

**Palladium and Platinum Paramagnetic Complexes formed by Oxidation of Catecholate Derivatives of these Elements**

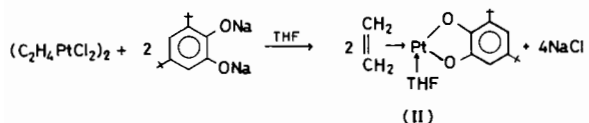
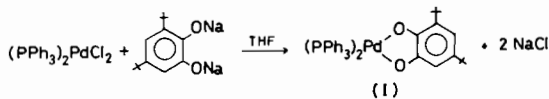
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Earlier we have shown, that the oxidation of platinum bistrisphenylphosphine complexes with catecholate ligands leads to the formation of paramagnetic derivatives unstable at room temperature, in which the unpaired electron is essentially located on *o*-semiquinolate ligand [1]. In the present work these oxidation reactions of catecholate derivatives have been studied using the palladium and platinum complexes.

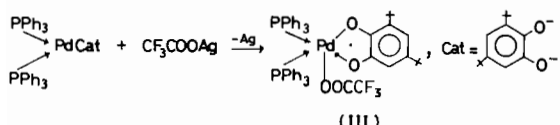
The initial catecholate derivatives of these elements have been obtained by the following reactions:



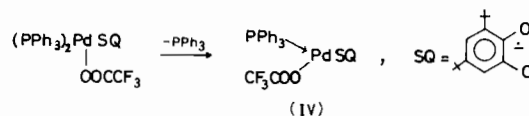
Bis(triphenylphosphine)palladium-3,5-di-tert-butyl catecholate represents itself diamagnetic blue-green finely crystalline substance, which is stable to the oxygen action both in solid state and in solution. On the contrary, tetrahydrofuranate of ethene-platinum-3,5-di-tert-butyl catecholate (diamagnetic red-brown substance) is quickly enough oxidized in solution to form paramagnetic derivative, whose structure will be discussed lower.

(PPh<sub>3</sub>)<sub>2</sub>PdCat interacts easily with such reagents as silver trifluoroacetate, copper(II) chloride, benzoyl peroxide and aroxil radical.

The reaction of bis(triphenylphosphine) palladium-3,5-di-tert-butylcatecholate with silver trifluoroacetate leads to the isolation of metallic silver and the formation of palladium paramagnetic derivative (III):

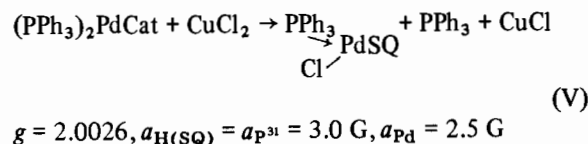


The ESR spectrum parameters of (III) indicate, that there is a pentacoordinative complex ( $g = 2.0031$ ,  $a_{H(SQ)} = 3.2$  G,  $a_{P^{31}} = 2.2$  G). In this derivative both phosphine ligands occupy the equivalent position in palladium coordination sphere and situate practically in the same plane as *o*-semiquinolate fragment. During the reaction proceeding the ESR spectrum of (I) is quickly changed by the ESR spectrum of another palladium semiquinolate complex with only a triphenylphosphine ligand:



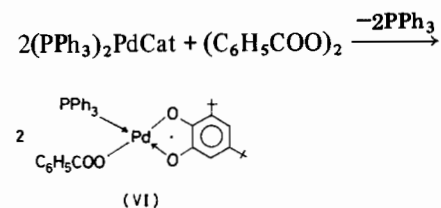
By analogy, we may assume, that the structure of (IV) approximates to the plane square. It should be noted, that in the case of analogous platinum complex [2] there is no derivative formation of the (IV) type.

Copper(II) chloride use as the oxidant leads only to the formation of square palladium complex (V):



In this case it is impossible to fix the intermediate pentacoordinative derivative of the (III) type.

The reaction of (PPh<sub>3</sub>)<sub>2</sub>PdCat with benzoyl peroxide in THF solution occurs immediately after reagents mixing, the ESR signal-triplet appearing. The analysis of ESR spectrum parameters allows us to treat this triplet belonging to the complex of the type (VI).



Stable radicals can be used as oxidants of palladium catecholate derivatives. Thus, the action of 2,4,6-tri-tert-butylphenoxil radical on (I) leads to the formation of palladium paramagnetic complex (VII) at the room temperature.

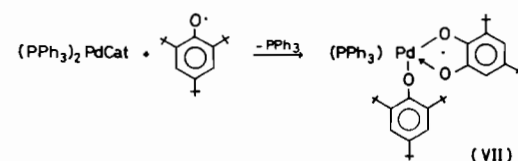
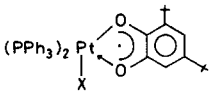
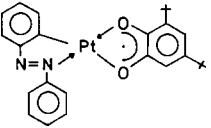
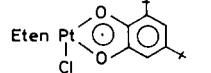


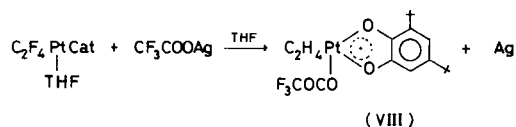
TABLE I. ESR Spectra Data of Platinum *o*-semiquinolate Complexes.

Complex	<i>g</i>	<sup>a</sup> H(SQ)	<sup>a</sup> Pt <sup>195</sup>	<sup>a</sup> P <sup>31</sup>
	1.9990	3.3	13.0	3.3
	1.9960	2.7	14.8	—
	2.0070	—	34	—

It should be particularly emphasized, that this reaction is unprecedented and shows that palladium catecholate complexes may be used as spin traps for fixation of free radicals with unpaired electron centered on heteroatom.

It is of interest, that  $(PPh_3)_2PtCat$  does not take part in the interaction with such free radicals.

The novel olefine platinum complex, tetrahydrofuranate etheneplatinum-3,5-di-tert-butylcatecholate, being firstly obtained in the present work, very easily enters into oxidation reactions in solution. Unlike other platinum catecholate derivatives its interaction with oxygen,  $CF_3COOAg$ ,  $CuCl_2$  leads to the formation of the stable paramagnetic product.

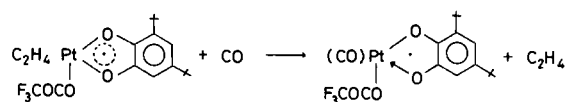


Attention is drawn to the ESR spectrum parameters of this novel platinum complex (Table I). There is a considerably large value of *g*-factor, the great constant of hyperfine splitting on platinum and the absence of hyperfine splitting constant on hydrogen atom of catecholate ring. For comparison, Table I shows the ESR spectra data of earlier obtained platinum complexes.

The proximity of hyperfine splitting (HFS) constants and *g*-factor in *o*-semiquinolate platinum derivatives with triphenylphosphine and arylazoaryl ligands [2, 3] to such values in alkali metals *o*-semiquinolates [4] allows us to treat these complexes as compounds in which the unpaired electron is essentially located on *o*-semiquinolate ligand. On the contrary, in the case of ethene platinum complex there is no such conformity between constants, the essential increase of spin density taking place on platinum atom.

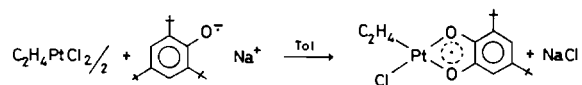
Thus the complexes obtained with *o*-quinone ligands (this term unites all possible cases of

*o*-quinone coordination with transition metal: in the form of neutral molecule, one-electron reduction form — *o*-semiquinone and two-electron reduction one — catecholate) clearly demonstrates the dependence of spin density distribution according to the nature of ligands surrounding. The reaction of (VIII) with CO confirms this fact:

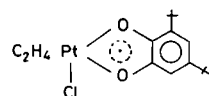


The displacement of ethene with CO in the complex (VIII) leads to a considerable change of ESR spectrum parameters and consequently to the redistribution of spin density as compared with (VIII). There is electron localization on *o*-semiquinone fragment in the carbonyl derivative (IX).

It should be noted, that the complex (VIII) can be prepared by the reaction of  $(C_2H_4PtCl_2)_2$  with 3,5-di-tert-butylbenzosemiquinolate of thallium in toluene solution.



It is of interest, that the interaction of



with triphenylphosphine and  $C_2H_4PtCat$  with  $PPh_3$

occurs differently. (II) reacts with  $PPh_3$  to liberate ethene and to form catecholate platinum complex  $(PPh_3)_2PtCat$ . (VIII) with  $PPh_3$  does not react.

## Experimental

### $(PPh_3)_2PdCat$

Disodium-3,5-di-tert-butylcatecholate in ether solution was added to suspension of  $(PPh_3)_2PdCl_2$  in benzene to give green solution. Addition of hexane precipitated blue-green crystals of bistrisphenylphosphinepalladium catecholate. *Anal.* Found: C, 70.36; H, 5.88; P, 7.00; Pd, 12.02%. Calcd. for  $C_{50}H_{50}O_2P_2Pd$ : C, 70.58; H, 5.88; P, 7.29; Pd, 12.42%.

### $C_2H_4Pt$ Cat | THF

$Na_2Cat$  in THF solution was added to THF solution of  $(C_2H_4PtCl_2)_2$  obtained by known procedure [5]. Immediately the solution colour changed from yellow to red-brown. After one hour THF was removed and the residue was extracted with hexane to give a red-brown substance, whose composition was confirmed by elemental analysis. Found: C, 46.53; H, 6.16; Pt, 37.20%. Calcd. for  $C_{20}H_{32}O_3Pt$ : C, 46.60; H, 6.21; Pt, 47.20%.

## Oxidation Reactions of Platinum and Palladium Catecholate Complexes

The oxidation of catecholate complexes was carried out under molar ratio of reagents 1:1, in evacuated tubes.  $CuCl_2$ ,  $CF_3COOAg$  were used as oxidants. The control for reaction proceeding was made by the means of ESR spectroscopy. The ESR spectra were registered on RE-1301 instrument.

## References

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