Contribution from the Istituto di Chimica Generale, Università di Pisa, 56100 Pisa, Italy, Chemistry Department, Columbia University, New York, New York 10027, and Istituto di Strutturistica Chimica, Centro di Studio per la Strutturistica Diffrattometrica del CNR, Università di Parma, 43100 Parma, Italy

Copper(I)–Phenoxide Complexes: Synthesis and Ligand-Induced Transformations of the Copper(I)–Phenoxo Functionality

Paolo Fiaschi,[†] Carlo Floriani,*[†,‡] Marco Pasquali,[†] Angiola Chiesi-Villa,[§] and Carlo Guastini[§]

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Synthesis and structural characteristics of copper(I) complexes containing the [Cu–OAr] unit are reported. Ancillary ligands promote transformations into the various forms in which this unit occurs. These forms are closely related to those found in copper(I)–alkyl and –aryl chemistry. Reaction of copper(I) chloride with sodium phenoxides, NaOAr (Ar = Ph, 2,6-$Me_2C_6H_3$), under nitrogen in THF, gave solutions of Cu(I) phenoxides (I) that rapidly decomposed to copper metal. The same reaction under carbon monoxide, however, gave the compounds [S(CO)Cu(μ-OAr)$_2$Cu(CO)S] (II) (S = THF; Ar = Ph, 2,6-$Me_2C_6H_3$). By addition of monodentate ligands, L, to solutions of II, the complexes [L_2Cu(μ-OAr)$_2$CuL_2] (III) (L = PPh_3, *p*-MeC_6H_4NC; Ar = Ph) crystallized (ν(C–N): 2145 and 2125 cm^{-1}). The solid-state structure (L = *p*-MeC_6H_4NC) showed a close proximity of the two copper(I) atoms (Cu···Cu = 3.223 (1) Å), Cu–O bond distances of 2.066 (4) and 2.083 (4) Å, and a tetrahedral coordination around copper(I) as expected. By use of a tridentate ligand, the phenoxo group was forced to display a terminal bonding mode in [Cu(TRIPHOS)(OPh)] (V). The same result was achieved by using bulky substituents at the phenyl ring of the phenoxo group in [Cu(*p*-MeC_6H_4NC)$_2$(2,6-*t*-$Bu_2C_6H_3O$)] (VIII) (ν(C–N) (Nujol): 2145 and 2170 cm^{-1}). Bidentate ligands, in turn, caused the rearrangements of the bimetallic unit [Cu_2(μ-OAr)$_2$]. The ligand BEN (BEN = *N,N'*-ethylenebis(benzaldimine)), upon reaction with a solution of II (Ar = 2,6-$Me_2C_6H_3$), promoted a ligand disproportionation leading to the phenoxo–cuprate(I) complex [Cu(BEN)$_2$]$^+$[ArO–Cu–OAr]$^-$ (VII) (Ar = 2,6-$Me_2C_6H_3$), the structure of which was determined by X-ray analysis. The cuprato anion has a linear coordination (O–Cu–O = 169.8 (3)°) with short Cu–O bond distances (1.806 (6), 1.798 (8) Å). The reaction of dppe with a solution of II (Ar = Ph), however, gave the dinuclear compound [[Cu(OPh)(dppe)]$_2$(μ-dppe)]·4THF (VI), containing terminal phenoxo ligands (Cu–O = 2.023 (5) Å). This compound may be an intermediate through which the rearrangement of II occurs in the reaction with BEN. The Cu–O bond distance was found to increase as the coordination number of Cu(I) increased from 2 (VIII; Cu–O = 1.806 (6) Å) to 3 (III, L = *p*-MeC_6H_4NC; Cu–O = 1.917 (3) Å) to 4 (VI; Cu–O = 2.023 (5) Å). Crystallographic details for complex III (L = *p*-MeC_6H_4NC): space group $P2_1/n$ (monoclinic); *a* = 11.288 (3), *b* = 10.374 (3), *c* = 16.449 (4) Å; β = 95.62 (3)°; *V* = 1917.0 (9) Å^3; *Z* = 2; D_{calcd} = 1.35 g cm^{-3}. The final *R* factor was 0.052 (R_w = 0.059) for 1932 observed reflections. Crystallographic details for complex VIII: space group $P2_1/n$ (monoclinic); *a* = 23.179 (4), *b* = 9.456 (1), *c* = 12.509 (2) Å; β = 94.02 (2)°; *V* = 2735.0 (7) Å^3; *Z* = 4; D_{calcd} = 1.22 g cm^{-3}. The final *R* factor was 0.039 (R_w = 0.043) for 2623 observed reflections. Crystallographic details for complex VI: space group *Pbca* (orthorhombic); *a* = 23.524 (7), *b* = 21.746 (6), *c* = 18.572 (4) Å; *V* = 9501 (4) Å^3; *Z* = 4; D_{calcd} = 1.26 g cm^{-3}. The final *R* factor was 0.049 (R_w = 0.057) for 3837 observed reflections. Crystallographic details for complex VII: $P2_1/c$ (monoclinic); *a* = 13.643 (3), *b* = 21.528 (5), *c* = 15.538 (4) Å; β = 111.31 (3)°; *V* = 4252 (2) Å^3; *Z* = 4; D_{calcd} = 1.32 g cm^{-3}. The final *R* factor was 0.042 for 2410 observed reflections.

Introduction

The copper–alkoxo unit, which is usually synthesized in situ, plays a significant role in metal-promoted transformations of organic substrates by copper(I).[1,2] In addition, metal-promoted activation of small molecules containing oxygen, such as carbon monoxide and carbon dioxide, often produces the M–OR unit.[1,2] However, the high reactivity and relative instability of the Cu^I–OR[1,2] unit contrasts sharply with the inertness and stability of the [M–OR] unit of many transition metals.[3]

Both the [Cu–OR] moiety and the better known copper(I)–organometallic functionality [Cu–R], which are to bring about transformations of organic substrates, are synthesized and used in situ. In the case of copper(I)–alkyls, the "in situ" conditions are those promoting the formation of a cuprato-type derivative, which is believed to be the active form in the alkylation of organic substrates. The goal of this work was to determine the reaction form of the [Cu–OPh] unit. The present study provides fundamental information concerning synthesis, stability, environment, and simple ligand-induced transformations of the organometallic functionality [Cu–OAr].

There is a close relationship between the copper(I) [Cu–R] and [Cu–OR] functionalities, in both structure and related reactivity. The forms that copper(I) functionalities display may be summarized as follows:

(1) Homoleptic Compounds: [Cu–R]$_n$, [Cu–OR]$_n$. In this form, copper(I) is normally bicoordinate with the organic fragment displaying a bridging bonding mode. This structural mode, well-known for both functionalities, may be exemplified by some typical compounds: [Cu–CH_2SiMe_3]$_4$,[7] [Cu–Mes]$_5$[8] (Mes = 2,4,6-$Me_3C_6H_2$), [Cu–O-*t*-Bu]$_4$,[9] and [Cu–OCH-*t*-Bu_2]$_4$,[10] all having similar cyclic structures.

(2) Compounds Having the L_nCu–R and L_nCu–OR Formulas. Here, the organometallic functionality is "stabilized" by ancillary ligands. This class includes some complexes in which donor atoms

* To whom correspondence should be addressed at Columbia University.
† Università di Pisa.
‡ Columbia University.
§ Università di Parma.

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belong to the organic residue of the organometallic functionality. This is the most common form for both functionalities. Some phenoxo derivatives having this formula are known,[11] while examples are numerous for alkyl and aryl derivatives.[5]

(3) Alkyl- and Alkoxo-Cuprato Compounds. These have the simplified formulas $[R-Cu-R]^-$ and $[RO-Cu-OR]^-$. They denote the cuprato unit in the ion-separated form, rather than the structure of the neutral compound. Cuprato compounds can occur, however, in two forms, which differ significantly in their reactivities.

(a) Cuprato Compounds in the Ion-Pair Form. A significant number of these species are known in copper(I)-alkyl chemistry, primarily when lithium plays the role of the countercation.[5,12] Lithium, in fact, replaces copper(I) in polynuclear structures that are very similar to those found for homoleptic compounds. No compound of this sort is known for copper(I) alkoxo derivatives.

(b) Cuprato Compounds in the Ion-Separated Form. An example was reported for the copper(I)-phenyl derivative $[CuMes_2]^-$,[13] while the only known example of a phenoxo-cuprate(I) compound will be described below.

This paper describes the synthesis of the [Cu-OAr] unit, the forms in which it occurs, the bonding modes of the -OAr unit associated with these forms, and how the interconversions of the various forms cited above are brought about by the introduction of appropriate ancillary ligands. Some of these results have been briefly communicated.[14,15]

Experimental Section

All reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. Infrared spectra were recorded with a Perkin-Elmer Model 283 spectrophotometer. Copper(I) chloride was prepared as reported.[16] Sodium phenoxides were prepared from sodium sand in THF reacted with freshly distilled phenols and recovered as white crystalline solids by addition of *n*-hexane. The content of sodium phenoxide was checked by a standard acid-base titration.

Abbreviations: dppe = bis(1,2-diphenylphosphino)ethane; TRIPHOS = 1,1,1-tris((diphenylphosphino)methyl)ethane; BEN = *N,N'*-ethylenebis(benzaldimine).[17a]

Reaction of [CuCl] with Sodium Phenoxide. An acetonitrile (10 mL) solution of sodium phenoxide (1.16 mmol) was added dropwise to a suspension of [CuCl] (1.15 g, 1.16 mmol) in 30 mL of acetonitrile. The resulting yellow suspension was filtered out from the NaCl, giving a solution, from which the isolation of any compounds was prevented by a fast decomposition to copper metal. A stabilization of the solution was achieved by reacting it with carbon monoxide (ν(C-O) = 2080 cm^{-1}). It was not possible to isolate a product from the carbonylated solution.

Reaction of [Cu(CO)Cl] with Sodium Phenoxide: Complex II. Carbon monoxide was absorbed by a suspension of [CuCl] (1.00 g, 10.08 mmol) in methanol (30 mL).[17b] A methanolic solution (15 mL) of PhONa (10.0 mmol) was then added. The solid dissolved, forming a light yellow solution (ν(C-O) = 2080 cm^{-1}). The solution gave, on standing, a crystalline solid, which could be filtered and dried on a stream of carbon monoxide. The IR spectrum of the solid (Nujol) showed a CO band at 2090 cm^{-1}. Sometimes some impurity of [Cu(CO)Cl] (ν(C-O) = 2120 cm^{-1})[17b] was present in the solid. When the reaction was carried out in a gas-volumetric apparatus, 1.17 mmol of CO was absorbed per 1.18 mmol of CuCl. The same results have been found by carrying out the reaction in THF.

Reaction of [Cu(CO)Cl] with Sodium 2,6-Dimethylphenoxide. The reaction was carried out as reported for the unsubstituted phenoxide and gave similar results. The methanolic solution showed a CO band at 2095 cm^{-1}, while the lability of the carbonyl compound prevented the isolation of any solid, decomposition to copper metal being observed after a few hours.

Preparation of Tetrakis(*p*-tolyl isocyanide)bis(μ-phenoxo)dicopper(I) (III). A THF suspension of [CuCl] (0.80 g, 8.08 mmol) was reacted with *p*-tolyl isocyanide (1.86 g, 16.0 mmol) to form a colorless solution, to which a methanolic solution (15.0 mL) of PhONa (8.08 mmol) was added. The sodium chloride formed was filtered out and diethyl ether (10 mL) added to the resulting solution. A crystalline solid formed (yield ca. 45%). Anal. Calcd for $[[Cu(p\text{-}MeC_6H_4NC)_2]_2(\mu\text{-}OPh)_2]$, $C_{44}H_{38}N_4O_2Cu_2$: C, 67.58; H, 4.89; N, 7.16. Found: C, 67.52; H, 4.90; N, 7.08. C-N bands from the IR spectrum (Nujol) are at 2145 and 2125 cm^{-1}.

Reaction of [Cu(CO)Cl] with Sodium Phenoxide and Triphenylphosphine: Complex IV. Carbon monoxide was absorbed by a THF (15 mL) suspension of [CuCl] (0.79 g, 7.97 mmol), to which a THF solution (15 mL) of PhONa (8.0 mmol) was added. Immediate reaction occurred, forming a yellow solution containing solid NaCl, which was filtered out. Then the yellow solution was reacted with PPh_3 (4.20 g, 16.0 mmol) dissolved in THF (15 mL). Carbon monoxide evolved. By addition of Et_2O white crystalline solid formed (yield ca. 32.0%). Anal. Calcd for $[Cu_2(\mu\text{-}OPh)_2(PPh_3)_4]$, $C_{84}H_{70}P_4O_2Cu_2$: C, 74.0; H, 5.14; P, 9.11. Found: C, 73.25; H, 5.20; P, 8.95. The same reaction can be carried out in the absence of carbon monoxide.

Reaction of [Cu(CO)Cl] with Sodium Phenoxide and 1,1,1-Tris((diphenylphosphino)methyl)ethane: Complex V. A THF (10 mL) suspension of CuCl (0.33 g, 3.35 mmol) was kept under a carbon monoxide atmosphere.[17b] Sodium phenoxide (3.35 mmol) was then added. Sodium chloride was filtered out from the resulting yellow suspension, to which a THF solution (20 mL) of TRIPHOS (2.09 g, 3.35 mmol) was added. The resulting light yellow solution gave on standing white crystals of complex V, [Cu(TRIPHOS)(OPh)]·THF (yield ca. 50.5%). Anal. Calcd for $C_{47}H_{44}P_3OCu$: C, 72.26; H, 5.63; P, 11.9. Found: C, 71.0; H, 5.92; P, 11.53.

Synthesis of [[Cu(OPh)dppe]$_2$(μ-dppe)] (VI). A THF suspension of CuCl (0.62 g, 6.26 mmol) was reacted with a THF solution (25 mL) of PhONa (6.30 mmol). A light yellow solution suddenly formed, along with sodium chloride, which was filtered out. By addition of dppe (2.50 g, 6.26 mmol) dissolved in THF (25 mL), a white crystalline solid formed (yield ca. 51%), which was dried in vacuo. Anal. Calcd for $[Cu_2(dppe)_3(OPh)_2]$, $C_{90}H_{82}P_6Cu_2O_2$: C, 71.66; H, 5.48; P, 12.32. Found: C, 71.2; H, 5.54; P, 12.1. Complex VI was obtained independently of the dppe/Cu ratio. The complex recrystallized from THF gave a solvated species containing four THF molecules per unit.

Synthesis of $[Cu(BEN)_2]^+[Cu(2,6\text{-}Me_2C_6H_3O)_2]^-$ (VII). A THF solution (15 mL) of $2,6\text{-}Me_2C_6H_3ONa$ (8.12 mmol) was added to the suspension of [Cu(CO)Cl][17b] obtained from the carbonylation of [CuCl] (0.81 g, 8.12 mmol) in 25 mL of THF. The yellow solution filtered from NaCl was reacted with BEN (1.91 g, 8.12 mmol) dissolved in THF (15 mL). By addition of Et_2O (20 mL), yellow crystals of $[Cu(BEN)_2][Cu(2,6\text{-}Me_2C_6H_3O)_2]$ formed (yield ca. 43%). Anal. Calcd for $C_{44}H_{42}N_4O_2Cu_2$: C, 67.24; H, 5.38; N, 7.12. Found: C, 68.18; H, 6.10; N, 6.64. ν(C-N) (Nujol): 1627 cm^{-1}.

Synthesis of Bis(*p*-tolyl isocyanide)(2,6-di-*tert*-butylphenoxo)copper(I) (VIII). A THF (20 mL) suspension of [CuCl] (0.44 g, 4.51 mmol) was reacted with *p*-tolyl isocyanide (1.05 g, 9.10 mmol). A THF solution (10 mL) of sodium 2,6-di-*tert*-butylphenoxide (4.50 mmol) was then added. A red solution suddenly formed, from which sodium chloride was filtered out. The resulting solution gave, on standing, crystals (yield ca. 40%) of $[Cu(p\text{-}MeC_6H_4NC)_2(2,6\text{-}t\text{-}Bu_2C_6H_3O)]$. Anal. Calcd for $C_{30}H_{35}N_2OCu$: C, 71.64; H, 6.96; N, 5.57. Found: C, 71.06; H, 6.97; N, 5.45. The IR spectrum showed two strong C-N bands (Nujol) at 2145 and 2170 cm^{-1}.

Reaction of [Cu(CO)Cl] with $2,6\text{-}Me_2C_6H_3ONa$ and dppe. [Cu(CO)Cl] (0.46 g, 4.61 mmol) obtained by the normal procedure[17b] in THF (30 mL) was reacted with an equimolar amount of $2,6\text{-}Me_2C_6H_3ONa$ (4.62 mmol). Sodium chloride was filtered out from the resulting yellow suspension which was reacted with a THF (20 ml) solution of dppe (2.76 g, 6.93 mmol). The solution gave on cooling white crystals of complex (VI) (yield ca. 40%), $[Cu_2(dppe)_3(2,6\text{-}Me_2C_6H_3O)_2]$. Anal. Calcd for $C_{94}H_{90}O_2P_6Cu_2$: C, 72.18; H, 5.80; P, 11.90. Found: C, 71.59; H, 5.97; P, 11.5.

X-ray Structure Determination on $[[Cu(p\text{-}MeC_6H_4NC)_2]_2(\mu\text{-}OPh)_2]$ (III), [[Cu(OPh)dppe]$_2$(μ-dppe)]·4THF (VI), [Cu(PhCH=

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Table I. Crystal Data and Summary of Intensity Data Collection and Structure Refinement

	$C_{44}H_{38}Cu_2N_4O_2$ (III)	$C_{106}H_{114}Cu_2O_6P_6$ (VI)	$C_{48}H_{50}Cu_2N_4O_2$ (VII)	$C_{30}H_{35}CuN_2O$ (VIII)
mol wt	781.9	898.5	842.0	503.2
cell dimens at 295 K[a]				
a, Å	11.288 (3)	23.524 (7)	13.643 (3)	23.179 (4)
b, Å	10.374 (3)	21.746 (6)	21.528 (5)	9.456 (1)
c, Å	16.449 (4)	18.572 (4)	15.538 (4)	12.509 (2)
α, deg	90	90	90	90
β, deg	95.62 (3)	90	111.31 (3)	94.02 (2)
γ, deg	90	90	90	90
V, Å^3	1917.0 (9)	9501 (4)	4252 (2)	2735.0 (7)
Z	2	4	4	4
D_{calcd}, g cm^{-3}	1.35	1.26	1.32	1.22
radiation	graphite monochromated Mo Kα (λ = 0.7107 Å)	Ni-filtered Cu Kα (λ = 1.5418 Å)	*c*	*c*
space group	$P2_1/n$[b]	*Pbca*	$P2_1/c$	$P2_1/n$[b]
max cryst dimens, mm	0.15 × 0.28 × 0.40	0.29 × 0.39 × 0.45	0.11 × 0.34 × 0.40	0.11 × 0.30 × 0.39
μ, cm^{-1}	11.5	19.2	15.2	12.6
diffractometer	Philips PW 1100	Siemens AED	*c*	*c*
scan type	$\omega/2\theta$	$\theta/2\theta$	$\theta/2\theta$	$\theta/2\theta$
scan speed	0.075°/s	3–12°/min	3–12°/min	3–12°/min
scan width, deg	1.50	$(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]$	*c*	*c*
2θ range, deg	6–50	6–110	6–110	6–120
reflecns measd	$\pm h,k,l$	h,k,l	$\pm h,k,l$	$\pm h,k,l$
unique total data	3378	5930	4975	
unique obsd data	1932	3837	2410	2623
criterion for observn	$I > 3\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
no. of parameters varied	235	407	433	307
R[32]	0.052	0.049	0.042	0.039
R_w[32]	0.059	0.057		0.043
GOF[33]	0.65	0.89		0.67

[a] Unit cell parameters were obtained by least-squares refinement of the setting angles of 25 carefully centered reflections chosen from diverse regions of reciprocal space. [b] A nonstandard setting of C_{2h}^5 (No. 14). Coordinates of equivalent positions are as follows: x, y, z; $\bar{x}, \bar{y}, \bar{z}$; $^1/_2 + x, {}^1/_2 - y, {}^1/_2 + z$; $^1/_2 - x, {}^1/_2 + y, {}^1/_2 - z$. [c] As for VI. [d] $\Delta\theta = [(\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda] \tan\theta$.

Table II. Final Atomic Fractional Coordinates (×10^4) for $[[Cu(p\text{-}MeC_6H_4NC)_2]_2(\mu\text{-}OPh)_2]$ (III)

	x/a	*y/b*	*z/c*		*x/a*	*y/b*	*z/c*
Cu	4367 (1)	5989 (1)	4338 (1)	C(10)	7494 (5)	8702 (6)	1520 (4)
O	4630 (4)	4037 (4)	4530 (2)	C(11)	6787 (5)	9719 (6)	1220 (4)
N(1)	5612 (5)	7208 (6)	2974 (3)	C(12)	5662 (6)	9852 (7)	1523 (5)
N(2)	1943 (5)	7305 (5)	4314 (4)	C(13)	5273 (6)	9020((7)	2078 (5)
C(1)	4135 (5)	3059 (6)	4116 (3)	C(14)	7173 (7)	10636 (7)	589 (4)
C(2)	3198 (6)	3223 (7)	3505 (4)	C(15)	2836 (6)	6765 (7)	4339 (4)
C(3)	2696 (7)	2175 (9)	3089 (5)	C(16)	839 (5)	7967 (6)	4293 (4)
C(4)	3091 (8)	934 (9)	3247 (6)	C(17)	394 (6)	8540 (7)	3572 (4)
C(5)	4034 (8)	748 (8)	3835 (6)	C(18)	−710 (6)	9168 (6)	3550 (4)
C(6)	4541 (6)	1787 (7)	4280 (4)	C(19)	−1354 (5)	9188 (6)	4245 (4)
C(7)	5214 (6)	6657 (7)	3484 (4)	C(20)	−865 (6)	8595 (7)	4940 (4)
C(8)	6021 (6)	8032 (7)	2373 (4)	C(21)	232 (6)	7984 (6)	4981 (4)
C(9)	7117 (6)	7848 (6)	2100 (4)	C(22)	−2563 (6)	9828 (8)	4181 (5)

$NCH_2CH_2N{=}CHPh)_2]^+[Cu(2,6\text{-}Me_2C_6H_3O)_2]^-$ (VII), and $[Cu(2,6\text{-}t\text{-}Bu_2C_6H_3O)(p\text{-}MeC_6H_4NC)_2]$ (VIII). The crystals selected for study were wedged into thin-walled glass capillaries and sealed under nitrogen. The reduced cells were obtained with use of TRACER[1,18] (see Table I for crystal data and data collection parameters). Intensity data were collected at 295 K with analysis of individual reflection profiles[19] for complexes VI–VIII. For complex III the three-point technique was used. The structure amplitudes were obtained after the usual Lorentz and polarization reduction.[20] No correction for absorption was applied to the data. In the structure solution and refinement, only the observed reflections were used.

Full-matrix least-squares refinement was based on F, and the function minimized was $\sum w(|F_o| - |F_c|)^2$. Unit weights were used for complex VII, since these gave acceptable agreement analyses, while for the other complexes weights were applied according to the scheme $w = k/\sigma^2(F_0) + gF_0^2)$. At convergence the values for k and g were as follows: 0.7241 and 0.00988 for III; 0.6714 and 0.00346 for VI; 1.0000 and 0.00432 for VIII. The atomic scattering factors for all non-hydrogen atoms were taken from ref 21a and those for hydrogen from ref 22. The effects of anomalous dispersions were included in F_c by using the values of ref 21b. There was no evidence of secondary extinction among low-angle reflections for any of the complexes. Tables of observed and calculated structural factors are available (see paragraph at the end of the paper regarding supplementary material).

For each compound, the copper atom position was located from a three-dimensional Patterson function. Subsequent Fourier syntheses then served to establish all other non-hydrogen atom positions. Following introduction of anisotropic temperature factors for all non-hydrogen atoms, Fourier difference maps located most of the hydrogen atoms for VII and all of them for the others. In all the structures the hydrogen atom positions were introduced in calculations prior to the final refinement and held fixed (β_{iso} + 7.8 Å^2). For VI and VII the phenyl rings were treated as rigid hexagons during the refinement. No constraint was applied to III and VIII. The two independent tetrahydrofuran solvent molecules, detected by the X-ray analysis, in complex VI were affected

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Table III. Fractional Atomic Coordinates (×10[4]) for [[Cu(OPh)dppe]$_2$(μ-dppe)]·4THF (VI)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu	987 (1)	525 (1)	1189 (1)	C(36)	1819 (2)	2143 (1)	977 (2)
P(1)	1604 (1)	−323 (1)	1158 (1)	C(41)	315 (1)	1347 (1)	−302 (2)
P(2)	1674 (1)	1086 (1)	1778 (1)	C(42)	83 (1)	1363 (1)	−992 (2)
P(3)	714 (1)	669 (1)	18 (1)	C(43)	−216 (1)	1880 (1)	−1223 (2)
O(1)	342 (2)	303 (2)	1861 (2)	C(44)	−282 (1)	2383 (1)	−763 (2)
C(1)	1774 (2)	−759 (2)	335 (2)	C(45)	−50 (1)	2367 (1)	−73 (2)
C(2)	2280 (2)	−689 (2)	−47 (2)	C(46)	249 (1)	1849 (1)	158 (2)
C(3)	2352 (2)	−987 (2)	−706 (2)	C(51)	1301 (1)	647 (2)	−630 (2)
C(4)	1919 (2)	−1355 (2)	−982 (2)	C(52)	1312 (1)	251 (2)	−1220 (2)
C(5)	1413 (2)	−1426 (2)	−600 (2)	C(53)	1777 (1)	256 (2)	−1688 (2)
C(6)	1340 (2)	−1128 (2)	59 (2)	C(54)	2229 (1)	657 (2)	−1565 (2)
C(11)	1524 (2)	−930 (1)	1833 (2)	C(55)	2217 (1)	1053 (2)	−975 (2)
C(12)	1108 (2)	−858 (1)	2361 (2)	C(56)	1753 (1)	1049 (2)	−507 (2)
C(13)	1045 (2)	−1301 (1)	2898 (2)	C(57)	255 (2)	26 (2)	−249 (3)
C(14)	1398 (2)	−1816 (1)	2906 (2)	C(61)	−56 (2)	675 (2)	2125 (2)
C(15)	1814 (2)	−1888 (1)	2378 (2)	C(62)	−73 (2)	1302 (2)	1970 (2)
C(16)	1877 (2)	−1445 (1)	1841 (2)	C(63)	−495 (2)	1671 (2)	2274 (2)
C(17)	2290 (2)	33 (2)	1419 (3)	C(64)	−899 (2)	1413 (2)	2732 (2)
C(18)	2180 (2)	481 (2)	2056 (3)	C(65)	−882 (2)	786 (2)	2888 (2)
C(21)	1540 (2)	1488 (2)	2629 (2)	C(66)	−460 (2)	416 (2)	2584 (2)
C(22)	1865 (2)	1987 (2)	2857 (2)	O(1A)	4538 (6)	4396 (7)	4513 (8)
C(23)	1726 (2)	2294 (2)	3493 (2)	C(2A)	4356 (7)	4964 (7)	4212 (7)
C(24)	1260 (2)	2102 (2)	3900 (2)	C(3A)	3726 (6)	5017 (6)	4388 (8)
C(25)	935 (2)	1602 (2)	3672 (2)	C(4A)	3634 (7)	4559 (7)	5055 (7)
C(26)	1074 (2)	1295 (2)	3036 (2)	C(5A)	4168 (8)	4107 (8)	5003 (9)
C(31)	2105 (2)	1641 (1)	1273 (2)	O(1B)	552 (6)	3128 (6)	1386 (7)
C(32)	2685 (2)	1563 (1)	1146 (2)	C(2B)	645 (7)	3057 (7)	2131 (9)
C(33)	2979 (2)	1987 (1)	723 (2)	C(3B)	1079 (6)	3509 (7)	2237 (8)
C(34)	2693 (2)	2489 (1)	428 (2)	C(4B)	1287 (6)	3879 (6)	1581 (8)
C(35)	2113 (2)	2567 (1)	555 (2)	C(5B)	815 (6)	3669 (7)	1024 (8)

Table IV. Fractional Atomic Coordinates (×10[4]) for [Cu(PhCH=NCH$_2$CH$_2$N=CHPh)$_2$]$^+$[Cu(2,6-Me$_2$C$_6$H$_3$O)$_2$]$^-$ (VII)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu(1)	2339 (1)	493 (1)	2610 (1)	C(13B)	−842 (4)	1143 (2)	551 (4)
Cu(2)	1615 (1)	3383 (1)	2765 (1)	C(14B)	−1884 (4)	976 (2)	380 (4)
N(1A)	1622 (4)	1121 (2)	3212 (4)	C(15B)	−2123 (4)	373 (2)	566 (4)
N(2A)	2818 (4)	1290 (2)	2111 (4)	C(16B)	−1320 (4)	−63 (2)	924 (4)
C(1A)	778 (6)	1084 (3)	3388 (5)	C(21B)	5080 (4)	380 (2)	3998 (3)
C(2A)	2023 (6)	1747 (3)	3162 (6)	C(22B)	6126 (4)	346 (2)	4064 (3)
C(3A)	2194 (6)	1817 (3)	2243 (6)	C(23B)	6768 (4)	871 (2)	4311 (3)
C(4A)	3633 (6)	1430 (3)	1916 (5)	C(24B)	6363 (4)	1430 (2)	4493 (3)
C(11A)	321 (4)	499 (2)	3545 (4)	C(25B)	5317 (4)	1464 (2)	4427 (3)
C(12A)	944 (4)	−25 (2)	3890 (4)	C(26B)	4676 (4)	939 (2)	4180 (3)
C(13A)	484 (4)	−574 (2)	4033 (4)	O(1)	319 (4)	3206 (3)	2760 (5)
C(14A)	−599 (4)	−601 (2)	3832 (4)	O(2)	2785 (5)	3650 (3)	2603 (5)
C(15A)	−1221 (4)	−78 (2)	3487 (4)	C(31)	−91 (6)	2841 (2)	3223 (6)
C(16A)	−761 (4)	472 (2)	3343 (4)	C(32)	−1067 (6)	2565 (2)	2763 (6)
C(21A)	4336 (4)	968 (2)	1761 (3)	C(33)	−1532 (6)	2200 (2)	3251 (6)
C(22A)	5361 (4)	1155 (2)	1899 (3)	C(34)	−1022 (6)	2111 (2)	4199 (6)
C(23A)	6084 (4)	725 (2)	1812 (3)	C(35)	−45 (6)	2387 (2)	4659 (6)
C(24A)	5783 (4)	109 (2)	1586 (3)	C(36)	420 (6)	2752 (2)	4171 (6)
C(25A)	4758 (4)	−77 (2)	1448 (3)	C(37)	−1568 (8)	2651 (5)	1758 (8)
C(26A)	4034 (4)	352 (2)	1536 (3)	C(38)	1484 (8)	3046 (4)	4678 (7)
N(1B)	1513 (5)	−262 (2)	1868 (4)	C(41)	3694 (5)	3396 (2)	2674 (6)
N(2B)	3438 (5)	−178 (2)	3336 (4)	C(42)	3919 (5)	3300 (2)	1876 (6)
C(1B)	533 (7)	−373 (3)	1452 (5)	C(43)	4906 (5)	3081 (2)	1945 (6)
C(2B)	2215 (6)	−809 (3)	2092 (7)	C(44)	5669 (5)	2957 (2)	2810 (6)
C(3B)	2913 (7)	−789 (3)	3116 (6)	C(45)	5445 (5)	3053 (2)	3608 (6)
C(4B)	4441 (6)	−180 (3)	3716 (5)	C(46)	4457 (5)	3272 (2)	3539 (6)
C(11B)	−278 (4)	104 (2)	1095 (4)	C(47)	3081 (9)	3478 (6)	939 (7)
C(12B)	−39 (4)	707 (2)	909 (4)	C(48)	4225 (12)	3345 (6)	4408 (7)

by high thermal motion (or disorder) and were refined isotropically. Their hydrogen atoms were neither located nor introduced into calculated positions.

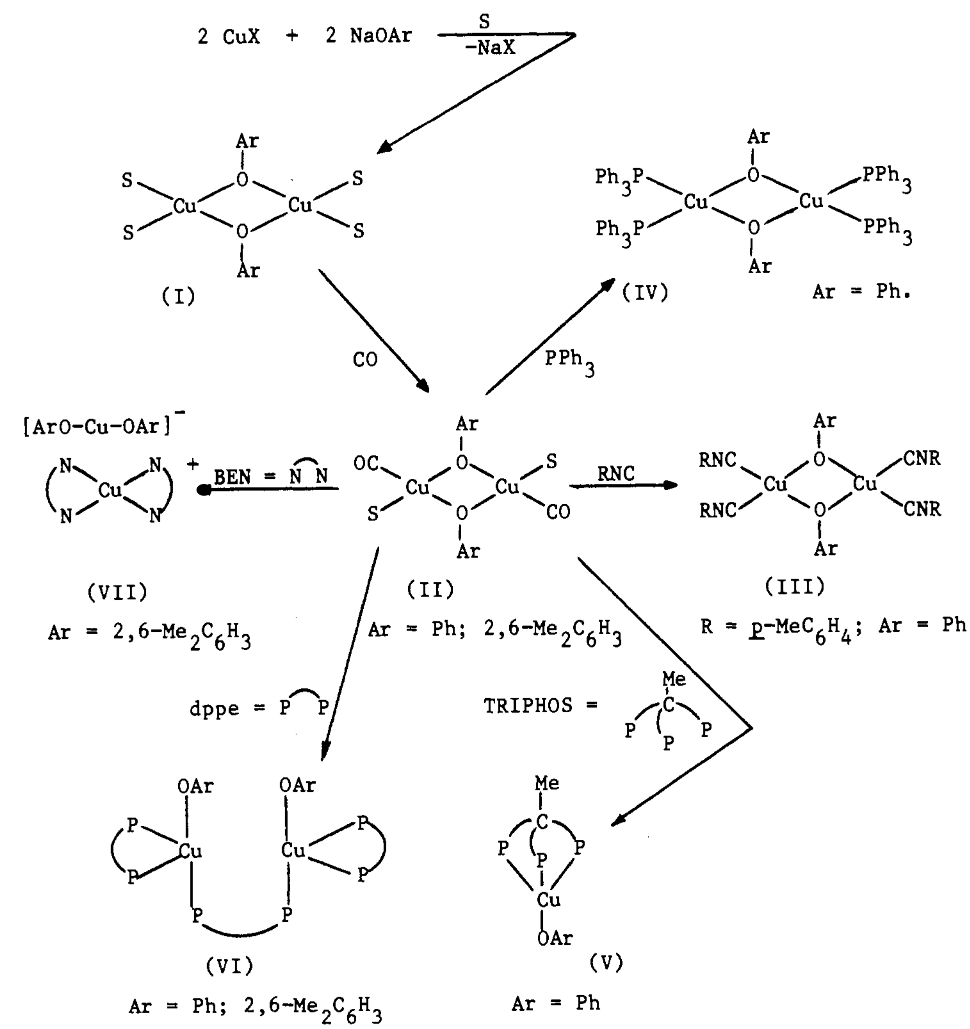
Results and Discussion

A main goal of this work was to establish both the stability of the [Cu–OAr] unit and the bonding mode of the ArO$^-$ group, depending on both the substituent at the Ar residue and the nature of ancillary ligands. In the absence of ancillary ligands, reaction of sodium phenoxides, ArONa (Ar = Ph, 2,6-Me$_2$C$_6$H$_3$, 2,6-*t*-Bu$_2$C$_6$H$_3$), with copper(I) halides, in either methanol or tetrahydrofuran, did not allow the isolation of well-defined compounds. Copper(I) phenoxide so formed in situ rapidly decomposed to copper metal. Due to their low coordinating ability, the solvents MeOH and THF were unable to stabilize the [Cu–OAr] unit. "Stabilization" was achieved, however, by carrying out the reaction in the presence of various ancillary ligands such as CO, isocyanides, phosphines, and Schiff bases (Scheme I). The nature of the solvated species I may be inferred from the structures of more stable compounds containing ancillary ligands different from solvent. Carbon monoxide can replace the solvent, S, providing higher stability for the complexes II. Stable molecules containing the Cu–OAr unit may then be prepared by initial reaction of copper(I) halides with various phenoxides under a carbon monoxide atmosphere, followed by replacement of CO by less labile ligand.

Table V. Fractional Atomic Coordinates (×10[4]) for [Cu(2,6-*t*-$Bu_2C_6H_3O$)(*p*-MeC_6H_4NC)$_2$] (VIII)

atom	x/a	y/b	z/c	atom	x/a	y/b	z/c
Cu	2184 (1)	2714 (1)	2257 (1)	N(1A)	3054 (1)	1670 (3)	4007 (2)
O	1400 (1)	3165 (2)	2517 (2)	C(2A)	3486 (1)	1320 (4)	4804 (3)
C(1)	1040 (1)	2743 (3)	3224 (2)	C(3A)	3544 (2)	2125 (4)	5727 (3)
C(2)	692 (1)	1506 (4)	3019 (3)	C(4A)	3973 (2)	1757 (5)	6509 (3)
C(3)	279 (2)	1162 (4)	3735 (3)	C(5A)	4335 (1)	634 (4)	6378 (3)
C(4)	195 (2)	1979 (5)	4621 (3)	C(6A)	4268 (1)	−146 (4)	5438 (3)
C(5)	540 (2)	3157 (4)	4840 (3)	C(7A)	3842 (1)	189 (4)	4636 (3)
C(6)	965 (1)	3556 (4)	4169 (2)	C(8A)	4809 (2)	231 (5)	7210 (3)
C(7)	1321 (1)	4900 (4)	4422 (2)	C(1B)	2440 (2)	3401 (4)	952 (3)
C(8)	1173 (2)	6040 (4)	3596 (3)	N(1B)	2632 (1)	3880 (3)	201 (2)
C(9)	1210 (2)	5522 (5)	5530 (3)	C(2B)	2855 (1)	4500 (4)	−698 (3)
C(10)	1976 (2)	4590 (5)	4475 (3)	C(3B)	2524 (2)	4542 (6)	−1645 (3)
C(11)	749 (2)	585 (4)	2016 (3)	C(4B)	2753 (2)	5138 (6)	−2522 (3)
C(12)	1353 (2)	−66 (4)	2018 (4)	C(5B)	3300 (2)	5696 (5)	−2472 (3)
C(13)	321 (2)	−665 (5)	1967 (4)	C(6B)	3620 (2)	5647 (5)	−1511 (4)
C(14)	614 (2)	1458 (5)	1001 (3)	C(7B)	3401 (2)	5061 (5)	−621 (3)
C(1A)	2704 (2)	1960 (4)	3342 (3)	C(8B)	3549 (2)	6309 (6)	−3453 (4)

Scheme I



Carbon monoxide stabilizes the cuprous phenoxide, preventing any disproportionation to copper metal and copper(II). Yet, carbon monoxide is lost very easily. Hence, regardless of the ArO^- used (Ar = Ph, 2,6-$Me_2C_6H_3$), isolation of carbonyls in the solid state was impossible. However, a rather stable tetranuclear copper(I)–alkoxo–carbonyl compound was recently reported.[23,24] The CO stretching frequency ranging from 2080 to 2095 cm^{-1} belongs to that of terminal carbon monoxide,[25] and a single CO per copper is absorbed. The structure proposed for the carbonylated species II is based on the proven structure of complexes III (vide infra) and IV[26] that result from reaction of the carbonylated solution with isocyanide and triphenylphosphine, respectively, assuming that these ligands replace the more labile S and CO molecules around the metal without changing the bonding mode of the phenoxo group. Two single-bridged phenoxo binuclear copper(I) complexes recently reported have two sets of

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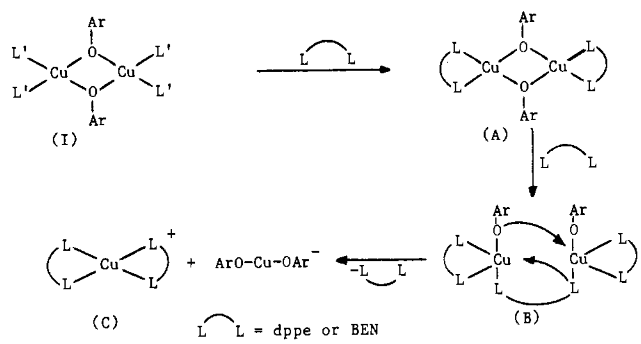
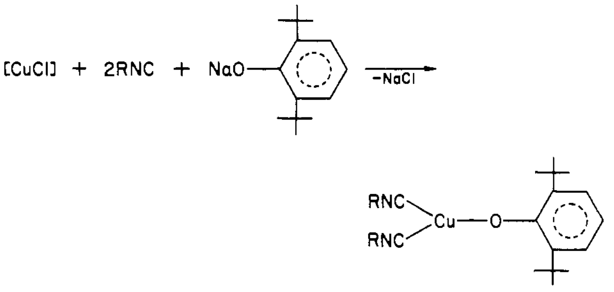
(26) Floriani, C.; Chiesi-Villa, A.; Guastini, C., preliminary data on the structure of IV.

Scheme II



nitrogen donor atoms which are attached to the phenyl group.[27] Isocyanides in complex III show only terminal C═N stretching bands (ν(C–N) = 2125, 2145 cm^{-1}). The dimeric fragment $[Cu–OAr]_2$, around which this molecule is built, is significant as both metal atoms could simultaneously interact with various substrates.[27,28]

The stability of the Cu–OPh unit is, however, not strictly associated with a bridging bonding mode for the phenoxo group. The terminal bonding mode of the phenoxo group can be achieved by the use of appropriate ancillary ligands or by introduction of bulky substituents at the ortho positions of the aromatic ring. The reaction of II with the ligand TRIPHOS produces complex V (Scheme I), having, very probably, the monomeric structure shown. The TRIPHOS ligand provides the saturation of the coordination sphere of Cu(I) necessary for stabilization of the Cu–OPh unit. A support to this comes from the isolation and structural determination of [Cu(TRIPHOS)(Ph)].[29] By the reaction of [CuCl] with 2,6-di-*tert*-butylphenoxide in the presence of *p*-tolyl isocyanide, VIII was isolated having a terminal phenoxo group:



(1)

VIII

In this case, *tert*-butyl substitution at the 2- and 6-positions on the phenyl ring prevents the formation of a bridged dimeric structure. The phenoxo group is forced to occupy a terminal position, and the mononuclear fragment [Cu–OAr] is stabilized by coordination, to Cu(I), of two *p*-tolyl isocyanide molecules. The C–N stretching frequencies (2170, 2145 cm^{-1}) are in the high range, as expected for coordination of the isocyanide molecules to an acidic center. The structure of VIII was determined by X-ray analysis and will be discussed below.

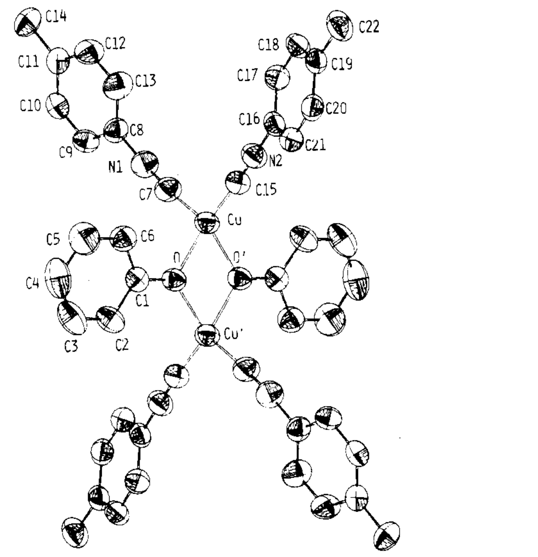


Figure 1. ORTEP drawing of the complex $[[Cu(p\text{-}MeC_6H_4NC)_2]_2(\mu\text{-}OPh)_2]$ (III). Primes indicate a transformation of $1 - x$, $1 - y$, $1 - z$ (50% probability ellipsoids).

The unexpected stepwise rearrangement of complex II, promoted by the bidentate ligands dppe and BEN, show how the [Cu–OAr] unit may be modified by appropriate ligands. The reaction goes further, leading to the formation of complex VI (in Scheme I). This complex, VI, formed independently of the Cu/dppe molar ratio used, is the only identifiable product of the reaction. Similar results were observed with use of sodium 2,6-dimethylphenoxide. When II (Ar = $2,6\text{-}Me_2C_6H_3$) is reacted with *N,N'*-ethylenebis(benzaldimine), BEN,[17a] a ligand disproportionation was observed, producing the phenoxocuprato group (VII) and the corresponding cation, the structure of which was determined by X-ray analysis.[17a] In general, 2,6-dimethyl substitution on the phenyl ring has little effect on the reaction reported for the phenoxo group but was introduced to increase slightly the solubility of the final compound so that crystalline solids, suitable for X-ray analysis, could be obtained.

Scheme II, supported by the results outlined above, may be proposed for the transformations undergone by the [Cu–OAr] unit in the presence of a bidentate ligand. Although complex A has not been identified, even in the case of dppe, its triphenylphosphine analogue IV has been isolated and structurally identified.[26] With dppe, the reaction goes further to the second complex B. Complex A seems the obvious precursor. The species B was isolated as the dppe complex VI. With use of the ligand BEN, rearrangement of species B may be responsible for the ligand disproportionation, leading to VII (species C).

A description of the structural transformations of the [Cu–OAr] unit, induced by reaction with ancillary ligands, is concluded in the following discussion of the structures of the key compounds (III and VI–VIII) reported above in Schemes I and II and reaction 1.

Description of the Structures. Structure of Complex III. An ORTEP view of $[[Cu(p\text{-}MeC_6H_4NC)_2]_2(\mu\text{-}OPh)_2]$ is reported in Figure 1. The dinuclear complex has a C_1 symmetry and copper(I) a pseudotetrahedral coordination geometry. The two coordination planes Cu, O, O′ and Cu, C(15), C(17) are mutually orthogonal, the dihedral angle being 92.8°. The Cu_2O_2 skeleton is planar. As the angles around copper(I) are imposed mainly by the bridging bonding mode of the phenoxo group, significant deviation from the ideal values is observed (Table VI). The phenoxo ligand is planar, and it forms a dihedral angle of 20.0 (1)° with the Cu_2O_2 plane (Table SX). Structural parameters of the Cu–C–N–R fragments are very close to those found in another copper(I) isocyanide complex.[30] A significant deviation

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Table VI. Selected Interatomic Distances (Å) and Angles (deg)

(a) $[[Cu(p\text{-}Me_6H_4NC)_2]_2(\mu\text{-}OPh)_2]$ (III)[a]

Cu–O	2.066 (4)	O–C(1)	1.316 (7)
Cu–O′	2.083 (4)	N(1)–C(7)	1.143 (9)
Cu–C(7)	1.905 (7)	N(1)–C(8)	1.418 (9)
Cu–C(15)	1.907 (7)	N(2)–C(15)	1.150 (9)
Cu···Cu′	3.223 (1)	N(2)–C(16)	1.420 (8)
O–Cu–O′	78.1 (2)	Cu–O–C(1)	129.0 (3)
O–Cu–C(7)	113.2 (2)	C(1)–O–Cu′	128.2 (4)
O–Cu–C(15)	122.0 (3)	Cu–C(7)–N(1)	170.0 (7)
O′–Cu–C(7)	113.3 (2)	Cu–C(15)–N(2)	175.3 (6)
O′–Cu–C(15)	114.7 (2)	C(7)–N(1)–C(8)	172.5 (7)
C(7)–Cu–C(15)	111.6 (3)	C(15)–N(2)–C(16)	179.3 (7)
Cu–O–Cu′	101.9 (2)		

(b) $[[Cu(OPh)dppe]_2(\mu\text{-}dppe)]\cdot4THF$ (VI)[b]

Cu–O(1)	2.023 (5)	C(17)–C(18)	1.554 (7)
Cu–P(1)	2.348 (3)	C(57)–C57′)	1.519 (7)
Cu–P(2)	2.301 (3)	O(1)–C(61)	1.331 (6)
Cu–P(3)	2.289 (3)		
O(1)–Cu–P(1)	106.9 (2)	P(2)–Cu–P(3)	125.2 (1)
O(1)–Cu–P(2)	111.1 (2)	Cu–O(1)–C(61)	127.6 (3)
O(1)–Cu–P(3)	114.0 (1)	O(1)–C(61)–C(62)	122.6 (4)
P(1)–Cu–P(2)	89.7 (1)	O(1)–C(61)–C(66)	117.3 (4)
P(1)–Cu–P(3)	104.9 (1)		

(c) $[Cu(PhCH{=}NCH_2CH_2N{=}CHPh)_2]^+[Cu(2,6\text{-}Me_2C_6H_3O)_2]^-$ (VII)

Cu(1)–N(1A)	2.080 (6)	Cu(2)–O(1)	1.806 (6)
Cu(1)–N(2A)	2.083 (6)	Cu(2)–O(2)	1.798 (8)
Cu(1)–N(1B)	2.073 (5)	O(1)–C(31)	1.319 (11)
Cu(1)–N(2B)	2.092 (5)	O(2)–C(41)	1.323 (10)
N(1A)–C(2A)	1.467 (8)	N(1B)–C(2B)	1.477 (9)
N(1A)–C(1A)	1.279 (11)	N(1B)–C(1B)	1.278 (10)
C(1A)–C(11A)	1.465 (9)	C(1B)–C(11B)	1.463 (9)
C(2A)–C(3A)	1.536 (14)	C(2B)–C(3B)	1.529 (12)
N(2A)–C(3A)	1.477 (9)	N(2B)–C(3B)	1.477 (8)
N(2A)–C(4A)	1.290 (11)	N(2B)–C(4B)	1.278 (10)
C(4A)–C(21A)	1.461 (9)	C(4B)–C(21B)	1.459 (8)
N(1B)–Cu(1)–N(2B)	84.1 (2)	O(1)–Cu(2)–O(2)	169.8 (3)
N(2A)–Cu(1)–N(2B)	120.6 (3)	Cu(2)–O(1)–C(31)	137.0 (5)
N(2A)–Cu(1)–N(1B)	128.3 (2)	Cu(2)–O(2)–C(41)	135.2 (5)
N(1A)–Cu(1)–N(2B)	124.6 (2)	O(1)–C(31)–C(32)	119.3 (7)
N(1A)–Cu(1)–N(1B)	120.7 (3)	O(1)–C(31)–C(36)	120.6 (6)
N(1A)–Cu(1)–N(2A)	83.9 (2)	O(2)–C(41)–C(42)	119.3 (7)
		O(2)–C(41)–C(46)	120.6 (7)

(d) $[Cu(2,6\text{-}t\text{-}Bu_2C_6H_3O)(p\text{-}MeC_6H_4NC)_2]$ (VIII)

Cu–O	1.917 (3)	C(1A)–N(1A)	1.154 (5)
Cu–C(1A)	1.891 (4)	N(1A)–C(2A)	1.402 (4)
Cu–C(1B)	1.891 (4)	C(1B)–N(1B)	1.160 (5)
O–C(1)	1.320 (4)	N(1B)–C(2B)	1.399 (5)
O–Cu–C(1A)	121.8 (2)	C(1A)–N(1A)–C(2A)	179.1 (3)
O–Cu–C(1B)	115.4 (2)	Cu–C(1B)–N(1B)	174.4 (4)
C(1A)–Cu–C(1B)	121.8 (2)	C(1B)–N(1B)–C(2B)	178.1 (4)
Cu–O–C(1)	134.3 (2)	O–C(1)–C(2)	120.1 (3)
Cu–C(1A)–N(1A)	171.2 (3)	O–C(1)–C(6)	120.7 (3)

[a] Primes indicate the symmetry transformation $1 - x$, $1 - y$, $1 - z$. [b] The prime indicates the symmetry transformation $\bar{x}$, $\bar{y}$, $\bar{z}$.

from linearity exists for the Cu–C–N–R moieties (Cu–C(7)–N(1) = 170.0 (7)°; Cu–C(15)–N(2) = 175.3 (6)°). The C–N distance is that expected for a triple bond (C(7)–N(1) = 1.143 (9); C(15)–N(2) = 1.150 (9) Å). Cu–O bond distances (Cu–O = 2.066 (4) Å; Cu–O′ = 2.083 (4) Å) are very close to those found in complex VI, while they are significantly longer than those in complexes VII and VIII. Similarly, the Cu–O bond distance in $[(CuO\text{-}t\text{-}Bu)_4]$ ($Cu–O_{av}$ = 1.854 (9) Å)[9] increased considerably after copper(I) coordination of carbon monoxide $[Cu(O\text{-}t\text{-}Bu)(CO)]_4$ (Cu–O = 2.060 (3)–2.072 (3) Å).[23] The structural parameters related to $[Cu(\mu\text{-}OPh)_2Cu]$ can be hardly compared with those of singly bridged dicopper–phenoxo complexes, because of the single bridge and the constraint on the structures reported.[27] Cu–O bond distances seems to become shorter as the coordination number about Cu(I) decreases (Table VII). The copper–copper

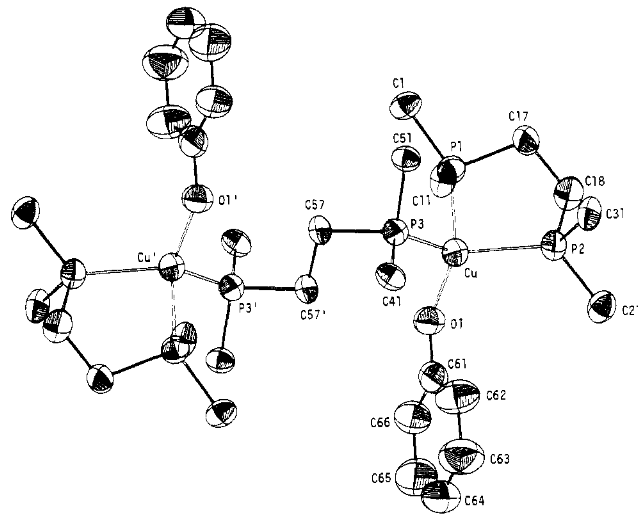

Figure 2. ORTEP drawing of the complex $[[Cu(OPh)dppe]_2(\mu\text{-}dppe)]\cdot4THF$ (VI). Primes denote a transformation of $\bar{x}$, $\bar{y}$, $\bar{z}$. Only the first carbon atoms of the phenyl rings of the phosphinic ligands are indicated for clarity (50% probability ellipsoids).

distance (3.223 (1) Å), while ruling out metal–metal interaction, provides two copper(I) centers at the appropriate separation for the bimetallic activation of small molecules.[27,28]

Structure of Complex VI, $[[Cu(OPh)dppe]_2(\mu\text{-}dppe)_2]$. Figure 2 is an ORTEP view of the dicopper complex VI. The dimer has a C_i crystallographic symmetry. The pseudotetrahedral coordination around copper(I) is achieved by three phosphorus donor atoms, from one chelating and one bridging dppe, and a phenoxo group. Due to constraints imposed by the phosphorus ligands, the bond angles of the coordination polyhedron are different from those expected for a tetrahedron (Tables VI and SIX). The difference in Cu–P bond distances[31] ranging from 2.289 (3) Å (Cu–P(3)) to 2.348 (3) Å (Cu–P(1)) is probably due to steric interaction between bulky ligands bonded to the metal atom. The five-membered chelating ring is twisted by the torsional angle P(1)–C(17)–C(18)–P(2) = −60.2 (4)°. The Cu–O bond distance (2.023 (5) Å) is only slightly shorter than that found in complex III (2.066 (4) and 2.082 (4) Å). This suggests that as long as the coordination number of the metal remains constant, the bonding mode of the phenoxo group is a secondary factor in determining the Cu–O bond distance (Table VII).

Structure of Complex VII, $[Cu(BEN)_2]^+[Cu(2,6\text{-}Me_2C_6H_3O)_2]^-$. The crystals of VII consist of cations $[Cu(BEN)_2]^+$ (Figure 3a)[17a] and anions $[Cu(2,6\text{-}Me_2C_6H_3O)_2]^-$ (Figure 3b). The four Cu–N bond distances in the cation are very small, and they fall in the usual range for amino– and azomethino–copper(I) complexes (Table VIc).[17a] The two chelating rings have a twist conformation, with torsional angles N(1A)–C(2A)–C(3A)–N(2A) = −50.5 (8)° and N(1B)–C(2B)–C(3B)–N(2B) = −52.2 (9)°. Bond distances and angles within the BEN ligand are as expected (Table SX).[17a] Nearly linear bicoordination is found in the diphenoxocuprate(I) derivative (Figure 3b) having a O(1)–Cu–O(2) angle of 169.8 (3)°. The Cu–O bond distances (Cu–O(1) = 1.806 (6) Å; Cu–O(2) = 1.798 (8) Å) are significantly shorter and the Cu–O–C angles (Cu(2)–O(1)–C(31) = 137.0 (5)°; Cu(2)–O(1)–C(41) = 135.2 (5)°) much larger than those found in complexes III and IV (Table VI). The Cu–O bond distance was found to increase as the coordination number of copper(I) increases. The two phenyl rings are rotated by an angle of 54.4 (2)°.

Structure of Complex VIII. Figure 4 is an ORTEP view of complex VIII, which consists of a monomeric unit, in which

(31) Gill, J. T.; Mayerle, J. J.; Welcker, P. S.; Lewis, D. F.; Ucko, D. A.; Barton, D. J.; Stovens, D.; Lippard, S. J. *Inorg. Chem.* **1976**, *15*, 1155–1168.
(32) $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w(|F_o| - |F_c|)^2/\sum wF_o^2]^{1/2}$.
(33) Defined as $[\sum w(|F_o| - |F_c|)^2/(N_o - N_v)]^{1/2}$, where N_o is the number of observations and N_v is the number of variable parameters.

Table VII. Copper(I)-Oxygen Bond Lengths in Copper(I)-Alkoxo Derivatives

compd[a]	coord no. of Cu(I)	bonding mode of the alkoxo group	Cu-O dist, Å	ref
[Cu-O-*t*-Bu]$_4$	2	bridging	1.813 (10)-1.878 (9)	9
[Cu-O-*t*-Bu(CO)]$_4$	4	bridging	2.060 (3)-2.072 (3)	23
[Cu(mhp)]$_4$	2	bridging	1.823 (4)-1.843 (4)	11d
[Cu(2Me-ox)(CO)]$_4$	4	bridging	2.01 (2)-2.08 (2)	24
[[Cu(RNC)$_2$]$_2$(μ-OPh)$_2$] (III)	4	bridging	2.066 (4)-2.082 (4)	this work
[[Cu(OPh)dppe]$_2$(μ-dppe)] (VI)	4	terminal	2.023 (5)	this work
[Cu(BEN)$_2$(2,6-Me$_2$C$_6$H$_3$O)$_2$] (VII)	2	terminal	1.806 (6)-1.798 (8)	this work
[Cu(2,6-*t*-BuC$_6$H$_3$O)(RNC)$_2$] (VIII)	3	terminal	1.917 (3)	this work

[a] Abbreviations: R = *p*-MeC$_6$H$_4$; mhp = 6-methyl-2-oxypyridine anion; 2Me-ox = 2-methyl-8-quinolinate anion.

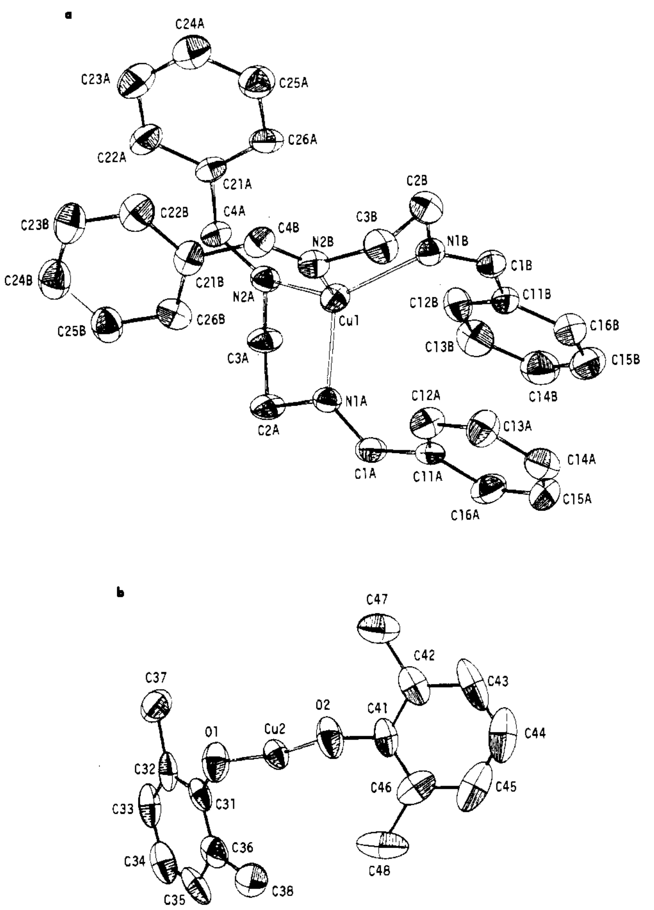

Figure 3. ORTEP drawings of (a) the cation and (b) the anion of the complex [Cu(PhCH=NCH$_2$CH$_2$N=CHPh)$_2$]$^+$[Cu(2,6-Me$_2$C$_6$H$_3$O)$_2$]$^-$ (VII) (50% probability ellipsoids).

copper(I) has a nearly planar trigonal coordination. Copper(I) is out by 0.114 (1) Å from the plane defined by the three donor atoms C(1A), C(1B), and O. The Cu-O bond distance, which is mainly determined by the coordination number of copper(I), has a value intermediate (1.917 (3) Å) between that found in the bicoordinate phenoxocuprate VII and those found in tetracoordinate species such as complexes III and VI. The Cu-O-C bond angle (134.3 (2)°) is very close to those of the terminal phenoxo groups of complex VII.

Conclusions

The results reported show that there is no intrinsic instability associated with the Cu-OAr unit. The phenoxo group displays either a bridging or a terminal bonding mode, depending on the substituent at the phenyl ring, and on the nature of ancillary ligands present. These were found to be the primary determinant of the various forms in which the [Cu-OPh] unit occurs. It is known that the reactivity of the [Cu-R] functionality is determined by the form in which the Cu-C bond occurs. In the present study, phenoxy [Cu-OPh] analogues for all the forms in which the Cu(I)-alkyl functionality occurs, outlined in the Introduction, were found. Thus, structure-reactivity relationships, closely akin to those operating in the reactions of Cu(I) alkyl and aryl derivatives with organic substrates, may be expected for the [Cu-OR] functionality.

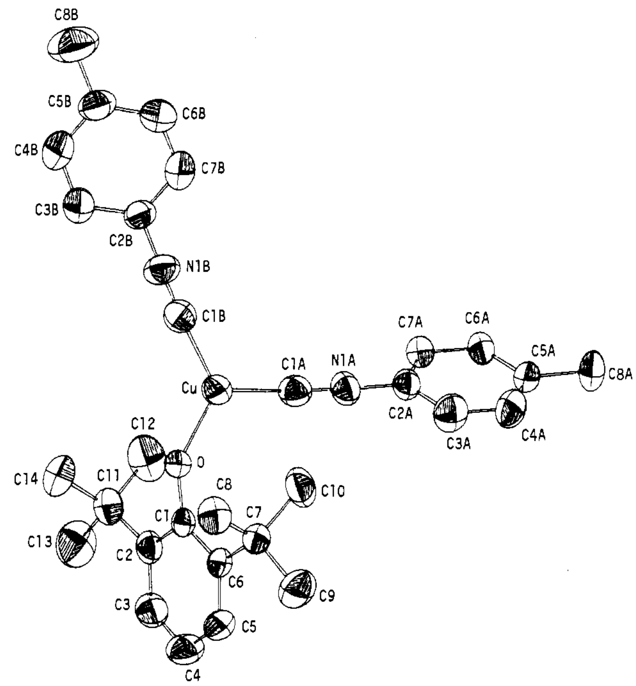

Figure 4. ORTEP drawing of the complex [Cu(2,6-*t*-Bu$_2$C$_6$H$_3$O)(*p*-MeC$_6$H$_4$NC)$_2$] (VIII) (50% probability ellipsoids).

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Registry No. II (R = Ph), 99642-99-6; II (R = 2,6-Me$_2$C$_6$H$_3$), 99632-84-5; III, 99665-07-3; IV, 34013-00-8; V, 99632-85-6; VI, 99632-87-8; VII, 94152-79-1; VIII, 99632-88-9; Cu(CO)Cl, 53513-40-9.

Supplementary Material Available: Listings of observed and calculated structure factors, unrefined hydrogen coordinates (Tables SI-SIV), thermal parameters (Tables SV-SVIII), nonessential bond distances and angles (Table SIX), and least-squares planes (Table SX) (58 pages). Ordering information is given on any current masthead page.