

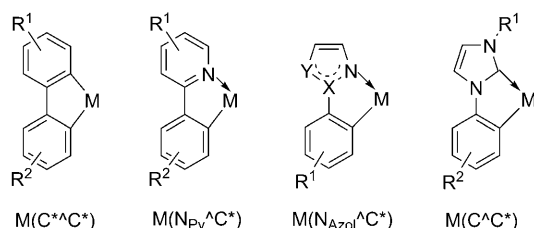
Light-Emitting Diodes

Green–Blue Emitters: NHC-Based Cyclometalated [Pt(C[∧]C*)(acac)] Complexes**

Yvonne Unger, Dirk Meyer, Oliver Molt, Christian Schildknecht, Ingo Münster, Gerhard Wagenblast, and Thomas Strassner*

Transition-metal complexes, which are suitable as emitters for phosphorescent organic light-emitting diodes (PhOLED) are currently of great interest.^[1] Especially iridium and platinum compounds with conjugated ligands are prominent examples because of their exceptional luminescence properties.^[1,2] Iridium complexes in most cases carry two or three cyclometalated bidentate ligands, either as homo- or heteroleptic complexes.^[1,2b] Platinum(II) complexes are known with bidentate as well as tri- and tetradentate ligands.^[2]

Cyclometalating ligands are often derived from compounds such as biphenyl,^[2a,3] 2-phenylpyridine,^[2,4] or phenylazoles such as phenylpyrazole^[1,2b] and 2-phenylimidazole^[5] (Scheme 1). But a new class of platinum compounds, to date



Scheme 1. Examples of cyclometalated complexes derived from biphenyl, 2-phenylpyridine, 2-phenylpyrazole (X = N, Y = CH), 2-phenylimidazole (X = C, Y = NR), or phenylimidazole.

only been mentioned in patents,^[6] was never investigated in detail: platinum(II) compounds with 1-phenylimidazole ligands, which cyclometalate into the phenyl ring (C^{*}) and interact with the metal by a strongly donating interaction of the carbene carbon atom (Scheme 1).

[*] Y. Unger, D. Meyer,^[†] Prof. Dr. T. Strassner
Physikalische Organische Chemie, Technische Universität Dresden
01069 Dresden (Germany)
Fax: (+49) 351-463-39679
E-mail: thomas.strassner@chemie.tu-dresden.de
Homepage: <http://www.chm.tu-dresden.de/oc3>
Dr. O. Molt, Dr. C. Schildknecht, Dr. I. Münster, Dr. G. Wagenblast
BASF SE
67056 Ludwigshafen (Germany)

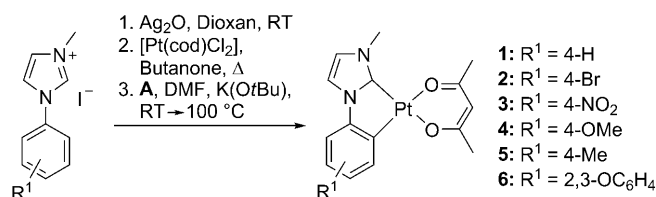
[†] Solid-state structure determination.

[**] We gratefully acknowledge the support of the project through the BMBF (FKZ: 13N10477) and the synthesis of the matrix material by Dr. N. Langer (BASF). D.M. thanks the “Degussa-Stiftung” for financial support. NHC = N-heterocyclic carbene, acac = acetylacetonone.

Supporting information for this article is available on the WWW under <http://dx.doi.org/10.1002/anie.201001316>.

The photophysical properties of cyclometalated β -diketonate platinum(II) complexes ([Pt(N[∧]C*)(O[∧]O)]) are strongly dependent on the substituents on the ligands.^[7] We therefore searched for a way to access the new class of compounds ([Pt(C[∧]C*)(O[∧]O)]). Herein we present the synthesis and photophysical properties of these new platinum(II) complexes, where N-heterocyclic carbene (NHC) compounds are used as cyclometalating (C[∧]C^{*}) ligands. The geometry of these new platinum(II) complexes is discussed on the basis of a solid-state structure and their performance as a light-emitting diode is demonstrated for one example.

To date, only one cyclometalated NHC-platinum(II)- β -diketonate complex ([Pt(C[∧]C*)(acac)] (acac = acetylacetonone)) with a cyano-substituent has been published.^[6f,g] Our synthesis of [Pt(C[∧]C*)(acac)] complexes starts with the reaction of the corresponding imidazolium salts with silver(I) oxide (Scheme 2). Without isolation of the resulting interme-



Scheme 2. Synthesis of the cyclometalated NHC-complexes 1–6. cod = cyclooctadiene.

diate it is transmetalated with (1,5-cyclooctadiene)dichloroplatinum(II). After changing the solvent (from dioxane/butanone to DMF) an excess of acac (**A**) and potassium *tert*-butanolate is added. The reaction mixture is stirred for several hours before the product is isolated. Complexes **1–6** could be synthesized in yields ranging from 16–67% (Scheme 2).

All the compounds were investigated by 1D and 2D NMR spectroscopy to unambiguously assign the NMR signals. The assignment of the protons is based on COSY and ROESY spectra, that of the carbon atoms on HSQC and HMBC spectra. The spectra of compound **4** are given in the Supporting Information. To unambiguously establish the three-dimensional structure, single crystals suitable for the X-ray diffraction (Figure 1)^[8] were obtained by slow evaporation of solvent from a saturated dichloromethane solution of complex **6**.

In complex **6** the central metal ion is square-planar coordinated. As expected, the Pt–C bond lengths are different, the distance between the metal and the cyclometalated

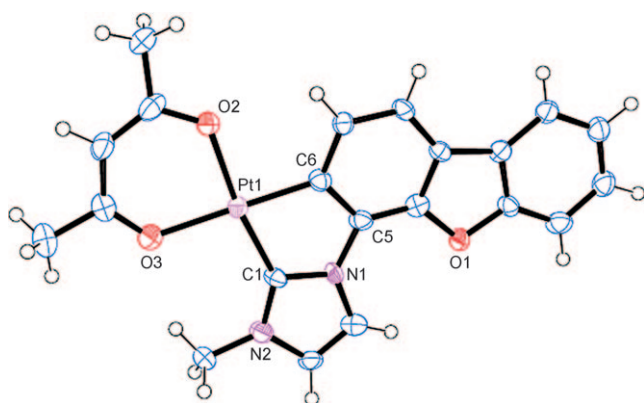


Figure 1. Solid-state structure of complex **6**. Thermal ellipsoids are set at 50% probability. Selected bond lengths [Å] and angles [°]: Pt1–C1 1.937 (8), Pt1–C6 1.960 (6), Pt1–O2 2.055 (6), Pt1–O3 2.089 (6); C1–Pt1–C6 80.5 (3), O2–Pt1–O3 90.0 (2), C6–Pt1–O2 91.4 (3), C1–Pt1–O3 98.0 (3), C1–N1–C5–C6 -2.8 (10).

carbon atom C6 is longer than the distance to the carbene carbon atom C1. The planarity of the system is clear from the small dihedral angle of all the atoms which form the central five-membered ring with the platinum(II) center (C1–N1–C5–C6 -2.8°). While the C1–Pt1–C6 angle (80.5°) deviates significantly from the perfect 90° angle, the O2–Pt1–O3-angle of the acetylacetonate ligand (90°) is ideal for a square-planar coordination geometry. Calculated quantum-chemical data (DFT calculations, see the Supporting Information) agree well with the experimentally determined values. Similar angles have been described before for other cyclometalated platinum(II) complexes with β -diketonate ligands.^[9]

To investigate the photophysical properties, the absorption and emission spectra were measured in a polymethylmethacrylate film (PMMA) at different temperatures. From the absorption spectra of complexes **1–6** (Figure 2a) it is clear that the absorption maximum is independent of the substituent at the phenyl ring. The maximum absorption is around 220 nm and another weaker absorption band can be observed between 300 nm and 350 nm.

The emission spectra of selected compounds are given in Figure 2b. The individual emission spectra of all the complexes are given in the Supporting Information. With the exception of complex **3**, the emission maximum of all the compounds lies in the blue part of the visible spectrum around 450–460 nm, whereas the strongly deactivating group on the phenyl ring in **3** leads to an emission maximum at about 550 nm.

Compound **3** shows a pronounced bathochromic shift of the emission, which might result from the formation of aggregates and a MMLCT (metal metal-to-ligand charge transfer) character of the transition. We therefore undertook concentration-dependent measurements, but the reason for the shift still remains unclear.^[10]

From other cyclometalated platinum(II) complexes the dependence of the emission wavelengths from the substituent at the phenyl ring is well known and can be observed also for this new class of compounds,^[7] which seems to open up possibilities to selectively address certain wavelengths.

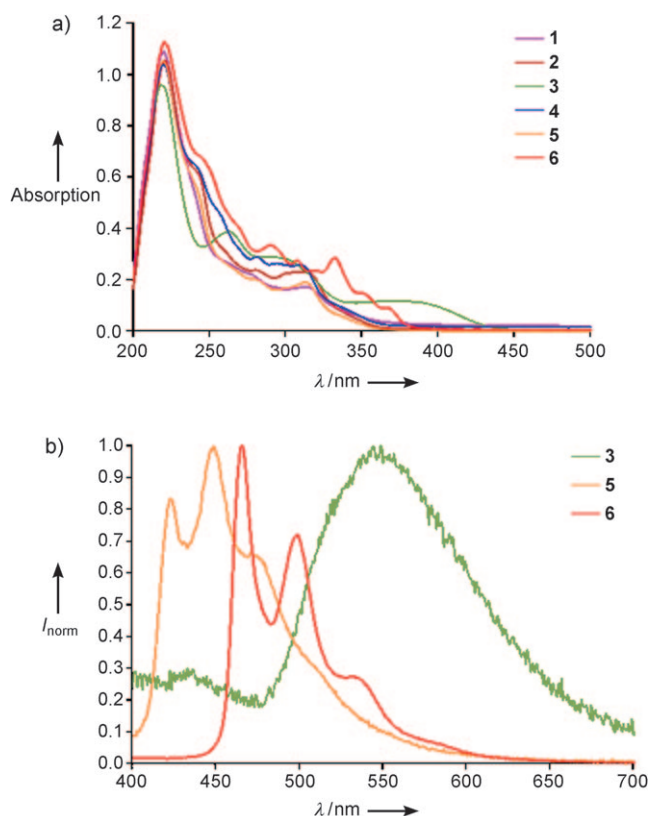


Figure 2. a) Absorption spectra of cyclometalated NHC-complexes **1–6** and b) emission spectra of **3**, **5**, and **6**.

Table 1 summarizes the photoluminescence data of compounds **1–6** at room temperature. The emission of compounds **1–5** contains a significant UV part which makes them less useful for the diodes, but the emission bands of **6** lie in the

Table 1: Photoluminescence data (2% in PMMA, room temperature) of cyclometalated NHC complexes **1–6**.

	λ_{exc} [nm] ^[a]	CIE x,y ^[b]	λ_{em} [nm] ^[c]	$\phi^{[d]}$	τ_0 [μs] ^[e]
1	320	0.190; 0.190	416, 441, 464	0.07	
2	310	0.171; 0.163	418, 446	0.05	
3	355	0.362; 0.469	546	0.11	91
4	355	0.167; 0.157	456	0.32	24
5	315	0.161; 0.131	419, 445	0.20	25
6	355	0.162; 0.314	463, 497	0.90	23

[a] Excitation wavelength. [b] CIE coordinates at room temperature. [c] Emission wavelength. [d] Quantum yield, excited with λ_{exc} , N_2 atmosphere. [e] Decay lifetimes (excited by laser pulses (355 nm, 1 ns)).

visible region of the spectrum. Complexes with electron-donating substituents at the phenyl ring show moderate to good quantum yields. Especially notable are the 90% quantum yield of complex **6**. The strongly structured bands and the relatively long lifetime of the triplet indicate a high LCT (ligand charge transfer) and a small MLCT (metal-to-ligand charge transfer) character of the emission.

Because of its promising emission properties, complex **6** was tested in a device with the new matrix material **7**.^[11] The layout of the diode is given in Figure 3. The device was

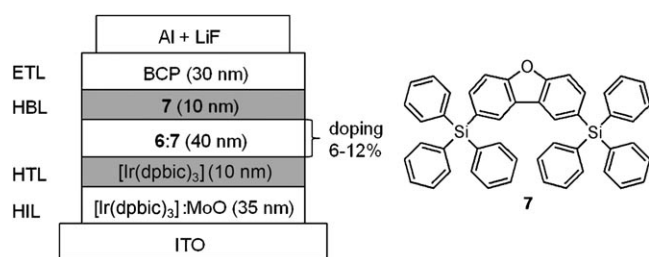


Figure 3. Construction of the device (left) and structure of the Ir complex and compound **7** (right). ELT = electron-transport layer, HBL = hole-blocking layer, HTL = hole transporting layer, HIL = hole injecting layer, BCP = 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline.

produced by thermal deposition under high vacuum conditions onto a glass substrate coated with indium-tin-oxide (ITO), where different concentrations (6, 8, 10, and 12 %) of complex **6** were doped into the new matrix material. The CIE (Commission Internationale de l'éclairage) coordinates of 0.162/0.314 promise a green–blue color which could also be observed in the experiment. Therefore **6** is a promising candidate for the blue component in white OLEDs, as for lighting applications a pure-blue emission is not needed. “Deeper blue compounds” such as **4** with CIE = 0.167/0.157 unfortunately show significantly lower quantum yields.

Independent of the dopant concentration, the electroluminescence spectra (see the Supporting Information) show their maxima at 480 nm and a pronounced progression of the emission band. The maximum luminance depends on the doping concentration and can be found in between 4900 cd m^{-2} (13 V, 6 % doping) and 6750 cd m^{-2} (13.2 V, 12 % doping). The maximum external quantum efficiency is reached at the highest doping concentration of 12 % (Table 2).

Table 2: Device performance.

Doping conc. ^[a]	Current density at 300 cd m^{-2} [mA cm^{-2}]	Voltage at 300 cd m^{-2} [V]	Luminance [cd m^{-2}]	EQE [%] ^[a]
6 %	3.7	8.6	4900	5.4
8 %	3.5	8.5	5000	5.6
10 %	3.2	8.5	5900	6.0
12 %	2.8	8.4	6750	6.2

[a] External quantum efficiency.

We were able to synthesize a new class of platinum(II) complexes with cyclometalated 1-phenylimidazole ligands and investigated their photophysical properties. The solid-state structure of these compounds could be shown for compound **6**. With the exception of **3** all complexes emit in the green–blue part of the visible spectrum and show interesting photophysical properties.

Received: March 4, 2010

Revised: September 30, 2010

Published online: November 29, 2010

Keywords: carbene ligands · cyclometalation · luminescence · OLEDs · platinum

- [1] H. Yersin, *Highly Efficient OLEDs with Phosphorescent Materials*, Wiley-VCH, Weinheim, **2008**.
- [2] a) J. A. G. Williams, *Top. Curr. Chem.* **2007**, *281*, 205–268; b) Y. Chi, P.-T. Chou, *Chem. Soc. Rev.* **2010**, *39*, 638–655.
- [3] C. B. Blanton, Z. Murtaza, R. J. Shaver, D. P. Rillema, *Inorg. Chem.* **1992**, *31*, 3230–3235.
- [4] L. Chassot, E. Mueller, A. Von Zelewsky, *Inorg. Chem.* **1984**, *23*, 4249–4253.
- [5] H. Li, J. Ding, Z. Xie, Y. Cheng, L. Wang, *J. Organomet. Chem.* **2009**, *694*, 2777–2785.
- [6] a) J. Li, Z. Wang, E. Turner (Arizona State University, USA), WO 2009111299, **2009**; b) T. Murakami, K. Yagi, S. Ichijima, T. Igarashi, T. Satou (Fuji Photo Film Co., Japan), WO 2006115301, **2006**; c) R. Pretot, P. A. Van Der Schaaf, J. Schmidt, B. Schmidhalter, T. Schaefer, B. Lamatsch (Ciba Specialty Chemicals Holding Inc., Switzerland), WO 2006067074, **2006**; d) M. E. Thompson, A. Tamayo, P. Djurovich, T. Sajoto, S. R. Forrest, P. B. Mackenzie, R. Walters, J. Brooks, X.-C. Li, B. Alleyne, J.-Y. Tsai, C. Lin, B. Ma, M. S. Barone, R. Kwong (The University of Southern California, USA, The Trustees of Princeton University; Universal Display Corporation), WO 2005113704, **2005**; e) R. Walters, P. B. MacKenzie, M. E. Thompson (USA), US 2005260445, **2005**; f) 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, H.-H. Johannes (BASF AG, Germany), WO 2006056418, **2006**; g) O. Molt, E. Fuchs, M. Egen, K. Kahle, C. Lennartz (BASF AG, Germany), WO 2007088093, **2007**.
- [7] J. Brooks, Y. Babayan, S. Lamansky, P. I. Djurovich, I. Tsyba, R. Bau, M. E. Thompson, *Inorg. Chem.* **2002**, *41*, 3055–3066.
- [8] Crystallographic data for **6**: $\text{C}_{21}\text{H}_{18}\text{N}_2\text{O}_3\text{Pt}$, $M_w = 541.46$, $0.33 \times 0.13 \times 0.12 \text{ mm}^3$, monoclinic, $P2_1/c$, $a = 9.333(1)$, $b = 18.052(1)$, $c = 11.185(2) \text{ \AA}$, $\beta = 109.05(1)^\circ$, $V = 1781.3(4) \text{ \AA}^3$, $Z = 4$, $\rho_{\text{calcd}} = 2.019 \text{ Mg m}^{-3}$, $\mu = 7.902 \text{ mm}^{-1}$, Mo-K α irradiation, $\lambda = 0.71073 \text{ \AA}$, $T = 198(2) \text{ K}$, 18766 reflections, 3628 independent, $R_{\text{int}} = 0.0767$, $R_1 = 0.0460$ ($[F^2 > 2\sigma(F^2)]$), $wR^2 = 0.1291$ (all data), GOF = 1.226, $\theta = 4.84$ to 26.40° . Largest diff. peak and hole 2.685 and $-3.930 \text{ e \AA}^{-3}$. CCDC 794937 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.
- [9] a) B. Ma, P. I. Djurovich, M. Yousufuddin, R. Bau, M. E. Thompson, *J. Phys. Chem. C* **2008**, *112*, 8022–8031; b) Z. He, W.-Y. Wong, X. Yu, H.-S. Kwok, Z. Lin, *Inorg. Chem.* **2006**, *45*, 10922–10937; c) B. Yin, F. Niemeyer, J. A. G. Williams, J. Jiang, A. Boucekkinne, L. Toupet, H. Le Bozec, V. Guerschais, *Inorg. Chem.* **2006**, *45*, 8584–8596.
- [10] a) B. Ma, P. I. Djurovich, M. Yousufuddin, R. Bau, M. E. Thompson, *J. Am. Chem. Soc.* **2005**, *127*, 28–29; b) S.-W. Lai, H.-W. Lam, L. Wei, K.-K. Cheung, C.-M. Che, *Organometallics* **2002**, *21*, 226–234; c) A. F. Rausch, H. H. Homeier, P. I. Djurovich, M. E. Thompson, H. Yersin, *Proc. SPIE* **2007**, *6655*, 66550F1.
- [11] a) N. Langer, K. Kahle, C. Lennartz, O. Molt, E. Fuchs, J. Rudolph, C. Schildknecht, S. Watanabe, G. Wagenblast (BASF SE, Germany), WO 2009003919, **2009**; b) N. Langer, K. Kahle, C. Lennartz, O. Molt, E. Fuchs, J. Rudolph, C. Schildknecht, S. Watanabe, G. Wagenblast (BASF SE, Germany), WO 2009003898, **2009**.