Inorg. Chem. **1993**, *32*, 2018–2024

Splitting Dioxygen with Mesitylcopper(I). An Arylcopper(I) Intermediate, Formed in a Coupling Reaction, Containing Two Trapped Trigonal Pyramidally Coordinated Oxides

Mikael Håkansson,[*,†] Mikael Örtendahl,[†] Susan Jagner,[*,†] Michael P. Sigalas,[‡] and Odile Eisenstein[*,‡]

Department of Inorganic Chemistry, Chalmers University of Technology, S-412 96 Göteborg, Sweden, and Laboratoire de Chimie Théorique, Bât. 490, Université de Paris-Sud, 91405, Orsay, France

Received October 9, 1992

Oxidatively induced reductive coupling of mesityl from mesitylcopper(I) effected by dioxygen is shown to result in an intermediate, $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$, containing oxide ligands trapped in an unusual coordination mode on the surface of the cluster. $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ crystallizes in the monoclinic space group $C2/c$ with $a = 16.452(5)$ Å, $b = 33.947(8)$ Å, $c = 12.902(5)$ Å, $\beta = 125.66(1)°$, and $Z = 4$. The complex has approximate D_{3h} symmetry such that the two oxide ligands and a central copper(I) are situated on the approximate 3-fold axis while the remaining nine copper(I) centers form three wings, each with three copper(I) atoms participating in 2 electron–3 center bonds with two mesityl groups. Cu···Cu distances involved in the latter interactions range from 2.376(8) to 2.439(6) Å. The oxide ligands are trigonal pyramidally coordinated by four copper(I) atoms at distances of 1.81(2)–1.90(2) Å and are slightly displaced (0.1 Å) from the cluster surface, i.e. from the trigonal coordination plane, toward the central copper(I). The unusual coordination mode of oxygen on the surface of the cluster, the extreme instability of the complex, and its color are discussed in the context of extended Hückel (EHT) calculations.

Introduction

Dioxygen has been shown to undergo a variety of reactions, such as reversible binding,[1] with copper(I) complexes. With other transition metals, oxygen insertion into M–C bonds has been utilized for the preparation of metal alkoxides, phenoxides, and alkyl peroxo intermediates.[2] In the reaction between dioxygen and various arylcopper(I) compounds in apolar solvents, biaryls, arenes, and diaryl ethers have been obtained.[3] Similarly, oxidation of polynuclear aryl clusters such as $[\mathrm{Cu}_4(\mathrm{C}_6\mathrm{H}_4\mathrm{CH}_2\mathrm{NMe}_2\text{-}2)_4]$ with O_2 leads to the formation of the dimer, a trace of the arene, and the phenol.[4] Recently, "kinetic" mixed diaryl higher order cyanocuprates have been reacted with dioxygen at low temperature to give unsymmetrical biaryls in high and predictable yields.[5] We were interested in examining the reaction of dioxygen with a simple, structurally well-characterized arylcopper(I) complex, our choice being mesitylcopper(I).[6] We report dioxygen cleavage accompanied by oxidatively induced reductive elimination[7] of bimesityl, resulting in the formation of an oxidomesitylcopper(I) intermediate, $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$, viz.

$$10\mathrm{MesCu} + \mathrm{O}_2 \rightarrow [\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6] + 2(\mathrm{Mes{-}Mes})$$

The unusual coordination mode of the trapped oxide ligands in $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$, the color of the intermediate, and its extreme instability prompted us to examine bonding within the cluster by means of extended Hückel (EHT) calculations in order to account for these phenomena.

Experimental Section

Preparation of $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$. All operations were carried out under nitrogen or argon using standard Schlenk techniques. Oxidation reactions were performed with dry oxygen (99.998%). Solvents (dioxane, hexane, tetrahydrofuran, toluene) were distilled under nitrogen from sodium/benzophenone shortly prior to use. Copper(I) chloride was purified according to literature methods.[8] Mesitylcopper(I) was prepared from copper(I) chloride, 2-bromomesitylene, and magnesium according to methods described previously.[6,9] Mesitylcopper(I) (0.50 g; 2.7 mmol) was dissolved in 25 mL of hexane, and dry dioxygen (6.0 mL; 0.27 mmol) was added by means of a cannula. The solution was stirred at ambient temperature for approximately 12 h, during which time a red-orange precipitate of $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ was deposited in quantitative yield. The compound is virtually insoluble in hexane and dissolves with decomposition in more coordinating solvents such as toluene or THF. The orange-red precipitate of $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ is extremely air sensitive as indicated by a change of color to brown. Only traces of arene or phenol could be found after hydrolysis of the solution from which $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ was precipitated. The presence of bimesityl in the same solution was established by the following NMR data. ^{1}H NMR (CDCl_3): δ +1.93 (s, 12H); δ +2.16 (s, 6H); δ +6.69 (s, 4H).

For the synthesis of single crystals, suitable for X-ray diffraction analysis, a small amount of oxygen was allowed to diffuse slowly into the mesitylcopper/hexane solution at 4 °C, yielding large plates of $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ after several days. Crystals of $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ decompose rapidly on exposure to the atmosphere at ambient temperature, turning brownish-black.

X-ray Crystallography. Crystal and experimental data are summarized in Table I. A crystal of $[\mathrm{Cu}_{10}\mathrm{O}_2(\mathrm{Mes})_6]$ was mounted in a glass capillary, under argon, at −150 °C,[10] and transferred at the same temperature to a Rigaku AFC6R diffractometer. Diffracted intensities were measured using graphite-monochromated Mo Kα (λ = 0.710 69 Å) radiation from a RU200 rotating anode source operated at 9 kW (50 kV; 180 mA). The

---

[†] Chalmers University of Technology.

[‡] Université de Paris-Sud.

(1) See for example: Karlin, K. D.; Tyeklar, Z.; Farooq, A.; Haka, M. S.; Ghosh, P.; Cruse, R. W.; Gultneh, Y.; Hayes, J. C.; Toscano, P. J.; Zubieta, J. *Inorg. Chem.* **1992**, *31*, 1436 and references cited therein.

(2) Caulton, K. G.; Hubert-Pfalzgraf, L. G. *Chem. Rev.* **1990**, *90*, 969. Lubben, T. V.; Wolczanski, P. T. *J. Am. Chem. Soc.* **1987**, *109*, 424. Cleaver, W. M.; Barron, A. R. *J. Am. Chem. Soc.* **1989**, *111*, 8966. Arasasingham, R. D.; Balch, A. L.; Cornman, C. R.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1989**, *111*, 4357. Balch, A. L.; Cornman, C. R.; Olmstead, M. M. *J. Am. Chem. Soc.* **1990**, *112*, 2963. Arasasingham, R. D.; Balch, A. L.; Hart, R. L.; Latos-Grazynski, L. *J. Am. Chem. Soc.* **1990**, *112*, 7566.

(3) Camus, A.; Marsich, N. *J. Organomet. Chem.* **1972**, *46*, 385.

(4) van Koten, G.; Jastrzebski, J. T. B. H.; Noltes, J. G. *J. Org. Chem.* **1977**, *12*, 2047.

(5) Lipschutz, B. H.; Siegmann, K.; Garcia, E. *Tetrahedron* **1992**, *48*, 2579.

(6) (a) Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *J. Chem. Soc., Chem. Commun.* **1983**, 1156. (b) Meyer, E. M.; Gambarotta, S.; Floriani, C.; Chiesi-Villa, A.; Guastini, C. *Organometallics* **1989**, *8*, 1067.

(7) Kochi, J. K. *Organometallic Mechanisms and Catalysis*; Academic Press: New York, 1978.

(8) Keller, R. N.; Wycoff, H. D. *Inorg. Synth.* **1946**, *2*, 1.

(9) Tsuda, T.; Yazawa, T.; Watanabe, K.; Fujii, T.; Saegusa, T. *J. Org. Chem.* **1981**, *46*, 192. Tsuda, T.; Watanabe, K.; Miyata, K.; Yamamoto, H.; Saegusa, T. *Inorg. Chem.* **1981**, *20*, 2728.

(10) Håkansson, M. Ph.D. Thesis, Chalmers University of Technology, Göteborg, 1990.

0020-1669/93/1332-2018$04.00/0

Table I. Crystallographic Data for $[Cu_{10}O_2(Mes)_6]$

formula	$C_{54}H_{66}Cu_{10}O_2$	γ, deg	90
fw	1382.6	V, Å^3	5855(3)
cryst syst	monoclinic	Z	4
space group	$C2/c$ (No. 15)	d_{calc}, g/cm^3	1.57
a, Å	16.452(5)	μ, cm^{-1}	36.0
b, Å	33.947(8)	T, °C	−120
c, Å	12.902(5)	R^a	0.064
α, deg	90	$R_w{}^a$	0.086
β, deg	125.66(1)		

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

Table II. Fractional Atomic Coordinates and B_{eq} (for Cu) or B (Å^2) Values for the Non-Hydrogen Atoms in $[Cu_{10}O_2(Mes)_6]$

atom	x	y	z	B_{eq}/B
Cu(1)	0.5000	0.1859(2)	0.2500	2.6(4)
Cu(2)	0.3821(4)	0.1523(2)	0.0180(5)	2.8(3)
Cu(3)	0.3465(4)	0.2365(2)	0.0953(5)	2.6(2)
Cu(4)	0.5000	0.2721(2)	0.2500	3.2(4)
Cu(5)	0.5419(4)	0.1386(2)	0.0575(5)	3.1(3)
Cu(6)	0.3361(4)	0.1620(2)	0.2328(5)	2.7(2)
O	0.363(2)	0.1820(7)	0.118(2)	2.3(6)
C(1)	0.688(3)	0.147(1)	0.144(3)	2(1)
C(2)	0.732(3)	0.107(1)	0.165(4)	3(1)
C(3)	0.812(3)	0.104(1)	0.142(4)	3(1)
C(4)	0.838(3)	0.137(1)	0.100(4)	3(1)
C(5)	0.794(3)	0.173(1)	0.078(4)	3(1)
C(6)	0.721(3)	0.177(1)	0.102(4)	2(1)
C(7)	0.701(3)	0.072(1)	0.202(4)	4(1)
C(8)	0.919(3)	0.131(1)	0.074(4)	4(1)
C(9)	0.668(3)	0.214(1)	0.067(4)	2(1)
C(10)	0.371(3)	0.293(1)	0.095(4)	2(1)
C(11)	0.356(3)	0.319(1)	0.166(4)	3(1)
C(12)	0.357(3)	0.362(1)	0.149(4)	4(1)
C(13)	0.379(3)	0.374(1)	0.069(4)	3(1)
C(14)	0.391(3)	0.347(1)	−0.004(4)	3(1)
C(15)	0.387(3)	0.307(1)	0.005(4)	3(1)
C(16)	0.334(3)	0.309(1)	0.262(4)	4(1)
C(17)	0.382(4)	0.416(2)	0.052(5)	7(2)
C(18)	0.402(3)	0.283(1)	−0.067(4)	3(1)
C(19)	0.404(3)	0.118(1)	−0.078(3)	2(1)
C(20)	0.396(3)	0.129(1)	−0.191(4)	3(1)
C(21)	0.380(3)	0.103(1)	−0.284(4)	3(1)
C(22)	0.372(4)	0.066(2)	−0.269(5)	5(1)
C(23)	0.385(4)	0.052(2)	−0.169(5)	6(1)
C(24)	0.408(3)	0.077(1)	−0.065(4)	3(1)
C(25)	0.398(3)	0.172(1)	−0.217(4)	4(1)
C(26)	0.357(4)	0.035(2)	−0.364(5)	8(2)
C(27)	0.416(4)	0.064(2)	0.052(5)	7(1)

Table III. Selected Interatomic Distances (Å) and Angles (deg) for $[Cu_{10}O_2(Mes)_6]^a$

O–Cu(1)	1.88(2)	C(19)–Cu(2)	1.88(4)
O–Cu(2)	1.81(2)	C(19)–Cu(5)	2.02(4)
O–Cu(3)	1.87(2)	Cu(1)···Cu(2)	2.692(6)
O–Cu(6)	1.90(2)	Cu(1)···Cu(3)	2.727(7)
C(1)–Cu(5)	2.00(4)	Cu(1)···Cu(6)	2.698(5)
C(1)–Cu(6^i)	1.93(4)	Cu(5)···Cu(2)	2.414(7)
C(10)–Cu(3)	1.95(4)	Cu(5)···Cu(6^i)	2.376(8)
C(10)–Cu(4)	2.01(4)	Cu(4)···Cu(3)	2.439(6)

O–Cu(1)–O^i	172(1)	Cu(1)–O–Cu(2)	94(1)
O–Cu(2)–Cu(19)	176(1)	Cu(1)–O–Cu(3)	94(1)
O–Cu(3)–C(10)	163(1)	Cu(1)–O–Cu(6)	91(1)
O–Cu(6)–C(1^i)	175(1)	Cu(2)–O–Cu(3)	121(1)
C(10)–Cu(4)–C(10^i)	140(2)	Cu(2)–O–Cu(6)	125(1)
C(1)–Cu(5)–C(19)	156(1)	Cu(3)–O–Cu(6)	113(1)
Cu(5)–C(1)–Cu(6^i)	74(1)	Cu(3)···Cu(4)···Cu(3^i)	120.6(4)
Cu(3)–C(10)–Cu(4)	76(1)	Cu(2)···Cu(5)···Cu(6^i)	105.6(3)
Cu(5)–C(19)–Cu(2)	76(1)		

^{a} Symmetry code: (i) $1 - x$, y, $^1/_2 - z$.

$\omega/2\theta$ 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 for $5 < 2\theta < 41°$ ($+h,+k,\pm l$) for an orange platelet with approximate dimensions 0.20 × 0.20 × 0.05 mm, using an ω scan rate of 8°/min and a scan width of $(1.10 + 0.30 \tan\theta)°$. 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. No correction was made for the effects of absorption, owing to inability to measure and index the faces of the extremely unstable crystal and to failure to obtain a more satisfactory structural model from empirically corrected data (by means of azimuthal scans). Of the 3002 unique relections measured, 959 had $I > 3.0\sigma(I)$ and were considered observed. Cell constants were obtained by least-squares refinement from the setting angles of 12 reflections in the range $17.9 < 2\theta < 24.0°$.

The structure was solved by direct methods (MITHRIL[11]). Full-matrix least-squares refinement, including anisotropic thermal parameters for the copper atoms and isotropic thermal parameters for oxygen and carbon and with the hydrogen atoms as a fixed contribution, gave a final $R = 0.064$ ($R_w = 0.086$) for 159 parameters and 959 observed reflections. The maximum and minimum values in the final difference map were 1.15 and −0.59 e/Å^3, respectively. Reflections were weighted according to $w = [\sigma^2(F_o)]^{-1}$. Several attempts were made to obtain a more satisfactory refinement of the structure by measuring intensity data from crystals from different batches. Apart from being extremely unstable, crystals of $[Cu_{10}O_2(Mes)_6]$ diffract poorly, the results reported here thus representing the best we were able to obtain.

All calculations were carried out with the TEXSAN[12] program package. Atomic scattering factors and anomalous dispersion correction factors were taken from ref 13. Structural illustrations have been drawn with ORTEP.[14] Final positional parameters are listed in Table II, and selected interatomic distances and angles, in Table III.

Results and Discussion

In the present investigation we have shown that dioxygen effects oxidatively induced reductive elimination[7] of bimesityl from mesitylcopper(I) and simultaneously undergoes cleavage to oxide. Controlled reaction between mesitylcopper(I) and dioxygen has permitted isolation of an intermediate, $[Cu_{10}O_2(Mes)_6]$, the structure of which is depicted in Figures 1–3. Pairwise coupling of aryl groups by pyrolysis of the octamer to give a Cu(0)–Cu(I) cluster, $[m\text{-}(CF_3)C_6H_4]_6Cu_8$, has been demonstrated previously,[15] as has biaryl formation from the reaction of dioxygen with arylcopper(I) complexes[3,4] and with mixed diaryl higher order cyanocuprates.[5] We believe, however, this to be the first example of oxidatively induced reductive elimination[7] of a simple arylcopper(I) compound effected by dioxygen with the concomitant isolation and structural characterization of an intermediate.

Mesitylcopper(I) is currently widely used as a reagent for the preparation of a variety of new copper(I) complexes such as amides, phosphides, and alkoxides. Its popularity is mainly due to limited air sensitivity in the solid state and good solubility in many solvents, which are characteristics lacking in most other organocopper compounds. Furthermore, mesitylcopper(I) is very reactive toward any kind of proton donor and thus provides an excellent alternative whereby lithium or magnesium contamination (or complexation) of the product is avoided. Whereas crystals of mesitylcopper(I) are pale yellow, those of $[Cu_{10}O_2(Mes)_6]$ are orange-red and more sensitive to air. We were not able to dissolve $[Cu_{10}O_2(Mes)_6]$ in either toluene or THF without extensive decomposition of the compound. Since the complex is also virtually insoluble in hexane, from which it was precipitated, we were restricted to solid-state characterization.

Two different mechanisms have been proposed for the oxidation of $[Cu_4(C_6H_4CH_2NMe_2\text{-}2)_4]$ with dioxygen:[4,16a,b] viz. the formation of an activated species between O_2 and the Cu_4 core followed by *either* intraaggregate C–C coupling of two aryl groups

---

(11) Gilmore, C. J. *J. Appl. Crystallogr.* **1984**, *17*, 42.
(12) TEXSAN-TEXRAY Structure Analysis Package. Molecular Structure Corp., The Woodlands, TX, 1989.
(13) *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(14) Johnson, C. K. *ORTEP*. Report ORNL-3794; Oak Ridge National Laboratory: Oak Ridge, TN, 1965.
(15) Cairncross, A.; Sheppard, W. A. *J. Am. Chem. Soc.* **1971**, *93*, 247.

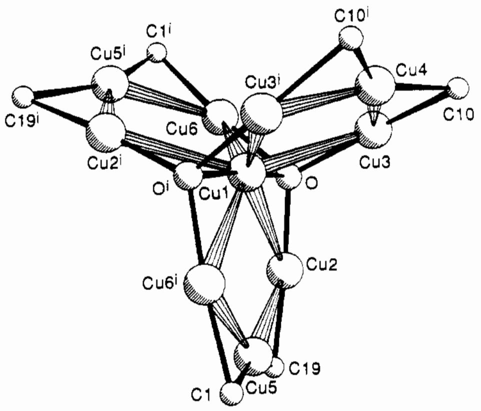


Figure 1. Core of $[Cu_{10}O_2(Mes)_6]$, showing the crystallographic numbering. In order to emphasize the structure of the core, Cu⋯Cu contacts have been drawn as open spoke "bonds". Symmetry code: (*i*): $1 - x, y, {}^1/_2 - z$.

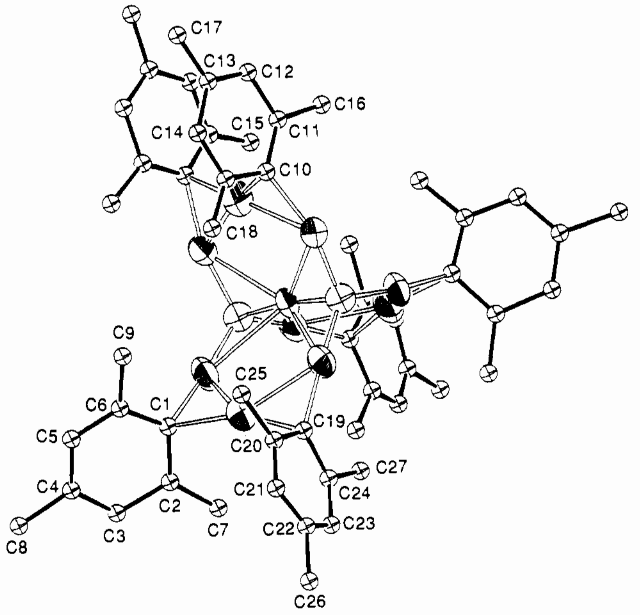


Figure 2. View of $[Cu_{10}O_2(Mes)_6]$, showing the crystallographic numbering of the mesityl groups. The core (cf. Figure 1) has been drawn with open bonds. The thermal ellipsoids of the copper atoms enclose 50% probability. For clarity, the carbon atoms have been drawn as spheres of radius 0.1 Å.

bonded to the same copper(I) center giving the biaryl *or* O_2 insertion into the Cu–C bond which results ultimately in the formation of the phenol. The present results demonstrate unequivocally that in the case of mesitylcopper(I) the former mechanism is that which occurs, intraaggregate C–C coupling of mesityl bonded to copper(I) being accompanied by simultaneous cleavage of dioxygen to oxide. Further reaction of the intermediate with oxygen induces coupling of the remaining mesityl groups, leading eventually to the formation of a brownish-black amorphous product which is presumably a mixture of copper(I) and copper(II) oxides.

The core of the $[Cu_{10}O_2(Mes)_6]$ complex (Figure 1) is composed of three wings, each containing three copper(I) centers, joined via a central copper(I), Cu(1). In order to emphasize the structure of the core, Cu⋯Cu contacts have been drawn as open spoke "bonds". As is seen from Table III, and will be discussed further below, the magnitude of these distances vary. Thus, Cu(1) is involved in relatively long Cu⋯Cu contacts (2.692(6)–2.727(7) Å) and can be regarded as being esssentially linearly coordinated by oxygen with Cu(1)–O = 1.88(2) Å and O–Cu(1)–O^i = 172(1)° (for symmetry code, see Table III). These connectivity relationships are in good agreement with values determined for e.g. Cu_2O,[17] in which copper(I) also exhibits linear coordination. The copper(I) centers nearest to Cu(1), viz. Cu(2), Cu(3), Cu(6), and their symmetry-related equivalents, are each approximately linearly coordinated by oxygen and a mesityl carbon with Cu–O = 1.81(2) and 1.87(2) Å, Cu–C in the range 1.88(4)–1.95(4) Å, and O–Cu–C from 163(1) to 176(1)°. These copper(I) atoms are involved in short Cu⋯Cu contacts to the peripheral copper(I) centers, Cu(4), Cu(5), and Cu(5^i), i.e. 2.376(8)–2.439(6) Å, of the magnitude commonly observed in connection with Cu–μ-(aryl)–Cu linkages of 2 electron–3 center (2e–3c) character.[6,16a]

Mesitylcopper(I) has been found to exist predominantly as a dimer in toluene solution at ambient temperature,[6b] whereas it is pentameric in the solid state.[6] From a tetrahydrofuran solution containing THT (tetrahydrothiophene), a tetrameric complex $[Cu_4(Mes)_4(THT)_2]$ has been isolated.[6] A linear, monomeric $[Cu(Mes)_2]^-$ anion has been prepared and characterized by means of crystal structure determination.[18] The copper(I)–mesityl–copper(I) fragments in the present structure (Figures 1–3) are closely similar to those in $[Cu_5(Mes)_5]$ and $[Cu_4(Mes)_4(THT)_2]$:[6] Cu–C distances range from 1.88(4) to 2.02(4) Å, the peripheral copper(I) centers, Cu(4) and Cu(5), being associated with the slightly longer Cu–C bonds. The C–Cu–C angles, 140(2) and 156(1)°, are also in good agreement with corresponding values determined for $[Cu_5(Mes)_5]$, viz. 149(1) – 160(1)°, and for $[Cu_4(Mes)_4(THT)_2]$, viz. 140.6(4) and 141.5(4)°.[6] The Cu–C–Cu angles (Table III) are consistent with values determined previously.[6,16a] The aryl groups in $[Cu_{10}O_2(Mes)_6]$ are approximately perpendicular to the relevant Cu–Cu–Cu planes (cf. Figure 3). Whereas Cu(1), Cu(3), Cu(4), and Cu(3^i) are constrained to be co-planar by symmetry, the plane through Cu(1), Cu(2), and Cu(6^i) is inclined at 175° to that through Cu(2), Cu(5), and Cu(6^i). The dihedral angles between the planes through the aryl groups bonded to Cu(2), Cu(5), and Cu(6^i) and the plane through the latter atoms are 95 and 90°, and that between the C(10) aryl group and the Cu(1), Cu(3), Cu(4), Cu(3^i) plane is 94°. As is seen from Figure 3, the planes through the aryl groups bonded to Cu(3), Cu(4), and Cu(3^i) are parallel, whereas the planes through those bonded to Cu(2), Cu(5), and Cu(6^i) are inclined at 126°. There are no intermolecular contacts significantly less than 3.6 Å.

The oxide ligands are trapped on the surface of the cluster in a rather unusual trigonal pyramidal coordination mode (Figures 1 and 3 and Table III). The oxygen atom is displaced 0.10 Å from the trigonal plane [through Cu(2), Cu(3), and Cu(6)] toward the apical copper(I) [Cu(1)]. At this level of structural precision, apical and equatorial O–Cu distances cannot be considered to differ.

Extended Hückel (EHT) calculations[19] were carried out on $[Cu_{10}O_2(Mes)_6]$, whose structure was modified to comply with D_{3h} symmetry (**1**) (Chart I), the copper(I) centers being hereafter denoted as Cu_A, Cu_B, and Cu_C in accordance with **1**. Mean values of the relevant distances were used for Cu–O, Cu_A–Cu_B, and Cu_B–Cu_C, respectively. Calculations were also carried out on an idealized model (D_{5h}) (**2**) of the pentanuclear $[Cu_5(Mes)_5]$ complex[6] in order to permit comparison between some of the properties of the two compounds.

---

[16] (a) van Koten, G.; Noltes, J. G. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon: Oxford, U.K., 1981; Chapter 14, p 709 and references therein. (b) *Ibid.*, p 745. (c) *Ibid.*, pp 737–740. (d) The interaction between the filled d block and the σ aryl orbital is net antibonding. However, in some of the molecular orbitals the d block combine in phase with the aryl orbitals. The net bonding is due to the s and p participation of Cu.

[17] Restori, R.; Schwarzenbach, D. *Acta Crystallogr.* **1986**, *B42*, 201.

[18] Leoni, P.; Pasquali, M.; Ghilardi, C. A. *J. Chem. Soc., Chem. Commun.* **1983**, 240.

[19] Extended Hückel calculations were done using the weighted H_{ij} formula (Ammeter, J. H.; Bürgi, H.-B.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1978**, *100*, 3686). The Cu parameters were taken from the literature: Hay, P. J.; Thibeault, J. C.; Hoffmann, R. *J. Am. Chem. Soc.* **1975**, *97*, 4884.

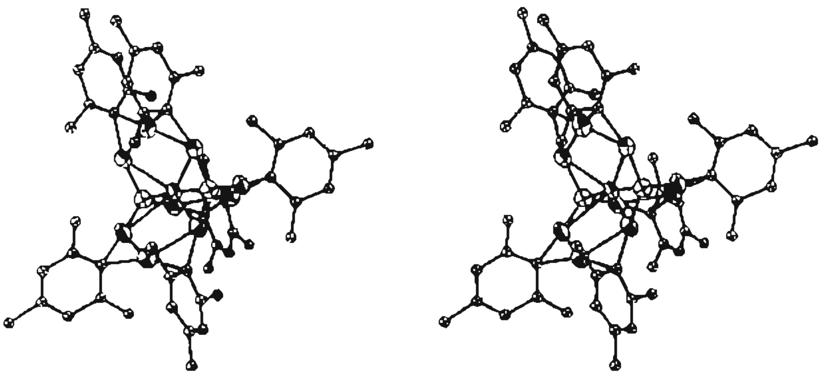
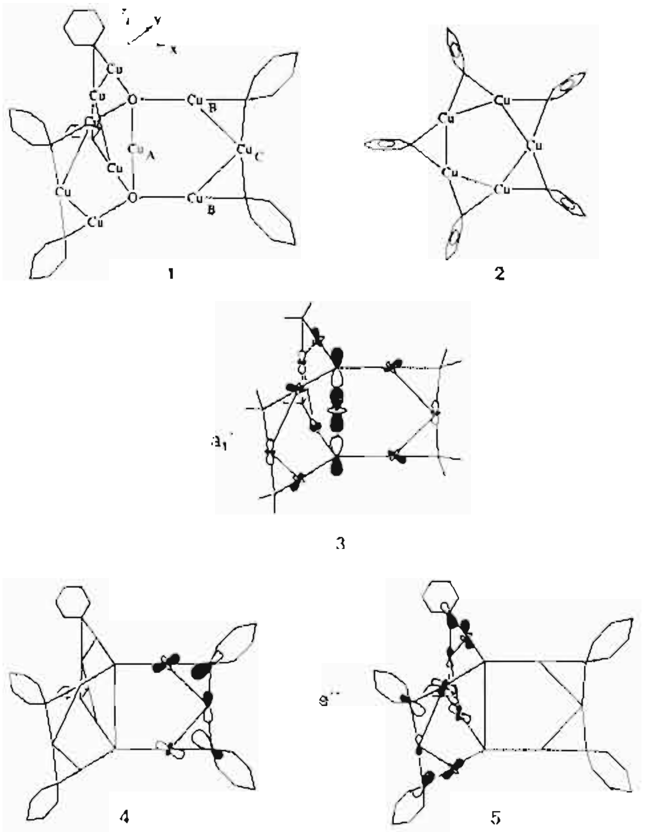


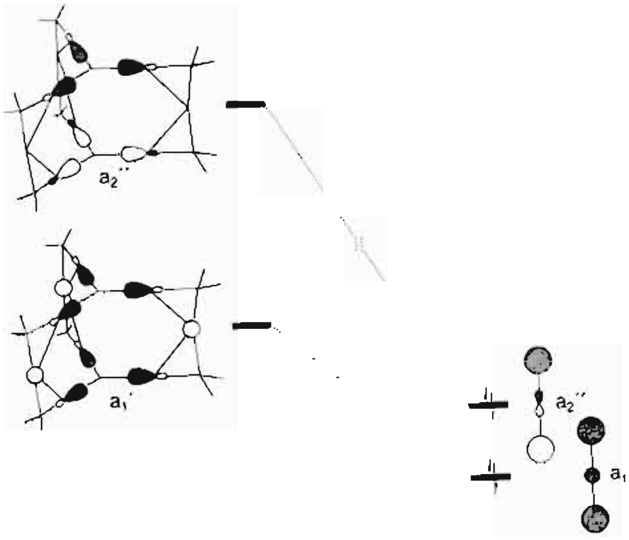
Figure 3. Stereoview of the $[Cu_{10}O_2(Mes)_6]$ cluster. The orientation is as in Figure 2.

Chart I



1 2 3 4 5

Scheme I



The large number of atoms in $[Cu_{10}O_2(Mes)_6]$ results in a concentration of molecular orbitals reminiscent of a band structure. We have therefore chosen a representation of the energy pattern adapted to large clusters and solids. Figure 4 shows the participation of the different atoms in terms of discrete DOS histograms in a meaningful energy range.

The highest occupied orbitals are mostly centered on the aryl ligands with contributions from the copper(I) atoms linked to the aryl groups. Participation of oxygen is small but not negligible and will play a role in the reactivity (see below). Going down in energy, one sees an increasing participation of the Cu atoms due mainly to the d orbitals. Other aryl orbitals appear below this d block. Those orbitals which have a major contribution from oxygen are considerably lower in energy, owing to the higher electronegativity of the oxygen atom. Other aryl orbitals are found both above and below the oxygen-centered orbitals (not shown in Figure 4). The empty orbitals can be described in a similar manner: The lower band is composed of aryl orbitals with no contribution from the copper atoms, whereas the next band is derived from the s and p orbitals of copper. Finally, the highest part of the band is composed of the remaining aryl orbitals.

As mentioned above, three features of the complex are of particular interest: the unusual coordination mode of oxygen on the surface of the cluster and the instability and the color of the compound. To determine the origin of these features a more detailed description of some of the orbitals is required.

The copper d orbitals interact only in an antibonding mode with the occupied orbitals of the ligands and in particular with the oxygen orbitals. The empty π orbitals of the aryl groups play a minor role due to the large gap in energy between these orbitals and the copper d block. Consequently, the d block of each copper atom can be considered to be filled effectively with 10 electrons, which is consistent with a +I oxidation state for copper as suggested by a conventional electron count. However, the antibonding interaction between copper and oxygen cannot be neglected since it raises the energy of part of the d block. The highest destabilization is found between Cu_A and O due to the large overlap between z^2 and the oxygen p_z orbitals. The resulting orbital delocalized (3) on Cu and O is found just below the HOMO. We believe that it is this orbital which would be responsible for high reactivity of the compound toward electrophiles and, in part, for its color (see below).

The ligand–Cu bonds are obtained by interaction of the valence orbitals of the ligands (oxide or aryl) with the empty s and p orbitals of the copper atoms: The oxide ligands coordinate to four copper centers resulting in the rather unusual trigonal pyramidal arrangement described above. It appears that in this bonding each oxygen orbital is stabilized by the proper combination of empty Cu s and p orbitals. Thus the oxygen s orbital can interact with an in-phase combination of all four neighbouring copper atoms as shown in Scheme I, whereas the oxygen p_x and p_y orbitals interact with the e combination of the Cu_B σ hybrid and the p_x or p_y orbitals of Cu_A (Scheme II). The oxygen p_z orbitals are essentially involved with the Cu_A atom. Both the

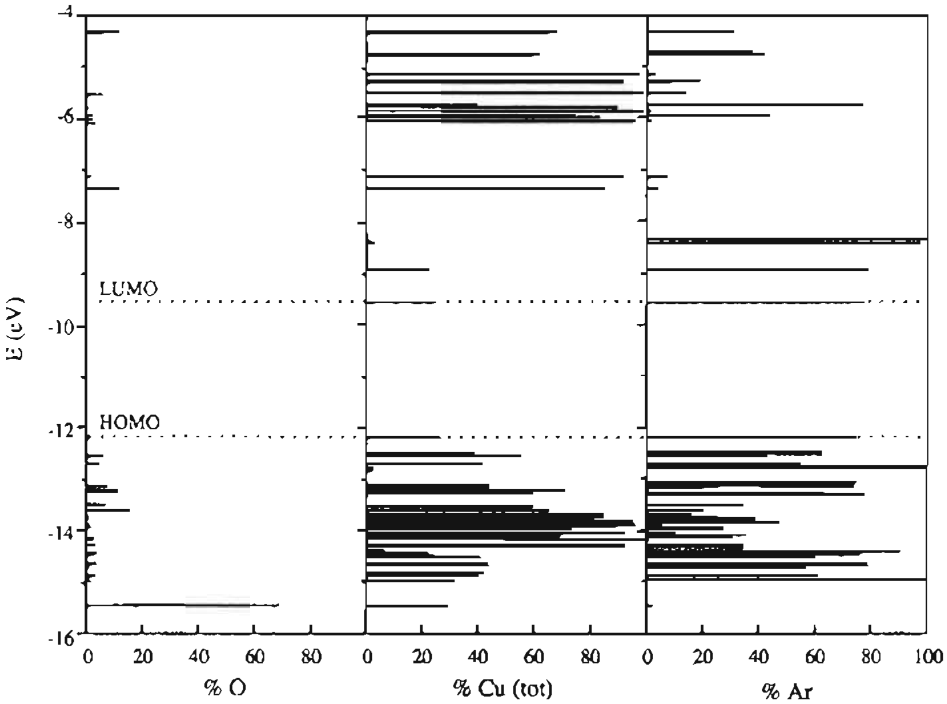
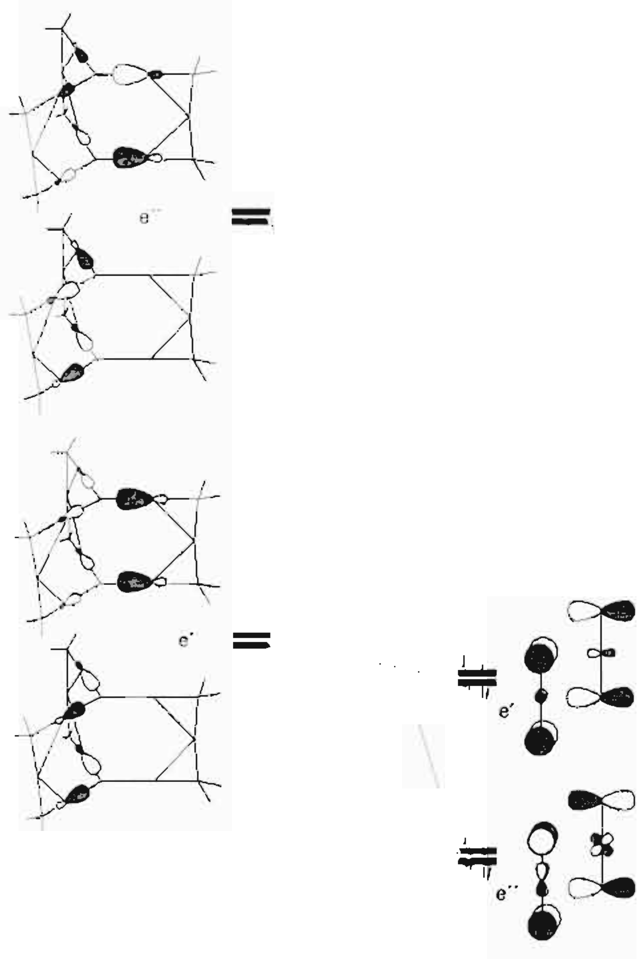
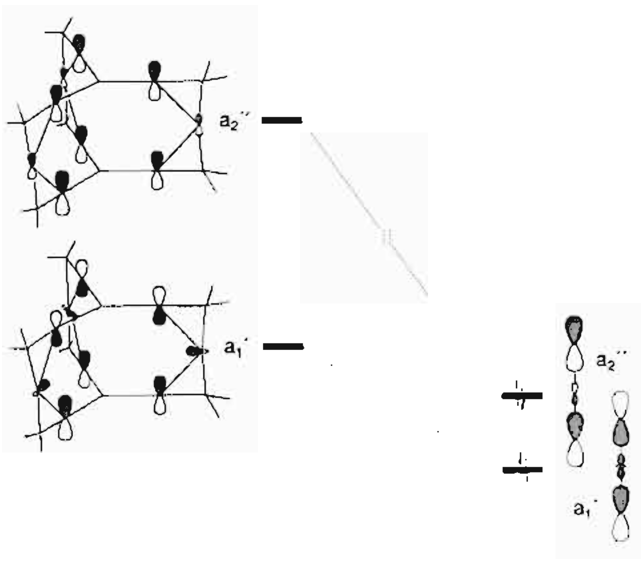


Figure 4. Distribution of the electron density on the copper(I) atoms, the oxide ligands, and the aryl groups in **1** as a function of the energy.

Scheme II



Scheme III



in-phase and out-of-phase combinations can be stabilized by the s and p_z orbitals of $\mathrm{Cu_A}$, respectively, because of a large overlap. Additional stabilization is provided by a weaker interaction with the high-lying orbitals centered on $\mathrm{Cu_B}$ (Scheme III).

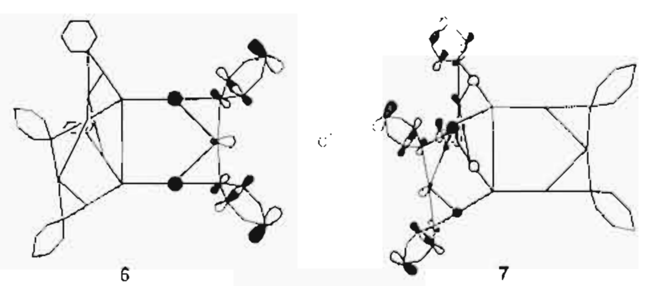
Although unusual, the oxygen coordination mode in the cluster is not totally unprecedented. For instance, oxygen was found to be coordinated in a square-planar manner in a $\mathrm{V_4O}$ cluster and the four metal center described in a similar way.[20] In the present case, trigonal pyramidal coordination geometry is predetermined by the ligands. In particular, the spatial orientation of the $\mathrm{Cu_B}$ σ hybrids (pointing away from the cluster), which is determined by the aryl groups and which has an important role to play in bonding with the oxygen p_x and p_y orbitals, would favor a geometry in which oxygen is coplanar with the $\mathrm{Cu_B}$ centers or even situated above this plane. Other forces, including the strong interaction with $\mathrm{Cu_A}$, induce a compromise, forcing the oxygen to enter the

---

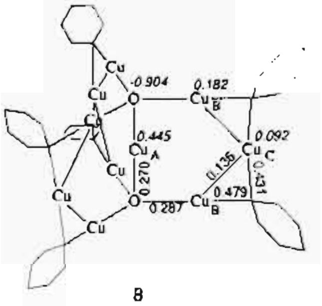
(20) Rambo, J. R.; Huffman, J. C.; Christou, G.; Eisenstein, O. *J. Am. Chem. Soc.* **1989**, *111*, 8027.

(21) (a) The oxygen atoms were allowed to move within the rigid framework of the $\mathrm{Cu_B(aryl)_6}$ backbone, the best position of each oxygen center being found to be 0.25 Å from the plane through the adjacent $\mathrm{Cu_B}$ atoms toward $\mathrm{Cu_A}$. In another optimization process, the oxygen centers were moved while keeping the sum of the O–Cu bond lengths constant, thus removing the rigid framework constraint. In this last process, the best results were obtained for a geometry similar to that observed experimentally, i.e. no tendency toward a tetrahedral distortion of the trigonal pyramid. (b) Our method of calculation does not, however, permit proof that the experimental coordination geometry is the optimum structure

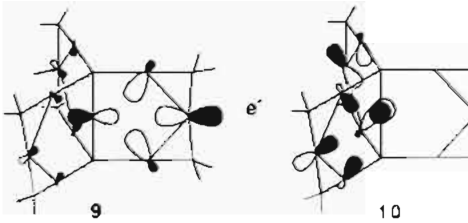
Chart II



6 7



8



9 10

cluster. According to our calculations, the "best" position for the oxygen ligands in the $Cu_{10}(aryl)_6$ framework is 0.25 Å from the plane through the three Cu_B centers toward Cu_A.[21a] Although such optimizations with EHT calculations have limited validity, we believe that they give a reasonable indication of the feasibility of bonding oxygen close to the surface of the cluster.[21b]

The aryl ligands are bonded to copper forming typical 2e–3c bonds,[16c,d] composed of the σ orbital of each aryl group, which is high in energy, and the s, p_x, and p_z orbitals of the two copper atoms. Since the aryl σ orbital is high in energy, the resulting bonding MO remains high and constitutes the HOMO (e'', **4**, **5**) (Chart I) of the complex. It is thus clear that the empty s and p orbitals of each copper have been properly utilized to stabilize all the ligands.

The LUMO (e', **6**, **7**) (Chart II) of the complex is composed of the π^* of the aryl slightly stabilized by the Cu_B and Cu_C centers. It is therefore at a rather high energy. The magnitude of the HOMO–LUMO gap implies that the complex is diamagnetic.

One of the questions usually raised in connection with Cu clusters is the existence of Cu–Cu bonding.[22] Hoffmann and others[22a,b] have shown that Cu–Cu bonding will result from the participation of s and p Cu orbitals in the bonding scheme since the interaction between the d block and the ligands is antibonding. The Mulliken overlap populations (MOP) and the charges are shown in **8**. For **1**, the Mulliken overlap population (0.136) indicates a significant bonding interaction between Cu_B and Cu_C and a much smaller one (0.016) between Cu_A and Cu_B. Our analysis is certainly biased since the MOP are calculated for different Cu–Cu distances (Cu_A–Cu_B > Cu_B–Cu_C). The result is, however, in agreement with the existence of a bond between those copper atoms (Cu_B and Cu_C) bridged by the aryl groups, i.e. those participating in 2e–3c bonds. The existence of bonding interactions between Cu_A and Cu_B is less clear since there is no reliable reference point and Cu–Cu bonds have been shown to be highly flexible.[22c]

It is clear from the previous description that the Cu centers play different roles. Cu_B and Cu_C have received significant density from the aryl ligands, while the oxide ligands interact mostly with Cu_B and less with Cu_A. In particular, p_x and p_y of Cu_A have little interaction with the p_x and p_y orbitals of oxygen and thus remain almost empty, an indication of appreciable unsaturation at Cu_A.

There would appear to be two reasons for the reactivity of the compound. First, the Cu s and p orbitals combine in a bonding manner to create low-lying molecular orbitals such as **9** and **10** which are directed toward the surface of the cluster and would thus be responsible for reactivity of the complex towards incoming nucleophiles. These orbitals are not strongly destabilized by the ligands (aryl and oxygen) and thus remain at low energy. In other words, the Cu centers remain unsaturated and ought therefore to be centers for reactivity. In this context, it is of interest that the central Cu (Cu_A) is more electron deficient than the peripheral Cu_B and Cu_C centers (**8**). This is because the p_x and p_y of Cu_A are only marginally destabilized by the p_x and p_y orbitals of oxygen, these last being well stabilized by the orbitals of the three neighboring Cu_B centers (Scheme II). Thus, as mentioned above, only the s and p_z orbitals of Cu_A are significantly occupied by electrons. This suggests that any multiple bonding between O and Cu_A is weak, which is also in accord with the observed Cu_A–O [Cu(1)–O] bond distance. It suggests, moreover, that the central Cu_A atom should be particularly susceptible to attack by a nucleophile, although access to Cu_A ought to be sterically hindered owing to its shielded position at the centre of the cluster. Similarly, the Cu_C centers are partially protected by the proximity of the mesityl groups.

Reactivity toward an electrophile would arise from the presence of the occupied orbital **3** centered on the oxygen and copper atoms which is very close to the frontier level. In other words, the unusual coordination geometry of the trapped oxide ligands, whereby these are positioned on the surface of the cluster, ought to make the compound also very susceptible to electrophilic attack.

In $Cu_5(Mes)_5$, the 2e–3c bonds involve Cu s, p_x, and p_y orbitals while the p_z orbitals perpendicular to the molecular plane remain essentially empty, indicating appreciable unsaturation at each Cu center. The reactivity of the compound toward nucleophilic attack thus has the same origin as in $[Cu_{10}(Mes)_6O_2]$. In $[Cu_5(Mes)_5]$ there is an in-phase combination of Cu hybrids in the plane of the five-membered ring. In addition, the in-phase combination of Cu p_z orbitals is sufficiently low to increase reactivity toward nucleophiles.

The transition from the HOMO (e'') into the LUMO (e') is permitted. We have seen that the aryl σ orbital is only moderately stabilized by Cu and that the LUMO is composed mostly of aryl π^*. The HOMO–LUMO energy gap corresponds to an absorption in the visible. Transition from **3** into the aryl π^*, which would also be permitted (a' → e'), would lie in the same range of energy values. Although EHT calculations are certainly inappropriate for the assignment of absorption bands, they can be used to rationalize the difference in color between $[Cu_{10}(Mes)_6O_2]$ and $[Cu_5(Mes)_5]$. In $[Cu_5(Mes)_5]$, the HOMO is lower in energy due to the smaller size of the cluster and the absence of oxygen, leading to fewer antibonding interactions. In contrast, the LUMO's of the two complexes are very similar in energy since they are mostly localized on the aryl π^*, which interact little with the rest of the cluster. Thus the HOMO →

---

[22] (a) Mehrotra, P. M.; Hoffmann, R. *Inorg. Chem.* **1978**, *17*, 2187. (b) Merz, K. M., Jr.; Hoffmann, R. *Inorg. Chem.* **1988**, *27*, 2120. Subramanian, L; Hoffmann, R. *Inorg. Chem.* **1992**, *31*, 1021. For an analysis of Cu–Cu interactions in chain systems, see: Cui, C. X.; Kertesz, M. *Inorg. Chem.* **1990**, *29*, 2568. (c) For a different point of view on the Cu···Cu interaction, see: Avdeef, A.; Fackler, J. P., Jr. *Inorg. Chem.* **1978**, *17*, 2182. Lee, S. W.; Trogler, W. C. *Inorg. Chem.* **1990**, *29*, 1659. (d) Burdett, J. K.; Eisenstein, O. *Inorg. Chem.* **1992**, *31*, 1758. (e) Solovcichik, G. L.; Eisenstein, O.; Poulton, J. T.; Streib, W. E.; Huffmann, J. C.; Caulton, K. G. *Inorg. Chem.* **1992**, *31*, 3306.

LUMO transition in $[Cu_5(Mes)_5]$ is blue shifted with respect to that in $[Cu_{10}(Mes)_6O_2]$, in agreement with the observed colors of the two compounds.

In conclusion, the transient orange-red color which is often observed to develop at ground joints and stopcocks of glassware containing mesitylcopper(I) can now be attributed to oxygen seepage resulting in the formation of the intermediate $[Cu_{10}(Mes)_6O_2]$. The present experimental and theoretical study of this complex has provided insights into the structure and reactivity of the intermediate itself but has, in addition, shed new light on the mechanism involved in biaryl formation from arylcopper(I) compounds effected by dioxygen.

Acknowledgment. This work has been supported by grants from the Swedish Natural Science Research Council and the CNRS. The Laboratoire de Chimie Théorique is associated with the CNRS (URA 506) and is a member of the ICMO and IPCM. The theoretical part of this work was initiated during a visit by O.E. to Göteborg sponsored by the Maxwell fellowship of the French Academy of Sciences. M.P.S. thanks the University of Thessaloniki and the CNRS for funding his stay in Paris.

Supplementary Material Available: Tables giving crystal data and details of the structure determination, anisotropic thermal parameters for the copper atoms, and atomic coordinates for the hydrogen atoms (4 pages). Ordering information is given on any current masthead page.