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

LITERATURE CITED


o-SEMIQUINOLATO COMPLEXES OF PALLADIUM AND PLATINUM WITH ARYLazoARYL LIGANDS

G. A. Razuvaev, G. A. Abakumov, I. A. Teplova, K. G. Shal'nova, L. G. Abakumova, and V. K. Cherkasov

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:

\[
\begin{align*}
N=N + \text{PdCl}_2 &\rightarrow \text{K}_2\text{PdCl}_4, \\
N=N + \text{PtCl}_2 &\rightarrow \text{K}_2\text{PtCl}_4
\end{align*}
\]

\[
\begin{align*}
R=R^1=R^2=R^3=H &\rightarrow (Ia, Ib), \\
R=H, R^1=OH, R^2=R^3=H &\rightarrow (II); \\
R=H, R^1=OH, R^2=R^3=\text{C}_2\text{H}_6 &\rightarrow (III). \quad M=\text{Pd}(Ia)\rightarrow (IHa, IIIa), \text{Pt}(Ib)\rightarrow (IIIb).
\end{align*}
\]

It is interesting to note that, when PdCl₂ 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-benzoquinolate to form paramagnetic complexes of the RMSQ type:

\[
\begin{align*}
\text{H} & \quad (\text{Ic})-(\text{IIIc}) \\
\text{M} & \quad \text{Pd} \quad (\text{Ic})-(\text{IId}) \quad \text{and} \quad \text{the} \quad \text{following} \quad X=C(CH_3)_2.
\end{align*}
\]

Complexes Ic-IIIc and IId were isolated in individual states, and IId and IIIId 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 (Ph₃P) 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-benzoquinolate with Ph₃P results only in the cleavage of the Pd + N bond and the formation of an adduct with Ph₃P, as is evidenced by the parameters of the ESR spectrum of the product (IV):

\[
\begin{align*}
\text{N} & \quad \text{PdCl₂} + \text{Ph₃P} \rightarrow \\
\text{PPh₃} & \quad \text{N=P} \quad \text{O} \quad \text{X} \\
\text{IV} & \quad \text{N} \quad \text{PdCl} \quad \text{X} \quad \text{PPh₃} \quad \text{N} \quad \text{O} \quad \text{X}
\end{align*}
\]

The small value of the constant α₃₄₃ (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:

\[
\begin{align*}
\text{N} & \quad \text{PdCl₂} + \text{Ph₃P} \rightarrow \\
\text{PPh₃} & \quad \text{N=P} \quad \text{O} \quad \text{X} \\
\text{(IV)+NaCl} & \quad \text{N} \quad \text{PdCl} \quad \text{X} \quad \text{PPh₃} \quad \text{N} \quad \text{O} \quad \text{X}
\end{align*}
\]

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-benzoquinolate [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 Ph₃P on IId-IIIId produces a complex with a diamagnetic pyrocatecholate structure of the type