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Phosphane copper(I) formate complexes stabilized by formic acid and acetic acid through H···O···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 HO_2CH (**4**) or HO_2CMe (**6**), molecules [(P($C_6H_2CH_2NMe_2$-2)$_3$)$CuO_2CH \cdot 2HO_2CH$] (**5**) and [(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 CuO_2CH entity, while the second HCO_2H molecule forms a N···H hydrogen bridge with the non-coordinating *ortho*-substituent Me_2NCH_2.

Keywords: Copper(I) formate; Formic acid; Acetic acid; Phosphane; Hydrogen-bonding; Molecular recognition; X-ray structure analysis; Thermolysis

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_nCuO_2R] 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 [CuO_2CH] 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 (O_2 traces: CuO catalyst, BASF AG, Ludwigshafen; H_2O: 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. ^1H, $^{13}C\{^1H\}$ and $^{31}P\{^1H\}$ 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 $CDCl_3$, δ 7.26); $^{13}C\{^1H\}$ NMR spectra were recorded at 67.890 MHz (internal standard, relative to $CDCl_3$, δ 77.16); $^{31}P\{^1H\}$ NMR spectra were recorded at 101.202 MHz in $CDCl_3$ with $P(OMe)_3$ as external standard (δ 139.0, relative to 85% H_3PO_4, 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 [CuO_2CH] (**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 *oil-pump 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 ($CDCl_3$): δ 2.29 (s, 18H, CH_3), 3.47 (d, $^2J_{HH} = 12.2$ Hz, 3H, CH_2), 3.82 (d, $^2J_{HH} = 12.2$ Hz, 3H, CH_2), 6.76 (dd, $^3J_{HH} = 7.7$ Hz, $^4J_{PH} = 7.7$ Hz, 3H, C_6H_4), 7.17–7.36 (m, 9H, C_6H_4), 8.42 (s, 1H, CH). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 47.3 (CH_3), 65.3 (d, $^3J_{PC} = 36.8$ Hz, CH_2), 128.5 (d, $J_{PC} = 4.3$ Hz, C_6H_4), 130.2 (C_6H_4), 131.7 (d, $J_{PC} = 25.2$ Hz, C_6H_4), 132.3 (d, $J_{PC} = 8.2$ Hz, C_6H_4), 133.9 (C_6H_4), 142.1 (d, $J_{PC} = 18.1$ Hz, $^{i}C/C_6H_4$), 168.5 (CO_2H). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −33.1.

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

Formic acid (**4**) (0.184 g, 4.0 mmol) dissolved in 10 mL of dichloromethane was 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 $C_{30}H_{41}CuN_3O_6P$ (634.19): C, 56.82; H, 6.52; N, 6.63. Found: C, 56.38; H, 6.46; N, 6.51%. IR (KBr) ν [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 ($CDCl_3$): δ 2.50 (s, 18H, CH_3), 3.43 (d, $^2J_{HH} = 10.2$ Hz, 3H, CH_2), 4.13 (d, $^2J_{HH} = 10.2$ Hz, 3H, CH_2), 6.77 (dd, $^3J_{HH} = 9.6$ Hz, $^4J_{PH} = 9.6$ Hz, 3H, C_6H_4), 7.26–7.55 (m, 9H, C_6H_4), 12.24 (s, 2H, $CO_2\underline{H}$), 8.38 (s, 2H, $HO_2C\underline{H}$). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ 46.5 (CH_3), 63.8 (d, $J_{CP} = 10.6$ Hz, CH_2), 129.8 (d, $J_{PC} = 4.3$ Hz, C_6H_4), 130.6 (d, $J_{PC} = 24.2$ Hz, C_6H_4), 131.2 (C_6H_4), 133.0 (d, $J_{PC} = 7.7$ Hz, C_6H_4), 133.5 (C_6H_4), 139.6 (d, $J_{PC} = 19.1$ Hz, $^{i}C/C_6H_4$), 168.5 ($H\underline{C}\ O_2$), 162.3 ($H\underline{C}O_2H$). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ −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,