Influence of solvents on the molecular and crystal structure of the complex of 1,3-diallyl-5-[3-(diphenylphosphino)propyl]-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione with palladium(II) dichloride

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X-ray diffraction study demonstrated that the molecular and crystal structures of the complexes of 1,3-diallyl-5-[3-(diphenylphosphino)propyl]-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**1**) with $PdCl_2$ are determined to a large degree by intra- and intermolecular short contacts between different-polarity groups of the complex molecules. The strength and the existence of the complexes may be affected by the solvents from which the crystals are grown.

Key words: X-ray diffraction analysis, tertiary phosphine, complexes with palladium(II) dichloride.

Interest in the use of phosphorylated derivatives of diallylisocyanuric acid in the synthesis of coordination compounds arises primarily from their polydentate properties. When developing approaches to realization of the coordination potentialities of these compounds, we found that not only monomeric *trans*-complexes, which are typical of tertiary phosphines containing bulky substituents at the phosphorus atom, but also binuclear and chelate compounds can be prepared by varying the number of carbon atoms in the methylene chain between the isocyanurate ring and the diphenylphosphine group.[1] It was also demonstrated that the coordination bonds in the complexes differ in stability and the complexes isolated from different solvents possess different physicochemical properties. Thus, the reactions of 1,3-diallyl-5-[3-(diphenylphosphino)propyl]-1,3,5-triazine-2,4,6(1*H*,3*H*,5*H*)-trione (**1**) with $PdCl_2$ in MeCN or EtOH afforded complexes **2** or **3**, respectively, of composition ligand : metal = 2 : 1. The resulting complexes were obtained as yellow powders.[2] Spectral studies demonstrated that both compounds are monomeric *trans*-complexes, but their melting points, frequencies of Pd—Cl stretching vibrations in the IR spectra, and the chemical shifts of the phosphorus signals in the ^{31}P NMR spectra are somewhat different.[2] In addition, the ^1H NMR spectra of complexes **2** and **3** have signals for the protons of MeCN and EtOH, respectively.[2] Previously,[1] it was suggested that the difference in the physicochemical characteristics of complexes **2** and **3** is associated with the fact that the crystals of the complexes contain molecules of the solvent in which these complexes have been synthesized. However, the question of whether the solvent is involved in the coordination sphere about the palladium ion remained open.

For tertiary phosphines, it was found[3] that the spectral characteristics of their complexes with salts of transition metals depend substantially on the bond angles at the phosphorus and palladium atoms, which are primarily associated with steric interactions between the substituents at the phosphorus atom and the ligands in the complex. At the same time, it is known that interactions, such as hydrogen bonds in which solvent molecules of solvation can also be involved, play an important role in structures of organic molecular crystals.[4] The formation of supramolecular structures in crystals and solutions of isocyanurates due to hydrogen bonding is well known.[5] In this connection and taking into account that complexes **2** and **3** contain identical ligands, it is reasonable to suppose that the difference in their physicochemical characteristics is a manifestation of the difference in the geometric parameters, which, in turn, can be caused by intra- and intermolecular short contacts between the different-polarity groups in the complex molecules.

Results and Discussion

With the aim of studying the effect of the solvents on the structures of complexes of tertiary phosphine **1** with $PdCl_2$, we prepared crystals **4** and **5** from different solutions of complexes **2** and **3** and studied these crystals by X-ray diffraction analysis.

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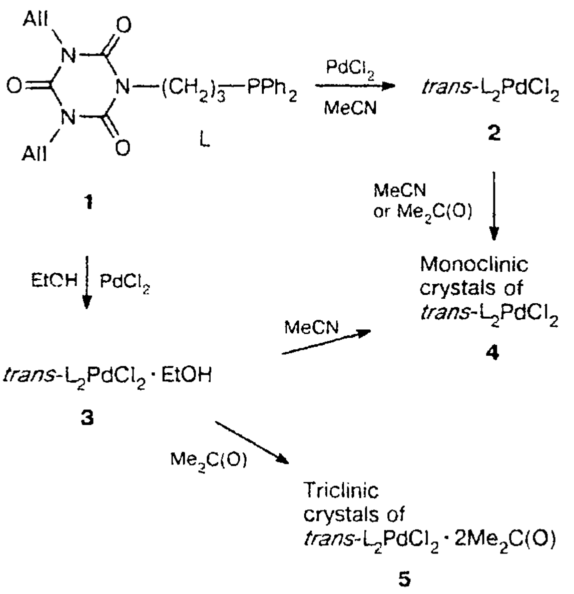

Crystals were grown from MeCN, in which complex **2** has been synthesized, and from acetone. Acetone was chosen because we failed to obtain crystals from EtOH (in which complex **3** has been synthesized) due to the poor solubility of the complexes in this solvent, while these complexes are rather readily soluble in acetone. In addition, acetone, like EtOH, is more prone to hydrogen bonding than MeCN. As a result, two types of crystals were prepared. In MeCN, both complexes (**2** and **3**) formed identical monoclinic crystals **4** with the space group *C*2/*c*. These crystals do not contain solvent molecules. When crystallization was performed in acetone instead of MeCN, neither the crystal symmetry changed nor was the solvent involved in the crystal lattice in the case of complex **2**, whereas compound **3** crystallized as solvate complex **5** with a solvent : complex composition of 2 : 1. Crystals **5** belong to the triclinic system (the space group $P\bar{1}$). The selected geometric parameters of the complexes in crystals **4** and **5** are given in Table 1. The molecular structures of the complexes under study are shown in Figs. 1 and 2. In crystals **4** and **5**, the palladium ions occupy inversion centers and are surrounded by two chloride ions and two molecules of tertiary phosphine, which coordinate the palladium atom through the phosphorus atoms located in the *trans* positions relative to one another. The Cl_2PdP_2 fragments in both crystals are planar, but their geometric parameters are different. Thus, the Cl(1)PdP(1) and Cl(1′)PdP(1) (Cl(1′): $-x$, $-y$, $2 - z$) angles (90.71(2)° and 89.29(2)°, respectively) in crystal **5** are close to the ideal values for planar-square coordination, whereas the corresponding angles in crystal **4** are 3° smaller and larger (87.03(3)° and 92.97(3)°), respectively, than 90°. Approximately the same distortions (2°) of the angles about the central ion have been observed previously[6] in the *trans*-complex $PdCl_2(PPh_3)_2$, in which the chlorine atom is shielded by the carbon atom of one of the phenyl radicals (the $ClPdPC_{Ph}$ torsion angle is 16.0(2)°). An analogous shielding is observed in crystals **4**, the Cl(1)PdP(1)C(22) angle being only 9.0(2)°. In crystals **5**, such shielding is absent. For the *trans*-complex $PdCl_2(PPh_3)_2$, the observed effects were attributed to steric interactions between the bulky phenyl groups at the phosphorus atom.[6] However, in the case of crystals **4** this explanation fails because the complexes in crystals **4** and **5** contain identical substituents at the phosphorus atoms. The fact that the Pd—Cl bonds in both crystals are elongated compared to the corresponding bonds in the *trans*-complex $PdCl_2(PPh_3)_2$ (2.291(1) Å) is quite unexpected. The elongation of the bonds in crystals **4** is larger (2.3609(8) Å) than that in crystals **5** (2.3356(6) Å). Note that this increase in the Pd—Cl bond lengths has not been observed previously even in sterically strained chelate *trans*-complexes of tertiary phosphines with $PdCl_2$ (for example, the Pd—Cl bond length in the complex *trans*-$PdCl_2[(Bu^t)_2P(CH_2)_3P(Bu^t)_2]$ is 2.326(4) Å).[6] The Pd—P bond lengths in crystals **4** (2.326(1) Å) and **5** (2.329(5) Å) are comparable with those in the complex *trans*-$PdCl_2(PPh_3)_2$ (2.337(1)).[6] The C_{Ph}—P—C_{Ph} and C_{Alk}—P—C_{Ph} angles are smaller than the tetrahedral value. However, this feature is typical of all complexes of tertiary phosphines with salts of transition metals.[3] The P—C_{Ph} bond lengths have standard values[3] (see Table 1).

Therefore, the data of X-ray diffraction analysis demonstrated that the environment about the central palladium ion in crystals **4** is distorted compared to the ideal geometry reported in the literature. Note that this distortion is not associated with steric effects of the substituents at the phosphorus atoms. This brings up the

Table 1. Selected bond lengths (*d*), bond angles (ω), and torsion angles (τ) in structures **4** and **5**

Parameter	**4**	**5**
Bond	*d*/Å	
Pd(1)—Cl(1)	2.3609(8)	2.3356(6)
Pd(1)—P(1)	2.326(1)	2.3296(5)
P(1)—C(15)	1.832(4)	1.823(3)
P(1)—C(16)	1.811(4)	1.827(3)
P(1)—C(22)	1.821(4)	1.818(3)
Bond angle	ω/deg	
Cl(1′)—Pd(1)—P(1)	87.03(3)	89.29(2)
Cl(1)—Pd(1)—P(1)	92.97(3)	90.71(2)
Pd(1)—P(1)—C(15)	111.4(1)	113.37(8)
Pd(1)—P(1)—C(16)	108.1(1)	118.57(9)
Pd(1)—P(1)—C(22)	119.5(1)	108.06
C(15)—P(1)—C(16)	107.1(2)	102.7(1)
C(15)—P(1)—C(22)	104.2(2)	107.8(1)
C(16)—P(1)—C(22)	105.8(2)	105.7(1)
Torsion angle	τ/deg	
Cl(1)—Pd(1)—P(1)—C(15)	−130.7(1)	151.4(1)
Cl(1)—Pd(1)—P(1)—C(16)	111.8(1)	30.9(1)
Cl(1)—Pd(1)—P(1)—C(22)	−9.2(2)	−89.1(2)

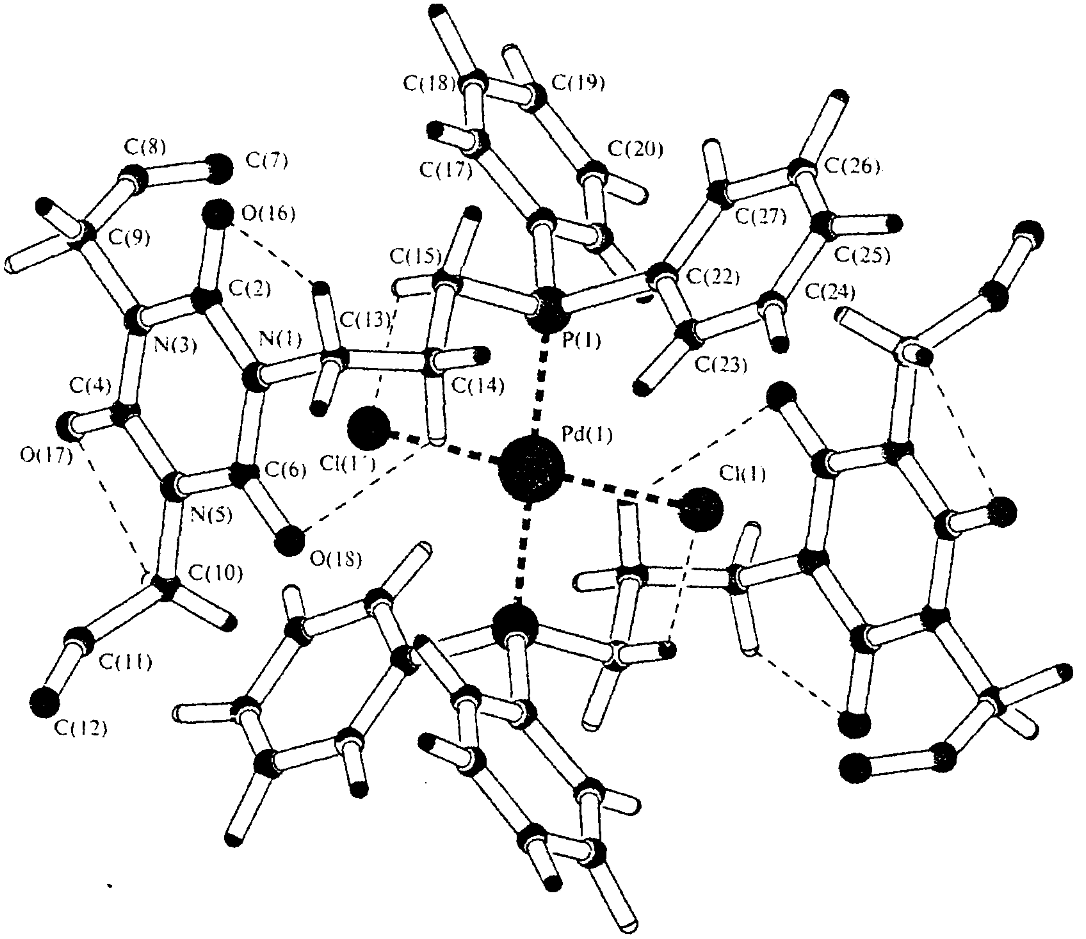

Fig. 1. Structure of complex **4** in the crystal. The intramolecular C—H...X hydrogen bonds are indicated by thin dashed lines.

questions: Why is the formation of crystals **4** favorable in the case of crystallization of complex **2** from acetone, and why does crystallization of complex **3** from different solvents afford crystals of two types?

We believe that the distortions of the geometric parameters of the molecules in crystals **4** are compensated by intramolecular short contacts between different-polarity groups, which is associated with the presence of the isocyanurate fragments in the phosphine ligands. The formation of supramolecular structures by derivatives of isocyanuric acid through intermolecular nonbonded interactions between the carbonyl groups of the heterocycle and the protons of the alkyl substituents has been the subject of wide speculation in recent years.[5,7] It was also demonstrated that the solvent molecules can also be involved in these interactions.[8] However, it should be taken into account that the H-donor ability of the solvents is different. Crystals **4** obtained by crystallization of complex **2** from MeCN do not contain molecules of the solvating solvent due, apparently, to the weak H-donor ability of the latter. In our opinion, the formation of crystals with the same symmetry upon crystallization of complex **2** from acetone indicates that the system of nonbonded interactions observed in crystals **4** is formed even in complex **2** and this system is so strong that it is not destroyed by acetone. Ethanol should form stronger molecular complexes with isocyanurates compared to MeCN and hence, ethanol could be involved in the crystal lattice of complex **3**. However, we have demonstrated previously[2] (based on the data of ^{31}P and ^{1}H NMR spectroscopy) that EtOH can be displaced from the complex by MeCN. In this connection, it is not surprising that prolonged storage of complex **3** in MeCN afforded crystals identical to those obtained in the case of complex **2**. At the same time, complex **3** in acetone gave rise to crystals **5** in spite of the fact that the H-donor ability of ethanol is higher than that of acetone. Presumably, the driving force for both processes of displacement of EtOH from complex **3** is the tendency of the structures to form stronger intramolecular short contacts.

The above-mentioned conclusions are based on the following data of X-ray diffraction analysis. It was found that in the absence of the solvating solvent, the differ-

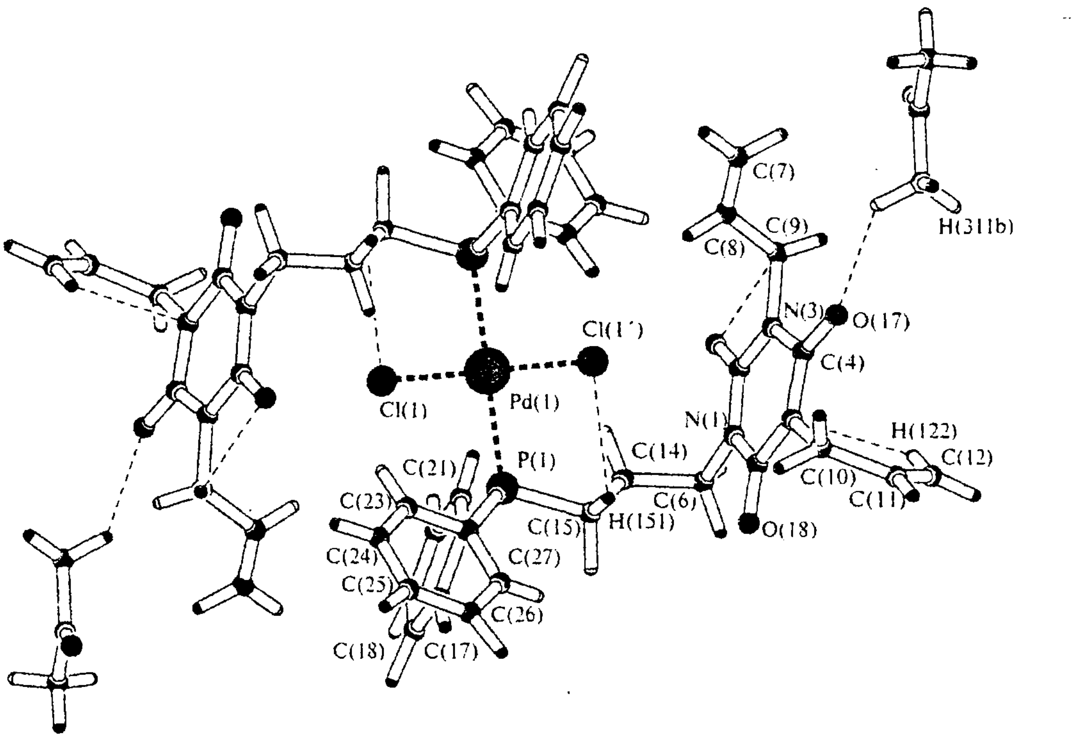

Fig. 2. Structure of complex **5** in the crystal. The intramolecular C—H...X hydrogen bonds and the hydrogen bonds with acetone molecules of solvation are indicated by thin dashed lines

ent-polarity groups in the isocyanurate heterocycle of the phosphine ligand in crystals **4** are involved in a number of stabilizing intramolecular short contacts. Among these contacts are interactions of the O(17) and O(16) atoms of the carbonyl groups of the isocyanurate ring with the H(102) proton of the allylic substituent and the H(131) proton of the methylene group of the propylene fragment, respectively (*d*(O(17)...H—C(10)) is 2.35(1) Å and the C(10)—H...O(17) angle is 101(1)°; *d*(O(16)...H—C(13)) is 2.28(6) Å and the C(13)—H...O(16) angle is 106(3)°). In addition, the position of the isocyanurate fragment in crystals **4** is favorable for hydrogen bonding between the O(18) atom and the H(141) proton of the methylene chain (*d*(O...H—C(14)) is 2.50(3) Å and the C(14)—H...O(18) angle is 117(2)°) and for the formation of rather short contacts between the chlorine atom and the H(151) proton of the methylene chain of the phosphine ligand (*d*(Cl...H—C(15)) is 2.69(5) Å and the C(15)—H...Cl angle is 132(3)°). Apparently, these interactions are responsible for the elongation of the Pd—Cl bonds to 2.3609(8) Å and for the decrease in the Cl(1)—Pd—P(1) and Pd—P(1)—C(15) angles to 87.03(3)° and 111.5(1)°, respectively, the latter angle being substantially smaller than the analogous angles in *trans*-complexes of palladium(II) salts with tertiary phosphines containing alkyl substituents (for example, the Pd—P—C_{Me} angles in *trans*-$PdI_2(PMe_2Ph)_2$ are in the range of 114—118°).[9] It should be noted that the observed intramolecular short contacts between the different-polarity groups in the complex molecule do not lead to noticeable distortions of the bond lengths and bond angles at the carbon and nitrogen atoms of the planar isocyanurate fragment compared to the geometric parameters of nonsubstituted isocyanuric acid.[10] Unfortunately, we failed to unambiguously establish the conformations of the allylic substituents in the isocyanurate heterocycle in crystals **4** due to rotational disorder of the substituents, which is manifested in the increase in the thermal parameters of the corresponding carbon atoms.

In crystals **5**, the isocyanurate fragment is rotated with respect to the N(1)—C(13) bond in such a way that the distance between the O(18) and H(141) atoms becomes larger than the sum of their van der Waals radii due to a short contact between the H(311) atom of the acetone molecule of solvation and the O(17) atom of the isocyanurate fragment of the complex (*d*(C(31)—H...O(17)) is 2.54(1) Å and the C(31)—H...O(17) angle is 136(1)°). In addition, the distance between the chlorine atom and the H(151) proton of the methylene group increases to 2.80(3) Å, whereas the Pd—Cl bond length decreases to 2.3356(6) Å. In crystals **5**, an intramolecular interaction between the O(16) atom of the isocyanurate heterocycle and the H(92) atom of the methylene group of the allylic radical is observed (*d*(O(16)...H—C(9)) is 2.33(3) Å and the

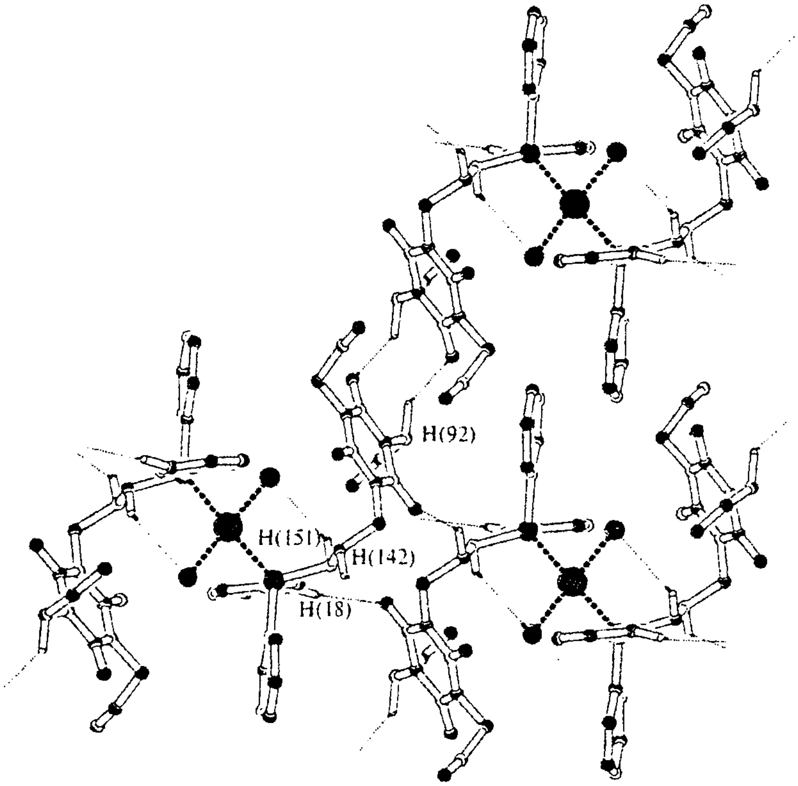

Fig. 3. System of intermolecular hydrogen bonds (indicated by thin lines) and the molecular packing in crystal **4**. The view along the *0Y* axis. Only protons involved in hydrogen bonding are shown.

C(9)—H...O(16) angle is 104(3)°), which is favored by the *trans* configuration of the C(7)—C(8) and C(9)—N(3) bonds (the N(3)—C(9)—C(8)—C(7) torsion angle is 142.4(6)°) in the symmetrically arranged isocyanurate fragments. The bonds of two other allylic groups in the isocyanurate fragments, *viz.*, C(12)—C(11) and C(10)—N(5), are in the eclipsed conformation (the C(12)—C(11)—C(10)—N(5) torsion angle is 2.2(5)°) due to the short contact between the N(5) atom and the H(122) proton (*d*(C(12)—H...N(5)) is 2.54(1) Å and the C(12)—H...N(5) angle is 101.0(2)°).

In both cases, the complex molecules are arranged in layers, but systems of intermolecular contacts between and within the layers are substantially different. In crystals **4**, hydrogen-bonded molecules are linked in infinite layers parallel to the *0YZ* plane through intermolecular contacts between the H(18) protons of the phenyl groups and the H(142) protons of the methylene groups of one molecule of the complex and the O(16′) and O(16′′) atoms of the isocyanurate rings of the adjacent molecules. Each molecule in the layer is linked to molecules of the upper and lower layers *via* pairs of short contacts between the O(17) atoms of the isocyanurate fragments and the H(92) atoms of the allylic groups of the adjacent molecules to form an infinite chain of molecules linked along the diagonal of the *X0Z* plane. Therefore, the complex molecules in the crystal are linked *via* a three-dimensional system of hydrogen bonds (Fig. 3). In addition, the parallel alignment of the phenyl rings of the molecules located in the lower and upper layers results in stabilizing stacking-type dispersion interactions.[11]

Of intermolecular interactions, only pairs of contacts between the corresponding O(18) atoms of the isocyanurate fragments and the H(132) protons of the methylene groups of two adjacent molecules of the complex related by the symmetry operation (1 − *x*, −*y*, 1 − *z*) (*d*(H...O(18)) is 2.43(3) Å and the C(13)—H...O(18) angle is 139(2)°) persist in crystals **5**. These contacts lead to the formation of infinite chains of molecules linked *via* hydrogen bonds. These chains lie in the *X0Z* plane and are extended along the diagonal of this face of the unit cell (Fig. 4). The π—π dispersion interactions are identical in both crystals. However, these interactions in crystals **4** are additional to those available in the three-dimensional network of hydrogen bonds. In crystals **5**, only stacks of complex molecules surrounded by acetone molecules of solvation are formed due to the participation of the O(17) atoms of the carbonyl groups in short contacts with acetone molecules. The latter, apparently, prevent the formation of contacts between the adjacent stacks. These stacks are

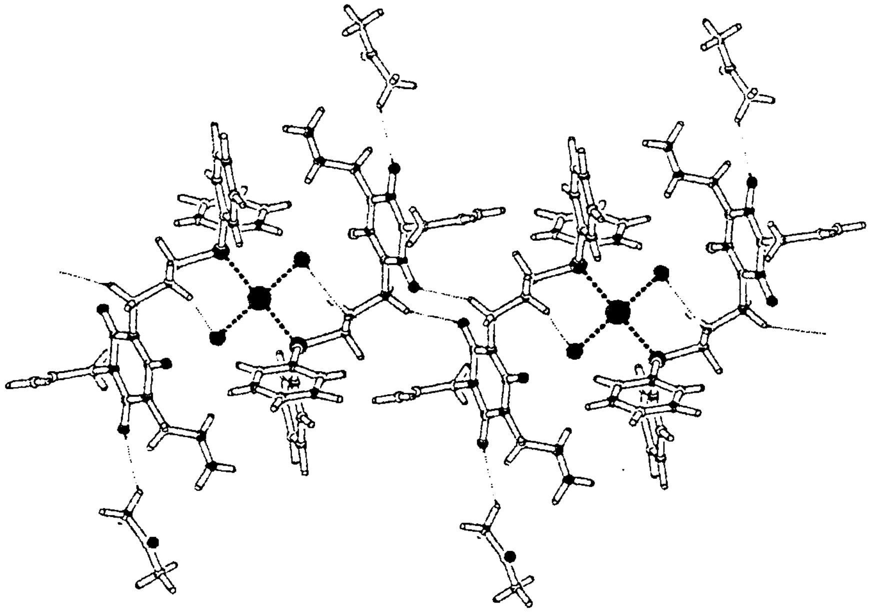

Fig. 4. Formation of stacks of the molecules linked *via* hydrogen bonds in the crystal of complex **5**. The view along the *0X* axis. The intermolecular hydrogen bonds are indicated by thin lines.

linked in layers and a three-dimensional structure only *via* dispersion interactions between the phenyl rings of the molecules from the adjacent chains. In crystal **5**, regions containing the solvent molecules are localized.

To summarize, X-ray diffraction study demonstrated that the geometric parameters of the complexes of isocyanurate-containing tertiary phosphine **1** with $PdCl_2$ are determined to a large extent by the system of intra- and intermolecular short contacts between the different-polarity groups, in which the solvent molecules of solvation can also be involved. The physicochemical characteristics of the complexes, in turn, depend on their geometric parameters. Hence, particular characteristics of two isocyanurate-containing complexes which have the same composition and identical configurations of the ligands about the central ion, but which are isolated from different solvents, can be different.

Experimental

X-ray diffraction studies were carried out on an automated four-circle Enraf-Nonius CAD-4 diffractometer.

Crystals **4**, L_2PdCl_2, are monoclinic. At 20 °C, a = 23.073(3), b = 9.848(2), c = 22.150(3) Å, β = 98.12(1)°, V = 4982(1) Å^3, Z = 4, d_{calc} = 1.45 g cm^{-3}, space group $C2/c$ (the molecules occupy special positions, *viz.*, centers of symmetry).

Crystals **5**, $L_2PdCl_2 \cdot EtOH$, are triclinic. At 20 °C, a = 9.735(2), b = 11.915(3), c = 13.721(2) Å, α = 80.17(2), β = 69.38(1), γ = 72.52(2)°, V = 1417.0(5) Å^3, Z = 1, d_{calc} = 1.49 g cm^{-3}, space group $P1$ (the molecules occupy special positions, *viz.*, centers of symmetry).

A total of 5501 (**4**) and 6018 (**5**) reflections were measured (λMo-Kα radiation, graphite monochromator, ω/2θ scanning technique, θ ≤ 26.3°) of which 3899 (**4**) and 5039 (**5**) reflections were with $I \geq 3\sigma$. The empirical absorption correction was applied (μMo were 5.92 (**4**) and 9.22 cm^{-1} (**5**)). The structures were solved by the direct method using the SIR program[12] and refined isotropically. Based on the thermal parameters, bond lengths, and bond angles of the allylic substituents in crystal **4**, we suggested that the terminal carbon atoms of these fragments are disordered. The difference electron density series revealed intense peaks around these atoms. We succeeded in resolving the positions of the C(7) atom disordered over two sites with occupancies of 0.4 and 0.6 and of the C(12) atom disordered over three sites with occupancies of 0.4, 0.2, and 0.4. Then these structures were refined anisotropically (except for the disordered carbon atoms in the allylic fragments in crystal **4**). Subsequently, the positions of the hydrogen atoms (except for the H atoms of the disordered fragments) were located from the difference electron density series. In crystal **4**, the contribution of the H atoms to the structure amplitudes was taken into account using fixed positional and isotropic temperature parameters. In crystal **5**, the hydrogen atoms were refined isotropically. The final values of the R factors were as follows: R = 0.046 and R_w = 0.061 based on 3706 independent reflections with $F^2 \geq 3\sigma$ in crystal **4** and R = 0.037 and R_w = 0.053 based on 4810 reflections with $F^2 \geq 3\sigma$ in crystal **5**. All calculations were carried out on an AlphaStation 200 computer using the MolEN program package.[13] The atomic coordinates and the temperature parameters were deposited with the Cambridge Structural Database. The molecules and the molecular packings in the crystals were drawn and the intra- and intermolecular interactions were calculated using the PLATON program.[14]

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