



Conjugated Systems

Diaryl-1,2,3-Triazolylidene Platinum(II) Complexes

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Abstract: Control of the excited state geometry by rational ligand design leads to a new class of phosphorescent emitters with extraordinary photophysical properties. Extension of the π -system in the triplet state leading to a significant bathochromic shift of the emission was avoided by introduction of additional steric demand. We report the synthesis, characterization and photophysical properties of novel platinum(II) complexes bearing C^C* cyclometalated mesoionic carbene (MIC) with different β -diketonate ligands. The MIC ligand precursors were prepared from 1-phenyl-1,2,3-triazole using arylation protocols, introducing phenyl or mesityl functionalities. A solid state structure confirming the NMR assignments is presented. The emission properties were investigated in detail at room temperature and 77 K and are supported by DFT calculations and cyclic voltammetry. All complexes, with emission maxima between 502-534 nm, emit with quantum efficiencies ranging from 70-84% in PMMA films.

donating abnormal NHCs (aNHCs),^[8] where the carbene did

Introduction

Photoluminescent organometallic compounds^[1] are an important pillar of applied chemistry. The interaction of organic components and metal center results in valuable material properties which allow for application in various fields, such as photocatalysis,^[2] dye-sensitized solar cells^[3] or organic light emitting diodes (OLEDs).^[4] The development of the first OLED setup^[5] ultimately required optimizations also for phosphorescent emitter molecules.

Phosphorescent organometallic complexes allow for quantum yields of up to 100%, but defined electronic states and molecular stability are essential to obtain a high-quality dopant. This can be achieved by electronic and steric modifications, which change the properties of the complexes. Especially platinum(II)^[6] and iridium(III)^[6q, r, 7] complexes bearing cyclometalating ligands based on phenylpyridines and aryl-substituted N-heterocyclic carbene (NHC) systems are promising candidates for these applications. Recent results indicated that a rigid geometry in the excited state is crucial for high quantum yields.^[6a]

A number of different N-heterocyclic carbene systems have been tested as ligands in platinum(II) complexes in recent years.^[6a, r] The majority of these motifs were derived from imidazolium-based ligands by deprotonation of the C2-hydrogen atom. In 2001, Crabtree and co-workers discovered strongly

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not form in the C2-position, but rather in the backbone of the heterocycle, resulting in a mesoionic structure. These aNHCs have inspired other motifs, such as 1,2,3-triazolylidenes, which also are mesoionic in nature.^[9] While these mesoionic carbenes (MICs) have been studied regarding their performance in homogeneous catalysis,^[9c] exploration of their prospect as ligands in luminescent transition metal compounds has only recently commenced.^[6b, 10] Here, we present four novel phosphorescent diaryl-1,2,3-triazole-based MIC platinum(II) complexes with remarkable photophysical properties due to the strongly donating heterocycle and their rigid geometry enforced by cyclometalation. We compare systems concerning their ability to include the second aryl ring into the π -system. By nuclear magnetic resonance studies and a solid state structure we confirmed the presence of a mesoionic carbene in the target compounds. We also studied the effect of aryl substituents on the β -diketonate which led to highly interesting phosphorescent emitter molecules.

Results and Discussion

Syntheses of the ligands starts from 1-phenyl-1,2,3-triazole 1 which was prepared according to a literature procedure from aniline (Scheme 1).^[6b, 11] The aryl substituents in 2 and 3 were introduced using hypervalent diaryliodonium tetrafluoroborates. In copper(II) acetate catalyzed reactions,^[12] diphenyliodonium tetrafluoroborate^[13] and bis(2,4,6-trimethylphenyl)iodonium tetrafluoroborate^[14] were reacted with the triazole substrate 1 to yield the quarternized products 2 and 3, respectively. The platinum(II) complexes were synthesized following a multi-step procedure.^[6b, 15] The ligand precursors 2 and 3 were reacted with silver(I)-oxide to give the respective silver(I) carbene complexes. Upon addition of Pt(COD)Cl₂ (COD = 1,5-cyclooctadiene), the NHC ligand is transmetalated to the plati-

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Scheme 1. Synthetic approach towards 4a–c and 5. (i) [Ph₂I][BF₄], Cu(OA-c)₂:H₂O, DMF, 100 °C. (ii) [Mes₂I][BF₄], Cu(OAc)₂:H₂O, DMF, 100 °C. (iii) Ag₂O, DMF, 75 °C. (iv) Pt(COD)Cl₂, RT to 125 °C. (v) β -diketone, base, RT to 100 °C.

num center and subsequently cyclometalated at elevated temperatures, followed by addition of the respective β -diketone ligand and base. Compounds **4a**–**c** and **5** were isolated by flash column chromatography.

All synthesized compounds were characterized by means of standard NMR techniques, mass spectrometry and elemental analysis. Due to its symmetry, compound **2** shows only one singlet resonance for its backbone protons at a chemical shift of $\delta = 9.79$ ppm. The mesitylated salt **3** on the other hand shows the expected two doublet resonances for these protons at 9.49 and 9.90 ppm, with the latter belonging to the proton adjacent to the phenyl ring (based on the NOESY assignment). These backbone hydrogen resonances are a useful probe for the determination of the binding situation. Changes in integration and chemical shift of these resonances are an indication for the formation of the respective mesoionic carbene structure. Interestingly, cyclometalation into the neighboring phenyl ring can also be confirmed by means of NMR spectroscopy as described below for complex **4a**.

The signal shape of the proton resonance at $\delta = 7.9$ ppm (and the coupling constant for its shoulders in the range of 50 Hz) is indicative for a proton-heteroatom coupling (Figure 1). The hetero nucleus responsible for this coupling is the platinum center, which is confirmed by the shape of the signal in the ¹⁹⁵Pt spectrum. Here, a doublet with a coupling constant of 53 Hz is found in the NMR experiment. The vicinal nuclear interaction was confirmed by 2D NMR techniques which allowed us to assign the proton resonance in question to the proton adjacent to the cyclometalating position in the phenyl ring of the metallacycle. Additionally, we were able to obtain a solid state structure for complex 4a which confirms the mesoionic binding mode of the N-heterocyclic ligand. The platinum(II) complex crystallizes in the monoclinic space group C2/c, with eight molecules per unit cell. The metal center forms a square planar coordination sphere, which is slightly twisted out of plane (Figure 2a). While the O(1)-Pt(1)-O(2) angle is close to the ideal value of 90° , the bite angle C(1)-



Figure 1. Relevant segments of the ¹H (CDCl₃, 600 MHz) and ¹⁹⁵Pt (CDCl₃, 64 MHz) NMR spectra for compound **4a** showing the heteroatom coupling between hydrogen and platinum nuclei.



Figure 2. ORTEP3 drawings of 4a. Ellipsoids are given at 50% probability level. a) Molecular structure. b) Packing diagram; view normal to (100). c) Packing diagram; view normal to (010). Selected bond lengths [Å] and angles [deg]: Pt(1)-C(1) 1.943(2); Pt(1)-C(4) 1.992(2); Pt(1)-O(1) 2.0802(16); Pt(1)-O(2) 2.0539(16); C(1)-Pt(1)-C(4) 81.07(9); O(1)-Pt(1)-O(2) 91.15(7); O(1)-Pt(1)-C(1)-C(2) 2.5(3); C(2)-N(1)-C(9)-C(14) -142.1(3).

Pt(1)-C(4) of the MIC ligand in the five-membered metallacycle is significantly smaller with 81.07(9)°. All platinum–carbon and platinum–oxygen bond lengths are within the expected range and compare to those of structurally related compounds.^[6b, 15b] The non-coordinating phenyl ring rotates out of the coordination plane by -142.1(3)°, which also impacts the packing in the solid state (Figure 2b). The molecules stack roughly 180° rotated against one another (Figure 2c), which allows the aforementioned phenyl group to use a gap between the MIC and the β -diketonate ligand. In this orientation, the closest Pt– Pt distance is observed to be 4.53 Å, which rules out a direct metal–metal interaction in this structure.

The photophysical properties of all complexes were investigated at room temperature and for **4a** and **5** additionally at low temperature. Absorption spectra were recorded in dichloromethane (DCM) solution and are given in Figure 3. Complexes **4a**–**c** show an absorption maximum at around 280 nm.

Compound **4a** further displays a broad band around 375 nm, while **4b** and **4c** absorb without distinct bands at higher wavelengths. The spectrum of **5** resembles that of **4a** in terms of structuring but is blue-shifted by approximately 15 nm. TD-DFT calculations using Gaussian 09^[16] were em-

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Figure 3. Absorption (solid) and emission (dotted) spectra of **4**a–**c** and **5**. Absorption spectra were measured in 5×10^{-5} mol L⁻¹ DCM solution. Emission spectra were measured using PMMA films with a 2 wt% emitter load.

ployed to assign the visible bands to electronic transitions (see Supporting Information, Figures S1–S4 and Tables S1–S6). The high energy bands at 280 nm (**4a–c**) and 265 nm (**5**) represent a complex mixture of transitions involving both ligands as well as the metal center. The bands at 375 nm (**4a–c**) and 355 nm (**5**) on the other hand can be attributed to transitions from the HOMO–1/HOMO to the NHC-centered LUMO, to which the MIC ligand, the platinum center and the β -diketonate contribute equally.

Emission properties for all complexes were investigated by preparing poly(methyl methacrylate) (PMMA) films with an emitter concentration of 2 wt %. Additionally, spectra in 2-MeTHF solution were measured (see Experimental Section, for PL data see Supporting Information Table S7). Figure 3 shows the emission spectra for all platinum compounds at room temperature. The emission maxima are flanked by weak shoulders on each side. The emission maximum of complex 4a is in the green region of the spectrum at a wavelength of 532 nm, which corresponds to a bathochromic shift of 39 nm compared to a recently published N-methylated analogous complex.^[6b] The introduction of the N-aryl functionality in 4a exhibits a profound effect on the emission process. To investigate this bathochromic shift we employed DFT calculations which show a distortion of the molecule for 4a when comparing the triplet with the singlet geometry. In the optimized ground state structure the non-coordinating phenyl ring is twisted out of plane with a dihedral angle of -149.8° to the triazole (Figure 4a).

Upon excitation from S₀ into the triplet state T₁ the phenyl ring of **4a** rotates into the molecular plane, effectively enlarging the conjugated π -system (Figure 4b). This results in a stabilization of the excited state, which corresponds to the observed bathochromic shift (see Supporting Information, Figure S5). A simulation of the spin density distribution in the excited state visualizes the contribution of the phenyl moiety (Figure 4c). As expected, this effect persists when introducing more sterically demanding β -diketonate systems like the mesityl and duryl substituents. The impact on the emission maxima



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Figure 4. DFT (B3LYP/6-31G(d)) optimized structures for complex **4a** (a and b) as well as **5** (d and e) with dihedral angles (red bonds). Spin density simulations for the excited states of **4a** (c) and **5** (f), plotted for an isovalue of 0.0008.

of **4b** (533 nm) and **4c** (534 nm) is small, since the intramolecular distance between the β -diketonate and the non-coordinating substituent of the MIC ligand is too large to hinder the rotation of the N-aryl moiety. Notably, in these complexes, the quantum yield is increased to 81% (**4b**) and 82% (**4c**), when compared to **4a**, which achieved a quantum efficiency of 70% (Table 1). The luminescence lifetimes changed only marginally and remained in the range of 12–15 µs upon introduction of the β -diketonate. To test our assumption concerning the planarization in the excited state, we synthesized the N-mesitylated compound **5** with a higher steric demand in the

Table 1. Photoluminescence (2 wt% emitter load in PMMA) and electrochemical data for $4a-c$ and 5 .									
	Photolu $\lambda_{ m exc}$ [nm] ^[a]	minescenc CIE <i>x;y</i> ^[b]	e data λ _{em} [nm] ^[c]	$arPhi^{[d]}$	τ _v [μs] ^[e]	τ _ο [μs] ^[f]	CV <i>E</i> _{1/2} (red) [V] ^[g]		
4a	360	0.349; 0.569	532 (527)	70	10.6	15.1	-2.09		
4b	360	0.340; 0.569	533 (526)	81	10.5	12.9	-2.07		
4c	360	0.337; 0.568	534 (524)	82	10.2	12.4	-2.07		
5	360	0.239; 0.474	502 (492)	84	9.2	11.0	-2.37		

[a] Excitation wavelength. [b] CIE coordinates at RT. [c] Maximum emission wavelength at RT. $\lambda_{\rm em}$ in degassed 2-MeTHF (c =4.5 × 10⁻⁵ mol L⁻¹) at 77 K given in parentheses. [d] Quantum yield at $\lambda_{\rm exc}$ = 360 nm and RT. [e] Experimental phosphorescence lifetime at RT. [f] Phosphorescence lifetime given as $\tau_0 = \tau_v / \Phi$. [g] Cyclic voltammetry experiments referenced to Fc/Fc⁺.

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non-coordinating N-aryl unit. DFT calculations suggest that the mesityl ring is oriented perpendicular to the coordination plane in the ground state (Figure 4d). In the triplet state geometry, the mesityl system and the triazole span a dihedral angle of -116.2° as the methyl groups in the *ortho*-position do not allow further rotation (Figure 4e). An extension of conjugation into the N-aryl unit in the excited state can thereby be attenuated, which is visible in the calculated spin density (Figure 4 f). Compared to 4a, the sterically demanding aryl group in 5 partakes in the emissive process to a significantly lower extent. Consequently, this is also reflected in the position of the emission maximum at 502 nm (Figure 3, Table 1); a hypsochromic shift of 30 nm compared to complex 4a. Additionally, the quantum yield is increased by 14% while the emission lifetimes are slightly shortened to 11 µs. Complexes 4a-c with the phenyl group and 5 carrying a mesityl ring differ significantly in emission color, while the emission band shapes are quite similar, pointing towards a related phosphorescence mechanism. In order to gain more resolved spectra, measurements at low temperature (77 K) were conducted for complexes 4a and 5 in degassed solutions of the emitters in 2-methyltetrahydrofuran. The results given in Figure 5 show resolved emissions



Figure 5. Emission spectra at RT and 77 K for compounds **4a** and **5**. RT measurements were carried out in 2 wt% PMMA films and at 77 K in 2Me-THF $(4.5 \times 10^{-5} \text{ mol L}^{-1})$ solutions.

which are blue-shifted by approximately 10 nm compared to the measurements at room temperature. The spectra at 77 K display three well defined bands and a weak fourth band at higher wavelengths. The first and the second band differ energetically by approximately 1297 cm⁻¹ (**4a**) or 1290 cm⁻¹ (**5**). These energy gaps correspond to infrared (IR) active $0 \rightarrow 1$ transitions, which were assigned to be centered on the MIC ligand by DFT simulations of the respective IR spectra. With these vibrations being represented in the emission spectra, it can be concluded that the heterocyclic ligand is strongly involved in the emissive process, which is consistent with the data presented earlier. Along with the theoretical results obtained from the time-dependent and excited state calculations (Figure 4 and Supporting Information Figure S5) we can characterize the emission as an ILCT/MLCT process.

Cyclic voltammetry experiments were performed on degassed DMF solutions of all complexes (see Supporting Information Figures S6–S9). Compounds 4a-c and 5 show a reversible reduction at -2.07-2.09 V and -2.37 V versus ferrocene (Table 1 and Figure 6), respectively, while the onset of oxidative



Figure 6. Cyclic voltammetry spectra of complexes 4a-c and 5 in degassed DMF solutions at a scan rate of 50 mV s⁻¹. Referenced against Fc/Fc⁺.

processes is between 0.0–0.25 V. The unaltered potential of the reductive event for 4a-c leads to the conclusion that the β -diketonate moiety of the complexes does not partake in the reductive process and the involved molecular orbitals. Moreover, electron-accepting, N-heterocyclic ligands are known to enable reversible reductive processes^[17] which hints towards the reduction taking place at the MIC ligand. This is also consistent with the LUMO plots obtained in the DFT calculations and the higher potential necessary to reduce **5**. DFT calculations of the radical anions of **4a** and **5** display a similar behavior compared to the neutral molecules in the excitation process (see Supporting Information, Figure S10). Unlike complex **5**, the phenylated compound **4a** is able to planarize, which aids in stabilizing the surplus electron and results in a significantly lower reduction potential.

Conclusion

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Four new platinum(II) complexes bearing C^C* cyclometalated mesoionic carbene ligands based on 1,2,3-triazole systems are presented. The phenyl and mesityl groups were introduced to the 1-phenyl-1,2,3-triazole system using the corresponding iodonium reagents. Cyclometalation of the MIC ligand was confirmed by a proton-heteroatom coupling found in the ¹H and ¹⁹⁵Pt spectra, as well as 2D NMR experiments and a solid state structure. All complexes proved to be strongly emissive at

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room temperature in PMMA films with quantum yields ranging from 70 to 84%. Depending on the aryl fragment a significant change of the emission color was noticed. Theoretical calculations confirmed that this effect is due to a distortion of the geometry in the excited state. In the case of the phenyl ligand, the aryl unit rotates into the molecular plane and enlarges the conjugated system. This causes a stabilization of the excited state, resulting in an emission maximum at $\lambda_{em} = 536$ nm, while for the mesityl ligand a planarization is hindered due to steric demand. This significantly reduces its contribution to the conjugated system and blue-shifts the emission by 33 nm.

Experimental Section

General considerations

All compounds were synthesized in flame dried Schlenk tubes and under argon atmosphere unless otherwise noted. Solvents of at least 99.0% purity were used in all reactions in this study. Dimethylformamide (DMF) was dried using standard techniques and stored over molecular sieve (3 Å). Dichloro(cycloocta-1,5-diene)platinum(1) was prepared according to a modified literature procedure.[15b] Bis-1,3-(2,4,6-trimethyl-phenyl)propan-1,3-dione and bis-1,3-(2,3,5,6-tetramethylphenyl)-propan-1,3-dione were prepared according to a modified literature procedure.^[18] All other chemicals were obtained from common suppliers and used without further purification. ¹H, ¹³C, ¹⁹F and ¹⁹⁵Pt spectra were acquired on Bruker NMR Avance 300, Bruker DRX 500 and Bruker Avance 600 NMR spectrometers. ¹H and ¹³C spectra were referenced internally (¹H: 7.26, 13C 77.0 for CDCl3; 1H: 2.50, 13C 39.43 for [D6]DMSO). 195Pt spectra were referenced externally by using potassium tetrachloroplatinate(1) in D₂O (PtCl₄²: -1617.2). ¹⁹F NMR spectra were also referenced externally against trifluoromethylbenzene (-63.72 ppm vs. CCl₃F). Chemical shifts are given in ppm, coupling constants J in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute on a Hekatech EA 3000 Euro Vector elemental analyzer. Melting points were determined by using a Wagner and Munz PolyTherm A system and are not corrected.

Photoluminescence measurements

The 2 wt% emitter films were prepared by doctor blading a solution of an emitter in a 10 wt% PMMA solution in dichloromethane on a quartz substrate with a 60 μ m doctor blade. The film was dried and the emission was measured under nitrogen atmosphere. Room temperature experiments in degassed 2-methyltetrahydrofuran (2-MeTHF) solution were carried out at a concentration of $1 \times$ 10⁻⁵ mol L⁻¹. Solutions for the low temperature measurements at 77 K were prepared by dissolving the emitter in degassed 2-MeTHF to give a concentration of 4.5×10^{-5} mol L⁻¹. The frozen samples in quartz cuvettes were inserted in a guartz finger dewar containing liquid nitrogen. Excitation was conducted in a wavelength range of 250-400 nm (Xe lamp with a monochromator), and the emission was detected with a calibrated quantum yield detection system (Hamamatsu, model C9920-02). The uncertainty of the guantum yield is $\pm 2\%$ for quantum yields of >10%. The phosphorescence decay was measured with an Edinburgh Instruments mini- τ by excitation with pulses of an EPLED (360 nm, 20 kHz) and time-resolved photon counting (TCSPC). Absorption spectra were measured on a PerkinElmer Lambda 25 UV/Vis spectrometer.

Electrochemistry

Cyclic voltammetry experiments were carried out using a Biologic SP-150 potentiostat in degassed, dry DMF solutions, employing a platinum wire counter electrode, a glassy carbon working electrode and a Ag/Ag⁺ pseudo reference electrode. All complexes were measured as 0.5 mm solutions along with 0.1 m supporting electrolyte ((*n*Bu)₄ClO₄) at a sweep rate of 50 mV s⁻¹. All measurements were internally referenced against Fc/Fc⁺.

Computational details

The Gaussian 09^[16] package was used to perform all quantum chemical calculations employing the hybrid functional B3LYP^[19] together with a 6-31G(d)^[20] and 6-31+G(d)^[20g,21] basis set. Platinum was described by a decontracted Hay–Wadt(n+1) ECP and basis set.^[22] All given structures were verified as true minima by vibrational frequency analysis and the absence of negative eigenvalues. Calculated geometries were visualized with CYLview and Gauss-View.

Synthesis and Characterization

1,3-Diphenyl-1,2,3-triazolium tetrafluoroborate (2): 0.726 g (5 mmol) 1-Phenyl-1,2,3-triazole 1, 2.759 g (7.5 mmol, 1.5 equiv) diphenyliodonium tetrafluoroborate and 0.050 g (0.25 mmol, 0.05 equiv) copper(II)-acetate monohydrate are placed in a Schlenk tube and are dissolved in 20 mL DMF. The mixture is heated to 100 °C and stirred for 17 h. The reaction is cooled to room temperature and all volatiles are removed under reduced pressure. The product (1.41 g, 91%) is isolated by crystallization from hot ethanol. M.p. 165 °C. ¹H NMR (300 MHz, [D₆]DMSO): δ = 9.79 (s, 2H, CH_{arom}), 8.21–8.08 (m, 4H, CH_{arom}), 7.86–7.71 ppm (m, 6H, CH_{arom}). ¹³C NMR (75 MHz, [D₆]DMSO): δ = 135.0 (C), 132.2 (CH_{arom}), 130.5 (CH_{arom}), 130.0 (CH_{arom}), 121.9 ppm (CH_{arom}). ¹⁹F NMR (282 MHz, [D₆]DMSO): δ = -148.8 (s, BF₄⁻¹), -148.9 ppm (s, BF₄⁻¹). MS (ESI, m/z): 222.0 (M-BF4)⁺. Anal Calcd for C₁₄H₁₂BF₄N₃: C 54.41, H 3.92, N 13.60, found: C 54.79, H 4.00, N 13.69.

1-Phenyl-3-(2,4,6-trimethylphenyl)-1,2,3-triazolium tetrafluoroborate (3): 0.363 g (2.5 mmol) 1-Phenyl-1,2,3-triazole 1, 1.356 g (3 mmol, 1.2 equiv) bis(2,4,6-trimethylphenyl)iodonium tetrafluoroborate and 0.025 g (0.125 mmol, 0.05 equiv) copper(II)-acetate monohydrate are placed in a Schlenk tube and are dissolved in 20 mL DMF. The mixture is heated to 100 $^\circ\text{C}$ and stirred for 17 h. The reaction is cooled to room temperature and all volatiles are removed under reduced pressure. The raw product is crystallized by addition of diethyl ether to a methanol solution of the reaction mixture. The analytically pure product (0.41 g, 47%) is obtained by extraction of the raw product with DCM and subsequent drying in vacuo. M.p. 203 °C. ¹H NMR (600 MHz, $[D_6]DMSO$): $\delta = 9.90$ (d, J =1.6 Hz, 1 H, CH_{arom}), 9.49 (d, J = 1.6 Hz, 1 H, CH_{arom}), 8.17–8.10 (m, 2 H, CH_{arom}), 7.83–7.73 (m, 3 H, CH_{arom}), 7.25 (d, J=0.8 Hz, 2 H, CH_{arom}), 2.39 (s, 3 H, CCH₃), 2.13 ppm (s, 6 H, CCH₃). ¹³C NMR (151 MHz, $[D_6]DMSO$): $\delta = 142.0$, (Ci), 134.9 (Ci), 134.3 (Ci), 133.7 (CH_{arom}), 131.9 (CH_{arom}), 131.2 (Ci), 130.2 (CH_{arom}), 130.0 (CH_{arom}), 129.5 (CH_{arom}), 121.8 (CH_{arom}), 20.63 (CCH₃), 16.75 ppm (CCH₃). ¹⁹F NMR (282 MHz, [D₆]DMSO): $\delta = -148.8$ (s, BF₄⁻), -148.9 ppm (s, BF_4^{-}). MS (ESI, m/z): 264.1 (M-BF₄)⁺; 615.2 (2M-BF₄)⁺. Anal Calcd for $C_{17}H_{18}BF_4N_3$: C 58.15, H 5.17, N 11.97; found: C 57.90, H 5.24, N 12.13.

Acetylacetonato- $\kappa O, \kappa O'$ -[1-phenyl-3-(phenyl- κC^2)-triazol-4-ylidene-

 κC^4] platinum(II) (**4a**): In a flame dried Schlenk tube, 0.247 g (0.8 mmol) 1,3-diphenyl-1,2,3-triazolium tetrafluoroborate (**2**) and 0.093 g (0.4 mmol, 0.5 equiv) silver(i)-oxide are dissolved in 20 mL

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dry DMF and heated to 85°C for 24 h. After adding 299 mg (0.8 mmol, 1 equiv) Pt(COD)Cl₂, the mixture is stirred at room temperature for three hours and subsequently heated to 130 °C for another 21 hours. The solution is cooled to room temperature, 0.160 mg (1.6 mmol, 2 equiv) acetylacetone and 221 mg (1.6 mmol, 2 equiv) potassium carbonate are added and stirred at room temperature for 21 hours and afterwards at 100 °C for six hours. All volatiles are removed in vacuo and the residue is washed with ca. 40 mL of distilled water. The remaining solid is filtered, dried at 60°C overnight and extracted with DCM. The product is purified by flash column chromatography with DCM as eluent. The product is obtained after washing with *iso*-hexanes and diethyl ether $(3 \times$ 5 mL each) and drying in vacuo. (185 mg, 45%). M.p. 220°C. ¹H NMR (600 MHz, CDCl₃): $\delta = 8.05$ (s, 1 H, NCH), 7.97–7.84 (m, 1 H, PtCCH), 7.84–7.78 (m, 2H, CH $_{\rm ortho}$ of N3-Ph), 7.65–7.59 (m, 2H, CH_{meta} of N3-Ph), 7.59–7.55 (m, 1H, CH_{para} of N3-Ph), 7.54 (dd, J =7.8, 1.4 Hz, 1 H, CH_{ortho} of N1-Ph), 7.18 (t, J=7.4 Hz, 1 H, CH_{para} of N1-Ph), 7.12 (t, J=7.5 Hz, 1 H, CH_{meta} of N1-Ph), 5.50 (s, 1 H), 2.06 ppm (s, 3 H), 2.00 (s, 3 H). $^{13}\mathrm{C}$ NMR (151 MHz, CDCl_3): $\delta\!=\!185.1$ (CO), 184.8 (CO), 145.4 (PtCCN), 139.4 (PtCN), 136.1 (Ci of N3-Ph), 132.4 (PtCCH), 130.3 (CH_{para} of N3-Ph), 130.1 (CH_{meta} of N3-Ph), 128.0 (CH_{para} of N1-Ph), 127.2 (PtCCN), 124.7 (NCH), 123.5 (CH_{meta} of N1-Ph), 120.8 (CH $_{\rm ortho}$ of N3-Ph), 113.6 (CH $_{\rm ortho}$ of N1-Ph), 102.2 (CH_{arom}), 27.9 (COCH₃), 27.8 ppm (COCH₃). ¹⁹⁵Pt NMR (64 MHz, CDCl₃): $\delta = -3410.3 \text{ ppm}$ (d, J = 53 Hz). MS (ESI, m/z): 515.2 (*M*+H)⁺; 929.3 (2M-acac)⁺. Anal Calcd for C₁₉H₁₇N₃O₂Pt 0.08 CH₂Cl₂: C 43.73, H 3.29, N 8.02; found: C 43.69, H 3.25, N 8.05.

[Bis-1,3-(2,4,6-trimethylphenyl)propane-1,3-dionato- $\kappa O, \kappa O'$][1-phenyl-3-(phenyl- κC^2)-triazol-4-ylidene- κC^4]platinum(II) (**4b**): Prepared analogously to 4a (see Supporting Information). 0.493 mg (1.6 mmol, 2 equiv) bis-1,3-(2,4,6-trimethylphenyl)propane-1,3-dione were used instead of acetylacetone and 180 mg (1.6 mmol, 2 equiv) potassium tert-butoxide instead of potassium carbonate (146 mg, 25 %). M.p. 269 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.02 (s, 1 H), 7.98– 7.70 (m, 3 H), 7.66–7.48 (m, 4 H), 7.17–7.04 (m, 2 H), 6.86 (d, J =3.7 Hz, 4H), 5.67 (s, 1H), 2.38 (s, 6H), 2.35 (s, 6H), 2.31 (s, 3H), 2.30 ppm (s, 3 H). 13 C NMR (75 MHz, CDCl₃): $\delta = 184.9$ (CO), 184.3 (CO), 145.6 (Ci), 139.8 (Ci), 139.6 (2 Ci), 137.7 (Ci), 137.6 (Ci), 136.3 (Ci), 134.3 (Ci), 134.1 (Ci), 133.1 (CH_{arom}), 130.4 (CH_{arom}), 130.3 (CH_{arom}), 128.6 (CH_{arom}), 128.3 (CH_{arom}), 128.2 (CH_{arom}), 127.1 (Ci), 125.0 (CH_{arom}), 123.8 (CH_{arom}), 120.8 (CH_{arom}), 113.7 (CH_{arom}), 107.1 (CH_{arom}), 21.2 (2 CCH₃), 20.0 (CCH₃), 19.8 ppm (CCH₃). ⁹⁵Pt NMR (64 MHz, CDCl₃): $\delta = -3350.4$ ppm. MS (ESI, *m/z*): 723.4 (*M*+H)⁺. Anal Calcd for $C_{35}H_{33}N_3O_2Pt$: C 58.16, H 4.60, N 5.81; found: C 58.34, H 4.57, N 5.42.

[Bis-1,3-(2,3,5,6-tetramethylphenyl)-propane-1,3-dionato-κO,κO'][1phenyl-3-(phenyl- κC^2)-triazol-4-ylidene- κC^4]platinum(II) (**4 c**): Prepared analogously to 4a (see Supporting Information). 0.538 mg (1.6 mmol, 2 equiv) bis-1,3-(2,3,5,6-tetramethylphenyl)propane-1,3dione were used instead of acetylacetone and 180 mg (1.6 mmol, 2 equiv) potassium tert-butoxide instead of potassium carbonate (246 mg, 41 %). M.p. > 325 °C. ¹H NMR (300 MHz, CDCl₃): δ = 8.05 (s, 1H, NCH), 7.89–7.82 (m, 1H, CH_{arom}), 7.82–7.75 (m, 2H, CH_{arom}), 7.65–7.50 (m, 4H, CH_{arom}), 7.18–7.05 (m, 2H, CH_{arom}), 6.95 (d, J =4.7 Hz, 2 H, CH_{arom}), 5.64 (s, 1 H, COCH), 2.28 (s, 6 H, CCH₃), 2.25 (s, 6H, CCH₃), 2.24 (s, 6H, CCH₃), 2.22 ppm (s, 6H, CCH₃). ^{13}C NMR (75 MHz, CDCl₃): δ = 185.8 (Ci), 185.3 (Ci), 145.4 (Ci), 142.7 (Ci), 142.5 (Ci), 139.5 (Ci), 136.1 (Ci), 133.7 (Ci), 133.6 (Ci), 133.0 (CH_{arom}), 132.0 (CH_{arom}), 131.0 (CH_{arom}), 131.0 (CH_{arom}), 130.2 (CH_{arom}), 130.1 (CH_{arom}), 129.7 (Ci), 129.5 (Ci), 128.0 (CH_{arom}), 127.0 (Ci), 124.9 (CH_{arom}), 123.6 (CH_{arom}) , 120.6 (CH_{arom}) , 113.5 (CH_{arom}) , 107.5 (CH_{arom}) , 19.7 (CCH_{3}) , 19.6 (CCH₃), 16.5 (CCH₃), 16.3 ppm (CCH₃). MS (ESI, m/z): 751.4

 $(M{+}H)^+.$ Anal Calcd for $C_{37}H_{37}N_3O_2Pt$ 0.27 $CH_2Cl_2\colon$ C 57.86, H 4.89, N 5.43; found: C 57.84, H 4.88, N 5.41.

Acetylacetonat- $\kappa O, \kappa O'$ -[3-(phenyl- κC^2)-1-(2,4,6-trimethylphenyl)-tria*zol-4-ylidene-* κC^{5} *]platinum(11)* (5): In a flame dried Schlenk tube, 0.351 g (1 mmol) 1-phenyl-3-(2,4,6-trimethylphenyl)-1,2,3-triazolium tetrafluoroborate (3) and 0.116 g (0.5 mmol, 0.5 equiv) silver(I)oxide are dissolved in 24 mL dry DMF and heated to 80 $^\circ\text{C}$ for 24 h. After adding 374 mg (1 mmol, 1 equiv) Pt(COD)Cl₂, the mixture was stirred at room temperature for three hours and subsequently heated to 130°C for another 21 hours. The solution is cooled to room temperature, 0.400 mg (4 mmol, 4 equiv) acetylacetone and 553 mg (4 mmol, 4 equiv) potassium carbonate are added and stirred at room temperature for 21 hours and afterwards at 100 °C for six hours. All volatiles are removed in vacuo and the residue is washed with ca. 40 mL of distilled water. The remaining solid is filtered, dried at 60 °C overnight and extracted with DCM. The product is purified by flash column chromatography with an eluent mixture of DCM/methanol (1% methanol). The product is obtained after drying in vacuo. (129 mg, 23%). M.p.: 255 °C. ¹H NMR (300 MHz, CDCl₃): $\delta = 8.07 - 7.74$ (m, 1 H, CH_{arom}), 7.63 (s, 1 H, CH_{arom}), 7.47 (dd, J=7.7, 1.5 Hz, 1 H, CH_{arom}), 7.18 (td, J=7.4, 1.5 Hz, 1 H, CH_{arom}), 7.10 (td, J=7.5, 1.5 Hz, 1 H, CH_{arom}), 7.04 (s, 2 H, CH_{arom}), 5.49 (s, 1H, COCH), 2.38 (s, 3H, CCH₃), 2.09 (s, 6H, CCH₃), 2.06 (s, 3H, CCH₃), 1.96 ppm (s, 3 H, CCH₃). ¹³C NMR (75 MHz, CDCl₃): $\delta = 185.2$ (CO), 185.0 (CO), 145.9 (Ci), 141.4 (Ci), 138.8 (Ci), 135.1 (Ci), 132.8 (Ci), 132.6 (CH_{arom}), 129.5 (CH_{arom}), 129.2 (CH_{arom}), 128.0 (CH_{arom}), 127.0 (Cì), 123.6 (CH_{arom}), 113.7 (CH_{arom}), 102.3 (CH_{arom}), 28.1 (CCH_3), 28.0 (CCH₃), 21.3 (CCH₃), 17.3 ppm (CCH₃). ¹⁹⁵Pt NMR (64 MHz, CDCl₃) $\delta = -3414.6$ ppm (d, J = 56.9 Hz). MS (ESI, m/z): 557.4 (M+H)⁺. Anal Calcd for C₂₂H₂₃N₃O₂Pt: C 47.48, H 4.17, N 7.55; found: C 47.15, H 4.05, N 7.54.

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Conflict of interest

The authors declare no conflict of interest.

Keywords: excited state · mesoionic · OLEDs · phosphorescence · platinum

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FULL PAPER





Conjugated Systems

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Diaryl-1,2,3-Triazolylidene Platinum(II) Complexes Excitation induced extension of the π -system leads to red-shifted emission So N-Ph So N-Ph So N-Mes T1 $\lambda_{em} = 532 \text{ nm}$ $\lambda_{em} = 502 \text{ nm}$ Control of excited state geometry by

rational ligand design leads to a new class of phosphorescent emitters with extraordinary photophysical properties. Extension of the π -system in the triplet state leading to a significant bathochromic shift of the emission was avoided by introduction of additional steric demand.