SUPPLEMENTARY INFORMATION

DOI:

Title: A Straightforward Approach to Oxide-free Copper Nanoparticles by Thermal Decomposition of a Copper(I) Precursor

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1 Experimental

The synthesis of the copper(I) and copper(II) complexes were performed under non-inert conditions in undried solvents. Nanoparticle synthesis was performed with standard Schlenk techniques in an argon atmosphere with solvents dried by standard techniques and degassed by multiple freeze-pump-thaw cycles. The educts copper(II) acetate (monohydrate, Sigma-Aldrich, ACS reagent, ≥98%), 2-[2-(methoxyethoxy)ethoxy]acetic acid (Sigma-Aldrich, technical grade) and triphenylphosphine (Sigma-Aldrich, ReagentPlus®, 99%) were used without further purification.

Copper(II)  2-[2-(methoxyethoxy)ethoxy]acetate (1): 4.99 g (25 mmol) Copper(II) acetate (monohydrate) and 8.91 g (50 mmol) of 2-[2-(methoxyethoxy)ethoxy]acetic acid were dispersed in 2 L of toluene. An azeotropic mixture of toluene, water and acetic acid were added. The title complex was obtained as colourless viscous oil. Yield: 100%. Mp. 69 °C. Anal. calcd. for C_{65}H_{89}O_{12}P_{2}Cu (1027.54): C 71.30, H 5.92, found: C 71.14, H 5.66. FTIR (ATR): v = 3051 (w), 2874 (w), 1607 (s), 1585 (m), 1381 (w), 1184 (w), 1092 (s), 1026 (w), 998 (w), 851 (w), 741 (s), 692 (s), 618 (w) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.32 (s, 3H, OCH₃), 3.42–3.44 (m, 12H, CH₂), 3.53–3.55 (m, 18H, CH), 7.17–7.20 (m, 18H, CH), 7.23–7.26 (m, 27H, CH) ppm. ¹³C(¹H) NMR (CDCl₃): δ = 59.0 (s, OCH₃), 69.3 (s, CH₂), 70.5 (s, CH₃), 70.7 (s, CH₃), 71.1 (s, CH₂), 72.0 (s, OCOCH₂), 128.6 (d, mCH), 129.6 (s, OCH₃), 134.1 (d, CH, J_Cp = 17.8 Hz), 178.2 (s, OCO) ppm. ³¹P(¹H) NMR (CDCl₃): δ = -3.3 ppm. HRMS (ESI) m/z = 829.1157 (M + Na⁺).

Bis(triphenylphosphine)copper(I) 2-[2-(methoxyethoxy)ethoxy]acetate (3): 5.13 g (5 mmol) tris(triphenylphosphine)copper(I) 2-[2-(methoxyethoxy)ethoxy]acetate (2) were dissolved in 3 mL of dichloromethane. Under vigorous stirring, 500 mL of hexane were added. The title complex precipitated as colourless solid. Yield: 98%. Mp. 148 °C. Anal. calcd. for C₁₅₃H₁₇₇O₁₄P₃Cu (765.29): C 67.49, H 5.66, found C 67.16, H 5.86. FTIR (ATR): v = 3054 (w), 2877 (w), 1593 (s), 1434 (s), 1403 (m), 1314 (m), 1119 (m), 997 (w), 853 (w), 745 (s), 694 (s) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.28 (s, 3H, OCH₃), 3.42–3.44 (m, 2H, CH₂), 3.50–3.54 (m, 6H, CH₃), 3.88 (s, 2H, OCOCH₂), 7.14–7.17 (m, 12H, CH), 7.24–7.27 (m, 18H, CH) ppm. ¹³C(¹H) NMR (CDCl₃): δ = 59.0 (s, OCH₃), 69.8 (s, CH₂), 70.1 (s, CH₃), 70.4 (s, CH₂), 70.7 (s, CH₃), 71.9 (s, OCOCH₂), 128.8 (d, mCH), 132.4 (d, CH, J_Cp = 30.1 Hz), 133.8 (d, CH, J_Cp = 12.5 Hz), 176.5 (s, OCO) ppm. ³¹P(¹H) NMR (CDCl₃): δ = -0.5 ppm. HRMS (ESI) m/z = 829.1157 (M + Cu⁺).
Preparation of copper nanoparticles: Bis(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)-ethoxy]acetate (3) was dissolved in 10 mL of 1-hexadecylamine in the desired concentration (0.5 mM and 1.0 mM) at 50 °C under inert conditions. After preheating the solution to 250 °C it was heated to 330 °C at a constant heating rate of 25 K·min⁻¹. While keeping the temperature for 10 min the formation of copper nanoparticles was observed by a sudden reddening of the reaction mixture. After air-cooling and dissolving the solidified reaction mixture in 10 mL of n-hexane, the particles were precipitated by the addition of 20 mL of ethanol. A fraction of 5 mL was submitted to centrifugation (30 min, 5300 min⁻¹). The particles were redispersed in 5 mL of ethanol, isolated by centrifugation and redispersed in 5 mL of n-hexane for further analysis.
2 Spectroscopical data

2.1 IR data
All infrared spectra were recorded at ambient conditions as ATR-FTIR spectra by using a Biorad FTS-165 or a Nicolet iS 10 from Thermo Scientific.

IR spectrum of copper(II)-2-[2-(2-methoxyethoxy)ethoxy]acetate (1):

IR spectrum of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (2):
IR spectrum of bis(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (3):
2.2. NMR data
All $^1$H NMR spectra were recorded in CDCl$_3$ at 25 °C with a Bruker Avance III 500 spectrometer operating at 500.30 MHz in the Fourier transform mode; $^{13}$C($^1$H) NMR spectra were recorded at 125.80 MHz. Chemical shifts are given relative to the internal standard tetramethylsilane.

$^1$H and $^{13}$C($^1$H) NMR spectra of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (2):
$^1\text{H}$ and $^{13}\text{C}[^1\text{H}]$ NMR spectra of bis(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (3):
3. Additional TEM images

All TEM measurements were performed with a PHILIPS CM 20 FEG instrument operated at 200 kV.

0.5 mM sample:

1.0 mM sample:
4. X-Ray and electron diffractograms

The non-volatile decomposition products of the thermal decompositions have been investigated by X-ray powder diffraction using a STOE-STAD IP device with Cu Kα (λ = 154.184 pm) radiation.

X-Ray powder diffractogram of the decomposition product of 3:

Selected area electron diffractogram of copper nanoparticles (1.0 mM sample), edited with reflections of copper (fcc, a = 3.61 Å, left side), copper(I) oxide (right side, top) and copper(II) oxide (right side, bottom):