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-(2-methoxyethoxy)ethoxy]acetic acid (Sigma-Aldrich, technical grade) and triphenylphosphine (Sigma-Aldrich, ReagentPlus®, 99%) were used without further purification.

Copper(II) 2-[2-(2-methoxyethoxy)ethoxy]acetate (1): 4.99 g (25 mmol) Copper(II) acetate (monohydrate) and 8.91 g (50 mmol) of 2-[2-(2-methoxyethoxy)ethoxy]acetic acid were dispersed in 2 L of toluene. An azeotropic mixture of toluene, water and acetic acid was distilled of. As soon as the boiling point of the pure solvent was reached, the residual solvent was removed *in vacuo* to yield the title complex as green viscous oil. Yield: 100 %. Anal. calcd. for $C_{14}H_{36}O_{10}Cu$ (417.19): C 42.72, H 6.77, found: C 42.54, H 6.97. FTIR (ATR): $\tilde{\nu}$ = 2873 (m), 1635 (s), 1575 (s), 1416 (m), 1329 (m), 1199 (w), 1081 (s), 1027 (w), 931 (w), 850 (w), 723 (w) cm^{-1}. HRMS (ESI): m/z = 440.0714 (M + Na$^+$).

Tris(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)ethoxy]acetate (2): 10.45 g (25 mmol) copper(II) 2-[2-(2-methoxyethoxy)ethoxy]acetate, 22.95 g (87.5 mmol) triphenylphosphine and 0.23 mL (12.5 mmol) of water were dissolved in 150 mL of methanol. The reaction mixture was boiled until it became colourless. Upon cooling, the title complex precipitated. After recrystallisation from methanol the title complex was obtained as colourless material. Yield: 65 %. Mp. 69 °C. Anal. calcd. for $C_{61}H_{58}O_5P_3Cu$ (1027.54): C 71.30, H 5.92, found: C 71.14, H 5.66. FTIR (ATR): $\tilde{\nu}$ = 3051 (w), 2874 (w), 1607 (s), 1585 (m), 1480 (m), 1381 (m), 1307 (w), 1184 (w), 1092 (s), 1026 (w), 998 (w), 851 (w), 741 (s), 692 (s), 618 (w) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.28 (s, 3H, OCH_3), 3.37–3.53 (m, 12H, CH_2), 3.88 (s, 2H, OCOCH_2), 7.17–7.20 (m, 18H, CH), 7.23–2.26 (m, 27H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 59.0 (s, OCH$_3$), 69.3 (s, CH$_2$), 70.5 (s, CH$_2$), 70.7 (s, CH$_2$), 71.1 (s, CH$_2$), 72.0 (s, OCOCH$_2$), 128.6 (d, ^{m}CH, $^{3}J_{CP}$ = 8.4 Hz), 129.6 (s, ^{p}CH), 133.9 (d, ^{o}CH, $^{2}J_{CP}$ = 16.3 Hz), 134.1 (d, ^{i}CH, $^{1}J_{CP}$ = 17.8 Hz), 178.2 (s, OCO) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = -3.3 ppm. HRMS (ESI) m/z = 829.1157 (M – PPh$_3$ + Cu$^+$).

Bis(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)ethoxy]acetate (3): 5.13 g (5 mmol) tris(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)ethoxy]acetate (**2**) were dissolved in 3 mL of dichloromethane. Under vigorous stirring, 500 mL of ^{n}hexane were added. The title complex precipitated as colourless solid. Yield: 98 %. Mp. 148 °C, Anal. calcd. for $C_{43}H_{43}O_5P_2Cu$ (765.29): C 67.49, H 5.66, found C 67.16, H 5.86. FTIR (ATR): $\tilde{\nu}$ = 3054 (w), 2877 (w), 1593 (s), 1481 (s), 1434 (s), 1403 (m), 1314 (m), 1119 (m), 1094 (s), 1026 (m), 997 (w), 853 (w), 745 (s), 694 (s) cm^{-1}. ^{1}H NMR ($CDCl_3$): δ = 3.28 (s, 3H, OCH_3), 3.42–3.44 (m, 2H, CH_2), 3.50–3.52 (m, 6H, CH_2), 3.88 (s, 2H, OCOCH_2), 7.14–7.17 (m, 12H, CH), 7.24–7.27 (m, 18H, CH) ppm. ^{13}C{^{1}H} NMR ($CDCl_3$): δ = 59.0 (s, OCH$_3$), 69.8 (s, CH$_2$), 70.1 (s, CH$_2$), 70.4 (s, CH$_2$), 70.7 (s, CH$_2$), 71.9 (s, OCOCH$_2$), 128.8 (d, ^{m}CH, $^{3}J_{CP}$ = 3.4 Hz), 129.9 (s, ^{p}CH), 132.4 (d, ^{i}CH, $^{1}J_{CP}$ = 30.1 Hz), 133.8 (d, ^{o}CH, $^{2}J_{CP}$ = 12.5 Hz), 176.5 (s, OCO) ppm. ^{31}P{^{1}H} NMR ($CDCl_3$): δ = -0.5 ppm. HRMS (ESI) m/z = 829.1157 (M + Cu$^+$).

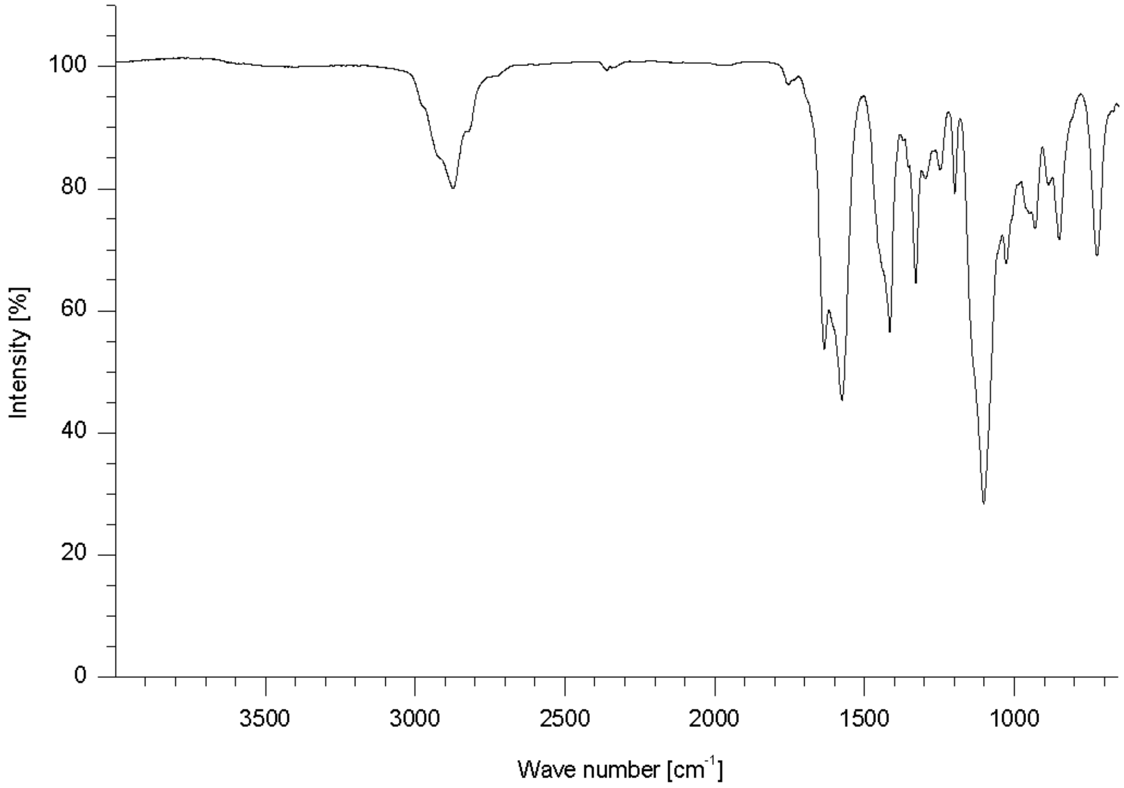
Preparation of copper nanoparticles: Bis(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)-ethoxy]acetate (**3**) was dissolved in 10 mL of 1-hexadecylamine in the desired concentration (0.5 mM and 1.0 mM) at 50 °C under inert conditions. After preheating the solution to 250 °C it was heated to 330 °C at a constant heating rate of 25 $\mathrm{K \cdot min^{-1}}$. 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 $\mathrm{min^{-1}}$). 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

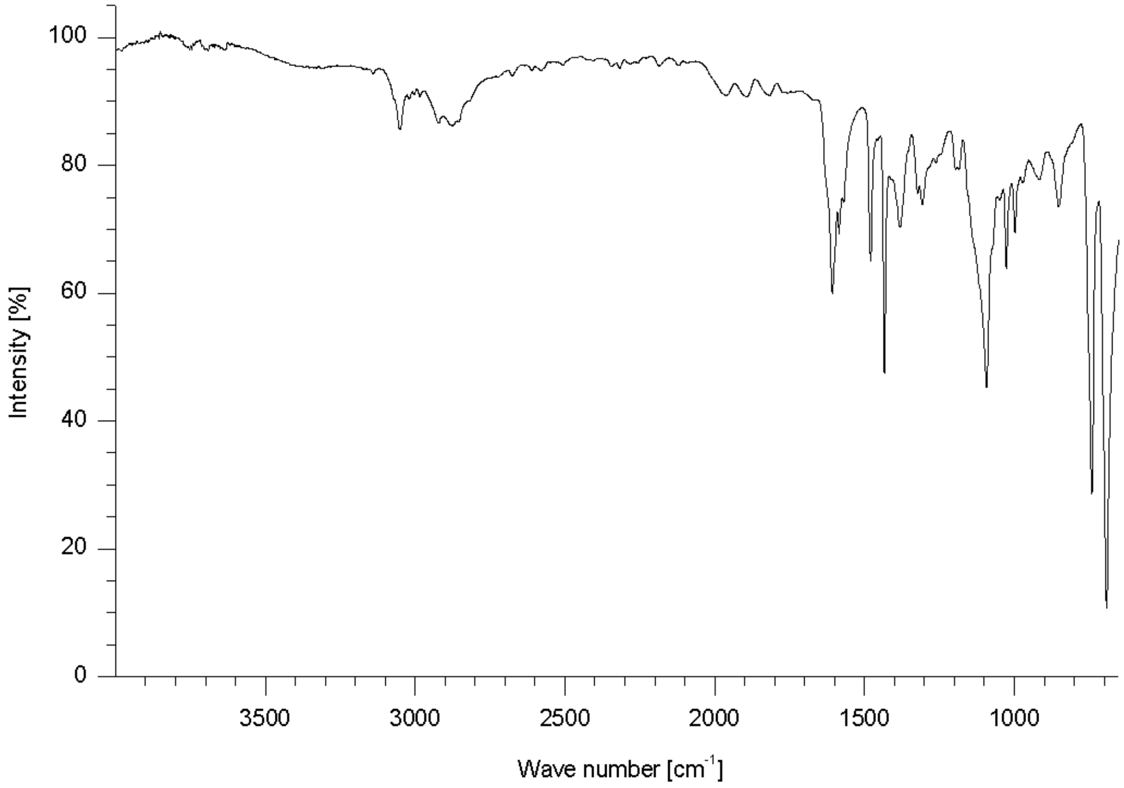
2.1 IR data

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.

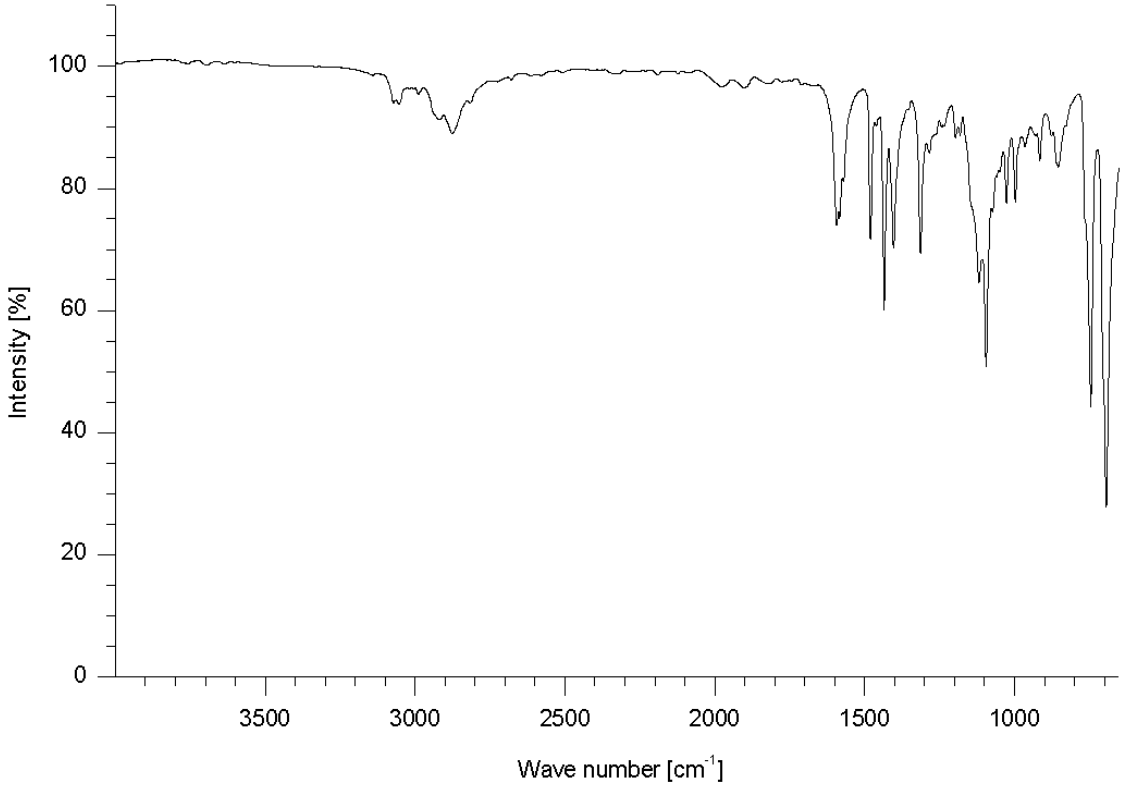
IR spectrum of copper(II)-2-[2-(2-methoxyethoxy)ethoxy]acetate (**1**):



IR spectrum of of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (**2**):



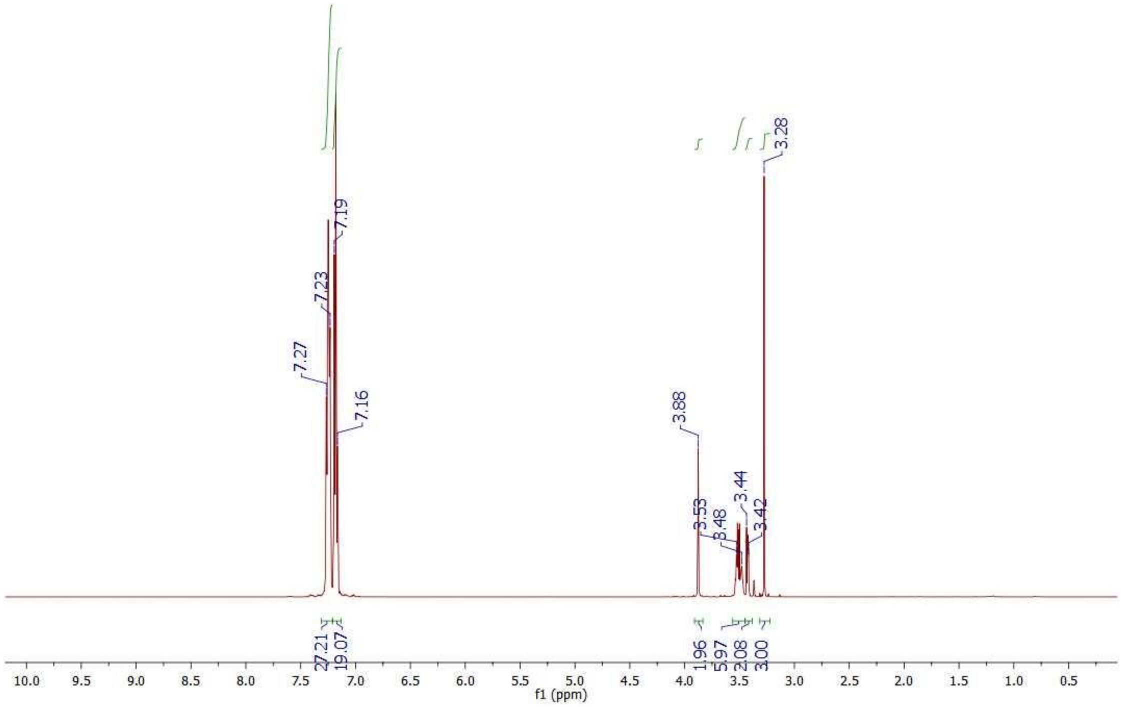
IR spectrum of of bis(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (**3**):

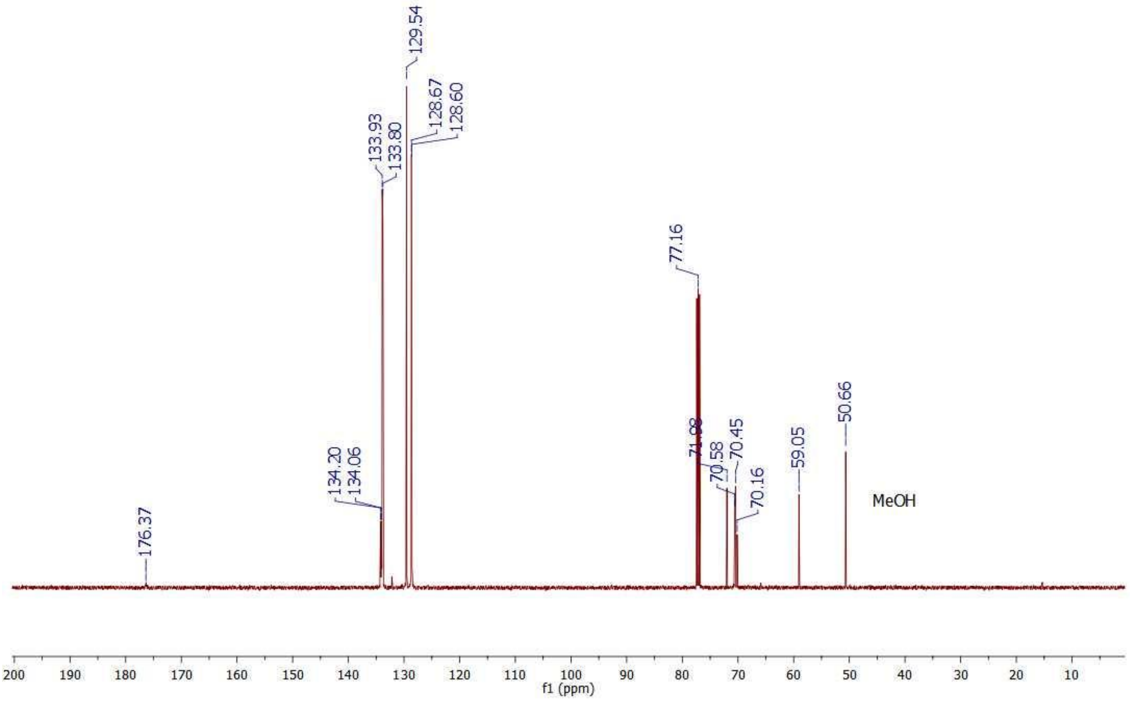


2.2. NMR data

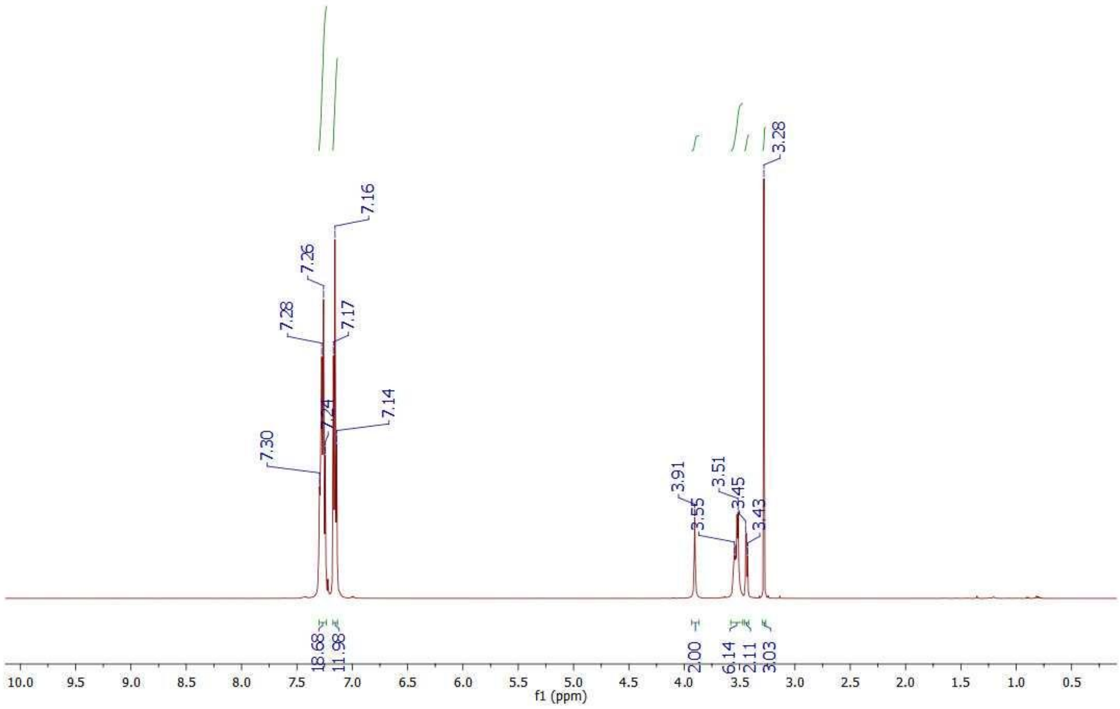
All ^{1}H NMR spectra were recorded in $CDCl_3$ at 25 °C with a Bruker Avance III 500 spectrometer operating at 500.30 MHz in the Fourier transform mode; $^{13}C\{^1H\}$ NMR spectra were recorded at 125.80 MHz. Chemical shifts are given relative to the internal standard tetramethylsilane.

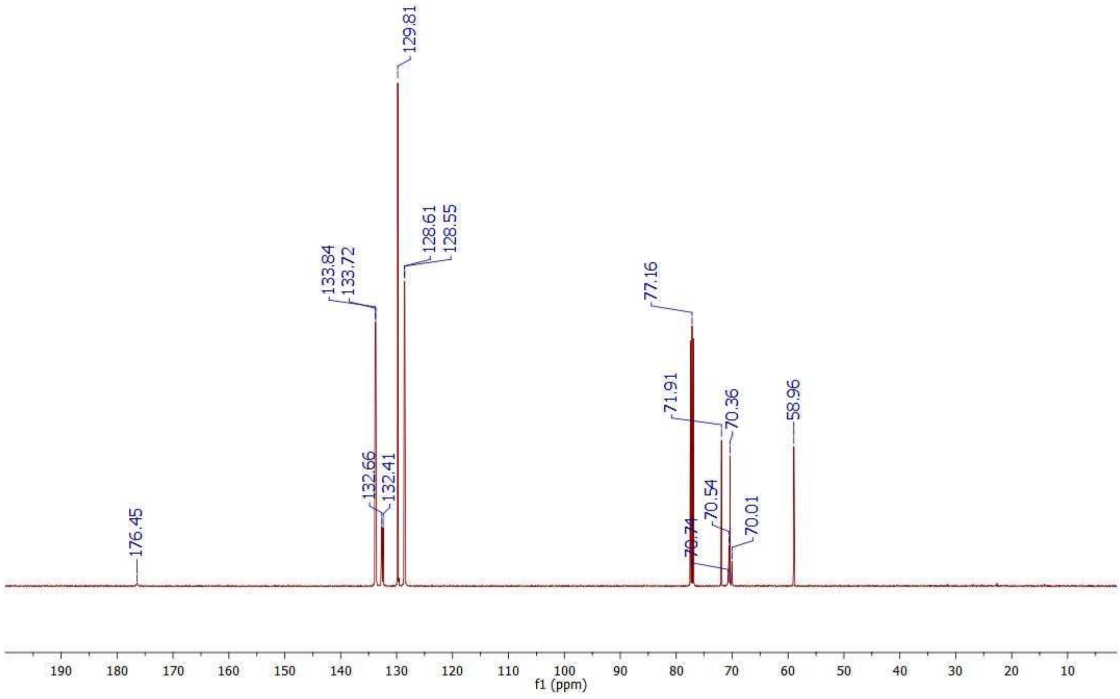
^{1}H and $^{13}C\{^1H\}$ NMR spectra of tris(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (**2**):





^{1}H and ^{13}C{^{1}H} NMR spectra of bis(triphenylphosphine)copper(I)-2-[2-(2-methoxyethoxy)ethoxy]acetate (**3**):

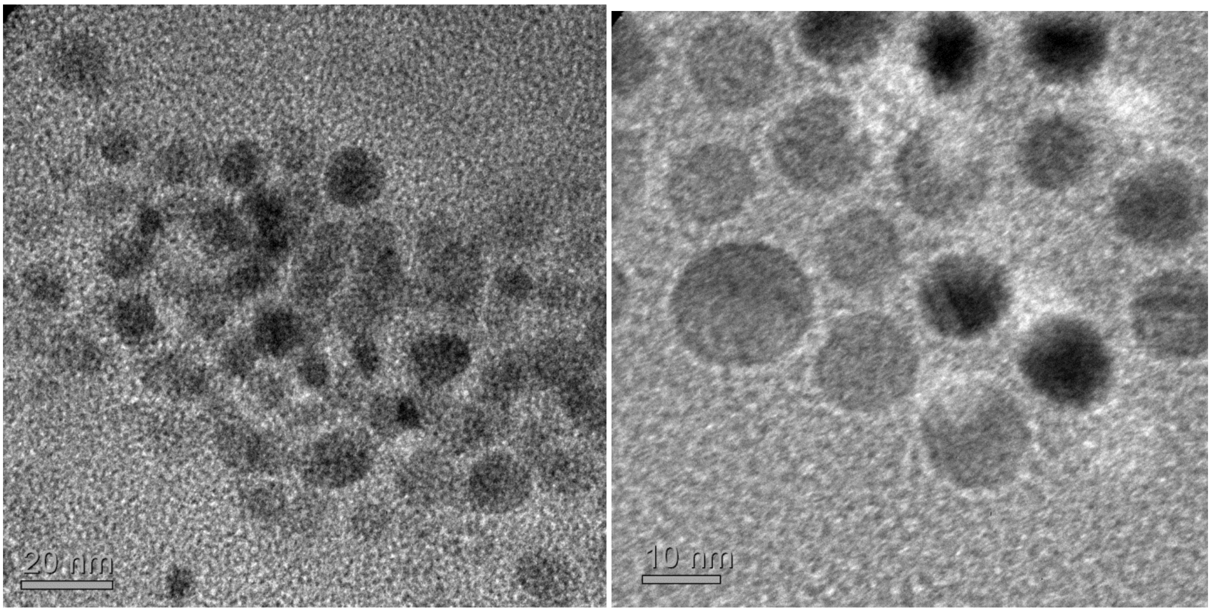




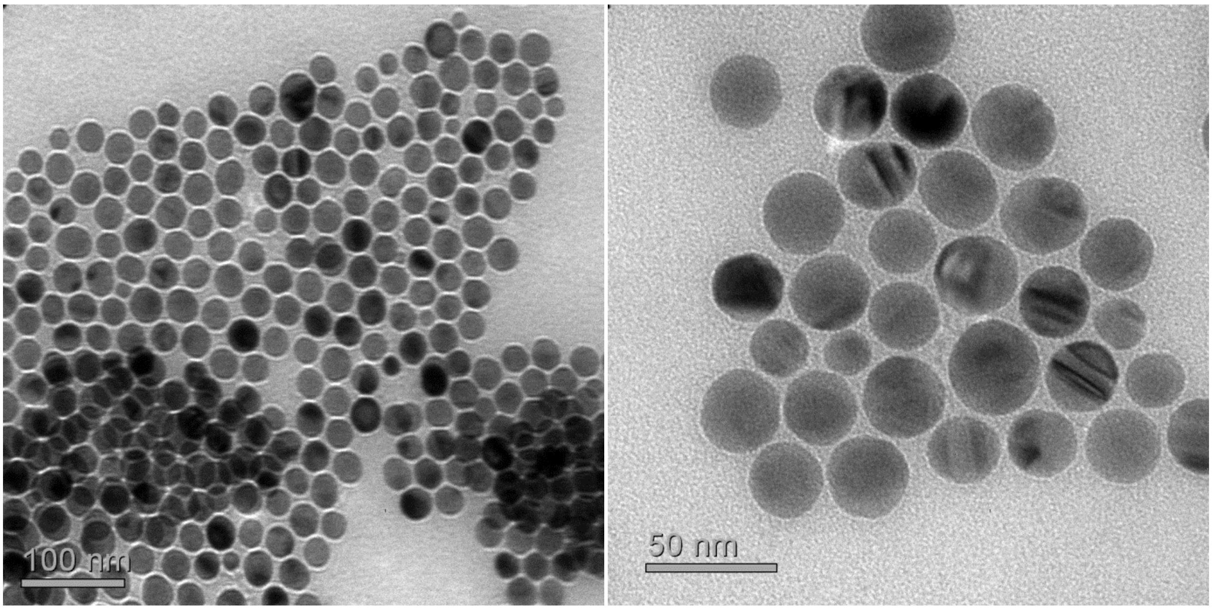
3. Additional TEM images

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

0.5 mM sample:



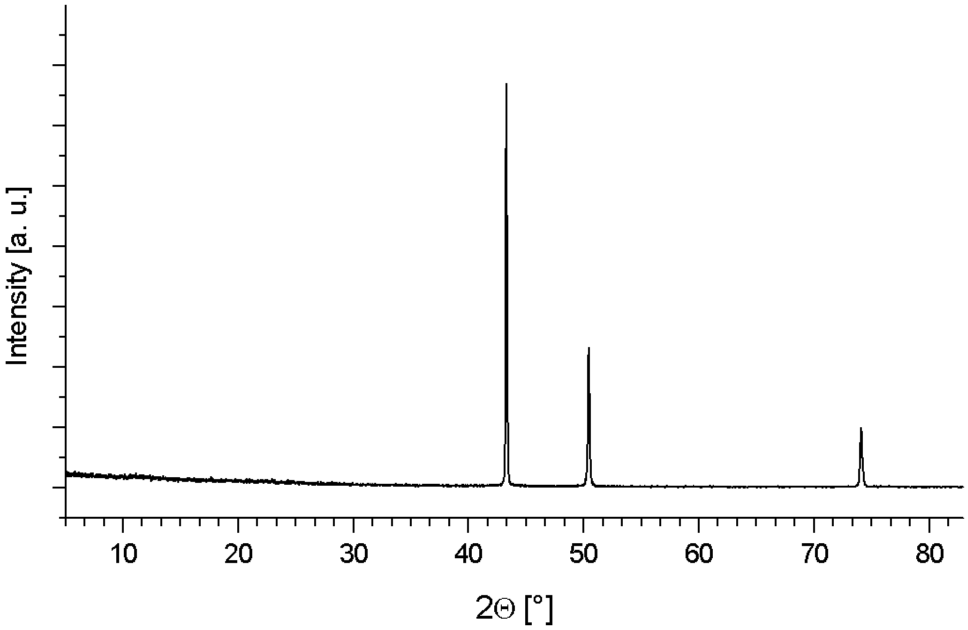
1.0 mM sample:



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 K_α (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):