1130 Russian Chemical Bulletin, International Edition, Vol. 50, No. 7, pp. 1130—1139, July, 2001

Structures and conformational behavior of phosphorothioites and their complexes with transition metals obtained from X-ray diffraction analysis

O. N. Kataeva★ *and O. G. Sinyashin*

A. E. Arbuzov Institute of Organic and Physical Chemistry, Kazan Research Center of the Russian Academy of Sciences,
8 ul. Akad. Arbuzova, 420088 Kazan, Russian Federation.
Fax: +7 (843 2) 76 7424. E-mail: ok@iopc.knc.ru

The data on the structures, conformational behavior, and coordination properties of phosphorothioites are summarized. Their complexes with transition metals are characterized by different modes of coordination depending on the nature of the metal atom, the substituents at the sulfur atoms, reaction conditions, and conditions of single-crystal growth. The principal differences in properties of phosphorothioites and their analogs containing the P—O and P—N bonds are analyzed.

Key words: phosphorotrithioites, conformations, mode of coordination, polydentate ligands, metal complexes.

Intensive studies of the chemistry of phosphorothioites performed in 1980—1990s added essentially to knowledge of the reactivity of trivalent phosphorus derivatives.[1,2] However, processes of complex formation involving phosphorothioites and transition metal compounds have long been beyond the scope of these investigations. For example, phosphorothioites have not even been mentioned in the recent review[3] devoted to P- and S-containing ligands although transition metal complexes containing phosphorothioite ligands have attracted considerable interest in recent years. This is associated, on the one hand, with the fact that these metal complexes have found use as catalysts of liquid-phase hydrogenation[4] and hydroformylation[5] and, on the other hand, with wide application of X-ray diffraction analysis to studies in the field of organophosphorus chemistry, which enables one to gain detailed information on the structures of organometallic and coordination compounds.

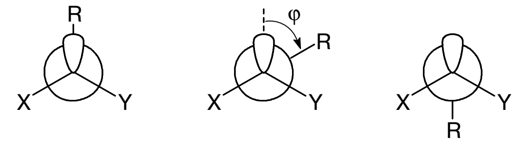
Analysis of the structures of metal complexes available in the Cambridge Structural Database[6] demonstrated that esters and amides of trivalent phosphorus acids, like phosphines, form complexes with transition metals in which the phosphorus atom is coordinated to the metal atom exclusively in the monodentate fashion.

At the same time, phosphorothioites represent unique ambident systems formed by Period III elements in which the sulfur atom serves as a competitive and, in some cases, dominant reaction center, which is manifested in the different chemical behavior[1,2] of phosphites and phosphorothioites. The observed differences in the reactivity of these classes of compounds are attributed to the unusual electronic structures of phosphorothioites. It is assumed that the orbitals of the lone electron pairs of the phosphorus and sulfur atoms are mixed in total thioesters of phosphorous acid, *viz.*, in phosphorotrithioites. This conclusion was made based on the ionization potentials determined by photoelectron spectroscopy.[7,8] It is these characteristic features of the electronic structures of phosphorothioites that are responsible for their reactivities, including those exhibited in complex formation. The conformational lability typical of phosphorothioites is in great part favorable for a wide diversity of their complexes with transition metals.

In the present review, we survey the results of studies of the structures and conformational behavior of "free" phosphorothioites and their complexes with transition metal compounds in the crystalline state performed in recent years at the A. E. Arbuzov Institute of Organic and Physical Chemistry of the Kazan Research Center of the Russian Academy of Sciencess. Particular attention is given to analysis of the factors governing the mode of coordination in the complexes and to consideration of the influence of the metal—phosphorus and metal—sulfur coordination on the structure and conformation of the organophosphorus ligand.

Conformational behavior of "free" phosphorotrithioites

Organic phosphorotrithioites. For phosphorothioites of the XYP—S—R type (X, Y, and R are various substituents), three orientations of the S—R bond with respect to the lone electron pair of the phosphorus atom can occur due to internal rotation about the P—S bond:



cis $-30^\circ \le \varphi \le 30^\circ$

±gauche $30^\circ \le |\varphi| \le 120^\circ$

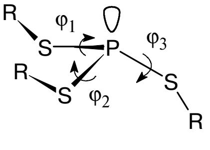
trans $120^\circ \le \varphi \le 240^\circ$

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 7, pp. 1079—1087, July, 2001.

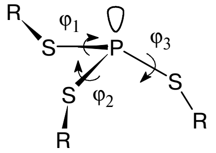
It was demonstrated[9] that five conformations are possible for phosphorotrithioites $P(SR)_3$ possessing three P—S axes of internal rotation on the assumption that the potentials of internal rotation about all three axes are equal:

cis,cis,cis (C_{3v}) ($\varphi_1 = \varphi_2 = \varphi_3 = 0°$);
cis,cis,trans (C_s) ($\varphi_1 = \varphi_2 = 0°$, $\varphi_3 = 180°$);
gauche,gauche,gauche (C_3) ($\varphi_1 = \varphi_2 = \varphi_3 = 60°$);
gauche,−gauche,trans (C_s) ($\varphi_1 = -\varphi_2 = 60°$, $\varphi_3 = 180°$);
gauche,gauche,trans (C_1) ($\varphi_1 = \varphi_2 = 60°$, $\varphi_3 = 180°$).

The last two mentioned conformations differ in symmetry due to the opposite directions of rotation about the same P—S bond:



gauche,gauche,trans
($\varphi_1 = \varphi_2$, C_1)



gauche,−gauche,trans
($\varphi_1 = -\varphi_2$, C_S)

According to the data from gas phase electron diffraction[10,11] and molecular spectroscopy[9,12,13] obtained for phosphorothioites in the gaseous and liquid phases and in solutions, complex mixtures of conformers with the *gauche* and *trans* orientations of the alkylthio groups relative to the lone electron pair of the phosphorus atom exist. Reliable evidence for the presence of *cis* conformers of phosphorotrithioites in the gaseous and liquid phases are lacking in the literature.

The results of studies on the conformational behavior of trialkyl phosphorotrithioites (R = Me and Et) in the crystalline state by vibrational spectroscopy and molecular mechanics[12] are also indicative of the presence of the *gauche,gauche,trans* conformers. The majority of phosphorotrithioites $P(SR)_3$ (R = Ph,[14] C(O)Ph,[15] C(S)OEt,[15] $C(S)NMe_2$,[16] $C(S)NEt_2$,[17] $P(S)(OMe)_2$,[15] or $P(S)(OPr^i)_2$ [14]) characterized by X-ray diffraction analysis adopt the propeller *gauche,gauche,gauche* conformation with the symmetry C_3. Thus, the S—C bonds in the molecule of triphenyl phosphorotrithioite are rotated with respect to the lone electron pair of the phosphorus atom by 41.0°, the P—S bonds being virtually orthogonal to the planes of the phenyl groups ($\tau = 96.6°$).

It should be noted that, according to the data from X-ray diffraction analysis, phosphonotetrathioates $(RS)_3PS$ (R = Ph[18] or Me_3Sn [19]), like phosphorotrithioites, have the propeller conformation in the crystalline state.

Therefore, most of phosphorotrithioites are conformationally labile. These substances occur in the gaseous and liquid phases as mixtures of conformers with the *gauche* and *trans* orientations of the substituents at the sulfur atoms relative to the lone electron pair of the phosphorus atom. In the crystalline phase, the majority of phosphorotrithioites as well as of phosphorotetrathioates adopt the propeller *gauche,gauche,gauche* conformation.

Organometallic phosphorotrithioites. In crystals, phosphorotrithioites containing organometallic substituents at the sulfur atoms have more diversified structures. The information on the structures of organometallic phosphorothioites in the crystalline phase are based on the results of X-ray diffraction analysis performed for tricymantrenyl and triferrocenyl phosphorotrithioites.[20,21]

In the crystal, the molecule of tricymantrenyl phosphorotrithioite (**1**) possessing nine axes of internal rotation is unsymmetrical (Fig. 1). According to the data from X-ray diffraction analysis, the cymantrenylthio groups have different orientations with respect to the lone electron pair of the phosphorus atom, *viz.*, *cis* ($\tau = 7.2°$), *gauche* ($\tau = 31.0°$), and *trans* ($\tau = 178.1°$). The P—S bonds are virtually orthogonal to the planes of the cyclopentadienyl rings. This conformation is untypical of organic phosphorotrithioites studied in the gaseous, liquid, and crystalline phases.

The conformational lability of the cymantrenyl fragments is, apparently, one of the reasons for the unusual *cis,gauche,trans* conformation of **1**. Virtually free metal—cyclopentadienyl rotation is observed in many half-sandwich metal carbonyl complexes in solutions.[22] As a result, three cymantrenyl substituents are nonequivalent in the crystalline state and the carbonyl groups have large thermal parameters. The P(1)—S(1)—C(11) bond angle is 7° larger than two other bond angles at the sulfur atoms due to steric interactions of the *trans*-cyclopentadienyl group with the S(2) and S(3) atoms (see Fig. 1). In addition, the carbonyl groups in the crystal of **1** are involved in short intermolecular C—H...O contacts. It is known[23—27] that such interactions can radically change the molecular conformation in the crystal in spite of the fact that their energies are at most 1 kcal mol^{-1}.

In the crystal, triferrocenyl phosphorotrithioite (**2**),[21,28] unlike tricymantrenyl phosphorotrithioite

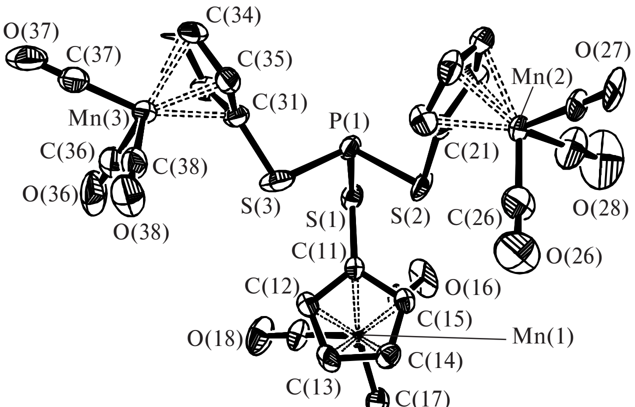


Fig. 1. Molecular structure of complex **1**.

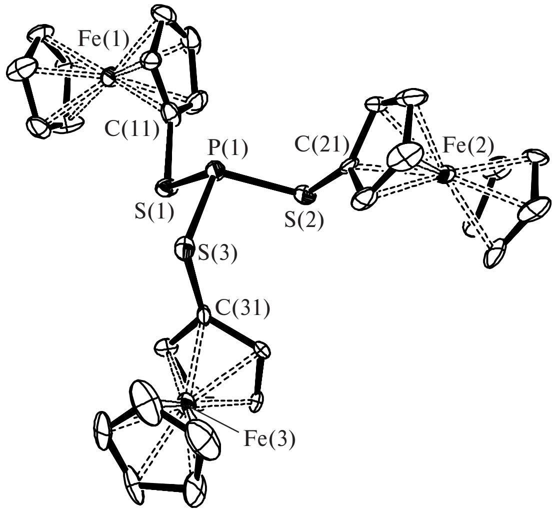


Fig. 2. Molecular structure of complex **2**.

(**1**) possessing an unusual structure, adopts the *gauche*,*gauche*,*trans* conformation (Fig. 2) similar to that observed in organic phosphorothioites.

In the crystal,[20] the corresponding triferrocenyl phosphorotrithioate (**3**) has a symmetrical propeller conformation (Fig. 3) typical of "classical" compounds of four-coordinate phosphorus, for example, of phosphorotetrathioates.

It should be noted that the geometric parameters of three ferrocenylthio groups, *viz*., the P—S and S—C bond lengths and the O=P—S and P—S—C bond angles, are equal to within the experimental error resulting in a symmetrical conformation. The structure of triferrocenyl phosphorotrithioate **3** differs fundamentally from the structure of its oxygen analog, *viz*., of triferrocenyl phosphate.[29] Thus, complex **3** in which the sulfur atoms are weak H acceptors and are not involved in hydrogen bonding has a propeller structure, whereas triferrocenyl phosphate whose four oxygen atoms are involved in C—H...O interactions has the *cis*,*gauche*,*trans* conformation, all three ferrocenyl groups adopting different orientations with respect to the P—O bonds.

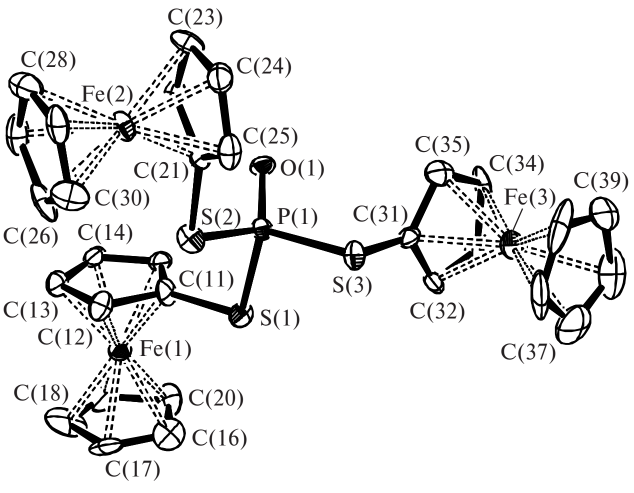


Fig. 3. Molecular structure of complex **3**.

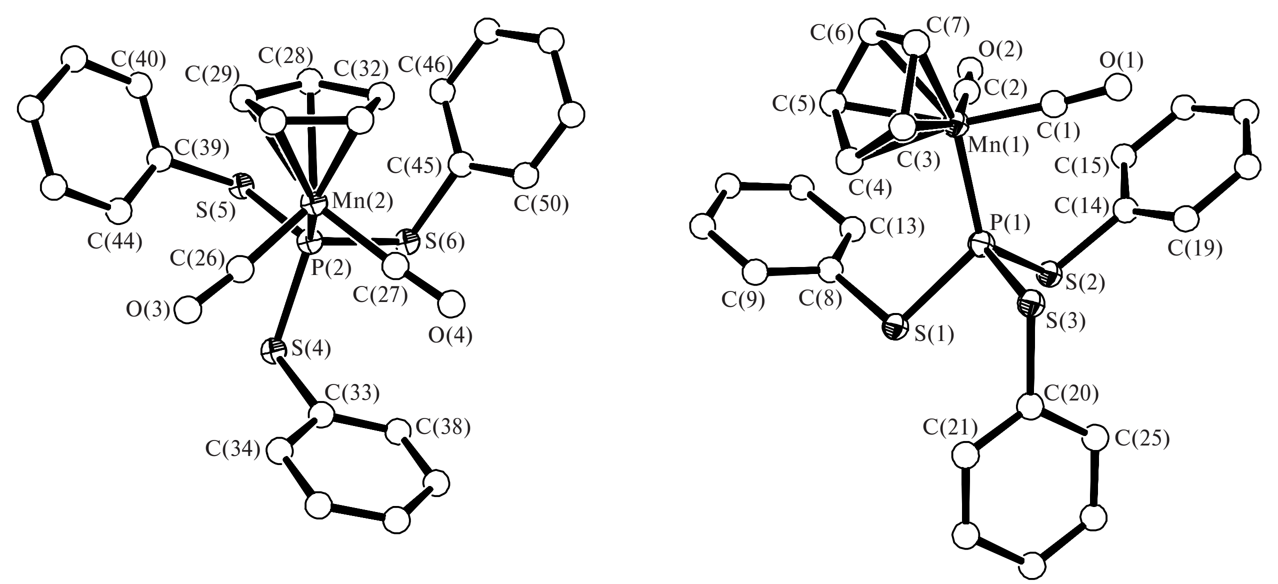
Conformational behavior of phosphorotrithioites in complexes with transition metals

The structures of phosphorothioites should be substantially changed upon complex formation with transition metal compounds. The electronic rearrangement of the structure on formation of the coordination bond, the steric crowding of the complex, and intra- and intermolecular interactions are responsible for changes in the structure of the ligand. Fundamental changes in the structure of the ligand lead to distortion of its symmetry. Thus, the threefold symmetry axis coinciding with the direction of the lone electron pair of the phosphorus atom disappears on formation of transition metal complexes even in the case of the monodentate mode of coordination.

Half-sandwich manganese and chromium complexes. When we started studies on the complex-forming properties of phosphorothioites, only two publications[30,31] devoted to the structures of iron carbonyl complexes with triphenyl phosphorotrithioite were available. These complexes are characterized by the monodentate coordination and the phenylthio group in the phosphorus-containing ligand has the *gauche*,*gauche*,*trans* conformation with respect to the P—Fe bond.

We sudied the cymantrene complexes of triisopropyl and triphenyl phosphorotrithioites, *viz*., cyclopentadienyl(dicarbonyl)[triisopropyl phosphorotrithioite]manganese (**4**) and cyclopentadienyl(dicarbonyl)[triphenyl phosphorotrithioite]manganese (**5**).[32] In these complexes, the phosphorus atom is also coordinated to manganese in the monodentate fashion, and the coordination environment about the manganese atom is a piano stool. There are two crystallographically independent molecules **A** and **B** in the crystal structures of **4** and **5**. In the case of the half-sandwich manganese complex **4** with triisopropyl phosphorotrithioite, the phosphorus-containing ligands in both molecules are similar in geometric parameters and conformations and the isopropylthio group has the *gauche*,*gauche*,*trans* orientation with respect to the Mn—P bond. The geometric parameters of the complex, primarily, the Mn—P—S bond angles, depend substantially on the conformation. Thus, the Mn—P—SPr^i bond angle for the *trans*-isopropylthio group is 10° smaller than the corresponding angle for the *gauche*-isopropylthio group.

The ligands in two independent molecules in the cymantrene complex **5** with triphenyl phosphorotrithioite, unlike those in complex **4**, adopt different conformations (Fig. 4). In molecule **A**, triphenyl phosphorotrithioite retains a propeller conformation of the "free" ligand, whereas one of the phenylthio groups in molecule **B** is in the *trans* orientation with respect to the Mn—P coordination bond.



Molecule A

Molecule B

Fig. 4. Structures of two independent molecules of complex **5**.

In the half-sandwich chromium complex, *viz*., in η-mesitylene(dicarbonyl)(triphenyl phosphorotrithioite)chromium (**6**), the conformation of triphenyl phosphorotrithioite differs from that described above. X-ray diffraction study of this complex[33] confirmed that the phosphorus atom is coordinated to chromium atom in the monodentate fashion (Fig. 5). The phosphorotrithioite ligand has an unsymmetrical structure. The phenyl groups along three P—S bonds have different conformations with respect to the Cr—P coordination bond (*cis*, *gauche*, and *trans*), the tetrahedral configuration of the phosphorus atom being distorted, which is manifested in an increase in the Cr—P—S bond angle to 125.3° in the case of the *cis* orientation of the phenyl group.

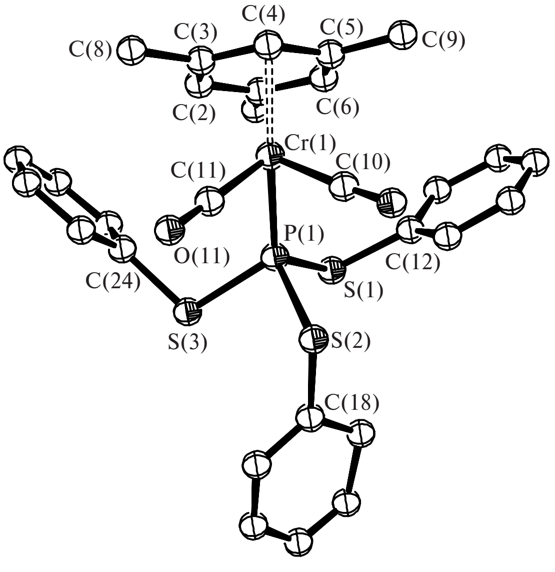
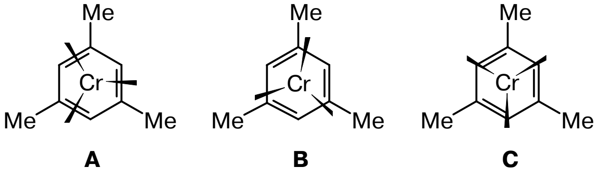


Fig. 5. Molecular structure of complex **6**.

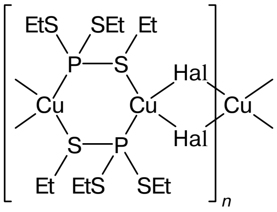
In our opinion, this structure is dictated by steric factors and by the presence of a short intramolecular O...S contact resulting from the virtually eclipsed arrangement of one of the carbonyl groups relative to the P—S bond. In addition, the methyl substituents of the arene fragment are in eclipsed positions with respect to the Cr—CO and Cr—P bonds. Hence, of three possible conformations, *viz*., the staggered conformation (**A**) and two eclipsed conformation (with the eclipsed arrangement of the C—Me (**B**) or C—H bonds of the arene fragment (**C**)), conformation **B** actually exists.



Therefore, the phosphorus—metal coordination bond and the intra- and intermolecular interactions involving molecules of triphenyl phosphorotrithioite are responsible for the existence of three different conformations in iron carbonyl complexes and in half-sandwich manganese and chromium complexes containing triphenyl phosphorotrithioite as a ligand, whereas "free" triphenyl phosphorotrithioite in the crystalline state adopts the propeller conformation.[14]

It should be noted that the conformation of the ligand in transition metal complexes not necessarily depends on the mode of coordination and the nature of the metal atom. Thus, the unusual *cis*,*gauche*,*trans* conformation of triphenyl phosphorotrithioite is observed not only in complex **6** with the monodentate coordination of the ligand, but also in the complex with monovalent copper chloride (**7**) characterized by the bidentate coordination.[34] In this connection, let us consider the crystal structures of phosphorothioite complexes with monovalent copper salts in more detail.

Complexes with copper(I) halides. The bidentate coordination of the copper atom was observed for the first time[35,36] in a series of isostructural complexes of triethyl phosphorotrithioite with copper(I) halides.



8a—c

Hal = Cl (**a**), Br (**b**), I (**c**)

According to the X-ray diffraction data, complexes **8a—c** form polymeric chains consisting of alternating centrosymmetrical six- and four-membered rings. The structure of bromo(triethyl phosphorotrithioite)copper(I) (**8b**) is shown in Fig. 6. The six-membered heterocycle adopts a chair conformation. The four-membered ring containing the bridging bromine atoms is planar. Both donor atoms of the ambident P—S system are involved in coordination bonding with the copper atom. Therefore, the copper atom has a tetrahedral configuration and is linked with two bromine atoms, the phosphorus atom of one phosphorotrithioite molecule, and the sulfur atom of another phosphorotrithioite molecule. The triethyl phosphorotrithioite ligand adopts an unsymmetrical conformation with the *gauche* (P—S(1)), *trans* (P—S(2)), and *cis* (P—S(3)) orientations of the ethylthio groups relative to the Cu—P coordination bond. The S(1) atom involved in the coordination bond with the copper atom has a trigonal-pyramidal configuration due to which the conformation about the S(1)—C(1) bond differs from those about two other S—C bonds.

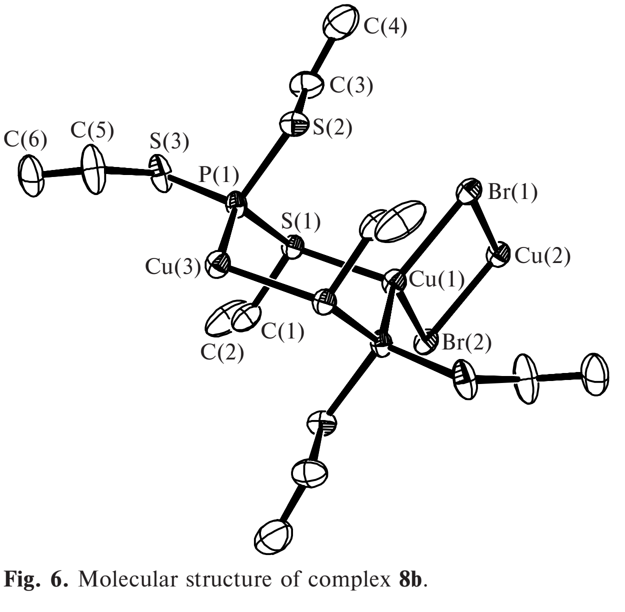


Fig. 6. Molecular structure of complex **8b**.

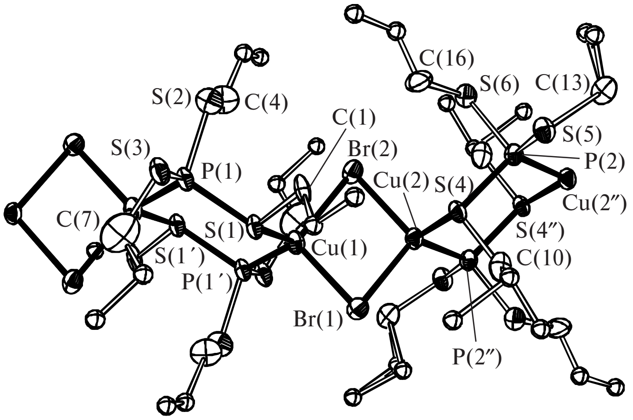
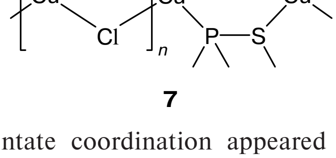


Fig. 7. Molecular structure of complex **9**.

The mode of coordination in the phosphorotrithioite complexes with copper(I) halides remains virtually the same regardless of the lengths of the alkyl substituent at the sulfur atom,[37,38] which is attributable to the similar stereoelectronic parameters of *n*-alkyl groups. The complexes of tripropyl phosphorotrithioite and tributyl phosphorotrithioite with copper(I) bromide (**9** and **10**, respectively) crystallize in a different space group ($P\bar{1}$) with two formula units per asymmetric unit (Fig. 7). In these complexes, the polymeric unit is doubled and consists of alternating six- and four-membered rings. The six-membered rings, like those in complexes **8a—c**, adopt a centrosymmetrical chair conformation, whereas the four-membered rings have a folded conformation. An increase in the length of the alkyl substituents at the sulfur atoms of trialkyl phosphorotrithioites leads to their conformational nonhomogeneity in complexes **9** and **10** giving rise to two conformations in the crystals, *viz.*, to the *gauche*,*gauche*,*trans* conformation with the local symmetry C_1 and to the *gauche*,−*gauche*,*trans* confirmation with the local symmetry C_S.

This mode of coordination is retained in the case of replacement of the alkyl groups at the sulfur atom by the phenyl fragments in complex **7**. The complex of triphenyl phosphorotrithioite with CuCl exists as a polymeric chain consisting of spiro-fused five-membered rings.[34] Each of these rings includes two copper atoms linked through the bridging chlorine atom and the P—S fragment.



7

The bidentate coordination appeared to be rather characteristic of phosphorotrithioite complexes with monovalent copper salts, the structure of the polymeric

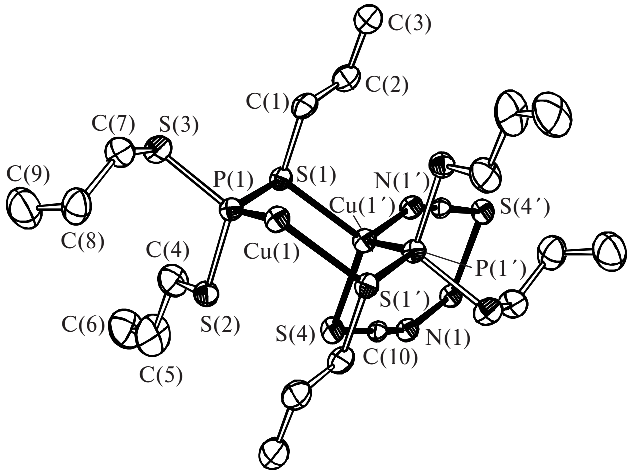
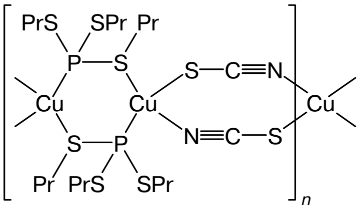


Fig. 8. Molecular structure of complex **11**.

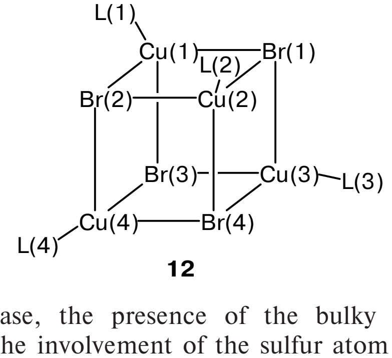
chain remaining virtually the same[38] when the halogen atom is replaced, for example, by rhodanide in complex **11**.



11

In this complex, tripropyl phosphorotrithioite has the *gauche* (P—S(1)), *gauche* (P—S(3)), *trans* (P—S(2)) conformation (Fig. 8).

The presence of bulky substituents at the sulfur atoms is the most evident factor, which can hinder the formation of bidentate copper complexes with phosphorotrithioites. This fact was confirmed in the study[38] of the crystal structure of the copper(I) bromide complex with triisopropy phosphorotrithioite:



12

In this case, the presence of the bulky substituent excludes the involvement of the sulfur atom in coordination with the metal atom resulting in the monodentate coordination of the phosphorus atom to the copper atom. Complex **12** has a tetrameric structure with the cubane-like core of the heavy atoms (Fig. 9).

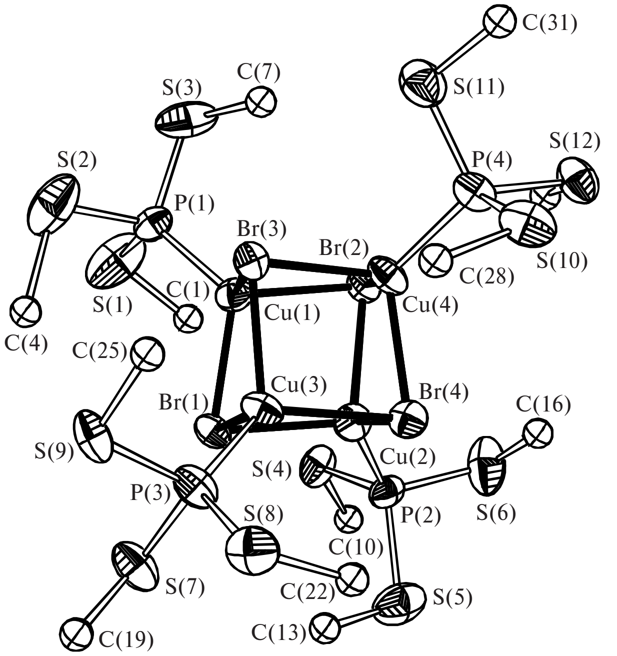
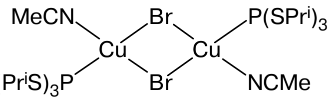


Fig. 9. Molecular structure of complex **12**.

It should be noted that complex **12** readily decomposes upon recrystallization from acetonitrile to give dimeric complex **13** in which the monodentate coordination of the phosphorus atom with the copper atom is retained and the solvent molecule is involved in the coordination sphere about copper.[36,38]



13

In tetrameric complex **12**, the triisopropyl phosphorotrithioite molecules bound through coordination bonds possess essential conformational lability, which is manifested in large thermal parameters of the atoms of the phosphorus-containing ligands and in their rotational disordering. In this case, the phosphorotrithioite ligands adopt three different conformations, including the *cis*,*gauche*,*cis* conformation, which has been observed previously in none of the phosphorotrithioite complexes with transition metal compounds, and two conformations with the *gauche* and *trans* orientations of the isopropylthio group typical of phosphorotrithioites. The same ligand in dimeric complex **13** is conformationally homogeneous and adopts the unsymmetrical *gauche*,*gauche*,*trans* conformation.

Along with steric factors, the electronic effects play a large role in the structure formation of the complex. For example, the replacement of the electron-withdrawing alkylthio group in the phosphorothioite ligand by the electron-donating dialkylamino group leads to changes not only in the donor properties of the phosphorus

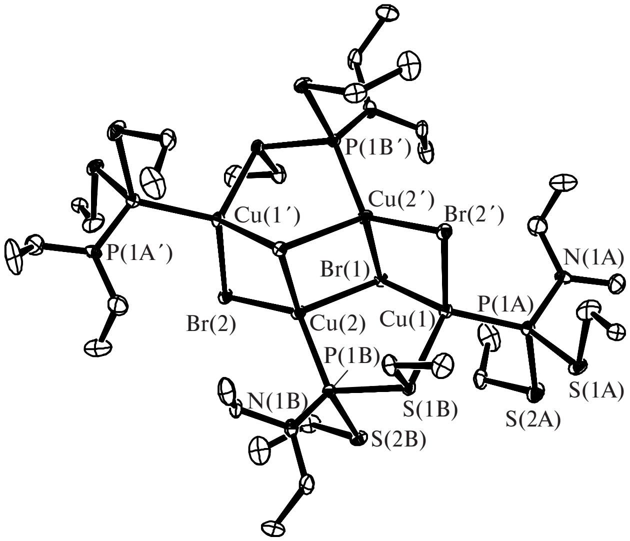
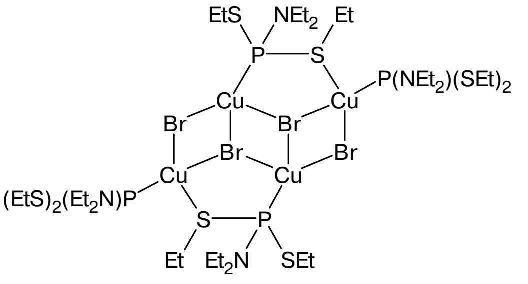


Fig. 10. Molecular structure of complex **14**.

atom, but also in the steric parameters of the corresponding ligand. In addition, the range of heteroatoms capable of forming coordination bonds with the copper atom is extended. X-ray diffraction study[37,38] of the complex of *N,N*-diethylamido-*S,S*-diethyl phosphorodithioite with CuBr (**14**) showed that the latter has a unique structure (Fig. 10) characterized by the monodentate coordination of the phosphorus atom to copper and by the bidentate coordination of the copper atom by the phosphorus and sulfur atoms.



14

The nitrogen atom is not involved in coordination bonding with the copper atom.

Further replacement of alkylthio groups by diethylamino groups leads to an increase in the steric volume of the ligand due to which only the monodentate coordination is realized in the complex of tris(diethylamido)phosphite with CuBr (**15**),[39] like in a number of other triamidophosphite complexes with copper halides.[40,41] Complex **15** (Fig. 11) has the monomeric structure $[(Et_2N)_3P]_2 \cdot CuBr$ with the planar-trigonal configuration of the copper atom, which is less typical of monovalent copper compounds than the tetrahedral configuration. This complex has the 2 : 1 stoichiometric composition, unlike the 1 : 1 composition of the above-described complexes.

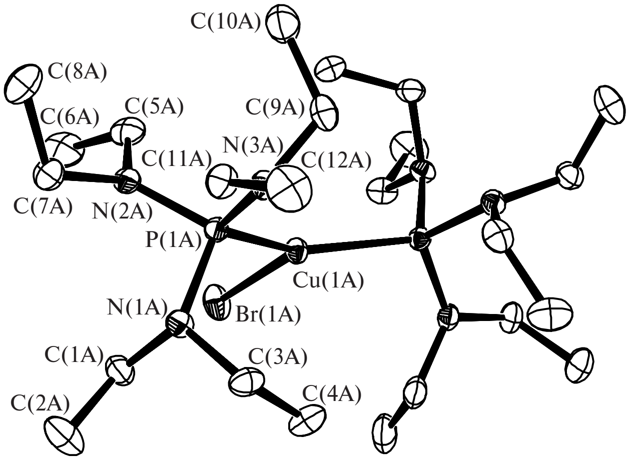
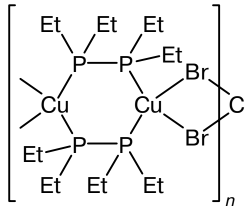


Fig. 11. Molecular structure of complex **15**.

Let us mention once again that the involvement of the second donor center of phosphorotrithioites, *viz.*, the sulfur atom, along with the phosphorus atom in coordination to the copper atom is explained, in our opinion, by the similarity of the electronic structures of the phosphorus and sulfur atoms, their sizes, and the energies of the lone electron pairs, as well as by mixing of the orbitals of the lone electron pairs of the phosphorus and sulfur atoms. This assumption is confirmed by the identity of the coordination properties[39] of the ligands containing the P—P, P—S, and S—S bonds, in particular, of triethyl phosphorotrithioite, tetraethyl diphosphine, and dialkyl disulfides. According to the X-ray diffraction data,[42] tetraethyl diphosphine forms a complex with copper bromide possessing the polymeric structure identical to that of the analogous copper complex with triethyl phosphorotrithioite:



In this case, the bidentate mode of coordination is observed, like in the complexes of dialkyl disulfides with copper(I) halides,[43,44] in particular, in the complex of diisopropyl disulfide with copper bromide (**16**)[39] studied by us (Fig. 12).

Therefore, the ligand molecules in transition metal complexes are characterized by a wider variety of different conformations (regardless of the mode of coordination and the nature of the metal atom) compared to the molecules of "free" phosphorothioites. In the crystals, phosphorotrithioites in transition metal complexes adopt all conformations typical of these ligands in the gaseous phase and solutions as well as conformations, which have not been observed previously for "free" phosphorotrithioites.

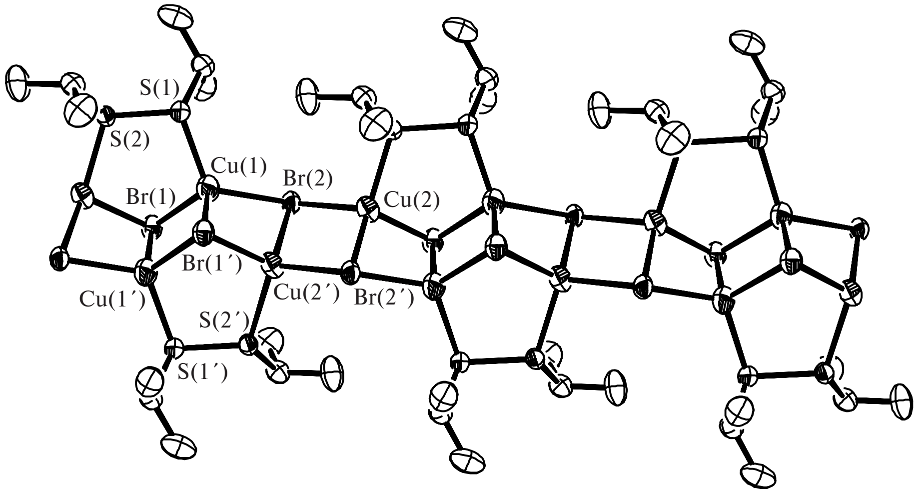


Fig. 12. Molecular structure of complex **16**.

Geometrical consequences of complex formation of phosphorothioites with transition metal compounds

It is reasonable that the conformational changes in the phosphorothioite molecules are the most noticeable consequences of complex formation, whereas changes in the bond angles and, the more so, in the bond lengths are less pronounced. The former changes depend substantially on the mode of coordination and the conformation of the ligand. Thus, the corresponding geometric parameters of the symmetrical conformations are identical on condition that the phosphorus atom is coordinated to the transition metal atom in the monodentate fashion. In the case of conformations with different orientations of the alkylthio and phenylthio groups, the observed variations in the geometric parameters reflect primarily the influence of the steric factors, which is particularly manifested in the bond angles at the phosphorus and sulfur atoms. Thus, the M—P—S and P—S—C bond angles (M is metal) in the fragments adopting different conformations differ by 10—15°.

One of the tendencies (Table 1) observed in all bidentate phosphorothioites complexes with copper(I) salts[38] is the formation of shorter P—Cu coordination bonds (2.218 Å) compared to S—Cu bonds (2.382 Å). This corresponds to the greater donor ability of the phosphorus atom in phosphorothioites. It should be noted that the P—C covalent bond (1.855 Å), unlike the P—Cu coordination bond, is generally[45] longer than the S—C bond (1.808 Å). At the same time, the presence of the S—Cu coordination bond in the bidentate complexes leads to a noticeable (~0.05 Å) elongation of the P—S covalent bond. As for a change in the P—S bond length in monodentate phosphorothioite complexes with transition metals, its value depends primarily on the nature of the metal atom. Thus, the average P—S bond length in a series of complexes of triphenyl phosphorotrithioite with various 3d metals changes as follows, *d*/Å: 2.110(2) (Cu) — 2.108(3) (Fe) — 2.132(3) (Mn) — 2.151(1) (Cr), which reflects the ability of the metal atom to perform back donation of the electron density to the σ*(P—S) orbitals.

Table 1. Principal bond lengths (*d*/Å) in bidentate phosphorotrithioite complexes with copper halides

Complex	*d*/Å				
	Cu—S(1)	Cu—P	P—S(1)*	P—S(2)	P—S(3)
$\mathrm{CuCl \cdot P(SEt)_3}$ (**8a**)	2.392(1)	2.208(1)	2.128(2)	2.086(2)	2.074(2)
$\mathrm{CuBr \cdot P(SEt)_3}$ (**8b**)	2.385(1)	2.224(1)	2.126(1)	2.074(1)	2.089(1)
$\mathrm{CuBr \cdot P(SPr)_3}$ (**9**)**	2.387(5)	2.199(7)	2.128(7)	2.072(9)	2.090(9)
	2.407(7)	2.215(6)	2.117(8)	2.099(9)	2.067(9)
$\mathrm{CuBr \cdot P(SBu)_3}$ (**10**)**	2.394(7)	2.192(7)	2.141(9)	2.065(9)	2.068(9)
	2.409(7)	2.231(7)	2.116(9)	2.084(9)	2.037(9)
$\mathrm{CuCl \cdot P(SPh)_3}$ (**7**)[34]	2.344(2)	2.243(2)	2.174(2)	2.117(2)	2.103(2)
$\mathrm{CuSCN \cdot P(SPr)_3}$ (**11**)	2.370(1)	2.240(1)	2.131(2)	2.074(2)	2.092(2)
$\mathrm{CuBr \cdot P(SEt)_2NEt_2}$ (**13**)	—	2.219(3)	—	2.111(4)	2.101(3)
	2.349(2)	2.196(2)	2.156(3)	2.100(3)	—
Average value	2.382	2.218	2.135	2.084	2.084

* The S(1) atom is involved in the coordination bond with Cu.

** The parameters are given for two independent molecules.

These changes in the geometric parameters of the phosphorothioite structure upon complex formation with transition metal compounds result from the electronic rearrangement of the molecule due to the appearance of coordination bonds, steric requirements, and intra- and intermolecular interactions involving phosphorothioites.

Conclusions

The data surveyed in the present review clearly demonstrate that the complex-forming properties of phosphorothioites differ radically from those of their oxygen- and nitrogen-containing analogs. Complexes with different structures are formed depending on the nature of the metal atom, the substituents in the phosphorothioite molecule, and conditions of the reaction and crystal growth. In these complexes, different modes of coordination are observed, *viz.*, the "classical" monodentate coordination involving the phosphorus atom, the unusual bidentate coordination involving both the phosphorus and sulfur atoms, and simultaneously both modes of coordination in one complex. In all cases, the phosphorus atom wins a competition with the sulfur atom for the formation of the coordination bond with the metal atom. On complex formation, the conformations of the ligand molecule become more diversified regardless of the nature of the metal atom and the mode of coordination.

Depending on the nature of the substituents at the sulfur atom and the mode of coordination, phosphorotrithioites form various structures with compounds of monovalent copper, *viz.*, monomeric, dimeric, tetrameric (of the cubane or staggered types), and polymeric with different structures. Analysis of the complexes of copper(I) halides with phosphorus-containing ligands, including compounds with the P—E bond (E is any heteroatom), which have been studied previously, demonstrated that dimers are the most widespread type of these complexes. In the latter complexes, two copper atoms are linked through the bridging halogen atoms. The copper atoms can adopt both the planar-trigonal and tetrahedral configurations depending on the nature and structure of the ligands. Cubane-like and staggered structures are less common. The four-membered rings containing the bridging halogen atoms are destroyed only in the case of sterically overcrowded phosphorus-containing ligands yielding monomeric complexes of different stoichiometric compositions, *viz.*, LCuHal, L_2CuHal, and L_3CuHal. The bidentate mode of coordination of phosphorotrithioites in complexes with copper(I) halides gives rise to complexes with unique polymeric structures, which offers possibilities for the construction of new materials.

We thank S. A. Katsyuba and V. A. Al′fonsov for helpful discussion.

This work was financially supported by the Russian Foundation for Basic Research (Project Nos. 98-03-32777 and 98-03-33074). We also thank the Russian Foundation for Basic Research (Project No. 99-07-90133) for partial paying for the license for the Cambridge Structural Database.

References

1. A. N. Pudovik, E. S. Batyeva, and O. G. Sinyashin, *Tioefiry kislot trekhvalentnogo fosfora* [*Thioesters of Trivalent Phosphorus Acids*], Nauka, Moscow, 1989 (in Russian).
2. A. N. Pudovik, E. S. Batyeva, O. G. Sinyashin, and V. A. Al′fonsov, in *Chemistry of Organophosphorus Compounds*, Ed. A. N. Pudovik, Mir Publishers, Moscow, 1989, pp. 93—118.
3. J. R. Dilworth and N. Wheatley, *Coord. Chem. Rev.*, 2000, **199**, 89.
4. US Pat. 3110747, 1963; *Chem. Abstrs.*, 1964, **60**, 7504a.
5. US Pat 3351666, 1967; *Chem. Abstrs.*, 1968, **68**, 42004p.
6. F. H. Allen, O. Kennard, and R. Taylor, *Acc. Chem. Res.*, 1983, **16**, 146, *Cambridge Structural Database System* (Search was performed with the October 2000 release, 224400 entries).
7. V. V. Zverev, Z. G. Bazhanova, N. V. Villem, and Ya. Ya. Villem, *Zh. Obshch. Khim.*, 1983, **53**, 1968 [*J. Gen. Chem. USSR*, 1983, **53** (Engl. Transl.)].
8. E. N. Ofitserov, Dr. Sc. (Chem). Thesis, *Konkurentsiya protsessov zameshcheniya i prisoedineniya v reaktsiyakh proizvodnykh trekhvalentnogo fosfora* [*Competitive Substitution and Addition in Reactions of Trivalent Phosphorus Derivatives*], Kazan, 1992, 30 (in Russian).
9. I. I. Patsanovskii, E. A. Ishmaeva, A. B. Remizov, F. S. Bilalov, E. N. Ofitserov, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR,* 1980, **254**, 414 [*Dokl. Chem.*, 1980 (Engl. Transl.)].
10. V. A. Naumov, O. N. Kataeva, and O. G. Sinyashin, *Zh. Strukt. Khim.,* 1984, **25**, 79 [*J. Struct. Chem. (USSR)*, 1984, **25** (Engl. Transl.)].
11. O. N. Kataeva and V. A. Naumov, *Zh. Strukt. Khim.,* 1987, **28**, 153 [*J. Struct. Chem. (USSR*, 1987, **28** (Engl. Transl.)].
12. E. A. Filippova, S. A. Katsyuba, R. R. Shagidullin, and O. G. Sinyashin, *Zh. Prikl. Spektrosk.,* 1987, **46**, 761 [*J. Appl. Spectrosc.,* 1987, **46** (Engl. Tranl.)].
13. E. A. Filippova, S. A. Katsyuba, V. N. Shegeda, R. R. Shagidullin, and A. G. Trusenev, *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1989, 1531 [*Bull. Acad. Sci. USSR, Div. Chem. Sci.*, 1989, **38** (Engl. Transl.)].
14. V. A. Al′fonsov, I. A. Litvinov, O. N. Kataeva, D. A. Pudovik, and S. A. Katsyuba, *Zh. Obshch. Khim.*, 1995, **65**, 1129 [*Russ. J. Gen.Chem.*, 1995, **65** (Engl. Transl.)].
15. I. A. Litvinov, M. B. Zuev, O. N. Kataeva, and V. A. Naumov, *Zh. Obshch. Khim.*, 1991, **61**, 1120 [*J. Gen. Chem. USSR*, 1991, **61** (Engl. Transl.)].
16. R. W. Light, L. D. Hutchins, R. T. Paine, and C. F. Campana, *Inorg. Chem.*, 1980, **19**, 3597.
17. D. S. Yufit, Yu. T. Struchkov, M. A. Pudovik, L. K. Kibardina, I. A. Aleksandrova, V. K. Khairullin, and A. N. Pudovik, *Dokl. Akad. Nauk SSSR,* 1980, **255**, 1190 [*Dokl. Chem.*, 1980 (Engl. Transl.)].
18. R. K. Shibao, N. L. Keder, and H. Eckert, *Acta Crystallogr., Sect. C*, 1992, **48**, 1525.
19. A.-F. Shihada and F. Weller, *J. Organomet. Chem.*, 1988, **342**, 177.
20. V. A. Milyukov, A. V. Zverev, S. M. Podlesnov, D. B. Krivolapov, I. A. Litvinov, A. T. Gubaidullin, O. N. Kataeva,

A. G. Ginzburg, and O. G. Sinyashin, *Eur. J. Inorg. Chem.*, 2000, 225.

21. O. N. Kataeva, A. T. Gubaidullin, D. B. Krivolapov, I. A. Litvinov, L. I. Kursheva, V. A. Milyukov, and O. G. Sinyashin, *Tez. dokl. VII Vseross. konf. po metalloorganicheskoi khimii* [*Abstrs. of Papers, VII All-Russian Conf. on Organometallic Chemistry*], Moscow, 1999, 65 (in Russian).
22. M. J. McGlinchey, in *Advances in Organometallic Chemistry*, Eds. F. G. B Stone and R. West, Acad. Press, Inc., 1992, 285—325.
23. D. Braga, F. Grepioni, and G. R. Desiraju, *Chem. Rev.*, 1998, **98**, 1375.
24. G. R. Desiraju, *Acc. Chem. Res.*, 1991, **24**, 290.
25. T. Steiner and W. Saenger, *J. Am. Chem. Soc.*, 1992, **114**, 10146.
26. G. R. Desiraju, *Acc. Chem. Res.*, 1996, **29**, 441.
27. U. Koch and P. L. A. Popelier, *J. Phys. Chem.*, 1995, **99**, 9747.
28. O. N. Kataeva, A. T. Gubaidullin, D. B. Krivolapov, and I. A. Litvinov, *Abstrs. XVIIIth IUCr Congress and General Assembly (4—13 August 1999, Glasgow, Scotland)*, Glasgow, 1999, 414.
29. M. Herberhold, A. Hofman, W. Milius, F. F. de Biani, and P. Zanello, *Inorg. Chim. Acta*, 1998, **273**, 24.
30. W. Bin-Fang, S. Han-Quan, Y. Xiu-Ying, H. Hiang, and L. Qi-Wang, *J. Strukt. Chem. (Chinese)*, 1992, **11**, 339.
31. L. Qi-Wang, W. Bin-Fang, H. Hiang, L. Shu-Tang, and Y. Xiu-Ying, *Acta Chim. Sinica (Chinese)*, 1992, **50**, 778.
32. O. G. Sinyashin, I. Yu. Gorshunov, V. A. Milyukov, E. S. Batyeva, I. A. Litvinov, O. N. Kataeva, A. G. Ginzburg, and V. I. Sokolov, *Izv. Akad. Nauk, Ser. Khim.*, 1994, 1116 [*Russ. Chem. Bull.*, 1994, **43**, (Engl. Transl.)].
33. V. A. Milyukov, A. V. Zverev, S. M. Podlesnov, D. B, Krivolapov, I. A. Litvinov, A. T. Gubaidullin, O. N. Kataeva, A. G. Ginzburg, and O. G. Sinyashin, *Zh. Obshch. Khim.*, 2000, **70**, 748 [*Russ. J. Gen. Chem.*, 2000, **70** (Engl. Transl.)].
34. P. G. Jones, A. K. Fischer, L. Frolova, and R. Schmutzler, *Acta Crystallogr., Sect. C*, 1998, **54**, 1842.
35. E. S. Batyeva, L. I. Kursheva, O. N. Kataeva, I. A. Litvinov, and O. G. Sinyashin, *Zh. Obshch. Khim.*, 1993, **63**, 225 [*Russ. J. Gen. Chem.*, 1993, **63** (Engl. Transl.)].
36. O. N. Kataeva, I. A. Litvinov, V. A. Naumov, L. I. Kursheva, and E. S. Batyeva, *Inorg. Chem.*, 1995, **34**, 5171.
37. O. N. Kataeva, A. T. Gubaidullin, I. A. Litvinov, L. I. Kursheva, E. S. Batyeva, and O. G. Sinyashin, *Phosphorus, Sulfur, Silicon, Relat. Elem.*, 1999, **144—146**, 733.
38. O. N. Kataeva, D. B. Krivolapov, A. T. Gubaidullin, I. A. Litvinov, L. I. Kursheva, and S. A. Katsyuba, *J. Mol. Struct.*, 2000, **554**, 127.
39. O. N. Kataeva, A. T. Gubaidullin, I. A. Litvinov, L. I. Kursheva, E. S. Batyeva, V. A. Milyukov, and O. G. Sinyashin, *Tez. dokl. VI Mezhdunarodnaya konferentsiya "Metalloorganicheskie soedineniya — materialy budushchego tysyacheletiya"* [*Abstrs. of Papers, International Conf. on Organic Compounds — Materials of the New Millenium*], Nizhnii Novgorod, 2000, 74 (in Russian).
40. T. M. Arkhireeva, B. M. Bulychev, A. I. Sizov, T. A. Sokolova, V. K. Belsky, and G. L. Soloveichik, *Inorg. Chim. Acta*, 1990, **169**, 109.
41. P. B. Hitchcock, M. F. Lappert, and M. Layth, *Eur. J. Inorg. Chem.*, 1998, 751.
42. J. Von Kaiser, H. Hartung, E. Lengies, R. Richter, and J. Sieler, *Z. Anorg. Allg. Chem.*, 1976, **422**, 149.
43. C.-I. Branden, *Acta Chem. Scand.*, 1967, **21**, 1000.
44. P. M. Boorman, K. A. Kerr, R. A. Kydd, K. J. Moynihan, and K. A. Valentine, *J. Chem. Soc., Dalton. Trans.*, 1982, 1401.
45. F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, and R. Taylor, *J. Chem. Soc., Perkin Trans. 2*, 1987, S1.

Received February 9, 2001;
in revised form April 25, 2001