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A straightforward approach to oxide-free copper nanoparticles by thermal decomposition of a copper(I) precursor†

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The synthesis of the novel copper(I) precursor [$Cu(PPh_3)_2(O_2CCH_2OC_2H_4OC_2H_4OCH_3)$] and its application in the straightforward solution synthesis of oxide-free copper nanoparticles by mere thermal decomposition are reported; depending on the precursor concentration particles of sizes of 10 nm or 30 nm are obtained in narrow size distributions.

Among various chemical[1] and physical[2] methods for the preparation of copper nanoparticles, the precursor approach[3] has received continuous attention during the last few years. It can be understood as a variation of the traditional chemical approach in which all necessary reactants (*i.e.* copper sources, stabilisers and reducing agents) are combined into one molecule. The particle generation is performed in solution by thermal decomposition of the precursor. The convenient processing and the high reproducibility of the first order reaction make the precursor approach an interesting alternative, *e.g.* for industrial applications.

To date, the main drawback of the precursor approach has been considered to be the high oxygen sensitivity of the particle preparation process, which arises from the absence of an excess of reducing equivalents. Hence, often only oxidised copper nanoparticles could be isolated.[3c,d,f,h] In the past, the problem had to be addressed by using advanced working procedures, such as the use of dry boxes[3b,k] or reducing solvents and atmospheres.[3a,e,g,j]

Completing our work on the use of gold[4] and silver[5] ethylene glycol carboxylates as precursor compounds for metal nanoparticle generation, we herein report the synthesis and application of the air-stable complex bis(triphenylphosphine)copper(I) 2-[2-(2-methoxyethoxy)ethoxy]acetate (**3**) as a new precursor for copper nanoparticle formation. Due to the presence of two phosphine ligands with reducing properties this metal–organic complex features a significantly lower oxidation sensitivity of the particle generation process and facilitates the preparation of oxide-free copper nanoparticles by the use of standard Schlenk techniques. Furthermore, to the best of our knowledge, it is the first copper(I) compound successfully applied in the solution synthesis of copper nanoparticles next to the highly air and moisture sensitive copper(I) acetate.[3h,i]

Metal–organic complex **3** was prepared from commercially available starting materials using copper(II) 2-[2-(2-methoxyethoxy)ethoxy]acetate, which itself was synthesised by an anion exchange reaction of the acid $CH_3O(C_2H_4O)_2CH_2CO_2H$ (**1**) with copper(II) acetate hydrate (Scheme 1, for experimental details see ESI†). Acetic acid and water were removed by azeotropic distillation with toluene as an entrainer. Copper(II) carboxylate was reduced by triphenylphosphine which was added in an excess, sufficient to stabilise the resulting copper(I) carboxylate, yielding tris(triphenylphosphine) copper(I) 2-[2-(2-methoxyethoxy)ethoxy]-acetate (**2**).[6] One of the three phosphine ligands in **2** could be removed by two-solvent recrystallisation, *i.e.* by dissolving **2** in dichloromethane and adding ^{n}hexane. This methodology allowed the isolation of **3** as a colourless air stable solid with an overall yield of 73% based on copper(II) acetate hydrate. The complex was characterised using elemental analysis, IR and NMR (^1H, $^{13}C\{^1H\}$) spectroscopy, mass spectrometry and single-crystal X-ray structure determination (see ESI†).

Complex **3** crystallises in the triclinic space group $P\bar{1}$ without any solvent molecules (Fig. 1).[7] The carboxylato group is monodentate-bonded to copper(I), resulting in the formulation of a 16-valence-electron complex. The copper(I) ion is located almost exactly in the plane defined by the three surrounding atoms P1, P2 and O1, protruding only 0.1135 Å. Regarding the ethylene glycol chains, the lowest energy conformation (*gauche* C–C bonds and *anti* C–O bonds)[8] is found to be one of the two conformations, which are about equally populated.

The thermal behaviour of **3** was studied by thermogravimetric (TG) and differential scanning calorimetric (DSC) investigations

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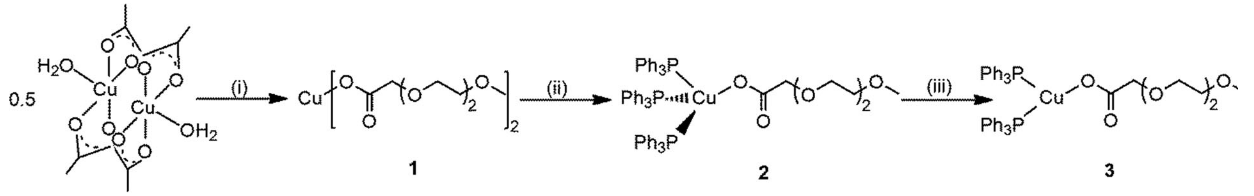

Scheme 1 Synthesis of **3**: (i) $2CH_3O(C_2H_4O)_2CH_2CO_2H$, toluene, 111 °C, 5 h, azeotropic distillation; (ii): $3.5PPh_3$, $0.5H_2O$, MeOH, 65 °C, 3 h; (iii): two-solvent recrystallisation from dichloromethane–^{n}hexane.

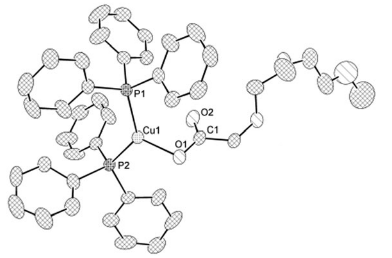

Fig. 1 ORTEP diagram (50% probability level) of **3**. All disordered atoms and all hydrogen atoms are omitted for clarity. Selected bond distances [Å] and angles [°]: Cu1–P1 2.2118(8), Cu1–P2 2.2547(7), Cu1–O1 2.063(2), Cu1–O2 2.539(3), C1–O1 1.275(4), C1–O2 1.230(3), P1–Cu–P2 130.17(3), O1–C1–O2 124.7(3), P1–Cu1–O1 109.31(6), P2–Cu1–O1 119.69(6).

to gain information about the decomposition behaviour of the complex (Fig. 2). It was found that the decomposition appears in two steps, of which the first resembled a slow mass decay starting at *ca.* 200 °C. In TG-MS coupling experiments performed for the complex bis(triphenylphosphine)copper(I) 2-(2-methoxyethoxy)acetate, the typical fragments of triphenylphosphine could be detected, which indicates that the decomposition of the complex starts with the loss of the phosphine ligands. In a second decomposition step at *ca.* 300 °C decarboxylation occurs, leading to the formation of copper(0). The process is overlaid with the decomposition of the ethylene glycol chain. The residual mass of 8.6% fits well to the formation of elemental copper (8.3% theoretical), whose presence was proven by X-ray powder diffraction (XRPD) measurements (see ESI†). The DSC measurement shows a melting point of 140 °C and portrays the thermal decomposition as a single endothermic process.

The decomposition temperature of **3** requires the application of high-boiling solvents for the nanoparticle formation (*vide supra*). We choose 1-hexadecylamine (mp 40 °C, bp 330 °C) because it is available in higher purity than the common oleylamine. Furthermore, presuming the amine coordinates to the metal, the long alkyl chain should be able to avoid oxidation more effectively than a short one, *e.g.* that of 1-octylamine.

A typical nanoparticle preparation protocol proceeded as follows: a solution of **3** in 1-hexadecylamine (0.5 mM or 1.0 mM) was prepared and preheated to 250 °C, followed by heating it to reflux at a constant heating rate of 25 °C min^{-1}. While keeping the temperature at 330 °C for 10 min the formation of copper nanoparticles was observed by the sudden reddening of the reaction mixture. After cooling it to ambient temperature the solidified mixture was dissolved in ^{n}hexane. The copper nanoparticles were precipitated by addition of ethanol, separated by centrifugation, washed once with ethanol and dried or redispersed in ^{n}hexane for analysis (see ESI† for details). In contrast to the nanoparticle dispersions the dried particles are stable *ad infinitum* under inert conditions, whereas they slowly form copper oxides when stored in air for weeks. By gravimetric measurements and assuming the organic shell to make up only a minor weight fraction we found virtually quantitative conversion of the precursor to copper(0).

The obtained nanoparticles were investigated using UV-vis, XRPD and electron transmission microscopy (TEM). The UV-vis spectra of the copper nanoparticles in ^{n}hexane showed the expected plasmon absorption which is due to the metallic properties of the particles.[9] It shifts from 570 cm^{-1} to 575 cm^{-1} for a precursor concentration rising from 0.5 mM to 1.0 mM, indicating the formation of larger nanoparticles at higher concentrations (Fig. 3).

The XRPD pattern of the nanoparticles (Fig. 3) shows the reflections of the (111), (200) and (220) planes of the face-centered cubic cell of copper (ICDD 00-004-0836). No reflections of copper(I) oxide or copper(II) oxide could be detected, meaning that the amount of crystalline impurities is below the detection limit. The peak broadening, which is characteristic of nanoparticles, can be used to estimate the crystallite size using the Scherrer equation.[10] By interpretation of the (111) peak, the size was calculated to be

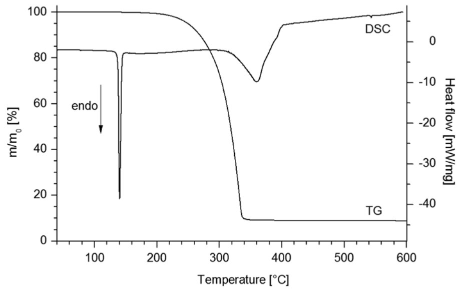

Fig. 2 TG and DSC traces of **3** (gas flow N_2 60 mL min^{-1} (TG) and N_2 20 mL min^{-1} (DSC), heating rate 10 K min^{-1}).

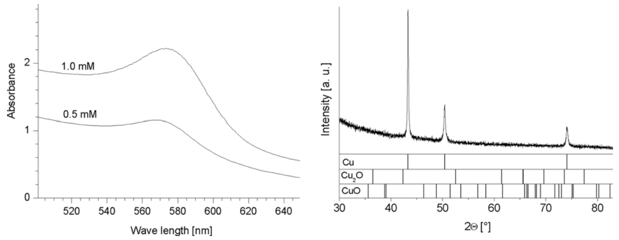

Fig. 3 UV-vis spectra of copper nanoparticles dispersed in ^{n}hexane (left); the XRPD pattern of copper nanoparticles (1.0 mM sample) with reflections of copper (ICDD 00-04-0836), copper(I) oxide (ICDD 01-071-3645) and copper(II) oxide (ICDD 01-073-6023) for comparison (right).

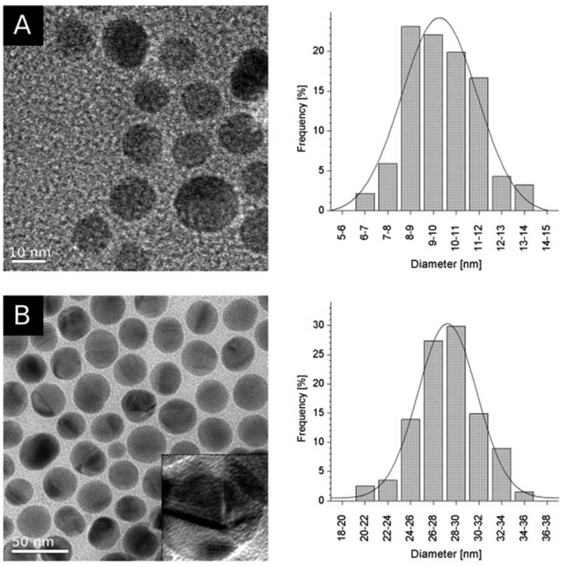

Fig. 4 TEM images and size distribution of copper nanoparticles obtained at different precursor concentrations. (A) $c = 0.5$ mM, $d = 9.8$ nm, $\sigma = 1.7$ nm; (B) $c = 1.0$ mM, $d = 28.2$ nm, $\sigma = 2.6$ nm, inset: multiply twinned particles.

31 ± 2 nm, which fits well to the size distributions obtained using electron microscopy (*vide infra*).

The copper nanoparticle size and size distribution were determined using TEM. At least 200 particles were counted for each sample. For the mathematical interpretation the size distributions were fitted by Gaussian functions.

For the 0.5 mM sample spherical particles with a mean diameter of $d = 9.8$ nm and a standard derivation of $\sigma = 1.7$ nm (size variation $c_v = 17\%$) were found (Fig. 4A). The 1.0 mM sample yielded larger particles with $d = 28.2$ nm in a narrower size distribution ($\sigma = 2.6$ nm, $c_v = 9\%$, Fig. 4B). Rounding these results to a reasonable accuracy we regard the particles to have sizes of 10 and 30 nm. The particles in both probes tend to form two- and three-dimensional close-packed arrangements with short interparticle distances of about 2 nm which are likely due to the presence of the long-chained amine (*vide supra*).[3b] In the 1 mM sample, simple and multiple twinning can be observed in about 5% of the particles (see the inset in Fig. 4B), which is a known feature of copper nanoparticles with a sufficient size.[11] Electron diffraction studies did not show any mark of the formation of either copper(I) or copper(II) oxides, even though the probe preparation was performed under non-inert conditions (see ESI†).

In terms of their microscopic images the particles prepared in this work are similar to the particles obtained in other precursor approach studies.[3b,c] The size variations are slightly larger than in comparable systems. However, the accessibility of a range of particle sizes by changing the copper precursor concentration seems to be unique to our system and will be part of future investigations.

In conclusion, the synthesis of the new copper(I) precursor $[Cu(PPh_3)_2(O_2CCH_2OC_2H_4OC_2H_4OCH_3)]$ (**3**) is discussed. This metal–organic complex allows the easy and straightforward solution synthesis of oxide-free copper nanoparticles by mere thermal decomposition, *i.e.* without the addition of any reducing agents. Compared with other copper precursors such as copper(II) carboxylates,[3d,e,h] complex **3** significantly reduces the oxidation sensitivity of the reaction mixtures due to the presence of its reducing triphenylphosphine ligands and allows the use of standard Schlenk techniques rather than that of dry boxes. Nanoparticles of different sizes, 10 nm and 30 nm, were obtained in narrow size distributions by changing the precursor concentration from 0.1 mM to 1.0 mM. We are confident that **3**, the respective tris(triphenylphosphine) copper(I) complex **2**, as well as the copper(II) carboxylate **1** 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.[12]

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Notes and references

1 (*a*) H. Hirai, H. Wakabayashi and M. Komiyama, *Bull. Chem. Soc. Jpn.*, 1986, **59**, 367; (*b*) R. A. Salkar, P. Jeevanandam, G. Kataby, S. T. Aruna, Y. Koltypin, O. Palchik and A. Gedanken, *J. Phys. Chem. B*, 2000, **104**, 893; (*c*) J. H. Kim, T. A. Germer, G. W. Mulholland and S. H. Ehrman, *Adv. Mater.*, 2002, **14**, 518; (*d*) S.-H. Wu and D.-H. Chen, *J. Colloid Interface Sci.*, 2004, **273**, 165; (*e*) P. X. Rutkowski and J. I. Zink, *Inorg. Chem.*, 2009, **48**, 1655.

2 (*a*) D. B. Pedersen and S. Wang, *J. Phys. Chem. C*, 2007, **111**, 17493; (*b*) G. H. Chan, J. Zhao, E. M. Hicks, G. C. Schatz and R. P. van Duyne, *Nano Lett.*, 2007, **7**, 1947.

3 (*a*) N. A. Dhas, C. P. Raj and A. Gedanken, *Chem. Mater.*, 1998, **10**, 1446; (*b*) J. Hambrock, R. Becker, A. Birkner, J. Weiß and R. A. Fischer, *Chem. Commun.*, 2002, 68; (*c*) S. U. Son, I. K. Park, J. Park and T. Hyeon, *Chem. Commun.*, 2004, 778; (*d*) X. Sun, Y.-W. Zang, R. Si and C.-H. Yan, *Small*, 2005, **11**, 1081; (*e*) M. Salavati-Niasari, F. Davar and N. Mir, *Polyhedron*, 2008, **27**, 3514; (*f*) M. Salavati-Niasari and F. Davar, *Mater. Lett.*, 2009, **63**, 441; (*g*) M. Salavati-Niasari, Z. Fereshteh and F. Davar, *Polyhedron*, 2009, **28**, 126; (*h*) G. Cheng and A. R. H. Walker, *Anal. Bioanal. Chem.*, 2010, **396**, 1057; (*i*) L.-I. Hung, C.-K. Tsung, W. Huang and P. Yang, *Adv. Mater.*, 2010, **22**, 1910; (*j*) M. H. Habibi, R. Mokhtari, M. Amirnasr and A. Amiri, *Spectrochim. Acta, Part A*, 2011, **79**, 1524; (*k*) M. Shi, H. S. Kwon, Z. Peng, A. Elder and H. Yang, *ACS Nano*, 2012, **6**, 2157.

4 (*a*) A. Tuchscherer, D. Schaarschmidt, S. Schulze, M. Hietschold and H. Lang, *Inorg. Chem. Commun.*, 2011, **14**, 676; (*b*) A. Tuchscherer, D. Schaarschmidt, S. Schulze, M. Hietschold and H. Lang, *Dalton Trans.*, 2012, **41**, 2738.

5 M. Steffan, A. Jakob, P. Claus and H. Lang, *Catal. Commun.*, 2009, **10**, 437.

6 B. Hammond, F. H. Jardine and A. G. Vohra, *J. Inorg. Nucl. Chem.*, 1971, **33**, 1017.

7 Crystal data for $[Cu(PPh_3)_2(OOCCH_2OC_2H_4OC_2H_4OCH_3)]$ (**3**): $C_{43}H_{43}CuO_5P_2$, $M_r = 765.25$ g mol^{-1}, crystal dimensions $0.20 \times 0.10 \times 0.05$ mm, $T = 110$ K, $\lambda = 154.184$ pm, triclinic, $P\bar{1}$, $a = 10.7844(5)$ Å, $b = 13.4639(6)$ Å, $c = 14.1917(6)$ Å, $\alpha = 71.163(4)^\circ$, $\beta = 77.783(4)^\circ$, $\gamma = 84.067(4)^\circ$, $V = 1904.74(15)$ Å^3, $Z = 2$, $\rho_{calcd} = 1.344$ g cm^{-3}, $\mu = 1.958$ mm^{-1}, θ range = 3.35–65.48°, reflections collected: 12 298, independent: 6090 ($R_{int} = 0.0380$), $R_1 = 0.0390$, w$R_2 = 0.0805$ [$I > 2\sigma(I)$]. CDCC 932859†.

8 P. Johansson, J. Grondin and J.-C. Lassègues, *J. Phys. Chem. A*, 2010, **114**, 10700.

9 J. A. Creighton and D. G. Eadon, *J. Chem. Soc., Faraday Trans.*, 1991, **87**, 3881.

10 (*a*) A. L. Patterson, *Phys. Rev.*, 1939, **56**, 978; (*b*) A. Kochendörfer, *Z. Kristallogr. Kristallgeom. Kristallphys. Kristallchem.*, 1944, **105**, 393.

11 S. I. Cha, C. B. Mo, K. T. Kim, Y. J. Jeong and S. H. Hong, *J. Mater. Res.*, 2006, **21**, 2371.

12 S. F. Jahn, T. Blaudeck, R. R. Baumann, A. Jakob, P. Ecorchard, T. Rüffer, H. Lang and P. Schmidt, *Chem. Mater.*, 2010, **22**, 3067; C. Schoner, A. Tuchscherer, T. Blaudeck, S. F. Jahn, R. R. Baumann and H. Lang, *Thin Solid Films*, 2013, **531**, 147.