A Reactive and Versatile Fourteen-electron Copper(I) Fragment for Binding Carbon Monoxide, Isocyanides, and Phosphines: Synthesis, Crystal Structure, and Reactivity of (2-Methylquinolin-8-olato)copper(I) Derivatives†

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The synthesis of the 14-electron copper(I) moiety [Cu(2Me-quin)] (2Me-quin = 2-methylquinolin-8-olate) having a bent arrangement of the donor atom is reported. The reaction of CuCl with Na(2Me-quin) led to the disproportionation of copper(I) to copper(II) and copper metal, while in the presence of CO, a thermally very stable carbonyl complex [{Cu(2Me-quin)(CO)}$_4$] (**2**) was isolated [ν(CO)(Nujol) 2 050 cm^{-1}]. Complex (**2**) has a tetranuclear cubane-like structure, with S_4 symmetry, in which the coppers are bridged by the oxygen atom of the quinolinolate anion [av. Cu–O 2.04, Cu ··· Cu, 3.615, Cu–C 1.76 Å). Carbon monoxide can be replaced in the tetranuclear structure by *p*-MeC$_6$H$_4$NC to form [{Cu(2Me-quin)(*p*-MeC$_6$H$_4$NC)}$_4$] (**4**) [ν(CN)(Nujol) 2 145 cm^{-1}], which was also formed directly from CuCl, Na(2Me-quin), and *p*-MeC$_6$H$_4$NC. Reaction of PPh$_3$ and dppe (Ph$_2$PCH$_2$CH$_2$PPh$_2$) replaced CO and led to monomeric complexes [Cu(2Me-quin)(PPh$_3$)$_2$] (**5**) and [Cu(2Me-quin)(dppe)] (**6**). Complex (**2**) was used as a source of dicopper(I), by treating it with dppm (Ph$_2$PCH$_2$PPh$_2$) which caused loss of CO and led to the formation of [Cu$_2$(2Me-quin)$_2$(μ-dppm)] (**7**). The two Cu(2Me-quin) fragments share the oxygen atom of the quinolinate ligand, forming a dimetallic fragment [Cu ··· Cu 2.790(2) Å], where the five-co-ordination of each copper(I) is completed by one of the P donor atoms from the dppm ligand. Compound (**2**) catalyses the reduction of nitrosobenzene to azoxybenzene and nitroalkanes to oximes and nitriles under a pressure of carbon monoxide (60—100 atm) at temperatures from 80 to 110 °C. Compounds (**2**), (**5**), and (**7**) were characterized by single-crystal *X*-ray analysis: (**2**), space group $P2_1/n$ (monoclinic): a = 15.591(3), b = 18.558(3), c = 15.850(3) Å; β = 90.08(2), Z = 4, R 0.069 (R' = 0.076) for 1 414 observed reflections; (**5**), space group $Pna2_1$ (orthorhombic), a = 27.478(4), b = 12.519(2), c = 11.031(3) Å, Z = 4, R 0.059 for 1 920 observed reflections; (**7**), space group $P\bar{1}$ (triclinic), a = 12.018(4), b = 17.540(4), c = 11.793(4) Å, α = 90.82(3), β = 119.02(2), γ = 78.00(3)°, Z = 2, R 0.051 (R' = 0.054) for 3 876 observed reflections.

Metallic fragments having a fourteen-electron configuration have played a significant role in reactions with the most unreactive substrates.[1] Only a few of these metal fragments can be directly synthesized, and they are usually generated from more stable complexes, *via* thermally or photochemically induced loss of labile ligands.[2] Considerable effort has been devoted to finding such highly reactive metallic fragments and providing the most appropriate genesis possible. Among the best known metal fragments, which have played the role of 'vedettes' in organometallic chemistry because of their ability to add organic functionalities and small molecules, are M(PR$_3$)$_2$ (M = Ni, Pd, or Pt) derivatives, M(η^5-C$_5$H$_5$)$_3$ (M = Co, Ir, or Rh),[4] M(η^5-C$_5$H$_5$)$_2$ and M(η^5-C$_5$Me$_5$)$_2$ (M = Ti or Zr),[5] and V(η^5-C$_5$H$_5$)$_2{}^+$.[6]

In the case of Group 1B metals there are no comparable reactive fourteen-electron species since the fourteen-electron configuration is a quite common and stable configuration and a number of stable complexes are known where the metal can have a nearly linear two-co-ordination.[7] Two-co-ordinate complexes having a fourteen-electron configuration would be expected to be unstable and reactive, if we were able to impose a bent arrangement of the two donor atoms. In such an event the metal will strongly tend to achieve a 16- or 18-electron configuration. In planning such a reactive 14-electron configuration for copper(I), the nature of the donor atoms has a major role. They have to be, preferentially, nitrogen and oxygen rather than sulphur or phosphorus, which impart great stability to the +I oxidation state for copper.[7] In addition, we expect neutral complexes to be more electron rich than the usual cationic copper(I) complexes. Ligands imposing the right arrangement of oxygen and nitrogen donor atoms, and being anionic, normally promote disproportionation of copper(I) to copper(II) and copper metal, unless the reactive metallic fragment can be stabilized. A rather unique example is the use of copper(I) acetylacetonate, Cu(acac), for binding olefins,[8a] phosphine,[8b] and isocyanides.[8b,c] The present paper reports the synthesis and the chemistry of the Cu(2Me-quin) moiety, where 2Me-quin = 2-methylquinolin-8-olate. This unit can be generated in the presence of ligands stabilizing the +I oxidation state for copper, *i.e.* carbon monoxide, isocyanides, phosphines,

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.
Non-S.I. unit employed: atm = 101 325 Pa.

etc., or can collapse to form a very stable polynuclear structure. Substantial differences exist between the chemistry of the two fragments Cu(acac) and Cu(2Me-quin) in terms of binding ability, stability, and formation of polynuclear compounds. Tetra-, bi-, and mono-nuclear complexes of Cu(2Me-quin) have been isolated and structurally characterized. Moreover the polynuclear carbonyl complex [{Cu(2Me-quin)(CO)}$_4$] was found to be a catalyst in the carbon monoxide–copper(I)-promoted deoxygenation of nitroso- and nitro-derivatives. A preliminary communication on the synthesis and the structure of [{Cu(2Me-quin)(CO)}$_4$] has been published.[9]

Experimental

All the reactions were carried out under an atmosphere of purified nitrogen. Solvents were dried and distilled before use by standard methods. The compounds CuCl,[10] CuI,[10] and *p*-tolyl isocyanide[11] were prepared by published procedures. Infrared spectra were recorded with a Perkin-Elmer 283 spectrophotometer. Gas chromatographic analyses were carried out using a HP 588 A and a HP 5995A gas chromatograph-mass spectrometer. The sodium salt of 2-methylquinolin-8-ol was prepared by treating the ligand with NaOMe. It was recrystallized from tetrahydrofuran (thf) and n-hexane and the content of the anion was determined by a usual acidimetric titration.

Syntheses.—*Bis*(2-*methylquinolin*-8-*olato*)*copper*(II), [Cu(2Me-quin)$_2$], (**1**). A thf suspension (40 cm^3) of CuCl (0.52 g, 5.25 mmol) was treated with an equimolar amount of Na(2Me-quin). A very rapid disproportionation of copper(I) to copper(II) and copper metal occurred. Sodium chloride and metallic copper were filtered from the brown solution from which [Cu(2Me-quin)$_2$], (**1**), crystallized (yield *ca.* 70%) (Found: C, 61.50; H, 4.20; N, 7.05. Calc. for $C_{20}H_{16}CuN_2O_2$: C, 63.25; H, 4.20; N, 7.4%).

Tetrakis[*carbonyl*(2-*methylquinolin*-8-*olato*)*copper*(I)], (**2**). (*a*) *At high pressure.* A thf suspension (40 cm^3) of CuCl (1.49 g, 15.0 mmol) and of Na(2Me-quin) (15.0 mmol) was pressurized with 60 atm of carbon monoxide in an autoclave and heated to 65 °C for 5 h. Then the autoclave was slowly cooled and the suspension recovered carefully under nitrogen. Large yellow crystals of complex (**2**) were formed mixed with fine NaCl, which was removed by filtering the suspension through a large-porosity filter (yield *ca.* 80%) (Found: C, 53.05; H, 3.65; N, 5.10. Calc. for $C_{44}H_{32}Cu_4N_4O_8$: C, 52.90; H, 3.20; N, 5.60%). Complex (**2**) is stable to air in the solid state, and sparingly soluble in organic solvents; ν(CO)(Nujol) 2 050br cm^{-1}, shifted to 2 070 cm^{-1} in thf.

(*b*) *At atmospheric pressure.* Carbon monoxide was absorbed by a thf suspension (30 cm^3) of CuCl (0.40 g, 4.04 mmol). After the absorption was complete, a thf solution (15 cm^3) of Na(2Me-quin) (4.05 mmol) was slowly added. During the addition a microcrystalline yellow solid formed along with NaCl, which was removed by washing the solid mixture with methanol (yield *ca.* 70%). The solid isolated was complex (**2**).

[Cu(2Me-quin)(dppe)], (**6**). (*a*) *Reaction of dppe with complex* (**2**). A thf solution (20 cm^3) of dppe ($Ph_2PCH_2CH_2PPh_2$) (1.17 g, 2.94 mmol) was slowly added to a thf suspension (20 cm^3) of complex (**2**) (0.78 g, 0.78 mmol). Loss of carbon monoxide occurred along with the formation of a yellow solution, from which on standing and cooling to 0 °C complex (**6**) crystallized out (yield *ca.* 52%). No carbonyl band was present in the i.r. spectrum of a solution of (**6**) (Found: C, 69.0; H, 5.15; N, 2.20; P, 9.75. Calc. for $C_{36}H_{32}CuNOP_2$: C, 69.75; H, 5.15; N, 2.25; P, 10.0%).

(*b*) *Direct synthesis.* A thf suspension (40 cm^3) of CuCl (0.53 g, 5.23 mmol) was mixed with dppe (2.12 g, 5.33 mmol), then stirred until a white crystalline solid formed. When Na(2Me-quin) (5.33 mmol) was added to the suspension, a yellow solution formed, while the insoluble NaCl was filtered out. Cooling the resulting solution to 0 °C precipitated complex (**6**) as yellow crystals.

[Cu(2Me-quin)(PPh$_3$)$_2$], (**5**). A thf solution (15 cm^3) of PPh$_3$ (0.49 g, 1.87 mmol) was added to a thf suspension (20 cm^3) of complex (**2**) (0.46 g, 0.46 mmol). The solid dissolved with loss of carbon monoxide. The resulting yellow solution did not show any CO band in the i.r. spectrum. On addition of Et$_2$O a crystalline light yellow solid formed (yield *ca.* 36%) (Found: C, 73.9; H, 5.20; N, 1.80; P, 8.10. Calc. for $C_{46}H_{38}CuNOP_2$: C, 74.1; H, 5.10; N, 1.90; P, 8.30%).

[{Cu(2Me-quin)(*p*-MeC$_6$H$_4$NC)}$_4$], (**4**). (*a*) *From complex* (**2**). A thf solution (20 cm^3) of *p*-MeC$_6$H$_4$NC (0.51 g, 4.33 mmol) was added to a thf (20 cm^3) suspension of complex (**2**) (0.87 g, 0.87 mmol). The solid dissolved losing carbon monoxide and forming a yellow solution, from which in a few minutes yellow complex (**4**) crystallized (yield *ca.* 65%). The i.r. spectrum of the solution showed a single band at 2 145 cm^{-1}, while in the solid state (Nujol) two bands at 2 145 and 2 125 cm^{-1} are present (Found: C, 62.55; H, 4.35; N, 8.10. Calc. for $C_{18}H_{15}CuN_2O$: C, 63.80; H, 4.45; N, 8.25%). The same compound was obtained using an excess of *p*-MeC$_6$H$_4$NC.

(*b*) *Direct synthesis.* Addition of *p*-tolyl isocyanide (1.34 g, 1.15 mmol) to a thf suspension (30 cm^3) of CuCl (0.50 g, 5.05 mmol) gave a white voluminous solid. The addition of an equimolar amount of Na(2Me-quin) (5.05 mmol) led to a deep yellow solution and a crystalline yellow solid. By gentle heating the solid dissolved and NaCl was removed by filtration. On cooling and standing at room temperature complex (**4**) crystallized out (yield *ca.* 68%). Analytical and spectroscopic data were identical to those of the solid from (*a*).

[Cu$_2$(2Me-quin)$_2$(μ-dppm)], (**7**). A thf solution (15 cm^3) of dppm ($Ph_2PCH_2PPh_2$) (0.73 g, 3.78 mmol) was added to a suspension of complex (**2**) (0.94 g, 0.94 mmol) in thf (20 cm^3). The addition caused loss of carbon monoxide and formation of a deep yellow solution, from which complex (**7**) crystallized on standing at room temperature (yield *ca.* 45%). The i.r. spectrum of the solution did not show any CO band (Found: C, 64.7; H, 4.70; N, 2.05; P, 7.30. $C_{45}H_{38}Cu_2N_2O_2P_2$: C, 65.3; H, 4.60; N, 3.40; P, 7.50%). The solid analysed did not contain thf since it had been stirred *in vacuo* for several hours.

Deoxygenation of Nitroso- and Nitro-derivatives.—Deoxygenation reactions were carried in a steel autoclave under a pressure of carbon monoxide at controlled temperature. The analysis of the organic compound was carried out by g.l.c. and mass spectrometry.

(*a*) *Nitrosobenzene.* A thf solution (40 cm^3) of nitrosobenzene (1.59 g, 14.9 mmol) containing complex (**2**) (0.66 g, 0.66 mmol) was pressurized at 60 atm of carbon monoxide, heated to 80 °C, and stirred for 30 h. The reaction gas contained CO$_2$. The solution contained 6.0 mmol of azoxybenzene, traces of hydrazobenzene, and traces of nitrosobenzene. Complex (**2**) was recovered (yield *ca.* 40%) by filtering the final suspension.

(*b*) *Nitrobenzene.* No deoxygenation was observed under the conditions specified above.

(*c*) *Pyridine* N-*oxide.* A thf solution (30 cm^3) of pyridine *N*-oxide (3.79 g, 48.0 mmol) was treated with complex (**2**) (0.80 g, 0.80 mmol) at 110 °C for 80 h under 100 atm of carbon monoxide. Carbon dioxide, 13.0 mmol of pyridine, and 35.0 mmol of unreacted pyridine *N*-oxide were found.

(*d*) *Nitroalkanes.* Reaction was carried out using RNO$_2$ (R = Et, Pr^n, or Bu^n) and gave very similar results for the three nitro-derivatives. Details for the deoxygenation of nitroethane are reported. A thf solution (40 cm^3) of nitroethane (2.62 g, 35.0 mmol) was treated with complex (**2**) (0.63 g, 0.63 mmol) and pressurized at 80 atm with carbon monoxide. Then the

Table 1. Experimental data for the *X*-ray diffraction studies

Complex	(2)	(5)	(7)
Crystal system	Monoclinic	Orthorhombic	Triclinic
Space group	$P2_1/n$	$Pna2_1$	$P\bar{1}$
Cell parameters[a]			
a/Å	15.591(3)	27.478(4)	12.018(4)
b/Å	18.558(3)	12.519(2)	17.540(4)
c/Å	15.580(3)	11.031(3)	11.793(4)
α/°	90	90	90.82(3)
β/°	90.08(2)	90	119.02(2)
γ/°	90	90	78.00(3)
U/Å^3	4 586(1)	3 795(1)	2 115(1)
Z	4	4	2
D_c/g cm^{-3}	1.447	1.306	1.413
M	998.9	746.3	899.9
Crystal dimensions, mm	0.10 × 0.13 × 0.32	0.12 × 0.18 × 0.29	0.18 × 0.64 × 0.72
μ/cm^{-1}	18.88	18.70	11.25
A[b]	1.19—1.32	1.20—1.33	1.18—1.89
Diffractometer	Philips PW 1100	Siemens AED	Philips PW 1100
Diffraction geometry	equatorial	equatorial	equatorial
Scan type	ω—2θ	θ—2θ	ω—2θ
Scan speed	0.04° s^{-1}	3—12° min^{-1}	0.075° s^{-1}
Scan width/°	1.60	*c*	1.20
Radiation	*d*	*e*	*d*
2θ range/°	4—40	6—120	6—47
Reflections measured	$\pm h\ k\ l$	$h\ k\ l$	$\pm h\ \pm k\ l$
Unique data	3 456	2 993	5 906
Observed data	1 414 [$I > 3\sigma(I)$]	1 920 [$I > 2\sigma(I)$]	3 876 [$I > 3\sigma(I)$]
No. of variables	214	351	457
Overdetermination ratio	6.6	5.5	8.5
Maximum shift/error in last cycle	0.1	0.4	0.3
$R = \Sigma\|\Delta F\|/\Sigma\|F_o\|$	0.069	0.059	0.051
$R' = \Sigma w^{\frac{1}{2}}\|\Delta F\|/\Sigma w^{\frac{1}{2}}\|F_o\|$	0.076	—	0.054
Goodness of fit $[\Sigma w\|\Delta F\|^2/(N_o - N_v)]$[f]	1.20	—	1.46

[a] Unit-cell parameters were obtained by least-squares analysis of the setting angles of 20—25 carefully centred reflections chosen from diverse regions of reciprocal space. [b] Minimum and maximum for absorption correction factor. [c] $(\theta - 0.5) - [\theta + (0.5 + \Delta\theta)]°$; $\Delta\theta = (\lambda_{\alpha_2} - \lambda_{\alpha_1})/\lambda$. [d] Graphite-monochromated Mo-K_α (λ = 0.7107 Å). [e] Nickel-filtered Cu-K_α (λ = 1.5418 Å). [f] N_o = Number of observations, N_v = number of variables.

suspension was stirred and heated to 100 °C for 20 h. The analysis of gases showed the presence of CO_2. Acetonitrile (6.6 mmol), acetamide (16.1 mmol), and nitroethane (3.5 mmol) were found in solution. A thf (35 cm^3) solution of 2-nitropropane (1.98 g, 22.3 mmol) was pressurized with 85 atm of carbon monoxide in the presence of complex (**2**) (0.37 g, 0.37 mmol). The suspension was heated to 80 °C and stirred for 65 h. Carbon dioxide was found in the gas phase and the solution contained acetone oxime (17.0 mmol), acetone (1.0 mmol), traces of unreacted 2-nitropropane, and other products.

X-*Ray Crystallography for Complexes* (**2**), (**5**), *and* (**7**).—Data reduction, structure solution, and refinement were carried out on a GOULD 32/77 computer using SHELX 76.[12] The crystals selected for study were mounted in a random orientation on a single-crystal four-circle diffractometer. Crystals of (**2**) and (**7**) were sealed in glass capillaries under nitrogen. Crystal data and details of the data collection and structure refinement parameters are given in Table 1. The reduced cells quoted were obtained with the use of TRACER.[13] Intensity data were collected at room temperature using the profile measurement technique[14] for (**5**) and the 'three-point' technique for (**2**) and (**7**). The structure amplitudes were obtained after the usual Lorentz and polarization corrections. The crystal quality was tested by ψ scans showing that crystal absorption effects could not be neglected for complex (**2**), so an absorption correction was made following ref. 15. No absorption corrections were applied for complexes (**5**) and (**7**).

Structure solution and refinement were based on the observed reflections. The structures were solved by the heavy-atom method starting from a three-dimensional Patterson map for (**5**) and (**7**). For complex (**2**) the co-ordinates of the copper atoms were obtained by direct methods.[12] Refinement was by blocked full-matrix least squares for (**5**) and (**7**) and by full-matrix least squares for (**2**) minimizing the function $\Sigma w|\Delta F|^2$. Unit weights were used for (**5**) since these gave acceptable agreement analyses. For (**2**) and (**7**) the reflections were weighted according to the scheme $w = k/[\sigma^2(F_o) + |g|F_o^2]$. At convergence the values for k and g were 1.0000 and 0.004 02 respectively for (**2**), 1.4635 and 0.000 76 for (**7**). Scattering factors for neutral atoms were taken from ref. 16*a* for non-hydrogen atoms and from ref. 17 for H. Anomalous scattering corrections were included in all structure-factor calculations.[16b] Among the low-angle reflections no correction for secondary extinction was deemed necessary.

Because of the low percentage of observed reflections, probably due to the small dimensions of the crystal available, refinement for complex (**2**) was carried out using isotropic thermal parameters except for the copper atoms which were allowed to vary anisotropically. So the accuracy of the analysis is rather poor as indicated by the high values of the estimated standard deviations (e.s.d.s). All but those associated with the methyl-group hydrogen atoms were placed in calculated positions and introduced in calculations by refining only an overall isotropic thermal parameter (U = 0.18 Å^2). In the final difference map there were a few peaks of about 0.8 e Å^{-3} with no chemical meaning.

Refinement of complex (**7**) was carried out anisotropically

Table 2. Fractional atomic co-ordinates for [{Cu(2Me-quin)(CO)}$_4$], (**2**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu(1)	0.378 1(3)	0.185 4(2)	0.091 3(2)	C(21)	0.675 3(11)	0.333 9(10)	0.115 3(12)
Cu(2)	0.522 1(2)	0.310 3(2)	0.001 1(2)	C(22)	0.681 9(11)	0.404 8(10)	0.086 7(12)
Cu(3)	0.619 2(2)	0.191 8(2)	0.145 3(2)	C(23)	0.746 4(11)	0.449 6(10)	0.118 0(12)
Cu(4)	0.466 6(2)	0.314 4(2)	0.229 0(3)	C(24)	0.804 2(11)	0.423 5(10)	0.177 9(12)
O(1)	0.378 1(12)	0.290 2(10)	0.138 6(12)	C(25)	0.797 7(11)	0.352 7(10)	0.206 5(12)
C(1)	0.312 2(12)	0.327 0(11)	0.105 9(12)	C(26)	0.733 2(11)	0.307 8(10)	0.175 2(12)
C(2)	0.298 9(12)	0.398 2(11)	0.130 9(12)	C(27)	0.856 0(20)	0.322 5(18)	0.263 2(19)
C(3)	0.228 9(12)	0.436 6(11)	0.099 5(12)	C(28)	0.846 5(24)	0.258 4(21)	0.292 2(23)
C(4)	0.172 2(12)	0.403 9(11)	0.043 2(12)	C(29)	0.777 1(22)	0.213 8(19)	0.262 6(22)
C(5)	0.185 5(12)	0.332 7(11)	0.018 3(12)	N(3)	0.719 2(15)	0.241 4(13)	0.205 5(15)
C(6)	0.255 5(12)	0.294 2(11)	0.049 6(12)	C(30)	0.761 3(22)	0.132 7(19)	0.294 8(21)
C(7)	0.134 0(29)	0.300 8(25)	−0.031 6(26)	O(4)	0.523 2(12)	0.215 0(10)	0.228 6(12)
C(8)	0.146 4(24)	0.231 5(21)	−0.056 7(23)	C(31)	0.491 8(12)	0.170 3(10)	0.289 1(10)
C(9)	0.218 0(23)	0.196 3(21)	−0.026 5(21)	C(32)	0.518 9(12)	0.099 3(10)	0.300 1(10)
N(1)	0.268 7(15)	0.226 2(13)	0.028 4(15)	C(33)	0.487 7(12)	0.058 7(10)	0.367 4(10)
C(10)	0.238 6(25)	0.115 3(21)	−0.044 0(24)	C(34)	0.429 3(12)	0.089 1(10)	0.423 7(10)
O(2)	0.473 6(12)	0.208 8(10)	0.009 1(12)	C(35)	0.402 2(12)	0.160 1(10)	0.412 7(10)
C(11)	0.503 6(12)	0.164 3(10)	−0.053 9(10)	C(36)	0.433 4(12)	0.200 7(10)	0.345 4(10)
C(12)	0.481 6(12)	0.091 5(10)	−0.058 1(10)	C(37)	0.339 1(22)	0.189 5(22)	0.467 0(22)
C(13)	0.512 9(12)	0.048 8(10)	−0.123 5(10)	C(38)	0.317 1(26)	0.259 5(23)	0.456 9(26)
C(14)	0.566 2(12)	0.078 8(10)	−0.184 8(10)	C(39)	0.351 8(22)	0.304 3(20)	0.386 2(21)
C(15)	0.588 2(12)	0.151 5(10)	−0.180 7(10)	N(4)	0.410 1(17)	0.270 1(15)	0.336 1(16)
C(16)	0.556 9(12)	0.194 3(10)	−0.115 2(10)	C(40)	0.324 0(24)	0.380 9(20)	0.370 1(23)
C(17)	0.640 3(20)	0.187 4(19)	−0.240 1(20)	C(41)	0.353 4(20)	0.116 5(18)	0.153 5(19)
C(18)	0.658 0(22)	0.256 8(19)	−0.230 4(22)	O(5)	0.323 3(17)	0.071 5(15)	0.196 3(17)
C(19)	0.631 4(19)	0.293 4(16)	−0.159 7(18)	C(42)	0.461 3(22)	0.390 4(20)	−0.010 8(21)
N(2)	0.577 9(15)	0.267 7(13)	−0.100 8(15)	O(6)	0.425 6(19)	0.445 4(18)	−0.029 1(18)
C(20)	0.658 5(22)	0.375 1(20)	−0.148 5(22)	C(43)	0.640 6(23)	0.110 7(20)	0.093 5(23)
O(3)	0.613 5(12)	0.289 2(10)	0.087 3(12)	O(7)	0.664 5(19)	0.063 5(16)	0.056 8(18)

Table 3. Fractional atomic co-ordinates (× 10^4) for [Cu(2Me-quin)(PPh$_3$)$_2$], (**5**)

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	959(1)	513(1)	2 500	C(36)	1 283(5)	585(9)	5 848(9)
P(1)	1 622(1)	−88(2)	3 589(5)	C(51)	1 170(3)	2 916(6)	1 126(9)
P(2)	849(1)	2 253(2)	2 400(7)	C(52)	1 338(3)	2 304(3)	156(9)
O(1)	1 115(3)	−285(6)	874(13)	C(53)	1 586(3)	2 792(6)	−799(9)
N(1)	444(3)	−684(7)	2 683(19)	C(54)	1 666(3)	3 892(6)	−784(9)
C(1)	119(5)	−797(14)	3 650(22)	C(55)	1 497(3)	4 505(6)	186(9)
C(2)	−96(6)	−1 883(16)	3 656(25)	C(56)	1 250(3)	4 017(6)	1 141(9)
C(3)	−4(8)	−2 665(15)	2 795(32)	C(41)*	1 120(5)	2 953(12)	3 893(13)
C(4)	454(7)	−3 250(14)	1 004(34)	C(42)	864(5)	3 100(12)	4 972(13)
C(5)	780(8)	−2 996(15)	64(36)	C(43)	1 096(5)	3 548(12)	5 976(13)
C(6)	1 018(6)	−1 981(11)	−20(25)	C(44)	1 584(5)	3 849(12)	5 901(13)
C(7)	909(5)	−1 208(9)	902(23)	C(45)	1 840(5)	3 702(12)	4 822(13)
C(8)	555(5)	−1 452(10)	1 846(19)	C(46)	1 608(5)	3 254(12)	3 818(13)
C(9)	325(6)	−2 499(11)	1 893(24)	C(61)	230(3)	2 784(9)	2 603(15)
C(10)	18(7)	57(16)	4 439(21)	C(62)	−132(3)	2 105(9)	2 163(15)
C(11)	1 757(3)	−1 510(4)	3 296(10)	C(63)	−607(3)	2 482(9)	2 019(15)
C(12)	2 172(3)	−1 858(4)	2 685(10)	C(64)	−719(3)	3 536(9)	2 316(15)
C(13)	2 242(3)	−2 945(4)	2 468(10)	C(65)	−357(3)	4 215(9)	2 756(15)
C(14)	1 896(3)	−3 684(4)	2 862(10)	C(66)	117(3)	3 838(9)	2 900(15)
C(15)	1 481(3)	−3 335(4)	3 472(10)	C(61B)	234(4)	2 704(11)	1 730(16)
C(16)	1 411(3)	−2 248(4)	3 689(10)	C(62B)	−133(4)	1 935(11)	1 681(16)
C(21)	2 162(2)	609(6)	3 050(13)	C(63B)	−606(4)	2 231(11)	1 371(16)
C(22)	2 494(2)	1 090(6)	3 837(13)	C(64B)	−713(4)	3 296(11)	1 111(16)
C(23)	2 886(2)	1 667(6)	3 372(13)	C(65B)	−346(4)	4 065(11)	1 160(16)
C(24)	2 946(2)	1 763(6)	2 121(13)	C(66B)	127(4)	3 769(11)	1 469(16)
C(25)	2 615(2)	1 282(6)	1 335(13)	C(41B)	1 028(8)	2 998(15)	3 425(16)
C(26)	2 222(2)	705(6)	1 799(13)	C(42B)	690(8)	3 485(15)	4 190(16)
C(31)	1 647(5)	−8(9)	5 279(9)	C(43B)	848(8)	4 016(15)	5 231(16)
C(32)	1 989(5)	−560(9)	5 973(9)	C(44B)	1 343(8)	4 059(15)	5 505(16)
C(33)	1 967(5)	−518(9)	7 236(9)	C(45B)	1 680(8)	3 572(15)	4 740(16)
C(34)	1 603(5)	75(9)	7 805(9)	C(46B)	1 523(8)	3 041(15)	3 700(16)
C(35)	1 261(5)	627(9)	7 111(9)				

* The site occupation factors for atoms from C(41) to C(46B) are 0.5.

Table 4. Fractional atomic co-ordinates (× 10^4) for [Cu_2(2Me-quin)$_2$(μ-dppm)], (**7**)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
Cu(1)	1 541(1)	2 664(1)	−201(1)	C(22)	−1 188(4)	4 415(2)	−2 685(4)
Cu(2)	4 033(1)	2 037(1)	145(1)	C(23)	−2 260(4)	5 038(2)	−3 009(4)
O(1)	3 339(4)	2 503(2)	1 617(4)	C(24)	−2 068(4)	5 746(2)	−2 479(4)
O(2)	2 301(4)	1 587(2)	−735(4)	C(25)	−805(4)	5 832(2)	−1 626(4)
N(1)	947(5)	2 240(3)	927(5)	C(26)	267(4)	5 209(2)	−1 302(4)
N(2)	4 820(5)	917(3)	958(4)	C(31)	1 347(4)	3 464(2)	−2 954(3)
C(1)	−227(7)	2 165(4)	624(7)	C(32)	1 261(4)	4 075(2)	−3 761(3)
C(2)	−441(9)	1 732(5)	1 472(9)	C(33)	1 319(4)	3 918(2)	−4 896(3)
C(3)	590(10)	1 368(5)	2 603(9)	C(34)	1 463(4)	3 151(2)	−5 224(3)
C(4)	2 968(10)	1 061(5)	4 129(8)	C(35)	1 549(4)	2 540(2)	−4 417(3)
C(5)	4 161(9)	1 166(5)	4 413(7)	C(36)	1 491(4)	2 697(2)	−3 283(3)
C(6)	4 328(7)	1 658(4)	3 592(7)	C(41)	5 684(4)	3 445(3)	1 267(3)
C(7)	3 254(6)	2 037(4)	2 413(6)	C(42)	6 799(4)	3 570(3)	1 279(3)
C(8)	2 011(7)	1 893(3)	2 102(6)	C(43)	7 828(4)	3 727(3)	2 428(3)
C(9)	1 860(8)	1 424(4)	2 878(7)	C(44)	7 742(4)	3 759(3)	3 566(3)
C(10)	−1 342(7)	2 526(5)	−666(9)	C(45)	6 627(4)	3 633(3)	3 554(3)
C(11)	6 082(6)	587(4)	1 742(6)	C(46)	5 598(4)	3 477(3)	2 405(3)
C(12)	6 479(7)	−162(4)	2 451(6)	C(51)	4 669(5)	3 367(2)	−1 492(4)
C(13)	5 549(7)	−536(4)	2 339(6)	C(52)	4 739(5)	4 107(2)	−1 834(4)
C(14)	3 183(8)	−545(4)	1 362(7)	C(53)	4 977(5)	4 220(2)	−2 858(4)
C(15)	1 915(7)	−173(4)	545(7)	C(54)	5 145(5)	3 591(2)	−3 540(4)
C(16)	1 595(7)	551(4)	−192(7)	C(55)	5 075(5)	2 851(2)	−3 198(4)
C(17)	2 554(6)	913(3)	−68(6)	C(56)	4 837(5)	2 739(2)	−2 174(4)
C(18)	3 893(6)	536(3)	815(6)	C(57)	2 910(6)	3 972(3)	−492(6)
C(19)	4 201(7)	−199(3)	1 509(6)	O(3)	9 066(14)	604(7)	5 833(12)
C(20)	7 037(7)	1 022(5)	1 856(8)	C(58)	8 032(14)	851(10)	6 134(19)
P(1)	1 399((2)	3 634(1)	−1 400(2)	C(59)	7 938(14)	1 620(10)	6 403(20)
P(2)	4 340(2)	3 170(1)	−183(2)	C(60)	8 703(20)	1 913(9)	6 043(25)
C(21)	75(4)	4 500(2)	−1 831(4)	C(61)	9 468(19)	1 303(13)	5 646(19)

for all non-hydrogen atoms. The hydrogen atoms were located from ΔF syntheses and introduced in calculations as fixed contributors prior to the final refinement (U_{iso} = 0.10 Å^2). The final difference map showed no unusual feature, with no significant peak above the general background of about 0.3 e Å^{-3}. The phenyl rings of the phosphine ligand were considered as rigid groups having D_{6h} symmetry (C–C 1.39 Å). The *X*-ray analysis revealed the presence of a thf molecule of crystallization.

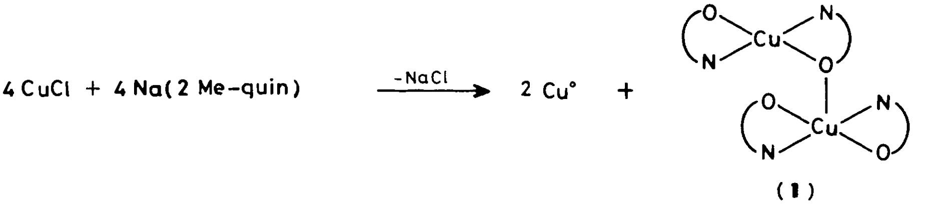
Some difficulties were encountered in the structure solution and refinement for complex (**5**). A Patterson map revealed the position of the copper atom and of two independent phosphorus atoms allowing exclusion of space group *Pnma*. The other non-hydrogen atoms were located from successive Fourier difference syntheses. Most of the Fourier peaks were smeared out in the *z* direction (including copper and phosphorus atoms). This is reflected in the high values of U_{33} which are considerably greater than those of the other components, indicating some kind of disorder in the [001] direction. Attempts to simulate the disorder by splitting all the atoms into two halves were successful only for the phenyl rings C(41)—C(46) and C(61)—C(66) which were split into C(41B)—C(46B) and C(61B)—C(66B) respectively with site occupation factors of 0.5. This model was refined anisotropically only for the non-disordered atoms to *R* 0.059 [$R_G = 0.064 = (\Sigma w|\Delta F|^2/\Sigma w F_o{}^2)^{\frac{1}{2}}$]. Since the space group is polar the chirality of the crystal was tested by inverting all co-ordinates *x*, *y*, *z* (−*x*, −*y*, −*z*) and refining to convergence once again. The resulting values (*R* = 0.061, R_G = 0.066) indicate that the original assignment of crystal chirality is correct. The hydrogen atoms were introduced in idealized position as fixed contributors (U_{iso} = 0.05 Å^2) prior to the final refinement. The phosphine phenyl rings were refined as rigid groups having D_{6h} symmetry. The final difference map showed no unusual feature with no peak greater than 0.4 e Å^{-3} and no hole less than −0.5 e Å^{-3}.

Final atomic co-ordinates are listed in Tables 2—4. Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

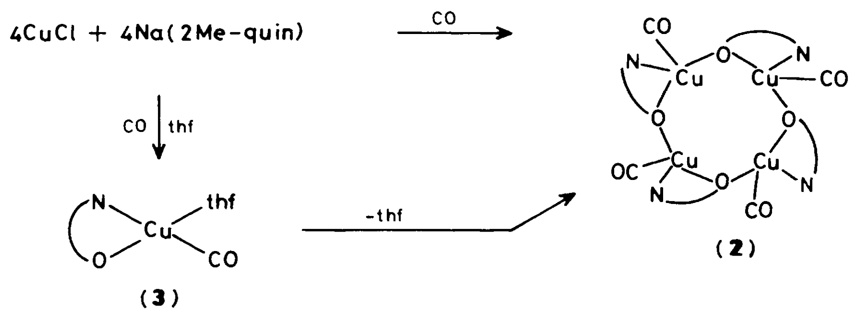
Results and Discussion

The attempts to synthesize a reactive fourteen-electron species in the case of copper(I) began by choosing a bidentate mono-anionic ligand imposing a bent arrangement of the two donor atoms around the metal and leading to a neutral species. Some ligands, like bidentate Schiff-base derivatives from salicylaldehyde and acetylacetone and quinolin-8-ol, caused mainly the disproportionation of copper(I) to copper(II) and copper metal. 2-Methylquinolin-8-ol was found to be a good ligand for our purposes, if the reaction is carried out in the presence of some additional ligands stabilizing the copper(I) state. By treating CuCl in thf with the sodium salt of 2-methylquinolin-8-ol, Na(2Me-quin), a very rapid disproportionation of copper(I) occurred and complex (**1**) was isolated and structurally characterized.[18] When reaction (1) was carried out under a pressure of carbon monoxide or using [Cu(CO)Cl][19] as starting material, complex (**2**) was formed [equation (2)].

Formation of the tetranuclear species can be viewed as occurring through the intermediacy of the mononuclear species, having a labile ligand, thf, on copper(I). Carbon monoxide has the major role in stabilizing the +I oxidation state for copper and in preventing the disproportionation reaction. Some of the properties of complex (**2**) are worth mentioning, like the unusual thermal stability and air stability in the solid state. The CO stretching frequency at 2 050 cm^{-1} (Nujol) is in the lower range for terminal copper(I) carbonyls in agreement with a high basicity of the ancillary ligand.[20] The significant increase of this band to 2 070 cm^{-1} in solution (thf) cannot be explained, unless the proposed intermediate (**3**) is formed. A related phenomenon



(1)



(2)

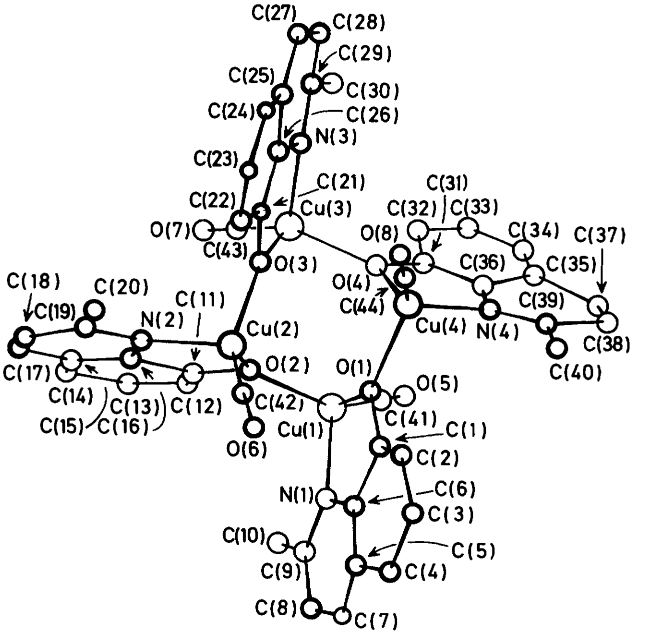


Figure 1. A view of the tetrameric complex [{Cu(2Me-quin)(CO)}$_4$], (**2**)

Table 5. Selected interatomic distances (Å) and angles (°) for [{Cu(2Me-quin)(CO)}$_4$], (**2**)

Cu(1)–O(1)	2.08(2)	Cu(2)–O(2)	2.04(2)
Cu(1)–O(2)	2.03(2)	Cu(2)–O(3)	2.01(2)
Cu(1)–N(1)	2.12(2)	Cu(2)–N(2)	2.00(2)
Cu(1)–C(41)	1.66(3)	Cu(2)–C(42)	1.77(4)
Cu(3)–O(3)	2.03(2)	Cu(4)–O(4)	2.05(2)
Cu(3)–O(4)	2.04(2)	Cu(4)–O(1)	2.04(2)
Cu(3)–N(3)	2.05(2)	Cu(4)–N(4)	2.08(2)
Cu(3)–C(43)	1.75(4)	Cu(4)–C(44)	1.86(7)
Cu(1) ⋯ Cu(2)	3.531(1)	Cu(2) ⋯ Cu(3)	3.514(1)
Cu(1) ⋯ Cu(3)	3.856(1)	Cu(2) ⋯ Cu(4)	3.7171(1)
Cu(1) ⋯ Cu(4)	3.520(1)	Cu(3) ⋯ Cu(4)	3.550(1)
C(41)–O(5)	1.17(4)	C(43)–O(7)	1.12(4)
C(42)–O(6)	1.20(4)	C(44)–O(8)	1.04(6)
O(1)–Cu(1)–O(2)	91.8(8)	O(2)–Cu(2)–O(2)	92.3(8)
O(1)–Cu(1)–N(1)	80.5(8)	O(2)–Cu(2)–N(2)	81.1(9)
O(1)–Cu(1)–C(41)	120.4(12)	O(2)–Cu(2)–C(42)	125.8(12)
O(2)–Cu(1)–N(1)	102.3(8)	O(3)–Cu(2)–N(2)	99.4(8)
O(2)–Cu(1)–C(41)	135.9(12)	O(3)–Cu(2)–C(42)	127.8(12)
N(1)–Cu(1)–C(41)	111.6(12)	N(2)–Cu(2)–C(42)	118.7(12)
O(3)–Cu(3)–O(4)	94.2(8)	O(4)–Cu(4)–O(1)	95.2(8)
O(3)–Cu(3)–N(3)	80.9(9)	O(4)–Cu(4)–N(4)	80.2(9)
O(3)–Cu(3)–C(43)	124.3(12)	O(4)–Cu(4)–C(44)	127.8(18)
O(4)–Cu(3)–N(3)	99.3(8)	O(1)–Cu(4)–N(4)	101.5(9)
O(4)–Cu(3)–C(43)	128.7(13)	O(1)–Cu(4)–C(44)	120.9(18)
N(3)–Cu(3)–C(43)	117.5(13)	N(4)–Cu(4)–C(44)	121.7(20)
Cu(1)–C(41)–O(5)	170(3)	Cu(3)–C(43)–O(7)	170(4)
Cu(2)–C(42)–O(6)	171(3)	Cu(4)–C(44)–O(8)	170(7)

occurs in the case of isocyanide derivatives (see below). Figure 1 shows a view of complex (**2**). The complex consists of four copper atoms, arranged at the vertices of a distorted tetrahedron, symmetrically bridged by the oxygen atoms of four quinolinato anions. The molecule as a whole has approximately S_4 symmetry, with the copper and the bridging oxygen atoms having a cubane-like structure. Each copper has a pseudo-tetrahedral co-ordination provided by the bidentate quinolato anion, carbon monoxide, and the bridging oxygen. Bond distances and angles are reported in Table 5. The Cu–O bond distances range from 2.01(2) to 2.08(2) Å (av. 2.04 Å), and Cu–N from 2.00(2) to 2.12(2) Å (av. 2.06 Å). The copper–copper separations vary from 3.514(1) to 3.856(1) Å (av. 3.615 Å) and the average Cu ⋯ Cu ⋯ Cu angle is 60.0°. The Cu–C (mean 1.76 Å) and C–O(carbon monoxide) (mean 1.13 Å) bond distances compare very well with the values reported for other copper(I) carbonyls.[20] These structural parameters can be related to those of the analogous [{Cu(OCMe$_3$)}$_4$],[21] [{Cu(mpyo)}$_4$] (mpyo = 6-methylpyridin-2-onate),[22] and [{Cu(OCMe$_3$)(CO)}$_4$].[23]

The polynuclear structure of complex (**2**) is built up by a phenoxo group bridging two copper atoms.[24] A bridging oxygen atom has been invoked as the crucial ligand for the activity of the dicopper unit in binding dioxygen. The Cu ⋯ Cu separation (av. 3.615 Å) is suitable for the binuclear activation of small molecules. Each copper(I) has only one co-ordination site filled by a labile ligand, which can easily be replaced. The N and O donor atoms surrounding copper(I) are attached to an organic residue which has considerable electronic flexibility, a property which is necessary for the metal to bind small molecules like dioxygen and carbon monoxide. The thermal stability is rather surprising considering the presence of a carbon monoxide molecule and of a Cu–OR bond which is believed to be unstable.[24] Reactions of complex (**2**) led either to maintenance or to the release of the monomeric fragment Cu(2Me-quin) [equation (3), R = *p*-MeC_6H_4NC].

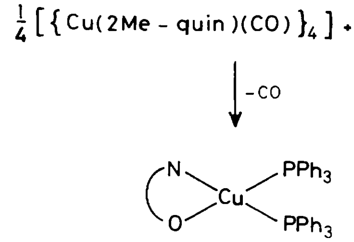
$$4\,CuCl + 4\,RNC + 4\,Na(2Me\text{-}quin) \xrightarrow{-NaCl} \frac{4}{n}[\{Cu(2Me\text{-}quin)(RNC)\}_n] \quad (3)$$

(**4**)

$$[\{Cu(2Me\text{-}quin)(CO)\}_4] + 4\,RNC \xrightarrow[-CO]{}$$

(**2**)

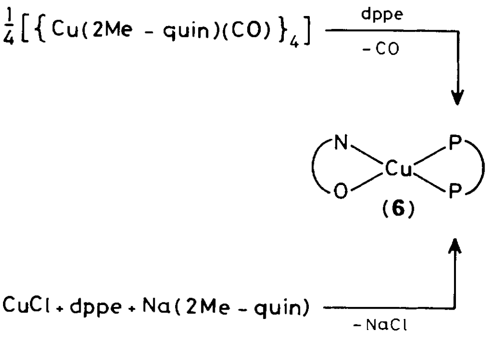
The reaction of complex (**2**) with *p*-tolyl isocyanide led to compound (**4**), which could be also independently synthesized by reaction of CuCl with *p*-tolyl isocyanide and Na(2Me-quin). Formation of (**4**), which was isolated as crystalline solid, was independent of the Cu : RNC molar ratio used. The i.r. spectrum showed a significant difference from solid state to solution, having two bands at 2 125 and 2 145 cm^{-1} in the solid and a single band at 2 145 cm^{-1} in solution (thf). This suggests there exists an equilibrium between the oligomeric and a monomeric species analogous to (**3**) in solution, explaining why a single band occurs in the i.r. spectrum of (**4**) in solution. Additionally, significant differences in the chemical environment in the solid state alter the chemical environment in the oligomeric structure. Based on the known structure of (**2**) and on the Cu : RNC molar ratio, an analogous tetrameric structure for (**4**) is very likely, the genesis of which may require the intermediacy of a monomeric species like (**3**). The use of ligands for which copper(I) has a very high affinity allowed isolation of monomeric species [Cu(2Me-quin)], though in this case the reactivity of the metal is highly depressed. Triphenylphosphine breaks down the tetrameric structure of (**4**) to a monomeric phosphine complex [equation (4)].



(**5**)

(4)

An enhancement in the formation of a monomeric species was obtained by using a bidentate phosphine like dppe [equation (5)]. A view of the structure of (**5**) is shown in Figure 2, showing the tetrahedral co-ordination around copper(I). The most relevant bond distances and angles are given in Table 6, though, due to the low quality of the *X*-ray data, a detailed discussion of them is meaningless. This notwithstanding the structural parameters of the Cu(2Me-quin) fragment are close to those found for (**2**) and (**7**). Complex (**2**) reacts with dppm in thf as in equation (6). An ORTEP view of the dimer (**7**) is shown in Figure 3, while selected bond distances and angles are listed in Table 7. The two Cu(2Me-quin) fragments share the oxygen atom of the quinolinato ligand, forming a dimetallic fragment [Cu···Cu 2.790(2) Å], where each copper(I) completes five-



(5)

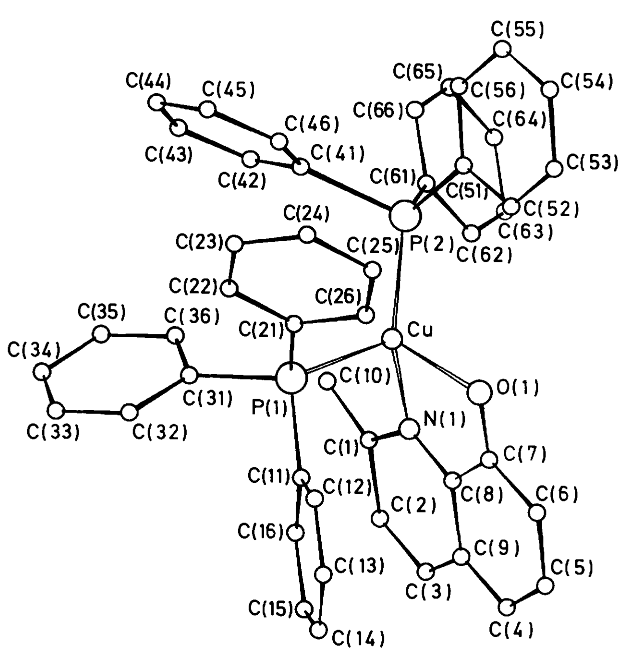
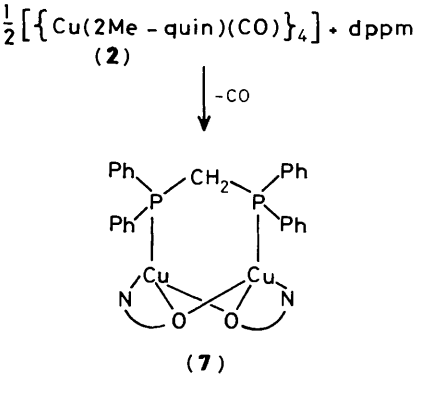


Figure 2. A view of the monomeric complex [Cu(2Me-quin)$(PPh_3)_2$], (**5**). The disorder affecting the two phenyl rings C(41)—C(46) and C(61)—C(66) is not shown for clarity

Table 6. Selected interatomic distances (Å) and angles (°) for [Cu(2Me-quin)$(PPh_3)_2$], (**5**)

Cu(1)–O(1)	2.088(14)	Cu–N(1)	2.071(9)
Cu–P(1)	2.308(4)	Cu–P(2)	2.202(3)
O(1)–Cu–N(1)	83.0(4)	N(1)–Cu–P(1)	104.6(3)
O(1)–Cu–P(1)	97.4(2)	N(1)–Cu–P(2)	128.8(2)
O(1)–Cu–P(2)	117.2(4)	P(1)–Cu–P(2)	117.2(2)



(6)

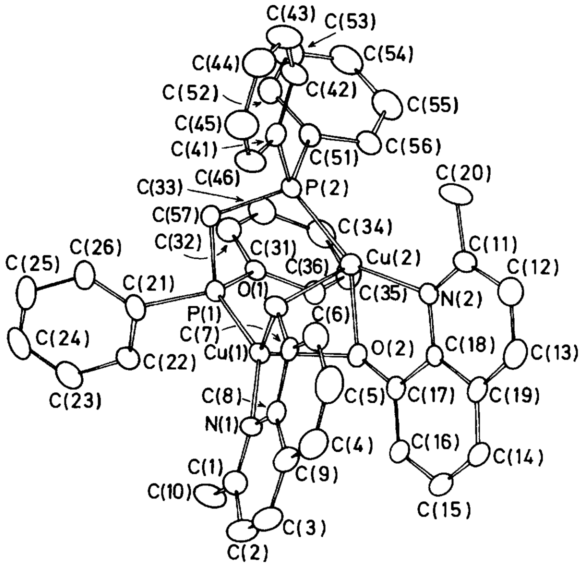
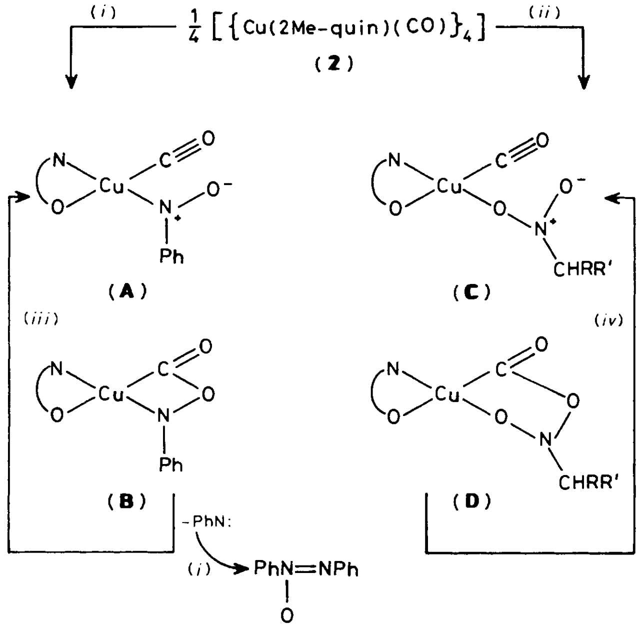


Figure 3. A view of the complex $[Cu_2(2Me\text{-}quin)_2(\mu\text{-}dppm)]$, (7)

Table 7. Selected interatomic distances (Å) and angles (°) for $[Cu_2(2Me\text{-}quin)_2(\mu\text{-}dppm)]$, (7)

Cu(1)–O(1)	2.153(4)	Cu(2)–O(1)	2.336(6)
Cu(1)–O(2)	2.141(4)	Cu(2)–O(2)	2.144(5)
Cu(1)–N(1)	2.010(7)	Cu(2)–N(2)	2.018(5)
Cu(1)–P(1)	2.147(3)	Cu(2)–P(2)	2.168(3)
P(1)–C(21)	1.825(4)	P(2)–C(41)	1.840(4)
P(1)–C(31)	1.826(5)	P(2)–C(51)	1.823(7)
P(1)–C(57)	1.827(7)	P(2)–C(57)	1.862(6)
Cu(1)···Cu(2)	2.790(2)		
O(1)–Cu(1)–N(1)	81.6(2)	O(2)–Cu(2)–N(2)	80.6(2)
O(1)–Cu(1)–O(2)	89.7(2)	O(1)–Cu(2)–O(2)	85.0(2)
O(1)–Cu(1)–P(1)	109.0(2)	O(2)–Cu(2)–P(2)	130.8(2)
O(2)–Cu(1)–N(1)	99.6(2)	O(1)–Cu(2)–N(2)	97.3(2)
O(2)–Cu(1)–P(1)	109.9(2)	O(1)–Cu(2)–P(2)	91.7(1)
N(1)–Cu(1)–P(1)	148.4(2)	N(2)–Cu(2)–P(2)	148.2(2)
Cu(1)–P(1)–C(57)	106.7(2)	Cu(2)–P(2)–C(57)	111.2(3)
Cu(1)–P(1)–C(31)	119.1(2)	Cu(2)–P(2)–C(51)	120.7(2)
Cu(1)–P(1)–C(21)	118.5(2)	Cu(2)–P(2)–C(41)	112.8(2)
C(31)–P(1)–C(57)	102.2(3)	C(51)–P(2)–C(57)	104.0(3)
C(21)–P(1)–C(57)	105.7(3)	C(41)–P(2)–C(57)	102.5(3)
C(21)–P(1)–C(31)	102.8(2)	C(41)–P(2)–C(51)	103.7(3)
P(1)–C(57)–P(2)	110.0(3)		

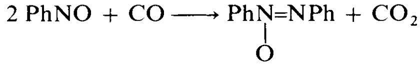


Scheme. R = R′ = Me; R = Me, R′ = H; R = Et, R′ = H; R = Pr^n, R′ = H. (*i*) PhNO; (*ii*) $RR'CHNO_2$; (*iii*) $-CO_2$; PhNO, CO; (*iv*) $-RR'C{=}NOH$, $-CO_2$; CO, $RR'CHNO_2$

co-ordination by using one of the P donor atoms from the dppm ligand. The co-ordination around each metal can be described as an approximate trigonal pyramid, though the N(1)–Cu(1)–P(1) [148.4(2)°], N(2)–Cu(2)–P(2) [148.2(2)°], O(1)–Cu(1)–N(1) [81.6(2)°], and O(2)–Cu(2)–N(2) [80.6(2)°] angles deviate significantly from the expected values. The trigonal planes are defined by N(1), P(1), O(2) for Cu(1), which is 0.162(2) Å out of their plane, and by N(2), P(2), O(2) for Cu(2), which is out of this plane by 0.075(2) Å. The Cu–O bond distances [Cu(1)–O(1) 2.153(4); Cu(1)–O(2) 2.141(4), and Cu(2)–O(2) 2.144(5) Å] are in the normal range for four-co-ordinate copper and phenoxo groups,[24] and compare well with that in complex (**5**) [2.088(14) Å], while they are significantly longer than those in complex (**2**) (mean 2.04 Å). The anomalous value for Cu(2)–O(1), 2.336(6) Å, is connected with the steric crowding around this bond. The Cu–P bond lengths are in the range found for phosphine(phenoxo)copper(I) complexes.[24] In the $Cu_2(2Me\text{-}quin)_2$ fragment the Cu···Cu distance [2.790(2) Å] is similar to that found in several dicopper complexes suggested as structural models for binding small molecules or organic functionalities.[25]

Reduction of Nitro- and Nitroso-compounds catalysed by Complex (**2**).—The thermal and air-stability of complex (**2**), together with its lability in the presence of organic functionalities, suggested it would be a potentially useful complex in copper(I)–carbon monoxide-promoted transformations of organic substrates, demonstrating the synthetic utility of the release of the reactive fourteen-electron species from complex (**2**).

Reactions (7)—(10) of (**2**) with nitro- and nitroso-derivatives

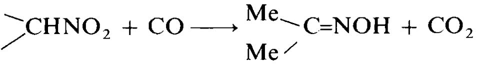


$$2\,PhNO + CO \longrightarrow \underset{\displaystyle O}{PhN}{=}NPh + CO_2 \qquad (7)$$

$$PhNO_2 + CO \longrightarrow \text{no reaction}$$

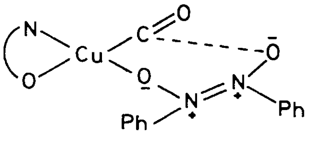
$$C_5H_5NO + CO \longrightarrow C_5H_5N + CO_2 \qquad (8)$$

$$RCH_2NO_2 + CO \xrightarrow[-H_2O]{} RC{\equiv}N + CO_2 \qquad (9)$$



$$\begin{matrix}Me\\Me\end{matrix}\!\!>CHNO_2 + CO \longrightarrow \begin{matrix}Me\\Me\end{matrix}\!\!>C{=}NOH + CO_2 \qquad (10)$$

have been carried out in a few exploratory cases under carbon monoxide pressure (6—100 atm) at relatively high temperature (80—110 °C) (see Experimental section). All these reactions are poorly catalytic, though an extended investigation on the catalytic potential of complex (**2**) was not carried out. The results described above may be rationalized on the basis of the Scheme for nitroso- and nitro-derivatives, where the initial reaction is the cleavage of the tetrameric structure by either the nitro- or nitroso-derivative which binds to the copper(I), followed by nucleophilic attack of the basic oxygen from the nitro- or nitroso-derivative on the electrophilic carbon monoxide.



(**E**)

Our results merit some additional comments in order to be understood on the basis of the Scheme. The almost selective formation of azoxybenzene in reaction (7) suggests that in the Scheme the co-ordination to copper(I) may also occur with the dimer of nitrosobenzene,[26] as depicted in (**E**). This may be further supported by the observation that we were never able to detect phenyl isocyanate in such a reaction. The lack of reactivity of $PhNO_2$ contrary to aliphatic nitro-derivatives may be due to the significant difference in oxygen basicity between the two species, so that $PhNO_2$ is not able to bind to copper(I) in the preliminary stage (**C**). Reduction of primary and secondary nitroalkanes leads to different results. Secondary derivatives produce exclusively oximes, while primary form nitriles, amides, and acids. There is, probably, no substantial difference between the two reactions. In case of secondary nitroalkanes the reduction product is of the nitroso (RR′CH–NO), in the stable tautomeric oxime form (RR′C=NOH). When the same reaction is carried out with primary nitroalkanes, the resulting oxime, undergoes, however, under the reaction conditions, dehydration to a nitrile. Partial or complete hydration of the nitrile is responsible for the presence of variable amounts of amide and carboxylic acid. The copper(I)-catalysed reduction of nitroalkanes to oximes was reported using substantially different copper(I) systems prepared *in situ* and very different reaction conditions.[27] The reaction conditions used in the latter case prevent the dehydration, occurring in our reaction, of primary oximes to nitriles.

Acknowledgements

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