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ESR INVESTIGATION OF THE SUBSTITUTION REACTIONS IN RHODIUM(I) COMPLEXES WITH SPIN-LABELED LIGANDS

V.I. NEVODCHIKOV, G.A. ABAKUMOV, V.K. CHERKASOV and G.A. RAZUVAEV *
Institute of Chemistry, USSR Academy of Sciences, Gorky (U.S.S.R.)

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Summary

A number of new spin-labelled Rh^I complexes containing both the 3,6-di-tert-butyl-*o*-benzosemiquinone (3,6-SQ) fragment and n- and π-donor ligands have been prepared. The tetracoordinate derivatives of the composition L_2Rh-(3,6-SQ), where L = CO, $P(OPh)_3$, L = 1/2 1,5-COD and the pentacoordinate complex $(PPh_3)_2$Rh(3,6-SQ)(CO) were isolated in individual state, the formation of other rhodium compounds was registered by ESR spectroscopy. The presence of an *o*-benzosemiquinolate ligand in the molecule with the unpaired electron located essentially on this fragment does not significantly influence on the reactivity of the metal ion in most cases; the n- and π-donor ligands exchange reactions studied by ESR confirm this fact. $(PPh_3)_2$Rh(3,6-SQ) has an abnormal distribution of spin density of the unpaired electron in the molecule, mostly located on the metal atom, this derivative bearing a close analogy to the rhodium(II) (d^7) complexes.

Some of the more general aspects of use of the "spin-label" method in the coordination chemistry of transition metals have been discussed previously [1]. At the present time the substituted *o*-benzosemiquinolates are the most suitable for use as spin-labelled ligands as:

1) Chelate complexes of *o*-semiquinones with transition metals are to be rather stable.

2) The unpaired electron is located essentially on the paramagnetic ligand, induces only a small perturbation of the energy of the metal ligand environment.

3) The small interaction of the unpaired electron with the metal orbitals is very sensitive both to the nature of ligands in the molecule and to the general spatial structure of the complex, and is seen as hyperfine structure of the ESR spectra.

The possibilities of spin-label ligands have been demonstrated for the example of the exchange reactions of n- and π-ligands in the *o*-semiquinolate-Cu^I complexes [2]. Analogously, we have studied some radical rhodium(I) derivatives in solution by the ESR method [3]. In the literature there are no another data regarding the preparation of *o*-semiquinolate-Rh^I complexes.

The present work deals with the synthesis of Rh^I *o*-benzosemiquinolate complexes and the investigation of substitution reactions occurring in the coordination sphere of the metal by ESR spectroscopy.

The complex $(CO)_2Rh(3,6\text{-}SQ)$ (I) was isolated from the reaction of $[(CO)_2RhCl]_2$ with thallium *o*-benzosemiquinolate in toluene. The ESR spectrum of this compound consists of a 1 : 2 : 1 triplet (splitting on two protons of semiquinolate ring). The solution of the complex shows thermochromism; as the temperature is reduced the colour of the solution changes from red-brown to green, the ESR signal disappearing simultaneously. Such behaviour is very likely to be due to association of the square planar molecules of the complex at the expense of Rh—Rh bond formation (analogous to the dicarbonylrhodium acetylacetonate [4]) with strong antiferromagnetic interaction of the semiquinolate ligands. The complex I enters into ligands exchange reactions with the majority of n- and π-donors. Figure 1 shows the general scheme of the reactions studied. The most characteristic reaction of complex I is the displacement one of the CO ligands to form mixed four-coordinate complexes of the type (3,6-SQ)RhCOL (II), where L = PPh_3, $P(OPh)_3$, $AsPh_3$. The ESR spectra hyperfine structure of these complexes has additional splitting in the ligand signals (Table 1), the hyperfine splitting constant of the L nucleus having a value

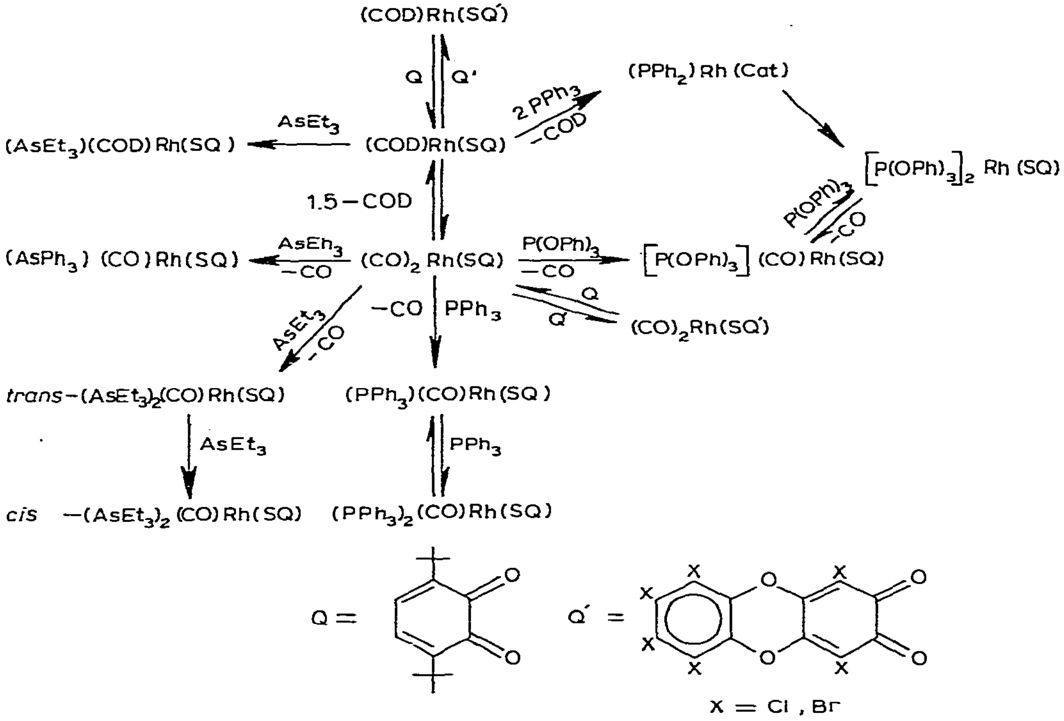


Fig. 1. The general scheme of the exchange reactions for Rh^I *o*-benzosemiquinolate complexes.

TABLE 1

ESR PARAMETERS OF THE COMPLEXES OBTAINED (G)

Complex	g	a_{HSQ}	a_{L^1}	a_{L^2}	a_{Rh}
$(CO)_2Rh(3,6\text{-}SQ)$	2.0020	3.2			
$P(OPh)_3CORh(3,6\text{-}SQ)$	2.0022	3.2	3.2		
$[P(OPh)_3]_2Rh(3,6\text{-}SQ)$	2.0039	3.2	3.2	3.2	
$PPh_3CORh(3,6\text{-}SQ)$	2.0045	3.2	3.2		
$(PPh_3)_2CORh(3,6\text{-}SQ)$	2.0011	3.2	17.0	17.0	1.6
$AsPh_3CORh(3,6\text{-}SQ)$	2.0058	3.4	3.4		
trans-$(AsEt_3)_2CORh(3,6\text{-}SQ)$	2.0025	3.2	17.1	17.1	
cis-$(AsEt_3)_2CORh(3,6\text{-}SQ)$	2.0006	3.2	8.6	2.6	2.6
$(1,5\text{-}COD)Rh(3,6\text{-}SQ)$	2.0039	3.2			
$(AsEt_3)(1,5\text{-}COD)Rh(3,6\text{-}SQ)$	2.0017	3.2	40.0		4.2

$\cong a_H$, corresponding to the square-planar geometry of the complex [2]. The action of two and more moles of donor ligand on the dicarbonyl complex I leads to different semiquinolate derivatives of monovalent rhodium, the latter's composition and structure depending on the ligand nature.

$P(OPh)_3$ displaces both carbonyl ligands from the coordination sphere of complex I to give the diphosphite derivative $[P(OPh)_3]_2Rh(3,6\text{-}SQ)$ (III). (ESR spectrum of III - quintet 1 : 4 : 6 : 4 : 1; splittings on two protons of SQ and two nuclei of ^{31}P, $a_H \cong a_P$.) This corresponds to four-coordinate planar complex. The compound III has been isolated for use in exchange reactions (eq. 1).

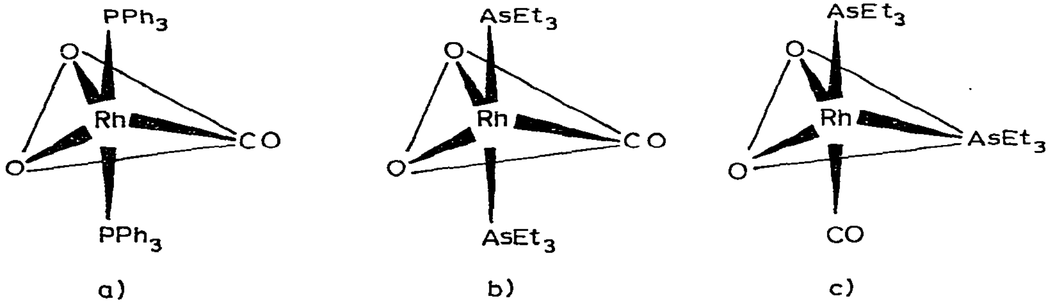
$$[P(OPh)_3]_2CORhCl + (3,6\text{-}SQ\text{-}Tl) \xrightarrow[-CO]{-TlCl} [P(OPh)_3]_2Rh(3,6\text{-}SQ) \qquad (1)$$

It should be noted that there is an equilibrium between the phosphitecarbonyl (II) and diphosphite (III) complexes, which readily shifts to the formation of III under lower CO concentration (eq. 2)

$$[P(OPh)_3]CORh(3,6\text{-}SQ) + P(OPh)_3 \rightleftharpoons [P(OPh)_3]_2Rh(3,6\text{-}SQ) + CO \qquad (2)$$

Both PPh_3 and $AsEt_3$ form pentacoordinate complexes of the type L_2CORh-(3,6-SQ) (IV) in the reaction with the dicarbonyl complex I.

In solution, $(PPh_3)_2CORh(3,6\text{-}SQ)$ (IV) is in equilibrium with the carbonylphosphine complex II, as was shown previously [3]. The position of the equilibrium depends on temperature and concentration. Low temperature favours the formation of V, which makes its isolation possible under low-temperature



a) b) c)

Fig. 2. The geometric configuration of o-benzosemiquinolate complexes IV, V and VI (a, b and c, respectively).

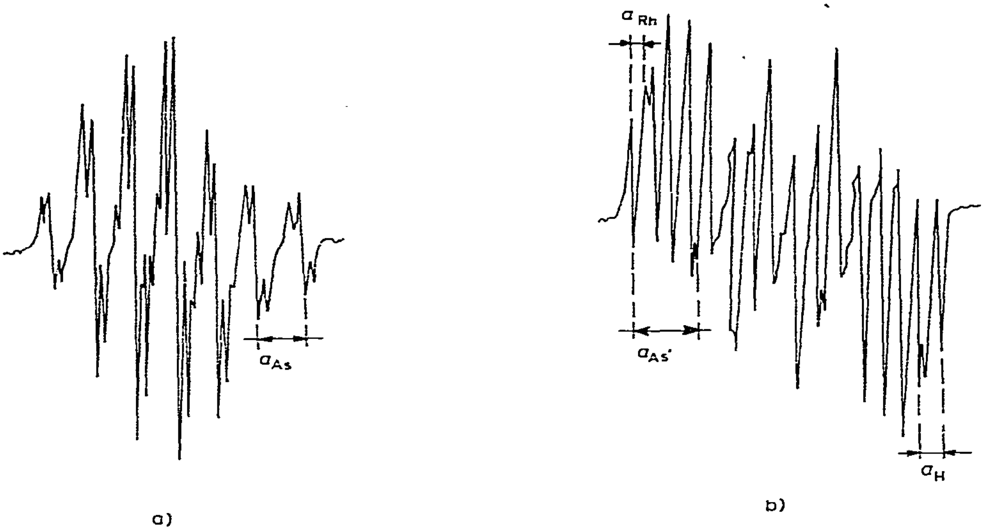


Fig. 3. ESR spectra of (3,6-SQ)Rh$(AsEt_3)_2$CO in toluene at room temperature; a) V, b) VI.

crystallization conditions. The ESR spectrum consists of a triplet of triplets of doublets (splitting on two ^{31}P nuclei, two protons of SQ and the Rh nucleus), $a_P >> a_H$. The large value of the phosphorous-31 hyperfine splitting (HFS) constant indicates that the phosphine ligands are situated out of the nodal plane of the molecular orbital occupied by the unpaired electron. Taking into account the geometry typical for pentacoordinate Rh^I complexes, the trigonal bipyramid geometry of IV can be pictured to be as is shown in Fig. 2a. This complex can be prepared by the exchange reaction of $(PPh_3)_2$CORhCl with 3,6-SQTl in toluene.

$(AsEt_3)_2$CORh(3,6-SQ) does not dissociate. However, as the ESR spectra indicate, the latter exists in two isomeric forms with different positions of the arsine ligands in relation to the SQ ligand. The isomer V primary formed rearranges in the presence of $AsEt_3$ to form the isomer VI. The ESR spectrum of V consists of a septet of triplets (there is splitting on two protons of SQ and two nuclei of ^{75}As, $I_{As} = 3/2$), $a_{As} >> a_H$ (Fig. 3), and points to a structure analogous to that of IV (Fig. 2b). The ESR spectrum of VI (Fig. 3), with splitting on two protons of SQ, two inequivalent ^{75}As nuclei and the Rh nucleus demonstates the inequivalent position of the arsine ligands in relation to SQ. In this complex one of the arsine groups is situated, as before, out of the plane of the semiquinolate ligand and the other group exchanges with the CO ligand and is in the nodal plane of the unpaired electron (Fig. 2c).

The dicarbonyl complex I reacts with 1,5-cyclooctadiene (COD) in THF to give an equilibrium mixture of the complexes (eq. 3); the equilibrium being shifted to the left in nonpolar solvents

$$(CO)_2Rh(3,6\text{-}SQ) + COD\text{-}1,5 \rightleftharpoons (COD\text{-}1,5)Rh(3,6\text{-}SQ) + 2\,CO \qquad (3)$$

The ESR spectrum of cyclooctadiene Rh^I *o*-semiquinolate consists of a triplet (splitting on two protons of SQ). The main method of preparation of VII is the exchange reaction between (COD-1,5)$RhCl_2$ and (3,6-SQ-Tl).

The 1,5-COD ligand in complex VII, as well as CO in complex I, is displaced by n-donor ligands to form a number of new Rh^{I} *o*-benzosemiquinolate derivatives. $P(OPh)_3$ reacts with VII along with the dicarbonyl complex I to form the previously described complex III.

The reaction of $AsEt_3$ is accomplished by the formation of a pentacoordinate complex. ESR spectrum: quartet of doublets of triplets (splitting on ^{75}As nucleus, Rh nucleus and two protons of SQ), a_{As} 75 = 40.0 G. The large value of ^{75}As HFS constant suggests that the complex has tetragonal pyramid structure, the arsine ligand being in its top. Thus, the overall formula of the complex is $AsEt_3Rh(1,5\text{-}COD)(3,6\text{-}SQ)$.

PPh_3, analogously to phosphite, displaces from complex II. The derivative formed according to the ESR spectrum differs from the other Rh^{I} complexes. The large value of $g = 2.017$, the large width of the absorption line (40—50 G) and the absence of hyperfine coupling with protons of the SQ ligand indicate that a considerable part of the spin density is located on the central atom. Some rhodium derivatives, $(MNT)_2Rh^{2-}$[5,6] and Cp_2Rh [7], which have been identified as d^7 complexes of Rh^{II} are known. The diphosphine complex obtained in the present work appears to take an intermediate position between d^8 complexes of Rh^{I} and d^7 complexes of Rh^{II}.

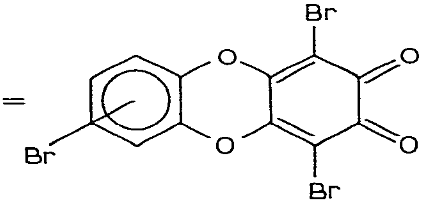
Phosphine ligands possessing poor acceptor and good donor properties induce redistribution of the electron density in such a manner that the structure of the SQ ligand approximates to the catecholate one and the spin density on the rhodium atom increases. Due to the difference in electronic structure of the rhodium(I) complexes I—VII from the derivative VIII we attribute the catecholate structure $(PPh_3)_2Rh(3,6\text{-}Cat)$ to the diphosphite compound VIII.

The replacement of the phosphine ligands in VIII by $P(OPh)_3$ and CO reduces the affectivity of the coupling between the metal *d* orbitals and the unpaired electron MO and lead to "pure" semiquinolate complexes of Rh^{I}: III and IV, respectively.

Some complexes of types I and II enter into substitution reactions not only with n- and π-donor ligands but with the *o*-semiquinolate fragment (eq. 4).

$$(3,6-SQ)RhL_2 \;+\; Q \;\rightleftharpoons\; SQRhL_2 \;+\; 3,6-Q\;, \qquad (4)$$

where Q =



SQ = corresponding semiquinolate , L = CO , ½ 1,5-COD

There is an equilibrium between the two semiquinolate complexes in the case of dicarbonyl complex I: temperature decrease shifting the equilibrium to the left. The ESR spectrum of $(CO)_2RhSQ$ consists of a singlet, $g = 2.0022$. The reaction of complex VII with perbromoxanthrenquinone-2,3 is completely shifted to the right. The ESR spectrum of the compound formed consists of a singlet, $g = 2.0042$.

Experimental

ESR spectra of the complexes described were registered on a PE-1301 radiospectrometer.

The Rh^I halides, $[(CO)_2RhCl]_2$, $[P(OPh)_3]_2CORhCl$, $(PPh_3)_2CORhCl$, $[(1,5\text{-}COD)RhCl]_2$, used for the synthesis of *o*-benzosemiquinolate complexes were prepared according to the known procedures [8,9,10,11].

$(CO)_2Rh(3,6\text{-}SQ)$

0.194 g (0.5×10^{-3} mol) of $[(CO)_2RhCl]_2$ in 30 ml of toluene was mixed with 0.424 g (10^{-3} mol) of (3,6-SQTl) in 20 ml of toluene in evacuated ampoules. As the reaction proceeded the solution colour became red-brown, and the TlCl precipitated out of solution. Toluene was removed after TlCl separation. The solid residue was recrystallized from hexane to give a dark brown precipitate of $(CO)_2Rh(3,6\text{-}SQ)$ Found: C, 50.71; H, 5.35; Rh, 27.37. Calcd. for $C_{16}H_{20}O_4Rh$: C, 50.65; H, 5.28; Rh, 27.17%.

$[P(OPh)_3]_2Rh(3,6\text{-}SQ)$

This derivative was synthesized by the above exchange reaction. During the reaction there was extensive gas evolution, and the solution colour became crimson. After TlCl and toluene removal, the solid residue was crystallized from hexane. Found: C, 64.40; H, 5.49; P, 6.21; Rh, 10.31. Calcd. for $C_{50}H_{50}O_8P_2Rh$: C, 63.63; H, 5.30; P, 6.5; Rh, 10.9%.

$(PPh_3)_2CORh(3,6\text{-}SQ)$

This was prepared according to above technique. The product crystallization was carried out from hexane at −80°C. Found: C, 68.9; H, 6.03; P, 7.0; Rh, 11.5. Calcd. for $C_{50}H_{50}O_2P_2Rh$; C, 70.0; H, 5.6; P, 7.1; Rh, 11.8%.

$(1,5\text{-}COD)Rh(3,6\text{-}SQ)$

This complex was obtained by the exchange reaction of the corresponding rhodium halide with 3,6-SQTl. The reaction took place in toluene in an evacuated ampoule, and the solution became an intense crimson of colour. The dark, finely crystalline product was crystallized from hexane. Found: C, 61.44; H, 7.75; Rh, 22.5. Calcd. for $C_{22}H_{32}O_2Rh$, C, 61.25; H, 7.42; Rh, 23.9%.

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