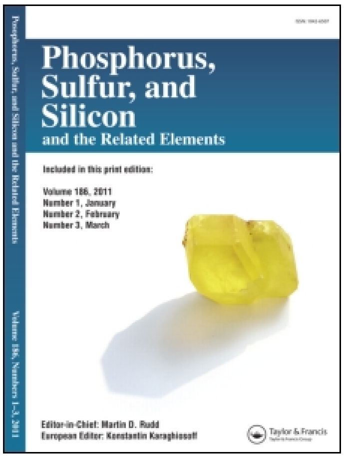

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REACTIONS OF THIOESTERS OF PHOSPHORUS ACIDS WITH CATIONIC COMPLEXES OF MANGANESE

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Abstract The thioesters of P(III) acids react with $[Cp(CO)_2Mn(NO)]^+$ by substituting one CO-group with formation of a stable cationic products with a Mn-P bond. Fourier transform infrared spectroscopy and a special program were used for the real-time monitoring of the mechanistic path of the reaction of S-ethyl-N,N-tetraethyldiamidothiophosphite with $[Cp(CO)_2Mn(NO)]^- BF_4^+$. The formation of a few intermediates is described.

INTRODUCTION

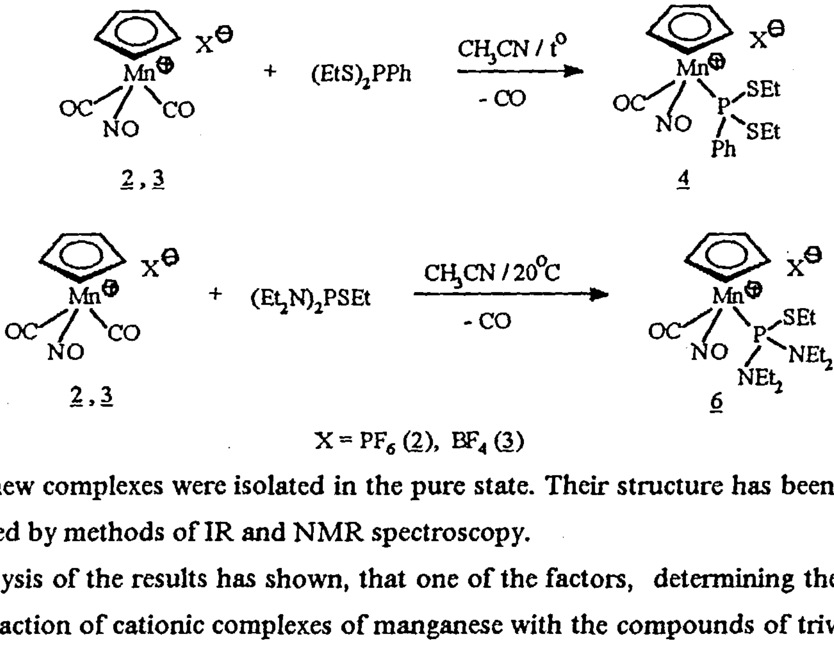
The chemistry of thioesters of P(III) acids is one of the promtly developing areas of organophosphorus compounds. However, until now there are insufficient works on the investigation of reactions of the thioesters of P(III) acid derivatives with organometallic compounds, including cymantrene and its derivatives.

We have reported[1] on the synthesis of similar complexes by interaction of thioesters of P(III) acids with intermediate (1). In this case, stable free-radical complexes of the this type with a manganese-sulfur bond, were isolated together with complexes of manganese, containig thioderivatives of P(III) acids as ligands. Isoelectronic analogues of cymantrene, nitrosyl cationic complexes of manganese (2,3) in reactions with thioesters of P(III) acids have not been studied.

RESULTS AND CONCLUSIONS

We have established, that triethyltrithiophosphite does not react with cationic complexes in solution of acetonitryle even at long heating with reflux.

If the number of electronegative alkylthio groups at phosphorus is reduced, the process of substitution of carbonyl on the phosphorus-containing ligands is facilitated. Prolonged heating with reflux of dithiophosphonite with a cationic complex in solution of acetonitrile results in the formation of a new complex (4), containing dithiophosphonite as a ligand. The interaction of cationic complexes with thiophosphinite in the same conditions is proceeds much more readily. The reaction proceeds up to the end during 5 hours with the formation of a new complex. The introduction of strong electron-seeking amidogroups to a phosphorus atom makes it possible to synthesize appropriate complexes (6) at room temperature in 1 hour.



$X = PF_6$ (2), BF_4 (3)

All new complexes were isolated in the pure state. Their structure has been confirmed by methods of IR and NMR spectroscopy.

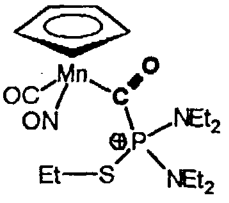
Analysis of the results has shown, that one of the factors, determining the rate of reaction of cationic complexes of manganese with the compounds of trivalent phosphorus, is the donor properties of phosphorus atom. The increase of the number of electronegative alkylthio groups reduces the rate of the subsititution of carbonyl. In the case of trithiophosphites the subsititution reaction actually does not take place. The introduction of electron-seeking amidogroups considerably accelerates the process of exchange of ligands. On the basis of these data a con-clusion can be drawn, that the rate of the reaction discussed decreases in the following series of the compounds of trivalent phosporus:

$$(EtO)_3P > Ph_3P \sim (Et_2N)_2PSEt > Ph_2PSEt > PhP(SEt)_2 > (EtS)_3P \sim PCl_3$$

In order to elucidate the mechanism of the reaction, we monitored the reaction of complex (3) with S-ethyl-N,N-tetraethyldiamidothiophosphite using Fourier Transform Infrared spectroscopy[2].

Meanwhile time in spectral range (1900-1700 cm^{-1}), the appearance of a new absorption band at 1752 cm^{-1} due to the vibration ν(CO) is noted. The intensity of this band steadily decreases until it disappears completely after about 40 minu-tes. The appearence of this new vibration ν(CO) can be explained by the fact that, during the reaction, a new intermediate is formed.

It is known[3] that, for cation (3) , the addition reaction of a suitable nucleophles to the carbon atom of the CO ligand is most specific. Taking into account the ambident nature of the P-S bond in the thioester of P(III) acid, it is possible to assume that the same type of reaction is attributable to the formation of either of the intermediates (7) or (8) in the reaction of a complex (3) with diamidothiophosphite.



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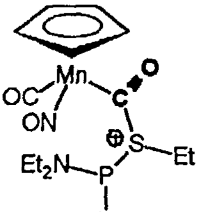

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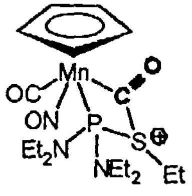

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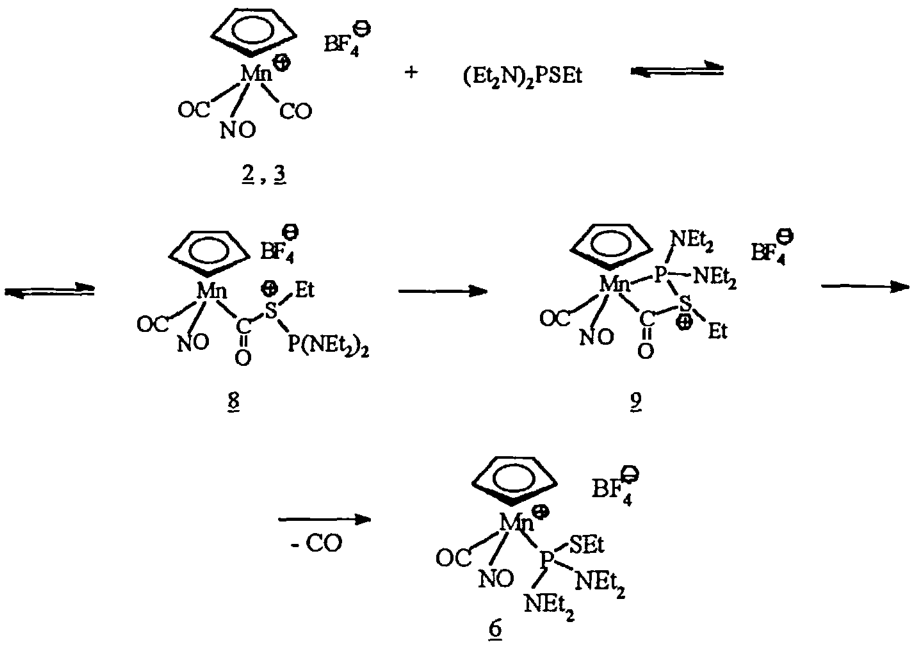
Perhaps both intermediates (7) and (8) are formed at the earlier stages of the reaction. It also seems reasonable to assume that compound (8) would be preferable as an intermediate product.

Besides, when analyzing the spectral map, it is seen that, while the 1752 cm^{-1} band decreases, the intensity of the absorption near 1776 cm^{-1} increases. This absorption band is related to the vibration of the carbonyl group of another intermediate (9) having a cycllic system, where the frequency of the ν(CO) is that of compound (8). Later, the alteration of the 1776 cm^{-1} band is masked by the beginning of growth of the 1799 cm^{-1} band related to the stretching mode ν(CO) of the final product.

On the basis of our results, and taking into account pertinent literature data, we assume that the reaction of the cationic complex (3) with the diamidothiophosphite proseeds as follows.



Thus, we have shown that the thioesters of P(III) acids react with cationic complexes of manganese by substituting one carbonyl and forming stable cationic products having a manganese-phosphorus bond. Our Fourier Transform Infrared investigation of the reaction of S-ethyl-N,N-tetraethyldiamidothiophosphite with the nitrosyl complex of manganese has made it possible for us to examine the spectral surface and spectral map approaches. We believe that we have established the formation of a few intermediates, and we are able to suggest a conceivable path for the reaction.

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