Russian Journal of General Chemistry, Vol. 71, No. 7, 2001, pp. 1151–1152. Translated from Zhurnal Obshchei Khimii, Vol. 71, No. 7, 2001, pp. 1221–1222.

LETTERS TO THE EDITOR

Synthesis and Properties of Platinum(II) 2-(2-Pyridyl)thiophenide Complexes and Ruthenium(II) Bisbipyridyl Complexes with 1,2-Bis(diphenylphosphino)ethene

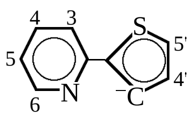
K. P. Balashev, M. V. Kulikova, O. R. Khanukaeva, A. D. Shashko, and A. Yu. Ershov

Gertsen Russian State Pedagogical University, St. Petersburg, Russia
St. Petersurg State University, St. Petersburg, Russia

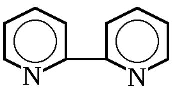
Received May 4, 2000

The presence of long-lived electronically exited states and the reversible nature of charge transfer in complexes of platinum metals with heterocyclic cyclometalating and polypyridine ligands make it possible to consider them as possible components for creating artificial molecularly-organized systems with directed charge and energy phototransfer [1]. In this respect special attention is attracted by coordinately unsaturated complexes which are capable of associating in molecular-organized systems via interactions between “ligand complexes” and “metal complexes” [2].

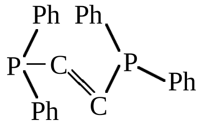
In this work we have prepared *trans*-N,P isomers of the complexes [Pt(tpy)Cl(dppe)] (**I**), [(Pt(tpy)Cl)2 · (μ-(dppe))] (**II**), and [Cl(tpy)Pt(μ-(dppe))Ru(bpy)$_2$Cl] · (BF$_4$) (**III**) (tpy is the deprotonated form of 2-(2-pyridyl) thiophene, dppe is *trans*-1,2-bis(diphenylphosphino)ethene, and bpy is 2,2'-bipyridyl). The complexes were characterized by ^{1}H and ^{31}P NMR and electronic spectroscopy, and also by cyclic voltammetry.



tpy



bpy



dppe

According to NMR data, the replacement of chloride ligands in the complexes [Pt(tpy)Cl$_2$]$^-$ and [Pt(tpy)(μ-Cl)]$_2$ by diphosphine ligands or by the [Ru(bpy)$_2$Cl(dppe)]$^+$ ligand complex are stereoselective and results in formation of *trans-N,P* isomers. This is proved by a strong screening of the H$^{4'}$ protons of the tpy ligand, which is characteristic of *trans-N,P*-[Pt(tpy)Cl(PZ$_3$)] complexes [3]. The coordination-induced shifts of the H$^{4'}$ protons under the anisotropic effect of phenyl substituents of the phosphine ligands in complexes **I**–**III** are –1.24, –1.24, and –1.33 ppm, respectively, and the coupling constants are as follows, Hz: J_{PtP} ~4150 and $^3J_{PtH}$ ~25 (H^6) and ~20 (H$^{4'}$). The nonequivalence of protons of the bipyridyl ligands in the NMR spectrum of compound **III** points to *cis-N,N* configuration of the {Ru(bpy)$_2$} fragment.

The optical and electrochemical properties of the complexes are mainly determined by the {Pt(tpy)} and {Ru(bpy)$_2$} groups, as the highest occupied molecular orbitals [d_{Pt} (**I, II**) and d_{Ru} (**III**)] are predominantly metal-centered and the lowest unoccupied orbitals [π^*_{tpy} (**I, II**) and π^*_{bpy} (**III**)] are predominantly ligand-centered. This results in the presence of low-energy d–π^* optical transitions in the electronic absorption and luminescence spectra of the complexes and in the metal-centered nature of their oxidation and in the ligand-centered nature of their electrolytic reduction. Comparison of the optical and electrochemical characteristics of complexes **I** and [Ru(bpy)$_2$Cl(dppe)]$^+$ [4] with those of binuclear systems **II** and **III** shows that the metal fragments {Pt(tpy)} and {Ru(bpy)$_2$} preserve their properties when linked by a diphosphine bridging ligand.

***trans-N,P*-Chloro[1,2-bis(diphenylphosphino)-ethene][2-(2-pyridyl)thiophen-3-ide]platinum(II) (I).** A deaerated solution of 0.06 mmol of [(C$_4$H$_9$)$_4$N] · [Pt(tpy)Cl$_2$] [5] and 0.08 mmol of 1,2-bis(diphenylphosphino)ethene in 12 ml of CH$_2$Cl$_2$ was stirred for 1 h at room temperature. After washing the reaction mixture with water and removal of the solvent in a vacuum, the residue was washed with ether and dissolved in deaerated CH$_2$Cl$_2$. The solution was treated with hexane until crystallization had began and left to

1070-3632/01/7107-1151 $25.00 © 2001 MAIK “Nauka/Interperiodica”

stand for 3 days at –20°C. The precipitate was washed with hexane and dried in a vacuum. Yield 72%. ^{1}H NMR spectrum (CD$_2$Cl$_2$), δ, ppm (J, Hz): 5.89 (H$^{4'}$, $^3J_{\mathrm{HPt}}$ 20), 6.89 d (H^3), 7.15 t (H^4), 7.3–7.8 m (42H), 9.51 d (H^6, $^3J_{\mathrm{HPt}}$ 26). ^{31}P NMR spectrum (CDCl$_3$), δ_P, ppm (J, Hz): 11.65 (J_{PPt} 4140). Electronic absorption spectrum (CH$_3$CN), λ_{max}, nm ($\varepsilon \times -10^{-3}$, l mol^{-1} cm^{-1}): 306 (14.1), 328 (10.7), 406 (4.1). Luminescent characteristics (CH$_3$CN), short-wave maximum, $\nu_{\mathrm{max}} \times 10^{-3}$, cm^{-1} (lifetime τ, μs; quantum yield F): 17.79 (15; 0.26). Electrochemical parameters (CH$_3$CN, reference Fc/Fc$^+$), V: $E_{1/2}$ –2.02; E_p (v 100 mV/s) 1.00.

***trans-N,P*-[μ-1,2-Bis(diphenylphosphino)ethene]-di(chloro[2-(2-pyridyl)thiophen-3-ide]platinum(II)) (II).** A deaerated suspension of 0.1 mmol of [Pt(tpy) · (μ-Cl)]$_2$ [5] and 0.1 mmol of 1,2-bis(diphenylphosphino)ethene in 20 ml of CH$_2$Cl$_2$ was stirred for 1 h at 40°C. The solution was filtered, and the product was precipitated with hexane. The precipitate was dissolved in CH$_2$Cl$_2$ and subjected to chomatography on neutral Al$_2$O$_3$ in a 1 : 1 CH$_2$Cl$_2$ · C$_2$H$_5$OH mixture. The solution containing the first chromatographic zone was evaporated to dryness in a vacuum, and the residue was dissolved in CHCl$_3$. The solution was filtered, the product was precipitated with hexane, washed with ether, and dried in a vacuum. Yield 65%. ^{1}H NMR spectrum (CD$_2$Cl$_2$), δ, ppm (J, Hz): 5.89 d (2H$^{4'}$, $^3J_{\mathrm{HPt}}$ 21), 6.94 d (2H^3), 7.22 t (2H^4), 7.3–7.9 m (44H), 9.48 d (2H^6, $^3J_{\mathrm{HPt}}$ 25). ^{31}P NMR spectrum (CDCl$_3$), δ_P, ppm (J, Hz): 11.68 (J_{PPt} 4170). Electronic absorption spectrum (CH$_3$CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 306 (20.9), 328 (15.9), 404 (6.9). Luminescent characteristics (CH$_3$CN), $\nu_{\mathrm{max}} \times 10^{-3}$, cm^{-1} ($\tau$, μs; F): 17.79 (14; 0.10). Electrochemical parameters (CH$_3$CN, reference Fc/Fc$^+$), V: $E_{1/2}$ –2.14, –2.34; E_p (v 100 mV/s) 1.05.

[μ-1,2-Bis(diphenylphosphino)ethene][*trans-N,P*-chloro(2-(2-pyridyl)thiophen-3-ide)platinum(II)]-[*cis-N,N*-chlorobis(2,2'-bipyridyl)ruthenium(II)] Tetrafluoroborate (III). A suspension of 0.1 mmol of [Pt(tpy)(μ-Cl)]$_2$ [5] and 0.05 mmol of [Ru(bpy)$_2$ · Cl(dppe)](BF$_4$) [4] in deaerated CH$_2$Cl$_2$ was stirred for 3 days at room temperature. The solvent was distilled off in a vacuum, the residue was dissolved in a 1 : 1 acetonitrile–toluene mixture, subjected to chromatography on Al$_2$O$_3$ in a 1 : 1 CH$_3$CN · H$_2$O mixture. The product was extracted with CHCl$_3$ from the solution containing the first chromatographic zone, the extract was evaporated in air, and the dry residue was washed with ether and dried in a vacuum. Yield 35%. ^{1}H NMR spectrum (CD$_2$Cl$_2$), δ, ppm (J, Hz): 5.80 d (H$^{4'}$, $^3J_{\mathrm{HPt}}$ 20), 7.0–7.8 m (26H), 7.9–8.2 m (8H), 8.42 d (2H), 8.46 d (2H), 9.1–9.3 M (2H), 9.48 d (H^6, $^3J_{\mathrm{HPt}}$ 25). ^{31}P NMR spectrum (CD$_3$CN), δ_P, ppm (J, Hz): 13.98 (J_{PPt} 4130), 43.02. Electronic absorption spectrum (CH$_3$CN), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 290 (37.5), 330 (15.4), 460 (9.5). Luminescent characteristics (CH$_3$CN), $\nu_{\mathrm{max}} \times 10^{-3}$, cm^{-1} ($\tau$, μs; F): 17.70 (7; 0.14). Electrochemical parameters (CH$_3$CN, reference Fc/Fc$^+$), V: $E_{1/2}$ –1.65, –1.92, 0.87.

The techniques of spectroscopic and electrochemical experiments have been described in [3].

ACKNOWLEDGMENTS

The work was financially supported by the Russian Foundation for Basic Research (project no. 97-03-32 272) and the *Obshchaya i tekhnicheskaya khimiya* Interinstitution Scientific and Technical Program (project no. P-70).

REFERENCES

1. Balzani, V., Juris, A., Venturi, M., Compagna, S., and Serroni, S., *Chem. Rev.*, 1996, vol. 96, no. 5, pp. 759–833.
2. *Supramolecular Chemistry,* Balzani, V. and De Cola, I., Eds., Dordrecht: Cluwer, 1992.
3. Kulikova, M.V., Balashev, K.P., Kvam, P.-I., and Songstad, I., *Zh. Obshcvh. Khim.*, 1999, vol. 69, no. 10, pp. 1585–1592.
4. Ershov, A.Yu., Veletskii, N.I., Dement'ev, I.A., Sokolova, N.I., and Nikol'skii, A.B., *Zh. Obshch. Khim.*, 1994, vol. 64, no. 8, pp. 1233–1241.
5. Kvam P.-I. and Songstad J., *Acta Chem. Scand.*, 1995, vol. 49, no. 5, pp. 313–324.