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LETTERS TO THE EDITOR

Carbonyl Complexes of Platinum (II) and Palladium(II) with Heterocyclic Cyclometalating Ligands

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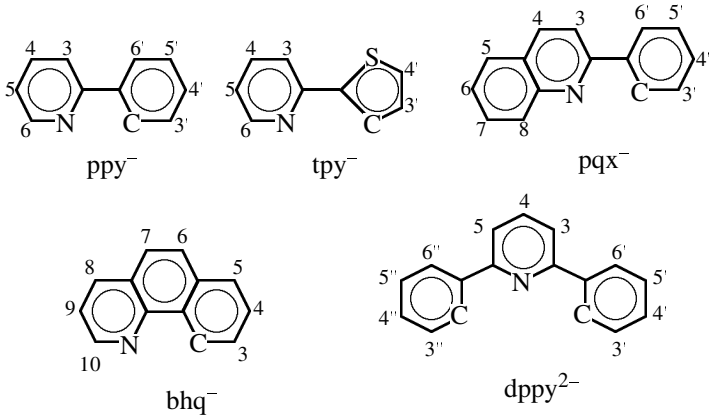
Mixed-ligand cyclometalated complexes of platinum metals have long-lived electronically excited states and can undergo reversible electron transfer and form polynuclear metal complex systems. Owing to such characteristic features, these complexes have found use as components of artificial molecularly organized systems with directed charge and energy phototransfer [1]. One of the most promising types of mixed-ligand cyclometalating complexes are those containing a photolabile carbonyl ligand [2].

In the present we work prepared and characterized by ^{1}H NMR, IR, and electronic spectroscopy the carbonyl mixed-ligand cyclometalated complexes [Pt(ppy)(CO)Cl] (**I**), [Pt(tpy)(CO)Cl] (**II**), [Pt(bhq)·(CO)Cl] (**III**), [Pt(pqx)(CO)Cl] (**IV**), [Pt(dppy)CO] (**V**), and [Pd(tpy)(CO)Cl] (**VI**) {ppy$^-$, tpy$^-$, pqx$^-$, and bhq$^-$ are deprotonated 2-phenylpyridine, 2-(2-thienyl)-pyridine, 2-phenylquinoxaline, and benzo[*h*]quinoline, respectively, and dppy^{2-} is a bisdeprotonated 2,6-diphenylpyridine}.



Compounds **I**–**III** were prepared in the following way: CO was passed over the course of 10 h through a saturated solution of 1 mmol of [N(Bu)$_4$][Pt(C^N)·Cl$_2$] [(C^N)$^-$ = ppy$^-$, tpy$^-$, or bhq$^-$] [3] in a mixed solvent (CH_2Cl_2–MeOH, 2 : 1), the reaction mixture was cooled to –20°C, and the precipitate that formed after 1 h was filtered off, washed with CH_2Cl_2 and diethyl ether, and dried in air.

***trans*-*N*,*C*-Cabonyl(chloro)[2-(2-pyridyl)phenyl-3-ido]platinum (I),** yield 85%. IR spectrum (KBr), ν(CO), cm^{-1}: 2100. ^{1}H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 9.46 d.d.d (H^6, $^3J_{HH}$ 5.9, $^4J_{HH}$ 1.6, $^3J_{HPt}$ 26), 8.01 t.d (H^4, $^3J_{HH}$ 7.6, 7.5, $^4J_{HH}$ 1.6), 7.84 d.d (H^3, $^3J_{HH}$ 8.1, $^4J_{HPt}$ 8), 7.68 d.d (H$^{6'}$, $^3J_{HH}$ 7.7, $^4J_{HH}$ 1.5), 7.52 d.d.d (H$^{3'}$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.6, $^5J_{HH}$ 0.6), 7.42 t.d (H^5, $^3J_{HH}$ 7.5, 7.1, $^4J_{HH}$ 1.3), 7.28 t.d.d (H$^{5'}$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.1, $^5J_{HPt}$ 7), 7.19 t.d.d (H$^{4'}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.3, $^4J_{HPt}$ 8). Electronic absorption spectrum (MeCN), λ_{max}, nm (ε × 10^{-3}, l mol^{-1} cm^{-1}): 274 (13.4), 314 (5.9), 326 (6.6), 366 (2.7).

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***trans*-*N,C*-Carbonyl(chloro)[2-(2-pyridyl)thienyl-3-ido]platinum (II),** yield 70%. IR spectrum (KBr), ν(CO), cm^{-1}: 2105. ^1H NMR spectrum [$(CD_3)_2CO$], δ, ppm (*J*, Hz): 9.21 d.d.d (H^6, $^3J_{HH}$ 5.8, $^4J_{HH}$ 1.3, $^3J_{HPt}$ 34), 8.16 t. d (H^4, $^3J_{HH}$ 7.9, $^4J_{HH}$ 1.8), 7.74 d ($H^{4'}$, $^3J_{HH}$ 5.3), 7.72 d.d (H^3, $^3J_{HH}$ 7.8, $^4J_{HH}$ 1.3), 7.49 d.d (H^5, $^3J_{HH}$ 5.8, 7.9), 7.14 d.d ($H^{3'}$, $^3J_{HH}$ 5.3, $^3J_{HPt}$ 28). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 298 (11.7), 331 (10.7), 406 (4.17), 505 sh (0.034), 555 sh (0.009).

***trans*-*N,C*-(Benzo[*h*]quinolyl-2-ido)(carbonyl)chloroplatinum (III),** yield 62%. IR spectrum (KBr), ν(CO), cm^{-1}: 2085. ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm (*J*, Hz): 9.68 d.d.d (H^{10}, $^3J_{HH}$ 5.5, $^4J_{HH}$ 1.6, $^3J_{HPt}$ 36), 8.73 d.d (H^8, $^3J_{HH}$ 8.1, $^4J_{HH}$ 1.4), 8.38 d.d (H^3, $^3J_{HH}$ 7.6, $^3J_{HPt}$ 43), 7.94 d (H^7, $^3J_{HH}$ 8.8), 7.89 d.d (H^9, $^3J_{HH}$ 8.1, 5.5), 7.83 d (H^6, $^3J_{HH}$ 8.8), 7.77 d.d (H^5, $^3J_{HH}$ 7.9, $^4J_{HH}$ 0.9), 7.53 d.d (H^4, $^3J_{HH}$ 7.9, 7.5). Electronic absorption spectrum (THF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 294 (17.6), 314 sh (9.4), 335 sh (3.6), 350 (3.9), 374 sh (2.6), 390 (2.6).

***trans*-*N,C*-Carbonyl(chloro)[2-(2-quinolyl)phenyl-3-ido]platinum (IV).** A solution of 1.33 mmol of 2-phenylquinoxaline in CH_2Cl_2, 10 ml, was added over the course of 4 h to 40 ml of a solution of 1.2 mmol of $[Bu_4N]_2[PtCl_4]$ in CH_2Cl_2–MeOH (2 : 1). The reaction mixture was heated with stirring for 1 h at 40°C and then evaporated to dryness. The residue was washed with 0.01 M HCl and water, dissolved in CH_2Cl_2, and the dimeric complex $[Pt(pqx)\cdot Cl]_2$ was precipitated with methanol. The precipitate was filtered off, mixed with 20 ml of CH_2Cl_2, and CO was passed through the resulting suspension. The precipitate completely dissolved within 30 min. Pentane vapor was passed through the solution for 3 days. An orange precipitate formed and was filtered off, washed with CH_2Cl_2 and diethyl ether, and dried in air; yield 36%. IR spectrum (KBr), ν(CO), cm^{-1}: 2097. ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 9.50 (H^8, $^3J_{HH}$), 8.42 (H^3, $^3J_{HH}$ 8.8), 7.94 (H^4, $^3J_{HH}$ 8.8, $^5J_{HPt}$ 7), 7.85 (H^5, $^3J_{HH}$ 8.3, $^4J_{HH}$ 1.5), 7.79 (H^7, $^3J_{HH}$ 8.8, 7.1, $^4J_{HH}$ 1.5), 7.75 ($H^{6'}$, $^3J_{HH}$ 8.0, $^4J_{HH}$ 1.3), 7.62 (H^6, $^3J_{HH}$ 7.6, 7.3, $^4J_{HH}$ 0.9), 7.54 ($H^{3'}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.3, $^3J_{HPt}$ 70), 7.31 ($H^{5'}$, $^3J_{HH}$ 7.5, $^4J_{HH}$ 1.3, $^5J_{HPt}$ 7), 7.20 ($H^{4'}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.3, $^4J_{HPt}$ 11).

Carbonyl[2,6-diphenylpyridyl-2,2'-ido]platinum (V). Carbon monoxide was passed through a saturate solution of $[Pt(dppy)(SO(CH_3)_2)]$ [4] in CH_2Cl_2 over the course of 30 min. The resulting red needle-like precipitate was filtered off, washed with cold CH_2Cl_2 and diethyl ether, and dried in air; yield 97%. IR spectrum, ν(CO), cm^{-1}: 2044 (KBr), 2062 (CH_2Cl_2). ^1H NMR spectrum (CD_2Cl_2), δ, ppm (*J*, Hz): 7.59 d (H^4, $^3J_{HH}$ 8.0), 7.56 ($H^{3',3''}$, $^3J_{HH}$ 7.4, $^4J_{HH}$ 1.4, $^3J_{HPt}$ 34), 7.41 ($H^{6',6''}$, $^3J_{HH}$ 7.8), 7.21 ($H^{3,5}$, $^3J_{HH}$ 7.8), 7.19 ($H^{4',4''}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.5), 7.10 ($H^{5',5''}$, $^3J_{HH}$ 7.3, $^4J_{HH}$ 1.5). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 285 sh (21.4), 335 (13.8), 350 (12.6), 420 (0.49), 445 (0.50), 470 sh (0.32), 515 (0.054).

***trans*-*N,C*-Carbonyl(chloro)[2-(2-pyridyl)thienyl-3-ido]palladium (VI).** Carbon monoxide was passed through a suspension of $[Pd(tpy)(\mu\text{-}Cl)]_2$ [5] in CH_2Cl_2 until the precipitate dissolved completely. The solution was treated with pentate to precipitate compound **VI**. The precipitate was filtered off, washed with CH_2Cl_2 and diethyl ether, and dried in air; yield 70%. IR spectrum (KBr), ν(CO), cm^{-1}: 2113. ^1H NMR spectrum [$(CD_3)_2SO$], δ, ppm: 9.00 (H^6, $^3J_{HH}$ 6.0), 7.84 (H^4, $^3J_{HH}$ 7.6, 6.6), 7.52 ($H^{4'}$, $^3J_{HH}$ 4.6), 7.40 (H^3, $^3J_{HH}$ 8.0), 7.29 ($H^{3'}$, $^3J_{HH}$ 5.2), 7.11 (H^5, $^3J_{HH}$ 6.6). Electronic absorption spectrum (DMF), λ_{max}, nm ($\varepsilon \times 10^{-3}$, l mol^{-1} cm^{-1}): 285 (19.3), 318 sh (9.0), 370 (5.0), 392 sh (4.2).

The NMR, IR, and electronic absorption spectra were obtained at 298 K on Bruker AC-200F, Perkin–Elmer FT-IR-1725X, and SF-121 instruments, respectively.

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