ISSN 1070-3632, Russian Journal of General Chemistry, 2008, Vol. 78, No. 4, pp. 567–574. © Pleiades Publishing, Ltd., 2008.
Original Russian Text © L.D. Popov, S.A. Borodkin, I.N. Shcherbakov, Yu.N. Tkachenko, V.A. Kogan, 2008, published in Zhurnal Obshchei Khimii, 2008, Vol. 78, No. 4, pp. 586–593.

Synthesis, Structure, and Properties of New Phosphorus Schiff Bases

L. D. Popov, S. A. Borodkin, I. N. Shcherbakov, Yu. N. Tkachenko, and V. A. Kogan

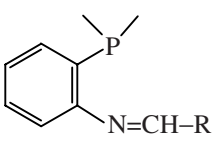
Southern Federal University,
ul. Zorge 7, Rostov-on-Don, 344090 Russia
e-mail: saborod@list.ru

Received August 13, 2007

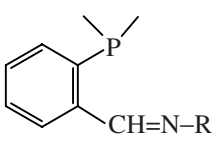
Abstract—A series of new Schiff bases has been synthesized on the basis of (2-aminophenyl)triphenylphosphonium chloride and substituted salicylaldehydes. The structure of the prepared compounds has been established by means of IR, UV, and ^{1}H NMR spectroscopy, as well as DFT B3LYP/6-31G(d,p) quantum-chemical simulation. The possible tautomerism and certain properties of the azomethines, including complex formation, have been studied.

DOI: 10.1134/S1070363208040099

Schiff bases are unique compounds due the possibility of easily varying fragments at the exocyclic C=N bond, which allows exploring such important aspects as tautomerism, conformational equilibria, acid&3base and donor–acceptor properties, etc. But, probably, the most important property of azomethines is their high complex-forming ability [1–4]. The interest in azomethines and their metal complexes is caused by their practical importance. Among them, luminophores, lubricant and fuel additives, photochromic materials, biologically active compounds, etc., were found [5]. Azomethines often serve as precursors for synthesis of other compounds, including heterocycles [6]. The number of papers on Schiff bases does not reduce, and the last review [7] contains about 700 references which cover the period since 2000 until present. In this connection we considered it of interest to synthesize new azomethines on the basis of aminophosphonium salts. Organophosphorus azomethines containing a P(III) atom, like **I** [8–17] and **II** [18–32] and their metal complexes, have been described in the literature, while *ortho*-hydroxyazomethines including a charged triarylphosphonium group have never been reported.

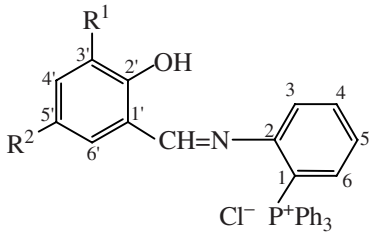


I



II

The goal of the present work was to synthesize new phosphorus-containing azomethines and to study their structure and some properties, including complex formation. (2-Aminophenyl)triphenylphosphonium chloride was reacted with substituted salicylaldehydes to obtain phosphonium anils **IIIa–IIIg**.



IIIa–IIIg

$R^1 = R^2 = H$ (**a**); $R^1 = H$, $R^2 = NO_2$ (**b**); $R^1 = H$, $R^2 = Br$ (**c**); $R^1 = H$, $R^2 = OCH_3$ (**d**); $R^1 = OCH_3$, $R^2 = Br$ (**e**); $R^1 = R^2 = Br$ (**f**); $R^1 = R^2 = Cl$ (**g**).

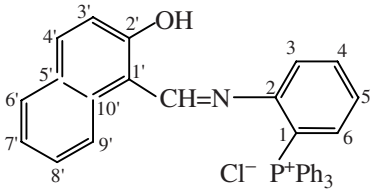
The ^{1}H NMR spectra of compounds **IIIa–IIIg** in DMSO-d_6 show a hydroxyl proton signal as a singlet at δ 10.10–12.42 ppm, which disappears upon deuteration. As expected, the most downfield OH proton signal (δ 12.42 ppm) is characteristic of nitro derivative **IIIb**. The azomethine CH proton gives a singlet at δ 8.77–9.18 ppm, the largest chemical shifts are observed in dichloro and dibromo derivatives **IIIf**

and **IIIg**. The spectra also contain P^+Ph_3 signals at δ 7.6–7.85 ppm, as a complex 15-proton multiplet.

The phosphorus-containing substituent complicates the shape of signals of its connected aromatic ring. This is explained by the fact that proton–phosphorus spin-spin coupling can reveal itself through 4–5 bonds. Thus, the H^3 signals appear as a doublet of doublets at δ 7.8–8.1 ppm ($^2J_{HH}$ 7.8 Hz, J_{HP} 6 Hz) and usually occur in the same field as triphenylphos-phonium proton signals. The H^4 signals at δ 7.9–8.1 ppm have a complex shape due to spin–spin coupling with H^5 which is *meta* to H^4 and long-range coupling with phosphorus. The observed coupling constants are $^2J_{HH}$ 7.5–8.0 and $^3J_{HH}$ 1.3 Hz. The H^5 signals are doublets at δ 7.40–7.60 ppm ($^2J_{HH}$ 7.4–7.7 Hz, J_{HP} 3.0–3.7 Hz). The H^6 proton gives a doublet of doublets at δ 7.12–7.25 ppm (J_{HP} 14 Hz, $^2J_{HH}$ 7–8 Hz).

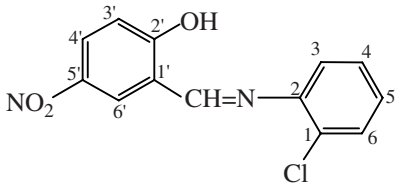
The shape and location of signals of the phenolic fragment are substitution-dependent. In the case of dichloro- and dibromo derivatives, the $H^{4'}$ and H6' protons give, as expected, doublets at δ 6.54–6.76 and 7.32–7.57 ppm , respectively ($^3J_{HH}$ 2.4–2.6 Hz). In the ^{1}H NMR spectrum of the compound with $R^1 = OCH_3$ and R^2 = Br, the same protons again appear as doublets at δ 6.31 and 6.94 ppm, respectively ($^3J_{HH}$ 2.3 Hz). The $H^{6'}$ signals of monosubstituted compounds appear as a doublet at δ 6.20–7.51 ppm ($^3J_{HH}$ 2.5–2.9 Hz). In this case, electronic effects of substituents are well-pronounced. Thus, the electron-donor methoxy group shifts the $H^{6'}$ signal upfield (to 6.20 ppm), while the electron-acceptor nitro group shifts the same signal downfield (to 7.51 ppm). The $H^{4'}$ signal is complicated and looks like a doublet of doublets at δ 6.75–8.0 ppm ($^2J_{HH}$ 9.0 Hz, $^3J_{HH}$ 3 Hz). The largest chemical shift, too, is observed for the nitro derivative. The H3' proton is detected as a doublet at δ 6.81–7.24 ppm ($^2J_{HH}$ 8.3–9.2 Hz).

The shapes and positions of the H^3–H^6 signals in the ^{1}H NMR spectrum of naphthyl derivative **IV** are similar to those in the spectra of azomethines **III**. The only distinguishing feature of the spectrum of this compound is that it contains signals of the naphthalene system at δ 7.00–8.23 ppm. These signals overlap with PPh_3 signals and, therefore, are difficult to assign.



IV

To assess the effect of the triphenylphosphonium group on the positions of ^{1}H NMR signals, we synthesized and explored model compound **V**.



V

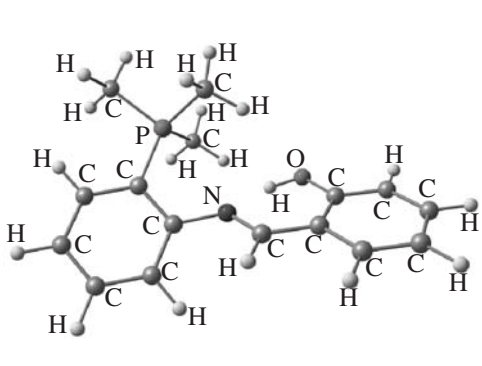
Compared to phosphonium derivative **IIIb**, nitro substitution exerts a stronger impact on the ^{1}H NMR spectrum of chloro derivative **V**. Thus, for example, the OH proton signal appears as a very downfield singlet (δ 14.23 ppm). The $H^{4'}$ (doublet of doublets, δ 8.24 ppm) and $H^{6'}$ (doublet, δ 8.69 ppm) signals in the ^{1}H NMR spectrum of compound **V** are also shifted downfield compared to compound **IIIb**. It is noteworthy that the H^4 signal in the spectrum of compound **V** is shifted upfield from the H^6 signals (δ 7.42 and 7.52 ppm, respectively). In the spectra of derivatives **III**, an opposite mutual location of these signals is observed (about 8.0 and 7.2 ppm, respectively). The H^3 and H^5 signals in the spectra of compounds **III** and **V** have a similar mutual location. It follows from the above data that the substitution of the chlorine atom by the positively charged triphenylphosphonium group exerts the strongest effect on the positions of the *ortho*- and *para*-proton signals.

The UV spectra of compounds **IIIa** in ethanol contain a strong π→π* transition band of the aromatic rings at λ_{max} 207 nm (log ε_{max} 4.80), a strong π→π* transition band (*E* band) at λ_{max} 276 nm (log ε_{max} 4.00), and a π→π* band (*K* band) at λ_{max} 358 nm (log ε_{max} 3.95). Addition of excess acid (HCl) to the solution of compound **IIIa**, the electronic spectrum changes insignificantly, which implies weak proton-acceptor properties of the imine nitrogen atom. In an alkaline medium (KOH), the spectrum changes significantly. The aromatic π→π* transition band undergoes a bathochromic shift of 20 nm and appears at λ_{max} 227 nm (log ε_{max} 4.62). The *E* band shifts bathochromically by 30 nm and appears at λ_{max} 306 nm (log ε_{max} 4.02). The *K* band undergoes the strongest bathochromic shift (by 87 nm) and increases in intensity (λ_{max} 435 nm, log ε_{max} 4.13), implying ionization of compound **IIIa**. The effect of the pH of the medium on the UV absorption

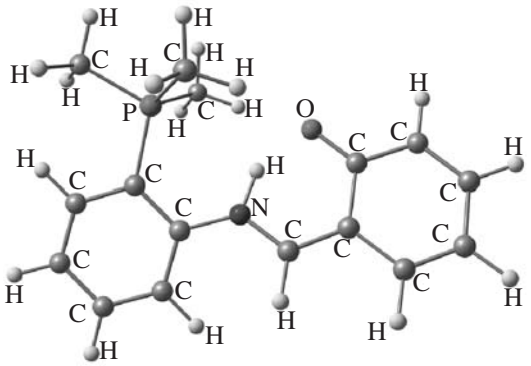
bands of nitro derivative **IIIb** is similar to that in unsubstituted compound **IIIa**: The aromatic π→π* transition band in a strongly alkaline medium (excess KOH) undergoes a 15-nm bathochromic shift compared to a neutral medium, and the *E* band is shifted bathochromically by 10 nm. The longest wave band corresponding to formation of a monodeprotonated structure is observed at λ_{max} 435 nm with log ε_{max} 3.93 (in neutral medium, λ_{max} 350 nm and log ε_{max} 3.85). The π→π* transition band of the nitro group (in a neutral medium, λ_{max} 302 nm and log ε_{max} 3.90) undergoes a 80-nm bathochromic shift as the solution is made alkaline (λ_{max} 382 nm, log ε_{max} 4.01). Noteworthy, this equilibrium in the solution is reversible, since adding acid to the alkaline solution (to pH 7) restores the spectrum of the neutral form.

Compounds like **III** and **IV** can undergo benzoid–quinoid tautomerism due to proton transfer from oxygen to the azomethine nitrogen [33–36]. To assess the relative stability of the tautomers, we accomplished DFT B3LYP/6-311G(d,p) quantum-chemical calculations of model anils **IIIa** and **IV** in which the triphenylphosphonium fragment of the synthesized azomethines is replaced by trimethylphosphonium. Figure 1 shows the steric models and calculated total energies (au) of the most stable conformations of the two tautomeric forms (benzoid and quinoid) and their relative stabilities (ΔE, kcal mol^{-1}).

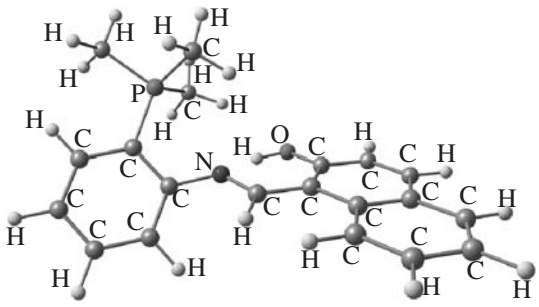
Like azomethine **IIIa**, compound **IV** prefers the benzoid tautomeric form, but the difference in the total energies in the case of naphthyl derivative **IV** is much smaller that in the case of compound **IIIa**, on account of a stronger stabilization of the quinoid tautomer due to π conjugation of the C=O bond with the more extended aromatic system of the naphthyl fragment. This conclusion is consistent with the ^{1}H NMR data for compounds **III** and **IV** which prefer the benzoid form in a polar solvent (DMSO).



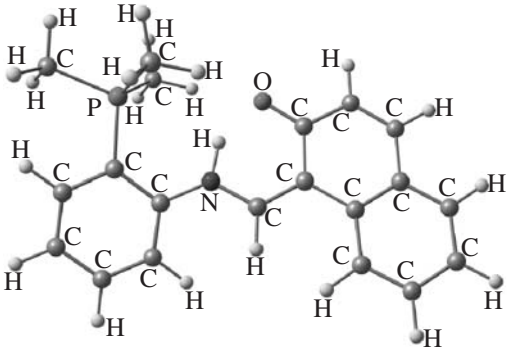
–1092.502624 au
ΔE 0 kcal mol^{-1}



–1092.491342 au
ΔE 7.1 kcal mol^{-1}



–1246.1789249 au
ΔE 0 kcal mol^{-1}



–1246.1737251 au
ΔE 3.3 kcal mol^{-1}

Fig. 1. Steric models and calculated total energies of the most stable conformers of the two tautomeric forms (benzoid and quinoid) and their relative stabilities (ΔE).

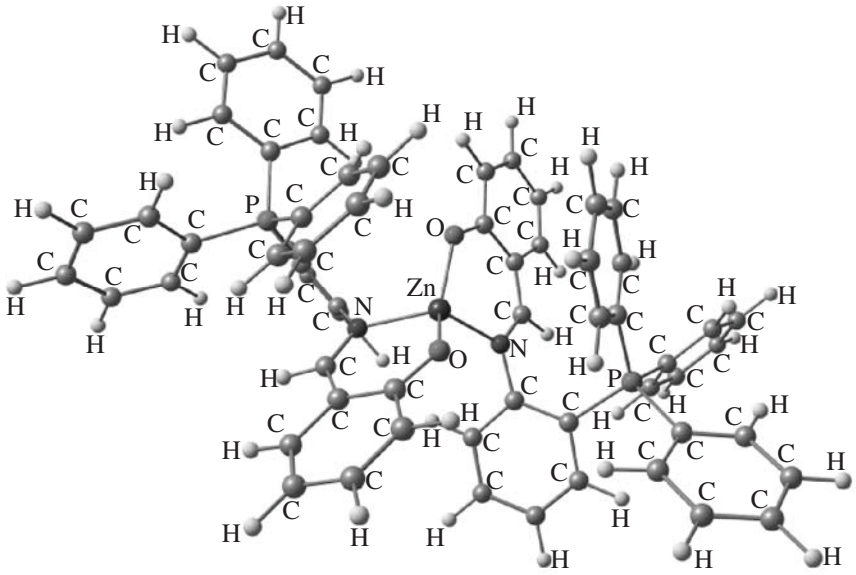


Fig. 2. Optimal geometry of zinc complex **VI**, obtained by the B3LYP/6-311G(d,p) method.

The azomethine nitrogen atom is involved into a strong hydrogen bond, which, together with the steric shielding by the bulky triphenylphosphonium substituent, is likely to prevent protonation of the investigated azomethines in an acid medium (experimental finding).

To study the complex-forming properties of these compound, we explored reaction of azomethines **IIIa–IIIg** and **IV** with Zn(II) and Cd(II) ions. The choice of these metals is primarily explained by the fact that many Zn(II) and Cd(II) azomethine complexes possess interesting and important luminescent properties and are used as organic light-emitting diodes [37–40]. The presence of a labile proton in the molecules of these ligands allowed us to prepare ML_2 chelate metal complexes **VI**. Let us note immediately that we could isolate and purify only three complexes: two zinc (with **IIIb** and **IIIc** as ligands) and one cadmium (with **IIIb**). Comparison of the IR spectra of these complexes with those of the free ligands reveals disappearance of the OH absorption band and a 10–15-nm bathochromic shift of the C=N group with simultaneous 10–15-nm hypsochromic shift the aldehyde Ph–O stretching vibration band, which suggests chelate formation. The ^{1}H NMR spectra of the complexes no longer show the OH proton signal, and the $H^{3'}$ signal is shifted upfield by about 1.0 ppm, which provides further evidence for chelate formation.

The possibility of existence of a tetrahedral zinc complex **VI**, even though it contains the bulky triphenylphosphonium substituent, was additionally confirmed by DFT calculations of its equilibrium geomety (Fig. 1).

The six-membered chelate rings are almost planar, except that they are folded by an angle of 11° along the line connecting the donor nitrogen and oxygen atoms. The pseudo-tetrahedral configuration of bonds around the complex-forming metal is slightly distorted: The angle between the chelate ring planes is 81°C. The Zn–O and Zn–N distances are 1.930 and 2.055 Å, respectively, that is typical of structurally similar zinc complexes.

Preliminary tests for photochemical activity showed that these complexes in the solid state possess luminescent properties. Detailed investigation of the photophysical properties of the complexes will be reported elsewhere.

EXPERIMENTAL

The IR spectra were recorded on a Varian Scimitar 1000 FT-IR spectrophotometer for suspensions in mineral oil. The ^{1}H NMR spectra were measured on a Bruker AM-300 spectrometer, internal reference TMS. The UV spectra were obtained on a Unicam Helious Gamma instrument for solutions in ethanol in the range 195–500 nm.

Quantum-chemical calculations. The electronic and steric structures of the compounds were calculated nonempirically in the framework of the density functional theory (DFT). The hybrid exchange correlation functional B3LYP [41], with Becke's exchange part [42] and Lee–Yang–Parr's correlation part [43] was applied. The molecular geometry was preliminary optimized over all natural variables without any symmetry constraints. Minima on the potential energy surface (PES) were found for each structure by calculating force constant matrix and normal mode frequencies. The calculations were performed using the PCGAMESS V.7.0 program [44]. For data treatment, visualization of the results, and presentation graphics the ChemCraft program was used [45].

(2-Aminophenyl)triphenylphosphonium chloride was prepared by the reaction of triphenylphosphine with anhydrous $NiCl_2$ by the procedure in [46].

[2-(1*E*)-(2-Hydroxyphenyl)methyleneaminophenyl]triphenylphosphonium chloride (IIIa). To a solution of 0.50 g of (2-aminophenyl)triphenylphosphonium chloride in 10 ml of ethanol, 0.13 ml of salicylaldehyde was added, and the mixture was heated under reflux for 4 h. The ethanol solution was then reduced by 2/3, and ethyl acetate was added until precipitation began. The yellow precipitate obtained after cooling was filtered off, washed with ethyl acetate, and recrystallized from ethanol–ethyl acetate, 1:4. Yield 67%, mp >300°C (EtOH). IR spectrum, cm^{-1}: 3350 (OH), 1604 (C=N), 1278 (Ph–O). ^1H NMR spectrum (DMSO-d_6), δ , ppm (*J*, Hz): 10.56 s (1H, OH), 8.80 s (1H, CH=N), 7.6–7.8 m [15H, $P(C_6H_5)_3$], 7.8 m [1H, H^3, obscured by $(C_6H_5)_3$ signals], 8.03 t.t (1H, H^4, $J_{H^4,H^{3(5)}}$ 7.9), 7.54 t.d (1H, H^5, $J_{H^5,H^{4(6)}}$ 7.5, $J_{H^5,P}$ 3.7), 7.20 d.d (1H, H^6, partially obscured by the $H^{4'}$ signal), 6.87 d.d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 8.3, $J_{H^{3'},H^{5'}}$ 0.8), 7.23 t.d (1H, $H^{4'}$, partially obscured by the H^6 signal), 6.47 t.d (1H, $H^{5'}$, $J_{H^{5'},H^{4'(6')}}$ 7.2, $J_{H^{5'},H^{3'}}$ 0.8), 6.71 d.d (1H, $H^{6'}$, $J_{H^{6'},H^{5'}}$ 7.9, $J_{H^{6'},H^{4'}}$ 1.7). Found, %: C 75.40; H 5.00; N 2.84; P 6.29. $C_{31}H_{25}ClNOP$. Calculated, %: C 75.38; H 5.10; N 2.84; P 6.27.

[2-(1*E*)-(2-Hydroxy-5-nitrophenyl)methyleneaminophenyl]triphenylphosphonium chloride (IIIb) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.214 g of 2-hydroxy-5-nitrobenzaldehyde. Yield 86%, mp >300°C. IR spectrum, cm^{-1}: 2450 (OH), 1605 (C=N), 1577, 1339 (NO_2), 1282 (Ph–O). ^1H NMR spectrum (DMSO-d_6), δ , ppm (*J*, Hz): 12.42 s (1H, OH), 8.89 s (1H, CH=N), 7.6–7.8 m [15H, $P(C_6H_5)_3$], 8.0 m (3H, H^3, H^4 и $H^{4'}$), 7.58 t.d (1H, H^5, partially obscured by $(C_6H_5)_3$ signals, $J_{H^5,H^{4(6)}}$ 7.5, $J_{H^5,P}$ 3.2), 7.24 d.d (1H, H^6, partially obscured by the $H^{3'}$ signal), 7.24 d (1H, $H^{3'}$, partially obscured by the H^6 signal, $J_{H^{3'},H^{4'}}$ 9.2), 7.51 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2.9). Found, %: C 68.78; H 4.47; N 4.93; P 5.79. $C_{31}H_{24}ClN_2O_3P$. Calculated, %: C 69.08; H 4.49; N 5.20; P 5.75.

[2-(1*E*)-(5-Bromo-2-hydroxyphenyl)methyleneaminophenyl]triphenylphosphonium chloride (IIIc) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.258 g of 5-bromo-2-hydroxybenzaldehyde. Yield 57%, mp >300°C. IR spectrum, cm^{-1}: 2750 (OH), 1608 (C=N), 1291 (Ph–O). ^1H NMR spectrum (DMSO-d_6), δ , ppm (*J*, Hz): 10.95 s (1H, OH), 8.83 s (1H, CH=N), 7.6 – 7.85 m [15H, $P(C_6H_5)_3$], 7.88 d.d [1H, H^3, partially obscured by $(C_6H_5)_3$ signals], 8.03 t (1H, H^4, $J_{H^4,H^{3(5)}}$ 7.9), 7.56 t.d (1H, H^5, $J_{H^5,H^{4(6)}}$ 7.7, $J_{H^5,P}$ 3.3), 7.20 d.d (1H, H^6, partially obscured by the $H^{4''}$ signal), 6.91 d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 8.8), 7.23 d.d (1H, $H^{4'}$, partially obscured by the H^6 signal), 6.67 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2.5). Found, %: C 65.28; H 4.20; N 2.17; P 5.29. $C_{31}H_{24}BrClNOP$. Calculated, %: C 65.00; H 4.22; N 2.45; P 5.41.

[2-(1*E*)-(2-Hydroxy-5-methoxyphenyl)methyleneaminophenyl]triphenylphosphonium chloride (IIId) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.195 g of 2-hydroxy-5-methoxybenzaldehyde. Yield 62%, mp >300°C. IR spectrum, cm^{-1}: 2750 (OH), 1598 (C=N), 1270 (Ph–O). ^1H NMR spectrum (DMSO-d_6), δ , ppm, (*J*, Hz): 10.10 s (1H, OH), 8.77 s (1H, CH=N), 7.6–7.8 m [15H, $P(C_6H_5)_3$], 7.8 m [1H, H^3, obscured by $(C_6H_5)_3$ signals], 8.03 t.t (1H, H^4, $J_{H^4,H^{3(5)}}$ 7,7), 7.53 t.d (1H, H^5, $J_{H^5,H^{4(6)}}$ 7,5, $J_{H^5,P}$ 3,3), 7.17 d.d (1H, H^6, $J_{H^6,P}$ 14,3, J_{H^6,H^5} 6,9), 6.81 d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 9,0), 6.75 d.d (1H, $H^{4'}$, $J_{H^{4'},H^{3'}}$ 9,0, $J_{H^{4',6'}}$ 3,0), 6.20 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2,9), 3.19 s (OCH_3). Found, %: C 73.50; H 4.98; N 2.57; P 5.89. $C_{32}H_{27}ClNO_2P$. Calculated, %: C 73.35; H 5.19; N 2.67; P 5.91.

[2-(1*E*)-(5-Bromo-2-hydroxy-3-methoxyphenyl)methyleneaminophenyl]triphenylphosphonium chloride (IIIe) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.297 g of 5-bromo-2-hydroxy-3-methoxybenzaldehyde. Yield 45%, mp >300°C. IR spectrum, cm^{-1}: 2730 (OH), 1602 (C=N), 1259 (Ph–O). ^1H NMR spectrum (DMSO-d_6), δ , ppm, (*J*, Hz): 10.06 s

(1H, OH), 8.90 s (1H, CH=N), 7.6–7.85 m [15H, P(C_6H_5)$_3$], 7.91 d.d (1H, H^3, $J_{H^3,P}$ 6.0, J_{H^3,H^4} 7.8), 8.03 t.t (1H, H^4, $J_{H^4,H^{3(5)}}$ 8.0), 7.56 t.d (1H, H^5, $J_{H^5,H^{4(6)}}$ 7.4, $J_{H^5,P}$ 3.0), 7.22 d.d.d (1H, H^6, $J_{H^6,P}$ 14.4, J_{H^6,H^5} 6.9), 6.31 d (1H, $H^{4'}$, $J_{H^{4',6'}}$ 2.2), 6.94 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2.3), 3.79 s (OCH_3). Found, %: C 63.77; H 4.27; N 2.27; P 5.17. $C_{32}H_{26}BrClNO_2P$. Calculated, %: C 63.75; H 4.35; N 2.32; P 5.14.

[2-(1*E*)-(3,5-Dibromophenyl-2-hydroxy)methyleneaminophenyl]triphenylphosphonium chloride (IIIf) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.359 g of 3,5-dibromo-2-hydroxybenzaldehyde in butan-1-ol. Yield 87%, mp >300°C. IR spectrum, cm^{-1}: 2700 (OH), 1609 (C=N), 1280 (Ph–O). ^{1}H NMR spectrum (DMSO-d_6), δ , ppm, (*J*, Hz): 11.21 s (1H, OH), 9.18 s (1H, CH=N), 7.6–7.8 m [15H, P(C_6H_5)$_3$], 8.1 m (2H, H^3 и H^4), 7.6 m [1H, H^5, obscured by (C_6H_5)$_3$ signals], 7.21 d.d (1H, H^6, $J_{H^6,P}$ 14.3, J_{H^6,H^5} 6.9), 6.76 d (1H, $H^{4'}$, $J_{H^{4',6'}}$ 2.4), 7.57 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2.4). Found, %: C 56.81; H 3.47; N 2.21; P 4.92. $C_{31}H_{23}Br_2ClNOP$. Calculated, %: C 57.13; H 3.56; N 2.15; P 4.75.

[2-(1*E*)-(3,5-Dichloro-2-hydroxyphenyl)methyleneaminophenyl]triphenylphosphonium chloride (IIIg) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.245 g of 3,5-dichloro-2-hydroxybenzaldehyde. Yield 65%, mp >300°C. IR spectrum, cm^{-1}: 2730 (OH), 1608 (C=N), 1280 (Ph–O). ^{1}H NMR spectrum (DMSO-d_6), δ , ppm (*J*, Hz): 11.12 s (1H, OH), 9.18 s (1H, CH=N), 7.65–7.85 m [15H, P(C_6H_5)$_3$], 8.1 m (2H, H^3 и H^4), 7.59 m [1H, H^5, partially obscured by (C_6H_5)$_3$ signals], 7.21 d.d (1H, H^6, $J_{H^6,P}$ 14.3, J_{H^6,H^5} 6.9), 6.54 d (1H, $H^{4'}$, $J_{H^{4',6'}}$ 2.6), 7.32 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2.6). Found, %: C 66.37; H 3.98; N 2.41; P 5.69. $C_{31}H_{23}Cl_3NOP$. Calculated, %: C 66.15; H 4.12; N 2.49; P 5.50.

[2-(1*E*)-(2-Hydroxy-1-naphthyl)methyleneaminophenyl]triphenylphosphonium chloride (IV) was prepared by the same procedure from 0.50 g of (2-aminophenyl)triphenylphosphonium chloride and 0.221 g of 2-hydroxy-1-naphthaldehyde. Yield 57%, mp >300°C. IR spectrum, cm^{-1}: 2670 (OH), 1592 (C=N), 1273 (Ph–O). ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, (*J*, Hz): 11.66 s (1H, OH), 9.07 s (1H, CH=N), 7.6–7.8 m [17H, P(C_6H_5)$_3$ + $2H_{naphth.}$], 8.23 d (1H, $H^{9'}$, $J_{H^{9'},H^{8'}}$ 8.5), 8.07 t.t (1H, H^4, $J_{H^4,H^{3(5)}}$ 7.7), 7.8 d.d (1H, H^3), 7.6 t.d [1H, H^5, partially obscured by (C_6H_5)$_3$ signals], 7.25 d.d (1H, H^6), 7.23 d (1H, H^6 *J* 7.2), 7.01 m (2H, $H_{naphth.}$). Found, %: C 76.93; H 4.81; N 2.67; P 5.87. $C_{35}H_{27}ClNOP$. Calculated, %: C 77.27; H 5.00; N 2.57; P 5.69.

2-(*E*)-(2-Chlorophenyliminomethyl)-4-nitrophenol (V). To a solution of 0.30 g of *ortho*-chloroaniline in 5 ml of ethanol, 0.393 g of 2-hydroxy-5-nitrobenzaldehyde in 5 ml of ethanol was added, and the mixture was heated under reflux. Two minutes later, a precipitate began to form. After 30 min under reflux, the precipitate was filtered off and washed with ethanol and recrystallized from ethanol–DMF. Yield 92%, mp 190°C. ^{1}H NMR spectrum (DMSO-d_6), δ, ppm, (*J*, Hz): 14.23 s (1H, OH), 9.20 s (1H, CH=N), 7.58 d.d (1H, H^3, J_{H^3,H^4} 8.0, J_{H^3,H^5} 1.5), 7.42 t.d (1H, H^4, $J_{H^4,H^{3(5)}}$ 7.6, J_{H^4,H^6} 1.4), 7.31 t.d (1H, H^5, $J_{H^5,H^{4(6)}}$ 7.6, J_{H^5,H^3} 1.5), 7.52 d.d (1H, H^6, J_{H^6,H^5} 7.9, J_{H^6,H^4} 1.3), 7.10 d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 9.2), 8.24 d.d (1H, $H^{4'}$, $J_{H^{4'},H^{3'}}$ 9.2, $J_{H^{4'},H^{6'}}$ 2.8), 8.69 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 2.8).

[2-(1*E*)-(2-Hydroxy-5-nitrophenyl)methyleneaminophenyl]triphenylphosphonium chloride zinc complex (VI). To a solution of 0.50 g of compound **IIIb** in 10 ml of absolute methanol, a solution of 0.102 g of $Zn(CH_3COO)_2 \cdot 2H_2O$ in 5 ml methanol was added. The mixture was refluxed for 4 h, and the precipitate that formed was filtered off and washed with methanol. Yield 47%, mp>300°C. IR spectrum, cm^{-1}: 1594 (C=N), 1572, 1298 (NO_2 + Ph–O). ^{1}H NMR spectrum (DMSO-d_6), δ , ppm, (*J*, Hz): 8.74 s (1H, CH=N), 7.6–7.85 m [15H, P(C_6H_5)$_3$], 7.8 m [1H, H^3, obscured by (C_6H_5)$_3$ signals], 7.96 t (1H, H^4, $J_{H^4,H^{3(5)}}$ 7.6), 7.49 t.d (1H, H^5, $J_{H^5,H^{4(6)}}$ 7.7, $J_{H^5,P}$ 3.3), 7.14 d.d (1H, H^6, $J_{H^6,P}$ 14.3, J_{H^6,H^5} 6.9), 6.10 d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 9.6), 7.62 d.d [1H, $H^{4'}$, partially obscured by (C_6H_5)$_3$ signals, $J_{H^{4'},H^{6'}}$ 3.2], 7.42 d (1H, $H^{6'}$, $J_{H^{6'},H^{4'}}$ 3.2). Found, %: Zn 5.54; P 5.53. $C_{62}H_{46}Cl_2N_4O_6P_2Zn$. Calculated, %: Zn 5.73; P 5.43.

[2-(1*E*)-(2-Hydroxy-5-nitrophenyl)methyleneaminophenyl]triphenylphosphonium chloride cadmium complex (VI) was prepared by the same procedure from 0.50 g of compound **IIIb** and 0.124 g of $Cd(CH_3COO)_2 \cdot 2H_2O$. Yield 28%, mp>300°C. IR spectrum, cm^{-1}: 1594 (C=N), 1575, 1311 (NO_2), 1299 (Ph–O). ^{1}H NMR spectrum (DMSO-d_6), δ , ppm, (*J*, Hz): 8.77 s (1H, CH=N), 7.6–7.85 m [15H, P(C_6H_5)$_3$], 7.8 m [1H, H^3, obscured by (C_6H_5)$_3$ signals], 7.90 t (1H, H^4, $J_{H^4,H^{3(5)}}$ 7.5), 7.4 m (1H, H^5, obscured by the $H^{6'}$ signal), 7.14 d.d (1H, H^6, $J_{H^6,P}$ 14.0, J_{H^6,H^5} 7.6), 6.00 d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 9.8), 7.56 d.d [1H, $H^{4'}$, $J_{H^{4'},H^{3'}}$ 9.7, $J_{H^{4'},H^{6'}}$ 3.2], 7.40 d (1H, $H^{6'}$, partially obscured by the H^5 signal, $J_{H^{6'},H^{4'}}$ 3.2). Found, %: Cd 9.72; P 5.41. $C_{62}H_{46}CdCl_2N_4O_6P_2$. Calculated, %: Cd 9.46; P 5.21.

[2-(1*E*)-(5-Bromo-2-hydroxyphenyl)methyleneaminophenyl]triphenylphosphonium chloride zinc complex (VI) was prepared by the same procedure from 0.50 g of compound **IIIc** and 0.096 g of Zn $(CH_3COO)_2 \cdot 2H_2O$. Yield 33%, mp > 300°C. IR spectrum, cm^{-1}: 1606 (C=N), 1300 (Ph–O). ^1H NMR spectrum (DMSO-d_6), δ , ppm, (*J*, Hz): 8.89 s (1H, CH=N), 7.6–7.85 m [15H, $P(C_6H_5)_3$], 7.8 m [1H, H^3, obscured by $(C_6H_5)_3$ signals], 7.90 br.t (1H, H^4), 7.42 br.t (1H, H^5), 7.12 d.d (1H, H^6, $J_{H^6,P}$ 14.5, J_{H^6,H^5} 8.0), 6.58 d (1H, $H^{3'}$, $J_{H^{3'},H^{4'}}$ 8.9), 6.96 br.d (1H, $H^{4'}$), 6.44 br.s (1H, $H^{6'}$). Found, %: Zn 5.37; P 5.09. $C_{62}H_{46}Br_2Cl_2N_2O_2P_2Zn$. Calculated, %: Zn 5.41; P 5.12.

ACKNOWLEDGMENTS

The work was financially supported by the internal grant of the Southern Federal University for 2007.

REFERENCES

1. Shoichiro, Y., *Coord. Chem. Rev*., 1999, vol. 190–192, p. 537.
2. Garnovskii, A.D., and Vasil'chenko, I.G., *Usp. Khim.,* 2005, vol. 74, no. 3, p. 211.
3. Garnovskii, A.D., *Koord. Khim*., 1993, vol. 19, no. 5, p. 394.
4. Kogan, V. A., Kharabaev, N.N., Osipov, O.A., and Kochin, S.G., *Zh. Strukt. Khim*., 1981, vol. 22, no. 1, p. 126.
5. Minbaev, B.U., *Shiffovy osnovaniya* (Schiff Bases), Alma-Ata: Nauka, 1989.
6. Kuznetsov, V.V., and Prostakov, I.S., *Khim. Geterotsikl. Soedin*., 1990, no. 1, p. 5.
7. Vigato, P.A., and Tamburini, S., *Coord. Chem. Rev.,* 2004, vol. 248, p. 1717.
8. Parr, J., and Slawin, A.M.Z., *Inorg. Chim. Acta*, 2000, vol. 303, no. 1, p. 116.
9. Shi, P.-Y., and Liu, Y.-H., *Organometallics*, 2002, vol. 21, no. 15, p. 3203.
10. Korupoju, S.R., Lai, R.-Y., Liu, Y.-H., Peng, S.-M., and Liu, S.-T., *Inorg. Chim. Acta*, 2005, vol. 358, no. 11, p. 3003.
11. Doherty, S., Knight, J.G., Scanlan, T.H., Elsegood, R.Y., and Clegg, W., *J. Organomet. Chem*., 2002, vol. 650, nos. 1–2, p. 231.
12. Dalili, S., Caiazzo, A., and Yudin, A.K., *J. Organomet. Chem*., 2004, vol. 689, no. 22, p. 3604.
13. Faller, J.W., Mason, G., and Parr, J., *J. Organomet. Chem*., 2002, vol. 650, nos. 1–2, p. 181.
14. Cameron, P.A., Gibson, V.C., Redshaw, C., Segal, J.A., White, J.P., and Williams, D.J., *J. Chem. Soc., Dalton Trans.*, 2002, vol. 2, no. 3, p. 415.
15. Bhattacharyya, P., Loza, M.L., Parr, J., and Slawin, A.M.Z., *J. Chem. Soc., Dalton Trans*., 1999, no. 17, p. 2917.
16. Dilworth, J.R., Howe, S.D., Hutson, A.J., Miller, J.R., Silver, J., Thompson, R.M., Harman, M., and Hursthouse, M.B., *J. Chem. Soc., Dalton Trans.*, 1994, no. 24, p. 53.
17. Bhattacharyya, P., Parr, J., and Slawin, A.M.Z., *J. Chem. Soc. Dalton Trans*., 1998, no. 21, p. 3609.
18. Bandoli, G., Dolmella, A., Crociani, L., Antonaroli, S., and Crociani, B., *Trans. Met. Chem.*, 2000, vol. 25, no. 1, p. 17.
19. Watkins, S.E., Craig, D.C., and Colbran, S.B., *Inorg. Chim. Acta*, 2000, vol. 307, nos. 1–2, p. 134.
20. Getty, A.D., and Goldberg, K.I., *Organometallics*, 2001, vol. 20, no. 12, p. 2545.
21. Ohtaka, A., Kato, N., and Kurosawa, H., *Organometallics*, 2002, vol. 21, no. 25, p. 5464.
22. Ankersmit, H.A., Loken, B.H., Kooijman, H., Spek, A.L., Vrieze, K., and Koten, G., *Inorg. Chim. Acta,* 1996, vol. 252, nos. 1–2, p. 141.
23. Sanchez, G., Serrano, J.L., Lopez, C.M., Garcia, J., Perez, J., and Lopez, G., *Inorg. Chim. Acta*, 2000, vol. 306, no. 2, p. 168.
24. Sanchez, G., Vives, J., Serrano, J.L., Perez, J., and Lopez, G., *Inorg. Chim. Acta*, 2002, vol. 328, no. 1, p. 74.
25. Barbaro, P., Bianchini, C., Laschi, F., Midollini, S., Moneti, S., Scapacci, G., and Zanello, P., *Inorg. Chem.,* 1994, vol. 33, no. 8, p. 1622.
26. Lane, H.P., Watkinson, M., Bricklebank, N., McAuliffe, C.A., and Pritchard, R.G., *Inorg. Chim. Acta*, 1995, vol. 232, nos. 1–2, p. 145.
27. Kbin, H.-F., Beck, R., Florke, U., and Haupt, H.-J., *Eur. J. Inorg. Chem.*, 2002, no, 12, p. 3305.
28. Del Zotto, A., Zangrando, E., Baratta, W., Felluga, A., Martinuzzi, P., and Rigo, P., *Eur. J. Inorg. Chem.*, 2005, no. 23, p. 4707.
29. Ainscough, E.W., Brodie, A.M., Burrell, A.K., and Kennedy, M.F., *J. Organomet. Chem*., 2000, vol. 609, nos. 1–2, p. 2.
30. Stephens, P.J., Devlin, F.J., Chabalowski, C.F., and Frisch, M.J., *J. Phys. Chem*., 1994, vol. 98, no. 45, p. 11623.
31. Sanchez, G., Serrano, J.L., Moral, M.A., Perez, J., Molins, E., and Lopez, G., *Polyhedron*, 1999, vol. 18, no. 23, p. 3057.
32. Chen, X., Femia, F.J., Babich, J.W., and Zubieta, J., *Inorg. Chim. Acta*, 2001, vol. 315, no. 2, p. 147.
33. Minkin, V.I., Olekhnovich, L.P., and Zhdanov, Yu.A., *Molecular Design of Tautomeric Compounds*, Boston: Kluwer, 1988.

34. Olekhnovich, L.P., and Zhdanov, Yu.A., *Acc. Chem. Res*., 1981, vol. 14, p. 210.
35. Minkin, V.I., *Pure Appl. Chem.*, 1989, vol. 61, p. 661.
36. Minkin, V.I., Olekhnovich, L.P., and Zhdanov, Yu.A., *Zh. Vses. Khim. O–va,* 1977, vol. 22, p. 274.
37. Metelitsa, A.V., Burlov, A.S., Bezuglyi, S.O., Borodkina, I.G., Bren', V.A., Garnovskii, A.D., and Minkin, V.I., *Koord. Khim*., 2006, vol. 32, no. 12, p. 894.
38. Katkova, M.A., Vitukhnovskii, A.G., and Bochkarev, M.N., *Usp. Khim.*, 2005, vol. 74, no. 12, p. 1193.
39. Veinot, J.G.C., and Marks, T.J., *Acc. Chem. Res*., 2005, vol. 38, no. 8, p. 632.
40. *Organic Light-Emmiting Devices*, Mueller, K., Schert, U. and Weinhein Eds., New York: Wiley–VCH, 2006, p. 426.
41. Stephens, P.J., Devlin, F.J., Chabalowski, C.F., and Frisch, M.J., *J. Phys. Chem.*, 1994, vol. 98, no. 45, p. 11 623.
42. Becke, A.D., *J. Chem. Phys.*, 1993, vol. 98, no. 7, p. 5648.
43. Lee, C., Yang, W., and Parr, R.G., *Phys. Rev. B*., 1988, vol. 37, no. 2, p. 785.
44. Granovsky, A.A., *web-reference http://classic.chem.msu.su/ gran/gamess/index.html.*
45. Zhurko, G.A., *Chemcraft, ver. 1.5 trial, build 266. http://www.chemcraftprog.com/description.html.*
46. Cooper, M.K., Downes, J.M., Duckworth, P.A., and Tiekins, E.R.T., *Aust. J. Chem*., 1992, vol. 45, no. 9, p. 595.