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# The "Enders Triazole": A well known molecule, but still a new ligand!!

Thomas Strassner<sup>a,\*</sup>, Yvonne Unger<sup>a</sup>, Dirk Meyer<sup>a</sup>, Oliver Molt<sup>b</sup>, Ingo Münster<sup>b</sup>, Gerhard Wagenblast<sup>b</sup>

<sup>a</sup> Physikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, 01062 Dresden, Germany

<sup>b</sup> BASF SE, 67056 Ludwigshafen, Germany

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# ABSTRACT

1,3,4-Triphenyl-1,2,4-triazolium salts have previously been used and described in the literature as precursors for carbenes, which have been reported as organocatalysts and as neutral monodentating N-heterocyclic carbene (NHC) ligands. We now report the synthesis of 1,3,4-tri-phenyl-4,5-dihydro-1H-1,2,4-triazole-5-ylidene-platinum(II)-acetylacetonate where the triazole binds to the metal in a new coordination mode ( $C^CC^*$ ) as an anionic bidentate ligand, where the NHC carbene interacts with the platinum center and one of the phenyl rings is cyclometalated. The complex shows phosphorescent emission in the blue region of the visible spectrum at 441 and 465 nm with a quantum yield of 42%. DFT calculations (BP86/6-31G\* as well as B3LYP/6-31G\*) were found to be well suited to determine the structure of the complex.

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**Introduction**. During the last decade the development of more energy efficient lighting was found to be an important goal and research activities lead to a significant improvement. Transition metal complexes containing metals with a high spin-orbit coupling and their promising photophysical properties of up to 100% quantum yield [1,2] have been identified as key components of phosphorescent organic light-emitting devices (PhOLEDs) [3–5]. Although a variety of metals has been tested, iridium(III) [1,6,7] and platinum(II) [8–11] complexes with cyclometalated bidentate ligands (often derived from biphenyl [12–14], phenylpyrazole [15] or 2-phenylpyridine [12,15,16]) have been found to be especially interesting. Complexes of the type [(C<sup>∧</sup>N)<sub>1-2</sub>M(O<sup>∧</sup>O)] (C<sup>∧</sup>N, 2-arylpyridinate or a related ligand; O<sup>∧</sup>O, a β-diketonate ligand, M = Pt, Ir) have been intensely studied due to their exceptional luminescence properties [17–19].

Significant progress has been made in the last years tuning the photophysical properties of these complexes. We as well as other groups recently reported cyclometalated mononuclear platinum(II) NHC complexes of the type [Pt(NHC)(acac)] where NHC is a monoanionic bidentate aryl-alkyl functionalized imidazole ligand [11,20–23]. These complexes, with the acetylacetonate auxiliary ligand, show moderate to excellent quantum yields and good thermal stability. We were now interested whether also phenyltriazoles can be cyclometalated to the platinum(II) center and as the 1,3,4-phenylsubstituted triazole first reported by Enders [24] is one of the best known phenyltriazoles we

\* Corresponding author. Tel.: +49 351 463 38571; fax: +49 351 463 39679. *E-mail address:* thomas.strassner@chemie.tu-dresden.de (T. Strassner). decided to investigate whether the new bonding mode can also be observed for that molecule which has previously been published in various roles.

The 1,3,4-triphenyl-1,2,4-triazolium perchlorate  $(1 \cdot ClO_4^-)$  as a precursor for a new stable carbene was first reported by Enders in 1995 [24]. By reaction with sodium methoxide in methanol they could successfully synthesize the methanol adduct, which liberates the free carbene upon heating under high vacuum conditions. They could isolate and characterize the free carbene and even get a solid-state structure of the stable carbene [25]. The triazolium salt can be synthesized in large scale with good yields and gives access to the free carbene [26–29], which was also successfully used as an organocatalyst [30] and for the dehydrogenation of ammonia borane with a relatively low activation barrier [31]. Even chiral analogues have been reported [32].

As carbenes they are also exceptional ligands and several metalorganic complexes have been reported which used the carbene as a monodentate ligand [33], e.g. for oxorhenium [34], palladium (II) [35], iridium(I) [36] or platinum(II) [37] complexes [38]. When we recently started to work on platinum(II) cyclometalated acetylacetonate (acac) complexes with NHC-donors (C^C\*) [20] as compared to the well known cyclometalated nitrogen donors (C^N) we got interested whether this would also be possible with the triazolium salt.

**Results and discussion**. The synthesis of the platinum complex 1,3,4-triphenyl-4,5-dihydro-1*H*-1,2,4-triazole-5-ylidene platinum(II) acetylacetonate (**2**) did not start from the perchlorate salt, but from the iodine salt ( $1\cdotI^-$ ) as given in Scheme 1. The synthesis of the ligand ( $1\cdotI^-$ ) from benzoylchloride, aniline and phenylhydrazine leads to the corresponding phenylhydrazone in 48.9% yield. Reaction of this intermediate with triethyl orthoformate (HC(OEt)<sub>3</sub>) and ammonium iodide proceeds smoothly with 91.5% yield. The synthesis of the platinum complex

Abbreviations: PMMA, polymethylmetacrylate.

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Scheme 1. Synthesis of the cyclometalated platinum(II) complex.

Table 1				
Photoluminescence measurements	(2% in	PMMA)	of <b>2</b> a	at RT.

$\lambda_{exc} \left[ nm  ight]^a$	$X_{\rm RGB}{}^{\rm b}$	Y <sub>RGB</sub> <sup>c</sup>	$\lambda_{em}  [nm]^d$	$\phi^{e}$
310	0.169	0.191	464	0.42
200	0.172	0.165	441, 405	0.42

<sup>a</sup> Excitation wavelength.

<sup>b,c</sup> CIE coordinates at room temperature.

<sup>d</sup> Emission maxima.

<sup>e</sup> Quantum yield, radiant exposure under N<sub>2</sub>.

by transmetalation of the silver complex with dichloro(cyclooctadiene) platinum(II) and addition of 2,4-pentanedione leads to the complex in 38.9% yield. Details of the syntheses are given in the Supporting Information.

As the imidazolium-based C<sup>C</sup>\* cyclometalated platinum(II) acac complexes showed interesting optical properties [20] we were interested in the photophysics of 2. We found that the complex also emits in the blue region of the spectrum (Table 1). The experimentally measured emission (Fig. 1) and absorption spectra (Fig. 2) show a similar line shape compared to the imidazolium-based complexes [20,39]. To unequivocally confirm the proposed structure of **2** we have also been able to grow crystals suitable for X-ray diffraction and to determine the solid-state structure (Fig. 3). Details of the solid-state structure determination are given in the Supporting Information together with details of the photophysical measurements. We also employed DFT calculations to compare the structural data to the results of the solid-state structure (Table 2). We used two established functionals (B3LYP, BP86) together with the 6-31G\* basis set. The photoluminescence was measured at two different excitation wavelengths, 310 nm and 355 nm. In both cases quantum yields of 42% were observed at room temperature. For the excitation at 310 nm the strongest band was found at 464 nm, while the emission spectrum for the excitation at 355 nm (Fig. 1) shows a complex fine structure with three main bands.



Fig. 1. Emission spectrum of 2 (excitation at 355 nm) at RT.

The emission maximum was found at 470 nm with a broad tail towards 550 nm, but also a strong shoulder between 430 and 450 nm with another maximum at 441 nm.

The observed bond lengths in the solid-state structure show interesting differences to the phenyl imidazolium derived complexes which have recently been reported [20,39,40]. In all cases the platinum carbene bond is relatively short (1.94 Å), while the cyclometalated bonds are longer and differ significantly (1.96–1.99 Å). Comparing the geometry of the substituted imidazole and the triazole rings, the effect seems to be independent from the change (CH vs. N-Ph) in the backbone of the five-membered ring. The angle C1–N1–C3 (115.4°) is very similar to the corresponding angle in the dibenzofuran substituted structure (114.5°) [20], but the lower electron density in the more delocalized dibenzofuran leads to an almost by 0.03 Å elongated platinum–carbon bond. On the other hand the platinum–oxygen bonds are identical in length, no influence of the longer cyclometalated bond can be observed. For the triazole complexes.

The new C<sup>C</sup>\* cyclometalation bonding mode which has only very recently been shown to be accessible for platinum(II) centers from 1-phenyl-3-methyl-imidazolium based precursors can also be found for the well-known "Enders triazole." The triazole does not only act as a monodentate carbene, but can also be cyclometalated in a C<sup>C</sup>\* fashion. This potentially gives rise to a new class of compounds which might have interesting photophysical properties based on the results reported here.

**Conclusion**. With this study we were able to show that triazoles carrying phenyl substituents can not only bind to metals in a monodentate way as regular "NHC-carbenes," but they can also cyclometalate to the phenyl ring forming a significantly more stable complex where the ligand binds in a bidentate fashion. Additionally we found that the complex shows a phosphorescent emission with a quantum yield of 42% and a decay time of 35.6 µs. The solid-state structure confirms the predictions by DFT calculations on the BP86/6-31G<sup>\*</sup> and B3LYP/6-31G<sup>\*</sup> level of theory.



Fig. 2. Absorption spectrum of 2 at RT.



**Fig. 3.** Solid-state structure of complex **2**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (°): Pt1-C1 1.937 (2), Pt1-C4 1.985 (2), Pt1-O1 2.0870 (17), Pt1-O2 2.0381 (17), C1-Pt1-C4 80.23 (10), O1-Pt1-O2 89.18 (7), C1-Pt1-O1 99.61 (8), C4-Pt1-O2 91.00 (9), C1-N1-C3-C4 -2.9 (3).

#### Table 2

Comparison of experimental data (solid-state structure) with DFT calculations (basis set  $6-31G^*$ ). Bond lengths in Å, angles in °. For the atom numbering see Fig. 3.

	X-ray	B3LYP	BP86
C1-Pt1	1.94	1.96	1.95
C4–Pt1	1.98	2.00	2.00
01-Pt1	2.09	2.15	2.14
02-Pt1	2.04	2.09	2.08
N1-C3	1.42	1.44	1.44
C1-Pt1-C4	80.3	79.9	80.1
C1-Pt1-O1	99.6	99.3	98.6
C1-Pt1-O2	171.2	172.2	171.7
01-Pt1-02	89.2	88.4	89.6
C1-01-02-C4	1.3	0.9	1.4
Pt1-C4-C3-C1	2.1	3.4	4.2

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### Appendix A. Supplementary material

Experimental details, details of the solid-state structure determination, photoluminescence measurements, xyz-coordinates and details of the quantum-chemical calculations. CCDC-877924 contains the supplementary crystallographic data for compound **2**. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. Supplementary data to this article can be found online at doi: http://dx.doi.org/10.1016/j. inoche.2013.01.018

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