1,3-Diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates in reactions of complex formation with palladium(II) dichloride

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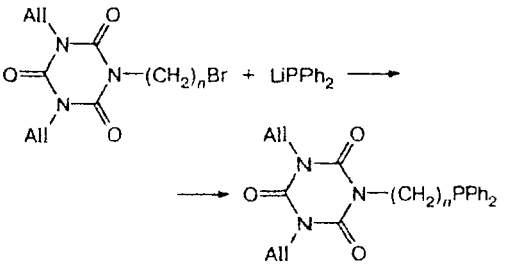
The reactions of phosphine derivatives of diallyl isocyanurates with palladium(II) dichloride lead to the formation of complexes, whose structure, composition, and stability depend on the length of the methylene chain between the isocyanurate and diphenylphosphine fragments in the ligand. 1,3-Diallyl-5-[5′-(diphenylphosphino)pentyl and 10′-(diphenylphosphino)decyl] isocyanurates with $PdCl_2$ form monomeric L_2PdCl_2 *trans*-complexes in which P atoms of the ligands participate in coordination with the metal. 1,3-Diallyl-5-[2′-(diphenylphosphino)ethyl] isocyanurate with $PdCl_2$ forms a dimeric $(LPdCl_2)_2$ complex, which decomposes in a solution to the monomer including solvent molecule into the coordination sphere of the metal. The reactions of 1,3-diallyl-5-[4′-(diphenylphosphino)butyl] isocyanurate and 1,3-diallyl-5-[6′-(diphenylphosphino)hexyl] isocyanurate with $PdCl_2$ give monomeric chelate $LPdCl_2$ complexes in which one of the allyl groups of the isocyanurate cycle participates in coordination with the central ion along with the phosphorus atom.

Key words: phosphorylated diallyl isocyanurates, tertiary phosphines; palladium(II) dichloride; monomeric, dimeric, and chelate complexes, synthesis, structure; ^1H, ^{31}P, and ^{13}C NMR and IR spectroscopy.

Previously we have shown for 1,3-diallyl-5-[3′-(diphenylphosphino)propyl] isocyanurate that phosphine derivatives of diallylisocyanuric acid (PDAIC) are capable of complex formation with transition metal chlorides.[1,2] In this connection, the compounds indicated are interesting objects for the preparation of metallopolymers, since the tendency of allyl isocyanurates to polymerization is well known.[3] It has been established for the compound studied that only the P atom of the diphenylphosphine group participates in coordination when a complex with the metal is formed. At the same time, PDAIC are polydentate ligands, and in our opinion, under certain steric conditions, allyl and carbonyl groups and N atoms of the isocyanurate cycle can coordinate with the central ion of the transition metal rather than the P atom. This provides possibilities for the formation of chelate or binuclear complexes.

For this purpose, we synthesized several 1,3-diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates in which the distance between the isocyanurate cycle and diphenylphosphine group was varied. The reaction of lithium diphenylphosphide with 1,3-diallyl-5-(ω-bromoalkyl) isocyanurates in THF (Scheme 1) is the general method for the preparation of the latter. As a result, we synthesized phosphine derivatives of diallylisocyanuric acid with the number (n) of methylene groups between the isocyanurate cycle and diphenylphosphine group equal to 2, 4, 5, 6, and 10.

Scheme 1



n = 2 (**1**), 4 (**2**), 5 (**3**), 6 (**4**), 10 (**5**)

Compounds **1**—**5** were isolated in the individual state by column chromatography. They are viscous transparent liquids. The structure of diallylisocyanurates was confirmed by ^{13}C, ^1H, and ^{31}P NMR and IR spectroscopy, and their composition was determined by elemental analysis (Tables 1—4).

Isocyanurates **1**—**5** enter readily reactions of complex formation with $PdCl_2$. All reactions were carried

Translated from *Izvestiya Akademii Nauk. Seriya Khimicheskaya*, No. 9, pp. 1859—1865, September, 1998.

Table 1. Yields and data of TLC and elemental analysis of 1,3-diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates **1**—**5**

Compound	R_f (petroleum ether : Et_2O)	Yield (%)	Found / Calculated (%) C	H	N	P	Molecular formula
1	0.64 (3 : 1)	63	65.02 65.59	5.75 5.70	9.68 9.97	7.52 7.36	$C_{23}H_{24}N_3O_3P$
2	0.69 (2 : 1)	66	66.61 66.81	6.34 6.23	9.31 9.35	6.87 6.90	$C_{25}H_{28}N_3O_3P$
3	0.52 (2 : 1)	72	67.31 67.39	6.79 6.48	9.21 9.07	6.47 6.69	$C_{26}H_{30}N_3O_3P$
4	0.80 (2 : 1)	78	67.74 67.92	6.70 6.71	8.60 8.81	6.45 6.49	$C_{27}H_{32}N_3O_3P$
5	0.56 (1 : 1)	50	69.18 69.79	7.38 7.50	7.87 7.68	5.85 5.82	$C_{31}H_{40}N_3O_3P$

Table 2. IR spectra of 1,3-diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates **1**—**5** and their complexes with $PdCl_2$ **6**—**10**

Number of methylene groups	Isocyanurate cycle, oil (solution in $CHCl_3$)				Allyl groups, oil (solution in $CHCl_3$)				ν(PdCl)/cm^{-1}, oil, [ML]
	ν(C=O)/cm^{-1}		δ(C=O)/cm^{-1}		ν(C=C)/cm^{-1}		δ(CH)/cm^{-1}		
(*n*)	L	[ML]	L	[ML]	L	[ML]	L	[ML]	
2	1690 (1696)	1691 (1694)	765	763	1645 (1645)	1645 (1645)	933, 995 (940, 988)	928, 995 (932, 988)	340, 299, 265 (359, 335, 290, 269)[a]
4	1694 (1700)	1691 (1696)	764	766	1644 (1645)	1645, 1536 (1645)	936, 992 (992)	940, 972, 1016 (972, 1006)	363
5	1696 (1696)	1692 (1693)	767	767	1646 (1645)	1644 (1645)	934, 993 (936, 988)	932, 992 (924, 972)	356
6	1692 (1700)	1692 (1696)	765	765	1645 (1645)	1645, 1536 (1645)	934, 992 (992)	940, 972, 1016 (972, 1006)	357
10	1693	1704	767	767	1645	1647	934, 993	923, 993	357

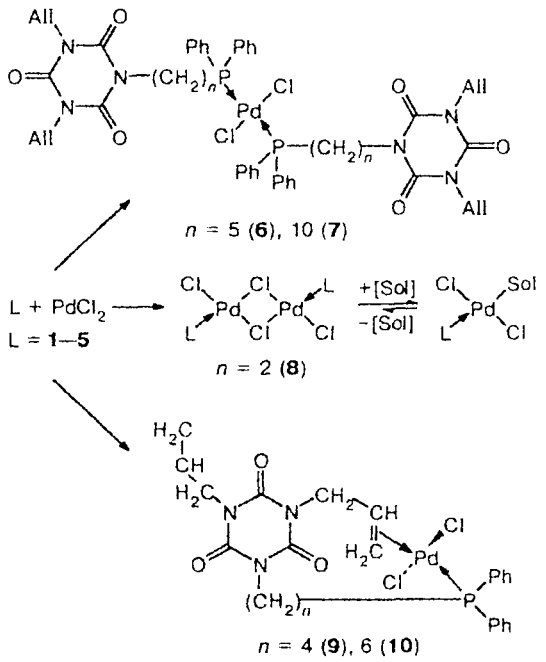
[a] Solution in toluene.

out in MeCN in a twofold excess of diallyl isocyanurates (Scheme 2). The complexes **6**, **8**—**10** that formed were stable in air, powdered yellow (**6**, **8**) and light-brown (**9**, **10**) substances, and complex **7** is a viscous orange liquid. It is noteworthy that the compounds isolated have different solubilities in organic solvents. For example, the solubility of complex **10** in benzene and $CHCl_3$ is much lower that of complexes **6**—**8**; therefore, ^1H and ^{13}C NMR spectra of the compounds under study were obtained in DMSO-d_6. Complex **9** is well soluble only in DMF, DMSO, and nitrobenzene. The determination of the specific electroconductivity in nitrobenzene of the compounds synthesized indicated that the solutions contained no charged structures.

The results of elemental analysis of complexes **6** and **7** and the molecular weight of complex **6** determined by cryoscopy corresponded to the L_2PdCl_2 composition, whereas the data of these methods for **8**—**10** corresponded to monomeric $LPdCl_2$ complexes (Table 5), which rules out the possibility of formation of binuclear complexes of the $(LPdCl_2)_2$ type in which each molecule of the ligand is coordinated to one metal ion *via* the P atom and to another metal ion due to the carbonyl or allyl group.

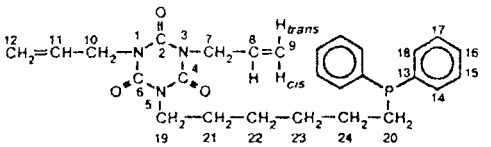
Complex **6** has the same composition as *trans*-bis{1,3-diallyl-5-[3′-(diphenylphosphino)propyl] isocyanurate}dichloropalladium(II) (n = 3) described previously.[2] The ^{31}P NMR spectrum of compound **6** exhib-

Scheme 2



its one signal shifted to the downfield region as compared to the position of the signal of the starting ligand (Table 6). This suggests that the P atom of the diphenylphosphine group of the corresponding isocyanurate participates in the coordination with the metal.[4] The participation of the phosphorus atom in complex formation is also indicated by the downfield shift of the signals of protons of the phenyl and methylene groups in the ^{1}H NMR spectrum of complex **6** as compared to their positions in the spectrum of the starting ligand (see Tables 3 and 6). The coupling constants of methylene protons with the P atom in the spectrum of complex **6** were not measured because of considerable broadening of the signals caused probably by both the formation of hydrogen bonds in the complex between protons of the methylene chain and carbonyl groups of the isocyanurate cycle and the steric influence on chemical shifts of protons by remote groups of atoms in structures stabilized by hydrogen bonds. As in the case of the complex with three methylene groups obtained previously,[2] the IR spectra of complex **6** recorded in Nujol and in $CHCl_3$ exhibited no shifts of the bands corresponding to the allyl and carbonyl groups of the isocyanurate cycle relative to similar bands in the spectra of the free ligand.

Table 3. ^{1}H NMR (in DMSO-d_6) and ^{31}P NMR spectra of 1,3-diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates **1**—**5**[a]



Parameter	Group	**1**	**2**	**3**[b]	**4**
δ ^{1}H	N—C(7,10)H_2 (4 H)	4.34 (d)	4.37 (d)	4.35 (d)	4.46 (d)
	N—C(19)H_2 (2 H)	3.98 (m)[c]	3.77 (m)[c]	3.75 (m)[c]	3.84 (m)[c]
	P—C(20)H_2 (2 H)	2.46 (m)[d]	2.12 (m)[d]	1.92 (m)[d]	2.14 (m)[d]
	C(21)H_2 (2 H)		1.74 (m)[e]	1.60 (m)[e]	1.60 (m)[e]
	C(22)H_2 (2 H)		1.14 (m)[e]	1.48 (m)[e]	1.60 (m)[e]
	C(23)H_2 (2 H)			1.48 (m)[e]	1.46 (m)[e]
	C(24)H_2 (2 H)				1.38 (m)[e]
	C(8,11)H (2 H)	5.84 (ddt)	5.84 (ddt)	5.75 (ddt)	5.92 (ddt)
	=C(9,12)H_{trans} (2 H)	5.23 (d)[f]	5.19 (d)[f]	5.22 (d)[f]	5.27 (d)[f]
	=C(9,12)H_{cis} (2 H)	5.17 (d)[f]	5.14 (d)[f]	5.09 (d)[f]	5.21 (d)[f]
	Ph (10 H)	7.38—7.50 (m)	7.37—7.43 (m)	7.38—7.50 (m)	7.35—7.50 (m)
$^3J_{HH}$/Hz	C(7,10)H_2—C(8,11)H	5.0	5.2	6.0	5.9
	C(8,11)=C(9,12)H_{trans}	17.5	16.0	18.0	17.3
	C(8,11)=C(9,12)H_{cis}	10.6	10.5	10.0	10.1
	C(19)H_2—CH_2	7.6	6.8	7.0	7.2
$^nJ_{PH}$/Hz	$^2J_{PC(20)H_2}$	≤1.0	≤1.0	6.0	
	$^3J_{PCCH_2}$	7.3	7.3	6.0	
δ ^{31}P		−22.2 (C_6H_6)	−17.6 (C_6H_6); −17.4 ($CHCl_3$)	−16.1 (C_6H_6)	−18.0 (C_6H_6)

[a] For compound **5**, ^{31}P NMR (C_6H_6), δ: −16.0. [b] In CCl_4.
[c] Center of a multiplet of the AA′ part of the AA′XX′K system (K = ^{31}P) with an additional doublet splitting with $^3J_{PCCH}$ for compound **1**.
[d] Center of a multiplet of the XX′ part of the AA′XX′K system (K = ^{31}P) with an additional doublet splitting with $^2J_{PCH}$.
[e] Centers of unsolved multiplets.
[f] For all compounds, $^2J_{H_{cis}H_{trans}}$ < 1.0 Hz.

The low-frequency region of the IR spectrum contains one absorption band of the Pd—Cl bonds indicating their *trans*-arrangement in the planar-square configuration of the complex[5,6] (see Table 2). Thus, the data of

Table 4. ^{13}C NMR spectra of compounds **1**, **4**, **8**, and **10** (in DMSO-d_6)

Atom	δ ($^1J_{CH}$; $^nJ_{CH}$/Hz)			
	1	**8**	**4**	**10**
C(4)	147.91 (s)	148.06 (s)	148.21 (s)	148.22 (s)
C(2), C(6)	148.15 (s)	148.27 (s)	148.41 (s)	148.40 (s)
C(7), C(10)	44.03 (tm, 142.0; 7.4)	44.11 (tm, 140.0)[a]	44.00 (tm, 141.0; 6.8)	43.98 (tm, 143.4)
C(8), C(11)	131.64 (dm, 158.3; 5.0)	131.76 (dm, 156.8)[a]	131.87 (dm, 161.0)[a]	131.18 (dm, 161.4);[a,b] 130.92 (dm, 161.0)[a,c]
C(9), C(12)	116.99 (tm, 157.0; 5.1)	116.58 (tm, 155.4)[a]	116.99 (tm, 157.4; 4.2)	116.53 (tm, 158.4)[a]
C(13)	137.41 (d, $^1J_{CP}$ = 13.4)	128.12 (d, $^1J_{CP}$ = 58.4)	138.41 (d, $^1J_{CP}$ = 14.2)	133.95 (d, $^1J_{CP}$ = 95.5)
C(14), C(18)	132.00 (dm, 159.8; 6.8; $^2J_{CP}$ = 19.0)	132.69 (dm, 157.2; $^2J_{CP}$ = 19.0)[a]	132.13 (dm, 160.0; 7.0; $^2J_{CP}$ = 18.4)	130.17 (dm, 160.4; $^2J_{CP}$ = 9.1);[a,b] 134.17 (dm, 160.0; $^2J_{CP}$ = 9.4)[a,c]
C(15), C(17)	128.22 (dm, 160.6; 6.8; $^3J_{CP}$ = 6.5)	128.33 (dm, 163.9; $^3J_{CP}$ = 11.4)[a]	128.29 (dm, 160.0; 5.0; $^3J_{CP}$ = 6.0)	128.38 (dm, 158.0; $^3J_{CP}$ = 10.8);[a,b] 128.03 (dm, 158.0, $^3J_{CP}$ = 10.0)[a,c]
C(16)	128.40 (dm, 161.1; 7.1)	131.19 (dm, 162.3)[a]	128.23 (dm, 160.0)[a]	131.90 (dm, 167.5)[a]
C(19)	44.05 (tm, 142.0; $^2J_{CP}$ = 5.0)	41.87 (tm, 142.0; $^2J_{CP}$ = 0)	42.07 (tm, 142.2)[a]	41.95 (tm, 146.4)[a]
C(20)	25.37 (tm, 130.4; $^1J_{CP}$ = 13.4)	24.90 (d, $^1J_{CP}$ = 34.0)[d]	29.83 (tm, 123.7; $^1J_{CP}$ = 12.8)	25.18 (d, $^1J_{CP}$ = 39.9)[d]
C(21)			26.86 (t, 126.9)	28.40 (t, 125.0)
C(22)			25.00 (t, 125.7)	26.77 (t, 125.1)
C(23)			25.24 (tm, 125.9; $^3J_{CP}$ = 16.2)[a]	29.42 (d, $^3J_{CP}$ = 12.0)[d]
C(24)			26.52 (tm, 129.0; $^2J_{CP}$ = 11.2)	25.24 (d, $^2J_{CP}$ = 16.0)[d]

[a] $^2J_{CH}$ and $^3J_{CH}$ were not determined due to broadening of the signals.
[b] Parameters of the main component.
[c] Parameters of the minor component.
[d] The coupling constants were determined from the spectra recorded with complete decoupling of protons.

Table 5. Yields and data of elemental analysis and molecular weights (M) for complexes of 3,5-diallyl-1-[ω-(diphenylphosphino)alkyl] isocyanurates with $PdCl_2$ **6—10**

Compound	Yield (%)	M.p. /°C	M, found[a] / calculated (solvent)	Found / Calculated (%) C	H	Cl	N	P	Pd	Molecular formula
6	95	75	1182 1103 (C_6H_6)	56.32 56.57	5.56 5.44	6.21 6.43	7.84 7.61	5.57 5.42	9.42 9.61	$C_{52}H_{32}Cl_2N_6O_6P_2Pd$
7	57			59.56 59.86	6.25 6.44	5.51 5.71	6.43 6.76	4.82 4.99	8.41 8.53	$C_{62}H_{80}Cl_2N_6O_6P_2Pd$
8	98	217	607 676 (C_6H_6)	46.35 46.15	3.91 4.01	11.86 11.87	6.83 7.02	4.86 5.18	17.51 17.72	$C_{23}H_{24}Cl_2N_3O_3PPd$
9	98	Does not melt to 250	645 626 (DMSO)	47.55 47.92	4.62 4.47	11.41 11.34	6.36 6.70	4.64 4.95	16.54 16.93	$C_{25}H_{28}Cl_2N_3O_3PPd$
10	94	Does not melt to 250	666 654 (C_6H_6)	49.77 49.54	5.19 4.89	10.93 10.86	6.21 6.42	4.74 4.46	16.51 16.20	$C_{27}H_{32}Cl_2N_3O_3PPd$

[a] Molecular weights were determined by cryoscopy.

Table 6. ^1H and ^{31}P NMR spectra of complexes of 1,3-diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates with $PdCl_2$ **6—10**[a]

Parameter	Group	6		8		9	10
		DMSO-d_6	$CDCl_3$	DMSO-d_6	$CDCl_3$	DMSO-d_6	DMSO-d_6
δ ^1H	N—C(7,10)H_2 (4 H)	4.37 (d)	4.48 (d)	4.43 (d)	4.43 (d)	4.36 (d) 4.31 (d)	4.35 (d) 4.31 (d)
	N—C(19)H_2 (2 H)	3.70 (m)[b]	3.81 (m)[b]	3.90 (m)[b]	3.99 (m)[b]	3.75 (m)[b]	3.70 (m)[b]
	P—C(20)H_2 (2 H)	2.46 (m)[c]	2.43 (m)[c]	2.90 (m)[c]	[d]	2.22 (m)[c]	2.21 (m)[c]
	C(21)H_2 (2 H)	1.50 (m)[e]	1.41 (m)[e]			1.79 (m)[e]	2.11 (m)[e]
	C(22)H_2 (2 H)	1.38 (m)[e]	1.41 (m)[e]			1.68 (m)[e]	1.77 (m)[e]
	C(23)H_2 (2 H)	1.27 (m)[e]	1.30 (m)[e]				1.41 (m)[e]
	C(24)H_2 (2 H)						1.26 (m)[e]
	C(8,11)H (2 H)	5.85 (ddt)	5.88 (ddt)	5.84 (ddt)	5.87 (ddt)	5.81 (ddt); 5.68 (m)[e]	5.83 (ddt); 5.63 (m)[e]
	=C(9,12)H_{trans} (2 H)	5.20 (d)[f]	5.31 (d)[f]	5.23 (d)[f]	5.29 (d)[f]	5.20 (m);[e] 5.46 (m)[e]	5.18 (d);[f] 5.60 (m)[e]
	=C(9,12)H_{cis} (2 H)	5.15 (d)[f]	5.25 (d)[f]	5.15 (d)[f]	5.20 (d)[f]	5.14 (m);[e] 5.51 (m)[e]	5.12 (d);[f] 5.39 (m)[e]
	Ph (10 H)	7.52— 7.68 (m)	7.42— 7.68 (m)	7.62— 7.85 (m)	7.46— 7.66 (m)	7.77— 7.81 (m)	7.55— 7.74 (m)
$^nJ_{HH}$/Hz	C(7,10)H_2—C(8,11)H	[g]	5.9	5.0	[g]	5.0	5.0
	C(8,11)=C(9,12)H_{trans}	17.5	17.0	17.2	17.0	16.6	16.6
	C(8,11)=C(9,12)H_{cis}	10.1	10.3	10.4	9.0	10.1	10.1
	C(19)H_2—CH_2	[g]	7.2	7.6	[g]	[g]	[g]
$^nJ_{PH}$/Hz	$^2J_{PC(20)H_2}$	[g]	[g]	6.4	[g]	[g]	[g]
	$^3J_{PCCH_2}$			6.0	[g]		
δ ^{31}P		18.0 (C_6H_6)		11.5, 23.95 (32 : 1) (C_6H_6)		31.5 (DMSO)	32.6 (C_6H_6)

[a] For complex **7**, ^{31}P NMR (C_6H_6), δ: 19.9.
[b] Center of the broadened multiplet of the AA′ part of the AA′XX′K system (K = ^{31}P).
[c] Center of the broadened multiplet of the XX′ part of the AA′XX′K system (K = ^{31}P).
[d] Could not be identified due to broadening of signals.
[e] Centers of broadened multiplets.
[f] For all compounds, $^2J_{H_{cis}H_{trans}} < 1.0$ Hz.
[g] Coupling constants were not determined due to broadening of the signals.

physicochemical methods presented above are evidence that at $n = 5$ phosphorylated diallylisocyanurate forms with $PdCl_2$ a monomeric 2 : 1 *trans*-complex in which only the P atom of the diphenylphosphine group participates in coordination with the central ion. According to the data of elemental analysis and IR spectroscopy, complex **7** has a similar structure (see Tables 2 and 5).

As mentioned above, complexes **8—10** have the composition $LPdCl_2$. Either dimers with Pd—Cl bridges or structures in which more than one functional group of the isocyanurate ligand participate in coordination with the metal (chelate structures) can correspond to this composition. The magnitude of shifts of the signals of phosphorus atoms in the ^{31}P NMR spectra of these compounds as compared to the signals in the spectra of free ligands suggests that the P atoms participate in complex formation (see Tables 3 and 6). The ^{31}P NMR spectrum of complex **8** exhibits two signals with δ 11.5 and 23.95 (the ratio of intensities 32 : 1). The position of the first of them coincides with that of the signals of the P atoms of complexes **6** and **7**, and the second signal appears in the region of lower fields. The signals of the phosphorus atoms in the ^{31}P NMR spectra of complexes **9** and **10** are observed in the region of lower fields as compared to the corresponding signals of compounds **2** and **4** and complexes **6** and **7**. This difference in chemical shifts in the ^{31}P NMR spectra of the complexes considered is explained by their different structures. The positions of the signals of the P atoms of compounds **6** and **7** and that of the first signal of compound **8** is characteristic of monomeric *trans*-complexes of tertiary phosphine with transition metal salts.[5,6] The second signal in the spectrum of compound **8** corresponds to either the *cis*-configuration of the complex[5,7] or its dimeric structure.[8] The positions of the signals in the ^{31}P NMR spectra of compounds **9** and **10** indicate that their structures differ from those of complexes **6—8**.

Let us consider in more detail the structure of complex **8**. The parameters of the IR spectrum of this compound indicate that the allyl and carbonyl groups of the isocyanurate ligand are not involved in coordination with the metal (see Table 2). In the low-frequency region

of the IR spectrum of complex **8** recorded in both Nujol and polyethylene matrix, unlike the spectra of the complexes with three, five, and ten methylene groups, three absorption bands are observed (see Table 2). According to the published data,[8,9] this pattern of the spectrum corresponds to the dimeric structure of a complex with two Pd—Cl bridges. However, it has been mentioned above that the molecular weight of complex **8** corresponds to the monomeric structure. To answer this question, we recorded the IR spectrum of complex **8** in toluene as the most appropriate (in the spectral aspect) solvent. As a result, one intense absorption band at 359 cm^{-1} appeared instead of three absorption bands in the frequency region from 100 to 400 cm^{-1}. However, it should be mentioned that low-intense bands at 335, 290, and 269 cm^{-1} are retained in the spectrum. Removal of the solvent resulted in recovering of intensities of the three absorption bands under discussion and disappearance of the band at 359 cm^{-1} in the IR spectrum of the already solid sample. Based on these data, we concluded that in toluene the dimeric structure of complex **8** is decomposed to form monomers. It is likely that in the solution there is an equilibrium between the dimer and monomer, which is strongly shifted toward the latter, which also agrees with the data of ^{31}P NMR spectroscopy (see Table 6). The fact that low-intensity bands of the dimeric structure are retained in the spectrum of a toluene solution of complex **8** rules out the assignment of the signal with δP 23.95 in the ^{31}P NMR spectrum to the *cis*-form of the complex. Probably, in the solution, the fourth coordination vacancy in the planar-square configuration of complex **8** is occupied by a solvent molecule. In the IR spectrum of this compound recorded in $CHCl_3$, the region from 400 to 4000 cm^{-1} exhibits no changes as compared to the spectrum of a solution of the free ligand. The conclusions on the structure of complex **8** in the solution also agree with the parameters of its ^1H and ^{13}C NMR spectra. The ^{13}C NMR spectrum exhibits the shifts of the signals of only the carbon atoms that are localized in the vicinity of the P atom (C(13), C(19), and C(20)) coordinated to the metal (see Table 4). The changes in coupling constants of the C(20) and C(13) atoms with the P atom ($^1J_{PC}$) are characteristic of the changes corresponding to the participation of the diphenylphosphine group in complex formation.[10,11] In the ^1H NMR spectrum of complex **8**, as compared to that of the free ligand of **1**, only the signals of protons of the methylene group and phenyl substituents at the P atom undergo the characteristic shifts (see Tables 3 and 6). As in the case of complex **7**, we cannot determine the coupling constants with the P atom in the ^1H NMR spectrum of complex **8** due to strong the broadening of the signals of methylene protons.

To confirm the dimeric structure of complex **8** in the solid state, we studied its reaction with pyridine. According to the elemental analysis data, this reaction results in the formation of the $LPdCl_2Py$ complex (**11**). In the ^{31}P NMR spectrum of the latter obtained in benzene, one signal with δP 10.5 is observed. This value indicates that the coordination P→Pd bond is retained and corresponds to the monomeric *trans*-complex. In the IR spectrum of complex **11**, the region form 100 to 500 cm^{-1} contains only one absorption band of the Pd—Cl bond at 358 cm^{-1}, and the absorption bands at 340, 299, and 265 cm^{-1}, which are observed in the spectrum of complex **6**, disappear. The ^1H NMR spectrum of complex **11** also agrees with its monomeric structure.

Thus, a decrease in the number of methylene groups separating the isocyanurate cycle and diphenylphosphine group in PDAIC molecules to two results in the formation of complex **8**, which exists in the solid state as a dimer with Pd—Cl bridges. The latter is decomposed in solutions of benzene, chloroform, toluene, and DMSO to monomers in which a solvent molecule occupies the fourth coordination vacancy in the planar-square configuration of the complex.

The analysis of the ^{31}P NMR spectroscopy data for complexes **9** and **10** suggests that these compounds have chelate structures[5] in which not only the P atom of the ligand but also donating groups of the isocyanurate fragment participate in coordination with the metal. The IR spectra of complexes **9** and **10** obtained in Nujol and polyethylene matrix are evidence for their *trans*-configuration (see Table 2). In the IR spectra of the complexes in the frequency range from 400 to 4000 cm^{-1}, on the one hand, no shifts of the bands assigned to the absorption of C=O bonds are observed, and on the other hand, the bands corresponding to vibrations of the $CH{=}CH_2$ fragments of allyl substituents in the isocyanurate cycle change their positions and intensities. For example, in the spectra of the free ligands, the absorption bands at 1644 (**2**) and 1645 cm^{-1} (**4**) of stretching vibrations of the C=C bond and two bands of deformation vibrations of the C—H bonds (at 936 and 992 cm^{-1} (**2**) and 934 and 992 cm^{-1} (**4**)) correspond to the free ligands.[12,13] The bands under discussion undergo changes in the spectra of the complexes obtained in Nujol and $CHCl_3$. The intensities of the bands at 1644 and 1645 cm^{-1} decrease sharply, and they look like shoulders on the absorption bands of carbonyl groups. In addition, a low-intensity band appear at 1546 cm^{-1}, which is characteristic of olefin bonds coordinated to the metal.[5,12] In the region of deformation vibrations, several broad low-intensity bands (940, 972, and 1016 cm^{-1}) appear instead of two strong absorption bands.[14]. It is noteworthy that similar changes in the spectra of the complexes, as compared to those of the free ligands, are also observed in solutions of these compounds in $CHCl_3$ in the regions free from absorption of the solvent (see Table 2). According to the published data,[5,12,14] these changes in the IR spectra of the complexes, as compared to those of the free ligands, can be evidence that compounds **9** and **10** in the solid state in a solution of $CHCl_3$ have chelate structures in which one allyl group of isocyanurate participates in coordination with the metal along with the P atom. The ^1H NMR spectra of complexes **9** and

10 exhibit two types of signals of protons of allyl groups with different chemical shifts, which are substantially broadened as compared to the corresponding signals in the spectra of the free ligands. The existence of two types of signals with the 1 : 1 ratio of intensities suggests that only one of the allyl groups of the ligand participates in coordination with palladium in complex **9**. Broadening of the signals indicates that exchange processes occur between the coordinated and free allyl groups in the complexes at room temperature.[15] The ratio of intensities of two types of signals of protons of the allyl groups in the ^{1}H NMR spectrum of complex **10** is equal to 1 : 2, and their position and shape (the first group of signals is broadened, and the second group is similar to the signals in the starting ligand) cannot be explained by the presence of only free allyl group in the complex. The ^{13}C NMR spectrum of complex **10** in DMSO-d_6 was recorded to answer this question. The spectrum obtained also exhibits two groups of signals of carbon atoms of allyl and phenyl groups with the 1 : 2 ratio of intensities. The chemical shifts of one group of signals changed as compared to their values in the spectrum of the ligand (see Table 4). In our opinion, this picture of the ^{1}H and ^{13}C NMR spectra of complex **10** is explained by its partial decomposition in DMSO and the existence of complexes with chelate and monomeric structures in the solution.

Thus, the data of physicochemical methods presented above indicate that when the number of methylene groups in the isocyanurate ligand is equal to 4 and 6, the reactions of the latter with $PdCl_2$ give chelate $LPdCl_2$ complexes in which (in the solid state) both the P atom of the diphenylphosphine group and one of the allyl groups of isocyanurate are coordinated with the central ion. According to the data of ^{1}H and ^{31}P NMR and IR spectroscopy, complex **10** has the chelate structure in $CHCl_3$ and benzene, but in DMSO it exists as a monomer including the solvent molecule in the coordination sphere of the metal. Complex **9** in DMSO retains the chelate structure.

In should be mentioned in conclusion that the studies performed allowed us to establish that a change in the number of ethylene fragments separating the isocyanurate cycle and diphenylphosphine group of PDAIC makes it possible to synthesize Pd^{II} complexes with different compositions, structures, and stability in solutions. Evidently, differences in structures of the complexes reflect the competition between steric and electronic interactions of both intra- and intermolecular characters.

Experimental

IR spectra in the region of 400—4000 cm^{-1} were recorded on a Specord M-80 instrument in 0.5-mm cells in Nujol and in $CHCl_3$; in the frequency range of 700—100 cm^{-1}, spectra were obtained on a Bruker IFS-113V Fourier-spectrometer in Nujol or in the polyethylene matrix, and the spectrum of a toluene solution of complex **6** was recorded in a 2-mm polyethylene cell. ^{31}P NMR spectra were recorded on a Bruker CXP-100 instrument (36.47 MHz) relative to 85% H_3PO_4 (external standard). ^{1}H NMR spectra were recorded on a Bruker WM-250 instrument (250.13 MHz)), and ^{13}C NMR spectra were obtained on a Bruker WSL-400 instrument (100.62 MHz) relative to Me_4Si (internal standard). Molecular weights were determined by cryoscopy.

1,3-Diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates (1—5) were synthesized by the procedure described previously.[2] The compounds were purified by chromatography on a column filled with silica gel using a petroleum ether—Et_2O (1 : 10) mixture as the eluent. The yields, data of elemental analysis, and spectral parameters of complexes **1—5** are presented in Tables 1—4.

Complexes of 1,3-diallyl-5-[ω-(diphenylphosphino)alkyl] isocyanurates with $PdCl_2$ (6—10) (general procedure). A mixture of isocyanurate and $PdCl_2$ taken in the 2 : 1 molar ratio in anhydrous MeCN (20 mL) was refluxed for 2 h. The solvent was evaporated *in vacuo*, the residue was triturated with Et_2O, and the powdered complex was filtered off. Complexes **6** and **8—11** were purified by dissolution in MeCN and precipitation from the solution with Et_2O, and complex **7** was purified by chromatography on a column filled with silica gel using a petroleum ether—Et_2O (1 : 1) mixture as the eluent. The yields, elemental analysis data, and spectral parameters of complexes **6—10** are presented in Tables 2 and 4—6.

The specific electroconductivity (χ_{max}/Ohm^{-1} cm^{-1} mol^{-1}) of solutions of complexes **6** and **8—10** in nitrobenzene was the following: 0.3 (C = 0.0035 mol L^{-1}); 0.1 (C = 0.0077 mol L^{-1}); 0.9 (C = 0.0079 mol L^{-1}); and 1.1 (C = 0.0164 mol L^{-1}), respectively.

***trans*-{1,3-Diallyl-5-[2′-(diphenylphosphino)ethyl] isocyanurate}pyridinedichloropalladium(II) (11).** Pyridine (0.19 g, 2.4 mmol) was added to complex **8** (0.5 g, 0.8 mmol) in anhydrous C_6H_6 (20 mL) at ~20 °C. One hour after, the solvent was evaporated *in vacuo*, the residue was dissolved in C_6H_6, and complex **11** was precipitated with petroleum ether. The yield of compound **11** was 0.46 g (82%). Found (%): C, 49.83; H, 4.64; Cl, 10.76; N, 8.49; P, 4.11; Pd, 15.30. $C_{28}H_{29}Cl_2N_4O_3PPd$. Calculated (%): C, 49.63; H, 4.28; Cl, 10.48; N, 8.27; P, 4.57; Pd, 15.65. IR (Nujol), ν/cm^{-1}: 358 (Pd—Cl); 763, 1690 (C=O); 933, 992 (C—H); 1645 (C=C). ^{31}P NMR (C_6H_6), δ: 10.5. ^{1}H NMR ($CDCl_3$), δ: 2.90 (m, 2 H, PC(20)H_2); 4.04 (m, 2 H, NC(19)H_2); 4.47 (d, 4 H, NC(7,10)H_2, $^3J_{HH}$ = 5.3 Hz); 5.21 (d, 2 H, C(9,12)H_{cis}, $^3J_{HH}$ = 10.6 Hz); 5.27 (d, 2 H, C(9,12)H_{trans}, $^3J_{HH}$ = 17.3 Hz); 5.86 (m, 2 H, C(8,11)H); 7.98, 8.21 (both m, 15 H, Ph, Py).

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Received February 27, 1998;
in revised form April 29, 1998