Organometallic Chemistry

3,6-Di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) with bidentate bis(diphenylphosphine) ligands. Synthesis, structures, and properties

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New mononuclear 3,6-di-*tert*-butyl-*o*-benzosemiquinone complexes of copper(I) with bis(diphenylphosphine) ligands were synthesized: (DBSQ)Cu(dppe) (**1**) (DBSQ = 3,6-di-*tert*-butyl-*o*-benzosemiquinone and dppe = 1,2-bis(diphenylphosphino)ethane), (DBSQ)Cu(dppp) (**2**) (dppp = 1,3-bis(diphenylphosphino)propane), (DBSQ)Cu(dppn) (**3**) (dppn = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), and (DBSQ)Cu(dppfc) (**4**) (dppfc = 1,1′-bis(diphenylphosphino)ferrocene). The compositions and structures of complexes **1**—**4** were characterized by elemental analysis and electronic absorption, IR, and ESR spectroscopy. The molecular structures of complexes **3** and **4** were established by X-ray diffraction analysis. The reactions of elimination and replacement of neutral ligands in the coordination sphere of the complexes were studied by ESR spectroscopy.

Key words: copper(I) complexes, 3,6-di-*tert*-butyl-*o*-benzosemiquinone, bis(diphenylphosphines), synthesis, structure, X-ray diffraction analysis.

Owing to the presence of paramagnetic ligands, *o*-semiquinone complexes of metals are very convenient objects for studying the structure and dynamics of the coordination sphere in solutions by ESR spectroscopy.[1—3] In particular, using *o*-semiquinone complexes of copper as examples, the reactions of elimination, addition, and replacement of neutral ligands were studied,[4] the intramolecular metal—ligand electron transfer induced by replacement of neutral ligands was observed,[2,5] and the redox isomerism of diazadiene complexes[2,6] as well as the stereochemical nonrigidity of the coordination sphere of bis(triphenylphosphine) complexes of copper(I)[7] were found. The lability of the coordination sphere of bis(phosphine) complexes of copper substantially complicates their preparation because of the interaction of triphenylphosphine with the second *o*-quinone functional group as exemplified by mono- and binuclear *o*-semiquinone complexes of metals (derivatives of di-*o*-quinones).[8,9]

In this work, we report the preparation of *o*-semiquinone complexes of copper(I) with bidentate bis(diphenylphosphine) ligands, which are characterized by the kinetically stable coordination sphere.

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 11, pp. 2333—2340, November, 1998.

1066-5285/98/4711-2262$20.00

Results and Discussion

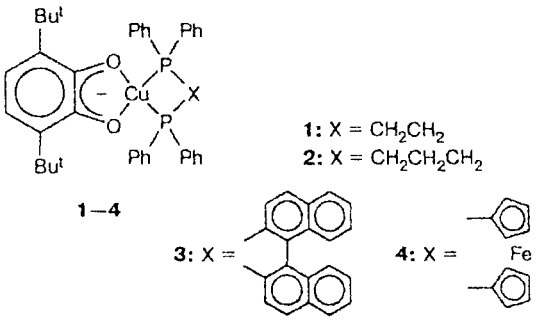
The mono- and binuclear complexes (DBSQ)Cu(dppe) (**1**, DBSQ = 3,6-di-*tert*-butyl-1,2-benzosemiquinone, dppe = 1,2-bis(diphenylphosphino)ethane), (DBSQ)Cu(dppp) (**2**, dppp = 1,3-bis(diphenylphosphino)propane), (DBSQ)Cu(dppn) (**3**, dppn = 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl), and (DBSQ)Cu(dppfc) (**4**, dppfc = 1,1′-bis(diphenylphosphino)ferrocene) were synthesized *in situ* from copper(I) chloride, the corresponding diphosphine, and thallium(I) *o*-semiquinolate according to a known procedure:[10]

$$CuCl + dppl + Tl(DBSQ) \longrightarrow (dppl)Cu(DBSQ) + TlCl, \quad (1)$$

dppl = dppe, dppp, dppfc, dppn.

The resulting complexes **1**—**4** were isolated in the individual form as solid air-stable compounds of different violet hues. These compounds are readily crystallized (toluene/hexane), readily soluble in ethers and aromatic hydrocarbons, and poorly soluble in alkanes and methanol.

Scheme 1



The IR spectra of complexes **1**—**4**, which are similar to the spectrum of the known complex $(DBSQ)Cu(PPh_3)_2$,[10] have bands of the *o*-semiquinone fragment at 960—970 cm^{-1} (νC—C Bu^t) and 1470—1480 cm^{-1} (νC—O) and bands of the bis(diphenylphosphine) ligand at 700, 750 ($\delta_\perp$CH of the Ph group), 1000, 1110 ($\delta_\perp$C—C of the Ph group), and 480—530 cm^{-1} (δPC)).

The electronic absorption spectra (EAS) of solutions of complexes **1**—**4** have intense ($\varepsilon > 1 \cdot 10^3$) double bands with λ_{max} 540—670 nm in the visible region. The presence of the long-wavelength band distinguishes these spectra from that of the known complex $(DBSQ)Cu(PPh_3)_2$,[10] which contains only one band with λ_{max} 535 nm. The electronic absorption spectra of complexes **1**—**4** differ only in the relative intensity of the bands. In the spectrum of complex **1**, the intensity of the short-wavelength band is almost half as large as that of the long-wavelength band while in the spectra of the mononuclear complexes (**2**—**4**), the intensities of these bands are nearly identical. In the spectrum of complex **4**, the short-wavelength band is the most intense one.

Table 1. Parameters of the isotropic ESR spectra of *o*-semiquinone complexes of copper(I) with bis(diphenylphosphine) ligands (toluene, 290 K)

Complex (ligand)	g_i	$A_i(^{63}Cu)/A_i(^{65}Cu)$	$A_i(^{31}P)$ /mT	$A_i(H_{SQ})$
1 (dppe)	2.0055	1.383/1.484	1.992	0.303(2H)
2 (dppp)	2.0046	1.344/1.443	2.068	0.301(2H)
3 (dppdn)	2.0059	1.344/1.450	2.018	0.299(2H)
4 (dppfc)	2.0057	1.191/1.283	1.863	0.299(2H)

All the compounds synthesized in this work are paramagnetic both in the solid state and in solutions. The ESR spectra of powders of these complexes are similar and contain symmetrical structureless lines with width $\Delta H \approx 3$ mT and $g_{eff} = 2.005$. The parameters of the isotropic ESR spectra of solutions of the complexes are given in Table 1. The ESR spectrum of complex **3** is shown in Fig. 1. The hyperfine structures of the ESR spectra of complexes **1**—**4** reflect hyperfine interactions of the unpaired electron with two protons of the *o*-semiquinone ligand (1 : 2 : 1 triplet), with the magnetic isotopes ^{63}Cu (69.09%; $I = 3/2$; $\mu_N = 2.2206$) and ^{65}Cu (30.91%; $I = 3/2$; $\mu_N = 2.3790$)[11] of one copper atom (1 : 1 : 1 : 1 quartets), and with the magnetic isotopes ^{31}P (100%; $I = 1/2$; $\mu_N = 1.1305$)[11] of two phosphorus atoms (1 : 2 : 1 triplet). The values g_i and the constants of hyperfine interactions with ^1H, ^{63}Cu, ^{65}Cu, and ^{31}P isotopes are typical of *o*-semiquinone complexes of copper(I) and agree with the published data.[4,10] Therefore, according to the data of IR, ESR, and electronic absorption spectroscopy, complexes **1**—**4** are *o*-semiquinone four-coordinate complexes of copper(I) containing the bidentate diphosphine ligand. The large values of the constants of hyperfine interac-

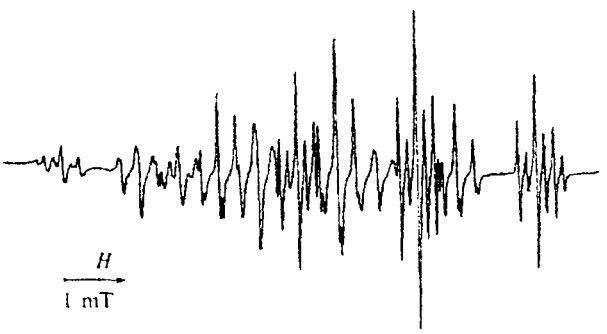


Fig. 1. ESR spectrum of complex **3** in solution.

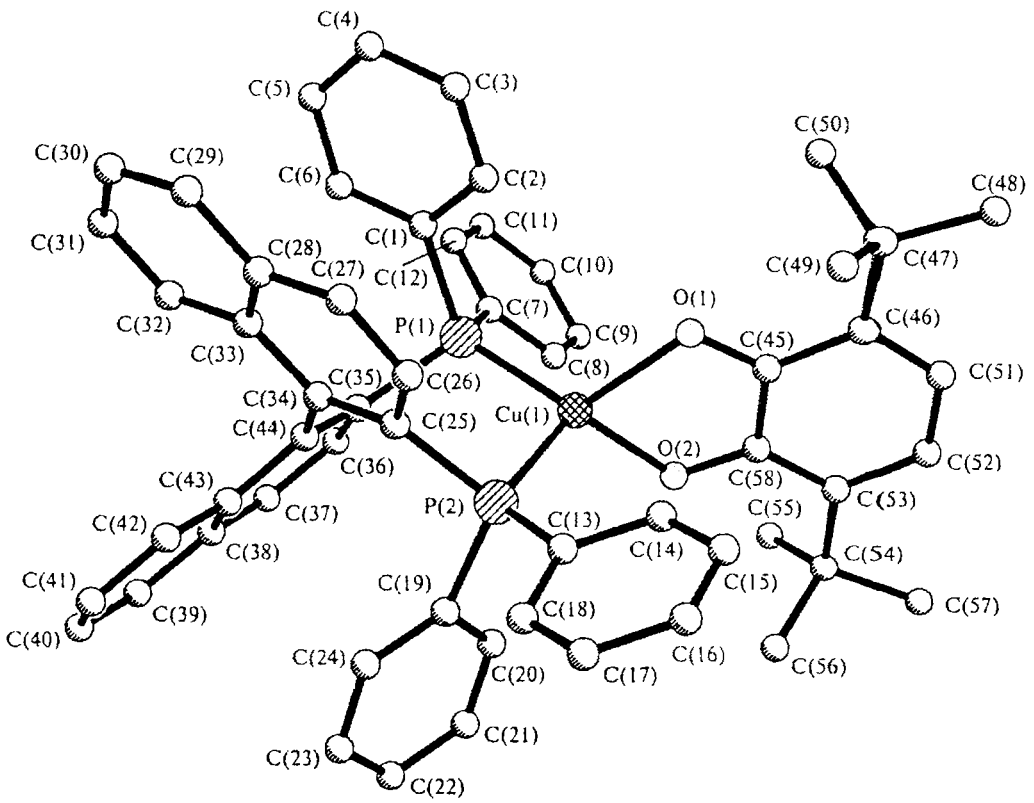


Fig. 2. Molecular structure of complex **3**.

tions with the copper and phosphorus nuclei are indicative of the nonplanar pseudotetrahedral geometry of the complexes, which is typical of copper(I) complexes containing phosphine ligands.[3,4]

Based on the data of X-ray diffraction analysis, the copper(I) atom in complex **3** (Fig. 2) is in a pseudotetrahedral environment and is coordinated to two oxygen atoms of the *o*-semiquinone ligand (O(1) and O(2)) and two phosphorus atoms of the diphosphine ligand (P(1) and P(2)). The Cu(1)—O(1) and Cu(1)—O(2) bond lengths (2.029(3) and 2.036(3) Å, respectively) are somewhat larger than those in the known semiquinone complexes of copper.[12,13] The Cu(1)—P(1) and Cu(1)—P(2) bonds are identical in length (2.222(1) Å). The P(1)—Cu(1)—P(2) bond angle is 102.0°. The angle between the O(1)Cu(1)O(2) and P(1)Cu(1)P(2) planes is close to a right angle (87.6°). The chelate O(1)Cu(1)O(2)C(58)C(45) ring is nonplanar because the copper atom deviates from the plane of the semiquinone ring by 0.863 Å. The O(1)—C(45), O(2)—C(58), and C(45)—C(58) bond lengths (1.284(5), 1.282(4), and 1.474(6) Å, respectively) that characterize the redox state of the ligand are typical of *o*-semiquinones.[14] The value of the O(1)—Cu(1)—O(2) bond angle (80.4°) is also typical of *o*-semiquinone complexes of metals.[14]

According to the data of X-ray diffraction analysis, single crystals of complex **4** (Fig. 3) contain two molecules of the complex per hexane molecule of solvation. As in the case of complex **3**, the copper(I) atom in molecule **4** is in a pseudotetrahedral environment and is directly bonded to two oxygen atoms (O(1) and O(2)) and two phosphorus atoms (P(1) and P(2)). The O(1)Cu(1)O(2) and P(1)Cu(1)P(2) planes are approximately orthogonal to each other. The angle between these planes is 86.6°. Although the Cu(1)—O(1) and Cu(1)—O(2) bond lengths (2.028(2) and 2.070(2) Å, respectively) are close to the corresponding values in complex **3**, the difference in their values is more pronounced. Note that the Cu(1)—P(1) and Cu(1)—P(2) bond lengths (2.218(1) and 2.238(1) Å, respectively) are also substantially different. These bonds are the shortest of the corresponding bonds in the known copper(I) complexes containing the dppfc ligand (Cu—P 2.243—2.286 Å).[15,16] The P(1)—Cu(1)—P(2) bond angle (112.9°) is comparable with the corresponding values in the known copper(I) complexes with the dppfc ligand.[15,16] The copper atom lies virtually in the plane of the semiquinone ligand (it deviates from this plane by only 0.079 Å). As in the case of complex **3**, the O(1)—C(11), O(2)—C(16), and C(11)—C(16) bond lengths (1.277(3), 1.273(3), and 1.476(4) Å, respec-

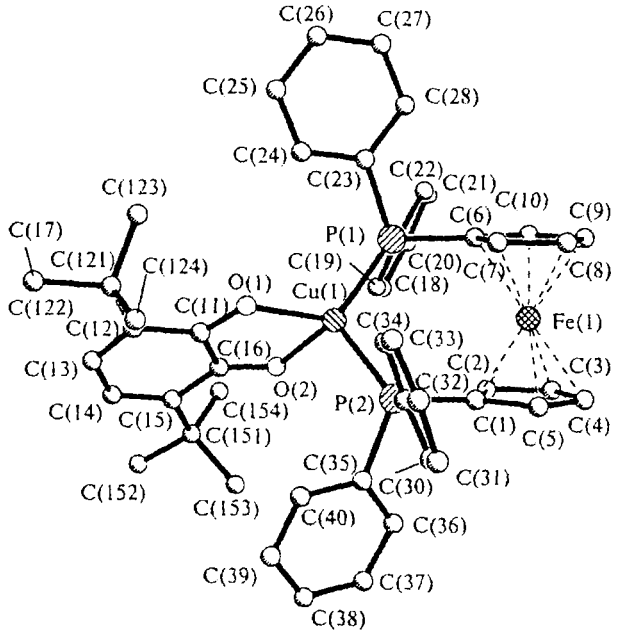


Fig. 3. Molecular structure of complex **4**.

Table 2. Crystallographic parameters of complexes **3** and **4** · $0.5C_6H_{14}$

Parameter	Complex **3**	Complex **4** · $0.5C_6H_{14}$
Formula	$C_{58}H_{52}CuO_2P_2$	$C_{51}H_{55}CuFeO_2P_2$
Space group	$P\bar{1}$	$P\bar{1}$
a/Å	10.969(3)	12.507(2)
b/Å	12.056(4)	14.443(3)
c/Å	18.998(6)	14.483(3)
α/deg	76.00(3)	113.29(3)
β/deg	87.82(2)	93.73(3)
γ/deg	88.58(3)	104.32(3)
V/Å^3	2435.8(13)	2288.9(8)
Z	2	2
ρ_{calc}/g cm^{-3}	1.236	1.279
Radiation	Mo-Kα (λ = 0.71073 Å)	Mo-Kα (λ = 0.71073 Å)
θ/2θ Scanning range/deg	2—50	2—50
Number of measured reflections	8373	8088
Number of reflections with $I > 4\sigma$	4894	6074
Weighting scheme	$w^{-1} = \sigma^{-2}(F) + 0.0048F^2$	$w^{-1} = \sigma^{-2}(F) + 0.0004F^2$
R	0.044	0.030
R_w	0.058	0.039

tively) and the O(1)—Cu(1)—O(2) bond angle (79.9°) have values typical of *o*-semiquinone complexes of metals.[14] The structure of the ferrocenyl fragment of the dppfc ligand is similar to those observed in the reported copper(I) complexes with this ligand.[15,16] The Cu—Fe distance is 4.053 Å.

Table 3. Bond lengths in complex **3**

Bond	d/Å	Bond	d/Å
Cu(1)—P(1)	2.222(1)	Cu(1)—P(2)	2.222(1)
Cu(1)—O(1)	2.029(3)	Cu(1)—O(2)	2.036(3)
P(1)—C(1)	1.827(5)	P(1)—C(7)	1.829(5)
P(1)—C(35)	1.840(4)	P(2)—C(13)	1.835(5)
P(2)—C(19)	1.822(4)	P(2)—C(25)	1.842(4)
O(1)—C(45)	1.284(5)	O(2)—C(58)	1.282(4)
C(1)—C(2)	1.375(7)	C(1)—C(6)	1.382(7)
C(2)—C(3)	1.36(1)	C(3)—C(4)	1.39(1)
C(4)—C(5)	1.34(1)	C(5)—C(6)	1.387(8)
C(7)—C(8)	1.362(7)	C(7)—C(12)	1.380(8)
C(8)—C(9)	1.399(8)	C(9)—C(10)	1.359(10)
C(10)—C(11)	1.339(9)	C(11)—C(12)	1.393(9)
C(13)—C(14)	1.356(6)	C(13)—C(18)	1.383(6)
C(14)—C(15)	1.398(9)	C(15)—C(16)	1.350(10)
C(16)—C(17)	1.347(7)	C(17)—C(18)	1.370(8)
C(19)—C(20)	1.376(7)	C(19)—C(24)	1.377(6)
C(20)—C(21)	1.375(8)	C(21)—C(22)	1.363(8)
C(22)—C(23)	1.37(1)	C(23)—C(24)	1.402(8)
C(25)—C(26)	1.412(6)	C(25)—C(34)	1.383(6)
C(26)—C(27)	1.358(7)	C(27)—C(28)	1.405(7)
C(28)—C(29)	1.428(7)	C(28)—C(33)	1.401(6)
C(29)—C(30)	1.351(9)	C(30)—C(31)	1.400(8)
C(31)—C(32)	1.342(7)	C(32)—C(33)	1.416(6)
C(33)—C(34)	1.445(6)	C(34)—C(44)	1.505(5)
C(35)—C(36)	1.403(6)	C(35)—C(44)	1.381(5)
C(36)—C(37)	1.363(6)	C(37)—C(38)	1.406(7)
C(38)—C(39)	1.409(6)	C(38)—C(43)	1.410(6)
C(39)—C(40)	1.358(8)	C(40)—C(41)	1.397(8)
C(41)—C(43)	1.377(6)	C(43)—C(44)	1.448(5)
C(45)—C(46)	1.424(5)	C(45)—C(58)	1.474(6)
C(46)—C(47)	1.532(6)	C(46)—C(51)	1.364(6)
C(47)—C(48)	1.541(6)	C(47)—C(49)	1.524(7)
C(47)—C(50)	1.517(8)	C(51)—C(52)	1.422(7)
C(52)—C(53)	1.361(6)	C(53)—C(54)	1.527(6)
C(53)—C(58)	1.426(6)	C(54)—C(55)	1.521(8)
C(54)—C(56)	1.516(6)	C(54)—C(57)	1.532(8)

It is known[4] that in solutions four-coordinate *o*-semiquinone complexes of copper(I) with the triphenylphosphine and other neutral ligands dissociate to form the corresponding three-coordinate complex and the neutral ligand.

$$(PPh_3)_2Cu(DBSQ) \rightleftharpoons (PPh_3)Cu(DBSQ) + PPh_3. \quad (2)$$

Equilibrium (2) is particularly noticeable in dilute ($C \leq 1 \cdot 10^{-4}$ mol L) solutions whose ESR spectra are superpositions of the spectra of three- and four-coordinate complexes. This equilibrium reaction is also the key stage in the course of replacement of neutral ligands in the coordination sphere of *o*-semiquinone complexes of copper(I) by alternative ligands. Reaction (2) also complicates the synthesis of mononuclear bis(phosphine) complexes of copper(I) with di-*o*-quinones due to interactions of the *o*-quinone groups with free PPh_3 molecules that are present in solutions.

We examined the possibility of the change of the mode of coordination of the diphosphine ligand from bidentate to monodentate and studied the replacement

reactions of neutral ligands in the coordination sphere of complexes **1**—**4** by ESR spectroscopy.

It was found that three-coordinate complexes with the monodentate diphosphine ligand were not formed in dilute toluene solutions of complexes **1**—**4** ($C = 5 \cdot 10^{-5}$ mol L^{-1}) upon heating up to 380 K. Under the same conditions, the $(PPh_3)_2Cu(DBSQ)$ complex in a solution partially (~70%) dissociated.

The reactions of 2,6-dimethylphenylisonitrile (RNC) and the corresponding diphosphine were used as the test reactions that characterize the stability of the complexes in the replacement reactions of neutral ligands. It is

Table 4. Bond angles in complex **3**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
P(1)—Cu(1)—P(2)	102.0(1)	C(27)—C(28)—C(33)	118.8(4)	P(1)—Cu(1)—O(2)	122.0(1)	C(29)—C(28)—C(33)	119.4(4)
P(2)—Cu(1)—O(1)	118.4(1)	C(28)—C(29)—C(30)	120.0(5)	O(1)—Cu(1)—O(2)	80.4(1)	C(29)—C(30)—C(31)	120.5(6)
P(2)—Cu(1)—O(2)	115.7(1)	C(30)—C(31)—C(32)	120.5(5)	Cu(1)—P(1)—C(7)	113.8(2)	C(31)—C(32)—C(33)	121.5(4)
Cu(1)—P(1)—C(1)	115.3(2)	C(28)—C(33)—C(32)	118.0(4)	Cu(1)—P(1)—C(35)	111.7(1)	C(28)—C(33)—C(34)	119.8(4)
C(1)—P(1)—C(7)	104.5(2)	C(32)—C(33)—C(34)	122.1(4)	C(7)—P(1)—C(35)	105.6(2)	C(25)—C(34)—C(33)	119.2(3)
C(1)—P(1)—C(35)	105.0(2)	C(25)—C(34)—C(44)	123.5(4)	Cu(1)—P(2)—C(19)	114.6(2)	C(33)—C(34)—C(44)	117.3(3)
Cu(1)—P(2)—C(13)	118.1(1)	P(1)—C(35)—C(36)	118.6(3)	Cu(1)—P(2)—C(25)	106.4(1)	P(1)—C(35)—C(44)	121.4(3)
C(13)—P(2)—C(19)	103.8(2)	C(36)—C(35)—C(44)	119.7(3)	C(19)—P(2)—C(25)	109.4(2)	C(35)—C(36)—C(37)	121.5(4)
C(13)—P(2)—C(25)	103.9(2)	C(36)—C(37)—C(38)	121.2(4)	Cu(1)—O(2)—C(58)	112.9(2)	C(37)—C(38)—C(39)	121.6(4)
Cu(1)—O(1)—C(45)	112.9(2)	C(37)—C(38)—C(43)	118.6(4)	P(1)—C(1)—C(6)	121.8(3)	C(39)—C(38)—C(43)	119.8(4)
P(1)—C(1)—C(2)	118.0(4)	C(38)—C(39)—C(40)	120.5(5)	C(1)—C(2)—C(3)	119.6(6)	C(39)—C(40)—C(41)	120.4(5)
C(2)—C(1)—C(6)	120.2(5)	C(40)—C(41)—C(43)	120.0(5)	C(3)—C(4)—C(5)	121.2(7)	C(41)—C(43)—C(43)	121.0(4)
C(2)—C(3)—C(4)	119.7(7)	C(38)—C(43)—C(43)	118.2(3)	C(1)—C(6)—C(5)	120.1(5)	C(38)—C(43)—C(44)	119.6(4)
C(4)—C(5)—C(6)	119.2(7)	C(43)—C(43)—C(44)	122.2(4)	P(1)—C(7)—C(12)	124.6(4)	C(34)—C(44)—C(35)	123.4(3)
P(1)—C(7)—C(8)	117.4(4)	C(34)—C(44)—C(43)	117.0(3)	C(7)—C(8)—C(9)	121.2(6)	C(35)—C(44)—C(43)	119.4(3)
C(8)—C(7)—C(12)	117.8(5)	O(1)—C(45)—C(46)	122.6(4)	C(9)—C(10)—C(11)	120.0(6)	O(1)—C(45)—C(58)	116.8(3)
C(8)—C(9)—C(10)	119.7(6)	C(46)—C(45)—C(58)	120.6(4)	C(7)—C(12)—C(11)	120.6(6)	C(45)—C(46)—C(47)	121.1(4)
C(10)—C(11)—C(12)	120.6(6)	C(45)—C(46)—C(51)	116.1(4)	P(2)—C(13)—C(18)	124.9(3)	C(47)—C(46)—C(51)	122.7(3)
P(2)—C(13)—C(14)	116.6(4)	C(46)—C(47)—C(48)	111.5(4)	C(13)—C(14)—C(15)	120.2(5)	C(46)—C(47)—C(49)	109.3(4)
C(14)—C(13)—C(18)	118.4(4)	C(48)—C(47)—C(49)	107.1(4)	C(15)—C(16)—C(17)	119.0(6)	C(46)—C(47)—C(50)	110.7(4)
C(14)—C(15)—C(16)	120.7(5)	C(48)—C(47)—C(50)	107.6(4)	C(13)—C(18)—C(17)	120.2(4)	C(49)—C(47)—C(50)	110.7(4)
C(16)—C(17)—C(18)	121.5(5)	C(46)—C(51)—C(52)	123.5(4)	P(2)—C(19)—C(24)	124.1(4)	C(51)—C(52)—C(53)	122.9(4)
P(2)—C(19)—C(20)	116.3(3)	C(52)—C(53)—C(54)	123.1(4)	C(19)—C(20)—C(21)	121.0(5)	C(52)—C(53)—C(58)	116.7(4)
C(20)—C(19)—C(24)	119.6(4)	C(54)—C(53)—C(58)	120.2(4)	C(21)—C(22)—C(23)	121.2(6)	C(53)—C(54)—C(55)	110.0(4)
C(20)—C(21)—C(22)	119.3(6)	C(53)—C(54)—C(56)	110.6(4)	C(19)—C(24)—C(23)	119.4(5)	C(55)—C(54)—C(56)	109.5(4)
C(22)—C(23)—C(24)	119.4(5)	C(53)—C(54)—C(57)	111.5(4)	P(2)—C(25)—C(34)	122.7(3)	C(55)—C(54)—C(57)	107.7(4)
P(2)—C(25)—C(26)	116.6(3)	C(56)—C(54)—C(57)	107.5(5)	C(25)—C(26)—C(27)	120.9(4)	O(2)—C(58)—C(45)	116.5(3)
C(26)—C(25)—C(34)	119.8(4)	O(2)—C(58)—C(53)	123.4(4)	C(27)—C(28)—C(29)	121.8(4)	C(45)—C(58)—C(53)	120.1(3)
C(26)—C(27)—C(28)	121.5(4)	P(1)—Cu(1)—O(1)	118.9(1)				

Table 5. Bond lengths in complex **4**

Bond	d/Å	Bond	d/Å	Bond	d/Å	Bond	d/Å
Cu(1)—P(1)	2.218(1)	Cu(1)—P(2)	2.238(1)	C(121)—C(124)	1.529(6)	C(13)—C(14)	1.408(6)
Cu(1)—O(1)	2.028(2)	Cu(1)—O(2)	2.070(2)	C(14)—C(15)	1.365(4)	C(15)—C(151)	1.527(5)
Fe(1)—C(1)	2.041(2)	Fe(1)—C(2)	2.033(3)	C(15)—C(16)	1.443(4)	C(151)—C(152)	1.532(6)
Fe(1)—C(3)	2.056(4)	Fe(1)—C(4)	2.050(3)	C(151)—C(153)	1.532(4)	C(151)—C(154)	1.527(5)
Fe(1)—C(5)	2.046(2)	Fe(1)—C(6)	2.039(2)	C(17)—C(18)	1.384(5)	C(17)—C(22)	1.389(3)
Fe(1)—C(7)	2.036(3)	Fe(1)—C(8)	2.060(4)	C(18)—C(19)	1.390(6)	C(19)—C(20)	1.370(5)
Fe(1)—C(9)	2.048(3)	Fe(1)—C(10)	2.042(2)	C(20)—C(21)	1.379(6)	C(21)—C(22)	1.383(6)
P(1)—C(6)	1.815(3)	P(1)—C(17)	1.832(3)	C(23)—C(24)	1.377(4)	C(23)—C(28)	1.388(4)
P(1)—C(23)	1.825(3)	P(2)—C(1)	1.801(3)	C(24)—C(25)	1.395(5)	C(25)—C(26)	1.365(5)
P(2)—C(29)	1.831(3)	P(2)—C(35)	1.823(2)	C(26)—C(27)	1.372(6)	C(27)—C(28)	1.373(4)
O(1)—C(11)	1.277(3)	O(2)—C(16)	1.273(3)	C(29)—C(30)	1.391(3)	C(29)—C(34)	1.382(5)
C(1)—C(2)	1.428(5)	C(1)—C(5)	1.431(4)	C(30)—C(31)	1.394(7)	C(31)—C(32)	1.363(7)
C(2)—C(3)	1.416(5)	C(3)—C(4)	1.408(6)	C(32)—C(33)	1.368(5)	C(33)—C(34)	1.389(7)
C(4)—C(5)	1.403(5)	C(6)—C(7)	1.439(4)	C(35)—C(36)	1.378(5)	C(35)—C(40)	1.381(4)
C(6)—C(10)	1.418(4)	C(7)—C(8)	1.410(4)	C(36)—C(37)	1.393(4)	C(37)—C(38)	1.363(5)
C(8)—C(9)	1.407(5)	C(9)—C(10)	1.416(5)	C(38)—C(39)	1.373(6)	C(39)—C(40)	1.381(4)
C(11)—C(12)	1.431(4)	C(11)—C(16)	1.476(4)	C(1S)—C(2S)	1.51(2)	C(1S)—C(1SA)	1.43(2)
C(12)—C(121)	1.533(5)	C(12)—C(13)	1.364(5)	C(2S)—C(3S)	1.49(2)		
C(121)—C(122)	1.544(6)	C(121)—C(123)	1.530(4)				

Table 6. Bond angles in complex **4**

Angle	ω/deg	Angle	ω/deg	Angle	ω/deg
P(1)—Cu(1)—P(2)	112.9(1)	Cu(1)—P(1)—C(23)	116.0(1)	C(12)—C(121)—C(123)	110.2(3)
P(1)—Cu(1)—O(1)	120.4(1)	C(6)—P(1)—C(23)	102.3(1)	C(122)—C(121)—C(123)	106.8(3)
P(2)—Cu(1)—O(1)	113.3(1)	C(17)—P(1)—C(23)	105.2(1)	C(12)—C(121)—C(124)	109.0(3)
P(1)—Cu(1)—O(2)	119.6(1)	Cu(1)—P(2)—C(1)	113.4(1)	C(122)—C(121)—C(124)	108.8(4)
P(2)—Cu(1)—O(2)	106.2(1)	Cu(1)—P(2)—C(29)	118.2(1)	C(123)—C(121)—C(124)	110.9(3)
O(1)—Cu(1)—O(2)	79.9(1)	C(1)—P(2)—C(29)	104.3(1)	C(12)—C(13)—C(14)	123.4(3)
C(1)—Fe(1)—C(2)	41.0(1)	Cu(1)—P(2)—C(35)	112.7(1)	C(13)—C(14)—C(15)	123.5(3)
C(1)—Fe(1)—C(3)	68.4(1)	C(1)—P(2)—C(35)	104.4(1)	C(14)—C(15)—C(151)	123.5(3)
C(2)—Fe(1)—C(3)	40.5(1)	C(29)—P(2)—C(35)	102.4(1)	C(14)—C(15)—C(16)	116.4(3)
C(1)—Fe(1)—C(4)	68.3(1)	Cu(1)—O(1)—C(11)	113.8(2)	C(151)—C(15)—C(16)	120.2(2)
C(2)—Fe(1)—C(4)	68.0(1)	Cu(1)—O(2)—C(16)	112.3(2)	C(15)—C(151)—C(152)	111.5(3)
C(3)—Fe(1)—C(4)	40.1(2)	Fe(1)—C(1)—P(2)	122.4(1)	C(15)—C(151)—C(153)	109.6(3)
C(1)—Fe(1)—C(5)	41.0(1)	Fe(1)—C(1)—C(2)	69.2(1)	C(152)—C(151)—C(153)	106.8(3)
C(2)—Fe(1)—C(5)	68.5(1)	P(2)—C(1)—C(2)	122.1(2)	C(15)—C(151)—C(154)	110.4(3)
C(3)—Fe(1)—C(5)	67.7(1)	Fe(1)—C(1)—C(5)	69.7(1)	C(152)—C(151)—C(154)	108.3(3)
C(4)—Fe(1)—C(5)	40.1(1)	P(2)—C(1)—C(5)	130.9(3)	C(153)—C(151)—C(154)	110.2(3)
C(1)—Fe(1)—C(6)	113.6(1)	C(2)—C(1)—C(5)	106.8(3)	O(2)—C(16)—C(11)	117.1(2)
C(2)—Fe(1)—C(6)	109.6(1)	Fe(1)—C(2)—C(1)	69.8(2)	O(2)—C(16)—C(15)	123.1(3)
C(3)—Fe(1)—C(6)	34.8(1)	Fe(1)—C(2)—C(3)	70.6(2)	C(11)—C(16)—C(15)	119.7(2)
C(4)—Fe(1)—C(6)	174.2(1)	C(1)—C(2)—C(3)	108.2(3)	P(1)—C(17)—C(18)	117.6(2)
C(5)—Fe(1)—C(6)	144.8(1)	Fe(1)—C(3)—C(2)	68.9(2)	P(1)—C(17)—C(22)	123.1(3)
C(1)—Fe(1)—C(7)	110.1(1)	Fe(1)—C(3)—C(4)	69.7(2)	C(18)—C(17)—C(22)	119.2(3)
C(2)—Fe(1)—C(7)	135.7(1)	C(2)—C(3)—C(4)	107.9(3)	C(17)—C(18)—C(19)	120.0(3)
C(3)—Fe(1)—C(7)	175.5(1)	Fe(1)—C(4)—C(3)	70.2(2)	C(18)—C(19)—C(20)	120.2(4)
C(4)—Fe(1)—C(7)	143.9(1)	Fe(1)—C(4)—C(5)	69.8(2)	C(19)—C(20)—C(21)	120.3(4)
C(5)—Fe(1)—C(7)	114.3(1)	C(3)—C(4)—C(5)	108.7(3)	C(20)—C(21)—C(22)	119.7(3)
C(6)—Fe(1)—C(7)	41.4(1)	Fe(1)—C(5)—C(1)	69.3(1)	C(17)—C(22)—C(21)	120.5(3)
C(1)—Fe(1)—C(8)	135.2(1)	Fe(1)—C(5)—C(4)	70.1(2)	P(1)—C(23)—C(24)	117.5(2)
C(2)—Fe(1)—C(8)	175.3(1)	C(1)—C(5)—C(4)	108.3(3)	P(1)—C(23)—C(28)	123.5(2)
C(3)—Fe(1)—C(8)	143.7(1)	Fe(1)—C(6)—P(1)	123.7(1)	C(24)—C(23)—C(28)	118.9(3)
C(4)—Fe(1)—C(8)	114.1(1)	Fe(1)—C(6)—C(7)	69.2(1)	C(23)—C(24)—C(25)	120.2(3)
C(5)—Fe(1)—C(8)	110.3(1)	P(1)—C(6)—C(7)	122.6(2)	C(24)—C(25)—C(26)	119.7(4)
C(6)—Fe(1)—C(8)	68.7(1)	Fe(1)—C(6)—C(10)	69.8(1)	C(25)—C(26)—C(27)	120.6(3)
C(7)—Fe(1)—C(8)	40.3(1)	P(1)—C(6)—C(10)	130.8(2)	C(26)—C(27)—C(28)	119.9(3)
C(1)—Fe(1)—C(9)	174.5(1)	C(7)—C(6)—C(10)	106.6(3)	C(23)—C(28)—C(27)	120.6(3)
C(2)—Fe(1)—C(9)	143.9(1)	Fe(1)—C(7)—C(6)	69.4(2)	P(2)—C(29)—C(30)	121.8(3)
C(3)—Fe(1)—C(9)	114.0(1)	Fe(1)—C(7)—C(8)	70.8(2)	P(2)—C(29)—C(34)	118.8(2)
C(4)—Fe(1)—C(9)	110.1(1)	C(6)—C(7)—C(8)	108.5(3)	C(30)—C(29)—C(34)	119.4(3)
C(5)—Fe(1)—C(9)	134.5(1)	Fe(1)—C(8)—C(7)	68.9(2)	C(29)—C(30)—C(31)	119.8(3)
C(6)—Fe(1)—C(9)	68.5(1)	Fe(1)—C(8)—C(9)	69.5(2)	C(30)—C(31)—C(32)	120.0(3)
C(7)—Fe(1)—C(9)	67.8(1)	C(7)—C(8)—C(9)	107.9(3)	C(31)—C(32)—C(33)	120.6(5)
C(8)—Fe(1)—C(9)	40.0(1)	Fe(1)—C(9)—C(8)	70.4(2)	C(32)—C(33)—C(34)	120.2(4)
C(1)—Fe(1)—C(10)	144.2(1)	Fe(1)—C(9)—C(10)	69.5(2)	C(29)—C(34)—C(33)	120.0(3)
C(2)—Fe(1)—C(10)	113.8(1)	C(8)—C(9)—C(10)	108.5(3)	P(2)—C(35)—C(36)	124.0(2)
C(3)—Fe(1)—C(10)	110.1(1)	Fe(1)—C(10)—C(6)	69.6(1)	P(2)—C(35)—C(40)	117.0(2)
C(4)—Fe(1)—C(10)	134.8(1)	Fe(1)—C(10)—C(9)	70.0(1)	C(36)—C(35)—C(40)	118.8(3)
C(5)—Fe(1)—C(10)	174.0(1)	C(6)—C(10)—C(9)	108.5(3)	C(35)—C(36)—C(37)	119.5(3)
C(6)—Fe(1)—C(10)	40.7(1)	O(1)—C(11)—C(12)	123.1(3)	C(36)—C(37)—C(38)	121.1(4)
C(7)—Fe(1)—C(10)	68.3(1)	O(1)—C(11)—C(16)	116.7(2)	C(37)—C(38)—C(39)	119.7(3)
C(8)—Fe(1)—C(10)	67.9(1)	C(12)—C(11)—C(16)	120.2(2)	C(38)—C(39)—C(40)	119.6(3)
C(9)—Fe(1)—C(10)	40.5(1)	C(11)—C(12)—C(121)	119.9(3)	C(35)—C(40)—C(39)	121.3(3)
Cu(1)—P(1)—C(6)	115.2(1)	C(11)—C(12)—C(13)	116.6(3)	C(2S)—C(1S)—C(1SA)	117.8(9)
Cu(1)—P(1)—C(17)	114.3(1)	C(121)—C(12)—C(13)	123.5(3)	C(1S)—C(2S)—C(3S)	117.3(9)
C(6)—P(1)—C(17)	102.2(1)	C(12)—C(121)—C(122)	111.1(3)		

known[4] that in the case of bis(phosphine) semiquinone complexes of copper(I), replacement (reaction (3)) occurs in stages and both mixed-ligand and completely replaced complexes, which exist in the equilibrium with the initial complex, can be observed in solutions by ESR spectroscopy.

$$(PPh_3)_2Cu(DBSQ) + RNC \rightleftharpoons (PPh_3)(RNC)Cu(DBSQ) + PPh_3. \quad (3a)$$

$$(PPh_3)(RNC)Cu(DBSQ) + RNC \rightleftharpoons (RNC)_2Cu(DBSQ) + PPh_3. \quad (3b)$$

Table 7. Atomic coordinates ($\times 10^4$) and equivalent temperature factors ($\times 10^3$) for complex **3**

Atom	*x*	*y*	*z*	U_{iso}
Cu(1)	3244(1)	492(1)	7274(1)	45(1)
P(1)	3039(1)	−1120(1)	6922(1)	41(1)
P(2)	2441(1)	37(1)	8396(1)	40(1)
O(1)	2720(2)	1991(2)	6601(1)	44(1)
O(2)	4854(3)	1333(2)	7147(1)	48(1)
C(1)	1583(4)	−1272(4)	6522(2)	49(2)
C(2)	887(6)	−305(5)	6277(3)	82(3)
C(3)	−204(8)	−389(9)	5955(5)	131(5)
C(4)	−587(8)	−1446(9)	5891(5)	137(5)
C(5)	65(6)	−2405(7)	6155(3)	87(3)
C(6)	1172(4)	−2323(4)	6470(3)	58(2)
C(7)	4187(4)	−1330(4)	6241(2)	50(2)
C(8)	5247(5)	−738(5)	6191(3)	72(2)
C(9)	6148(6)	−810(6)	5665(4)	92(3)
C(10)	5957(6)	−1436(5)	5171(3)	85(3)
C(11)	4926(7)	−2025(5)	5214(3)	92(3)
C(12)	4018(6)	−1958(5)	5738(3)	83(3)
C(13)	1856(4)	1199(3)	8790(2)	46(2)
C(14)	1919(7)	2272(4)	8358(3)	90(3)
C(15)	1481(9)	3210(5)	8614(4)	119(4)
C(16)	1011(6)	3048(5)	9302(4)	88(3)
C(17)	976(6)	1987(5)	9734(3)	80(3)
C(18)	1385(5)	1061(4)	9492(3)	68(2)
C(19)	3459(4)	−771(3)	9076(2)	49(2)
C(20)	4692(5)	−620(4)	8920(3)	67(2)
C(21)	5558(6)	−1116(5)	9418(4)	92(3)
C(22)	5159(8)	−1792(6)	10069(4)	91(3)
C(23)	3949(9)	−1994(5)	10233(3)	84(3)
C(24)	3078(6)	−1472(4)	9727(3)	62(2)
C(25)	1081(3)	−819(3)	8365(2)	37(1)
C(26)	−61(4)	−243(4)	8320(2)	50(2)
C(27)	−1083(5)	−744(4)	8185(3)	60(2)
C(28)	−1057(4)	−1863(4)	8092(2)	50(2)
C(29)	−2127(5)	−2410(6)	7945(3)	72(2)
C(30)	−2070(6)	−3473(6)	7860(3)	82(3)
C(31)	−962(5)	−4090(5)	7920(3)	72(2)
C(32)	67(5)	−3598(4)	8053(3)	53(2)
C(33)	58(4)	−2466(3)	8143(2)	42(1)
C(34)	1157(3)	−1916(3)	8266(2)	36(1)
C(35)	3169(4)	−2387(3)	7686(2)	40(1)
C(36)	4204(4)	−3101(4)	7708(3)	58(2)
C(37)	4399(5)	−4000(4)	8284(3)	68(2)
C(38)	3593(4)	−4228(4)	8892(3)	58(2)
C(39)	3800(6)	−5139(4)	9502(3)	75(2)
C(40)	3009(6)	−5346(5)	10080(3)	82(2)
C(41)	1974(6)	−4656(4)	10081(3)	72(2)
C(42)	1740(5)	−3763(4)	9496(2)	57(2)
C(43)	2544(4)	−3521(3)	8886(2)	42(1)
C(44)	2339(3)	−2580(3)	8265(2)	38(1)
C(45)	3561(4)	2742(3)	6477(2)	39(1)
C(46)	3365(4)	3884(3)	6064(2)	41(1)
C(47)	2121(4)	4280(3)	5749(2)	50(2)
C(48)	2136(6)	5540(4)	5326(3)	67(2)
C(49)	1164(6)	4190(6)	6368(4)	74(2)
C(50)	1763(7)	3576(5)	5228(4)	75(3)
C(51)	4335(4)	4593(4)	5983(3)	55(2)
C(52)	5491(5)	4244(4)	6286(3)	57(2)
C(53)	5729(4)	3166(4)	6684(2)	47(2)
C(54)	6969(4)	2791(4)	7012(2)	59(2)
C(55)	7531(6)	1866(7)	6679(4)	81(3)
C(56)	6802(8)	2353(9)	7835(3)	93(3)
C(57)	7849(7)	3806(7)	6867(4)	92(3)
C(58)	4757(4)	2376(3)	6787(2)	39(1)

In none of the reactions of complexes **1**—**4** with RNC was the formation of the mixed-ligand complex detected. The ESR spectra of solutions of these complexes in toluene ($C = 2 \cdot 10^{-3}$ mol L^{-1}) in the presence of a tenfold excess of the isonitrile ligand are superpositions of the spectrum of the initial complex and the spectrum of the bis(isonitrile) complex $(RNC)_2Cu(DBSQ)$. The relative stability of complexes **1**—**4** in the replacement reactions of the ligands can be estimated by comparing the ratios of the intensities of the ESR spectra. Based on our results, the stability of the complexes increases in the series **4** < **1** ≈ **2** < **3**.

The difference in the behavior of complexes **1**—**4** was also observed in the reactions of these complexes with the corresponding diphosphines (reaction (4)). Only in the case of complexes **1** and **2** did bis(phosphine) complexes **1a** and **2a** appear in solutions when a fivefold excess of a diphosphine ligand was used.

$$\underset{\mathbf{1,\ 2}}{(\eta^2\text{-dppl})Cu(DBSQ)} + dppl \longrightarrow \underset{\mathbf{1a,\ 2a}}{(\eta^1\text{-dppl})_2Cu(DBSQ)} \quad (4)$$

Under similar conditions, analogous complexes **3a** and **4a** were not obtained.

Experimental

Thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate,[17] thallium 3,6-di-*tert*-butyl-4-methoxy-*o*-benzosemiquinolate,[17] and anhydrous CuCl [18] were synthesized according to known procedures. Commercial (Aldrich and Strem) bis(diphenylphosphino)methane, 1,2-bis(diphenylphosphino)ethane, 1,3-bis(diphenylphosphino)propane, 2,2′-bis(diphenylphosphino)-1,1′-binaphthyl, and 1,1′-bis(diphenylphosphino)ferrocene were used.

The IR spectra were recorded on a Specord M80 spectrometer. The electronic absorption spectra were measured on Specord M40 and SF-14 spectrometers. The ESR spectra were obtained on a Bruker ER 200D-SRC spectrometer equipped with an ER 4105DR double-mode resonator (operating at ~9.5 GHz) and an ER 4111 VT temperature-controlled block. The values of the g factor were determined with the use of diphenylpicrylhydrazyl as the standard.

[1,2-Bis(diphenylphosphino)ethane]-3,6-di-*tert*-butyl-1,2-benzosemiquinone copper(I) (1). A mixture of anhydrous copper(I) chloride (0.106 g, 1.06 mmol) and dppe (0.42 g, 1.06 mmol) was shaken with degassed THF (50 mL) in an evacuated tube until copper chloride was completely dissolved. A solution of thallium 3,6-di-*tert*-butyl-*o*-benzosemiquinolate, which was prepared from DBSQ (0.236 g, 1.06 mmol), was added to the resulting solution. The reaction mixture turned violet. The solvent was changed for toluene. The thallium chloride that precipitated was filtered off *in vacuo*. The volume of the filtrate was decreased by a factor of ~10. Hot hexane was added to the solution warmed to 60 °C. The reaction mixture was allowed to cool to ~20 °C. After 4—6 h, dark-violet crystals of **1** precipitated. The crystals were separated from the solution by filtration, washed with cold hexane, and dried *in vacuo*. The yield was 0.409 g (60%), m.p. 225—226 °C. Found (%): C, 70.00; H, 6.48; P, 8.96; Cu, 9.18. $C_{40}H_{44}CuO_2P_2$. Calculated (%): C, 70.43; H, 6.46; P, 9.10; Cu, 9.32. IR, ν/cm^{-1}: 495, 530, 700, 750, 960, 970, 1100, 1440, 1475. EAS (toluene), λ_{max}/nm: 544 (ε 1950), 664 (ε 3600).

Table 8. Atomic coordinates ($\times 10^4$) and equivalent temperature factors ($\times 10^3$) for complex **4**

Atom	*x*	*y*	*z*	U_{iso}
Cu(1)	1741(1)	2289(1)	3691(1)	37(1)
Fe(1)	−803(1)	2437(1)	5288(1)	37(1)
P(1)	1951(1)	3475(1)	5288(1)	35(1)
P(2)	−47(1)	1321(1)	3008(1)	33(1)
O(1)	2603(1)	2672(1)	2690(1)	42(1)
O(2)	2673(1)	1233(1)	3357(1)	39(1)
C(1)	−882(2)	1190(2)	3941(2)	37(1)
C(2)	−457(3)	1033(2)	4791(2)	43(1)
C(3)	−1287(3)	1028(3)	5410(3)	56(1)
C(4)	−2212(3)	1197(3)	4963(2)	57(1)
C(5)	−1979(2)	1290(2)	4064(2)	46(1)
C(6)	657(2)	3640(2)	5730(2)	38(1)
C(7)	−198(2)	3820(2)	5165(2)	40(1)
C(8)	−1107(3)	3872(2)	5691(2)	51(1)
C(9)	−842(3)	3716(3)	6567(2)	55(1)
C(10)	242(2)	3582(2)	6599(2)	47(1)
C(11)	3242(2)	2102(2)	2323(2)	36(1)
C(12)	3932(2)	2243(2)	1610(2)	41(1)
C(121)	3955(2)	3135(2)	1282(2)	52(1)
C(122)	4854(4)	3225(4)	615(4)	83(3)
C(123)	4261(3)	4196(3)	2222(3)	66(2)
C(124)	2806(4)	2902(4)	663(4)	77(2)
C(13)	4539(2)	1551(3)	1252(2)	51(1)
C(14)	4526(2)	740(2)	1562(2)	50(1)
C(15)	3913(2)	570(2)	2257(2)	38(1)
C(151)	3903(2)	−308(2)	2594(2)	47(1)
C(152)	4623(4)	−988(4)	2025(4)	76(2)
C(153)	2705(3)	−1045(3)	2341(3)	57(2)
C(154)	4358(3)	159(3)	3740(3)	66(2)
C(16)	3254(2)	1277(2)	2678(2)	34(1)
C(17)	2621(2)	3169(2)	6249(2)	41(1)
C(18)	2794(3)	2188(2)	5924(3)	57(1)
C(19)	3252(3)	1896(3)	6630(3)	75(2)
C(20)	3559(3)	2587(3)	7643(3)	71(2)
C(21)	3402(3)	3571(3)	7975(3)	62(2)
C(22)	2935(3)	3862(2)	7279(2)	50(1)
C(23)	2751(2)	4826(2)	5566(2)	37(1)
C(24)	3499(2)	4965(2)	4941(2)	48(1)
C(25)	4144(3)	5979(3)	5121(3)	62(2)
C(26)	4026(3)	6833(3)	5918(3)	62(2)
C(27)	3270(3)	6705(2)	6536(3)	59(1)
C(28)	2631(3)	5709(2)	6359(2)	48(1)
C(29)	−873(2)	1741(2)	2243(2)	38(1)
C(30)	−1886(2)	1071(3)	1599(2)	51(1)
C(31)	−2469(3)	1414(4)	1008(3)	68(2)
C(32)	−2057(4)	2410(4)	1075(3)	76(2)
C(33)	−1061(4)	3072(3)	1702(3)	68(2)
C(34)	−456(3)	2738(2)	2282(2)	50(1)
C(35)	−183(2)	−34(2)	2124(2)	36(1)
C(36)	−655(3)	−903(2)	2302(2)	50(1)
C(37)	−649(3)	−1899(3)	1610(3)	62(2)
C(38)	−193(3)	−2031(3)	754(3)	59(1)
C(39)	273(3)	−1170(3)	569(2)	58(1)
C(40)	286(3)	−177(2)	1259(2)	50(1)
C(1S)	9492(8)	4733(6)	−373(5)	146(5)
C(2S)	8399(12)	4794(8)	−5(9)	180(7)
C(3S)	7343(10)	4174(7)	−776(9)	176(6)

Complexes **2**—**4** were prepared analogously.

[1,3-Bis(diphenylphosphino)propane]-3,6-di-*tert*-butyl-1,2-benzosemiquinone copper(I) (2). The yield was 0.452 g (65%), m.p. 211—212 °C. Found (%): C, 70.27; H, 7.78; P, 8.75; Cu, 8.97. $C_{41}H_{46}CuO_2P_2$. Calculated (%): C, 70.74; H, 6.62; P, 8.91; Cu, 9.14. IR, ν/cm^{-1}: 440, 460, 505, 510, 705, 745, 760, 960, 970, 1040, 1115, 1440, 1470. EAS (toluene), λ_{max}/nm: 568 (ε 3060), 654 (ε 4100).

[2,2′-Bis(diphenylphosphino)-1,1′-binaphthyl]-3,6-di-*tert*-butyl-1,2-benzosemiquinone copper(I) (3). The yield was 0.543 g (60%), m.p. 278—279 °C. Found (%): C, 76.13; H, 6.25; P, 7.21; Cu, 7.39. $C_{58}H_{52}CuO_2P_2$. Calculated (%): C, 76.86; H, 5.74; P, 6.85; Cu, 7.01. IR, ν/cm^{-1}: 505, 700, 745, 775, 820, 960, 970, 1100, 1360, 1400, 1440, 1470. EAS (toluene), λ_{max}/nm: 538 (ε 3400), 670 (ε 4425).

[1,1′-Bis(diphenylphosphono)ferrocene]-3,6-di-*tert*-butyl-1,2-benzosemiquinone copper(I) (4). The yield was 0.572 g (65%), m.p. 221—222 °C. Found (%): C, 69.24; H, 5.96; P, 6.30; Cu, 6.42; Fe, 5.64. $C_{48}H_{48}CuFeO_2P_2$. Calculated (%): C, 68.78; H, 5.73; P, 7.40; Cu, 7.58; Fe, 6.69. IR, ν/cm^{-1}: 495, 530, 705, 760, 960, 975, 1450, 1480. EAS (toluene), λ_{max}/nm: 568 (ε 2900), 640 (ε 2650).

X-ray diffraction analysis of complexes 3 and 4. Single crystals of the complexes were glued to glass needles using epoxy resin in air and transferred on a diffractometer. The X-ray diffraction data sets were collected on automated four-circle Siemens P3/PC (for **3**) and Enraf Nonius CAD-4 (for **4**) diffractometers (θ/2θ scanning technique, λMo-Kα radiation, λ = 0.71073 Å) at ~20 °C. The unit cell parameters for both crystals were determined and refined using 24 equivalent reflections with 2θ < 24—28°. Three strong reflections with 0 < χ< 60° were used as the standards. In the course of data collection, no significant variation in these standards was observed, and therefore, corrections were not applied. The structures were solved by direct methods to reveal all nonhydrogen atoms. The positions of all hydrogen atoms were located from difference Fourier syntheses. All nonhydrogen atoms were refined anisotropically by the full-matrix least-squares method. The hydrogen atoms were refined isotropically. All calculations were carried out using the SHELXTL PLUS program package (PC version).[19] The crystallographic parameters of complexes **3** and **4** and selected details of the refinement are given in Table 2. The principal geometric characteristics of the molecules are listed in Tables 3—6. The atomic coordinates of complexes **3** and **4** are given in Tables 7 and 8, respectively.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 95-03-09455, 96-15-97520, and 98-03-32939) and by the International Center "Foundation for the Promotion of Advanced Studies in Nizhny Novgorod" (Grant 97-3-01). The spectral studies were carried out in the Analytical Center (G. A. Razuvaev Institute of Organometallic Chemistry, Russian Academy of Sciences) and were financially supported by the Russian Foundation for Basic Research (Project No. 96-03-40042g). X-ray diffraction analysis was performed in the Center of X-ray Diffraction Studies (A. N. Nesmeyanov Institute of Organoelement Compounds, Russian Academy of Sciences).

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Received June 8, 1998