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1 Introduction

Persistent innovations in the field of nanotechnology led to the development of numerous new methods for the preparation of copper nanoparticles, among which are the preparation in micelles,¹ spray pyrolysis,² sputtering approaches,³ nanosphere lithography,⁴ chemical vapor deposition (CVD)⁵ as

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Copper(II) and triphenylphosphine copper(I) ethylene glycol carboxylates: synthesis, characterisation and copper nanoparticle generation + +

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Ethylene glycol-functionalised copper(II) carboxylates $Cu[O_2CCR_2(OC_2H_4)_nOCH_3]_2$ (n = 0-3; R = H, Me) (2a–e) have been prepared by the reaction of $[Cu_2(OAC)_4:2H_2O]$ with $CH_3O(C_2H_4O)_nCR_2CO_2H$ (1a–e). Upon reduction of 2a–e with triphenylphosphine, the corresponding tris(triphenylphosphine)copper(I) complexes 3a–e were obtained, which could be converted to the bis(triphenylphosphine)copper(I) complexes 4a–e by removal of one phosphine ligand. Based on IR spectroscopy and single crystal X-ray structure analysis the binding motif of the carboxylato group on the copper ion is discussed. DSC, TG and TG-MS experiments were performed to analyse the thermal decomposition mechanism of 2–4. Complex 4c was used as a precursor for the generation of copper nanoparticles by thermal decomposition in hexadecylamine without the need of any further reactants. Depending on the precursor concentration, spherical copper nanoparticles with a mean diameter ranging from 10 to 85 nm as well as nanorods with a length of up to 1.3 µm (aspect ratios ranging between 2 and 32) were obtained. Electron diffraction analysis of the rods suggested that they consist of five domains which are arranged around a fivefold rotational axis.

well as sonochemical⁶ and sonoelectrochemical methods.⁷ These techniques are alternatives to the traditional three-component approach in which copper nanoparticles are prepared by adding a reducing agent to a solution of a copper compound in the presence of a stabilising agent.⁸

A non-classical nanoparticle preparation method with growing importance is the single-source precursor approach which aims to simplify the particle generation process by combining two or three of the traditional components (*vide supra*) in one molecule.⁹ Usually, the compounds used as precursors are metal–organic complexes which decompose thermally to generate the respective copper(0), *e.g.* by the decomposition of copper(π) acetylacetonate at 230 °C in oleylamine.^{9c, f,i}

The thermal decomposition route for nanoparticle synthesis has considerable advantages, *e.g.* it allows easy reaction control because the system is much less complex than in multi-component approaches. Usually the decomposition is a reaction of first order and no injection rates or concentration effects have to be considered, which provides a high reproducibility.^{9b} No addition of strong reducing agents such as hydrazine is necessary; this simplifies the application of the particles in catalytic or biological processes and makes the actual particle generation more secure and economical.¹⁰ Despite the low complexity of the reaction system systematic

[†] Dedicated to Prof. Dr Werner Uhl, Universität Münster, on the occasion of his $60^{\rm th}$ birthday.

 $[\]pm$ Electronic supplementary information (ESI) available: IR and NMR (¹H, ¹³C{¹H}) spectra, crystal structures and data, TG and TG-MS measurements, XRPD data, additional TEM images, electron diffractograms. CCDC 932855–932857 and 933501. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt51913a

optimisation is possible, *e.g.* by variation of the chemical structure of the precursor.

A common family of single-source precursors for the generation of copper is its carboxylates. In the absence of oxygen they are known to generate copper(0) by decarboxylation at temperatures between 200 and 300 °C.¹¹ For the solution synthesis of copper nanoparticles a variety of carboxylates such as copper(1) acetate, ^{9f,g} copper(1) formate, ^{9d} copper(1) oxalate^{9e} and copper(1) hydrazine carboxylate^{9a} have been investigated. Besides carboxylates, copper CVD precursors, such as copper(1) acetylacetonate^{9c,f,i} and copper(1) 1-dimethylamino-2-propanolate, ^{9b} were used.

Despite the large number of investigated precursors, systematic optimisation of the precursor properties is rarely performed. One of the most prevalent problems in all investigated precursors is reported to be the high oxidation sensitivity of the particle generation process, which often prevented the isolation of pure copper nanoparticles^{9c,d,f} or demanded advanced working techniques such as the use of gloveboxes.^{9b,i} This issue is due to the limited number of reducing equivalents, which does not exceed one in all mentioned precursors. An easy way to raise the number of reducing equivalents and thus to lower the oxidation sensitivity of the particle preparation process is the use of phosphine copper(1) carboxylates, since phosphine ligands possess reducing properties. Furthermore, triphenylphosphine copper(1) carboxylates are stable species which are easy to handle and to synthesise.¹²

Recently, we reported about the use of ethylene glycol-functionalised metal carboxylates for the straightforward generation of silver,¹³ gold¹⁴ and rhodium¹⁵ nanoparticles at low temperatures. Thermally initiated decarboxylation was used to afford reactive metal(0) colloids, whereas the ethylene glycol chains were sufficient to stabilise the nanoparticles of silver and gold even in non-coordinating solvents. First results concerning the synthesis and characterisation of bis(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)ethoxy]acetate (4c) and its use as a single-source precursor for the generation of spherical copper nanoparticles were reported lately.¹⁶ Herein, we give a full report of the synthesis and characterisation of a series of novel copper(I) and copper(II) ethylene glycol carboxylates. In addition, the application of 4c to the solution synthesis of spherical as well as rod-like copper nanoparticles without the addition of any reducing agents is described.

2 Synthesis and characterisation

The ethylene glycol-functionalised copper(π) carboxylates **2a–e** have been prepared by an anion exchange reaction of the carboxylic acids CH₃O(C₂H₄O)_nCR₂CO₂H (n = 0-3; R = H, Me) (**1a–e**) with copper(π) acetate hydrate (Scheme 1). Acetic acid and water were removed from the reaction mixture by an azeotropic distillation with toluene as entrainer, thus shifting the equilibrium to the product side. After removal of the solvent no further workup was necessary. The acids **1a–c** were commercially available, **1d–e** have been synthesised by the reaction of the corresponding methyl ethylene glycol with 2-bromo-2-methylpropanoic acid or 2-bromoacetic acid (see the Experimental section for details).¹⁷

Copper(π) methoxyacetate **2a** was obtained as a green solid, whereas **2b–e** are green oils which show a decrease of viscosity with increasing chain length. They are highly soluble in protic and aprotic solvents, *e.g.* in water as well as in toluene. The identity of the paramagnetic copper(π) carboxylates was proven by elemental analysis, IR spectroscopy and ESI-TOF mass spectrometry.

The tris(triphenylphosphine)copper(I) carboxylates 3a-e are accessible by the reaction of the copper(II) carboxylates 2a-e with 3.5 equiv. of triphenylphosphine in the presence of 0.5 equiv. of water, of which copper(II) is reduced to copper(I) by 0.5 equiv. of the phosphine.¹² The reaction involves a nucleophilic attack of the carboxylate on the phosphine and the hydrolysis of the resulting phosphonium ion by water to form triphenylphosphine oxide and the corresponding carboxylic acid. Three molar equivalents of PPh₃ act as ligands to stabilise the soft copper(I) ion. After recrystallisation from methanol, the products are obtained as colourless, air stable solids. One of the three ligands is bound only weakly to the metal and can be removed by two-solvent recrystallisation, *i.e.* by solving the compounds in dichloromethane and adding ^{*n*}hexane. In this manner the bis(triphenylphosphine)copper(1) carboxylates 4a-e were obtained as colourless solids. Analyses of 3-4 included elemental analysis, IR and NMR spectroscopy (¹H, ¹³C{¹H}, ³¹P{¹H}), ESI-TOF mass spectrometry as well as singlecrystal X-ray structure analysis.

IR-spectroscopy has proven to be a fast and in most cases reliable method to investigate the binding motif of the carboxylato group to a metal.¹⁸ With reference to ionic carboxylates



Scheme 1 Synthesis of the ethylene glycol-functionalised copper(II) and copper(I) carboxylates 2–4: (i) toluene, 111 °C, 5 h, azeotropic distillation; (ii) 3.5PPh₃, 0.5H₂O, MeOH, 65 °C, 3 h; (iii) two-solvent recrystallisation from dichloromethane/ⁿhexane.

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(e.g., their sodium or potassium salts), bridging and chelating carboxylates show a smaller difference $\Delta \tilde{\nu}_{CO_2}$ of the symmetric and asymmetric $\tilde{\nu}_{CO_2}$ valence absorptions, whereas monodentate bonded groups show a significantly increased $\Delta \tilde{\nu}_{CO_2}$. As reference substances we prepared the potassium carboxylates of the acids 1c and 1d,¹⁹ their $\tilde{\nu}_{CO_2}$ differences were found to be 185 cm⁻¹ and 193 cm⁻¹, respectively.

The $\tilde{\nu}_{CO_2}$ values of complexes 2 are indicative of monodentate coordination (Table 1). This corresponds well to the crystal structures of the hydrates of 2a and 2b as determined by Rossotti et al.²⁰ and Hawkins et al.²¹ In contrast to the well known dimeric paddle-wheel structure of copper(II) acetate hydrate, monomeric structures with $\eta^1\mbox{-bonded}$ carboxylato groups were found in which one ether oxygen per chain completes the coordination sphere of the metal. For the tris(triphenylphosphine)copper(I) carboxylates 3a-e the $\Delta \tilde{\nu}_{CO_2}$ values are between 223 cm⁻¹ (**3b**) and 230 cm⁻¹ (**3e**). This indicates a monodentate binding motif, which was confirmed by X-ray structure analysis for 3a, b and d (see ESI[‡]). For the bis(triphenylphosphine) compounds 4a–e the $\Delta \tilde{\nu}_{CO_2}$ values are generally smaller than for 2 and 3. This resembles the expected trend to η^2 -bonded carboxylato groups which compensate for the missing third ligand. However, the $\Delta \tilde{\nu}_{CO_2}$ values show a distinct variation, ranging from 153 cm⁻¹ to 190 cm⁻¹. For 4b and d (153 and 154 cm $^{-1}$, resp.) η^2 -bounded carboxylato groups can be assumed but no certain conclusions can be made about 4a, c and e (166–190 cm^{-1}), since these values are close to the values of the respective potassium salts (vide supra).

For a precise investigation of the questionable structures 4a-e we performed single crystal X-ray structure analysis (Fig. 1), out of which we recently reported the structure of 4c.¹⁶ The remaining complexes crystallise in monoclinic $(P2_1/n, 4e)$, triclinic (*P*1; 4a and d) or orthorhombic (*Pbca*, 4b) space groups without any additional solvent molecules. Selected bond lengths and angles are summarised in Table 2, while selected crystallographic and measurement data are given in the ESI.‡

Complexes 4a, b, d and e show a similar structure to the copper(I) ion situated in the expected distorted tetrahedral arrangement formed by the two PPh₃ ligands and the two oxygen atoms of the bidentate carboxylato group. The P1-Cu1-P2 angle is enlarged due to the spatially demanding triphenylphosphine units, whereas the O1-Cu1-O2 angle is significantly smaller since it is part of a four-membered ring. Complexes 4b and 4d evince quite similar Cu-O-bond lengths which correlate well with the small differences of the $\Delta \tilde{\nu}_{CO_{2}}$ valence absorptions (Table 1). In complexes 4a and e the Cu-Obond lengths differ more, but the carboxylato group is still clearly η^2 -bond in both cases. With these results, the structures of 4a, b, d and e are in contrast to the structure of 4c, for which we found a n¹-bonded carboxylato group.¹⁶ Furthermore, we noted a distinct intermolecular van der Waals interaction

Table 1 \tilde{v}_{CO_2} absorptions and $\Delta \tilde{v}_{CO}$ values for complexes 2–4

Compd.	$\Delta \tilde{v}_{\mathrm{CO}_2} [\mathrm{cm}^{-1}]$	$\Delta \tilde{v}_{\mathrm{CO}_2} [\mathrm{cm}^{-1}]$	$\Delta \tilde{\nu}_{\rm CO_2}{}^a [{\rm cm}^{-1}]$
2a	1393	1602	209
2b	1415	1630	215
2c	1416	1635	219
2d	1412	1625	213
2e	1416	1635	219
3a	1373	1597	224
3b	1373	1596	223
3c	1381	1607	226
3d	1380	1599	229
3e	1379	1599	230
4a	1407	1582	175
4b	1410	1564	153
4c	1403	1593	190
4d	1402	1556	154
4e	1433	1599	166

 ${}^{a}\Delta\tilde{\nu}_{\rm CO_2} = \tilde{\nu}_{\rm CO_2, asym} - \Delta\tilde{\nu}_{\rm CO_2, sym}.$

Table 2 Selected bond lengths [Å] and angles [°] of 4a, b, d and e^a

	4a	4b	4d	4e
Cu1-P1	2.2410(8)	2.2074(6)	2.2218(7)	2.2526(6)
Cu1-P2	2.2507(7)	2.2504(6)	2.2533(7)	2.2048(6)
Cu1-O1	2.1126(18)	2.1388(15)	2.1959(19)	2.1202(14)
Cu1-O2	2.3575(19)	2.2556(16)	2.2193(19)	2.3013(14)
C1-O1	1.254(3)	1.257(3)	1.257(3)	1.256(2)
C1-O2	1.242(3)	1.250(3)	1.2611(3)	1.261(2)
P1-Cu1-P2	125.81(3)	132.75(2)	129.50(3)	131.72(2)
O1-Cu1-O2	58.58(6)	60.30(6)	60.13(7)	59.93(5)
O1-C1-O2	123.4(2)	123.6(2)	123.0(2)	123.22(19)
P1-Cu1-O1	104.54(5)	102.23(5)	100.77(6)	98.76(4)
P2-Cu1-O2	116.64(5)	116.05(5)	109.88(5)	117.16(4)

^a The estimated standard deviations of the last significant digits are shown in parentheses.



Fig. 1 ORTEP diagrams (50% probability level) of 4a, 4b, 4d and 4e (from left to right). In the case of 4b, only one conformation of the disordered chain is shown. All hydrogen atoms are omitted for clarity.

between the ethylene glycol chains in **4c** and **d**, which might serve as an explanation for the aberrant structure of **4c**.

3 TG, DSC and TG-MS investigations

The thermal behaviour of 2–4 was studied by thermogravimetry (TG) and differential scanning calorimetry (DSC) to gain information on the decomposition temperature and the degradation mechanism of these species. Exemplarily, the TG and DSC traces of **2b** and **4b** are shown in Fig. 2. Please notice that the traces of the tris(triphenylphosphine)copper(1) complexes **3** are similar to that of the bis(triphenylphosphine) carboxylates **4** and hence are depicted in the ESI‡ along with further TG traces of complexes **2** and **4**.

The thermal decomposition of the monosubstituted carboxylate 2b starts at an onset temperature of 220 °C (Fig. 2).

Fig. 2 Thermal decomposition of copper carboxylates **2b** (top) and **4b** (bottom). Upper parts: TG, TG' and DSC traces; lower parts: selected MS scans of the decomposition products. Fragments: m/z = 29 (C₂H₂⁺), 31 (OCH₃⁺), 44 (CO₂⁺, C₂H₄O⁺), 45 (C₂H₅O⁺), 60 (C₂H₄O₂⁺), 78 (C₆H₆⁺), 89 (CH₃OC₂H₄OCH₂⁺), 108 (C₆H₅P⁺). Ar gas flow 60 mL min⁻¹, heating rate 5 K min⁻¹.

Complexes **2a**, **c** and **e** have the same decomposition temperature, whereas the decomposition of the dimethyl-substituted derivate **2d** starts already at 190 °C. The significant lower decomposition temperature of **2a–e** in comparison with copper(π) acetate (260 °C) can be explained by a lower energy of the radical decarboxylation products due to the presence of the stabilising aliphatic groups. The residual masses of all samples fit well to the copper content of the compounds. The identity of the residues was proven by X-ray powder diffraction (XRPD) measurements, confirming the formation of elemental copper (see ESI‡). The first derivative of the TG curve indicates that the decomposition occurs in two steps. The DSC measurement shows both to be endothermic processes.

The TG traces of the bis- and tris(triphenylphosphine) complexes **3** and **4** show mass decays starting slowly at *ca*. 200 °C and ending at 330 °C. No dependence of the decomposition temperature on the degree of substitution at the α -position of the carboxylato group is found. The residual masses of all probes fit well to the exclusive formation of copper. The DSC measurements show melting points ranging from 52 to 132 °C (**3e** and **3a**, resp.) for the tris(triphenylphosphine)copper(1) carboxylates and from 110 °C to 181 °C (**4e** and **4b**, resp.) for the bis(triphenylphosphine)copper(1) compounds. The thermal decompositions give rise to single endothermic signals in the DSC studies.

TG-MS studies have been performed to investigate the decomposition behaviour of 2–4 in detail (2 and 4: Fig. 2; 3: ESI‡). The two decomposition steps of the copper(II) carboxylate **2b** can be clearly distinguished by the observation of different characteristic fragments. The first step is characterised by the mass fragments m/z = 44 (CO₂⁺) as well as m/z = 28 (CO) and m/z = 22 (CO₂⁺⁺) (both not shown), indicating the step to be a decarboxylation. It involves homolytic C–C- and C–O-bond cleavage and is accompanied by the formation of copper(0). The remaining organic radicals might decompose or recombine to form longer ethylene glycol chains. The second decomposition step is observed at higher temperatures and gives rise to fragments such as m/z = 29 (C₂H₅⁺), 31 (OMe⁺), 45 (C₂H₅O⁺) and 60 (C₂H₄O₂⁺) as well as to the ion characteristic for the intact chain at m/z = 89 (CH₃OC₂H₄OCH₂⁺).

Regarding **4b**, the typical fragmentation products of triphenylphosphine (m/z = 78, 108) are observed to begin at a temperature of *ca.* 200 °C, which proves that the decomposition starts with the loss of the phosphine ligands. A similar behaviour has been described by W. Reichle *et al.* for tris(triphenylphosphine)copper(i) chloride²² and was also found for bis-(tri^{*n*}butylphosphine)copper(i) carboxylates.²³ In a second decomposition step beginning at a temperature of 260 °C, decarboxylation and decomposition of the chain are observed as simultaneous processes by fragment formation of m/z =31 (OMe⁺), 44 (CO₂⁺) and 60 (C₂H₄O₂⁺).

The formation of metallic copper by thermolysis of **2–4** in defined decomposition mechanisms makes the compounds suitable precursors for the generation of copper(0) in various applications, *e.g.* in the preparation of copper nanoparticles or in metal–organic inks.



4 Nanoparticle formation and characterisation

The copper(I) and copper(I) carboxylates 2-4 were applied as precursors in the solution synthesis of copper nanoparticles without the addition of any reducing agents. As a high-boiling solvent we have chosen 1-hexadecylamine (mp. 40 °C, bp. 330 °C), which is available in a higher purity than the common oleylamine. By coordination to the metal it acts as a stabilising component and, by its long alkyl chain, it is able to retard oxidation of the particles more effectively than shortchained amines, e.g. 1-octylamine. After preliminary studies we focused on the triphenylphosphine copper(1) carboxylates 3 and 4 because, due to the reducing properties of the phosphine ligands, the reaction system is much less sensitive to oxygen than a system with the copper(π) carboxylates 2a-e. We found no significant differences between the bis- and tris(triphenylphosphine)copper(1) complexes and decided to use the former due to their higher copper content.

For the nanoparticle synthesis, solutions of the bis(triphenylphosphine)copper(i) carboxylate **4c** in 1-hexadecylamine were heated to reflux. While keeping the temperature at 330 °C for 10 min the formation of copper nanoparticles was observed by the sudden appearance of a red colour. After cooling the reaction mixture to ambient temperature, the solidified reaction mixtures were dissolved in ^{*n*}hexane. Addition of ethanol led to the precipitation of the particles which were separated by centrifugation, washed with ethanol and redispersed in ^{*n*}hexane for further analysis.

Different concentrations of the precursor solutions were investigated to study the influence of concentration on the particle size, shape and size distribution (Table 3).

Copper nanoparticle dispersions are known to absorb electromagnetic radiation at wavelengths of 550–600 nm due to excitation of the particles plasmon resonance, whereby the resonance frequency depends on the size and shape of the particles.²⁴ However, interpretation is more difficult for copper than for its higher homologues due to further influences specific for this metal, such as the degree of surface oxidation.²⁵ It was found that the plasmon absorption of the prepared nanoparticles in *n*hexane shifts from 570 nm to 580 nm for precursor concentration rising from 0.5 mM to 2.0 mM (Fig. 3). This indicates that larger particles were formed at higher concentrations.

Table 3 Comparison of spherical copper nanoparticles obtained by thermal decomposition of **4c** in hexadecylamine (*d*: mean diameter, σ : standard deviation)¹⁶

<i>c</i> [mM]	$T[^{\circ}C]$	d^{a} [nm]	$\sigma^{a} [\mathrm{nm}]$
0.5	330	9.8	1.7
1.0	330	28.2	2.6
2.0	330	85.6	15.0

^a Obtained by TEM measurements (vide infra).



Fig. 3 Characterisation of copper nanoparticles. Left: UV-vis spectra, measured in *n*hexane; right: XRPD of 1 mM sample and reflex pattern of copper (ICDD 00-04-0836), copper(I) oxide (ICDD 01-071-3645) and copper(II) oxide (ICDD 01-073-6023) for comparison.

The copper nanoparticles obtained from the 1 mM batch were investigated by XRPD (Fig. 3). Three reflexes were observed which were assigned to the (111) plane at 43.3°, the (200) plane at 50.4° and the (220) plane at 74.1° of the face-centred cubic cell of copper (ICDD 00-004-0836). No reflexes of copper(I) or copper(II) oxide were found, which indicates that the amount of crystalline oxides is below the detection level. The reflex broadening, which is characteristic for nanoparticles, was used to estimate the crystallite size using the Scherrer equation. By analysis of the (111) reflex, a size of about 31 ± 2 nm was calculated. This result is in accordance with the data obtained by microscopic measurements (*vide infra*).

The exact size, size distribution and shape of the copper nanoparticles were determined by transmission electron microscopy (TEM, Fig. 4 and 5). All particles in a selected area on the TEM grid were counted (at least 200 particles), excluding only those in undistinguishable aggregates. For the



Fig. 4 TEM images and size distributions of copper nanoparticles at different precursor concentrations: (A) c = 0.5 mM; (B) c = 1.0 mM, inset: penta-twinned particle.



Fig. 5 TEM image and size distribution of copper nanoparticles at a precursor concentration of c = 2.0 mM.

mathematical interpretation, the size distributions were fitted by Gaussian functions.

For a precursor concentration of 0.5 mM copper particles with a mean diameter of d = 9.8 nm and a standard deviation of $\sigma = 1.7$ nm were generated (Fig. 4A), whereas a moderate increase in precursor concentration to 1.0 mM resulted in the formation of significantly larger particles which had a mean diameter of d = 28.2 nm ($\sigma = 2.6$ nm, Fig. 4B).¹⁶ The particles of both samples were spherical and had size variations $c_v =$ $d/\sigma \times 100\%$ of 17% (0.5 mM sample) and 9% (1.0 mM sample). By this, they cannot be regarded as monodisperse by strict criteria ($c_v < 5\%$), however, they are in the order of the also common 15% criterion.²⁶ Due to their rather small size variation, the particles tend to form two- and three-dimensional close-packed arrangements. The interparticle distance is typical for particles stabilised by long alkyl chains. It varies between 1.5 and 3.5 nm, which is shorter than the length of two stretched hexadecyl chains $(2 \times 2.1 \text{ nm})$ and indicates interpenetrating organic matrices. An influence of the ethylene glycol chains is not visible. Occasionally, simple and multiple twinning can be observed in the 1 mM sample by different absorbance of the electron beam on different oriented lattices in a particle (inset Fig. 4B).

A precursor concentration of 2 mM generated an ensemble of irregular particles. The size distribution is still monomodal, but broad with a maximum of 85.6 nm (σ = 15 nm). Next to spherical particles anisotropic shapes were found, *e.g.* oval and triangular plates as well as short rods. The generation of anisotropic particles in the isotropic crystal-system of copper can be explained as a consequence of symmetry breaking by twinning, *e.g.* by the assumption of a twin plane parallel to the plates faces.²⁷

In addition, experiments at a higher precursor concentration of 10 mM were performed. Next to spherical nanoparticles significantly elongated nanoparticles ("nanorods") were observed, both in about equal proportions (Fig. 6A). The formation of copper nanorods is well investigated for template assisted growth²⁸ and for CVD processes.²⁹ Furthermore, it has been observed for thermal decomposition at high precursor concentrations, but no further investigations were carried out for the latter.^{9b}

The rods of our samples have a narrow diameter distribution between 40 and 50 nm and a length ranging from



Fig. 6 (A) TEM image of copper rods obtained from 10 mM solution; (B) schematic representation of the rod structure and cross sections of the rods (gray: contribution to the diffractogram, white: no contribution to the diffractogram); (C) diffractogram of nanorod lying on a side as well as calculated <100> (solid lines, bold numbers) and <112> (dashed lines, italic numbers) reciprocal lattices; (D) diffractogram of nanorod lying on edge as well as calculated <110> (solid lines, bold numbers) and <111> (dashed lines, italic numbers) reciprocal lattices.

100 nm to 1.3 μ m. Usually the short rods have slightly larger diameters than the longer ones. The aspect ratio is between 2 and 32. Regarding the spherical particles, a size distribution maximum of 38.3 nm (σ = 13 nm) is found.

A peculiar feature of copper nanorods is their optical properties, as their UV-vis absorption is reported to shift to shorter wavelengths with increasing rod lengths.³⁰ However, we were not able to distinguish the absorption resulting from the elongated particles from the absorption of the spherical ones, most likely because of broad length variation of the rods.

To gain information about the internal structure of the copper rods we performed selected area electron diffraction (SAED) on single rods. Investigation of about 25 rods revealed two different diffraction patterns (Fig. 6C and D) in about equal proportions. The diffractograms are similar to the ones found by investigation of copper nanorods prepared by growth in micelles^{28c} as well as to the patterns obtained from silver³¹ and gold^{27a} nanorods.

The two obtained diffraction patterns cannot be interpreted as a single crystallographic zone but are found to be superpositions of two zones. In Fig. 6C the square reciprocal lattice made up of the reflections of the ($\overline{2}00$), (020) and (220) planes corresponds to the <100> zone. It is overlaid by the rectangular reciprocal lattice of the <112> zone consisting of the reflections of the ($1\overline{1}1$), (311) and (220) planes. Some reflections (marked by an asterisk) cannot be assigned to a single zone but are double diffractions. The second diffractogram (Fig. 6D) is made up of the rectangular reciprocal lattice of the <110> zone with the reflections from the ($1\overline{1}\overline{1}$), ($11\overline{1}$), (220) and ($00\overline{2}$) planes and the hexagonal reciprocal lattice of the <111> zone with $(0\bar{2}\bar{2})$, (202) and (220) reflections. These superpositions prove that the rods are not formed by a single domain. However, they are consistent with a penta-twinned rod structure as shown in Fig. 6B. In this structure, the rods are built up by five elongated tetrahedra which are radially arranged along a common [110] axis. Neighbouring tetrahedra are connected by {110} boundaries. This arrangement is possible with only a little strain, because the interfacial angle between the {111} planes of 70.53° is close to $360^\circ/5 = 72^\circ$. The basic area of the tetrahedra and hence the surface of the rods consist of {100} planes. The rod ends might be made up of {111} planes which results in the overall form of an elongated pentagonal bipyramide (Fig. 6B). However, rods can also be terminated by {110} planes.³¹

In the penta-twinned arrangement a rod cannot be oriented in a way that allows the contemporary observation of the Bragg reflections of all five domains, but only three of them (Fig. 6B). If a rod lying on its side interacts with an electron beam perpendicular to this side the domains T1, T3 and T4 contribute to the diffractogram. T1 is oriented along <100> and T3 and T4 along <112>. The interaction results in the diffractogram presented in Fig. 5C. If the rod is tilted around its axis by $72^{\circ}/4 =$ 18° or if the rod lies on its edge in such a way that the electron beam is parallel to its side, domain T5 will cause diffractions of the <110> zone and T2 and T3 that of <111>, resulting in the diffractogram shown in Fig. 6D.

The experimental results may be explained by the following approach: as soon as the reaction mixture reaches the necessary temperature, simultaneous decomposition of the precursor molecules leads to a high supersaturation, followed by nucleation and 3D particle growth. Twins are formed by stacking faults or by collision of small metal clusters in this early stage of growth. Both processes are more likely at higher growth speed which explains the more frequent observation of twins at higher precursor concentration. At a low precursor concentration ($c \le 2$ mM) the growth stays in the 3D regime for twinned as well as for untwinned particles, which has recently been explained under the assumption of diffusion controlled growth.³² A high precursor concentration can lead to 1D growth of twinned particles, resulting in the formation of copper rods. However, particles whose symmetry is not broken by twinning will grow homogeneously in all three dimensions and cannot convert into rods.^{27a} If one-dimensional growth starts, the rods diameter corresponds to that of its spherical seed particle; that is why the short rods which are formed towards the end of the reaction time have larger diameters. The generation of monodisperse rods in solution is possible by seed mediated growth, as shown for gold.^{27a} However, to the best of our knowledge, seed mediated growth was not yet observed for copper.

5 Summary and conclusions

A straightforward synthetic methodology for the preparation of ethylene glycol functionalised copper(II) carboxylates

Cu[O₂CCR₂(OC₂H₄)_nOCH₃]₂ (n = 0-3; R = H, Me) (**2a-e**) as well as the corresponding tris- and bis(triphenylphosphine)copper(1) carboxylates **3a-e** and **4a-e** is described. Investigation of the thermal decomposition by TG-MS experiments showed that the carboxylates decompose in two steps starting with a decarboxylation in the case of the copper(1) carboxylates **2a-e** and with the loss of the ligand for the triphenylphosphinecopper(1) complexes **3** and **4**. It was shown that substitution at the carbon in α -position of the carboxylato group results in a lower decomposition temperature for the copper(1) complexes. In all thermally induced decompositions copper(0) was formed. The straightforward synthesis, the defined decomposition mechanism and the possibility to influence the decomposition qualifies the respective complexes as excellent precursors for the generation of metallic copper.

The application of the copper carboxylates was demonstrated by employing complex **4c** as a precursor for the generation of oxide-free copper nanoparticles by thermal decomposition in a long-chained amine, *i.e.* without the addition of any further reducing or stabilising reagents. A considerable advantage of this single-source precursor approach is its reproducibility, since only few reaction parameters (as precursor concentration and reaction temperature) have to be controlled. Whereas known precursors such as copper(π) acetylacetonate^{9c_if_i often give rise to air sensitive reaction mixtures, complex **4c** features a significantly lower oxygen sensibility, which is due to the presence of its reducing phosphine ligands, and hence allows to generate oxide free copper nanoparticles by the use of standard Schlenk techniques.}

Systematic variation of the precursor concentration between 0.5 mM and 2.0 mM allowed one to obtain nanoparticles with size-distribution maxima between 10 nm and 85 nm and moderate size variations. To the best of our knowledge, the possibility to vary the particle size to a similar extent is unprecedented for copper nanoparticle generation by the precursor approach. Using a precursor concentration of 10 mM, copper nanorods with aspect ratios of up to 32 have been obtained. Electron diffraction studies showed that the rods are not single domain crystals but consist of five domains. Compared with other rod preparation methods, the herein described single-source precursor approach provides access to copper nanorods by a much simpler procedure.

We are confident that the copper(i) and copper(ii) complexes can be applied successfully in further applications such as the preparation of metal–organic inks for inkjet printing, spray pyrolysis or spin-coating of conductive copper patterns and layers as successfully shown for the respective silver and gold carboxylates.³³

6 Experimental section

6.1. Instruments and materials

The synthesis of the copper(1) and copper(11) complexes were performed under non-inert conditions in undried solvents. Nanoparticle synthesis was performed with standard Schlenk techniques under an argon atmosphere with solvents dried by standard techniques³⁴ and degassed by multiple freeze–pump–thaw cycles. All chemicals were commercially available and were used without further purification. For synthesis and spectroscopic characterisation of **2–4c** please refer to ref. 16.

Inert centrifugation was performed using a Labofuge 200 from Heraeus. Elemental analyses were performed using a Thermo FLASHEA 112 Series instrument. Infrared spectra were recorded using a Biorad FTS-165 or using a Nicolet iS 10 from Thermo Scientific. ¹H NMR spectra were recorded using a Bruker Avance III 500 spectrometer operating at 500.30 MHz in the Fourier transform mode; ¹³C{¹H} NMR spectra were recorded at 125.80 MHz; ³¹P{¹H} NMR spectra at 202.53 MHz. Chemical shifts are given relative to the internal standard tetramethylsilane for ¹H and ¹³C¹₁H NMR spectra and to the external standard 85% phosphoric acid for ³¹P{¹H} NMR spectra. Mass spectra were recorded using a micrOTOF QII Bruker Daltonite workstation. TG, DSC and TG-MS experiments were performed using a Mettler Toledo TGA/DSC1 1600 system with an MX1 balance coupled with a Pfeiffer Vacuum MS ThermoStar GSD 301 T2 mass spectrometer at a heating rate of 5 K min⁻¹ under a flowing argon atmosphere (40 mL min⁻¹). The DSC measurements were used to determine the melting point. UV-vis spectra were recorded using a Thermo Genesys 6 spectrometer. XRPD was carried out on a STOE-S-TAD IP device using CuK α (λ = 154.184 pm) radiation. TEM imaging was performed using a PHILIPS CM 20 FEG instrument operated at 200 kV.

6.2. Synthesis

2-[2-(2-Methoxyethoxy)ethoxy]-2-methylpropanoic acid (1d) was prepared following a protocol by J. A. Ragan *et al.*^{17*a*} Yield: 56%. Bp: 185 °C at 2 Pa. Anal. calcd for C₉H₁₈O₅ (206.23): C 52.41, H 8.80, found C 51.82, H 8.96. FTIR (ATR): $\tilde{\nu}$ = 3253(w), 2984(m), 2877(m), 1735(s), 1489(m), 1359(m), 1320(m), 1133(s), 1083(s), 977(m), 845(m), 747(m) cm⁻¹. ¹H NMR (CDCl₃): δ = 1.47 (s, 6H, CCH₃), 3.39 (s, 3H, OCH₃), 3.56–3.60 (m, 4 H), 3.67–3.72 (m, 4 H) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 24.5 (s, CCH₃), 59.2 (s, OCH₃), 64.7 (s, CH₂), 70.1 (s, CH₂), 71.0 (s, CH₂), 71.9 (s, CH₂), 79.0 (s, CCH₂), 176.6 (s, CO₂H) ppm.

2-{2-[2-(2-Methoxy)ethoxy]ethoxy]ethoxy]acetatic acid (1e) was prepared following a protocol by W. Kunz *et al.*^{17b} Yield: 58%. Bp: 198 °C at 2 Pa. Anal. calcd for C₉H₁₈O₆ (222.28): C 48.63, H 8.16, found C 47.85, H 8.47. FTIR (ATR): $\tilde{\nu} = 3201$ (w), 2875(m), 1756(s), 1604(w), 1432(m), 1351(w), 1199(m), 1092(s), 849(m), 743(s), 692(s) cm⁻¹. ¹H NMR (CDCl₃): $\delta = 3.37$ (s, 3H, OCH₃), 3.55–3.56 (m, 2H, CH₂), 3.62–3.65 (m, 4H, CH₂), 3.67–3.68 (m, 4H, CH₂), 3.74–3.76 (m, 2H, CH₂), 4.15 (s, 2H, OCOCH₂). ¹³C{¹H} NMR (CDCl₃): $\delta = 58.9$ (s, OCH₃), 68.8 (s, CH₂), 70.3 (s, CH₂), 70.4 (s, CH₂), 70.4 (s, CH₂), 70.6 (s, CH₂), 71.5 (s, CH₂), 72.0 (s, OCOCH₂), 172.8 (s, CO₂H) ppm.

Copper(II) carboxylates (2a, b, d, e): two equivalents of the carboxylic acid were added to a suspension of copper(II) acetate monohydrate in a sufficient volume of toluene. Upon boiling, a mixture of water, acetic acid and toluene was distilled. When reaching the boiling point of pure toluene, the

residual solvent was removed in vacuo to give the products as green solids or viscous fluids (vide supra) in quantitative yields. Copper(II) 2-methoxyacetate (2a): Mp. 219 °C. Anal. calcd for C₆H₁₀O₆Cu (241.68): C 29.82, H 4.17; found C 29.87, H 4.12. FTIR (ATR): $\tilde{\nu} = 2944$ (m), 1602(s), 1579(s), 1435(m), 1393(m), 1340(m), 1244(w), 1115(m), 1072(m), 1072(m), 988(w), 966(m), 942(m), 731(w) cm⁻¹. HRMS (ESI): m/z =263.9666 ($M + Na^+$). Copper(II) 2-(2-methoxyethoxy)acetate (2b): Anal. calcd for C₁₀H₁₈O₈Cu (329.79): C 36.42, H 5.50, found C 36.20, H 5.82. FTIR (ATR): $\tilde{\nu} = 2883(m)$, 1756(w), 1630(s), 1415(s), 1574(s), 1415(m), 1432(s), 1329(s), 1260(s), 1199(m), 1093(s), 1027(m), 947(w), 894(w), 849(m), 753(m), 694(m) cm⁻¹. HRMS (ESI): m/z = 352.0190 (M + Na⁺). Copper(II) 2-[2-(methoxyethoxy)ethoxy]-2-methylpropanoate (2d): Anal. calcd for C18H34O10Cu (473.14): C 45.69, H 7.24, found C 45.98, H 7.27. FTIR (ATR): $\tilde{\nu} = 2978(m), 2929(m), 2875(m),$ 1625(s), 1472(w), 1412(m), 1357(w), 1181(m), 1081(s), 979(w), 848(w), 813(w), 779(w) cm⁻¹. HRMS (ESI) m/z = 496.1363 $(M + Na^{\dagger})$. Copper(II) 2-{-2-[2-(2-methoxyethoxy)ethoxy]ethoxy}acetate (2e): Anal. calcd for C₁₈H₃₀O₁₂Cu (501.96): C 42.72, H 6.77, found C 42.54, H 6.97. FTIR (ATR): $\tilde{\nu} = 2871(m)$, 1635(s), 1577(s), 1416(m), 1329(m), 1247(s), 1199(w), 1081(s), 934(w), 851(w), 724(w) cm⁻¹. HRMS (ESI) m/z = 528.1238 (M + Na⁺).

Tris(triphenylphosphine)copper(1) carboxylates (3a, b, d, e): Copper(II) carboxylates 2a, b, d, e, 3.5 equiv. of triphenylphosphine and 0.5 equiv. of water were dissolved in methanol (200 mL for a 20 mmol reaction). The mixture was heated to reflux until it became colourless. Upon cooling to -20 °C the respective products precipitated. Recrystallisation from methanol and drying in vacuo gave the title complexes as colourless solids. Tris(triphenylphosphine)copper(1) 2-methoxyacetate (3a): Yield: 88%. Mp. 132 °C. Anal. calcd for C₅₇H₅₀O₃P₃Cu (939.44): C 72.87, H 5.36, found C 72.65, H 5.42. FTIR (ATR): $\tilde{\nu} = 3053(w), 1614(m), 1597(s), 1480(m), 1434(s), 1373(m),$ 1109(m), 1093(s), 997(m), 738(s), 691(s), 618(w) cm⁻¹. ¹H NMR $(CDCl_3)$: $\delta = 3.26$ (s, 3H, OCH₃), 3.83 (s, 2H, CH₂), 7.26–7.29 (m, 18H, CH), 7.34–7.37 (m, 27H, CH) ppm. ¹³C{¹H} NMR $(\text{CDCl}_3): \delta = 58.7 \text{ (s, OCH}_3), 72.1 \text{ (s, CH}_2), 128.7 \text{ (d, }^mCH, {}^3J_{CP} =$ 8.2 Hz), 129.6 (s, ${}^{p}CH$), 133.9 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 16.2 Hz), 134.1 (d, ${}^{1}CH$, ${}^{1}J_{CP}$ = 18.2 Hz), 176.3 (OCO) ppm. ${}^{31}P{}^{1}H$ NMR (CDCl₃): δ = -3.3 ppm. HRMS (ESI) m/z = 739.0648 (M - PPh₃ + Cu⁺). Tris(triphenylphosphine)copper(1) 2-(2-methoxyethoxy)acetate (3b): Yield: 85%. Mp. 86 °C. Anal. calcd for C₅₉H₅₄O₄P₃Cu (983.49): C 72.05, H 5.53, found C 71.90, H 5.53. FTIR (ATR): $\tilde{\nu} = 3053(w), 2938(w), 2813(w), 1596(m), 1480(w), 1433(s),$ 1394(m), 1373(m), 1111(w), 1092(s), 1026(s), 744(s), 693(s) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.24 (s, 3H, OCH₃), 3.41–3.42 (m, 2H, CH₂), 3.45-3.46 (m, 2H, CH₂), 3.88 (s, 2H, OCOCH₂), 7.16-7.19 (m, 18H, CH), 7.23–2.27 (m, 27H, CH) ppm. ¹³C{¹H} NMR $(CDCl_3)$: $\delta = 58.0$ (s, OCH_3), 69.0 (s, CH_2), 69.7 (s, CH_2), 71.0 (s, OCOCH₂), 127.3 (d, ^{*m*}CH, ³ J_{CP} = 8.3 Hz), 128.6 (s, ^{*p*}CH), 132.9 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 16.3 Hz), 133.2 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 17.6 Hz), 175.5 (s, OCO) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = -3.3$ ppm. HRMS (ESI) m/z = 783.0910 (M – PPh₃ + Cu⁺). Tris(triphenylphosphine)-2-[2-(2-methoxyethoxy]-2-methylpropanoate copper(1) (3d): Yield: 53%. Mp. 94 °C. Anal. calcd for $C_{63}H_{62}O_5P_3Cu$

(1055.64): C 71.68, H 5.92, found C 71.71, H 5.94. FTIR (ATR): $\tilde{\nu} = 3052(w), 2979(w), 2927(w), 1599(s), 1585(w), 1479(m),$ 1433(s), 1380(m), 1347(w), 1091(m), 1026(m), 842(w), 742(s), 692(s), 607(w) cm⁻¹. ¹H NMR (CDCl₃): δ = 1.38 (s, 6H, CCH₃), 3.30-3.32 (m, 2H, CH₂), 3.24 (s, 3H, OCH₃), 3.46-3.48 (m, 2H, CH_2), 3.50–3.52 (m, 2H, CH_2), 3.54–3.56 (m, 2H, CH_2), 7.22–7.25 (m, 18H, CH), 7.31–7.35 (m, 27H, CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 25.7 (s, CCH₃), 59.1 (s, OCH₃), 63.7 (s, CH₂), 70.4 (s, CH₂), 71.3 (s, CH₂), 72.1 (s, CH₂), 78.8 (s, CCH₃), 128.7 (d, ${}^{m}CH$, ${}^{3}J_{CP}$ = 8.9 Hz), 129.8 (s, ${}^{p}CH$), 133.3 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 25.3 Hz), 134.0 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 15.5 Hz), 181.7 (s, OCO) ppm. ${}^{31}P{}^{1}H$ NMR (CDCl₃): $\delta = -3.3$ ppm. HRMS (ESI) m/z =857.1470 (M – PPh₃ + Cu⁺). Tris(triphenylphosphine)copper(1) 2-{2-[2-(2-methoxy)ethoxy]ethoxy}acetate (3e): Yield: 43%. Mp. 52 °C. Anal. calcd for C₆₃H₆₂O₅P₃Cu (1055.59): C 70.61, H 5.83, found C 70.19, H 5.85. FTIR (ATR): $\tilde{\nu} = 3047$ (w), 2890(w), 1606(s), 1599(s), 1480(m), 1432(s), 1379(m), 1092(s), 1026(w), 850(w), 743(s), 692(s) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.28 (s, 3H, OCH₃), 3.44-3.47 (m, 4H, CH₂), 3.51-3.53 (m, 8H, CH₂), 3.88 (s, 2H, OCOCH₂), 7.17-7.20 (m, 18H, CH), 7.23-2.27 (m, 27H, CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 59.1 (s, OCH₃), 70.1 (s, CH₂), 70.5 (m, CH₂), 70.6 (s, CH₂), 70.7 (s, CH₂), 72.0 (s, OCOCH₂), 128.6 (d, ^{*m*}CH, ³ J_{CP} = 8.4 Hz), 129.5 (s, ^{*p*}CH), 133.9 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 16.3 Hz), 134.2 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 17.8 Hz), 177.6 (s, OCO) ppm. ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta = -3.3$ ppm.

Bis(triphenylphosphine)copper(1) carboxylates (4a, b, d, e): A concentrated solution of a tris(triphenylphosphine)copper(I) carboxylate 3a, b, d, e in dichloromethane was added dropwise to ⁿhexane under vigorous stirring at ambient conditions (for a 20 mmol reaction about 10 mL dichloromethane and 500 mL ⁿhexane). The respective title complexes precipitated as colourless solids which were isolated by filtration, washed with ^{*n*}hexane and dried *in vacuo*. Bis(triphenylphosphine)copper(1) 2-methoxyacetate (4a): Yield: 98%. Mp. 145 °C. Anal. calcd for C₃₉H₃₅O₃P₂Cu (677.19): C 69.17, H 5.21, found C 69.25, H 5.26. FTIR (ATR): $\tilde{\nu} = 3052(w), 2874(w), 2811(w),$ 1582(s), 1479(s), 1434(s), 1407(m), 1315(m), 1194(w), 1123(s), 1095(s), 1024(m), 996(m), 855(w), 735(s), 692(s) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.19 (s, 3H, OCH₃), 3.75 (s, 2H, CH₂), 7.16-7.19 (m, 12H, CH), 7.26–7.29 (m, 18H, CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 58.7 (s, OCH₃), 72.1 (s, CH₂), 128.7 (d, ^mCH, ³J_{CP} = 8.3 Hz), 129.6 (s, ${}^{p}CH$), 133.8 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 16.0 Hz), 134.2 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 18.6 Hz), 176.3 (s, OCO) ppm. ${}^{31}P{}^{1}H$ NMR (CDCl₃): $\delta = -2.4$ ppm. HRMS (ESI) m/z = 739.0648 (M + Cu⁺). Bis(triphenylphosphine)copper(1) 2-(2-methoxyethoxy)acetate (4b): Yield: 95%. Mp. 181 °C. Anal. calcd for C₄₁H₃₉O₄P₂Cu (721.22): C 68.28, H 5.45, found C 68.20, H 5.52. FTIR (ATR): $\tilde{\nu} = 3064(\text{w}), 2895(\text{w}), 1564(\text{s}), 1478(\text{m}), 1433(\text{s}), 1410(\text{m}),$ 1321(m), 1120(s), 1094(s), 997(w), 853(w), 738(s), 691(s) cm⁻¹. ¹H NMR (CDCl₃): δ = 3.24 (s 3H, OCH₃), 3.43–3.47 (m, 4H, CH₂), 3.89 (s, 2H, OCOCH₂), 7.15-7.19 (m, 12 H, CH), 7.25–7.28 (m, 18H, CH) ppm. ${}^{13}C{}^{1}H$ NMR (CDCl₃): δ = 58.9 (s, OCH₃), 69.8 (s, CH₂), 70.7 (s, CH₂), 71.9 (s, OCOCH₂), 128.6 (d, ${}^{m}CH$, ${}^{3}J_{CP}$ = 4.3 Hz), 129.9 (s, ${}^{p}CH$), 132.6 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 30.1 Hz), 133.9 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 12.6 Hz), 176.5 (s, OCO) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = -2.4$ ppm. HRMS (ESI) m/z =

783.0910 (M + Cu⁺). Bis(triphenylphosphine)copper(I) 2-[2-(2methoxyethoxy]-2-methylpropanoate (4d): Yield: 89%. Mp. 122 °C. Anal. calcd for C₄₅H₄₇O₅P₂Cu (793.32): C 68.12, H 5.97, found C 68.03, H 5.93. FTIR (ATR) $\tilde{\nu}$ = 2866(m), 1583(m), 1556(s), 1479(m), 1434(s), 1402(m), 1355(w), 1093(s), 1026(m), 847(m), 744(s), 692(s) cm⁻¹. ¹H NMR (CDCl₃): δ = 1.37 (s, 6H, CCH₃), 3.31-3.32 (m, 2H, CH₂), 3.32 (s, 3H, OCH₃), 3.45-3.47 (m, 2H, CH₂), 3.50-3.52 (m, 2H, CH₂), 3.54-3.55 (m, 2H, CH₂), 7.19–7.22 (m, 12H, CH), 7.30–7.32 (m, 18H, CH) ppm. ¹³C{¹H} NMR (CDCl₃): δ = 25.7 (s, CCH₃), 59.0 (s, OCH₃), 63.7 (s, CH₂), 70.3 (s, CH₂), 71.2 (s, CH₂), 72.0 (s, CH₂), 78.7 (s, CCH₃), 128.6 (d, ${}^{m}CH$, ${}^{3}J_{CP}$ = 6.8 Hz), 129.9 (s, ${}^{p}CH$), 132.7 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 31.5 Hz), 133.9 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 13.5 Hz), 181.6 (s, OCO) ppm. ³¹P{¹H} NMR (CDCl₃): $\delta = -2.4$ ppm. Bis(triphenylphosphine)copper(1) 2-{2-[2-(2-methoxyethoxy)ethoxy]ethoxy}acetate (4e): Yield: 87%. Mp. 110 °C. Anal. calcd for C₄₅H₄₇O₆P₂Cu (809.32): C 66.78, H 5.85, found C 66.25, H 6.00. FTIR (ATR): $\tilde{\nu}$ = 3051 (w), 2861(w), 1599(m), 1478(s), 1433(s), 1410(w), 1379(w), 1093 (s), 1026(m), 997(m), 850(w), 742(s), 692(s) cm⁻¹. ¹H NMR $(CDCl_3): \delta = 3.34$ (s, 3H, OCH_3), 3.50–3.53 (m, 4H, CH_2), 3.57-3.61 (m, 8H, CH₂), 3.94 (s, 2H, OCOCH₂), 7.19-7.22 (m, 12H, CH), 7.30–7.33 (m, 18H, CH) ppm. ¹³C{¹H} NMR (CDCl₃): $\delta = 59.1$ (s, OCH₃), 70.1 (s, CH₂), 70.5 (m, CH₂), 70.6 (s, CH₂), 70.7 (s, CH_2), 72.0 (s, $OCOCHH_2$), 128.7 (d, ${}^{m}CH$, ${}^{3}J_{CP}$ = 5.7 Hz), 129.9 (s, ${}^{p}CH$), 132.6 (d, ${}^{i}CH$, ${}^{1}J_{CP}$ = 30.8 Hz), 133.8 (d, ${}^{o}CH$, ${}^{2}J_{CP}$ = 12.9 Hz), 176.6 (s, OCO) ppm. ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): δ = -2.34 ppm.

Generation of spherical and rod-like copper nanoparticles: Complex 4c was dissolved in 10 mL of 1-hexadecylamine to obtain the desired concentration (0.5 mM, 1.0 mM, 2.0 mM, 10.0 mM). After preheating the solution to 250 °C it was further heated to 330 °C at a constant heating rate of 25 K min⁻¹ and was kept at this temperature for 10 min. The generation of nanoparticles was observed by the sudden appearance of red colour. After air-cooling the solution to ambient temperature, the solidified reaction mixture was dissolved in 10 mL of ^{*n*}hexane. The particles were precipitated by addition of 20 mL ethanol. A sample of 5 mL was subjected to centrifugation (30 min, 5300 min⁻¹). The particles were redispersed in 5 mL of ^{*n*}hexane by the use of ultrasound for further analysis.

For TEM measurement, one drop of the particle dispersions was placed on a polymer-coated, copper-supported carbon grid. After removing the drop by the use of filter paper the grid was dried *in vacuo*.

Single-crystal X-ray diffraction analysis: Single crystals of 4a, b, d and e suitable for X-ray diffraction analysis were obtained by diffusion of ^{*n*}hexane into a concentrated solution of the respective complexes in dichloromethane. Data were collected using an Oxford Gemini S diffractometer using MoK α (λ = 71.073 pm) or CuK α (λ = 154.184 pm) radiation. The structures were solved by direct methods and refined by full matrix least squares procedures on $F^{2,35}$ All non-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen-atom positions. CCDC-932857 (4a), 933501 (4b), 932855 (4d) and 932856 (4e) contain the supplementary crystallographic data for this paper.

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Notes and references

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