Organometallics **1998,** *17,* 210−215

Homoleptic Copper(I) Alkoxide and Phenoxide Clusters Stabilized by Intramolecular *π*-Coordination: Tetrameric *o*-Allylphenoxocopper(I) and Hexameric 2-Methyl-3-buten-2-oxocopper(I)

Mikael Håkansson,* Cesar Lopes, and Susan Jagner

Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden

Received July 30, 1997[⊗]

Built-in *π*-alkene functionalities have been found to yield homoleptic copper(I) phenoxide and alkoxide clusters exhibiting tetrameric cubane- or hexameric ribbon-shaped structures. While tetrameric *o*-allylphenoxocopper(I) (**1**) is remarkably stable, retains its structure in solution, and resists carbonylation, hexameric methylbutenoxocopper(I) (**2**) dissolves in such a way that oxo-bridged copper(I) is retained, whereas *π*-alkene−copper(I) coordination is destroyed, leaving copper(I) free to accept carbon monoxide as a ligand.

Introduction

Very few homoleptic alkoxides of copper(I) have been prepared[1] and in only one case, $[(\mathrm{CuO^tBu})_4]$, structurally characterized.[1c] While a homoleptic aryloxidocuprate(I) anion[2] has been reported, uncharged aryl oxides of copper(I) have, so far, been isolated only in the presence of stabilizing ancillary ligands, such as phosphines[2a,3a−e] or isocyanides,[2b,3f] or with stabilizing heteroatomic substituents.[3g] Very recently, however, we have prepared $[(\mathrm{CuOC_6H_3Ph_2})_4]$ from mesitylcopper(I) and 2,6-diphenylphenol and also isolated its carbonylation product, dimeric, μ_2-phenoxo-bridged $[(\mathrm{Cu(OC_6H_3Ph_2)(CO)})_2]$.[4]

Homoleptic arylcopper complexes predominantly form tetrameric, square-planar aggregates like structure I in Chart 1. For a long time it seemed as if the Cu-OR unit behaved in a similar manner (structure II), since the only crystal structure of a homoleptic copper(I) alkoxide without coordinating heteroatoms, *tert*-butoxocopper(I), displays a tetramer with a planar $\mathrm{Cu_4O_4}$ core,[1c] and the first crystal structure of a homoleptic aryloxocopper compound, namely, $[(\mathrm{CuOC_6H_3Ph_2})_4]$, also reveals the familiar square-planar tetranuclear structure II in Chart 1.

Chart 1

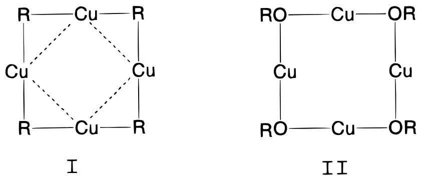
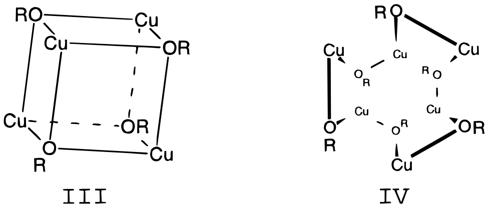


Chart 2



However, as a result of our efforts to study the effects—on stability, reactivity, and structure—of using ligands with built-in *π*-alkene functionalities, we can now report on a seemingly richer structural diversity among the homoleptic Cu-OR compounds as compared to the homoleptic Cu-R compounds. Thus, while *o*-vinylphenylcopper[5] in the solid state has the planar structure I (the vinyl group is not coordinated), we now demonstrate how *o*-allylphenoxocopper(I) and 2-methyl-3-buten-2-oxocopper(I) exhibit the new structures III and IV in Chart 2, attained by intramolecular *π*-alkene coordination.

Experimental Section

General. All operations were carried out under nitrogen or argon using standard Schlenk techniques. Solvents were distilled under nitrogen from sodium/benzophenone shortly prior to use (tetrahydrofuran, toluene, hexane/tetraglyme) or dried with molecular sieves (dichloromethane, chloroform). Copper(I) chloride was purified according to literature meth-

---

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1997.

(1) (a) Tsuda, T.; Hashimoto, T.; Saegusa, T. *J. Am. Chem. Soc.* **1972**, *94*, 658. (b) Greiser, T.; Weiss, E. *Chem. Ber.* **1976**, *109*, 3142. (c) Wilkinson, G.; Young, G. B.; Hursthouse, M. B.; Malik, K. M. A. *J. Chem. Soc., Dalton Trans.* **1980**, 1863.

(2) (a) Fiaschi, P.; Floriani, C.; Pasquali, M.; Chiesi-Villa, A.; Guastini, C. *Inorg.* Chem. **1986**, *25*, 462. (b) Fiaschi, P.; Floriani, C.; Pasquali, M.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc. Chem. Commun.* **1984**, 888.

(3) See, for example: (a) Reichle, W. T. *Inorg. Chim. Acta* **1971**, *5*, 325. (b) Kubota, M.; Yamamoto, A.; *Bull. Chem. Soc. Japan* **1978**, *51*, 2909. (c) Eller, P. G.; Kubas, J. G. *J. Am. Chem. Soc.* **1977**, *99*, 4346. (d) Osakada, K.; Takizawa, T.; Tanaka, M.; Yamamoto, T. *J. Organomet. Chem.* **1994**, *473*, 359. (e) Lopes, C.; Håkansson, M.; Jagner, S. *Inorg. Chim. Acta, in* the press. (f) Pasquali, M.; Fiaschi, P.; Floriani, C.; Gaetani-Manfredotti, A. *J. Chem. Soc. Chem. Commun.* **1983**, 197. (g) Berry, M.; Clegg, W.; Garner, C. D.; Hillier, I. H. *Inorg. Chem.* **1982**, *21*, 1342.

(4) Lopes, C.; Håkansson, M.; Jagner, S. *Inorg. Chem.* **1997**, *36*, 3232.

(5) Eriksson, H.; Örtendahl, M.; Håkansson, M. *Organometallics* **1996**, *15*, 4823.

S0276-7333(97)00657-2 CCC: $15.00
Publication on Web 01/19/1998

ods.[6] Mesitylcopper(I) was prepared from copper(I) chloride, 2-bromomesitylene, and magnesium according to methods described previously.[7]

Preparation of $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ (1). Mesitylcopper(I) (5.5 mmol, 1.0 g) was dissolved in 10 mL of toluene to give a yellow solution, and excess of *o*-allylphenol (11 mmol, 1.6 mL) was added by means of a cannula while the solution was stirred, whereupon it became almost colorless and a white precipitate was formed during the ensuing exothermic reaction. The reaction was allowed to proceed for approximately 12 h, during which time a white precipitate of $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ was deposited. The precipitate was washed twice with 5 mL of toluene and once with 5 mL of hexane to give **1** in approximately 80% yield. The compound is sparingly soluble in toluene and hexane and is slightly soluble in dichloromethane and THF. That this powder was identical with the crystalline product used for structural characterization was confirmed by means of X-ray powder diffraction, an *I* centered unit cell with the dimensions $a = b = 17.870$ Å, $c = 10.279$ Å, and $\alpha = \beta = \gamma = 90°$ being obtained at ambient temperature.

For the preparation of single crystals, suitable for X-ray diffraction analysis, mesitylcopper(I) (0.2 mmol, 0.036 g) was dissolved in toluene (5 mL) and excess of *o*-allylphenol (0.7 mmol, 0.1 mL) was added using a cannula. The resulting solution was stirred for a few seconds and then allowed to stand at ambient temperature, colorless rods of **1** being deposited after 2−3 days. Attempts to determine the melting point of the compound failed, owing to decomposition of the crystals starting at ca. 160 °C. Crystals of **1** are otherwise relatively stable, decomposing completely only after several days of exposure to the atmosphere.

Preparation of $[Cu_6(OCMe_2CH{=}CH_2)_6]$ (**2**). Mesitylcopper(I) (22.7 mmol, 4.15 g) was dissolved in toluene (20 mL), and the solution was centrifuged. Excess 2-methyl-3-buten-2-ol (34.1 mmol, 2.93 g) was added to the clear pale yellow solution of mesitylcopper(I) in toluene. After the mixture was stirred for 10 min, a white precipitate of **2** started to form. Stirring of the mixture was continued overnight, after which the solvent was evaporated almost to dryness. The precipitate was washed four times with 5-mL portions of hexane and then dried carefully under reduced pressure. On extensive drying the compound becomes gray. Yield of **2**: 83%. The compound is soluble in chloroform but only sparingly soluble in THF, toluene, and benzene, precluding cryoscopic determination of the molecular weight of **2** in solution.

Single crystals of **2** for X-ray analysis were grown from a saturated toluene/hexane solution (2 mL of toluene/5 mL of hexane) at 4 °C. Crystals of **2** decompose completely within minutes when exposed to the atmosphere. Rapid decomposition of **2** precluded an X-ray powder diffraction investigation of the compound in microcrystalline form as well as elemental analysis.

Carbonylation of $[Cu_6(OCMe_2CH{=}CH_2)_6]$ (2). Methylbutenoxocopper(I), **2**, was prepared as above and carbonylated in chloroform, benzene, or toluene, yielding deep-yellow (chloroform) or deep-red sensitive solutions (benzene, toluene), respectively. Evaporation of the solvent under reduced pressure yielded an extremely sensitive yellow compound (**3**). Attempts to obtain single crystals of **3** have so far been unsuccessful. Cryoscopic determination of the molecular weight of **3** (assuming a Cu/CO ratio of 1) in benzene, calculated for $[Cu_n(OCMe_2CH{=}CH_2)_n(CO)_n]$: 636 g/mol^{-1} corresponding to an aggregation number, *n*, of 3.6.

All attempts to carbonylate $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ (**1**) failed.

Infrared Spectroscopy. Infrared spectra were recorded on a Mattson Polaris FTIR spectrometer with a resolution of 2 cm^{-1}. Solid samples have been prepared under argon or carbon monoxide, using CaF_2 or KBr mull cells. Liquid samples have been measured in standard solution cells equipped with CaF_2 or KBr windows.

$[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ (1): IR (Nujol mull, CaF_2 windows, cm^{-1}) $\nu_{C=C}$ 1517, 1522; (in dichloromethane, CaF_2 cell, cm^{-1}) $\nu_{C=C}$ 1524 sh; (in THF, CaF_2 cell, cm^{-1}) $\nu_{C=C}$ 1525 vw. IR of $HOC_6H_4CH_2C(H){=}CH_2$ (CaF_2 cell, cm^{-1}): $\nu_{C=C}$ 1638 (in dichloromethane $\nu_{C=C}$ also 1638).

$[Cu_6(OCMe_2CH{=}CH_2)_6]$ (2): IR (Fluorolube mull, CaF_2 windows, cm^{-1}) $\nu_{C=C}$ 1502; (in chloroform, CaF_2 cell, cm^{-1}) $\nu_{C=C}$ 1635 sh; (in dichloromethane, CaF_2 cell, cm^{-1}) $\nu_{C=C}$ 1635, 1644. IR of $HOC(CH_3)_2CH{=}CH_2$ (CaF_2 cell, cm^{-1}): $\nu_{C=C}$ 1647 (in chloroform and dichloromethane $\nu_{C=C}$ 1646).

3: IR (Fluorolube mull, CaF_2 windows, cm^{-1}) ν_{CO} 2021 vw, 2066 sh, $\nu_{C=C}$ 1641, 1501; (in chloroform, CaF_2 cell, cm^{-1}) ν_{CO} 2065, 2082, $\nu_{C=C}$ 1644; (in toluene, CaF_2 cell, cm^{-1}) ν_{CO} 2018 vw, 2061.

NMR Spectroscopy. ^1H NMR spectra (400 MHz) were recorded on a Varian XL 400 spectrometer (s = singlet, d = doublet, dd = doublet of doublets, t = triplet, m = multiplet, b = broad). A ^{13}C NMR spectrum (100 MHz) was also recorded for **3**, using the same spectrometer. For solutions of **1** and *o*-allylphenol in THF, ^1H NMR spectra (ppm) were recorded at 50 °C using THF-d_8 and the most downfield signal from THF as an internal standard. For solutions of **2**, **3**, and $HOC(CH_3)_2CH{=}CH_2$ in chloroform-*d* and benzene-*d*, spectra were recorded at 19 °C using the relevant solvent as internal standard.

***o*-Allylphenoxocopper(I) (1):** δ 3.21 (b, 2H, $-CH_2-$), 3.76 (b, 2H, $=CH_2$), 4.50 (b, 1H, $-CH=$), 6.58 (s, 1H, phenyl), 6.96 (m, 3H, phenyl).

***o*-Allylphenol:** δ 3.34 (d, 2H, $-CH_2-$), 4.98 (dd, 2H, $=CH_2$), 5.97 (m, 1H, $-CH=$), 6.68 (m, 2H, phenyl), 6.98 (m, 2H, phenyl), 7.89 (s, 1H, $-OH$).

Methylbutenoxocopper(I) (2): (in chloroform) δ 1.33 (s, 6H, $-C(CH_3)_2-$), 4.95 (d, 1H, $=CH_2$), 5.24 (d, 1H, $=CH_2$), 6.03 (dd, 1H, $-CH=$); (in benzene) δ 1.31 (s, b, 6H, $-C(CH_3)_2-$), 4.92 (d, b, 1H, $=CH_2$), 5.29 (s, b, 1H, $=CH_2$), 6.01 (s, b, 1H, $-CH=$).

Solution of 3 in chloroform: δ 1.47 (s, 6H, $-C(CH_3)_2-$), 4.97 (d, 1H, $=CH_2$), 5.08 (d, 1H, $=CH_2$), 6.22 (dd, 1H, $-CH=$); no carbonyl ^{13}C NMR signal was observed.

Solution of $HOC(CH_3)_2CH{=}CH_2$ in chloroform: δ 1.23 (s, 6H, $-C(CH_3)_2-$), 2.45 (s, 1H, $-OH$), 4.90 (d, 1H, $=CH_2$), 5.12 (d, 1H, $=CH_2$), 5.91 (dd, 1H, $-CH=$).

Solution of $HOC(CH_3)_2CH{=}CH_2$ in benzene: δ 1.21 (s, 6H, $-C(CH_3)_2-$), 2.84 (s, 1H, $-OH$), 4.89 (d, 1H, $=CH_2$), 5.19 (d, 1H, $=CH_2$), 5.90 (dd, 1H, $-CH=$).

X-ray Crystallography. Crystal and experimental data are summarized in Table 1. Crystals of **2** were mounted using a special low-temperature technique.[8] Diffracted intensities were measured using a Rigaku AFC6R diffractometer and graphite-monochromated Mo Kα ($\lambda = 0.710\,73$ Å) radiation from a RU200 rotating anode source operated at 9 kW (50 kV, 180 mA). The $\omega/2\theta$ scan mode was employed, and stationary background counts were recorded on each side of the reflection, the ratio of peak counting time vs background counting time being 2:1. Data were measured at −110 °C for $5° < 2\theta < 50°$ ($+h$, $+k$, $+l$) for a colorless rod of **1** with approximate dimensions 0.20 × 0.10 × 0.10 mm, using an ω scan rate of 8°/min and a scan width of $(1.21 + 0.30 \tan\theta)°$. For **2**, diffracted intensities from a pale-yellow cube with dimensions 0.10 × 0.10 × 0.10 mm were measured at −115 °C for $5° < 2\theta < 50°$ ($\pm h$, $+k$, $+l$),using an ω scan rate of 8°/min and a scan

---

[6] Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

[7] (a) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192. (b) Tsuda, T.; Watanabe, K.; Miyata, K.; Yamamoto, H.; Saegusa, T. *Inorg. Chem.* **1981**, *20*, 2728. (c) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc. Chem. Commun.* **1983**, 1156. (d) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

[8] Håkansson, M. *Inorg. Synth.* accepted for publication.

Table 1. Crystallographic Data for $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ (1) and $[Cu_6(OCMe_2CH{=}CH_2)_6]$ (2)

	1	**2**
formula	$C_{36}H_{36}Cu_4O_4$	$C_{30}H_{54}Cu_6O_6$
fw	786.9	892.0
cryst syst	tetragonal	trigonal
space group	$I4_1/a$ (No. 88)	$R\bar{3}c$ (hex) (No. 167)
a, Å	17.710(3)	17.768(3)
c, Å	10.197(6)	18.94(6)
V, Å	3198(2)	5179(16)
Z	4	6
d_{calcd} g/cm^3	1.63	1.72
μ, cm^{-1}	26.7	36.7
T, °C	−110	−120
R^a	0.051	0.034
$R_w{}^b$	0.059	0.038

[a] $R = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $R_w = [(\sum w(|F_o| - |F_c|)^2/\sum wF_o{}^2)]^{1/2}$.

width of $(0.89 + 0.30 \tan \theta)°$. In both cases, weak reflections ($I < 10.0\sigma(I)$) were rescanned up to three times and counts accumulated to improve counting statistics. The intensities of three reflections monitored regularly after measurement of 150 reflections indicated crystal stability during data collection. Correction was made for Lorentz and polarization effects; empirical corrections based on azimuthal scans for several reflections were made for the effects of absorption (minimum/maximum transmission factors = 0.95/1.00 (**1**), 0.93/1.00 (**2**)). Of the 1491 unique reflections measured for **1**, 706 had $I > 3.0s(I)$ and were considered observed; for **2**, 533 of the 1130 unique reflections had $I > 3.0\sigma(I)$. Cell constants were obtained by least-squares refinement from the setting angles of 20 reflections in the range $10.8° < 2\theta < 18.5°$ (for **1**) and $13.9° < 2\theta < 21.9°$ (for **2**).

The structures were solved by direct methods (MITHRIL).[9] Two carbon atoms of the allyl function in **1** (C(7) and C(8)) were found to be disordered and were each resolved into two positions (cf. the Supporting Information). Full-matrix least-squares refinement, including anisotropic thermal parameters for all non-hydrogen atoms except the split C(7) and C(8) carbons, which were refined with isotropic thermal parameters, and with the hydrogen atoms as a fixed contribution ($B = 1.2B_{eq}$ of the carrying carbon atom), gave a final $R = 0.051$ ($R_w = 0.059$) for 98 parameters and 706 observed reflections. Those hydrogen atoms associated with the phenyl group were included in calculated positions (C−H = 0.95 Å), while those bonded to C(9) were located from a difference map but not refined. Refinement of **2** with anisotropic thermal parameters for the non-hydrogen atoms, with isotropic thermal parameters for the hydrogen atoms of the alkene group, located from a difference map, and with the hydrogen atoms of the methyl groups as a fixed contribution (C−H = 0.95 Å, $B = 1.2B_{eq}$ of the carrying carbon atom) gave a final $R = 0.034$ ($R_w = 0.038$) for 76 parameters and 533 observed reflections. The maximum and minimum values in the final difference map were 0.45 and −0.79 e/Å^3 for **1** and 0.41 and −0.46 e/Å^3, respectively. Reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$.

All calculations were carried out with the TEXSAN[10,11] program package. Atomic scattering factors and anomalous dispersion correction factors were taken from ref 11. Final positional parameters are listed in the Supporting Information, and selected interatomic distances and angles are in Tables 2 and 3. Figures 1 and 3 have been drawn with ZORTEP and Figures 2 and 4 with PLUTON.

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ (1)[a]

Cu−O	1.962(5)	C(2)−C(3)	1.39(1)
Cu−O^i	1.933(5)	C(3)-C(4)	1.37(1)
Cu−C(8a)	2.07(2)	C(4)−C(5)	1.38(1)
Cu−C(8b)	2.02(2)	C(5)−C(6)	1.39(1)
Cu−C(9)	2.02(1)	C(2)−C(7a)	1.53(2)
Cu−Xa	1.90	C(2)−C(7b)	1.60(2)
Cu−Xb	1.90	C(7a)−C(8a)	1.49(3)
Cu···O^{ii}	2.785(6)	C(7b)−C(8b)	1.56(2)
O−C(1)	1.363(9)	C(8a)−C(9)	1.51(2)
C(1)−C(2)	1.39(1)	C(8b)−C(9)	1.42(2)
O−Cu−O^i	97.1(2)	C(2)−C(1)−C(6)	119.1(8)
O−Cu−Xa	116.3	C(1)−C(2)-C(3)	119.6(8)
O−Cu−Xb	117.4	C(1)−C(2)−C(7a)	120.5(10)
O^i−Cu−Xa	144.9	C(1)−C(2)−C(7b)	120.7(9)
O^i−Cu−Xb	144.2	C(3)−C(2)−C(7a)	118.4(10)
O−Cu−O^{ii}	82.3(2)	C(3)−C(2)−C(7b)	115.7(9)
O^i−Cu−O^{ii}	74.0(2)	C(2)−C(3)-C(4)	121.3(8)
O^{ii}−Cu−Xa	120.5	C(3)−C(4)-C(5)	119.1(9)
O^{ii}−Cu−Xb	102.8	C(5)−C(6)-C(1)	120.5(9)
Cu−O−C(1)	124.0(5)	C(2)−C(7a)−C(8a)	109(2)
Cu−O−Cu^{iii}	106.8(2)	C(2)−C(7b)−C(8b)	109(1)
Cu^{iii}−O−C(1)	125.8(5)	C(7a)−C(8a)−C(9)	114(2)
O−C(1)−C(2)	121.7(8)	C(7b)−C(8b)−C(9)	112(1)
O−C(1)−C(6)	119.2(7)		

[a] Symmetry code: (*i*) $^3/_4 + x$, $^5/_4 - y$, $^1/_4 - z$; (*ii*) $2 - x$, $^1/_2 - y$, z; (*iii*) $^5/_4 - y$, $x - ^3/_4$, $^1/_4 - z$.

Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $[Cu_6(OCMe_2CH{=}CH_2)_6]$ (2)[a]

Cu−O	1.980(5)	O−C(1)	1.425(8)
Cu−O^i	1.927(5)	C(1)-C(2)	1.53(1)
Cu−C(4^{ii})	1.986(8)	C(1)−C(3)	1.54(1)
Cu−C(5^{ii})	1.979(9)	C(1)−C(4)	1.51(1)
Cu−X	1.863	C(4)−C(5)	1.36(1)
Cu···O^{ii}	2.747(5)	Cu···Cu^i	3.142(2)
O−Cu−O^i	95.1(2)	O−C(1)−C(2)	109.1(6)
O−Cu−X	123.7	O−C(1)-C(3)	109.4(6)
O^i−Cu−X	141.1	O−C(1)−C(4)	109.4(6)
O^{ii}−Cu−X	68.4	C(2)−C(1)−C(3)	107.7(6)
O−Cu−O^{ii}	128.7(2)	C(2)−C(1)−C(4)	110.1(7)
O^i−Cu−O^{ii}	73.1(2)	C(3)−C(1)-C(4)	109.9(7)
Cu−O−Cu^{ii}	107.1(2)	C(1)−C(4)-C(5)	126.3(9)
Cu−O−C(1)	119.3(4)	Cu^{ii}−O−C(1)	133.5(4)

[a] Symmetry code: (*i*): $y, -x + y, -z$; (*ii*) $x - y, x, -z$.

Results and Discussion

In addition to introducing the new alkoxo- and aryloxocopper structures shown in Chart 2, the present study demonstrates the possibility of utilizing a built-in π-alkene function as a stabilizing ligand for copper(I) alkoxides and phenoxides. Conversely, both compounds provide novel examples of alkene π-coordination to copper(I) without the presence of ancillary coordinating or noncoordinating anions such as halide.[12] The present study affords, moreover, a comparison with respect to resistance to carbonylation and dissolution between a homoleptic copper(I) alkoxide and an analogous phenoxide.

The reaction between methylcopper(I) and phenols or alcohols has been demonstrated to be an effective preparatory method for copper(I) alkoxides and phe-

---

[9] Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.

[10] TEXSAN-TEXRAY Structure Analysis Package; Molecular Structure Corp.: Texas, 1989.

[11] *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.

[12] (a) Håkansson, M.; Jagner, S.; Walther, D. *Organometallics* **1991**, *10*, 1317. (b) Håkansson, M.; Jagner, S. *J. Organomet. Chem.* **1990**, *397*, 383. (c) Håkansson, M.; Wettström, K.; Jagner, S. *J. Organomet. Chem.* **1991**, *421*, 347. (d) Håkansson, M.; Jagner, S.; Clot, E.; Eisenstein, O. *Inorg. Chem.* **1992**, *31*, 5389.

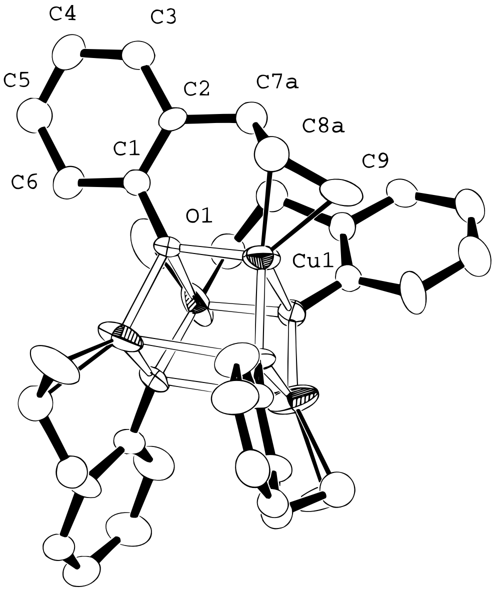


Figure 1. Crystallographic numbering in *o*-allylphenolatocopper (**1**). The cubane-type Cu_4O_4 core is illustrated by means of open "bonds". For clarity, the disordered carbon atoms, C(7) and C(8), are depicted in one of the two possible sites, viz. C(7a) and C(8a).

noxides.[13] Mesitylcopper(I) has been used analogously to prepare copper(I) amides from the relevant amines,[7b] and copper(I) silyl oxides from the corresponding silanols.[14] Here, we have shown that this general approach can be utilized successfully for the preparation of *o*-allylphenoxocopper(I), **1**, and methylbutenoxocopper(I), **2**, from mesitylcopper(I), *o*-allylphenol, and 2-methyl-3-buten-2-ol, both of the compounds per se and of single crystals suitable for X-ray diffraction work. As discussed further below, whereas methylbutenoxocopper(I) decomposes rapidly on exposure to air and is soluble in chloroform but only sparingly soluble in THF, toluene, hexane, and benzene, *o*-allylphenoxocopper(I) is surprisingly stable in the solid state; it is, however, only sparingly soluble in nonpolar solvents and slightly soluble in coordinating solvents.

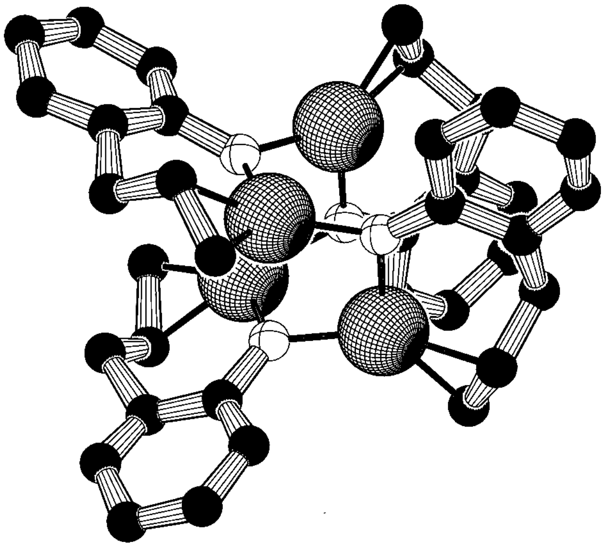


Figure 2. The cubane-shaped core in **1** is markedly distorted. The long Cu−O interactions (2.79 Å) are not indicated. An alkene group and the two closest oxygens arrange in an approximate trigonal-pyramidal geometry around copper.

o-Allylphenoxocopper(I), **1**, crystallizes as a $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ tetramer (cf. Figure 1). As is seen from Figure 2, the complex has a distorted Cu_4O_4 cubane-type core, the distortion being similar to that exhibited by one of the two possible $Cu_4X_4(olefin)_4$ cubane isomers.[12b,d] These isomers arise from the two ways in which the four long Cu−X bonds can be aligned, i.e., either all four parallel or pairs of parallel long Cu−X bonds mutually orthogonal,[12d] the $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ tetramer being of the latter isomeric type (cf. Figure 2). The short Cu−O bonds in $[Cu_4(OC_6H_4CH_2C(H){=}CH_2)_4]$ are 1.933(5) and 1.962(5) Å, while the long Cu···O contact is 2.785(6) Å (see Table 2). Copper(I) thus exhibits trigonal-pyramidal coordination geometry, similar to that found in complexes between alkenes and copper(I) chloride,[12,15] the trigonal plane being defined by O, O^i, and X, the midpoint of the C=C bond (cf. Table 2). Owing to the disorder there are two such planes: Cu being displaced 0.14 Å from that through O, O^i, and Xa and 0.08 Å, in the opposite direction, from that through O, O^i, and Xb. Thus, the distortion from trigonal-pyramidal toward tetrahedral coordination geometry would seem to be somewhat more pronounced than in many of the chloro complexes studied[12c,d] and reminiscent of one of the copper(I) centers in the complex between isoprene and copper(I) chloride.[12a] The asymmetry between O−Cu−X and O^i−Cu−X angles (cf. Table 2) is indicative of appreciable olefin sliding for both olefin orientations.[16a]

As expected, the distortion of the copper(I) coordination polyhedron from trigonal pyramidal towards tetrahedral is accompanied by an appreciable olefin twist, viz. 20 and 24°, respectively, out of the relevant O, O^i, X plane. Values associated with essentially trigonally coordinated copper(I) centers have been found to be of the order of 4°.[12c] One might envision that the disordered orientation of the olefin in the present complex might be a consequence of equal preferences for "quasicubical" and "quasidocecahedral" olefin twists[16] as the coordination polyhedron of copper(I) distorts from trigonal pyramidal to tetrahedral.[12a] In both cases the coordinated olefin can be considered to exhibit a twist approaching the "quasicubical" rather than "quasidodecahedral",[16] with dihedral angles between the Cu, C(8a), C(9) plane and the planes through Cu, Xa, O; Cu, Xa, O^i; and Cu, Xa, O^{ii} of 20°, 42°, and 63°, respectively.[12a] Corresponding values for the other orientation, viz. involving C(8b) and Xb, are similar, i.e., 19°, 30°, and 69°, respectively. Thus the disorder does not appear to be attributable to an equal preference for the two possible olefin twisting modes.

Methylbutenoxocopper(I), **2**, has a unique ribbon-shaped hexameric structure, as shown in Figures 3 and 4. Hitherto, the few homoleptic copper(I) alkoxides or phenoxides whose structures are known are tetrameric

---

(13) Whitesides, G. M.; Sadowski, J. S.; Lilburn, J. *J. Am. Chem. Soc.* **1974**, *96*, 2829.

(14) McGeary, M. J.; Wedlich, R. C.; Coan, P. S.; Folting, K.; Caulton, K. G. *Polyhedron* **1992**, *11*, 2459.

(15) Camus, A.; Marsich, N.; Nardin, G.; Randaccio, L. *Inorg. Chim. Acta* **1977**, *23*, 131.

(16) (a) Ittel, S. D.; Ibers, J. A. *Adv. Organomet. Chem.* **1976**, *14*, 33. (b) Rösch, N; Hoffmann, R. *Inorg. Chem.* **1974**, *11*, 2656.

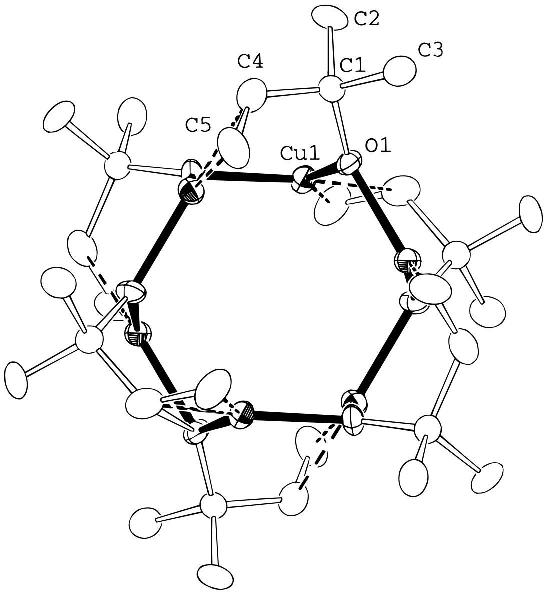


Figure 3. Crystallographic numbering in methylbutenoxocopper (**2**). Top view of the twelve-membered Cu-O ring core which is indicated with bold bonds, while π-alkene-to-copper interactions are indicated with dashed lines.

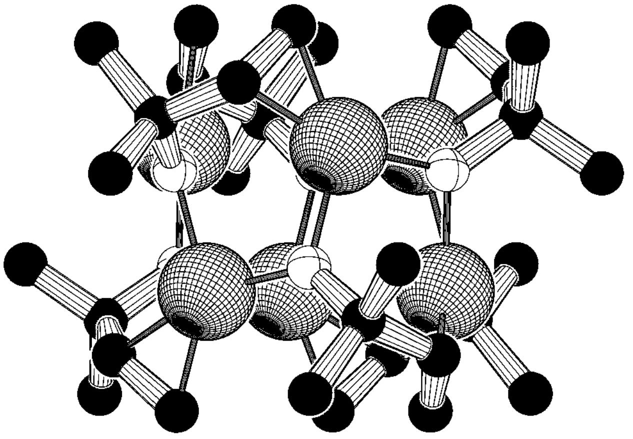


Figure 4. Side view of the ribbon-shaped core in **2**. The core atoms can be considered to lie in two separate planes.

with planar Cu_4O_4 core—$[(CuO^tBu)_4]$[1c] and $[(CuOC_6H_3Ph_2)_4]$, Ph = C_6H_5[4]—or cubane-type—*o*-allylphenoxocopper(I), **1**. As is seen from Figure 4, the Cu_6O_6 core of $[Cu_6(OCMe_2CH{=}CH_2)_6]$, **2**, bears resemblance to a crown-6 ether.

In methylbutenoxocopper(I), **2**, copper(I) is perhaps best described as being three-coordinated by oxo functionalities of two methylbutenoxo ligands and the alkene group of a third (see Figure 3 and Table 3). The oxygen atom of this third ligand is at 2.747(5) Å from Cu (cf. Table 3), but Cu is displaced 0.03 Å from the plane through O, O^i and the midpoint of the $C(4^{ii})-C(5^{ii})$ bond in the opposite direction, i.e., *away from* O^{ii}. Thus, although it would be possible to describe copper(I) as having trigonal-pyramidal rather than trigonal-planar coordination geometry, there is no tendency toward distortion from trigonal-pyramidal toward tetrahedral coordination geometry as observed in **1**. The olefin is twisted 5° out of the trigonal plane. As in **1**, the asymmetry between O−Cu−X and O^i−Cu−X angles (Table 3) demonstrates appreciable olefin sliding.[16a]

As in **1**, one of the Cu−O distances in the trigonal coordination plane is shorter than the other, this feature being more marked in **2** than in **1**. The Cu−O distances in both **1** and **2** are, of course, considerably longer than in 2,6-diphenylphenoxocopper(I) (1.834(7)−1.86587) Å), in which copper(I) is two-coordinated.[4] Cu−C and Cu−X distances in both compounds (where X is the midpoint of the C=C linkage) are within the normal range.[12,14,15]

The lowering of $\nu_{C=C}$ (≈118 cm^{-1}) in **1** on coordination is similar to that found for *o*-allylphenoxo complexes of palladium(II) and platinum(II) in which the double bond coordinates to the metal,[17] and is slightly larger than values observed previously by us in π-olefinic complexes of copper(I).[12] The C=C bond is unusually long (1.51(2), 1.42(2) Å, Table 2),[12,14,15] but owing to the disorder associated with C(7) and C(8), it is impossible to assess whether this reflects the slightly larger $\Delta\nu_{C=C}$ than usually observed or whether it is an artifact of the disorder. The lowering of $\nu_{C=C}$ in **2** on coordination (≈145 cm^{-1}) is considerably larger than normally observed,[12] but paradoxically, this is not reflected in the length of the C=C bond, which is 1.36(1) Å. Whereas **1** retains copper(I)−alkene coordination on dissolution in THF, it is noteworthy than on dissolution of **2** in chloroform the copper(I)−alkene bond is broken and the C=C stretching frequency is identical with that determined for the free ligand dissolved in chloroform. It has not been possible to determine the molecular weights of either dissolved **1** or **2**. The IR and NMR investigations of **1** suggest that the solid-state structure is retained on dissolution. On the basis of an analogy with the carbonylated derivative of **2**, namely **3**, and with *tert*-butoxocopper(I) and 2,6-diphenylphenoxocopper(I), we believe that **2** dissolves to form an oxo-bridged tetramer, probably with a planar Cu_4O_4 core. Both *tert*-butoxocopper(I)[1c] and 2,6-diphenylphenoxocopper(I)[4] have been shown to have planar Cu_4O_4 cores in the solid state, and since they both seem to retain their aggregation state on dissolution,[1b,4] it seems reasonable to assume that the solution structures of these compounds are similar to those in the solid state.

As mentioned above, the Cu_6O_6 core of $[Cu_6(OCMe_2CH{=}CH_2)_6]$, **2**, bears resemblance to a crown-6 ether, but the cavity is not big enough to accommodate noncoordinating small molecules. In the case of carbon monoxide, coordination to copper(I) rather than simple occupation of the cavity appears to occur. Thus on the basis of the IR results, the carbonylation product of $[Cu_6(OCMe_2CH{=}CH_2)_6]$, **3**, contains, in the solid state, both ligands π-coordinated to copper(I) through the alkene group and ligands in which the alkene group does not participate in copper(I) coordination. The IR spectra indicate an equal number of coordinated and free alkene groups. On dissolution, however, **3** exhibits behavior similar to **2**, i.e. copper(I)−alkene coordination is destroyed, as indicated by both IR and ^{1}H NMR measurements. Cryoscopic molecular weight determination of **3** suggests that it is tetrameric in solution. The carbonyl stretching frequencies are consistent with terminally bonded carbon monoxide (see ref 4 and references therein) both in solution and in the solid state. Thus **3** in solution may contain either a planar Cu_4O_4 core or a core of cubane type as in $[(Cu(O^tBu)$-

---

(17) Aresta, M.; Nyholm, R. S. *J. Organomet. Chem.* **1973**, *56*, 395.

(CO))$_4$].[18] Since nothing is yet known concerning the aggregation state, or structure of solid **3**, we are pursuing our attempts to obtain single crystals.

The ^{1}H NMR spectra of **1** provide an opportunity to examine shifts in a compound in which π-alkene coordination to copper(I) has been ascertained. **1** shows upfield shifts of the olefinic proton signals on complexation between *o*-allylphenoxide and copper(I), viz. $\Delta\delta(-\mathrm{CH}=) = 1.47$ ppm and $\Delta\delta(=\mathrm{CH_2}) = 1.22$ ppm. These shifts are similar to those reported for (β-diketonato)copper(I) complexes with norbornadiene ligands[19] and support the now well-accepted mechanistic model for the initial formation of a copper(I)−alkene π-complex on organocuprate addition to α,β-unsaturated compounds, which is thought to comprise the first step in the copper(I) promoted conjugate addition process.[20] For example, ^{1}H NMR spectra of solutions of Me_2CuLi and methyl cinnamate were found to exhibit proton signals shifted strongly upfield: from δ 7.73 to 4.6 and 6.55 to 4.3 (for the protons analogous to those mentioned above), these being interpreted as indicating the formation of a π-alkene−copper(I) complex.[20] Measurements on cationic copper(I)−alkene complexes show, however, substantially smaller ^{1}H NMR shifts.[21]

In conclusion, we have here reported the preparation and characterization of a well-defined, homoleptic copper(I) phenoxide and an analogous copper(I) alkoxide stabilized by π-alkene coordination. Both complexes exhibit structures previously not associated with homoleptic Cu-OR compounds: cubane-shaped tetrameric (**1**) and ribbon-shaped hexameric (**2**). In the case of *o*-allylphenoxocopper(I), **1**, the results are in accordance with the previous findings that, although there is no intrinsic instability associated with the Cu−OAr unit,[2] an ancillary ligand, here a built-in π-alkene function, appears to be vital for the formation of a stable uncharged species. *o*-Allylphenoxocopper(I), once formed, dissolves only sparingly in polar solvents and is insoluble in nonpolar solvents, seemingly retaining its structure in solution, which would account for its resistance to carbonylation. Methylbutenoxocopper(I), **2**, on the other hand, dissolves in such a way that oxo-bridged copper(I) is retained, whereas π-alkene−copper(I) coordination is destroyed, leaving copper(I) free to accept carbon monoxide as a ligand. On formation of solid **3**, rearrangement occurs so as to accommodate some ligands coordinated to copper(I) via the π-alkene functionality.

Acknowledgment. Financial support from the Swedish Natural Science Research Council is gratefully acknowledged.

Supporting Information Available: Tables of anisotropic thermal parameters for the non-hydrogen atoms and atomic coordinates (4 pages). Ordering information is given on any current masthead page.

OM9706572

---

(18) Geerts, R. L; Huffman, J. C.; Folting, K.; Lemmen, T. H.; Caulton, K. G. *J. Am. Chem. Soc.* **1983**, *105*, 3503.

(19) Chi, K-M.; Hou, H.-C.; Hung, P.-T.; Peng, S.-M.; Lee, G.-H. *Organometallics* **1995**, *14*, 2641.

(20) Hallnemo, G.; Olsson, T.; Ullenius, C. *J. Organomet. Chem.* **1985**, *282*, 133. Ullenius, C.; Christenson, B. *Pure Appl. Chem.* **1988**, *60*, 57.

(21) Salomon, R. G.; Kochi, J. K. *J. Am. Chem. Soc.* **1973**, *95*, 1889.