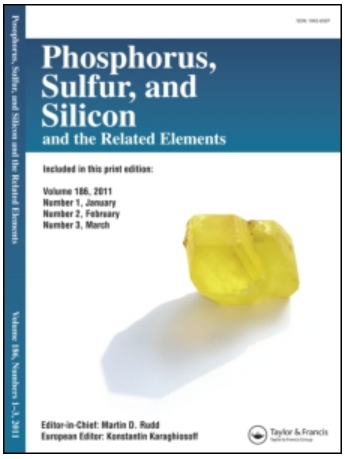

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REACTIONS OF THIOL DERIVATIVES OF ACIDS OF TRIVALENT PHOSHORUS WITH TRANSITION METAL HALIDES.

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Abstract Reactions of thiol derivatives of acids of trivalent phosphorus ($(RS)_3P$ $RSP(NR_2)_2$, $(RS)_2PCl$) with transition metal halides (Cu(I), Cu (II), Ag(I), Pd (II), Pt (II)) have been investigated.

Key words trialkyltrithiophosphite, transition metal halides, complex, coordination

Compounds containing a P-S -bond are of great interest in terms of their coordination chemistry.[1] The presence of two donor atoms in a ligand and their ability to form a bond with transition metals with one or both centers of the ambident system provides wide possibilities of obtaining new phosphorus-sulfur containing metal complexes and studying their structure and properties.

Our investigations began with the reaction of trialkyltrithiophosphites with copper (I) and copper(II) halides.[2] We have studied the reactions of triethyl, -n-propyl-, -i-propyl-, -phenyltrithiophosphite with CuCl, CuBr, CuI and have established, that in all cases the interactions result in the formation of complexes of the 1:1 ratio with the metal.

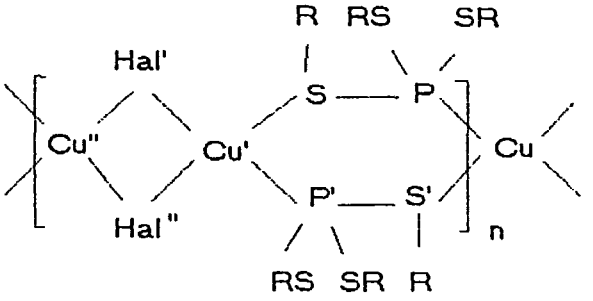

FIGURE 1. $(RS)_3PCuHal$, where $R=C_2H_5$; Hal=Cl, Br, J.

With X-ray data it was established, that triethyl- and triphenyltrithiophosphites react with the copper(I) halides with the formation of crystalline complexes, in which the copper atoms are bonded to the phosphorus atom of one trithiophosphite fragment and the sulfur atom of another fragment. They form regular polymer chains with alternating 4- and 6- membered cycles(I).

Such a kind of coordination with both atoms of the ambident >P-S- system in a series of derivatives of P(III) acids is novel, as other derivatives of the P(III)- atom (amides, esters of P(III)) coordinate only with the participation of the phosphorus atom.

It is of interest, that the bulkier substituted triisopropyltrithiophosphite forms complexes coordinated with copper(I) bromide only with the phosphorus atom of the thiophosphite. The structure of the product has been established by X-ray data. It should be noted that one molecule of acetonitrile was drawn into the coordination sphere of copper when the complex was recrystallized from CH_3CN.

It is of interest to compare the X-ray data for the molecules of complexes of triethyl- and triphenyltrithiophosphites with CuCl (Table 1). Firstly, the CuCl and CuCl' bonds are essentially different in their length in the alkyl-complex.

TABLE 1. Some bond lengths for complexes of $CuCl\,P(SEt)_3$, $CuCl\,P(SPh)_3$ and $P(SPh)_3$ according to X-ray analysis data.

bond	$CuCl\,P(SPh)_3$	$CuCl\,P(SEt)_3$	$P(SPh)_3$
Cu-P	2.243(2)	2.208(1)	———
Cu'-S_3	2.344(2)	2.392(1)	———
Cu-Cl	2.323(2)	2.373(1)	———
Cu-Cl'	2.335(2)	2.312(1)	———
P-S_1	2.117(2)	2.074(2)	2.127(0)
P-S_2	2.103(2)	2.086(2)	2.127(0)
P-S_3	2.174(2)	2.128(2)	2.127(0)

Secondly, it is observed lengthening of the Cu-P bond on the transition from the alkyl to the phenyl complex (0.035Å) and the shorten of the S-Cu bond in the phenyl containing complex on (0.048Å). All the above shows that the interaction between the metal atom and the sulfur atom of one of the thiols groups of the ligand becomes stronger. On the other hand it leads to the lengthening of the P-S bond, the sulfur atom of which is bonded with the copper atom, when compared with triphenyltrithiophosphite and complexes with trialkyltrithiophosphites.

If we proceed from the crystal state to the solution , one can observe, that this tendency is preserved in the NMR ^{31}P data of trithiophosphites. If we compare the value of the displacement of ligand shift in the complexes of triphenyltrithiophosphite with the free triphenyltrithiophosphite, we can see, that the value of this displacement is very small (<5ppm) (Table 2).

Table 2. Changes in chemical shifts of ^{31}P NMR spectra for complexes of transition metals of a number of trithiophosphites ($\Delta\delta^{31}P = \delta^{31}P$ complex - $\delta^{31}P$ ligand).

SUBSTANCE	$\delta^{31}P$, ppm	$\Delta\delta^{31}P$, ppm
$CuCl \cdot P(SEt)_3$	104	12
$CuBr \cdot P(SEt)_3$	99	17
$CuCl \cdot P(SPh)_3$	130	2
$CuBr \cdot P(SPh)_3$	128	4
$CuBr \cdot P(S\ n\text{-}Pr)_3$	92	26
$CuBr \cdot P(S\ i\text{-}Pr)_3$	96	22
$P(SPh)_3$	132	—
$P(SEt)_3$	116	—
$P(S\ n\text{-}Pr)_3$	118	—
$P(S\ i\text{-}Pr)_3$	117	—

Meanwhile the value of displacement of the shift for the complexes of triethyltrithiophosphite exceeds 10 ppm, for the pure phosphorus coordinated complexes these values are about 20 ppm.

For the determination of the influence of the oxidation state of the metal on the direction of interaction the reactions of triethyltrithiophosphite with $CuCl_2$ and $CuBr_2$ have been studied. The reactions proceed as complicated redox processes with the formation of the complex of thiophosphite with copper (I) halide, which are coordinated on both centers of the >P-S- ambident system, cited above; dithiochlorophosphite or bromphosphite, tetrathiophosphite and disulfide.

$$2CuHal_2 \xrightarrow{P(SEt)3} 2CuHal + Hal_2$$

$$2CuHal + 2P(SEt)_3 \longrightarrow 2CuHal\,P(SEt)_3$$

$$Hal_2 + P(SEt)_3 \longrightarrow HalP(SEt)_2 + [EtSHal]$$

$$P(SEt)_3 + [EtSHal] \xrightarrow{Hal=Cl} HalP(SEt)_2 + EtSSEt$$

$$P(SEt)_3 + [EtSHal] \xrightarrow{Hal=Br} S{=}P(SEt)_3 + [EtHal]$$

It is of interest to note, that the increase in nucleophility of the phosphorus atom by introducing of the amido groups into the molecule of thiophosphite also results in a complex with the metal being coordinated to the phosphorus atom.

Diethyldithiochlorphosphite also react with CuCl in accordance with NMR ^{31}P data with the formation of a complex with the coordination of a phosphorus atom.. However this substance is unstable and destroyes in a solution with the formation of the complex of tryethyltrithiophosphite with CuCl and ethylthiodichlorphosphite.

Besides copper (I,II) halides we attempt to investigate the reactions of tryalkyltrithiophosphite with AgCl, AgBr, $PdCl_2$, K_2PtCl_4. But it appeared, that the reaction with AgCl in the same conditions doesn't take place. In the case of $PdCl_2$ by NMR ^{31}P the formation of an intermediate complex was observed (δ=110.9 ppm) but it is unstable and disintegrate with the formation of diethyldithiochlorophosphite and diethyldisulfide.

In the case of K_2PtCl_4 by NMR ^{31}P the formation of phosphorus coordinated complex, of $PtCl_2 \cdot 2P(SEt)_3$ was observed (δ=82.5 ppm, $J_{P\text{-}Pt}$=4140 Hz), This complex we have also obtained by the reaction of $(EtS)_3P$ with $PtCl_2 \cdot TOD$ (tetraoctadehalin).

Very interesting results have been obtained by us in the reactions of complexes of trithiophosphite with CuCl and CuBr with the proton containing compounds (EtOH, Et_2NH).

Pure trithiophosphite does not react with absolute ethyl alcohol neither at room temperature nor when boiled during several days. Meanwhile the complex has begun the reaction with the absolute ethanol at room temperature. The product of this reaction is diethylphosphoric acid.

The reaction of trithiophosphite with diethylamine does not take place at all. However if instead of thiophosphite in this reaction we take the thiophosphite complex with copper (I) halide the substitution reaction at the phosphorus (III) atom proceeds readily with the substitution of the thiogroups by amido groups. In accordance with the NMR ^{31}P data complex copper(I)halides with triamidophosphite and phosphorus containing compound with P-H bond are formed.

These first results demonstrate that with complexes we can conduct reactions which in ordinary conditions do not take place at all and we can pass over to other derivatives of phosphorus acids without sulfur atoms.

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