

## Reaction of Triphenylphosphine with Copper Complexes derived from 2-Nitrosophenols (1,2-Quinone Mono-oximes)

Robert G. Buckley, John Charalambous,\* Malcolm J. Kensett, Mary McPartlin, and Deepak Mukerjee

School of Chemistry, The Polytechnic of North London, Holloway, London N7 8DB

Edward G. Brain

Beecham Pharmaceuticals, Research Centre, Brockham Park, Betchworth, Surrey RH3 7AJ

John M. Jenkins

Propellants Explosives and Rocket Motor Establishment, Waltham Abbey, Essex EN9 1BP

Reaction of triphenylphosphine with the copper(II) complexes of 5-methoxy-2-nitrosophenol, 4-methyl-2-nitrosophenol, 1-nitroso-2-naphthol, and 2-nitroso-1-naphthol involves deoxygenation of one of the ligands to give 2-amino-7-methoxy-3*H*-phenoxazin-3-one, 4-methyl-2-aminophenol, 1-amino-2-naphthol, and 2-amino-*N*<sup>4</sup>-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine respectively as the major organic products. In all cases reduction of the metal occurs to give a complex of type Cu(qo)-(PPh<sub>3</sub>)<sub>2</sub> (qoH = nitrosophenol). The reactions are rationalised in terms of nitrene intermediacy. An X-ray diffraction study of Cu(qo)(PPh<sub>3</sub>)<sub>2</sub> (qoH = 1-nitroso-2-naphthol) has been undertaken.

Metal complexes derived from 2-nitrosophenols (1,2-quinone mono-oximes) can be employed as starting reagents in the synthesis of a wide variety of organic materials.<sup>1-3</sup> In an earlier communication preliminary results of reactions between copper 1,2-benzoquinone mono-oximate complexes and triphenylphosphine were reported.<sup>2</sup> Here we further describe these reactions and also reactions involving copper complexes derived from the 1,2-naphthoquinone mono-oximes. Recently we have reported on the reaction between the complexes and amines.<sup>4</sup>

### Results

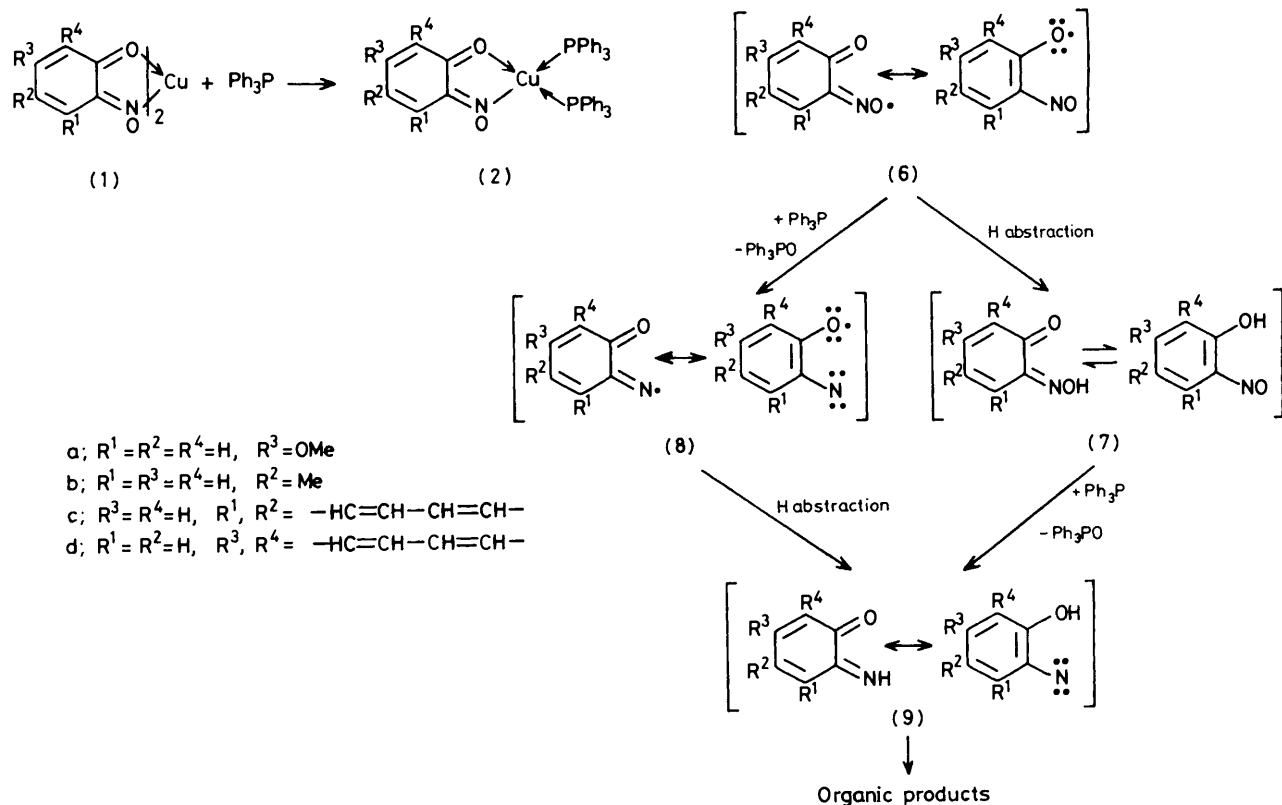
Interaction of triphenylphosphine with the complexes (1a-d) gave, in each case, triphenylphosphine oxide, a diamagnetic copper-containing solid, and a complex mixture of organic products (Scheme 1). The elemental analysis, i.r. spectra, and measured relative molecular masses of the copper-containing solids suggested that they were quinone oximate-bis(triphenylphosphine)copper(I) complexes of type (2). This was in keeping with the well documented reduction of copper(II) bischelates by triphenylphosphine.<sup>5,6</sup> Further confirmation of the nature of these solids was obtained through an X-ray crystallographic study of the product from the bis(1,2-naphthoquinone 1-oximate)copper(II) (1c) reaction which showed it to have the structure (2c) (Figure). The complexes were obtained in 55-75% yield. Another product isolated in 56% yield from the bis-(5-methoxy-1,2-benzoquinone 2-oximate)copper(II) (1a) reaction was 2-amino-7-methoxy-3*H*-phenoxazin-3-one (3). Previously this compound was reported as 1,6-dihydroxy-3,8-dimethoxyphenazine<sup>2</sup> but its formulation as the phenoxazinone has been established by X-ray crystallography.<sup>7</sup> The bis(4-methyl-1,2-benzoquinone 2-oximate)copper(II) (1b) reaction afforded 2-amino-4-methylphenol in low yield. The major organic product isolated from the reaction involving bis-(1,2-naphthoquinone 1-oximate)copper(II) was 1-amino-2-naphthol (26%). Other compounds obtained in trace quantities from the product mixture were 1-phenylamino-2-naphthol and 6-hydroxydibenz[*b,k*]acridin-8-one (4). From the reaction involving bis(1,2-naphthoquinone 2-oximate)copper(II) (1d) was isolated 2-amino-*N*<sup>4</sup>-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (5) in 37% yield.

### Discussion

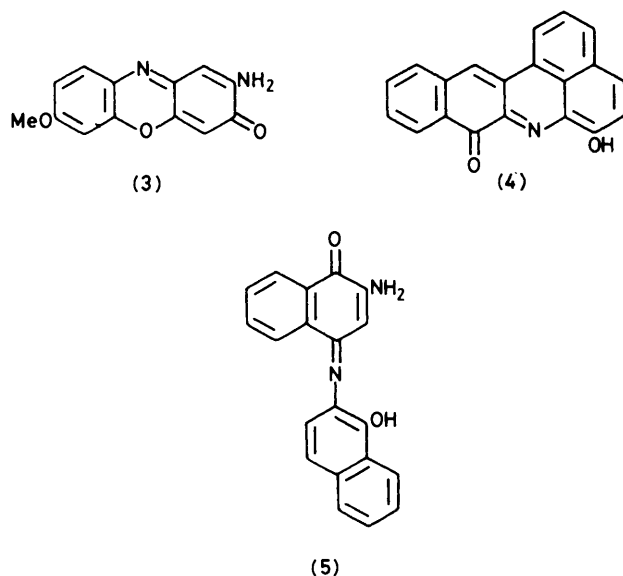
It is widely accepted that trivalent phosphorus derivatives deoxygenate nitroso-compounds to yield nitrene intermediates.<sup>8,9</sup> For the reactions described here it is also possible that nitrenes are involved. Support for the suggestion is provided by the formation of amino-compounds. Amine formation in deoxygenation reactions of nitro-compounds with trivalent phosphorus reagents or in azide decomposition reactions is considered to be indicative of nitrene participation.<sup>10</sup> The reactions may proceed through routes involving nitrene precursors<sup>11</sup> but such mechanisms are considered less likely.

The reactions studied can be accounted as indicated in Scheme 1. The initial stage is the reduction of the copper(II) co-ordination centre by triphenylphosphine. This gives the copper(II) complex (2) and the ligand radical (6) which affords the free ligand (7) and the nitrene/quinone imine species (8) and (9) *via* deoxygenation and/or hydrogen abstraction reactions.

The 2-amino-4-methylphenol and 1-amino-2-naphthol arise through further hydrogen abstraction reactions of the corresponding intermediate (9). 2-Amino-7-methoxy-3*H*-phenoxazin-3-one may arise through reactions involving attack of (9a) or of the corresponding amine on the nitrosophenolic or quinone oximic tautomers of (7a) respectively (Scheme 2). The formation of 2-amino-*N*<sup>4</sup>-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine can be rationalised similarly by assuming attack on the 4-position of the ring system. In 1,2-naphthoquinonoid compounds this kind of attack is well known<sup>12,13</sup> and is supported by the formation of 2-amino-*N*<sup>4</sup>-phenyl-1,4-naphthoquinone 4-imine from the reaction of 1,2-naphthoquinone 2-oxime with aniline.<sup>14</sup> The formation of the acridinone (4) from the reaction can be explained by postulating hydrolysis of the corresponding nitrene/quinone imine intermediate (9) to 1,2-naphthoquinone which reacts with 1-amino-2-naphthol to give the acridinone. The reaction of 1-amino-2-naphthol hydrochloride with 1,2-naphthoquinone is known to give the acridinone.<sup>15</sup> It is not certain how 1-phenylamino-2-naphthol is formed but it could point to a reactive intermediate such as a nitrene, utilising a phenyl group from triphenylphosphine. This novel behaviour has also been observed in related systems (*e.g.* the reaction between triphenylphosphine and zinc(II) naphthoquinone-oximate-complexes).<sup>14</sup>



Scheme 1



*Crystal and Molecular Structure of 1,2-Naphthoquinone 1-oximatobis(triphenylphosphine)copper(I) (2d).*—*Crystal data.*  $C_{46}H_{36}CuNO_2P_2$ , Monoclinic,  $P2_1/m$ ,  $a = 16.083(4)$ ,  $b = 13.517(4)$ ,  $c = 18.100(6)$  Å,  $\beta = 104.484(3)^\circ$ ,  $U = 3809.77$  Å<sup>3</sup>,  $D_m = 1.32$ ,  $D_c = 1.33$  g cm<sup>-3</sup>,  $Z = 4$ . Intensity data were collected on a Philips PW1100 four-circle diffractometer using graphite monochromated Mo- $K_\alpha$  radiation. The structure was solved and refined using 1882 unique reflections [ $I > 3\sigma(I)$ ] to a final  $R$  factor of 0.060.<sup>16</sup> Anisotropic temperature factors were refined for the Cu, N, the carbonyl O and both P

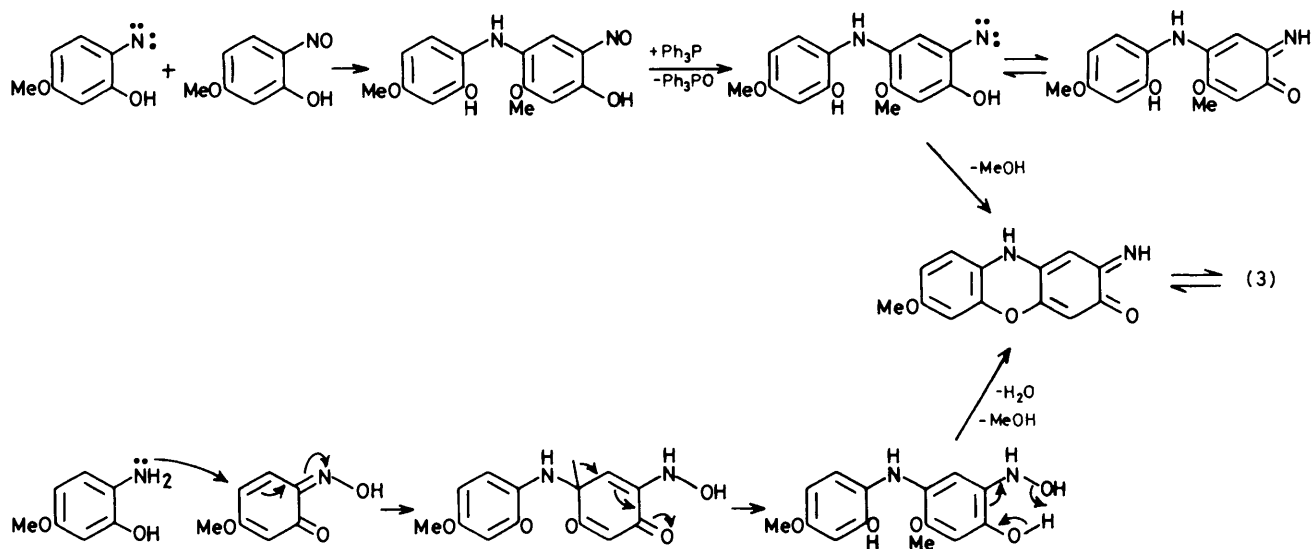
atoms. The phenyl groups were constrained to have C-C bond distances of 1.395 Å and C-C-C bond angles of 120°. All hydrogen atoms were included in calculated positions as earlier difference maps had not unambiguously located them. Lists of structure factors, rigid group positional parameters, and thermal parameters for all atoms are given in Supplementary Publication No. SUP 23533 (13 pp.).\* The positional parameters are listed in Table 1 and the bond lengths and angles in Table 2. The atomic numbering is explained in the Figure.

As with other 1,2-quinone oximate-complexes the chelate ring in 1,2-naphthoquinone 2-oximatobis(triphenylphosphine)-copper(I) is five membered. The bond lengths in the chelate ring agree well with results for other 1,2-quinone oximate-complexes.<sup>17</sup> The P-Cu-P bond angle [124.5(1)°] is much greater than the idealized value of 109.5°. This can be attributed to the steric factors involving the bulky Ph<sub>3</sub>P groups and is in keeping with results obtained from related complexes.<sup>18</sup>

### Experimental

<sup>1</sup>H N.m.r. spectra were measured using a Perkin-Elmer R12B Spectrometer and the 220 MHz instrument at the Physico-Chemical Measurements Unit at Harwell. I.r. spectra were recorded with a Pye Unicam SP2000 spectrophotometer. The mass spectra were obtained using A.E.I. MS9 and MS50 spectrometers. Magnetic measurements were made at room temperature using a Gouy balance equipped with a permanent magnet of 3 600 Oe. Relative molecular masses were determined osmotically using a Mechrolab 301A osmo-

\* For details of the Supplementary publications scheme, see the Instructions for Authors in *J. Chem. Soc., Perkin Trans. I*, 1983, Issue 1.



Scheme 2

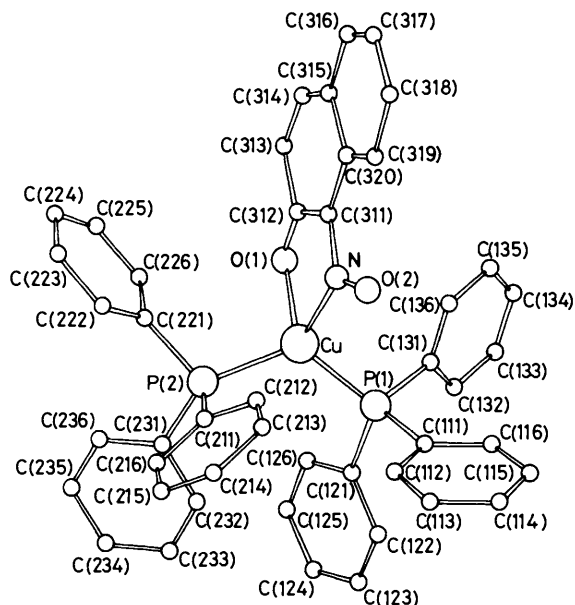


Figure. Structure of compound (2d)

meter in chloroform. The adsorbent used in the chromatography columns was Merck Kieselgel 60 (70–230 mesh). Thin layer and preparative plate chromatography were carried out using pre-coated Merck Kieselgel 60 F<sub>254</sub> plates. All of the reactions were carried out in a nitrogen atmosphere.

**Reaction of Bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) (1a) with Triphenylphosphine.**—Bis(5-methoxy-1,2-benzoquinone 2-oximato)copper(II) (3.7 g, 10.1 mmol) and triphenylphosphine (13.1 g, 49.9 mmol) in pyridine (100 cm<sup>3</sup>) were stirred at 20 °C for 5 days. Silica (20.0 g) was added and the solvent removed under reduced pressure. The residue was then extracted (Soxhlet) with diethyl ether. After concentration to low volume, the extract was filtered. The diamagnetic residue was yellow 5-methoxy-1,2-benzoquinone 2-oximatobis(triphenylphosphine)copper(I) (2a) (5.5 g, 74%) (Found: C, 69.6; H, 4.6; Cu, 9.0; N, 1.8%; *M*, 757. C<sub>43</sub>H<sub>36</sub>CuNO<sub>3</sub>P<sub>2</sub> requires C, 69.8; H, 4.9; Cu, 8.6; N, 1.9%; *M*, 739).

The filtrate was chromatographed on silica gel. Elution with light petroleum (b.p. 60–80 °C) gave unchanged triphenylphosphine (4.2 g) (identified by t.l.c.). Elution with toluene gave a further quantity of 5-methoxy-1,2-benzoquinone 2-oximatobis(triphenylphosphine)copper(I) (0.2 g). Elution with tetrahydrofuran gave triphenylphosphine oxide (3.0 g) (identified by t.l.c.). Continued extraction of the Soxhlet residue with ethyl acetate gave red 2-amino-7-methoxy-3*H*-phenoxazin-3-one (3) (0.7 g, 56%), m.p. 268–270 °C (decomp), identical in respect of t.l.c., i.r. and mass spectra, and mixed m.p. with an authentic sample.<sup>7</sup> Extraction of the Soxhlet residue with methanol gave unchanged (1a) (0.5 g, 14% recovery) (identified by i.r.).

**Reaction of Bis(4-methyl-1,2-benzoquinone 2-oximato)copper(II) (1b) with Triphenylphosphine.**—Bis(4-methyl-1,2-benzoquinone 2-oximato)copper(II) (3.4 g, 10.1 mmol) and triphenylphosphine (13.1 g, 49.9 mmol) in pyridine (100 cm<sup>3</sup>) were stirred at 20 °C for 2 days. The mixture was then filtered. The diamagnetic residue was red 4-methyl-1,2-benzoquinone 2-oximatobis(triphenylphosphine)copper(I) (2b) (3.8 g, 53%) (Found: C, 72.8; H, 5.2; Cu, 9.3; N, 1.9%; *M*, 730. C<sub>43</sub>H<sub>36</sub>CuNOP<sub>2</sub> requires C, 72.0; H, 5.1; Cu, 9.0; N, 2.0%; *M*, 723). Chromatography of the filtrate (silica gel) gave, with light petroleum (b.p. 60–80 °C) as eluant, unchanged triphenylphosphine (3.8 g) (identified by t.l.c.). Elution with toluene gave a yellow solid (0.8 g) (mixture by t.l.c.) from which 2-amino-4-methylphenol (ca. 5%) (identified by t.l.c. and mass spectroscopy) was obtained using plate chromatography. Elution with tetrahydrofuran gave triphenylphosphine oxide (2.5 g) (identified by t.l.c.).

**Reaction of Bis(1,2-naphthoquinone 1-oximato)copper(II) (1c) with Triphenylphosphine.**—Bis(1,2-naphthoquinone 1-oximato)copper(II) (2.0 g, 4.9 mmol) and triphenylphosphine (6.6 g, 25.2 mmol) in pyridine (40 cm<sup>3</sup>) were stirred at 20 °C for 7 days. Diethyl ether (175 cm<sup>3</sup>) was added and the mixture stirred for 12 h and then filtered. The diamagnetic residue recrystallised from toluene as green rods of 1,2-naphthoquinone 1-oximatobis(triphenylphosphine)copper(I) (2c) (1.50 g, 40%) (Found: C, 73.0; H, 5.0; Cu, 8.3; N, 1.8%; *M*, 722. C<sub>46</sub>H<sub>36</sub>CuNO<sub>2</sub>P<sub>2</sub> requires C, 72.7; H, 4.8; Cu, 8.4; N, 1.8%; *M*, 760).

**Table 1.** Fractional co-ordinates for (2d).

Independent atoms with standard deviations in parentheses

Atom	x	y	z
Cu	0.154 9(1)	0.135 4(1)	0.420 4(1)
P(1)	0.105 9(2)	0.273 8(2)	0.463 1(2)
P(2)	0.290 1(2)	0.081 9(2)	0.457 9(2)
N	0.109 9(5)	0.118 1(6)	0.306 1(5)
O(1)	0.064 2(5)	0.020 9(5)	0.415 6(5)
O(2)	0.139 5(5)	0.163 3(6)	0.255 5(5)
C(311)	0.042 4(7)	0.054 5(9)	0.281 6(7)
C(312)	0.022 6(8)	0.009 3(9)	0.347 2(8)
C(313)	-0.052 1(8)	-0.061 3(10)	0.330 9(8)
C(314)	-0.092 3(9)	-0.074 4(10)	0.258 5(8)
C(315)	-0.078 6(8)	-0.031 5(10)	0.194 9(8)
C(316)	-0.126 0(8)	-0.050 1(10)	0.117 3(8)
C(317)	-0.110 1(10)	-0.003 0(11)	0.059 3(9)
C(318)	-0.043 8(10)	0.065 7(12)	0.064 9(9)
C(319)	0.008 6(8)	0.082 5(9)	0.141 1(8)
C(320)	-0.006 0(7)	0.036 9(9)	0.203 3(7)

Atoms in rigid groups

Atom	x	y	z
C(111)	0.1306	0.3851	0.4163
C(112)	0.1309	0.4793	0.4479
C(113)	0.1504	0.5617	0.4091
C(114)	0.1696	0.5500	0.3385
C(115)	0.1692	0.4558	0.3069
C(116)	0.1497	0.3734	0.3458
C(121)	0.1421	0.3081	0.5637
C(122)	0.0848	0.3325	0.6073
C(123)	0.1157	0.3589	0.6837
C(124)	0.2039	0.3609	0.7166
C(125)	0.2613	0.3365	0.6730
C(126)	0.2304	0.3101	0.5965
C(131)	-0.0108	0.2732	0.4449
C(132)	-0.0631	0.3514	0.4107
C(133)	-0.1521	0.3441	0.3976
C(134)	-0.1889	0.2586	0.4187
C(135)	-0.1367	0.1804	0.4529
C(136)	-0.0477	0.1877	0.4660
C(211)	0.3588	0.1412	0.4052
C(212)	0.3502	0.2432	0.3942
C(213)	0.3997	0.2925	0.3526
C(214)	0.4579	0.2398	0.3221
C(215)	0.4665	0.1378	0.3331
C(216)	0.4169	0.0885	0.3746
C(221)	0.3035	0.9500	0.4430
C(222)	0.3605	0.8902	0.4950
C(223)	0.3682	0.7902	0.4791
C(224)	0.3189	0.7499	0.4112
C(225)	0.2620	0.8096	0.3593
C(226)	0.2543	0.9097	0.3751
C(231)	0.3475	0.1006	0.5572
C(232)	0.4307	0.1387	0.5780
C(233)	0.4717	0.1524	0.6549
C(234)	0.4295	0.1281	0.7110
C(235)	0.3463	0.0900	0.6902
C(236)	0.3053	0.0763	0.6133

The filtrate was chromatographed on silica gel. Elution with diethyl ether yielded triphenylphosphine (0.20 g) (identified by t.l.c.). Further elution gave a multicomponent eluate. Elution with ethyl acetate gave triphenylphosphine oxide (2.30 g) (identified by t.l.c.). Slow evaporation of the multicomponent ethereal eluate yielded a second crop of 1,2-naphthoquinone 1-oximatobis(triphenylphosphine)copper(I) (0.51 g, 14%) followed by 1-amino-2-naphthol (0.21 g, 26%) (identified by i.r. and mass spectroscopy). 6-Hydroxydibenz[*b,k*]acridin-8-one (4) (trace) (identical t.l.c. and mass spectroscopy with authen-

**Table 2.** Bond lengths (Å) and bond angles (°) in (2d)

Bond lengths			
Cu-P(1)	2.241(4)	O(1)-C(312)	1.262(15)
Cu-P(2)	2.230(3)	C(311)-C(312)	1.44(2)
Cu-N	2.028(9)	C(312)-C(313)	1.50(2)
Cu-O(1)	2.115(8)	C(313)-C(314)	1.32(2)
P(1)-C(111)	1.819(9)	C(314)-C(315)	1.36(2)
P(1)-C(121)	1.826(9)	C(315)-C(316)	1.44(2)
P(1)-C(131)	1.823(6)	C(316)-C(317)	1.31(2)
P(2)-C(211)	1.816(8)	C(317)-C(318)	1.40(2)
P(2)-C(221)	1.823(8)	C(318)-C(319)	1.44(2)
P(2)-C(231)	1.821(7)	C(319)-C(320)	1.35(2)
N-O(2)	1.287(13)	C(320)-C(315)	1.47(2)
N-C(311)	1.368(14)	C(320)-C(311)	1.46(2)
Bond angles			
P(1)-Cu-P(2)	124.5(1)	C(311)-N-O(2)	118.2(9)
N-Cu-P(1)	112.4(3)	C(312)-O(1)-Cu	108.8(8)
N-Cu-P(2)	110.2(3)	C(312)-C(311)-N	109(1)
O(1)-Cu-P(1)	109.0(2)	C(320)-C(311)-N	127(1)
O(1)-Cu-P(2)	112.7(2)	C(320)-C(311)-C(312)	124(1)
O(1)-Cu-N	78.9(3)	C(311)-C(312)-O(1)	126(1)
C(111)-P(1)-Cu	113.1(3)	C(313)-C(312)-O(1)	118(1)
C(121)-P(1)-Cu	120.2(3)	C(313)-C(312)-C(311)	116(1)
C(131)-P(1)-Cu	111.7(2)	C(314)-C(313)-C(312)	117(1)
C(111)-P(1)-C(121)	101.6(4)	C(315)-C(314)-C(313)	130(1)
C(111)-P(1)-C(131)	104.7(3)	C(315)-C(320)-C(311)	115(1)
C(121)-P(1)-C(131)	103.8(4)	C(319)-C(320)-C(311)	125(1)
C(211)-P(2)-Cu	111.8(2)	C(319)-C(320)-C(315)	120(1)
C(221)-P(2)-Cu	114.5(2)	C(320)-C(315)-C(314)	118(1)
C(231)-P(2)-Cu	118.0(3)	C(316)-C(315)-C(314)	126(1)
C(211)-P(2)-C(221)	104.1(4)	C(316)-C(315)-C(320)	115(1)
C(211)-P(2)-C(231)	103.5(3)	C(317)-C(316)-C(315)	122(1)
C(221)-P(2)-C(231)	103.4(3)	C(318)-C(317)-C(316)	124(1)
O(2)-N-Cu	124.7(6)	C(319)-C(318)-C(317)	115(1)
C(311)-N-Cu	117.1(8)	C(318)-C(319)-C(320)	123(1)

tic sample<sup>15</sup>) and 1-phenylamino-2-naphthol (trace) identical t.l.c. and mass spectroscopy with authentic sample<sup>14,19</sup>) were obtained by plate chromatography of the mother liquor.

**Reaction of Bis(1,2-naphthoquinone 2-oximato)copper(II) (1d) with Triphenylphosphine.**—Bis(1,2-naphthoquinone 2-oximato)copper(II) (1d) (2.0 g, 4.9 mmol) and triphenylphosphine (6.6 g, 25.2 mmol) in pyridine (40 cm<sup>3</sup>) were stirred at 20 °C for 5 days. A mixture of diethyl ether (200 cm<sup>3</sup>) and light petroleum (b.p. 60–80 °C) was added and the whole stirred for 12 h and then filtered. The diamagnetic residue crystallised from toluene as gold 1,2-naphthoquinone 2-oximatobis(triphenylphosphine)copper(I) (2d) (1.0 g, 27%) (Found: C, 72.8; H, 4.8; N, 1.5. C<sub>46</sub>H<sub>36</sub>CuNO<sub>2</sub>P<sub>2</sub> requires C, 72.7; H, 4.8; N, 1.8%). The filtrate was chromatographed on silica gel. Elution with toluene gave triphenylphosphine (2.1 g) (identified by t.l.c.). Elution with dichloromethane gave a purple solid (0.31 g) and elution with dichloromethane-diethyl ether gave a brown solid which, after washing with diethyl ether, yielded a further quantity of 1,2-naphthoquinone 2-oximatobis(triphenylphosphine)copper(I) (1.63 g, 44%) (identified by t.l.c.). Elution with ethyl acetate gave triphenylphosphine oxide (2.0 g) (identified by t.l.c.). The purple substance obtained from the dichloromethane eluate was rechromatographed on silica gel. Elution with dichloromethane yielded purple 2-amino-N<sup>4</sup>-(1-hydroxy-2-naphthyl)-1,4-naphthoquinone 4-imine (5) (0.28 g, 37%), m.p. 275–276 °C (Found: C, 76.6; H, 4.5; N, 9.1. C<sub>20</sub>H<sub>14</sub>N<sub>2</sub>O<sub>2</sub> requires C, 76.4; H, 4.5; N, 8.9%),  $\nu_{\text{max}}$  (CHCl<sub>3</sub> soln.) 1 665 (quinonoid CO), 3 390, and 3 510 cm<sup>-1</sup>;  $\lambda_{\text{max}}$  (CHCl<sub>3</sub>) 545 nm ( $\epsilon$  834 m<sup>2</sup> mol<sup>-1</sup>);  $\delta$ [(CD<sub>3</sub>)<sub>2</sub>SO] 6.20 (1 H, s,

naphthoquinonoid 3-H), 6.46br (3 H, s, NH/OH, exchanged with D<sub>2</sub>O) and 7.07—8.64 (10 H, m, aromatic); *m/z* 314 (*M*<sup>+</sup>).

### Acknowledgement

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