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Phosphane copper(I) formate complexes stabilized by formic acid and acetic acid through $H \cdots O \cdots H$ bridges

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Abstract

The formate copper(I) complex $[(P(C_6H_2CH_2NMe_2-2)_3)CuO_2CH]$ (3) is accessible by the reaction of equimolar amounts of $P(C_6H_2CH_2NMe_2-2)_3$ (1) with $[CuO_2CH]$ (2). When 3 is treated with HO₂CH (4) or HO₂CMe (6), molecules $[(P(C_6H_2CH_2NMe_2-2)_3)CuO_2CH \cdot HO_2CMe]$ (7), respectively, are formed.

In 3, 5, and 7 the phosphane unit is acting as a tripodal PN_2 ligand as it could be shown by ¹H NMR spectroscopy. IR studies showed that the formate building block in 3 and in its solvated form in 5 and 7 is σ -bonded by one oxygen atom to Cu(I). The thermal decomposition behavior of 3 is discussed.

The solid state structure of **5** is reported. The crystal structure consists of two chemical identical crystallographic independent molecules. In **5** a four-coordinated copper(I) ion is present with the $P(C_6H_4CH_2NMe_2-2)_3$ ligand occupying three of the coordination sites, while the 4th site is occupied by the formate anion. One of the two formic acid molecules in **5** is thereby hydrogen-bonded to the CuO₂CH entity, while the second HCO₂H molecule forms a N···H hydrogen bridge with the non-coordinating *ortho*-substituent Me₂NCH₂.

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1. Introduction

Copper(I) carboxylates are known since quite some time and have prooved to be very useful as reagents in organic, organometallic and metal–organic synthesis [1–3]. In general, copper(I) carboxylates are highly aggregated species in which the carboxylic units are μ -bridging the respective copper(I) ions. Complexes of higher nuclearity can be transferred to lower aggregated assemblies on addition of Lewis-bases L (L = neutral or ionic 2-electron donor) [4,5]. Depending on the ratio of L, cubane- or staircase-like (1:1), dimeric (1:2) or monomeric (1:3) [L_nCuO₂R] complexes (R = singly-bonded organic ligand, H; n = 1, 2, 3; L = phosphane, phosphate, alkyne, alkene) are formed. However, only less is known about the solid state structure of the latter molecules [1–5]. More recently, copper(I) and silver(I) carboxylates have gained an inherent interest, since such complexes play an important role, for example, as catalysts in organic transfer reactions and in the isomerization of olefines [2,3]. In addition, these species can successfully be used as precursors in the deposition of metal films on (structured) oxidized silicon wafers by applying chemical vapor deposition (CVD), atomic layer deposition (ALD), or spin-coating processes [6–8]. Decomposition studies both in the solid state and in the gas phase were carried out [9].

As the simplest carboxylate ligand, the formate ion HCO_2^- is of importance in metal–organic chemistry, since copper(I) formats are of interest with respect to some important industrial reactions involving the synthesis and selective partial oxidation of methanol, which may be carried out over copper and silver catalysts [10]. Also, carbox-

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ylic- and formate-functionalized metal complexes can be used as precursors for the preparation of self-assembled monolayers [11]. Considering these topics, it is of interest to study Lewis-base copper(I) formates involving coordinated formic acid or other carboxylic acids, since [CuO₂CH] in its non-coordinated form is very sensitive to moisture, oxygen and temperature.

We report here on the synthesis and characterization of the phosphane copper(I) formate $[(P(C_6H_4CH_2NMe_2-2)_3)-CuO_2CH]$ and its reaction behavior towards formic and acetic acid.

2. Experimental

2.1. General methods

All reactions were carried out under an atmosphere of purified nitrogen (O2 traces: CuO catalyst, BASF AG, Ludwigshafen; H₂O: molecular sieve 4 Å, Aldrich) using standard Schlenk techniques. Diethyl ether was purified by distillation from sodium/benzophenone ketyl and acetonitrile by distillation from calcium hydride. Infrared spectra were recorded with a Perkin-Elmer FT-IR 1000 spectrometer. ${}^{1}H$, ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectra were recorded with a Bruker Advance 250 spectrometer operating in the Fourier transform mode. ¹H NMR spectra were recorded at 250.130 MHz (internal standard, relative to CDCl₃, δ 7.26); ${}^{13}C{}^{1}H$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to $CDCl_3$, δ 77.16); ³¹P{¹H} NMR spectra were recorded at 101.202 MHz in CDCl₃ with P(OMe)₃ as external standard (δ 139.0, relative to 85% H₃PO₄, δ 0.00). Chemical shifts are reported in δ units (ppm) downfield from tetramethylsilane ($\delta = 0.0$) with the solvent as the reference signal. Melting points were determined using sealed nitrogen purged capillaries on a Büchi MP 510 melting point apparatus. Microanalyses were performed by the Institute of Organic Chemistry, Chemnitz, Technical University.

3. General remarks

 $P(C_6H_4CH_2NMe_2-2)_3$ (1) [12] and $[CuO_2CH]$ (2) [13] were prepared by published procedures. All other chemicals were purchased from commercial providers and were used as received.

3.1. Synthesis of
$$[(P(C_6H_4CH_2NMe_2-2)_3)CuOC(O)H]$$

(3)

 $P(C_6H_4CH_2NMe_2-2)_3$ (1) (0.88 g, 2.0 mmol) was dissolved in 20 mL of dichloromethane, and [CuO₂CH] (2) (0.22 g, 2.0 mmol) suspended in 20 mL of dichloromethane was slowly added at -20 °C. After 2 h of stirring at this temperature, the reaction solution was filtered through a pad of Celite. Evaporation of all volatile materials in *oilpump vacuum* gave the title compound as a yellow solid. Yield: 0.94 g (1.7 mmol, 87% based on 1).

M.p.: 197–199 °C (decomp.). Elemental *Anal.* Calc. for $C_{28}H_{37}CuN_3O_2P$ (542.14): C, 62.03; H, 6.88; N, 7.75. Found: C, 61.78; H, 6.75; N, 7.46%. IR (KBr) ν [cm⁻¹]: 3053 (m), 2966 (m), 2939 (m), 2857 (m), 2818 (s), 2775 (s), 2709 (w), 1607 (s) (CO, asym.), 1458 (s), 1364 (m) (CO, sym.), 1309 (m), 1264 (m), 1172 (m), 1124 (w), 1097 (w), 1028 (s), 1003 (m), 840 (m), 756 (s), 735 (s), 531 (w), 501 (w), 484 (w). ¹H NMR (CDCl₃): δ 2.29 (s, 18H, CH₃), 3.47 (d, ²J_{HH} = 12.2 Hz, 3H, CH₂), 3.82 (d, ²J_{HH} = 12.2 Hz, 3H, CH₂), 6.76 (dd, ³J_{HH} = 7.7 Hz, ⁴J_{PH} = 7.7 Hz, 3H, C₆H₄), 7.17–7.36 (m, 9H, C₆H₄), 8.42 (s, 1H, CH). ¹³C{¹H} NMR (CDCl₃): δ 47.3 (CH₃), 65.3 (d, ³J_{PC} = 36.8 Hz, CH₂), 128.5 (d, J_{PC} = 4.3 Hz, C₆H₄), 130.2 (C₆H₄), 131.7 (d, J_{PC} = 25.2 Hz, C₆H₄), 132.3 (d, J_{PC} = 8.2 Hz, C₆H₄), 133.9 (C₆H₄), 142.1 (d, J_{PC} = 18.1 Hz, ⁱC/C₆H₄), 168.5 (CO₂H). ³¹P{¹H} NMR (CDCl₃): δ –33.1.

3.2. Synthesis of $[(P(C_6H_4CH_2NMe_2-2)_3)CuOC(O)H \cdot 2HOC(O)H]$ (5)

Formic acid (4) (0.184 g, 4.0 mmol) dissolved in 10 mL was of dichloromethane drop-wise added to $[(P(C_6H_4CH_2NMe_2-2)_3)CuO_2CH]$ (3) (1.08 g, 2.0 mmol) dissolved in 20 mL of dichloromethane at 0 °C. After 1 h of stirring at this temperature, the reaction solution was filtered through a pad of Celite. Evaporation of all volatiles in oil-pump vacuum afforded 5 as a yellow solid. Yield: 1.05 g (1.66 mmol, 83% based on 1). Single crystals of 5 suitable for X-ray structure determination could be obtained by slowly cooling a dichloromethane solution containing 5 to -20 °C.

M.p.: 105-106 °C (decomp.). Elemental Anal. Calc. for C₃₀H₄₁CuN₃O₆P (634.19): C, 56.82; H, 6.52; N, 6.63. Found: C, 56.38; H, 6.46; N, 6.51%. IR (KBr) v [cm⁻¹]: 3453 (m), 3060 (m), 2997 (m), 2959 (s), 2924 (s), 2778 (s), 2834 (s), 2777 (m), 2703 (m), 2679 (m), 1692 (s) (CO asym., formic acid), 1598 (vs) (CO asym., formate), 1496 (s), 1443 (m), 1377 (m) (CO sym., formate), 1327 (m), 1309 (m), 1268 (m), 1207 (s) (CO, sym., formic acid), 1172 (m), 1148 (m), 1129 (m), 1108 (m), 1076 (m), 1029 (m), 992 (m), 966 (m), 883 (m), 837 (m), 757 (vs), 735 (m), 701 (m), 531 (m), 504 (m), 483 (m), 465 (m), 440 (m). ¹H NMR (CDCl₃): δ 2.50 (s, 18H, CH₃), 3.43 (d, ${}^{2}J_{HH} = 10.2$ Hz, 3H, CH₂), 4.13 (d, ${}^{2}J_{HH} = 10.2$ Hz, 3H, CH₂), 6.77 (dd, ${}^{3}J_{HH} = 9.6$ Hz, ${}^{4}J_{\rm PH} = 9.6 \text{ Hz}, 3 \text{H}, C_{6}\text{H}_{4}), 7.26-7.55 \text{ (m, 9H, } C_{6}\text{H}_{4}),$ 12.24 (s, 2H, CO_2H), 8.38 (s, 2H, HO_2CH). ¹³C{¹H} NMR (CDCl₃): δ 46.5 (CH₃), 63.8 (d, J_{CP} = 10.6 Hz, CH₂), 129.8 (d, $J_{PC} = 4.3$ Hz, C₆H₄), 130.6 (d, $J_{PC} =$ 24.2 Hz, C₆H₄), 131.2 (C₆H₄), 133.0 (d, $J_{PC} = 7.7$ Hz, C₆H₄), 133.5 (C₆H₄), 139.6 (d, $J_{PC} = 19.1$ Hz, ${}^{i}C/C_{6}H_{4}$), 168.5 (H<u>C</u> O₂), 162.3 (H<u>C</u>O₂H). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta - 40.1.$

3.3. Structure determination and refinement of 5

X-ray structure measurement was performed with a BRUKER SMART CCD 1K diffractometer. Crystal data,

data collection and refinement parameters for **5** are given in Table 1. The unit cell was determined with the program SMART [14]. For data integration and refinement of the unit cell, the program SAINT [14] was used. Space group determination was done with XPREP [14]. The structure was solved with direct methods using SHELX-97 [15], the structure refinement was based on least-square methods based on F^2 with SHELX-97 [15]. All non-hydrogen atoms were fully refined in the calculated positions. The hydrogen atoms of the formate ion and of the formic acid building blocks were taken from the electron density difference map and refined freely. All other hydrogen atoms were positioned as riding on their neighboring atoms.

3.4. Synthesis of $[(P(C_6H_4CH_2NMe_2-2)_3)CuOC(O)H \cdot HOC(O)Me]$ (7)

Complex 7 was synthesized in the same manner as 5 (see above). Thus, HO₂CMe (6) (0.12 g, 2.0 mmol) was added to $[(P(C_6H_4CH_2NMe_2-2)_3)CuO_2CH](3)$ (1.08 g, 2.0 mmol). After appropriate work-up, complex 7 was obtained as a yellow solid. Yield: 1.0 g (1.7 mmol, 83% based on 3).

M.p.: 193–195 °C (decomp.). Elemental *Anal.* Calc. for $C_{30}H_{41}CuN_3O_4P$ (602.19): C, 59.84; H, 6.86; N, 6.98.

Table 1

Crystal data, collection and refinement parameters for 5

· /	1
Formula	$C_{30}H_{41}O_6PN_3$
Formula weight	634.17
Crystal dimensions (mm)	$0.45 \times 0.35 \times 0.25$
Crystal system	monoclinic
Space group	P2(1)/c
a (Å)	18.357(4)
b (Å)	19.577(4)
<i>c</i> (Å)	17.684(3)
β (°)	90.776(16)
$V(Å^3)$	6355(2)
Z	8
D_{calc} (g/cm ³)	1.326
Index ranges	$-22 \leq h \leq 22, -24 \leq k \leq 24,$
-	$-21 \leq l \leq 21$
<i>F</i> (000)	2672
μ (Mo K α) (cm ⁻¹)	7.82
Radiation, Mo Ka (Å)	$\lambda = 0.71073$
Temperature (K)	223(2)
$2\theta_{\max}$ (°)	52.00
Number of reflections measured	12486
Independent reflections observed	10416
$[I \ge 2\sigma(I)]$	
Number of refined parameters	779
$R_1 \left[I > 2\sigma(I) \right]^a$	0.0530/0.0429
$wR_2 [I > 2\sigma(I)]^b$	0.1384/0.1325
Goodness-of-fit on F^{2c}	1.060
$\Delta \rho_{\rm max} ({\rm e}^{{\rm \AA}-3})$	2.607
$\Delta \rho_{\rm min} (e^{{\rm \AA}-3})$	0.392
$(\Delta/\sigma)_{\rm max}$	0.083
	1/2

^a $R = \sum (||F_o| - |F_c||) / \sum |F_o|; \ wR_2 = \left[\sum (w(F_o^2 - F_c^2)^2) / \sum (wF_o^4) \right]^{1/2}.$ ^b $w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 4.1728P], \ P = (F_o^2 + 2F_c^2)/3.$ ^c $S = \left[\sum w(F_o^2 - F_c^2)^2 \right] / (n - p)^{1/2} \ (n = \text{number of reflections, } p = \text{parameters used}).$

Found: C, 59.54; H, 6.58; N, 6.74%. IR (KBr) v [cm⁻¹]: 3433 (w), 3054 (m), 2964 (s), 2936 (m), 2857 (s), 2812 (s), 2764 (s), 2711 (m), 1613 (s) (CO asym., acetic acid), 1583 (s) (CO asym., formate), 1457 (s), 1440 (s), 1365 (s) (CO sym., formate), 1306 (m), 1264 (s) (CO asym., acetic acid), 1171 (m), 1125 (w), 1097 (w), 1025 (s), 1001 (m), 880 (w), 840 (s), 754 (s), 730 (s), 702 (w), 673 (w), 531 (w), 500 (w), 488 (w). ¹H NMR (CDCl₃): δ 2.07 (s, 3H, CH₃), 2.40 (s, 18H, CH₃), 3.45 (d, ${}^{2}J_{HH} = 10.2$ Hz, 3H, CH₂), 4.01 (d, ${}^{2}J_{HH} = 10.2$ Hz, 3H, CH₂), 6.76 (dd, ${}^{3}J_{HH} =$ 7.8 Hz, ${}^{4}J_{\rm PH} = 7.8$ Hz, 3H, C₆H₄), 7.20–7.41 (m, 9H, C₆H₄), 8.40 (s, 1 H, CHCO₂), 12.98 (s, 1H, MeCO₂H). ¹³C{¹H} NMR (CDCl₃): δ 23.4 (MeCO₂H), 47.1 (Me₂N), 64.5 (d, ${}^{3}J_{PC} = 36.8 \text{ Hz}$, CH₂), 129.0 (d, $J_{PC} = 4.3 \text{ Hz}$, C_6H_4), 130.7 (C_6H_4), 132.6 (d, $J_{PC} = 8.0$ Hz, C_6H_4), 133.7 (C₆H₄), 141.1 (d, $J_{PC} = 18.3$ Hz, ${}^{IC}/C_{6}H_{4}$), 168.9 (H<u>C</u>O₂), 176.8 (Me<u>C</u>O₂H). ${}^{31}P{}^{1}H{}$ NMR (CDCl₃): $\delta - 31.7$.

4. Results and discussion

4.1. Synthesis

The phosphane copper(I) formate $[(P(C_6H_4CH_2NMe_2-2)_3)CuOC(O)H]$ (3) is accessible by treatment of $P(C_6H_4CH_2NMe_2-2)_3$ (1) with 1 equiv. of $[CuO_2CH]$ (2) in dichloromethane or tetrahydrofuran as solvent at $-20 \degree C$ (Eq. (1)). After appropriate work-up, complex 3 could be isolated as a yellow solid in 87% yield (Section 2).



Complex **3** is obtained in solvent free form and hence, is the first example in copper(I) formate chemistry without a solvent molecule attached to copper(I). All other so far synthesized Lewis-base copper(I) formats include at least half of a solvent molecule, *i.e.* EtOH, which forms a $H \cdots O \cdots H$ hydrogen bridge with the CuOC(O)H core [16]. The stability of **3** is related to phosphane **1**, since this ligand acts as a multipodal protecting group and stabilizes the copper(I) formate. The phosphorus atom and two of the three Me₂NCH₂ ortho-substituents are datively-bonded to the Cu(I) ion [1]. Due to this bonding motif, the group-11 metal ion possesses coordination number 4 and hence, counts to 18-valence electrons.

While 3 is fairly stable to oxygen and moisture, even more stable molecules can be obtained, when 3 is subsequently reacted with formic acid (4) (Eq. (2)) and acetic acid (6) (Eq. (3)), respectively.

Treatment of **3** with an excess of HCO_2H (**4**) in dichloromethane as solvent produced [($P(C_6H_4CH_2NMe_2-2)_3$)-CuOC(O)H · 2HOC(O)H] (**5**) which is the solvated form of **3** at room temperature. Complex **5** could be isolated in the form of yellow crystals after crystallization from dichloromethane at room temperature.



In 5, one HCO₂H molecule solvates the copper(I) formate entity [CuOC(O)H], while the second formic acid is hydrogen-bonded to the free MeNCH₂ *ortho*-substituent through $H \cdots O \cdots H$ bond formation.

When acetic acid (6) is used, $[(P(C_6H_4CH_2NMe_2-2)_3)-CuOC(O)H \cdot HOC(O)Me]$ (7) is formed in which one MeCO₂H molecule is hydrogen-bonded to the keto-oxygen atom of the copper formate building block (Eq. (3)). The yield is 83% (Section 2). This differs from 5, where two carboxylic acids are coordinated to the phosphane copper(I) formate core (vide supra). However, a compound similar to 5 in which one of the three Me₂NCH₂ units is hydrogen-bridged by a carboxylic acid could not be isolated for 7 even, when 3 is reacted with an excess of MeCO₂H.



After appropriate work-up, complexes **3**, **5**, and **7** could be isolated as yellow crystalline materials. They are soluble in most common polar organic solvents such as tetrahydro-furan, diethyl ether, and dichloromethane.

A further method for the preparation of a phosphine copper formate is the insertion of carbon dioxide into a Cu–H bond in, for example, hexanuclear $[(Ph_3P)CuH]_6$ [5,17]. This prompted us to study the thermolysis of, *e.g.* **3**. On heating **3** to temperatures around 200 °C, gas evolution was observed and yellow colored **3** darkend to give $P(C_6H_4CH_2NMe_2-2)_3$ (1) along with elemental copper (Scheme 1). This shows that most probably **3** decarboxylates to give $[(P(C_6H_4CH_2NMe_2-2)_3)CuH]$ which then eliminates H_2 to produce copper along with **1**. The latter decomposition is also favoured in, for example, heterobimetallic organometallic π -tweezer chemistry. Here it was found that on heating $\{[Ti](\mu-\sigma,\pi-C \equiv CR)_2\}CuO_2CR'$ $[Ti] = (\eta^5-C_5H_4SiMe_3)_2Ti; (R, R' = singly-bonded organic group), CO₂ is eliminated to give the bis(alkynyl)titano-$



Scheme 1. Thermolysis of **3** $(P(^N)_3 = P(C_6H_4CH_2NMe_2-2)_3)$.

cene-stabilized copper(I) organyls {[Ti](μ - σ , π -C \equiv CR)₂}-CuR' [18]. Another favoured decomposition route for **3** is the elimination of the phosphine P(C₆H₄CH₂NMe₂-2)₃ to yield copper formate [CuO₂CH] which subsequently eliminates CO₂ and H₂ to give Cu(0) (Scheme 1). This decomposition path is also possible [17], although we could not isolate [(P(C₆H₄CH₂NMe₂-2)₃)CuH].

Decarboxylation and dehydrogenation of 3 is also observed, when 3 is refluxed in toluene or mesitylene, whereby elemental copper deposited at the Schlenk walls. On cooling such solutions to room temperature, colorless crystals of 1 precipitated.

4.2. Characterization

Complexes 3, 5, and 7 gave satisfactory elemental analyses. They were characterized by FT-IR, ${}^{1}H$, ${}^{13}C{}^{1}H$ and ${}^{31}P{}^{1}H$ NMR spectroscopy (Section 2). The solid state structure of 5 was established by single X-ray structure determination.

In the IR spectra of 3, 5, and 7, characteristic absorptions are found between 1200 and 1700 cm^{-1} for the formate, formic acid and acetic acid groups (Table 2).

Distinct $v(CO_2)$ frequencies for the copper formate unit in 3, 5, and 7 are found at 1607 and 1364 cm⁻¹ for 3, 1598 and 1377 cm⁻¹ for 5 and 1583 and 1365 cm⁻¹ for 7, whereby the frequencies at ca. 1600 cm⁻¹ can be assigned to the asymmetric and those at ca. 1360 cm⁻¹ to the symmetric O–C–O stretching modes of the coordinated CO₂H⁻

Table 2 Characteristic IR spectral frequencies for 3, 5, and 7 $[cm^{-1}]^a$

Compound	Formate		Formic/acetic acid	
	$v_{as}(CO_2)$	$v_{s}(CO_{2})$	$v_{as}(CO_2)$	$v_{\rm s}({\rm CO}_2)$
3	1607	1364		
5	1598	1377	1692	1207
7	1583	1365	1613	1264

^a $\Delta = v_{as} - v_s$; as = asymmetric, s = symmetric.

ion [16]. These absorptions appear at values which are typical for σ -bonded formates in transition metal chemistry. The separation Δ ($\Delta = v_{as} - v_{sym}$; as = asymmetric, sym = symmetric) allows to indicate if the formate unit is monodentate or bidentate bound to copper(I) [19], whereby the monodentate binding increases Δ between the v(CO₂) frequencies relative to the values of the free formate taken as those of the respective sodium ($\Delta = 241 \text{ cm}^{-1}$) [19] or potassium salts ($\Delta = 233 \text{ cm}^{-1}$). [20,21] This is also found for **3**, **5**, and **7** ($\Delta = 243$ (**3**), $\Delta = 221$ (**5**), $\Delta = 218 \text{ cm}^{-1}$ (7)) and is similar for, *e.g.* [(Ph₃P)₂CuO₂CH] ($\Delta = 231 \text{ cm}^{-1}$) [5a,16,22].

The CO₂ frequencies of the solvated formic acid molecules in **5** are observed at 1692 and 1207 cm⁻¹, respectively. The difference Δ (485 cm⁻¹) lies between the data characteristic for free formic acid (671 cm⁻¹) [23] and, for example, for Na[H(HCO₂)₂] (439 cm⁻¹), [24] but is typical to values found in the H-bridged formic acid dimers [HCO₂H]₂ (524 cm⁻¹) [25], [(PPh₃)₃CuOC(O)H · HCO₂H] [16] and [(PPh₃)₂AgOC(O)H · 2HCO₂H] [16,26].

In the case of "weak" to "medium" H bonds of general type A–H···B (v(AH)), an absorption band between 2000 and 3500 cm⁻¹ occurs, while for "strong" to "very strong" hydrogen bonds, very broad absorptions are observed below 1600 cm^{-1} [27]. This is illustrated by the following systems: in $[HCO_2H]_2$, a hydrogen-bonded O···O distance of 2.703 Å [28], $v(OH) = 2570-3490 \text{ cm}^{-1}$ (with the maximum at ca. 3100 cm^{-1}) is typical [26], while for K[H- $(O_2CH)_2$ an $O \cdots O$ bond separation of 2.45 Å and a broad v(OH) vibration with a maximum at 1400 cm⁻¹ is found [24,29]. A correlation of the v(OH) frequencies and the $O \cdots O$ bonds based on the above results, gives a predicted position of the v(OH) mode in $[(P(C_6H_4CH_2NMe_2-2)_3) CuO_2CH \cdot 2(HCO_2H)$] (5) at 1469 cm⁻¹ and 1440 cm⁻¹, respectively. The same is true for $[(P(C_6H_4CH_2NMe_2-2)_3) CuO_2CH \cdot HOC(O)Me$ (7). The very weak absorptions at 1974 cm^{-1} (5) and 1964 (7) can be assigned to the v(OH) vibration.

The ¹H NMR spectra of **3**, **5**, and **7** show well-resolved resonance signals and are consistent with the empirical formula $[(P(C_6H_4CH_2NMe_2)_3)CuO_2CH(HOC(O)R)_n]$ (**5**: n = 2, R = H; **7**: n = 1, R = Me). Characteristic for **3** is the appearance of a distinct signal at 8.42 ppm which can be assigned to the formate CH hydrogen atom. This proton can be detected at 8.38 ppm for **5** and at 8.40 ppm for **7**. The ¹H NMR spectra of **5** and **7** show for their solvated RCO₂H entities (R = H, CH₃), two typical signals at 8.40 (CH) and 12.24 ppm (HO) for **5** and at 2.57 (CH₃) and 12.98 ppm (HO) for **7**. In addition to the O₂CH and HO₂CR protons, the resonance signals for the P(C₆H₄-CH₂NMe₂-2)₃ moiety are observed in the range characteristic for this type of ligand [30].

In the ${}^{13}C{}^{1}H$ NMR spectra of 3, 5, and 7, the formate building block gives rise to a very characteristic resonance signal at ca. 168.5 ppm. In respect to the appropriate noncoordinated formic acid (171.3 ppm), an up-field shift of ca. 3 ppm is observed. For 5 two distinct resonances are observed at δ 162.3 and 168.5, which can be assigned to the coordinated formate ion and the formic acid solvate molecule. A similar behavior is found for 7. The ¹³C{¹H} NMR spectrum of the latter complex consists of two sharp resonance signals at 168.9 ppm (for the coordinated formate ion) and 176.8 ppm (for the sp²-hybridized carbon atom) of the MeCO₂H solvate molecule. The CH₃ entity is found at 23.4 ppm.

The coordination of $P(C_6H_4CH_2NMe_2-2)_3$ to copper(I) is nicely confirmed by ³¹P{¹H} NMR spectroscopy. For **3** and **5** a singlet appears at -33.1 (3) and -31.7 ppm (5) which is downfield-shifted (1: -37.2 ppm) compared with the starting material **1** [12]. In contrast to this finding it is of interest to note that for **7**, a up-field shift is observed (-40.1 ppm).

4.3. Solid state structure of 5

Single crystals of $[(P(C_6H_4CH_2NMe_2-2)_3)CuO_2CH \cdot 2(HOOCH)]$ (5) could be grown by slowly cooling a saturated dichloromethane solution containing 5 to -20 °C. The result of the X-ray structure analysis of 5 is depicted in Fig. 1. Selected bond distances (Å) and bond angles (°) are given in Table 3. Crystal data as well as collection and refinement parameters are summarized in Table 1 (Section 2).

Complex 5 crystallizes in the monoclinic space group $P2_1/c$. The asymmetric unit comprises two independent molecules (5a and 5b). In 5, a four-coordinated copper(I)



Fig. 1. ORTEP plot (50% probability level) of the molecular structure of one (5a) of the two crystallographically independent molecules of 5 showing the atom numbering scheme.

Table 3 Selected bond distances (Å) and angles (°) of the two independent molecules of ${\bf 5}^a$

5a		5b	
Bond distances			
Cu(1)–O(1)	2.041(2)	Cu(2)–O(7)	2.043(2)
Cu(1)–N(1)	2.127(2)	Cu(2)–N(4)	2.174(2)
Cu(1)-N(2)	2.172(2)	Cu(2)–N(5)	2.151(2)
Cu(1)–P(1)	2.1839(8)	Cu(2)–P(2)	2.1859(8)
O(1)-C(28)	1.254(3)	O(7)–C(58)	1.249(4)
O(2)-C(28)	1.242(4)	O(8)-C(58)	1.242(4)
O(3)-C(29)	1.294(4)	O(9)-C(59)	1.305(4)
O(4)-C(29)	1.163(4)	O(10)-C(59)	1.184(4)
O(5)-C(30)	1.235(4)	O(11)-C(60)	1.217(4)
O(6)-C(30)	1.189(6)	O(12)–C(60)	1.217(4)
Bond angles			
O(1)-Cu(1)-P(1)	130.82(6)	O(7)-Cu(2)-P(2)	129.58(6)
O(1)-Cu(1)-N(1)	102.18(9)	O(7)-Cu(2)-N(4)	106.24(9)
O(1)-Cu(1)-N(2)	106.26(9)	O(7)-Cu(2)-N(5)	104.53(9)
N(1)-Cu(1)-N(2)	121.66(9)	N(4)-Cu(2)-N(5)	121.18(9)
N(1)-Cu(1)-P(1)	99.06(6)	N(4)-Cu(2)-P(2)	99.37(6)
N(2)-Cu(1)-P(1)	99.08(7)	N(5)-Cu(2)-P(2)	97.79(6)
C(1)-P(1)-C(10)	103.7(1)	C(40)-P(2)-C(31)	103.0(1)
C(1)–P(1)–C(19)	104.8(1)	C(40)-P(2)-C(49)	103.9(1)
C(19)-P(1)-C(10)	104.8(1)	C(31)-P(2)-C(49)	104.2(1)
C(1)-P(1)-Cu(1)	109.80(8)	C(40)-P(2)-Cu(2)	110.50(9)
C(10)-P(1)-Cu(1)	104.08(9)	C(31)-P(2)-Cu(2)	104.07(8)
C(7)–N(1)–Cu(1)	111.4(2)	C(37)-N(4)-Cu(2)	109.1(2)
C(16)-N(2)-Cu(1)	108.8(2)	C(46)-N(5)-Cu(2)	111.9(2)
C(19)–P(1)–Cu(1)	127.35(8)	C(49)-P(2)-Cu(2)	128.43(8)
C(28)–O(1)–Cu(1)	124.2(2)	C(58)-O(7)-Cu(2)	121.2(2)
O(2)-C(28)-O(1)	127.0(3)	O(8)-C(58)-O(7)	126.9(3)
O(4)-C(29)-O(3)	123.5(3)	O(9)-C(59)-O(10)	125.6(3)
O(6)-C(30)-O(5)	127.5(5)	O(11)-C(60)-O(12)	126.7(4)

^a The estimated standard deviation(s) of the last significant digit are shown in parentheses.

ion is present with the $P(C_6H_4CH_2NMe_2-2)_3$ ligand occupying three of the coordination sites (PNN) and the formate anion binds through one oxygen atom to the 4th site, forming a distorted tetrahedral environment around copper. The range of the O–Cu–P angles are between 129.58(6) and 130.82(6)° (Table 3) which are larger than that of the ideal tetrahedron angle, while the angles of O–Cu–N (between 102.18(9) and 106.24(9)°) and N–Cu–P (between 97.79(6) and 99.37(6)°) are smaller (Table 3).

Table 4

Selected bond distances (Å) and angles (°) of the hydrogen bonds of molecules 5a and 5b

$D - H \cdot \cdot \cdot A^a$	D–H	$H{\cdots}A$	$D – H \cdot \cdot \cdot A$	D–H···A
Molecule 5a				
$O(2)-H(2H)\cdots O(3)$	1.13(7)	1.43(7)	2.551(3)	168(7)
$N(3)-H(3N)\cdots O(5)$	0.90(3)	1.74(3)	2.618(3)	166(3)
Molecule 5b				
$O(9)-H(9H)\cdots O(8)$	0.86(6)	1.71(6)	2.549(3)	167(5)
$N(6)-H(6N)\cdots O(11)$	1.01(3)	1.64(3)	2.637(3)	166(3)

^a D = donor atom; A = acceptor atom.

The O1–Cu1–P1 and O7–Cu2–P2 angles with 130.82(6) and 129.58(6)° are larger than those observed for $[(Ph_3P)_3-CuO_2CH \cdot HO_2CH]$ (97.35(8)–109.77(9)°), reflecting the different coordination mode (see Table 4).

The Cu-P separations with 2.1839(8) and 2.1859(8) Å (Table 3) are shorter than those ones found in, for example, $[(Ph_3P)_3CuO_2CH \cdot HO_2CH]$ (2.315–2.332 Å) and $[(Ph_3P)_3-$ CuO₂CH · 0.5EtOH] (2.332–2.341 Å), respectively [16]. The Cu-N distances of 5 are located between 2.127(2) and 2.174(2) Å, somewhat shorter than those characteristic for, *i.e.* $[(P(C_6H_4CH_2NMe_2-2)_3)Cu_2Br_2]$ (N-Cu = 2.17(2)-2.32(2) Å) [30]. However, they are almost identical with the separations found in $[(P(C_6H_4CH_2NMe_2-2)_3)Cu_2Cl_2]$ (N-Cu = 2.103(5)-2.215(5) Å) [30] and $[(Ph_3P)_2Cu(2,3-1)]$ $Py(CO_2)(COOH))$] (N-Cu = 2.109(2) Å) [31]. The Cu-O bond lengths are 2.041(2) and 2.043(2) Å. Comparing the observed bond distances of 5 with a unidentate and chelate-bonded HCO_2^- ion confirms this finding. The copper-oxygen bond length decreases from 2.226(3) Å for a bidentate formate ligand to 2.04-2.08 Å for a σ-coordinated HCO_2^- anion [5a].

One of the two formic acid molecules in 5 is hydrogenbonded to the formate anion to form an assembly that is best described as a biformate anion $[H(HCO_2)_2]^-$. This anion is the simplest member of a class of hydrogen complexes, involving carboxylic acids and carboxylate anions [32]. Theoretical studies on this matter exist [27]. Hydrogen bonds display an almost continuous distribution of $O \cdots O$ separations between 2.36 and 3.69 Å and have been subdivided into classes which are referred to us as "very strong" (<2.5 Å), "strong" (2.5–2.65 Å), "medium" (2.65– 2.80 Å), or "weak" (>2.80 Å) [33]. For 5 the hydrogen bond of the $[H(HCO_2)_2]^-$ unit with $O2 \cdot \cdot \cdot O3 = 2.552(3)$ Å can be considered as a "strong" interaction. This can be compared with the hydrogen bond length observed for $K[H(HCO_2)_2]$, where a $O \cdots O$ separation of 2.45 Å is typical [29]. The hydrogen bond distance for the respective $[H(HCO_2)_2]^{-1}$ entity in $[(Ph_3P)_3CuO_2CH \cdot HO_2CH]$ with $O \cdots O =$ 2.529(5) Å is similar [16]. The second formic acid molecule present in 5 is also hydrogen-bonded, however, to the free nitrogen atom N3 of the P(C₆H₄CH₂NMe₂-2)₃ ligand (Fig. 1). The N3···O5 distance with 2.619(3) Å indicates that a strong hydrogen bond exists as well (vide supra). The apparent reduction in hydrogen bond strength compared to the free biformate ion $[H(HCO_2^-)_2]^-$ can be explained by a competition of the formate ion electron density between the copper(I) ion and the formic acid molecule.

5. Supplementary material

CCDC 626529 contains the supplementary crystallographic data for **5**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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