2. The synergistic effect in such systems is due to the regeneration of the dithiocarbamates of copper and nickel under the action of TDS.

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o-SEMIQUINOLATO COMPLEXES OF PALLADIUM AND PLATINUM WITH ARYLAZOARYL LIGANDS

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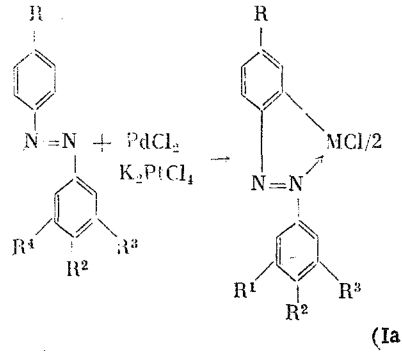
546.92:546.98

As a continuation of the investigation of the chemistry of o-semiquinolato complexes of elements of the nickel subgroup [1-4], we have synthesized new stable paramagnetic complexes of Pd and Pt with o-semiquinolato and arylazoaryl ligands and studied their reactivity.

The reaction of Pd(II) and Pt(II) salts with azoaryl derivatives is known to result in the o-metalation of the benzene ring [5, 6]. This method has been used by us to obtain azoaryl chlorides of Pd and Pt, which are the starting reagents for the synthesis of o-semiquinolato complexes of these elements:



(Ia, Ib) - (IIIa, IIIb)

$R=R^1=R^2=R^3=H$ (I); $R=OH$, $R^1=R^2=R^3=H$ (II);
$R=H$, $R^2=OH$, $R^1=R^3=t\text{-}C_4H_9$ (III). M=Pd(Ia)–(IIIa), Pt (Ib) - (IIIb).

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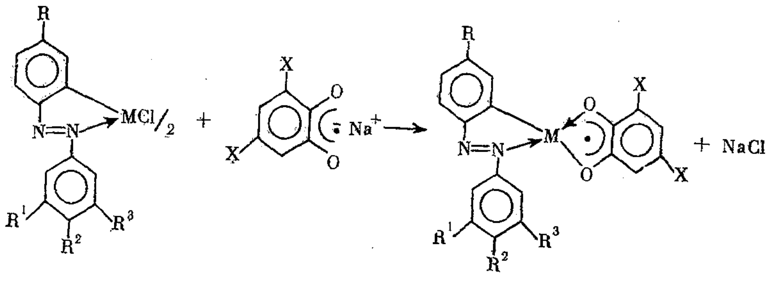
It is interesting to note that, when $PdCl_2$ is reacted with hydroxyphenylazobenzene, in contrast to the case of 3,5-di-tert-butyl-4-hydroxyphenylazobenzene [6], the hydroxyphenyl ring is metalated, as is evidenced by the presence in the IR spectrum of the compound obtained of an intense band at 690 cm^{-1}, which characterizes the deformation vibrations of the C–H bonds in the monosubstituted benzene ring.

All the Pd and Pt complexes obtained with arylazoaryl ligands react with sodium 3,5-di-tert-butyl-1,2-benzosemiquinolate to form paramagnetic complexes of the RMSQ type:



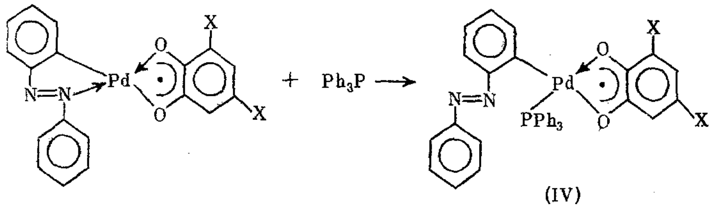
(Ic)-(IIIc)

(2)

M=Pd (Ic)-(IIIc), Pt (Id)-(IIId). Here and in the following $X{=}C(CH_3)_3$.

Complexes Ic-IIIc and Id were isolated in individual states, and IId and IIId were investigated in solution. All the arylazoaryl o-semiquinolates of Pd and Pt are paramagnetic.

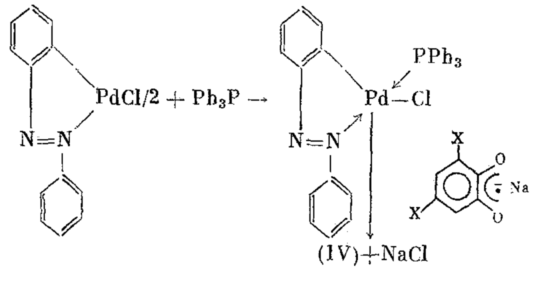
Compounds I-IIIc and IIId are very reactive and react with donor molecules (Ph_3P) and benzoyl peroxide, as well as with o-quinones, which have stronger acceptor properties than does 3,5-di-tert-butyl-1,2-benzoquinone. It should be noted that the reactions of Pd and Pt derivatives proceed differently. The reaction of 2-(phenylazo)phenylpalladium 3,5-di-tert-butyl-1,2-benzosemiquinolate with Ph_3P results only in the cleavage of the Pd ← N bond and the formation of an adduct with Ph_3P, as is evidenced by the parameters of the ESR spectrum of the product (IV):



(IV)

(3)

The small value of the constant $a_{^{31}P}$ (Table 1) indicates that the P atom scarcely departs from the plane of the o-semiquinolato ligand, i.e., IV may be treated as a square planar complex. Complex IV was synthesized in another way:

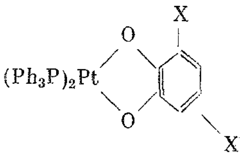


(4)

The parameters of the ESR spectrum of IV obtained according to reactions (3) and (4) are identical, confirming the structure of this compound.

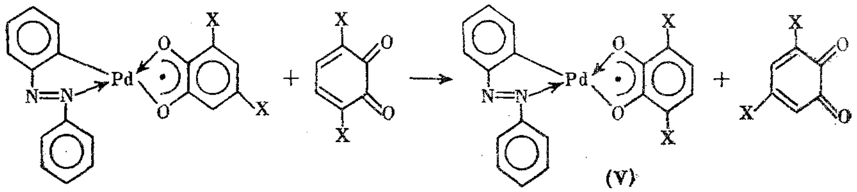
Unlike π-allylpalladium 3,5-di-tert-butyl-1,2-benzosemiquinolate [1], intramolecular reduction of the o-semiquinolato ligand and the formation of a complex with a pyrocatecholate structure do not occur in the present case.

Conversely, the action of Ph_3P on Id-IIId produces a complex with a diamagnetic pyrocatecholate structure of the type



whose oxidation yields pentacoordinate Pt complexes, which are unstable at ∿20°C and were described in [4].

Like the other o-semiquinolato complexes of Pd [1, 2], compounds Ic-IIIc readily undergo oxidation-reduction displacement reactions:

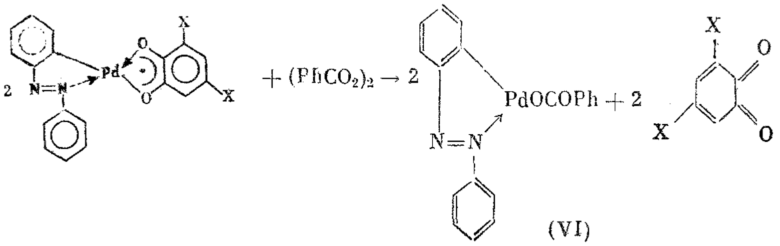


(V)

(5)

This reaction does not occur for the Pt analogs.

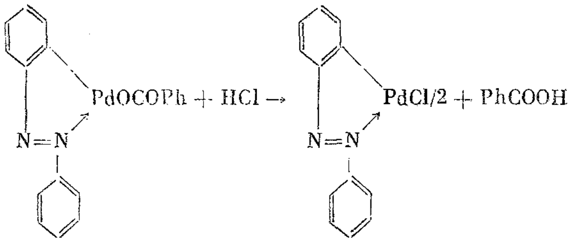
The reaction of Ic-IIIc with benzoyl peroxide results in the splitting of the palladium-o-semiquinolato-ligand bond and the formation of diamagnetic Pd derivatives



(VI)

(6)

The formation of complex VI in reaction (6) is proved by the fact that orange crystals of Ia and PhCOOH are obtained when aqueous HCl is reacted with VI:



(7)

EXPERIMENTAL

Commercial azobenzene was used in the work, and II and III were synthesized according to a standard nitrogen coupling procedure.

2-(Phenylazo)phenylpalladium 3,5-Di-tert-butyl-1,2-benzosemiquinolate (Ic). A solution of 2 mmoles of sodium 3,5-di-tert-butyl-1,2-benzosemiquinolate was added to a suspension of 0.65 g (1 mmole) of Ia in THF. At the conclusion of the reaction (the color of the solution becomes reddish brown), THF was removed in a vacuum. For the extraction of Ic the precipitate was repeatedly washed with hexane. After the evaporation of hexane, Ic remained in the

TABLE 1. Parameters of the ESR Spectra of o-Semiquinolato Complexes of Palladium and Platinum with Arylazoaryl Ligands

Complex	g_i	a_{HSQ}	a_M	Complex	g_i	a_{HSQ}	a_M
(Ic)	2,0016	3,3	1,8	(IId)	1,9980	3,4	12,7
(IIc)	2,0014	3,3	2,0	(IIId)	1,9980	3,3	13,5
(IIIc)	2,0017	3,3	1,7	(IV)	2,0029	3,7	–
(Id)	1,9960	2,7	14,8	(V)	2,0014	3,3	1,6

form of a reddish brown substance. The yield was 84%. Found: C 62.21; H 5.79; Pd 20.98%. Calculated for $C_{26}H_{29}N_2O_2$: C 61.48; H 5.90; Pd 20.97%.

The complexes IIc, IIIc, and Id-IIId were obtained in a similar manner. The IR spectra were recorded on a UR-20 spectrometer, and the ESR spectra were recorded on an RÉ-1301 radiospectrometer.

CONCLUSIONS

1. New stable paramagnetic o-semiquinolates of palladium and platinum with arylazoaryl ligands have been synthesized.

2. The reactions of the o-semiquinolato complexes of palladium and platinum with triphenylphosphine proceed differently and result, in the case of palladium, in the cleavage of the Pd ← N coordinate bond and the preservation of the o-semiquinolate structure of the original complex, and, in the case of platinum, displacement of the azo ligand and the formation of a pyrocatecholate derivative of platinum are observed.

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STERIC STRUCTURE OF N-(HALOMETHYL)IMIDES

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Compounds containing geminal nitrogen and halogen atoms have unique physical and chemical properties. Many data indicate the existence of α-(chloromethyl)amines in the form of immonium salts [1]. The absence of chlorine nuclear-quadrupole-resonance signals indicates partial shift of the free pair of nitrogen electrons to the C—Cl σ bond [2]. Thus, in the series of α-(haloalkyl)amines, the α effect is most pronounced; this effect has been widely investigated for α-halo ethers [3, 4] and is explained by transfer of electrons of the unshared electron pair of the donor atom to the nonbonding σ* orbital of the C—Hal bond (n—σ* interaction).

In investigation of the α effect, a decisive role is played by determination of the mutual orientation of the unshared electron pair and the acceptor bond, i.e., the conformation of the molecule. Addition to the N atom of electron-acceptor substituents preventing transfer of the unshared electron pair to the σ* orbital of the C—Hal bond stabilizes the structure.

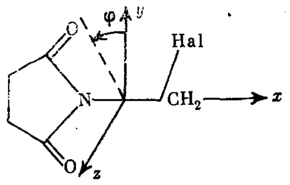

Fig. 1. Conformation of the investigated molecules and orientation in the system of coordinates.

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Branch of the Academy of Sciences of the USSR. Translated from Izvestiya Akademii Nauk SSSR, Seriya Khimicheskaya, No. 11, pp. 2487-2490, November, 1980. Original article submitted December 17, 1979.

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