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Mononuclear cycloplatinated complexes derived from 2-tolylpyridine with N-donor ligands: Reactivity and structural characterization

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ABSTRACT

The cycloplatinated dichloro-bridged complex $[(2\text{-Tolpy})Pt(\mu\text{-}Cl)]_2$ (**1**), obtained by treatment of 2-tolylpyridine with K_2PtCl_4, reacts with different N-donor ligands in a 1:2 molar ratio in chloroform to give the corresponding mononuclear complexes [(2-Tolpy)Pt(L)Cl] [L = pyridine (**2**), 2-trifluoromethylpyridine (**3**), 3-trifluoromethylpyridine (**4**), 4-trifluoromethylpyridine (**5**), 2,6-dibromopyridine (**6**), 2-tolylpyridine (**7**) and morpholine (**8**)]. Compounds **2–5** and **8** exist as a single isomer in solution which show a *trans*-C,Cl geometry. In the case of compounds **6** and **7** a mixture of two isomers (*trans*-C,Cl and *trans*-C,L) was obtained and its relative ratio depends on the temperature. The crystal and molecular structures of compounds **5** and **7** were determined by X-ray crystallography.

1. Introduction

The tendency of transition metal salts to give cyclometallated complexes with heteroaromatic ligands is well documented. Most of these complexes are halogen-bridged dimers. However, mononuclear complexes with the general formula [M(C^N)LX] (M = Pd, Pt; C^N = orthometallated ligand; L = neutral monodentate ligand; X = halide ligand) have also been reported [1]. Pt(II) derivatives have been the most widely studied in recent years, one of the reasons is the interesting range of properties that platinum complexes exhibit, such as the efficient emission from triplet excited states which is extremely useful in order to incorporate these systems into organic light emitting devices (OLEDs) [2,3]. Another reason is that square-planar Pt(II) compounds may coordinate different substrates through covalent interactions and undergo inner-sphere interactions and atom transfer reactions.

It has been reported that heteroleptic complexes with a cyclometallated ligand and a non-cyclometallated ancillary chelate offer a number of advantages over the corresponding homoleptic complexes [4]. Moreover, the synthesis of heteroleptic complexes requires milder reaction conditions and the yields are generally higher than for homoleptic complexes [5]. The appropriate choice of ligands is also a means to achieve interesting properties such as solubility and stability. Furthermore, a number of sensors for biomolecules [6], gases and organic vapours have been obtained using these materials [7].

The photophysical properties of the corresponding complexes depend to a large extent on the withdrawing or donating character of the ligand [8]. This is due to the influence of the ligand on the relative electron density at the metal centre, which modifies the quantity of metal-to-ligand charge transfer (MLCT) character in the lowest energy transition state and, as a result, may alter the relative energy and lifetime of the excited state [5,9]. These aspects can therefore be used to tune the complexes in order to achieve the desired characteristics [8,10], and phosphorescent N,C,N-coordinated Pt(II) complexes [11] have proven to be excellent emitters for OLEDs [12]. An efficient method to enhance the luminescence quantum yields by preventing non-radioactive decay is the use of ligands with a very strong ligand-field, e.g. with a metallated aromatic carbon bonded to the platinum centre [13]; thus, wide ranges of emission wavelengths, decay times and quantum yields have been reported [14]. Furthermore, cycloplatinated complexes have become the focus of scientific interest because of their potential antitumoral activity [15].

In this paper we present the synthesis and characterization of several platinum complexes derived from 2-tolylpyridine and different monodentate N-donor ligands. The influence of the steric requirements on the structure is also described and some compounds show dynamic behaviour in solution that involves two different isomers. The molecular structures of some of the complexes are also reported.

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2. Results and discussion

2.1. Mononuclear cycloplatinated complexes

For the convenience of the reader the compounds and reactions are shown in Scheme 1. The compounds described in this paper were characterized by elemental analysis (C, H, N), mass spectrometry, and IR and ^{1}H, ^{13}C–{1H}, ^{19}F and ^{195}Pt NMR spectroscopy (data in Section 3).

The dichloro-bridged dinuclear complex $[(2\text{-Tolpy})Pt(\mu\text{-Cl})]_2$ (**1**) was obtained by heating 2-tolylpyridine with potassium tetrachloroplatinate(II) at 65 °C for 8 h in water/ethanol (see data in Section 3). Related cycloplatinated compounds derived from different heterocyclic systems including phenylpyridine have been obtained using K_2PtCl_4 but with ethylene glycol or a mixture of 2-ethoxyethanol/water as solvent [16].

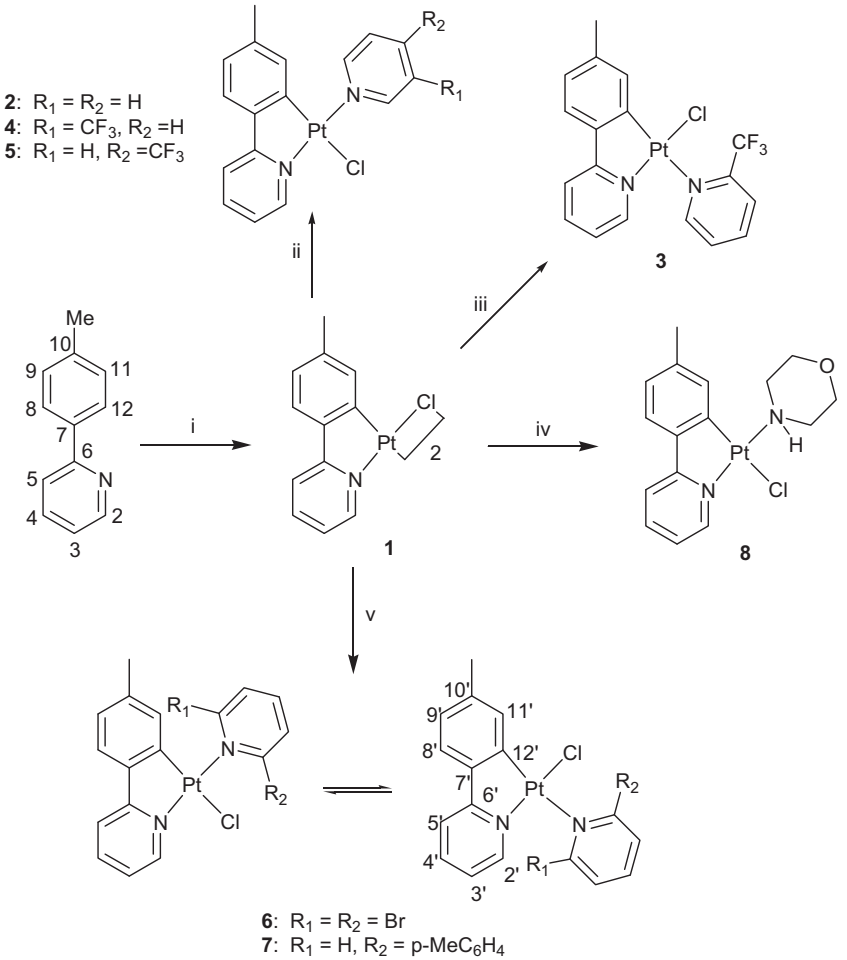
Treatment of the cycloplatinated dichloro-bridged dinuclear complex $[(2\text{-Tolpy})Pt(\mu\text{-Cl})]_2$ (**1**) with N-donor ligands in a 1:2 molar ratio in chloroform gave the corresponding mononuclear complexes [(2-Tolpy)Pt(L)Cl] [L = pyridine (**2**), 2-trifluoromethylpyridine (**3**), 3-trifluoromethylpyridine (**4**), 4-trifluoromethylpyridine (**5**), 2,6-dibromopyridine (**6**), 2-tolylpyridine (**7**) and morpholine (**8**)].

The microanalytical data were consistent with the empirical formula (see Section 3). The MS-FAB spectra showed the characteristic clusters of isotopic peaks due to the presence of the numerous platinum isotopes, and they were assigned to $[M]^+$, $[(2\text{-Tolpy})Pt(L)]^+$ and $[(2\text{-Tolpy})Pt]^+$ ions [17].

The IR spectra of the compounds showed a characteristic band at 1605–1609 cm^{-1} assigned to $\nu_{C=N}$, similar to that found in platinum complexes containing heterocyclic cyclometallated ligands [18,19]; for compounds **2**–**7** an additional band was observed at 1587–1591 cm^{-1} assigned to the C=N group of the coordinated pyridine ligands [20], which was shifted as a consequence of the Pt–N bond formation [21,22]. The IR spectrum of complex **8** showed a band at 3185 cm^{-1} assigned to the N–H stretching vibration of the morpholine ligand (*cf.* ν_{N-H} 3500–3310 cm^{-1} for secondary amines) consistent with $N_{morpholine}$–Pt bond formation.

The signals in the ^{1}H NMR spectra were assigned on the basis of the chemical shifts observed for similar complexes [24–26]. The resonances attributed to the protons adjacent to the five-membered metallacylce (H_2 and H_{11}) showed the satellites due to the coupling with 195Pt [^{3}J(Pt–H) = 19–24 Hz].

The H_{11} resonance for complexes **2**, **4**, **5** and **8** was high-field shifted (6.08–6.14 ppm, **2**, **4** and **5**; 6.97 ppm, **8**). The greater shift observed for **2**, **4** and **5** was attributed to the shielding effect of the aromatic ring of the pyridine ring situated *cis* to the metallated C_{12} carbon [25,27,28]. The spectra of complexes **2**, **4**, **5** and **8** showed the H_2 signal at 9.51–9.67 ppm low-field shifted due to the proximity of the pyridine nitrogen atom. The ^{1}H NOESY spectra showed close contacts between the hydrogen atoms of the pyridine coligand and the H11 hydrogen atom of the cycloplatinated ligand (e.g. in the spectrum for **4** a weak correlation between $H2_{4\text{-CF3py}}$ and H11 could be distinguished). These data confirm the isolation of the compound with a pyridine coligand *trans* to nitrogen



Scheme 1. (i) K_2PtCl_4, $EtOH/H_2O$, 65 °C, 8 h; (ii) L, $CHCl_3$, r.t., 2 h; (iii) 2-CF_3Py, $CHCl_3$, reflux, 24 h; (iv) $HN(CH_2CH_2)_2O$, CHCl3, r.t., 2 h; (v) 2,6-Br_2Py, $CHCl_3$, reflux, 24 h (**6**); 2-TolPy, CH_2Cl_2, r.t., 2 h (**7**).

disposition, in agreement with the *trans-choice* model [29] according to which in square planar Pd(II) complexes the ligand with the hardest donor atom choose as ancillary ligand in *trans* position the ligand with the softer one.

The ^{13}C NMR resonances, including the Pt satellites, were in accordance with the proposed structures (see Section 3) with the C_2 and C_{12} carbons showing the most noticeable low field shifts. In the case of complex **5** the expected quadruplet for the $-CF_3$ group [J(CF) = 3.53 Hz] was observed [23]. The ^{19}F NMR spectra of compounds **4** and **5** showed a singlet resonance which was assigned to the CF_3 groups (−62.99, **4** and −65.41, **5**, ppm). The chemical shifts in the ^{195}Pt NMR spectra of the complexes appeared between −3266 and −3200 ppm.

However, the ^1H NMR spectrum of compound **3** showed the H_2 and H_{11} resonances, at 8.88 [^3J(PtH$_2$) = 22.71 Hz] and 7.66 ppm, respectively; we suggest these data are in accordance with the pyridine ligand in a *cis* to nitrogen disposition. The ^1H NOESY spectrum showed a weak correlation between $H6_{2\text{-}CF3py}$ and H2, which is in agreement with the proposed structure. The ^{19}F NMR spectrum showed a singlet at −100.29 for the CF_3 group; the ^{195}Pt NMR spectrum showed a signal at −3540 ppm. The ^1H NMR spectra for complexes **2**–**5** and **8** recorded at high temperature showed no substantial changes.

For **6** and **7** the ^1H and ^{13}C NMR spectra showed two sets of signals attributable to the presence of two isomers in solution (see Section 3). For the convenience of the reader, the protons of one isomer are denoted as H_x and H_{xpy} (for the protons corresponding to the cyclometallated moiety and to the pyridine ligand, respectively) whereas for the other isomer they are denoted as $H_{x'}$ and $H_{x'py}$, (also, respectively). The most noticeable difference between the two sets of signals was for the $H_2/H_{2'}$ and $H_{11}/H_{11'}$ resonances. The signals corresponding to H_2 and H_{11} protons in one of the sets appeared at similar chemical shifts to those observed for **2**, **4** and **5** (*vide supra*) and consequently are consistent with a N-*trans*-N arrangement.

In the other set of signals the resonance coupled to the ^{195}Pt nucleus, assigned to the $H_{2'}$ proton was only slightly high-field shifted (*ca.* 0.3 ppm), but the singlet assigned to $H_{11'}$ appeared low-field shifted by more than 1 ppm as compared to H_{11} (at 7.26 and 7.59 ppm for **6** and **7**, respectively) and did not show coupling to the platinum nucleus. These results are in agreement with a N-*cis*-N arrangement, in which the shielding effect of the pyridine ring does not affect the $H_{11'}$ proton. The *cis*/*trans* molar ratio was 1:1 for both complexes, as calculated from the integrals in the ^1H NMR spectra.

The high temperature ^1H NMR spectrum of **6** was unchanged in comparison to the room temperature one. However, in the case of complex **7**, the high temperature ^1H NMR spectrum showed increase in the amount of the *trans* isomer (a 1:2 *cis*/*trans* ratio was determined). When the solution of complex **7** was cooled to room temperature the high temperature spectrum did not change. Different condition reactions, e.g., increasing the reaction time or refluxing the corresponding mixtures, were tested, but substantial changes were not observed.

These results were in contradiction with the *trans-choice* model (*vide supra*). In the case of complexes **6** and **7** the *trans* disposition is only partially achieved and the two theoretical isomers were observed in solution and, in the case of **3**, only the *cis* isomer was detected. It has been reported that the steric effects may play an essential role in the geometry of pyridine complexes [20] and consequently we suggest that this behaviour may be attributable to steric requirements of pyridine coligands in which the substituents are adjacent to the coordinated nitrogen (CF_3, **3**; Br, **6**; p-MeC_6H_4, **7**). The *cis* arrangement may ease the steric repulsion between this substituent and the methyl group of the *p*-tolyl-cyclometallated ring [20]. The molecular structure of the isomer with a *trans*-N,N geometry for compound **7** could be determined by X-ray single-crystal diffraction (*vide infra*).

2.2. X-ray diffraction analysis

Suitable crystals of compounds **5** and **7** were obtained by recrystallization from dichloromethane/hexane. Both crystals consisted of discrete molecules separated by typical van der Waals distances. The molecular structures of the complexes together with the labelling schemes used are given in Figs. 1 and 2, respectively. Selected bond distances and angles are given in Table 1. Crystallographic data are listed in Table 2.

The crystal structures of complexes [(2-Tolpy)Pt(4-CF_3py)Cl] (**5**) and [(2-Tolpy)Pt(TolpyH-κ^1N)Cl] (**7**) consist of one and two mononuclear molecules per asymmetric unit, respectively. In both cases the platinum atom is in a slightly distorted square-planar coordination environment and is bonded to an adjacent *ortho*-carbon atom and to the nitrogen atom of the 2-tolylpyridine ligand, a nitrogen atom (*trans* to N, from the 4-CF_3-pyridine ring in **5** and from the 2-tolylpyridine coligand in **7**) and to a chlorine atom (*trans* to C). The sum of the angles around the metal centre is very close to 360°, with the most noticeable distortion in the somewhat reduced "bite" angle upon chelation. The requirements of the five-membered chelate ring force the C(1)–Pt(1)–N(1) bond angle to 80.5(3)° (**5**) and to 81.51(12)° and 81.48(12)° [**7**, for Pt(1) and Pt(2), respectively].

In all of the molecules the phenyl and the pyridine rings of the cyclometallated ligand are almost coplanar, with a dihedral angle of 4.62° (**5**) and 3.20° and 2.86° (**7**). In complex **5** the platinum atom, the metallated carbon atom and both nitrogen atoms are almost coplanar, and the chlorine atom is located 0.448 Å above the plane defined by aforementioned atoms. In complex **7** the displacement is smaller (0.205 and 0.07 Å), i.e. in one of the molecules the chlorine atom is almost coplanar with the aforementioned atoms.

In complex **5** the 4-CF_3py ring is tilted with respect to the cyclometallated 2-Tolpy moiety, with an angle between these planes of 60.34°. In complex **7** the values for the dihedral angles described by the two rings of the non-cyclometallated 2-tolylpyridine ligand and the cyclometallated ring are 44.25° and 43.28°.

The Pt–C bond lengths are 2.004(8) Å for **5** and 1.985(3) and 1.982(3) Å for **7** and these are within the range of values obtained for analogous complexes in which a *trans*-C,Cl geometry is present [1c,d,25,30,31]. These values are consistent with a reinforced bond through π back donation.

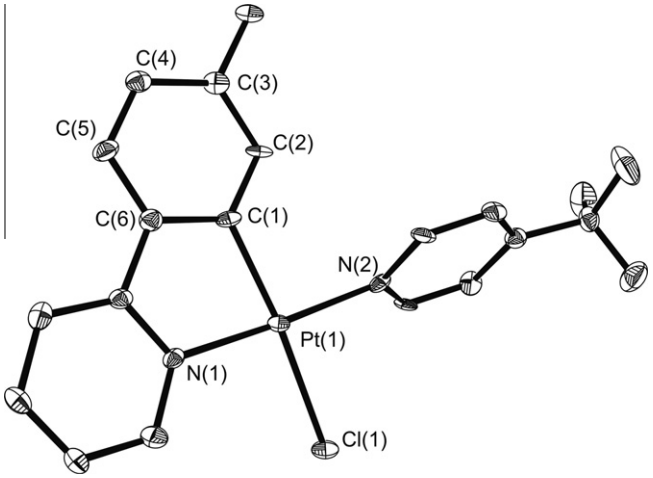


Fig. 1. Crystal structure of [(2-Tolpy)Pt(4-CF_3py)Cl] (**5**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

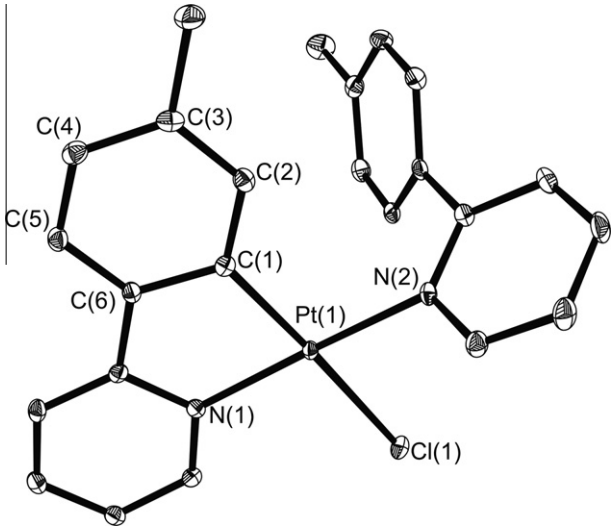


Fig. 2. Crystal structure of [(2-Tolpy)Pt(TolpyH-κ^{1}N)Cl] (**7**), with labelling scheme. Hydrogen atoms have been omitted for clarity.

Table 1
Selected bond lengths (Å) and angles (°) for complexes [(2-Tolpy)Pt(4-CF_3py)Cl] (**5**) and [(2-Tolpy)Pt(TolpyH-κ^{1}N)Cl] (**7**).

	5	7
C(1)–Pt(1)	2.004(8)	1.985(3)
N(1)–Pt(1)	2.012(7)	2.016(3)
N(2)–Pt(1)	2.020(7)	2.038(3)
Cl(1)–Pt(1)	2.413(2)	2.4091(8)
C(25)–Pt(2)		1.982(3)
N(3)–Pt(2)		2.017(3)
N(4)–Pt(2)		2.036(3)
Cl(2)–Pt(2)		2.4104(8)
C(1)–Pt(1)–N(1)	80.5(3)	81.51(12)
C(1)–Pt(1)–N(2)	95.9(3)	96.07(12)
N(1)–Pt(1)–N(2)	173.2(2)	173.41(10)
C(1)–Pt(1)–Cl(1)	172.1(2)	176.77(9)
N(1)–Pt(1)–Cl(1)	96.60(17)	95.50(8)
N(2)–Pt(1)–Cl(1)	87.68(18)	87.04(8)
C(25)–Pt(2)–N(3)		81.48(12)
C(25)–Pt(2)–N(4)		98.93(12)
N(3)–Pt(2)–N(4)		177.22(10)
C(25)–Pt(2)–Cl(2)		176.13(9)
N(3)–Pt(2)–Cl(2)		95.53(8)
N(4)–Pt(2)–Cl(2)		87.01(8)

The Pt–N bond lengths (see Table 1) of 2.012(7) and 2.020(7) Å are in agreement with the expected values in complexes with an N-*trans*-N arrangement [1d,c,5,25].

The Pt–Cl bond length, 2.413(2) Å, is in accordance with the strong *trans* effect of the carbon atom [1d,c,25,30,31] and it is longer than the corresponding distance found in compounds with N-donor atoms [18,32–34] or chlorine atoms [35] in a *trans* disposition.

3. Experimental

3.1. General remarks

Solvents were distilled prior use from appropriate drying agents [36]. All chemicals were used as supplied from commercial sources and were used without further purification. Elemental analyses (C, H, N) were carried out on a Carlo-Erba 1108 elemental analyser. IR spectra were recorded as KBr pellets on a Perkin-Elmer 1330 spectrophotometer. Mass spectra were obtained on a QUATRO mass spectrometer with a Cs ion-gun and 3-NBA matrix. NMR spectra were obtained as $CDCl_3$ or CD_3CN solutions and were recorded on a Bruker AC-200F spectrometer (200.0 MHz for ^{1}H, 50.3 MHz for ^{13}C–{1H}, 188.3 MHz for ^{19}F). ^{195}Pt NMR spectra were recorded on a Bruker DRX-500 spectrometer (107.5 MHz, using a saturated solution of K_2PtCl_4 in D_2O as internal standard).

Table 2
Crystal data and structure refinement data for complexes **5** and **7**.

Complex	5	7
Empirical formula	$C_{18}H_{14}ClF_3N_2Pt$	$C_{24}H_{21}ClN_2Pt$
Formula mass	545.85	567.97
Crystal system	monoclinic	triclinic
Space group	$P2(1)$	$P\bar{1}$
Unit cell dimensions		
a (Å)	4.7616(3)	11.0507(4)
b (Å)	13.5232(8)	14.1465(5)
c (Å)	13.1212(8)	14.3145(5)
α (°)	90	67.520(2)
β (°)	96.248(4)	79.671(2)
γ (°)	90	89.157(2)
V (Å^3)	839.88(9)	2030.65(12)
Z	2	4
D_{calc} (Mg m^{-3})	2.158	1.858
μ(Mo Kα) (mm^{-1})	8.546	7.053
F(000)	516	1096
Crystal size (mm)	0.20 × 0.07 × 0.03	0.30 × 0.16 × 0.08
T (K)	100(2)	100(2)
No. of reflections collected	11123	36506
No. of independent reflections	4047	10013
Goodness of fit (GOF) on F^2	0.993	1.097
R^a	0.0365	0.0186
$wR_2{}^b$	0.0789	0.0499

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $[F > 4\sigma(F)]$.
[b] $wR_2 = [\Sigma[w(F_o^2-F_c^2)^2]/\Sigma w(F_o^2)^2]^{1/2}]$, all data.

3.2. Synthesis of the complexes

3.2.1. [(2-Tolpy)Pt(μ-Cl)]$_2$ (*1*)

K_2PtCl_4 (1.226 g, 2.95 mmol) was dissolved in the minimum amount of warm water in a Schlenk vessel and 2-tolylpyridine (500 mg, 2.95 mmol, 520 μL) in ethanol (40 ml) was added. The resultant pink suspension was heated at 65 °C for 8 h under Schlenk conditions and the resulting green-yellow suspension was filtered off and the solid washed with hexane and Et_2O. Yield: 975 mg (41.4%). *Anal.* Calc. for $(C_{12}H_{10}NPtCl)_2$: C, 36.1; H, 2.5; N, 3.5. Found: C, 36.4; H, 2.3; N, 3.5%. FAB-Mass: 797 [M$^+$]; 532 [(2-Tolpy)$_2$Pt]; 362 [(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3029 (w), 1608 (m).

3.2.2. [2-(p-tolpy)PtPyCl] (*2*)

Complex **1** (100 mg, 0.125 mmol) was suspended in chloroform and pyridine (21.82 mg, 0.276 mmol, 22.32 μL) was added. The initial suspension became a yellow solution immediately and the mixture was stirred at room temperature for 2 h. The solvent was removed under reduced pressure, the resulting yellow solid was washed with Et_2O and recrystallized from dichloromethane/*n*-hexane. Yield: 66 mg (55.0%). *Anal.* Calc. for $C_{17}H_{15}N_2PtCl$: C, 42.7; N, 5.8; H, 3.2. Found: C, 42.6; N, 5.7; H, 3.2%. FAB-Mass: 478 [M$^+$]; 442 [(2-Tolpy)PtPy]; 363 [(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3024 (w), 1606 (s), 1587 (s). ^{1}H NMR ($CDCl_3$): δ(ppm) = 9.67 (dd; 1H, H_2; $^3J(H_2H_3)$ = 5.8 Hz; $^4J(H_2H_4)$ = 0.5 Hz; $^3J(PtH_2)$ = 21.7 Hz); 9.01 (dd with Pt; 2H; $H_{2,6\text{-py}}$; $^3J(H_{2,6\text{-py}}H_{3,5\text{-py}})$ = 6.5 Hz; $^4J(H_{2,6\text{-py}}H_{4py})$ = 1.4 Hz; $^3J(PtH_{2,6\text{-py}})$ = 21.4 Hz); 7.99 (d, 1H; H_5; $^3J(H_5H_4)$ = 7.8 Hz); 7.91 (tt, 1H; $H_{4\text{-py}}$; $^3J(H_{4\text{-py}}H_{3,5\text{-py}})$ = 1.0 Hz); 7.78 (dd, 1H; H_4; $^3J(H_4H_3)$ = 1.5 Hz); 7.44 (dd, 2H; $H_{3,5\text{-py}}$); 7.37 (d, 1H; H_9; $^3J(H_9H_8)$ = 7.8 Hz;); 7.24 (dd, 1H; H_3); 6.92 (d, 1H; H_8); 6.14 (s, broad; 1H, H_{11}; $^3J(PtH_{11})$ = 23.9 Hz); 2.19 (s, CH_3). ^{13}C–{1H} NMR: δ(ppm) = 154.08 (s, $C_{2,6\text{-py}}$); 151.29 (s, C_2); 125.95 (s, C_{12};

$J(PtC_{12})$ = 22.1 Hz); 21.80 (s, CH_3); rest of aromatic carbons: 142.10–117.87 ppm. ^{195}Pt NMR: δ(ppm) = −3266.

3.2.3. [(2-Tolpy)Pt(2-CF_3py)Cl] (**3**)

2-Trifluoromethylpyridine (36.7 mg, 0.125 mmol, 29.7 μL) was added to a suspension of **1** (100 mg, 0.125 mmol) in chloroform. The mixture was stirred and heated under reflux for 24 h. The resulting solid was filtered off and washed with Et_2O and hexane. Yield: 59 mg (43.2%). *Anal.* Calc. for $C_{18}H_{14}F_3N_2PtCl$: C, 39.6; N, 5.1; H, 2.6. Found: C, 39.9; N, 5.3; H, 2.4%. FAB-Mass: 544 [M^+]. IR (KBr, cm^{-1}): 3027 (w), 1651 (s), 1607 (s), 1588 (s). ^{1}H NMR (CD_3CN): δ(ppm) = 9.48 (broad, 1H, H_{6py}), 8.80 (dd; 1H, H_2; $^3J(H_2H_3)$ = 5.5 Hz; $^3J(PtH_2)$ = 22.7 Hz); 8.00 (dd, 1H; H_4; $^3J(H_4H_5)$ = 7.8 Hz; $^3J(H_4H_3)$ = 1.2 Hz); 7.90 (broad, 1H, H_{3py}), 7.77 (d, 1H; H_5); 7.66 (s, 1H; H_{11}); 7.55 (broad, 2H, H_{3py}, H_{4py}), 7.40 (d, 1H; H_9; $^3J(H_9H_8)$ = 7.9 Hz); 7.18 (dd, 1H; H_3); 6.94 (d, 1H; H_8); ^{13}C–{1H} NMR (CD_3CN): δ(ppm) = 168.69 (C_2); 150.82 (s, C_{2py}; $^2J(PtC_{2py})$ = 9.8 Hz); 133.59 (s; C_{12}; $J(PtC_{12})$ = 32.4 Hz); 124.59 (s; C_{3py}; $^3J(PtC_{3py})$ = 20.8 Hz); 122.68 (s; C_{6py}; $^2J(PtC_{6py})$ = 19.4 Hz); 119.44 (s; C_{5py}; $^4J(PtC_{5py})$ = 22.2 Hz); rest of aromatic carbons: 143.79–125.71; 21.77 (CH_3). ^{19}F NMR (CD_3CN): δ = −100.29 ppm. ^{195}Pt NMR: δ(ppm) −3540.

3.2.4. [(2-Tolpy)Pt(3-CF_3py)Cl] (**4**)

3-Trifluoromethylpyridine (36.7 mg, 0.250 mmol, 29.71 μL) was added to a suspension of **1** (100 mg, 0.125 mmol) in chloroform. The initial green suspension became a yellow solution which was stirred for 2 h at room temperature. The solvent was removed under reduced pressure and the resulting green-yellow solid was washed with Et_2O and hexane. Yield: 99 mg (72.6%). *Anal.* Calc. for $C_{18}H_{14}F_3N_2PtCl$: C, 39.6; N, 5.1; H, 2.6. Found: C, 39.4; N, 5.0; H, 2.9%. FAB-Mass: 1054 [$(2\text{-Tolpy})_2Pt_2(3\text{-}CF_3py)_2Cl$]; 545 [$M^+$]; 510 [(2-Tolpy)Pt(3-$CF_3$py)]; 363 [(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3077 (w), 1609 (s), 1590 (s). ^{1}H NMR ($CDCl_3$): δ(ppm) = 9.62 (dd; 1H; H_2; $^3J(H_2H_3)$ = 5.8 Hz; $^4J(H_2H_4)$ = 0.7 Hz; $^3J(PtH_2)$ = 19.7 Hz); 9.34 (s, broad; 1H, H_{2py}; $^3J(PtH_{2py})$ = 23.3 Hz); 9.26 (d, broad; 1H; H_{6py}; $^3J(H_{6py}H_{5py})$ = 5.0 Hz; $^3J(PtH_{6py})$ = 22.1 Hz); 8.17 (d, broad; 1H; H_{4py}; $^3J(H_{4py}H_{3py})$ = 8.1 Hz; $^5J(PtH_{4py})$ = 53.7 Hz); 7.79 (dd, 1H; H_{5py}); 7.62–7.59 (complicated multiplet; 2H, H_3 and H_4); 7.37 (d, 1H; H_9; $^3J(H_9H_8)$ = 7.9 Hz); 7.11 (d, 1H; H_5; $^3J(H_5H_4)$ = 6.6 Hz; $^4J(H_5H_3)$ = 1.3 Hz); 6.92 (d, 1H; H_8); 6.08 (s; 1H, H_{11}; $^3J(PtH_{11})$ = 23.1 Hz); 2.19 (s, 3H; CH_3). ^{13}C–{1H} NMR ($CDCl_3$) δ(ppm) = 167.31 (C_{2py}); 157.18 (C_2); 121.50 (C_{12}; $J(PtC_{12})$ = 83.5 Hz); rest of the aromatic carbons: 151.50–118.00; 21.77 (CH_3). ^{19}F NMR ($CDCl_3$): δ = −62.99 ppm. ^{195}Pt NMR: δ(ppm) −3260.

3.2.5. [(2-Tolpy)Pt(4-CF_3py)Cl] (**5**)

A suspension of **1** (100 mg, 0.125 mmol) in chloroform was treated with 4-trifluoromethylpyridine (36.7 mg, 0.250 mmol, 29.85 μL). The resultant yellow solution was stirred for 2 h at room temperature. The solvent was removed under reduced pressure to give a green oil which was triturated with Et_2O and hexane to give a green-yellow solid, which was filtered off and dried *in vacuo*. Yield: 48.5 mg (35.5%). *Anal.* Calc. for $C_{18}H_{14}F_3N_2PtCl$: C, 39.6; N, 5.1; H, 2.6. Found: C, 39.4; N, 5.1; H, 2.9%. FAB-Mass: 1054 [$(2\text{-Tolpy})_2Pt_2(4\text{-}CF_3py)_2Cl$]; 545 [$M^+$]; 510 [(2-Tolpy)Pt(4-$CF_3$py)]; 363 [(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3028 (w), 1609 (s), 1590 (s). ^{1}H NMR: δ = 9.62 (d, broad; 1H, H_2; $^3J(H_2H_3)$ = 5.9 Hz; $^3J(PtH_2)$ = 19.7 Hz); 9.26 (d, 2H; $H_{2,6\text{-py}}$ $^3J(H_{2,6py}H_{3,5\text{-py}})$ = 6.5 Hz; $^3J(PtH_{2,6\text{-py}})$ = 22.3 Hz); 7.82 (dd, 1H; H_4; $^3J(H_4H_5)$ = 7.4 Hz; $^3J(H_4H_3)$ = 1.5 Hz; 7.71 (d, 2H; $H_{3,5\text{-py}}$); 7.60 (d, 1H; H_5); 7.37 (d, 1H; H_9; $^3J(H_9H_8)$ = 7.9 Hz); 7.11 (dd, 1H; H_3); $^3J(H_3H_2)$ = 1.4 Hz; 6.93 (d, 1H; H_8); 6.11 (s; 1H, H_{11}; $^3J(PtH_{11})$ = 23.2 Hz). ^{13}C–{1H} NMR: δ = 167.25 (s, C2); 155.24 (s; $C_{3,5\text{-py}}$; $^3J(PtC_{3,5\text{-py}})$ = 6.2 Hz); 151.30 (s; $C_{2,6\text{-py}}$; $^2J(PtC_{2,6\text{-py}})$ = 9.8 Hz); 121.93 (q, CF_3; $J(CF)$ = 3.5 Hz); rest of aromatic carbons: 142.04–117.98; 21.81 (CH_3). ^{19}F NMR ($CDCl_3$): δ = −65.41 ppm. ^{195}Pt NMR: δ(ppm) −3257. Crystals suitable for X-ray diffraction studies were obtained by recrystallization from a CH_2Cl_2/hexane solution.

3.2.6. [(2-Tolpy)Pt(2,6-Br_2py)Cl] (**6**)

A suspension of **1** (100 mg, 0.125 mol) in $CHCl_3$ was treated with 2,6-dibromopyridine (59.22 mg, 0.250 mmol) and this mixture was stirred and heated under reflux for 24 h to give a yellow solution. The solvent was removed under reduced pressure and the resulting yellow oil triturated with Et_2O and hexane to give an olive green solid. Yield: 61 mg (38.4%). *Anal.* Calc. for $C_{17}H_{13}N_2Br_2PtCl$: C, 32.1; N, 4.4; H, 2.0. Found: C, 32.4; N, 4.7; H, 2.2%. FAB-Mass: 592 [(2-Tolpy)Pt(2,6-Br_2py)]; 532 [$(2\text{-Tolpy})_2Pt$]; 363 [(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3028 (w), 1605 (s), 1588 (s). ^{1}H NMR: δ(ppm) = 9.59 (dd; 1H, H_2; $^3J(H_2H_3)$ = 5.8 Hz; $^4J(H_2H_4)$ = 0.8 Hz; $^3J(PtH_2)$ = 19.7 Hz); 9.23 (dd; 1H, $H_{2'}$; $^3J(H_{2'}H_{3'})$ = 5.9 Hz; $^3J(H_{2'}H_{4'})$ = 0.9 Hz; $^3J(PtH_{2'})$ = 22.6 Hz); 7.99 (d, 2H; $H_{3,5\text{-py}}$; $^3J(H_{3,5\text{-py}}H_{4\text{-py}})$ = 8.0 Hz); 7.69 (t, 1H; $H_{4\text{-py}}$); 7.91 (dd, broad; 1H, H_4; $^3J(H_4H_3)$ = 1.5 Hz); 7.46 (d, broad; 1H, H_9; $^3J(H_9H_8)$ = 7.9 Hz); 7.33 (d, broad; 1H, H_3); 7.26 (s, 1H, $H_{11'}$); 7.21 (d, broad; 1H, H_5; $^3J(H_5H_4)$ = 7.2 Hz); 7.13 (d, 2H; $H_{3,5\text{-py}'}$; $^3J(H_{3,5\text{-py}'}H_{4py'})$ = 7.0 Hz); 7.01 (t, 1H; $H_{4py'}$); 6.80 (d, broad; 1H, H_8); 6.00 (s; 1H, H_{11}; $^3J(PtH_{11})$ = 24.2 Hz); 2.26 (s, 3H, CH_3); 2.15 (s, 3H, CH_3). ^{13}C–{1H} NMR: δ(ppm) = 167.25 and 162.36 ($C_{2,6\text{-py}}$); 154.34 and 151.12 (C_2); 141.54–117.62 (rest of aromatic carbons); 21.82 and 21.41 (CH_3). The ^{1}H NMR spectrum at high temperature in $CDCl_3$ was also recorded and no changes were observed. ^{195}Pt NMR: δ(ppm) −3201.

3.2.7. [(2-Tolpy)Pt(TolpyH-κ^1N)Cl] (**7**)

2-Tolylpyridine (42.50 mg, 0.250 mmol, 42.88 μL) was added to a suspension of **1** (100 mg, 0.125 mmol) was in dichloromethane. The initial suspension became a yellow solution immediately which was stirred at room temperature for 2 h. The mixture was filtered and the solvent was removed under reduced pressure. The resulting brown oil which was triturated with Et_2O and hexane to five a brown solid which was filtered off. Yield: 68.3 mg (48.1%). *Anal.* Calc. for $C_{24}H_{21}N_2PtCl$: C, 50.7; N, 4.9; H, 3.7. Found: C, 51.0; N, 4.8; H, 3.8%. FAB-Mass: 567 [M^+], 532 [(2-Tolpy)Pt(TolpyH-κ^1N)]; 363[(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3031 (w), 1606 (s), 1591 (s). ^{1}H NMR: δ(ppm) = 9.58 (dd; 1H, H_2; $^3J(H_2H_3)$ = 5.9 Hz; $^3J(PtH_2)$ = 19.0 Hz); 9.23, (dd; 1H, $H_{2'}$; $^3J(H_{2'}H_{3'})$ = 5.9 Hz; $^4J(H_{2'}H_{4'})$ = 1.0 Hz; $^3J(PtH_{2'})$ = 10.9 Hz); 9.14; (m; 1H, $H_{6py'}$; $^3J(H_{6py'}H_{5py'})$ = 5.9 Hz; $^4J(H_{6py'}H_{4py'}$ = 1.5 Hz; $^5J(H_{6py'}H_{3py'})$ = 0.6 Hz; $^3J(PtH_{6py'})$ = 18.5 Hz); 8.77 (s, broad; 1H, H_{6py}); 7.59 (s, $H_{11'}$); 6.00 (s; 1H, H_{11}; $^3J(PtH_{11})$ = 23.9 Hz); 2.44, 2.41, 2.26, 2.15 (s, CH_3). Rest of aromatic protons: 8.13–6.63 ppm. ^{13}C–{1H} NMR: δ = 167.26–117.62 (aromatic carbons); 21.81–20.27 (methyl groups). ^{195}Pt NMR: δ(ppm) -3200 ppm. Crystals suitable for X-ray diffraction studies were obtained by recrystallization from a CH_2Cl_2/hexane solution.

3.2.8. [(2-Tolpy)Pt(morpholine-κ^1N)Cl] (**8**)

The dimeric complex **1** (100 mg, 0.125 mmol) was suspended in chloroform and morpholine (21.78 mg, 0.250 mmol, 21.86 μL) was added. The initial suspension became an olive green solution, which was stirred at room temperature for 2. The solvent was removed under reduced pressure to give a green-yellow solid. Yield: 47 mg (38.7%). *Anal.* Calc. for $C_{16}H_{19}N_2PtClO$: C, 39.53; N, 5.76; H, 3.91. Found: C, 36.80; N, 5.12; H, 3.64%. FAB-Mass 486 [M^+]; 451 [(2-Tolpy)Pt(morpholine-κ^1N)]; 363 [(2-Tolpy)Pt]. IR (KBr, cm^{-1}): 3185 (m), 2845 (m), 1605 (s), 1587 (s). ^{1}H NMR: δ = 9.57 (dd; 1H, H_2; $^3J(H_2H_3)$ = 6.4 Hz; $^4J(H_2H_4)$ = 0.8 Hz; $^3J(PtH_2)$ = 19.4 Hz); 7.74 (dd, 1H; H_4; $^3J(H_4H_5)$ = 7.2 Hz; $^3J(H_4H_3)$ = 1.5 Hz); 7.56 (d, 1H; H_9; $^2J(H_9H_8)$ = 8.0 Hz); 7.39 (d, 1H, H_8); 7.04 (dd, 1H; H_3); 6.98 (d,

1H; H_5); 6.97 (s; 1H, H_{11}; $^3J(PtH_{11})$ = 21.5 Hz); 4.77 (s, broad; 1H, NH; $^2J(PtH_{NH})$ = 81.7 Hz); 3.97–3.19 (m, 8H, morpholine protons); 2.43 (s, 3H; CH_3). ^{13}C NMR–{1H}: δ(ppm) = 166.75 (s, C_2); 117.89 (s; C_{12}; $J(PtC_{12})$ = 21.5 Hz); 68.54 (s; $C_{3,5\text{-morphol}}$; $^2J(PtC_{3,5\text{-morphol}})$ = 24.8 Hz); 51.82 (s; $C_{2,6\text{-morphol}}$; $^3J(PtC_{2,6\text{-morphol}})$ = 7.1 Hz); 22.13 (s, CH_3); rest of aromatic carbons: 151.42–124.49 ppm. ^{195}Pt NMR: δ(ppm) −3222 ppm.

3.2.9. X-ray crystallographic study

Three dimensional X-ray data were collected on Bruker Smart 1 K and Bruker AXS CCD diffractometers using graphite-monochromated Mo Kα radiation. All the measured reflections were corrected for Lorentz and polarization effects and for absorption by semi-empirical methods based on symmetry-equivalent and repeated reflections. The structures were solved by direct methods and refined by full matrix least-squares on F^2.

Hydrogen atoms were included in calculated positions and refined in riding mode. All non-hydrogen atoms were refined anisotropically. The structure solution and refinement were carried out using the program package SHELX-97 [37].

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Appendix Appendix. A. Supplementary data

CCDC 791986 and 791987 contain the supplementary crystallographic data for **5** and **7**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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