## Spectroscopic and Electrochemical Properties of Cyclopalladated Complexes Derived from 2,3-Diphenylpyrazine

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Received October 18, 2006

**Abstract**—A comparative study of complexes [Pd(dphpz)(N^N)]PF<sub>6</sub> [dphpz<sup>-</sup> is the deprotonated form of 2,3-diphenylpyrazine; (N^N) is ethylenediamine (En), 2,2'-bipyridine (bpy), *o*-phenanthroline (phen), dipyrido-[*a*,*c*]phenazine (dppz), 6,7-dicyanopyrido[*f*,*h*]quinoxaline (dicnq)] was made, using <sup>1</sup>H NMR, electronic absorption, and emission spectroscopy, and also cyclic voltammetry. Steric interaction of the dphpz<sup>-</sup> phenyl rings leads to significant proton shielding in the carbanionic moiety of the cyclometallated ligand. Introduction of heterocyclic dimines instead of ethylenediamine decreases the deshielding of the dphpz<sup>-</sup> protons adjacent to the coordination center. Irrespective of the nature of the N^N ligands, the cyclopalladated complexes are characterized by specific parameters of photo- and electrostimulated electron transfer processes involving the Pd(dphpz) orbitals, namely, by the long-wave absorption band with  $\lambda_{max}$  395±6 nm and  $\varepsilon$  (2.2±1.2)×10<sup>3</sup> 1 mol<sup>-1</sup> cm<sup>-1</sup>, the vibrationally structured low-temperature (77 K) luminescence resulting from the spin-forbidden optical transfer from the excited to the ground state of the complex (energy  $E^{00}$  19.27±0.07 kK, lifetime  $\tau$  160±30 µs), and the one-electron electroreduction wave with  $E_1 - (2.0\pm0.1)$ V. For the [Pd(dphpz)·(N^N)]<sup>+</sup> complexes containing diazine derivatives of phenanthroline (dppz, dicnq), the degradation of the photoexcitation energy from two electronically excited states can occur as isolated process with successive transfer of electrons to the  $\pi$  orbitals localized on the remote moieties: [Pd(dphpz)] and diazine fragments of the N^N ligands.

**DOI:** 10.1134/S1070363207080191

The development of photo- and electroactive molecularly organized metal complexes capable of directed transfer and accumulation of charge or energy on the reaction center due to the definite steric and structural organization of the individual components stimulates studies of coordination-unsaturated complexes with variable optical and electrochemical parameters as structural components of such systems [1, 2].

It was shown previously that the cyclopalladated ethylenediamine complexes based on deprotonated forms of diphenyl- and dibenzo-substituted 1,4-diazines have a long-lived electronically excited state responsible for their luminescence. They are also characterized by a quasireversible one-electron electroreduction process [3, 4]. Introduction of heterocyclic diimine ligands with the low-energy delocalized  $\pi^*$  orbitals instead of the aliphatic ethylenediamine expands the possibility of modification of the optical and electrochemical parameters of such complexes. This paper deals with a comparative study of the spectroscopic and electrochemical properties of the mixed-ligand complexes  $[Pd(dphpz)(N^N)]PF_6$   $[(dphpz)^-$  is the deprotonated form of 2,3-diphenyl-pyrazine; (N^N) is ethylenediamine (En), 2,2'-bi-pyridine (bpy), *o*-phenanthroline (phen), dipyrido-[a,c]phenazine (dppz), or 6,7-dicyanopyrido[f,h]-quinoxaline (dichq)] (see scheme).

The <sup>1</sup>H NMR spectra of the complexes confirm the mononuclear structure and the mode of the ligand coordination in the complexes [Pd(dphpz)(N^N)]. The coordination-induced chemical shifts of protons in ligands  $[\Delta \delta = \delta_c - \delta_l]$  reflecting the character of changes in their chemical shifs in the course of complex formation, resulting from the donor-acceptor ligand  $\rightarrow$  metal and anizotropic interactions, are listed in Table 1.

The mononuclear structure of the complexes is characterized by almost orthogonal arrangement of the noncoordinated phenyl ring of the dphpz<sup>-</sup> ligand



[Pd(dphpz)(dicnq)]<sup>+</sup>

relative to the plane of complex [5]. This leads to strong and practically constant shielding of the H<sup>6</sup> and  $H^5$  protons ( $\Delta\delta$  –0.9 and –0.7 ppm, respectively), resulting from the anisotropic effect of the ring current. The  $\Delta\delta$  value of the H<sup>3'</sup>, H<sup>6</sup>, and H<sup> $\alpha/\alpha'$ </sup> ligand protons nearest to palladium is determined mainly by the efficiency of the donor-acceptor ligand  $\rightarrow$  metal interaction. The presence of ethylenediamine, a typical  $\sigma$ donor, in the inner sphere is accompanied by shielding of the  $H^3$  and  $H^6$  dphpz<sup>-</sup> protons and deshielding of the  $H^{\alpha/\alpha}$  En proton. Difference in the *trans* effect of the carbanionic and pyrazine moieties of the cyclometallated ligand leads to the magnetic nonequivalence of the  $H^{\alpha}$  and  $H^{\alpha'}$  ethylenediamine protons. At the same time, weakening of the donor-acceptor  $(N^N) \rightarrow$ Pd interaction resulting from a decrease in the  $\sigma$ -donor properties on introduction of heterocyclic diimines instead of the aliphatic ethylenediamine leads to a decrease in the deshielding and to magnetic equivalence of the H<sup> $\alpha$ </sup> and H<sup> $\alpha$ </sup> dimine protons, as well as to a decrease in the deshielding of the  $H^5$  and  $H^3$ dphpz<sup>-</sup> protons.

A decrease in the basicity of diimines in the Bpy >

Table 1. Coordination-induced chemical shifts  $(\delta_c - \delta_l)$  of complexes  $[Pd(dphpz)(N^N)]^+$ ligand protons in (DMSO- $d_6$  solutions)

(N^N)	En	bpy	phen	dppz	dicnq
H <sup>5</sup>	0.00	-0.01	0.00	0.00	0.00
H <sub>o</sub>	-0.26	-0.13	-0.09	-0.04	-0.04
$H^{3}$	-0.3	0.4	0.4	0.3	0.4
$\mathrm{H}^{4'}$	-0.4	-0.5	-0.4	-0.5	-0.5
$H^{5}$	-0.6	-0.7	-0.7	-0.7	-0.7
$\mathrm{H}^{6}$	-0.8	-1.0	-0.9	-1.0	-0.9
$\mathrm{H}^{o,m,p}$	0.2	0.2	0.2	0.2	0.2
$H^{\alpha}/H^{\alpha}$	2.67/1.84	0.45	0.27	0.19	1.10
$\mathrm{H}^{\mathrm{eta}}/\mathrm{H}^{\mathrm{eta}}$	1.32/1.30	0.37	0.43	0.26	-0.48
$H^{\gamma}/H^{\gamma'}$	—	0.46	0.54	0.26	0.17
$\mathrm{H}^{\delta}/\mathrm{H}^{\delta'}$	_	0.20	0.38	_	0.15
$H^{\epsilon}\!/H^{\epsilon'}$	_	-	_	_	0.1

phen > dpq > dppz ~ dicnq series is accompanied by a regular decrease in the deshielding of the  $H^{\alpha}$ diimine protons and in the shielding of the H<sup>6</sup> protons from the pyrazine moiety of the dphpz anion.

Compound	Absorption, $\lambda_{max}$ , nm ( $\epsilon \times 10^{-3}$ , 1 mol <sup>-1</sup> cm <sup>-1</sup>	Reduction, $-E_{1/2}$ , V ( $\Delta E$ , mV) <sup>b</sup>		
	(π–π*)	$(\pi_{\text{Ph/d}} - \pi^*)$	$\pi^*_{(dphpz)}$	$\pi^*_{(N \wedge N)}$
Hdphpz bpy phen dppz	207 (25.8), 219 (15.8) sh, 280 (7.3), 318 (4.9) 235 (12.7), 243 (19.5), 283 (16.3) 226 (47.3), 267 (27.7) 268 (27.3), 363 (10.4), 378 (7.9) <sup>b</sup>	2.29 <sup>°</sup>  _	2.52 ° _ _	$\begin{array}{c} - \\ 2.55 & (60) \\ 2.51 & (60) \\ 1.59 & (60) \\ 2.49 & (60) \end{array}$
dicnq	265 (43.6), 307 (23.1), 364 (7.4) sh <sup>b</sup>	-	_	$\begin{array}{c} 2.19 \ (00) \\ 1.09 \ (70) \\ 2.10^{\circ} \\ 2.57^{\circ} \end{array}$
[Pd(dphpz)En] <sup>+</sup> [Pd(dphpz)bpy] <sup>+</sup> [Pd(dphpz)phen] <sup>+</sup>	207 (29.5), 232 (12.5) sh, 279 (7.6), 338 (3.6) 209 (28.9), 254 (7.5), 304 (5.9), 312 (6.1) 208 (28.9), 230 (12.9) sh, 264 (6.2) sh, 275 (7.2), 324 (2.7)	388 (2.1) 388 (0.9) 399 (4.1)	1.85 (70) 1.95 <sup>c</sup> 2.05 <sup>c</sup>	1.27 <sup>c</sup> 1.30 <sup>c</sup>
[Pd(dphpz)dppz] <sup>+</sup> [Pd(dphpz)dicnq] <sup>+</sup>	206 (27.7), 241 (10.6), 270 (16.7), 295 (7.9) sh, 359 (4.6), 363 (4.4), 377 (4.9) 206 (28.1), 266 (6.9), 273 (1.6)	400 (2.2) 399 (1.6)	2.00 (70) 2.05 <sup>°</sup>	1.61 (90) 1.16 (80) 1.59 <sup>c</sup>

**Table 2.** Parameters of the electronic absorption spectra and reduction voltammograms of the ligands and  $[Pd(dphpz)(N^{N})]^{+}$  complexes

<sup>a</sup> CH<sub>3</sub>OH. <sup>b</sup> DMF. <sup>c</sup> Potential of the irreversible reduction wave at a potential sweep rate of 50 mV s<sup>-1</sup>.

The electro- and photostimulated processes in the mixed-ligand complexes within the framework of the model of localized molecular orbitals [6] are classed as metal- or ligand-centered depending on the character of the participating orbitals. Provided that the Koopmans theorem is valid [7], the orbital nature of the redox and spectroscopic LUMO and HOMO of the complexes is observed. Contrary to the reversible character of the ligand-centered electroreduction processes for the complexes with the heterocyclic ligands, involving the electron transfer to the delocalized  $\pi^*$  orbitals, the metal-centered electroreduction of Pd(II) complexes is irreversible. This is due to the high rate of the subsequent chemical reactions of Pd(I) complexes, the primary products of the oneelectron electroreduction. The optical and electrochemical properties of the ligands and the cyclopalladated complexes derived from them are given in Table 2.

Comparison of electronic absorption spectra of the free ligands and the related complexes shows that, along with superposition of the overlapping intraligand spin-allowed absorption bands in the UV range ( $\lambda < 380$  nm), the [Pd(dphpz)(N^N)]<sup>+</sup> complexes exhibit a long-wave absorption band (Fig. 1). Its location and the extinction coefficient [ $\lambda_{max}$  395±6 nm,  $\epsilon$  (2.2±1.2) 10<sup>3</sup> 1 mol<sup>-1</sup> cm<sup>-1</sup>] only slightly depend on particular ligand. This fact allows absorption band to be assigned to the spin-allowed optical transition between the HOMO and LUMO of complexes localized mainly on the metal complex fragment Pd(dphpz). Quantum-chemical calculations of the platinum cyclometallated complexes derived from phenyl-substituted imines [8] show that the HOMO and LUMO of complexes have  $\pi$  symmetry. The LUMO is localized mainly on the  $\pi^*$  orbital of the imine moiety of cyclometallated ligands, whereas the HOMO has mixed  $\pi_{Ph/d}$  phenyl-metal character. Within the framework of the model of localized molecular orbitals, this band may be classed as the spin-allowed transfer of the  $\pi_{ph/d}$ - $\pi^*$  type.

Voltammograms of electroreduction of the free ligands are characterized by one-electron reduction waves caused by consecutive transfer of electron to the unoccupied  $\pi^*$  orbitals. The specific features of the electronic structure of the 1,4-diazine derivatives of *o*-phenanthroline (dppz, dicnq) are determined by the presence of two heterocycles, phenanthroline and diazine, and hence, of the corresponding predominantly localized  $\pi^*$ (phen) and  $\pi^*$ (diaz) orbitals. Weak electronic interaction between them leads to essentially isolated character of the corresponding electro- and photostimulated electron transfer processes [9, 10]. The reduction voltammograms of

*o*-phenanthroline as well as of its 1,4-diazine derivatives contain one-electron waves with the practically constant half-wave (phen, dppz) or peak current (dicnq) potential ( $E = -2.53 \pm 0.03$  V). They were assigned to the electron transfer to the  $\pi^*$ (phen) redox orbitals of the ligands. At the same time, the diazine derivatives of *o*-phenanthroline the exhibit additional anodically shifted reversible reduction waves (Table 2) caused by the electron transfer to the lowest  $\pi^*$ (diaz) redox orbitals of the ligands [9, 10].

In accordance with data of electronic absorption spectroscopy, the reduction voltammograms of all the mononuclear complexes are characterised by a oneelectron wave (Fig. 2) with virtually the same potential  $(E = -2.0\pm0.1 \text{ V})$ , which allows its assignment to the electron transfer to the  $\pi^*(\text{diaz})$  orbitals of the Pd(dphpz) fragment. The anodic shift of the wave potential of the cyclopalladated complexes as compared to the free Hdphpz ligand ( $\Delta E \ 0.3 \text{ V}$ ) agrees with the expected decrease in energy of the  $\pi^*(\text{diaz})$ orbital of the ligand resulting from the donor-acceptor ligand  $\rightarrow$  metal interaction.

The presence of heterocyclic chelating ligands (N^N) with their own unoccupied low-energy  $\pi^*$  orbitals in the inner sphere of the complexes [Pd(dphpz).  $(N^N)$ ]<sup>+</sup> leads to appearance of additional reversible one-electron reduction waves. Comparison of the voltammograms of reduction of the 1,4-diazine derivatives of o-phenanthroline (dppz, dicnq) and complexes [Pd(dphpz)(N^N)]<sup>+</sup> derived from them allows the additional electroreduction waves of complexes to be assigned to the electron transfer to the  $\pi^*(\text{diaz})$ orbitals of the (N^N) ligands. Thus, in accordance with the remoteness of the diazine moiety of the ligands from the coordination center, the complex formation does not noticeably affect the isolated character of the  $\pi^*$  orbitals localized on the diazine and phenanthroline moieties of the dipyridodiazine lidands. The reduction voltammograms of the complexes [Pd(dphpz)(bpy)]<sup>+</sup> and [Pd(dphpz)(phen)]<sup>+</sup> also contain an additional one-electron reduction wave  $(E_r)$ -1.27 and -1.30 V, respectively) which may be caused by the electron transfer to the  $\pi^*$  orbitals of the diimine ligand.

Photoexcitation of complexes in a frozen glassy matrix (77 K, DMF-toluene, 1:1) leads to intense luminescence (Fig. 3). The spectral and kinetic luminescence parameters of the complexes  $[Pd(dphpz) \cdot (N^N)]^+$  [(N^N) = En, bpy, phen] (Table 3) are essentially independent of the nature of the ligands. The luminescence spectra are characterized by the vibrational progression with the energy of the purely electronic transition ( $E^{00}$  19.27±0.07 kK) and the





**Fig. 1.** Absorption spectra: (1) Hdphp, (2)  $[Pd(dphp)En]^+$ , and (3)  $[Pd(dphpz)dppz]^+$ .



**Fig. 2.** Cyclic voltammograms: (a)  $[Pd(dphp)En]^+$  and (b)  $[Pd(phpz)(dppz)]^+$ .

vibrational frequency (v  $1.00\pm0.07$  kK) corresponding to the C=N vibration of the cyclometallated (dphpz) ligand [11]. The kinetics of the luminescence decay is exponential with the lifetime of the elec-

Compound	Pd(dphpz)	Pd (N^N)	
Compound	$\lambda_{\max}$ , nm	τ, μs	$\lambda_{max}$ , nm
[[Pd(dphpz)En] <sup>+</sup> [[Pd(dphpz)bpy] <sup>+</sup> [[Pd(dphpz)phen] <sup>+</sup> [[Pd(dphpz)dppz] <sup>+</sup> [Pd(dphpz)dicnq] <sup>+</sup>	517 sh, 623 sh, 542, 573 sh 521, 541 sh, 551, 570 sh 519, 547 516, 546 <sup>b</sup> 519, 549	190 140 140 _c _c	546, <sup>b</sup> 585 440, 475 sh

**Table 3.** Luminescence characteristics of complexes [Pd(dphpz))(N^N)]<sup>+a</sup>

<sup>a</sup> 77 K, DMF-toluene, 1:1. <sup>b</sup> Superposition of two bands. <sup>c</sup> Nonexponential kinetics of luminescence decay.

tronically excited states responsible for the luminescence ( $\tau 160 \pm 30 \mu s$ ) typical of cyclopalladated complexes. The whole set of the spectral and kinetic luminescence parameters of these complexes allows the luminescence to be considered as a spin-forbidden

(a)



spectra complexes: Fig. 3. Luminescence of (a) 1)  $[Pd(dphpz)En]^+$  and (2) [Pd(dphpz)phen]<sup>+</sup>; [Ph(dphpz)(dppz)]<sup>+</sup>, (1)dppz, (b) (2)and (*3*) [Pd(dphpz)(dppz)]<sup>+</sup>–dppz.

radiative process of degradation of the photoexcitation energy from the electronically excited state localized on the metal complex fragment Pd(dphpz).

The low-temperature luminescence of the complexes  $[Pd(dphpz)(N^N)]^+$  with the diazine derivatives of phenanthroline has the nonexponential decay kinetics. The vibronically structured luminescence spectra (Fig. 3) are determined by the superposition of the vibronic transitions from two electronically excited states. The parameters of these transitions are close to those of the radiative transitions from the state localized on the Pd(dbpz) fragment and the diazine part of free (N^N) ligands [10]. Although the energy transfer to the lowest electronically excited state is thermodynamically favorable, weak electronic interaction of the excited states localized on the spatially separated diazine part of the (N^N) ligand and Pd(dphpz) fragment leads to low efficiency of the energy transfer between them. This effect determines the isolated character of the energy degradation from two electronically excited states and leads to lowtemperature multiluminescence of complexes  $[Pd(dphpz)(N^N)]^+$  with the diazine derivatives of o-phenanthroline. Strong temperature quenching of the luminescence, characteristic of optical transitions localized on the Pd(dphpz) fragment as well as on the diazine part of (N^N) ligands, leads to its absence in liquid solutions of all the complexes at 293 K.

The whole set of the data obtained shows that the coordination-unsaturated cyclopalladated complexes derived from 2,3-diphenylpyrazine have the fixed and predictable parameters determining their optical and electrochemical properties in the ground and electronically excited states. Therefore, they can be successfully used as photo- and electroactive components of molecularly organized metal complex systems.

## **EXPERIMENTAL**

The <sup>1</sup>H NMR spectra were taken on a Bruker AC-200F spectrometer. The electronic absorption spectra were recorded on an SF-200 spectrophotometer. The luminescence studies were carried out on a KSVU-1 device with a pulse laser photoexcitation (LGI-21,  $\lambda$  337 nm) at 77 K in a glassy DMF-toluene (1:1) matrix and at 298 K in DMF solutions [12]. The parameters of cyclic voltammograms were determined on a modified SVA-1B installation at 298 K in a three-electrode cell with the separated compartments of the working (Pt), auxiliary (Pt), and reference (Ag) electrodes in the presence of 0.1 M [N(C<sub>4</sub>H<sub>9</sub>)<sub>4</sub>]BF<sub>4</sub> in DMF solutions [13]. The half-wave and current peak potential and are given vs. the ferricenium/ferrocene redox system.

Dipyrido-substituted 1,4-diazines were prepared by condensation of 1,10-phenantroline-5,6-dione with the corresponding diamines, *o*-phenylenediamine (dppz), and diaminomaleonitrile (dicnq) [14, 15]. The complexes [Pd(dphpz)(N^N)]PF<sub>6</sub> complexes were prepared according to [4] by reaction of the complexes [Pd(dphpz)( $\mu$ -Cl)]<sub>2</sub> prepared in advance with the (N^N) ligand.

[2-(3-Phenyl-2-ido)phenylpyrazine](ethylenediamine)palladium(II) hexafluorophosphate. Yield 85%. <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm (<sup>3</sup> $J_{HH}$ , Hz): Pd(dphpz): 8.71 s (H<sup>5</sup>), 8.45 d (H<sup>6</sup>, 3.0), 7.55 m (5H<sup>o,m,p</sup>), 7.08 d (H<sup>3</sup>, 6.9), 7.01 t (H<sup>4</sup>, 6.9), 6.74 t (H<sup>5</sup>, 6.9), 6.53 d (H<sup>6</sup>, 6.9); PdEn: 5.29 s (H<sup> $\alpha$ </sup>), 4.46 s (H<sup> $\alpha$ </sup>), 2.75 s (H<sup> $\beta$ </sup>), 2.73 (H<sup> $\beta$ </sup>).

[2-(3-Phenyl-2-ido)phenylpyrazine](2,2'-bipyridine)palladium(II) hexafluorophosphate . Yield 90%. <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm ( ${}^{3}J_{\rm HH}$ , Hz): Pd(dphpz): 8.72 s (H<sup>5</sup>), 8.58 s (H<sup>6</sup>), 7.72 m (H<sup>3'</sup>), 7.57 m (5H<sup>*o*,*m*,*p*), 6.87 m (H<sup>4'</sup>), 6.75 m (H<sup>5'</sup>), 6.40 m (H<sup>6'</sup>); Pd(bpy): 9.14 d (2H<sup> $\alpha/\alpha'$ </sup>, 5.1), 8.59 d (2H<sup> $\delta/\delta'$ </sup>, 8.0), 8.37 d.d (2H<sup> $\gamma/\gamma'$ </sup>, 7.3, 8.0), 7.82 d.d (2H<sup> $\beta/\beta'$ </sup>, 5.1, 7.3).</sup>

[2-(3-Phenyl-2-ido)phenylpyrazine](*o*-phenanthroline)palladium(II) hexafluorophosphate. Yield 76%. <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm (<sup>3</sup> $J_{HH}$ , Hz): Pd(dphpz): 8.71 s (H<sup>5</sup>), 8.60 s (H<sup>6</sup>), 7.74 m (H<sup>3</sup>), 7.56 m (5H<sup>*o*,*m*,*p*</sup>), 6.98 m (H<sup>4</sup>), 6.67 m (H<sup>5</sup>), 6.43 m (H<sup>6</sup>); Pd(phen): 9.35 d (2H<sup>α/α'</sup>, 5.1), 8.98 d (2H<sup>γ/γ'</sup>, 8.0), 8.29 s (2H<sup>δ/δ'</sup>), 8.14 d.d (2H<sup>β/β'</sup>, 5.1, 8.0).

[2-(3-Phenyl-2-ido)phenylpyrazine](dipyrido-[*a,c*]phenazine)palladium(II) hexafluorophosphate. Yield 89%. <sup>1</sup>H NMR spectrum (DMSO- $d_6$ ),  $\delta$ , ppm (<sup>3</sup> $J_{\rm HH}$ , Hz): Pd(dphpz): 8.71 s (H<sup>5</sup>), 8.67 s (H<sup>6</sup>), 7.72 m (H<sup>3</sup>), 7.56 m (5H<sup>o,m,p</sup>), 6.87 m (H<sup>5</sup>), 6.66 m (H<sup>5</sup>), 6.42 m (H<sup>6'</sup>); Pd(dppz): 9.61 d (2H<sup> $\gamma/\gamma'$ </sup>, 8.0), 9.24 d (2H<sup> $\alpha/\alpha'$ </sup>, 4.6), 8.42 d.d (2H<sup> $\delta/\delta'$ </sup>, 4.6), 8.10 m (2H<sup> $\epsilon/\epsilon'$ </sup>), 7.38 d.d (2H<sup> $\beta/\beta'$ </sup>, 5.1, 8.0).

[2-(3-Phenyl-2-ido)phenylpyrazine](6,7-dicyanodipyrido[*f*,*h*]quinoxaline)palladium(II) hexafluorophosphate. Yield 84%. <sup>1</sup>H NMR spectrum (DMSO-*d*<sub>6</sub>), δ, ppm (<sup>3</sup>*J*<sub>HH</sub>, Hz): Pd(dphpz): 8.71 s (H<sup>5</sup>), 8.67 s (H<sup>6</sup>), 7.66 m (H<sup>3</sup>), 7.57 m (5H<sup>o,m,p</sup>), 6.82 m (H<sup>4</sup>), 6.62 m (H<sup>5</sup>), 6.37 m (H<sup>6</sup>); Pd(dicnq): 9.69 d (2H<sup>γ/γ'</sup> 8.0), 9.54 d (H<sup>α/α'</sup>, 5.1), 8.33 d.d (2H<sup>β/β'</sup>, 5.3, 8.0).

## REFERENCES

- Balzani, V., Juris, A., Venturi, M., Compagna, S., and Serroni, S., *Chem. Rev.*, 1996, vol. 96, no. 5, p. 759.
- 2. Balzani, V. and Scandola, F., *Supramolecular Pho-tochemistry*, Chichester: Horwood, 1991.
- Kulikova, M.V., Balashev, K.P., Kvam, P.-I., and Songstad, J., *Zh. Obshch. Khim.*, 2000, vol. 70, no. 2, p. 177.
- Cherezova, E.A., Taraskina, T.V., Kulikova, M.V., and Balashev, K.P., *Zh. Obshch. Khim.*, 2003, vol. 73, no. 7, p. 1229.
- Kulikova, M.V., Kotlyar, V.S., Kvam, P.-I., and Songstad, J., *Zh. Obshch. Khim.*, 1997, vol. 67, no. 6, p. 1027.
- DeArmond, M. and Carlin, D., Coord. Chem. Rev., 1985, vol. 63, p. 325.
- 7. Koopmans, T., Physics, 1933, vol. 1, no. 1, p. 104.
- Brooks, J., Babayan, Y., Lamansky, S., Djurovich, P.I., Tsyba, I., Bau, R., and Thomson, M.E., *Inorg. Chem.*, 2002, vol. 41, no. 12, p. 3035.
- Fees, J., Kaim, W., Moscherosch, M., Matheis, W., Klima, J., Krejcik, M., and Zalis, S., *Inorg. Chem.*, 1993, vol. 32, no. 2, p. 166.
- Balashev, K.P., Cherezova, E.A., Ivanov, M.A., and Tkacheva, T.A., *Zh. Obshch. Khim.*, 2006, vol. 76, no. 7, p. 1198.
- 11. Steel, P.J. and Cugill, G.B., J. Organomet. Chem., 1990, vol. 395, no. 3, p. 359.
- 12. Vasil'ev, V.V., Balashev, K.P., and Shagisultanova, G.A., *Opt. Spektrosk.*, 1983, vol. 54, no. 4, p. 876.
- 13. Kotlyar, V.S. and Balashev, K.P., *Elektrokhimiya*, 1996, vol. 32, no. 11, p. 1358.
- 14. Che, C.-M., Yang, M., Wong, K.-H., Chan, H.-L., and Lam, W., *Chem. Eur. J.*, 1999, vol. 5, no. 11, p. 3350.
- 15. Arounaguiri, S. and Maiya, B.G., *Inorg. Chem.*, 1999, vol. 38, no. 5, p. 842.
- 16. Dickenson, J.E. and Summers, L.A., Aust. J. Chem., 1970, vol. 23, no. 6, p. 1023.

RUSSIAN JOURNAL OF GENERAL CHEMISTRY Vol. 77 No. 8 2007