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 ..........................................................2
2. Nanoparticles synthesis and characterizations ..................3
3. Reaction profiles using the ATR FTIR cell ......................6
4. Catalytic tests ..........................................................11
5. Experiments with pure Copper foil ..............................17
6. TEM imaging with various hydride sources ..................21
1. General details

All syntheses and procedures were carried under inert gas (N\textsubscript{2} or Ar) using an inert glovebox (H\textsubscript{2}O: ≤ 0.5 ppm, O\textsubscript{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 K\textalpha 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: \textsuperscript{1}H NMR, and \textsuperscript{31}P{}\textsuperscript{(1}H\textsuperscript{)} 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(\textsuperscript{1}H) = 7.26 ppm for the residual signal of CDCl\textsubscript{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)]\textsubscript{2} (>99.9% Aldrich), copper foil (thickness 0.25 mm, 99.98%), phenylsilane (97+% , Acros), diphenylsilane (97%, Aldrich), triphenylsilane (97%, Aldrich), triethoxysilane (95%, Aldrich), triethylsilane (99%, Acros), TMDS (1,1,3,3-tetramethyldisiloxane) (97%, Acros), PMHS (polymethylhydrosiloxane) (Fluka), (9-BBN-H)\textsubscript{2} (Aldrich), sodium borohydride (NaBH\textsubscript{4}) (98%, Alfa-Aesar), sodium hydride (NaH) (95%, Aldrich).
2. Nanoparticles synthesis and characterizations

Preparation of copper nanoparticles with oleylamine.

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 N₂ three times. Under N₂, [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 N₂, 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 N₂ flow and stored in a glovebox (H₂O: ≤ 0.5 ppm, O₂: ≤ 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.

![XRD on the powder of the isolated Cu NPs.](image)
\(^1\text{H} \text{NMR Analysis of the supernatant of the Cu NPs synthesis:}\)

![H NMR Analysis of the supernatant of the Cu NPs synthesis](image)

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

Two side-products could be identified in the crude after elimination of the Cu NPs and concentration under vacuum, by \(^1\text{H} \text{NMR and GC/MS. Comparison with the spectrum of pure OAm shows the complete conversion of OAm into various products. Among them, N-oleylacetamide (mass 309 g.mol}^1) \text{and oleanitrile (mass 263 g.mol}^1) \text{can be identified with signature chemical shifts at 3.22 ppm (q, } J = 7 \text{ Hz, N-CH} \text{, red dot), 1.96 ppm (s, COCH} \text{, blue dot) and 2.60 ppm (bs, NH, green dot) for N-oleylacetamide}^2 \text{ and 2.32 ppm (t, } J = 7 \text{ Hz, NC-CH}_2, \text{ orange dot), 1.65 ppm (quint., } J = 7 \text{ Hz, NC-CH}_2-\text{CH}_2-\text{CH}_2, \text{ purple dot) for oleanitrile.}^3\)
**ATR FT-IR cell at SMIS beamline (SOLEIL)**

![Figure S3 - FTIR cell used for the IR study](image)

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](image)

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), PhSiH₃ (0.24 mL) and P(n-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 PhSiH₃ (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-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-Bu)₃. Light-gray spectra as the first ones in the series. The last spectrum is the black one.](image)

Observations: no change of the signal of benzaldehyde (green dots), the ν(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 PhSiH₃ (0.240 mL) in THF (5 mL) is prepared. Under a flow of N₂, 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 ν(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 N₂, 0.1 mL of this solution is added to the FIIR 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.

![Reaction scheme](image)

**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.**

![Integration plot](image)

**Figure S9 - Integration of the υ(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 (5mL) 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), PhSiH₃ (0.24 mL) is added with a syringe on the layer of Cu NPs and the spectra are recorded every 80 s.

![Diagram showing reaction profile](image)

**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 PhMe₂SiH instead of PhSiH₃:

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), PhMe₂SiH (0.08 mL) and is added with a syringe on the layer of Cu NPs and the spectra are recorded every 80 s.

![Reaction profile diagram]

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 ¹H NMR in CDCl₃ to determine the conversion of benzaldehyde.

Figure S12 - ¹H NMR in CDCl₃ of aliquots of the reaction mixture: A = Benzaldehyde with (Cu NPs + P(n-Bu)_3 (0.6 mol%)) in THF; B = after addition of PhSiH₃, 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 \(^1\)H NMR in CDCl\(_3\) to determine the conversion of benzaldehyde. The results are detailed in Table S1.

![Chemical reaction diagram]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Phosphine</th>
<th>NMR yield(^{(a)}) (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>P((n)-Bu)(_3))</td>
<td>93%</td>
</tr>
<tr>
<td>2</td>
<td>PhBu(_3))</td>
<td>2%</td>
</tr>
<tr>
<td>3</td>
<td>PCy(_3))</td>
<td>59%</td>
</tr>
<tr>
<td>4</td>
<td>PPh(_3))</td>
<td>85%</td>
</tr>
<tr>
<td>5</td>
<td>dppBz(^{(b)}))</td>
<td>76%</td>
</tr>
<tr>
<td>6</td>
<td>Triphos(^{(c)}))</td>
<td>&lt;1%</td>
</tr>
</tbody>
</table>

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

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 CH₃CN (low energy)

Figure S14 - ESI positive mode in CH₃CN (low energy).
Figure S15 - ESI positive mode in CH$_3$CN (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 HNO₃ (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 HNO₃ 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, PhSiH₃ (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 ¹H NMR in CDCl₃ 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 $P(n$-$Bu)_3$

![Reaction Scheme](image)

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

![Chemical structure and NMR spectra](image)

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

![Diagram]

\[
\text{[Diagram showing TEM imaging process with various hydride sources]}
\]

<table>
<thead>
<tr>
<th>Entry</th>
<th>Hydride source</th>
<th>Conversion(^{(a)})</th>
<th>TEM observation</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>PhSiH(_3)</td>
<td>&gt;99(^{(b)})</td>
<td>![TEM image]</td>
</tr>
<tr>
<td>2</td>
<td>Ph(_2)SiH(_2)</td>
<td>&gt;99%</td>
<td>![TEM image]</td>
</tr>
<tr>
<td>3</td>
<td>(EtO)(_3)SiH</td>
<td>&gt;99%</td>
<td>![TEM image]</td>
</tr>
<tr>
<td>4</td>
<td>TMDS</td>
<td>31%</td>
<td>![TEM image]</td>
</tr>
<tr>
<td>5</td>
<td>PhMe(_2)SiH</td>
<td>n.d.</td>
<td>![TEM image]</td>
</tr>
<tr>
<td></td>
<td>Compound</td>
<td>Purity</td>
<td></td>
</tr>
<tr>
<td>---</td>
<td>--------------</td>
<td>--------</td>
<td></td>
</tr>
<tr>
<td>6</td>
<td>Et&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>7</td>
<td>Ph&lt;sub&gt;3&lt;/sub&gt;SiH</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>8</td>
<td>PMHS</td>
<td>n.d.</td>
<td></td>
</tr>
<tr>
<td>9&lt;sup&gt;(c)&lt;/sup&gt;</td>
<td>NaH</td>
<td>&gt;99%</td>
<td></td>
</tr>
<tr>
<td>10</td>
<td>NaBH&lt;sub&gt;4&lt;/sub&gt;</td>
<td>&gt;99%</td>
<td></td>
</tr>
<tr>
<td>11</td>
<td>(9-BBN-H)&lt;sub&gt;2&lt;/sub&gt;</td>
<td>&gt;99%</td>
<td></td>
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<td></td>
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<tr>
<td>---</td>
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</tr>
<tr>
<td>12</td>
<td>HCO₂NH₄</td>
<td>n.d.</td>
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</tr>
<tr>
<td>13</td>
<td>H₂</td>
<td>n.d.</td>
<td></td>
</tr>
</tbody>
</table>

(a) ¹H 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.

References


