Synthesis and complexing properties of phosphoryl-substituted salicylaldimines*

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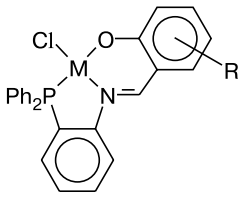
Starting from *meta* and *ortho* isomers of (diphenylphosphorylmethyl)anilines **2a,b**, procedures were developed for the synthesis of new phosphoryl-substituted Schiff bases **3a,b** serving as tridentate ligands. In alcoholic solutions, ligands **3a,b** form complexes of different composition with praseodymium and neodymium nitrates. Only the $M(L)_2(NO_3)_3$ complexes crystallized from solution regardless of the reactant ratio. According to the X-ray diffraction study and IR spectroscopy, one of the ligands in the complexes with *ortho* ligand **3b** is coordinated in a bidentate fashion *via* the oxygen atom of the P=O group and the phenoxy oxygen atom, whereas the second ligand molecule forms a coordination bond with metal only *via* the phosphoryl oxygen atom. In the $Pr(\mathbf{3a})_2(NO_3)_3$ complexes, both *meta* ligands **3a** are involved in the bidentate *O*,*O*-coordination.

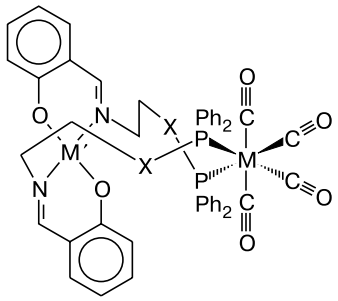
Key words: Schiff bases, (diphenylphosphorylmethyl)anilines, (diphenylphosphorylmethyl)nitrobenzenes, complexes, lanthanides, structure, X-ray diffraction study, hydrogen bonds.

Schiff bases form catalytically active metal complexes, whose structures are determined by both the structure of the ligand and the nature of the metal.[1,2] Salicylaldehyde azomethines containing substituents with the coordination-active donor HO, H_2N, or HS centers at the imine nitrogen atom have been studied in most detail. Data on the related compounds bearing an additional phosphorus-containing donor center are limited to a few phosphine-containing structures,[3—5] which can form both chelate mononuclear compounds involving all coordinating groups of the molecules (**A**),[5] and dinuclear complexes (**B**) with the chelate-chain coordination of the ligands.[4]



A

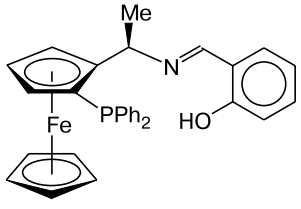
M = Ni^{II}, Pd^{II}



B

M = Cr, Mo; X = NH, $(CH_2)_n$ (n = 0, 1, 2);
M′ = Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}

It should also be noted that the use of the phosphine-substituted ligand **C** in the alkylation of aromatic aldehydes with diethylzinc in the presence of chiral ferrocenyl-substituted salicylaldimines as the basic catalysts results in high enantioselectivity (up to 100% *ee*).



C

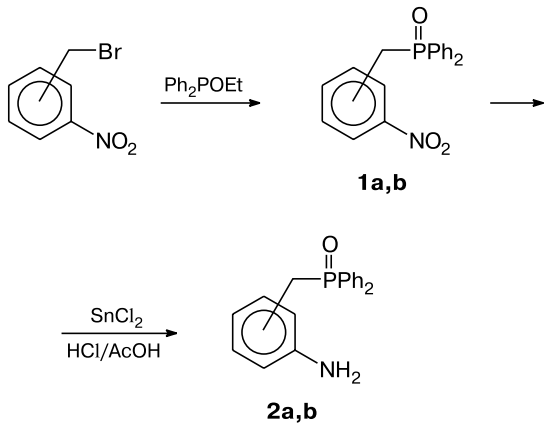
* Dedicated to Academician G. A. Abakumov on the occasion of his 70th birthday.
† Deceased.

Published in Russian in *Izvestiya Akademii Nauk. Seriya Khimicheskaya,* No. 9, pp. 1827—1835, September, 2007.
1066-5285/07/5609-1891

Taking into account that tertiary phosphine oxides can form strong coordination bonds with various metals through the lone electron pair of the phosphoryl oxygen atom, we carried out the condensation of salicylaldehyde with *ortho*- and *meta*-substituted α-diphenylphosphoryltoluidines and synthesized new phosphoryl-substituted oligodentate ligands, *viz.*, salicylaldimines containing the phosphoryl substituent in the *N*-aryl ring.

We used *ortho*- and *meta*-substituted (diphenylphosphorylmethyl)nitrobenzenes **1a**,**b** as the precursors of the amino component in the synthesis of Schiff bases. Compounds **1a**,**b** were synthesized by the Arbuzov reaction starting from the corresponding nitrobenzyl bromides and ethyl diphenylphosphinite. The target α-diphenylphosphoryltoluidines **2a,b** were synthesized by the reduction of aromatic nitro derivatives with tin chloride in an acidic medium, which is widely employed in synthetic organic chemistry. This approach proved to be very efficient. The yields of phosphoryl-substituted anilines were 94% (**2a**) and 87% (**2b**) (Scheme 1).

Scheme 1



The spectroscopic study of the structures of nitro derivatives **1a**,**b** showed that the positions of the absorption bands of the functional nitro and phosphoryl groups in the IR spectra depend only slightly on the mutual arrangement of the substituents, whereas these differences in the ^{1}H NMR spectra are substantial. For example, the signal of the methylene protons in *ortho* isomer **1b** is shifted downfield compared to that for *meta* analog **1a** ($\Delta\delta$ ~0.5) due to the orienting effect of the *o*-NO_2 group. The X-ray crystal structures of isomers **1a**,**b** are also different. The molecular structures of compounds **1a** and **1b** are presented in Figs 1 and 2, respectively. Selected bond lengths and bond angles are given in Table 1.

Molecules **1a** and **1b** have a different arrangement of the nitro-substituted benzyl fragment. In the crystal structures, compounds **1a** and **1b** exhibit planar chirality with respect to the mutual arrangement of the oxygen atom

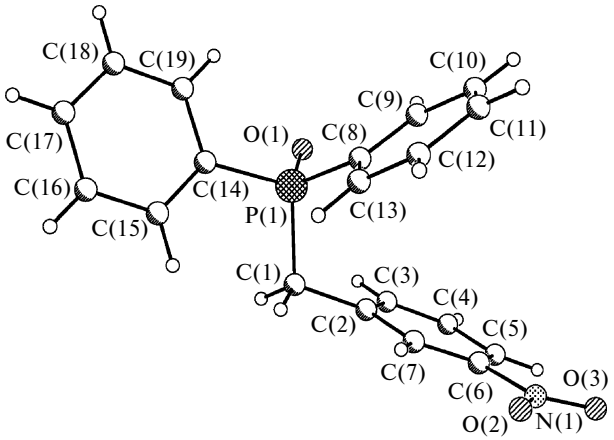


Fig. 1. Molecular structure of compound **1a**.

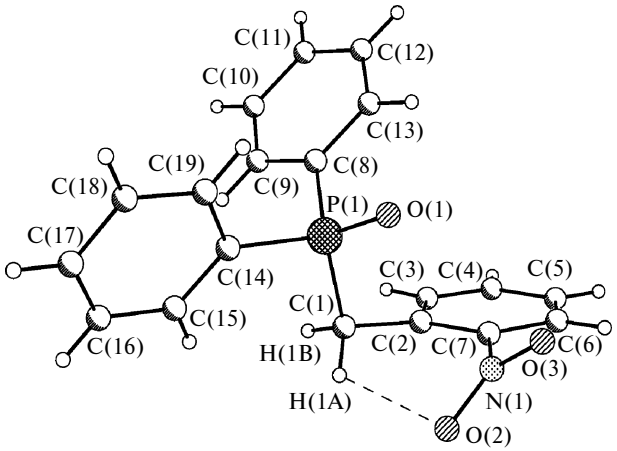


Fig. 2. Molecular structure of compound **1b**.

of the P=O fragment and the nitro group. In *ortho* derivative **1b**, these groups are on the same side of the P(1)C(1)C(2) plane, whereas these groups in *meta* analog **1a** are on opposite sides.

The nitro group in *ortho* derivative **1b** is rotated with respect to the plane of the phenyl ring bound to this group by 44.2(2)°. The N—O bonds are nonequivalent; the N(1)—O(2) distance is 0.012 Å longer than the N(1)—O(3) distance. The nonequivalence of the bonds in the nitro group and the large angle of rotation of this group suggest that there is a moderate-strength intramolecular C—H...O contact with the geometric parameters characteristic of very weak hydrogen bonds (O(2).....C(1), 2.928(3) Å; O(2).....H(1A), 2.29 Å; C(1)H(1A)O(1), 121°). At the same time, the nitro group in *meta* isomer **1a** is nearly parallel to the plane of the phenyl ring (the angle between the planes is 6.2(3)°), and the N—O bond lengths are equal within experimental error.

An analysis of the crystal packings of **1a** and **1b** showed that weak C—H...O and O...π interactions are the predominant contacts in the crystals of these compounds. The shortest contacts are observed in *ortho* isomer **1b**

Table 1. Selected bond lengths (*d*) and bond angles (ω) in isomeric (diphenylphosphorylmethyl)nitrobenzenes **1a**,**b**

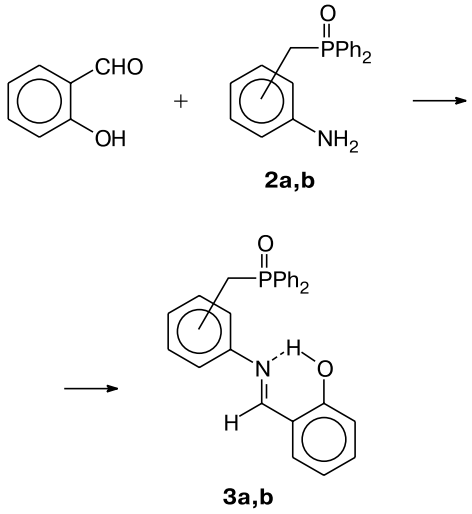
Parameter	Value	
	1a	**1b**
Bond length	*d*/Å	
P(1)—O(1)	1.496(1)	1.484(2)
P(1)—C(1)	1.807(2)	1.822(2)
P(1)—C(8)	1.802(2)	1.807(2)
P(1)—C(14)	1.806(2)	1.799(2)
C(1)—C(2)	1.513(3)	1.503(3)
C(2)—C(7)	1.393(3)	1.395(3)
C(6)—C(7)	1.377(3)	1.380(3)
C(7)—N(1)	—	1.471(3)
C(6)—N(1)	1.479(2)	—
N(1)—O(2)	1.228(2)	1.232(2)
N(1)—O(3)	1.230(2)	1.219(2)
Bond angle	ω/deg	
O(1)—P(1)—C(1)	113.85(8)	112.95(9)
O(1)—P(1)—C(8)	111.71(9)	111.49(9)
O(1)—P(1)—C(14)	111.50(9)	112.21(9)
C(1)—P(1)—C(14)	106.62(9)	106.7(1)
C(8)—P(1)—C(14)	106.22(9)	106.57(9)
P(1)—C(1)—C(2)	111.5(1)	108.8(2)
C(1)—C(2)—C(7)	119.2(2)	124.1(2)
C(2)—C(7)—C(6)	118.9(2)	123.2(2)
C(2)—C(7)—N(1)	—	120.5(2)
C(7)—C(6)—N(1)	118.7(2)	—

(O(3)...C(17), 3.149(3) Å; O(3)...C(2), 3.163(3) Å). In *meta* isomer **1a**, the O(2)...C(4) distance is 3.218(4) Å. In both isomers **1a,b**, the oxygen atom of the phosphoryl group forms a C—H...O contact with the hydrogen atom of the methylene group. This contact is substantially stronger in *ortho* isomer **1b** than in *meta* isomer **1a** (the O...H distance is 2.28 and 2.52 Å in the *ortho* and *meta* isomers, respectively).

The ^{1}H NMR spectra of toluidines **2a,b**, unlike those of nitro derivatives **1a**,**b**, show no substantial difference in the position of the signals for the methylene protons. It should be noted that the signals for the protons of the central aromatic ring in **1a**,**b** overlap with the signals for the protons of the phenyl rings at the phosphoryl group, whereas two distinct groups signals of aromatic protons with different intensities are observed in this spectral region for compounds **2a,b**. The IR spectra of toluidines **2a**,**b** contain a set of bands in the 3400—3200 cm^{-1} region characteristic of stretching vibrations of the primary amino group, which is, apparently, associated with the formation of inter- and intramolecular hydrogen bonds with the phosphoryl oxygen atom. The low-frequency shift of the stretching band of the PO group and the presence of several maxima at 1170 cm^{-1} in the spectrum of *ortho* isomer **2b** are consistent with this assumption.

The condensation of salicylaldehyde with α-phosphoryltoluidines **2a,b** readily proceeds on heating in ethanol to give the target phosphorylmethylphenyl-substituted salicylaldehyde imines **3a**,**b** (Scheme 2).

Scheme 2



Both isomeric salicylaldimines **3a**,**b** were isolated in the individual state as yellow crystalline compounds in high yields after recrystallization from a 1 : 1 benzene—diethyl ether system. The ^{31}P NMR spectra show singlets with similar chemical shifts (δ_P 29.4 for **3a** and 29.2 for **3b**). The ^{1}H NMR spectra of imines **3a**,**b** contain signals of the aromatic protons along with signals of the protons of the hydroxy (δ_{OH} 13.13 for **3a** and 12.92 for **3b**) and aldimine groups ($\delta_{HC=N}$ 8.38 for **3a** and 7.86 for **3b**). Doublets of the methylene protons with the spin-spin coupling constant of ~13.5 Hz are observed at δ 3.68 (**3a**) and 3.93 (**3b**). The ^{13}C NMR spectra of compounds **3a**,**b** show signals of the carbon atoms of the aromatic rings along with the characteristic signals of the carbon atoms of the methylene group (**3a**: δ_C 37.93 ($^1J_{P,C}$ = 65.6 Hz); **3b**: δ_C 33.34 ($^1J_{P,C}$ = 66.4 Hz)) and the azomethine fragment ($\delta_{C=N}$ 162.72 (**3a**) and 163.14 (**3b**)).

It should be noted that the ^{13}C, ^{31}P, and ^{1}H NMR spectra of compounds **3a**,**b** in $CDCl_3$ show only one set of the corresponding signals, which is apparently associated with stabilization of the only isomeric form in solution. This isomer contains the stable intramolecular hydrogen-bonded ring involving the C=N bond. The presence of this isomer in the crystal structure of **3a** was confirmed by X-ray diffraction.

In the IR spectra of aldimines **3a**,**b** in solution (c = 0.1 mol L^{-1}; $CHCl_3$), the positions of the stretching bands of the imino and phosphoryl groups depend on their mutual arrangement, each compound existing at least as two conformers. The IR spectrum of *meta* isomer **3a** shows one intense ν(P=O) absorption band at 1190 cm^{-1} (with a shoulder at lower frequencies) and two absorption bands,

which can be assigned to ν(C=N), a strong band at 1622 cm^{-1} and a medium-intensity band at 1600 cm^{-1}. On the contrary, the ν(P=O) vibrations of *ortho* isomer **3b** are observed as two bands at 1198 cm^{-1} (with a shoulder at lower frequencies) and 1176 cm^{-1}, and the ν(C=N) vibration is observed as one band at 1617 cm^{-1} with a shoulder at ~1620 cm^{-1}. The spectra of polycrystalline samples of compounds **3a** and **3b** are comparable with the spectra in solutions and, apparently, they also cannot be interpreted as those corresponding to the only conformer. The 2300—3300 cm^{-1} region in the spectra of compounds **3a**,**b** contains a broad low-intensity band characteristic of stretching vibrations of OH groups involved in weak hydrogen bonding. This band overlaps with the CH stretching bands of the aromatic and methylene groups.

Apparently, these spectroscopic manifestations are attributed not only to the mutual arrangement of the phosphoryl group and the salicylaldimine fragment but also to the characteristic features of different hydrogen bonds between the OH, C=N, and P=O groups. Taking into account the NMR spectroscopic data, the most probable conformers are those, in which the intramolecular C=N...H—O hydrogen bond is present and the hydrogen bond with the phosphoryl oxygen atom is absent (the highest ν(P=O) frequencies; ν(C=N) 1617—1622 cm^{-1}),* and those containing a bifurcated hydrogen bond formed by the phosphoryl oxygen atom and the nitrogen atom characterized by a decrease in the ν(C=N) frequency to 1600 cm^{-1},[7] as was observed for *meta* isomer **3a**.

Upon the repeated recrystallization of *meta*-salicylaldimine **3a** from a CH_2Cl_2—Bu^tOMe system, the product was isolated as the only conformer, whose structure was confirmed by single-crystal X-ray diffraction. In the crystal structure of *meta* isomer **3a**, the rather strong intramolecular O—H...N hydrogen bond is characterized by the O(2)...N(1) distance of 2.592(2) Å (Fig. 3, Table 2). The presence of this hydrogen bond leads to the expected averaging of the other bond lengths. In the crystal structure of *meta* isomer **3a**, the salicylaldimine fragment is nearly planar (the dihedral angle between the aromatic ring of the central aromatic moiety and the C(9)—C(14) ring is 13°), and the phosphoryl group is perpendicular to the mean plane of this fragment. A slight distortion of the planar conformation in the crystal structure of **3a** is, apparently, associated with the crystal packing effects, to be more precise, with stacking interactions between the aromatic rings C(2)—C(6) (the shortest C...C contacts are 3.384(2) Å), resulting in the formation of dimers. In addition to the stacking interactions, these dimers are stabilized by a rather strong C—H...O contact (H...O, 2.39 Å) formed by the hydrogen atom at the C=N bond and the phosphoryl oxygen atom.

* For comparison, ν(C=N) for analogous unphosphorylated salicylaldimines is 1628 cm^{-1}.[6]

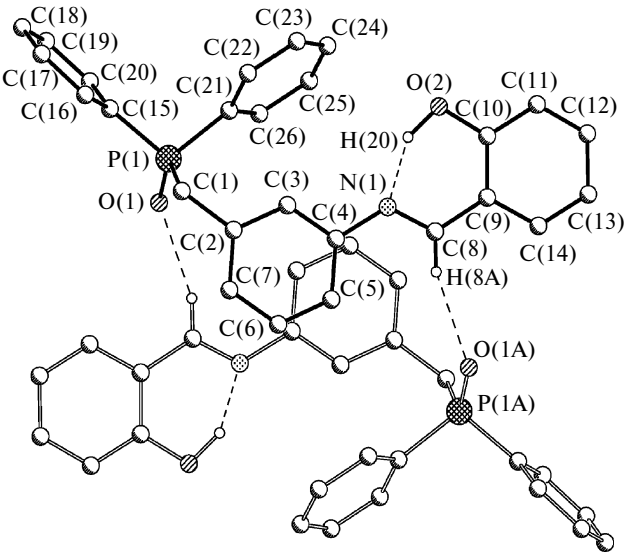


Fig. 3. Formation of dimers in the crystal structure of *meta* isomer **3a**. The atomic numbering scheme is given only for one symmetrically independent molecule.

Presumably, ligands **3a**,**b** form complexes with lanthanide ions with the involvement not only of the phosphoryl group but also of the hydroxyazomethine fragment. The coordination properties of ligands **3a**,**b** were studied in the reactions with praseodymium and neodymium nitrates. Upon the mixing of the reagents in molar ratios from 1 : 1 to 1 : 3 in an ethanolic solution, the ^{31}P NMR spectra show singlets shifted downfield with respect to the signal of the free ligand in the same solvent (δ_P = 33.5 (**3a**) and 32.7 (**3b**); see Table 3), whereas the signal of the free ligand is absent. The positions of the signals are indicative of fast exchange processes and the formation of complexes of different composition. The downfield shifts of the signals of the complexes provide unambiguous evidence for the involvement of the phosphine oxide group in the complexation.

The $[LnL_2(NO_3)_3]$ complexes (**4a—c**: L = **3a**, Ln = Pr (**4a**); L = **3b**, Ln = Pr (**4b**); L = **3b**, Ln = Nd (**4c**)) precipitate with time from solutions at different ligand-to-metal molar ratios.

The identity of complexes **4a—c** isolated from the reaction mixtures containing the starting reagents in different ratios was confirmed by comparing the physicochemical constants (melting points, IR spectra, and unit cell parameters (**4b**)) and the elemental analysis data.

According to the X-ray diffraction study, the praseodymium atom in the crystal structure of complex **4b** is coordinated by two neutral ligands (L = **3b**) and three nitrate anions (Fig. 4). The latter are coordinated to the metal atom in a bidentate fashion with a slight asymmetry (the Pr—O bond lengths in the NO_3 ligands vary in a range of 0.03—0.07 Å). Complex **4b** contains ligands **3b** with different denticities. One of the ligands (**B**) serves as a

Table 2. Selected bond lengths (*d*) in ligand *meta*-**3a** and complex **4b**

3a		**4bA**		**4bB**	
Bond	*d*/Å	Bond	*d*/Å	Bond	*d*/Å
P(1)—O(1)	1.481(1)	P(1)—O(1)	1.525(5)	P(1′)—O(1′)	1.522(5)
P(1)—C(1)	1.817(1)	P(1)—C(1)	1.814(7)	P(1′)—C(1′)	1.833(2)
P(1)—C(15)	1.807(1)	P(1)—C(15)	1.797(8)	P(1′)—C(15′)	1.780(8)
P(1)—C(21)	1.811(2)	P(1)—C(21)	1.812(8)	P(1′)—C(21′)	1.787(8)
N(1)—C(4)	1.431(1)	N(1)—C(3)	1.435(10)	N(1′)—C(3′)	1.447(9)
N(1)—C(8)	1.288(1)	N(1)—C(8)	1.301(9)	N(1′)—C(8′)	1.315(9)
O(2)—C(10)	1.359(1)	O(2)—C(10)	1.354(9)	O(2′)—C(10′)	1.292(9)
C(8)—C(9)	1.462(1)	C(8)—C(9)	1.457(11)	C(8′)—C(9′)	1.429(10)
C(9)—C(10)	1.406(1)	C(9)—C(10)	1.419(11)	C(9′)—C(10′)	1.444(10)
C(10)—C(11)	1.388(1)	C(10)—C(11)	1.390(11)	C(10′)—C(11′)	1.409(10)
C(11)—C(12)	1.398(1)	C(11)—C(12)	1.399(11)	C(11′)—C(12′)	1.369(11)
C(12)—C(13)	1.387(2)	C(12)—C(13)	1.401(11)	C(12′)—C(13′)	1.392(10)
C(13)—C(14)	1.3962(15)	C(13)—C(14)	1.349(11)	C(13′)—C(14′)	1.382(11)
C(9)—C(14)	1.404(1)	C(14)—C(9)	1.429(11)	C(9′)—C(14′)	1.420(11)
		Pr(1)—O(1)	2.370(5)	Pr(1)—O(1′)	2.401(5)
		Pr(1)—O(1N)	2.570(5)	Pr(1)—O(2′)	2.341(5)
		Pr(1)—O(2N)	2.607(5)	Pr(1)—O(7N)	2.565(5)
		Pr(1)—O(4N)	2.585(5)	Pr(1)—O(8N)	2.636(5)
		Pr(1)—O(5N)	2.535(5)		

Table 3. ^{31}P NMR spectroscopic data (EtOH) for mixtures of $Ln(\mathbf{L})_n(NO_3)_3$ (L = **3a,b**)

Ligand/Metal	L : M = 1 : 1		L : M = 2 : 1		L : M = 3 : 1	
	δ_P	$\Delta\delta$	δ_P	$\Delta\delta$	δ_P	$\Delta\delta$
3a/Pr	55.22	11.7	40.2	6.7	35.3	1.8
3b/Pr	50.8	18.1	59.9	27.2	52.0	19.3
3b/Nd	73.1	40.4	43.7	11.0	52.8	20.1

bidentate ligand and forms coordination bonds with the involvement of the oxygen atoms of the phosphoryl and hydroxy groups, whereas another ligand (**A**) is coordinated to the metal atom in a monodentate fashion and forms the coordination bond only *via* the phosphoryl oxygen atom. Therefore, the coordination number of praseodymium in complex **4b** is nine.

The difference in the coordination mode of two molecules of ligand **3b** results in the unexpected stabilization of its different forms in complex **4b**. Actually, coordinated ligand **3bA**, like free molecule **3a**, exists in the enol-imine form, whereas the structure of ligand **3bB** is characterized by the localization of the proton at the nitrogen atom and is stabilized, apparently, by the Pr(1).....O(2′) coordination bond. The latter structure can be interpreted as either a keto-enamine tautomer (the quinomethide form) or a zwitterionic form.[2] The above-mentioned differences in the structure of molecules **A** and **B** of ligand **3b**, in turn, lead to a substantial redistribution of the bond lengths in the region of the hydrogen-bonded rings (see Table 2) and a distortion of the planarity of the salicylaldimine fragment in **3bB** (the C(8′)N(1′)C(3′)C(2′) torsion angle is 135.6°). It should be noted that keto-enamine form **3bB** contains, along with the intramolecular hydrogen bond with the O(2′) atom (N(1′)...O(2′), 2.68 Å; N(1′)H(1N′)O(2′), 141°), the hydrogen bond with the phosphoryl group (N(1)′...O(1′), 2.94 Å; N(1′)H(1N′)O(1′), 126°). Apparently, the bifurcated hydrogen bond also contributes to the stabilization of form **3bB** and is responsible for a substantial rotation of the aromatic ring C(2′)—C(7′) with respect to the ring C(9′)—C(14′).

The mutual arrangement of the ligands in complex **4b** is influenced not only by steric factors and the coordination to the metal atom but also by the intramolecular stacking interaction between the salicylidene fragment of ligand **3bA** and the phenyl ring C(15)—C(20) of ligand **3bB**. Actually, the dihedral angle between these aromatic rings is 11.7°, and the shortest C(14′)...C(18) and C(10′)...C(16) contacts are 3.38 and 3.41 Å, respectively.

The IR spectrum of complex **4b** (Fig. 5, spectrum *d*) shows two absorption bands of differently coordinated phosphoryl groups. The band at 1161 cm^{-1} is assigned

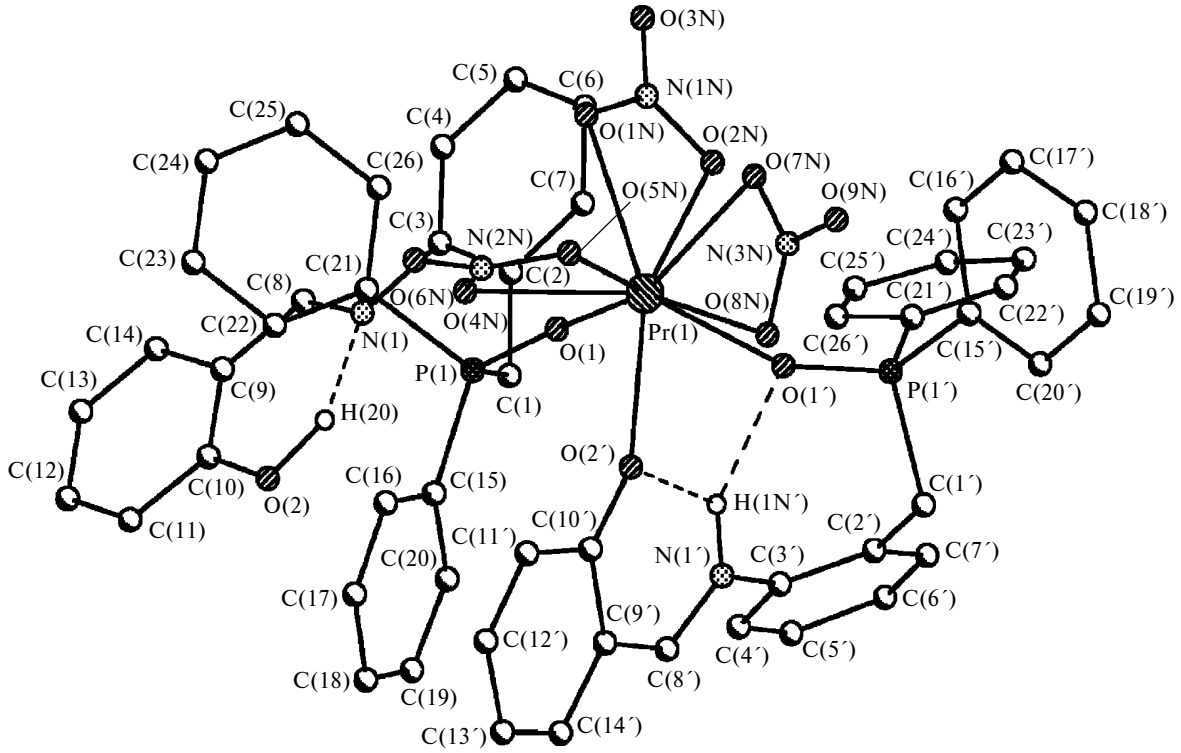


Fig. 4. Molecular structure of complex **4b**.

to monodentate ligand **3bA** and is characteristic of P=O groups bound to metal. Another band has a maximum at 1133 cm^{-1}; the additional low-frequency shift is attributed to the hydrogen bonding between the P=O group and the phenol proton in ligand **3bB**. Earlier, we have documneted this phenomenon upon complexation.[8] A complicatedly structured band with a maximum at 1626 cm^{-1} and a shoulder at 1615 cm^{-1} is observed in the absorption region of the C=N bond. It should be noted that the assignment of the observed absorption bands to the pure C=N vibration is incorrect due to the redistribution of the bond orders in the salicylaldimine fragment associated with intramolecular hydrogen bonding, which was established by X-ray diffraction. This vibration is mixed with the vibration of the conjugated C_{Ar}—N bond and with the skeletal vibrations of the aromatic rings. This, in particular, accounts for the fact that it is impossible to unambiguously determine the coordination mode of the ligands in complexes **4a—c** based on the IR spectra. It should also be noted that if the observed frequencies assigned to ν(C=N) are correlated to the lengths of this bond determined by X-ray diffraction (see Table 2), no length—frequency relationships are observed. However, the fact that the IR spectra of complexes **4b,c** formed by the same ligand **3b** are identical suggests that complexes **4b,c** have identical structures.

The spectrum of complex **4a** (L = **3a**) shows that both phosphoryl groups are coordinated. Thus, the ν(P=O) band is shifted to 1153 cm^{-1}, and the band of the free P=O group is absent. Three absorption maxima at 1634, 1620, and 1602 cm^{-1} can be assigned to mixed vibrations of the CNC fragment (Fig. 5, spectrum *c*). This fact is indicative of the *O*,*O*-bidentate coordination of both ligands **3a** in complex **4a** with a pronounced shift of the phenol proton to the nitrogen atom. It should be noted that the nitrate groups in complexes **4a—c** are coordinated to the metal ion in a bidentate fashion, as evidenced by the characteristic absorption bands ν(N=O) at ~1480 cm^{-1} and $\nu_{as}(NO_2)$ at ~1297 cm^{-1}.

Therefore, the new tridentate ligands, *viz.*, phosphoryl-substituted Schiff bases, synthesized in the present study readily form complexes with lanthanides, whose structures are determined by the mutual arrangement of the complex-forming fragments in the ligands. It should be noted that, in contrast to typical salicylaldimines, the nitrogen atom in the new ligands is not involved in the coordination to metal.

Experimental

The ^1H, ^{13}C, and ^{31}P NMR spectra were recorded on Bruker AMX-400 (400.13, 100,61, and 161.98 MHz, respectively) and Bruker AV-300 (300.09, 75.47, and 121.49 MHz, respectively) instruments in $CDCl_3$ with the use of the signal of the residual protons of the deuterated solvent as the internal standard (^1H and ^{13}C) and 85% H_3PO_4 as the external standard (^{31}P). For

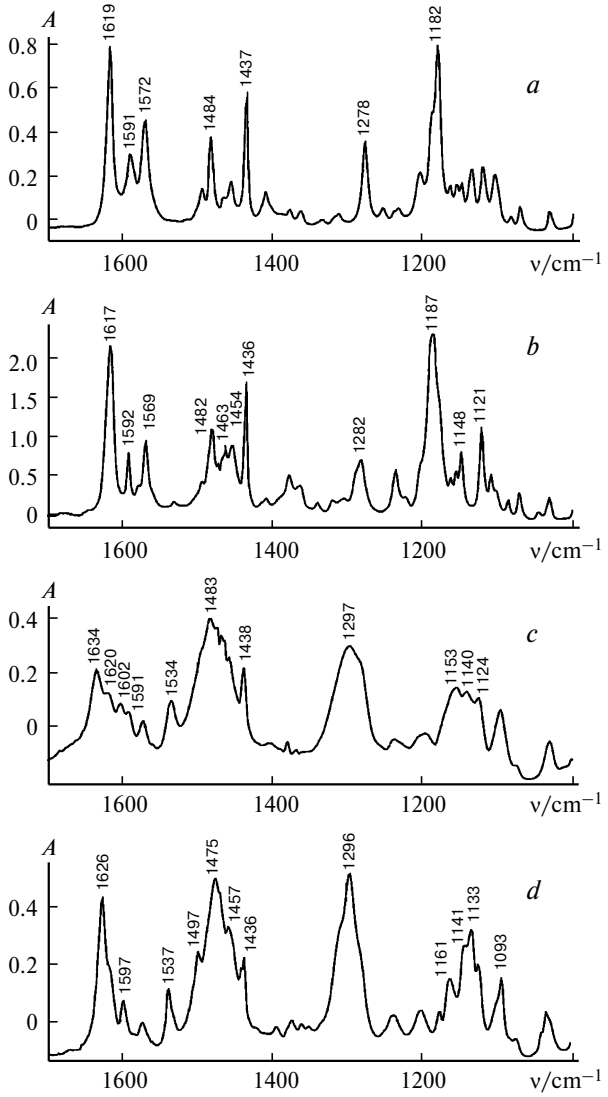


Fig. 5. Fragments of the IR spectra (Nujol) of crystalline samples of compounds **3a** (*a*) and **3b** (*b*) and praseodymium complexes **4a** (*c*) and **4b** (*d*). Bands associated with Nujol are excluded.

the ^{31}P NMR spectra of the reaction mixtures, D_2O was used as the external standard. The IR spectra were measured on a Nicolet Magna-IR 750 infrared Fourier-transform spectrometer; the resolution was 2 cm^{-1}, the number of scans was 128 (KBr pellets or Nujol mulls).

Nitrobenzyl bromides were synthesized from *o*- or *m*-nitrobenzaldehyde by the Cannizzaro reaction[9] followed by the bromination of nitrobenzyl alcohols that formed with phosphorus tribromide according to known procedures.[10,11]

(*m*-Nitrobenzyl)diphenylphosphine oxide (1a). Ethyl diphenylphosphinite (29.0 g, 0.126 mol) was slowly added dropwise to a solution of *m*-nitrobenzyl bromide (27.2 g, 0.126 mol) in refluxing toluene. The reaction mixture was refluxed with stirring for 2 h and then cooled. The precipitate was filtered off and recrystallized from ethanol. Compound **1a** was obtained in a yield of 42.4 g (85%) as a white crystalline compound (needle-like crystals). M.p. 214—216 °C (EtOH). ^{31}P NMR ($CDCl_3$), δ: 28.91. ^1H NMR ($CDCl_3$), δ: 3.72 (d, 2 H, CH_2, $^2J_{P,H}$ =13.3 Hz); 7.38 (t, 1 H, C_6H_4N, $^3J_{H,H}$ = 7.8 Hz); 7.43—7.48 and 7.51—7.55 (both m, 6 H each, PhP); 7.56 (d, 1 H, C_6H_4N, $^3J_{H,H}$ = 7.8 Hz); 7.66—7.71 (m, 4 H, PhP); 7.81 (dd, 1 H arom., $^4J_{H,H}$ = 1.4 Hz, $^4J_{P,H}$ = 4.3 Hz); 8.03 (d, 1 H, C_6H_4—N, $^3J_{H,H}$ = 7.8 Hz). IR (KBr), ν/cm^{-1}: 1524, 1349 (NO_2); 1187 (PO). Found (%): C, 67.64; H, 4.71; N, 4.27. $C_{19}H_{16}NO_3P$. Calculated (%): C, 67.65; H, 4.78; N, 4.15.

***o*-Nitrobenzyldiphenylphosphine oxide (1b)** was synthesized according to an analogous procedure. The yield was 76%, m.p. 178—179 °C (*cf.* lit. data[12]: m.p. 179—180 °C). ^{31}P NMR ($CDCl_3$), δ: 29.35. ^1H NMR ($CDCl_3$), δ: 4.32 (d, 2 H, CH_2, $^2J_{P,H}$ = 13.9 Hz); 7.38—7.60 (m, 8 H, arom.); 7.67—7.77 (m, 5 H, arom.); 7.89 (d, 1 H, C_6H_4—N, $^3J_{H,H}$ = 8.2 Hz). IR (KBr), ν/cm^{-1}: 1525, 1357 (NO_2); 1187 (PO).

***m*-(Diphenylphosphorylmethyl)aniline (2a).** A solution of $SnCl_2$ (8 g, 0.035 mol) in concentrated hydrochloric acid (20 mL) was slowly added dropwise to a solution of (*m*-nitrobenzyl)diphenylphosphine oxide **1a** (3.4 g, 0.01 mol) in glacial acetic acid (20 mL) for 2.5 h. The temperature of the reaction mixture raised to 35 °C without external heating. Then the mixture was stirred at 40—42 °C for 2 h, cooled, and poured onto ice, pH was brought to 12 with a NaOH solution, and the mixture was extracted with chloroform (3×25 mL). The combined extracts were dried over sodium sulfate and filtered. The solvent was evaporated *in vacuo*, and the residue was recrystallized from benzene. Compound **2a** was obtained in a yield of 2.9 g (94%) as white crystals, m.p. 132—134 °C (C_6H_6). ^{31}P NMR ($CDCl_3$), δ: 29.65. ^1H NMR ($CDCl_3$), δ: 3.40 (br.s, 2 H, NH_2); 3.54 (d, 2 H, CH_2, $^2J_{P,H}$ = 13.8 Hz); 6.38 (d, 1 H, C_6H_4N, $^3J_{H,H}$ =7.7 Hz); 6.47 (d, 1 H, C_6H_4N, $^3J_{H,H}$ = 7.7 Hz); 6.54 (br.d, 1 H, C_6H_4—N, J = 1.9 Hz); 6.92 (t, 1 H, C_6H_4N, $^3J_{H,H}$ = 7.7 Hz); 7.41—7.50 and 7.62—7.72 (both m, 6 H + 4 H, PhP). IR (KBr), ν/cm^{-1}: 3425, 3364, 3328, 3200 (NH_2), 1190 (PO). Found (%): C, 74.37; H, 5.96; N, 4.42. $C_{19}H_{18}NOP$. Calculated (%): C, 74.25; H, 5.90; N, 4.56.

***o*-(Diphenylphosphorylmethyl)aniline (2b)** was synthesized according to an analogous procedure from **1b** in 87% yield, m.p. 198—200 °C (C_6H_6). ^{31}P NMR ($CDCl_3$), δ: 34.06. ^1H NMR ($CDCl_3$), δ: 3.72 (d, 2 H, CH_2, $^2J_{P,H}$ = 12.8 Hz); 4.75 (br.s, 2 H, NH_2); 6.56 (t, 1 H, C_6H_4—N, $^3J_{H,H}$ = 7.3 Hz); 6.63 (d, 1 H, C_6H_4—N, $^3J_{H,H}$ = 7.3 Hz); 6.76 (d, 1 H arom., $^3J_{H,H}$ = 8.0 Hz); 7.04 (dd, 1 H, C_6H_4N, $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 8.0 Hz); 7.42—7.55 and 7.75—7.80 (both m, 6 H + 4 H, PhP). IR (KBr), ν/cm^{-1}: 3402, 3305, 3250, 3219 (NH_2); 1173 (PO). Found (%): C, 74.14; H, 5.76; N, 4.51. $C_{19}H_{18}NOP$. Calculated (%): C, 74.25; H, 5.90; N, 4.56.

2-[3-(Diphenylphosphorylmethyl)phenyliminomethyl]phenol (3a). A solution of salicylaldehyde (0.36 g, 0.003 mol) in ethanol (2 mL) was slowly added dropwise to a solution of *meta* isomer **2a** (0.9 g, 0.003 mol) in ethanol. The reaction mixture was refluxed for 2 h. The solution was concentrated to dryness, and the residue was recrystallized from a 1 : 1 benzene—diethyl ether mixture. Imine **3a** was obtained in a yield of 0.8 g (67%) as a yellow crystalline compound, m.p. 164—166 °C. ^{31}P NMR ($CDCl_3$), δ: 29.43. ^1H NMR ($CDCl_3$), δ: 3.68 (d, 2 H, CH_2, $^2J_{P,H}$ = 13.5 Hz); 6.92 (dt, 1 H, arom., $^3J_{H,H}$ = 7.3 Hz, $^3J_{H,H}$ = 8.0 Hz); 6.94 (br.d, 1 H, arom., $^3J_{H,H}$ = 7.4 Hz); 6.98 (d, 1 H, arom., $^3J_{H,H}$ = 8.0 Hz); 7.02 (d, 1 H, arom., $^3J_{H,H}$ = 7.4 Hz); 7.09 (d, 1 H, arom., $^3J_{H,H}$ = 7.4 Hz); 7.23 (t, 1 H, arom.,

Table 4. Principal crystallographic data and the refinement statistics for **1a,b**, **3a**, and **4b**

Parameter	**1a**	**1b**	**3a**	**4b**
Molecular formula	$C_{19}H_{16}NO_3P$	$C_{19}H_{16}NO_3P$	$C_{26}H_{22}NO_2P$	$C_{52}H_{44}N_5O_{13}P_2Pr$
Molecular weight	337.30	337.30	411.42	1149.77
Crystal dimensions	0.19×0.18×0.15	0.26×0.18×0.15	0.4×0.2×0.2	0.11×0.04×0.02
T/K	120	120	120	100
Crystal system	Triclinic	Orthorhombic	Monoclinic	Triclinic
Space group	$P\bar{1}$	$P2_12_12_1$	$P2_1/n$	$P\bar{1}$
$Z(Z')$	2(1)	4(1)	4(1)	2(1)
a/Å	5.7534(9)	5.6835(6)	13.208(2)	9.9318(13)
b/Å	11.125(2)	13.872(1)	7.3837(1)	11.601(2)
c/Å	13.844(3)	20.501(2)	16.025(3)	23.540(3)
α/deg	112.257(5)			84.688(9)
β/deg	98.96(3)		92.371(4)	80.645(8)
γ/deg	96.319(5)			71.769(6)
V/Å^3	801.3(2)	1616.3(3)	1561.5(5)	2539.4(7)
d_{calc}/g cm^{-3}	1.398	1.368	1.635	1.504
μ/cm^{-1}	1.89	1.87	1.42	10.92
F(000)	352	704	808	1168
$2\theta_{max}$/deg	60	60	58	54
Number of measured reflections (R_{int})	10445 (0.0723)	12573 (0.0473)	12087 (0.0203)	24352 (0.1745)
Number of independent reflections	4680	4642	5411	11034
Number of reflections with $I > 2\sigma(I)$	2386	2958	4155	5060
Number of variables	217	217	329	652
R_1	0.0489	0.0454	0.0417	0.0747
wR_2	0.1226	0.0827	0.1124	0.1356
GOOF	0.848	0.952	1.079	0.935
Residual electron density/e Å^{-3} (d_{min}/d_{max})	0.48/−0.55	0.43/−0.38	0.42/−0.25	1.114/−1.717

$J_{H,H}$ = 8.0 Hz); 7.32 (dt, 1 H, arom., $^3J_{H,H}$ = 7.4 Hz, $^4J_{P,H}$ = 1.6 Hz); 7.35 (dt, 1 H, arom., $^3J_{H,H}$ = 8.0 Hz, $^4J_{P,H}$ = 1.6 Hz); 7.43—7.55, 7.68—7.73 (m, 6 H + 4 H, PhP); 8.38 (s, 1 H, CH=N); 13.13 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ:* 37.93 (d, C1, $J_{P,C}$ = 65.6 Hz); 117.06 (s, C(11)); 118.91 (s, C(13)); 119.01 (s, C(9)); 120.32 (d, C(7), $^4J_{P,C}$ = 2.9 Hz); 122.06 (d, C(6), $^5J_{P,C}$ = 5.1 Hz); 128.47 (d, C(17), C(23), C(19), C(25), $^3J_{P,C}$ = 11.7 Hz); 128.58 (s, C(5)); 129.20 (d, C(3), $^3J_{P,C}$ = 2.9 Hz); 131.05 (d, C(16), C(22), C(20), C(26), $^2J_{P,C}$ = 8.7 Hz); 131.83 (d, C(18), C(24), $^4J_{P,C}$ = 2.2 Hz); 131.97 (d, C(15), C(21), $^1J_{P,C}$ = 99.2 Hz); 132.14 (s, C(14)); 132.46 (d, C(2), $^2J_{P,C}$ = 8.0 Hz); 133.00 (s, C(12)); 148.29 (s, C(4)); 160.96 (s, C(10)); 162.72 (s, C(8)). IR (Nujol), ν/cm^{-1}: 512, 524, 694, 719, 755, 793, 891, 946, 998, 1119, 1148, 1182, 1278, 1437, 1484, 1572, 1591, 1619, 2300—3300. Found (%): C, 75.98; H, 5.36; N, 3.31. $C_{26}H_{22}NO_2P$. Calculated (%): C, 75.90; H, 5.39; N, 3.40.

The *ortho* isomer of salicylaldimine **(3b)** was synthesized analogously in 85% yield, m.p. 158—160 °C (benzene—diethyl ether, 1 : 1). ^{31}P NMR ($CDCl_3$), δ: 29.20. ^{1}H NMR ($CDCl_3$), δ: 3.93 (d, 2 H, CH_2, $^2J_{P,H}$ = 13.7 Hz); 6.91—7.02 (m, 2 H, arom.); 7.08 (d, 1 H, arom., $^3J_{H,H}$ = 8.0 Hz); 7.21 (t, 1 H, arom., $^3J_{H,H}$ = 7.5 Hz); 7.29—7.47 (m, 9 H, arom.); 7.63—7.69 (m, 5 H, arom.); 7.86 (s, 1 H, CH=N); 12.92 (s, 1 H, OH). ^{13}C NMR ($CDCl_3$), δ: 33.34 (d, C(1), $^1J_{P,C}$ = 66.4 Hz); 116.98 (s, C(11)); 118.45 (d, C(4), $^4J_{P,C}$ = 2.9 Hz); 118.93 (s, C(13)); 119.16 (s, C(9)); 125.16 (d, C(2), $^2J_{P,C}$ = 8.7 Hz); 126.84 (d, C(6), $^4J_{P,C}$ = 2.9 Hz); 128.19 (d, C(17), C(23), C(19), C(25), $^3J_{P,C}$ = 11.7 Hz); 128.28 (s, C(5)); 130.94 (d, C(16), C(22), C(20), C(26), $^2J_{P,C}$ = 8.7 Hz); 131.50 (d, C(18), C(24), $^4J_{P,C}$ = 2.2 Hz); 131.90 (d, C(7), $^3J_{P,C}$ = 4.4 Hz); 131.96 (d, C(15), C(21), $^1J_{P,C}$ = 97.8 Hz); 132.45 (s, C(14)); 133.07 (s, C(12)); 147.64 (d, C(3), $^3J_{P,C}$ = 5.8 Hz); 160.57 (s, C(10)); 163.14 (s, C(8)). IR (Nujol), ν/cm^{-1}: 512, 524, 694, 719, 746, 767, 910, 1121, 1148, 1187, 1282, 1436, 1482, 1569, 1592, 1617, 2300—3300. Found (%): C, 75.71; H, 5.27; N, 3.34. $C_{26}H_{22}NO_2P$. Calculated (%): C, 75.90; H, 5.39; N, 3.40.

Bis{2-[3-(diphenylphosphorylmethyl)phenyliminomethyl]phenol}praseodymium trinitrate (4a). The $Pr(NO_3)_3 \cdot 6H_2O$ compound (51.8 mg, 0.12 mmol) was added to a solution of salicylaldimine **3a** (97.9 mg, 0.24 mmol) in ethanol (2.5 mL), and the reaction mixture was heated until the reagents were completely dissolved. Then the mixture was kept for 12 h, and the precipitate that formed was separated and recrystallized from EtOH. The complex was obtained in a yield of 125.1 mg (90.1%), m.p. 158—160 °C (with decomp.). IR (Nujol), ν/cm^{-1}: 518, 694, 736, 756, 817, 1028, 1094, 1124, 1140, 1153, 1297, 1438, 1462, 1483, 1534, 1571, 1592, 1602, 1620, 1634. ^{31}P NMR (EtOH), δ: 40.2. Found (%): C, 54.14; H, 3.87; N, 6.12. $C_{52}H_{44}N_5O_{13}P_2Pr$. Calculated (%): C, 54.32; H, 3.86; N, 6.09.

Under analogous conditions, **bis{2-[2-(diphenylphosphorylmethyl)phenyliminomethyl]phenol}praseodymium trinitrate (4b)**

* For comparison, ν(C=N) for analogous unphosphorylated salicylaldimines is 1628 cm^{-1}.[6]

was synthesized from imine **(3b)** (82.0 mg) and $Pr(NO_3)_3 \cdot 6H_2O$ (43.3 mg) in a yield of 102.1 mg (89.2%), m.p. 220—222 °C. IR (Nujol), ν/cm^{-1}: 521, 692, 748, 818, 1032, 1093, 1122, 1133, 1141, 1161, 1296, 1436, 1457, 1475, 1497, 1537, 1571, 1597, 1617, 1626. ^{31}P NMR (EtOH), δ: 59.9. Found (%): C; 54.66; H, 3.84; N, 5.77. $C_{52}H_{44}N_5O_{13}P_2Pr$. Calculated (%): C, 54.32; H, 3.86; N, 6.09.

Neodymium complex **4c** was synthesized under analogous conditions from ligand **3b** (88.5 mg, 0.215 mmol) and $Nd(NO_3)_3 \cdot 6H_2O$ (47.2 mg, 0.1075 mmol). The yield was 91%, m.p. 165—167 °C (with decomp.). IR (Nujol mulls), ν/cm^{-1}: 520, 691, 720, 755, 818, 1040, 1092, 1122, 1132 (PO); 1143, 1161 (PO); 1297 (NO_3); 1377, 1436, 1463, 1480 (NO_3); 1536, 1595, 1615, 1623 (NCN). ^{31}P (EtOH), δ: 43.7. Found (%): C, 54.19; H, 3.85; N, 6.34. $C_{52}H_{44}N_5NdO_{13}P_2$. Calculated (%): C, 54.16; H, 3.85; N, 6.07.

X-ray diffraction study. X-ray diffraction data for compounds **1a,b** and **3a** were collected on a SMART 1000 CCD diffractometer; for complex **4b**, on a SMART APEXII CCD diffractometer (Mo-Kα radiation, graphite monochromator, ω-scanning technique). Crystals suitable for X-ray diffraction were grown from EtOH (**1a,b**), CH_2Cl_2—Bu^{t}OMe (**3a**), and CH_3CN (**4b**). Semiempirical absorption corrections were applied based on equivalent reflections with the use of the Sadabs program. The rather high R_{int} factor for complex **4b** is accounted for by small crystal sizes and the low reflecting ability even when the exposure time of 60 s per frame was used. The structures were solved by direct methods and refined anisotropically by the full-matrix least-squares method based on F^2_{hkl}. The hydrogen atoms at the nitrogen and oxygen atoms in **3a** and **4b** were located in difference Fourier maps. The other hydrogen atoms were positioned geometrically. An analysis of difference Fourier maps for *meta* isomer **3a** showed that one phenyl ring is disordered over two positions with occupancies of 0.4 and 0.6. Principal crystallographic data and the refinement statistics are given in Table 4. All calculations were carried out with the use of the SHELXTL PLUS program package.

This study was financially supported by the Russian Foundation for Basic Research (Project Nos 05-03-33094 and 05-03-32692).

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Received April 4, 2007;
in revised form June 8, 2007