

Copper(I) Carboxylates of Type $[(n\text{Bu}_3\text{P})_m\text{CuO}_2\text{CR}]$ ($m = 1, 2, 3$) – Synthesis, Properties, and their Use as CVD Precursors

Alexander Jakob^a, Yingzhong Shen^a, Thomas Wächtler^b, Stefan E. Schulz^b, Thomas Gessner^b, Ralf Riedel^c, Claudia Fasel^c, and Heinrich Lang^{a,*}

Chemnitz, Technische Universität Chemnitz, ^a Fakultät für Naturwissenschaften, Institut für Chemie, Lehrstuhl für Anorganische Chemie, ^b Fakultät für Elektrotechnik und Informationstechnik, Zentrum für Mikrotechnologien

^c Darmstadt/Germany, Technische Universität Darmstadt, Fachbereich 21, Materialwissenschaften, Fachgebiet Disperse Feststoffe

Received May 16th, 2008.

Dedicated to Professor Bernt Krebs on Occasion of his 70th Birthday

Abstract. Copper(I) carboxylates of type $[(n\text{Bu}_3\text{P})_m\text{CuO}_2\text{CR}]$ ($m = 1$: **3a**, R = Me; **3b**, R = CF₃; **3c**, R = Ph; **3d**, R = CH=CHPh. $m = 2$: **4a**, R = Me; **4b**, R = CF₃; **4c**, R = Ph; **4d**, R = CH=CHPh. $m = 3$: **8a**, R = Me; **8b**, R = CF₃; **8c**, R = CH₂Ph; **8d**, R = (CH₂OCH₂)₃H; **8e**, R = ^cC₄H₇O) are accessible by following synthesis methodologies: the reaction of $[\text{CuO}_2\text{CR}]$ (**1a**, R = Me; **1b**, R = CF₃; **1c**, R = Ph; **1d**, R = CH=CHPh) with m equivalents of $n\text{Bu}_3\text{P}$ (**2**) ($m = 1, 2, 3$), or treatment of $[(n\text{Bu}_3\text{P})_m\text{CuCl}]$ (**5a**, $m = 1$; **5b**, $m = 2$) with $[\text{KO}_2\text{CCF}_3]$ (**6**). A more straightforward synthesis method for **8a** – **8e** is the electrolysis of copper in presence of HO₂CR (**7a**, R = Me; **7b**, R = CF₃; **7c**, R = CH₂Ph; **7d**, R = (CH₂OCH₂)₃H; **7e**, R = ^cC₄H₇O) and **2**, respectively. This method allows to prepare the appropriate copper(I) carboxylate complexes in virtually quantitative yield, analytically pure form, and on an industrial scale.

IR spectroscopic studies reveal that the carboxylic units in **4**, **5**, and **8** bind in a unidentate, chelating or μ -bridging fashion to copper(I) depending on m and R.

The thermal properties of **4**, **6**, and **8** were determined by TG and DSC studies. Based on TG-MS experiments a conceivable mechanism for the thermally induced decomposition of these species is presented.

Hot-wall Chemical Vapor Deposition experiments (CVD) with precursor **4b** showed that copper could be deposited at 480 °C onto a TiN-coated oxidized silicon substrate. The copper films were characterized by SEM and EDX studies. Pure layers were obtained with copper particles of size 200 – 780 nm.

Keywords: Copper; Carboxylates; Tri-*n*-butylphosphane; Electrolysis; CVD; TG; DSC; SEM; EDX

Introduction

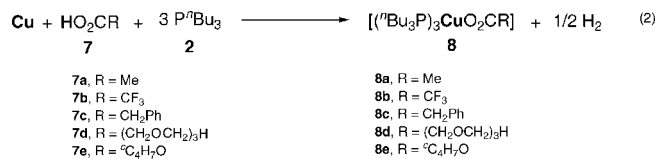
Copper is widely applied as interconnect material in Ultra-Large Scale Integrated (ULSI) microprocessors, due to its low resistivity (bulk value: 1.7 $\mu\Omega$ cm) compared to afore used aluminium (bulk resistivity: 2.7 $\mu\Omega$ cm) [1, 2]. Furthermore, Cu exhibits high thermal conductivity and superior electromigration resistance, which is up to four orders of magnitude higher than for Al as well as increased resistance to stress-induced voiding in comparison to Al or W. However, with decreasing feature size, physical vapor deposition techniques are becoming more and more problematic with respect to film conformality and step-coverage in nanoscale trenches. Chemical Vapor Deposition (CVD) represents an alternative, due to its ability to form continuous films of equal thickness also on complex surfaces. However, for the

CVD of copper appropriate precursors are required [3–8].

CVD precursors should be volatile, low molecular weighted, easy to handle in the deposition experiments, and available in high yield and straightforward reactions. Among them, Lewis-base copper(I) β -diketonates (for example, β -diketonate = 2,4-pentanedionate (acac), dipivaloylmethanate, 1,1,1-trifluoro-2,4-pentanedionate, 1,1,1,5,5,5-hexafluoro-2,4-pentanedionate (hfac), ...) have been intensively studied as CVD precursors, since they possess, when compared with the corresponding copper(II) systems, a higher vapor pressure and a lower deposition temperature [7]. As ancillary Lewis-base ligands in metal-organic complexes $[\text{L}_m\text{Cu}(\beta\text{-diketonate})]$ ($m = 1, 2$) [9], phosphanes, phosphites [10], alkenes [1] or alkynes can be used [2]. Meanwhile, copper(I) β -diketonates are commercially available, e. g. ($\eta^2\text{-H}_2\text{C}=\text{CHSiMe}_3$)Cu(hfac) (*Cupra-Select*[®]) [11a,b] and (MHY)Cu(hfac) (*Gigacopper*[®]) (MHY = 2-methyl-1-hexene-3-yne) [11c], respectively, which makes this class of metal precursors still the most important in industrial applications. These precursors deposit copper either by direct reduction with hydrogen or by a thermally induced disproportionation. Within the latter reactions the β -diketonate ligand is removed in form of $[\text{Cu}(\beta\text{-diketonate})_2]$ and the desorption of neutral Lewis-

* Prof. Dr. H. Lang
Technische Universität Chemnitz
Fakultät für Naturwissenschaften, Institut für Chemie
Lehrstuhl für Anorganische Chemie
Straße der Nationen 62
D-09111 Chemnitz (Germany)
E-mail: heinrich.lang@chemie.tu-chemnitz.de

and analytically pure. Additionally this synthesis method allows the preparation of **8a–8e** on an industrial scale. In contrast, the synthesis of **8a–8e** by the method described in Equation (2) only gives minor amounts of the appropriate phosphane copper(I) carboxylate complexes (Experimental Part). Nevertheless, the electrolytic procedure privileges the formation of tris-ⁿBu₃P copper(I) systems.



Complexes **3a–3d**, **4a–4d**, and **8a–8e** gave satisfactory elemental analyses and were characterized by FT-IR and ¹H-, ¹³C{¹H}- and ³¹P{¹H}-NMR spectroscopy (Experimental Part).

Carboxylate ions RCO₂⁻ can bind to transition metals in a monodentate [21], chelating [22, 23], or μ-bridging [24, 25] fashion, whereby a relationship between the relevant bonding motifs of the carboxylic ligands and the carbon-oxygen stretching frequencies exists, allowing to determine the coordination number at the metal atom [26–28]. Monodentate bonded R(O)CO⁻ carboxylate groups increase the separation Δν (Δν = ν_{asym} – ν_{sym}) of the corresponding ν_{CO2} frequencies relative to the values of the free carboxylate ion, usually taken from the respective sodium or potassium salts [29]. Typical Δν values for sodium and potassium trifluoroacetate are 223 and 241 cm⁻¹ [30, 31]. The ν_{CO} absorptions for complexes **3a–3d**, **4a–4d**, and **8a–8e** are summarized in Table 2.

Table 2 Δν values of the ν_{CO} vibrations of complexes **3a–3d**, **4a–4d**, and **8a–8e**.

Compd.	ν _{asym} / cm ⁻¹	ν _{sym} / cm ⁻¹	Δν / cm ⁻¹
3a	1594	1460	134
3b	1672	1461	211
3c	1705	1600	105
3d	1639	1553	86
4a	1594	1460	134
4b	1682	1464	218
4c	1708	1654	54
4d	1640	1555	85
8a	1575	1464	111
8b	1691	1464	227
8c	1577	1463	114
8d	1607	1463	144
8e	1608	1463	145

As it can be seen from Table 2, the Δν values for **3b**, **4b** and **8b** are 211, 218 and 227 cm⁻¹ and point to monodentate bonded CO₂CF₃ entities [33]. A similar structural motif is found for isostructural silver(I) carboxylates [34]. All other complexes show Δν values between 50–145 cm⁻¹ portending to chelate-bonded or μ-bridged copper(I) carboxylate units. For example, the separations found for **3a** and **4a** suggest a μ-bridging acetate [32].

The ¹H NMR spectra of **3**, **4**, and **8** show well-resolved resonance signals for the organic groups R and *n*-Bu and are consistent with the empirical formula [(ⁿBu₃P)_mCuO₂CR] (m = 1, 2, 3; R = Me, CF₃, Ph, CH₂Ph, CH=CHPh, (CH₂OCH₂)₃H, ⁿC₄H₉O) (Experimental Part).

In the ¹³C{¹H} NMR spectra of **3**, **4** and **8** for the carboxylic building block a very characteristic resonance signal is found between 160–180 ppm, in a region in which no other resonance signals appear. In comparison with free carboxylic acids an up-field shift by 1–3 ppm is observed for **3c** and **4c** [34]. However, for **4d** the CO₂ carbon atom is shifted to lower field (173.3 ppm), when compared with the corresponding free acid PhCH=CHCO₂H (172.8 ppm).

In the ³¹P{¹H} NMR spectra of all newly synthesized metal-organic complexes relatively broad signals are observed between –20.1 to –13.8 (**3a–3d**), –25.0 to –17.6 (**4a–4d**), and –26.2 to –22.9 ppm (**8a–8e**). These signals are down-field shifted in contrast to *non*-coordinated ⁿBu₃P (–32.3 ppm) which is typical in copper(I) phosphane chemistry [23, 39]. The difference in the chemical shifts of **3**, **4** and **8** relates to the number of Lewis-base ligands coordinating to copper(I). In all ³¹P{¹H} NMR spectra broad lines are observed, explainable by the quadrupolar effect of copper (⁶³Cu and ⁶⁵Cu isotopes). Exchange processes involving either the ⁿBu₃P ligands or the carboxylate units could be another reason [37].

TG-, DSC- and TG-MS-Studies

The thermal stability of metal-organic **3a–3d**, **4a–4d**, and **8a–8d** were investigated by ThermoGravimetry (TG) and Differential Scanning Calorimetry (DSC) under an atmospheric pressure of N₂ to show if these species may be suitable precursors for chemical vapor deposition (CVD) experiments. These studies allow to optimize the temperature at which the appropriate copper(I) complex should be maintained during the CVD experiments without decomposition. All copper carboxylates decompose in a two-step process (exception of **3b**, **3d**, and **8c** which decompose in three steps) of which the first decomposition takes place between 95–360 °C, while the second step is observed in the temperature range of 205–500 °C depending on the nature of the CO₂R group. Metal-organic **3a** shows the lowest decomposition temperature (95 °C), while complex **4b** with 170 °C possesses the highest initial temperature. Exemplary, the TG trace of **4b** is shown in Figure 1.

Thermogravimetric studies of [(ⁿBu₃P)₂CuO₂CCF₃] (**4b**) give evidence for a thermal decomposition process that starts at about 170 °C and has a maximal rate at 250 °C (Figure 1). The weight loss of the 1st decomposition interval (170–360 °C) is 77.4 % corresponding to the loss of CO₂ and elimination of the ⁿBu₃P ligands. Further heating to 450 °C induces a weight loss of 12 %. This can be interpreted as the elimination of fluorine-carbon fragments. The final thermogravimetric residue at 500 °C is 10.2 %, which almost confirms the theoretically calculated value for the formation of elemental copper (10.9 %). Similar obser-

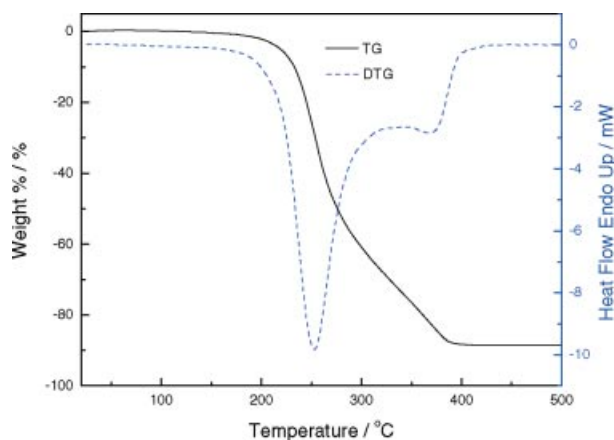


Figure 1 TG and DTG (Derivative ThermoGravimetry) traces of complex **4b** (N₂, heating rate 8 K/min).

variations were made for all other copper(I) carboxylate complexes (Table 3, Experimental Part).

As expected, complexes **3a–3d** appear to be less volatile than **4a–4d** and **8a–8e**, since the latter complexes possess one or even two more ⁿBu₃P Lewis-base ligands at copper(I) resulting in lower aggregated species. For example, it could be shown by single X-ray structure determination that [(F₃CCH₂O)₃P]CuO₂CCF₃)₄ with only one phosphite coordinated to copper is tetrameric showing a distorted cubane-like Cu₄O₄ structure, [(F₃CCH₂O)₃P)₂CuO₂CCF₃)₂ with two Lewis-base ligands is dimeric with μ-bridging carboxylic units, while [(F₃CCH₂O)₃P)₃CuO₂CCF₃] is mononuclear.

In addition, TG-MS experiments were enforced to obtain first information on the decomposition mechanism of metal-organic **3**, **4**, and **8** and hence, to learn more about the volatility and stability of these precursors. Exemplarily, complex **4b** was studied by TG-MS and the result is shown in Figure 2. At 240 °C a fragment with *m/z* = 44 could be detected which corresponds to the elimination of carbon dioxide. Fragments characteristic for P⁺ (*m/z* = 31), C₃H₇⁺

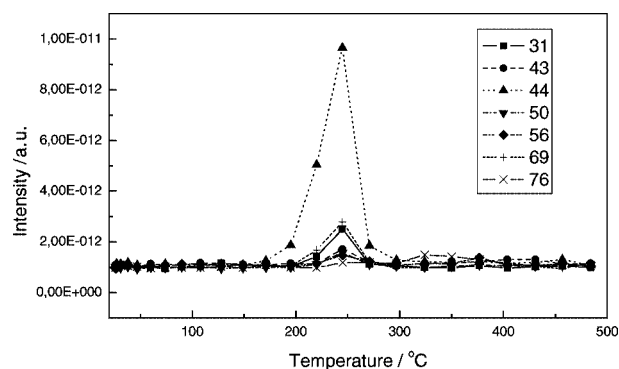
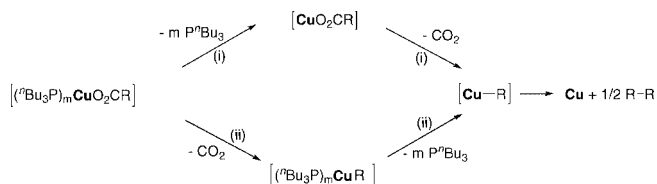


Figure 2 TG-MS curves of **4b** (heating rate 8 K/min, Ar atmosphere, gas flow 75 sccm).

(*m/z* = 43), Me₂C=CH₂⁺ (*m/z* = 56) and C₃H₉P⁺ (*m/z* = 76) have also been detected at this temperature. These ions result from the ionization of the ⁿBu₃P ligand. Furthermore, CF₃⁺ (*m/z* = 69) is found in the dynamic mass spectra as characteristic ion. Resulting from CF₃⁺, which appears in high intensity, also CF₂⁺ ions (*m/z* = 50) of lower intensity were generated.

Based on these data a possible mechanism for the thermal decomposition of complexes **3**, **4** and **8** is proposed (Scheme 1).



Scheme 1 Proposed thermally induced decomposition mechanism for complexes **3**, **4** and **8** (*m* = 1, 2, 3; R = singly-bonded organic ligand as outlined in Table 1).

The decomposition of complexes **3**, **4**, and **8** corresponds to the thermolysis of similar phosphane silver(I) car-

Table 3 TG and DSC data for complexes **3a–3d**, **4a–4d**, and **8a–8e**.

Compd.	TG			Residue ^{b)} / %	DSC		
	T ₁ (Δ <i>m</i> ₁) ^{a)} / °C	T ₂ (Δ <i>m</i> ₂) ^{a)} / °C	T ₃ (Δ <i>m</i> ₃) ^{a)} / °C		Δ <i>H</i> ₁ ^{c)} / J g ⁻¹	Δ <i>H</i> ₂ ^{c)} / J g ⁻¹	Δ <i>H</i> ₃ ^{c)} / J g ⁻¹
3a	95-204 (46.3)	204-300 (45.3)		8.5	28.8	-61.8	-12.9
3b	167-287 (47.6)	287-310 (24.4)	310-570 (14.0)	14.1	-120.4	42.2	-107.9
3c	140-280 (49.3)	280-495 (33.8)		16.1	5.3	162.6	-8.8
3d	100-242 (53.8)	242-300 (16.4)	300-500 (13.6)	16.2	15.3	144.1	-60.9
4a	100-216 (58.3)	216-300 (33.1)		8.1	45.6	-101.4	-6.7
4b	170-360 (77.4)	360-450 (12.3)		10.2	-168.9	-10.1	-47.0
4c	150-300 (85.7)	300-500 (5.2)		8.9	3.3	182.6	-2.9
4d	143-300 (82.1)	300-500 (5.0)		12.9	5.01	175.84	73.76
8a	62-204 (48.6)	204-217 (14.3)	217-253 (28.3)	8.5	58.6	overlapping processes	
8b	96-199 (18.2)	199-262 (51.1)	262-370 (21.9)	8.7		-81.8	
8c	90-214 (38.5)	214-321 (51.4)		10.1	-146.0	-63.5	
8d	80-209 (35.6)	209-279 (54.7)	279-405 (1.8)	7.9	-178.0	-178.3	
8e	80-197 (23.1)	197-325 (69.3)		7.6	11.1	-65.7	108.3

^{a)} T₁, T₂, T₃ = Temperature range for the 1st, 2nd and 3rd decomposition step; Δ*m*₁, Δ*m*₂, Δ*m*₃ = weight loss for the 1st, 2nd and 3rd step in %. ^{b)} Remaining residue at 500 °C in % based on charged complex. ^{c)} Δ*H*₁, Δ*H*₂, Δ*H*₃ = enthalpy of the 1st, 2nd and 3rd decomposition step.

boxylates [12, 19]. For example, $[(^n\text{Bu}_3\text{P})_2\text{AgO}_2\text{CC}_6\text{F}_5]$ undergoes a consecutive decomposition, producing $[(^n\text{Bu}_3\text{P})_2\text{AgC}_6\text{F}_5]$ by decarboxylation at first. Elimination of $^n\text{Bu}_3\text{P}$ then gives $[\text{AgC}_6\text{F}_5]$, which produces elemental silver and fluorine-containing organics by homolytical cleavage of the silver-carbon bond [38]. Likewise, it is also possible that the appropriate copper complexes **3**, **4**, and **8** may also eliminate $^n\text{Bu}_3\text{P}$ at first, followed by decarboxylation of the remaining copper carboxylate $[\text{CuO}_2\text{CR}]$. Nevertheless, it is difficult to decide which route is more favored in copper carboxylate chemistry since the loss of CO_2 and $^n\text{Bu}_3\text{P}$ appears simultaneously (Figure 3). However, we favor route (ii) (Scheme 1) because this pattern takes also place in the thermally induced decomposition of heterobimetallic organometallic π -tweezers of type $[(\eta^5\text{-C}_5\text{H}_4\text{SiMe}_3)_2\text{Ti}(\mu\text{-}\sigma,\pi\text{-C}\equiv\text{CSiMe}_3)]\text{CuO}_2\text{CR}$ (R = organic rest) [12].

Besides TG analyses (*vide supra*) also DSC studies were carried out with **3**, **4**, and **8** to determine the change of entropy during thermolysis. The endothermic and/or exothermic processes of these complexes are summarized in Table 3. DSC plots of selected samples are presented in Figure 3.

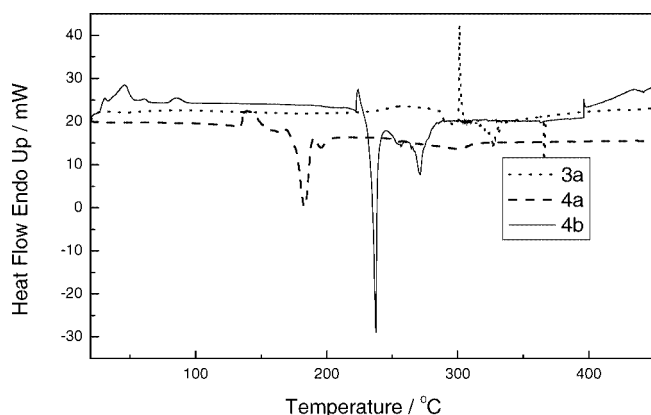


Figure 3 DSC traces of **3a**, **4a**, and **4b** (heating rate 8 K/min, N_2 atmosphere).

Most of the synthesized complexes show endothermic and exothermic peaks. For example, complex **4b** possesses endothermic and overlapping exothermic signals between 225 and 385 °C. These data suggest that this compound indeed undergoes a stepwise decomposition (*i. e.*, loss of CO_2 , $^n\text{Bu}_3\text{P}$ and R) (*vide supra*) (Table 3).

Chemical Vapor Deposition

On the basis of the thermal properties obtained from TG and DSC studies we chose complex **4b** as potential CVD copper precursor. This complex is more stable than the other ones and exhibits a higher vapor pressure, due to the *non*-existence of hydrogen bonds.

The CVD experiments were conducted with **4b** using a horizontal CVD hot-wall reactor without any addition of a reducing agent. In a typical deposition experiment, copper

metal was deposited onto a TiN-coated oxidized silicon substrate at 480 °C during a process time of 120 min. The precursor temperature was maintained at 120 °C with a nitrogen flow of 44 sccm. The total pressure was kept at 7.0×10^{-2} mbar with nitrogen as carrier gas. The film deposited is copper colored. In the precursor flow direction, the color appears lighter with increasing distance from the gas inlet, related to lower film thickness. In this region the precursor concentration was lower. The surface morphology of the copper film was examined by scanning electron microscopy (SEM). An image is depicted in Figure 4. The film was formed at 480 °C is partly rough, coarse-grained and not completely continuous. Rather the deposit consists of loose clusters which tend to coalesce.

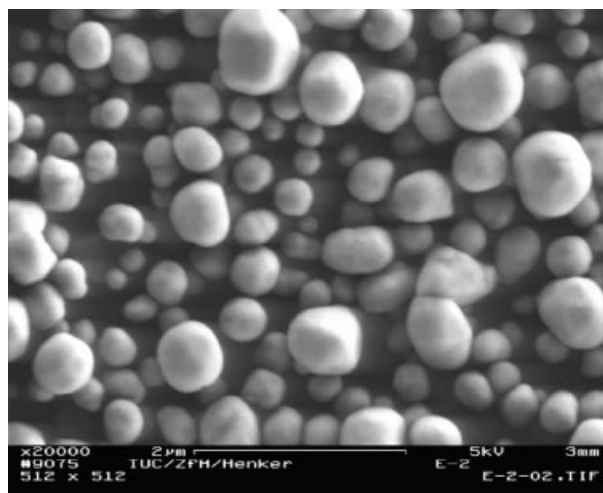


Figure 4 Surface SEM image showing the morphology of the copper film obtained from **4b** on a TiN-coated oxidized silicon substrate at 480 °C and a total gas pressure of 7.0×10^{-2} mbar.

Two kinds of copper grains are visible: small grains of about 200 nm size, the nucleation layer, which are evenly formed and are in the state of coalescence, and large, irregularly shaped copper grains of size 780 nm which are situated on the nucleation layer. The larger grains may be the result of an agglomeration process of copper particles at this temperature. There may be several reasons for this change, which are not longer comprehensible, *e.g.* a low carrier gas flow or temperature variation. Another reason for the formation of the larger particles rather than a continuous film may be the strong tendency of agglomeration at elevated temperatures which is known for copper on substrates such as refractory metals and their nitrides [39, 40].

The copper clusters were additionally studied by energy-dispersive X-ray spectroscopy (EDX) (Figure 5). Besides a clear Cu signal, only a minor Si peak resulting from the substrate was detected. No impurities were found within the detection limits of this method.

The result of this deposition experiment shows that **4b** is a promising candidate for further CVD processes of Cu nanoclusters or Cu films.

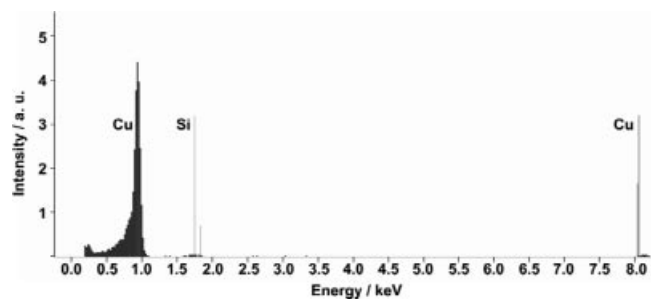


Figure 5 EDX spectrum of the copper clusters obtained from **4b** ($T_s = 480\text{ }^\circ\text{C}$, $p_{\text{total}} = 7.0 \times 10^{-2}\text{ mbar}$; carrier gas N_2 ; flow rate = 44 sccm).

Conclusion

A series of tri-*n*-butyl phosphane copper(I) carboxylates has been synthesized by three different synthesis methodologies, including complexation, metathesis, and electrolysis. It appeared that the latter method is straightforward and allows to prepare the respective metal-organic complexes in a “one-pot” synthesis procedure on an industrial scale, whereby the molecules are formed in analytically pure form. The thermodynamics of selected samples was studied by TGA, DSC, TG/DTG and TG-MS. Based on these investigations a decomposition mechanism is proposed including decarboxylation-elimination-homolytical coupling. In first deposition experiments complex [${}^n\text{Bu}_3\text{P}$] ${}^n\text{CuO}_2\text{CCH}_3$] was used as CVD precursor to grow copper layers on TiN-coated oxidized silicon substrates at $480\text{ }^\circ\text{C}$ deposition temperature, carrier gas flow 44 sccm, and a total pressure of $7.0 \times 10^{-2}\text{ mbar}$, respectively. The film that was formed is partly rough and coarse-grained. The EDX results showed that the obtained layer composed of pure copper within the detection limit of EDX.

Experimental Section

Materials and Methods

Complexes **5a** and **5b** [7, 9], and the copper carboxylates **1a–1d** [41] were prepared by published procedures. All other chemicals were purchased by commercial providers and were used as received.

All reactions were carried out under an atmosphere of purified nitrogen (O_2 traces: copper oxide catalyst, BASF AG, Ludwigshafen; H_2O : molecular sieve 4 Å, Aldrich Company) using standard Schlenk techniques. The electrolysis reactions were carried out under Ar atmosphere (4.6; AirLiquide) in a heatable one-pot cell, with copper (>99.9%) as anode and cathode material. Dichloromethane was purified by distillation from P_2O_5 ; diethyl ether was purified by distillation from sodium/benzophenone ketyl; *n*-pentane was purified by distillation from calcium hydride. Infrared spectra were recorded on a Perkin Elmer FT-IR spectrometer (Spectrum 1000).

${}^1\text{H}$ NMR spectra were recorded on a Bruker Avance 250 spectrometer operating at 250.130 MHz in the Fourier transform mode; ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR spectra were recorded at 62.895 MHz. Chemical shifts are reported in δ units (parts per million) downfield from tetramethylsilane ($\delta = 0.0\text{ ppm}$) with the solvent as the reference

signal (${}^1\text{H}$ NMR, CDCl_3 $\delta = 7.26$; ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR, CDCl_3 $\delta = 77.55$). ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR spectra were recorded at 101.255 MHz in CDCl_3 with $\text{P}(\text{OMe})_3$ as external standard ($\delta = 139.0$, rel. to H_3PO_4 (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 K min^{-1} under N_2 (1.0 sccm). TG-MS studies were carried out with a Netzsch STA 429 equipment with an orifice coupling system and a Quadrap 01 MS analysis system of Balzers QMA 400. DSC experiments were carried out with the Perkin Elmer System Pyris DSC 6 with a constant heating rate of 8 K min^{-1} under N_2 (1.0 sccm). The CVD experiments were carried out in a horizontal quartz tube hot-wall CVD reactor with 40 mm in diameter. Heating was achieved by a resistively heated tube oven (HORST company). The temperature was set by a temperature controller HAT 520 (HORST company) and was calibrated with a thermocouple type GTH 1150 digital thermometer. The precursor was placed in a glass container in direct contact with the reactor quartz tube. The precursor container was heated with a heating band for evaporation of the precursor. The precursor vapor was transported to the reactor tube by N_2 carrier gas. The carrier gas flow was regulated using a MKS type 247 mass flow controller which was connected to the apparatus by a section of flexible stainless steel tubing. The pressure control system consists of an Edwards Active Gauge Controller, a cooling trap, and a turbomolecular pump with a backing pump. The trap prevents the reactor effluents from entering the vacuum pump. SEM micrographs were recorded on a SEM instrument type DSM 982, Gemini from LEO company. EDX analysis was performed on the EDX system EDWIN (Röntec company) attached to the SEM. Microanalyses were performed by the Institute of Organic Chemistry, University of Heidelberg and partly by the Institute of Organic and Inorganic Chemistry, Chemnitz University of Technology.

Synthesis of [CuO_2CCH_3] (**1a**) [41]

Acetic acid (0.6 g, 10.0 mmol) was added in a single portion to [CuCl] (0.99 g, 10.0 mmol) suspended in 40 mL of dichloromethane at $25\text{ }^\circ\text{C}$. After 10 min of stirring, 1.0 g of NEt_3 (1.39 mL, 10.0 mmol) dissolved in 5 mL of dichloromethane, was added. During 5 h of stirring at $25\text{ }^\circ\text{C}$, [CuO_2CCH_3] (**1a**) precipitated as a colorless solid. The reaction mixture was filtered and the colorless residue was washed with 10 mL of dichloromethane and then dried in oil-pump vacuum. Yield: 0.77 g (6.3 mmol, 63% based on [CuCl]).

Synthesis of [${}^n\text{Bu}_3\text{P}$] CuO_2CCH_3] (**3a**)

To a suspension of **1a** (1.23 g, 10.0 mmol) in 40 mL of diethyl ether, ${}^n\text{Bu}_3\text{P}$ (**2**) (2.02 g, 10.0 mmol) dissolved in 20 mL of diethyl ether was added dropwise at $-20\text{ }^\circ\text{C}$. After 1 h of stirring at this temperature, the reaction solution was filtered through a pad of Celite. Evaporation of all volatiles from the filtrate in oil-pump vacuum afforded a colorless liquid. Yield of **3a**: 2.69 g (8.27 mmol, 83% based on **1a**). Elemental analysis: Calcd. for $\text{C}_{14}\text{H}_{30}\text{CuO}_2\text{P}$ (324.91) C, 51.75; H, 9.31. Found: C, 51.32; H, 9.29%.

IR (NaCl): ν [cm^{-1}] 1594 (s) (CO , asym.), 1460 (s) (CO , sym.). ${}^1\text{H}$ NMR (CDCl_3): 1.03 (t, $J_{\text{HH}} = 7.0\text{ Hz}$, 9 H, $(\text{CH}_2)_3\text{CH}_3$), 1.51 (m, 18 H, $(\text{CH}_2)_3\text{CH}_3$) δ 1.59 (s, 3 H, CH_3CO_2). ${}^{13}\text{C}\{{}^1\text{H}\}$ NMR (C_6D_6): δ 175.8 (CH_3CO_2), 23.9 (CH_3CO_2), 26.85 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{PC}} = 4.8\text{ Hz}$), 25.5 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{PC}} = 6.2\text{ Hz}$), 24.8 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$, $J_{\text{PC}} = 11.5\text{ Hz}$), 13.8 ($\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$). ${}^{31}\text{P}\{{}^1\text{H}\}$ NMR (CDCl_3): δ -20.1.

Synthesis of [ⁿBu₃P]CuO₂CCF₃ (**3b**)

Complex **3b** was accessible by the reaction of [ⁿBu₃P]CuCl (**5a**) (3.01 g, 10.0 mmol) dissolved in 40 mL of diethyl ether with [CF₃CO₂K] (**6**) (1.52 g, 10.0 mmol) suspended in 30 mL of diethyl ether at -20 °C. After 4 hours of stirring at this temperature, all volatiles were removed in oil-pump vacuum and to the remaining liquid 100 mL of *n*-pentane were added. Filtration through a pad of Celite and evaporation of the solvent from the filtrate in oil-pump vacuum gave a colorless liquid. Yield: 3.16 g (8.35 mmol, 83 % based on **5a**). Elemental analysis: Calcd. for C₁₄H₂₇CuF₃O₂P (378.88) C, 44.43; H, 7.20. Found: C, 44.32; H, 7.26 %.

IR (NaCl): ν [cm⁻¹] 1672 (s) (CO, asym.), 1461 (vs) (CO, sym.), 1412 (m), 1199 (vs) (CF₃). ¹H NMR (CDCl₃): δ 1.32 (m, 18 H, (CH₂)₃CH₃), 0.95 (t, $J_{\text{HH}} = 7.4$ Hz, 9 H, (CH₂)₃CH₃). ¹³C{¹H} NMR (CDCl₃): δ 14.1 (CH₂CH₂CH₂CH₃), 25.0 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 13.0$ Hz), 25.4 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 17.0$ Hz), 27.4 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 4.3$ Hz), 118.1 (CF₃CO₂, $J_{\text{CF}} = 289$ Hz), 161.4 (CF₃CO₂, $J_{\text{CF}} = 25.9$ Hz). ³¹P{¹H} NMR (CDCl₃): δ -18.4.

Synthesis of [ⁿBu₃P]CuO₂CPh (**3c**)

[CuO₂CPh] (**1c**) was synthesized similar to the preparation of **1a** (see above). In this respect, benzoic acid (1.22 g, 10.0 mmol) was reacted with [CuCl] (0.99 g, 10.0 mmol) in presence of NEt₃ (1.01 g, 1.39 mL, 10.0 mmol). After appropriate work-up, colorless [CuO₂CPh] (**1c**) was obtained in 1.13 g yield (61 % based on [CuCl]). 2.02 g (10.0 mmol) of **2** were dissolved in 20 mL of diethyl ether and this solution was added dropwise to the suspension of [CuO₂CPh] (**1c**) (1.85 g, 10.0 mmol) in 40 mL of diethyl ether at -20 °C. The reaction mixture was stirred for 2 hours at this temperature. Filtration through a pad of Celite and evaporation of the solvent from the filtrate in oil-pump vacuum gave colorless, liquid **3c**. Yield: 3.06 g (7.8 mmol, 79 % based on **2**). Elemental analysis: Calcd. for C₁₉H₃₂CuO₂P (386.98) C, 58.97; H, 8.33. Found: C, 58.76; H, 7.97 %.

IR (NaCl): ν [cm⁻¹] 1705 (s) (CO, asym.), 1600 (s) (CO, sym.). ¹H NMR (CDCl₃): δ 0.83 (t, 9 H, $J_{\text{HH}} = 7.1$ Hz, (CH₂)₃CH₃), 1.2–1.5 (m, 18 H, (CH₂)₃CH₃), 7.3 (m, 3 H, C₆H₅), 8.0 (m, 2 H, C₆H₅). ¹³C{¹H} NMR (CDCl₃): δ 14.0 (CH₂CH₂CH₂CH₃), 24.7 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 13.0$ Hz), 25.0 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 20.2$ Hz), 27.4 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 2.8$ Hz), 128.1 (Ph), 130.1 (Ph), 131.5 (Ph), 135.0 (Ph), 171.8 (CO₂Ph). ³¹P{¹H} NMR (CDCl₃): δ -14.8.

Synthesis of [ⁿBu₃P]CuO₂CCH=CHPh (**3d**)

Cinnamic acid (1.48 g, 10 mmol) was reacted with [CuCl] (0.99 g, 10.0 mmol) in a similar manner as described above. After appropriate work-up, yellow [CuO₂CCH=CHPh] (**1d**) could be isolated in 1.84 g yield (87 % based on [CuCl]). ⁿBu₃P (**2**) (2.02 g, 10.0 mmol) was dissolved in 20 mL of diethyl ether and then added dropwise to a suspension of **1d** (1.84 g, 8.73 mmol) in 30 mL diethyl ether at -20 °C. After stirring the reaction mixture for 3 hours at this temperature, it was filtered through a pad of Celite and all volatiles were removed in oil-pump vacuum to give a colorless liquid. Yield: 3.39 g (8.2 mmol, 82 % based on **1a**). Elemental analysis: Calcd. for C₂₁H₃₄CuO₂P (413.02) C, 61.07; H, 8.30. Found: C, 60.78; H, 7.97 %.

IR (NaCl): ν [cm⁻¹] 1670 (m) ($\nu_{\text{C}=\text{C}}$), 1639 (s) (CO, asym.), 1553 (vs) (CO, sym.). ¹H NMR (CDCl₃): δ 0.84 (t, $J_{\text{HH}} = 6.9$ Hz, 9 H, (CH₂)₃CH₃), 1.4 (m, 18 H, (CH₂)₃CH₃), 6.45 (d, 1 H, CH, $J_{\text{HH}} = 12.0$ Hz), 7.2–7.4 (m, 5 H, Ph), 7.50 (d, 1 H, CH, $J_{\text{HH}} = 12.0$ Hz). ¹³C{¹H} NMR (CDCl₃): δ 14.1 (CH₂CH₂CH₂CH₃), 24.8 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 12.5$ Hz), 25.1 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 15.4$ Hz), 27.2 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 2.9$ Hz),

126.8 (=CH), 127.9 (Ph), 128.9 (Ph), 129.2 (Ph), 136.4 (Ph), 141.1 (=CH), 171.8 (CO₂). ³¹P{¹H} NMR (CDCl₃): δ -13.8.

Synthesis of [ⁿBu₃P]₂CuO₂CCH₃ (**4a**)

ⁿBu₃P (**2**) (4.04 g, 20.0 mmol) dissolved in 40 mL of diethyl ether was added dropwise to [CuO₂CCH₃] (**1a**) (1.23 g, 10.0 mmol) suspended in 40 mL of diethyl ether at -20 °C. After 2 hours of stirring, all volatiles were removed in oil-pump vacuum to leave a colorless liquid. Yield: 4.16 g (7.9 mmol, 79 % based on **1a**). Elemental analysis: Calcd. for C₂₆H₅₇CuP₂O₂ (527.23) C, 59.23; H, 10.90. Found: C, 59.59; H, 10.85 %.

IR (NaCl): ν [cm⁻¹] 1594 (s) (CO, asym.), 1460 (s) (CO, sym.). ¹H NMR (CDCl₃): δ 0.59 (t, $J_{\text{HH}} = 4.3$ Hz, 18 H, (CH₂)₃CH₃), 1.10 (m, 36 H, (CH₂)₃CH₃), 1.13 (s, 3 H, CO₂CH₃). ¹³C{¹H} NMR (CDCl₃): δ 13.8 (CH₂CH₂CH₂CH₃), 24.1 (CO₂CH₃), 24.8 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 11.1$ Hz), 26.0 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 6.8$ Hz), 175.4 (CO₂CH₃). ³¹P{¹H} NMR (CDCl₃): δ -25.0.

Synthesis of [ⁿBu₃P]₂CuO₂CCF₃ (**4b**)

Complex **4b** was synthesized in the same manner as **3b**. In this respect, [ⁿBu₃P]₂CuCl (**5b**) (5.03 g, 10.0 mmol) was reacted with **6** (1.52 g, 10.0 mmol). After appropriate work-up, complex **4b** was obtained as a colorless liquid. Yield: 4.88 g (8.4 mmol, 84 % based on **5b**). Elemental analysis: Calcd. for C₂₆H₅₄CuF₃O₂P₂ (581.20) C, 53.77; H, 9.38. Found: C, 53.76; H, 9.21 %.

IR (NaCl): ν [cm⁻¹] 1682 (s) (CO, asym.), 1464 (vs) (CO, sym.). ¹H NMR (CDCl₃): δ 1.39 [m, 36 H, (CH₂)₃CH₃], 0.82 [t, $J_{\text{HH}} = 6.9$ Hz, 18 H, (CH₂)₃CH₃]. ¹³C{¹H} NMR (CDCl₃): δ 13.9 (CH₂CH₂CH₂CH₃), 24.8 (CH₂CH₂CH₂CH₃), 27.3 (CH₂CH₂CH₂CH₃), 117.2 (CF₃, $J_{\text{CF}} = 308$ Hz), 161.5 (CO, $J_{\text{CF}} = 35.0$ Hz). ³¹P{¹H} NMR (CDCl₃): δ -17.6.

Synthesis of [ⁿBu₃P]₂CuO₂CPh (**4c**)

Complex **4c** was synthesized similarly to the procedure used for the synthesis of **3c**. In this respect, **2** (4.04 g, 20.0 mmol) was reacted with **1c** (1.85 g, 10.0 mmol). After appropriate work-up, complex **4c** was isolated as a colorless liquid. Yield: 4.89 g (8.3 mmol, 83 % based on **1c**). Elemental analysis: Calcd. for C₃₁H₅₉CuO₂P₂ (589.30): C, 63.18; H, 10.09. Found: C, 62.78; H, 9.88 %.

IR (NaCl): ν [cm⁻¹] 1708 (s) (CO, asym.), 1654 (s) (CO, sym.). ¹H NMR (CDCl₃): δ 1.1–1.4 [m, 36 H, (CH₂)₃CH₃], 7.2 (m, 3 H, C₆H₅), 0.68 [t, 18 H, $J_{\text{HH}} = 4.2$ Hz, 7.9 (m, 2 H, C₆H₅), (CH₂)₃CH₃]. ¹³C{¹H} NMR (CDCl₃): δ 14.0 (CH₂CH₂CH₂CH₃), 24.7 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 13.1$ Hz), 25.0 (CH₂CH₂CH₂CH₃, $J_{\text{PC}} = 20.4$ Hz), 27.3 (CH₂CH₂CH₂CH₃), 128.0 (Ph), 129.9 (Ph), 131.2 (Ph), 135.4 (Ph), 171.9 (CO₂). ³¹P{¹H} NMR (CDCl₃): δ -18.5.

Synthesis of [ⁿBu₃P]₂CuO₂CCH=CHPh (**4d**)

Complex **4d** was accessible in an analogous way as **3d**. Therefore, ⁿBu₃P (**2**) (4.04 g, 20.0 mmol) was reacted with **1d** (2.11 g, 10.0 mmol). After appropriate work-up, complex **4d** could be isolated as a colorless liquid. Yield: 4.67 g (7.6 mmol, 76 % based on **1d**). Elemental analysis: Calcd. for C₃₃H₆₁CuP₂O₂ (615.34) C, 64.41; H, 9.99. Found: C, 63.92; H, 9.70 %.

IR (NaCl): ν [cm⁻¹] 1640 (m) (CO, asym.), 1579 (s) ($\nu_{\text{C}=\text{C}}$), 1555 (vs) (CO, sym.). ¹H NMR (CDCl₃): δ 0.89 [t, 18 H, $J_{\text{HH}} = 6.8$ Hz, (CH₂)₃CH₃], 1.5 [m, 36 H, (CH₂)₃CH₃], 7.3–7.4 (m, 5 H, Ph), 6.82 (d, 1 H, CH, $J_{\text{HH}} = 15.8$ Hz), 7.47 (d, 1 H, CH, $J_{\text{HH}} = 15.8$ Hz). ¹³C{¹H} NMR (CDCl₃): δ 14.2 (CH₂CH₂CH₂CH₃), 25.0 (CH₂CH₂CH₂CH₃, $J_{\text{CP}} = 12.3$ Hz), 25.4 (CH₂CH₂CH₂CH₃, $J_{\text{CP}} = 12.8$ Hz), 27.4 (CH₂CH₂CH₂CH₃, $J_{\text{CP}} = 3.5$ Hz), 126.6 (=CH), 127.7 (Ph), 128.5 (Ph), 128.8 (Ph), 137.2 (Ph), 138.4 (=CH), 173.3 (CO₂). ³¹P{¹H} NMR (C₆D₆): δ -19.4.

Synthesis of [ⁿBu₃P]₃CuO₂CCH₃] (8a)

Complex **8a** was prepared by electrolysis. 274 mg (2.74 mmol, 0.16 mL) of acetic acid (**7a**), 2.05 mL (8.22 mmol) of **2**, and 0.38 mL (2.74 mmol) of triethylamine were dissolved in 60 mL of acetonitrile in a electrolysis cell equipped with copper electrodes. The reaction was preformed with a cell potential of 4.5 V at 40 °C over a period of 30 min and was continued with 3 V for 5.5 hours. Afterwards, the colorless solution was transferred to a 250 mL Schlenk tube and all volatiles were evaporated in *oil-pump* vacuum. Complex **8a** was isolated as an colorless oil. Yield: 1.90 g (2.60 mmol, 95 % based on **7a**). Elemental analysis: Calcd. for C₃₈H₈₄CuO₂P₃ (729.55) C, 62.56; H, 11.61. Found: C, 62.44; H, 11.83 %.

IR (NaCl): ν [cm⁻¹] 1575 (CO, asym.), 1464 (CO, sym.). ¹H NMR (CDCl₃): δ 0.91 (t, ³J_{HH} = 7.1 Hz, 27 H, P(CH₂)₃CH₃), 1.30 – 1.52 (m, 54 H, P(CH₂)₃CH₃), 2.00 (s, 3 H, C(O)CH₃). ¹³C{¹H} NMR (CDCl₃): δ 14.0 (P(CH₂)₃CH₃), 24.3 (C(O)CH₃), 24.7 (d, J_{CP} = 12 Hz, P(CH₂)₂CH₂CH₃), 26.0 (PCH₂CH₂CH₂CH₃), 27.7 (d, J_{CP} = 8 Hz, PCH₂(CH₂)₂CH₃), 176.1 (CO). ³¹P{¹H}-NMR [δ]: –26.2 (bs).

Synthesis of [ⁿBu₃P]₃CuO₂CCF₃] (8b)

Compound **8b** was synthesized by the appropriate method described above. As starting materials were used 290 mg (2.55 mmol, 0.19 mL) of trifluoroacetic acid (**7b**) and 1.91 mL (7.74 mmol) of **2**. The reaction was performed with a cell potential of 2.0 V at 40 °C over a period of 2.5 hours. Complex **8b** was isolated as an colorless oil. Yield: 1.95 g (2.49 mmol, 98 % based on **7b**). Elemental analysis: Calcd. for C₃₈H₈₁CuF₃O₂P₃ (783.51) C, 58.25; H, 10.42. Found: C, 58.45; H, 11.12 %.

IR (NaCl): ν [cm⁻¹] 1691 (CO, asym.), 1464 (CO, sym.). ¹H NMR (CDCl₃): δ 0.70 (t, ³J_{HH} = 7.2 Hz, 27 H, P(CH₂)₃CH₃), 1.05 – 1.42 (m, 54 H, P(CH₂)₃CH₃). ¹³C{¹H} NMR (CDCl₃): δ 14.1 (P(CH₂)₃CH₃), 25.1 (d, J_{CP} = 12 Hz, P(CH₂)₂CH₂CH₃), 25.5 (d, J_{CP} = 9 Hz, PCH₂CH₂CH₂CH₃), 27.2 (PCH₂(CH₂)₂CH₃), 117.2 (q, ¹J_{CF} = 292.4 Hz, CF₃), 161.5 (q, ²J_{CF} = 35.0 Hz, CO). ³¹P{¹H}-NMR [δ]: –22.9 (bs).

Synthesis of [ⁿBu₃P]₃CuO₂CCH₂Ph] (8c)

Complex **8c** was prepared as described for **8a**: 339 mg (2.49 mmol) of phenylacetic acid (**7c**), 1.86 mL (7.48 mmol) of **2**, and 0.35 mL (2.49 mmol) of triethylamine were reacted. The cell potential was 4.0 V at 40 °C over a period of 4.5 hours. Complex **8c** was isolated as a colorless oil. Yield: 1.95 g (2.42 mmol, 97 % based on **7c**). Elemental analysis: Calcd. for C₄₄H₈₈CuO₂P₃ × NEt₃ (906.83) C, 66.22; H, 11.45; N, 1.55. Found: C, 66.44; H, 11.83; N, 1.35 %.

IR (NaCl): ν [cm⁻¹] 1577 (CO, asym.), 1463 (CO, sym.). ¹H NMR (CDCl₃): δ 0.89 (t, ³J_{HH} = 6.6 Hz, 27 H, P(CH₂)₃CH₃), 1.00 (t, 9 H, NEt₃), 1.23 – 1.45 (m, 54 H, P(CH₂)₃CH₃), 2.50 (q, 6 H, NEt₃), 3.57 (s, 2 H, CH₂Ph), 7.08 – 7.36 (m, 5 H, Ph). ¹³C{¹H} NMR (CDCl₃): δ 11.6 (NEt₃), 14.0 (P(CH₂)₃CH₃), 24.8 (d, J_{CP} = 12 Hz, P(CH₂)₂CH₂CH₃), 25.7 (d, J_{CP} = 4 Hz, PCH₂CH₂CH₂CH₃), 27.3 (d, J_{CP} = 7 Hz, PCH₂(CH₂)₂CH₃), 44.2 (CH₂Ph), 46.3 (NEt₃), 125.7 (C/Ph), 128.0 (C/Ph), 129.6 (C/Ph), 138.2 (C/Ph), 176.1 (CO). ³¹P{¹H}-NMR [δ]: –26.2 (bs).

Synthesis of [ⁿBu₃P]₃CuO₂C(CH₂OCH₂)₃H] (8d)

Complex **8d** was synthesized as described above. 0.63 mL (3.53 mmol) of **7d**, 0.50 mL (3.53 mmol) of triethylamine, and 2.65 mL (10.6 mmol) of **2** were dissolved in 60 mL of acetonitrile. The reaction was performed with a cell potential of 4.0 V at 40 °C over a period of 1 h and then with 2.0 V for 4 hours. When a deposition of crystalline or black copper at the cathode was observed,

the reaction was finished. Afterwards, the colorless solution was transferred to a 250 mL Schlenk tube and all volatile materials were removed in *oil-pump* vacuum. Complex **8d** was obtained as a pale yellow oil. Yield: 2.94 g (3.47 mmol, 98 % based on **7d**). Elemental analysis: Calcd. for C₄₃H₉₄CuO₃P₃ (847.67) C, 60.93; H, 11.18. Found: C, 60.97; H, 11.70 %.

IR (NaCl): ν [cm⁻¹] 1607 (CO, asym.), 1463 (CO, sym.). ¹H NMR (CDCl₃): δ 0.88 (t, ³J_{HH} = 6.8 Hz, 27 H, P(CH₂)₃CH₃), 1.20 – 1.65 (m, 56 H, P(CH₂)₃CH₃), 3.34 (s, 3 H, OCH₃), 3.44 – 3.75 (m, 8 H, (OCH₂CH₂)₂), 4.01 (s, 2 H, O₂CCH₂). ¹³C{¹H} NMR (CDCl₃): δ 14.2 (P(CH₂)₃CH₃), 25.0 (d, J_{PC} = 12 Hz, CH₂CH₂CH₂CH₃), 26.1 (s, CH₂CH₂CH₂CH₃), 27.7 (d, J_{PC} = 6 Hz, CH₂CH₂CH₂CH₃), 59.3 (OCH₃), 70.5 ((OCH₂CH₂)₂), 70.6 ((OCH₂CH₂)₂), 70.8 ((OCH₂CH₂)₂), 71.0 ((OCH₂CH₂)₂), 72.3 (O₂CCH₂), 174.2 (CO). ³¹P{¹H}-NMR [δ]: –25.6 (bs).

Synthesis of [ⁿBu₃P]₃CuO₂CⁿC₄H₇O] (8e)

Complex **8e** was prepared by the same method as described for the synthesis of **8a**, whereby 0.61 mL (6.4 mmol) of tetrahydrofuran-2-carboxylic acid (**7e**), and 4.80 mL (19.2 mmol) of **2** were dissolved in 60 mL of acetonitrile. Reaction conditions: potential 4.0 V, reaction time 5 hours, temperature 40 °C. After appropriate work up, complex **8e** was obtained as a pale greenish oil. Yield: 4.54 g (5.83 mmol, 91 % based on **7e**). Elemental analysis: Calcd. for C₄₁H₈₈CuO₃P₃ (785.60) C, 62.68; H, 11.29. Found: C, 63.05; H, 11.34 %.

IR (NaCl): ν [cm⁻¹] 1608 (CO, asym.), 1463 (CO, sym.). ¹H-NMR [δ]: 0.87–0.99 (m, 27 H, P(CH₂)₃CH₃), 1.35–1.42 (m, 54 H, P(CH₂)₃CH₃), 1.81–2.05 (m, 2 H, OCH₂CH₂CH₂), 2.19–2.31 (m, 2 H, CH₂CH₂CHCO₂), 3.80–4.11 (m, 2 H, OCH₂CH₂), 4.39 (dd, ³J_{HH} = 6.0 Hz (*trans*), ³J_{HH} = 8.2 Hz (*cis*), 1 H, CH₂CHCO₂). ¹³C{¹H}-NMR [δ]: 13.9 (P(CH₂)₃CH₃), 24.8 (d, J_{PC} = 12 Hz, P(CH₂CH₂CH₂CH₃), 25.8 (PCH₂CH₂CH₂CH₃), 26.7 (PCH₂CH₂CH₂CH₃), 27.5 (C_β/C₄H₇O), 30.7 (C_β/C₄H₇O), 68.9 (C_α/C₄H₇O), 78.3 (C_α/C₄H₇O), 177.6 (CO₂). ³¹P{¹H}-NMR [δ]: –25.1 (bs).

Acknowledgements. Financial support from the Deutsche Forschungsgemeinschaft (International Research Training Group GRK 1215, “Materials and Concepts for Advanced Interconnects”), the Fonds der Chemischen Industrie, and the BASF AG, Ludwigshafen is gratefully acknowledged.

References

- [1] H. K. Shin, K. M. Chi, M. J. Hampden-Smith, T. T. Kodas, M. F. Paffett, J. D. Farr, *Chem. Mater.* **1992**, *4*, 788.
- [2] T. H. Baum, C. E. Larson, *Chem. Mater.* **1992**, *4*, 365.
- [3] A. Grodzicki, I. Łakomska, P. Piszczek, I. Szymańska, E. Szyłk, *Coord. Chem. Rev.* **2005**, *249*, 2232.
- [4] J. Li, R. Blewer, J. W. Mayer, *MRS Bull.* **1993**, *18*, 18.
- [5] T. L. Alford, J. Li, J. W. Mayer, S. Q. Wang, *Thin Solid Films* **1995**, *262*, VII.
- [6] P. L. Pai, C. H. Ting, *IEEE Electron Device Lett.* **1989**, *10*, 423.
- [7] T. T. Kodas, M. J. Hampden-Smith, *The Chemistry of Metal CVD VCH*, Weinheim **1994**.
- [8] A. Jain, K. M. Chi, H. K. Shin, J. Farkas, T. T. Kodas, M. J. Hampden-Smith, *Semicond. Int.* **1993**, *16*, 128.
- [9] H. K. Shin, M. J. Hampden-Smith, E. N. Duesler, *Can. J. Chem.* **1992**, *70*, 2954.
- [10] D. B. Beach, F. K. Legoues, C. K. Hu, *Chem. Mater.* **1990**, *2*, 216.
- [11] a) G. Papadimitropoulos, D. Davazoglou, *Surf. Coat. Technol.*, **2007**, *201*, 8935; b) D. Garg, H. Cheng, J. A. T. Norman, E. Machado, P. Ordejon, *US Pat. Appl. Publ.* **2004**, US

- 20040234704; c) M. Joulaud, C. Angekört, P. Doppelt, T. Mourier, D. Mayer, *Microelectron. Eng.* **2002**, *64*, 107.
- [12] H. Lang, D. S. A. George, G. Rheinwald, *Coord. Chem. Rev.* **2000**, *206–207*, 101.
- [13] N. A. Clinton, J. K. Kochi, *J. Organomet. Chem.* **1972**, *42*, 229.
- [14] D. J. Darensbourg, M. W. Holteamp, B. Khandelwal, J. H. Reibenspies, *Inorg. Chem.* **1994**, *33*, 531–537.
- [15] B. Goinez-lor, M. Iglesias, C. Cascales, E. Gutierrez-Puebla, M. A. Monge, *Chem. Mater.* **2001**, *13*, 1364.
- [16] M. B. Dines, *Inorg. Chem.* **1972**, *11*, 2949.
- [17] A. Bayler, A. Schier, H. Schmidbaur, *Inorg. Chem.* **1998**, *37*, 4353.
- [18] T. Miyaji, Z. Xi, K. Nakajima, T. Takahashi, *Organometallics* **2001**, *20*, 2859.
- [19] E. Szytk, P. Piszczek, A. Grodzicki, M. Chaberski, A. Golin-ski, J. Szatkowski, T. Blaszczyk, *Chem. Vap. Deposition* **2001**, *7*(3), 111.
- [20] H. Schmidt, Y. Shen, M. Leschke, Th. Haase, K. Kohse-Höinghaus, H. Lang, *J. Organomet. Chem.* **2003**, *669 (1-2)*, 25.
- [21] a) F. A. Cotton, W. H. Tbsley, *Inorg. Chem.* **1982**, *21*, 300; b) M. A. Gil, W. Maringgele, S. Dechert, F. Meyer, *Z. Anorg. Allg. Chem.* **2007**, *633*, 2178.
- [22] J. N. Van Niekerk, F. R. L. Schoening, J. H. Talbot, *Acta Crystallogr.* **1953**, *6*, 720.
- [23] N. W. Alcock, V. L. Tracy, *Acta Crystallogr.* **1971**, *B35*, 406.
- [24] Y. B. Koh, G. G. Christoph, *Inorg. Chem.* **1978**, *17*, 2590.
- [25] J. E. Davis, B. M. Gatehouse, K. S. Murray, *J. Chem. Soc., Dalton Trans.* **1973**, 2523.
- [26] A. V. R. Varrier, R. S. Krishnan, *Spectrochim. Acta*, Part A, **1971**, 1243.
- [27] R. G. Griffin, J. D. Ellett, Jr. M. Mehring, J. G. Bullitt, J. S. Wagh, *J. Chem. Phys.* **1972**, *57*, 2147.
- [28] G. B. Deacon, R. J. Phillips, *Coord. Chem. Rev.* **1980**, *33*, 227.
- [29] K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*, Wiley, New York, **1963**, 198.
- [30] W. Klemperer, G. C. Pimentel, *J. Chem. Phys.* **1954**, *22*, 1399.
- [31] C. D. Garner, B. Hughes, *Adv. Inorg. Chem. Radiochem.* **1975**, *17*, 1.
- [32] D. A. Edwards, R. Richards, *J. Chem. Soc., Dalton Trans.* **1975**, 637.
- [33] M. Leschke, *Ph. D. Thesis*, Chemnitz, Technical University, Germany **2002**, <http://archiv.tu-chemnitz.de/pub/2002/0031>.
- [34] Y. Shen, H. Pritzkow, B. Walfort, T. Ruffer, H. Lang, *Acta Crystallogr.* **2004**, *E60*, m91.
- [35] E. Szyk, I. Lakomska, A. Grodzicki, *Thermochim. Acta* **1993**, *223*, 207.
- [36] G. A. Bowmaker, Effendy, J. V. Hanna, P. C. Healy, J. C. Reid, C. E. F. Rickard, A. H. White, *J. Chem. Soc., Dalton Trans.* **2000**, 753.
- [37] a) Z. Yuan, N. H. Dryden, J. J. Vittal, R. J. Puddephatt, *Chem. Mater.* **1995**, *7*, 1696; b) S. Berger, S. Braun, H. O. Kalinowski, *NMR-Spektroskopie von Nichtmetallen*, Georg Thieme Verlag, Stuttgart, **1993**, 88, and references therein.
- [38] H. Schmidt, *Diploma thesis*, TU Chemnitz, Germany, **2002**.
- [39] A. Furuya, N. Hosoi, Y. Ohshita, *J. Appl. Phys.* **1995**, *78*, 5989.
- [40] F. Fillot, Zs. Tökei, G. P. Beyer, *Surf. Sci.* **2007**, *601*, 986.
- [41] D. A. Edwards, R. Richards, *J. Chem. Soc., Dalton Trans.* **1973**, 2463.