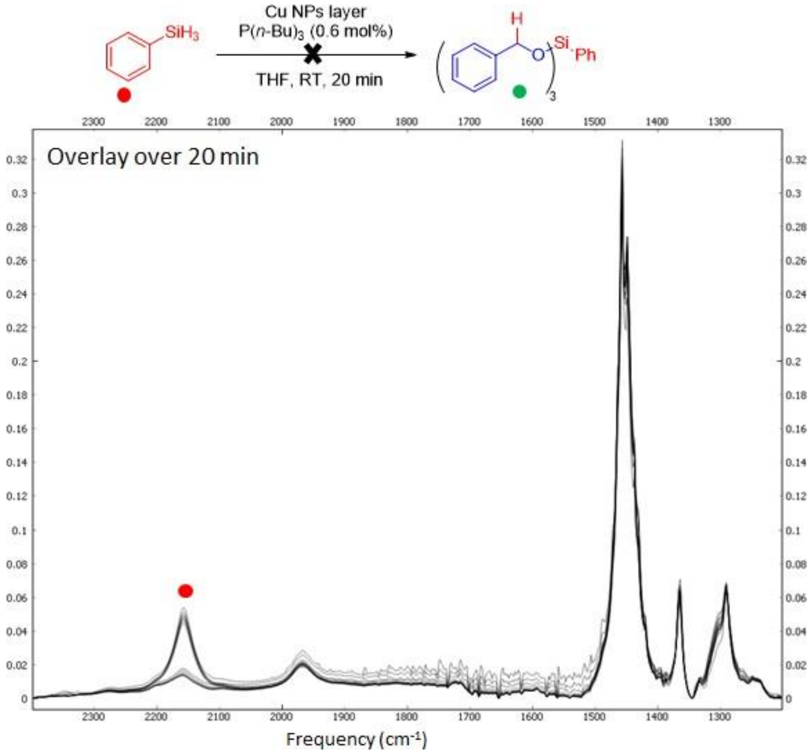


Figure S6 - Overlay of FTIR evolution of the reaction medium in the absence of benzaldehyde. Light-gray spectra as the first ones in the series. The last spectrum is the black one.

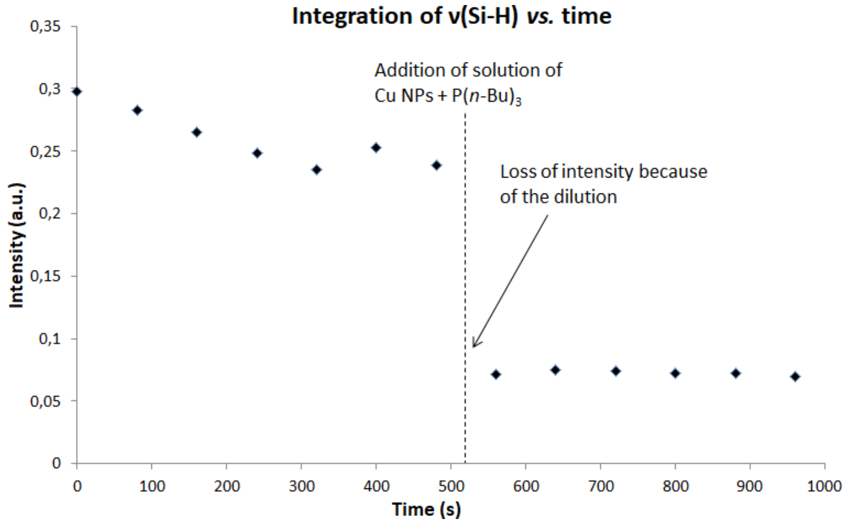


Figure S7 – Integration of the v(Si-H) band over time

Without phenylsilane:

In a glovebox, a solution of PhCHO (0.5 mL) in THF (5 mL) is prepared. Under a flow of N_2, 0.1 mL of this solution is added to the FIIR cell. Then, 0.1 mL of a well-dispersed THF solution (5mL) containing 2 mg of Cu NPs and 0.02 mL of P(*n*-Bu)$_3$, is added to the cell through the inlet. The spectra are recorded every 80 s.

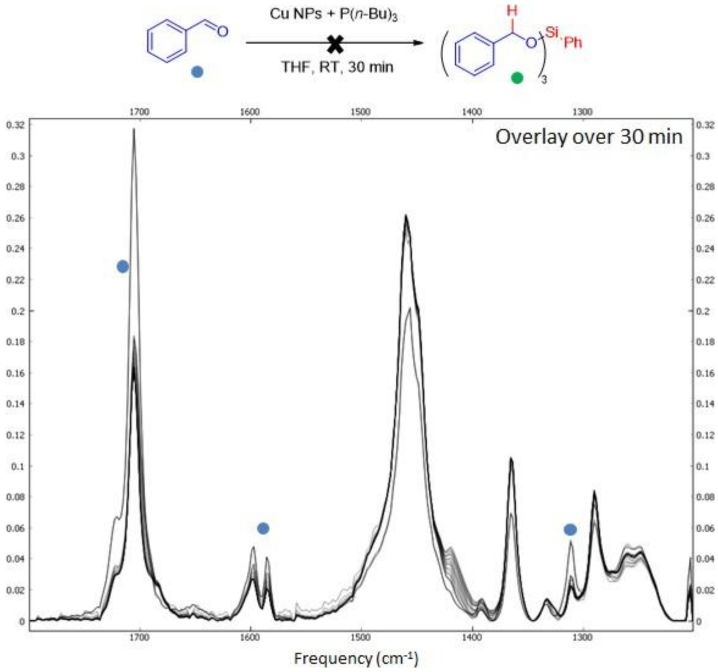


Figure S8 - Overlay of FTIR evolution of the reaction medium in the absence of phenylsilane. Light-gray spectra as the first ones in the series. The last spectrum is the black one.

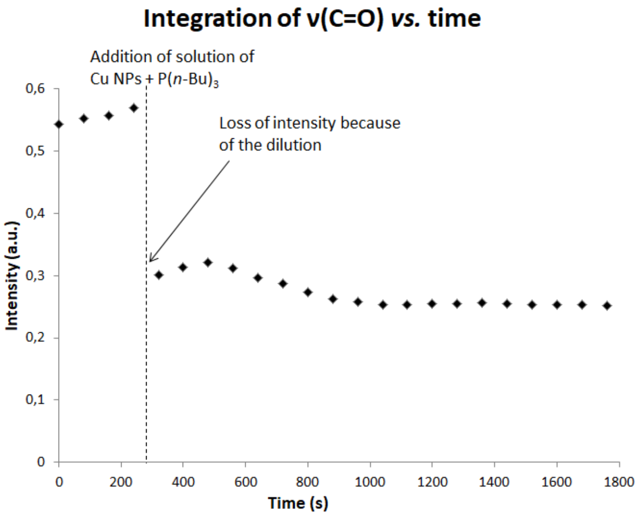


Figure S9 – Integration of the ν(C=O) band over time

Reaction profile with a layer of Cu NPs dispersed in an excess of DBU (instead of P(*n*-Bu)$_3$):

In a glovebox, a layer of Cu NPs + xsDBU was prepared by dropcasting a suspension of Cu NPs (1mg) + DBU (1mL) in THF (5 mL) on the ATR crystal. The crystal was then placed in the IR-cell and sealed. The FT-IR analysis takes place under a nitrogen flushed box. In the FT-IR cell, a THF solution (5 mL) containing PhCHO (0.5 mL), PhSiH$_3$ (0.24 mL) is added with a syringe on the layer of Cu NPs and the spectra are recorded every 80 s.

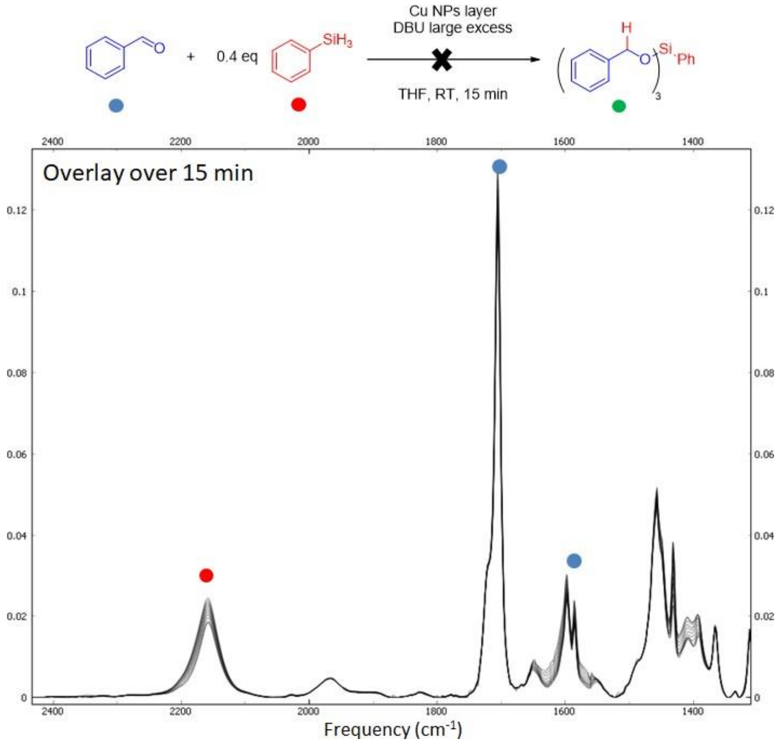


Figure S10 - Overlay of FTIR evolution of the reaction medium in the presence of DBU instead of P(*n*-Bu)$_3$. Light-gray spectra as the first ones in the series. The last spectrum is the black one.

Reaction profile with PhMe$_2$SiH instead of PhSiH$_3$:

In a glovebox, a layer of Cu NPs was prepared by dropcasting a suspension of Cu NPs (1 mg) + P(*n*-Bu)$_3$ (0.02 mL) in THF (5 mL) on the ATR crystal. The crystal was then placed in the IR-cell and sealed. The FT-IR analysis takes place under a nitrogen flushed box. In the FT-IR cell, 0.1 mL of a THF solution (0.5 mL) containing PhCHO (0.05 mL), PhMe$_2$SiH (0.08 mL) and is added with a syringe on the layer of Cu NPs and the spectra are recorded every 80 s.

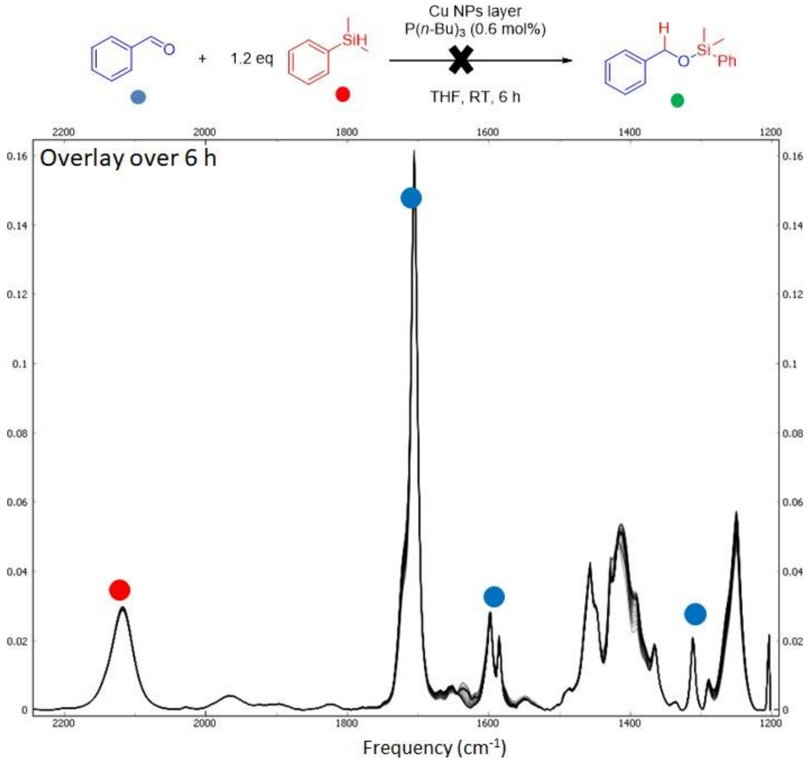


Figure S11 - Overlay of FTIR evolution of the reaction medium in the presence of dimethylphenylsilane instead of phenylsilane. Light-gray spectra as the first ones in the series. The last spectrum is the black one.

4. Catalytic tests

In a 10 mL vial, Cu NPs (2 mg, 0.03 mmol) were suspended in THF (5 mL). After the addition of 300 µL of a 0.1 M solution of P(*n*-Bu)$_3$ in THF, the mixture was put in a sonication bath for 1 min. To this dark red suspension, $PhSiH_3$ (250 µL, 2.03 mmol) and PhCHO (500 µL, 4.92 mmol) are added. Self-heating of the medium and formation of bubbles is observed at this point. After 2 h of agitation at room temperature, an aliquot of the crude is analyzed by ^{1}H NMR in $CDCl_3$ to determine the conversion of benzaldehyde.

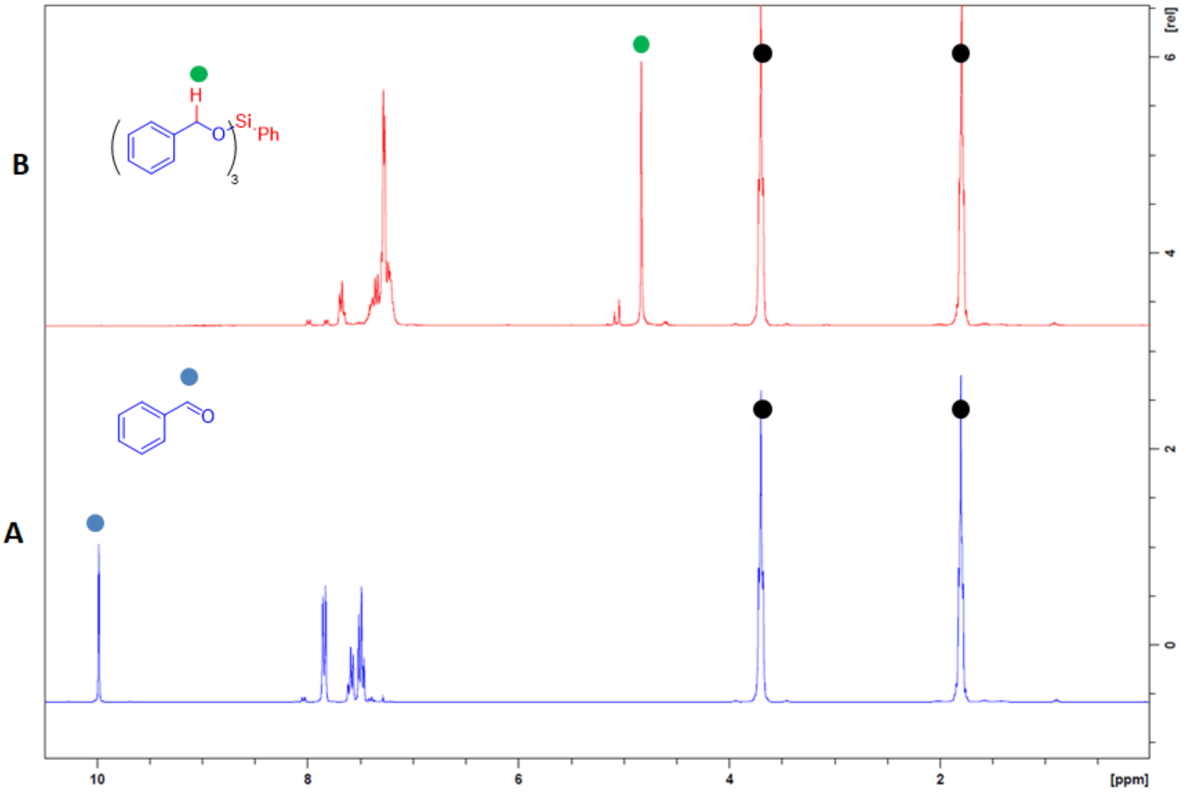


Figure S12 - ^{1}H NMR in $CDCl_3$ of aliquots of the reaction mixture: A = Benzaldehyde with (Cu NPs + P(*n*-Bu)$_3$ (0.6 mol%)) in THF; B = after addition of $PhSiH_3$, room temperature, 2 h.

*Observations using [Cu(acac)$_2$] + P(*n*-Bu)$_3$ as catalyst:*

To the blue solution of [Cu(acac)$_2$] in THF, addition of P(*n*-Bu)$_3$ did not give any visible change. At the addition of $PhSiH_3$, the solution quickly changed from blue to yellow then dark brown. A TEM grid was prepared with an aliquot, showing the formation of NPs (Figure S13).

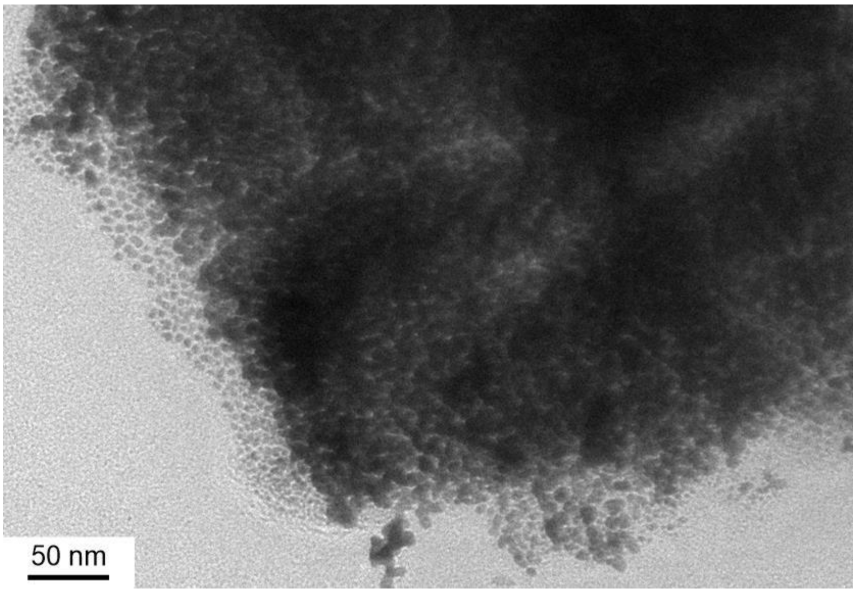
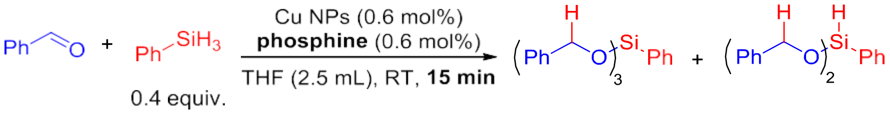


Figure S13 - TEM image of the nanoparticles formed during after the addition of $PhSiH_3$ to the solution of Cu(acac)$_2$ + P(*n*-Bu)$_3$ in THF

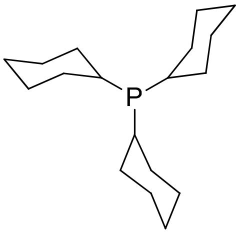
Comparison of benzaldehyde conversion in the presence of various phosphines:

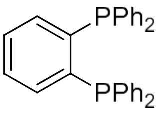
In a 10 mL vial, Cu NPs (1 mg, 0.016 mmol) were suspended in THF (2.5 mL). After the addition of 0.015 mmol of the corresponding phosphine, the mixture was put in a sonication bath for 1 min. To this dark red suspension, $PhSiH_3$ (125 µL, 1.01 mmol) and PhCHO (250 µL, 2.46 mmol) are added. After 15 min of agitation at room temperature, an aliquot of the crude is analyzed by ^1H NMR in $CDCl_3$ to determine the conversion of benzaldehyde. The results are detailed in Table S1.



Entry	Phosphine	NMR yield[(a)] (%)
1	P(*n*-Bu)$_3$	93%
2	P*t*Bu$_3$	2%
3	PCy$_3$	59%
4	PPh$_3$	85%
5	dppBz$^{(b)}$	76%
6	Triphos$^{(c)}$	<1%

(a) based on benzaldehyde conversion into silylated benzylic alcohol species. (b) 0.5 equiv. *vs* Cu (c) 0.33 equiv. *vs* Cu


PCy$_3$


dppBz

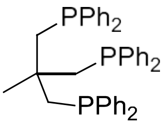

triphos

Table S1 - Influence of the phosphine.

ESI-MS analysis

ESI/MS was acquired using a mass spectrometer LC ESI/LTQ Orbitrap.

Sample preparation:

Under inert atmosphere, 2 mg of Cu NPs were suspended in 2 mL of pure P(*n*-Bu)$_3$ and agitated at RT for 1 week. The suspension was then diluted with THF (5 mL) and centrifuged at 30,000 g for 25 min. The supernatant was eliminated and the resulting solid redispersed in 5 mL of THF and centrifuged again (operation repeated twice). The resulting powder was redispersed in THF (1 mL). For the ESI-MS analysis, 15 µL of this suspension was diluted in 1 mL of acetonitrile.

ESI Positive mode ESI in CH_3CN (low energy)

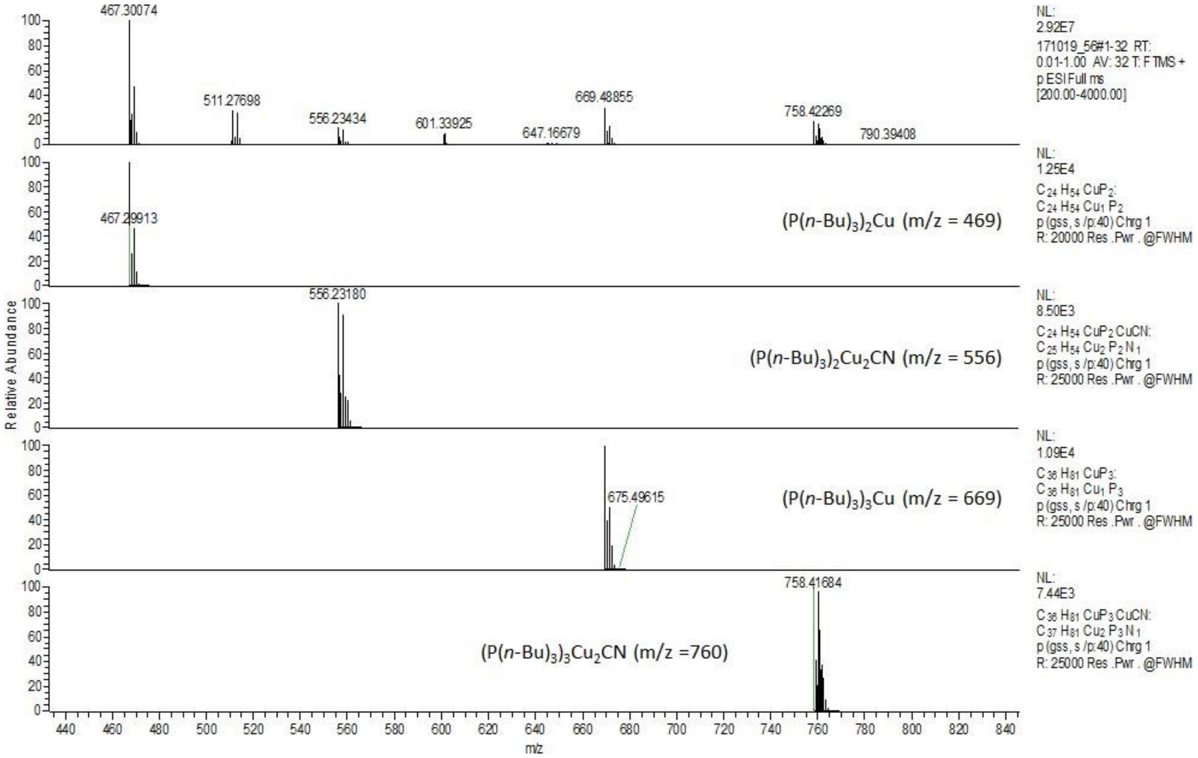


Figure S14 - ESI positive mode in CH_3CN (low energy).

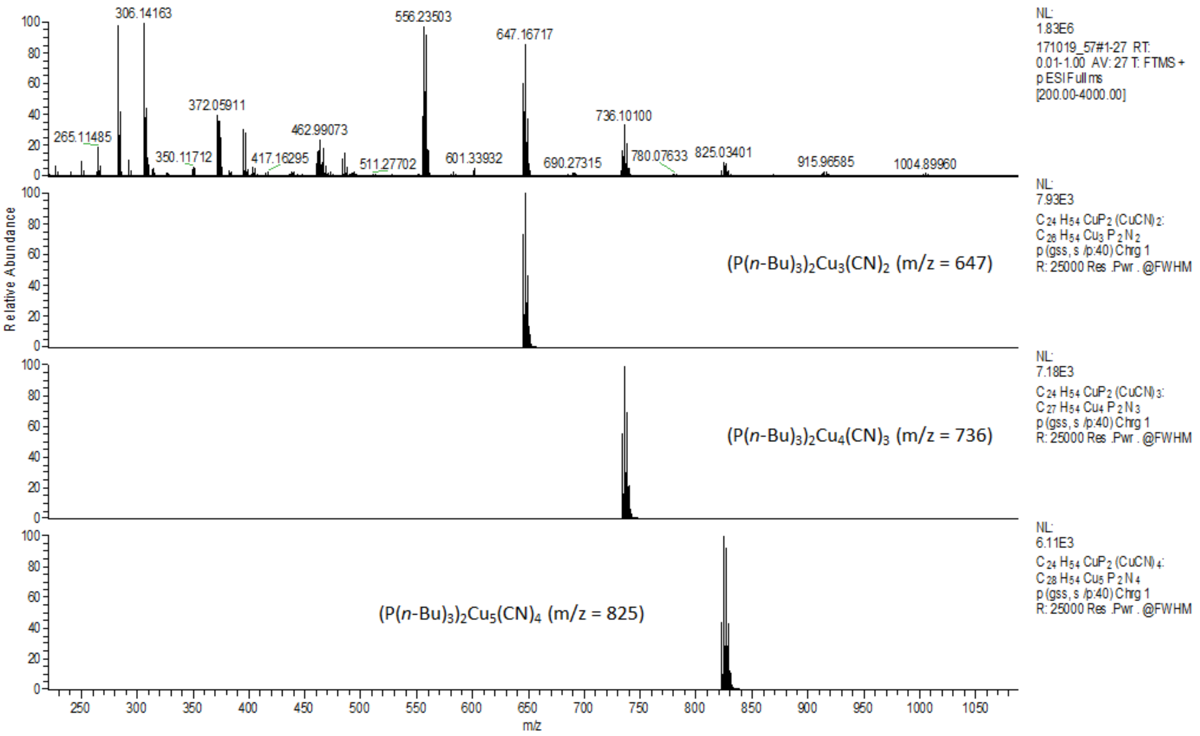


Figure S15 – ESI positive mode in CH_3CN (high energy).

ICP-MS analysis

The analysis was conducted on a iCAP 6000 ICP-AES Thermo Fisher. The calibration has been realized with ICP standard copper solutions (1000 ± 3 g.mL^{-1}) in HNO_3 (4 w%), PlasmaCAL from SCP science.

Sample preparation:

Under inert atmosphere, 2 mg of Cu NPs (0.032 mmol of Cu atoms) were suspended in 5 mL of THF in the presence of a phosphine (1 equiv. *vs*. Cu atom), TMDS (0.500 mL, 2.82 mmol) and benzaldehyde (0.500 mL, 5 mmol) and agitated at RT for 15 min. The reaction medium was then centrifuged at 10,000 g for 30 min. The colorless supernatant was carefully separated and the volatiles were removed under vacuum. The resulting oil was dissolved in HNO_3 5 w% (10 mL) and the aqueous phase was analyzed by ICP, using the 324.7 and 327.3 nm wavelength of copper for the dosage.

The analysis was recorded on two samples prepared independently: the concentration of Cu leached species in solution after workup steps were 0.15 and 0.12 mM, corresponding to respectively a leaching of 5.1% and 4.3% of the quantity of copper initially introduced.

5. Experiments with pure Copper foil

In a 10 mL vial, a Cu foil (approx. 45 mg, 0.5 cm x 0.5 cm) put in THF (2.5 mL). After the addition of 150 µL of a 0.1 M solution of P(*n*-Bu)$_3$ in THF , PhSiH$_3$ (120 µL, 0.97 mmol) and PhCHO (250 µL, 2.46 mmol) are added. After 18 h of agitation at room temperature, an aliquot of the crude is analyzed by ^{1}H NMR in CDCl$_3$ to determine the conversion of benzaldehyde and phenylsilane.

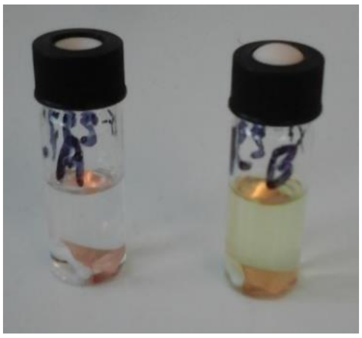
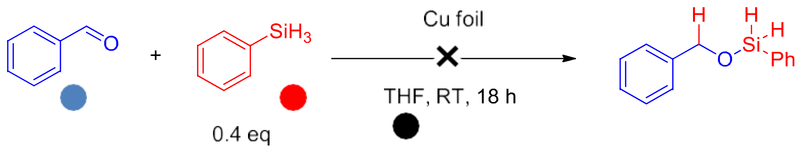


Figure S16 - Photographs of the reactions: left: with Cu foil without P(*n*-Bu)$_3$; right: with Cu foil with P(*n*-Bu)$_3$.

Without P(n-Bu)$_3$



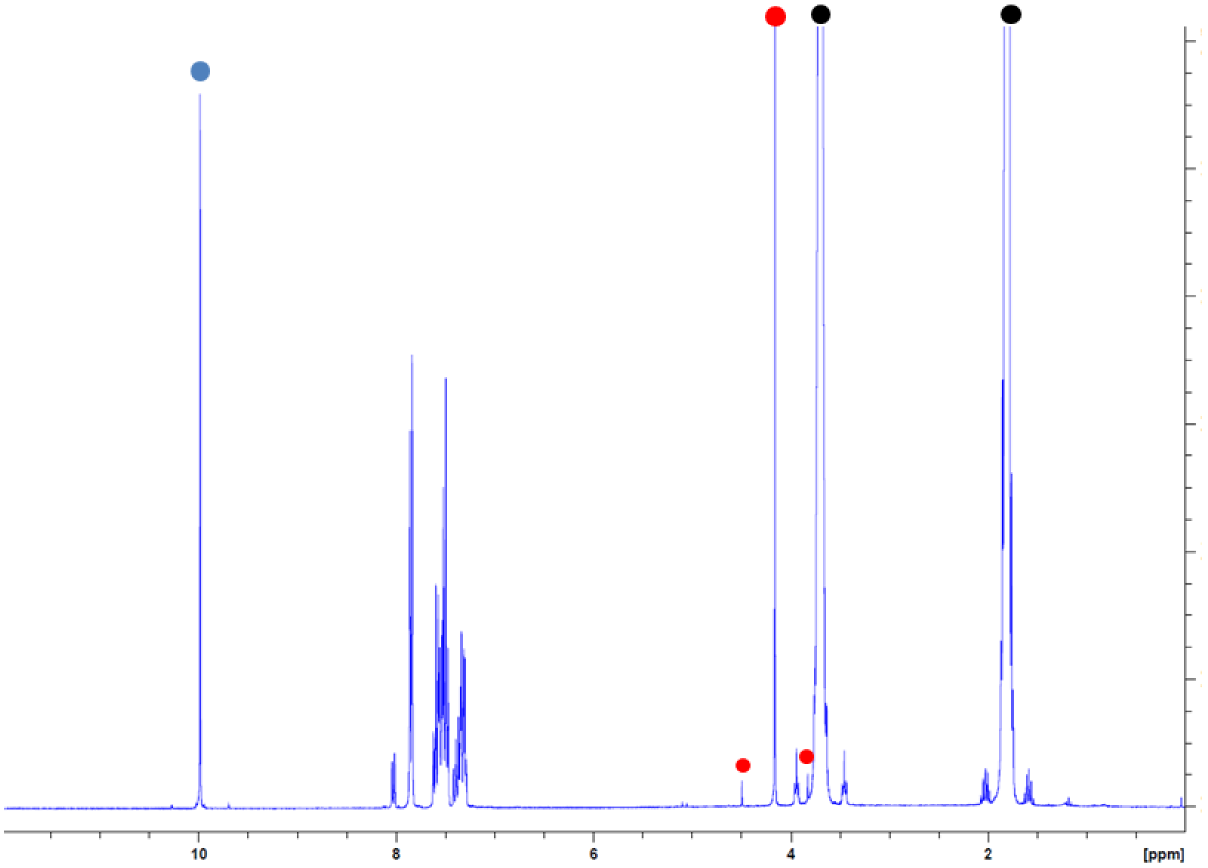
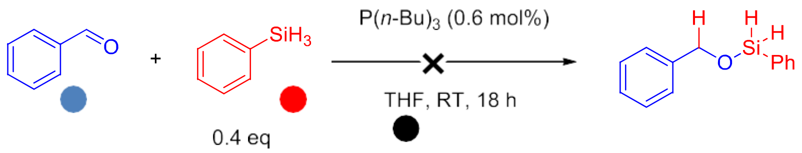


Figure S17 - *^{1}H NMR spectrum of the reaction crude (without P(*n*-Bu$_3$)).*

Without Cu foil



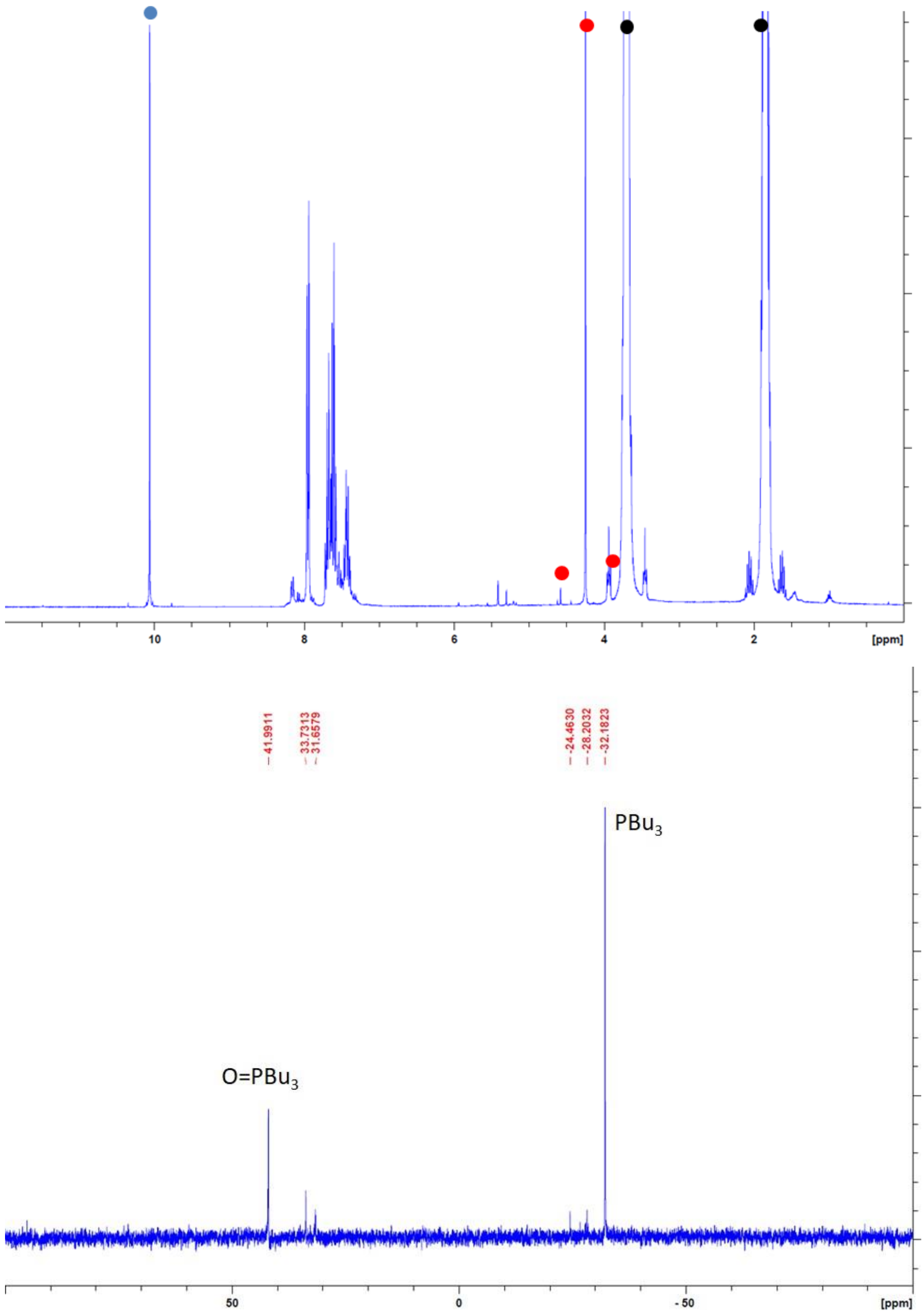
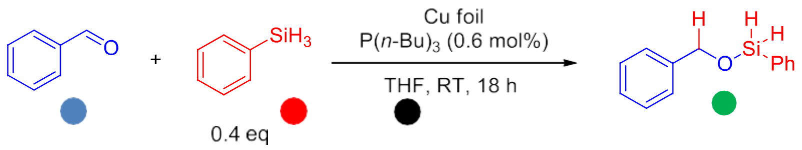


Figure S18 – ^{1}H NMR and ^{31}P{^{1}H} NMR spectra of the reaction crude (without Cu foil).

with Cu foil and P(n-Bu)$_3$



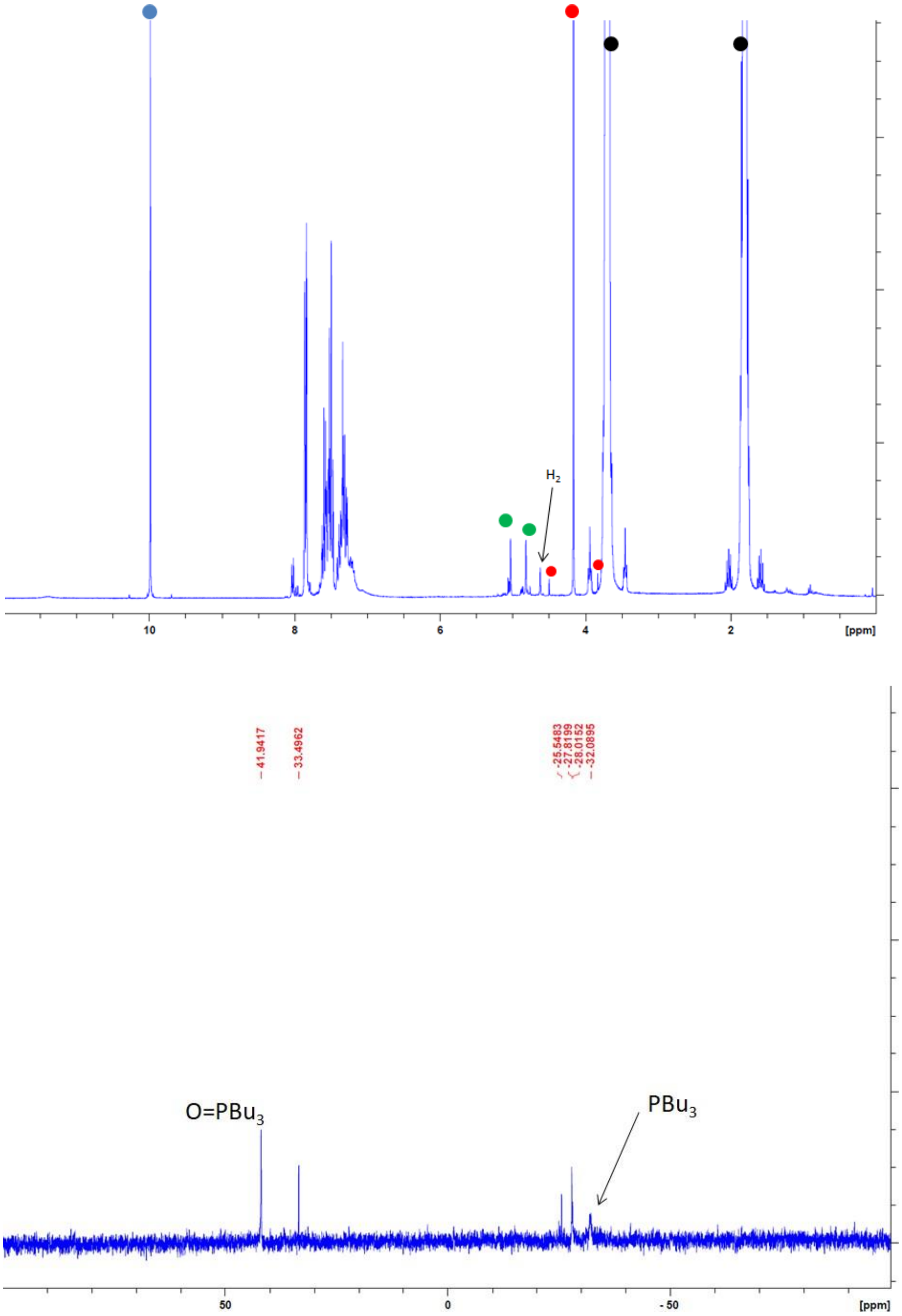
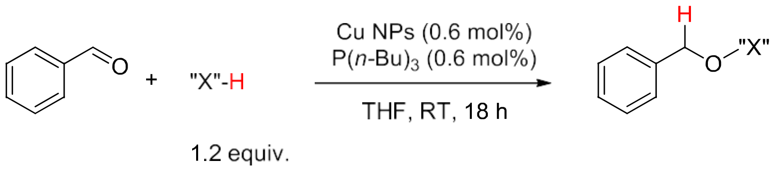
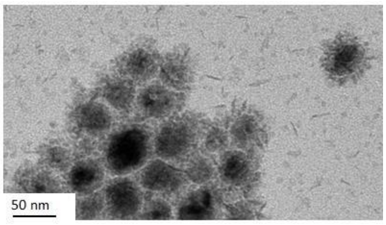
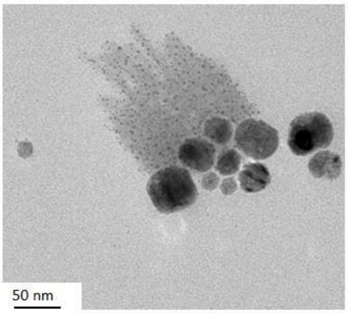
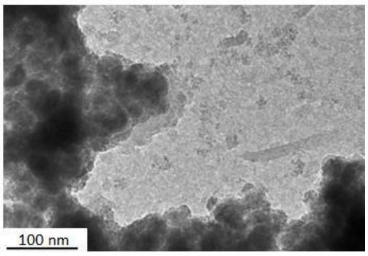
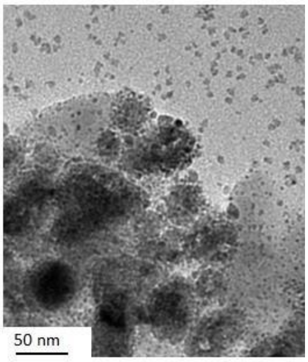
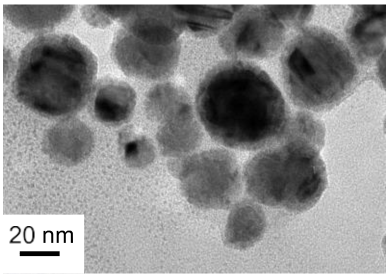


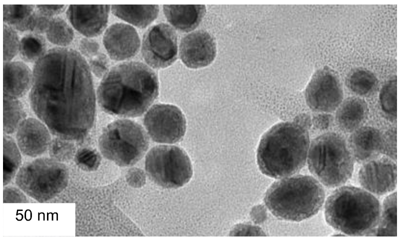
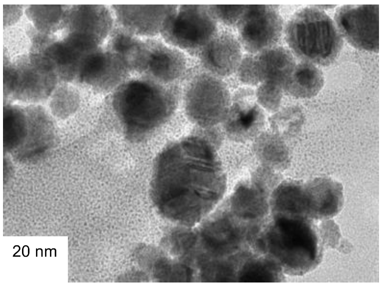
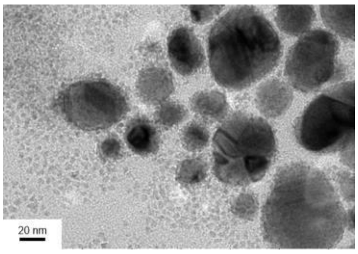
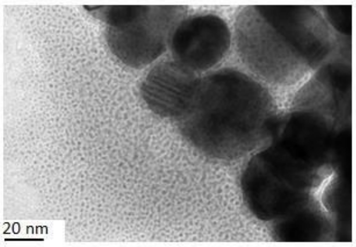
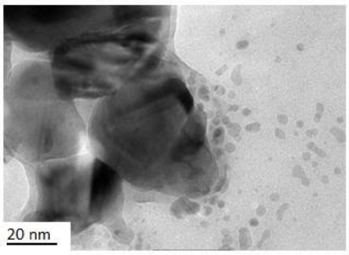
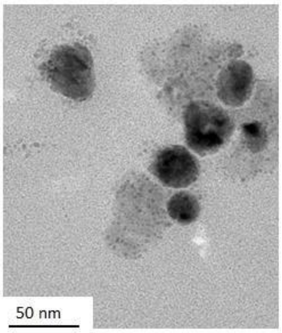
Figure S19 - ^{1}H NMR and $^{31}P\{^{1}H\}$ NMR spectra of the reaction crude (with Cu foil and P(*n*-Bu)$_3$).

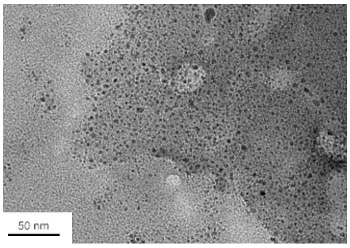
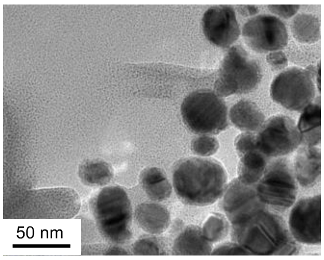
6. TEM imaging with various hydride sources



(XX)

Entry	Hydride source	Conversion[a]	TEM observation
1	$PhSiH_3$	>99%[b]	
2	Ph_2SiH_2	>99%	
3	$(EtO)_3SiH$	>99%	
4	TMDS	31%	
5	$PhMe_2SiH$	n.d.	

6	Et_3SiH	n.d.	
7	Ph_3SiH	n.d.	
8	PMHS	n.d.	
9(c)	NaH	>99%	
10	$NaBH_4$	>99%	
11	$(9\text{-BBN-H})_2$	>99%	

12	HCO_2NH_4	n.d.	
13	H_2	n.d.	

(a) ^{1}H NMR yield given for the conversion of benzaldehyde to the corresponding alcohol; n.d. = not detected (b) Complete after 20 min. (c) benzaldehyde is fully converted into benzyl benzoate.

Table S2 – TEM observations of table 2 of the main text.

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