

Carbonylation of a Tetrameric Aryloxocopper(I) Cluster

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Carbonylation of 2,6-diphenylphenoxocopper(I), tetrameric $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ (**1**, Ph = C₆H₅), has been shown to result in a $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ dimer (**2**). The parent aryl oxide, $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$, which has been prepared from mesitylcopper(I) and 2,6-diphenylphenol, has an approximately planar Cu₄O₄ core, in which copper(I) is two-coordinated and Cu–O bonds range from 1.834(7) to 1.865(7) Å. Its carbonylation product **2** is a μ_2 -phenoxo-bridged dimer, containing three-coordinated copper(I), with longer Cu–O bonds, *viz.* 1.953(7)–1.995(7) Å. Cu–C bond lengths in $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ are 1.78(1) and 1.79(1) Å, respectively, with both carbonyl C–O distances equal to 1.12(1) Å, and Cu–C–O angles of 174(1) and 179(1)°, respectively. Carbonyl stretching frequencies in the infrared are 2099, 2103, and 2112 cm^{−1} for the solid and 2102 cm^{−1} in toluene solution, and the ¹³C NMR signal (toluene solution) is at 168 ppm. From comparison with other carbonyl complexes of copper(I), the Cu–C bond is judged to be predominantly of σ character, with minimal metal \rightarrow ligand π^* contribution. Both $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ and $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ retain their aggregation states on dissolution in nonpolar solvents, as ascertained by cryoscopic molecular weight determinations of the compounds in benzene. Crystal data: **1**, triclinic, space group $P\bar{1}$ (No. 2), $a = 12.738(9)$, $b = 22.426(5)$, and $c = 9.984(3)$ Å, $\alpha = 101.62(2)$, $\beta = 91.02(4)$, and $\gamma = 85.93(3)^\circ$, $Z = 2$, $R = 0.052$ ($R_w = 0.058$) for 721 parameters and 3843 reflections; **2**, triclinic, space group $P\bar{1}$ (No. 2), $a = 10.67(3)$, $b = 15.72(1)$, and $c = 10.05(1)$ Å, $\alpha = 96.99(8)$, $\beta = 104.66(16)$, and $\gamma = 101.46(12)^\circ$, $Z = 2$, $R = 0.049$ ($R_w = 0.054$) for 397 parameters and 2152 reflections.

Introduction

Copper(I) carbonyl complexes and, more specifically, the nature of the copper(I)–carbonyl bond and reversible binding of carbon monoxide by copper continue to be subjects of much interest.^{1–8} Although carbonylation of $[(\text{CuO}^i\text{Bu})_4]$, which is tetrameric in the solid state,² yields a remarkably stable $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$ compound retaining the tetrameric aggregation state of the parent alkoxide, both in the solid and on dissolution,³ carbonyl derivatives of aryl oxides have, hitherto, defied solid state isolation.^{1a} In connection with our current investigations into aryl oxides of copper(I),^{9,10} we therefore considered it of interest to attempt to isolate and characterize both the parent aryl oxides and their carbonylation products. We here report the preparation and characterization of 2,6-diphenylphenoxocopper(I), $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ (Ph = C₆H₅), and its carbonylated derivative, $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$.

Experimental Section

General. All operations were carried out under nitrogen or argon using standard Schlenk techniques. Solvents [hexane (after addition of a small amount of tetraglyme) and toluene] were distilled under nitrogen from sodium/benzophenone shortly prior to use. Copper(I) chloride was purified according to literature methods.¹¹ Mesitylcopper(I) was prepared from copper(I) chloride, 2-bromomesitylene, and magnesium according to methods described previously.¹²

Preparation of $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$. Mesitylcopper(I) (12.7 mmol, 2.33 g) was dissolved in toluene (15 mL), and the resulting yellow solution was centrifuged and transferred to a Schlenk tube containing 2,6-diphenylphenol (10.6 mmol, 2.61 g). After stirring of the mixture for 20 min, 2,6-diphenylphenol had dissolved. Stirring was continued, and, after 2 days, white microcrystalline $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ had precipitated from a pale yellow solution. The mixture was centrifuged, the solvent removed, and the precipitate washed four times with 5 mL portions of hexane and dried under reduced pressure. The pale yellow solution was evaporated to half its volume, 10 mL of hexane was added, and the solution was stirred overnight, resulting in a second crop of microcrystalline $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$, which was washed and dried as above. Yield: 2.6 g (79%). The compound decomposes rapidly on exposure to the atmosphere at ambient temperature.

For the preparation of single crystals suitable for X-ray diffraction work, 0.5 mmol (0.1 g) of mesitylcopper(I), dissolved in a mixture of toluene (1 mL) and hexane (3 mL), was allowed to react, as above, with 0.5 mmol (0.13 g) of 2,6-diphenylphenol. The mixture was stirred until 2,6-diphenylphenol dissolved, and the solution was allowed to stand, colorless plates of $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ being deposited after 1–2 days.

Preparation of $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$. Microcrystalline $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ was prepared, washed, and dried as above. Toluene (5 mL) was added to 2,6-diphenylphenoxocopper(I) (1.6 mmol, 0.5

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Table 1. Crystallographic Data for [(CuOC₆H₃Ph₂)₄] (**1**) and [{Cu(OC₆H₃Ph₂)(CO)}₂] (**2**)

	1	2
formula	C ₇₂ H ₅₂ Cu ₄ O ₄	C ₃₈ H ₂₆ Cu ₂ O ₄
fw	1235.4	673.7
cryst syst	triclinic	triclinic
space group	<i>P</i> 1̄ (No. 2)	<i>P</i> 1̄ (No. 2)
<i>a</i> , Å	12.738(9)	10.67(3)
<i>b</i> , Å	22.426(5)	15.72(1)
<i>c</i> , Å	9.984(3)	10.05(1)
α, deg	101.62(2)	96.99(8)
β, deg	91.02(4)	104.66(16)
γ, deg	85.93(3)	101.46(12)
<i>V</i> , Å ³	2784(2)	1573(5)
<i>Z</i>	2	2
<i>d</i> _{calc} , g/cm ³	1.47	1.42
radiation (λ)	Mo Kα (0.71073 Å)	Mo Kα (0.71073 Å)
μ, cm ⁻¹	15.6	13.9
<i>T</i> , °C	-120	-120
<i>R</i> ^a	0.052	0.049
<i>R</i> _w ^a	0.058	0.054

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

g), and the slurry was stirred under carbon monoxide for 30 min, during which time the white precipitate dissolved, giving a yellow solution. The solution was evaporated almost to dryness, 3 mL of hexane was added, and the resulting white microcrystalline [{Cu(OC₆H₃Ph₂)(CO)}₂] was isolated. Yield: 0.52 g (96%). [{Cu(OC₆H₃Ph₂)(CO)}₂] decomposes rapidly on exposure to the atmosphere at ambient temperature.

The compound can also be prepared in a way analogous to the preparation of [(CuOC₆H₃Ph₂)₄], under an atmosphere of carbon monoxide instead of argon. In order to obtain single crystals suitable for X-ray diffraction work, 0.4 mmol (0.08 g) of mesitylcopper(I) was dissolved in a mixture of toluene (0.6 mL) and hexane (3.5 mL). The solution was added to 0.4 mmol (0.10 g) of 2,6-diphenylphenol, and the mixture was stirred under an atmosphere of carbon monoxide. After prolonged stirring (for 3 h), excess [{Cu(OC₆H₃Ph₂)(CO)}₂] was deposited as a white precipitate. This was removed by centrifuging the mixture, and the colorless solution was allowed to stand at -18 °C for approximately 1 week, after which time colorless rods of [{Cu(OC₆H₃Ph₂)(CO)}₂] had formed.

Cryoscopy. [(CuOC₆H₃Ph₂)₄] dissolves slowly in toluene and is also soluble in benzene. Cryoscopic determination of the molecular weight of the compound in benzene solution yielded a value of 1176 g mol⁻¹ (calculated for [(CuOC₆H₃Ph₂)₄], 1235 g mol⁻¹). Cryoscopic measurement on the solution obtained by carbonylation of **1** in benzene: experimental, 655 g mol⁻¹; calculated for [{Cu(OC₆H₃Ph₂)(CO)}₂], 674 g mol⁻¹. Similarly, [(CuOC₆H₃Ph₂)₄] was carbonylated in toluene prior to investigation of **2** by ¹H and ¹³C NMR spectroscopy.

NMR and Infrared Spectroscopy. ¹H NMR spectra (400 MHz) for **1**, **2**, and 2,6-diphenylphenol in toluene, and a ¹³C NMR spectrum (100 MHz) for **2** in toluene, were recorded at 20 °C on a Varian XL 400 spectrometer using toluene-*d*₈ and the most upfield signal from toluene as an internal standard (s = singlet, d = doublet, t = triplet, m = multiplet, b = broad).

¹H NMR (ppm): For 2,6-diphenylphenol, δ 5.07 (s, 1H, -OH), 6.85 (t, 1H), 7.04–7.17 (m, 8H), 7.37 (s, 2H), 7.39 (d, 2H). For **1**, δ 6.76–7.44 (m). For **2**, δ 6.88 (t, 1H), 7.00 (t, 2H), 7.18 (t, 4H), 7.27 (d, 2H), 7.60 (d, 4H). No trace of uncarbonylated **1** was observed in the spectrum.

¹³C NMR (ppm): For **2**, δ(CO) 168.2 (s, b) (Δ*ν*_{1/2} = 10 Hz). No coupling with the quadrupolar copper nucleus was observed.

Carbonyl stretching frequencies for **2** were recorded on a Mattson Polaris FTIR spectrometer with a resolution of 2 cm⁻¹.

IR: for [{Cu(OC₆H₃Ph₂)(CO)}₂] (s) (**2**, Nujol mull, CaF₂ windows, cm⁻¹), *ν*_{CO} 2099 s, 2103 s, 2112 m (¹³CO, 2052 w, 2058 w). Crystals of **2** dissolved in toluene (CaF₂ cell, cm⁻¹), *ν*_{CO} 2102. **1** carbonylated in toluene (CaF₂ cell, cm⁻¹), *ν*_{CO} 2102.

X-ray Crystallography. Crystal and experimental data are summarized in Table 1. Crystals were mounted using low-temperature methods.⁴ Diffracted intensities were measured at -120 °C using a Rigaku AFC6R diffractometer and graphite-monochromated Mo Kα

Table 2. Selected Interatomic Distances (Å) and Angles (deg) for [(CuOC₆H₃Ph₂)₄] (**1**)

Cu(1)–O(1)	1.865(7)	Cu(2)–O(1)	1.859(6)
Cu(1)–O(4)	1.861(7)	Cu(2)–O(2)	1.861(7)
Cu(3)–O(2)	1.834(7)	Cu(4)–O(3)	1.855(7)
Cu(3)–O(3)	1.857(8)	Cu(4)–O(4)	1.837(7)
O(1)–C(1)	1.35(1)	O(2)–C(19)	1.36(1)
O(3)–C(37)	1.36(1)	O(4)–C(55)	1.34(1)
Cu(1)···Cu(2)	2.933(3)	Cu(2)···Cu(3)	2.926(2)
Cu(1)···Cu(4)	2.798(2)	Cu(3)···Cu(4)	2.962(3)
O(1)–Cu(1)–O(4)	173.4(3)	O(1)–Cu(2)–O(2)	160.0(3)
O(2)–Cu(3)–O(3)	166.7(3)	O(3)–Cu(4)–O(4)	165.1(3)
Cu(1)–O(1)–Cu(2)	103.9(3)	Cu(2)–O(2)–Cu(3)	104.7(3)
Cu(3)–O(3)–Cu(4)	105.9(4)	Cu(1)–O(4)–Cu(4)	98.4(3)
Cu(1)–O(1)–C(1)	118.0(6)	Cu(3)–O(3)–C(37)	128.2(7)
Cu(2)–O(1)–C(1)	137.4(6)	Cu(4)–O(3)–C(37)	125.6(7)
Cu(2)–O(2)–C(19)	123.3(7)	Cu(1)–O(4)–C(55)	126.1(7)
Cu(3)–O(2)–C(19)	131.3(7)	Cu(4)–O(4)–C(55)	134.9(7)
Cu(4)···Cu(1)···Cu(2)	95.17(7)	Cu(2)···Cu(3)···Cu(4)	91.91(6)
Cu(3)···Cu(2)···Cu(1)	85.54(7)	Cu(1)···Cu(4)···Cu(3)	87.33(6)

(λ = 0.71073 Å) radiation from an RU200 rotating anode source operated at 9 kW (50 kV, 180 mA). The ω/2θ 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 for 5 < 2θ < 50° (+h, ±k, ±l) for a pale yellow plate of **1**, with approximate dimensions 0.25 mm × 0.20 mm × 0.10 mm, using an ω scan rate of 8 deg/min and a scan width of (1.21 + 0.30 tan θ)°. For **2**, a colorless rod with approximate dimensions 0.20 mm × 0.05 mm × 0.05 mm was used under identical experimental conditions. In both cases, weak reflections (*I* < 10.0σ(*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. For **1**, correction was made for Lorentz and polarization effects; an empirical correction based on azimuthal scans for several reflections was made for the effects of absorption (minimum/maximum transmission factors = 0.61/1.00). For **2**, correction was made for Lorentz and polarization effects but not for the effects of absorption. Of the 9782 unique reflections measured for **1**, 3843 had *I* > 3.0σ(*I*) and were considered observed. Cell constants for **1** were obtained by least-squares refinement from the setting angles of 20 reflections in the range 14.1 < 2θ < 18.9°. Of the 5528 unique reflections measured for **2**, 2152 had *I* > 3.0σ(*I*) and were considered observed. Cell constants for **2** were obtained by least-squares refinement from the setting angles of eight reflections in the range 14.4 < 2θ < 26.9°.

Both structures were solved by direct methods (MITHRIL¹³). Full-matrix least-squares refinement, including anisotropic thermal parameters for the non-hydrogen atoms, and with the hydrogen atoms as a fixed contribution (C–H = 0.95 Å, *B* = 1.2*B*_{eq} of the carrying carbon atom), gave final residuals of *R* = 0.052 (*R*_w = 0.058) for 721 parameters and 3843 observed reflections for **1** and *R* = 0.049 (*R*_w = 0.054) for 397 parameters and 2152 observed reflections for **2**. The maximum and minimum values in the final difference map were 0.88 and -0.74 e/Å³ for **1** and 0.54 and -0.58 e/Å³ for **2**, respectively. Reflections were weighted according to *w* = [σ²(*F*_o)]⁻¹.

All calculations were carried out with the TEXSAN¹⁴ program package. Atomic scattering factors and anomalous dispersion correction factors were taken from ref 15. Selected interatomic distances and angles are given in Tables 2 and 3.

Results and Discussion

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

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Table 3. Selected Interatomic Distances (Å) and Angles (deg) for $[(\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO}))_2]_2$ (**2**)

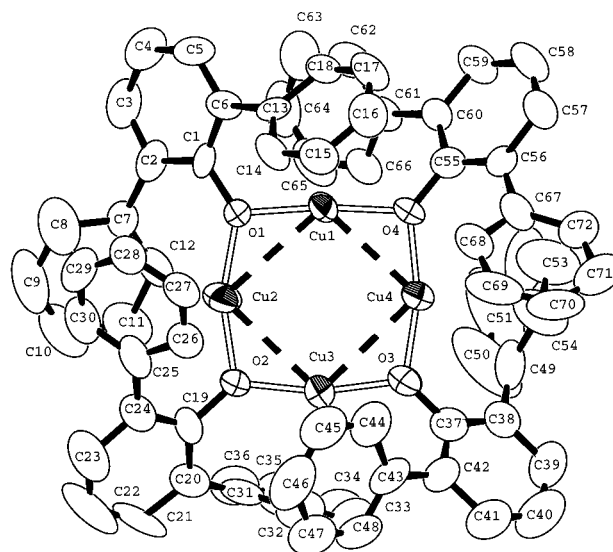
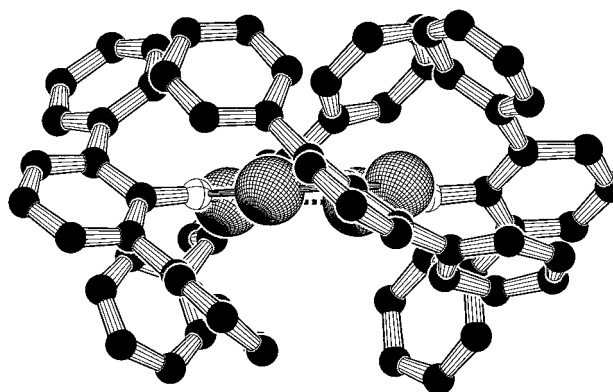
Cu(1)—C(1)	1.78(1)	Cu(2)—C(2)	1.79(1)
C(1)—O(1)	1.12(1)	C(2)—O(2)	1.12(1)
Cu(1)—O(3)	1.953(7)	Cu(2)—O(3)	1.965(7)
Cu(1)—O(4)	1.995(7)	Cu(2)—O(4)	1.966(7)
O(3)—C(3)	1.36(1)	O(4)—C(21)	1.34(1)
Cu(1)···Cu(2)	3.012(3)		
Cu(1)—C(1)—O(1)	174(1)	Cu(2)—C(2)—O(2)	179(1)
O(3)—Cu(1)—O(4)	79.6(3)	O(3)—Cu(2)—O(4)	80.0(3)
O(3)—Cu(1)—C(1)	148.5(4)	O(3)—Cu(2)—C(2)	139.4(4)
O(4)—Cu(1)—C(1)	130.9(4)	O(4)—Cu(2)—C(2)	140.4(4)
Cu(1)—O(3)—Cu(2)	100.5(3)	Cu(1)—O(4)—Cu(2)	99.0(3)
Cu(1)—O(3)—C(3)	132.3(6)	Cu(1)—O(4)—C(21)	126.9(6)
Cu(2)—O(3)—C(3)	127.2(6)	Cu(2)—O(4)—C(21)	133.4(6)

for copper(I) alkoxides and aryl oxides.¹⁶ Mesitylcopper(I) has been used analogously to prepare copper(I) amides from the relevant amines^{12b} and copper(I) silyl oxides from the corresponding silanols.¹⁷ We have shown recently that this general approach can be utilized successfully for the preparation of *o*-allylphenoxocopper(I) and methylbutenoxocopper(I) from mesitylcopper(I) and *o*-allylphenol and 2-methyl-3-buten-2-ol, respectively.¹⁰ A further example is provided by the present preparation of 2,6-diphenylphenoxocopper(I), which is tetrameric both in solution and in the solid state.

Whereas $[(\text{CuO}^t\text{Bu})_4]$ retains its tetrameric aggregation state, albeit with a different type of Cu_4O_4 core, on carbonylation to $[(\text{Cu}(\text{O}^t\text{Bu})(\text{CO}))_4]$,³ we have found that carbonylation of the 2,6-diphenylphenoxo analogue, tetrameric $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$, results in a $[(\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO}))_2]_2$ dimer (**2**) and that preparation from mesitylcopper(I) and 2,6-diphenylphenol under carbon monoxide also yields **2**. As for $[(\text{Cu}(\text{O}^t\text{Bu})(\text{CO}))_4]$, which is tetrameric both in solution and in the solid state,³ the degree of aggregation of **2** in the solid state, here dimeric, would appear to persist in solution.

The parent aryl oxide, $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$, provides a unique example of a homoleptic copper(I) aryl oxide without the presence of stabilizing ancillary ligands or functions. The compound has an approximately planar Cu_4O_4 core, in which copper(I) is two-coordinated, with Cu—O bonds ranging from 1.834(7) to 1.865(7) Å and O—Cu—O angles close to 180° (*cf.* Figures 1 and 2 and Table 2). As can be seen from Figure 2, the Cu_4O_4 core in **1** is approximately planar, with a mean atomic deviation from the best plane through these eight atoms of 0.05 Å. (Alternatively, the core could be described in terms of a planar, to within 0.005 Å, O_4 unit, with the copper(I) atoms deviating between 0.02 and 0.10 Å from this plane). The four copper atoms form an approximate square, less regular than that in $[(\text{CuO}^t\text{Bu})_4]$,² in which the copper(I)···copper(I) separations are somewhat shorter, ranging from 2.646(2) to 2.771(3) Å. The irregularity of the "square" Cu_4 core and the long Cu···Cu separations, 2.798(2)–2.962(3) Å, provide perhaps the most significant difference between tetrameric copper(I) aryl oxides and tetrameric copper(I) aryls, Cu···Cu distances in the latter being of the order of 2.4 Å or less,¹⁸ due to the presence of three-center two-electron Cu—C—Cu bonds.

In $[(\text{CuO}^t\text{Bu})_4]$,^{2,19} the ^tBu substituents are all bent in the same direction away from the Cu_4O_4 core. This is not the case in

**Figure 1.** ZORTEP drawing of $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ (**1**), showing the crystallographic numbering. The Cu_4O_4 square in the Cu_4O_4 core is emphasized by means of dashed lines.**Figure 2.** PLUTON drawing of $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ (**1**) with the Cu_4O_4 core viewed side-on. Cu, "globe" pattern; O, crossed pattern; and C, filled.

$[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$, as can be seen from Figure 2. The phenoxo phenyl rings situated diametrically opposite one another with respect to the core of **1** (*cf.* Figure 1) are approximately perpendicular to one another, *i.e.*, mutually inclined at angles of 78.7 and 87.1°, respectively. Within each $\text{C}_6\text{H}_3\text{Ph}_2$ fragment, the outer rings are also appreciably inclined, the dihedral angles between these pairs of outer phenyl rings within the four $\text{C}_6\text{H}_3\text{Ph}_2$ groups being 74.2, 53.0, 66.5, and 74.1°, respectively. There are a few Cu···C(arene) distances less than 3 Å, *viz.* Cu(1)···C(13) = 2.80(1), Cu(1)···C(66) = 2.90(1), Cu(2)···C(12) = 2.62(1), Cu(2)···C(25) = 2.81(1), Cu(2)···C(26) = 2.76(1), Cu(3)···C(32) = 2.80(1), Cu(4)···C(49) = 2.90(1), and Cu(4)···C(54) = 2.88(1) Å.

Carbonylation of $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$ yields dimeric $[(\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO}))_2]_2$ (**2**, Figures 3 and 4), containing three-coordinated copper(I), with, as expected, longer Cu—O bonds than those in $[(\text{CuOC}_6\text{H}_3\text{Ph}_2)_4]$, *viz.* 1.953(7)–1.995(7) Å (*cf.* Table 3). Cu(1) and Cu(2) are displaced by 0.099 and 0.047 Å, respectively, from the trigonal planes through the relevant ligand atoms. The Cu_2O_2 core is planar to within 0.07 Å, the dihedral angle between the planes through Cu(1), O(3), and O(4) and Cu(2), O(3), and O(4) being 171°. As can be seen from Figure 4, this slight folding is accompanied by bending of the carbonyl groups

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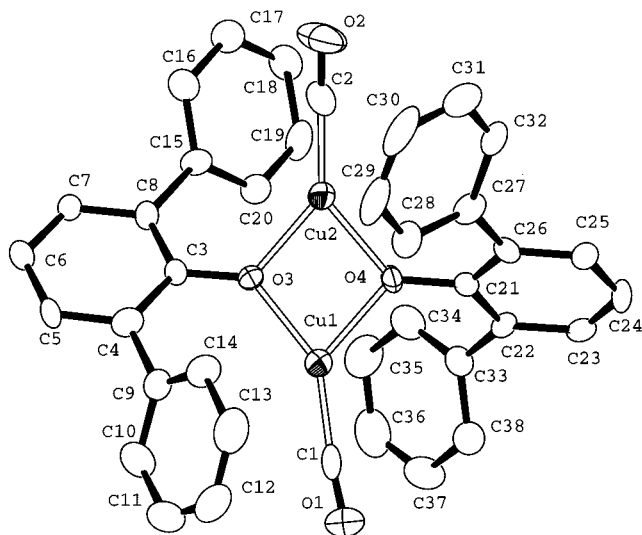


Figure 3. ZORTEP drawing of $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ (**2**), showing the crystallographic numbering.

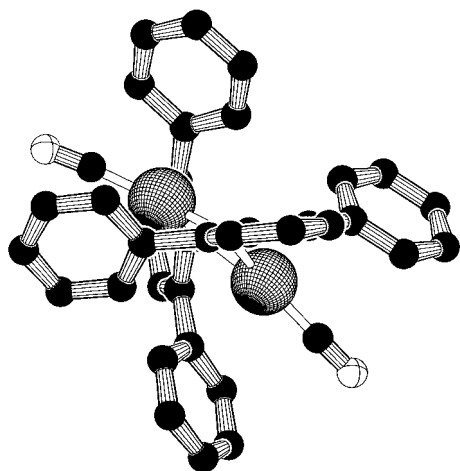


Figure 4. PLUTON drawing of $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ (**2**) with the Cu_2O_2 core viewed side-on. Cu, "globe" pattern; O, crossed pattern; and C, filled.

toward one another. We estimate the angle between the $\text{O}(1)-\text{C}(1)$ and $\text{O}(2)-\text{C}(2)$ bond vectors to be approximately 153° . The phenoxo phenyl rings of the aryloxo ligands situated diametrically opposite to one another with respect to the Cu_2O_2 core are mutually perpendicular, with a dihedral angle of 94.2° . Likewise, the outer rings within each $\text{C}_6\text{H}_3\text{Ph}_2$ fragment are also approximately perpendicular to one another and exhibit dihedral angles of 90.3 and 83.8° , respectively. The closest $\text{Cu}\cdots\text{C}$ -(arene) distances are of the order of 3 \AA , *viz.* $\text{Cu}(1)\cdots\text{C}(14) = 3.14(1)$, $\text{Cu}(2)\cdots\text{C}(15) = 3.08(1)$, $\text{Cu}(2)\cdots\text{C}(20) = 3.03(1)$, and $\text{Cu}(2)\cdots\text{C}(28) = 3.10(1) \text{ \AA}$.

It is noteworthy that it is the aryloxo rather than the carbonyl ligands which bridge the copper(I) centers. This is in accordance with the previous findings of Floriani *et al.*^{1a} Further attempts to isolate carbonylated phenoxocopper(I) derivatives with bulky substituents adjacent to the oxo ligand have resulted in dimeric species essentially similar to $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$, with bridging aryloxo and terminal carbonyl ligands.¹⁰

In the solid state, three carbonyl stretching frequencies have been observed for **2**, *viz.* 2099 (s), 2103 (s), and 2112 (m) cm^{-1} . Corresponding weak ^{13}C peaks were found at 2052 and 2058 cm^{-1} , in good agreement with the isotope effect predicted by the diatomic harmonic oscillator for a 2100 cm^{-1} vibration, 47 cm^{-1} . As a first approximation, one would expect a single vibration in this region for a planar $\text{OC}-\text{Cu}_2\text{O}_2-\text{CO}$ unit,

namely the out-of-phase coupling of the two individual CO stretchings. However, we also have to consider that, in this case, the CO bond vectors make a non-zero angle, the deviation from linearity being of the order of 27° , also causing the in-phase combination to be IR-active, although with a lower intensity.²⁰ Furthermore, intermolecular interactions may be of importance, since the $\text{O}\cdots\text{O}$ separation of carbonyl groups of the nearest neighboring dimer is only $3.76(2) \text{ \AA}$ [*i.e.*, $\text{O}(1)\cdots\text{O}-(1^i)$, where $i = -x, -y, 2 - z$], and intermolecular CO couplings could lead to further splittings according to the correlation field approximation.²¹ A complete, unambiguous assignment would, however, require more detailed investigations beyond the scope of the present report.

$[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ loses carbon monoxide somewhat more slowly than $[\text{Cu}(\text{CO})\text{Cl}]$,⁵ from which carbon monoxide is released extremely rapidly. That $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$ is resistant to decarbonylation has been attributed to its "kinetic stability", *i.e.*, the unfavorable pyramidal coordination geometry for copper(I) which would occur in the initial decarbonylation product.³ Similar reasoning has also been exploited to account for the formation of a copper(I) carbonyl complex stabilized by a tris-chelating oxygen donor ligand.²² Such reasoning might also be used to rationalize the more rapid decarbonylation of $[\text{Cu}(\text{CO})\text{Cl}]$ as compared to that of **2**, since, in the former compound, the proximity of chloride ligands to an initially pyramidal decarbonylated copper(I) center provides ready access to tetrahedral coordination,⁵ whereas loss of a carbonyl group from $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ would result initially in a two-coordinated copper(I) center with nonlinear coordination geometry.

As in $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$,³ the ^{13}C O shift of CO bonded to copper(I) in $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ (168 ppm) is upfield of that of free CO (184 ppm)²³ and slightly lower than the 173 ppm observed for $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$.³ The values for both $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$ and $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$ lie in the range of ^{13}C chemical shifts exhibited by transition metal carbonyls, in which the $\text{OC}\rightarrow\text{M}$ interaction is considered to be predominantly of σ character.²⁴

Similar conclusions concerning bonding within the $\text{Cu}-\text{C}-\text{O}$ unit in copper(I) carbonyls have been drawn from infrared stretching frequencies, ν_{CO} , in these complexes invariably being high, approaching and sometimes even exceeding²⁵ (see below) the value of 2143 cm^{-1} observed for the gaseous molecule.²⁶ The observed carbonyl stretching frequencies for **2**, *viz.* 2099 , 2103 , and 2112 cm^{-1} (solid) and 2102 cm^{-1} (toluene solution) are in good agreement with values determined¹ for carbonyl ligands terminally bonded to copper(I) and are intermediate between those found for $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$ (in toluene)³ and $[(\text{Cu}(\text{CO})\text{Cl})]$ (s),^{5,6} *i.e.*, 2063 and 2127 cm^{-1} , respectively. This trend is matched by the $\text{Cu}-\text{C}$ bond lengths in the three compounds, which are shortest ($1.767(6)$ and $1.783(9) \text{ \AA}$) in $[(\text{Cu}(\text{O}^i\text{Bu})(\text{CO}))_4]$,³ slightly, if not significantly, longer in $[\{\text{Cu}(\text{OC}_6\text{H}_3\text{Ph}_2)(\text{CO})\}_2]$, *i.e.*, $1.78(1)$ and $1.79(1) \text{ \AA}$, and longest, $1.856(16) \text{ \AA}$, in $[\text{Cu}(\text{CO})\text{Cl}]$.⁵ Owing to the low precision

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associated with the determination of C–O distances, it is not possible to detect any differences or trends in these distances between the three compounds.

Furthermore, as has been pointed out in a recent review,²⁷ copper(I) and CO may be considered to be poorly matched reaction partners, in that CO relies heavily on back-bonding for the strength of the M–C bond, whereas copper(I) is reluctant to participate strongly in back-bonding. Thus, the Cu–C bond is considered to be primarily a dative bond, with negligible multiple bond character.²⁷ This has later been supported by an investigation of matrix-isolated monomeric Cu(CO)Cl, exhibiting ν_{CO} of 2157 cm⁻¹, in which the Cu–C bond is predominantly a σ -bond and π^* back-donation is considered to play a minor role.²⁵ *Ab initio* calculations on the Cl–Cu–CO species now, however, suggest that π^* back-donation is not negligible.²⁸ Moreover, the presence of π back-bonding, in addition to the stronger σ -donor interaction in the Cu(I)–CO interaction, as compared with that involving Zn(II), has been demonstrated to be crucial for enhancement of methanol formation from CO by Cu(I)-promoted ZnO catalysts.²⁹ Very recently, solid cationic [Cu(CO)_n]⁺ ($n = 1, 2, 3$) complexes with very high $\nu(\text{CO})$

stretching frequencies, 2164–2178 cm⁻¹, have been isolated, providing further evidence for the importance of nonclassical OC–Cu(I) bonding, predominantly of σ type.⁷ In any event, it may be concluded that the copper(I)–carbonyl interaction is weak and that carbonyl derivatives of, *e.g.*, aryl oxides and alkoxides (*cf.* ref 3) can probably be isolated only when the structure is such that initial decarbonylation of a copper(I) center would result in an unfavorable coordination geometry for this center.

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Supporting Information Available: Tables giving crystal data and details of the structure determinations, fractional coordinates and equivalent isotropic thermal parameters for the non-hydrogen atoms, anisotropic thermal parameters, atomic coordinates for the hydrogen atoms and bond distances and angles involving the non-hydrogen atoms for **1** and **2** (25 pages). Ordering information is given on any current masthead page.

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