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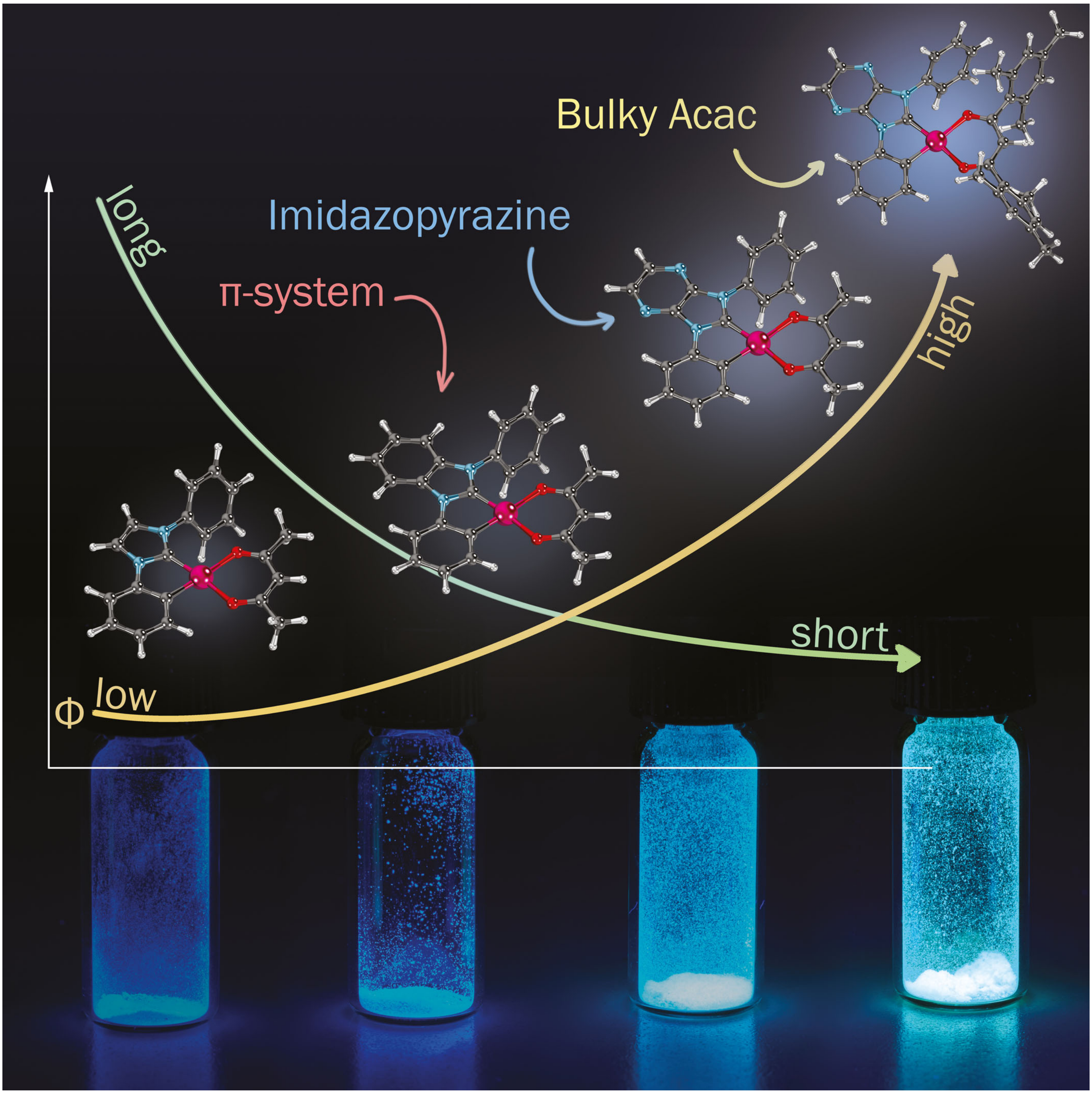
Organometallic Chemistry

Sky-Blue Triplet Emitters with Cyclometalated Imidazopyrazine-Based NHC-Ligands and Aromatic Bulky Acetylacetonates

Piermaria Pinter, Johannes Soellner, and Thomas Strassner*[a]

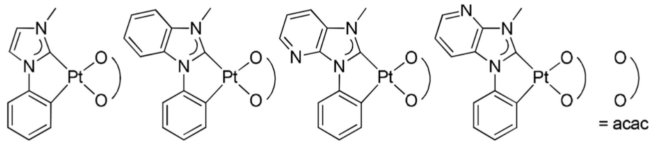


Abstract: Platinum(II) complexes with an *N*-heterocyclic carbene and a cyclometalating phenyl ligand (C^C*) are excellent candidates as efficient blue triplet emitters for OLED applications. The electronic and photophysical properties of these complexes can be fine-tuned with the objective to increase the quantum yields and lower the phosphorescence decay times. We found that platinum complexes with an imidazopyrazine C^C* ligand and bulky acetylacetonates are sky-blue triplet emitters, characterised by an almost unitary quantum yield and short phosphorescence decay times.

Introduction

Current sources of illumination are not efficient. For instance, the incandescent bulb, which is the most widely used form of artificial illumination, dissipates more than 90 % of the energy as heat.[1] Powering these sources of illumination requires more than 20 % of the overall energy production.[2] This energy demand is responsible for more than one-third of the world's greenhouse gas production.[3] Considering that we are facing both an energy and an environmental crisis, it is imperative to find more efficient sources of illumination. A promising alternative to the incandescent bulb is offered by the PhOLED (phosphorescent organic light emitting diode) technology. In a PhOLED an organometallic molecule, called triplet emitter, is electrically excited. After the excitation, the triplet emitter relaxes from the excited triplet state to the ground state, emitting a photon. The emission has a well-defined wavelength, which depends on the energy gap between the excited triplet and the ground state. Hence, by accurate molecular design of the triplet emitters, different emission colours can be obtained. During the last decade, there has been great interest from both academia and industry to develop new triplet emitters with improved photophysical properties. Efficient and stable triplet emitters have been obtained for red,[4] orange,[5] yellow,[5a,6] and green[7] emissions; however, the blue colour is still an open challenge.[8] Efficient blue triplet emitters are difficult to obtain because the energies of the emissive and metal-centred (^{3}MC) states are comparable. If the energy difference between an excited triplet state and a ^{3}MC state is small, then the ^{3}MC state can be accessible at room temperature.[9] The population of ^{3}MC states leads to a geometrical distortion of the triplet emitter,[10] which in some cases may lead to a bond-breaking process.[9a,10–11] Therefore, the population of ^{3}MC states is associated with the degradation of the triplet emitter with consequent reduction of the performance and lifetime of a PhOLED device.

To overcome these shortcomings, the scientific community proposed some strategies to prevent the population of ^{3}MC states.[9b,c,12] Efficient blue triplet emitters can be obtained using strong-field ligands which provide strong metal–ligand bonds.[12–13] Also, the rigidity of the complexes is important.[8b,14] Strong-field ligands (those ligands with excellent σ-donor and π-acceptor properties) destabilise ^{3}MC states.[11b,14d] Strong metal–ligand bonds prevent the breaking of bonds,[15] and rigid systems prevent the distortions in the excited state. In this perspective, *N*-heterocyclic carbenes with a cyclometalated fragment[16] (C^C* ligands) distinguished themselves as excellent systems for photophysical applications.[17] These exceptional ligands form strong metal–ligand bonds, and their complexes are, in general, rigid. Also, the electronic properties of both the cyclometalated and the carbene fragments can be fine-tuned. For example, modifying the π-conjugation on the C^C* ligand, the phosphorescent decay time can be changed between 8 and 400 μs.[18] Recently we also reported[19] that the introduction of a heteroatom in the backbone of the *N*-heterocyclic carbene changes the photophysical properties of the C^C* platinum(II) complexes. For example, platinum(II) complexes with an imidazopyridine ligand (Figure 1 c, and d), showed higher quantum yields and at the same time shorter decay times than structurally related phenyl imidazole (Figure 1 a) and benzimidazole (Figure 1 b) platinum(II) C^C* complexes. Additionally, we have shown that the use of bulky aromatic acetylacetonates improves the photophysical properties of the emitters. For example, using bulky aromatic acetylacetonates we observed an increase in phosphorescence quantum yields.



(**a**) QY: 7% (**b**) QY: 45% (**c**) QY: 65% (**d**) QY: 65%

Figure 1. Selected C^C* platinum complexes reported by our group **a**,[13c] **b**,[18], **c**,[19a] **d**[19b]. The measured quantum yields are given for comparison. acac = pentane-2,4-dione.

These results recently prompted us to study the electronic and photophysical properties resulting from the introduction of a second nitrogen atom. In the literature imidazopyrazine complexes of gold(I),[20] silver(I),[21] rhodium(I),[21] copper(I),[22] and platinum(II)[23] are known. We compared the electronic and spectroscopic properties of the imidazopyrazine complex with those observed for related systems (Figure 2, complexes **1**–**3**). Then, we investigated the electronic and photophysical properties of platinum(II) complexes with an imidazopyrazine and bulky aromatic acetylacetonates. We found that the imidazopyrazine complexes with bulky aromatic acetylacetonates are among the most efficient and fastest platinum sky-blue triplet emitters.

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[a] *P. Pinter, J. Soellner, Prof. Dr. T. Strassner*
Physikalische Organische Chemie
Technische Universität Dresden, 01069 Dresden (Germany)
E-mail: thomas.strassner@chemie.tu-dresden.de

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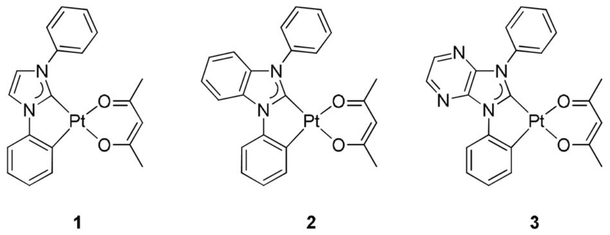
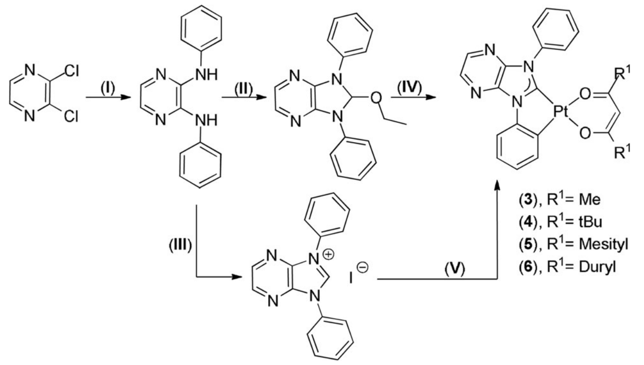


Figure 2. The C^C*platinum(II) complexes **1**–**3**; complex **1**[18] derived from imidazole, complex **2**[18] derived from benzimidazole, and complex **3** derived from imidazopyrazine.

Results and Discussion

The platinum(II) C^C*complexes with the imidazopyrazine ligand can be obtained following two distinct procedures (Scheme 1). We prepared the N^2,N^3-diphenylpyrazine-2,3-diamine by a reaction at elevated temperatures between commercially available 2,3-dichloropyrazine and aniline (**I**). In a second step, a ring-closure reaction gave 2-ethoxy-1,3-diphenyl-2,3-dihydro-1*H*-imidazo[4,5-b]pyrazine by the reaction of the N^2,N^3-diphenyl-pyrazine-2,3-diamine with triethyl orthoformate in the presence of HCl (**II**). The imidazolium salt can be obtained by reaction of N^2,N^3-diphenylpyrazine-2,3-diamine with triethyl orthoformate and NH_4I (**III**). The platinum(II) complexes can be prepared either from the ethoxy-imidazopyrazine derivate (**IV**) or the imidazolium salt (**V**). The C^C* precursor is reacted with Ag_2O to form the silver(I) carbene, which is then transmetallated by reaction with dichloro(1,5-cyclooctadiene)-platinum(II) [Pt(COD)Cl_2] (COD = 1,5-cyclooctadiene), followed by cyclometalation at elevated temperature. Afterwards, the respective acetylacetone (HR$_2$acac) and potassium *tert*-butanolate are added to the reaction mixture to effort the C^C* acetylacetonate platinum complexes in yields of 9–49 %. We observed that the procedure using the ethoxy derivative (**IV**) provides a significantly higher yield compared to the route via the imidazolium salt (**V**). For example, we obtained complex **3** in 49 % yield by route **IV**, but in only 9 % by route **V**.



Scheme 1. Preparation of the platinum(II) complexes **3**–**6**: (**I**) aniline neat, 160 °C, 78 %; (**II**) triethyl orthoformate, HCl, 93 %; (**III**) triethyl orthoformate, NH_4I, 48 %; (**IV**) DMF, Ag_2O, [Pt(COD)Cl_2], HR$_2$acac, KO*t*Bu, 43–49 % (**V**) DMF, Ag_2O, [Pt(COD)Cl_2], HR$_2$acac, KO*t*Bu, 9–17 %.

We were able to obtain single crystals of complex **6** suitable for solid-state structure determination by slow evaporation of a concentrated DMF solution of the complex. The solid-state structure and some important structural parameters of complex **6** are reported in Figure 3 and Figure S19, Supporting Information. In the solid-state structure of complex **6**, the Pt–Pt distance is 8.3914(8), which is long enough to exclude any possible metallophilic interaction (Figure 5).

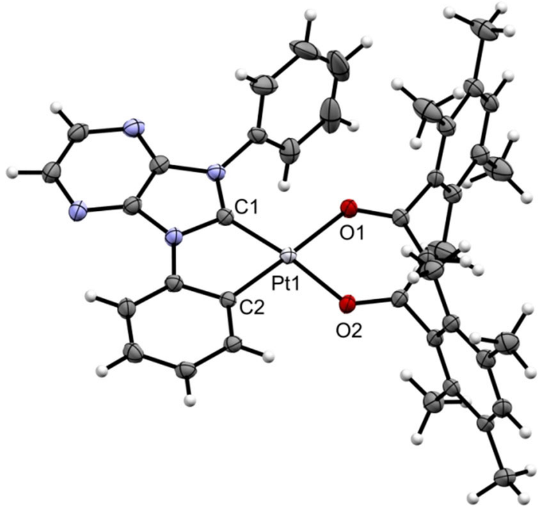


Figure 3. Solid-state structure of complex **6**, thermal ellipsoids are drawn at 50 % probability. Selected bond lengths [Å]: Pt(1)–C(1): 1.926(2), Pt(1)–C(2): 1.991(2), Pt(1)–O(1): 2.082(2), and Pt(1)–O(2): 2.038(2).

The electronic properties of the C^C* ligands show up on the differences of the spectroscopic properties of the platinum(II) complexes; for example, in the UV/Vis absorption spectra of complexes **1**–**3**. The transitions at low energies of complexes **1** and **2** have comparable energies ($\lambda_{abs} = 316$ and 327 nm, respectively for complex **1** and **2**) whereas in the case of complex **3** this transition is redshifted ($\lambda_{abs} = 358$ nm).

Complexes **1**–**3** are characterised by different emission profiles. The emission spectra of complexes **1** and **2** are partially resolved, whereas the emission spectrum of complex **3** is broad and structureless (Figure 4). This difference is maintained at 77 K; the emission profiles of complexes **1** and **2** are well resolved in contrast to the emission profile of complex **3** (Figure S20, Supporting Information). Complex **3** is a more efficient emitter compared to complexes **1** and **2**. Its quantum yield is four times higher than that of **1** and the phosphorescent decay time shorter (Table 1).

At low temperatures, all complexes show a unitary quantum yield. Therefore, the low quantum yields observed at room temperature for **1** and **2** can be attributed to a temperature dependent non-radiative deactivation mechanism. It is commonly accepted that this nonradiative mechanism proceeds through the population of a metal-centred state ^{3}MC. Because the imidazopyrazine-based complex has a remarkably higher room temperature quantum yield with respect to complexes **1** and **2**, the ^{3}MC state of complex **3** is less accessible than the

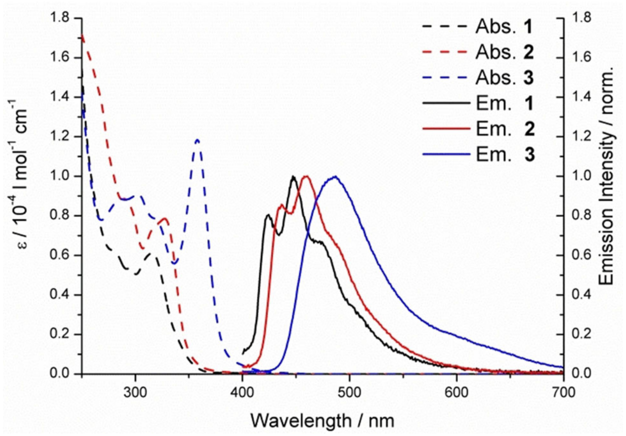


Figure 4. (-----) The absorption spectra of complexes **1**–**3** obtained from a 0.1 mm solution of the complex in DCM measured at room temperature. (——) The normalised emission spectrum of complexes **1**–**3** obtained from a 60 μm PMMA film doped with 2.0 wt % of the emitter.

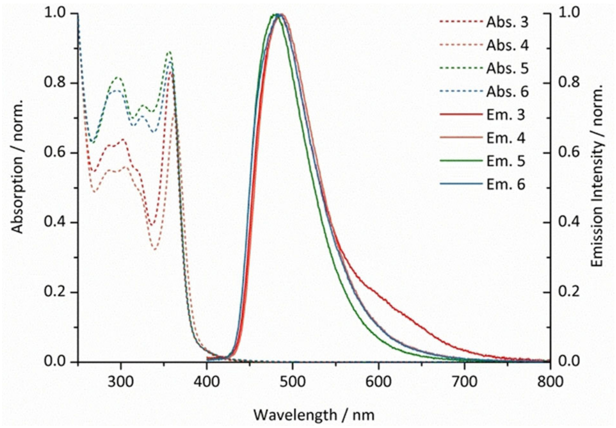


Figure 5. (-----) The normalised absorption spectra of complexes **3**–**6** obtained from a 0.05 mm solution of the complex in DCM measured at room temperature. (——) The normalised emission spectrum of complexes **3**–**6** obtained from a 60 μm PMMA film doped with 2.0 wt % of the emitter.

^{3}MC states of **1** and **2**. The excellent photophysical properties of complex **3**, motivated us to investigate this class of complexes further. In detail, it has previously been experimentally observed that using bulky acetylacetonates has a beneficial effect on the photophysical properties of the emitters. For example, platinum(II) complexes with sterically demanding acetylacetonates show in general higher quantum yields than analogous acetylacetonate complexes. Therefore, we prepared some complexes analogous to complex **3**, but with sterically demanding acetylacetonates (complexes **4**–**6**). The absorption and emission spectra and the photophysical properties of complexes **4**–**6** are reported in Figure 5 and Table 1. Complexes **4**–**6** are excellent sky-blue triplet emitters. For **5** and **6** approximately a unitary quantum yield and at the same time a short decay time was found, among the shortest for platinum(II) C^C* blue emitters.

Conclusions

We observed[19] that the introduction of a nitrogen atom in the backbone of the (benz)imidazole, independent of the position, drastically changes the photophysical properties of the complexes (Figure 1 c,d). But the introduction of a second nitrogen atom in the backbone of the (benz)imidazole system has an even larger beneficial effect on the photophysical properties of platinum(II) C^C* blue emitters. The combination of the imidazopyrazine-based ligands with bulky acetylacetonates leads to very efficient emitters characterised by an almost unitary quantum yield and at the same time very short decay times.

Conflict of interest

The authors declare no conflict of interest.

Keywords: blue triplet emitters · N-heterocyclic carbenes · OLEDs · phosphorescence · quantum yields

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Table 1. Photophysical data for complexes **1**–**6** from a 60 μm PMMA film doped with 2.0 wt % of the emitter.[a]

Compd.	Φ [%][b]	λ_{em} [nm][c]	CIE (*x*,*y*)[d]	τ_0[e] [μs]	k_r [$10^3 \cdot s^{-1}$][f]	k_{nr} [$10^3 \cdot s^{-1}$][g]
1	19 [100]	447 [424]	0.16, 0.13 [0.16, 0.10]	19.6	50.9	41.3
2	48 [100]	461 [419]	0.16, 0.16 [0.16, 0.10]	9.9	101.5	52.8
3	84 [100]	487 [448]	0.22, 0.35 [0.15, 0.15]	3.6	275.2	44.0
4	84	483	0.19, 0.36	3.8	266.6	42.7
5	99	482	0.17, 0.30	3.4	290.2	2.9
6	98	483	0.19, 0.33	3.6	278.7	5.6

[a] Measured under a nitrogen atmosphere at room temperature with $\lambda_{exc.} = 300$ nm. In square brackets obtained from a glassy matrix of a frozen 0.5 mm solution of the complex in 2-MeTHF, measured under an argon atmosphere at 77 K with $\lambda_{exc.} = 300$ nm. [b] Absolute quantum yield ±5 %. [c] Maximum emission wavelength. [d] CIE coordinates. [e] Decay lifetime (excited by laser pulses 360 nm, 20 kHz) given as $\tau = \tau_{exp}/\Phi$. [f] Radiative decay rate constant given as $k_r = (\Phi/\tau_{exp})$. [g] Non-radiative decay rate constant given as $k_{nr} = (1-\Phi)/\tau_{exp}$.

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*P. Pinter, J. Soellner, T. Strassner**

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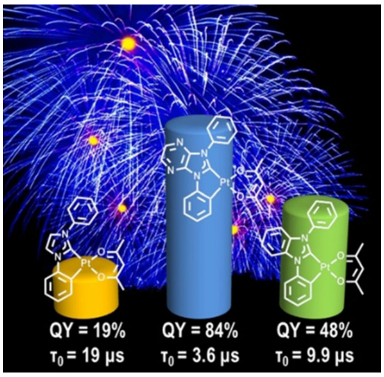

Platinum(II) complexes with imidazopyrazine-based C^C* ligands are excellent sky-blue emitters with an almost unitary quantum yield and very short phosphorescence decay times (see scheme).

Platinum(II) complexes with a cyclometalated NHC ligand (C^C*) are very efficient blue triplet emitters for OLED applications. In their Full Paper on page ■■., Strassner et al. describe the use of C^C* ligands based on the imidazopyrazine motif together with a bulky acetylacetonate co-ligand to provide platinum(II) complexes with exceptional phosphorescent properties, such as high quantum yields and among the shortest decay times observed for this class of complexes.