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**Blue phosphorescent nitrile containing C<sup>∧</sup>C\* cyclometalated NHC  
platinum(II) complexes**

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Blue phosphorescent nitrile containing C<sup>∧</sup>C\*  
cyclometalated NHC platinum(II) complexes†Cite this: *Dalton Trans.*, 2014, **43**,  
3297Alexander Tronnier,<sup>a</sup> Stefan Metz,<sup>b</sup> Gerhard Wagenblast,<sup>b</sup> Ingo Muenster<sup>b</sup> and  
Thomas Strassner\*<sup>a</sup>

Since C<sup>∧</sup>C\* cyclometalated Pt(II) complexes with N-heterocyclic carbene (NHC) ligands have been identified as potential emitter materials in organic light-emitting devices (OLEDs), very promising results regarding quantum yields, colour and stability have been presented. Herein, we report on four nitrile substituted complexes with a chelating NHC ligand (1-(4-cyanophenyl)-3-isopropyl-1*H*-benzo[d]imidazole or 4-(*tert*-butyl)-1-(4-cyanophenyl)-3-methyl-1*H*-imidazole) and a bidentate monoanionic auxiliary ligand (acetylacetonone or dimesitylmethane). The complexes have been fully characterized including extensive 2D NMR studies (COSY, HSQC, HMBC, NOESY, <sup>195</sup>Pt NMR), three of them also by solid-state structures. Photo-physical measurements in amorphous PMMA films and pure emitter films at room temperature reveal the impact of the mesityl groups in the auxiliary ligand, which led to a significant increase of the quantum yield, while the decay lifetimes decreased. The electron withdrawing nitrile groups shift the emission towards blue colour coordinates.

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## Introduction

The invention of luminescent organic devices in 1993<sup>1</sup> had a large impact on the field of organic electronics. Many groups since then focused their research activities on organic conductors, isolators, optical sensors and emissive compounds.<sup>2</sup> Especially the field of organic light-emitting devices (OLEDs) has seen rapid development. A breakthrough came with the incorporation of transition metal complexes in 1998<sup>3</sup> which enabled quantum yields beyond the fluorescence limit of 25% leading to the new class of phosphorescent organic light-emitting devices (PhOLEDs).<sup>4</sup> Therein the heavy atom is responsible for effective spin-orbit coupling (SOC) and *triplet harvesting*, leading to exceptional photophysical properties and quantum yields as high as 100%.<sup>5</sup> Although different transition metals were investigated as emitting compounds,<sup>6</sup> neutral iridium(III)<sup>7</sup> and platinum(II)<sup>8</sup> complexes with cyclometalated ligands show the most promising results so far.

Prominent motifs in such Pt(II) complexes are bidentate cyclometalated aryl pyridine ligands which have been tested

together with acetylacetonate auxiliary ligands and derivatives thereof.<sup>9</sup> Based on this class of complexes (type A, Chart 1) a lot of variations regarding substituents, size of the  $\pi$  systems, heterocycles and auxiliary ligands were investigated to tune the photophysical properties.

A new class of complexes (type B) derived from these emitters was developed and the first complex was presented in a patent in 2006.<sup>10</sup> In this system the pyridine ring is replaced by a 3-methylimidazolylidene. Although similar complexes were prepared much earlier,<sup>11</sup> their potential as emitter molecules in OLEDs has only recently been shown.<sup>12</sup> First device tests with a complex of this class showed EQEs as high as 6.2% at 300 cd m<sup>-2</sup> and a maximum luminance of 6750 cd m<sup>-2</sup>. Since this discovery, continuing studies led to a whole new class of C<sup>∧</sup>C\* cyclometalated highly emissive complexes.<sup>13</sup>

It became obvious that extended  $\pi$  systems (type C) have a beneficial effect on the quantum yield<sup>14</sup> while sterically demanding groups are necessary to prevent stacking of

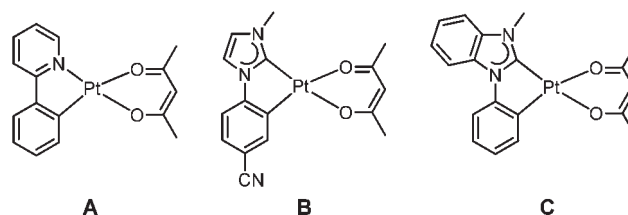


Chart 1 Examples of cyclometalated Pt(II) complexes.

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†Electronic supplementary information (ESI) available: Details of the photo-physical measurements and solid-state structures, 2D NMR spectra as well as Cartesian coordinates for the optimized structures. CCDC 972158–972160. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c3dt53264j

complex molecules<sup>15</sup> and the formation of excimers, which frequently results in red-shifted emission colours.<sup>16</sup>

Herein we report a series of new complexes derived from type B which incorporate a different size of the  $\pi$  system and sterically demanding substituents that show NHC centred emission in the blue to green region of the visible spectrum. Since electron withdrawing groups like fluoro or  $\text{CF}_3$  groups, which are often necessary to achieve blue emission, may cause problems in terms of stability, the nitrile group was chosen as an alternative substituent.

The influence of the auxiliary ligand on the steric shielding of the central Pt(II) atom and the photophysical properties is investigated by replacing acetylacetonate with 1,3-dimesitylpropane-1,3-dionate.

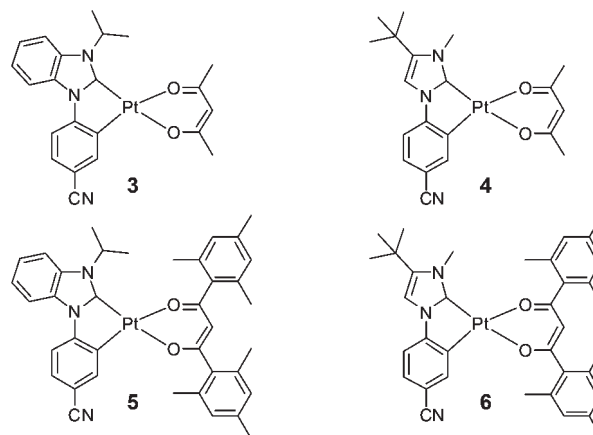


Chart 2 Synthesized complexes 3–6.

## Results and discussion

### Synthesis

The synthesis of the ligand precursors **1** and **2** has been reported previously (Scheme 1).<sup>10</sup> Compound **1** was prepared following a multi-step methodology starting with the synthesis of the unsymmetric *N*-(4-cyanophenyl)-*N'*-(2-isopropyl)phenylene-diamine with subsequent ring closure. Thus, the corresponding NHC ligand has an extended  $\pi$  system, the benzimidazole fragment, and a sterically shielding isopropyl group.

Ligand precursor **2** was prepared by nucleophilic aromatic substitution to generate the imidazole with the sterically demanding *tert*-butyl group already in the backbone followed by quaternization. The auxiliary ligand acetylacetonate (acac) is commercially available and dimesitylmethane (mesacac) could be readily obtained through published literature procedures.

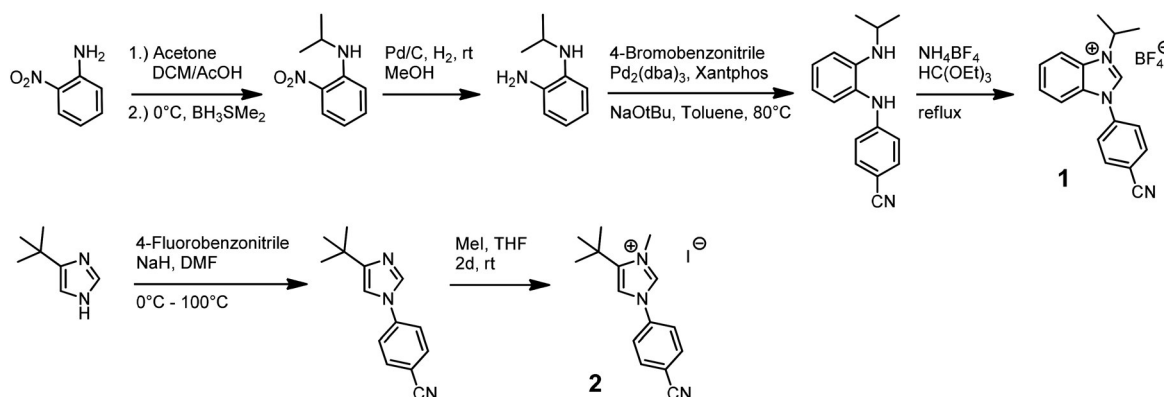
The complexes (Chart 2) were prepared in a one-pot synthesis using our established route: deprotonation of the imidazolium salt with silver(I) oxide and subsequent formation of a silver(I) NHC complex, transmetalation to dichloro(1,5-cyclooctadiene) platinum(II), and cyclometalation at elevated temperature followed by the reaction with the auxiliary ligand in the

presence of potassium *tert*-butanolate as a base. The complexes were obtained in yields of 25% to 36% after flash chromatography.

### Characterization

All complexes were characterized by standard techniques. The formation of an NHC bound cyclometalated species was verified by the disappearance of the imidazolium proton and the formation of a different coupling pattern for the cyclometalated ring in the <sup>1</sup>H NMR. 2D NMR measurements (see ESI, Fig. S1–S12†) revealed the carbene carbon signal at 150.8–151.7 ppm.

The <sup>195</sup>Pt NMR experiments showed signals typical for Pt(II) complexes of this class in the range of –3320 ppm (**5**) to –3380 ppm (**4**) in deuterated chloroform with the lowest values for the mesacac substituted complexes. The complexes show high thermal stability in air with melting points as high as 310 °C. The compounds with 1-(4-cyanophenyl)-3-isopropyl-1*H*-benzo[*d*]-imidazole as a NHC ligand were found to decompose at 265 °C (**3**) and 309 °C (**5**). Generally we found higher melting points for the complexes with the mesityl group in the auxiliary ligand as well as better solubility in methylene chloride or even diethyl ether.



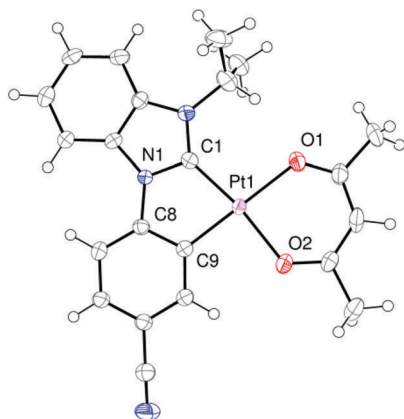
Scheme 1 Preparation of the ligand precursors **1** and **2**.

Single-crystals suitable for X-ray diffraction measurements could be obtained for **3**, **4** and **5** by slow evaporation of saturated methylene chloride solutions. The solid-state structures reveal a square-planar coordination of the central Pt(II) atom. The methyl substituents (of the isopropyl or *tert*-butyl group) at the NHC ligands are always rotated out of the complex plane which is comprised of the two metallacycles at the central platinum atom. In all complexes, the angles of these two cycles show some significant differences. While the O1–Pt1–O2 angle shows the nearly perfect 90° angle of a square-planar coordination, the C1–Pt1–C9 angles are about 10 degree smaller (80.26(15)–80.46(18)°). The bonds from the carbon atoms to the platinum centre are always shorter than the oxygen platinum contacts. The carbene carbon platinum bond (1.940(4)–1.957(7) Å) is the shortest of all four platinum–ligand bonds. Both oxygen platinum bond lengths differ only slightly (2.030(4)–2.087(3) Å).

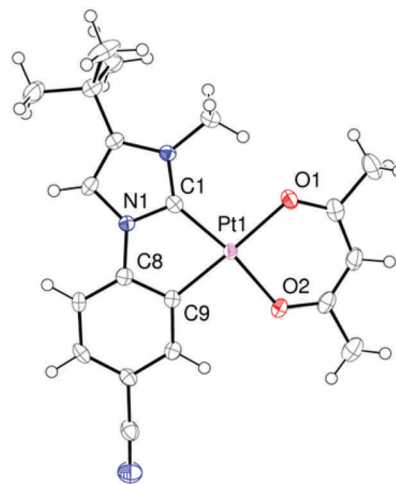
Complex **3** as shown in Fig. 1 crystallizes in a monoclinic crystal system. The molecules form pairs with a Pt...Pt distance of 3.26 Å which is just below the sum of van der Waals radii and may hint at a weak metal–metal closed-shell interaction (see ESI, Fig. S13†).<sup>17</sup> These pairs are oriented with an angle of 86° to each other. The molecules in each pair are rotated in such a way that the NHC moieties face the acac group of the other complex and the nitrile groups are facing towards the opposite direction.

For the other acac complex **4** (Fig. 2) a similar superimposed arrangement is found in the solid state (see ESI, Fig. S14†). The pairs form a zigzag pattern with an angle of 81.2°, a Pt...Pt distance of 3.28 Å between them and a similar orientation as found for **3**. Additionally, a Pt–H contact of 2.83 Å is found between two complexes of different pairs.

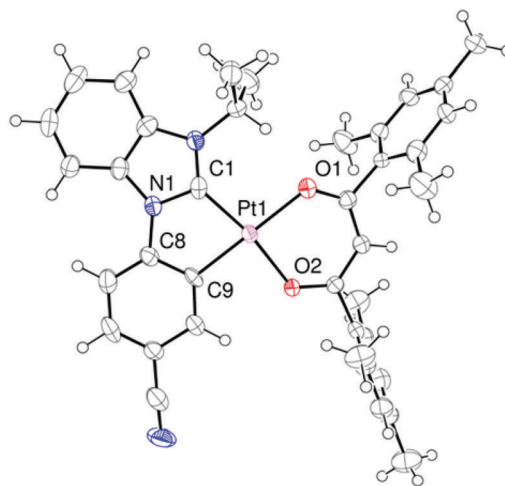
Fig. 3 shows the solid-state structure of the mesacac substituted complex **5**. It becomes obvious that the bulky mesityl groups at the auxiliary ligand have a significant impact on the steric situation around the platinum centre. The complex crystallizes in an orthorhombic system. Due to the shielding effect



**Fig. 1** Solid-state structure of **3**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Pt1–C1 1.940(4); Pt1–C9 1.969(4); Pt1–O1 2.087(3); Pt1–O2 2.059(3); C1–Pt1–C9 80.46(18); O1–Pt1–O2 89.35(13); Pt1–C1–N1–C8 –1.5(5); N1–C1–Pt1–O1 177.1(3).



**Fig. 2** Solid-state structure of **4**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Pt1–C1 1.954(4); Pt1–C9 1.986(4); Pt1–O1 2.083(3); Pt1–O2 2.047(3); C1–Pt1–C9 80.26(15); O1–Pt1–O2 90.22(11); Pt1–C1–N1–C8 3.5(4); N1–C1–Pt1–O1 171.1(3).



**Fig. 3** Solid-state structure of **5**. Thermal ellipsoids are drawn at 50% probability. Selected bond lengths [Å] and angles [°]: Pt1–C1 1.957(7); Pt1–C9 1.999(7); Pt1–O1 2.082(5); Pt1–O2 2.030(4); C1–Pt1–C9 80.4(3); O1–Pt1–O2 89.26(17); Pt1–C1–N1–C8 4.2(8); N1–C1–Pt1–O1 171.2(5).

of the auxiliary ligand no pairs of complexes can be formed. Neither the NHC ligand nor the metal centre can interact with other molecules. Thus, the shortest Pt...Pt distance is as long as 7.88 Å. The only contact from the metal centre to another molecule is an agostic interaction to an aryl hydrogen atom (2.89 Å). Interestingly, the metallacycles and the NHC backbone form no planar unit any more with parts of the complex showing significant twisting (see ESI, Fig. S15†).

The bond lengths and angles around the metal centre obtained from the X-ray diffraction experiments are in good agreement with previously published structures. Complexes **3** and **4** with the acetylacetonato ligand are able to form pairs of

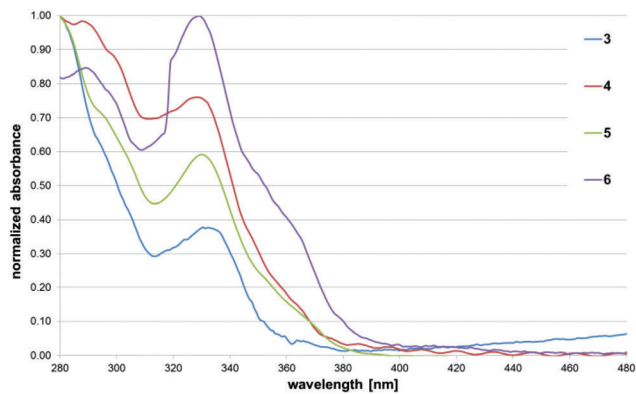


Fig. 4 Absorption spectra of complexes 3–6 at room temperature (2 wt% in PMMA).

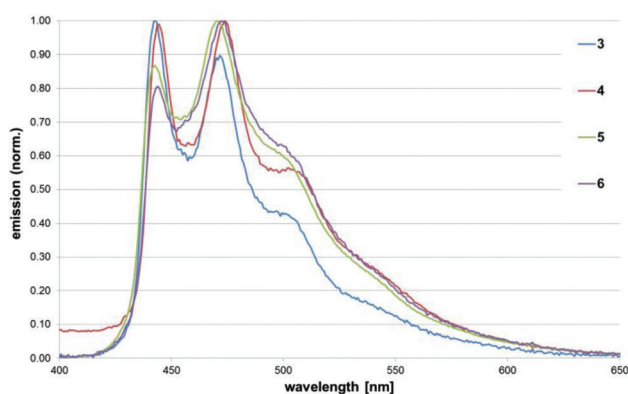


Fig. 5 Emission spectra of complexes 3–6 at room temperature (2 wt% in PMMA).

molecules with Pt...Pt distances slightly below the sum of van der Waals radii. A further similarity for this class of compounds is the arrangement of the complexes in the solid state where within the pairs each NHC ligand faces an acetylacetonato ligand. The steric shielding induced by the mesityl groups at the auxiliary ligand in 5 effectively suppresses the formation of pairs and should thus be useful in more concentrated emitter films.

### Photophysical properties

To investigate the photophysical properties of the complexes, the absorption (Fig. 4) and emission spectra (Fig. 5) were measured in amorphous poly(methyl methacrylate) films

(PMMA) at room temperature with a concentration of 2 wt% emitter.

All complexes show an absorption between 270 nm and 290 nm with an additional band at 330 nm. While the high energy transitions can be ascribed to spin-allowed  $^1\pi-\pi^*$  intra-ligand charge transfer (ILCT) processes mainly located on the NHC ligand, the weaker absorptions at higher wavelengths include the metal d-orbitals and are more of metal-to-ligand charge transfer (MLCT) nature.

All complexes show intense phosphorescence at room temperature (Table 1). The luminescence measurements (Fig. 5) show broad spectra ranging from the blue (450 nm) to green (540 nm) region of the visible spectrum with strong vibronic coupling. For all four complexes three discernible bands are found with an additional weak shoulder at 540 nm. With the exception of complex 3 the second band of the emission spectrum at around 470 nm is the most intense. The vibronic progression between the first and second transition band is about  $1400\text{ cm}^{-1}$  for all compounds, which corresponds to vibrations of the NHC ligand frame (as taken from the frequency analysis from the density functional theory (DFT) calculations).

A comparison of the acac substituted complexes with the ones bearing the dimesitylmethanato auxiliary ligand reveals a strong enhancement of the quantum yields (28% from 4 to 6) and significantly lowered excited-state lifetimes while the emission maxima remain in the same region, retaining the blue colour coordinates.

The obtained lifetimes and quantum yields are indicative of a fast radiative relaxation which is nearly twice as fast for the mesacac substituted complexes 5 and 6.

Furthermore, amorphous, pure emitter films were prepared to probe for changes caused by the steric demand introduced by the mesityl groups in the auxiliary ligand for complexes 5 and 6. For compound 3 no such films could be prepared due to early crystallization. All measured complexes show absorption bands between 240 nm and 330 nm and emission in the same region as for the measurement with 2% emitter concentration (see ESI, Fig. S16 and S17†) with quantum yields ranging from 11% (5) to 22% (6).

### DFT calculations

The optimized geometries for the singlet and triplet states have been calculated for the four complexes by DFT methods (B3LYP/6-31G(d) level with a Hay-Wadt-ECP for platinum).

Table 1 Photoluminescence data (2 wt% in PMMA, room temperature) of cyclometalated complexes 3–6

#	$\lambda_{\text{exc}}^a$ [nm]	CIE $x; y^b$	$\lambda_{\text{em}}^c$ [nm]	$\Phi^d$ [%]	$\tau_o^e$ [ $\mu\text{s}$ ]	$k_r^f$ [ $10^3\text{ s}^{-1}$ ]	$k_{\text{nr}}^g$ [ $10^3\text{ s}^{-1}$ ]
3	330	0.158; 0.161	444, 473	63	15.5	64.4	37.8
4	355	0.164; 0.216	443, 474	57	17.0	59.1	44.6
5	370	0.164; 0.212	442, 471	80	8.9	114.9	28.7
6	370	0.166; 0.229	443, 471	85	8.4	118.9	21.0

<sup>a</sup> Excitation wavelength. <sup>b</sup> CIE coordinates at rt. <sup>c</sup> Emission wavelength. <sup>d</sup> Quantum yield in % at  $\lambda_{\text{exc}}$ ,  $\text{N}_2$  atmosphere. <sup>e</sup> Decay lifetimes (excited by laser pulses (355 nm, 1 ns)) given as  $\tau_o = \tau_v/\phi$ . <sup>f</sup>  $k_r = \phi/\tau_v$ . <sup>g</sup>  $k_{\text{nr}} = (1 - \phi)/\tau_v$ .



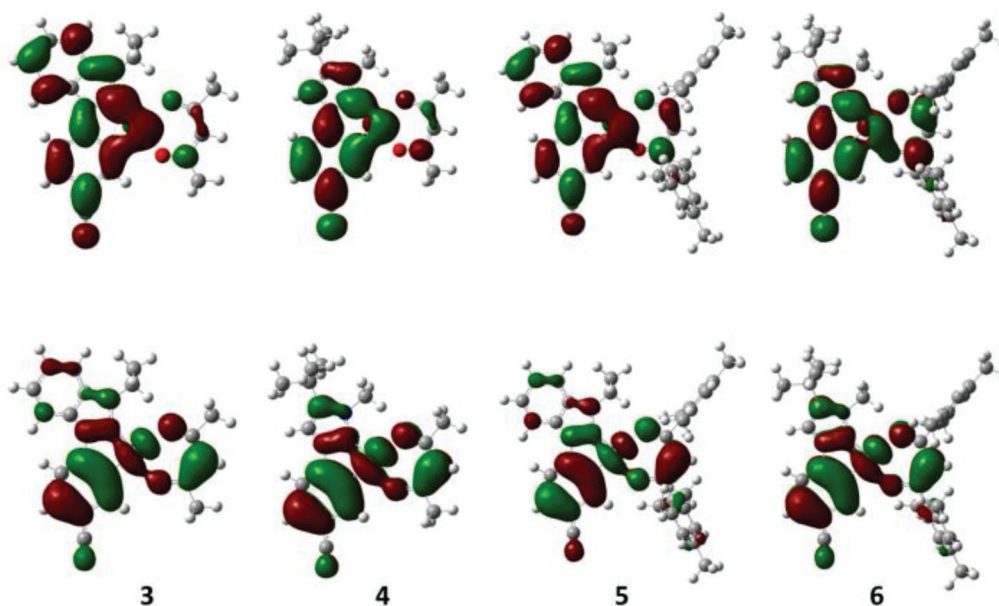


Fig. 6 Frontier molecular orbitals for complexes 3–6 (HOMO bottom, LUMO top; B3LYP/6-31G(d), isovalue = 0.02).

The results obtained from these calculations agree well with the structural data from the X-ray diffraction experiments (see ESI, Tables S2–S4, Fig. S18†).

Upon changing the multiplicity from the singlet to the excited triplet state most complexes retain their geometries with only slightly altered bond lengths around the platinum centre. For 5 an additional flipping of the auxiliary ligand out of the central complex plane, created by the two metallacycles, was observed (see ESI, Fig. S19†). A rotation of the two aryl groups in the diketonato ligand into the central plane, as observed for other complexes of this class,<sup>15d</sup> did not occur. The methyl groups in the *ortho* position at the aryl moieties effectively suppress any significant rotations so that the mesityl groups retain their function of shielding the metal centre from interactions even in the triplet state.

A possible side product in the synthesis of complex 3, a species where the platinum is not bound to the 4-cyanophenyl group but rather to a carbon of the isopropyl group, has been taken into account during the calculations (see ESI, Fig. S19†). This C(sp<sup>3</sup>)–Pt cyclometalated compound, which also forms a five-membered metallacycle, was found to be thermodynamically less favoured by 10.5 kcal mol<sup>−1</sup> and could indeed not be observed experimentally.

The frontier molecular orbitals (FMOs, Fig. 6) show a major contribution from the NHC ligand to the HOMO and LUMO, which are both of  $\pi$  character and show some contributions from metal d-orbitals and the  $\pi$  system of the auxiliary ligand as well. This is in good agreement with an MLCT/ILCT emission process as expected from the observed photophysical experiments. Since complexes 3 and 5 have a larger conjugated  $\pi$  electron system, a different HOMO–LUMO gap and consequently a different emission colour would be expected in comparison to the imidazole complexes 4 and 6. However, an

analysis of the FMOs reveals only a minor contribution of the benzimidazole phenyl ring to the HOMO, which might explain the very similar emission wavelengths observed for all four complexes.

Additionally computed spin densities of the lowest triplet state agree well with the findings from the FMO analysis and support an MLCT/ILCT process (see ESI, Fig. S20†).

A recently developed method to reliably predict the emission wavelength of transition-metal complexes helped with the development of these blue emitting complexes. *We a priori* computed the emission maxima of several complexes and synthesized only those which were predicted to have a blue emission colour.<sup>18</sup> The values obtained from the calculations are in very good agreement with the ones measured in the experiments (see ESI, Table S5†).

## Conclusions

Four new C<sup>^</sup>C\* cyclometalated Pt(II) NHC complexes with interesting photophysical properties were prepared and fully characterized. The choice of NHC ligands with nitrile substituents at the cyclometalated ring resulted in compounds with blue emission colour and wavelength maxima as low as 445 nm. The complexes with acetylacetonato as an auxiliary ligand showed good quantum yields (60%) and common excited state lifetimes of 15–17  $\mu$ s in amorphous PMMA films at room temperature. Based on DFT calculations we propose that the emission process is of <sup>3</sup>ILCT/<sup>3</sup>MLCT character, which is in good agreement with the strong vibronic coupling observed in the emission spectra. Solid-state structure determination by X-ray diffraction experiments showed the formation of a superstructure with Pt...Pt distances slightly below the

sum of van der Waals radii. A second auxiliary ligand with bulky mesityl substituents was chosen for comparison and we obtained dimesitylmethanato substituted complexes with significantly higher quantum yields (>80%), shorter decay lifetimes (8–9  $\mu$ s) and a different superstructure in the solid state. These results are in agreement with experimental data from the measurements of amorphous 100 wt% emitter films. Thus, the mesacac ligand is a promising alternative auxiliary ligand for this class of emitters compared to the generally used acetylacetonate.

## Experimental section

### General considerations

Solvents of at least 99.5% purity were used throughout this study. 1,4-Dioxane and DMF were dried using standard techniques and stored under an argon atmosphere over molecular sieve (3 Å). Dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl<sub>2</sub>)<sup>19</sup> was prepared following a modified literature procedure.<sup>12</sup> Dimesitylmethane was prepared according to a known procedure.<sup>20</sup> Potassium tetrachloroplatinate(II) was obtained from Pressure Chemicals Co. All other chemicals were obtained from common suppliers and used without further purification. <sup>1</sup>H, <sup>13</sup>C and <sup>195</sup>Pt NMR spectra were recorded on a Bruker 300 MHz, 500 MHz and 600 MHz NMR spectrometer. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally using the resonances of the solvent (<sup>1</sup>H: 7.26, <sup>13</sup>C: 77.0 for CDCl<sub>3</sub>; <sup>1</sup>H: 2.50, <sup>13</sup>C: 39.43 for DMSO-*d*<sub>6</sub>). <sup>19</sup>F NMR spectra were referenced externally against trifluoromethylbenzene (F<sub>3</sub>C-C<sub>6</sub>H<sub>5</sub>). <sup>195</sup>Pt NMR spectra were referenced externally using potassium tetrachloroplatinate(II) in D<sub>2</sub>O (−1617.2 (PtCl<sub>4</sub><sup>2−</sup>), −2654.1 (PtCl<sub>2</sub>)). Shifts are given in ppm, coupling constants *J* in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute on a Hekatech elemental analyser. Melting points have been determined using a Wagner and Munz Poly Therm A system and are not corrected. The emitter films were prepared by doctor blading a solution of emitter (2 mg mL<sup>−1</sup>) in a 10 wt% PMMA solution in dichloromethane on a substrate with a 60  $\mu$ m doctor blade. Quantum yields were determined by an absolute method using the integrated sphere technique of a Hamamatsu Quantaaurus apparatus.

### Syntheses of ligands

**1-(4-Cyanophenyl)-3-isopropyl-1H-benzo[d]imidazolium tetrafluoroborate (1).** The synthesis followed known literature procedures.<sup>10,21</sup> <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  10.25 (s, 1H, NCHN), 8.26–8.30 (m, 3H, CH<sub>arom</sub>), 8.10 (d, *J* = 8.6 Hz, 2H, CH<sub>arom</sub>), 7.93 (d, *J* = 8.5 Hz, 1H, CH<sub>arom</sub>), 7.73–7.82 (m, 2H, CH<sub>arom</sub>), 5.18 (td, *J* = 6.6 Hz, *J* = 13.3 Hz, 1H, CH<sub>3</sub>CHCH<sub>3</sub>), 1.72 (d, *J* = 6.7 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  141.4 (NCHN), 136.9 (C<sub>i</sub>), 134.3 (CH<sub>arom</sub>), 130.8 (C<sub>i</sub>), 130.6 (C<sub>i</sub>), 127.6 (CH<sub>arom</sub>), 127.0 (CH<sub>arom</sub>), 126.4 (CH<sub>arom</sub>), 117.8 (C<sub>i</sub>), 114.3 (CH<sub>arom</sub>), 113.5 (CH<sub>arom</sub>), 112.9 (C<sub>i</sub>), 51.1 (CH<sub>3</sub>CHCH<sub>3</sub>), 21.4 (CH<sub>3</sub>) ppm. <sup>19</sup>F NMR (282 MHz, DMSO-*d*<sub>6</sub>):

$\delta$  −148.9, −149.0 ppm. M.p.: 193–194 °C. Anal. calcd for C<sub>17</sub>H<sub>16</sub>BF<sub>4</sub>N<sub>3</sub>: C 58.48, H 4.62, N 12.04; found: C 58.38, H 4.77, N 12.08%.

**1-(4-Cyanophenyl)-3-methyl-4-(1-methylprop-2-yl)-1H-imidazolium iodide (2).** The synthesis followed known literature procedures.<sup>10</sup> <sup>1</sup>H NMR (300 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  9.85 (s, 1H, NCHN), 8.18–8.22 (m, 3H, CH<sub>arom</sub>), 8.03 (d, *J* = 8.9 Hz, 2H, CH<sub>arom</sub>), 4.03 (s, 3H, NCH<sub>3</sub>), 1.42 (s, 9H, CCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (75 MHz, DMSO-*d*<sub>6</sub>):  $\delta$  143.4 (C<sub>i</sub>), 137.7 (NCHN), 134.3 (CH<sub>arom</sub>), 122.1 (CH<sub>arom</sub>), 117.7 (C<sub>i</sub>), 116.7 (CH<sub>arom</sub>), 112.0 (C<sub>i</sub>), 36.6 (NCH<sub>3</sub>), 31.1 (C<sub>i</sub>), 28.4 (CCH<sub>3</sub>) ppm. M.p.: 297–298 °C. Anal. calcd for C<sub>15</sub>H<sub>18</sub>IN<sub>3</sub>: C 49.06, H 4.94, N 11.44; found: C 48.75, H 5.04, N 11.47%.

### Syntheses of complexes

The established synthetic route for the general synthesis of the platinum(II) complexes 3–6 uses silver(I) oxide (93 mg, 0.4 mmol) and the NHC ligand precursor (0.8 mmol) in 20 mL of dry 1,4-dioxane at room temperature under argon. Pt(COD)Cl<sub>2</sub> (299 mg, 0.8 mmol) and 10 mL of 2-butanone were added to the reaction mixture. The mixture was then refluxed for 21 h and all volatile compounds removed *in vacuo*. Afterwards, potassium *tert*-butanolate (357 mg, 3.2 mmol), 3.2 mmol of the corresponding auxiliary ligand and 20 mL of DMF were added to the crude reaction mixture. In the last reaction step the solution was stirred for 21 h at room temperature and 6 h at 100 °C. Upon completion all volatiles were removed *in vacuo* again, the remaining solid washed with water, dried and the complexes isolated by flash chromatography with methylene chloride–isohexane as the eluent.

**[1-(4-Cyanophenyl)-3-isopropyl-1H-benzo[d]imidazol-2-ylidene- $\kappa$ C<sup>2</sup>, $\kappa$ C<sup>2</sup>]platinum(II)acetylacetonate (3).** The synthesis followed the general procedure. 279 mg (0.8 mmol) of **1** and 0.33 mL (3.2 mmol) acetylacetonate were used. Yield: 133 mg, 22%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.18 (d, *pseudo-t*, *J*<sub>H,H</sub> = 1.7 Hz, *J*<sub>H,Pt</sub> = 28.6 Hz, 1H, PtCCH<sub>arom</sub>), 7.95 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, CH<sub>arom</sub>), 7.69 (d, *J*<sub>H,H</sub> = 7.5 Hz, 1H, CH<sub>arom</sub>), 7.54 (d, *J*<sub>H,H</sub> = 8.2 Hz, 1H, CH<sub>arom</sub>), 7.46 (dd, *J*<sub>H,H</sub> = 1.7 Hz, *J*<sub>H,H</sub> = 8.2 Hz, 1H, CH<sub>arom</sub>), 7.40 (dt, *J*<sub>H,H</sub> = 1.3 Hz, *J*<sub>H,H</sub> = 7.8 Hz, 1H, CH<sub>arom</sub>), 7.34 (dt, *J*<sub>H,H</sub> = 1.3 Hz, *J*<sub>H,H</sub> = 7.8 Hz, 1H, CH<sub>arom</sub>), 6.47 (m, 1H, CH<sub>3</sub>CHCH<sub>3</sub>), 5.59 (s, 1H, CH), 2.13 (s, 3H, CH<sub>3</sub>), 2.03 (s, 3H, CH<sub>3</sub>), 1.74 (d, *J*<sub>H,H</sub> = 7.0 Hz, 6H, CHCH<sub>3</sub>) ppm. <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>):  $\delta$  185.9 (OC<sub>i</sub>), 185.3 (OC<sub>i</sub>), 159.9 (C<sub>i</sub>), 151.6 (NCN), 134.2 (CH<sub>arom</sub>), 133.1 (C<sub>i</sub>), 132.2 (C<sub>i</sub>), 128.8 (CH<sub>arom</sub>), 126.7 (C<sub>i</sub>), 124.3 (CH<sub>arom</sub>), 123.1 (CH<sub>arom</sub>), 120.1 (C<sub>i</sub>), 113.7 (CH<sub>arom</sub>), 111.3 (CH<sub>arom</sub>), 111.2 (CH<sub>arom</sub>), 106.2 (C<sub>i</sub>), 102.3 (OCCH), 49.5 (CH<sub>3</sub>CHCH<sub>3</sub>), 28.0 (CH<sub>3</sub>), 27.9 (2 × CH<sub>3</sub>), 21.1 (CH<sub>3</sub>) ppm. <sup>195</sup>Pt NMR (128 MHz, CDCl<sub>3</sub>):  $\delta$  −3365.2 ppm. M.p.: dec. >265 °C. Anal. calcd for C<sub>22</sub>H<sub>21</sub>N<sub>3</sub>O<sub>2</sub>Pt·0.65CH<sub>2</sub>Cl<sub>2</sub>: C 44.62, H 3.69, N 6.89; found: C 44.63, H 3.77, N 6.92%.

**[1-(4-Cyanophenyl)-3-methyl-4-(1-methylprop-2-yl)-1H-imidazol-2-ylidene- $\kappa$ C<sup>2</sup>, $\kappa$ C<sup>2</sup>]platinum(II)acetylacetonate (4).** The synthesis followed the general procedure. 294 mg (0.8 mmol) of **2** and 0.33 mL (3.2 mmol) acetylacetonate were used. Yield: 145 mg, 34%. <sup>1</sup>H NMR (300 MHz, CDCl<sub>3</sub>):  $\delta$  8.04 (d, *pseudo-t*, *J*<sub>H,H</sub> = 1.7 Hz, *J*<sub>H,Pt</sub> = 27.9 Hz, 1H, PtCCH<sub>arom</sub>), 7.33 (dd, *J*<sub>H,H</sub> =

1.7 Hz,  $J_{\text{H,H}} = 8.0$  Hz 1H,  $\text{CH}_{\text{arom}}$ ), 6.96 (s, 1H,  $\text{CH}_{\text{arom}}$ ), 6.89 (d,  $J_{\text{H,H}} = 8.0$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 5.53 (s, 1H, CH), 4.23 (s, 3H,  $\text{NCH}_3$ ), 2.09 (s, 3H,  $\text{CH}_3$ ), 1.98 (s, 3H,  $\text{CH}_3$ ), 1.43 (s, 9H,  $\text{CCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.4 ( $\text{OC}_i$ ), 184.8 ( $\text{OC}_i$ ), 151.7 (NCN), 150.8 (CN), 142.2 ( $\text{C}_i$ ), 134.5 ( $\text{CH}_{\text{arom}}$ ), 128.4 ( $\text{CH}_{\text{arom}}$ ), 126.6 ( $\text{C}_i$ ), 120.2 ( $\text{C}_i$ ), 110.3 ( $\text{CH}_{\text{arom}}$ ), 109.7 ( $\text{CH}_{\text{arom}}$ ), 106.5 ( $\text{C}_i$ ), 102.1 (CH), 34.6 ( $\text{NCH}_3$ ), 31.5 ( $\text{C}_i\text{CH}_3$ ), 29.2 ( $\text{CCH}_3$ ), 27.9 ( $2 \times \text{CH}_3$ ) ppm.  $^{195}\text{Pt}$  NMR (128 MHz,  $\text{CDCl}_3$ ):  $\delta$  -3379.8 ppm. M.p.: 292–293 °C. Anal. calcd for  $\text{C}_{20}\text{H}_{23}\text{N}_3\text{O}_2\text{Pt}$ : C 45.11, H 4.35, N 7.89; found: C 45.25, H 4.55, N 7.51%.

[1-(4-Cyanophenyl)-3-isopropyl-1H-benzo[d]imidazol-2-ylidene- $\kappa\text{C}^2, \kappa\text{C}^2$ ]platinum(II)-1,3-dimesitylpropane-1,3-dionate (5). The synthesis followed the general procedure. 279 mg (0.8 mmol) of 1 and 987 mg (3.2 mmol) dimesitylmethane were used. Yield: 221 mg, 36%.  $^1\text{H}$  NMR (600 MHz,  $\text{CDCl}_3$ ):  $\delta$  8.08 (d,  $J_{\text{H,H}} = 1.7$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.96 (d,  $J_{\text{H,H}} = 8.2$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.66 (d,  $J_{\text{H,H}} = 8.2$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.57 (d,  $J_{\text{H,H}} = 8.2$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.47 (dd,  $J_{\text{H,H}} = 1.7$  Hz,  $J_{\text{H,H}} = 8.2$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.40 (t,  $J_{\text{H,H}} = 7.8$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.33 (t,  $J_{\text{H,H}} = 7.8$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 6.89 (s, 2H,  $\text{CH}_{\text{arom}}$ ), 6.84 (s, 2H,  $\text{CH}_{\text{arom}}$ ), 6.39 (m, 1H,  $\text{CH}_3\text{CHCH}_3$ ), 5.79 (s, 1H, CH), 2.35 (s, 6H,  $\text{CH}_3$ ), 2.32 (s, 3H,  $\text{CH}_3$ ), 2.31 (s, 6H,  $\text{CH}_3$ ), 2.30 (s, 3H,  $\text{CH}_3$ ), 1.55 (d,  $J_{\text{H,H}} = 7.0$  Hz, 6H,  $\text{CH}(\text{CH}_3)_2$ ) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.7 (CO), 185.6 (CO), 159.4 ( $\text{C}_i$ ), 151.6 (NCN), 139.1 ( $\text{C}_i$ ), 138.6 ( $\text{C}_i$ ), 138.0 ( $\text{C}_i$ ), 137.5 ( $\text{C}_i$ ), 134.3 ( $\text{CH}_{\text{arom}}$ ), 133.9 ( $\text{C}_i$ ), 133.4 ( $\text{C}_i$ ), 133.0 ( $\text{C}_i$ ), 132.2 ( $\text{C}_i$ ), 129.1 ( $\text{CH}_{\text{arom}}$ ), 128.4 ( $\text{CH}_{\text{arom}}$ ), 128.0 ( $\text{CH}_{\text{arom}}$ ), 124.4 ( $\text{CH}_{\text{arom}}$ ), 123.1 ( $\text{CH}_{\text{arom}}$ ), 120.1 ( $\text{C}_i$ ), 113.8 ( $\text{CH}_{\text{arom}}$ ), 111.4 ( $\text{CH}_{\text{arom}}$ ), 111.2 ( $\text{CH}_{\text{arom}}$ ), 107.3 (CH), 106.3 ( $\text{C}_i$ ), 49.5 ( $\text{CH}(\text{CH}_3)_2$ ), 21.1 ( $\text{CH}_3$ ), 20.9 ( $\text{CH}_3$ ), 19.9 ( $\text{CH}_3$ ), 19.6 ( $\text{CH}_3$ ), 19.4 ( $\text{CH}_3$ ) ppm.  $^{195}\text{Pt}$  NMR (64 MHz,  $\text{CDCl}_3$ ):  $\delta$  -3320.0 ppm. M.p.: dec. >309 °C. Anal. calcd for  $\text{C}_{38}\text{H}_{37}\text{N}_3\text{O}_2\text{Pt}$ : C 59.83, H 4.89, N 5.51; found: C 59.69, H 4.96, N 5.37%.

[1-(4-Cyanophenyl)-3-methyl-4-(1-methylprop-2-yl)-1H-imidazol-2-ylidene- $\kappa\text{C}^2, \kappa\text{C}^2$ ]platinum(II)-1,3-dimesitylpropane-1,3-dionate (6). The synthesis followed the general procedure. 294 mg (0.8 mmol) of 2 and 987 mg (3.2 mmol) dimesitylmethane were used. Yield: 147 mg, 25%.  $^1\text{H}$  NMR (300 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.94 (d, *pseudo-t*,  $J_{\text{H,H}} = 1.7$  Hz,  $J_{\text{H,Pt}} = 27.2$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 7.33 (dd,  $J_{\text{H,H}} = 1.7$  Hz,  $J_{\text{H,H}} = 8.0$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 6.98 (s, 1H,  $\text{CH}_{\text{arom}}$ ), 6.92 (d,  $J_{\text{H,H}} = 8.0$  Hz, 1H,  $\text{CH}_{\text{arom}}$ ), 6.87 (s, 2H,  $\text{CH}_{\text{arom}}$ ), 6.83 (s, 2H,  $\text{CH}_{\text{arom}}$ ), 5.73 (s, 1H, CH), 4.10 (s, 3H,  $\text{NCH}_3$ ), 2.33–2.28 ( $3 \times$  s, 18H,  $\text{CH}_3$ ), 1.39 (s, 9H,  $\text{CCH}_3$ ) ppm.  $^{13}\text{C}$  NMR (150 MHz,  $\text{CDCl}_3$ ):  $\delta$  185.2 (CO), 184.8 (CO), 151.0 ( $\text{C}_i$ ), 150.8 (NCN), 142.4 ( $\text{C}_i$ ), 139.4 ( $\text{C}_i$ ), 138.7 ( $\text{C}_i$ ), 137.9 ( $\text{C}_i$ ), 137.5 ( $\text{C}_i$ ), 134.6 ( $\text{CH}_{\text{arom}}$ ), 133.9 ( $\text{C}_i$ ), 133.6 ( $\text{C}_i$ ), 128.8 ( $\text{CH}_{\text{arom}}$ ), 128.4 ( $\text{CH}_{\text{arom}}$ ), 128.1 ( $\text{CH}_{\text{arom}}$ ), 126.1 ( $\text{C}_i$ ), 120.1 ( $\text{C}_i$ ), 110.2 ( $\text{CH}_{\text{arom}}$ ), 109.7 ( $\text{CH}_{\text{arom}}$ ), 107.2 (CH), 106.7 ( $\text{C}_i$ ), 34.6 ( $\text{NCH}_3$ ), 31.4 ( $\text{C}(\text{CH}_3)_3$ ), 29.2 ( $\text{C}(\text{CH}_3)_3$ ), 21.1 ( $\text{CH}_3$ ), 21.0 ( $\text{CH}_3$ ), 19.8 ( $\text{CH}_3$ ), 19.5 ( $\text{CH}_3$ ) ppm.  $^{195}\text{Pt}$  NMR (128 MHz,  $\text{CDCl}_3$ ):  $\delta$  -3330.0 ppm. M.p.: 308–310 °C. Anal. calcd for  $\text{C}_{36}\text{H}_{39}\text{N}_3\text{O}_2\text{Pt}$ : C 58.37, H 5.31, N 5.67; found: C 58.69, H 5.45, N 5.63%.

### Computational details

All calculations were performed with the Gaussian09 package.<sup>22</sup> The density functional hybrid model B3LYP<sup>23</sup> and

the gradient-corrected density functional BP86<sup>24</sup> were used together with the 6-31G(d)<sup>25</sup> basis set. No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. In all cases platinum was described using a decontracted Hay–Wadt ( $n + 1$ ) ECP and basis set.<sup>26</sup> Approximate free energies were obtained through thermochemical analysis, using the thermal correction to Gibbs free energy as reported by Gaussian09. This takes into account zero-point effects, thermal enthalpy corrections, and entropy. All energies reported in this paper, unless otherwise noted, are Gibbs free energies at standard conditions ( $T = 298$  K,  $p = 1$  atm), using unscaled frequencies. For visualization GaussView<sup>27</sup> and CYLview<sup>28</sup> were used.

### X-ray crystallography

Preliminary examination and data collection were carried out on an area detecting system (Kappa-CCD; Nonius, FR590) using graphite monochromated Mo  $\text{K}_\alpha$  radiation ( $\lambda = 0.71073$  Å) with an Oxford Cryosystems cooling system at the window of a sealed fine-focus X-ray tube. The reflections were integrated. Raw data were corrected for Lorentz, polarization, decay and absorption effects. The absorption correction was applied using SADABS.<sup>29</sup> After merging, the independent reflections were used for all calculations. The structure was solved by a combination of direct methods<sup>30</sup> and difference Fourier syntheses.<sup>31</sup> All non-hydrogen atom positions were refined with anisotropic displacement parameters. Hydrogen atoms were placed in ideal positions using the SHELXL riding model. Full-matrix least-squares refinements were carried out by minimizing  $\Sigma w(F_o^2 - F_c^2)^2$  with the SHELXL-97 weighting scheme and stopped at shift/err < 0.001. Details of the structure determinations are given in the ESI.† Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from International Tables for Crystallography.<sup>32</sup> All calculations were performed with the programs COLLECT,<sup>33</sup> DIRAX,<sup>34</sup> EVALCCD,<sup>35</sup> SIR92,<sup>30</sup> SADABS,<sup>29</sup> PLATON<sup>36</sup> and the SHELXL-97 package.<sup>31,37</sup> For the visualization Mercury<sup>38</sup> and ORTEP-III<sup>39</sup> were used.

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## Notes and references

- 1 J. Kido, M. Kimura and K. Nagai, *Science*, 1995, **267**, 1332.
- 2 (a) S. R. Forrest, *Nature*, 2004, **428**, 911; (b) N. Koch, *ChemPhysChem*, 2007, **8**, 1438.



- 3 M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson and S. R. Forrest, *Nature*, 1998, **395**, 151.
- 4 H. Yersin, *Top. Curr. Chem.*, 2004, **241**, 1.
- 5 (a) C. Adachi, M. A. Baldo, S. R. Forrest and M. E. Thompson, *Appl. Phys. Lett.*, 2000, **77**, 904; (b) H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH, Weinheim, Germany, 2008.
- 6 (a) P.-T. Chou and Y. Chi, *Chem.–Eur. J.*, 2007, **13**, 380; (b) Y. Chi and P.-T. Chou, *Chem. Soc. Rev.*, 2010, **39**, 638.
- 7 (a) S. Lamansky, P. Djurovich, D. Murphy, F. Abdel-Razzaq, H.-E. Lee, C. Adachi, P. E. Burrows, S. R. Forrest and M. E. Thompson, *J. Am. Chem. Soc.*, 2001, **123**, 4304; (b) T. Sajoto, P. I. Djurovich, A. Tamayo, M. Yousufuddin, R. Bau, M. E. Thompson, R. J. Holmes and S. R. Forrest, *Inorg. Chem.*, 2005, **44**, 7992; (c) M. K. Nazeeruddin and M. Gratzel, *Struct. Bonding*, 2007, **123**, 113; (d) J. A. G. Williams, A. J. Wilkinson and V. L. Whittle, *Dalton Trans.*, 2008, 2081; (e) C. Ulbricht, B. Beyer, C. Friebe, A. Winter and U. S. Schubert, *Adv. Mater.*, 2009, **21**, 4418; (f) T. Sajoto, P. I. Djurovich, A. B. Tamayo, J. Oxgaard, W. A. Goddard and M. E. Thompson, *J. Am. Chem. Soc.*, 2009, **131**, 9813.
- 8 (a) M. Maestri, D. Sandrini, V. Balzani, L. Chassot, P. Jolliet and A. Von Zelewsky, *Chem. Phys. Lett.*, 1985, **122**, 375; (b) D. Sandrini, M. Maestri, M. Ciano, V. Balzani, R. Lueoend, C. Deuschel-Cornioley, L. Chassot and A. Von Zelewsky, *Gazz. Chim. Ital.*, 1988, **118**, 661; (c) C. M. Che, K. T. Wan, L. Y. He, C. K. Poon and V. W. W. Yam, *J. Chem. Soc., Chem. Commun.*, 1989, 943; (d) M. Maestri, C. Deuschel-Cornioley and A. Von Zelewsky, *J. Photochem. Photobiol., A*, 1992, **67**, 173; (e) M. Hissler, W. B. Connick, D. K. Geiger, J. E. McGarrah, D. Lipa, R. J. Lachicotte and R. Eisenberg, *Inorg. Chem.*, 2000, **39**, 447; (f) S.-C. Chan, M. C. W. Chan, Y. Wang, C.-M. Che, K.-K. Cheung and N. Zhu, *Chem.–Eur. J.*, 2001, **7**, 4180; (g) V. Adamovich, J. Brooks, A. Tamayo, A. M. Alexander, P. I. Djurovich, B. W. D'Andrade, C. Adachi, S. R. Forrest and M. E. Thompson, *New J. Chem.*, 2002, **26**, 1171; (h) I. E. Pomestchenko, C. R. Luman, M. Hissler, R. Ziessel and F. N. Castellano, *Inorg. Chem.*, 2003, **42**, 1394; (i) J. A. G. Williams, *Top. Curr. Chem.*, 2007, **281**, 205; (j) Z. M. Hudson, C. Sun, M. G. Helander, H. Amarné, Z.-H. Lu and S. Wang, *Adv. Funct. Mater.*, 2010, **20**, 3426; (k) G. Zhou, Q. Wang, X. Wang, C.-L. Ho, W.-Y. Wong, D. Ma, L. Wang and Z. Lin, *J. Mater. Chem.*, 2010, **20**, 7472; (l) Z. M. Hudson, M. G. Helander, Z.-H. Lu and S. Wang, *Chem. Commun.*, 2011, **47**, 755; (m) J. Kalinowski, V. Fattori, M. Cocchi and J. A. G. Williams, *Coord. Chem. Rev.*, 2011, **255**, 2401; (n) A. F. Rausch, L. Murphy, J. A. G. Williams and H. Yersin, *Inorg. Chem.*, 2012, **51**, 312; (o) E. Rossi, A. Colombo, C. Dragonetti, D. Roberto, R. Ugo, A. Valore, L. Falciola, P. Brulatti, M. Cocchi and J. A. G. Williams, *J. Mater. Chem.*, 2012, **22**, 10650; (p) K. Li, G. Cheng, C. Ma, X. Guan, W.-M. Kwok, Y. Chen, W. Lu and C.-M. Che, *Chem. Sci.*, 2013, **4**, 2630; (q) S. C. F. Kui, P. K. Chow, G. Cheng, C.-C. Kwok, C. L. Kwong, K.-H. Low and C.-M. Che, *Chem. Commun.*, 2013, **49**, 1497.
- 9 J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau and M. E. Thompson, *Inorg. Chem.*, 2002, **41**, 3055.
- 10 M. Egen, K. Kahle, M. Bold, T. Gessner, C. Lennartz, S. Nord, H.-W. Schmidt, M. Thelakkat, M. Baete, C. Neuber, W. Kowalsky, C. Schildknecht and H.-H. Johannes, WO2006056418A2, 2006.
- 11 K. Hiraki, M. Onishi, K. Ohnuma and K. Sugino, *J. Organomet. Chem.*, 1981, **216**, 413.
- 12 Y. Unger, D. Meyer, O. Molt, C. Schildknecht, I. Muenster, G. Wagenblast and T. Strassner, *Angew. Chem., Int. Ed.*, 2010, **49**, 10214.
- 13 (a) A. Tronnier, A. Risler, N. Langer, G. Wagenblast, I. Münster and T. Strassner, *Organometallics*, 2012, **31**, 7447; (b) Z. M. Hudson, C. Sun, M. G. Helander, Y.-L. Chang, Z.-H. Lu and S. Wang, *J. Am. Chem. Soc.*, 2012, **134**, 13930; (c) T. Strassner, Y. Unger, D. Meyer, O. Molt, I. Muenster and G. Wagenblast, *Inorg. Chem. Commun.*, 2013, **30**, 39; (d) A. Tronnier and T. Strassner, *Dalton Trans.*, 2013, **42**, 9847; (e) A. Tronnier, A. Pöthig, E. Herdtweck and T. Strassner, Submitted.
- 14 A. Tronnier, Unpublished results.
- 15 (a) S. J. Farley, D. L. Rochester, A. L. Thompson, J. A. K. Howard and J. A. G. Williams, *Inorg. Chem.*, 2005, **44**, 9690; (b) X.-H. Zhao, G.-H. Xie, Z.-D. Liu, W.-J. Li, M.-d. Yi, L.-H. Xie, C.-P. Hu, R. Zhu, Q. Zhao, Y. Zhao, J.-F. Zhao, Y. Qian and W. Huang, *Chem. Commun.*, 2012, **48**, 3854; (c) T. Shigehiro, S. Yagi, T. Maeda, H. Nakazumi, H. Fujiwara and Y. Sakurai, *J. Phys. Chem. C*, 2013, **117**, 532; (d) A. Tronnier, N. Nischan, S. Metz, G. Wagenblast, I. Münster and T. Strassner, *Eur. J. Inorg. Chem.*, 2013, DOI: 10.1002/ejic.201301398.
- 16 T. W. Thomas and A. E. Underhill, *Chem. Soc. Rev.*, 1972, **1**, 99.
- 17 (a) P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597; (b) G. Gervasio, R. Bianchi and D. Marabello, *Chem. Phys. Lett.*, 2004, **387**, 481; (c) C.-M. Che and S.-W. Lai, *Coord. Chem. Rev.*, 2005, **249**, 1296.
- 18 Y. Unger, T. Strassner and C. Lennartz, *J. Organomet. Chem.*, 2013, **748**, 63.
- 19 D. Drew and J. R. Doyle, *Inorg. Synth.*, 1990, **28**, 346.
- 20 C. Zhang, P. Yang, Y. Yang, X. Huang, X.-J. Yang and B. Wu, *Synth. Commun.*, 2008, **38**, 2349.
- 21 A. Figge, H. J. Altenbach, D. J. Brauer and P. Tielmann, *Tetrahedron: Asymmetry*, 2002, **13**, 137.
- 22 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene,

- J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski and D. J. Fox, *Gaussian 09, Rev. B 0.1*, Gaussian, Inc., Wallingford, CT, 2009.
- 23 (a) S. H. Vosko, L. Wilk and M. Nusair, *Can. J. Phys.*, 1980, **58**, 1200; (b) C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B: Condens. Matter*, 1988, **37**, 785; (c) B. Miehlich, A. Savin, H. Stoll and H. Preuss, *Chem. Phys. Lett.*, 1989, **157**, 200; (d) A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648; (e) P. J. Stephens, F. J. Devlin, C. F. Chabalowski and M. J. Frisch, *J. Phys. Chem.*, 1994, **98**, 11623.
- 24 (a) J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **33**, 8822; (b) J. P. Perdew, *Phys. Rev. B: Condens. Matter*, 1986, **34**, 7406; (c) A. D. Becke, *Phys. Rev. A*, 1988, **38**, 3098.
- 25 (a) R. Ditchfield, W. J. Hehre and J. A. Pople, *J. Chem. Phys.*, 1971, **54**, 724; (b) W. J. Hehre, R. Ditchfield and J. A. Pople, *J. Chem. Phys.*, 1972, **56**, 2257; (c) P. C. Hariharan and J. A. Pople, *Chem. Phys. Lett.*, 1972, **16**, 217; (d) P. C. Hariharan and J. A. Pople, *Theor. Chim. Acta*, 1973, **28**, 213; (e) P. C. Hariharan and J. A. Pople, *Mol. Phys.*, 1974, **27**, 209; (f) V. A. Rassolov, J. A. Pople, M. A. Ratner and T. L. Windus, *J. Chem. Phys.*, 1998, **109**, 1223; (g) V. A. Rassolov, M. A. Ratner, J. A. Pople, P. C. Redfern and L. A. Curtiss, *J. Comput. Chem.*, 2001, **22**, 976.
- 26 (a) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 299; (b) P. J. Hay and W. R. Wadt, *J. Chem. Phys.*, 1985, **82**, 270; (c) W. R. Wadt and P. J. Hay, *J. Chem. Phys.*, 1985, **82**, 284.
- 27 R. Dennington II, T. Keith, J. Millam, K. Eppinnett, W. L. Hovell and R. Gilliland, *GaussView, 3.09*, Semichem, Inc., Shawnee Mission, 2003.
- 28 C. Y. Legault, *CYLVview, 1.0b*, Université de Sherbrooke, 2009.
- 29 G. M. Sheldrick, *SADABS, Version 2.10*, University of Goettingen, Goettingen, Germany, 2002.
- 30 A. Altomare, G. Cascarano, C. Giacovazzo, A. Guagliardi, M. C. Burla, G. Polidori and M. Camalli, *J. Appl. Crystallogr.*, 1994, **27**, 435.
- 31 G. M. Sheldrick, *Acta Crystallogr., Sect. A: Fundam. Crystallogr.*, 2008, **A64**, 112.
- 32 *International Tables for Crystallography, Vol. C; Mathematical, Physical and Chemical Tables*, ed. A. J. C. Wilson, Kluwer, 1992.
- 33 R. W. W. Hooft, *Data Collection Software for Nonius-Kappa CCD*, Nonius B.V., Delft, The Netherlands, 1999.
- 34 A. J. M. Duisenberg, *J. Appl. Crystallogr.*, 1992, **25**, 92.
- 35 A. J. M. Duisenberg, L. M. J. Kroon-Batenburg and A. M. M. Schreurs, *J. Appl. Crystallogr.*, 2003, **36**, 220.
- 36 A. L. Spek, *Acta Crystallogr., Sect. D: Biol. Crystallogr.*, 2009, **D65**, 148.
- 37 G. M. Sheldrick, *SHELXL-97, Program for the Refinement of Structures*, University of Goettingen, Goettingen, Germany, 1997.
- 38 C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek and P. A. Wood, *J. Appl. Crystallogr.*, 2008, **41**, 466.
- 39 (a) L. J. Farrugia, *J. Appl. Crystallogr.*, 1997, **30**, 565; (b) M. N. Burnett and C. K. Johnson, *ORTEP-III*, Oak Ridge National Laboratory, Oak Ridge, TN, USA, 2000.