Synthesis, Structure, and Dynamic Behaviour of (*p*-Quinone)copper(I) Complexes. Crystal Structure Determination of a Copper *p*-Benzoquinone Complex stabilized by a Tridentate Oxygen Ligand†

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The quinonecopper(I) complexes [Cu(olefin)L] [olefin = *p*-benzoquinone (bq), methyl-*p*-benzoquinone, or 1,4-naphthoquinone] of the tridentate oxygen ligand $L^- = [(C_5H_5)Co\{P(O)(OCH_3)_2\}_3]^-$ have been prepared by the reaction of NaL and the appropriate quinone with $[Cu(CH_3CN)_4]PF_6$ and by carbon monoxide substitution from [Cu(CO)L]. The complex [Cu(bq)L] crystallizes in space group $P\bar{1}$ ($Z = 2$) with $a = 11.358(6)$, $b = 12.138(7)$, $c = 12.465(6)$ Å, $\alpha = 92.18(2)$, $\beta = 134.24(2)$, $\gamma = 99.49(4)$°, and its *X*-ray crystal structure was refined to $R = 0.056$ for 4 140 reflections [$|F_o| > 2.5\sigma(F_o)$]. The co-ordination about the copper atom is distorted tetrahedral with one long [2.184(2) Å] and two short [1.966(2), 2.001(2) Å] copper–oxygen contacts. *p*-Benzoquinone co-ordinates through one olefinic double bond to the copper atom. The complex dismutates in solution according to the equilibrium 2 [Cu(bq)L] $\rightleftharpoons$ [LCu(μ-bq)CuL] + bq. In addition, it exhibits several other dynamic processes, the lowest-energy of which is olefin rotation. The intramolecular exchange of the free and the co-ordinated double bond gives rise to a coalescence temperature of about 305 K in the ^{1}H n.m.r. spectrum, corresponding to an activation barrier of *ca.* 60 kJ mol^{-1}. Intermolecular exchange of co-ordinated and non-co-ordinated bq becomes rapid on the n.m.r. time-scale above *ca.* 370 K.

Solutions of simple copper(I) salts readily absorb carbon monoxide and olefins. This is a unique feature of copper(I) chemistry but it is frequently difficult to isolate stable crystalline solids. The first isolation of a solid copper(I) carbonyl, namely $[Cu(CF_3CO_2)(CO)]$, was described in 1969.[1] The first copper carbonyl derivative characterized by a crystal structure determination was reported by Bruce and Ostazewski[2,3] in 1972. Now the structures of a considerable number of copper carbonyls are known.[4] Copper complexes with olefins and carbonyls occur in a variety of structures and stoicheiometries. An overview of the known structural types is given by Hathaway[5] in a recent account of copper co-ordination chemistry. It is an intriguing fact that although copper(I) behaves as a class b acceptor (a soft acid), it forms stable olefin and carbonyl derivatives almost exclusively with hard ligands and then preferentially with aliphatic nitrogen ligands.[6]

We have recently introduced a class of tris-chelating oxygen ligands of the general composition $[(C_5R'_5)M\{P(O)R_2\}_3]^-$. They are monoanionic, facially co-ordinating, six-electron ligands formally resembling the cyclopentadienyl and the tris(pyrazolyl)borate ligands but having electronic properties like oxide or fluoride ions.[7] We have observed that the ligand $[(C_5H_5)Co\{P(O)(OCH_3)_2\}_3]^-$, abbreviated in this paper as L$^-$ or tripod, is able to stabilize carbonyl- and ethylene-copper(I) fragments.[8] The ethylene in $[Cu(C_2H_4)L]$ is very labile towards substitution and at room temperature its exchange with non-co-ordinated ethylene is rapid on the n.m.r. time-scale. We have not established the reaction mechanism although there are some indications that it is associative. Very little is known about the reaction mechanism and the kinetics of ligand exchange in copper(I) compounds. This made us curious to see whether the possible co-ordination numbers of copper(I) complexes carrying an oxygen tripod ligand could be determined by synthesizing compounds of the type [Cu(olefin)L] with potentially bidentate olefins like *p*-benzoquinone. In this report we describe the synthesis and the dynamics of *p*-quinonecopper(I) complexes in solution and the solid-state structure of [Cu(bq)L] (bq = *p*-benzoquinone).

Results

Synthesis, Crystal Structure, and N.M.R. Spectra of [Cu(bq)L].—The complex [Cu(bq)L] was prepared from NaL, the sodium salt of the tripod ligand, *p*-benzoquinone (bq), and $[Cu(CH_3CN)_4]PF_6$ in dichloromethane [see equation (1)]. It

$$NaL + [Cu(CH_3CN)_4]PF_6 + bq \longrightarrow [Cu(bq)L] + 4\,CH_3CN + NaPF_6 \quad (1)$$

was purified by recrystallization from diethyl ether to give dark crimson rhombic crystals stable in dry air but sensitive to moisture. In the solid state decomposition occurs above *ca.* 120 °C. The schematic structure of [Cu(bq)L] is shown in Figure 1(*a*).

Single crystals of [Cu(bq)L] suitable for an *X*-ray crystal-structure determination were grown from diethyl ether at −20 °C. The molecular structure together with the numbering scheme is displayed in Figure 2. Important distances and angles are presented in Table 1 and the positional parameters in Table 2. In this complex the ligand L$^-$ acts as a chelating oxygen ligand. There are one long [2.184(2) Å] and two short [1.966(2), 2.001(2) Å] copper–oxygen contacts. The *p*-benzoquinone ligand co-ordinates through one double bond to copper. The idealized molecular point symmetry is C_s. The 2 + 1 distorted

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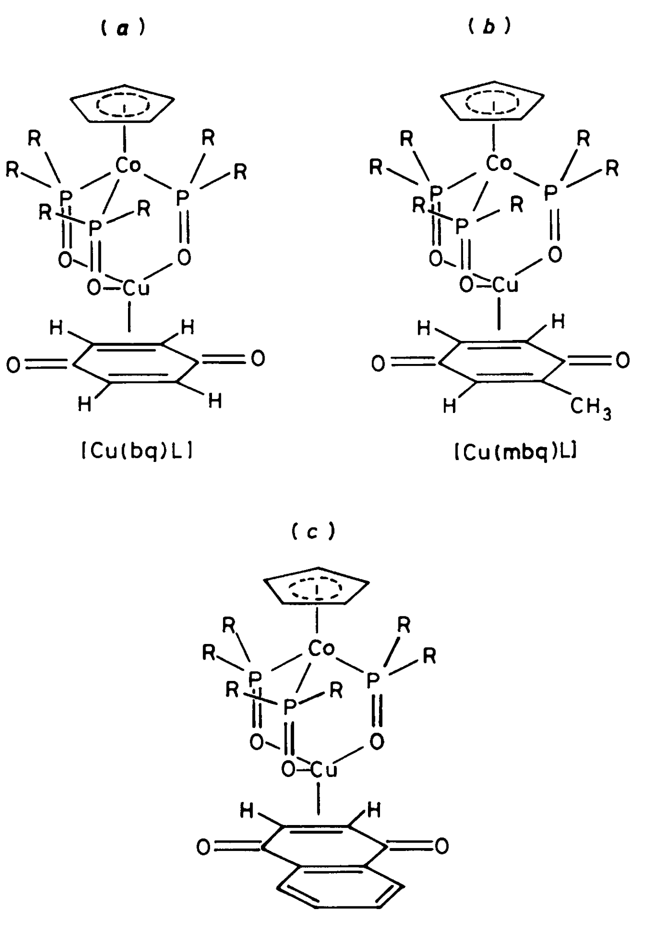
† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.



[Cu(bq)L]

[Cu(mbq)L]

[Cu(nq)L]

Figure 1. Schematic structures of the complexes; R = OCH_3

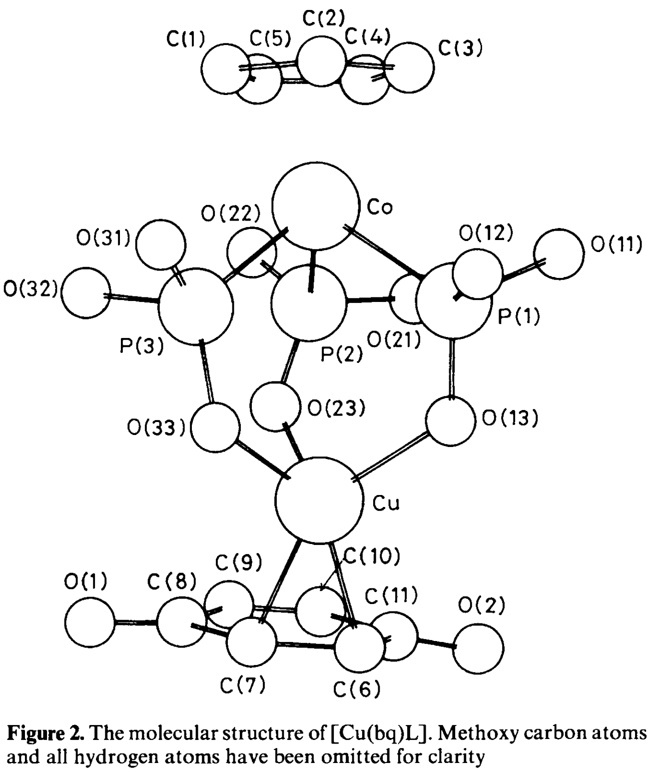


Figure 2. The molecular structure of [Cu(bq)L]. Methoxy carbon atoms and all hydrogen atoms have been omitted for clarity

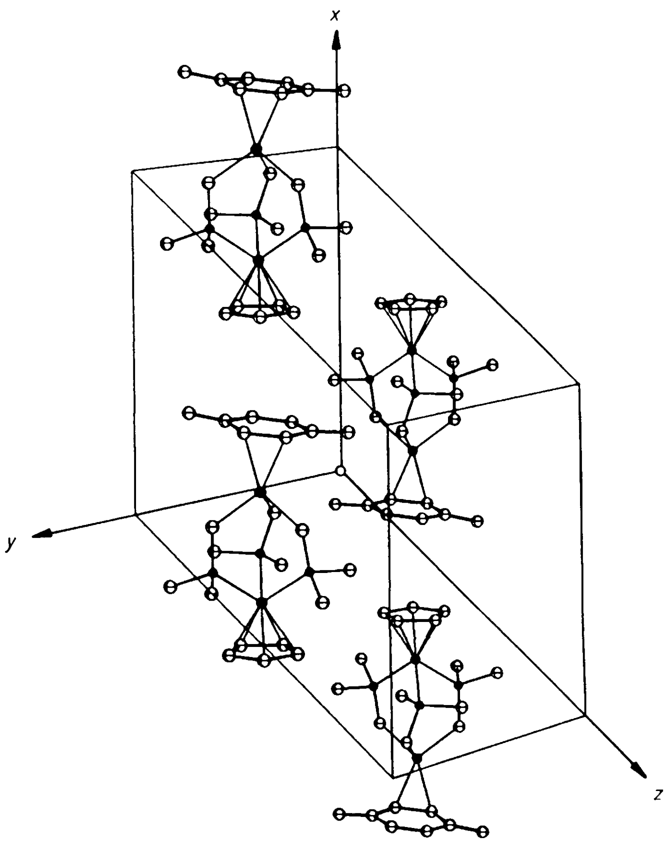


Figure 3. Packing of [Cu(bq)L] molecules. Methoxy carbon atoms and all hydrogen atoms have been omitted for clarity

co-ordination of the tripod ligand is reflected in the P=O distances. The P(2)=O(23) bond length of the weakly co-ordinating phosphonate group is slightly shorter than the other two P=O bond lengths [1.503(1) compared to 1.520(1) and 1.513(1) Å]. Correspondingly the angle Cu–O–P is smaller at the weakly bonded oxygen O(23) than at O(13) and O(33) [117.8(1) *vs.* 124.0(1) and 121.8(2)°]. The deviation of the copper co-ordination from a regular tetrahedral arrangement is marked; the angles O–Cu–O [91.31(8), 95.91(8), and 97.54(7)°] are significantly smaller than the tetrahedral angle of 109.5°.

The bite of the tripod ligand, *i.e.*, the non-bonding O···O distances between the P=O oxygen atoms, varies from 2.98 to 3.09 Å and is in the expected range.[8,9] The centre of the cyclopentadienyl ring, the cobalt, and the copper atom form a nearly linear arrangement, the angle being 177.4°.

Copper and the co-ordinated C=C double bond of the quinone ligand form essentially an isosceles triangle with Cu–C distances of 1.998(2) and 2.031(1) Å. The C(6)=C(7) bond is elongated to 1.375(5) Å whereas the non co-ordinated double bond remains mainly unchanged [1.318(6) Å] compared to that in free *p*-benzoquinone.[10] The angle Co–Cu–(C=C bond centre) is 169.5°.

The co-ordinated quinone molecule adopts a flattened boat conformation. Relative to the plane of the olefinic carbon atoms [C(6)–C(7)–C(9)–C(10)] the two planes containing each a carbonyl group and the two adjacent carbon atoms [C(9)–C(7)–C(8)–O(1)] and [C(10)–C(6)–C(11)–O(2)] are tilted away from the copper atom by only 3.8 and 2.7°, respectively. All other angles and distances of the co-ordinated quinone ligand correspond to those observed in free *p*-benzoquinone.

Table 1. Selected bond angles (°) and distances (Å) in [Cu(bq)L] with estimated standard deviations (e.s.d.s) in parentheses

Co–P(1)	2.147(1)	C(5)–H(5)	0.93(3)	O(32)–C(321)	1.435(3)	Cu–C(7)	1.998(2)
Co–P(2)	2.185(1)	P(1)–O(11)	1.602(2)	C(321)–H(321)	0.99(4)	Cu–O(13)	1.966(2)
Co–P(3)	2.177(1)	O(11)–C(111)	1.439(4)	C(321)–H(332)	0.93(5)	Cu–O(23)	2.184(2)
Co–C(1)	2.077(2)	C(111)–H(111)	0.93(4)	C(321)–H(333)	0.94(3)	Cu–O(33)	2.001(2)
Co–C(2)	2.081(2)	C(111)–H(112)	0.88(2)	P(3)–O(33)	1.513(1)	Cu–$\mathrm{M_{C=C}}$[b]	1.892
Co–C(3)	2.085(2)	C(111)–H(113)	0.92(5)	P(2)–O(21)	1.617(3)	C(6)–C(7)	1.375(5)
Co–C(4)	2.068(3)	P(1)–O(12)	1.607(2)	O(21)–C(211)	1.432(3)	C(6)–H(6)	0.93(3)
Co–C(5)	2.079(3)	O(12)–C(121)	1.441(3)	C(211)–H(211)	0.89(4)	C(7)–C(8)	1.480(4)
Co–$\mathrm{L_{Cp}}$[a]	1.697	C(121)–H(121)	0.95(2)	C(211)–H(212)	1.05(4)	C(7)–H(7)	0.92(3)
C(1)–C(2)	1.408(5)	C(121)–H(122)	0.96(4)	C(211)–H(213)	0.99(3)	C(8)–O(1)	1.213(4)
C(1)–H(1)	0.88(4)	C(121)–H(123)	1.03(5)	P(2)–O(22)	1.610(2)	C(8)–C(9)	1.475(5)
C(2)–C(3)	1.400(6)	P(1)–O(13)	1.520(1)	O(22)–C(221)	1.436(5)	C(9)–C(10)	1.318(6)
C(2)–H(2)	0.83(3)	P(3)–O(31)	1.601(2)	C(221)–H(221)	0.99(4)	C(9)–H(8)	0.89(3)
C(3)–C(4)	1.382(6)	O(31)–C(311)	1.440(5)	C(221)–H(222)	0.88(4)	C(10)–C(11)	1.474(4)
C(3)–H(3)	0.90(3)	C(311)–H(311)	1.02(3)	C(221)–H(223)	1.01(2)	C(10)–H(10)	0.92(3)
C(4)–C(5)	1.404(7)	C(311)–H(312)	0.99(3)	P(2)–O(23)	1.503(1)	C(11)–O(2)	1.223(4)
C(4)–H(4)	0.85(4)	C(311)–H(313)	0.86(4)	Cu–C(6)	2.031(1)	C(11)–C(6)	1.474(5)
C(5)–C(1)	1.387(6)	P(3)–O(32)	1.614(2)				

P(1)–Co–P(2)	88.61(2)	Co–P(2)–O(23)	118.29(9)	O(13)–Cu–O(23)	95.91(8)	C(7)–C(8)–C(9)	116.4(3)
P(1)–Co–P(3)	92.81(3)	Co–P(3)–O(33)	121.24(11)	O(13)–Cu–O(33)	97.54(7)	C(7)–C(8)–O(1)	122.1(3)
P(2)–Co–P(3)	92.00(3)	C(6)–Cu–C(7)	39.9(1)	O(23)–Cu–O(33)	91.31(8)	O(1)–C(8)–C(9)	121.6(3)
C(2)–C(1)–C(5)	108.9(4)	C(7)–C(6)–Cu	68.8(1)	Cu–O(13)–P(1)	124.0(1)	C(8)–C(9)–C(10)	122.6(3)
C(1)–C(2)–C(3)	106.6(3)	C(6)–C(7)–Cu	71.3(1)	Cu–O(23)–P(2)	117.8(1)	C(9)–C(10)–C(11)	121.8(3)
C(2)–C(3)–C(4)	108.9(4)	O(13)–Cu–$\mathrm{M_{C=C}}$	128.9	Cu–O(33)–P(3)	121.8(2)	C(10)–C(11)–C(6)	117.3(4)
C(3)–C(4)–C(5)	108.1(4)	O(23)–Cu–$\mathrm{M_{C=C}}$	112.4	C(11)–C(6)–C(7)	120.5(3)	C(10)–C(11)–O(2)	121.0(3)
C(4)–C(5)–C(1)	107.5(3)	O(33)–Cu–$\mathrm{M_{C=C}}$	122.1	C(6)–C(7)–C(8)	121.2(3)	O(2)–C(11)–C(6)	121.7(3)
Co–P(1)–O(13)	120.33(8)						

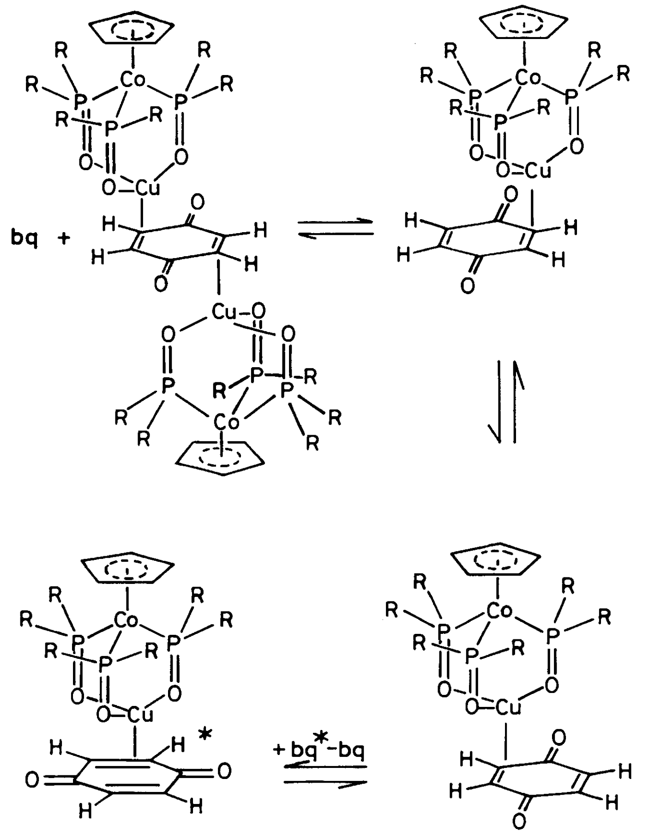
[a] $\mathrm{L_{Cp}}$ means the point where the normal from the cobalt atom onto the plane of the cyclopentadienyl ring intersects this plane. [b] $\mathrm{M_{C=C}}$ is the midpoint of the co-ordinating double bond of the quinone.

Table 2. Fractional atomic co-ordinates for [Cu(bq)L]

Atom	*X/a*	*Y/b*	*Z/c*	Atom	*X/a*	*Y/b*	*Z/c*
Cu	0.312 96(5)	0.837 67(3)	0.361 14(5)	O(22)	0.903 9(3)	0.504 4(2)	0.161 5(3)
Co	0.924 09(5)	0.746 75(4)	0.287 69(5)	C(221)	0.003 1(8)	0.441 1(4)	0.278 3(6)
C(1)	0.838 9(5)	0.699 6(4)	0.3865	H(221)	−0.058(6)	0.359(4)	0.230(5)
H(1)	0.912(5)	0.695(3)	0.483(5)	H(222)	0.013(7)	0.478(4)	0.347(6)
C(2)	0.801 5(5)	0.802 8(4)	0.339 0(5)	H(223)	0.119(6)	0.446(4)	0.321(6)
H(2)	0.846(5)	0.866(3)	0.397(5)	O(23)	0.158 7(3)	0.660 4(2)	0.266 6(3)
C(3)	0.691 9(5)	0.778 9(4)	0.179 9(5)	P(3)	0.187 17(11)	0.789 64(8)	0.512 09(10)
H(3)	0.656(5)	0.836(3)	0.130(5)	O(31)	0.196 2(3)	0.865 6(2)	0.626 6(3)
C(4)	0.666 6(5)	0.665 4(5)	0.131 4(5)	C(311)	0.353 3(6)	0.903 1(5)	0.787 0(5)
H(4)	0.619(5)	0.629(3)	0.045(5)	H(311)	0.320(6)	0.946(4)	0.831(5)
C(5)	0.756 5(6)	0.615 2(4)	0.259 6(6)	H(312)	0.443(6)	0.953(4)	0.801(5)
H(5)	0.763(5)	0.544(3)	0.258(5)	H(313)	0.366(7)	0.840(4)	0.817(6)
P(1)	0.974 94(11)	0.888 88(7)	0.212 88(10)	O(32)	0.226 8(3)	0.675 5(2)	0.580 3(3)
O(11)	0.804 2(3)	0.886 3(2)	0.039 1(2)	C(321)	0.379 3(6)	0.643 3(4)	0.649 8(6)
C(111)	0.796 4(6)	0.903 5(4)	0.920 9(5)	H(321)	0.373(6)	0.562 (4)	0.658(5)
H(111)	0.808(6)	0.982(4)	0.927(5)	H(322)	0.454(6)	0.684(4)	0.750(6)
H(112)	0.858(6)	0.868(4)	0.921(6)	H(323)	0.404(7)	0.646(4)	0.592(6)
H(113)	0.689(6)	0.863(4)	0.830(6)	O(33)	0.332 9(3)	0.848 6(2)	0.534 1(2)
O(12)	0.001 2(3)	0.003 1(2)	0.304 5(3)	C(6)	0.464 2(4)	0.871 1(3)	0.326 4(4)
C(121)	0.005 0(6)	0.109 6(3)	0.258 3(5)	H(6)	0.483(4)	0.949(3)	0.328(4)
H(121)	0.066(6)	0.122(4)	0.232(6)	C(7)	0.544 8(4)	0.832 7(3)	0.459 6(4)
H(122)	0.033(6)	0.171(4)	0.329(5)	H(7)	0.616(4)	0.883(3)	0.553(4)
H(123)	−0.117(6)	0.109(4)	0.159(6)	C(8)	0.552 1(4)	0.712 2(3)	0.465 2(4)
O(13)	0.119 9(3)	0.905 2(2)	0.225 2(2)	O(1)	0.631 9(4)	0.678 6(3)	0.583 8(3)
P(2)	0.977 84(12)	0.638 97(7)	0.189 31(10)	C(9)	0.461 2(5)	0.635 5(3)	0.319 2(5)
O(21)	0.850 9(3)	0.646 5(2)	0.011 0(3)	H(9)	0.462(4)	0.562(3)	0.319(4)
C(211)	0.895 5(6)	0.625 6(4)	0.930 8(5)	C(10)	0.386 2(5)	0.672 2(3)	0.191 8(5)
H(211)	0.819(6)	0.644(4)	0.840(5)	H(10)	0.333(4)	0.627(3)	0.100(4)
H(212)	0.873(6)	0.537(4)	0.904(5)	C(11)	0.385 5(4)	0.793 2(3)	0.185 8(4)
H(213)	0.006(6)	0.672(4)	0.975(5)	O(2)	0.326 5(4)	0.827 7(3)	0.070 0(3)

The dihedral angle between the plane defined by the copper atom and the co-ordinated C=C bond and the plane of the four olefinic carbon atoms is 97.5°.

The molecular packing of [Cu(bq)L] is illustrated in Figure 3. The unit cell contains two molecules which are identical with respect to distances and angles and related to each other by the centre of symmetry (space group $P\bar{1}$). The molecules are stacked approximately parallel to the [100] direction and such rows of



Scheme. Intra- and inter-molecular ligand-exchange processes occurring in toluene solutions of [Cu(bq)L]; R = OCH_3

molecules are packed in the fashion of the hexagonal packing of a bundle of broomsticks.

The proton n.m.r. spectrum of [Cu(bq)L] in toluene is not in accord with the solid-state structure described above. At room temperature there are two sets of tripod signals and three benzoquinone signals. The tripod signals occur in the ratio 2:3 and of the benzoquinone signals one is very broad and the other two are sharp. Upon cooling to 250 K the broad benzoquinone signal splits into two signals whereas the tripod signals remain sharp and their ratio is unchanged. At temperatures above 345 K all signals are broad and at 370 K only one set of tripod signals and one benzoquinone signal is observed. This complex solution behaviour can be explained by a combination of fluxional processes: an intramolecular exchange of the co-ordinated and the non-co-ordinated double bond in [Cu(bq)L] together with a dismutation reaction (2) and then intermolecular exchange of free and co-ordinated benzoquinone. The three

$$2\,[\mathrm{Cu(bq)L}] \rightleftharpoons [\mathrm{LCu}(\mu\text{-bq})\mathrm{CuL}] + \mathrm{bq} \qquad (2)$$

processes are summarized in the Scheme.

The proton n.m.r. data of the individual species involved are given in the Experimental section. We have performed further independent experiments to substantiate the mechanism of this dynamic behaviour. They are described in the Discussion.

[Cu(mbq)L] *and* [Cu(nq)L].—The complexes [Cu(mbq)L] (mbq = methyl-*p*-benzoquinone) and [Cu(nq)L] (nq = 1,4-naphthoquinone) were prepared from NaL, $[Cu(CH_3CN)_4]PF_6$, and methyl-*p*-benzoquinone and 1,4-naphthoquinone in dichloromethane in the same way as for [Cu(bq)L]. The complex [Cu(mbq)L] [see Figure 1(*b*)] is very substitution labile and the isolated product always contained a small amount of methylbenzoquinone. In chloroform solutions at room temperature it disproportionates completely within 1 h to give $[CuL_2]$, metallic copper, and free methylbenzoquinone. The naphthoquinone complex [Figure 1(*c*)] on the other hand could be isolated as air-stable red crystals. The proton n.m.r. spectrum of [Cu(mbq)L] * shows that the unsubstituted double bond is co-ordinated to copper. In the spectrum of the naphthoquinone complex there is, compared to the free ligand, a 1.8 p.p.m. upfield shift of the olefinic proton signals, from which we conclude that here too the unsubstituted double bond is the donor site. We note that both the methylbenzoquinone and the naphthoquinone copper complex do not dismutate as the *p*-benzoquinone complex does.

Discussion

Solid State Molecular Structure of [Cu(bq)L].—A prominent feature of the structure of [Cu(bq)L] is the 2 + 1 distorted tripod ligand co-ordination (Figure 2). The Cu–O bond of the weakly co-ordinating P=O unit is about 0.20 Å longer than the other two Cu–O bonds. So far, in most structures known containing the tripod ligand it exhibits nearly perfect C_{3v} symmetry. For example, the copper–oxygen bond lengths in [Cu(CO)L] are 2.033(3), 2.060(3), and 2.026(3) Å.[8] Even in $[CuL'_2]$ ($L'^- = [(C_5H_5)Co\{P(O)(OCH_2CH_3)_2\}_3]^-$) there is only a small 4 + 2 Jahn–Teller distortion of the CuO_6 octahedron; Cu–O distances are 2.04, 2.05, and 2.14 Å.[11] The irregular co-ordination of the tripod ligand in [Cu(bq)L] is therefore surprising. However, the 2 + 1 co-ordination of the tripod ligand fits in with the trend observed in the structures of other copper(I) compounds. In its carbonyl complexes copper clearly prefers a co-ordination number of four (in rare cases five),[12] whereas there seems to be a tendency for a co-ordination number of three in copper–olefin complexes. For instance the copper centre in $[Cu(CO)\{HB(pz)_3\}]$ (pz = pyrazolyl)] is four-co-ordinate and the molecule has approximate C_{3v} symmetry,[2] whilst in the related olefin compounds $[Cu(C_2H_4)\{HB(pz)_3\}\cdot CuCl]$[13] and $[Cu(C_6H_{10})\{HB(pz)_3\}\cdot CuCl]$[14] the geometry about the olefin-bearing copper ions is trigonal planar.

It is interesting that the oxygen tripod ligand L^- seems more strongly co-ordinated to the copper-*p*-benzoquinone fragment than to the copper–carbon monoxide fragment.[8] This is evident from the slightly shorter copper–oxygen contacts as well as from the longer P=O distances. We have observed earlier that increasing co-ordinative interaction of the tripod ligand correlates with increasing P=O bond lengths (and decreasing P=O stretching frequencies).[15]

The compound [Cu(bq)L] is the first molecular copper complex of unsubstituted *p*-benzoquinone whose crystal structure has been reported. The only other *p*-benzoquinone metal complexes with known crystal structures are the polymeric compound $[NH_4][Cu_3Cl_4(bq)_{1.5}]$[16] and the platinum complex $[Pt(bq)(PPh_3)_2]$.[17] The geometry of the *p*-benzoquinone ligand in [Cu(bq)L] is only slightly altered upon co-ordination. There is a weak deformation of the *p*-benzoquinone ligand toward a boat conformation, similar to that in $[NH_4][Cu_3Cl_4(bq)_{1.5}]$. This deformation, as measured by the dihedral angles between the plane defined by the olefinic carbon atoms and the planes containing the keto groups, is much more pronounced in $[Pt(bq)(PPh_3)_2]$ (16 and 11°). The length of the co-ordinated C=C bond in [Cu(bq)L] is also similar to that in $[NH_4][Cu_3Cl_4(bq)_{1.5}]$ (1.366 and 1.351 Å), whereas the co-ordinated C=C bond in $[Pt(bq)(PPh_3)_2]$ (1.49 Å) is much longer.

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* δ_H (80 MHz, $CDCl_3$) 2.0 [3 H, d, ^4J(HCCCH) = 1.5, HC=CCH_3], 3.6 [18 H, virt. q, ^3J (HCOP) = 11.0, OCH_3], 5.0 [5 H, q, ^3J (HCCoP) = 0.6 Hz, C_5H_5], 5.1 (2 H, s, HC=CH), and 6.4 (1 H, br s, *H*C=CCH_3).

Solution Behaviour of [Cu(bq)L], [Cu(mbq)L], *and* [Cu(nq)-L].—The i.r. spectrum of *p*-benzoquinone dissolved in dichloromethane does not change upon addition of an equimolar amount of the copper(I)-acetonitrile complex. Obviously no complexes of the type $[Cu(bq)(CH_3CN)_n]^+$ are formed to a significant degree under these conditions. In contrast to this carbon monoxide forms a carbonyl complex with $[Cu(CH_3CN)_4]PF_6$ in dichloromethane.[8] A stable copper–benzoquinone complex is obtained only after addition of the sodium salt of the oxygen tripod ligand. This is in accord with our observation that copper–olefin bonds become more stable through the presence of additional hard ligands and especially so by ligands with π-donor properties like L^- or Cl^-.

The dismutation (2) yields [LCu(μ-bq)CuL] and [Cu(bq)L] in a molar ratio of *ca.* 1:3, which is nearly constant in the temperature range 250–340 K. To study this equilibrium reaction in more detail we prepared [LCu(μ-bq)CuL] by an independent route [equations (3) and (4)], namely by substitution of carbon monoxide from [Cu(CO)L]. An isolable intermediate of the reaction is [Cu(bq)L]. When we added an equimolar amount of *p*-benzoquinone to [LCu(μ-bq)CuL] in dichloromethane a mixture of [LCu(μ-bq)CuL], [Cu(bq)L], and bq was obtained. The equilibrium position reached is the same as from pure [Cu(bq)L] [see equation (2)].

$$[\mathrm{Cu(CO)L}] + \mathrm{bq} \xrightleftharpoons{-\mathrm{CO}} [\mathrm{Cu(bq)L}] \qquad (3)$$

$$[\mathrm{Cu(bq)L}] \xrightleftharpoons{+[\mathrm{Cu(CO)L}]\,-\,\mathrm{CO}} [\mathrm{LCu(\mu\text{-}bq)CuL}] \qquad (4)$$

We did not determine the equilibration kinetics but noticed that the exchange of co-ordinated and non-co-ordinated *p*-benzoquinone becomes rapid on the n.m.r. time-scale upon heating. The coalescence temperature for this intermolecular exchange was 370 K. The equilibrium system summarized in equations (3) and (4) formally resembles (5), a reaction that has been described by Minematsu *et al.*[18]

$$[\mathrm{Pd(PBu_3)}_n] + \mathrm{bq} \rightleftharpoons [\mathrm{Pd(bq)(PBu_3)_2}] \rightleftharpoons [\mathrm{(Bu_3P)_2Pd(\mu\text{-}bq)Pd(PBu_3)_2}] \qquad (5)$$

The naphthoquinone ligand has no tendency to act as a bridging ligand and therefore the only intermolecular process occurring is the exchange of co-ordinated and non-co-ordinated naphthoquinone. The coalescence temperature measured in a toluene solution containing [Cu(nq)L] and naphthoquinone in the ratio 2:3 was 385 K.

The rotation of the olefin ligand relative to the oxygen tripod ligand is the most rapid process. It makes the six OCH_3 groups appear isochronous over the whole temperature range as if the molecules [Cu(bq)L], [LCu(μ-bq)CuL], [Cu(mbq)L], and [Cu(nq)L] had C_{3v} symmetry. Mingos[19] has recently pointed out that extended Hückel molecular-orbital (EHMO) calculations predict indeed very low olefin rotational barriers in d^{10} complexes of the type [M(olefin)(two-electron ligand)$_3$].

The intramolecular exchange of the free and the co-ordinated double bond in [Cu(bq)L] (see the second equilibrium depicted in the Scheme) leads to a very broad room-temperature n.m.r. signal of the olefinic protons. Below 275 K two separate signals at δ 4.9 and 6.2 can be discerned for the co-ordinated and the free double bond, respectively with the coalescence temperature, $T_C \approx 305$ K. Using equation (6)[20] one can estimate the activation enthalpy for this process to be $\Delta G^\ddagger \approx 60$ kJ mol^{-1} where δν is the difference in resonance frequencies of the two signals in the low-temperature limit.

$$\Delta G^\ddagger = 19.13\, T_C[9.97 + \log(T_C/\delta\nu)]\ \mathrm{J\ mol^{-1}} \qquad (6)$$

It is interesting that the olefinic protons in the analogous methylbenzoquinone complex [Cu(mbq)L] do not give rise to an exchange-broadened signal. At first sight it looks as if [Cu(mbq)L] were a rigid molecule. The reason for this is that although the exchange process very probably has a similar activation energy one simply cannot observe it when the two interconverting species are too different in energy (> 10 kJ mol^{-1}). In the whole accessible temperature range only the isomer with the unsubstituted double bond co-ordinated to copper is populated to a measurable extent. The preference for the unsubstituted double bond is in accord with our earlier findings[8] about the relative stabilities of tripod copper–olefin complexes.

Conclusion

The unexpected distorted structure of the *p*-benzoquinone copper complex described in this paper clearly shows that the tridentate oxygen ligand L^- can easily adjust its co-ordination mode to the electronic requirements of the copper–olefin fragment. This flexibility should allow an energetically favourable exchange of carbon monoxide and olefin ligands by an associative mechanism without evoking a 20-electron intermediate. The tripod ligand L^-, like tris(pyrazolyl)borate, is formally equivalent to a cyclopentadienyl ligand and the change bidentate/tridentate corresponds to the η^3/η^5 'slipping' of a cyclopentadienyl ligand that has been postulated to explain the S_N2 replacement of ethylene and carbon monoxide in compounds of the type $[M(C_2H_4)_2(C_5H_5)]$ and $[M(CO)_2(C_5H_5)]$ (M = Co, Rh, or Ir).[21]

Experimental

All reactions were performed under an atmosphere of dry nitrogen in conventional Schlenk glassware. Infrared spectra were recorded on a Perkin-Elmer PE 580 spectrometer, n.m.r. spectra on a Bruker WP80 (80 MHz) spectrometer. Chemical shifts are given (positive downfield) relative to $SiMe_4$. Carbon and hydrogen analyses were performed on a Carlo Erba Elemental Analizer model 1106. Membrane filters (regenerated cellulose, 1.0 μm, Schleicher & Schuell, RC60) were used to remove small particles. Tetrakis(acetonitrile)copper(I) hexafluorophosphate[22] was prepared according to the published procedure.

Preparation of [Cu(bq)L].—To a solution of $[Cu(CH_3CN)_4]PF_6$ (243 mg, 0.65 mmol) in dichloromethane (25 cm^3) were added with stirring benzoquinone (73 mg, 0.67 mmol) and NaL (328 mg, 0.69 mmol). After 30 min the solvent was distilled off *in vacuo* and the resulting powder dried *in vacuo*. The benzoquinonecopper complex was extracted from this residue with dry diethyl ether (25 cm^3). The solution was filtered through a membrane, concentrated to about 10 cm^3, and cooled to −20 °C for 1 d. The supernatant diethyl ether phase was decanted and the crystals which had formed were washed with three portions (10 cm^3) of pentane and dried for 2 h at 10^{-4} Torr (*ca.* 1.33×10^{-2} Pa); 216 mg of [Cu(bq)L] (0.35 mmol, 53%) were isolated in the form of red crystals, decomp. above 120 °C (Found: C, 32.90; H, 4.45. $C_{17}H_{27}CoCuO_{11}P_3$ requires C, 32.80; H, 4.35%). $\nu_{max.}$ 1 655(sh) and 1 650s (CO), 1 125vs cm^{-1} (P=O) (KBr). δ_H($C_6D_5CD_3$, 100 °C) 5.6 (4 H, s, br, $C_6H_4O_2$), 4.8 (5 H, s, C_5H_5), and 3.5 [18 H, virt. q, ^3J(HCOP) = 11, OCH_3]; (30 °C) 5.9 (s), 5.5 (vbr), 5.1 (s) (sum 4 H $C_6H_4O_2$) 4.82 [q, ^3J(HCCoP) = 0.4], and 4.77 [q, ^3J(HCCoP) = 0.5 Hz], ratio of intensity *ca.* 2:3 (sum 5 H), and 3.5 (18 H, m, OCH_3). (−25 °C) 6.2 {s, br, non-co-ordinated double bond of [Cu(bq)L]}, 5.8 (s, free quinone), 5.1 {s, quinone of [(CuL)$_2$bq]}, and 4.9 {s, br, co-ordinated double bond of

Table 3. Crystal data for [Cu(bq)L]

Formula	$C_{17}H_{27}CoCuO_{11}P_3$
M	622.80
Crystal system	Triclinic
Space group	$P\bar{1}$ (no. 2)
a/Å, α/°	11.358(6), 92.18(2)
b/Å, β/°	12.138(7), 134.24(2)
c/Å, γ/°	12.465(6), 99.49(4)
U/Å^3	1 185.5
Z	2
D_c/g cm^{-3}	1.74
Crystal shape	Rhombus, length 0.5 mm, 0.1 mm thick
λ(Mo-K_α)/Å	0.710 69
Monochromator	Graphite
μ/cm^{-1}	13.48
F(000)	628
Scan range/°	$3 < \theta < 26$, ω scan profile fit method*
Temperature	Ambient
Data corrections	Background, Lorentz, polarization
Absorption correction	ψ scan for 10 reflections
Transmission coefficients	0.795—0.998
No. of reflections measured	11 372
symmetrically independent	5 377 ($R_{int} = 0.026$)
with $\lvert F_o \rvert > 2.5\sigma(F_o)$	4 140
R	0.056
$R'(w = 2.148\ \sigma^{-2}\lvert F_o \rvert)$	0.034
Residual electron density	1.3 e Å^{-3}

* W. Clegg, *Acta Crystallogr., Sect. A*, 1981, **37**, 22.

[Cu(bq)L]} (sum of intensity 4 H), 4.82 {q, ^3J(HCCoP) = 0.4, C_5H_5 of [(CuL)$_2$bq]}, and 4.76 {q, ^3J(HCCoP) = 0.5 Hz, C_5H_5 of [Cu(bq)L], ratio of intensity *ca.* 2:3, sum 5 H}, and 3.5 (18 H, m, OCH_3).

Reaction of [Cu(CO)L] *with* bq.—When a dichloromethane solution of the yellow carbonyl complex [Cu(CO)L] was treated with an equimolar amount of *p*-benzoquinone the colour of the solution became dark crimson. As judged from the CO band intensity only about 10% of [Cu(bq)L] had been formed. To bring the equilibrium completely to the product side it was necessary to keep the solution under vacuum or to boil it under nitrogen gas for some time. Bubbling CO gas through the solution regenerated about 90% of the original intensity of the copper carbonyl band.

The dinuclear compound [LCu(μ-bq)CuL] was formed in nearly quantitative yield when [Cu(CO)L] and *p*-benzoquinone were heated in the ratio 2:1 instead of 1:1 in dichloromethane solution for 3 h. It could be isolated as an orange-red powder. δ_H ($C_6D_5CD_3$) 5.1 (4 H, s, $C_6H_4O_2$), 4.8 [10 H, q, ^3J (HCCoP) = 0.4, C_5H_5], and 3.5 [18 H, virt. q, ^3J(HCOP) = 11 Hz, OCH_3].

Preparation of [Cu(nq)L].—The complex [Cu(CH_3CN)$_4$]-PF_6 (1.308 g, 3.51 mmol) was added to an orange brown solution (60 cm^3) of naphthoquinone (555 mg, 3.51 mmol) in dichloromethane. No colour change occurred. During the addition of NaL (1.73 g, 3.64 mmol) the colour changed immediately to deep red and a light precipitate, presumably $NaPF_6$, was observed. The mixture was stirred for 90 min and then filtered. The filtrate was taken to dryness, dissolved in dry diethyl ether (60 cm^3), and filtered again through a membrane. Red crystals precipitated when the solution was stored at −20 °C overnight. They were separated, washed twice with hexane (10 cm^3), and identified as [Cu(nq)L] (321 mg, 14%). The mother-liquor yielded another 1.72 g of [Cu(nq)L] as a red powder containing some naphthoquinone as the main impurity. M.p. 205 °C (slow decomposition above 175 °C) (Found: C, 37.60; H, 4.40. $C_{21}H_{29}CoCuO_{11}P_3$ requires C, 37.50; H, 4.35%). $\nu_{max.}$ 1 665s and 1 595m (CO), 1 133(sh), 1 122vs, and 1 116(sh) cm^{-1} (P=O) (KBr). δ_H ($C_6D_5CD_3$) 7.6 (4 H, m, aromatic protons of nq), 5.2 (2 H, s, olefinic protons of nq), 4.8 [5 H, q, ^3J(HCCoP) = 0.4, C_5H_5], and 3.4 [18 H, virt. q, ^3J(HCOP) = 11 Hz, OCH_3].

X-*Ray Crystallography for* [Cu(bq)L].—Single crystals of [Cu(bq)L] suitable for *X*-ray structure determination were grown from diethyl ether. The quality of some crystals was checked by film techniques (oscillation and Weissenberg photographs). With the information derived therefrom and four-circle diffractometer data (Siemens AED 2), a triclinic unit cell emerged. The lattice constants were refined from the Bragg angles of 20 reflections. Subsequently, a complete intensity data set was collected.

The crystal structure of [Cu(bq)L] was solved by a combination of direct methods and Fourier techniques making use of the program system SHELX 76[23] with scattering factors taken from ref. 24. The positional parameters of copper, cobalt, and phosphorus were obtained through direct methods, refined by the full-matrix least-squares techniques, and used to calculate a Fourier difference map from which oxygen and carbon positions could be selected. The positional parameters of the hydrogen atoms could be found from a Fourier difference map that was calculated with all other atomic positions at an *R* of 0.067 and with anisotropic thermal parameters. Isotropic thermal parameters were introduced for the hydrogen atoms and fixed in three groups. The whole structural model was then refined by the blocked-matrix least-squares technique to a final (conventional) *R* of 0.056 ($R' = 0.034$), see Tables 2 and 3.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

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