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# Lewis-base copper(I) formates: Synthesis, reaction chemistry, structural characterization and their use as spin-coating precursors for copper deposition

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# ABSTRACT

Consecutive synthesis methodologies for the preparation of a series of copper(I) formates  $[L_mCuO_2CH]$  $(L = {}^{n}Bu_{3}P; 4a, m = 1; 4b, m = 2; 5, L = [Ti](C = CSiMe_{3})_{2}, m = 1, [Ti] = (n^{5}-C_{5}H_{4}SiMe_{3})_{2}Ti)$  and  $[L_mCuO_2CH HO_2CR]$  (L = <sup>n</sup>Bu<sub>3</sub>P: **7a**, m = 1, R = H; **7b**, m = 2, R = H; **7c**, m = 2, R = Me; **7d**, m = 2, R = CF<sub>3</sub>; **7e**, m = 2, R = Ph.  $L = ({}^{c}C_{6}H_{11})_{3}P$ , R = H: **8a**, m = 2; **8b**, m = 3.  $L = (CF_{3}CH_{2}O)_{3}P$ , R = H: **9a**, m = 2; **9b**, m = 3.  $L = (CH_3CH_2O)_3P$ , R = H: **10a**, m = 2; **10b**, m = 3.  $L = [Ti](C \equiv CSiMe_3)_2$ ; m = 1: **11a**, R = H; **11b**, R = Ph) is reported using [CuO<sub>2</sub>CH] (1) and L (2a,  $L = {}^{n}Bu_{3}P$ ; 2b, L ( ${}^{c}C_{6}H_{11})_{3}P$ ; 2c,  $L = (CF_{3}CH_{2}O)_{3}P$ ; 2d, L =  $(CH_3CH_2O)_3P$ ; **3**, L =  $[Ti](C \equiv CSiMe_3)_2$ ) as key starting materials. Addition of formic acid (**6a**) or carboxylic acid HO<sub>2</sub>CR (**6b**, R = Me; **6c**, R = CF<sub>3</sub>; **6d**, R = Ph) to the afore itemized copper(I) formates **4** and **5** gave metal-organic or organometallic 7-11. The molecular structures of 8a and 11a in the solid state are reported showing a threefold coordinated copper(I) ion, setup by either two coordinatively-bonded phosphorus atoms and one formate oxygen atom (**8a**) or two  $\pi$ -bonded alkyne ligands and one oxygen atom (11a). A formic acid molecule is additionally hydrogen-bonded to the CuO<sub>2</sub>CH moiety. The use of 7b as suitable precursor for the deposition of copper onto TiN-coated oxidized silicon wafers by the spin-coating process below 300 °C is described. Complex 7b offers an appropriate transformation behavior into metal phase by an elimination-decarboxylation mechanism. The morphology of the copper films strongly depends on the annealing conditions. A closed grain network densified by a post-treatment is obtained (8 °C min<sup>-1</sup>, N<sub>2</sub>/H<sub>2</sub> carrier gas). Hydrogen post-anneal to 420 °C after film deposition gave a copper film showing resistivities from 2.5 to 3.7  $\mu\Omega$  cm. This precursor was also used for gap-filling processes.

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#### 1. Introduction

Copper(I) formate in its *non*-coordinated form is a reactive metal–organic compound and is sensitive to moisture and temperature [1]. Nevertheless, it can be stabilized either by Lewis-base ligands L (L = neutral or ionic 2–4-electron donor) and/or hydrogen-bonded formic acid or carboxylic acids [2]. Depending on the nature and number of L in [L<sub>m</sub>CuO<sub>2</sub>CR] (m = 1, 2, 3; R = H, singlebonded organic group) different aggregated species are formed, for example, tetra-nuclear cubane- or staircase-like structured molecules, dinuclear or monometallic copper(I) complexes [3].

Recently, it could be shown that volatile phosphane, phosphite, or alkyne copper(I) carboxylates can successfully be used as CVD (Chemical Vapor Deposition) precursors in the deposition of thin copper layers on different substrate materials [4]. In contrast to

the above mentioned transition metal compounds only less is known about the use of copper(I) formate in metal deposition processes [5].

This prompted us to synthesize coordination complexes of general composition  $[L_mCuO_2CH]$  (L =  ${}^{n}Bu_3P$ , ( ${}^{c}C_6H_{11}$ )\_3P, (CF\_3CH\_2O)\_3P, (CH\_3CH\_2O)\_3P; *m* = 1, 2, 3; L = [Ti](C=CSiMe\_3)\_2, *m* = 1, [Ti] = ( $\eta^{5}-C_5H_4SiMe_3$ )\_2Ti). Their reaction behavior towards formic acid and carboxylic acids RCO\_2H (R = Me, CF\_3, Ph) is discussed. The use of  $[({}^{n}Bu_3P)_2CuO_2CH\cdot CH_2O]$  as spin-coating precursors for the deposition of pure copper layers is reported as well.

### 2. Experimental section

#### 2.1. Materials and methods

Complexes [ $L_mCuO_2CH$ ] (L = P(<sup>c</sup>C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>, P(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub>, P(OCH<sub>2</sub>-CF<sub>3</sub>)<sub>3</sub>; *m* = 2, 3) were prepared by published procedures [5]. All



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other chemicals were purchased by commercial providers and were used as received.

All reactions were carried out under an atmosphere of purified nitrogen (O<sub>2</sub> traces: copper oxide catalyst, BASF AG, Ludwigshafen; H<sub>2</sub>O: molecular sieve 4 Å, Aldrich Company) using standard Schlenk techniques. Dichloromethane was purified by distillation from P<sub>2</sub>O<sub>5</sub>; diethyl ether was purified by distillation from sodium/benzophenone ketyl; n-pentane was purified by distillation from calcium hydride. Infrared spectra were recorded with a Perkin Elmer FT-IR spectrometer (Spectrum 1000). <sup>1</sup>H NMR spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 62.895 MHz. Chemical shifts are reported in  $\delta$ units (parts per million) downfield from tetramethylsilane  $(\delta = 0.0 \text{ ppm})$  with the solvent as the reference signal (<sup>1</sup>H NMR. CDCl<sub>3</sub>  $\delta$  = 7.26; <sup>13</sup>C{<sup>1</sup>H} NMR, CDCl<sub>3</sub>  $\delta$  = 77.55). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 101.255 MHz in CDCl<sub>3</sub> with P(OMe)<sub>3</sub> as external standard ( $\delta$  = 139.0, rel. to H<sub>3</sub>PO<sub>4</sub> (85%) with  $\delta$  = 0.0). Thermogravimetric studies were carried out with the Perkin Elmer System Pyris TGA 6 with a constant heating rate of  $8 \text{ Kmin}^{-1}$  under N<sub>2</sub>  $(1.0 \text{ cm}^3 \text{ min}^{-1})$ . For the film preparation a spin-coating track RC8 with the Gyrset system from Suss Microtec Corp. was used. In a typical spin-coating experiment 2 mL of the appropriate precursor was dispensed under a stream of argon on the wafer material, which rotated with a spin-off speed between 300-2000 rpm adjusted for the desired film thickness. After the deposition was finished, the wafer was transferred to a Vacutherm VT 6060 oven from Heraeus Corp. and was heated under an oxygen-free argon atmosphere to 400 °C for 30 min with a variable heating ramp  $(1-15 \circ C \min^{-1})$  for optimized transformation of the precursor material into metallic copper. Thus, copper films could be obtained on silicon wafers priory isolated by silicon oxide and coated with a metal diffusion barrier layer, for example, TiN or TaN/Ta. Specific resistivity measurements were carried out as follows: sheet resistance was measured by current/voltage measurements at 81 points distributed over the whole wafer surface with a four-point probe using a sheet resistivity mapping system OmniMap<sup>®</sup> RS50/efrom Prometrix Corp. The film thicknesses were determined by etching at least three dots and surveying steps in the film using a TENCOR profilometer. The chemical composition profile was detected by AES and RBS (Rutherford Backscattering Spectrometry). TEM and EFTM were used to investigate the grain structure and composition. SEM micrographs were recorded with a SEM instrument type DSM 982, Gemini from LEO Corp. EDX analysis was performed with the EDX system EDWIN (Röntec Corp.) attached to the SEM. Microanalyses were performed by the Institute of Organic Chemistry, Chemnitz University of Technology (Foss Heraeus Vario EL C, H, N-Analyzer), and by the Institute of Organic Chemistry, University of Heidelberg (Heraeus C, H, N-Analyser). Melting points were determined using analytically pure samples, sealed off in nitrogen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus.

#### 2.2. Synthesis of $[(^{n}Bu_{3}P)CuO_{2}CH]$ (4a)

[CuO<sub>2</sub>CH] (1) (1.0 g, 10.0 mmol) was suspended in 30 mL of dichloromethane at -20 °C and <sup>n</sup>Bu<sub>3</sub>P (2.02 g, 10.0 mmol) was dropwise added. After 1 h of stirring at this temperature, the reaction mixture was filtered through a pad of Celite. All volatiles were removed in oil-pump vacuum to afford a colorless liquid. Yield: 2.29 g (7.4 mmol, 74% based on 1).

Elemental analysis: Anal. Calc. for  $C_{13}H_{28}CuO_2P$  (310.88): C, 50.23; H, 9.08. Found: C, 50.10; H, 8.96%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2957 (vs), 2930 (vs), 2870 (vs), 1633 (s) (CO, asym), 1592 (vs), 1461 (s), 1414 (m), 1378 (m), 1346 (m) (CO, sym), 1278 (m), 1209 (m), 1093 (m), 1054 (m), 907 (s), 779 (m), 728 (s). <sup>1</sup>H NMR

(CDCl<sub>3</sub>):  $\delta$  0.74 (t, 9 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 14.3 Hz), 1.20–1.30 (m, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 8.27 (s, 1 H, HCO<sub>2</sub><sup>-</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  13.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.6 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 5.8 Hz), 24.9 (CH<sub>2</sub>-CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 12.0 Hz), 27.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 3.4 Hz), 167.2 (CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –16.7.

# 2.3. Synthesis of $[({}^{n}Bu_{3}P)_{2}CuO_{2}CH]$ (4b)

The title compound was synthesized by applying the same procedure as used in the preparation of **4a** (Section 2.2). Thus,  ${}^{n}Bu_{3}P$  (**2a**) (4.04 g, 20.0 mmol) was reacted with **1** (1.08 g, 10.0 mmol). After appropriate work-up, complex **4b** could be isolated as a colorless liquid. Yield: 3.95 g (7.7 mmol, 77% based on **1**).

*Elemental analysis: Anal.* Calc. for C<sub>25</sub>H<sub>55</sub>CuO<sub>2</sub>P<sub>2</sub> (513.20): C, 58.51; H, 10.80. Found: C, 58.34; H, 10.77%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2956 (vs), 2929 (vs), 2869 (vs), 1607 (vs) (CO, asym), 1562 (s), 1460 (s), 1418 (m), 1377 (m), 1335 (m) (CO, sym), 1207 (m), 1127 (m), 1092 (m), 1053 (m), 1007 (m), 904 (s), 775 (m), 724 (s), 693 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.77 (t, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 6.9 Hz), 1.30–1.40 (m, 36 H, (*CH*<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 8.44 (s, 1 H, HCO<sub>2</sub><sup>-1</sup>). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  14.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 25.0 (CH<sub>2</sub>CH<sub>2</sub>-CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 11.5 Hz), 25.2 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 11.0 Hz), 27.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 2.4 Hz), 166.8 (HCO<sub>2</sub><sup>-1</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -20.8. TG: *T*<sub>begin</sub> = 60 °C, *T*<sub>end</sub> = 136 °C, *Δm* = 3.64%; *T*<sub>begin</sub> = 136 °C, *T*<sub>end</sub> = 284 °C, *Δm* = 82.95%; *T*<sub>begin</sub> = 284 °C, *Δm* = 400 °C, *Δm* = 2.26%.

#### 2.4. Synthesis of $[{[Ti](\mu-\sigma,\pi-C \equiv CSiMe_3)_2}CuO_2CH]$ (5)

Complex **5** was accessible by the reaction of  $[Ti](C \equiv CSiMe_3)_2$ (**3**) (165.3 mg, 0.32 mmol) dissolved in 30 mL of dichloromethane with **1** (34.72 mg, 0.32 mmol) dissolved in 30 mL of dichloromethane, whereby the dichloromethane solution of **1** is slowly added to **3** at -20 °C. After 1 h of stirring at this temperature, the reaction solution was filtered through a pad of Celite and all volatiles were removed in oil-pump vacuum to afford a deep brown solid material. Yield: 170 mg (0.27 mmol, 85% based on **1**).

M.p.: 145 °C (dec.). *Elemental analysis: Anal.* Calc. for  $C_{27}H_{45}$ CuO<sub>2</sub>Si<sub>4</sub>Ti (626.42): C, 51.77, H, 7.24. Found: C, 51.43; H, 7.12%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 1920 (s) ( $\nu_{C}\equiv_C$ ), 1611 (s) (CO,  $\nu_{as}$ ), 1454 (s) (CO,  $\nu_s$ ). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.23 (s, 18 H, SiMe<sub>3</sub>), 0.37 (s, 18 H, SiMe<sub>3</sub>), 5.99 (pt, 4 H, C<sub>5</sub>H<sub>4</sub>, J<sub>HH</sub> = 2.2 Hz), 6.14 (pt, 4 H, C<sub>5</sub>H<sub>4</sub>, J<sub>HH</sub> = 2.2 Hz), 8.55 (bs, 1 H, HCO<sub>2</sub><sup>-</sup>).

#### 2.5. Synthesis of $[(^{n}Bu_{3}P)CuO_{2}CH \cdot HO_{2}CH]$ (7a)

*Method a:* Formic acid (**6a**) (0.46 g, 10.0 mmol) dissolved in 20 mL of dichloromethane was added to **4a** (3.11 g, 10.0 mmol) dissolved in 30 mL of dichloromethane at -20 °C. After 1 h of stirring at this temperature the reaction solution was filtered through a pad of Celite. Afterwards, all volatiles were removed from the filtrate in oil-pump vacuum to produce a colorless liquid: Yield: 2.78 g (7.8 mmol, 78% based on **4a**).

*Method b*: Tri-*n*-butylphosphane (**2a**) (2.02 g, 10 mmol) was dissolved in 10 mL of dichloromethane and this solution was dropwise added to [CuO<sub>2</sub>CH] (**1**) (1.09 g, 10.0 mmol) and formic acid (**6a**) (0.46 g, 10.0 mmol) dissolved in 30 mL of dichloromethane at -20 °C. After 1 h of stirring at this temperature, the reaction solution was filtered through a pad of Celite. Afterwards, all volatiles were removed in oil-pump vacuum to produce a colorless liquid. Yield: 2.89 g (8.1 mmol, 81% based on **1**).

*Elemental analysis: Anal.* Calc. for  $C_{14}H_{30}CuO_4P$  (356.91): C, 47.11; H, 8.47. Found: C, 47.09; H, 8.32%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3419 (w) (OH), 2958 (vs), 2930 (vs), 2871 (s), 1715 (s) (C=O, HCO<sub>2</sub>H), 1647 (s), 1593 (s) (CO, asym), 1461 (m), 1378 (m), 1343 (m) (CO, sym), 1257 (m), 1208 (m) (C-O, HCO<sub>2</sub>H), 1123 (m),

1093 (m), 1063 (m), 1006 (m), 963 (m), 905 (m), 791 (m), 720 (m), 690 (m), 666 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.54 (t, 9 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 6.2 Hz), 1.00–1.20 (m, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 8.10 (s, 2 H, HCO<sub>2</sub><sup>-/</sup> HCO<sub>2</sub>H), 13.7 (s, 1 H, HCO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  13.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.4 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 6.2 Hz), 24.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 13.0 Hz), 27.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 2.4 Hz), 165.7 (CO, HCO<sub>2</sub><sup>-/</sup>HCO<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –14.6. TG: *T*<sub>bec</sub> gin = 70 °C, *T*<sub>end</sub> = 111 °C,  $\Delta m$  = 17.4%; *T*<sub>begin</sub> = 111 °C, *T*<sub>end</sub> = 233 °C,  $\Delta m$  = 53.6%; *T*<sub>begin</sub> = 233 °C, *T*<sub>end</sub> = 300 °C,  $\Delta m$  = 10.5%.

#### 2.6. Synthesis of $[(^{n}Bu_{3}P)_{2}CuO_{2}CH \cdot HO_{2}CH]$ (**7b**)

Formic acid HO<sub>2</sub>CH (**6a**) (0.46 g, 10.0 mmol) dissolved in 20 mL of dichloromethane was dropwise added to **4b** (5.13 g, 10.0 mmol) dissolved in 30 mL of dichloromethane at -20 °C. After stirring for 2 h at this temperature, the reaction mixture was filtered through a pad of Celite and all volatiles were evaporated in oil-pump vacuum to produce a colorless liquid: Yield: 4.53 g (8.1 mmol, 81% based on **4b**).

*Elemental analysis: Anal.* Calc. for C<sub>26</sub>H<sub>57</sub>CuO<sub>4</sub>P<sub>2</sub> (559.23): C, 55.84; H, 10.27. Found: C, 55.67; H, 10.12%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2956 (vs), 2920 (vs), 2872 (s), 2737 (m), 2693 (m), 2503 (m), 1738 (s), 1710 (s) (C=O, HO<sub>2</sub>CH), 1575 (s) (CO, asym), 1465 (s), 1418 (s), 1379 (m) (CO, sym), 1275 (m), 1206 (s) (C-O, HO<sub>2</sub>CH), 1128 (m), 1094 (s), 1068 (m), 1006 (m), 969 (m), 904 (s), 777 (m), 725 (m), 694 (m), 668 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.64 (t, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, J<sub>HH</sub> = 6.5 Hz), 1.10–1.30 (m, 36 H, (*CH*<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 8.10 (s, 2 H, HCO<sub>2</sub><sup>-</sup>/HCO<sub>2</sub>H), 14.40 (s, 1 H, HCO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  14.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J<sub>PC</sub> = 1.9 Hz), 25.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J<sub>PC</sub> = 3.4 Hz), 27.2 (*CH*<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 165.7 (CO, HCO<sub>2</sub><sup>-</sup>/HCO<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –17.7. TG: T<sub>begin</sub> = 90 °C, T<sub>end</sub> = 130 °C, Δm = 12.63%; T<sub>begin</sub> = 130 °C, T<sub>end</sub> = 280 °C, Δm = 75.16%.

#### 2.7. Synthesis of $[(^{n}Bu_{3}P)_{2}CuO_{2}CH \cdot HO_{2}CMe]$ (7c)

Complex **7c** was synthesized in the same manner as **7b** (Section 2.6). In this respect,  $[({^nBu_3})_2PCuO_2CH]$  (**4b**) (5.13 g, 10.0 mmol) was reacted with CH<sub>3</sub>CO<sub>2</sub>H (**6b**) (0.60 g, 10.0 mmol). After appropriate work-up, complex **7c** could be isolated as a colorless liquid. Yield: 4.64 g (8.1 mmol, 81% based on **4b**).

*Elemental analysis: Anal.* Calc. for C<sub>27</sub>H<sub>59</sub>CuP<sub>2</sub>O<sub>4</sub> (573.26): C, 56.57; H, 10.37. Found: C, 56.43; H, 10.22%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3407 (w) (OH), 2957 (vs), 2931 (vs), 2871 (s), 1748 (s) (CO, asym), 1720 (s) (CO, asym), 1587 (s) (CO, sym), 1463 (s) (CO, sym), 1415 (m), 1378 (m), 1261 (m), 1210 (m), 1130 (w), 1093 (m), 1068 (m), 1007 (m), 969 (m), 904 (s), 791 (m), 723 (m), 666 (w), 603 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.85 (t, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 6.7 Hz), 1.3–1.5 (m, 36 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.97 (s, 3 H, CH<sub>3</sub>), 8.47 (s, 1 H/HCO<sub>2</sub><sup>-</sup>), 12.19 (s, 1 H, CH<sub>3</sub>CO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  14.0 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 2.4 Hz), 27.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 2.4 Hz), 175.1 (CH<sub>3</sub>CO<sub>2</sub>), 162.7 (HCO<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –19.0. TG: *T*<sub>begin</sub> = 68 °C, *T*<sub>end</sub> = 135 °C, *Δm* = 11.25%; *T*<sub>begin</sub> = 135 °C, *Δm* = 74.56%.

#### 2.8. Synthesis of $[(^{n}Bu_{3}P)_{2}CuO_{2}CH \cdot HO_{2}CF_{3}]$ (7d)

Complex **7d** was synthesized in the same manner as **7b** (Section 2.6):  $[(^{n}Bu_{3})_{2}PCuO_{2}CH]$  (**4b**) (5.13 g, 10.0 mmol), CF<sub>3</sub>CO<sub>2</sub>H (**6c**) (1.14 g, 10 mmol). After appropriate work-up, **7d** could be isolated as a colorless liquid. Yield: 4.77 g (7.6 mmol, 76% based on **4b**).

*Elemental analysis: Anal.* Calc. for  $C_{27}H_{56}CuF_3P_2O_4$  (627.23): C, 51.70; H, 9.00. Found: C, 51.56; H, 8.97%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2960 (vs), 2967 (vs), 2873 (s), 1737 (s) (CO, asym), 1683 (s) (CO, asym), 1666 (s) (CO, sym), 1463 (s) (CO, sym), 1416 (m), 1380

(m), 1287 (s) (CF<sub>3</sub>, str.), 1140 (s), 1094 (m), 1050 (m), 1003 (m), 967 (m), 906 (s), 795 (m), 720 (m), 703 (m), 670 (m), 516 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.69 (t, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, *J*<sub>HH</sub> = 6.1 Hz), 1.2–1.5 (m, 36 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 8.17 (s, 1 H, HCO<sub>2</sub><sup>-</sup>), 14.81 (s, 1 H, CF<sub>3</sub>CO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  13.7 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.5 (d, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 2.4 Hz), 24.6 (d, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, *J*<sub>PC</sub> = 2.4 Hz), 26.9 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>), 163.6 (HCO<sub>2</sub>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  –19.0. TG: *T*<sub>begin</sub> = 85 °C, *T*<sub>end</sub> = 232 °C,  $\Delta m$  = 50.20%; *T*<sub>begin</sub> = 232 °C, *T*<sub>end</sub> = 300 °C,  $\Delta m$  = 39.50%.

# 2.9. Synthesis of $[(^{n}Bu_{3}P)_{2}CuO_{2}CH \cdot HO_{2}CPh]$ (7e)

Complex **7e** was prepared as described for **7b** (Section 2.6):  $[(^{n}Bu_{3})_{2}PCuO_{2}CH]$  (**4b**) (5.13 g, 10.0 mmol), PhCO<sub>2</sub>H (**6d**) (1.22 g, 10.0 mmol). After appropriate work-up, complex **7e** could be isolated as a colorless liquid. Yield: 4.64 g (7.3 mmol, 73% based on **4b**).

Elemental analysis: Anal. Calc. for C<sub>32</sub>H<sub>61</sub>CuP<sub>2</sub>O<sub>4</sub> (635.33): C, 60.50; H, 9.68. Found: C, 60.32; H, 9.46%. IR (NaCl):  $\tilde{v}$  [cm<sup>-1</sup>] 3060 (w), 2956 (vs), 2927 (vs), 2871 (s), 2737 (m), 1713 (s) (CO, asym), 1650 (m) (CO, asym), 1597 (m) (CO, sym), 1583 (m) (CO, sym), 1556 (m) (CO, sym), 1463 (s) (CO, sym), 1417 (m), 1379 (s), 1312 (m), 1264 (s), 1172 (m), 1116 (m), 1094 (m), 1067 (m), 1025 (m), 970 (m), 904 (m), 789 (m), 714 (s), 690 (m), 656 (m), 518 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.82 (t, 18 H, (CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>, J<sub>HH</sub> = 6.4 Hz), 1.2–1.5 (m, 36 H, (*CH*<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 7.2–7.4 (m, 3 H, Ph), 7.98 (s, 1 H, Ph), 8.02 (s, 1 H, Ph), 8.63 (s, 1 H, HCO<sub>2</sub><sup>-</sup>), 14.22 (s, 1 H, PhCO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  14.1 (CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.9 (d, CH<sub>2</sub>CH<sub>2</sub> CH<sub>2</sub>CH<sub>3</sub>, J<sub>PC</sub> = 9.1 Hz), 25.1 (d, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J<sub>PC</sub> = 10.1 Hz), 27.5 (d, CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>, J<sub>PC</sub> = 2.9 Hz), 128.1 (Ph), 130.1 (Ph), 132.1 (Ph), 133.1 (Ph), 167.4 (HCO<sub>2</sub><sup>-</sup>), 170.0 (PhCO<sub>2</sub>H). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  -19.3. TG:  $T_{\text{begin}} = 70 \text{ °C}$ ,  $T_{\text{end}} = 200 \text{ °C}$ ,  $\Delta m = 36.36\%$ ;  $T_{\text{begin}} = 200 \,^{\circ}\text{C}, T_{\text{end}} = 354 \,^{\circ}\text{C}, \Delta m = 47.30\%.$ 

#### 2.10. Synthesis of $[(({}^{c}C_{6}H_{11})_{3}P)_{2}CuO_{2}CH \cdot HO_{2}CH]$ (**8a**)

Formic acid (**6a**) (0.46 g, 10.0 mmol) was dissolved in 20 mL of dichloromethane and was dropwise added to [CuO<sub>2</sub>CH] (**1**) (1.08 g, 10 mmol) dissolved in 20 mL of dichloromethane at -20 °C. After stirring the reaction mixture for 30 min at this temperature, (<sup>c</sup>C<sub>6</sub>H<sub>11</sub>)<sub>3</sub>P (**2b**) (5.61 g, 20 mmol) dissolved in 20 mL of dichloromethane was drop-wise added to the reaction solution. After stirring for another 1 h at this temperature, the obtained reaction mixture was filtered through a pad of Celite and all volatiles were evaporated in oil-pump vacuum to give a colorless solid of **8a**. Yield: 6.22 g (8.7 mmol, 87% based on **1**). Crystallization from a dichloromethane solution containing **8a** at -20 °C afforded colorless single crystals of **8a**.

M.p.: 85 °C. *Elemental analysis: Anal.* Calc. for  $C_{38}H_{69}CuO_4P_2$  (715.46): C, 63.79; H, 9.72. Found: C, 63.58; H, 9.64%. IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3144 (m), 2926 (s), 2850 (s) ( $\nu_{CH}$ ), 2668 (m) ( $\nu_{CH}$ ), 2515 (m), 2267 (m), 1943 (m) (broad, OH), 1737 (s) (CO, asym, HCO<sub>2</sub>H), 1576 (vs) (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1447 (s) (CO, sym, HCO<sub>2</sub>H), 1365 (m), (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1295 (m), 1269 (m), 1177 (s), 1128 (m), 1073 (m), 1049 (m), 1004 (m), 916 (m), 888 (m), 852 (s), 819 (m), 781 (m), 750 (m), 693 (s), 669 (m), 512 (m), 489 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.20–2.27 (m, 66 H, C<sub>6</sub>H<sub>11</sub>), 8.47 (s, 2 H, CH), 12.75 (s, 1 H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  26.5 (C<sub>6</sub>H<sub>11</sub>), 27.8 (C<sub>6</sub>H<sub>11</sub>), 30.8 (C<sub>6</sub>H<sub>11</sub>), 32.9 (C<sub>6</sub>H<sub>11</sub>), 165.7 (HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  11.29.

#### 2.11. Synthesis of $[(({}^{c}C_{6}H_{11})_{3}P)_{3}CuO_{2}CH \cdot HO_{2}CH]$ (**8b**)

Complex **8b** was synthesized in the same manner as **8a** (Section 2.10): [CuO<sub>2</sub>CH] (1) (1.08 g, 10.0 mmol), ( ${}^{c}C_{6}H_{11}$ )<sub>3</sub>P (**2b**) (8.42 g, 30 mmol), HO<sub>2</sub>CH (**6a**) (0.46 g, 10.0 mmol). After appropri-

ate work-up, complex **8b** could be obtained as a colorless solid. Yield: 8.86 g (8.9 mmol, 89% based on **1**).

M.p.: 76 °C. *Elemental analysis: Anal.* Calc. for  $C_{56}H_{102}CuO_4P_3$  (995.89): C, 67.54; H, 10.32. Found: C, 67.43; H, 9.97%. IR (KBr):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2921 (vs), 2848 (s), 2665 (m) ( $\nu_{CH}$ ), 2605 (w) ( $\nu_{CH}$ ), 1942 (m) (broad, OH), 1743 (s) (CO, asym, HCO<sub>2</sub>H), 1702 (m), (CO, asym, HCO<sub>2</sub><sup>-</sup>), 1576 (s) (CO, sym, HCO<sub>2</sub>H), 1446 (s) (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1353 (m), 1294 (m), 1207 (m), 1175 (m), 1129 (w), 1107 (m), 1048 (w), 1003 (m), 916 (m), 888 (m), 850 (s), 819 (m), 781 (m), 750 (m), 693 (s), 669 (m), 512 (m), 489 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.23–1.82 (m, 99 H, C<sub>6</sub>H<sub>11</sub>), 8.44 (s, 2 H, CH), 12.75 (s, 1 H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  26.73 (C<sub>6</sub>H<sub>11</sub>), 27.98 (C<sub>6</sub>H<sub>11</sub>), 30.92 (C<sub>6</sub>H<sub>11</sub>), 32.81 (C<sub>6</sub>H<sub>11</sub>), 166.56 (HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  10.19.

# 2.12. Synthesis of $[((CF_3CH_2O)_3P)_2CuO_2CH \cdot HO_2CH]$ (9a)

Complex **9a** was synthesized as described earlier (Section 2.10): [CuO<sub>2</sub>CH] (**1**) (1.08 g, 10.0 mmol), (CF<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>P (**2c**) (6.56 g, 20.0 mmol), HO<sub>2</sub>CH (**6a**) (0.46 g, 10 mmol). Yield of colorless **9a**: 6.90 g (8.5 mmol, 85% based on **1**).

*Elemental analysis: Anal.* Calc. for C<sub>14</sub>H<sub>15</sub>CuF<sub>18</sub>O<sub>10</sub>P<sub>2</sub> (*810.73*): C, 20.74; H, 1.86. Found: C, 20.75; H, 1.63%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] (NaCl): 2962 (m), 2893 (w) ( $\nu_{CH}$ ), 2803 (w) ( $\nu_{CH}$ ), 1915 (m) (broad, OH), 1698 (s) (CO, asym, HCO<sub>2</sub>H), 1456 (m) (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1417 (s) (CO, sym, HCO<sub>2</sub>H), 1373 (m), (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1284 (vs), 1173 (s), 1107 (s), 1067 (vs), 992 (m), 963 (vs), 856 (s), 656 (s), 579 (m), 547 (m), 517 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.37 (m, 12 H, CF<sub>3</sub>CH<sub>2</sub>O), 6.80 (s, 2 H, CH), 9.70 (s, 1 H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  61.88 (CF<sub>3</sub>CH<sub>2</sub>O, J<sub>FC</sub> = 37.9 Hz, J<sub>PC</sub> = 4.8 Hz), 123.18 (CF<sub>3</sub>CH<sub>2</sub>O, J<sub>FC</sub> = 277.4 Hz, J<sub>PC</sub> = 8.6 Hz), 159.21 (HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  117.33.

#### 2.13. Synthesis of $[((CF_3CH_2O)_3P)_3CuO_2CH \cdot HO_2CH]$ (**9b**)

Complex **9b** was synthesized as described earlier (Section 2.10): [CuO<sub>2</sub>CH] (1) (1.08 g, 10.0 mmol), (CF<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>P (**2c**) (9.84 g, 30.0 mmol), HO<sub>2</sub>CH (**6a**) (0.46 g, 10 mmol). After appropriate work-up, complex **9b** was obtained as a colorless liquid. Yield: 9.33 g (8.2 mmol, 82% based on **1**).

*Elemental analysis: Anal.* Calc. for C<sub>20</sub>H<sub>21</sub>CuF<sub>27</sub>O<sub>13</sub>P<sub>3</sub> (1138.80): C, 21.09; H, 1.86. Found: C, 20.97; H, 1.73%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] (NaCl): 2970 (s), 2885 (s) ( $\nu_{CH}$ ), 2715 (m) ( $\nu_{CH}$ ), 2524 (m), 1920 (m) (broad, OH), 1706 (s) (CO, asym, HCO<sub>2</sub>H), 1455 (s) (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1417 (s), 1284 (s), 1171 (vs), 1063 (vs), 963 (vs), 854 (s), 657 (m), 572 (m), 511 (m), 433 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  4.36 (m, 18 H, CF<sub>3</sub>CH<sub>2</sub>O), 6.81 (s, 2 H, CH), 10.25 (s, 1 H, OH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  159.0 (HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup>), 122.7 (CF<sub>3</sub>CH<sub>2</sub>O,  $J_{FC}$  = 277.3 Hz,  $J_{PC}$  = 5.8 Hz), 61.7 (CF<sub>3</sub>CH<sub>2</sub>O,  $J_{FC}$  = 37.8 Hz,  $J_{PC}$  = 4.7 Hz). <sup>31</sup>P{<sup>1</sup>H</sup> NMR (CDCl<sub>3</sub>):  $\delta$  120.0.

#### 2.14. Synthesis of $[((CH_3CH_2O)_3P)_2CuO_2CH HO_2CH]$ (10a)

Complex **10a** was synthesized as described earlier (Section 2.10):  $[CuO_2CH]$  (1) (1.08 g, 10.0 mmol),  $(CH_3CH_2O)_3P$  (2d) (3.33 g, 20.0 mmol), HO\_2CH (6a) (0.46 g, 10 mmol). After appropriate work-up, **10a** was obtained as a colorless liquid. Yield: 4.24 g (8.7 mmol, 87% based on **1**).

*Elemental analysis: Anal.* Calc. for C<sub>14</sub>H<sub>33</sub>CuO<sub>10</sub>P<sub>2</sub> (486.90): C, 34.54; H, 6.83. Found: C, 34.43; H, 6.67%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3439 (w), 2982 (vs), 2930 (s), 2904 (s), 2708 (m) ( $\nu_{CH}$ ), 2509 (m) ( $\nu_{CH}$ ), 1956 (m) (broad, OH), 1722 (vs) (CO, asym, HCO<sub>2</sub>H), 1589 (vs) (CO, asym, HCO<sub>2</sub><sup>-</sup>), 1477 (m) (CO, asym, HCO<sub>2</sub>H), 1444 (m) (CO, sym, HCO<sub>2</sub><sup>-</sup>), 1391 (s), 1347 (m), 1296 (m), 1185 (m), 1163 (s), 1097 (s), 1025 (vs), 947 (vs), 777 (s), 691 (m), 665 (w), 538 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>): δ 1.14 (t, 18 H, CH<sub>3</sub>, J<sub>HH</sub> = 7.0 Hz), 3.88 (m,

12 H, CH<sub>2</sub>), 8.72 (s, 2 H, HCO<sub>2</sub>/ $^{-}$ O<sub>2</sub>CH), 13.84 (s, 1 H, CO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  16.7 (CH<sub>3</sub>), 60.8 (d, CH<sub>2</sub>, *J<sub>PC</sub>* = 24.8 Hz), 165.4 (s, HCO<sub>2</sub>H), 174.2 (s, HCO<sub>2</sub> $^{-}$ ). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  117.0.

#### 2.15. Synthesis of $[((EtO)_3P)_3CuO_2CH \cdot HO_2CH]$ (**10b**)

Complex **10b** was synthesized in the same manner as **8a** (Section 2.10): [CuO<sub>2</sub>CH] (**1**) (1.08 g, 10.0 mmol), (CH<sub>3</sub>CH<sub>2</sub>O)<sub>3</sub>P (**2d**) (4.99 g, 30.0 mmol), HO<sub>2</sub>CH (**6a**) (0.46 g, 10 mmol). After appropriate work-up, complex **10b** was obtained as a colorless liquid. Yield: 5.81 g (8.9 mmol, 89% based on **1**).

*Elemental analysis: Anal.* Calc. for C<sub>20</sub>H<sub>48</sub>CuO<sub>13</sub>P<sub>3</sub> (653.06): C, 36.78; H, 7.41. Found: C, 36.49; H, 7.21%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 2983 (vs), 2930 (s), 2900 (s), 2708 (m) ( $\nu_{CH}$ ), 2509 (m) ( $\nu_{CH}$ ), 1952 (m) (broad, OH), 1723 (vs) (CO, asym, HCO<sub>2</sub>H), 1585 (vs), (CO, asym, HCO<sub>2</sub><sup>-</sup>), 1477 (m) (CO, sym, HCO<sub>2</sub>H), 1443 (m) (CO, sym HCO<sub>2</sub><sup>-</sup>), 1391 (s), 1292 (m), 1188 (m), 1163 (s), 1093 (s), 1023 (vs), 946 (vs), 777 (s), 691 (m), 538 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  1.19 (t, 27 H, CH<sub>3</sub>,  $J_{HH}$  = 7.1), 3.90 (tq, 18 H, CH<sub>2</sub>,  $J_{HH}$  = 7.0 Hz), 8.73 (s, 2 H, HO<sub>2</sub>CH/HCO<sub>2</sub><sup>-</sup>), 13.38 (s, 1 H, CO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  16.5 (CH<sub>3</sub>), 60.4 (d, CH<sub>2</sub>,  $J_{PC}$  = 25.6 Hz), 165.0 (s, HCO<sub>2</sub>H/HCO<sub>2</sub><sup>-</sup>). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  116.9.

### 2.16. Synthesis of [{[Ti]( $\mu$ - $\sigma$ , $\pi$ -C=CSiMe<sub>3</sub>)<sub>2</sub>}CuO<sub>2</sub>CH·HO<sub>2</sub>CH] (**11a**)

To [CuO<sub>2</sub>CH] (1) (32.57 mg, 0.30 mmol) in 30 mL of dichloromethane was added formic acid (**6a**) (14.12 mg, 0.30 mmol) in a single portion at 20 °C. The reaction mixture was stirred for 20 min at this temperature. Afterwards, [Ti](C $\equiv$ CSiMe<sub>3</sub>)<sub>2</sub> (**3**) (155 mg, 0.30 mmol) dissolved in 20 mL of dichloromethane was dropwise added to the reaction solution and stirring was continued for 1 h. Then the reaction mixture was filtered through a pad of Celite and all volatiles were removed in oil-pump vacuum to give a deep brown solid. Yield: 200 mg (0.295 mmol, 98% based on **1**). Crystallization from a dichloromethane solution containing **11a** at -20 °C gave deep brown single crystals of **11a**.

M.p.: 133 °C (dec.). *Elemental analysis: Anal.* Calc. for  $C_{28}H_{47}$ -CuO<sub>4</sub>Si<sub>4</sub>Ti (671.44): C, 50.10; H, 7.06. Found: C, 50.40; H, 7.53%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3396 (broad) ( $\nu_{OH}$ ), 1918 (m) ( $\nu_{C=C}$ ), 1727 (s) (CO, asym), 1621 (s) (CO, asym), 1455 (s) (CO, sym), 1406 (s) (CO, sym), 1380 (m), 1295 (m), 1261 (s), 1183 (m). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  0.19 (s, 18 H, SiMe<sub>3</sub>), 0.24 (s, 18 H, SiMe<sub>3</sub>), 6.11 (pt, 4 H, C<sub>5</sub>H<sub>4</sub>, J<sub>HH</sub> = 2.34 Hz), 6.69 (pt, 4 H, C<sub>5</sub>H<sub>4</sub>, J<sub>HH</sub> = 2.34 Hz), 8.53 (s, 2 H, CO<sub>2</sub>H), 11.95 (s, 1 H, HO<sub>2</sub>CH). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  0.9 (SiMe<sub>3</sub>), 1.4 (SiMe<sub>3</sub>), 114.1 (CH/C<sub>5</sub>H<sub>4</sub>), 117.0 (CH/C<sub>5</sub>H<sub>4</sub>), 122.8 (<sup>i</sup>C/C<sub>5</sub>H<sub>4</sub>), 135.0 (C=CSi), 167.9 (TiC=C), 170.1 (CO<sub>2</sub>), 170.8 (CO<sub>2</sub>). ESI-MS ([*m/z* (rel. inten.)] (Thf)): [[Ti](C=CSiMe<sub>3</sub>)<sub>2</sub>]<sup>+</sup>, 581 (50).

#### 2.17. Synthesis of [{[Ti]( $\mu$ - $\sigma$ , $\pi$ -C=CSiMe<sub>3</sub>)<sub>2</sub>}CuO<sub>2</sub>CH·HO<sub>2</sub>CPh] (**11b**)

To  $[CuO_2CH]$  (1) (30.00 mg, 0.276 mmol) dissolved in 30 mL of dichloromethane was added HO<sub>2</sub>CPh (**6d**) (33.75 mg, 0.276 mmol) in 30 mL of dichloromethane at ambient temperature. The reaction solution was stirred for 30 min and then  $[Ti](C \equiv CSiMe_3)_2$  (3) (142.83 mg, 0.276 mmol) was added in a single portion. The work-up procedure according to the preparation of **6** gave a deep brown solid. Yield: 170 mg (0.2276 mmol, 86% based on **1**).

M.p.: 140 °C (dec.). *Elemental analysis: Anal.* Calc. for  $C_{34}H_{51}$ CuO<sub>4</sub>Si<sub>4</sub>Ti (747.543): C, 54.63; H, 6.88. Found: C, 54.56; H, 6.53%. IR (NaCl):  $\tilde{\nu}$  [cm<sup>-1</sup>] 3486 (broad), 1916 (m) ( $\nu_{c} =_{C}$ ), 1724 (vs) (C=O, HO<sub>2</sub>CPh), 1696 (vs) (CO, asym), 1404 (s) (C–O, sym), 1374 (s) (CO, sym). <sup>1</sup>H NMR (D<sub>6</sub>-acetone):  $\delta$  0.20 (s, 18 H, SiMe<sub>3</sub>), 0.25 (s, 18 H, SiMe<sub>3</sub>), 6.27 (pt, 4 H, C<sub>5</sub>H<sub>4</sub>, J<sub>HH</sub> = 2.2 Hz), 6.35 (pt, 4 H, C<sub>5</sub>H<sub>4</sub>, J<sub>HH</sub> = 2.2 Hz), 6.77 (m, 1 H, Ph), 7.62 (bs, 2 H, Ph), 8.10 (bs, 2 H, Ph), 9.61 (bs, 1 H, <sup>-</sup>O<sub>2</sub>CH). <sup>13</sup>C{<sup>1</sup>H} NMR (D<sub>6</sub>-acetone):  $\delta$  0.8 (SiMe<sub>3</sub>), 1.0 (SiMe<sub>3</sub>), 114.4 (CH/C<sub>5</sub>H<sub>4</sub>), 117.1 (CH/C<sub>5</sub>H<sub>4</sub>), 123.1

#### Table 1

Crystal data, collection parameter and refinement parameter for complexes  $\mathbf{8a}$  and  $\mathbf{11a}$ .

	8a	11a
Formula	$C_{38}H_{69}CuO_4P_2$	C <sub>28</sub> H <sub>47</sub> CuO <sub>4</sub> Si <sub>4</sub> Ti
Formula weight	715.41	671.46
Crystal color	colorless	dark brown
Crystal dimensions (mm)	$0.7\times0.3\times0.3$	$0.4 \times 0.3 \times 0.2$
Crystal system	monoclinic	triclinic
Space group	$P2_1/n$	ΡĪ
a (Å)	10.095(2)	11.068(4)
b (Å)	27.427(6)	12.451(4)
<i>c</i> (Å)	14.605(4)	14.752(5)
α (°)	90.0	96.287(6)
β (°)	99.062(6)	110.109(6)
γ (°)	90.0	98.767(7)
$V(Å^3)$	3993.6(15)	1857.7(11)
Z value	4	2
$D_{\text{calc}}$ (g cm <sup>-3</sup> )	1.190	1.199
Index ranges	$-12\leqslant h\leqslant 12$ ,	$-13\leqslant h\leqslant 12$ ,
	$0\leqslant k\leqslant$ 35,	$-15\leqslant k\leqslant 15$ ,
	$0\leqslant l\leqslant 18$	$0 \leqslant l \leqslant 18$
F(0 0 0)	1552	706
$\mu$ (Mo K $\alpha$ ) (mm <sup>-1</sup> )	0.662	0.943
$\theta$ Range for data collection	1.48-27.16	1.68-26.68
Radiation. Mo Kα (Å)	$\lambda = 0.71073$	$\lambda = 0.71073$
Temperature (K)	298	298
Number of reflections measured	49 462	14611
Independent reflections observed	9030	7184
$[I > 2\sigma(I)]$		
Data/restraints/parameters	8827/493/548	7184/0/367
T <sub>maximum/minimum</sub>	0.99999/	0.99999/
	0.43452	0.75234
$R_1 [I > 2\sigma(I)]/all^a$	0.0406/0.0691	0.0447/0.0635
$wR_2 [I > 2\sigma(I)]/all^b$	0.0903/0.1005	0.1209/0.1311
Goodness of fit (GOF) on $F^{2c}$	1.028	1.029
$\Delta ho_{ m max}$ (e Å $^{-3}$ )	0.278	0.398
$\Delta  ho_{\min} (e  \text{\AA}^{-3})$	-0.248	-0.459

<sup>a</sup>  $R_1 = \Sigma |F_{obs} - F_{calc}| / \Sigma F_{calc}$ 

<sup>b</sup>  $wR_2 = [\Sigma w (F_{obs}^2 - F_{calc}^2)]^2 / [\Sigma w (F_{obs}^2)]^2.$ 

 $S = [\Sigma W(F_{obs}^2 - F_{calc}^2)]/(n - p)^{1/2}, n = number of reflections; p = parameters used.$ 

 $({}^{i}C(C_{5}H_{4}), 123.9 \text{ (Ph)}, 128.6 \text{ (Ph)}, 130.3 \text{ (Ph)}, 131.9 \text{ (Ph)}, 135.0 \text{ (C=CSi)}, 169.7 \text{ (TiC=C)}, 171.9 \text{ (CO}_{2}), 172.6 \text{ (CO}_{2}).$ 

#### 2.18. Structure determination of 8a and 11a

Crystal data crystal data, collection parameter and refinement parameter of **8a** and **11a** are presented in Table 1. Data were col-





**Scheme 1.** Synthesis of **7–11** by reacting **1**, **4**, and **5** with **2**, **3**, and **6**, respectively. (i) Dichloromethane, 1 h, -20 °C; (ii) dichloromethane, 0.5–2 h, -20 °C.

The structures were solved by direct methods using SHELXS 97 [6]. The structures were refined by full-matrix least-squares procedures on  $F^2$  using SHELXL 97 [7]. All *non*-hydrogen atoms were refined anisotropically. In complex **11a** the hydrogen atom positions at the formiate and the formiat acid have been taken from the difference Fourier map and refined isotropically. All other hydrogen atom positions were refined using a riding model. In complex **8a** the hydrogen atom positions less H200 have been refined using the atom corresponding riding model. The positions of H200 have been taken from the difference Fourier map and refined freely. Two cyclohexyl rings and the formate molecule are disordered and have been refined to split occupancies of 0.63/0.37 (C19 to C24), 0.65/0.35 (C31 to C36) and 0.57/0.43 (O3 to O4), respectively.

### 3. Results and discussion

#### 3.1. Synthesis

A straightforward synthesis methodology for the high-yield preparation of the copper(I) formates  $[L_mCuO_2CH]$  (L =  ${}^nBu_3P$ : **4a**, m = 1; **4b**, m = 2. **5**, L = [Ti](C $\equiv$ CSiMe<sub>3</sub>)<sub>2</sub>, m = 1, [Ti] = ( $\eta^{5}$ -C<sub>5</sub>H<sub>4</sub>Si-Me<sub>3</sub>)<sub>2</sub>Ti) is given in Reaction 1 and includes the treatment of [CuO<sub>2</sub>CH] (**1**) with L (**2a**, L =  ${}^nBu_3P$ ; **3**, L = [Ti](C $\equiv$ CSiMe<sub>3</sub>)<sub>2</sub>) in the ratio of 1:1 (synthesis of **4a** and **5**) or 1:2 (**4b**) in dichloromethane as solvent. The synthesis of the appropriate copper(I) formates with L = P({}^cC\_6H\_{11})\_3, P(OCH<sub>2</sub>CH<sub>3</sub>)<sub>3</sub> and P(OCH<sub>2</sub>CF<sub>3</sub>)<sub>3</sub> is described elsewhere [5].

$$[L_mCuO_2CH]$$
(1)

**4a**: 
$$L = {}^{n}Bu_{3}P, m = 1$$
  
**4b**:  $L = {}^{n}Bu_{3}P, m = 2$   
**5**:  $L = [Ti](C = CSiMe_{3})_{2}, m = 1$ 

nn

lected with a Bruker Smart CCD diffractometer at 298 K using Mo K $\alpha$  radiation ( $\lambda$  = 0.71073 Å). Reflections were collected in the  $\theta$  scan modus in 0.3° steps and an exposure time of 20 s per frame.

After appropriate work-up, complexes **4a** and **4b** could be isolated as colorless liquids, while heterobimetallic **5** forms a dark brown solid with a decomposition point of 145 °C (Experimental Part).

Most likely, **4a** and **4b** are tetramers or dimers [3], though **5** features a low-valent copper(I) formate moiety stabilized by the chelating effect of the organometallic  $\pi$ -tweezer [Ti](C=CSiMe<sub>3</sub>)<sub>2</sub> [8]. Organometallic **5** is fairly stable both in the solid state and in solution, while **4a** and **4b**  $t_{end}$  to decompose on prolonged storage even in the solid state upon formation of greenish products, *i.e.* copper oxide-containing materials.

Reaction of **4a**, **4b**, and **5** with an excess of formic acid (**6a**), acetic acid (**6b**), trifluoroacetic acid (**6c**) or benzoic acid (**6d**) produced the more stable metal–organic complexes  $[L_mCuO_2CH \cdot HO_2CR]$  and  $[{[Ti](\mu-\sigma,\pi-C=CSiMe_3)_2}CuO_2CH \cdot HO_2CR]$  ([Ti] =  $(\eta^5-C_5H_4SiMe_3)_2$ -Ti; R = H, C<sub>6</sub>H<sub>5</sub>) (synthesis of **7a–7e**, **11a**, and **11b**) (Scheme 1, Table 2) in which a formic acid or a carboxylic acid molecule is additionally hydrogen-bonded to the keto-oxygen atom of the copper formate building block. Another possibility to synthesize the formic or carboxylic acid adducts **7–11** (Table 2) is given by the consecutive reaction of [CuO\_2CH] (**1**) with m equivalents of L (**2a**, L =  $^nBu_3P$ ; **2b**, L ( $^cC_6H_{11})_3P$ ; **2c**, L = (CF\_3CH\_2O)\_3P; **2d**, L = (CH\_3CH\_2O)\_3P; **3**, L = [Ti](C=CSiMe\_3)\_2) followed by addition of HO\_2CR (**6a**, R = H; **6b**, R = Me) (Scheme 1). The yield of individual **7–11** is 73–98% (Experimental Part, Table 2).

Complexes **7–11** are, compared with their *non*-coordinated, *non*-solvated counter parts **4** and **5**, significantly more stabile and can, for example, be handled even in air for a short period of time.

The *non*-solvated as well as formic acid and carboxylic acid mono-solvated adducts were characterized by elemental analysis and IR and NMR ( $^{1}$ H,  $^{13}$ C( $^{1}$ H) spectroscopy. The molecular structures of **8a** and **11a** in the solid state were determined by single X-ray structure analysis.

Most characteristic in the IR spectra of all complexes are the strong  $v(CO_2)$  vibrations of the carboxylato units between 1284– 1454  $(v_s(CO_2))$  and 1455–1702 cm<sup>-1</sup>  $(v_a(CO_2))$   $(v_s = symmetric,$  $v_a$  = anti-symmetric O-C-O stretching mode) (Experimental Part), which is typical in transition metal chemistry [9]. Whereas the anti-symmetric  $v(CO_2)$  bands can always be detected, the respective symmetric vibrations only at times, which is attributed to additional ligand absorptions in this region. The frequencies of the  $v(CO_2)$ modes of the hydrogen-bonded solvated  $RO_2CH$  acids (R = H, CH<sub>3</sub>,  $CF_3$ ,  $C_6H_5$ ) are observed between 1698–1748 cm<sup>-1</sup> for v(C=O) and 1163–1278 cm<sup>-1</sup> for v(C–O). The differences between these values range from 450 to 570 cm<sup>-1</sup> and show that the formic and carboxylic acids are situated between the data for the free acid molecules (e.g.,  $HCO_2H$ , 671 cm<sup>-1</sup>) and, for example, Na[H(HCO\_2)\_2] (439 cm<sup>-1</sup>), which is similar to the hydrogen-bonded dimer of formic acid (524 cm<sup>-1</sup>) [10a]. These data are also characteristic for other solvated transition complexes including [(Ph<sub>3</sub>P)<sub>m</sub>MO<sub>2</sub>CH·HO<sub>2</sub>CH] (M = Cu, Ag; m = 2, 3) [2a],  $[(Ph_3P)_2CuO_2CH \cdot 1/2EtOH]$  [2a], and  $[((C_6H_4-2-NMe_2)_3P)CuO_2CH \cdot HO_2CR]$  (R = H, CH<sub>3</sub>) [2b]. In general,

#### Table 2

Synthesis of complexes  $[L_mCuO_2CH \cdot HO_2CR]$  and  $[{[Ti](\mu - \sigma, \pi - C \equiv CSiMe_3)_2} CuO_2CH \cdot HO_2CR]$  (7–11).

Compounds	L	М	R	Yield <sup>a</sup>
7a	<sup>n</sup> Bu <sub>3</sub> P	1	Н	78
7b	<sup>n</sup> Bu <sub>3</sub> P	2	Н	81
7c	<sup>n</sup> Bu <sub>3</sub> P	2	Me	81
7d	<sup>n</sup> Bu <sub>3</sub> P	2	CF <sub>3</sub>	76
7e	<sup>n</sup> Bu <sub>3</sub> P	2	Ph	73
8a	$({}^{c}C_{6}H_{11})_{3}P$	2	Н	87
8b	$({}^{c}C_{6}H_{11})_{3}P$	3	Н	89
9a	$(CF_3CH_2O)_3P$	2	Н	85
9b	$(CF_3CH_2O)_3P$	3	Н	82
10a	(CH <sub>3</sub> CH <sub>2</sub> O) <sub>3</sub> P	2	Н	87
10b	$(CH_3CH_2O)_3P$	3	Н	89
11a	[Ti](C=CSiMe <sub>3</sub> ) <sub>2</sub>	1	Н	98
11b	[Ti](C=CSiMe <sub>3</sub> ) <sub>2</sub>	1	Ph	86

<sup>a</sup> Based on **1** (Scheme 1, reaction (i)).

for "weak" to "medium" hydrogen bonds of type  $A-H \cdots B$  (v(AH)) an absorption in the range of 2000–3500 cm<sup>-1</sup> occurs, for compounds with "strong" to "very strong" hydrogen bonds very broad vibrations are found below 1600 cm<sup>-1</sup> [11], which is illustrated by, for example, hydrogen-bridged [HCO<sub>2</sub>H]<sub>2</sub> [12,13]. There a O···O distance of 2.703 Å [13] and a v(OH) vibration with the maximum at ca. 3100 cm<sup>-1</sup> [12] is observed, while for the potassium salt K[H(O<sub>2</sub>CH)<sub>2</sub>] an O···O separation of 2.45 Å and a v(OH) at 1400 cm<sup>-1</sup> is characteristic [14] (for comparison see also, single solid state structure of **8a**, Fig. 1).

The <sup>1</sup>H NMR spectra of all newly synthesized transition metal complexes (Table 2) show well-resolved resonance signals with the expected coupling patterns and are consistent with the empirical formula given in the Experimental Part. Most characteristic for all complexes is the appearance of a very characteristic signal between 8.1 and 8.7 ppm (**9a,b**: 6.8 ppm) which can be assigned to the formate CH hydrogen atom of the *non*-solvated complexes. For the appropriate mono-solvated formic acid and carboxylic acid adducts (Table 2) a second signal is observed between 9.6 and 14.8 ppm typical for the HO hydrogen atom. In addition to the formate, formic acid and carboxylic acid resonances, signals for the auxiliary ligands  $L = P^n Bu_3$ ,  $P(^cC_6H_{11})_3$ ,  $P(OCH_2CH_3)_3$ ,  $P(OCH_2CF_3)_3$  and the chelating [Ti](C=CSiMe\_3)\_2 building block are observed in the range characteristic for this type of coordinating ligands (Experimental Part) [5].

As the <sup>1</sup>H NMR spectra of **4**, **5**, and **7–11**, also the <sup>13</sup>C{<sup>1</sup>H} NMR spectra of these molecules show well-resolved signals with resonances for the  $HCO_2^-$  anions and  $RCO_2H$  solvates (R = H, CH<sub>3</sub>, CF<sub>3</sub>, C<sub>6</sub>H<sub>5</sub>) being most typical (Experimental Part). For the *non*-solvated copper(I) formats [CuO<sub>2</sub>CH] one signal for the formate carbon atom is found at ca. 167 ppm, while in the corresponding mono-solvated species this signal is somewhat shifted to higher field. For the hydrogen-bonded formic and carboxylic acid molecules resonances are found between 159 and 175 ppm depending on the organic groups. The signals of the formic and carboxylic acid are observed as expected (Experimental Part).



**Fig. 1.** ORTEP diagram (30% probability level) of the molecular structure of **8a**. All cyclohexyl-bonded hydrogen atoms have been omitted for clarity. Only one atomic position is displayed of disordered atoms (C19–C24, C31–C36, and O3, O4, C38, respectively). Selected bond distances (Å) and bond angles (°): Cu(1)–O(1) 2.0657(19), Cu(1)–P(1) 2.2381(6), Cu(1)–P(2) 2.2431(7), C(37)–O(1) 1.218(4) C(37)–O(2) 1.210(4), C(38)–O(3) 1.297(15), C(38)–O(4) 1.175(13); O(1)–Cu(1)–P(1) 114.34(6), P(1)–Cu(1)–P(2) 143.31(2), C(37)–O(1) 111.7(2), O(1)–Cu(1)–P(2) 102.07(6), O(2)–C(37)–O(1) 124.7(3), O(4)–C(38)–O(3) 122.0(12). Standard deviations are given as the last significant figure(s) in parentheses.

The coordination of the phosphane and phosphite ligands to copper(I) can nicely been verified from <sup>31</sup>P{<sup>1</sup>H} NMR studies. For example, upon coordination of the free, *non*-coordinated <sup>*n*</sup>Bu<sub>3</sub>P



**Fig. 2.** ORTEP diagram (30% probability level) of the molecular structure of **11a**. All cyclopentadienyl- and trimethylsilyl-bonded hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): Cu(1)-Ti(1) 2.9938(10), Cu(1)-O(1) 1.949(2), C(1)-Ti(1) 2.131(3), C(6)-Ti(1) 2.116(3), Cu(1)-C(1) 2.084(2), Cu(1)-C(6) 2.098(3), Cu(1)-C(2) 2.156(3), Cu(1)-C(7) 2.165(3), Cu(27)-O(1) 1.242(4), C(27)-O(2) 1.244(5), C(28)-O(3) 1.285(5), C(28)-O(4) 1.176(5), Ti(1)-D(1) 2.067(1), Ti(1)-D(2) 2.074(1); C(6)-Ti(1)-C(1) 88.59(10), C(2)-C(1)-Ti(1) 166.6(2), C(7)-C(6)-Ti(1) 166.1(2), C(6)-C(7)-Si(2) 163.2(2), C(1)-C(28)-O(3) 128.4(5), D(1)-Ti(1)-D(2) 47.9(1), O(1)-Cu(1)-Ti(1) 172.68(7). D(1) = centroid of C11-C15; D(2) = centroid of C19-C23. The estimated standard deviations of the last significant digits are shown in parentheses.

#### Table 3

Selected bond distances (Å) and angles (°) of the intermolecular hydrogen bonds of metal–organic 8a.

$D - H \cdots A^a$	D-H	H···A	D···A	$D{-}H{\cdots}A$
$\begin{array}{c} O(2) - H(200) \cdots O(3) \\ O(2) - H(200) \cdots O(3')^b \end{array}$	0.95(6)	1.65(2)	2.598(10)	174(8)
	0.95(6)	1.82(6)	2.583(14)	132(8)

<sup>a</sup> D = donor atom; A = acceptor atom

<sup>b</sup> Label ' refers to the atom O3' of the disordered formate anion.

ligand (-32.3 ppm) [15] to copper a typical downfield-shift is observed (**4a**, -16.7; **4b**, -20.8 ppm). The phosphorus signals of the appropriate mono-solvated adducts are found at somewhat lower field (**7a**: -14.6; **7b**: -17.7). Similar observations were made for all the other phosphane or phosphite copper(I) species (Experimental Part) [5].

#### 3.2. Molecular structures of 8a and 11a in the solid state

The molecular structures of **8a** and **11a** in the solid state were elucidated by single crystal X-ray diffraction studies (complex **8a**, Fig. 1; complex **11a**, Fig. 2). Single crystals were grown by slowly cooling a saturated dichloromethane solution containing either **8a** or **11a** to -20 °C, whereby colorless (**8a**) or brown (**11a**) crystals were obtained. Selected bond distances (Å) and bond angles (°) are given in the captions of Figs. 1 and 2 and Table 1. Crystal data and collection and refinement parameters of both compounds are summarized in Table 1 (Experimental Part).

Mono solvated **8a** crystallized in the monoclinic space group  $P_21/n$ . The [( ${}^{c}C_{6}H_{11}$ )\_{3}P)\_{2}CuO\_{2}CH] molecular unit in **8a** comprises a *tri*-coordinate copper atom with the crystallographically independent P( ${}^{c}C_{6}H_{11}$ )\_{3} ligands occupying two of the three coordination sites and the formate anion is  $\sigma$ -bonded through one oxygen atom to the third site forming a somewhat distorted trigonal planar environment around copper(I) (Fig. 1). The atoms Cu1, P1, P2, and O1 are thereby in-plane bound (RMS deviation 0.028 Å, highest deviation from planarity observed for Cu1: 0.0479(5) Å). The range of the angles around Cu1 is 359.72(9)°, displaying in addition its distorted trigonal planar environment.

Of complex **8a**, the Cu1–O1 distance is 2.0657(19) Å while the Cu–P distances are 2.2381(6) and 2.2431(7) Å. Comparing these separations with a *uni*-dentate [2a] and chelate-bonded formate anion confirms this finding [2c]. The Cu–O/Cu–P distances, respectively, decreases from ca. 2.2/2.3 Å for a chelate-bonded format ligand [2c] to 2.04–2.08/2.24 Å for a  $\sigma$ -bonded HCO<sub>2</sub><sup>-</sup> anion [2a]. It should be noted, that **8a** represents the first monomeric Cu(I) carboxylato complex with the cupper(I) atom possessing an almost trigonal planar CuP<sub>2</sub>O setup.

The formic acid solvate present in **8a** is hydrogen-bonded to the copper(I) formate unit to form a building block which best can be described as a bi-formate anion  $[H(HCO_2)_2]^-$ . This moiety is the simplest form of a family in which formic or carboxylic acid molecules are bonded to metal formate building blocks by molecular recognition, and have been the subject of a number of theoretical studies [16]. For **8a**, the hydrogen bond with a O···O distance of 2.598(10) and 2.583(14) Å (Table 3) of the  $[H(HCO_2)_2]^-$  unit falls into the category of "very strong", which is also verified and typical for the potassium formate salt  $K[H(HCO_2)_2]$  [14a] (d<sub>0··O</sub> = 2.45 Å). This finding, when compared with the appropriate free bi-formate



Fig. 3. TG studies of complexes 7a (left) and 7b (right) (nitrogen, flow rate 20 L h<sup>-1</sup>, heating rate 8 K min<sup>-1</sup>).



Fig. 4. Surface SEM image showing the morphology of the copper film obtained from 7b deposited on a TiN-coated oxidized silicon substrate at 400 °C (left), spin-off speed vs. film thickness (right).

ion, can be resulting from the competition of the formate ion electron density between the copper ion and the formic acid adduct part. A similar situation was recently found for  $[(Ph_3P)_3 AgO_2CH \cdot (HCO_2H)_2]$  [10a].

The titanium–copper organometallic  $\pi$ -tweezer compound **11a** (Fig. 2) crystallized in the triclinic space group  $P\bar{1}$ .

The molecular solid state structure of 11a resembles to the structures typically found for heterobimetallic organometallic  $\pi$ tweezer complexes of general type { $[M](\mu-\sigma,\pi-C \equiv CR)_2$ }M'L  $([M] = (\eta^5 - C_5 H_4 R')_2 Ti (Zr, Hf); M'L = 10-12$  valence electron complex fragment, such as Ni(CO), Co(CO), CuX, AgX, AuX, FeCl<sub>2</sub>, NiCl<sub>2</sub>,  $CoCl_2$ ; R = single-bonded organic or organometallic ligand; R' = H, Me, SiMe<sub>3</sub>; X = halide, pseudo-halide, inorganic, organic or organometallic ligand) with M' in a planar (M' = Ni, Co, Cu, Ag, Au) or pseudo-tetrahedral coordination sphere (M' = Fe, Ni, Co) [17], and hence the bis(alkynyl)titanocene framework is not discussed here in detail. Concerning the [CuO<sub>2</sub>CH·HCO<sub>2</sub>H] building block following trends can be seen: (i) the copper-oxygen bond is with 1.949(2) Å shorter than the corresponding bond distances found in phopshine or phosphite copper formate systems (vide supra and Ref. [2a]) but is in the range of similar Ti-Cu tweezer molecules [3f,8a]. This shows that in 11a the bi-formate unit is somewhat stronger bonded to copper, compared with the appropriate copper phosphane complexes (Refs. [3a-g]). The oxygen-oxygen distance in the bi-formate building block is 2.571(5) Å and can be considered as "very strong" (vide supra). Selected bond distances (Å) and angles (°) of the intermolecular hydrogen bond D-H···A (O2-H29...O3) of **11a** are: D-H (1.14(8)), H...A (1.49(8)), D...A (2.571(5)); and D-H···A (156(7)), whereby D = donor atom and A = acceptor atom.

#### 3.3. TG- and spin-coating-studies

Metal thin film deposition by using the spin-coating process is a technique for coating a thin metal layer of *non*-volatile precursors within a few tens up to several hundred of nanometers onto a substrate or onto previously deposited layers [18]. On heating, a chemical change at the surface takes place leaving a metal film. This method is, when compared with other deposition techniques [19], a very cost effective method because it does not require complicated technical and hence, expensive equipment.

TG (ThermoGravimetry) studies were carried out to obtain first information on the decomposition temperature and on the relative stability of some of the newly synthesized complexes. Experiments were conducted at atmospheric pressure under a nitrogen purge. Exemplary, the TG studies of **4**, **7** and **9** are discussed. It was found that these complexes show a 2–4 step decomposition. In general, the thermal degradation starts at 80 °C and is completed above 400 °C (Experimental Part). The weight losses were accompanied by residues in the TG pan, the amount of which was comparable to the theoretical percentage of metallic copper present in the complex, though small amounts (0.5–3%) of additional material are also formed (Experimental Part). Evidently, these complexes eliminate first the solvated acid, followed by the ligands <sup>*n*</sup>Bu<sub>3</sub>P or (RO)<sub>3</sub>P upon heating without significant volatilization of the intact copper formiate. Thus, at atmospheric pressure the majority of the studied copper species showed a high utility for spin-coating. Following TG studies of complexes [(<sup>*n*</sup>Bu<sub>3</sub>P)<sub>*m*</sub>CuO<sub>2</sub>CH·CH<sub>2</sub>O] (**7a**, m = 1; **7b**, m = 2) are discussed in detail, *i.e.* the thermal gravimetric curves of both molecules are depicted in Fig. 3.

For both metal-organic complexes it was found that the mass loss of 81.49% (7a) and 88.64% (7b) is almost in accordance with the theoretical percentage calculated for the formation of elemental copper, the difference is less then 1% (C, O impurities). Similar results were recently reported for the decomposition of phosphane and phosphite copper(I) and silver(I) carboxylates, respectively [4a,4b,10]. Organic products formed during the redox process of the internal formiate/formic acid entities are in general volatile and vaporize during the decomposition process. These investigations prove that both complexes should be suitable as spin-coating precursors. Since **7b** with its two tri-*n*-butyl phosphane ligands is more stable towards air and moisture then 7a this molecule was chosen for further detailed TG and finally spin-coating studies. Attempts to remove impurities (vide supra) we repeated the TG measurement of 7b in presence of a reducing agent and hence, as carrier gas nitrogen containing 2% of hydrogen was applied. It was found that **7b** decomposes in a similar decomposition pattern as without addition of H<sub>2</sub>. An overall decomposition starting at 84 and ending at 360 °C is observed (Experimental Part). The mass loss of 88.85% is now in accordance with the theoretical percentage (88.64%) calculated for the formation of elemental copper from **7b**. This shows that sintering of the spin-coated wafer should best be carried out under reducing conditions (vide infra). From the data obtained (Experimental Part) it is most likely that the mono-solvated complexes (7-11) eliminate at first the hydrogen-bonded formic acid or carboxylic acid units giving the appropriate non-solvated species  $[(R_3P)_mCuO_2CH]$  (R = <sup>*n*</sup>Bu, <sup>*c*</sup>C<sub>6</sub>H<sub>11</sub>, OCH<sub>2</sub>CF<sub>3</sub>, OCH<sub>2</sub>CH<sub>3</sub>; m = 1, 2, 3). On further heating these molecules eliminate in the temperature range of 100-400 °C, depending on m and R, ligands  $R_3P$  or  $(RO)_3P$  to afford [CuO<sub>2</sub>CH]. Decarboxylation finally leads to elementary copper. Comparable decomposition pathways are found for dicopper and disilver dicarboxylates (e.g., oxalate, squarate) as it could be demonstrated by TG-MS studies [20].

Based on the TG studies (vide supra) metal–organic **7b** was applied as spin-coating precursor in the deposition of copper onto TiN-coated oxidized silicon wafer materials. The spin-coating



**Fig. 5.** AES spectrum of the copper film obtained by the spin-coating process using **7b** as precursor material at 400 °C (deposition occurred on a TiN-coated SiO<sub>2</sub> wafer material).

technique was chosen over physical or Chemical Vapor Deposition processes (for example, PVD (Physical Vapor Deposition), CVD (Chemical Vapor Deposition), ALD (Atomic Layer Deposition)) and electroplating because next to their benefits they do possess some drawbacks. PVD has, for example, limited gap-fill capabilities [21], CVD may yield uniformity issues with high areas, especially on large wafers and is not suitable for films thicker than 100 nm, and finally the costs for the appropriate precursors as well as equipment is high (see above) [22]. In contrast, electroplating is much more effective and hence, more widespread in microelectronics technology but there are also some challenges like control of metal crystal growth from nano-scale (feature filling) up to the macro-scale (uniformity across the wafers) or the introduction of bath additives into the deposited films increasing their resistivity. Thus, we favor the low cost spin-coating process as an alternative technique for metal film deposition. The process benefits of superior thickness uniformity, due to *non*-conformal coatings, the high potential to fill small gaps (<100 nm) with high aspect ratios, and atmospheric-like ambient process conditions.

Mono-solvated highly viscous 7b (vide supra) was used as a *non*-volatile material in first spin-coating studies for the deposition of copper films. Film deposition were verified as follows: In a typical deposition process 7b dissolved in tetrahydrofuran was dispensed under argon from a pipette onto a pre-cleaned and afterwards oxidized silicon wafer coated with a double layer of sputter deposited TiN diffusion barrier and Cu with a thickness of 40/100 nm with 150 rpm rotation speed. A spin-off speed of 2000 rpm was chosen in order to get a thin homogeneous liquid film on the wafer after 30 s of dispersion time. An industrial spin-coating system (Suss Microtec) with a closed deposition chamber and a protecting nitrogen stream was used for these studies. The treated wafers were transferred to an oven and have then been heated with a defined ramp rate of 8 K min<sup>-1</sup> up to 400 °C. The decomposition temperature followed the thermal gravimetric curve shown in Fig. 3. The film was annealed at 400 °C for 30 min in an N<sub>2</sub>/H<sub>2</sub> (ratio of 98:2) atmosphere. A SEM image of the obtained copper film is shown in Fig. 4 (left). As it can be seen from this figure, the copper film is not completely homogeneous and shows some defects. This can be explained by the different film thickness as result of the spin-coating process, which upon heating produce defects due to unequal evaporation of the *in situ* formed reaction products leading to partially cracked copper films.

Additionally, the behavior between the spin speed and film thickness was studied (Fig. 4, right). As it can be seen from this figure the exponent of -3 obtained from the spin speed curve is high as compared with other spin-coating metal–organic precursors including polyimide complexes (0.2–0.8) [23], which is explainable by the fact that the deposition process described (vide supra) is not

optimized towards the key parameters for mass flow (viscosity), film formation (surface tension, wetting, etc.) and film thickness. Since the films always contained traces of solvent molecules resulting from the precursor material the films are not completely solidifying during the spinning process. Better results were obtained by higher spin speeds ( $\geq 2000$  rpm), however, at a low film thickness the precursor films were destroyed during wetting processes. In addition, the low copper yield obtained during thermolysis (vide supra) causes open grain network structures, especially, when solidification takes place before the decomposition process is finished and hence, the deposited films still contain low boiling organic molecules. As summary, a film thickness of ca. 300 nm is necessary in order to guarantee comparable sheet resistance results.

The chemical composition versus film thickness relation was studied by AES (Auger Electron Spectroscopy) (Fig. 5). As result, small amounts of organic materials as well as phosphorus-containing residues could be detected. Nevertheless, these deposits could nicely be removed by hydrogen post-treatment (see above).

#### Supplementary material

CCDC 765261 and 765262 contain the supplementary crystallographic data for **8a** and **11a**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif.

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