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### The Synthesis, Chemical and Physical Properties of Silver(I) Carboxylates and their Use in Copper-to-Copper Joining

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#### Abstract

The synthesis of  $[AgO_2CCR_2OC(O)OMe]$  (6, R = H; 7, R = Me) by treatment of HO<sub>2</sub>CCR<sub>2</sub>OC(O)OMe (4, R = H; 5, R = Me) with  $[AgNO_3]$  in presence of NEt<sub>3</sub> is reported. The reaction of 6 and 7 with 2 equiv of PPh<sub>3</sub> gave  $[AgO_2CCR_2OC-$ 

(O)OMe(PPh<sub>3</sub>)<sub>2</sub>] (8, R = H; 9, R = Me). The thermal behavior of 6 and 7 was studied by TG, DSC and TG-MS of which the latter evinced decarboxylation as initial decomposition step followed by Ag–C, C–C and C–O bond cleavages giving silver. For copper-to-copper joining, 6 and 7 were processed to spreadable pastes by mixing them with ethylene glycol (EG) or diethylene glycol (DEG). On contact of 7-EG with Cu sheets [Cu<sub>2</sub>(O<sub>2</sub>CCMe<sub>2</sub>OC(O)OMe)<sub>4</sub>·2H<sub>2</sub>O] (12) was formed. Hereafter, 6-EG and 6-DEG were solely applied in pressureless Cu joining at 250 °C. Thru addition of Ag µm-particles a tensile shear strength of 19 MPa was achieved, showing a significant higher value as received with commercially Ag nanopastes. The solid state structure of 5, 8, 9 and 12 was determined by single crystal X-ray structure analysis, showing [3+1] (P<sub>2</sub>O + O) (8), distorted tetrahedral (9) or octahedral (12) coordination spheres at the metal ion.

**KEYWORDS**: Silver(I) carboxylate, TG–(MS)/DSC, Solid state structure, Silver sintering, Copper-to-copper joining.

#### 1. Introduction

The continuous miniaturization process of electronic assemblies results in higher thermal stresses of electronic modules, due to an increase of power densities [1]. As consequence thereof, higher temperatures generated may result in the remelting of the joints and hence sufficient reliability cannot be assured [1,2]. This is a major challenge for conventional soldering materials. Likewise, a high content of lead in Sn–Pb solders restricts their use in electronic and automobile industries [2,3] and hence the development of lead–free joining alternatives for low temperature joining processes is a challenging task [4].

One approach for low temperature joining is given by using nanoparticles (NPs) (high surface-to-volume ratio) [5–8], enabling joining processes at temperatures far below the melting point of the corresponding bulk material, due to a reduced sintering and melting temperature of the NPs with decreased particle size [9–13]. Beneficial of NPs in the sintering process is the generation of high-strength and temperature resistant joints at low temperature [10–16].

In this regard, different joining procedures of bulk copper were recently reported [10–14,16,17–27]. One methodology is based on the use of commercial available silver NPs pastes [11–13,17]. However, these pastes show some limitations, *e.g.* they are cost-expensive and reveal higher decomposition temperatures due to aging processes during prolonged storage [11].

Silver NP-containing powders and pastes are accessible by the reduction of AgNO<sub>3</sub> by sodium citrate [18–20] or AgNO<sub>2</sub> by ethylene glycol in presence of polyvinylpyrrolidone as stabilizing component [19,21], and, for example, by admixing AgNO<sub>3</sub> with primary or secondary amines RR`NH containing different carbon chain lengths R and R', respectively, in the presence of ascorbic acid as reducing agent [28, 29]. A further methodology to produce silver NPs is given by the thermal decomposition of amino silver(I) complexes of type  $[Ag(C_{12}H_{25}NH_2)_2]NO_3$  [22], or applying silver(I) carboxylates such as  $[Ag(O_2CC_nH_{2n+1})]$  (n = 7, 13, 17) in a mixture of RNH<sub>2</sub> or NR'<sub>3</sub> (R = C<sub>n</sub>H<sub>2n+1</sub> (n = 8, 12, 18); R' = C<sub>n</sub>H<sub>2n+1</sub> (n = 2, 8)) [23]. However, the organic particle periphery can negatively impact the joining process, in particular for large joining areas, since a high amount of organic materials can cause voids in the joining seam. Out of this reason, either a thinning of the protecting layer [21,24,25], or the use of a mixture of nano- and micron-sized particles [26] is beneficial.

Another approach for low temperature copper-to-copper joining processes is based on the usage of single-source complexes such as silver(I) carboxylates, which *in situ* generate silver NPs, when heated to temperatures around 250 °C without any addition of reducing reagents and/or organic stabilizing components [27]. A further advantage of this approach is the possibility to influence the decomposition behavior, the metal content and the solubility of the silver(I) carboxylate complexes by their modification. Hence, the *in situ* formation of NPs from silver(I) carboxylates during the joining process facilitates a simplified handling of the material. Moreover, silver(I) carboxylates are cost–effective and straightforward to prepare and remain stable for a long time in solution and in the solid state. As recently shown, silver(I) carboxylates are favored over silver(I)-*n*-alkylamines [30]. Thus, to complete the sinter process prolonged holding times and/or higher temperatures would be required for the respective silver(I)-*n*-alkylamines [30].

In this study, the synthesis, chemical and physical properties of silver(I) carboxylates  $[AgO_2CCR_2OC(O)OMe]$  (R = H, Me) are described. They can serve as filler material in pressureless joining processes of copper sheets at 250 °C, since the *O*-carbomethoxy unit induces a low decomposition temperature and good solubility of the respective complexes.

#### 2. Experimental

#### 2.1. General

All synthetic methodologies were carried out under an atmosphere of argon with the solvents degassed prior to use. Chloroform was dried by heating it with  $P_2O_5$  at reflux and storing it afterwards over a 4 Å molecular sieve. Ethanol was distilled from

sodium/diethyl phthalate and acetonitrile was purified by distillation from calcium hydride. Dichlormethane and diethyl ether were dried with a solvent purification system (MB SPS–800, MBraun). All reagents were obtained from commercial suppliers and were used without further purification.

NMR spectra (500.3 MHz for <sup>1</sup>H, 125.8 MHz for <sup>13</sup>C and 202.5 MHz for <sup>31</sup>P) were recorded with a Bruker Avance III 500 NMR spectrometer at ambient temperature. Chemical shifts are reported in  $\delta$  (ppm) downfield from tetramethylsilane with the solvent as reference signal (<sup>1</sup>H NMR, CDCl<sub>3</sub>  $\delta$  = 7.26, DMSO– $d_6 \delta$  = 2.50, D<sub>2</sub>O  $\delta$  = 4.79, CD<sub>2</sub>Cl<sub>2</sub>  $\delta$  = 5.32; <sup>13</sup>C{<sup>1</sup>H} NMR, CDCl<sub>3</sub>  $\delta$  = 77.16 ppm, DMSO– $d_6 \delta$  = 39.52, CD<sub>2</sub>Cl<sub>2</sub>  $\delta$  = 53.84) or by external standards (<sup>31</sup>P{<sup>1</sup>H} NMR relative to 85 % H<sub>3</sub>PO<sub>4</sub> at 0.0 ppm and P(OMe)<sub>3</sub> at 139.0 ppm).

The FTIR spectra were recorded with a Thermo Nicolet IR 200 instrument. Elemental analyses were performed with a Thermo FLASHEA 1112 Series instrument. High-resolution mass spectra were recorded with a Bruker Daltonik micrOTOF-QII mass spectrometer performing in the ESI mode. The melting points were determined by using a Gallenkamp MFB 595 010 M melting point apparatus. The TG, DSC and TG-MS experiments were performed with a Mettler Toledo TGA/DSC1 1600 system with a MX1 balance coupled with Pfeifer Vacuum MS Thermostar GSD 301 T2 mass spectrometer.

#### 2.2. Single–Crystal X–ray Diffraction Analysis

Data of **5**, **8**, **9** and **12** were collected with an Oxford Gemini S diffractometer at 115 K (**5**), 110 K (**8**), 120 K (**9**) and 111 K (**12**) using Mo K<sub> $\alpha$ </sub> ( $\lambda$  = 0.71073 Å) radiation (for more details see Table S1, Supplementary Data). The molecular structures were solved by direct methods using SHELXS–13 [31] and refined by full–matrix least squares procedures on *F*<sup>2</sup> with SHELXL–13 [32,33]. All non–hydrogen atoms were

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refined anisotropically and a riding model was employed in the treatment of the hydrogen atom positions. Graphics for the molecular structures have been created by using ORTEP [34].

The carboxylic hydrogen atom in **5** has been refined as an idealized OH group with the torsion angle derived from electron density (AIFX 147). The water-hydrogens in **12** were derived from residual electron density and fixed by using DFIX and DANG instructions. Crystallographic data for **5**, **8**, **9** and **12** have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository numbers CCDC 1815468 (**5**), 1815469 (**8**), 1815470 (**9**·CH<sub>2</sub>Cl<sub>2</sub>) and 1815471 (**12**); (http://www.ccdc.cam.ac.uk).

#### 2.3. Synthesis of carboxylic acids 4 and 5

The preparation of the title complexes was carried out on the basis of the procedure by Fischer *et al.* [35]. Since for the characterization of **4** only the elemental analysis data were reported, high–resolution ESI–TOF mass spectrometric as well as IR and NMR ( $^{1}$ H,  $^{13}$ C{ $^{1}$ H}) spectroscopic data of **4** are added here for completeness. For the synthesis of **5**, 2–hydroxy–2–methylpropanoic acid was used as reactant. After appropriate work–up, **5** was obtained as analytically pure compound.

**2–((Methoxycarbonyl)oxy)acetic acid (4)**. 2–Hydroxyacetic acid (1) (7.00 g, 92.04 mmol), *N*,*N*–dimethylaniline (34.8 mL, 276 mmol) and methyl chloroformate (21.4 mL, 276 mmol) were reacted as described in reference [35]. Distillation (100 °C, 3 x  $10^{-2}$  mbar) afforded the title compound as a colorless oil. Yield: 8.00 g (59.7 mmol, 65 % based on 1).

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Anal. Calcd. for C<sub>4</sub>H<sub>6</sub>O<sub>5</sub> (134.09 g mol<sup>-1</sup>): C, 35.83; H, 4.51. Found: C, 35.41; H, 4.74. Bp.: 100 °C at  $3 \cdot 10^{-2}$  mbar. IR (CHCl<sub>3</sub>, NaCl; cm<sup>-1</sup>):  $\tilde{v}$  = 2963 (br), 1764 (s, C=O,<sub>MeOC(O)O</sub>), 1743 (s, C=O), 1446 (m), 1419 (w), 1293 (m), 1238 (m), 1009 (m), 913 (w), 783 (vs), 757 (vs). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 10.90 (s, br, 1H, CO<sub>2</sub>H), 4.67 (s, 2H, CH<sub>2</sub>), 3.82 (s, 3H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 173.33 (C<sub>q</sub>-CO<sub>2</sub>H), 155.44 (C<sub>q</sub>-H<sub>3</sub>COCO<sub>2</sub>), 62.97 (CH<sub>2</sub>), 55.60 (CH<sub>3</sub>). HRMS (ESI-TOF, m/z): calcd. for C<sub>4</sub>H<sub>6</sub>O<sub>5</sub>Na [M + Na]<sup>+</sup>: 157.0107, found 157.0079.

**2–((Methoxycarbonyl)oxy)–2–methylpropanoic** acid (5). 2–Hydroxy–2– methylpropanoic acid (2) (9.50 g, 91.3 mmol), *N*,*N*–dimethylaniline (34.6 mL, 274 mmol) and methyl chloroformate (21.2 mL, 274 mmol) were reacted on the basis of the procedure reported by Fischer *et al.* [35]. The title compound was obtained as a colorless solid. Yield: 12.0 g (74.0 mmol, 81 % based on **2**).

Anal. Calcd. for C<sub>6</sub>H<sub>10</sub>O<sub>5</sub> (162.14 g mol<sup>-1</sup>): C, 44.45; H, 6.22. Found: C, 44.52; H, 6.30. Mp.: 96 °C. IR (KBr; cm<sup>-1</sup>):  $\tilde{v}$  = 3019 (br), 2965 (m), 2907 (m), 2689 (w), 2581 (w), 1746 (vs, C=O,<sub>MeOC(O)O</sub>), 1717 (vs, C=O), 1474 (m), 1456 (m), 1441 (s), 1376 (m), 1297 (vs), 1246 (s), 1201 (s), 1152 (vs), 1095 (m), 964 (m), 928 (m), 890 (m), 793 (m), 626 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 11.63 (s, br, 1H, CO<sub>2</sub>H), 3.77 (s, 3H, OCH<sub>3</sub>), 1.62 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 178.59 (C<sub>q</sub>-CO<sub>2</sub>H), 154.35 (C<sub>q</sub>-H<sub>3</sub>COCO<sub>2</sub>), 79.92 (C<sub>q</sub>-C(CH<sub>3</sub>)<sub>2</sub>), 54.96 (OCH<sub>3</sub>), 24.48 (CH<sub>3</sub>). HRMS (ESI-TOF, m/z): calcd. for C<sub>6</sub>H<sub>10</sub>O<sub>5</sub>Na [M + Na]<sup>+</sup>: 185.0420, found 185.0409.

#### 2.4. Synthesis of silver(I) carboxylates 6 and 7

**General procedure**. Silver(I) nitrate was dissolved in 100 mL of ethanol and acetonitrile (2.7 mL for the synthesis of **6**, 3 mL for the synthesis of **7**) at ambient

temperature. To this solution the carboxylic acid **4** or **5** and NEt<sub>3</sub> in 10 mL of ethanol were added at 0 °C with a syringe within 10 min. Immediately, a colorless solid began to precipitate. Stirring of the reaction mixture was continued for 1 h at ambient temperature. Subsequently, the colorless suspension was filtered off and washed twice with cold ethanol (each 30 mL, 0 °C) and then twice with diethyl ether (each 10 mL,

20 °C). Removal of all volatiles under reduced pressure gave 6 or 7.

**2–((Methoxycarbonyl)oxy)–ethane–1–carboxylatosilver(l) (6)**. Compound **4** (4.50 g, 33.6 mmol) and NEt<sub>3</sub> (5.10 mL, 36.8 mmol) were reacted with silver(l) nitrate (5.71 g, 33.6 mmol) as described above. After appropriate work–up, the title complex was obtained as a colorless solid. Yield: 7.69 g (31.9 mmol, 95 % based on **4**).

Anal. Calcd. for C<sub>4</sub>H<sub>5</sub>AgO<sub>5</sub> (240.95 g mol<sup>-1</sup>): C, 19.94; H, 2.09. Found: C, 19.99; H, 1.98. Mp.: 215 °C (decomposition). IR (KBr; cm<sup>-1</sup>):  $\tilde{v}$  = 2955 (w), 1753 (s, C=O,<sub>MeOC(O)O</sub>), 1614 (vs, CO<sub>2,asym</sub>), 1448 (m, CO<sub>2,sym</sub>), 1422 (s), 1342 (m), 1282 (vs), 987 (m), 914 (m), 792 (m), 664 (m). <sup>1</sup>H NMR (DMSO–*d*<sub>6</sub>,  $\delta$ ): 4.39 (s, 2H, C*H*<sub>2</sub>), 3.68 (s, 3H, OC*H*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO–*d*<sub>6</sub>,  $\delta$ ): 170.55 (C<sub>q</sub>–CO<sub>2</sub>Ag), 155.31 (C<sub>q</sub>– H<sub>3</sub>COCO<sub>2</sub>), 65.97 (CH<sub>2</sub>), 54.43 (OCH<sub>3</sub>). HRMS (ESI–TOF, m/z): calcd. for C<sub>4</sub>H<sub>5</sub>AgO<sub>5</sub>Na [M + Na]<sup>+</sup>: 262.9080, found 262.9099.

**2–((Methoxycarbonyl)oxy)–2–methylpropane–1–carboxylatosilver(I) (7)**. Carboxylic acid **5** (6.00 g, 37.0 mmol) and NEt<sub>3</sub> (5.60 mL, 40.4 mmol) were reacted with silver(I) nitrate (6.29 g, 37.0 mmol) as described above. After appropriate work–up, the title complex was obtained as a colorless solid. Yield: 9.15 g (34.0 mmol, 92 % based on **5**).

Anal. Calcd. for C<sub>6</sub>H<sub>9</sub>AgO<sub>5</sub> (269.00 g mol<sup>-1</sup>): C, 26.79; H, 3.37. Found: C, 26.88; H, 3.29. Mp.: 205 °C. IR (KBr; cm<sup>-1</sup>):  $\tilde{v} = 2991$  (w), 1740 (vs, C=O,<sub>MeOC(O)O</sub>), 1596 (vs, CO<sub>2,asym</sub>), 1448 (m), 1407 (s, CO<sub>2,sym</sub>), 1367 (m), 1299 (vs), 1214 (m), 1144 (s), 1102 (m), 961 (m), 820 (m), 794 (m). <sup>1</sup>H NMR (DMSO– $d_6$ ,  $\delta$ ): 3.60 (s, 3H, OCH<sub>3</sub>), 1.48 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (DMSO– $d_6$ ,  $\delta$ ): 175.11 (C<sub>q</sub>–CO<sub>2</sub>Ag), 153.75 (C<sub>q</sub>–H<sub>3</sub>COCO<sub>2</sub>), 82.35 (C<sub>q</sub>–C(CH<sub>3</sub>)<sub>2</sub>), 53.76 (OCH<sub>3</sub>), 25.69 (CH<sub>3</sub>). HRMS (ESI–TOF, m/z): calcd. for C<sub>6</sub>H<sub>9</sub>AgO<sub>5</sub>Na [M + Na]<sup>+</sup>: 290.9393, found 290.9407.

#### 2.5. Synthesis of silver(I) complexes 8 and 9

**General procedure**. The silver carboxylates **6** and **7**, respectively, were dissolved in 15 mL of dichloromethane and PPh<sub>3</sub> was added in a single portion at 0 °C. The respective reaction solution was stirred for 2 h at ambient temperature. Afterwards, the reaction solution was filtered through a pad of Celite and all volatiles were removed from the filtrate in vacuum, whereby a colorless solid of **8** or **9** remained.

**2–((Methoxycarbonyl)oxy)–ethane–1–carboxylato(bistriphenylphosphane)– silver(I) (8).** Complex **6** (200 mg, 0.83 mmol) and PPh<sub>3</sub> (435 mg, 1.66 mmol) were reacted as described above. The title complex was obtained as a colorless solid. Yield: 574 mg (0.75 mmol, 90 % based on **6**).

Anal. Calcd. for  $C_{40}H_{35}AgO_5P_2$  (765.49 g mol<sup>-1</sup>): C, 62.76; H, 4.61. Found: C, 62.94; H, 4.58. Mp.: 171 °C. IR (KBr; cm<sup>-1</sup>):  $\tilde{v} = 3051$  (w), 3004 (w), 2955 (w), 1753 (vs, C=O,\_MeOC(O)O), 1601 (vs, CO<sub>2,asym</sub>), 1479 (s, CO<sub>2,sym</sub>), 1435 (vs), 1408 (s,) 1340 (m), 1254 (vs), 1183 (w), 1096 (s), 1070 (w), 1027 (m), 990 (m), 910 (m), 792

(m), 746 (vs), 695 (vs), 516 (vs). <sup>1</sup>H NMR (CDCl<sub>3</sub>,  $\delta$ ): 7.40–7.28 (m, 30H, C<sub>6</sub>H<sub>5</sub>), 4.56 (s, 2H, C*H*<sub>2</sub>), 3.78 (s, 3H, OC*H*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 172.89 (C<sub>q</sub>–CO<sub>2</sub>Ag), 156.12 (C<sub>q</sub>–H<sub>3</sub>COCO<sub>2</sub>), 134.05 (d, *J*<sub>PC</sub> = 16.54 Hz, C<sub>6</sub>H<sub>5</sub>) 132.21 (d, *J*<sub>PC</sub> = 28.15 Hz, C<sub>q</sub>–C<sub>6</sub>H<sub>5</sub>), 130.32 (s, C<sub>6</sub>H<sub>5</sub>), 128.99 (d, *J*<sub>PC</sub> = 9.76 Hz, C<sub>6</sub>H<sub>5</sub>), 66.54 (CH<sub>2</sub>), 54.65 (OCH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>,  $\delta$ ): 9.40 (s).

2–((Methoxycarbonyl)oxy)–2–methylpropane–1–carboxylato(bistriphenyl– phosphane)silver(I) (9). Complex 7 (300 mg, 1.12 mmol) and PPh<sub>3</sub> (588 mg, 2.24 mmol) were reacted as described above. The title complex was obtained in analytically pure form as a colorless solid. Yield: 841 mg (1.06 mmol, 95 % based on 7).

Anal. Calcd. for  $C_{42}H_{39}AgO_5P_2$  (793.57 g mol<sup>-1</sup>): C, 63.57; H, 4.95. Found: C, 64.04; H, 4.97. Mp.: 160 °C (decomposition). IR (KBr; cm<sup>-1</sup>):  $\tilde{v}$  = 3054 (m), 3000 (w), 2972 (w), 1751 (vs, C=O,<sub>MeOC(O)O</sub>), 1592 (vs, CO<sub>2,asym</sub>), 1479 (s, CO<sub>2,sym</sub>), 1434 (vs), 1401 (s,) 1362 (m), 1272 (vs), 1210 (m), 1181 (w), 1147 (s), 1097 (s), 1027 (m), 997 (w), 960 (m), 932 (w), 817 (m), 784 (m), 746 (vs), 695 (vs), 516 (s). <sup>1</sup>H NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 7.47–7.33 (m, 30H, C<sub>6</sub>H<sub>5</sub>), 3.66 (s, 3H, OC*H*<sub>3</sub>) 1.62 (s, 6H, C*H*<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 177.64 (C<sub>q</sub>– CO<sub>2</sub>Ag), 154.79 (C<sub>q</sub>–H<sub>3</sub>COCO<sub>2</sub>), 134.32 (d, J<sub>PC</sub> = 16.71 Hz, C<sub>6</sub>H<sub>5</sub>) 132.73 (d, J<sub>PC</sub> = 27.41 Hz, C<sub>q</sub>–C<sub>6</sub>H<sub>5</sub>), 130.61 (C<sub>6</sub>H<sub>5</sub>), 129.23 (d, J<sub>PC</sub> = 9.72 Hz, C<sub>6</sub>H<sub>5</sub>), 83.49 (C<sub>q</sub>–C(CH<sub>3</sub>)<sub>2</sub>), 54.08 (OCH<sub>3</sub>), 26.14 (CH<sub>3</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CD<sub>2</sub>Cl<sub>2</sub>,  $\delta$ ): 8.92 (s).

**2.6. Synthesis of sodium carboxylates 10 and 11** (Reference substances for IR studies)

**General procedure**. Sodium hydroxide was dissolved in 12 mL of methanol at ambient temperature. To this solution carboxylic acid **4** or **5** in 5 mL of methanol was added in a single portion at ambient temperature. Stirring of the reaction mixture was continued for 10 h at ambient temperature. Subsequently, all volatiles were removed under reduced pressure to give **10** or **11**.

Sodium 2–((methoxycarbonyl)oxy)–ethane–1–carboxylate (10). Sodium hydroxide (86.0 mg, 2.15 mmol) and carboxylic acid 4 (288 mg, 2.15) were reacted as described above. The title complex was obtained as a colorless solid. Yield: 335 mg (2.15 mmol, 100 % based on 4).

Anal. Calcd. for C<sub>4</sub>H<sub>5</sub>NaO<sub>5</sub> (156.07 g mol<sup>-1</sup>): C, 30.78; H, 3.23. Found: C, 30.77; H, 3.16. Mp.: 250 °C decomposition. IR (KBr; cm<sup>-1</sup>):  $\tilde{v}$  = 2982 (w), 1751 (vs, C=O,<sub>MeOC(O)O</sub>), 1607 (vs, CO<sub>2,asym</sub>), 1457 (s), 1439 (s, CO<sub>2,sym</sub>), 1352 (m), 1291 (vs), 1253 (s), 993 (s), 952 (m), 923 (m), 786 (s), 675 (m). <sup>1</sup>H NMR (D<sub>2</sub>O,  $\delta$ ): 4.44 (s, 2H, CH<sub>2</sub>), 3.78 (s, 3H, OCH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O,  $\delta$ ): 175.03 (C<sub>q</sub>-CO<sub>2</sub>Na), 156.38 (C<sub>q</sub>-H<sub>3</sub>COCO<sub>2</sub>), 65.64 (CH<sub>2</sub>), 55.24 (OCH<sub>3</sub>). HRMS (ESI-TOF, m/z): calcd. for C<sub>4</sub>H<sub>5</sub>NaO<sub>5</sub>H [M + H]<sup>+</sup>: 157.0107, found 157.0103.

Sodium 2–((methoxycarbonyl)oxy)–2–methylpropane–1–carboxylate (11). Sodium hydroxide (95.0 mg, 2.38 mmol) and carboxylic acid **5** (386 mg, 2.38) were reacted as described above. The title complex was obtained as a colorless solid. Yield: 438 mg (2.38 mmol, 100 % based on **5**).

Anal. Calcd. for C<sub>6</sub>H<sub>9</sub>NaO<sub>5</sub> (184.12 g mol<sup>-1</sup>): C, 39.14; H, 4.93. Found: C, 39.13; H, 4.94. Mp.: 138 °C. IR (KBr; cm<sup>-1</sup>):  $\tilde{v} = 2992$  (w), 1738 (vs, C=O,<sub>MeOC(O)O</sub>), 1601 (vs, CO<sub>2,asym</sub>), 1447 (s), 1409 (s, CO<sub>2,sym</sub>), 1367 (m), 1302 (vs), 1214 (m), 1145 (s), 1103 (m), 962 (m), 935 (w), 794 (m). <sup>1</sup>H NMR (D<sub>2</sub>O,  $\delta$ ): 3.71 (s, 3H, OCH<sub>3</sub>), 1.48 (s, 6H, CH<sub>3</sub>). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>2</sub>O,  $\delta$ ): 179.71 (C<sub>q</sub>-CO<sub>2</sub>Ag), 155.02 (C<sub>q</sub>-H<sub>3</sub>COCO<sub>2</sub>), 83.38 (C<sub>q</sub>-C(CH<sub>3</sub>)<sub>2</sub>), 54.69 (OCH<sub>3</sub>), 24.29 (CH<sub>3</sub>). HRMS (ESI-TOF, m/z): calcd. for C<sub>6</sub>H<sub>9</sub>NaO<sub>5</sub>H [M + H]<sup>+</sup>: 185.0420, found 185.0420.

2.7. Tetra- $\mu$ -(2-((methoxycarbonyl)oxy)-2-methylpropane-1-carboxylato)bis(aqua)-dicopper(II) (12). A paste made from 7 and ethylene glycol was applied on a copper sheet. After an application time of 1 h the paste underwent a color change from off-white to turquoise. The formed turquoise colored solid was suspended in water, filtered off and the obtained aqueous solution was subsequently evaporated at ambient temperature. The title complex was obtained as turquoise crystals.

Anal. Calcd. for  $C_{24}H_{40}Cu_2O_{22}$  (807.64 g mol<sup>-1</sup>): C, 35.69; H, 4.99. Found: C, 35.77; H, 4.82. Mp.: 121 °C. IR (KBr; cm<sup>-1</sup>):  $\tilde{v} = 3495$  (br), 2995 (w), 1758 (vs, C=O,\_{MeOC(O)O}), 1627 (vs, CO<sub>2,asym</sub>), 1564 (m), 1478 (s), 1462 (s), 1423 (s, CO<sub>2,sym</sub>), 1368 (m), 1308 (vs), 1215 (s), 1163 (vs), 1102 (m), 966 (m), 935 (m), 829 (m), 795 (m), 783 (vs), 652 (m). HRMS (ESI-TOF, m/z): calcd. for  $C_{24}H_{36}Cu_3O_{20}$  [2 M\* + Cu]<sup>+</sup>: 834.9668, found 834.9676;  $C_{36}H_{54}Cu_4O_{30}$  [3 M + Cu]<sup>+</sup>: 1219.9866, found 1219.9851. M\* = [Cu(O<sub>2</sub>CCMe<sub>2</sub>OC(O)OMe)<sub>2</sub>].

#### 2.8. Joining process

For the joining experiments, copper sheets (ISO: Cu–ETP, EN: CW004A, DIN material number 2.0060) with a purity of  $\geq$  99.9 % were used. Due to the most suitable thermal behavior (see Section *Results and Discussion*), complex **6** was selected as filler material for the joining experiments. To ensure an efficient and hence straightforward application, **6** (initial state: solid) was mixed with two different solvents (ethylene glycol (EG) and diethylene glycol (DEG)) to prepare the corresponding joining pastes **6**–EG and **6**–DEG, respectively. With these spreadable pastes, an application similar to conventional soldering or brazing pastes is possible. Furthermore, the addition of Ag particles (0.7 – 1.2 µm, 99.9 %, Chempur) to **6** in different mass ratios was examined to analyze the influence on the achievable strengths and the resulting microstructure of the joints.

All joining experiments were carried out pressureless with a joining temperature of 250 °C and a holding time of 10 min. The heating of the samples was carried out in air by means of induction. The determination of the tensile shear strength as well as the microstructure investigations were performed using the sample geometry shown in Figure 1. The joining area was 9.0 mm x 7.5 mm. The examination of all tensile specimens – at least five individual samples per variation – was performed with a universal tensile testing machine Zwick/Roell Z020 at ambient temperature and at a strain rate of  $10^{-3}$  s<sup>-1</sup>. The microstructure of the joints was analyzed with a scanning electron microscope (LEO 1455VP) to correlate the resulting microstructure with the achievable strengths.



Overlap: 7.5 mm Sheet thickness: 3 mm Jocki

Figure 1. Sample geometry for joining experiments.

#### 3. Results and Discussion

#### 3.1. Synthesis and characterization

The synthesis of carboxylic acids **4** and **5** was carried out as shown in Scheme 1 according to reference [35]. Subsequent treatment of **4** and **5** with equimolar amounts of  $[AgNO_3]$  in presence of NEt<sub>3</sub> in ethanol afforded silver(I) carboxylates **6** and **7** in excellent yields as colorless solids (Scheme1). Complexes **6** and **7** are soluble in polar organic solvents such as acetonitrile and dimethyl sulfoxide.



Scheme 1. Synthesis of 4 – 7.

Since, from **6** and **7** no single crystals suitable for X–ray diffraction analysis could be obtained, they were reacted with 2 equiv of PPh<sub>3</sub> in dichloromethane at ambient temperature to give  $[AgO_2CCR_2OC(O)OMe(PPh_3)_2]$  (**8**, R = H; **9**, R = Me) (Equation (1)) in a yield of 90 % (**8**) or 95 % (**9**).



The identity of **4–9** was confirmed by elemental analysis, IR, <sup>1</sup>H, <sup>13</sup>C{<sup>1</sup>H} and <sup>31</sup>P{<sup>1</sup>H} NMR spectroscopy and high–resolution ESI–TOF mass spectrometry (**4–7**) (Experimental). The molecular structure of **5**, **8** and **9** in the solid state was determined by single crystal X–ray structure analysis.

The IR spectra of **6–9** show the symmetric and asymmetric stretching vibrations  $(\tilde{v}_{CO2,sym}; \tilde{v}_{CO2,asym})$  of the carboxylato groups at about 1407 and 1614 cm<sup>-1</sup> (Table 1). The obtained separations  $\Delta \tilde{v}_{CO2} = \tilde{v}_{CO2,asym} - \tilde{v}_{CO2,sym}$  are 166 cm<sup>-1</sup> for **6** and 189 cm<sup>-1</sup> for **7**. These values are close to the differences of the corresponding sodium carboxylates **10** and **11** (reference substances, Table 1 and Experimental), implying a bidentate bridging coordination mode [36–38]. For **8** and **9** differences of  $\Delta \tilde{v}_{CO2} = 122$  and 113 cm<sup>-1</sup> were found (Table 1), indicating a chelating binding mode [36–38], which was also verified by single crystal X–ray structure analysis (vide infra).

Compd.	${\widetilde v}_{ ext{CO2,asym}}$ [cm <sup>-1</sup> ]	${\widetilde v}_{ m CO2, sym}$ [cm <sup>-1</sup> ]	$\Delta \widetilde{v}_{CO2}{}^{a)}$ [cm <sup>-1</sup> ]
6	1614	1448	166
7	1596	1407	189
8	1601	1479	122
9	1592	1479	113
10	1607	1439	168
11	1601	1409	192

Table 1.  $\tilde{v}_{CO2}$  Absorptions and  $\Delta \tilde{v}_{CO2}$  values for 6–11.

a)  $\Delta \tilde{v}_{CO2} = \tilde{v}_{CO2,asym} - \tilde{v}_{CO2,sym}$ 

<sup>1</sup>H NMR spectroscopy allows to trace the reaction of **4**/**5** to **6**/**7** since upon treatment of **4**/**5** with [AgNO<sub>3</sub>] and NEt<sub>3</sub> the carboxylic proton is removed. The introduction of PPh<sub>3</sub> in **6** and **7** to produce **8** and **9** is accompanied by a typical downfield shift of the <sup>31</sup>P NMR resonance signal from -5.47 ppm (free PPh<sub>3</sub> [39]) to 9.40 ppm for **8**, and 8.92 ppm for **9** [40, 41] (Experimental).

#### 3.2. Solid state structures

Single crystals of **5** (Figure 2), **8** and **9** (Figure 3) suitable for X-ray diffraction studies were obtained by layering a dichloromethane solution containing the respective compounds with hexane at ambient temperature. Selected bond distances (Å) and bond angles (°) are summarized in the captions of Figures 2 and 3. Compounds **5** and **9** crystallize in the monoclinic space group  $P2_1/c$  and **8** in triclinic P-1, each with one molecule in the asymmetric unit. The carboxylic functionality in **5** forms hydrogen bridge bonds to an adjacent molecule, resulting in the formation of a dimer (Figure 2). The C-O single bond (C6-O4) of 1.3053(15) Å can clearly be distinguished from the C=O double bond (C6-O5) with 1.2190(16) Å.



**Figure 2.** ORTEP (50 % probability level) of the molecular structure of **5** involved in intermolecular hydrogen bridge–bond formation (pale blue). C–bonded hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): C6–O4 1.3053(15), C6–

O5 1.2190(16), O2–C2–O1 126.71(13), O2–C2–O3 125.72(13), O1–C2–O3 107.57(12), O5–C6–O4 124.35(13). Symmetry operation for generating equivalent atoms ('): 1–x, 2–y, –z. Hydrogen bridge–bond properties: O4···O5' 2.6155(13) Å, O1–H1···O2 178 °.

Silver complexes **8** and **9** consist of the bidentate bonded carboxylato and two datively-bonded PPh<sub>3</sub> groups. In **8**, the atoms P1, P2 and O1 form a 3-fold coordinated planar geometry at Ag1, whereby the P1-Ag1-P2 angle of 128.70(2) ° is the largest one observed in **8**. This angle and P-Ag1-O1 (122.35(5), 107.72(5) °) are in the range to recently published phosphane coordinated silver(I) carboxylates [40,42]. The O2 atom stabilizes the complex as a weakly coordinating ligand with 1.955(2) Å above the P<sub>2</sub>O1 plane (Figure 3). This causes a slight shift of Ag1 out of this P<sub>2</sub>O1 plane towards O2 by 0.1552(7) Å resulting in a [3+1] coordination geometry. This is also supported by different Ag–O bond distances, which are decreased to 2.3238(18) Å for O1, compared to more weakly bonded O2 (2.6194(16) Å). This is due to the presence of a C–O single bond between C1 and O1 (1.255(3) Å) and a carbonyl moiety for the C1–O2 bond (1.225(3) Å).



**Figure 3**. ORTEPs (probability level: 50 %, **8** and **9**) of the molecular structures of **8** (left) and **9** (right) with the atom numbering schemes. All hydrogen atoms and one disordered molecule of dichloromethane (**9**) have been omitted for clarity. Selected bond distances (Å) and angles (°) for **8**: C1–O1 1.255(3), C1–O2 1.225(3), Ag1–O1 2.3238(18), Ag1–O2 2.6194(16), Ag1–P1 2.4270(6), Ag1–P2 2.4181(6), O1–Ag1–O2 52.59(6), P1–Ag1–P2 128.70(2), P2–Ag1–O1 122.35(5), P1–Ag1–O1 107.72(5) and **9**: C1–O1 1.226(9), C1–O2 1.250(9), Ag1–O1 2.465(5), Ag1–O2 2.444(5), Ag1–P1 2.431(3), P1–Ag1–P2 126.59(6), P1–

Ag1–O2 119.81(15), P2–Ag1–O2 109.34(15), P1–Ag1–O1 110.80(15), P2–Ag1–O1 114.64(16), O1–Ag1–O2 53.44(15).

In contrast, complex **9** exhibits equal Ag1–O distances of 2.465(5) (O1) and 2.444(5) Å (O2) and thus, a symmetrical complexation of the Ag ion by the carboxylato group in a distorted tetrahedral environment is present (Figure 3). This is supported by shifts of O1 and O2 out of the AgP<sub>2</sub> plane by 1.259(7) (O1) and 0.922(7) (O2) Å, which are in close range compared to **8**, where O1 is solely shifted by 0.485(2) Å and O2 by 1.5213(19) Å (Figure 4). The plane intersection of the AgCO<sub>2</sub> unit towards the AgP<sub>2</sub> fragment in **9** is 82.01(19) °, further evidencing a tetrahedral coordination sphere at Ag1. In **8**, the AgCO<sub>2</sub> plane is rotated by 66.18(5) ° towards the AgP<sub>2</sub> unit, due to the weakly bonded O2. However, the carboxylato group restricts the O1–Ag1–O2 angle to 53.44(15) ° in **9**, causing a large distortion from the ideal value of 109.5 °.



**Figure 4.** ORTEP (50 % probability level) of the molecular structures of **8** (top) and **9** (bottom) showing the distances of the carboxylato oxygen atoms towards the  $AgP_2$  plane (grey). All hydrogen atoms and the phenyl rings have been omitted for clarity.

#### 3.3. Thermal properties

The thermal behavior of **6** and **7** in the solid state and as pastes (processing **6** and **7** into pastes using ethylene glycol (EG) or diethylene glycol (DEG)) as the solvents was studied by thermogravimetry (= TG/DTG) and differential scanning calorimetry (= DSC). In addition, TG–coupled mass-spectrometric (= TG–MS) experiments were carried out, to study the detailed decomposition behavior of **6** and **7**.

The respective TG/DTG and DSC studies of **6** and **7** were performed in a stream of  $O_2$  and  $N_2$  (gas flow 20 mL min<sup>-1</sup>) with a heating rate of 10 °C min<sup>-1</sup> in the temperature range of 100 – 500 °C. For all measurements, a continuous nitrogen carrier gas flow of 40 mL min<sup>-1</sup> was used. The corresponding TG/DTG and DSC traces of solid **6** are depicted in Figure 5.



**Figure 5.** TG/DTG (top) and DSC (bottom) traces for the thermal behavior of **6** in  $O_2$  (**a**) and in  $N_2$  (**b**) (gas flow 20 mL min<sup>-1</sup>,  $N_2$  carrier gas flow 40 mL min<sup>-1</sup>, heating rate 10 °C min<sup>-1</sup>).

The decomposition of **6** in oxygen occurs in consecutive steps starting at 215 °C (onset temperature), also detectable by DSC as an endothermic process and following by further exothermic events at 236 °C and 247 °C, respectively (Figure 5a). The decomposition of **6** is completed at 260 °C (according to DSC) which was quantified with a residue of 44.9 %, matching the formation of elemental silver (theoretical silver content of **6**, 44.8 %) as it was confirmed by PXRD measurements (Figure S1, ESI).

A similar thermal behavior of **6** was observed in an atmosphere of nitrogen, except that the decomposition of **6** was completed at a slightly higher temperature (280 °C, according to DSC) (Figure 5b). The as-obtained residue was 44.6 %, which agrees with the theoretical silver content of 44.8 %.

The appropriate TG/DTG and DSC traces of solid **7** (in  $O_2$  as in  $N_2$ ) are depicted in Figure 6.



**Figure 6.** TG/DTG (top) and DSC (bottom) traces for the thermal behavior of **7** in  $O_2$  (**a**) and in  $N_2$  (**b**) (gas flow 20 mL min<sup>-1</sup>,  $N_2$  carrier gas flow 40 mL min<sup>-1</sup>, heating rate 10 °C min<sup>-1</sup>).

The onset temperature of **7** in  $O_2$  is 206 °C, decomposition is completed at 400 °C. The appropriate DSC trace shows that decomposition of **7** occurs in consecutive steps (Figure 6a). Under N<sub>2</sub>, the decomposition starts at 196 °C, which is about 10 °C

lower as compared to its decomposition in  $O_2$  and is completed at 310 °C (Figure 6b). According to the DTG and DSC traces, **7** decomposes in three steps in which the 1<sup>st</sup> one at 206 °C and the 3<sup>rd</sup> one at 260 °C constitute to endothermic events, whereas the 2<sup>nd</sup> process at 210 °C is exothermic. The obtained residues at 500 °C correspond to 40.6 %, which points to the formation of elemental silver (40.1 % theoretical).

The presence of the  $\alpha$ -positioned Me groups in **7** leads to slightly lower onset temperatures, when compared to **6**. This can be explained with a higher thermodynamic stability of the decarboxylation products (organic radicals) of **7**, as recently evidenced for [Cu(O<sub>2</sub>CCMe<sub>2</sub>(C<sub>2</sub>H<sub>4</sub>O)<sub>2</sub>OMe)<sub>2</sub>] [43,44]. The decomposition of **7** takes place within a broader temperature range in O<sub>2</sub> and N<sub>2</sub>.

To obtain a deeper insight into the thermal decomposition behavior of **6** and **7**, TG–coupled mass spectrometric experiments were carried out (Figure 7).



**Figure 7**. TG trace (top) and selected mass spectrometric scans (bottom) of **6** (**a**):  $m/z = 15 (CH_3^+)$ ,  $m/z = 28 (CO^+)$ ,  $m/z = 31 (CH_3O^+)$ ,  $m/z = 44 (CO_2^+)$  and **7** (**b**):  $m/z = 15 (CH_3^+)$ ,  $m/z = 31 (CH_3O^+)$ ,  $m/z = 44 (CO_2^+)$ ,  $m/z = 58 (C_3H_6O^+)$ ,  $m/z = 59 (C_2H_3O_2^+)$  (nitrogen gas flow 20 mL min<sup>-1</sup>, heating rate 5 °C min<sup>-1</sup>).

In the 1<sup>st</sup> decomposition step of **6** and **7**  $CO_2^+$  (m/z = 44) and CO<sup>+</sup> (m/z = 28) as typical fragments could be detected, indicating that initially most probably the cleavage of the Ag–O bond takes place, forming [AgCR<sub>2</sub>OC(O)OMe] (R = H, Me). This assumption is in good agreement with previous investigations on, for example,

[AgO<sub>2</sub>C(CH<sub>2</sub>OCH<sub>2</sub>)<sub>3</sub>H] and [AuO<sub>2</sub>CCH<sub>2</sub>(OCH<sub>2</sub>CH<sub>2</sub>)<sub>2</sub>OMe(<sup>*n*</sup>Bu<sub>3</sub>P)] [45–47]. Subsequently, [AgCR<sub>2</sub>OC(O)OMe] decomposes via Ag–C, C–C and C–O homolytical bond cleavages, which was verified by the detection of characteristic fragments (**6**: m/z = 28 (CO<sup>+</sup>), 31 (CH<sub>3</sub>O<sup>+</sup>), 15 (CH<sub>3</sub><sup>+</sup>); **7**: m/z = 59 (C<sub>2</sub>H<sub>3</sub>O<sub>2</sub><sup>+</sup> = CH<sub>3</sub>CO<sub>2</sub>), 58 (C<sub>3</sub>H<sub>6</sub>O<sup>+</sup>), 31 (CH<sub>3</sub>O<sup>+</sup>), 15 (CH<sub>3</sub><sup>+</sup>)) (Figure 7).

#### 3.4. Copper-to-copper joining

To ensure a simplified application for copper-to-copper joining, the formation of spreadable pastes of **6** and **7** based on ethylene glycol (EG) and diethylene glycol (DEG) were applied. For the pastes with **7** a slow color change from off–white to turquoise was observed, when it was applicated to the Cu sheets (Figure S2, ESI). Obviously a redox reaction took place between **7** and the copper surface according to Equation 2.

$$2 \operatorname{Ag-O} \xrightarrow{O} O_{O_{1}} \xrightarrow{Cu(0)} Cu \left( O \xrightarrow{O_{1}} O_{O_{1}} \right)_{2} + 2 \operatorname{Ag(0)} \downarrow (2)$$

$$7 \qquad 12$$

A possible explanation for this behavior is the improved solubility of **7** in the pastes, due to the presence of the  $\alpha$ -methyl groups, which increase an interaction of **7** with the Cu surface.

To investigate more closely this behavior, the formed turquoise colored solid was suspended in water, filtered off and the obtained aqueous solution was subsequently evaporated to give suitable single crystals for X–ray diffraction study. For further characterization (IR, ESI-TOF, XRD) of **12** see the ESI.

Based on the results obtained from the thermal behavior, complex **6** represents the most eligible precursor for the low temperature joining of copper sheets, due to a narrow decomposition temperature range and a higher metal content in comparison to **7**.

To select the suitable solvent (EG or DEG) for paste formation, the appropriate pastes were investigated by TG/DTG and DSC analysis (Figure 8).



**Figure 8**. TG/DTG (top) and DSC (bottom) traces for the thermal behavior of **6**–EG (**a**) and **6**–DEG (**b**) ( $O_2$  flow 20 mL min<sup>-1</sup>,  $N_2$  carrier gas flow 40 mL min<sup>-1</sup>, heating rate 10 °C min<sup>-1</sup>).

As it can be seen from Figure 8, the solvents shift the onset temperature to lower values for **6**–EG (100 °C) and **6**–DEG (45 °C) as compared to solid **6**. This is related to the reducing properties of the respective solvents, which are responsible for Ag(I)/Ag(0) reduction forming, *e.g.* acetaldehyde on the example of EG [50]. In case of **6**–EG, the decomposition starts at 116 °C and is completed at 260 °C (Figure 8a). According to the DTG and DSC traces, the decomposition involves three events in which the 1<sup>st</sup> process at 135 °C is endothermic, whereas the following two processes at 186 and 230 °C are exothermic.

The decomposition process of **6**–DEG starts at 170 °C and is completed at 310 °C (Figure 8b). The DSC trace comprises several endothermic and exothermic peaks.

The obtained residue after the thermal heating of the paste with EG is 33.2 % and with DEG 30.6 %, respectively, corresponding to the formation of elemental silver,

which was proven by PXRD measurements.

Copper-to-copper joining experiments with pastes **6**–EG and **6**–DEG were carried out. The joining process was performed at 250 °C for 10 min without applying a pressure. The strength tests (Figure 9) show that with **6**–DEG higher joint strengths (8 MPa) could be achieved in comparison to **6**–EG (5 MPa). This is most likely a result of the much denser microstructure of the joining seam received with **6**–DEG than with **6**–EG (Figure 10).

The reason for this different behavior may be the difference between the joining temperature and decomposition temperature of the two pastes. Presumably, for the complete decomposition of **6**–EG the last two exothermic processes (186, 230 °C) are crucial, which indicates a higher mass loss compared to the 1<sup>st</sup> process at 135 °C. In contrast, with **6**–DEG the thermal processes, which are relevant for the complete decomposition, occur at a lower temperature thus correlating with the onset temperature of 170 °C.

The seams of the as-joint Cu sheets produced with paste **6**–DEG exhibit in comparison with **6**–EG higher tensile shear strengths and a denser microstructure at lower temperature. Therefore, only DEG as solvent was used for further joining experiments.





(b) Cu substrate Ag joining seam Cu substrate

**Figure 9**. Tensile shear strengths of joints obtained with **6**–EG and **6**–DEG (joining temperature 250 °C, holding time 10 min, joining pressure 0 MPa).

**Figure 10**. SEM images of joints obtained with **6**–EG (**a**) and **6**–DEG (**b**) (joining temperature 250 °C, holding time 10 min, joining pressure 0 MPa).

Furthermore, the addition of Ag particles of size  $0.7 - 1.2 \ \mu m$  to **6** was examined. Therefore, the influence of different mass ratios (Table in Figure 11) on the strength behavior and the resulting microstructure of the joints was investigated. The addition of  $\mu m$ -sized Ag particles to increase the metal content in conventional nanoparticle– containing pastes is known [2,11,19,51] and commercialized [11,52].

Figure 11 shows that the amount of the added particles has an essential influence on the strength behavior. The highest strengths of about 19 MPa could be achieved with **6**–DEG:Ag particles in the mass ratio of 1:1 (paste 2). The strengths are more than twice as high when compared to the pure precursor paste (joining paste 1) with a strength of 8 MPa.

Moreover, with joining paste 2 at 250 °C higher strength values (19 MPa) could be



achieved as compared to a commercial Ag nanopaste (10 MPa) (300 °C) (same sample geometry, Figure 11) [11,13].

Joining paste 1	6–DEG
Joining paste 2	<b>6</b> –DEG + Ag μm (1:1)
Joining paste 3	<b>6</b> –DEG + Ag μm (2:1)
Joining paste 4	6–DEG + Ag μm (1:2)

**Figure 11**. Left: Tensile shear strengths of joints obtained using **6**–DEG with addition of Ag µm particles in different mass ratios (joining temperature 250 °C, holding time 10 min, joining pressure 0 MPa) and a commercial Ag nanopaste (joining temperature 300 °C, holding time 10 min, joining pressure 0 MPa). Right: Mass ratios of the joining pastes.

A comparison of the microstructure of joints obtained with pastes 1 and 2 shows that with paste 2 a lower and finer porosity in the joining seam could be achieved (Figure 12). This is most likely the result of the Ag particle addition, which results in a higher metal content of paste 2 and therefore produces a denser microstructure and hence higher strength values of the joints. In addition, due to the addition of Ag particles, the joining seam with paste 2 is significantly thicker ( $\approx$ 16 µm) compared with the one obtained by using paste 1 (4 – 5 µm, Figure 12).



**Figure 12**. Comparison of SEM images of joints obtained with joining pastes 1 (**a**) and 2 (**b**) (joining temperature 250 °C, holding time 10 min, joining pressure 0 MPa). (Composition of pastes 1 and 2, see Figure 11).

It is interesting to note that the other mixture ratios (joining pastes 3 and 4) lead to lower strengths (Figure 11). Paste 3 shows with 8 MPa the same strength as the pure precursor paste (paste 1). This value is significantly lower than the strengths with joining paste 2 (19 MPa). The image of the microstructure (Figure 13a) shows that with paste 3 the joining seam exhibits a very porous structure, which is the reason for the lower strength values compared to joining paste 2. The seam seems like fluffed and is with approx. 80 µm comparatively thick. With paste 4, the strengths of 11 MPa are only slightly higher compared to pastes 1 and 3, but decidedly lower than paste 2. The microstructure of the seam with paste 4 (Figure 13b) exhibits a denser microstructure when compared with the one of joining paste 3 (Figure 13a), but possesses a higher porosity compared to the seam with paste 2 (Figure 12b). Therefore, also the strength values with paste 4 are between the values of joining pastes 2 and 3 (Figure 11).



**Figure 13**. Comparison of SEM images of joints obtained with joining pastes 3 (**a**) and 4 (**b**) (joining temperature 250 °C, holding time 10 min, joining pressure 0 MPa). (Composition of pastes 3 and 4, see Figure 11).

#### 4. Conclusion

The synthesis of silver(I) carboxylates  $[AgO_2CCR_2OC(O)OMe]$  (6, R = H; 7, R = Me) is reported. For investigation of their molecular structure in the solid state by single crystal X-ray diffraction analysis the respective PPh<sub>3</sub>-coordinated complexes  $[AgO_2CCR_2OC(O)OMe(PPh_3)_2]$  (8, R = H; 9, R = Me) were prepared. In 8 a [3+1]  $(P_2O + O)$  coordination geometry is present, due to an unsymmetrical bonding of the carboxylato molety to the silver ion. Therefore, the oxygen atom, involved in a C-O single bond acts as the strong and the carbonyl oxygen as a weaker bonded donor. Complex 9 exhibits a distorted tetrahedral environment with a symmetrical complexation of the carboxylato group towards the Ag ion and similar C–O distances within the CO<sub>2</sub> fragment. IR spectra of 8 and 9 confirm the chelate binding of the carboxylato group. In contrast, 6 and 7 show a bidentate bridging coordination motif as evidenced by IR spectroscopy. The investigation of the thermally induced decomposition of 6 and 7 in the solid state by TG/DSC indicated lower onset temperatures for 7 in comparison to 6. The decomposition of 7 is finished at higher temperatures, with 400 ( $O_2$ ) and 310 °C ( $N_2$ ), when compared to **6** (260 ( $O_2$ ), 280 °C (N<sub>2</sub>)). TG–MS experiments of **6** and **7** confirmed that initially decarboxylation occurs, followed by Ag-C, C-C and C-O bond cleavages. The obtained residues were characterized as silver by PXRD analysis.

To enable a simplified application for copper-to-copper sheet joining, **6** and **7** were mixed with ethylene glycol (EG) or diethylene glycol (DEG) to spreadable pastes. By application of **7**–EG to Cu sheets a redox reaction was observed resulting in the formation of  $[Cu_2(O_2CCMe_2OC(O)OMe)_4:2H_2O]$  (**12**). In comparison to **7**, complex **6** showed the most suitable thermal behavior for low temperature joining. Therefore, the influence of the used solvents (EG and DEG) on the decomposition behavior of **6** was investigated by TG/DTG and DSC. Due to the reducing properties of the

solvents EG and DEG towards the respective Ag(I) complexes, the onset temperature of the pure precursor was shifted to significant lower values. In addition, pressureless joining experiments (250 °C, 10 min) with 6-EG and 6-DEG were carried out and the resulting joining seams were investigated regarding to the strength behavior and the microstructure to select the convenient solvent. These results indicated that 6-DEG positively impacts the joining results, enabling a denser microstructure and higher strengths compared to 6-EG. Additionally, to increase the metal content in the joining pastes, Ag µm-sized particles in different mass ratios were added to 6-DEG (1:1, 1:2 and 2:1) and their influence was examined regarding the achievable strengths and the resulting microstructure of the joints. The results showed that the mass ratio 6-DEG:Ag µm particles has an essential influence on the strength behavior. The highest strengths of about 19 MPa were achieved with particles in the mass ratio of 1:1 (paste 2). The value of 19 MPa (250 °C, 10 min, pressureless) is significantly higher compared to 10 MPa, which is characteristic for a commercial Ag nanopaste (300 °C, 10 min, pressureless) [11,13]. In combination with the described advantages of the presented silver(I) carboxylate precursors (cost-effective and straightforward synthesis, long-term stability and considerably simplified handling), they pose a promising alternative for conventional nanopastes. Comparing the silver(I) carboxylates reported herein with recently reported silver(I)-nalkylamine complexes, discussed as potentially joining materials for copper-to-copper silver joints [30], show better decomposition properties, a higher chemical stability and, for example, an enhanced resistance against light. In addition, it was reported that after sintering of silver(I)-n-alkylamines large amounts of tar-like organic residues remained on the generated silver layers, which may result in the formation of less strong adhesions between the silver-substrate interface [30].

However, some challenges have to be overcome by using silver(I) carboxylates as precursors in copper-to-copper joining, especially in terms of minimization of the porosity in the joining seam to achieve a homogenous microstructure and higher tensile strength values. This requires further efforts in the optimization of the composition of the joining pastes. Jock

#### Notes

The authors declare no competing financial interests

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Appendix A. Supplementary data

Table S1 and S2, Figure S1-S3 and CIF files giving additional crystallographic data.

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![](_page_34_Figure_1.jpeg)

- Highlights: **Synthesis** [AgO<sub>2</sub>CCR<sub>2</sub>OC(O)OMe] and structure of and [AgO<sub>2</sub>CCR<sub>2</sub>OC(O)OMe(PPh<sub>3</sub>)<sub>2</sub>]
- ed. • The thermal decomposition of these complexes is studied by TG,