

Luminescent Platinum(II) Complexes Containing Cyclometallated Diaryl Ketimine Ligands: Synthesis, Photophysical and Computational Properties

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A new series of platinum(II) complexes containing cyclometallated diaryl ketimine ligands has been synthesised. The route involves reaction of diaryl ketimines with $K[PtCl_3(dmsO)]$ to obtain *trans*- $[PtCl_2(imine)(dmsO)]$ species, which underwent cyclometallation upon heating in toluene to give $[PtCl(Ar'(ArC=NH))(dmsO)]$ complexes **12b–17b**. *N*-Hydroxy and *N*-phenyl analogues **18b** and **21** were also synthesised. In complexes **19** and **20** the auxiliary chlorido and dmsO ligands were replaced by an acetylacetonato ligand. The photophysical properties of the cyclometallated complexes are reported. The emission bands at $\lambda_{max} \approx 450$ and 550 nm are assigned to mixed-ligand and MLCT states having significant singlet and triplet character, respectively. By

varying the structure of the aromatic ligand the efficiency of phosphorescence can be increased to 4.3 % for **15b** ($Ar' = 1$ -naphthyl). Theoretical calculations show that the low-energy transitions in all the cyclometallated systems involve mainly the frontier orbitals, HOMO and LUMO. These are mixed chlorido–metal–ligand to largely $\pi^* - C=N$ transitions. Most of the observed phosphorescence data can be explained by the geometric change on going from the S_0 to the T_1 states. An organic light-emitting device has been fabricated by using complex **15b** as the emissive dopant in a poly(vinylcarbazole) host. Broad electroluminescence spanning the range 500–750 nm was observed.

Introduction

Luminescent transition metal complexes enjoy a diverse range of applications, e.g. sensors, photocatalysis, nonlinear optical materials for data storage and organic light-emitting diodes (OLEDs).^[1,2] In this context, platinum complexes have attracted considerable interest due to their efficient room-temperature phosphorescence, short emission lifetimes and broad emission range.^[3] For example, platinum(II)–porphyrins are highly luminescent with high quantum yields.^[4,5] Room-temperature phosphorescence can be achieved from cyclometallated Pt^{II} complexes due to radiative decay from either excited $\pi-\pi^*$ or MLCT states. Ligands such as 2-phenylpyridine and its analogues have been extensively studied for this purpose (Figure 1). For specific examples, complexes **1**,^[6] **2**,^[7] **3**,^[8] **4**^[9] and **5**^[10] are representative. The emission profile is largely dependent on the substituents on the cyclometallated ligands and also the type of coordinating ligand, e.g. $[N^{\wedge}C^{\wedge}N]$ ^[11–15] $[N^{\wedge}N^{\wedge}C]$ ^[16–19]

or $[C^{\wedge}N^{\wedge}C]$ ^[20] coordination mode. The phosphorescence quantum yields of $[N^{\wedge}N^{\wedge}C]$ and $[C^{\wedge}N^{\wedge}C]$ platinum(II) systems tend to be much lower than those of $[N^{\wedge}C^{\wedge}N]$ -based systems.^[11,15] Whereas a number of such cycloplatinated ligands have been studied in reference to their luminescence properties, there have been few reports of other types of ligands.

Our aim was an integrated, synthetic, photophysical and computational study of a new family of platinum(II) complexes containing cyclometallated diaryl ketimine ligands where emission properties might be tuned by varying the imine ligand structure. It is worth noting that, while several luminescent platinum complexes with aldimines as ligands have been reported,^[21] complexes of ketimines are very rare and appear to be restricted to benzophenone imine. At the outset of our work Scaffidi-Domianello et al. reported (benzophenone imine)platinum(II) compounds, *trans*- $[PtCl_2(Ph_2C=NH)(RR'SO)]$ containing a range of different dialkyl(aryl) sulfoxide ligands.^[22] The solution photoluminescence quantum yields of the derived cyclometallated complexes were very low, the maximum being $\Phi_{em} = 0.019$. Solid-state quantum yields and device fabrication studies were not reported, and no other imine derivatives were studied in this work. Our series of complexes described herein comprise new structural modifications. The diaryl ketimine ligands are systematically varied, and in two cases

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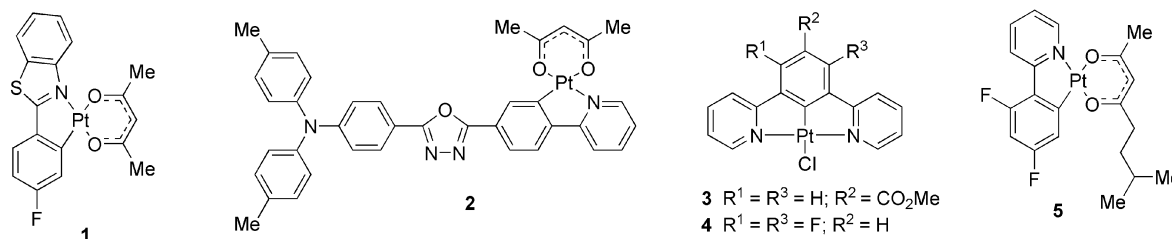


Figure 1. Selection of cyclometallated Pt^{II} complexes of (hetero)arylpuridine ligands.

substituents are attached to the imine nitrogen atom. Solution and solid-state photophysical properties of the cyclometallated complexes are reported along with theoretical calculations to support the experimental observations.

Results and Discussion

Synthesis of Cyclometallated Diaryl Ketimine Platinum(II) Complexes

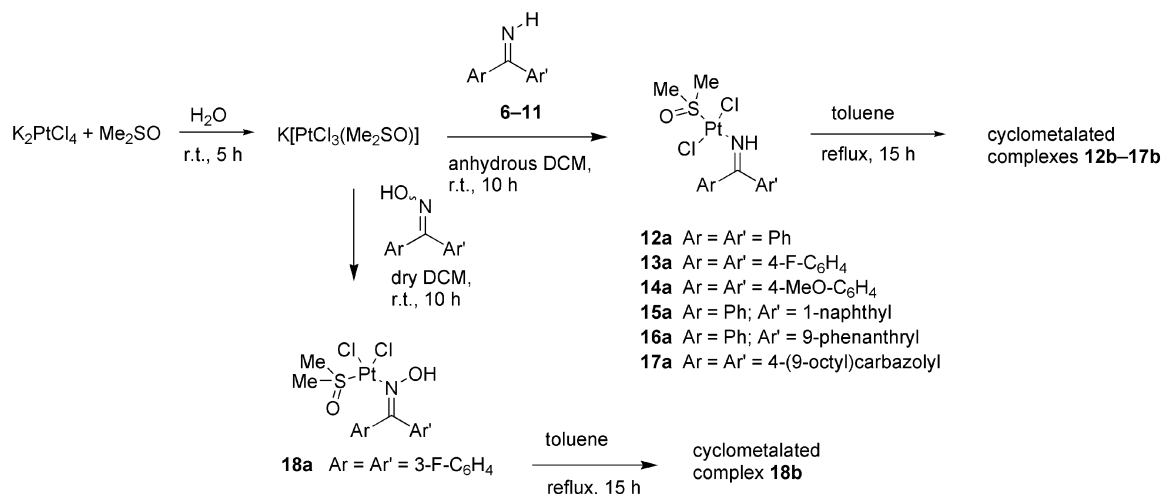
A series of *N*-unsubstituted diaryl ketimines **6–11** were synthesised either by: (i) thermal decomposition of oximes^[23] or (ii) by Grignard reaction of a nitrile.^[24] Different substituents were attached to the aryl rings [electron-withdrawing fluoro (**7**), electron-releasing methoxy (**8**), π -extended aryl (**9–11**)] to study the effect of these electronic and steric modifications on the cyclometallation reactivity and the subsequent photophysical properties of the complexes. The diaryl ketimines were all used as prepared, without purification, due to their instability.

The imines were treated with K[PtCl₃(dmsO)] obtained *in situ* by reaction of K₂PtCl₄ and dmsO (Scheme 1). The major products obtained were the *trans*-[PtCl₂(imine)(dmsO)] complexes **12a–17a** in variable yields. Small amounts of *cis*-[PtCl₂(imine)(dmsO)] (12–15%), *cis*-[PtCl₂(imine)₂] (6–8%) and μ -[PtCl(imine)(dmsO)] complexes were also detected in the NMR spectra of the crude product mixture. The yield for this step of the reaction sequence was low due to the instability of the imines **6–11** and the forma-

tion of side products. The purified complexes **12a–17a** were then subjected to cyclometallation by heating in toluene for 15 h. The corresponding complexes **12b–17b** were isolated in low yields and were observed to be luminescent on TLC (SiO₂-coated plate) under 365 nm irradiation and were notably more soluble in common organic solvents compared to their precursors **12a–17a**. The low yield for the cyclometallation step was due to the instability of the complexes **12b–17b** in the reaction mixture; after isolation and purification, **12b–17b** were stable to storage as solids.

In the case of 3,3'-difluorobenzophenone oxime, despite several attempts, vacuum pyrolysis did not yield the corresponding imine. Ryabov et al. have reported orthoplatinations of aryl oximes using dichloridobis(sulfoxide/sulfide)-platinum(II) complexes in moderate yields, although no photophysical properties were reported.^[25] We therefore proceeded to obtain compound **18a** and the derived cyclometallated product **18b**. The structure of *cis*-PtCl₂(oxime)(dmsO) complex **18a** was confirmed by X-ray analysis (see below). Complex **18b**, upon irradiation with 365 nm light, showed considerably weaker luminescence than complexes **12b–17b**.

Replacement of the auxiliary chlorido and dmsO ligands with a bidentate acetylacetonato ligand considerably improved the stability of the products. Complexes **19** and **20** were prepared in good yields in a one-pot procedure by treating *cis*-[PtCl₂(dmsO)₂]^[26] with the respective imines (**6** and **10**) in dry toluene followed by addition of acetylacetonate and sodium carbonate (Scheme 2). In contrast to



Scheme 1. Synthetic routes to cyclometallated complexes **12b–18b**. The structures of **12b–18b** are shown in Figure 2.

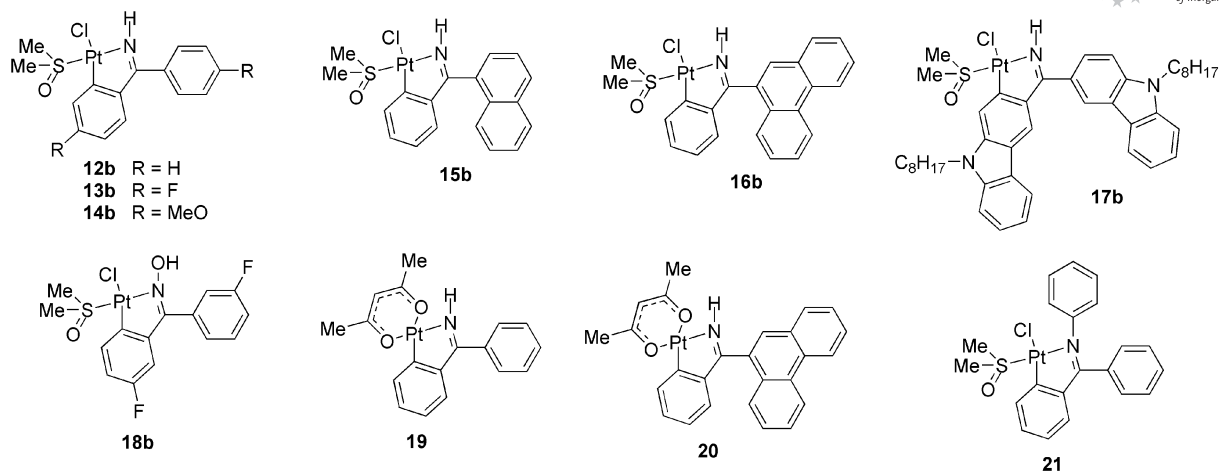
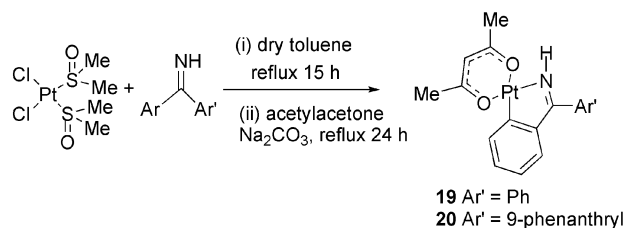


Figure 2. Structures of the cyclometallated Pt complexes synthesised in the present study.

12b–18b, complexes **19** and **20** were stable to storage in solution (in chloroform, dichloromethane or toluene, no change was observed by ^1H NMR analysis after one week). One example of an *N*-phenyl-substituted ketimine complex **21** was prepared (see the Supporting Information). However, this complex did not show any phosphorescence, so *N*-substitution in this series was not explored further.



Scheme 2. Synthesis of complexes **19** and **20**.

The structures of the cyclometallated complexes synthesised in the study are shown in Figure 2. The precursor complexes **12a–18a** and the cyclometallated products **12b–18b**, **19–21** were characterised by ^1H and ^{13}C NMR spectroscopy, mass spectrometry (ES $^+$ mode), IR spectroscopy and – where possible – also by CHN elemental analysis. In the latter series the aromatic proton of the cyclometallated ring displays characteristic satellites from $^3J_{\text{Pt,H}}$ coupling to the ^{195}Pt nucleus. The methyl signal of the dmsf ligand is also shifted downfield in the series **12b–18b** ($\Delta\delta \approx 0.1$ – 0.3 ppm) with clearly resolved satellites from $^3J_{\text{Pt,Me}}$ with $J \approx 21$ Hz. The IR stretching frequency of the C=N bond generally decreases by ca. 10 – 20 cm^{-1} in **12b–18b** compared to **12a–18a**, and the peak due to the coordinated dmsf is seen at ca. 1120 – 1130 cm^{-1} , shifted from that of free dmsf (1037 – 1124 cm^{-1}) and consistent with coordination to the platinum atom through the sulfur atom.^[27]

It is interesting to note that cyclometallation of the unsymmetrical diaryl ketimine complexes **15a** and **16a** occurred exclusively onto the phenyl ring and not the naphthyl or phenanthryl rings to yield **15b** and **16b**, respectively, as proved by COSY NMR spectroscopy (see Figure S2 in

the Supporting Information). No isomeric product was detected in the ^1H NMR analysis of the crude reaction mixtures.

X-ray Crystal Structure of **18a**

The asymmetric unit of **18a** comprises two molecules of similar conformation (Figure 3), related by a pseudo-glide plane $a(x,y,1/4)$ and linked by N–OH $\cdots$ O=S hydrogen bonds into an infinite chain parallel to the crystallographic x axis. The Pt atom has a *cis*-square coordination with a small tetrahedral distortion (5.4° twist between the PtCl $_2$ and PtSN planes). The bond lengths are usual for *cis*-R $_2$ (O)SPt(N-ligand)Cl $_2$ complexes,^[28] although it is noteworthy that PtCl $_2$ (SOMe $_2$)(HON=CPhMe), close to **18a** in composition, has a *trans*-square structure.^[25b] There is a 7.5° twist around the N=C(1) double bond of **18a**; the bonding plane of the N atom [N,O(1),Cl(1),Pt] is inclined by ca. 70° to the

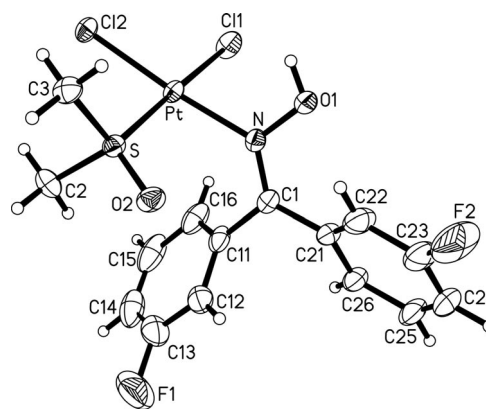


Figure 3. X-ray molecular structure of **18a**, showing the atomic displacement ellipsoids at 50% probability level. Selected bond lengths (for two independent molecules) [Å]: Pt–Cl(1) 2.314(1) & 2.315(1), Pt–Cl(2) 2.286(1) & 2.293(1), Pt–S 2.212(1) & 2.215(1), Pt–N 2.015(3) & 2.017(3), N=C(1) 1.295(5) & 1.296(5), N–O(1) 1.389(4) & 1.384(4).

metal coordinating plane (PtCl_2SN), whereas the benzene rings are inclined to the plane of C(1) by 40–50° in a propeller-like fashion.

Photophysical Properties

Figures 4 and 5 depict the PL spectra of the complexes shown in Figure 2. Complexes **12b**, **13b** and **14b** (Figure 4) have two broad bands each showing vibronic features, one band centred at ca. 450 nm and the other at ca. 550 nm, the latter one blueshifted by ca. 20 nm for complex **13b**.

We observed that bubbling nitrogen through the solution affects only the 550 nm band, whereas the other band does not change.

The other notable feature of the broad bands centred at ca. 550 nm is the very long lifetime even in a non-degassed toluene solution. The lifetime data for complex **12b** (144 ns) is shown in Figure S3 in the Supporting Information. This contrasts with the sub-nanosecond lifetime of the bands centred at ca. 450 nm. Due to technical limitations, our lifetime-measurement system could not measure such short lifetimes precisely. Thus, there is clear indication that the bands at ca. 450 nm are of singlet character since the lifetimes are very short and are not affected by oxygen, whereas the bands at ca. 550 nm are of triplet character since their lifetimes are much longer than that of conventional fluorophores and the 550 nm bands are quenched by oxygen (see Figure S4 in the Supporting Information).

The bands centred at ca. 450 nm (Figure 4) are not due to Raman scattering (there is a Raman scattering peak in toluene at ca. 455 nm when excited at 400 nm). Firstly, we depict the spectra of highly concentrated (10^{-3} M) solutions in Figure 4 in order to increase the luminescence emission. This is valid as we did not observe any significant luminescence spectral shape changes with an increase of concentration from 10^{-5} to 10^{-3} M. Furthermore, the band position does not change when the excitation wavelength is changed (Figure S6 in Supporting Information). This would not be the case for Raman bands. The same argument, based on changing the excitation wavelength, is valid for **17b** (Figures 5 and S7 in Supporting Information). For complexes **19** and **20** (Figure 5b) peaks at 456 nm are indeed due to Raman scattering as we observe a shift with the excitation wavelength. However, there is no singlet character emission at ca. 450 nm for these complexes. In complex **18b** the peak at 455 nm is additionally a Raman peak, but unlike in **19** and **20** the singlet character emission at ca. 450 nm is present. This is clearly demonstrated in Figure S8 in the Supporting Information. We could not conceal the Raman peaks in **18b**, **19** and **20** by increasing the concentration (as was done with the complexes in Figure 4), because they exhibited very efficient concentration quenching, and high concentration solutions were very weakly emissive.

In addition, variable-temperature studies of complex **13b** were performed. The isoemissive point, which is clearly present (Figure 6), shows that both species are interdepen-

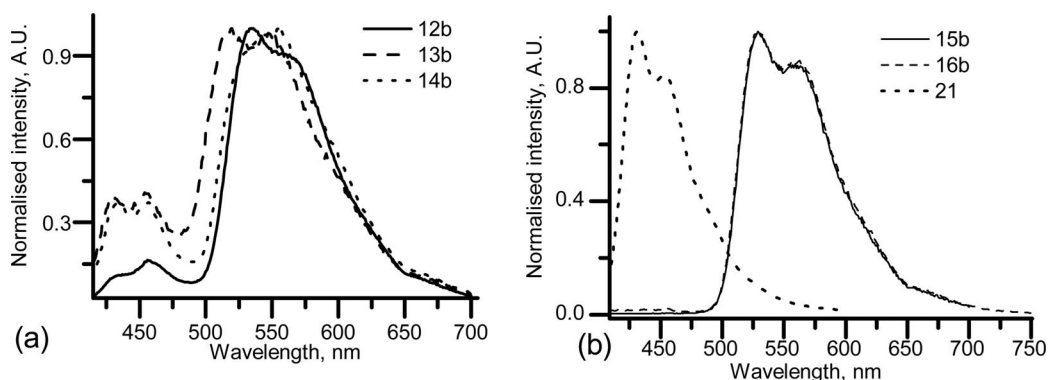


Figure 4. Photoluminescence spectra of complexes **12b**, **13b**, **14b** (a) and **15b**, **16b**, **21** (b) in 10^{-3} M toluene solution excited at 400 nm.

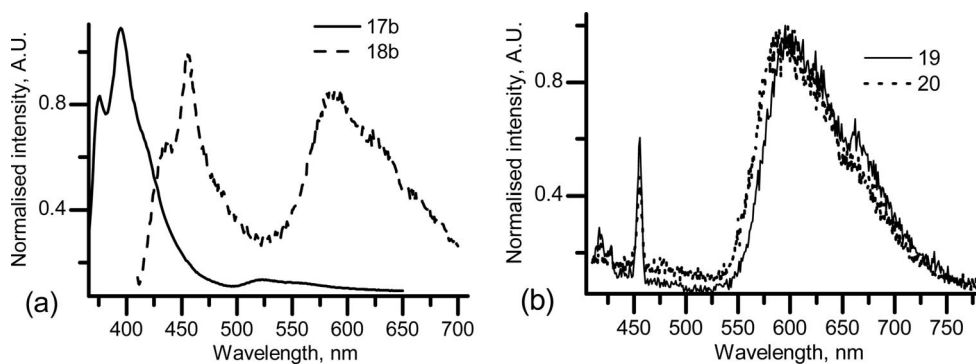


Figure 5. Photoluminescence spectra of complexes **17b**, **18b** (a) and **19**, **20** (b) in 10^{-5} M toluene solution. Excited at 400 nm (except **17b**, at 355 nm).

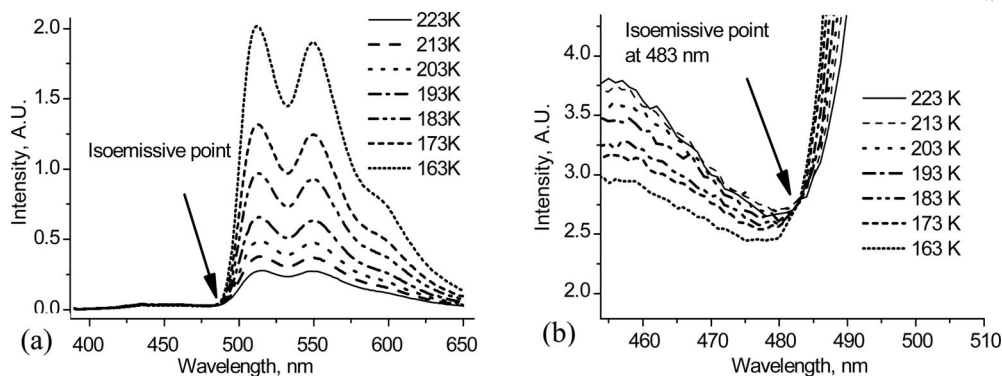


Figure 6. Photoluminescence spectra of complex **13b**: (a) in non-degassed 10^{-3} M toluene solution over the temperature range between 163 and 223 K, excited at 385 nm, and (b) expansion to show the isoemissive point at 483 nm.

Table 1. Photophysical data.

Complex	Fluorescence maxima [nm]	Phosphorescence maxima [nm]	Phosphorescence quantum yield Φ_{PL} [%]
12b	434, 457	534, 567	0.007 ^[d]
13b	431, 455	518, 549	<0.007 ^[e]
14b	433, 455	531, 553	<0.007 ^[e]
15b	— ^[a]	529, 562	4.3 ^[c]
16b	— ^[a]	529, 562	3.0 ^[c]
17b	375, 395	525, 556	<0.007 ^[e]
18b	— ^[b]	588	<0.007 ^[e]
19	— ^[a]	598	<0.007 ^[e]
20	— ^[a]	591	<0.007 ^[e]
21	431, 454	— ^[a]	0

[a] No emission observed. [b] Not possible to determine due to Raman peak of toluene at 455 nm. [c] Determined by using 9,10-diphenylanthracene as a standard^[30] for the lower-energy band from 483 to 700 nm; errors $\pm 5\%$. [d] Taken from ref.^[22] [e] Emission was much less than that of compound **12b**.

dent on one another, i.e. in that temperature range species with triplet character increase at the expense of singlet-character species. Similar isoemissive-point observations have been reported in the literature.^[29]

Furthermore, the absorption band at ca. 400 nm (Figure S5 in the Supporting Information) can be assigned mixed-ligand and MLCT character based on theoretical calculations (see below) and similarities in the energy and intensity of MLCT transitions in other platinum complexes.^[22] The emission bands at $\lambda_{\text{max}} \approx 450$ and 550 nm are assigned to mixed-ligand and MLCT states having significant singlet and triplet character, respectively, in agreement with the theoretical calculations (see below).

Until now the reported quantum efficiencies of cyclometallated diaryl ketimine platinum(II) complexes have been very low.^[22] However, by varying the ligand structure we have succeeded in increasing the efficiency of phosphorescence almost 500-fold for **15b** and **16b** (Table 1) in comparison to that of the parent complex **12b**.^[22]

From these observations, we see that for systems with incomplete intersystem crossing (ISC), very poor total emission quantum yields are measured, whereas in the two complexes **15b** and **16b**, where no obvious fluorescence type emission is observed, there is a concomitant dramatic increase in total emission, which must all arise from phosphorescence. This implies that in this family of complexes there

is an efficient non-radiative singlet decay channel, which effectively quenches all the singlets and/or singlet-to-triplet harvesting,^[31] and only those states survive that cross to the triplet manifold.

Application in Organic Light-Emitting Devices

Preliminary experiments were performed to demonstrate the applicability of cyclometallated diaryl ketimine platinum(II) complexes as emitters in OLEDs. As complex **15b** showed the highest PL efficiency it was chosen as an emissive dopant in a poly(vinylcarbazole) (PVK) host. The device structure used was ITO/PEDOT-PSS/PVK:40% PBD:12% **15b**/Ba/Al. The turn-on voltage is ca. 8 V (Figure 7), which mostly depends not on the dopant but on the carrier injection barriers into PVK. The maximum external quantum efficiency of the devices was 0.25% with a maximum brightness of ca. 18 cd/m² (Figures S9 and S10 in the Supporting Information). Optimisation of the device architecture to enhance these values is beyond the scope of this study. It should be noted that the broad electroluminescence band spanning the 500–775 nm range (Figure 8) makes these complexes attractive candidates for white OLEDs.^[32] Comparison with the solid-state spectrum of the parent complex **12b** and the electroluminescence spectrum are shown in Figure S11 in the Supporting Information.

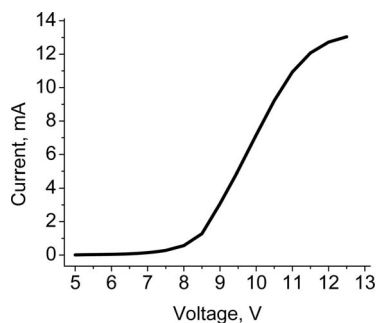


Figure 7. I/V characteristics for an OLED with complex **15b** as the emissive dopant.

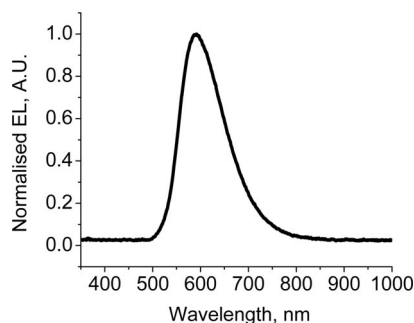


Figure 8. Electroluminescence (EL) spectrum of an OLED with complex **15b** as the emissive dopant.

Theoretical Calculations

Given the varied photophysical data obtained for the cyclometallated systems here, their geometries and electronic structures were investigated computationally. The optimised ground-state (S_0) geometry for **12b** at the B3LYP//LANL2DZ/6-311G** level of theory is in reasonable agreement with the experimentally (X-ray) determined geometry of **12b**.^[22] (See the Supporting Information for the computational and geometric details.) This level of theory was applied to calculations on all cyclometallated systems synthesised here.

The HOMO and LUMO for the S_0 geometry of **12b** are depicted in Figure 9. The HOMO is located on the Cl–Pt–C₆H₄ axis, whereas the LUMO is located mainly on the C=N bond. The HOMO contains 37% Pt character, whereas the LUMO has 8% Pt character. Thus, the ex-

pected lowest-energy transition (HOMO→LUMO) in the absorption spectrum of **12b** would be a mixed chlorido–metal–ligand to mainly π^* -C=N charge transfer. The frontier orbitals (HOMO and LUMO) for **13b–16b**, **19–21** are also of similar characteristics with HOMOs containing 34–38% Pt- d_{xz} character (Table 2; see Supporting Information for MO details). Whereas the LUMOs are similar, the HOMOs for **17b** and **18b** are different, and these compounds are discussed in detail later.

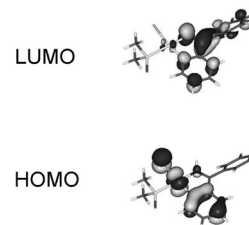


Figure 9. HOMO and LUMO for **12b** plotted at $0.04 \text{ (e/bohr}^3)^{1/2}$. These orbitals were similarly found for **13b–16b**, **19–21**.

TD-DFT data on the S_0 geometries of the cyclometallated complexes **12b–16b**, **19–21** show the lowest-energy transitions to be at 486–523 nm for $S_0 \rightarrow T_1$ and 401–434 nm for $S_0 \rightarrow S_1$ with low oscillation strengths. The latter values are in good agreement with the weak bands observed at 386–405 nm in the absorption spectra for six of the ten complexes (Figure S13 in the Supporting Information). We were not able to observe the expected very weak $S_0 \rightarrow T_1$ bands at around 500 nm here. The strong bands predicted at around 300 nm for these complexes correspond to the aryl- $\pi \rightarrow \pi^*$ -C=N, aryl- π^* transitions and are in agreement with intense bands observed elsewhere^[22] in the region of 300 nm for **12b** and related complexes.

As the HOMOs and LUMOs of **12b–16b** and **19–21** and their HOMO–LUMO energy gaps are similar, their emission data might have been expected to be similar. However, the emission data are different with both fluorescence and phosphorescence (dual emission) observed for **12b–14b**, strong phosphorescence for the fused ring systems (**15b** and **16b**) and strong fluorescence for the *N*-phenyl system **21**. Very weak luminescence was found for the acac systems, **19** and **20**. The HOMO–1 and LUMO+1 were therefore examined as they are expected to be involved in these emissions. Figure 10 shows these orbitals for **12b**, **15b**, **19**, **20**

Table 2. Orbital energies in eV and % Pt-MO compositions for frontier orbitals of complexes **12b–18b** and **19–21**.

	12b	13b	14b	15b	16b	17b	18b	19	20	21
LUMO+1	−1.09	−1.38	−0.97	−1.79	−1.78	−1.41	−1.42	−1.06	−1.55	−1.20
% Pt	16	3	4	2	2	1	37	2	3	33
LUMO	−2.37	−2.55	−2.04	−2.34	−2.34	−1.97	−2.39	−2.06	−2.06	−2.26
% Pt	8	8	8	8	8	8	8	8	7	7
HOMO	−6.02	−6.28	−5.84	−6.04	−6.09	−5.59	−6.19	−5.73	−5.73	−5.93
% Pt	37	37	38	37	35	19	27	34	34	37
HOMO−1	−6.65	−6.87	−6.13	−6.54	−6.46	−5.63	−6.89	−5.87	−5.85	−6.41
% Pt	83	63	10	3	1	3	17	41	40	17
HLG ^[a]	3.65	3.73	3.80	3.70	3.75	3.62	3.80	3.67	3.67	3.67

[a] HOMO–LUMO energy gap.

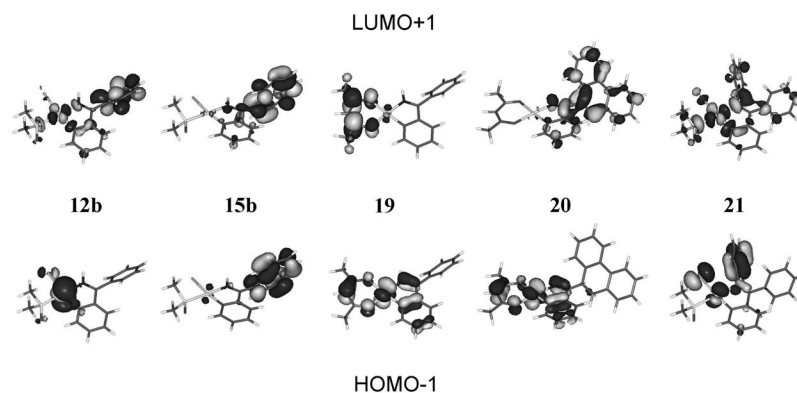


Figure 10. HOMO–1 and LUMO+1 plots for **12b**, **15b**, **19**, **20** and **21** at 0.04 (e/bohr³)^{1/2}.

and **21**. Clearly, these orbitals vary with significant metal character in the HOMO–1s for **12b**, **19** and **20** and in the LUMO+1 for **21**. The Pt-*d*_{xz} orbitals are found in the HOMO–1s for the acac complexes close in energies (differences of only 0.12–0.14 eV) with their HOMOs containing Pt-*d*_{yz} orbitals. Compound **12b**, on the other hand, has the Pt-*d*_{z²} orbital character in HOMO–1. The LUMO+1 of **21** contains substantial Pt*–*d*_{xy} orbital character.

Whereas the S₀→S₁ data from TD-DFT computations on S₀ geometries are in agreement with fluorescence data (S₀←S₁) for the acac systems **19** and **20**, the S₀→T₁ data do not tally with their observed phosphorescence (S₀←T₁) data. The S₁ geometries may, therefore, be similar to S₀ geometries, but the T₁ geometries may be significantly different in **19** and **20**. The excited triplet-state (T₁) geometries of all the systems were thus optimised to aid interpretation of the phosphorescence data. The optimised T₁ geometry of **12b** contains some significant geometrical changes compared to the S₀ geometry, notably the C=N bond length from

1.299 Å in S₀ to 1.378 Å in T₁ (see Figure S8 in the Supporting Information for details). Table 3 lists the C=N bond lengths for both geometries of all systems studied here. There are significantly longer C=N bonds in the T₁ geometries for **19–21** compared to those for **12b–16b**.

The energies of the optimised T₁ geometries at S₀ single-point energy calculations [T₁(S₀)] indicate how different the T₁ geometries are compared to the S₀ geometries. The [T₁(S₀)] energies for **19–21** are large (0.47–0.54 eV) with respect to **12b–16b** (0.33–0.37 eV). The well-known efficient emitter Ir(ppy)₃ has a [T₁(S₀)] value of only 0.22 eV^[33] reflecting little geometric change between these two states. Table 3 also lists the computed energy differences between S₀ and T₁ geometries (T₁ – S₀), which agree remarkably well with the observed phosphorescence data (Figure 11). The least successful fits involve **14b** and **18b**, where hydroxy and methoxy groups are present, and thus orientations of these groups are likely to have subtle effects on the energies of the geometries.

Table 3. Energies and C=N bond lengths for S₀ and T₁ optimised geometries and comparison of observed and computed photophysical data for complexes **12b–18b**, **19–21**.

	12b	13b	14b	15b	16b	17b	18b	19	20	21
S ₀ →T ₁ [eV] ^[a]	2.47	2.54	2.55	2.51	2.51	2.47	2.30	2.37	2.38	2.47
S ₀ →S ₁ [eV] ^[a]	2.90	3.00	3.09	2.96	2.97	2.92	3.07	2.85	2.88	2.95
T ₁ – S ₀ [eV] ^[b]	2.32	2.40	2.42	2.35	2.36	2.36	2.01	2.13	2.14	2.22
[T ₁ (S ₀)] [eV] ^[c]	0.37	0.36	0.33	0.35	0.33	0.26	0.65	0.51	0.47	0.54
S ₀ (C=N) [Å]	1.299	1.300	1.303	1.297	1.297	1.304	1.298	1.305	1.304	1.307
T ₁ (C=N) [Å]	1.378	1.391	1.398	1.374	1.372	1.382	1.438	1.428	1.429	1.432
Δ(C=N) [Å] ^[d]	0.079	0.091	0.095	0.077	0.075	0.078	0.140	0.123	0.125	0.125
S ₀ →T ₁ [nm] ^[a]	501	487	486	494	493	501	540	523	522	503
T ₁ – S ₀ [nm] ^[b]	534	512	517	525	525	525	617	582	582	558
S ₀ ←T ₁ phosphorescence ^[e]	534 (w)	518 (w)	531 (w)	529 (s)	529 (s)	525 (w) ^[f]	588 (vw)	598 (vw)	591 (vw)	— ^[g]
S ₀ →S ₁ [nm] ^[a]	427	413	401	419	417	425	400	434	430	421
S ₀ →S ₁ absorption ^[c,h]	400 (w)	386 (w)	— ^[i]	405 (w)	405 (w)	— ^[i]	— ^[i]	— ^[i]	400 (w)	386 (w)
S ₀ ←S ₁ fluorescence ^[e]	434 (w)	431 (w)	433 (w)	—	435 (vw)	375 (s) ^[f]	—	—	—	431 (s)

[a] From TD-DFT data on optimised S₀ geometries. [b] Difference between energies of optimised T₁ and S₀ geometries. [c] Difference between the energy of a single-point S₀ calculation on the optimised T₁ geometry and the energy of the optimised S₀ geometry. [d] Difference between C=N bond lengths of S₀ and T₁ geometries. [e] Observed data, the intensities listed (s = strong, w = weak, vw = very weak) are relative, excitation at 400 nm. [f] Excitation at 355 nm. [g] No emission observed. [h] The expected S₀→T₁ absorption bands were too weak to be observed. [i] Not recorded.

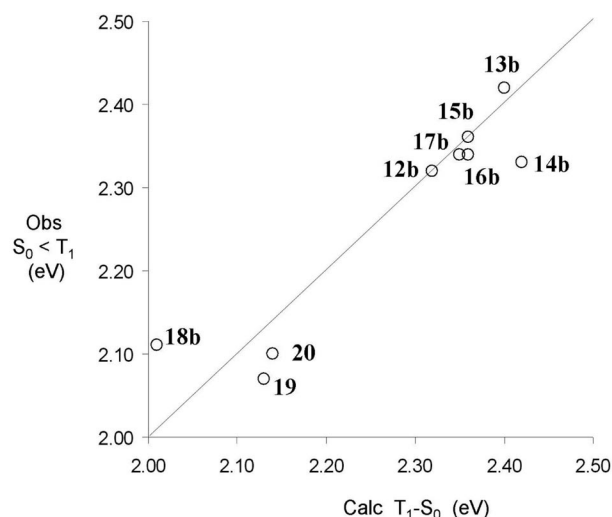


Figure 11. Correlation between observed phosphorescence data for **12b–18b**, **19** and **20** and the differences between computed total energies of optimised T_1 and S_0 geometries.

It is clear that the T_1 excited-state geometries of the acac complexes **19** and **20** are very different to the ground-state geometries, and thus the phosphorescence $S_0 \leftarrow T_1$ transitions are lower in energy than those of the related dmso complexes **12b** and **16b**, as observed experimentally. The energy-gap law predicts that the non-radiative decay rate constant increases with decreasing energy difference between the optimised T_1 and S_0 geometries.^[34]

The significantly different S_1 and T_1 geometries (assuming S_1 has a similar geometry to S_0) for the acac complexes **19** and **20** are responsible for the low phosphorescence observed for these complexes. The presence of unfavourable acac (26% in HOMO and 26–30% in HOMO–1) and metal character in the highest occupied orbitals are likely to be responsible for the low fluorescence observed for the acac complexes. Strong fluorescence is often associated with aryl- $\pi \rightarrow \pi^*$ transitions.

The *N*-phenyl system **21** also has a substantially different T_1 geometry. The absence of phosphorescence emission in **21**, where the maximum would be predicted to be at 558 nm, is most likely due to significantly different S_1 and T_1 geometries (assuming S_1 has a similar geometry to S_0). The unfavourable Pt(d) $\rightarrow$ Pt(d*) quenching of the radiative decay with the LUMO+1 as the Pt* orbital may also have a role in the lack of phosphorescence emission observed for **21**.^[3] The strong fluorescence observed for **21** (Figure 4) arises from *N*-phenyl π -orbital contributions (38% in HOMO–1) to the Pt, aryl- $\pi \leftarrow \pi^* \text{-C=N, aryl-}\pi^*$ transitions.

The strong phosphorescence observed for the fused-ring dmso complexes **15b** and **16b** is due to three highly favourable conditions. Firstly, the LUMO+1s and HOMO–1s consist of essentially the π^* (81–83%) and π (90–92%) orbitals of the naphthyl and anthracyl groups, respectively, with the LUMO+1s considerably close to the LUMOs in energies (0.55–0.56 eV). The second condition is the substantial heavy-metal character in the HOMOs promoting intersystem crossing (ISC) from singlet to triplet states. The

third factor is the relatively small geometric change observed between the S_0 and T_1 optimised geometries, promoting the radiative decay. Thus, from the phosphorescence band shapes observed for **15b** and **16b**, the transitions involved are likely to be a mixture of ^3LLT and $^3\text{MLCT}$ in character where the fused-ring π , π^* , Pt and $\pi^* \text{-C=N}$ orbitals are major contributors.

Both weak fluorescence and weak phosphorescence are observed for the parent dmso complex **12b** and the fluorine- and methoxy-substituted analogues, **13b** and **14b**, respectively. They have no such conditions that would either result in strong fluorescence (like **21**) or very weak luminescence (like **19** and **20**). The metal character in the HOMOs and T_1 geometries for **12b–14b** with the fused-ring systems (**15b** and **16b**) are similar. It is suggested that the weak dual emissions observed in **12b–14b** are due to the larger energy differences between the aryl- π^* LUMO+1 and HOMO orbitals in **12b–14b** (4.9 eV) compared to those in **15b** and **16b** (4.3 eV). The luminescence-band patterns observed for these systems indicate Pt, aryl- $\pi \leftarrow \pi^* \text{-C=N, aryl-}\pi^*$ transitions with LLT and MLCT character in both singlet and triplet states.

The frontier orbitals for **17b** and **18b** are shown in Figure 12. Methyl groups are used instead of octyl groups for **17b** to reduce the computational effort. The HOMOs have lower Pt character at 19% for **17b** and 27% for **18b** compared to other complexes discussed above. The carbazole ligands dominate the HOMO–1 (88% on cyclometallated carbazole ligand), HOMO (74% on cyclometallated carbazole ligand) and LUMO+1 (96% on second carbazole ligand) in **17b**. The much smaller heavy-metal contribution in **17b** (and thus little ISC promotion) accounts for very weak phosphorescence. The strong fluorescence in **17b** effectively arises from carbazolyl- $\pi \leftarrow \pi^* \text{-C=N, carbazolyl-}\pi^*$ transitions.

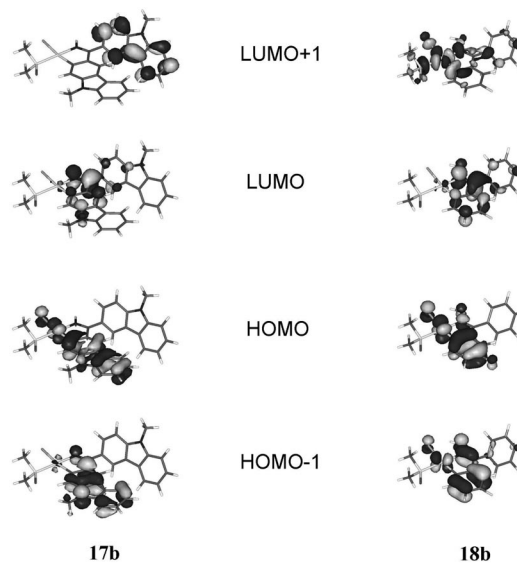


Figure 12. Frontier orbitals for **17b** and **18b** plotted at 0.04 (e/bohr^3)^{1/2}.

The very weak phosphorescence observed experimentally for the *N*-hydroxy system **18b** can be explained by the significantly different S_1 and T_1 geometries (assuming S_1 has a similar geometry to S_0) increasing the nonradiative decay rate constant. The undesirable $Pt-Pt^*-d \rightarrow d^*$ quenching of the radiative decay with the LUMO+1 as the Pt^* orbital may also have a role in the weak phosphorescence emission.^[3] The very weak fluorescence observed experimentally for the *N*-hydroxy system **18b** may be due to the unfavourable substantial Pt character in LUMO+1 (Figure 12) and the low aryl character of the phenyl group in the frontier orbitals.

Conclusions

A series of platinum(II) complexes containing cyclometallated diaryl ketimine ligands has been synthesised. Their photophysical properties are characterised by emission bands at $\lambda_{max} \approx 450$ and 550 nm, which are assigned to singlet and triplet species, respectively. By varying the structure of the aromatic ligand the efficiency of phosphorescence can be increased from $<0.007\%$ for several derivatives to 3.0 and 4.3% for **16b** and **15b**, respectively. Comprehensive theoretical calculations have rationalised the observed photophysical properties of these systems. Computations have shown that the low-energy transitions in all systems involve mainly the frontier orbitals, HOMO and LUMO. These are mixed chlorido-metal-ligand to largely $\pi^*-C=N$ transitions. Most of the phosphorescence data observed here can be explained by the geometric change on going from the S_0 to the T_1 states. The very weak (or zero) phosphorescence emissions observed for some systems (**18b**, **19–21**) are due to the large changes in geometry and energy between the S_0 and T_1 states. The relatively strong phosphorescence emissions observed in fused-ring systems (**15b** and **16b**) are due to significant aryl- π or $-\pi^*$ character in their HOMO–1, HOMO and LUMO+1 and substantial Pt character (35–37%) in the HOMO promoting favourable ISC combined with the relatively small geometric change on going from the S_0 to the T_1 states. The carbazole system **17b** has very weak phosphorescence due to little metal character (19%) in the HOMO (thus negligible ISC takes place) but has strong fluorescence with substantial aryl- π or $-\pi^*$ character in the frontier orbitals involved in the transitions. Weak dual emissions observed for the simpler systems (**12b–14b**), compared to strong phosphorescence found for fused-ring systems, are attributed to much less aryl- π^* character in the transitions. This work should stimulate further studies on luminescent platinum(II) complexes incorporating new ligands, aimed at exploring fundamental photophysical properties and practical applications.

Experimental Section

General Procedure for the Reaction of Diaryl Ketimines 6–11 with $K[PtCl_3(Me_2SO)]$: A solution of dimethyl sulfoxide (1.04 equiv.) in water was added dropwise to a solution of $K_2[PtCl_4]$ (1 equiv.) in

water. The solution was stirred at room temperature for 4–5 h, until the colour turned from red to yellow indicating that $K[PtCl_3(Me_2SO)]$ had been generated. A solution of the diaryl ketimine (1 equiv.) in dry dichloromethane was added dropwise to the yellow solution. The mixture was stirred at room temperature for 10 h. The organic layer was separated and the solvent removed under reduced pressure to give the crude product, which was purified by column chromatography to afford **12a–17a** as yellow solids.

General Procedure for Cyclometallation of the Complexed Imine: A solution of complex **12a–17a** in dry toluene (40 mL) was refluxed for ca. 15 h. The solvent was removed under reduced pressure to give the crude product, which was then purified by column chromatography to give **12b–17b** as yellow-orange solids.

Photophysical Measurements: The complexes were dissolved in toluene. Steady-state absorption spectra and luminescence emission and excitation spectra of the solutions were recorded by using a UV/Vis spectrophotometer (Lambda 19 from Perkin–Elmer) and a commercial spectrofluorimeter (Fluorolog from Jobin Yvon), respectively. Lifetime measurements were made by using a system consisting of excitation source, pulsed YAG laser emitting at 355 nm (EKSMA or CryLas GmbH). Samples were excited at 45° angle to the substrate plane, and the energy of each pulse could be tuned from μJ up to mJ. With the help of a spectrograph and other optics, luminescence data were collected by a sensitive ICCD camera (Stanford Computer Optics) with sub-nanosecond resolution. For low-temperature measurements (down to 77 K) samples were placed in a cryostat. Quantum efficiencies were determined by using 9,10-diphenylanthracene as a standard,^[30] where samples were degassed by using at least three pump-thaw cycles before measurements of the quantum efficiencies.

Supporting Information (see footnote on the first page of this article): Details of the synthesis and characterisation of all new compounds; additional photophysical data and spectra; X-ray crystallographic data for **18a**; device fabrication and characterisation; computational data for **12b–18b, 19–21**.

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