# Cyclometalated Platinum(II) Complexes with Nitrile and Isocyanide Ligands: Synthesis, Structure, and Photophysical Properties

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**Abstract**—A series of cyclometalated platinum(II) complexes with nitrile and isocyanide ligands (RCN and RNC; R = *t*-Bu, Bn, Ph) have been synthesized in 60–80% yields from the dimer [{Pt(ppy)Cl}$_2$] (Hppy is 2-phenylpyridine) and the corresponding nitriles and isocyanides. The structure of the synthesized complexes was determined by mass spectrometry, IR and NMR spectroscopy, and X-ray diffraction. The contributions of different intermolecular interactions to the crystal packing were estimated by Hirshfeld surface analysis. Photophysical properties of the synthesized complexes in solution and solid state were studied.

**Keywords:** platinum complexes, nitriles, isocyanides, luminescence

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In recent years, studies of C,N-cyclometalated platinum(II) complexes have become a rapidly developing field of coordination and organometallic chemistry due to interesting photophysical properties of this class of compounds [1–4]. Rational design of cyclometalating (C^N) and auxiliary ligands (L$^1$, L$^2$) in compounds like [Pt(C^N)(L$^1$,L$^2$)]$^Z$ allows fine tuning of photophysical properties, so that such complexes can be used as materials for emitting layer in light-emitting devices [5, 6], photocatalysts in organic synthesis and hydrogen generation processes [7], sensitized dyes in solar cells [8], and biosensors for diagnostics of diseases [9].

Nitriles and isocyanides are auxiliary ligands with a linear structure which ensures the absence of steric hindrances to various intermolecular noncovalent interactions [10] and hence increases structural rigidity of molecules in crystal, thus reducing nonradiative energy dissipation [4, 11–14]. Reported examples of cyclometalated platinum(II) complexes with nitrile or isocyanide ligands are highly efficient luminophores [1, 15–20] and photocatalysts [21–23]. However, only a few published studies on cyclometalated platinum(II) complexes with such ligands are available. Moreover, no simultaneous studies of C,N-cyclometalated platinum(II)

complexes with isostructural nitrile and isocyanide ligands have been performed.

In this work we synthesized two series of cyclometalated platinum(II) complexes with nitrile [Pt(ppy)Cl{NCR}] and isocyanide [Pt(ppy)Cl{CNR}] (R = *t*-Bu, Bn, Ph) ligands (Scheme 1) and examined their photophysical properties in solid phase and in solution.

Nitrile platinum(II) complexes [Pt(ppy)Cl{NCR}] [R = *t*-Bu (**2a**), Bn (**2b**), Ph (**2c**)] were prepared by stirring a suspension of the μ-chloro dimer [{Pt(ppy)Cl}$_2$] (**1**) in the corresponding nitrile (excess) at 40°C for 24 h (Scheme 1). Complexes **2a**–**2c** were isolated as analytically pure yellow finely crystalline powders in 60–70% yield. Crystalline complexes **2a**–**2c** are stable on exposure to air at room temperature; however, they are decomposing to initial dimer **1** and nitrile in CH$_2$Cl$_2$, CH(D)Cl$_3$, or MeOH solutions. According to the $^1$H NMR data, the complete decomposition was achieved in 6–24 h. As reported previously for the complex [Pt(ppy)Cl{NCMe}] [24], the formation of nitrile complexes **2a**–**2c** and their decomposition in solution are equilibrium processes. This was indirectly confirmed by the presence of the [Pt(ppy)Cl{NCR}]$^+$ ion peaks in the

**Scheme 1.**



**2a–2c**

**3a–3c**

R = *t*-Bu (**a**), CH$_2$Ph (**b**), Ph (**c**).
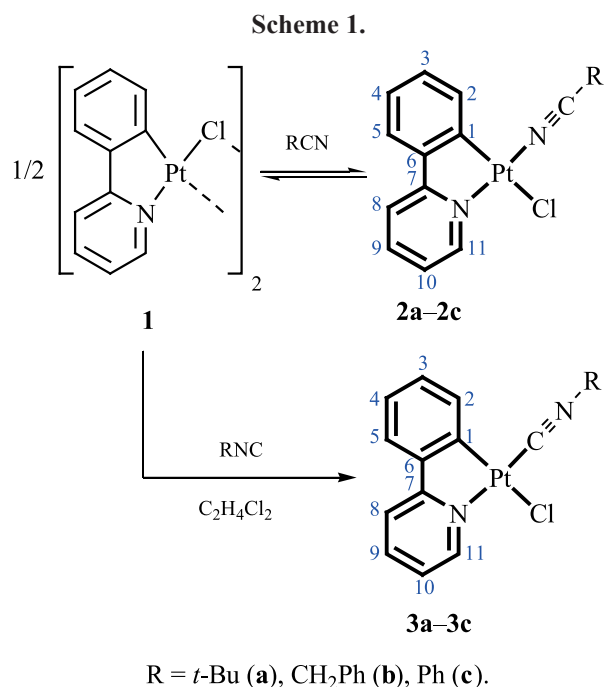
mass spectra of suspensions of stoichiometric amounts of dimer **1** and nitriles in methanol.

Isocyanide complexes [Pt(ppy)Cl{CNR}] [R = *t*-Bu (**3a**), Bn (**3b**), Ph (**3c**)] were prepared by reacting dimer **1** with 2 equiv of CNR in 1,2-dichloroethane. Compounds **3a**–**3c** were isolated in 72–80% yield as analytically pure yellow finely crystalline powders. Unlike nitrile complexes **2a**–**2c**, their isocyanide analogs **3a**–**3c** are stable both in the crystalline state and in solution (CH$_2$Cl$_2$, CHCl$_3$, MeOH).

Newly synthesized complexes **2b**, **2c**, and **3a**–**3c** were characterized by high-resolution mass spectrometry and IR and $^1$H, $^{13}$C–{$^1$H}, $^{195}$Pt–{$^1$H}, $^1$H–$^1$H COSY/$^1$H–$^1$H NOESY, and $^1$H–$^{13}$C HSQC/$^1$H–$^{13}$C HMBC NMR spectroscopy. In addition, the structures of **2c** and **3b** were determined by X-ray analysis. As shown by $^1$H NMR spectroscopy, compound **2a** in CDCl$_3$ solution is partially converted to dimer **1** and free nitrile ligand even in 15 min after dissolution; therefore, this complex in solution was studied only by mass spectrometry and $^1$H NMR. The spectral characteristics of **3c** fully agree with those reported previously [20].

In the mass spectra of solutions of **2a**–**2c** and **3a**–**3c** in methanol, the base peak was that of the [*M* – Cl]$^+$ ion with a characteristic isotope distribution. The IR spectra of isocyanide complexes **3a**–**3c** showed a strong C≡N stretching band in the region 2180–2200 cm$^{-1}$, which is

typical of isocyanide platinum(II) complexes [18, 25–28]. In the IR spectra of nitrile complexes **2a**–**2c**, the C≡N stretching band was located at 2218–2277 cm$^{-1}$.

The $^1$H, $^{13}$C{$^1$H}, and $^{195}$Pt–{$^1$H} NMR spectra of **2a**–**2c** and **3a**–**3c** displayed only one set of signals, indicating the presence of only one isomer in solution. The formation of a single geometric isomer of **2a**–**2c** and **3a**–**3c** with *trans*-(C$_{ppy}$,Cl) configuration can be rationalized by the thermodynamic *trans*-effect which makes *trans* orientation of the donor atoms C$_{ppy}$/Cl and N$_{ppy}$/C$_{CNR}$ (or N$_{ppy}$/N$_{NCR}$) preferred [26]. Signals of the ppy moiety in the $^1$H and $^{13}$C{$^1$H} NMR spectra were assigned using 2D NMR correlation techniques ($^1$H–$^1$H COSY, $^1$H–$^{13}$C HSQC, $^1$H–$^{13}$C HMBC), and our assignment was consistent with published data for other complexes containing a [Pt(ppy)] fragment [29–31]. In the $^1$H NMR spectra[1] of **2a**–**2c** and **3a**–**3c**, a characteristic signal was that located at δ 9.50–9.70 ppm, which was assigned to the H$^{11}$ proton of the phenylpyridine fragment; its downfield position is determined by the strong deshielding effect of the pyridine nitrogen atom [30–32], and its multiplicity originates from spin–spin coupling with the magnetically active $^{195}$Pt nucleus [30]. Likewise, the C$^2$–C$^6$ and C$^8$ atoms of isocyanide complexes **3a**–**3c** resonated as multiplets in the $^{13}$C NMR spectra. The platinum signal in the $^{195}$Pt NMR spectra appeared in the δ$_{Pt}$ range from –3945 to –3893 ppm, which is typical of cyclometalated platinum(II) complexes with isocyanide ligands [18, 25].

The structure of complexes **2c** and **3b** in the solid state was studied by X-ray diffraction (Fig. 1). The crystal structure of **3c** was reported by us previously [20], and the corresponding data are used here for comparison. The crystallographically independent part of unit cells of **2c** and **3b** is represented by one [Pt(ppy)Cl(L)] molecule (Fig. 1) against two molecules for complex **3c**. The selected bond lengths and bond angles in the complexes are given in Table 1 (the molecule of **3c** with shorter bonds was selected). In all structures, the nitrile/isocyanide ligand and phenylpyridine carbon atom coordinated to Pt(II) are oriented *cis*, which is consistent with the X-ray diffraction data for other isocyanide and nitrile complexes of platinum halides with cyclometalated phenylpyridine ligand [16, 18]. The Pt–C bond with the isocyanide ligand of complexes **3b** and **3c** is shorter by about 0.1 Å than the Pt–C bond with the phenylpyridine ligand. A similar pattern is observed for complex **2c** where the Pt–N bond with the nitrile ligand is shorter by ~0.05 Å

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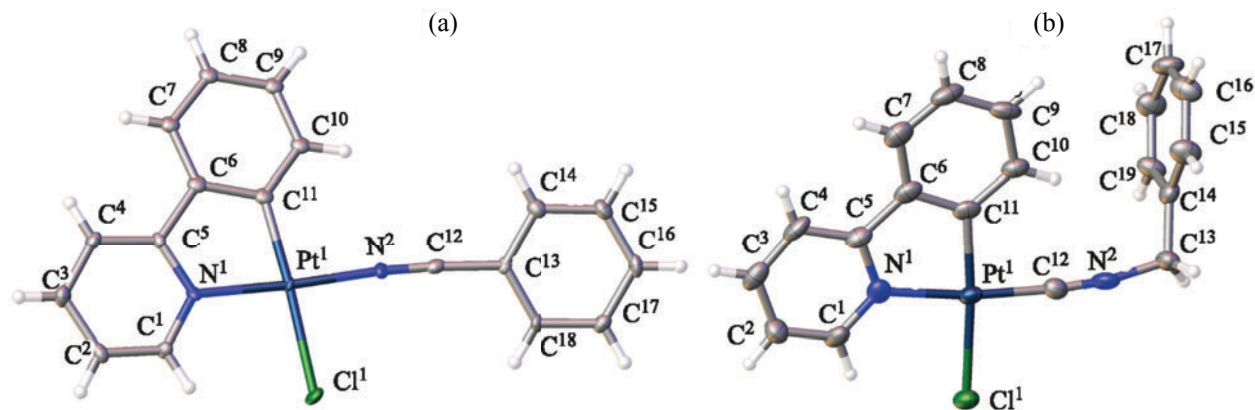[1] Hereinafter, for atom numbering, see Fig. 1.

**Fig. 1.** Structures of complexes (a) **2c** and (b) **3b** in crystal according to the X-ray diffraction data.

than the Pt–N bond with the phenylpyridine fragment. In all cases, the nitrile or isocyanide C≡N triple bond length is similar to the lengths of analogous bonds in other platinum(II) complexes [34, 35]. All other bond lengths were in good agreement with interatomic distances in other cyclometalated nitrile and isocyanide platinum(II) complexes [15, 19, 36].

In order to estimate contributions of different intermolecular contacts to the crystal packing, Hirshfeld surface analysis was performed for complexes **2c** and **3b**, and previously reported complex **3c** [20] (Table 2). It was found that intermolecular interactions involving hydrogen atoms contribute most to the crystal packing of all these complexes. However, it should be noted that these contacts predominate due to higher fraction of hydrogen atoms in all structures. Apart from hydrogen contacts, interactions between carbon atoms, on the one hand, and carbon and nitrogen atoms, on the other, that are responsible for π–π interactions, as well as contacts with

the platinum atoms (which could affect photophysical properties of the complex) were revealed. All complexes displayed Pt–H and Pt–C interactions, whereas no Pt–Pt contacts typical of bis-isocyanide and bis-nitrile platinum(II) complexes [26, 34–36, 39, 40] were found.

Photophysical properties of complexes **2a–2c** and **3a–3c** were studied in the solid state and $CH_2Cl_2$ solution (Table 3). In particular, their electronic absorption and emission spectra were recorded, and the lifetimes excited state of luminescence were measured. The electronic absorption spectra of the complexes in solution (Table 3, Fig. 2) showed several types of optical transitions. In keeping with published data [15, 16, 18, 36, 41–43], the strong high-energy absorption bands in the region λ 200–300 nm correspond to intraligand π–π* transitions. Less intense low-energy bands at λ 320–380 nm were assigned to spin-allowed charge transfer between the ligands ($^1$LLCT, ppy, π→π*) and from the metal to ligand [$^1$MLCT, dπ(Pt)→π*(ppy)] [5–7, 18, 29].

**Table 1.** Selected bond lengths and bond angles in complexes **2c**, **3b**, and **3c**

| Complex no. | R | $d$(Pt–C≡N), nm | $d$(Pt–N≡C), nm | $d$(Pt–$C_{ppy}$) | $d$(Pt–$N_{ppy}$) | $d$(C≡N) | Angle (CPtN) | Angle (CPtCl) |
|---|---|---|---|---|---|---|---|---|
| **2c** | Ph | – | 1.960(5) | 1.987(6) | 2.008(4) | 1.133(7) | 81.7(2) | 95.7(13) |
| **3b** | Bn | 1.894(8) | – | 2.009(9) | 2.050(7) | 1.148(11) | 81.0(3) | 94.7(2) |
| **3c** | Ph | 1.891(4) | – | 1.997(4) | 2.068(4) | 1.63(5) | 81.3(1) | 94.9(1) |

**Table 2.** Hirshfeld surface analysis of complexes **2c**, **3b**, and **3c**

| Complex no. | Contributions of interatomic contacts to the Hirshfeld surface, % |
|---|---|
| **2c** | H–H 38.7, C–H 28.1, Cl–H 13.8, C–C 5.6, N–H 4.5, C–N 2.9, Pt–C 2.5, Pt–H 2.2, C–Cl 1.3 |
| **3b** | H–H 38.7, C–H 30.3, Cl–H 13.8, C–C 5.6, N–H 5.0, Pt–H 4.0, C–N 0.6, Pt–C 0.4, Pt–N 0.3, C–Cl 0.2, N–Cl 0.2 |
| **3c** | H–H 44.3, C–H 21.4, Cl–H 13.5, C–C 8.2, C–N 4.7, N–H 2.2, Pt–C 3.9, Pt–H 0.6, Pt–N 0.6, C–Cl 0.3, N–Cl 0.3 |

**Table 3.** Photophysical characteristics of complexes **2a–2c** and **3a–3c** in solution and solid state

| Complex no. | $\lambda_{max}$,[a] nm ($\varepsilon \times 10^{-3}$, L mol$^{-1}$ cm$^{-1}$) | $\lambda_{em}$, nm ($\lambda_{excit}$, nm) | $\tau$,[b] μs |
|---|---|---|---|
| **2a** | 276 (22.5), 325 (10.0), 350 (7.5), 385 sh (3.5) | 480, 520, 560 sh (320)[a] | |
| | | 470, 520, 630 sh (350)[b] | 0.1 |
| **2b** | 270 (30.0), 326 (15.0), 380 (5.0) | 480, 520, 550 sh (325)[a] | |
| | | 490, 518, 575 sh (350)[b] | 0.9 |
| **2c** | 326 (26.0), 380 (5) | 480, 510, 550 (330)[a] | |
| | | 480, 517, 570[b] | 0.5 |
| **3a** | 268 (37.2), 308 (10.0), 326 (9.3), 359 (3.9) | 481, 512, 554 sh (350)[a] | |
| | | 592 sh (435)[b] | 0.9 |
| **3b** | 285 (21.5), 320 (9), 326 (8), 380 (3.7) | 482, 515, 549 sh (300)[a] | |
| | | 485, 516, 571 sh (360)[b] | 1.2 |
| **3c** | 248 (36.5), 278 (19.6), 298 (15.6), 312 (12.2), 325 (10.1), 372 (3.4) | 421, 446, 475, 506, 549 sh (320)[a] | |
| | | 480, 518, 548 sh (370)[b] | 1.0 |

[a] In methylene chloride ($c = 5 \times 10^{-4}$ M), 293 K.
[b] Solid state.

Both nitrile (**2a–2c**) and isocyanide complexes (**3a–3c**) in solution displayed a common vibrationally structured emission profile. Taking into account available literature data, including those for cyclometalated platinum(II) complexes with isocyanide ligands [7, 15, 38, 44], this means that orbitals of the CNR and NCR ligands in the complexes do not contribute to the radiative excited state and that the emission could originate from intraligand $^3$LC (ppy) transitions (with participation of the metal atom) with a small contribution of $^3$MLCT transitions. In accordance with the mixed $^3$LC/$^3$MLCT transitions, the emission maxima of all complexes are almost similar.

The solid-state emission spectra of the complexes are characterized by similar profiles with a small shift of the emission maximum to the long-wavelength region, which may be due to noncovalent interactions occurring in the solid state. The solid-state emission spectrum
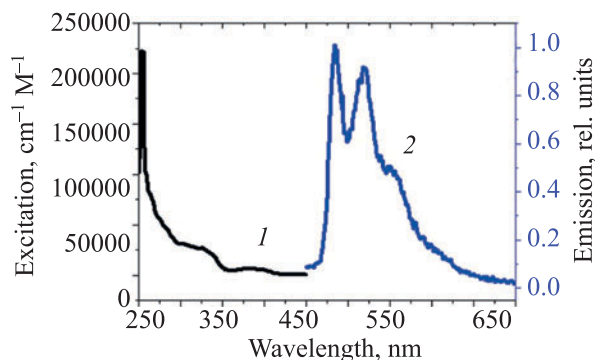


**Fig. 2.** (*1*) Luminescence excitation and (*2*) emission spectra of a solution of complex **2c** in methylene chloride ($c = 5 \times 10^{-4}$ M, 293 K).

of isocyanide complex **3a** is represented by a broad structureless band maximized at $\lambda$ 592 nm [25]. The large Stokes shift and lifetime values in the microsecond domain (0.1–0.9 μs) indicate the triplet character of luminescence of the complexes, i.e., phosphorescence.

Thus, our study of C,N-cyclometalated platinum(II) complexes with isomeric nitrile [Pt(ppy)Cl{NCR}] and isocyanide ligands [Pt(ppy)Cl{CNR}] (R = *t*-Bu, Bn, Ph) has shown that both types of the ligands exert similar effects on the photophysical properties. However, isocyanide complexes are stable in solution, whereas their nitrile analogs decompose to the initial μ-chloro dimer and nitrile ligand in a solution. Furthermore, the synthesized isocyanide complexes are potential precursors to N-heterocyclic and acyclic aminocarbene complexes (M-NHC and M-ADC, respectively) [45–47].

## EXPERIMENTAL

Commercial reagents and solvents (Aldrich) were used without further purification. 1,2-Dichloroethane and methylene chloride were distilled over $P_2O_5$, and diethyl ether was distilled over metallic sodium in the presence of benzophenone. Dinuclear complex **1** was synthesized from $K_2[PtCl_4]$ according to the procedure described in [29].

The high-resolution mass spectra (electrospray ionization) were recorded on a Bruker micrOTOF instrument using methanol as solvent; *m/z* values are given for most abundant isotopologues. The IR spectra were measured with a Shimadzu 8400S spectrometer in the range 4000–400 cm$^{-1}$ from samples prepared

as KBr pellets. The $^1H$, $^{13}C\{^1H\}$, and $^{195}Pt\{^1H\}$ NMR spectra were recorded at room temperature on a Bruker Avance II+ spectrometer operating at 400.13, 100.61, and 86 MHz, respectively, using $CDCl_3$ as solvent. The electronic absorption spectra were run on a Shimadzu UV-1800 spectrophotometer. The emission and luminescence excitation spectra were recorded, and the excited state lifetimes were measured, with a Horiba Jobin Yvon Fluorolog-3 spectrofluorometer.

**Complexes 2a–2c** (*general procedure*). A suspension of 100 mg (0.13 mmol) of [{Pt(ppy)Cl}₂] in 1 mL of the corresponding nitrile RCN (R = *t*-Bu, $PhCH_2$, Ph) was stirred at 50°C for 24 h until it became homogeneous. The solution was diluted with 4 mL of toluene–diethyl ether (1 : 3), and the precipitate was filtered off, washed with diethyl ether (2×4 mL), and dried in air. In the reaction with *t*-BuCN, light green luminescing solid precipitated and was filtered off, washed with diethyl ether (2×4 mL), and dried in air.

**[Pt(ppy)Cl(NCBu-*t*)] (2a).** Yield 73 mg (60%). IR spectrum, ν, cm⁻¹: 2231 (C≡N), 1485 (C=N). $^1H$ NMR spectrum, δ, ppm: 1.59 s (9H, *t*-Bu), 7.10–7.17 m (3H, 3-H, 4-H, 10-H), 7.26–7.28 m (1H, 5-H), 7.43–7.45 m (1H, 2-H), 7.61–7.63 m (1H, 8-H), 7.82 t.d (1H, 9-H, $^3J_{HH}$ = 8.0, 1.5 Hz), 9.66 d.d (1H, 11-H, $^3J_{HH}$ = 5.9, $^3J_{PtH}$ = 45.3 Hz). Mass spectrum: *m/z* 432.1088 $[M - Cl]^+$. Calculated for $C_{16}H_{17}N_2Pt$: 432.1034.

**[Pt(ppy)Cl(NCCH₂Ph)] (2b).** Yield 91 mg (70%). IR spectrum, ν, cm⁻¹: 2218 (C≡N), 1485 (C=N). $^1H$ NMR spectrum, δ, ppm: 4.22 s (2H, $CH_2$), 7.01 t.d (1H, 3-H, $^3J_{HH}$ = 8.0, 1.2 Hz), 7.11–7.17 m (2H, 4-H, 10-H), 7.33–7.47 m (7H, Ph, 2-H, 5-H), 7.60–7.62 m (1H, 8-H), 7.81 t.d (1H, 9-H, $^3J_{HH}$ = 8.0, 1.4 Hz), 9.63 d.d (1H, 11-H, $^3J_{HH}$ = 5.3, $^3J_{PtH}$ = 45.8 Hz). $^{13}C$ NMR spectrum, δ$_C$, ppm: 25.58 ($CH_2$), 118.30 (C⁸), 121.86 (C¹⁰), 123.62 (C⁴), 124.13 (C⁵), 127.57 (Ph), 127.93 (Ph), 128.05 (Ph), 128.28 (Ph), 128.81 (Ph), 129.14, 129.60, 130.38 (C³), 131.84 (C²), 132.15 (CN), 139.34 (C⁹), 139.66 (C¹), 143.85 (C⁶), 150.83 (C¹¹), 167.69 (C⁷). Mass spectrum: *m/z* 466.0865 $[M - Cl]^+$. Calculated for $C_{19}H_{15}N_2Pt$: 466.0877.

**[Pt(ppy)Cl(NCPh)] (2c).** Yield 86 mg (68%). IR spectrum, ν, cm⁻¹: 2278 (C≡N), 1486 (C=N). $^1H$ NMR spectrum, δ, ppm: 7.10–7.16 m (3H, 3-H, 4-H, 10-H), 7.35–7.49 m (1H, 5-H, 2-H), 7.58–7.66 m (3H, Ph, 8-H), 7.77 t (1H, Ph, $^3J_{HH}$ = 7.6 Hz), 7.82–7.86 m (1H, 9-H), 7.90 d (2H, Ph, $^3J_{HH}$ = 7.6 Hz), 9.70 d.d (1H, 11-H, $^3J_{HH}$ = 5.8, $^3J_{PtH}$ = 44.8 Hz). $^{13}C$ NMR spectrum, δ$_C$, ppm: 118.35

(C⁸), 121.91 (C¹⁰), 123.72 (C⁴), 124.27 (C⁵), 129.19, 129.58, 130.52 (C³), 131.79 (C²), 132.15 (CN), 133.14 (Ph), 134.65 (Ph), 139.42 (C⁹), 139.90 (C¹), 143.66 (C⁶), 150.90 (C¹¹), 167.70 (C⁷). Mass spectrum: *m/z* 452.0703 $[M - Cl]^+$. Calculated for $C_{18}H_{13}N_2Pt$: 452.0721.

**Complexes 3a and 3b** (*general procedure*). A suspension of 100 mg (0.13 mmol) of [{Pt(ppy)Cl}₂] in 20 mL of 1,2-dichloroethane was heated to 50°C, and a solution of the corresponding isocyanide CNR (R = *t*-Bu, $PhCH_2$; 0.26 mmol) in 10 mL of 1,2-dichloroethane was added with stirring over a period of 1 h. The mixture was stirred at 80°C for 2 h and evaporated to a minimum volume, and 10 mL of diethyl ether was added to the residue. The precipitate was filtered off and purified by recrystallization from methylene chloride–diethyl ether (2 : 1).

Complex **3c** was synthesized according to the procedure described in [20].

**[Pt(ppy)Cl(CNBu-*t*)] (3a).** Yield 88 mg (72%), decomposition point 165°C. IR spectrum: ν 2206 cm⁻¹ (N≡C). $^1H$ NMR spectrum, δ, ppm: 1.69 s (9H, *t*-Bu), 7.10 t.d (1H, 3-H, $^3J_{HH}$ = 7.4, 1.5 Hz), 7.16 t.d (1H, 4-H, $J_{HH}$ = 7.5, 1.4 Hz), 7.27 d.d.d (1H, 10-H, $J_{HH}$ = 7.3, 5.8, 1.4 Hz), 7.46 d.d (1H, 5-H, $J_{HH}$ = 7.4, 1.2 Hz), 7.53 d.d (1H, 2-H, $J_{HH}$ = 7.6, 1.4 Hz), 7.71–7.73 m (1H, 8-H), 7.87 t.d (1H, 9-H, $J_{HH}$ = 7.9, 1.6 Hz), 9.50–9.59 m (1H, 11-H). $^{13}C$ NMR spectrum, δ$_C$, ppm: 30.31 ($CH_3$), 58.50 [**C**($CH_3$)], 118.39 (C⁸, $J_{CPt}$ = 35.4 Hz), 122.13 (C¹⁰, $J_{CPt}$ = 26.8 Hz, Pt satellites), 124.08 s (Pt satellites), (C⁵, $J_{CPt}$ = 40.0 Hz, Pt satellites), 124.35 (C⁴), 131.20 (C³, $J_{CPt}$ = 72.9 Hz, Pt satellites), 136.81 (C², $J_{CPt}$ = 106.9 Hz, Pt satellites), 139.96 (C⁹), 140.98 (C¹), 144.11 (C⁶, $J_{CPt}$ = 34.3 Hz, Pt satellites Pt), 148.55 (C¹¹, $J_{CPt}$ = 22.2 Hz, Pt satellites), 166.34 (C⁷); no C≡N signal was detected. $^{195}Pt-\{^1H\}$ NMR spectrum: δ$_{Pt}$ –3945 ppm. Mass spectrum: *m/z* 432.1038 $[M - Cl]^+$. Calculated for $C_{16}H_{17}N_2Pt$: 432.1034.

**[Pt(ppy)Cl(CNCH₂Ph)] (3b).** Yield 104 mg (80%), decomposition point 160°C. IR spectrum: ν 2220 cm⁻¹ (C≡N). $^1H$ NMR spectrum, δ, ppm: 5.01 s (2H, $CH_2$), 6.95 t (1H, 3-H, $^3J_{HH}$ = 7.1 Hz), 7.09 t (1H, 4-H, $^3J_{HH}$ = 7.3 Hz), 7.22–7.29 m (2H, 10-H, Ph), 7.38–7.48 m (6H, 2-H, 5-H, Ph), 7.67–7.69 m (1H, 8-H), 7.84 t (1H, 9-H, $^3J_{HH}$ = 7.5 Hz), 9.50 d.d (1H, 11-H, $^3J_{HH}$ = 5.5, $^3J_{HPt}$ = 32.4 Hz). $^{13}C$ NMR spectrum, δ$_C$, ppm: 48.57 ($CH_2$), 118.50 (C⁸, $J_{CPt}$ = 36.6 Hz, Pt satellites), 122.14 (C¹⁰, $J_{CPt}$ = 25.5 Hz, Pt satellites), 124.09 (C⁵), 124.42 (C⁴, $J_{CPt}$ = 15.6 Hz, Pt satellites), 127.18 (Ph), 129.05 (Ph),

129.32 (Ph), 131.08 (Ph), 131.19 ($C^3$, $J_{CPt}$ = 72.6 Hz, Pt satellites), 136.13 ($C^2$, $J_{CPt}$ = 106.5 Hz, Pt satellites), 140.11 ($C^9$), 140.97 ($C^1$), 143.94 ($C^6$), 148.84 ($C^{11}$, $J_{CPt}$ = 23.0 Hz, Pt satellites), 166.31 ($C^7$); no C≡N signal was detected. $^{195}$Pt–{$^1$H} NMR spectrum: $\delta_{Pt}$ –3943 ppm. Mass spectrum: $m/z$ 466.0875 $[M - Cl]^+$. Calculated for $C_{19}H_{15}N_2ClPt$: 466.0867. Found, %: C 45.47; H 3.01; N 5.58. $C_{19}H_{15}N_2ClPt$. Calculated, %: C 44.03; H 3.12; N 5.33.

**X-Ray diffraction.** The X-ray diffraction data for complexes **2c** (CCDC entry no. 1408594) and **3b** (CCDC entry no. 1408607) were obtained with an Xcalibur Eos diffractometer at 100 K (monochromatized Mo$K_\alpha$ radiation, λ 0.71073 nm). The structures were solved by the direct method and were refined using SHELX [48] implemented in OLEX2 [49]. A correction for absorption was applied empirically by SCALE3 ABSPACK algorithm included in CrysAlisPro [50].

**Complex 2c.** $C_{18}H_{13}N_2ClPt$, $M$ 487.84; monoclinic crystal system, space group $P2_1/n$; unit cell parameters: $a$ = 8.1493(3), $b$ = 18.7526(7), $c$ = 10.4496(4) Å; $\beta$ = 105.839(4)°; $V$ = 1536.27(11) Å$^3$; $Z$ = 4; $d_{calc}$ = 2.109 g/cm$^3$; $\mu$ = 9.304 mm$^{-1}$. Total of 7103 reflection intensities were measured from a 0.1×0.1×0.1-mm single crystal, including 3308 reflections with $I > 2\sigma(I)$ ($R_{int}$ = 0.0386); $R_1(|F_o| \geq 4\sigma F)/R_1$ (all reflections) 0.0326/0.0395, $wR_2(|F_o| \geq 4\sigma F)/wR_2$ (all reflections) 0.0678/0.0719; $\rho_{min}/\rho_{max}$ 2.38/–2.68 $e$/Å$^3$.

**Complex 3b.** $C_{19}H_{15}N_2ClPt$, $M$ 501.87; monoclinic crystal system, space group $P2_1/n$; unit cell parameters: $a$ = 5.3540(3), $b$ = 14.3896(10), $c$ = 21.1589(10) Å; $\beta$ = 90.169(5)°; $V$ = 1630.11(16) Å$^3$; $Z$ = 4; $d_{calc}$ = 2.045 g/cm$^3$; $\mu$ = 8.771 mm$^{-1}$; Total of 7327 reflection intensities were measured from a 0.1×0.1×0.1-mm single crystal, including 3491 reflections with $I > 2\sigma(I)$ ($R_{int}$ = 0.0389); $R_1(|F_o| \geq 4\sigma F)/R_1$ (all reflections) 0.0456/0.0616, $wR_2(|F_o| \geq 4\sigma F)/wR_2$ (all reflections) 0.1084/0.1084; $\rho_{min}/\rho_{max}$ 3.26/–1.33 $e$/Å$^3$.

The Hirshfeld surface analysis of the crystal structures of complexes **2c**, **3b**, and **3c** was performed using CrystalExplorer 3.1 [51] in terms of the normalized contact length formalism ($d$norm) based on Bondi's van der Waals radii [38].

## CONFLICT OF INTEREST

No conflict of interest was declared by the authors.

## REFERENCES

1. Chen, Y., Lu, W., and Che, C.M., *Organometallics*, 2013, vol. 32, no. 1, p. 350. https://doi.org/10.1021/om300965b

2. Li, K., Tong, G.S.M., Wan, Q.Y., Cheng, G., Tong, W.Y., Ang, W.H., Kwong, W.L., and Che, C.M., *Chem. Sci.*, 2016, vol. 7, no. 3, p. 1653. https://doi.org/10.1039/c5sc03766b

3. Chi, Y. and Chou, P.T., *Chem. Soc. Rev.*, 2010, vol. 39, no. 2, p. 638. https://doi.org/10.1039/b916237b

4. Yam, V.W.W. and Law, A.S.Y., *Coord. Chem. Rev.*, 2020, vol. 414, article no. 213298. https://doi.org/10.1016/j.ccr.2020.213298

5. Yang, S.Y., Meng, F.Y., Wu, X.G., Yin, Z., Liu, X.Z., You, C.F., Wang, Y.F., Su, S.J., and Zhu, W.G., *J. Mater. Chem. C*, 2018, vol. 6, no. 21, p. 5769. https://doi.org/10.1039/c8tc01142g

6. Chan, A.K.W., Ng, M., Wong, Y.C., Chan, M.Y., Wong, W.T., and Yam, V.W.W., *J. Am. Chem. Soc.*, 2017, vol. 139, no. 31, p. 10750. https://doi.org/10.1021/jacs.7b04952

7. Schneider, J., Du, P.W., Jarosz, P., Lazarides, T., Wang, X.Y., Brennessel, W.W., and Eisenberg, R., *Inorg. Chem.*, 2009, vol. 48, no. 10, p. 4306. https://doi.org/10.1021/ic801947v

8. Pashaei, B., Shahroosvand, H., Graetzel, M., and Nazeeruddin, M.K., *Chem. Rev.*, 2016, vol. 116, no. 16, p. 9485. https://doi.org/10.1021/acs.chemrev.5b00621

9. Wong, K.M.C., Tang, W.S., Lu, X.X., Zhu, N.Y., and Yam, V.W.W., *Inorg. Chem.*, 2005, vol. 44, no. 5, p. 1492. https://doi.org/10.1021/ic049079p

10. Kinzhalov, M.A., Kashina, M.V., Mikherdov, A.S., Mozheeva, E.A., Novikov, A.S., Smirnov, A.S., Ivanov, D.M., Kryukova, M.A., Ivanov, A.Yu., Smirnov, S.N., Kukushkin, V.Yu., and Luzyanin, K.V., *Angew. Chem., Int. Ed.*, 2018, vol. 57, no. 39, p. 12785. https://doi.org/10.1002/anie.201807642

11. Solomatina, A.I., Aleksandrova, I.O., Karttunen, A.J., Tunik, S.P., and Koshevoy, I.O., *Dalton Trans.*, 2017,

vol. 46, no. 12, p. 3895.
https://doi.org/10.1039/c7dt00349h

12. Wang, W.Z., Zhang, Y., and Jin, W.J., *Coord. Chem. Rev.*, 2020, vol. 404, article no. 213107.
https://doi.org/10.1016/j.ccr.2019.213107

13. Koshevoy, I.O., Krause, M., and Klein, A., *Coord. Chem. Rev.*, 2020, vol. 405, article no. 213094.
https://doi.org/10.1016/j.ccr.2019.213094

14. Eremina, A.A., Kinzhalov, M.A., Katlenok, E.A., Smirnov, A.S., Andrusenko, E.V., Pidko, E.A., Suslonov, V.V., and Luzyanin, K.V., *Inorg. Chem.*, 2020, vol. 59, no. 4, p. 2209.
https://doi.org/10.1021/acs.inorgchem.9b02833

15. Diez, A., Fornies, J., Fuertes, S., Lalinde, E., Larraz, C., Lopez, J.A., Martin, A., Moreno, M.T., and Sicilia, V., *Organometallics*, 2009, vol. 28, no. 6, p. 1705.
https://doi.org/10.1021/om800845c

16. Fornies, J., Sicilia, V., Borja, P., Casas, J.M., Diez, A., Lalinde, E., Larraz, C., Martin, A., and Moreno, M.T., *Chem. Asian J.*, 2012, vol. 7, no. 12, p. 2813.
https://doi.org/10.1002/asia.201200585

17. Shahsavari, H.R., Aghakhanpour, R.B., Hossein-Abadi, M., Haghighi, M.G., Notash, B., and Fereidoonnezhad, M., *New J. Chem.*, 2017, vol. 41, no. 24, p. 15347.
https://doi.org/10.1039/c7nj03110f

18. Martinez-Junquera, M., Lara, R., Lalinde, E., and Moreno, M.T., *J. Mater. Chem. C*, 2020, vol. 8, no. 21, p. 7221.
https://doi.org/10.1039/d0tc01163k

19. Sivchik, V.V., Grachova, E.V., Melnikov, A.S., Smirnov, S.N., Ivanov, A.Y., Hirva, P., Tunik, S.P., and Koshevoy, I.O., *Inorg. Chem.*, 2016, vol. 55, no. 7, p. 3351.
https://doi.org/10.1021/acs.inorgchem.5b02713

20. Katkova, S.A., Kinzhalov, M.A., Novikov, A.S., and Luzyanin, K.V., *New J. Chem.*, 2021, vol. 45, no. 6, p. 2948.
https://doi.org/10.1039/D0NJ05457G

21. Anderson, C., Crespo, M., Morris, J., and Tanski, J.M., *J. Organomet. Chem.*, 2006, vol. 691, no. 26, p. 5635.
https://doi.org/10.1016/j.jorganchem.2006.09.012

22. Wang, H., Bisoyi, H.K., Wang, L., Urbas, A.M., Bunning, T.J., and Li, Q., *Angew. Chem., Int. Ed.*, 2018, vol. 57, no. 6, p. 1627.
https://doi.org/10.1002/anie.201712781

23. Boterashvili, M., Lahav, M., Shankar, S., Facchetti, A., and van der Boom, M.E., *J. Am. Chem. Soc.*, 2014, vol. 136, no. 34, p. 11926.
https://doi.org/10.1021/ja5066587

24. Zaitceva, O., Beneteau, V., Ryabukhin, D.S., Eliseev, I.I., Kinzhalov, M.A., Louis, B., Vasilyev, A.V., and Pale, P., *Tetrahedron*, 2020, vol. 76, no. 14, article no. 131029.
https://doi.org/10.1016/j.tet.2020.131029

25. Katkova, S.A., Leshchev, A.A., Mikherdov, A.S., and Kinzhalov, M.A., *Russ. J. Gen. Chem.*, 2020, vol. 90, no. 4, p. 648.
https://doi.org/10.1134/S1070363220040143

26. Kinzhalov, M.A., Kashina, M.V., Mikherdov, A.S., Katkova, S.A., and Suslonov, V.V., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 6, p. 1180.
https://doi.org/10.1134/S107036321806021x

27. Kinzhalov, M.A., Zolotarev, A.A., and Boyarskiy, V.P., *J. Struct. Chem.*, 2016, vol. 57, no. 4, p. 822.
https://doi.org/10.1134/S0022476616040302

28. Kinzhalov, M.A., Timofeeva, S.A., Luzyanin, K.V., Boyarskiy, V.P., Yakimanskiy, A.A., Haukka, M., and Kukushkin, V.Y., *Organometallics*, 2016, vol. 35, no. 2, p. 218.
https://doi.org/10.1021/acs.organomet.5b00936

29. Kinzhalov, M.A., Katkova, S.A., Doronina, E.P., Novikov, A.S., Eliseev, I.I., Ilichev, V.A., Kukinov, A.A., Starova, G.L., and Bokach, N.A., *Z. Kristallogr. Cryst. Mater.*, 2018, vol. 233, p. 795.
https://doi.org/10.1515/zkri-2018-2075

30. Pawlak, T., Niedzielska, D., Vícha, J., Marek, R., and Pazderski, L., *J. Organomet. Chem.*, 2014, vol. 759, p. 58.
https://doi.org/10.1016/j.jorganchem.2014.02.016

31. Niedzielska, D., Pawlak, T., Wojtczak, A., Pazderski, L., and Szlyk, E., *Polyhedron*, 2015, vol. 92, p. 41.
https://doi.org/10.1016/j.poly.2015.02.028

32. Pazderski, L., Pawlak, T., Sitkowski, J., Kozerski, L., and Szlyk, E., *Magn. Reson. Chem.*, 2009, vol. 47, no. 11, p. 932.
https://doi.org/10.1002/mrc.2491

33. Kashina, M.V., Kinzhalov, M.A., Smirnov, A.S., Ivanov, D.M., Novikov, A.S., and Kukushkin, V.Yu., *Chem. Asian J.*, 2019, vol. 14, no. 21, p. 3915.
https://doi.org/10.1002/asia.201901127

34. Mikherdov, A.S., Tiuftiakov, N.Yu., Polukeev, V.A., and Boyarskii, V.P., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 4, p. 713.
https://doi.org/10.1134/S1070363218040151

35. Dobrynin, M.V. , Sokolova, E.V., Kinzhalov, M.A., Smirnov, A.S., Starova, G.L., Kukushkin, V.Y., and Islamova, R.M., *ACS Appl. Polym. Mater.*, 2021, vol. 3, no. 2, p. 857.
https://doi.org/10.1021/acsapm.0c01190

36. Diez, A., Fornies, J., Larraz, C., Lalinde, E., Lopez, J.A., Martin, A., Moreno, M.T., and Sicilia, V., *Inorg. Chem.*, 2010, vol. 49, no. 7, p. 3239.
https://doi.org/10.1021/ic902094c

37. McKinnon, J.J., Jayatilaka, D., and Spackman, M.A., *Chem. Commun.*, 2007, no. 37, p. 3814.
https://doi.org/10.1039/b704980c

38. Bondi, A., *J. Phys. Chem.*, 1964, vol. 68, p. 441.
https://doi.org/10.1021/j100881a503

39. Ivanov, D.M., Kirina, Y.V., Novikov, A.S., Starova, G.L., and Kukushkin, V.Y., *J. Mol. Struct.*, 2016, vol. 1104, p. 19.
https://doi.org/10.1016/j.molstruc.2015.09.027

40. Mikherdov, A.S., Orekhova, Yu.A., and Boyarskii, V.P., *Russ. J. Gen. Chem.*, 2018, vol. 88, no. 10, p. 2119.
https://doi.org/10.1134/S1070363218100158

41. Jamshidi, M., Babaghasabha, M., Shahsavari, H.R., and Nabavizadeh, S.M., *Dalton Trans.*, 2017, vol. 46, no. 45, p. 15919.
https://doi.org/10.1039/c7dt03599c

42. Forniés, J., Fuertes, S., Larraz, C., Martín, A., Sicilia, V., and Tsipis, A.C., *Organometallics*, 2012, vol. 31, no. 7, p. 2729.
https://doi.org/10.1021/om201036z

43. Solomatina, A.I., Chelushkin, P.S., Abakumova, T.O., Zhemkov, V.A., Kim, M., Bezprozvanny, I., Gurzhiy, V.V., Melnikov, A.S., Anufrikov, Y.A., Koshevoy, I.O., Su, S.H., Chou, P.T., and Tunik, S.P., *Inorg. Chem.*, 2019, vol. 58, no. 1, p. 204.
https://doi.org/10.1021/acs.inorgchem.8b02204

44. Kui, S.C.F., Hung, F.-F., Lai, S.-L., Yuen, M.-Y., Kwok, C.-C., Low, K.-H., Chui, S.S.-Y., and Che, C.-M., *Chem. Eur. J.*, 2012, vol. 18, no. 1, p. 96.
https://doi.org/10.1002/chem.201101880

45. Mikherdov, A.S., Kinzhalov, M.A., Novikov, A.S., Boyarskiy, V.P., Boyarskaya, I.A., Dar'in, D.V., Starova, G.L., and Kukushkin, V.Y., *J. Am. Chem. Soc.*, 2016, vol. 138, no. 42, p. 14129.
https://doi.org/10.1021/jacs.6b09133

46. Kinzhalov, M.A. and Boyarskii, V.P., *Russ. J. Gen. Chem.*, 2015, vol. 85, no. 10, p. 2313.
https://doi.org/10.1134/s1070363215100175

47. Kinzhalov, M.A. and Luzyanin, K.V., *Coord. Chem. Rev.*, 2019, vol. 399, article no. 213014.
https://doi.org/10.1016/j.ccr.2019.213014

48. Sheldrick, G.M., *Acta Crystallogr., Sect. A*, 2008, vol. 64, no. 1, p. 112.
https://doi.org/10.1107/S0108767307043930

49. Dolomanov, O., Bourhis, L., Gildea, R., Howard, J., and Puschmann, H., *J. Appl. Crystallogr.*, 2009, vol. 42, p. 339.
https://doi.org/10.1107/S0021889808042726

50. CrysAlisPro A.T., Version 1.171.36.20 (release 27-06-2012).

51. Wolff, S.K., Grimwood, D.J., McKinnon, J.J., Turner, M.J., Jayatilaka, D., and Spackman, M.A., *Crystal Explorer, Version 3.1*, University of Western Australia, 2012.