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Structure and spectroscopic properties of luminescent cyclometalated platinum(II) complexes with chiral phosphine substituted carbohydrate ligands

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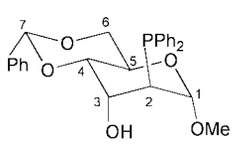
A series of new chiral cyclometalated platinum(II) complexes containing carbohydrate phosphine ligands have been prepared. The reaction of $[Pt(ppy)Cl]_2$ (Hppy = 2-phenylpyridine) with the chiral phosphines *n*-Hmbpa (methyl 4,6-*O*-benzylidene-*n*-deoxy-*n*-(diphenylphosphino)-α-D-altropyranoside, *n* = 2 or 3) afforded *cis*-[Pt(ppy)(*n*-Hmbpa)Cl] (*n* = 2 **2a** or 3 **2b**) in high yields. Treatment of **2a** or **2b** with an excess of $NaOCH_3$ gave the alkoxoplatinum(II) complexes *trans*-[Pt(ppy)(*n*-mbpa)] (*n* = 2 **3a** or 3 **3b**). The crystal structure of **3b** shows that the phosphorus atom is located *trans* to the nitrogen atom of the ppy ligand and the pyranose ring is in a boat conformation. Moderately intense UV-vis absorption bands assigned to metal-to-ligand charge-transfer (MLCT) transitions are shifted from *ca.* 376–382 to *ca.* 414–416 nm when the chloride ligand is substituted by the pendant alkoxide group. In solid state and 77 K MeOH–EtOH (4 : 1) glass solution, complexes **2** and **3** show a vibronic structured emission in the range 450–650 nm. Complex **2** is non-emissive in fluid solution at room temperature whereas **3** shows a long-lived ^{3}MLCT emission in both CH_3CN and CH_2Cl_2 at room temperature.

Introduction

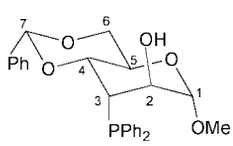
Transition metal complexes with long-lived and emissive excited states as exemplified by $Ru(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) and its derivatives have useful applications.[1] One of which that has been receiving current attention is new luminescence probes for biomolecules.[2–4] In this context, we are interested in square planar luminescent platinum(II) complexes, because they have a vacant co-ordination site for substrate binding reaction at the metal atom.[3,5–8] Recent studies revealed that platinum(II) complexes containing planar aromatic diimine ligands are good metallointercalators for DNA base pairs and other biomolecules.[3,4d,9]

Cyclometalated platinum(II) complexes are structurally similar to their aromatic diimine analogues, display rich photoluminescence properties and interesting photochemistry,[3,8,10,11] and are promising candidates for the design of new luminescent probes for biomolecules.[3] Both bis(cyclometalated) and mono-(cyclometalated) platinum complexes have been reported;[3,10,11] the latter class such as $[Pt(ppy)L^1L^2]^z$ ($z = -1$, 0 or +1: Hppy = 2-phenylpyridine) offer a convenient means to tune the excited state properties through varying the electronic and steric properties of the ligands L^1 and L^2. The luminescence properties of $[Pt(ppy)L^1L^2]^z$ ($z = -1$, $L^1 = L^2 = Cl^-$; $z = 0$, $L^1 = Cl^-$, L^2 = tris(morpholino)phosphine; $z = +1$: $L^1 = L^2$ = 2,2′-bipyridine, 1,10-phenanthroline or 1,2-diaminoethane) have previously been studied.[12] We envisaged that Pt^{II}–ppy complexes containing strong σ-donor ligands such as alkoxide will have a low energy and emissive MLCT excited state.

Studies on DNA binding reactions with chiral octahedral metal complexes have been receiving much attention.[2c] Since square-planar d^8 platinum(II) complexes are well suited to interact with DNA,[3,4d,9] chiral luminescent platinum(II) complexes would have useful applications.[8b,10b,c] Here, we describe the syntheses, characterization, and spectroscopic properties of a series of chiral cyclometalated platinum(II) complexes *cis*-[Pt(ppy)(*n*-Hmbpa)Cl] and *trans*-[Pt(ppy)(*n*-mbpa)] (*n*-Hmbpa = methyl 4,6-*O*-benzylidene-*n*-deoxy-*n*-(diphenylphosphino)-α-D-altropyranoside, *n* = 2 or 3), which contain a chelating carbohydrate phosphine ligand. The chiral ligands *n*-Hmbpa (*n* = 2 or 3) were chosen because of their chirality, their pendant hydroxy group, and potential as alkoxide ligands, and their platinum(II) derivatives were found to display antitumour activities.[13]



2-Hmbpa



3-Hmbpa

Results and discussion

Syntheses

A series of cyclometalated platinum(II) complexes containing the chiral phosphine ligands *n*-Hmbpa were prepared by the reactions depicted in Scheme 1. The starting material, $[Pt(ppy)Cl]_2$ **1**, was synthesized by a modification of the literature method[12a] using glycerol instead of dichloromethane and the isolated yield raised from 30 to 77%. Treatment of complex **1** with an equimolar amount of *n*-Hmbpa gave the new complexes *cis*-[Pt(ppy)(*n*-Hmbpa)Cl] (*n* = 2 **2a** or 3 **2b**) in nearly quantitative yields. The phosphine donor is located *trans* to the nitrogen atom of the ppy ligand. This assignment is based on the large Pt–P coupling constants[14] (4297 Hz for **2a** and 4423 Hz for **2b**) and is consistent with previous crystallographic studies on the analogues *cis*-$[Pt(ppy)(P(mor)_3)Cl]$ ($P(mor)_3$ = tris(morpholino)phosphine)[12c] and *cis*-[Pt(ppy)(POH)Cl] (POH = 2-diphenylphosphinoethanol).[15] Under strongly basic conditions, the co-ordinated chloride in **2a** or **2b** was substituted by the alkoxide derived from the pendant hydroxy groups of the *n*-Hmbpa ligands, leading to the formation of

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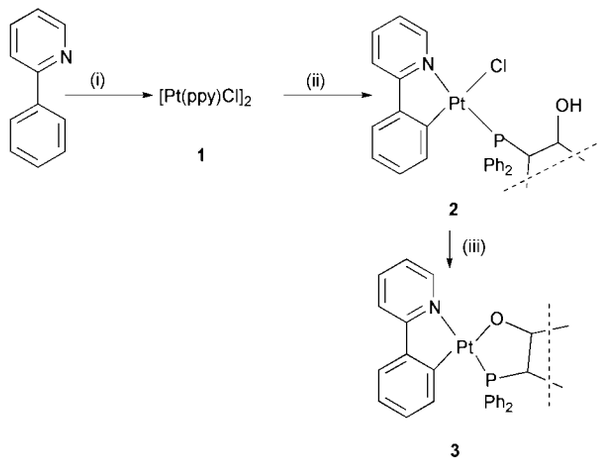
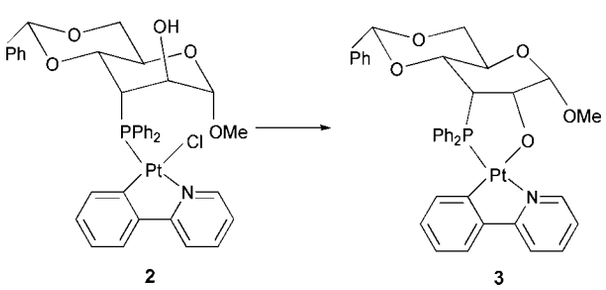


Scheme 1 (i) $PtCl_2$, $HOCH(CH_2OH)_2$; (ii) 2-Hmbpa or 3-Hmbpa, CH_2Cl_2; (iii) CH_3OH, $NaOCH_3$.

alkoxoplatinum(II) complexes *trans*-[Pt(ppy)(*n*-mbpa)] (*n* = 2 **3a** or 3 **3b**). The ^{31}P resonances are significantly shifted downfield from δ 16.5 for **2a** and 16.8 for **2b** to δ 35.0 for **3a** and 36.1 for **3b**, respectively, suggesting the formation of a P,O five-membered chelate ring.[16] The large Pt–P coupling constants (4375 Hz for **3a** and 4276 Hz for **3b**) indicate that the phosphorus atoms are *trans* to the nitrogen donors of the ppy ligands.[14]

^{1}H NMR

The assignments of the ^{1}H NMR signals were aided by ^{1}H–^{1}H COSY and ^{1}H–^{13}C HSQC (heteronuclear single quantum coherence) spectroscopies and by comparison to the literature data on related compounds.[13b] The chemical shifts and coupling constants are compiled in the Experimental section. The correlated peaks of H(1)–H(2) and H(2)–H(3) for **2a** and **2b** have not been observed in their ^{1}H–^{1}H COSY spectra, and the observed doublet of H(1) in complex **2a** is assigned to a three-bond ^{31}P–H coupling ($^3J_{PH}$ = 8.9 Hz). These findings suggest that the H(1)–C(1)–C(2)–H(2) and H(2)–C(2)–C(3)–H(3) torsion angles in **2a** and **2b** are close to 90°, the axial MeO, Ph_2P, and OH groups have a similar orientation as that in the "free" ligands,[17] and the phosphine ligands co-ordinate to the Pt^{II} through the phosphorus atom only.[18] However, the H(1)–H(2) and H(2)–H(3) couplings for **3a** and **3b** could be observed, implying a change in the conformation of the pyranose ring upon co-ordination of the alkoxy group to Pt^{II}. Both the diphenylphosphino and hydroxy groups must twist to allow for simultaneous co-ordination. Since O(4) and C(6) are fixed by the 4,6-*O*-benzylidene ring which is in a chair conformation, only the methoxy groups can change orientation, resulting in the pyranose rings of the deprotonated ligands 2- and 3-mbpa adopting a boat conformation (see Scheme 2).



Scheme 2

Crystal structure of complex 3b

Fig. 1 shows the ORTEP[19] drawing of complex **3b** with atom numbering; the hydrogen atoms are omitted for brevity. The

Table 1 Selected atomic distances (Å) and bond angles (°) for complex **3b**

Pt–P	2.227(1)	Pt–O(1)	2.058(3)
Pt–N(1)	2.069(4)	Pt–C(14)	2.011(5)
P–C(3)	1.847(5)	P–C(25)	1.830(5)
P–C(31)	1.839(6)	O(1)–C(2)	1.395(6)
N(1)–C(20)	1.349(7)	N(1)–C(24)	1.341(7)
C(14)–C(15)	1.388(8)	C(14)–C(19)	1.422(7)
C(14)–Pt–O(1)	171.1(2)	C(14)–Pt–N(1)	81.1(2)
O(1)–Pt–N(1)	90.4(2)	C(14)–Pt–P	102.9(2)
O(1)–Pt–P	85.7(1)	N(1)–Pt–P	175.4(1)
C(25)–P–Pt	113.9(2)	C(31)–P–Pt	118.1(2)
C(3)–P–Pt	100.0(2)	C(2)–O–Pt	114.1(3)
C(24)–N(1)–Pt	123.6(4)	C(20)–N(1)–Pt	115.3(4)
C(15)–C(14)–Pt	130.6(4)	C(19)–C(14)–Pt	113.0(4)

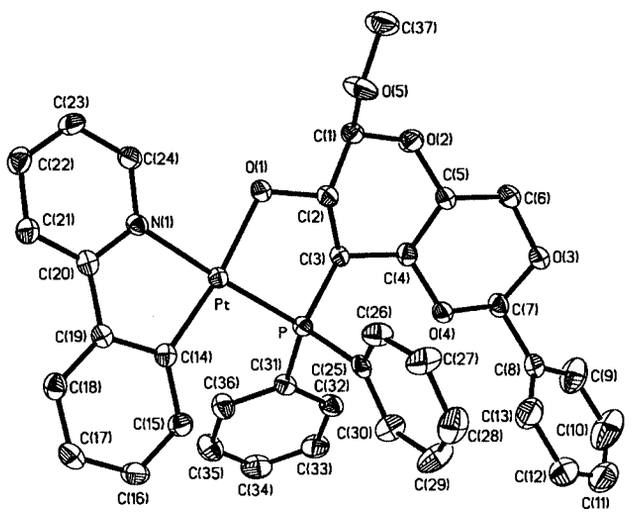


Fig. 1 Crystal structure of *trans*-[Pt(ppy)(3-mbpa)] **3b** showing the atom-labeling scheme.

absolute configuration of the 3-mbpa ligand is the same as that of free 3-Hmbpa.[17]

The phosphorus atom is located *trans* to the nitrogen atom of the ppy ligand, consistent with the NMR results. Although the Pt, P, O(1), N(1), and C(14) atoms are nearly coplanar, the Pt atom has a slightly distorted planar geometry as indicated by the angle P–Pt–C(14) of 102.9(2)° compared to C(14)–Pt–N(1) of 81.1(2)°.

Selected bond distances and angles are listed in Table 1. The nitrogen atom was assigned based on the shorter bond distance to its neighboring carbon atoms: N(1)–C(20) 1.349(7), N(1)–C(24) 1.341(7) Å *vs.* C(14)–C(15) 1.388(8), C(14)–C(19) 1.422(7) Å (Table 1), and the longer Pt–N(1) than the Pt–C(14) distances. The Pt–N(1) (2.069(4) Å) distance is comparable to related values in $[Pt(bpy)_2]^{2+}$ and $[Pt(phen)_2]^{2+}$,[20] but slightly shorter than those of 2.13–2.17 Å in *cis*-bis(cyclometalated)platinum(II) complexes.[10b,c] This is attributable to the *trans* effect of carbon-bound ligands. The Pt–O(1) distance (2.058(3) Å) is slightly longer than those of *cis*-[Pt(2-mbpa)$_2$] (average 1.98),[13b] and comparable to the related values in bis(3-diphenylphosphino-2-methylpropan-2-olato-*O*,*P*)platinum(II) (average 2.043(3) Å) and bis(3-diphenylphosphinoethoxo-*O*,*P*)platinum(II) (2.039(5) Å). The Pt–C(14) distance (2.011(5) Å) is slightly longer than those of 1.947(17)–2.009(10) Å observed for the *cis*-bis(cyclometalated)platinum(II) complexes.[10] Considering the normal difference of 0.11 Å between C–C and C–O bonds, the fact that the Pt–O distance is comparable to that of Pt–C in **3b** suggests that the former has no anomalous weakening.

As seen from Fig. 1, the 4,6-*O*-benzylidene ring in complex **3b** has a chair conformation and the pyranose ring exhibits a

Table 2 Spectral and emission data of complexes **2** and **3**

Complex	Medium (T/K)	Absorption [λ_{max}/nm($\varepsilon \times 10^{-3}$/dm^3 mol^{-1} cm^{-1})]	λ_{em}/nm/τ/μs	φ_{em}	k_r/10^4 s^{-1}
2a	CH_2Cl_2 (298)	315 (6.4), 327 (5.6), 376 (2.6)	Non-emissive		
	CH_3CN (298)		Non-emissive		
	Solid (298)		474/0.27, 506/0.32		
	Glass (77)		477/24, 515/24		
2b	CH_2Cl_2 (298)	316 (7.5), 327 (7.0), 382 (3.3)	Non-emissive		
	CH_3CN (298)	313 (7.8), 324 (6.4), 376 (3.2)	517/0.3	0.0004	0.13
	Solid (298)		516/0.53		
	Glass (77)		483/22, 518 /22		
3a	CH_2Cl_2 (298)	302 (15.3), 414 (2.7), 488 (0.04)	510/0.83	0.048	5.78
	CH_3CN (298)		516/0.92	0.053	5.76
	Solid (298)		528/4.9		
	Glass (77)		481/21, 517/21		
3b	CH_2Cl_2 (298)	303 (10.1), 416 (2.1), 488 (0.03)	510/0.24	0.014	5.83
	CH_3CN (298)		512/0.55	0.036	6.55
	Solid (298)		533/7.2		
	Glass (77)		483/18, 517/18		

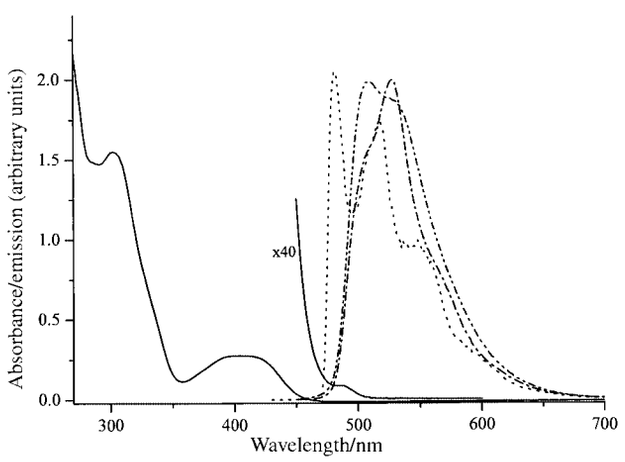


Fig. 2 Absorption and emission spectra of *trans*-[Pt(ppy)(2-mbpa)] **3a**: (——) absorption in CH_2Cl_2; (– – –) emission in 4 : 1 (v/v) methanol–ethanol rigid matrix at 77 K; (–••–••–) emission in degassed CH_2Cl_2 solution at room temperature; (–•–•–) emission in the solid state at room temperature.

boat conformation. The torsion angles of 125.3° for P–C(3)–C(2)–O(1) and −102.6° for O(1)–C(2)–C(1)–O(5) indicate that the diphenylphosphino, methoxy, and alkoxo groups are in equatorial position.

Absorption spectra and luminescence properties

The spectral data of complexes **2** and **3** are summarized in Table 2. The absorption and emission spectra of **3a** are presented in Fig. 2.

The intense absorption around 300–330 nm for all the complexes can be assigned to intraligand (IL) ($\pi \longrightarrow \pi^*$) transitions of the ppy ligand since free Hppy exhibits similar absorption bands in the same spectral region.[12c] The moderately intense absorptions around 375 nm for **2a** and **2b** shift to *ca.* 415 nm for **3a** and **3b**, which can be attributed to unresolved spin-allowed ^{1}MLCT ($d_{Pt} \longrightarrow \pi^*_{ppy}$) transition. Contribution from purely d–d transitions is unlikely to be important for absorption with $\varepsilon > 10^3$ dm^3 mol^{-1} cm^{-1}. The strong ligand-field strength of the ligands in the cyclometalated platinum(II) complexes would be expected to decrease the MLCT transition energy of Pt^{II}.[8b] Here, the $^1J_{PtP}$ values reflect that OR^- is a better σ donor to Pt^{II} than Cl^-. In line with this finding, the MLCT transition energy red-shifts from complex **2** (λ_{max} = 379 nm) to **3** (λ_{max} = 415 nm). As shown in Fig. 2, there is a weak absorption band at 488 nm with a low ε value for complex **3a**; we tentatively assign this peak to a ^{3}MLCT $^3[Pt \longrightarrow \pi^*(ppy)]$ transition. A similar ^{3}MLCT transition at 465 nm has been reported for $[Pt(^tBu_3terpy)Cl]^+$ ($^tBu_3terpy$ = 4,4′,4″-tri-*tert*-butyl-2,2′ : 6′,2″-terpyridine) by Che and co-workers.[6e]

In a 4 : 1 (v/v) methanol–ethanol glassy matrix at 77 K all the complexes are emissive with well resolved vibronic peaks. The lifetimes of the glassy emission measured at each vibronic peak maximum are the same indicating that these peaks originate from the same electronic state. The vibrational progressions ranging from 1000 to 1600 cm^{-1} are close to the C=C stretching frequencies of the cyclometalated diimine ligands. The vibrational satellite structure combined with the long emission lifetimes (18–24 μs) at 77 K for all the complexes suggests that their lowest excited states can be assigned to the ^{3}MLCT or ^{3}LC (ligand centered) state.

Photoluminescence of complexes **2a** and **2b** is too weak to be detected in CH_2Cl_2 solution, and **2b** shows a weak emission in CH_3CN. At room temperature, **3a** and **3b** show a strong broad emission in both CH_2Cl_2 and CH_3CN solutions, with their emission lifetimes significantly smaller than those measured in MeOH–EtOH glassy solution at 77 K. We assign the solution emission of complex **3** to be predominantly ^{3}MLCT since the emission spectra are significantly red-shifted (*ca.* 1600 cm^{-1}) as compared with that of $[Pt(ppy)_2(CH_2Cl)Cl]$, for which the lowest excited state is a ^{3}LC state localized on the ppy ligands,[21] and the radiative rate constants, 10^4 s^{-1} (Table 2), are typical of spin-forbidden MLCT excited states[22] and larger than that of *ca.* 10^3 s^{-1} for spin-forbidden LC excited states of platinum(II) complexes. As with other MLCT emissions, the temperature effect on the ^{3}MLCT emission lifetimes of complexes **3a** and **3b** (Table 2) is related to an upper-lying LF excited state, which can easily be populated by thermal activation, and provides fast deactivation pathways *via* molecular distortion.[5] Replacement of chloride by alkoxide would increase the energy gap between the emitting ^{3}MLCT and the upper-lying LF excited state, and decrease the non-radiative decay of the former. This explains why **3a** and **3b** are emissive in fluid solution at room temperature whereas **2a** and **2b** are weakly or non-emissive.

Conclusions

A series of cyclometalated platinum(II) complexes containing carbohydrate phosphine ligands have been prepared and characterized, and their absorption spectra and luminescence properties investigated. Data from absorption and emission spectra suggest that the emitting states of **3** are $[d_{Pt} \longrightarrow \pi^*_{ppy}]$ MLCT in nature. Replacement of chloride by alkoxide and the formation of a five-membered chelate ring increase both the energy gap between the emitting and the upper-lying LF excited state and the molecular rigidity of the auxiliary phosphine ligand.

As a result, the alkoxoplatinum(II) complexes **3a** and **3b** are strongly emissive with long-lived ^{3}MLCT excited states in solution at room temperature.

Experimental

Spectroscopic procedure

Infrared spectra were recorded with KBr disks on a Bio-Rad FTS 165 FT-IR spectrometer, fast atom bombardment (FAB) mass spectra obtained on a Finnigan Mat 95 mass spectrometer. Elemental analyses were performed by Butterworth Laboratory, UK. NMR spectra were recorded in $CDCl_3$ on a Bruker DRX 300 or 500 MHz FT-NMR spectrometer with TMS for ^{1}H and ^{13}C and external 85% H_3PO_4 for ^{31}P as standards. UV-vis absorption spectra were measured on a Milton Roy Spectronic 3000 diode-array spectrophotometer.

Emission spectra and lifetimes

Steady-state emission was recorded on a SPEX 1681 FLOUROLOG-2 series F111AI spectrophotometer and corrected for monochromator and photomultiplier efficiency and xenon lamp stability. Emission quantum yields were determined relative to quinine sulfate in 2.0 M sulfuric acid at low concentrations ($\varphi_{em} = 0.546$) or $[Ru(bpy)_3]^{2+}$ ($\varphi_{em} = 0.042$).[23] Low-temperature (77 K) emission spectra for glass and solid-state samples were recorded in a 5 mm diameter quartz tube placed inside a liquid nitrogen Dewar equipped with quartz windows. Emission lifetimes were measured with a Quanta Ray DCR-3 pulsed Nd:YAG laser system (pulse output 355 nm, 8 ns). The emission signals were detected by a Hamamatsu R928 photomultiplier tube and recorded on a Tektronix model 2430 digital oscilloscope.

Materials

Analytical grade solvents were used without further purification. Methyl 4,6-*O*-benzylidene-2-deoxy-2-(diphenylphosphino)-α-D-altropyranoside (2-Hmbpa), and methyl 4,6-*O*-benzylidene-3-deoxy-3-(diphenylphosphino)-α-D-altropyranoside (3-Hmbpa) were prepared by the literature methods.[13a] Sodium methoxide was prepared by dissolving sodium metal in dry methanol and then evaporating the solvent and drying under reduced pressure. All manipulations concerning phosphines were carried out under an argon atmosphere using standard Schlenk techniques.

Preparation of complexes

[Pt(ppy)Cl]$_2$ 1 was prepared by a modification of the literature method.[12a] To a suspension of $PtCl_2$ (2.62 g, 9.8 mmol) in glycerol (15 cm^3) was added the ligand Hppy (1.84 g, 11.9 mmol) in a round-bottom flask. The mixture was stirred vigorously and heated at 150 °C for three hours in the air. After cooling to room temperature, hydrochloric acid (1 M, 30 cm^3) was added and the reaction mixture stirred for 15 minutes. The precipitate was collected, washed with dichloromethane and dried in air (2.9 g, 77%). The product **1** was purified by the literature method (2.3 g, 61%).[12a]

***cis*-[Pt(ppy)(2-Hmbpa)Cl] 2a.** A suspension of $[Pt(ppy)Cl]_2$ (384 mg, 0.5 mmol) in dichloromethane (20 cm^3) was mixed with the ligand 2-Hmbpa (450 mg, 1.0 mmol) in dichloromethane (10 cm^3) and stirred until all the solid had dissolved. Removal of the solvent followed by addition of *n*-hexane gave complex **2a** in nearly quantitative yield. Found: C, 53.34; H, 4.40; N, 1.47%. Calc. for $C_{37}H_{35}ClNO_5PPt$: C, 53.21; H, 4.22; N, 1.68%. IR (cm^{-1}): *ν*(OH), 3508w; *ν*(C–H), 3050w, 2971w, 2930w; 2832w; *ν*(C=N, C=C), 1654m, 1607s, 1486s, 1438s; *ν*(C–O), 1123s, 1100s, 1048s. ^{1}H NMR (*δ*): 9.85–6.64 [m, aryl H], 5.17 [d, 1 H, H(1), $^3J_{PH}$ = 8.9], 4.82 [s, 1 H, H(7)], 4.68 [dt, 1 H, H(3), 8.5, 4.0 Hz], 4.43 [d, 1 H, H(2), $^2J_{PH}$ = 16.2], 4.12 [m, 1 H, H(5)], 4.10 [m, 1 H, H(6)], 3.26 [s, 3 H, CH_3], 3.17 [d, 1 H, OH, *J* 4.3 Hz], 3.10 [m, 1 H, H(6′)] and 2.10 [m, 1 H, H(4)]. ^{13}C NMR (*δ*): 166–118 [aryl C], 101.9 [C(7)], 99.0 [C(1), $^2J_{PC}$ = 17.4], 76.1 [C(4)], 69.4 [C(6)], 65.7 [C(3), $^2J_{PC}$ = 6.2 Hz], 56.9 [C(5)], 55.7 [CH_3] and 44.7 [C(2), $^1J_{PC}$ = 36.2]. ^{31}P NMR (*δ*): 16.5 ($^1J_{PtP}$ = 4297 Hz). MS (FAB, %): *m*/*z* 835 ($M^+ + 1$, 2), 819 ($M^+ - Me$, 1), 799 ($M^+ - Cl$, 100), 781 (($M^+ - Cl - H_2O$, 2) and 767 ($M^+ - Cl - MeOH$, 45).

***cis*-[Pt(ppy)(3-Hmbpa)Cl] 2b.** The procedure was similar to that for complex **2a**, except 3-Hmbpa was used. Found: C, 53.38; H, 4.32; N, 1.55%. Calc. for $C_{37}H_{35}ClNO_5PPt$: C, 53.21; H, 4.22; N, 1.68%. IR (cm^{-1}): *ν*(OH), 3450w; *ν*(C–H), 3058w, 2926w, 2855w; *ν*(C=N, C=C), 1655m, 1607m, 1561s, 1509s 1481s; *ν*(C–O), 1111s, 1068s, 1012s. ^{1}H NMR (*δ*): 9.79–6.51 [m, aryl H], 5.32 [s, 1 H, H(7)], 5.03 [dd, 1 H, H(2), $^3J_{PH}$ = 8.0, 5.1], 4.72 [m, 1 H, H(3), $^2J_{PH}$ = 14.2, 8.3, 1.5], 4.58 [s, 1 H, H(1)], 4.41 [dt, 1 H, H(4), $^3J_{PH}$ = 22.2, 8.9], 4.03 [d, 1 H, OH, *J* 5.1], 4.01 [m, 1 H, H(6)], 3.54 [t, 1 H, H(6′), *J* 10.2], 3.05 [m, 1 H, H(5), *J* 10.2, 8.9, 5.1 Hz] and 2.84 [s, 3 H, CH_3]. ^{13}C NMR (*δ*):166–118 [aryl C], 101.4 [C(7)], 100.8 [C(1), $^3J_{PC}$ = 3.1], 77.6 [C(4), $^2J_{PC}$ = 8.3], 71.5 [C(2), $^2J_{PC}$ = 10.4], 69.6 [C(6)], 58.3 [C(5)], 53.5 [CH_3] and 42.9 [C(3), $^1J_{PC}$ = 32.2 Hz]. ^{31}P NMR (*δ*): 16.8 ($^1J_{PtP}$ = 4423 Hz). MS (FAB, %): *m*/*z* 835 ($M^+ + 1$, 2), 816 ($M^+ - H_2O$, 1), 799 ($M^+ - Cl$, 100), 781 (($M^+ - Cl - H_2O$, 18) and 767 ($M^+ - Cl - MeOH$, 4).

***trans*-[Pt(ppy)(2-mbpa)] 3a.** A solution of complex **2a** (167 mg, 0.2 mmol) in dichloromethane (20 cm^3) was treated with an excess of NaOMe (27 mg, 0.5 mmol) in methanol (20 cm^3). The resulting solution was stirred for 3 hours at room temperature. The solvent was evaporated under reduced pressure. The residue was dissolved in dichloromethane (50 cm^3) and washed with water (20 cm^3 × 3); the dichloromethane solution was then dried over $MgSO_4$, filtered, and concentrated to *ca.* 5 cm^3. The product **3a** was precipitated by addition of *n*-hexane. Yield: 136 mg, 85%. Found: C, 55.49; H, 4.13; N, 1.65%. Calc. for $C_{37}H_{34}NO_5PPt$: C, 55.64; H, 4.29; N, 1.75%. IR (cm^{-1}): *ν*(C–H), 3054w, 2967w, 2923w, 2855w; *ν*(C=N, C=C), 1654m, 1606s, 1561m, 1483s, 1438s; *ν*(C–O), 1105s, 1078s, 1049s. ^{1}H NMR (*δ*): 9.12–6.61 [m, aryl H], 5.60 [s, 1 H, H(7)], 4.46 [m, 1 H, H(3), *J* 12.0, 9.5, 8.3], 4.43 [m, 1 H, H(1), *J* 9.5, 5.6], 4.36 [dd, 1 H, H(6), *J* 9.8, 4.7], 4.23 [m, 1 H, H(5), *J* 9.5, 4.7], 3.87 [t, 1 H, H(4), *J* 9.5, 5.6], 3.66 [t, 1 H, H(6′), *J* 9.8 Hz], 3.27 [m, 1 H, H(2)] and 3.20 [s, 3 H, CH_3]. ^{13}C NMR (*δ*): 166–118 [aryl C], 103.0 [C(7)], 100.1 [C(1), $^2J_{PC}$ = 4.2], 80.8 [C(4), $^3J_{PC}$ = 16.6], 76.1 [C(3)], 69.4 [C(6)], 65.7 [C(5)], 56.9 [CH_3] and 52.6 [C(2), $^1J_{PC}$ = 38.5 Hz]. ^{31}P NMR (*δ*): 35.0 ($^1J_{PtP}$ = 4375 Hz). MS (FAB, %): *m*/*z* 815 ($M^+ + H_2O - 1$, 3), 799 ($M^+ + 1$, 100), 782 ($M^+ - CH_4$, 1), 767 ($M^+ - MeO\cdot$, 5), 591 (30), 534 (22) and 154 (47).

***trans*-[Pt(ppy)(3-mbpa)] 3b.** The procedure was similar to that for complex **3a**, except **2b** was used. Yield: 137 mg, 86%. Found: C, 55.61; H, 4.26; N, 1.69%. Calc. for $C_{37}H_{34}NO_5PPt$: C, 55.64; H, 4.29; N, 1.75%. IR (cm^{-1}): *ν*(C–H), 3058w, 2967w, 2882w, 2810w; *ν*(C=N, C=C), 1604m, 1483s, 1437m; *ν*(C–O), 1101m, 1059s, 1028m. ^{1}H NMR (*δ*): 9.20–6.60 [m, aryl H], 5.41 [s, 1 H, H(7)], 4.70 [m, 2 H, H(1), H(2)], 4.30 [dd, 1 H, H(6), *J* 10.2, 4.6], 4.15 [m, 1 H, H(4), *J* 10.0, 9.8, 5.8], 3.91 [m, 1 H, H(5), *J* 9.6, 9.3, 4.4], 3.61 [t, 1 H, H(6′), *J* 10.0 Hz], 3.60 [s, 3 H, CH_3] and 3.00 [m, 1 H, H(3)]. ^{13}C NMR (*δ*): 166–118 [aryl C], 108.8 [C(1), $^3J_{PC}$ = 19.7], 101.8 [C(7)], 77.2 [C(4)], 76.1 [C(2), $^2J_{PC}$ = 5.2], 70.3 [C(6)], 63.9 [C(5)], 53.5 [CH_3] and 53.4 [C(3), $^1J_{PC}$ = 34.3 Hz]. ^{31}P NMR (*δ*): 36.1 ($^1J_{PtP}$ = 4276 Hz). MS (FAB, %): *m*/*z* 815 ($M^+ + H_2O - 1$, 2), 799 ($M^+ + 1$, 97), 782 ($M^+ - CH_4$, 17), 767 ($M^+ - MeO\cdot$, 10), 631 (10), 604 (58), 576 (42), 534 (22) and 154 (100).

Table 3 Crystallographic data, collection, and refinement details for complex **3b**

Formula	$C_{37}H_{34}NO_5PPt$
Formula weight	798.71
Crystal system	Orthorhombic
Space group	$P2_12_12_1$
a/Å	9.5498(1)
b/Å	9.5847(1)
c/Å	34.8584(4)
V/Å^3	3190.66(6)
Z	4
μ(Mo-Kα)/cm^{-1}	44.93
T/K	295
Reflections measured	24911
Observed reflections ($I \geq 2\sigma(I)$)	7327
Refined parameters	407
R, R_w	0.031, 0.067

Structure determination

A suitable single crystal of complex **3b** was mounted on a glass fiber tip and then onto a goniometer head. The details of the crystal parameters and data collection and refinement procedure are listed in Table 3. The X-ray diffraction data were collected on a Siemens SMART CCD four-circle area detector using graphite-monochromatized Mo-Kα radiation ($\lambda = 0.71073$ Å). Unit cell parameters and an orientation matrix were obtained from least-squares refinement on 8912 reflections. The intensity data were collected using the ω-scan technique within the limits $1 < \theta < 27.5°$. The collected frames were processed by SAINT software for integration; an absorption correction was applied together with merging (SADABS).[24]

The structure was solved by direct methods (SIR 92)[25] and Fourier difference methods and subsequently refined by full-matrix least squares against F_o^2 using the program SHELXTL 93[26] on a Silicon Graphics Indigo computer. Atomic scattering factors and anomalous dispersion corrections were taken from the internal library of SHELXL 97. All non-hydrogen atoms were given anisotropic displacement parameters.

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