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# Phosphane Copper(I) Dicarboxylates: Synthesis and Their Potential Use as Precursors for the Spin-coating Process in the Deposition of Copper

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**Phosphane Copper(I) Dicarboxylates: Synthesis and Their  
Potential Use as Precursors for the Spin-coating Process in  
the Deposition of Copper**

Journal:	<i>Zeitschrift für Anorganische und Allgemeine Chemie</i>
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Keywords:	Copper, Dicarboxylic Acids, Electrolysis, Spin-Coating, Copper Deposition



**Table 1.** Bond distances (Å) and angles (°) of the intermolecular hydrogen bonds of **6d**.<sup>a)</sup>

D-H...A	D-H	H...A	D...A	D-H...A
O7-H7O...O1	1.13(3)	1.35(3)	2.4753(19)	177(3)
O4-H4O...O6	1.05(4)	1.43(4)	2.463(2)	168(3)

a) D = Donor, A = Acceptor.

**Table 2.** Crystal and Intensity Collection Data for **5a**, **6a**, and **6d**.

	<b>5a</b>	<b>6a</b>	<b>6d</b>
Empirical formula	C <sub>78</sub> H <sub>68</sub> Cl <sub>8</sub> Cu <sub>2</sub> O <sub>4</sub> P <sub>4</sub>	C <sub>38</sub> H <sub>82</sub> CuO <sub>4</sub> P <sub>3</sub>	C <sub>31</sub> H <sub>58</sub> CuNO <sub>4</sub> P <sub>2</sub>
Formula weight	1603.88	759.49	634.26
<i>T</i> /K	298(2)	293(2)	100(1)
Radiation, $\lambda$ /Å	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, <i>P</i> 2 <sub>1</sub> / <i>n</i>	monoclinic, <i>P</i> 2 <sub>1</sub> / <i>c</i>	triclinic, <i>P</i> 1
Unit cell dimensions <i>a, b, c</i> /Å	12.656(5)	13.246(3)	13.3023(9)
	21.622(9)	13.785(3)	15.6730(11)
	30.730(13)	25.771(5)	19.1704(10)
$\alpha, \beta, \gamma$ /°			93.788(5)
	97.958(8)	93.863(4)	105.727(5)
			111.759(7)
<i>V</i> /Å <sup>3</sup>	8328(6)	4695.0(15)	3510.5(4)
<i>Z</i> , Calculated density / g·cm <sup>-3</sup>	4, 1.279	4, 1.074	4, 1.200
Absorption coefficient /mm <sup>-1</sup>	0.888	0.599	0.745
<i>F</i> (000)	3288	1664	1368
Crystal size /mm	0.3 x 0.2 x 0.2	0.5 x 0.1 x 0.05	0.2 x 0.2 x 0.18
$\theta$ range /°	1.34 to 23.26	1.68 to 25.35	2.89 to 26.08
Index ranges	-14 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 24, 0 ≤ <i>l</i> ≤ 34	-15 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 16, -31 ≤ <i>l</i> ≤ 31	-16 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 19, -23 ≤ <i>l</i> ≤ 23
Reflections collected	67882	45083	26289
Reflections unique	15686 [ <i>R</i> (int) = 0.0600]	8374 [ <i>R</i> (int) = 0.0667]	13314 [ <i>R</i> (int) = 0.0219]
Completeness to theta max.	99.6	97.5	95.6
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.99999 and 0.33977	1 and 0.712398	1.00656 and 0.99347
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	11888 / 192 / 977	8374 / 0 / 415	13314 / 0 / 711
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.040	1.020	0.945

Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0969$ , $wR_2 = 0.2716$	$R_1 = 0.0667$ , $wR_2 = 0.1750$	$R_1 = 0.0311$ , $wR_2 = 0.0696$
$R$ indices (all data)	$R_1 = 0.1439$ , $wR_2 = 0.3273$	$R_1 = 0.1491$ , $wR_2 = 0.2087$	$R_1 = 0.0596$ , $wR_2 = 0.0760$
Largest diff. peak and hole / $e \text{ \AA}^{-3}$	2.410 and $-0.458$	0.558 and $-0.378$	0.438 and $-0.363$

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$R_1 = [\sum(|F_o| - |F_c|)/\sum|F_o|]$ ;  $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$ .  $S = [\sum w(F_o^2 - F_c^2)^2]/(n-p)^{1/2}$ .  $n$  = number of reflections,  $p$  = parameters used.

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3 Considered to be published in *Zeitschrift für Anorganische und Allgemeine Chemie* (Alex8.doc)  
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7 **Phosphane Copper(I) Dicarboxylates: Synthesis and Their Potential Use as**  
8 **Precursors for the Spin-coating Process in the Deposition of Copper<sup>†</sup>**  
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17 **Alexander Jakob, Tobias Rüffer, Petra Ecorchard, Bernhard Walfort, Kathrin Körbitz,**  
18 **Swantje Frühauf,<sup>a)</sup> Stefan E. Schulz,<sup>a)</sup> Thomas Gessner,<sup>a)</sup> and Heinrich Lang\*<sup>)</sup>**  
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27 Chemnitz, Technische Universität, Fakultät für Naturwissenschaften, Institut für Chemie,  
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29 Lehrstuhl für Anorganische Chemie  
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36 Zentrum für Mikrotechnologien, Reichenhainerstr. 70, 09126 Chemnitz (Germany)  
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43 Bei der Redaktion eingegangen am ...  
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50 **Abstract.**  
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52  
53 Dicopper dicarboxylates [(R<sub>3</sub>P)<sub>m</sub>CuXCu(PR<sub>3</sub>)<sub>m</sub>] (**5a**, X = O<sub>2</sub>CCO<sub>2</sub>, R = Ph, *m* = 2; **5b**, X =  
54 O<sub>2</sub>CCO<sub>2</sub>, R = <sup>n</sup>Bu, *m* = 3) were prepared by treatment of [Cu<sub>2</sub>O] (**1a**) with HO<sub>2</sub>CCO<sub>2</sub>H (**2a**) in  
55 presence of PR<sub>3</sub> (**4a**, R = Ph; **4b**, R = <sup>n</sup>Bu). A further synthesis approach to mono- and dicop-  
56 per dicarboxylates is given using an electrolysis cell equipped with Cu electrodes and charged  
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<sup>†</sup> Dedicated to Prof. Dr. Rüdiger Kniep on occasion of his 65<sup>th</sup> birthday.

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3 with acids  $H_2X$  and phosphanes  $R_3P$ . Without addition of a base mononuclear  
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5  $[(^nBu_3P)_mCuXH]$  (**6a**,  $m = 3$ ,  $XH = O_2CCO_2H$ ; **6b**,  $m = 3$ ,  $XH = O_2CCH_2CO_2H$ ; **6c**,  $m = 3$ ,  
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7  $XH = O_2CCH_2CH_2CO_2H$ ; **6d**,  $m = 2$ ,  $XH = O_2C-2-C_5H_4N-6-CO_2H$ ) was formed, while in  
8  
9 presence of  $NEt_3$  the dicopper systems  $[(R_3P)_mCuXCu(PR_3)_m]$  (**5a**,  $X = O_2CCO_2$ ,  $R = Ph$ ,  $m =$   
10  
11  $2$ ; **5b**,  $X = O_2CCO_2$ ,  $R = ^nBu$ ,  $m = 3$ ; **5c**,  $X = O_2CCH_2CO_2$ ,  $R = ^nBu$ ,  $m = 3$ ; **5d**,  $X =$   
12  
13  $O_2CCH_2CH_2CO_2$ ,  $R = ^nBu$ ,  $m = 3$ ; **5e**,  $X = O_2C-2-C_5H_4N-6-CO_2$ ,  $R = ^nBu$ ,  $m = 3$ ) were pro-  
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15 duced. When **6a** was reacted with  $[(tmeda)Zn^nBu_2]$  (**7**), trimetallic  $[(tmeda)Zn(^nBu_3P)_3Cu-$   
16  
17  $O_2CCO_2)_2]$  (**8**) was accessible. In this heterobimetallic complex the  $Zn(tmeda)$  unit spans two  
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19  $CuO_2CCO_2$  entities. The molecular structures of **5a**, **6a** and **6d** in the solid state were deter-  
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21 mined by single X-ray structure analysis. Complexes **5a** and **6a** are monomers, while **6d** cre-  
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23 ates in the solid state a linear open chain coordination polymer by hydrogen bridge formation.  
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25 Characteristic for **6d** is the somewhat distorted trigonal bipyramidal geometry around Cu with  
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27 the  $^nBu_3P$  ligands in axial and the  $C_5H_3NCO_2H$  oxygen and nitrogen atoms in equatorial posi-  
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29 tions. In **5a** the oxalate connectivity binds in a  $\mu-1,2,3,4$  fashion being part of a planar  
30  
31  $Cu_2(oxalate)$  core. TG studies of several mono- and dicopper dicarboxylates were carried out.  
32  
33 Release of the  $PR_3$  ligands is recognized and the remaining Cu-(di)carboxylate unit decom-  
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35 poses to afford elemental Cu and  $CO_2$ . The deposition of Cu onto pieces of PVD-Cu oxidized  
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37 silicon wafers by applying the spin-coating process and using **5c** and **5d** as precursors is dis-  
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39 cussed.  
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**Keywords:** Copper; Dicarboxylic Acids; Electrolysis; Spin-coating; Copper Deposition

## Introduction

Copper deposition processes play, for example, an important role in micro- and nanoelectronics industry [1]. Numerous deposition methods, such as ionized metal plasma, physical, chemical and atomic vapor deposition, plasma-assisted and plasma-enhanced chemical vapor deposition, as well as electroplating and electroless plating have been used to deposit metal films on different surfaces [2]. For copper CVD (= Chemical Vapor Deposition) and ALD (= Atomic Layer Deposition) processes several copper(I) and copper(II) organometallics and metal-organic complexes were developed as precursor materials [3]. Among them copper(I)- $\beta$ -diketonates [ $L_m\text{Cu}(\beta\text{-diketonate})$ ] ( $L$  = phosphane, phosphite, alkene, alkyne, ...;  $m = 1, 2$ ) were prepared to obtain an assortment of precursors with different physical and chemical properties [4]. However, these species decompose by a thermally induced disproportionation giving elemental copper along with Cu(II)- $\beta$ -diketonates and the free Lewis-bases  $L$  [3o, 4]. Very recently, the successful use of copper(I) and silver(I) carboxylates as efficient CVD precursors was reported [3c, 5]. Their gas-phase behavior using temperature-programmed and *in-*

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3 *situ* mass spectrometry was established [5d-f]. The advantage of these compounds in compari-  
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5 son with the appropriate  $\beta$ -diketonate species is that they produce pure metal films in quanti-  
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7 tative yield [3c,o, 5g, 6]. Next to CVD and ALD metallization processes the spin-coating  
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9 process is an alternative technique for the deposition of metals [7].  
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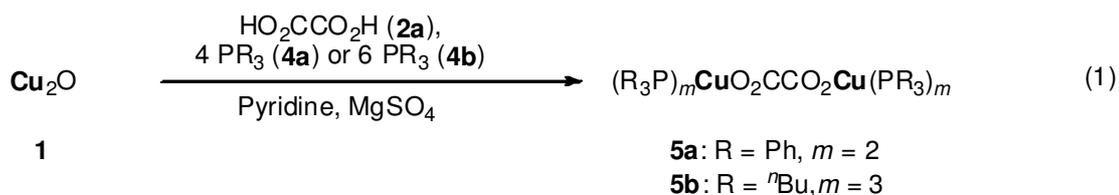
12 We here describe the synthesis of phosphane mono- and dicopper dicarboxylates by using  
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14 chemical and electrochemical synthesis methodologies. The use of these compounds as spin-  
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16 coating precursors for the deposition of copper onto pieces of PVD-copper oxidized silicon  
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18 wafer materials will be discussed.  
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## 27 **Results and discussion**

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29 The preparation of copper(I) dicarboxylates can be realized by using chemical [8] and  
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31 electrochemical [5g, 9] procedures of which the latter method proved to be more efficient and  
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33 additionally allows the straightforward synthesis of mono- and di-copper dicarboxylates de-  
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35 pending on the chemical composition of the electrolyte solution.  
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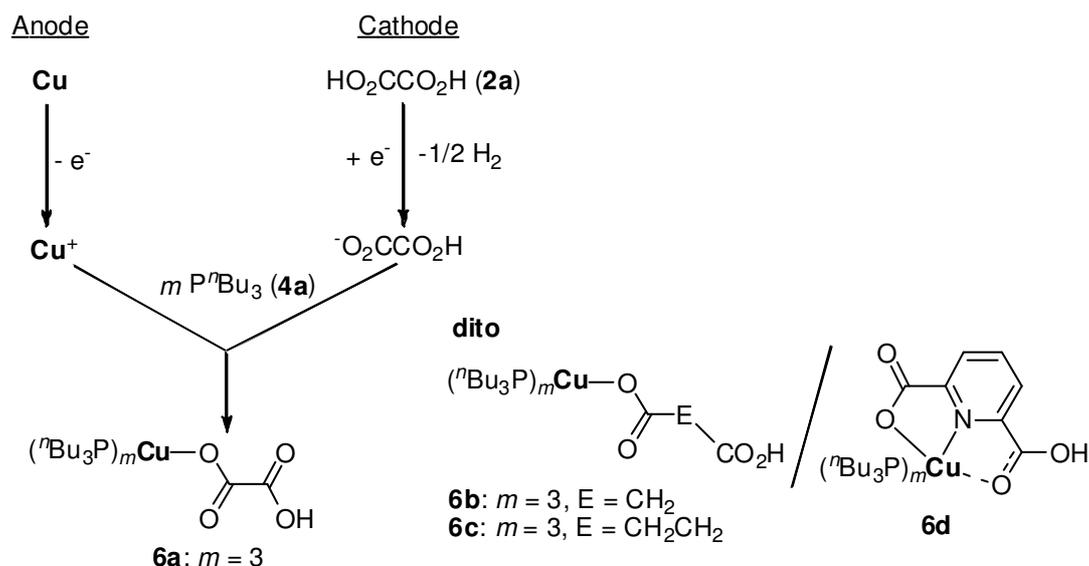
### 41 *Synthesis, reaction chemistry, and characterization*

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43 One possibility to synthesize dicopper dicarboxylates  $[(R_3P)_mCuXCu(PR_3)_m]$  (**5a** [10], X =  
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45  $O_2CCO_2$ , R = Ph,  $m = 2$ ; **5b**, X =  $O_2CCO_2$ , R =  $^nBu$ ,  $m = 3$ ) is given by the reaction of  $Cu_2O$   
46  
47 (**1a**) with  $HO_2CCO_2H$  (**2a**) and  $PR_3$  (**4a**, R = Ph; **4b**, R =  $^nBu$ ) in presence of  $MgSO_4$ ,  
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49 whereby the phosphanes are added in a 1:4 or 1:6 molar ratio in pyridine at 50 °C (Reaction  
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51 1). After appropriate work-up, **5a** and **5b** could be isolated in virtually quantitative yield.  
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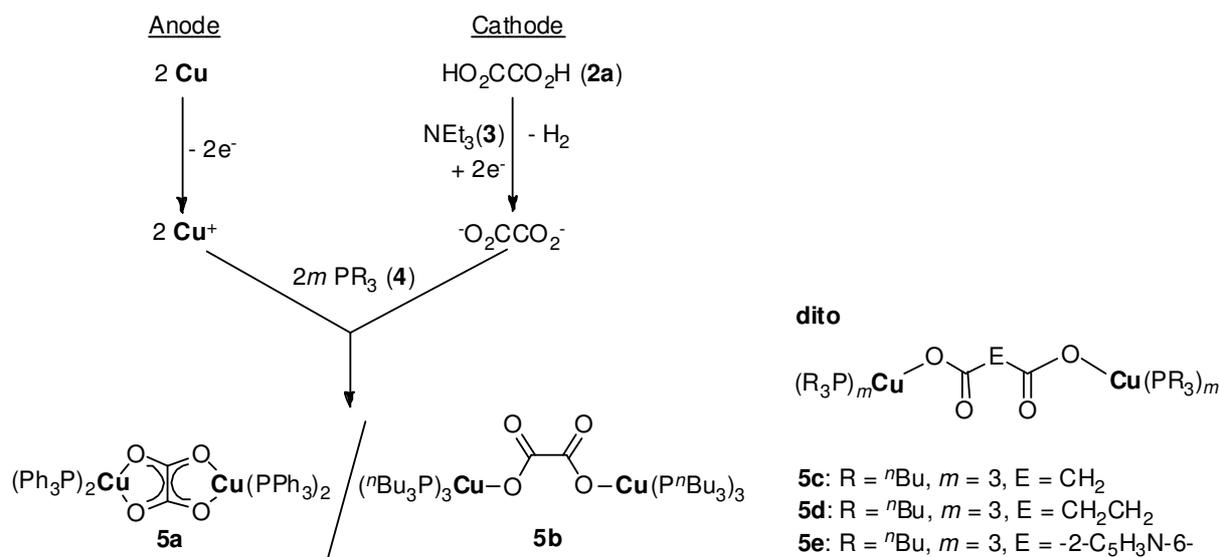
Though the latter synthesis methodology gives pure **5**, the disadvantage of this method is that only small quantities of the corresponding copper complexes are accessible per batch (5 g scale) and that work-up requires purification steps. This inspired us to search for another and hence, more straightforward synthesis procedure, which resulted in the electrochemical preparation of copper dicarboxylates by the oxidation of a sacrificial anode in a *non*-aqueous solution in presence of the appropriate acid H<sub>2</sub>X and PR<sub>3</sub> (Schemes 1 and 2). It was not necessary to add any extra electrolyte.

In a typical experiment, the direct electrochemical oxidation of copper was carried out in acetonitrile containing H<sub>2</sub>X and PR<sub>3</sub> at 40 °C (Scheme 2). The initial voltage was 2 – 6 V depending on the nature of H<sub>2</sub>X and PR<sub>3</sub>. Electrolysis was carried out until insignificant deposition of copper metal on the cathode was observed (1 – 4.5 hours). The formation of hydrogen, as consequence of the cathodic reduction of H<sup>+</sup>, was visually observed. After electrolysis the reaction solutions were transferred to Schlenk flasks and all volatiles were removed in *vacuum* to exclusively leave mononuclear complexes [(<sup>n</sup>Bu<sub>3</sub>P)<sub>m</sub>CuXH] (**6a**, *m* = 3, XH = O<sub>2</sub>CCO<sub>2</sub>H; **6b**, *m* = 3, XH = O<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>H; **6c**, *m* = 3, XH = O<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>H; **6d**, *m* = 2, XH = O<sub>2</sub>C-2-C<sub>5</sub>H<sub>4</sub>N-6-CO<sub>2</sub>H) as colorless (**6a** - **6c**) or yellow (**6d**) solids (Scheme 1).



**Scheme 1:** Schematic representation of the electrochemical synthesis of mononuclear copper complexes **6a** – **6d**.

From Scheme 1 it can be seen that a convenient and hence, straightforward synthesis route to a variety of mono-copper(I) dicarboxylates exists, when no additional electrolyte is added. However, to selectively obtain dicopper(I) dicarboxylates it is necessary to add triethylamine to the reaction solution to increase the conductivity of the electrolyte solution by formation of ammonium salts [Et<sub>3</sub>NH]<sub>2</sub>X and hence, the formation of hydrogen from Et<sub>3</sub>NH<sup>+</sup> is facilitated. The electrochemical preparation of [(R<sub>3</sub>P)<sub>m</sub>CuXCu(PR<sub>3</sub>)<sub>m</sub>] (**5a**, X = O<sub>2</sub>CCO<sub>2</sub>, R = Ph,  $m = 2$ ; **5b**, X = O<sub>2</sub>CCO<sub>2</sub>, R = <sup>n</sup>Bu,  $m = 3$ ; **5c**, X = O<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>, R = <sup>n</sup>Bu,  $m = 3$ ; **5d**, X = O<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>, R = <sup>n</sup>Bu,  $m = 3$ ; **5e**, X = O<sub>2</sub>C-2-C<sub>5</sub>H<sub>4</sub>N-6-CO<sub>2</sub>, R = <sup>n</sup>Bu,  $m = 3$ ) followed essentially the same procedure as described earlier, phosphanes PR<sub>3</sub> had to be added in a 1:4 or 1:6 ratio based on H<sub>2</sub>X (Scheme 2). Metal-organics **5a** - **5d** are colorless solids, **5e** is yellow. Complexes **5b** – **5e** dissolve in common organic solvents including *n*-pentane, toluene, diethyl ether, dichloromethane, and tetrahydrofuran, **5a** is only soluble to a minor extent in acetonitrile. All coordination compounds should best be stored under inert gas atmosphere, handling without significant decomposition for a period of 30 minutes under air is possible.



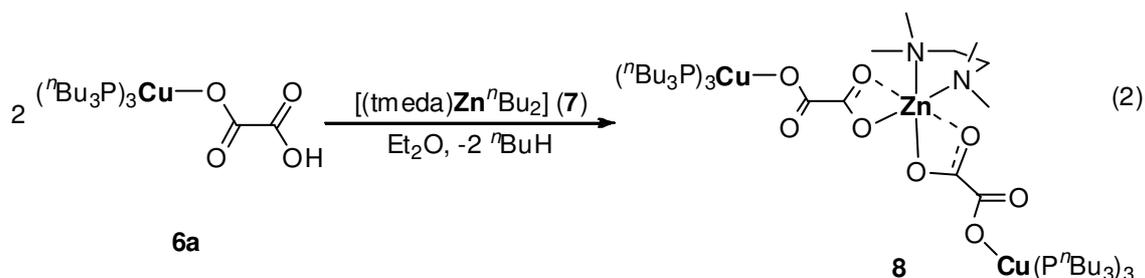
**Scheme 2:** Electrolytic synthesis of the dicopper dicarboxylates **5a** – **5e**.

The use of  $\text{Ph}_3\text{P}$  and  ${}^n\text{Bu}_3\text{P}$  phosphanes influence the formation of products **5a** – **5e** which results in either two ( $\text{Ph}_3\text{P}$ ) or three ( ${}^n\text{Bu}_3\text{P}$ ) auxiliary ligands on the copper atom. This different behavior, most probably attributed to steric hindrance [11], has a significant influence on the binding mode of the appropriate carboxylic unit to copper. In the case of  $\text{Ph}_3\text{P}$  the oxalato unit is chelate-bonded, while  ${}^n\text{Bu}_3\text{P}$  favors a mono-dentate binding.

The synthesis of complexes **5** and **6** by electrolysis (Schemes 1 and 2) allows the preparation of analytically pure mono- and dicopper carboxylates in virtually quantitative yields without extensive purifications methods. This makes them excellent starting materials for the deposition of elemental copper by, for example, the spin-coating process (vide infra).

Furthermore, mono-nuclear **6a** – **6e** with their *non*-coordinated  $\text{HO}_2\text{C}$  functionality should allow the introduction of a further metal-organic building block. Exemplary, we reacted **6a** with  $[(\text{tmeda})\text{Zn}{}^n\text{Bu}_2]$  (**7**) ( $\text{tmeda} = N,N'$ -*tetramethylethylenediamine*) in a 2:1 molar ratio in diethyl ether at ambient temperature (Reaction 2). After appropriate work-up, the trimetallic  $\text{Cu}_2\text{Zn}$  complex **8** could be isolated as colorless oil in quantitative yield. Complex **8** dissolves

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3 in most organic solvents and can be handled in air for a short period (3 hours). In **8** two  
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5 (<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>Cu-oxalato entities are connected by a hexa-coordinated Zn(tmeda) unit, whereby a  
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7 dynamic exchange behavior of the ligands and a fluctuation of the oxalate binding mode at  
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9 ambient temperature could not be excluded. Most likely one of the two CO<sub>2</sub> oxalato moieties  
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11 is chelate-bonded to zinc(II) and the other unit is σ-bonded to copper(I). [12]  
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The identities of **3**, **5** – **6** and **8** have been 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 (if soluble). The molecular structures of **5a**, **6a** and **6b** in the solid state were determined by single X-ray structure analysis, thus confirming the structural assignment made from spectroscopic analyses.

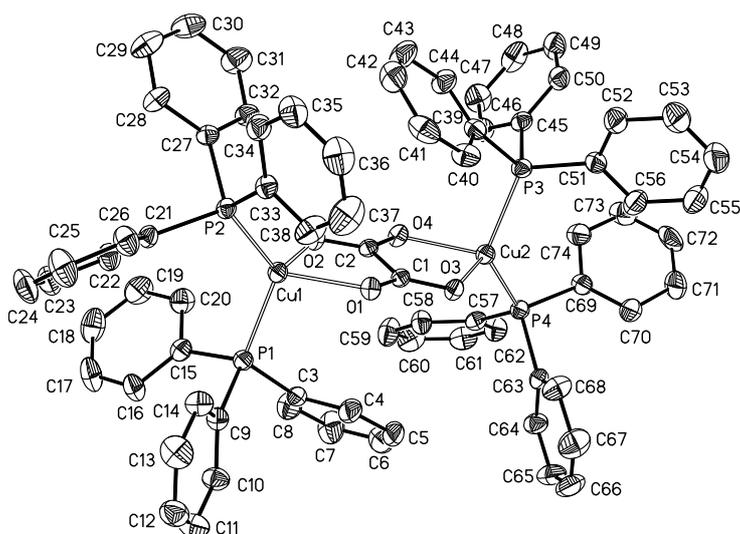
Most characteristic in the IR spectra of all complexes are the strong  $\tilde{\nu}_{CO}$  vibrations of the carboxylato units between 1350 - 1732 cm<sup>-1</sup> (Experimental Section). Whereas, the asymmetric  $\tilde{\nu}_{CO}$  bands (1578 – 1732 cm<sup>-1</sup>) can be always detected, the respective symmetric vibrations (1388 to 1464 cm<sup>-1</sup>) only at times, which is attributed to additional ligand absorptions in this region. The difference of the asymmetric and symmetric CO vibrations ( $\Delta\tilde{\nu}$ ) gives an indication of the binding mode of the carboxylate ligand. [13] For complexes **5a**, **5b** and **5e**  $\Delta\tilde{\nu}$  was determined to 187, 172, and 167 cm<sup>-1</sup>, respectively, indicating that the RCO<sub>2</sub> units are in a  $\mu$ -bridging mode as characteristic for ionic acetate species ( $\Delta\tilde{\nu} = 164$  cm<sup>-1</sup>). [13] Complexes **5c** ( $\Delta\tilde{\nu} = 225$  cm<sup>-1</sup>) and **5d** ( $\Delta\tilde{\nu} = 203$  cm<sup>-1</sup>) show a typical monodentate binding of the carboxylate groups, while it appeared that for **6a** – **6d** possessing a CO<sub>2</sub>H and a MCO<sub>2</sub> fragment it is difficult to unequivocally assigning the appropriate vibrations. The IR spectra of **6a** - **6d** dis-

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3 play, as expected, typical broad  $\tilde{\nu}_{OH}$  bands at ca. 3400  $\text{cm}^{-1}$  for the free  $\text{CO}_2\text{H}$  moieties point-  
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5 ing to hydrogen bridge formation.  
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10  $^{31}\text{P}\{^1\text{H}\}$  NMR spectroscopy can be used to monitor the progress of the formation of **5** and  
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12 **6** during electrolysis (Experimental Section). For example, the resonance signal for **4a** at  
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14 -32.2 ppm is shifted to lower field (-22.1 ppm, **5b**; -22.3 ppm, **6a**) upon complexation of the  
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16 phosphorus atom to copper(I), which is representative in transition metal phosphane chemis-  
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18 try. [5g, 14] The  $^{31}\text{P}\{^1\text{H}\}$  resonances are usually observed as broad signals, due to possible  
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20 ligand exchange processes and the quadrupole effect of copper. [5g, 15]  
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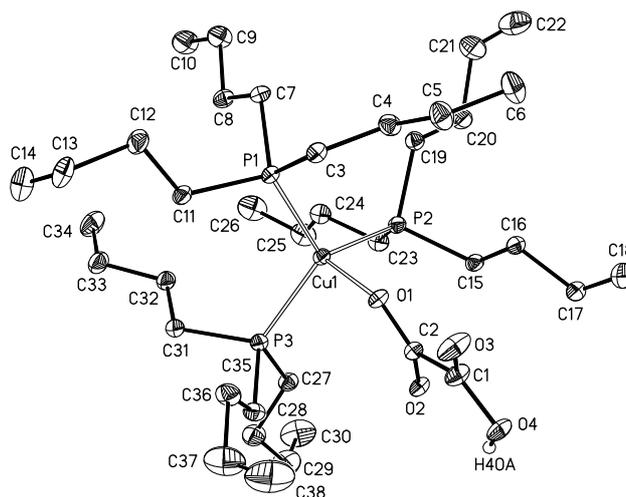
27 The successful formation of phosphane copper(I) complexes **5** and **6** were also confirmed  
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29 by  $^1\text{H}$  and  $^{13}\text{C}\{^1\text{H}\}$  NMR spectroscopies. The appropriate spectra show the expected signals  
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31 together with the typical coupling patterns for the  $\text{PR}_3$ ,  $\text{XH}$  or  $\text{X}$  ligands (Experimental Sec-  
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33 tion).  
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38 The molecular structures of **5a**, **6a** and **6d** in the solid state were determined by single X-  
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40 ray crystallographic analysis. Suitable crystals of **5a** were obtained by the diffusion of *n*-  
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42 hexane into a dichloromethane solution containing **5a** at 25 °C, while crystals of **6a** and **6d**  
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44 could be grown by cooling a concentrated *n*-hexane solution containing either **6a** or **6d** to -30  
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46 °C. ORTEP diagrams and selected bond distances (Å) and angles (°) are shown in Figures 1  
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48 (**5a**), 2 and 3(**6a**), as well as 4 and 5 (**6d**), respectively. Crystal and intensity collection data  
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50 are summarized in Table 2 (Experimental Section).  
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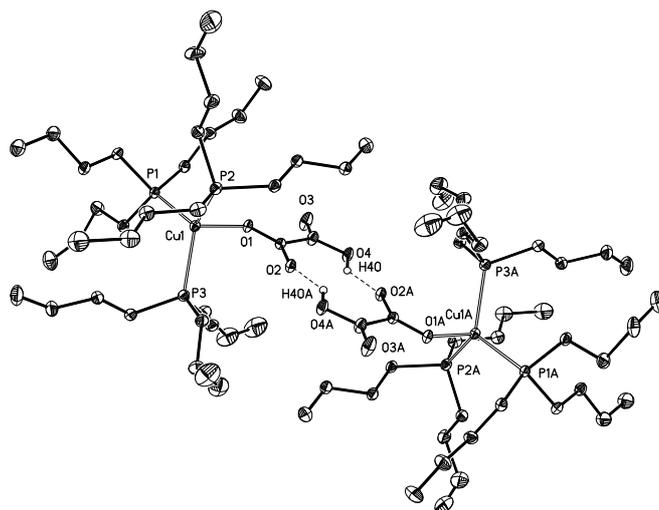
**Figure 1.** ORTEP diagram of **5a** with the atom numbering scheme. Thermal ellipsoids are shown at the 30 % probability level. All hydrogen atoms and the four dichloromethane solvent molecules are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1–P1 2.262(3), Cu1–P2 2.203(2), Cu1–O1 2.103(5), Cu1–O2 2.104(5), Cu2–P3 2.265(3), Cu2–P4 2.204(2), Cu2–O3 2.087(5), Cu2–O4 2.117(6), C1–C2 1.541(12); P1–Cu1–P2 125.02(9), O1–Cu1–O2 79.3(2), P1–Cu1–O1 103.90(17), P2–Cu1–O1 118.84(16), P3–Cu2–P4 126.20(10), O3–Cu2–O4 79.5(2), P3–Cu2–O3 104.29(17), P3–Cu2–O4 101.11(18), Cu1–O1–C1 117.4(7), Cu1–O2–C2 112.8(5), Cu2–O3–C1 112.6(5), Cu2–O4–C2 112.5(5), O1–C1–C2 117.3(7), O1–C1–O3 124.8(7), O2–C2–C1 117.4(7), O2–C2–O4 125.8(7), O3–C1–C2 117.8(7), O4–C2–C1 116.9(7).

Complex **5a** features a planar Cu<sub>2</sub>(oxalato) core with the oxalato unit in a  $\mu$ -1,2,3,4 bridging mode (Figure 1). Each copper(I) ion (Cu1, Cu2) is thereby coordinated by two phosphorus (P1, P2; P3, P4) and two oxygen atoms (O1, O2; O3, O4) resulting in an pseudo-tetrahedral environment at copper. The copper-phosphorus and copper-oxygen separations are comparable to similar bond distances found in other (di)copper(I) oxalato and copper-phosphane complexes [8a, 16].



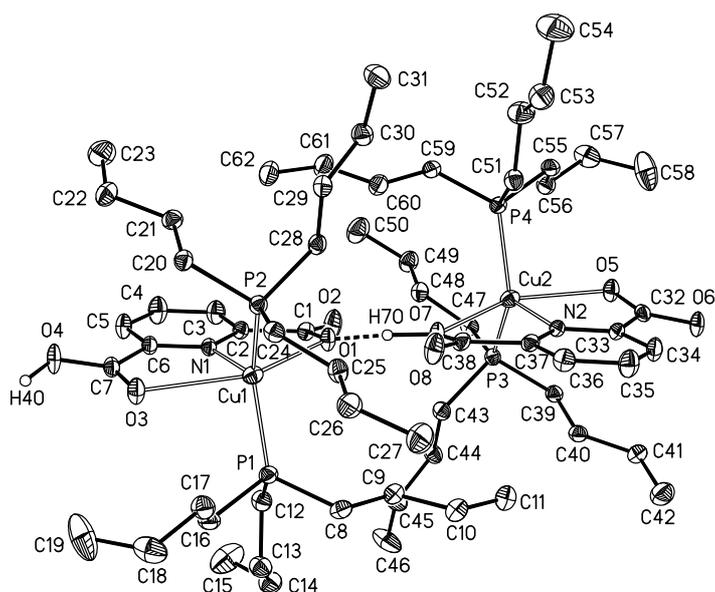
**Figure 2.** ORTEP diagram (30 % probability level) of the molecular structure of **6a**. All carbon-bonded hydrogen atoms are omitted for clarity. Selected bond distances (Å) and angles (°): Cu1–O1 2.134(3), Cu1–P1 2.2812(12), Cu1–P2 2.2762(13), Cu1–P3 2.2745(14); Cu1–O1–C2 124.5(3), O1–Cu1–P3 100.93(10), O1–Cu1–P1 94.55(8), P1–Cu1–P2 116.96(5), P1–Cu1–P3 116.51(5).

Complex **6a** crystallized in the monoclinic space group  $P2_1/c$ . The molecular structure of **6a** shows a somewhat distorted tetrahedral geometry around Cu1 with three phosphorus (P1, P2, P3) and one oxalato oxygen atom(s) (O1) bonded to Cu1 (Figure 2). All bond distances and angles are comparable to those values found elsewhere [8b, 17 – 19]. Two molecules of **6a** interact with each other, due to the formation of intermolecular hydrogen bridges. A graphical illustration of a selected dimer is shown in Figure 3 together with geometrical details of the hydrogen bridge.



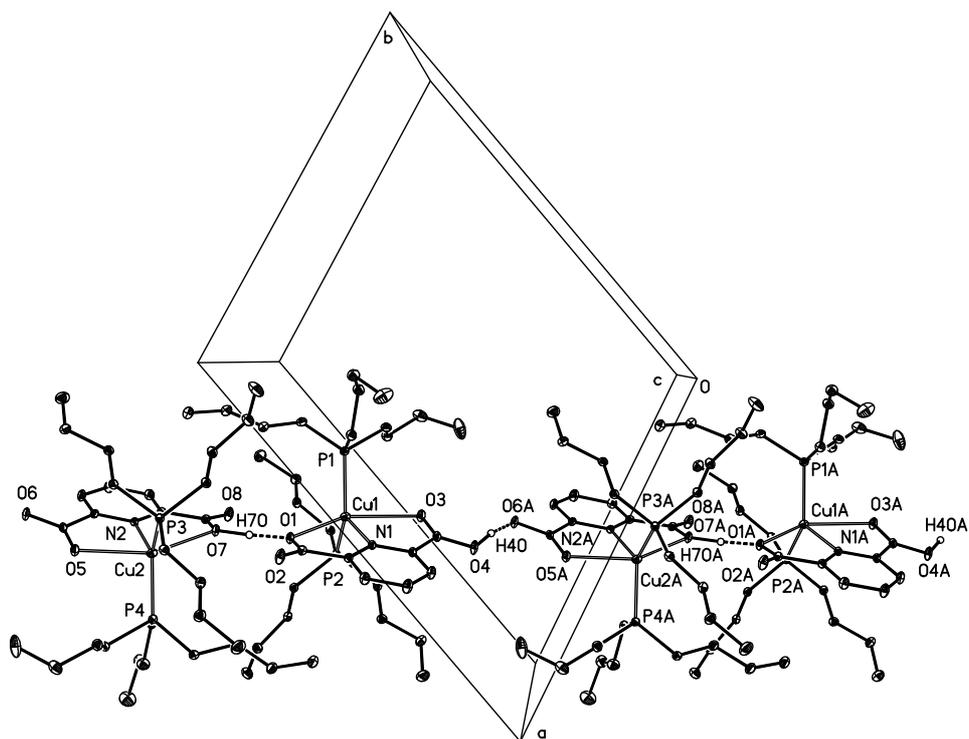
**Figure 3.** The dimer of **6a** in the solid state formed by intermolecular hydrogen bonds. Label 'A' refers to atoms of a symmetry generated molecule of **6a**. Hydrogen bridge bond lengths and angles:  $\angle$  D–H $\cdots$ A (O4–H4O $\cdots$ O2) = 144(6) °, D–H (O4–H4O) = 0.89(7) Å, H $\cdots$ A (H4O $\cdots$ O2) = 1.92(7) Å, D $\cdots$ A (O4 $\cdots$ O2) = 2.688(5) Å. (D = donor, A = acceptor.)

Molecule **6d** crystallized with two crystallographically independent molecules **6dA** and **6dB** (**6dA**: possessing the Cu(I) ion labeled Cu1, **6dB**: possessing the Cu(I) ion labeled Cu2) in the asymmetric unit in the triclinic space group *P1* (Figure 4). Related bond distances of **6dA** and **6dB** differ up to 2.5 %, while related bond angles show higher differences (up to 5 %). The two crystallographically independent molecules of **6d** are connected to each other by the formation of an intermolecular hydrogen bond between the carboxylic acid functionality of **6dB** (O7–H7o) and the carboxylic group of **6dA** (O1) (Figure 4, Table 1).



**Figure 4.** ORTEP diagram (50 % probability level) of the two crystallographically independent molecules of **6d** with the atom numbering scheme. All carbon-bonded hydrogen atoms have been omitted for clarity. Selected bond distances (Å) and angles (°): *Molecule A*: Cu1–N1 2.0696(14), Cu1–P1 2.2295(6), Cu1–P2 2.2234(6), Cu1–O1 2.3962(13), Cu1–O3 2.5658(14); P1–Cu1–N1 109.43(4), P2–Cu1–N1 115.13(4), P1–Cu1–P2 134.09(2), P1–Cu1–O1 100.92(4), P2–Cu1–O1 101.16(4). *Molecule B*: Cu2–N2 2.0672(15), Cu2–P3 2.2112(6), Cu2–P4 2.2241(6), Cu2–O5 2.4521(14), Cu2–O7 2.5058(13); P3–Cu2–N2 118.73(4), P4–Cu2–N2 106.79(4), P3–Cu2–P4 134.11(2), P3–Cu2–O5 93.47(4), P4–Cu2–O5 93.87(4).

Furthermore, a second intermolecular hydrogen bridge is formed by the carboxylic acid function of **6dA** (O4–H4o) and the carboxylic unit of a symmetry generated molecule of **6dA** (O6) (Figure 5, Table 1). Thus, complex **6d** forms in the solid state a 1D chain, due to repeated formation of intermolecular hydrogen bonds (Figure 5).



**Figure 5.** Representative part of one 1D chain formed by molecules of **6d** in the solid state by intermolecular hydrogen bonds. All hydrogen atoms, except the *O*-bonded ones, have been omitted for clarity.

In **6d** the nitrogen atom of individual  $\text{O}_2\text{C}-2-\text{C}_5\text{H}_4\text{N}-6-\text{CO}_2\text{H}$  moieties is coordinated to Cu(I). In addition, the Cu(I) ions interact with two oxygen donors of the  $\text{O}_2\text{C}-2-\text{C}_5\text{H}_4\text{N}-6-\text{CO}_2\text{H}$  group, whereby one oxygen refers to the negatively charged  $\text{O}_2\text{C}$  oxygen atom (**6dA**:  $d(\text{Cu1}-\text{O1})$ : 2.3962(13) Å; **6dB**:  $d(\text{Cu2}-\text{O5})$ : 2.4521(14) Å) and the second oxygen donor refers to the carbonyl  $\text{HO}_2\text{C}$  oxygen (**6dA**:  $d(\text{Cu1}-\text{O3})$ : 2.5658(14) Å; **6dB**:  $d(\text{Cu2}-\text{O7})$ : 2.5058(13) Å). All Cu(I)–O distances are significantly longer than the sum of the ionic radii (2.17 Å) of participating ions but, on the other side, significantly shorter than the sum of the van-der-Waals radii of copper and oxygen (2.90 Å), respectively. [20] Thus, all Cu–O interactions of **6dA** and **6dB** can be regarded as weak, giving rise to a trigonal-bipyramidal coordination geometry around Cu1 ( $\tau = 0.193$ ) and Cu2 ( $\tau = 0.187$ ). [21] As usually observed for

trigonal-bipyramidal coordination geometries, the more electronegative ligands occupy the apical positions. [22]

**Table 1.** Bond distances (Å) and angles (°) of the intermolecular hydrogen bonds of **6d**.<sup>a)</sup>

D–H···A	D–H	H···A	D···A	D–H···A
O7–H7O···O1	1.13(3)	1.35(3)	2.4753(19)	177(3)
O4–H4O···O6	1.05(4)	1.43(4)	2.463(2)	168(3)

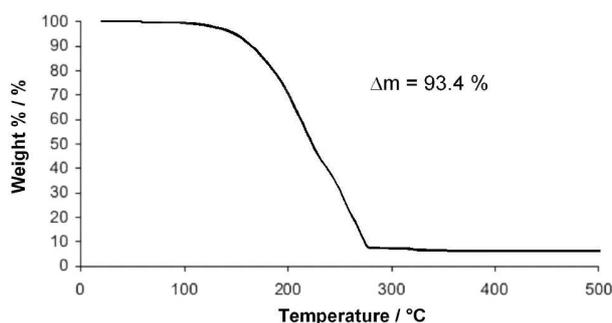
a) D = Donor, A = Acceptor.

### *Thermal gravimetric and spin-coating deposition experiments*

Metal thin film deposition, by using the spin-coating process, is a technique for coating a thin metal film of *non-volatile* precursor materials within a few tens up to several hundred of nanometers onto a substrate or onto previously deposited layers. [7] On heating, a chemical change at the surface takes place leaving a metal film. This method is, when compared with other deposition techniques, [2] a very cost-effective method because it does not require complicated technical and hence, expensive equipment.

It is helpful before carrying out such deposition experiments that the thermal solid state behavior of the metal organic precursors is known. Thus, thermal gravimetric analysis (TGA) was carried out with selected samples of **5** and **6** to evaluate the decomposition behavior with increasing temperature. It was found that the appropriate phosphane copper(I) oxalato complexes decompose to elemental copper by release of  $\text{PR}_3$  and  $\text{CO}_2$ , respectively. The thermal decomposition pattern for all other complexes is somewhat different since minor impurities of carbon are observed as well (Experimental Section). The decomposition of all complexes is completed at 450 °C. Exemplarily, the thermal gravimetric curve for **5c** is shown in Figure 6.

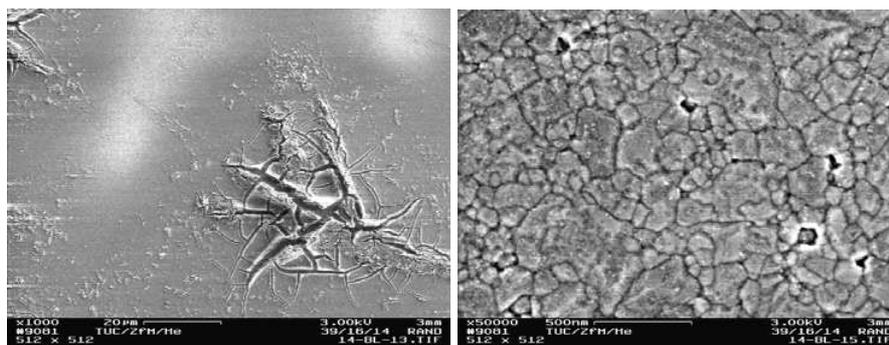
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3 Under typical TG conditions, complex **5c** undergoes a decomposition which starts at 95 °C  
4 and ends at 330 °C. The mass loss of 93.4 % is in accordance with the theoretical percentage  
5 calculated for the formation of elemental copper, the difference is less than 2.5 %. Organic  
6 products formed during the redox process of the internal dicarboxylic entity are in general  
7 volatile and vaporize during the decomposition process.  
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30 **Figure 6.** TG trace for metal-organic **5c** (heating rate 8 K min<sup>-1</sup>, nitrogen atmosphere, flow  
31 20 L h<sup>-1</sup>).  
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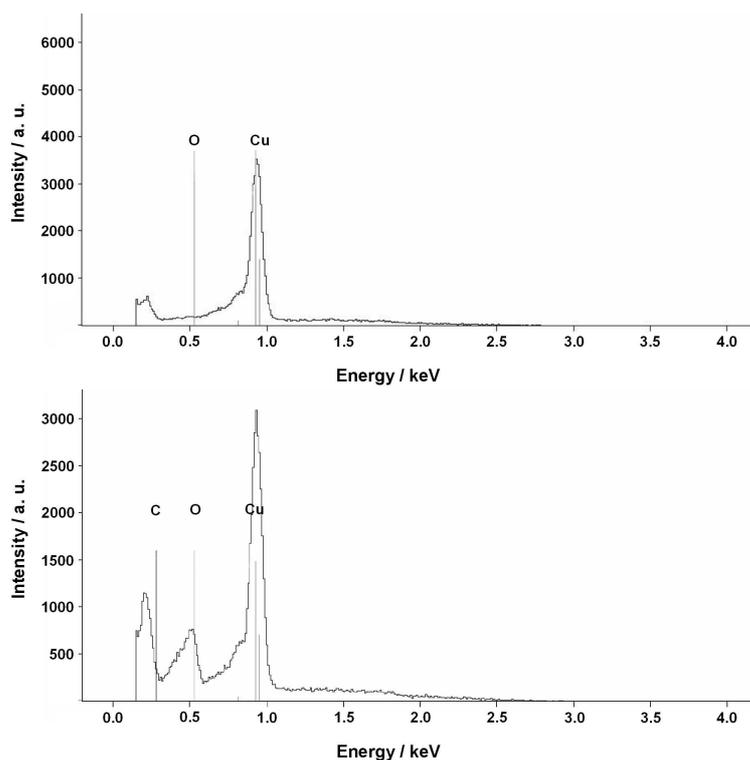
36  
37 Based on the thermal properties obtained from TG studies we chose **5c** and **5d** as potential  
38 spin-coating precursors. Precursor samples obtained from both complexes had a high viscos-  
39 ity. They were dispensed from a pipette onto a pre-cleaned and afterwards oxidized silicon  
40 wafer coated with a double layer of sputter deposited TiN diffusion barrier and Cu with a  
41 thickness of 40/100 nm. A spin-off speed of 1100 rpm was chosen in order to get a thin ho-  
42 mogeneous liquid film on the wafer after 30 seconds of dispersion time. An industrial spin-  
43 coating system (Suss Microtec) with a closed deposition chamber and a protecting nitrogen  
44 stream was used for these studies. The treated wafers were transferred to an oven and have  
45 then been heated with a defined ramp rate of 8 K min<sup>-1</sup> up to 450 °C. The decomposition tem-  
46 perature followed the thermal gravimetric curve shown in Figure 6. The films have been an-  
47 nealed at 400 °C for 1 h in N<sub>2</sub>/H<sub>2</sub> (ratio 98:2) atmosphere. SEM images of obtained copper  
48 films from **5c** and **5d** are shown in Figures 7 (**5c**) and 9 (**5d**). As it can be seen from Figure 7,  
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3 the copper film obtained from **5c** is not completely homogeneous and shows defects. This can  
4 be explained by the different film thickness obtained from the spin-coating process, which  
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6 be explained by the different film thickness obtained from the spin-coating process, which  
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8 upon heating produced defects due to unequal evaporation of the *in-situ* formed reaction prod-  
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10 ucts leading to partially cracked copper films.  
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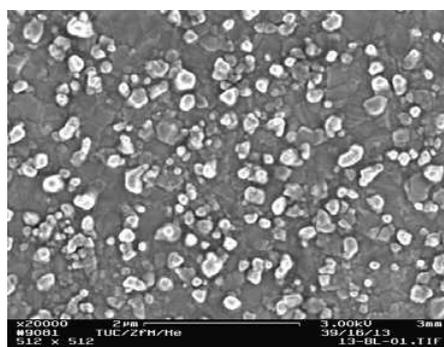


27 **Figure 7.** Surface SEM images showing the morphology of the copper film obtained from  
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29 **5c** on a PVD-copper coated oxidized silicon substrate (350 °C, heating rate 8 K  
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31 min<sup>-1</sup>, 1000 rpm, 10 s).  
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37 The results of EDX studies at the formed copper metal layers are shown in Figure 8. The  
38 sample deposited from **5c** displays a pure copper film without major contaminations from the  
39 precursor (Figure 8). In contrast, for the sample with the copper film derived from **5d** an oxy-  
40  
41 gen as well as an increased carbon signal has been detected. This is assumed to result from an  
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43 incomplete decomposition of the precursor and formation of copper oxides, rather than result-  
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45 ing from the silicon oxide from the substrate, since no silicon signal was detected.  
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**Figure 8.** EDX spectra of the copper films obtained from **5c** (top) and **5d** (bottom).



**Figure 9.** Surface SEM image showing the morphology of the copper film obtained from **5d** on a PVD-copper coated oxidized silicon substrate (350 °C, heating rate 8 K min<sup>-1</sup>, 1000 rpm, 10 s).

## Conclusion

Straightforward synthesis methodologies for the preparation of mono- and dicopper dicarboxylates of structural type  $[(^n\text{Bu}_3\text{P})_m\text{CuXH}]$  and  $[(\text{R}_3\text{P})_m\text{CuXCu}(\text{PR}_3)_m]$  ( $\text{X} = \text{O}_2\text{CCO}_2$ ,

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3 O<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>, O<sub>2</sub>C(CH<sub>2</sub>)<sub>2</sub>CO<sub>2</sub>, O<sub>2</sub>C-2-C<sub>5</sub>H<sub>3</sub>N-6-CO<sub>2</sub>;  $m = 2, 3$ ; R = <sup>n</sup>Bu, Ph) is discussed. The  
4  
5 molecular structures of [(Ph<sub>3</sub>P)<sub>2</sub>CuO<sub>2</sub>CCO<sub>2</sub>Cu(PPh<sub>3</sub>)<sub>2</sub>], [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCO<sub>2</sub>H], and [(<sup>n</sup>Bu<sub>3</sub>-  
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7 P)<sub>3</sub>CuO<sub>2</sub>C-2-C<sub>5</sub>H<sub>3</sub>N-6-CO<sub>2</sub>H] in the solid state were determined, whereby these are the first  
8  
9 single x-ray crystal structures of (<sup>n</sup>Bu<sub>3</sub>P)<sub>m</sub>Cu carboxylates. While complex [(Ph<sub>3</sub>P)<sub>2</sub>CuO<sub>2</sub>C-  
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11 CO<sub>2</sub>Cu(PPh<sub>3</sub>)<sub>2</sub>] is monomeric and contains chelated carboxylic moieties, compound [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>-  
12  
13 CuO<sub>2</sub>CCO<sub>2</sub>H]<sub>2</sub> is a dimer setup by hydrogen bridges between the CO<sub>2</sub>H moieties. Complex  
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15 [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>C-2-C<sub>5</sub>H<sub>3</sub>N-6-CO<sub>2</sub>H] forms a linear open 1D coordination polymer. The dif-  
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17 ferent coordination behavior of the carboxylic units in L<sub>2</sub>Cu and L<sub>3</sub>Cu compounds is attrib-  
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19 uted to the number of the auxiliary ligands present and hence, to the steric hindrance and elec-  
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21 tronic nature at copper(I). The reaction chemistry of [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCO<sub>2</sub>H] towards  
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23 [(tmeda)Zn<sup>n</sup>Bu<sub>2</sub>] (tmeda = *N,N,N',N'*-tetramethylethylene-1,2-diamine) is reported, whereby a  
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25 zinc reagent complex of higher nuclearity is obtained.  
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32 The thermal decomposition of dicopper dicarboxylates shows in all cases that the PR<sub>3</sub>  
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34 ligands are well separated from the internal redox processes of the internal Cu<sub>2</sub>-dicarboxylate  
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36 units. The deposition of elemental copper onto pieces of PVD-copper coated oxidized silicon  
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38 wafer materials by applying the spin-coating process and using [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>Cu-  
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40 (P<sup>n</sup>Bu<sub>3</sub>)<sub>3</sub>] and [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Cu(P<sup>n</sup>Bu<sub>3</sub>)<sub>3</sub>] as potential precursors is discussed.  
41  
42 The obtained layers are, however, not defect free. The EDX results of these films showed that  
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44 pure copper films were obtained with the [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>Cu(P<sup>n</sup>Bu<sub>3</sub>)<sub>3</sub>] precursor,  
45  
46 while it could not be satisfactorily shown that copper films obtained from [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>C-  
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48 CH<sub>2</sub>CH<sub>2</sub>CO<sub>2</sub>Cu(P<sup>n</sup>Bu<sub>3</sub>)<sub>3</sub>] are not free of carbon and oxygen impurities.  
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## 58 Experimental Section

### 59 Materials and Methods

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3       Complexes [(tmeda)Zn<sup>n</sup>Bu<sub>2</sub>] (**7**) was prepared in analogy to a published procedure [23].  
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6       Chemicals were purchased from commercial providers and were used as received.

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8       All reactions were carried out under an atmosphere of nitrogen using standard Schlenk  
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10       techniques. Tetrahydrofuran, diethyl ether and *n*-hexane were purified by distillation from  
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12       sodium/benzophenone ketyl; dichloromethane was purified by distillation from calcium hy-  
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14       dride. Celite (purified and annealed, Erg. B.6, Riedel de Haen) was used for filtrations. Infra-  
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16       red spectra were recorded with a Perkin Elmer FT-IR spectrometer Spectrum 1000. <sup>1</sup>H NMR  
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18       spectra were recorded with a Bruker Avance 250 spectrometer operating at 250.130 MHz in  
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20       the Fourier transform mode; <sup>13</sup>C{<sup>1</sup>H} NMR spectra were recorded at 62.860 MHz. Chemical  
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22       shifts are reported in  $\delta$  units (parts per million) downfield from tetramethylsilane with the  
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24       solvent as reference signal (<sup>1</sup>H NMR: CDCl<sub>3</sub> (99.8 %),  $\delta$  = 7.26; (CD<sub>3</sub>)<sub>2</sub>CO (99.9 %),  $\delta$  =  
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26       2.05; CD<sub>3</sub>CN (99.8 %),  $\delta$  = 1.94. <sup>13</sup>C{<sup>1</sup>H} NMR: CDCl<sub>3</sub> (99.8 %),  $\delta$  = 77.16; (CD<sub>3</sub>)<sub>2</sub>CO (99.9  
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28       %),  $\delta$  = 29.84, 206.26). <sup>31</sup>P{<sup>1</sup>H} NMR spectra were recorded at 101.255 MHz in CDCl<sub>3</sub> with  
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30       P(OMe)<sub>3</sub> as external standard ( $\delta$  = 139.0, rel. to H<sub>3</sub>PO<sub>4</sub> (85 %) with  $\delta$  = 0.00). Thermogra-  
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32       vimetric studies were done with the Perkin Elmer System Pyris TGA 6 with a constant heat-  
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34       ing rate of 8 °C min<sup>-1</sup> under N<sub>2</sub> (20.0 dm<sup>3</sup> h<sup>-1</sup>). DSC experiments were carried out with the  
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36       Perkin Elmer System Pyris DSC 6 with a constant heating rate of 8 °C min<sup>-1</sup> under N<sub>2</sub> (20.0  
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38       dm<sup>3</sup> h<sup>-1</sup>). Melting points were determined using analytically pure samples, sealed off in nitro-  
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40       gen purged capillaries on a Gallenkamp MFB 595 010 M melting point apparatus. Micro-  
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42       analyses were performed with a C, H, N-analyzer FlashAE 1112 (Thermo Company). The  
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44       Spin-coating experiments were carried out on an industrial spin-coating system from Suss  
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46       Microtec Inc. with a closed deposition chamber. A precursor sample of 1.6 g of the respective  
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48       complex was diluted in 0.4 mL of tetrahydrofuran and was mixed for 2 minutes under a nitro-  
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50       gen stream. Since tetrahydrofuran is volatile, a rotation speed of 1100 rpm was chosen. The  
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52       sample was dispensed on pre-cleaned PVD-copper oxidized silicon wafers and after spin-off  
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54       for 10 seconds the film was almost dry. The applied heating rate was 15 °C min<sup>-1</sup>, maximum  
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3 thermolysis temperature 450 °C, and dwell time 0.5 hours. SEM micrographs were recorded  
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5 on a SEM instrument type DSM 982 Gemini from LEO Corp. EDX analysis was performed  
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7 on the EDX system EDWIN (Röntec Corp.) attached to the SEM.  
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12 Synthesis of  $(\text{Ph}_3\text{P})_2\text{CuO}_2\text{CCO}_2\text{Cu}(\text{PPh}_3)_2$  (**5a**) and  $(^n\text{Bu}_3\text{P})_3\text{CuO}_2\text{CCO}_2\text{Cu}-$   
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14  $(\text{P}^n\text{Bu}_3)_3$  (**5b**)  
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#### 17 18 *Method A*

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20 To 20 mL of pyridine were added 430 mg (3.00 mmol) of copper(I) oxide (**1b**), 252 mg  
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22 (2.80 mmol) of oxalic acid (**2a**), 2.94 g (11.20 mmol) of **4a** or 3.90 g (16.80 mmol) of **4b**, and  
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24 2.0 g of  $\text{MgSO}_4$ . After 4 hours of stirring at 25 °C, the reaction mixture was filtered through a  
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26 pad of Celite and all volatiles were removed under reduced pressure. The title compounds  
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28 were obtained as a colorless solid (**5a**) or oil (**5b**). Yield: 3.49 g (2.76 mmol, 99 %, based on  
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30 **2a**) **5a**; 3.89 g (2.72 mmol, 97 %, based on **2a**). Both complexes should best be stored at -30  
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32 °C to prevent them for decomposition.  
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#### 40 41 *Method B*

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43  $[(\text{Ph}_3\text{P})_2\text{CuO}_2\text{CCO}_2\text{Cu}(\text{PPh}_3)_2]$  (**5a**) [10]

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45 0.48 g (5.32 mmol) of oxalic acid (**2a**), 5.59 g (21.29 mmol) of triphenylphosphane (**4b**)  
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47 and 0.54 g (5.323 mmol, 0.74 mL) of triethylamine were dissolved in 60 mL of acetonitrile in  
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49 an electrolysis cell equipped with copper electrodes and a stirring bar. The reaction was per-  
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51 formed with a cell potential of 2 V at 40 °C over a period of 3 hours. After 1.5 hour a color-  
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53 less compound precipitated. The supernatant solution was decanted and the remaining residue  
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55 was washed twice with diethyl ether (20 mL). Yield: 6.73 g (5.32 mmol, 99 % based on **2a**).  
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59 **Mp**: 185 °C. Anal. calc. for  $\text{C}_{74}\text{H}_{60}\text{Cu}_2\text{O}_4\text{P}_4$  (1264.25) C 70.30, H, 4.78; found C 70.09, H,  
60  
4.91 %. **IR** (KBr,  $\text{cm}^{-1}$ ):  $\tilde{\nu}$  = 1620 (vs, CO), 1433 (vs, CO).  **$^1\text{H NMR}$**  ( $\text{CDCl}_3$ ):  $\delta$  = 6.50 - 7.85

(m, 60 H, Ph).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 128.5$  ( $^o\text{C}/\text{C}_6\text{H}_5$ ),  $129.2$  ( $^p\text{C}/\text{C}_6\text{H}_5$ ),  $134.0$  (d,  $J_{\text{CP}} = 15$  Hz,  $^m\text{C}/\text{C}_6\text{H}_5$ ),  $134.7$  ( $^i\text{C}/\text{C}_6\text{H}_5$ ),  $160.0$  (CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -5.3$ .

$[(^n\text{Bu}_3\text{P})_3\text{CuO}_2\text{CCO}_2\text{Cu}(\text{P}^n\text{Bu}_3)_3]$  (**5b**)

Complex **5b** was prepared by the method, as described for the synthesis of **5a**: 0.50 g (5.55 mmol) of oxalic acid (**2a**), 6.74 g (33.32 mmol) of **4a** and 0.56 g (5.323 mmol, 0.77 mL) of triethylamine in 60 mL of acetonitrile. Reaction conditions: potential 2 V, reaction time 4.5 hours, temperature 40 °C. After appropriate work up, complex **5b** was obtained as colorless oil. Yield: 7.936 g (5.55 mmol, 99 %, based on **2a**).

Anal. calc. for  $\text{C}_{74}\text{H}_{162}\text{Cu}_2\text{O}_4\text{P}_6$  (1429.01) C 62.20, H 11.43; found C 62.61, H 11.56 %.

IR (NaCl,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 1635$  (s, CO),  $1463$  (s, CO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 0.89$  (t,  $J_{\text{HH}} = 6.8$  Hz, 54 H,  $\text{P}(\text{CH}_2)_3\text{CH}_3$ ),  $1.27 - 1.48$  (m, 108 H,  $\text{P}(\text{CH}_2)_3\text{CH}_3$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 14.0$  ( $\text{P}(\text{CH}_2)_3\text{CH}_3$ ),  $24.6$  (d,  $J_{\text{CP}} = 12$  Hz,  $\text{P}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ),  $26.2$  (d,  $J_{\text{CP}} = 6$  Hz,  $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ),  $27.5$  (d,  $J_{\text{CP}} = 8$  Hz,  $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$ ),  $163.1$  (CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -22.1$ .

Synthesis of  $(^n\text{Bu}_3\text{P})_3\text{CuO}_2\text{CCH}_2\text{CO}_2\text{Cu}(\text{P}^n\text{Bu}_3)_3$  (**5c**)

Compound **5c** was prepared as described for **5a**: 0.18 g (1.73 mmol) of malonic acid (**2b**), 2.10 g (10.38 mmol, 2.56 mL) of **4a** and 0.35 g (1.73 mmol, 0.48 mL) of triethylamine. Cell potential 4 V, 40 °C, 1.5 hours. After appropriate work-up complex **5c** was isolated as colorless oil. Yield: 2.50 g (1.70 mmol, 99 %, based on **2b**).

Anal. calc. for  $\text{C}_{75}\text{H}_{164}\text{Cu}_2\text{O}_4\text{P}_6$  (1443.06) C 62.42, H, 11.46; found C 62.32, H, 11.50 %.

IR (NaCl,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 1602$  (vs, CO),  $1377$  (vs, CO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 0.87$  (t,  $^3J_{\text{HH}} = 7.0$  Hz, 54 H,  $\text{CH}_3$ ),  $1.32 - 1.40$  (m 108 H,  $\text{P}(\text{CH}_2)_3\text{CH}_3$ ),  $3.04$  (s, 2 H,  $\text{O}_2\text{CCH}_2\text{CO}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 13.9$  ( $\text{P}(\text{CH}_2)_3\text{CH}_3$ ),  $24.7$  (d,  $^3J_{\text{CP}} = 12$  Hz,  $\text{P}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ),  $26.1$  ( $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ),  $27.6$  (d,  $^1J_{\text{CP}} = 8$  Hz,  $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$ ),  $38.7$  ( $\text{O}_2\text{CCH}_2\text{CO}_2$ ),  $173.7$  (CO).

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3  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -26.5$ . TGA (8 K/min): Step 1:  $T_{\text{start}} = 95\text{ }^\circ\text{C}$ ,  $T_{\text{end}} = 230\text{ }^\circ\text{C}$ ,  $\Delta m =$   
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6 58.7 %; Step 2:  $T_{\text{start}} = 230\text{ }^\circ\text{C}$ ,  $T_{\text{end}} = 333\text{ }^\circ\text{C}$ ,  $\Delta m = 34.7\text{ }%$ . DSC (8 K/min): Peak 1:  $T = 182$   
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8  $^\circ\text{C}$ ,  $\Delta H_1 = -40.1\text{ J/g}$ ; Peak 2:  $T = 193\text{ }^\circ\text{C}$ ,  $\Delta H_2 = -7.3\text{ J/g}$ .

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### Synthesis of $(^n\text{Bu}_3\text{P})_3\text{CuO}_2\text{CCH}_2\text{CH}_2\text{CO}_2\text{Cu}(P^n\text{Bu}_3)_3$ (**5d**)

Complex **5d** was synthesized as described earlier (synthesis of **5a**). Starting materials: 0.20 g (1.72 mmol) of succinic acid (**2c**), 2.08 g (21.29 mmol) of **4a**, and 0.35 g (1.73 mmol, 0.48 mL) of triethylamine. Cell potential 6 V, 40  $^\circ\text{C}$ , 2 hours. After appropriate work-up, **5b** was isolated as colorless oil. Yield: 2.50 g (1.70 mmol, 99 %, based on **2c**).

Anal. calc. for  $\text{C}_{76}\text{H}_{166}\text{Cu}_2\text{O}_4\text{P}_6$  (1457.09) C 62.64, H, 11.48; found C 62.38, H, 11.08 %.

IR (NaCl,  $\text{cm}^{-1}$ ):  $\tilde{\nu} = 1620$  (vs, CO), 1417 (vs, CO).  $^1\text{H}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 0.86$  (t,  $^3J_{\text{HH}} = 7.0$  Hz, 54 H,  $\text{CH}_3$ ), 1.30 - 1.42 (m 108 H,  $\text{P}(\text{CH}_2)_3\text{CH}_3$ ), 2.53 (s, 4 H,  $\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2$ ).  $^{13}\text{C}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = 13.9$  ( $\text{P}(\text{CH}_2)_3\text{CH}_3$ ), 24.7 (d,  $^3J_{\text{CP}} = 12$  Hz,  $\text{P}(\text{CH}_2)_2\text{CH}_2\text{CH}_3$ ), 26.1 ( $\text{PCH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ ), 27.6 (d,  $^1J_{\text{CP}} = 9$  Hz,  $\text{PCH}_2(\text{CH}_2)_2\text{CH}_3$ ), 32.6 ( $\text{O}_2\text{CCH}_2\text{CH}_2\text{CO}_2$ ), 177.5 (CO).  $^{31}\text{P}\{^1\text{H}\}$  NMR ( $\text{CDCl}_3$ ):  $\delta = -27.1$ . TGA (8 K/min): Step 1:  $T_{\text{start}} = 61\text{ }^\circ\text{C}$ ,  $T_{\text{end}} = 197\text{ }^\circ\text{C}$ ,  $\Delta m = 37.8\text{ }%$ ; Step 2:  $T_{\text{start}} = 197\text{ }^\circ\text{C}$ ,  $T_{\text{end}} = 256\text{ }^\circ\text{C}$ ,  $\Delta m = 41.8\text{ }%$ ; Step 3:  $T_{\text{start}} = 256\text{ }^\circ\text{C}$ ,  $T_{\text{end}} = 412\text{ }^\circ\text{C}$ ,  $\Delta m = 11.7\text{ }%$ . DSC (8 K/min): Peak 1:  $T = 107\text{ }^\circ\text{C}$ ,  $\Delta H_1 = 66.2\text{ J/g}$ ; Peak 2:  $T = 207\text{ }^\circ\text{C}$ ,  $\Delta H_2 = -78.5\text{ J/g}$ .

### Synthesis of $[(^n\text{Bu}_3\text{P})_3\text{CuO}_2\text{C}-2-\text{C}_6\text{H}_4\text{N}-6-\text{CO}_2\text{Cu}(P^n\text{Bu}_3)_3]$ (**5e**)

Complex **5e** was synthesized as described earlier (synthesis of **5a**). 0.50 g (2.99 mmol) of 2,6-pyridine-dicarboxylic acid (**2e**), 3.63 g (17.95 mmol, 4.48 mL) of **4a**, and 0.30 g (2.99 mmol, 0.42 mL) of triethylamine in 60 mL of acetonitrile. The reaction was performed with a cell potential of 4 V at 40  $^\circ\text{C}$  over a period of 3 hours. When elemental copper or black copper deposited at the cathode, the reaction was immediately stopped. Afterwards, the yellow

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3 solution was transferred to a 250 mL Schlenk tube and all volatiles were removed in *oil-pump*  
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5 vacuum giving **5e** as yellow oil. Yield: 4.51 g (2.99 mmol, 99 %, based on **2e**).  
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8 Anal. calc. for C<sub>79</sub>H<sub>165</sub>Cu<sub>2</sub>NO<sub>4</sub>P<sub>6</sub> (1506.09) C 63.00, H, 11.04; N, 0.93; found C 63.04, H,  
9 11.33; N, 0.97 %. IR (NaCl, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1630 (vs, CO), 1463 (s, CO). <sup>1</sup>H NMR (CDCl<sub>3</sub>):  $\delta$  =  
10 0.90 (t,  $J_{\text{HH}}$  = 6.6 Hz, 54 H, P(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.20 - 1.75 (m, 108 H, P(CH<sub>2</sub>)<sub>3</sub>), 7.71 (s, 1 H,  
11 C<sub>5</sub>H<sub>3</sub>N<sup>4</sup>H), 8.32 (d,  $J_{\text{HH}}$  = 7.7 Hz, 2 H, C<sub>5</sub>H<sub>3</sub>N<sup>3,5</sup>H). <sup>13</sup>C{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = 13.7 (CH<sub>3</sub>),  
12 24.4 (d,  $J_{\text{CP}}$  = 14 Hz, CH<sub>2</sub>CH<sub>3</sub>), 25.5 (PCH<sub>2</sub>CH<sub>2</sub>), 27.3 (PCH<sub>2</sub>), 126.0 (C<sub>5</sub>H<sub>3</sub>N), 136.3  
13 (C<sub>5</sub>H<sub>3</sub>N), 153.0 (C<sub>5</sub>H<sub>3</sub>N); 168.1 (CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -25.0.  
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#### 24 Synthesis of [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCO<sub>2</sub>H] (**6a**)

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27 0.63 g (7.00 mmol) of oxalic acid (**2a**) and 4.25 g (21.00 mmol, 5.24 mL) of tri-*n*-  
28 butylphosphane (**4a**) were dissolved in 60 mL of acetonitrile in an electrolysis cell equipped  
29 with copper electrodes and a stirring bar. The reaction was preformed with a cell potential of  
30 2 V at 40 °C over a period of 1 h. Afterwards the colorless solution was transferred to a 250  
31 mL Schlenk tube and all volatiles were removed in *oil-pump* vacuum. Complex **6a** was  
32 thereby obtained as colorless oil. Yield: 5.31 g (7.00 mmol, 99 %, based on **2a**).  
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41 **Mp**: 35 °C. Anal. calc. for C<sub>38</sub>H<sub>82</sub>CuO<sub>4</sub>P<sub>3</sub> (759.49) C 60.09, H 10.88; found C 60.38, H,  
42 10.77 %. IR (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3417 (w, CO<sub>2</sub>H), 1635 (vs, CO), 1405 (vs, CO). <sup>1</sup>H NMR  
43 (CDCl<sub>3</sub>):  $\delta$  = 0.91 (t, 27 H, CH<sub>3</sub>), 1.21 - 1.75 (m, 54 H, CH<sub>2</sub>), 10.92 (s, 1 H, CO<sub>2</sub>H). <sup>13</sup>C{<sup>1</sup>H}  
44 NMR (CDCl<sub>3</sub>):  $\delta$  = 14.2 (P(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 25.0 (P(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 25.3 (PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>),  
45 27.2 (PCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 163.1 (CO), 163.2 (CO). <sup>31</sup>P{<sup>1</sup>H} NMR (CDCl<sub>3</sub>):  $\delta$  = -22.3.  
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#### 56 Synthesis of [(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCH<sub>2</sub>CO<sub>2</sub>H] (**6b**)

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58 Compound **6b** was synthesized as described for the preparation of **6a**. As starting materi-  
59 als were used: 0.27 g (2.59 mmol) of malonic acid (**2b**) and 1.57 g (7.76 mmol) of tri-*n*-  
60 butylphosphane (**4a**). The reaction was performed with a cell potential of 2 V at 40 °C over a

period of 2 hours. After appropriate work-up, compound **6b** was obtained as colorless oil.  
Yield: 1.95 g (2.52 mmol, 97 %, based on **2b**).

Anal. calc. for  $C_{39}H_{84}CuO_4P_3$  (773.55) C 60.55, H 10.95; found C 60.28, H, 11.23 %. **IR** (NaCl,  $cm^{-1}$ ):  $\tilde{\nu}$  = 3420 (w,  $CO_2H$ ), 1731 (s, CO), 1602 (s, CO), 1463 (s, CO).  **$^1H$  NMR** ( $CDCl_3$ ):  $\delta$  = 0.86 (t,  $^3J_{HH}$  = 7.0 Hz, 27 H,  $P(CH_2)_3CH_3$ ), 1.26 - 1.36 (m, 54 H,  $P(CH_2)_2$ ), 2.57 (bs, 4 H,  $CH_2$ ), 10.93 (bs, 1 H,  $CO_2H$ ).  **$^{13}C\{^1H\}$  NMR** ( $CDCl_3$ ):  $\delta$  = 13.7 ( $P(CH_2)_3CH_3$ ), 24.7 (d,  $J_{CP}$  = 12 Hz,  $P(CH_2)_2CH_2CH_3$ ), 25.3 (d,  $J_{CP}$  = 12 Hz,  $PCH_2CH_2CH_2CH_3$ ), 26.9 ( $PCH_2(CH_2)_2CH_3$ ), 38.6 ( $CH_2CO_2H$ ), 173.3 (CO), 173.4 (CO).  **$^{31}P\{^1H\}$  NMR** ( $CDCl_3$ ):  $\delta$  = -22.6.

### Synthesis of [ $(nBu_3P)_3CuO_2CCH_2CH_2CO_2H$ ] (**6c**)

Complex **6c** was prepared as described for **6a**: 0.30 g (2.54 mmol) of succinic acid (**2c**) and 1.54 g (7.61 mmol) of tri-*n*-butylphosphane (**4a**) were reacted. The cell potential was 2 V at 40 °C over a period of 4 hours. Complex **6c** was obtained as colorless oil. Yield: 1.89 g (2.40 mmol, 95 %, based on **2c**).

Anal. calc. for  $C_{40}H_{86}CuO_4P_3$  (787.58) C 61.00, H 11.01; found C 61.09, H, 11.14 %. **IR** (NaCl,  $cm^{-1}$ ):  $\tilde{\nu}$  = 3420 (w,  $CO_2H$ ), 1724 (s, CO), 1565 (s, CO), 1511 (s, CO), 1464 (s, CO).  **$^1H$  NMR** ( $CDCl_3$ ):  $\delta$  = 0.92 (t,  $^3J_{HH}$  = 7.2 Hz, 27 H,  $P(CH_2)_3CH_3$ ), 1.45 - 1.58 (m, 36 H,  $PCH_2(CH_2)_2CH_3$ ), 1.48 - 1.55 (m, 18 H,  $PCH_2(CH_2)_2CH_3$ ), 2.49 (bs, 2 H,  $CH_2$ ), 3.03 (bs, 2 H,  $CH_2$ ), 11.71 (bs, 1 H,  $CO_2H$ ).  **$^{13}C\{^1H\}$  NMR** ( $CDCl_3$ ):  $\delta$  = 13.8 ( $P(CH_2)_3CH_3$ ), 24.6 (d,  $J_{CP}$  = 12 Hz,  $P(CH_2)_2CH_2CH_3$ ), 25.0 (d,  $J_{CP}$  = 12 Hz,  $PCH_2(CH_2)_2CH_3$ ), 27.0 (d,  $J_{CP}$  = 3 Hz,  $P(CH_2)_2CH_2CH_3$ ), 32.6 ( $O_2(CH_2)_2CO_2$ ), 32.8 ( $O_2(CH_2)_2CO_2$ ), 178.3 (CO), 177.5 (CO).  **$^{31}P\{^1H\}$  NMR** ( $CDCl_3$ ):  $\delta$  = -22.6.

### Synthesis of [ $(nBu_3P)_3CuO_2C-2-C_6H_4-6-CO_2H$ ] (**6d**)

Complex **6d** was synthesized as described earlier (synthesis of **6a**). 1.00 g (5.98 mmol) of 2,6-pyridine-dicarboxylic acid (**2e**) and 2.42 g (11.97 mmol) of tri-*n*-butylphosphane (**4a**) were dissolved in 60 mL of acetonitrile. The reaction was performed with a cell potential of 2 V at 40 °C over a period of 4 hours. After appropriate work-up, **6d** was obtained as yellow oil. Yield: 3.79 g (5.98 mmol, 99 %, based on **2e**).

**Mp**: 72 °C. Anal. calc. for C<sub>31</sub>H<sub>58</sub>CuO<sub>4</sub>P<sub>2</sub> (634.27) C 58.70, H 9.22; N, 2.21; found C 59.11, H, 9.13; N 2.21 %. **IR** (KBr, cm<sup>-1</sup>):  $\tilde{\nu}$  = 3463 (w, CO<sub>2</sub>H), 1736 (s, CO), 1355 (s, CO). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>):  $\delta$  = 0.77 (t, <sup>3</sup>J<sub>HH</sub> = 6.5 Hz, 27 H, CH<sub>3</sub>), 1.18 - 1.69 (m, 54 H, CH<sub>2</sub>), 8.00 (pt, <sup>3</sup>J<sub>HH</sub> = 7.9 Hz, 1 H, <sup>4</sup>H/py), 8.42 (d, <sup>3</sup>J<sub>HH</sub> = 7.8 Hz, 2 H, <sup>3</sup>H, <sup>5</sup>H/Ph), 12.81 (s, 1 H, CO<sub>2</sub>H). **<sup>13</sup>C{<sup>1</sup>H} NMR** (CDCl<sub>3</sub>):  $\delta$  = 13.9 (P(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 24.6 (P(CH<sub>2</sub>)<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 24.7 (PCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>3</sub>), 26.5 (PCH<sub>2</sub>(CH<sub>2</sub>)<sub>2</sub>CH<sub>3</sub>), 127.6 (<sup>3</sup>C/py), 138.6 (<sup>4</sup>C/py) 148.9 (<sup>2</sup>C/py), 166.5 (CO). **<sup>31</sup>P{<sup>1</sup>H} NMR** (CDCl<sub>3</sub>):  $\delta$  = -20.8.

### Synthesis of [(tmeda)Zn(<sup>n</sup>Bu<sub>3</sub>P)<sub>3</sub>CuO<sub>2</sub>CCO<sub>2</sub>)<sub>2</sub>] (**8**)

To 0.39 g (1.32 mmol) of **7** dissolved in 30 mL of diethyl ether were dropwise added 2.00 g (2.63 mmol) of **6a** dissolved in 30 mL of diethyl ether at -30 °C. After 1 h of stirring at this temperature the reaction solution was warmed to 25 °C and stirring was continued for another hour at this temperature. All volatiles were removed under reduced pressure, whereby the title complex was obtained as colorless oil. Yield: 2.24 g (1.32 mmol, 99 %, based on **7**).

Anal. calc. for C<sub>82</sub>H<sub>178</sub>Cu<sub>2</sub>N<sub>2</sub>O<sub>8</sub>P<sub>6</sub>Zn (1698.62) C 57.98, H, 10.56; N, 1.65; found C 57.73, H, 10.65; N, 1.38 %. **IR** (NaCl, cm<sup>-1</sup>):  $\tilde{\nu}$  = 1679 (s, CO), 1616 (vs, CO), 1464 (s, CO). **<sup>1</sup>H NMR** (CDCl<sub>3</sub>):  $\delta$  = 0.83 (t, J<sub>HH</sub> = 7.0 Hz, 54 H, P(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 1.20 - 1.80 (m, 108 H, P(CH<sub>2</sub>)<sub>3</sub>), 2.32 (bs, 12 H, NCH<sub>3</sub>), 2.45 (bs, 4 H, NCH<sub>2</sub>). **<sup>13</sup>C{<sup>1</sup>H} NMR** (CDCl<sub>3</sub>):  $\delta$  = 13.9 (P(CH<sub>2</sub>)<sub>3</sub>CH<sub>3</sub>), 24.7 (CH<sub>2</sub>CH<sub>3</sub>), 25.1 (PCH<sub>2</sub>CH<sub>2</sub>), 27.1 (PCH<sub>2</sub>), 47.2 (NCH<sub>3</sub>), 56.6 (NCH<sub>2</sub>), 168.3 (CO), 168.5 (CO), 168.6 (CO), 168.7 (CO). **<sup>31</sup>P{<sup>1</sup>H} NMR** (CDCl<sub>3</sub>):  $\delta$  = -23.7.

## Crystal Structure Determinations

Crystal data for **5a**, **6a**, and **6d** are presented in Table 2. Data were collected with a Oxford Gemini 5 (**6d**) or a Bruker SMART CCD 1K diffractometer at 298 K (**5a** and **6a**) or 100 K (**6d**) using Mo K $\alpha$  radiation ( $\lambda = 0.71073 \text{ \AA}$ ). The molecular solid state structures were solved by direct methods using SHELXS-97 [24] and refined by full-matrix least-square procedures on F<sup>2</sup> using SHELXL-97 [25]. All *non*-hydrogen atoms were refined anisotropically and a riding model was employed in the refinement of the hydrogen atom positions. In case of **6a** and **6d** the positions of *O*-bonded hydrogen atoms were taken from the difference Fourier map and refined isotropically. In case of **5a** the four dichloromethane molecules as packing solvents have been refined disordered on two positions with occupation factors of 0.52/0.48 (C75, C11, C12/C75', C11', C12'), 0.445/0.555 (C76, C13, C14/C76', C13', C14'), 0.427/0.573 (C77, C15, C16/C77', C15', C16') and 0.644/0.356 (C78, C17, C18/C78', C17', C18').

**Table 2.** Crystal and Intensity Collection Data for **5a**, **6a**, and **6d**.

	<b>5a</b>	<b>6a</b>	<b>6d</b>
Empirical formula	C <sub>78</sub> H <sub>68</sub> Cl <sub>8</sub> Cu <sub>2</sub> O <sub>4</sub> P <sub>4</sub>	C <sub>38</sub> H <sub>82</sub> CuO <sub>4</sub> P <sub>3</sub>	C <sub>31</sub> H <sub>58</sub> CuNO <sub>4</sub> P <sub>2</sub>
Formula weight	1603.88	759.49	634.26
<i>T</i> /K	298(2)	293(2)	100(1)
Radiation, λ /Å	0.71073	0.71073	0.71073
Crystal system, space group	monoclinic, <i>P2<sub>1</sub>/n</i>	monoclinic, <i>P2<sub>1</sub>/c</i>	triclinic, <i>P1</i>
Unit cell dimensions <i>a, b, c</i> /Å	12.656(5)	13.246(3)	13.3023(9)
	21.622(9)	13.785(3)	15.6730(11)
	30.730(13)	25.771(5)	19.1704(10)
<i>α, β, γ</i> /°			93.788(5)
	97.958(8)	93.863(4)	105.727(5)
			111.759(7)
<i>V</i> /Å <sup>3</sup>	8328(6)	4695.0(15)	3510.5(4)
<i>Z</i> , Calculated density / g·cm <sup>-3</sup>	4, 1.279	4, 1.074	4, 1.200
Absorption coefficient /mm <sup>-1</sup>	0.888	0.599	0.745
<i>F</i> (000)	3288	1664	1368
Crystal size /mm	0.3 x 0.2 x 0.2	0.5 x 0.1 x 0.05	0.2 x 0.2 x 0.18
<i>θ</i> range /°	1.34 to 23.26	1.68 to 25.35	2.89 to 26.08
Index ranges	-14 ≤ <i>h</i> ≤ 13, 0 ≤ <i>k</i> ≤ 24, 0 ≤ <i>l</i> ≤ 34	-15 ≤ <i>h</i> ≤ 15, -16 ≤ <i>k</i> ≤ 16, -31 ≤ <i>l</i> ≤ 31	-16 ≤ <i>h</i> ≤ 16, -16 ≤ <i>k</i> ≤ 19, -23 ≤ <i>l</i> ≤ 23
Reflections collected	67882	45083	26289
Reflections unique	15686 [ <i>R</i> (int) = 0.0600]	8374 [ <i>R</i> (int) = 0.0667]	13314 [ <i>R</i> (int) = 0.0219]
Completeness to theta max.	99.6	97.5	95.6
Absorption correction	Semi-empirical from equivalents	Semi-empirical from equivalents	Semi-empirical from equivalents
Max. and min. transmission	0.99999 and 0.33977	1 and 0.712398	1.00656 and 0.99347
Refinement method	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>	Full-matrix least-squares on <i>F</i> <sup>2</sup>
Data / restraints / parameters	11888 / 192 / 977	8374 / 0 / 415	13314 / 0 / 711
Goodness-of-fit on <i>F</i> <sup>2</sup>	1.040	1.020	0.945

Final $R$ indices [ $I \geq 2\sigma(I)$ ]	$R_1 = 0.0969$ , $wR_2 = 0.2716$	$R_1 = 0.0667$ , $wR_2 = 0.1750$	$R_1 = 0.0311$ , $wR_2 = 0.0696$
$R$ indices (all data)	$R_1 = 0.1439$ , $wR_2 = 0.3273$	$R_1 = 0.1491$ , $wR_2 = 0.2087$	$R_1 = 0.0596$ , $wR_2 = 0.0760$
Largest diff. peak and hole /e Å <sup>-3</sup>	2.410 and -0.458	0.558 and -0.378	0.438 and -0.363

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$R_1 = [\sum(|F_o| - |F_c|)/\sum|F_o|]$ ;  $wR_2 = [\sum(w(F_o^2 - F_c^2)^2)/\sum(wF_o^4)]^{1/2}$ .  $S = [\sum w(F_o^2 - F_c^2)^2/(n - p)]^{1/2}$ .  $n$  = number of reflections,  $p$  = parameters used.

## Supplementary Material

Crystallographic data for the structural analyses of **5a**, **6a**, and **6d** have been deposited with the Cambridge Crystallographic Data Centre, CCDC No. 764731 for **5a**, CCDC No. 764729 for **6a**, and CCDC No. 764730 for **6d**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 1EZ UK (Fax. +44-1223-336033; E-mail: deposit@ccdc.cam.ac.uk or www: <http://www.ccdc.cam.ac.uk>).

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15 **Phosphane Copper(I) Dicarboxylates: Synthesis and Their Potential Use as**  
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37 Two synthesis methodologies, and the reaction chemistry of a series of phosphane cop-  
38 per(I) dicarboxylates is discussed. Their use as precursors in the spin-coating process for  
39 copper deposition is reported.  
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