

Blue phosphorescent emitters: new *N*-heterocyclic platinum(II) tetracarbene complexes†‡

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Photoluminescence measurements show that platinum(II) tetracarbene complexes, which could be obtained via different synthetic routes, are interesting lead structures for the development of blue emitters for PhOLEDs with good quantum yields and high photostability.

In the last decade novel transition metal complexes of *N*-heterocyclic carbenes have found applications in many fields of chemistry. Fig. 1 shows some published examples of *N*-heterocyclic tetracarbenes of the group 10 metals nickel(II) and palladium(II).^{2–10} Complexes derived from protonated imidazoles with different substituents (Fig. 1, **I**),⁴ with crown ether topology (Fig. 1, **II**)⁹ and with biscarbene ligands (Fig. 1, **III**) have been published. There are also other examples with different bridges (e.g. BH₂, *o*-xylene)^{2,6} or derived from benzimidazoles^{8,11} which are not shown here.

With one exception published by Herrmann and co-workers,⁸ all previously reported tetracarbene complexes with chelating *N*-heterocyclic biscarbenes have been homoleptic ones (Fig. 1, **III**).^{3,5,7,8,10} Examples of platinum(II) tetracarbenes with the general structure of **III** are rare in the literature, only one example was reported as a byproduct.¹² We also found that tetracarbenes are formed in small amounts during the corresponding biscarbene synthesis^{13,14} and set out to selectively make homo- and heteroleptic platinum(II) tetracarbene complexes. Here we report the syntheses of these new platinum(II) tetracarbenes (Scheme 1) and the interesting photophysical properties of selected complexes.¹ The bis-imidazolium salts **1a–1d** were synthesized as previously described.^{12–24}

The homoleptic tetracarbenes bis(1,1'-dimethyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (**3aa**) and bis(1,1'-di-*n*-butyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (**3dd**) can be obtained in a one-pot reaction (Scheme 1, path 1) due to the lower steric demands of the methyl and *n*-butyl substituents, while the synthesis of bis(1,1'-di-isopropyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (**3bb**) and bis(1,1'-

dicyclohexyl-3,3'-methylene-diimidazoline-2,2'-diylidene)platinum(II) diiodide (**3cc**) with the sterically more demanding isopropyl and cyclohexyl substituents requires a two-step strategy. First the corresponding biscarbenes **2b–2d** need to be synthesized and isolated followed by conversion to the tetracarbene (Scheme 1, path 2), which is also necessary for the heteroleptic tetracarbenes **3ab–3ad**.

The homoleptic tetracarbene complexes **3aa–3dd** show two signals in the ¹H-NMR spectra in the range between δ = 7–8 ppm, which can be assigned to the imidazole backbone, while for the bridging CH₂-group two doublets in the range δ = 6–7 ppm are observed. It is well known from the biscarbene complexes that the two hydrogen atoms become different if the complex is conformationally restricted. This is even more pronounced in the case of the tetracarbenes, which cannot dynamically invert the central six-membered ring (Pt–C–N–CH₂–N–C). As expected, the ¹H-NMR spectra of the heteroleptic complexes **3ab–3ad** show four signals for the imidazole ring protons and four doublets for the methylene protons. The ¹³C-NMR spectra of **3ab–3ad** show two signals for the non-equivalent carbene carbon atoms while for the homoleptic tetracarbenes **3aa–3dd** only one signal for the carbene carbon atom can be observed.

Suitable crystals for the X-ray diffraction study were obtained by slow diffusion of methanol into a saturated solution of the metal complex in dimethyl sulfoxide. Fig. 2 shows the solid-state structure of the tetracarbene complex **3aa**. The metal is well protected by the two biscarbene ligands with the methyl groups above and below the plane formed by the four carbene carbon atoms and the platinum center. The two iodide anions are non-coordinating (distance platinum–anion

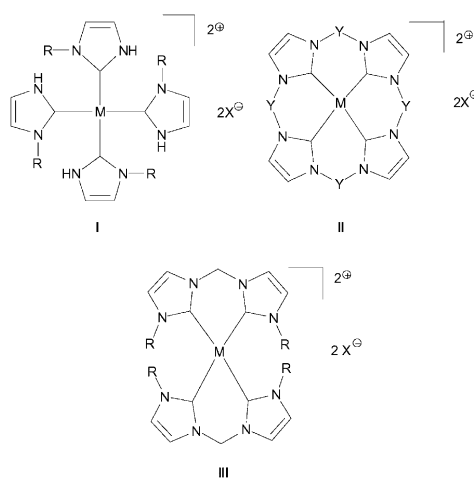


Fig. 1 General structures of tetracarbene complexes.

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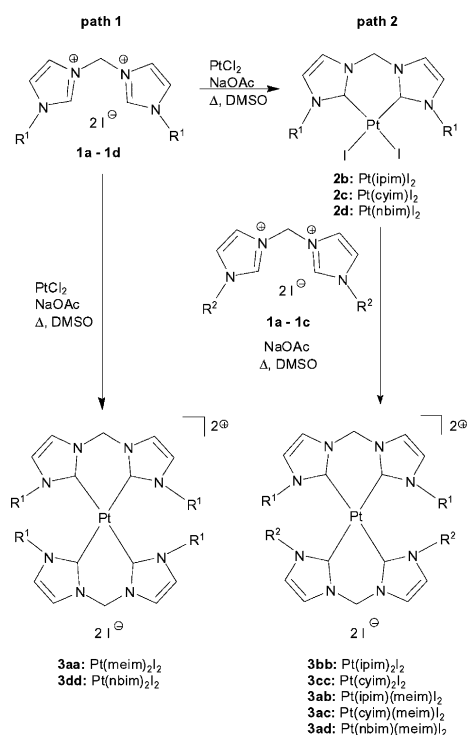
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‡ Electronic supplementary information (ESI) available: Experimental details, X-ray data, excitation spectra. CCDC 680958 (**3aa**). See DOI: 10.1039/b804019b

§ X-Ray analysis.



Scheme 1 Synthetic routes to homo- and heteroleptic Pt(II) tetracarbenes.

> 5 Å). Selected bond lengths and angles are given in the ESI† together with additional 3D-views of the complex.

Phosphorescent organic light-emitting devices (PhOLED) promise to be very efficient light sources in the future and have become more and more important in recent years because of their high efficiency based on their triplet emission.^{26–29} Their quantum efficiency can reach 100%, which is particularly important for practical applications. But currently there is one major problem as no emitters for the deep blue region of the spectrum are available. Many platinum compounds have been reported to be efficient triplet emitters^{30–32} and we were therefore interested in the photophysical properties of the platinum tetracarbenes.

We were surprised to find that some of the tetracarbenes show high quantum yields together with a high photostability at an emission wavelength of 386 nm. The CIE color coordinates of the PL emission are given in Table 1, and a diagram is also in the ESI†. The absorption and emission spectra are

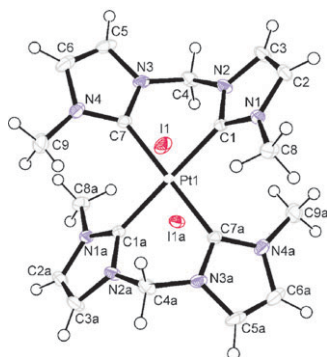


Fig. 2 ORTEP²⁵ representation of complex **3aa**; thermal ellipsoids are drawn at the 50% probability level.

Table 1 Photoluminescence data for selected tetracarbenes complexes

	$\lambda_{\text{exc}}/\text{nm}^a$	X_{RGB}^b	Y_{RGB}^c	$\lambda_{\text{em}}/\text{nm}^d$	ϕ^e
3aa	307	0.165	0.072	386	0.45
3cc	307	0.174	0.121	386	0.06
3ac	307	0.168	0.087	387	0.39

^a Excitation wavelength. ^b CIE coordinates at room temperature. ^c CIE coordinates at room temperature. ^d Emission wavelength. ^e Quantum yield, radiant exposure under N₂.

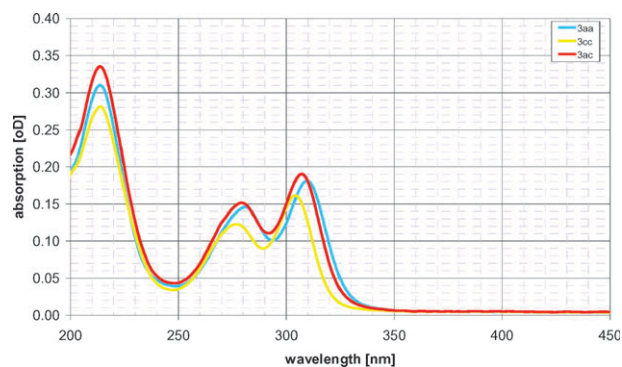


Fig. 3 Absorption spectra of complexes **3aa**, **3ac** and **3cc**, measured as 2% pva-films on qs.

given as Fig. 3 and Fig. 4, the corresponding excitation spectra is in the ESI†. They visualize the different quantum yields given in Table 1 and suggest that this new class of compounds is an interesting lead structure for emitters in the deep blue region of the visible spectrum. It makes them promising candidates for future applications as dopants in displays, although their emission wavelength still needs some tuning.

Table 1 summarizes the photoluminescence data for complexes **3aa**, **3ac** and **3cc**. The emission wavelengths are independent of the substituents, but the quantum yields differ significantly. Smaller substituents are obviously favorable as the best quantum yield was obtained for complex **3aa**. We also studied the complexes using quantum-chemical calculations. The differences between the geometries calculated for the singlet and triplet state of **3aa** are small, which might be favorable for the quantum yield as the complexes with sterically more demanding ligands (**3cc**) show larger differences in the calculated geometries. On the other hand, one larger

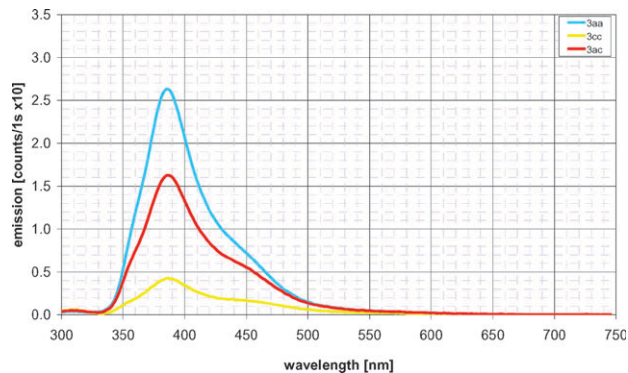


Fig. 4 Emission spectra of complexes **3aa**, **3ac** and **3cc**, measured as 2% pva-films on qs with an excitation wavelength of 307 nm.

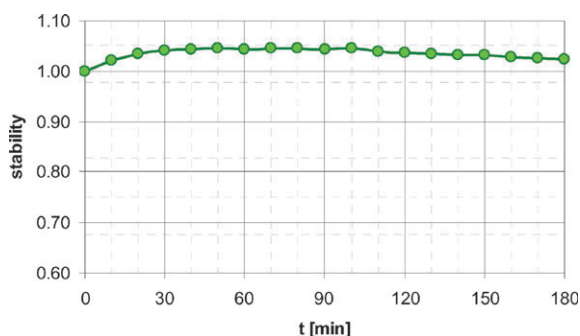


Fig. 5 Photostability of complex **3aa** (2% in pva on qs), excitation wavelength $\lambda_{\text{exc}} = 325$ nm, radiant exposure under N_2 [1.91 mW].

substituent seems to be tolerated with a moderate decrease in quantum efficiency (**3ac**).

The tetracarbene complexes also show an extraordinary stability, chemically (decomposition >340 °C) as well as photochemically. Fig. 5 shows the photostability of complex **3aa**. No significant decrease in the stability over the measurement time is observable.

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