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# Morphology Control in AgCu Nanoalloy Synthesis by Molecular Cu(I) **Precursors**

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Supporting Information



ABSTRACT: As nanoparticle preparation methods employing bottom-up procedures rely on the use of molecular precursors, the chemical composition and bonding of these precursors have a decisive effect on nanoparticle formation and their resulting morphology and properties. We synthesized the Cu(I) complexes  $[Cu(PPh_3)_2(bea)]$  (1, bea = benzoate) and  $[Cu(PPh_3)_3(Hphta)]$  (2, phta = phthalate) by reducing the corresponding Cu(II) mono- and dicarboxylates with triphenylphosphine. We characterized 1 and 2 by single-crystal X-ray diffraction analysis, elemental analyses, infrared and nuclear magnetic resonance spectroscopy, and mass spectrometry and obtained complete information about their structures in the solid state and in solution. Also, we examined their thermal stability in oleylamine and determined their decomposition temperatures to be used as the minimal reaction temperature in metal nanoparticle synthesis. The complexes 1 and 2 differ in the number of reducing PPh<sub>3</sub> ligands and the strength of carboxylate bonding to the Cu(I) center. Therefore, we employed them in combination with  $[Ag(NH_2C_{12}H_{25})_2]NO_3$  as molecular precursors in the solvothermal hot injection synthesis of AgCu nanoalloys in oleylamine and demonstrated their influence on the elemental distribution, phase composition, particle size distribution, shape, morphology, and optical properties of the resulting nanoparticles. The nanoalloy particles from the benzoate complex 1 were oblate and polydisperse and exhibited two surface plasmons at 393 and 569 nm, which is caused by their Janustype structure. The nanoparticles prepared from the phthalate complex 2 were round and monodisperse and exhibited one plasmon at 413 nm, as they formed an AgCu solid solution with a random distribution of the elements in a particle.

# INTRODUCTION

The combination of inorganic and material chemistry approaches enables the design and synthesis of novel precursors and their application in the preparation of new materials. Particularly noteworthy is the development of advanced molecular precursors to metal and alloy nanoparticles. Bimetallic nanoalloys exhibit different properties from their macroscopic (bulk) counterparts, such as surface plasmon resonance (SPR),<sup>1</sup> spinodal decomposition,<sup>2</sup> depression of melting point,<sup>3,4</sup> increased component miscibility,<sup>5</sup> and higher catalytic activity.<sup>6–8</sup> The resulting size, shape, and size

distribution of alloy nanoparticles are determined by many reaction parameters; one of the most important is the chemical nature of the reactants. This fact is a strong motivation for the preparation and study of new molecular metal complexes that can serve as effective precursors.

An opportunity to influence the final nanoparticle properties is offered by employing carefully selected metal sources. New molecular and single-source precursors were applied in

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gold<sup>9–11</sup> and AuAg nanoalloy<sup>12</sup> synthesis by microwaveassisted reactions. Another example is the CuNi nanoalloy synthesis by hydrazine reduction of double complex salts.<sup>13</sup> Molecular precursors based on triphenylphosphine were used for the preparation of silver and copper nanoparticles. Triphenylphosphine complexes were studied in the 1960s<sup>14</sup> and 1970s,<sup>15,16</sup> but they have only recently been used as molecular precursors for nanoparticle synthesis. Although bis(triphenylphosphine)silver(I) myristate<sup>17</sup> and Cu(I) triphenylphosphine derivatives of ethylene glycol carboxylates<sup>18,19</sup> have been used for the preparation of nanoparticles of individual metals, triphenylphosphine carboxylate complexes have not been previously used in the synthesis of bimetallic nanoalloys.

A silver/copper nanoalloy was prepared by the reduction of a solution of metal precursors with hydrazine<sup>20,21</sup> or NaBH<sub>4</sub><sup>22</sup> in the presence of polyvinylpyrrolidone (PVP) or by thermal decomposition in long-chain alkyl amines, which act as highboiling-point solvents, reducing agents, and surfactants.<sup>23</sup> Oleylamine is the most frequently used long-chain alkyl amine in nanoalloy synthesis (e.g., CuAg,<sup>2,24,25</sup> CuNi,<sup>7</sup> CoNi,<sup>26</sup> AuAg,<sup>27</sup> and AuCu<sup>28</sup>). Silver/copper bimetallic nanoalloys are currently being studied for their thermal<sup>29</sup> and optical properties and potential industrial applications in catalysis,<sup>22,30</sup> electronics,<sup>31</sup> and medicine.<sup>32</sup>

In this work, we compared two triphenylphosphine Cu(I) complexes of aromatic carboxylic acids, 1 and 2, as copper precursors in the AgCu nanoparticle synthesis. They differ in the number of reducing phosphine ligands and also in the strength of carboxylate binding (chelating vs terminal). These structural factors may influence their reactivity in solvothermal decomposition into alloy nanoparticles. We combined them with  $[Ag(NH_2C_{12}H_{25})_2]NO_3^{33}$  as a precursor of silver in a hot mixture of oleylamine and 1-octadecene and prepared the AgCu nanoalloys. We determined the influence of precursor type on the course of the reaction and different properties of the prepared nanoparticles, such as elemental distribution, particle shape, size and size distribution, and surface plasmon resonance maxima.

#### EXPERIMENTAL SECTION

**Materials.** Benzoic acid (Hbea), phthalic acid (H<sub>2</sub>phta), copper-(II) hydroxide, and silver(I) nitrate were of house stock, triphenylphosphine (99%) was purchased from Acros Organics, and methanol (p.a.) was purchased from Lach-Ner. Oleylamine (80– 90%) and 1-octadecene (90%) were purchased from Sigma-Aldrich, dried over sodium, distilled under reduced pressure, and stored in Schlenk flasks over molecular sieves.

Synthesis of Copper(II) Carboxylate Precursors.  $Cu(bea)_2$ . 3H<sub>2</sub>O and  $Cu(phta) \cdot H_2O$  were prepared according to literature procedures<sup>34,35</sup> and characterized by TG/DSC in a synthetic air atmosphere (Figures S1 and S2). The content of Cu was determined by ICP-OES, and for both compounds the contents found matched the theoretical values. For details, see the Supporting Information.

**Synthesis of [Cu(PPh<sub>3</sub>)<sub>2</sub>(bea)] (1).** Copper(II) benzoate (1.799 g, 5.000 mmol) was reduced with PPh<sub>3</sub> (4.590 g, 17.5 mmol, a molar ratio of 1:3.5) in boiling methanol (30 cm<sup>3</sup>). When the reaction was performed for 1.5 h, the final solution was colorless. The reaction mixture was cooled to 25 °C, and colorless crystals formed. The solid was filtered off, washed with diethyl ether, and dried in the ambient atmosphere. Yield: 1.565 g, 44.13%.

FTIR (ATR, cm<sup>-1</sup>):  $\nu$  420 m, 488 s, 502 vs, 513 s, 530 m, 679 s, 694 vs, 722 s, 746 s, 842 m, 997 w, 1026 m, 1067 m, 1096 s, 1394 s ( $\nu_s$  COO), 1435 s, 1479 m, 1539 s ( $\nu_a$  COO), 1591 m, 2901 w, 2988 w, 3049 w, 3067 w. ESI-MS (+): m/z 587.1115 [Cu(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 40%;

603.1063 [Cu(PPh<sub>3</sub>)<sub>2</sub>O]<sup>+</sup>, 100%; 667.0443 [Cu<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>OH]<sup>+</sup>, 5%; 681.0599 [Cu<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(OCH<sub>3</sub>)]<sup>+</sup>, 10%; 709.0909 [Cu<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(OC<sub>3</sub>H<sub>7</sub>)]<sup>+</sup>, 20%; 771.0699 [M + Cu]<sup>+</sup>, 25%. TG/ DSC: thermal degradation in oleylamine at 227 °C (Figure S3). <sup>31</sup>P{<sup>1</sup>H} NMR (300 MHz, CDCl<sub>3</sub>): δ –2.5 ppm. Anal. Found: Cu, 9.28; C, 73.03; H, 4.85. Calcd for C<sub>43</sub>H<sub>35</sub>O<sub>2</sub>P<sub>2</sub>Cu: Cu, 8.96; C, 72.82; H, 4.97.

Synthesis of  $[Cu(PPh_3)_3(Hphta)]$  (2). Copper(II) phthalate hydrate (1.228 g, 5.000 mmol) was reduced with PPh<sub>3</sub> (4.590 g, 17.5 mmol, a molar ratio of 1:3.5) for 56 h in boiling methanol (30 cm<sup>3</sup>). A light blue precipitate was obtained. The solid product was filtered off, washed with diethyl ether, and dried in the ambient atmosphere. Yield: 2.678 g, 52.74%.

FTIR (ATR, cm<sup>-1</sup>):  $\nu$  414 w, 447 m, 495 s, 515 vs, 638 m, 692 vs, 726 m, 740 s, 794 w, 998 w, 1027 m, 1072 m, 1090 s, 1159 w, 1217 m, 1365 s ( $\nu_s$  COO), 1433 s, 1456 s, 1473 m, 1558 m ( $\nu_{as}$  COO), 1684 w, 2901 w, 2988 m, 3055 w. ESI-MS (+): *m/z* 587.1102 [Cu(PPh<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 70%; 603.1049 [Cu(PPh<sub>3</sub>)<sub>2</sub>O]<sup>+</sup>, 100%; 815.0586 [Cu<sub>2</sub>(PPh<sub>3</sub>)<sub>2</sub>(C<sub>8</sub>H<sub>5</sub>O<sub>4</sub>)]<sup>+</sup>, 15%; 1139.0709 [Cu<sub>3</sub>(PPh<sub>3</sub>)<sub>3</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)]<sup>+</sup>, 15%; 1695.0302 [Cu<sub>4</sub>(PPh<sub>3</sub>)<sub>3</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>4</sub>]<sup>+</sup>, 15%; 1957.1214 [Cu<sub>4</sub>(PPh<sub>3</sub>)<sub>4</sub>(C<sub>8</sub>H<sub>4</sub>O<sub>4</sub>)<sub>4</sub>]<sup>+</sup>, 20%. TG/DSC: thermal degradation in oleylamine at 221 °C (Figure S4). <sup>31</sup>P{<sup>1</sup>H} NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  –1.9 ppm. Anal. Found: Cu, 6.30; C, 73.29; H, 4.88. Calcd for C<sub>62</sub>H<sub>50</sub>O<sub>4</sub>P<sub>3</sub>Cu: Cu, 6.26; C, 73.33; H, 4.96.

Synthesis of  $[Ag(NH_2C_{12}H_{25})_2]NO_3$ . The synthesis of  $[Ag(NH_2C_{12}H_{25})_2]NO_3$  has been described by Wakuda et al.<sup>33</sup> AgNO<sub>3</sub> (11.05 g, 65.03 mmol) was mixed with NH<sub>2</sub>C<sub>12</sub>H<sub>25</sub> (24.10 g, 130.0 mmol, a 1:2 molar ratio). Acetonitrile (350 cm<sup>3</sup>) was added, and the mixture was stirred for 3 h at ambient temperature. Then a white precipitate was filtered off, washed with acetonitrile and diethyl ether, and dried at ambient temperature, avoiding light. TG/DSC: thermal degradation in oleylamine at 199 °C.

Synthesis of AgCu Nanoparticles. In a typical synthesis,  $[Cu(PPh_3)_2(bea)]$  or  $[Cu(PPh_3)_3(Hphta)]$  and  $[Ag(NH_2C_{12}H_{25})_2]$ -NO<sub>3</sub> were combined in the eutectic Ag:Cu ratio of 60.1:39.9 mol % in a total amount of 0.4 mmol and placed into a Schlenk flask, and the flask was evacuated/refilled with dry N2 three times. Then dry oleylamine (4 cm<sup>3</sup>) was added via a syringe. The mixture was heated to 85 °C to dissolve the precursors to a clear colorless solution. Olevlamine (16 cm<sup>3</sup>) and 1-octadecene (20 cm<sup>3</sup>) were preheated in a three-neck Schlenk flask to 120 °C under vacuum to remove residual water and oxygen. After 20 min, the vacuum was replaced with a dry N<sub>2</sub> atmosphere, and the temperature was increased to 230 °C. The precursor solution was rapidly injected into the hot mixture of solvents. After 10 min, the black reaction mixture was cooled to room temperature in a water bath, 20 cm<sup>3</sup> of acetone was added, and the suspension was centrifuged. Acetone (20 cm<sup>3</sup>) was added to increase the yield by aggregating nanoparticles that could then be easily separated by centrifugation (6000 rpm, 10 min). The precipitate was washed twice with a mixture of hexane and acetone (a 1:3 volume ratio), and then it was dispersed in hexane and characterized. Oleylamine acts as a reducing and capping agent,<sup>36-39</sup> and 1octadecene dilutes oleylamine to give the most regular shape.

Characterization Methods. Single-crystal X-ray diffraction data were collected on a Rigaku diffraction system equipped with a rotating anode X-ray source with multilayer optics (Mo K $\alpha$ , 7.107 nm). The final structures were adjusted by Mercury<sup>40</sup> and Olex2<sup>41</sup> software. See Table S1 in the Supporting Information. IR spectra were recorded on a Bruker Tensor T27 spectrometer (4000-400 cm<sup>-1</sup>). The ATR (Bruker Platinum ATR) technique was used. Electrospray ionization mass spectrometry (ESI-MS) was performed on an Agilent 6224 Accurate-Mass TOF mass spectrometer. Positive and negative modes were measured under the following conditions: nitrogen flow 5 dm<sup>3</sup> min<sup>-1</sup>, gas temperature 325 °C, nebulizer pressure 45 psi, capillary voltage -2500 V in positive mode and 2500 V in negative mode. Samples were dissolved in methanol and injected directly into the spectrometer using a syringe pump. The thermal stability of nanoparticle precursors was studied by the thermogravimetrydifferential scanning calorimetry (TG-DSC) technique on a Netzsch STA 449C Jupiter apparatus from 25 to 500 °C under flowing

nitrogen (70 cm<sup>3</sup> min<sup>-1</sup>) with a heating rate of 5  $^{\circ}$ C min<sup>-1</sup>. Complexes 1 and 2 were placed into alumina crucibles and heated without and with an excess of olevlamine. The hydrodynamic nanoparticle diameter was determined by the dynamic light scattering (DLS) technique on a Zetasizer Nano ZS (Malvern) instrument in a hexane solution at 25 °C. Samples were diluted and filtered by a syringe filter (pore size 450 nm). Small-angle X-ray scattering (SAXS) measurements were carried out on a Biosaxs 1000 (Rigaku) system at 25 °C with  $\lambda$  = 14 nm for 5 min. Samples were sealed into 1.5 mm borosilicate glass capillaries (WJM-Glas). Data were analyzed by the Primus<sup>42</sup> and GNOM<sup>43</sup> software. The UV-vis spectra were obtained on a Unican UV4 (Chromspec) instrument. Samples were prepared by the same procedure as for DLS, but they were diluted to onefourth. The TEM measurements were carried out on a Philips CM 12 TEM/STEM microscope with an EDAX Phoenix EDS detector and on JEOL JEM2010 and 3010 microscopes equipped with an EDX detector and a CCD camera with a resolution of  $1024 \times 1024$  pixels. The samples for TEM measurements were dispersed in hexane, and one drop of colloidal solution was placed on a carbon-coated copper grid and allowed to dry by evaporation at ambient temperature. Image analyses were performed by the ImageJ software.44 STEM-EDS measurements were performed on a FEI Titan Themis instrument with a combination of a spherical aberration image (Cs) corrector, a monochromator system, sensitive ChemiSTEM technology, and a high-end GATAN GIF Quantum energy filter for EELS and EFTEM with a new enhanced piezo stage, FEI and GATAN software, and a FEI Ceta 16-megapixel CMOS camera. Powder X-ray diffraction (PXRD) measurements were carried out on a SmartLab diffractometer (Rigaku), with a Cu lamp, fine focus  $\lambda(K\alpha_1) = 15.4060$  nm,  $\lambda(K\alpha_2) = 15.4443$  nm, and  $\lambda(K\beta) = 13.9225$  nm. Samples were measured in parallel beam order in transmission mode between two foils. The metal contents were analyzed by inductively coupled plasma optical emission spectroscopy (ICP-OES) on an iCAP 6500 Duo (Thermo) spectrometer. Dried nanoparticles were completely dissolved in HNO<sub>3</sub>, diluted, and characterized. Elemental analysis (C, H, and N) was performed on a Flash 2000 CHNS Elemental Analyzer (Thermo Scientific).

#### RESULTS AND DISCUSSION

Copper(I) Triphenylphosphine Carboxylate Com**plexes.** The complexes  $[Cu(PPh_3)_2(bea)]$  (1) and [Cu- $(PPh_3)_3(Hphta)$  (2) were synthesized from the corresponding Cu(II) carboxylates Cu(bea)<sub>2</sub>·3H<sub>2</sub>O and Cu(phta)·H<sub>2</sub>O by reduction with PPh<sub>3</sub> in boiling methanol and isolated as white solids in 44.13% and 52.74% yields, respectively. For a precise structural investigation of the prepared precursors, we performed single-crystal X-ray diffraction analyses. Suitable single crystals were grown from a chloroform solution by hexane diffusion. The complexes 1 and 2 crystallize in the  $P2_12_12_1$  and *Pbca* space groups, respectively, without any additional solvent molecules. Selected crystallographic data and structure refinement parameters are gathered in Table S1 in the Supporting Information. Relevant bond distances and angles are summarized in Table 1. The metal center of complex 1 is formed by a Cu(I) ion in a distorted-tetrahedral arrangement (Figure 1). The central atom is connected to both oxygen atoms of a chelating carboxylate group and two molecules of PPh<sub>3</sub>. The crystal structure of 1 has already been reported.<sup>45</sup> Our refinement converged to a substantially better value of R1(observed) = 2.21%.

The metal center of **2** is formed by a Cu(I) ion in a trigonalpyramidal arrangement (Figure 1). The copper ion is connected to one oxygen atom of a monodentate carboxylic group and phosphorus atoms of three PPh<sub>3</sub> ligands. There is a nonconnected oxygen atom (O2) of the carboxylic group and

Table 1. Selected Bond Lengths and Bond Angles of  $[Cu(PPh_3)_2(bea)]$  (1) and  $[Cu(PPh_3)_3(Hphta)]$  (2)

1		2				
Bond Lengths (Å)						
Cu1-P1	2.2228(7)	Cu1-P1	2.3325(6)			
Cu1-P2	2.2321(6)	Cu1-P2	2.3289(6)			
		Cu1-P3	2.3415(6)			
Cu1-O1	2.194(2)	Cu1-O1	2.126(1)			
Cu1-O2	2.187(2)					
Bond Angles (deg)						
P1-Cu1-P2	126.35(3)	P1-Cu1-P2	116.60(2)			
		P1-Cu1-P3	119.38(2)			
		P2-Cu1-P3	110.38(2)			
P1-Cu1-O1	117.32(5)	P1-Cu1-O1	92.85(4)			
P2-Cu1-O1	110.56(5)	P2-Cu1-O1	115.65(4)			
		P3-Cu1-O1	99.51(4)			
P1-Cu1-O2	110.33(5)					
P2-Cu1-O2	113.25(5)					
O1-Cu1-O2	60.74(6)					
P2-Cu1-O2 O1-Cu1-O2	113.25(5) 60.74(6)					

one free carboxylic group in the molecule. Refinement converged to R1(observed) = 3.04%.

The complex 1 contains two molecules of PPh<sub>3</sub> and a bidentate carboxylic group, which is symmetrically bound. The Cu–O distances are the same on the  $3\sigma$  criteria. The Cu–P bond lengths are between 2.223 and 2.233 Å. In contrast, complex 2 contains three molecules of  $PPh_3$  and a monodentate carboxylic group. The Cu-P bond lengths are substantially longer, between 2.329 and 2.342 Å. Both structure types are known in the literature, but Adner et al.<sup>19</sup> reported that complexes recrystallized from dichlomethane by the addition of *n*-hexane contained two PPh<sub>3</sub> molecules and a bidentate carboxylic group. The molecular structure of 1 agrees with this observation, but 2 differs because after the same recrystallization it contains three molecules of PPh<sub>3</sub>, which are more weakly bonded to the central Cu atom and also the Cu-P bonds are longer than in 1. These structural differences may influence the relative reactivities of 1 and 2 in thermolysis decomposition reactions (vide supra), as there are more equivalents of reducing PPh<sub>3</sub> per Cu in 2 in comparison to 1.

Infrared spectroscopy can be a reliable method for establishing the binding mode of carboxylato groups to a metal.<sup>46</sup> Regarding ionic carboxylates, the bridging and bidentate carboxylate complexes show a small difference in the value of  $\Delta\nu(\rm CO_2)$  ( $\Delta\nu(\rm CO_2) = \nu(\rm CO_{2,asym}) - \nu$ -( $\rm CO_{2,sym}$ )), while the parameter significantly increases for monodentate complexes. The values of  $\Delta\nu(\rm CO_2)$  are 145 cm<sup>-1</sup> (141 cm<sup>-1</sup> for Na-bea) and 193 cm<sup>-1</sup> (173 cm<sup>-1</sup> for Na<sub>2</sub>-terphta) for complexes 1 and 2, respectively. These values are in agreement with the crystal structure, as complex 1 contains a bidentate benzoate ligand while complex 2 possesses a monodentate phthalate.

For additional characterization of the prepared complexes, ESI-MS was used. Molecular peaks were not observed for **1** and **2**, but other fragments of both complexes could be assigned. Peaks at m/z 587 and 603 were observed in the spectra of both complexes, and they were assigned to  $[Cu(PPh_3)_2]^+$  and  $[Cu(PPh_3)_2O]^+$ , respectively. Fragments with multiple Cu atoms were also present, such as  $[M + Cu]^+$  for **1** and  $[M + 2Cu - H]^+$  for **2**.



Figure 1. Molecular structures of  $[Cu(PPh_3)_2(bea)]$  (1, left) and  $[Cu(PPh_3)_3(Hphta)]$  (2, right). Thermal ellipsoids are drawn at the 50% probability level.

The stabilities of the synthesized compounds in solution were characterized by NMR spectroscopy. Only one singlet was observed in the <sup>31</sup>P NMR spectrum of both 1 and 2 in CDCl<sub>3</sub>. Complex 1 displayed a resonance at -2.5 ppm ( $\Delta \nu_{1/2} = 53$  Hz) and 2 at -1.9 ppm ( $\Delta \nu_{1/2} = 18$  Hz). These singlets were broader than the singlet of free PPh<sub>3</sub> ( $\delta$  -5.2 ppm,  $\Delta \nu_{1/2} = 2.9$  Hz). The downfield chemical shift of phosphorus confirmed that a coordination reaction took place. The broadening of the signals is probably caused by the dynamic exchange of bound and free PPh<sub>3</sub>. When oleylamine was added in excess to the solutions of 1 and 2, the resonances shifted toward the value of free PPh<sub>3</sub> in oleylamine ( $\delta$  -5.5 ppm,  $\Delta \nu_{1/2} = 1.8$  Hz) and broadened, displaying values of -4.2 ppm ( $\Delta \nu_{1/2} = 115$  Hz) and -4.9 ppm ( $\Delta \nu_{1/2} = 42$  Hz), respectively.

The thermal behavior of both precursors was studied by TG/DSC in a nitrogen atmosphere. The melting points are 221.3 and 169.9 °C for 1 and 2, respectively. These melting events are not accompanied by decomposition, in contrast to their corresponding parent Cu(II) carboxylate complexes without the PPh<sub>3</sub> ligands. Thermal stability was determined in excess oleylamine under a nitrogen atmosphere. This arrangement simulated the reaction conditions of nanoparticle preparation in order to observe the thermal degradation of the metal precursors in the presence of alkylamine. The decomposition of 1 and 2 occurred at 227 and 221 °C, respectively, forming elemental copper (Figures S3 and S4). The measured data show that 1 is more thermally stable in the presence of alkylamine, and its melting point is higher than that of 2.

**AgCu Nanoparticles.** Colloidal solutions of AgCu nanoalloys were prepared by the hot injection technique in a preheated mixture of oleylamine and 1-octadecene. Oleylamine acts as a high-boiling-point solvent, reducing agent, and surfactant.<sup>23</sup> [Ag(NH<sub>2</sub>C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>]NO<sub>3</sub> served as the silver precursor because of its good solubility and reducing nature of its dodecylamine ligands. As a copper source, we used the two complexes [Cu(PPh<sub>3</sub>)<sub>2</sub>(bea)] (1) and [Cu-(PPh<sub>3</sub>)<sub>3</sub>(Hphta)] (2) with the aim to compare their performance in producing AgCu alloy nanoparticles. The resulting colloids were investigated by physical/chemical characterization methods. Their elemental composition, particle size, and SPR maxima are summarized in Table 2.

Table 2.	Summary	of AgCu	Nanoalloy	Characterization
Results				

		$ \begin{bmatrix} Cu(PPh_3)_2(bea) \end{bmatrix} \\ (1)$	[Cu(PPh <sub>3</sub> ) <sub>3</sub> (Hphta)] (2)
Ag/Cu	nominal content (mol %)	60.17/39.83	60.67/39.33
Ag/Cu	exptl ICP-OES (mol %)	50.83/49.17	59.69/40.31
DLS	$\overline{x}$ (nm)	24	24
	Z average (nm)	24	22
	PdI	0.262	0.070
SAXS	$D_{\max}$ (nm)	19.2	15.7
	5	5.50	4.50
TEM	$\overline{x}$ (nm)	13.3	14.1
	5	5.41	0.90
UV– vis	SPR (nm)	393/569	413

The starting eutectic Ag:Cu molar ratio (60:40) in the precursor mixture is well maintained in the nanoparticle elemental composition for the reaction of **2**, while the product of **1** contains less silver (50:50) (Table 2).

The size and dispersity of nanoparticles were determined by the DLS method. Their weighted-average diameters are the same in both cases, 24 nm. The AgCu nanoalloy prepared from 2 exhibits a slightly smaller Z average (the difference is 2 nm); however, its polydispersive index (PdI) is more than 3 times lower. This difference shows that the size distribution of nanoparticles prepared from 2 is narrower than that of 1. These results are confirmed by the TEM and SAXS analysis. Figure 2 shows the TEM images and size distribution histograms. Nanoparticles made from complex 2 are regular and almost monodisperse, and their average diameter is 14.1 nm with standard deviation s = 0.90. Nanoparticles from 1 have an oblate shape with broader size distribution and an average diameter of 13.3 nm and s = 5.41. The smaller average diameter is caused by the presence of smaller particles, but the most abundant diameter is in the range 15-17 nm, larger than



Figure 2. TEM images and size distribution histograms of AgCu prepared from 1,  $\overline{x} = 13.3$  nm (A), and 2,  $\overline{x} = 14.1$  nm (B).

for the nanoparticles from **2**. Larger diameter and a less regular shape were also determined by a SAXS analysis, where the most represented diameters of AgCu nanoparticles synthesized from **1** and **2** were 19.2 nm (s = 5.50) and 15.7 nm (s = 4.50), respectively. The less regular shape of nanoparticles from **1** is illustrated by the model calculated from the SAXS data, and Figure 3 displays average AgCu nanoparticles and higher values of standard deviation. While nanoparticles from **2** are spherical, those obtained from **1** are oblate with some irregularities in their shape. These models are in good agreement with the TEM observations, but the SAXS method, by its principle, provides information on a much larger set of particles. The



**Figure 3.** Models of average AgCu nanoparticles prepared from 1, d = 19.2 nm (A), and 2, d = 15.7 nm (B), obtained from the SAXS data analysis.

graphs of the distribution function and plots of the measured data are shown in Figures S5 and S6 in the Supporting Information.

The results of powder X-ray diffraction measurements of nanoparticles prepared from 1 revealed diffractions of phaseseparated silver and copper. Nanoparticles synthesized from 2 display broad diffractions assignable to an fcc AgCu solid solution. The lattice parameter of 4.070 Å, calculated by Vegard's law, corresponds to 3.4% of Cu in Ag.<sup>47,48</sup> However, broad diffractions of small AgCu crystallites can be composed of contributions from several metastable phases, as was observed in samples prepared by arc discharge,<sup>49</sup> ball milling,<sup>50</sup> solution reduction,<sup>51</sup> rapid quenching,<sup>52,53</sup> or sputtering<sup>54</sup> methods. The presence of an amorphous phase can also be considered.<sup>55</sup>

The spatial distribution of Ag and Cu elements in individual nanoparticles was examined by high-resolution STEM-EDS. Figurse 4 and 5 show the Ag and Cu elemental distribution in nanoparticles synthesized from 1 and 2, respectively. These images demonstrate differences in the morphology of the prepared nanoparticles. Some of the nanoparticles synthesized from 1 have a Janus-type morphology, and silver and copper phases are separated within a selected particle. There are also particles composed of only silver, which was in excess in the



Figure 4. STEM-EDS of AgCu nanoparticles prepared from 1: (A) bright field; (B) high angle annular dark field; (C) silver distribution; (D) copper distribution; (E) silver/copper distribution.



Figure 5. STEM-EDS of AgCu nanoparticles prepared from 2: (A) bright field; (B) high angle annular dark field; (C) silver distribution; (D) copper distribution; (E) silver/copper distribution.

reaction mixture due to the eutectic Ag:Cu ratio (60:40 mol %) used for the synthesis. On the other hand, nanoparticles prepared from 2 exhibit homogeneous distribution of both metals within one particle. This phenomenon demonstrates the crucial role of employed Cu precursor complexes, because different elemental distributions may influence nanoparticle properties, such as a less regular shape (Figure 3) and biphasic nature of AgCu nanoparticles prepared from 1 observed in HRTEM (Figure 6). Additional results from STEM-EDS analysis are shown in the Supporting Information (Figures S7–S10).



**Figure 6.** HRTEM of AgCu nanoalloys prepared from **1** (A, left) and **2** (B, right).

The results from STEM-EDS were confirmed by the HRTEM technique. Figure 6A shows a Janus structure of nanoparticles prepared from 1. Analysis of lattice distances showed that one particle is composed of two separated phases. A measurement of lattice distances demonstrates the presence of both Cu (111) and Ag (111) lattices in one single particle. The Cu (111) lattice constant was measured and calculated from the lattice distance, and its value is 358 pm, comparable to the theoretical value of 361 pm. Similarly, the Ag (111) lattice constant was 406 pm and is also close to the theoretical value of 408 pm. On the other hand, Figure 6B shows a AgCu solid solution with the composition 78 mol % of Ag and 22 mol % of Cu with a theoretical lattice constant of 398 pm.<sup>47,48</sup> The lattice constant for AgCu (111) was determined to be

equal to 400 pm. The formation of phase-separated (Janus) and solid solution nanoparticles from 1 and 2, respectively, could be tentatively explained by the different thermal stabilities of the copper precursors. Complex 2 decomposes at 221 °C, which is closer to the temperature degradation of  $[Ag(NH_2C_{12}H_{25})_2]NO_3$  in oleylamine (199 °C) in comparison to 1, which reacts at a slightly higher temperature of 227 °C. Silver and copper atoms are formed from 2 simultaneously to precipitate randomly mixed in one particle. In contrast, silver is formed more easily from its precursor than copper from 1, which results in particles with the Ag/Cu Janus morphology.

A comparison of the optical properties of the AgCu nanoalloys prepared from different precursors is shown in Figure 7. The AgCu nanoalloy prepared from 1 exhibited two local absorption maxima in the UV-vis spectrum (Figure 7A). The first band at 393 nm was assigned to the surface plasmon resonance (SPR) of neat silver and the second band at 569 nm to the SPR of neat copper. Two local maxima are caused by the Janus-type morphology of these nanoparticles<sup>56</sup> and are consistent with SPR of neat Cu and Ag metal nanoparticles prepared separately from the same precursors by an identical procedure. The AgCu nanoalloy prepared from 2 exhibited one absorption maximum in its UV-vis spectrum at 413 nm (Figure 7B). This SPR absorption maximum is slightly shifted to longer wavelengths in comparison to neat silver nanoparticles prepared from the  $[Ag(NH_2C_{12}H_{25})_2]NO_3$  precursor by the same route (393-395 nm). This red shift points to the formation of the solid solution of these metals with limited solubility of Cu in Ag. The SPR of copper occurs typically at longer wavelengths (around 570 nm), and its maximum is dependent on composition if alloy nanoparticles exhibit measurable SPR and particular metals are miscible. This assignment to SPR of AgCu is in accordance with the literature data.<sup>24</sup> These results are additional proof of the importance of the precursor in nanoalloy synthesis, because by changing the molecular precursors, we can influence the final optical properties of the nanoalloy.



Figure 7. UV-vis spectra of the AgCu nanoalloys prepared from 1 (A) and 2 (B). The intensity values for absorbance are plotted relative to the intensity of the oleylamine peak at 220 nm, which is considered to remain constant.

#### CONCLUSION

The two copper(I) molecular carboxylate complexes [Cu-(PPh<sub>3</sub>)<sub>2</sub>(bea)] (1) and [Cu(PPh<sub>3</sub>)<sub>3</sub>(Hphta)] (2) were prepared and structurally characterized, and their thermal stability was determined. They differ in the coordination mode of the carboxylate ligands and also in the number of bound triphenylphosphine ligands. We used them as precursors for the AgCu nanoalloy synthesis by the hot injection method together with the [Ag(NH<sub>2</sub>C<sub>12</sub>H<sub>25</sub>)<sub>2</sub>]NO<sub>3</sub> silver source. We have shown the effects of the precursor nature on the resulting nanoparticle size distribution, morphology, and optical properties. The AgCu nanoalloy particles prepared from 1 are phaseseparated featuring Janus-type morphology, a less regular shape, and broader size distribution. Their UV–vis absorption spectrum exhibited two local maxima assigned to separate surface plasmon resonances of Ag and Cu.

In contrast, the nanoalloy synthesized from 2 exhibited an increased Ag/Cu mixing, resulting in a AgCu solid-solution phase composition, a narrow size distribution, and regular spherical shape. The absorption spectrum exhibits only one SPR maximum, corresponding to the homogeneous AgCu alloy. One can speculate that complex 2 with its weaker association of the phthalate ligand to the Cu(I) center and the high number of coordinated phosphine molecules presents a more reactive precursor and, therefore, leads to a nucleation pathway that results in AgCu nanoparticles possessing a metastable solid-solution structure. The reactions of metal clusters and nanoparticles may be strongly influenced by small changes in the nature and arrangement of ligands, it was shown in the case of the destabilizing role of the triphenylphosphine shell in Au<sub>11</sub> clusters.<sup>57</sup> The presence of specific ligands has been demonstrated as a decisive factor in the formation of prenucleation species, which in fact control the final metal nanoparticle composition and architecture in the AuCu alloy.<sup>5</sup> To elucidate further this structure-property relationship, we continue our studies of other Ag/Cu carboxylate precursors.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.inorg-chem.9b02172.

Synthesis of starting compounds, TG/DSC curves, crystallographic data and structure refinement parameters, SAXS analyses, and STEM-EDS images and elemental maps (PDF)

#### **Accession Codes**

CCDC 1859625–1859626 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/data\_request/cif, or by emailing data\_request@ccdc.cam.ac.uk, or by contacting The Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223 336033.

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#### Notes

The authors declare no competing financial interest.

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