PAPER

C^C* cyclometalated platinum(II) N-heterocyclic carbene complexes with a sterically demanding β-diketonato ligand – synthesis, characterization and photophysical properties†

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Neutral cyclometalated platinum(II) N-heterocyclic carbene complexes [Pt(C^C*)(O^O)] with C^C* ligands based on 1-phenyl-1,2,4-triazol-5-ylidene and 4-phenyl-1,2,4-triazol-5-ylidene, as well as acetylacetonato (O^O = acac) and 1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato (O^O = mesacac) ancillary ligands were synthesized and characterized. All complexes are emissive at room temperature in a poly(methyl methacrylate) (PMMA) matrix with emission maxima in the blue region of the spectrum. High quantum efficiencies and short decay times were observed for all complexes with mesacac ancillary ligands. The sterically demanding mesityl groups of the mesacac ligand effectively prevent molecular stacking. The emission behavior of these emitters is in general independent of the position of the nitrogen in the backbone of the N-heterocyclic carbene (NHC) unit and a variety of substituents in 4-position of the phenyl unit, *meta* to the cyclometalating bond.

Introduction

Square-planar platinum(II) complexes have proven to be strong phosphorescent compounds, and have been extensively explored with respect to a broad field of promising applications, such as chemosensors,[1–6] non-linear optical (NLO) materials,[7–9] photocatalysts,[10–14] optical power limiting materials (OPL),[15] photovoltaic devices,[16,17] and organic light emitting devices (OLEDs).[18–25] Concerning the field of OLED technology especially blue emitting compounds are required to develop full-color displays and efficient lighting devices. Cyclometalated platinum(II) complexes represent a promising class for this purpose, as shown from several reports.[26–37] The remarkable phosphorescence of platinum(II) complexes originates from the metal ion, which promotes a strong spin–orbit coupling, and thereby allows for efficient intersystem crossing to the triplet state.[38] Cyclometalating ligands also allow for an efficient emission behavior as their strong ligand field ensures a high stability of the complexes and raises the energy of the metal centered (MC) states in the platinum(II) complexes to

avoid non-radiative decay.[21] In particular platinum(II) complexes with cyclometalating C^N ligands attract a lot of scientific interest. Especially those with the general structure [Pt(C^N)(O^O)] (O^O = β-diketonato) turned out to be a stable and strongly phosphorescent class of emitter molecules. They allow to cover a broad range of the visual spectrum by variation of the C^N cyclometalating ligands and β-diketonato ancillary ligands[39–52] Low-energy emissions are also accessible from dimeric or oligomeric complex species. As a consequence of their planar structure, cyclometalated platinum(II) complexes often show molecular stacking by Pt–Pt bonds and π–π interactions, which promotes the formation of broad emission bands at higher wavelengths when compared to the monomer emissions.[53–57] Thus planar cyclometalated platinum(II) complexes are often discussed as emitters for single dopant white-light emitting diodes.[19,34,58–61]

After the first report of a C^C* cyclometalated platinum(II) complex in 2006[62] C^C* cyclometalating ligands have also been used for the development of new phosphorescent platinum(II) emitters of the general structure [Pt(C^C*)(O^O)] (O^O = β-diketonato).[63–68] This class of complexes reveals an extraordinary photoluminescent behavior, which strongly depends on the structure of the C^C* cyclometalating ligand (C: carbene carbon atom; C*: cyclometalated carbon atom), as well as on the O^O chelating ligand. Recently, several promising [Pt(C^C*)(O^O)] emitters have been reported, which emit in the green-blue region of the spectrum with quantum efficiencies of more than 90%.[66,69,70] It also has been

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demonstrated that exceptionally high quantum yields can be achieved by using mesityl substituted β-diketonato ligands (mesacac = 1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato).[71]

Herein we report the synthesis and the photoluminescent properties of a series of new phenyl-1,2,4-triazol-5-ylidene complexes to discuss the influence of the mesityl substituted β-diketonato ligand 1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato (mesacac) and several modifications of the C^C* cyclometalating ligand on the emission behavior.

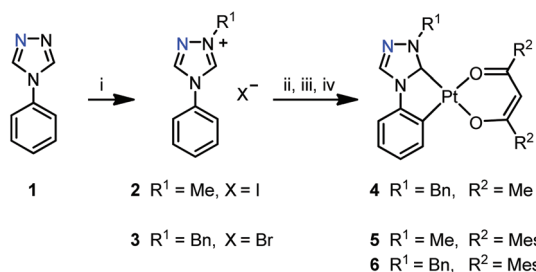## Results and discussion

Synthesis

The synthesis of the triazoles **1** and **7–9**, and the methyl substituted triazolium salts **2** and **10–12** (Schemes 1 and 2) has been reported previously.[68] The triazolium salts **3** and **13–15** were prepared by a quaternisation reaction using benzyl bromide (BnBr), **2** and **10–12** using iodomethane in tetrahydrofuran (THF). All complexes were synthesized in moderate to good yields by a multistep-reaction.[66,68] The triazolium salts were

Scheme 1 Synthesis of the ligand precursors **2**, **3** and complexes **4–6**. (i) Methyl iodide/benzyl bromide, THF, 100–110 °C; (ii) Ag$_2$O, 1,4-dioxane; (iii) Pt(COD)Cl$_2$, 1,4-dioxane/butanone solvent mixture (2 : 1), 115 °C; (iv) β-diketone, KO^{t}Bu, DMF, room temperature to 100 °C.

7 R^3 = H   **10** R^1 = Me, R^3 = H, X = I   **16** R^1 = Bn, R^2 = Me, R^3 = H
8 R^3 = OMe   **11** R^1 = Me, R^3 = OMe, X = I   **17** R^1 = Me, R^2 = Mes, R^3 = H
9 R^3 = Me   **12** R^1 = Me, R^3 = Me, X = I   **18** R^1 = Me, R^2 = Mes, R^3 = OMe

13 R^1 = Bn, R^3 = H, X = Br   **19** R^1 = Me, R^2 = Mes, R^3 = Me
14 R^1 = Bn, R^3 = OMe, X = Br
15 R^1 = Bn, R^3 = Me, X = Br   **20** R^1 = Bn, R^2 = Mes, R^3 = H
  21 R^1 = Bn, R^2 = Mes, R^3 = OMe
  22 R^1 = Bn, R^2 = Mes, R^3 = Me

Scheme 2 Synthesis of the ligand precursors **10–15** and complexes **16–22**. (i) Methyl iodide/benzyl bromide, THF, 100–110 °C; (ii) Ag$_2$O, 1,4-dioxane; (iii) Pt(COD)Cl$_2$, 1,4-dioxane/butanone solvent mixture (2 : 1), 115 °C; (iv) β-diketone, KO^{t}Bu, DMF, room temperature to 100 °C.

reacted with silver(I) oxide in 1,4-dioxane to generate a silver(I) carbene complex *in situ*, which was then transmetalated with dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl$_2$) in a 1,4-dioxane/butanone solvent mixture and cyclometalated at the C2 carbon atom of the phenyl ring at higher temperatures. The reported complexes were obtained after removal of the volatiles by reaction of the intermediate with the respective β-diketone and potassium *tert*-butoxide (KO^{t}Bu) in dimethylformamide (DMF).

Although this method was successful with imidazolium-based ligand precursors, the synthesis of platinum(II) triazol-5-ylidene complexes with mesacac ancillary ligands suffered from unsatisfying yields. Optimization of the reaction conditions leads to improved yields by using DMF already for the generation of the silver(I)carbene as well as for the transmetalation step. In comparison to the previously used 1,4-dioxane/butanone solvent mixture, we could more than double the yield of complex **17** (see exp. details, compound **17**, method B).

Solid state structure determination

Single crystals suitable for X-ray diffraction analysis were grown from **4** by slow vapor diffusion of diethyl ether into a highly concentrated solution of the respective complex in dichloromethane and from **20** by slow evaporation of the solvent from the solution of the complex in dichloromethane. All details of the solid state structure determinations are summarized in the ESI.† The complexes **4** (Fig. 1 and 2) and **20** (Fig. 3 and 4) crystallize in the monoclinic space group $P2_1/c$ and are devoid of any solvent molecules. X-ray diffraction analysis confirms a quasi-square planar coordination environment of the platinum(II) center with bond lengths of the
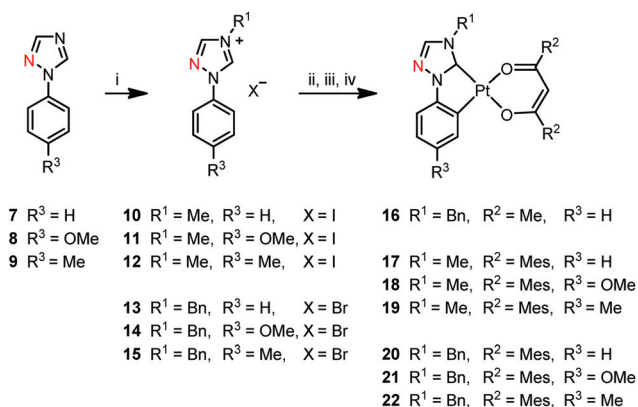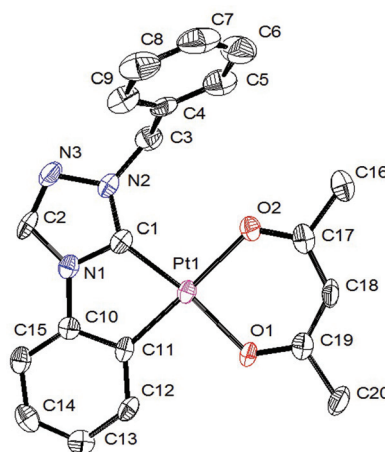
Fig. 1 Solid state structure of **4**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (°) and dihedral angles (°): Pt(1)−C(1) 1.930(5), Pt(1)−C(11) 1.985(5), Pt(1)−O(1) 2.045(3), Pt(1)−O(2) 2.094(3), C(1)−Pt(1)−C(11) 80.4(2), C(11)−Pt(1)−O(1) 91.72(16), C(1)−Pt(1)−O(2) 97.55(18), O(1)−Pt(1)−O(2) 90.24(13), C(11)−Pt(1)−C(1)−N(2) −176.6(6), O(2)−Pt(1)−C(1)−N(1) −176.6(3), O(1)−Pt(1)−O(2)−C(17) −2.6(4).
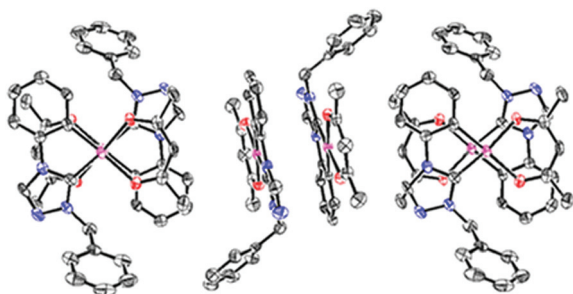
Fig. 2   Intermolecular arrangement of **4** in the solid state. All hydrogen atoms are omitted for clarity.

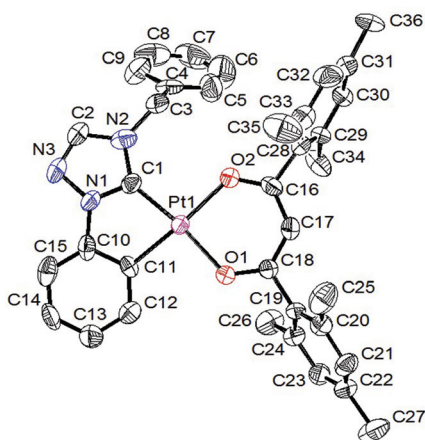
Fig. 3   Solid state structure of **20**. All hydrogen atoms are omitted for clarity. Selected bond lengths (Å), angles (°) and dihedral angles (°): Pt (1)–C(1) 1.938(12), Pt(1)–C(11) 2.012(11), Pt(1)–O(1) 2.042(8), Pt(1)–O(2) 2.064(8), C(1)–Pt(1)–C(11) 79.7(5), C(11)–Pt(1)–O(1) 93.0(4), C(1)–Pt(1)–O(2) 96.3(4), O(1)–Pt(1)–O(2) 91.1(3), C(11)–Pt(1)–C(1)–N(2) –178.5(16), O(2)–Pt(1)–C(1)–N(1) –176.8(10), O(1)–Pt(1)–O(2)–C(16) 4.5(10), C(17)–C(16)–C(28)–C(29) 77.3(16), C(20)–C(19)–C(18)–C(17) 68.7(16).
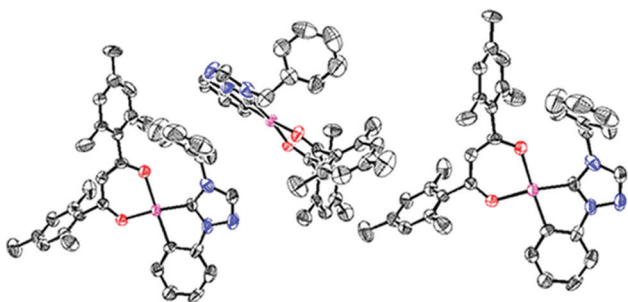

Fig. 4   Intermolecular arrangement of **20** in the solid state. All hydrogen atoms are omitted for clarity.

coordinative bonds similar to those of the previously reported [Pt(C^C*)(O^O)] complexes.[68,71,72]

The Pt(1)–O(2) bond lengths of both complexes are slightly elongated when compared to the Pt(1)–O(1) bond lengths, due to the *trans* effect of the cyclometalated phenyl ring.

The planar structure with coplanar arranged ligands allows **4** to stack with short intermolecular distances. In the solid state two of the molecules form dimers with a Pt–Pt contact shorter than twice the van-der-Waals radius of the platinum atom. However, in the case of **20** the sterically demanding mesityl groups of the β-diketonato ancillary ligand are twisted out of the coordination plane. This efficiently prevents molecular stacking of these complexes so that they are orthogonally arranged to each other.

Photoluminescence properties

This class of complexes shows very weak emissions from a solution in dichloromethane (see ESI†), but are significantly stronger emissive in a poly(methyl methacrylate) (PMMA) matrix. Therefore, the photophysical properties of all complexes were investigated from polymer films with 2% of the complexes in a PMMA matrix at room temperature. Emission spectra of **5–6** and **16–21** from neat complex films were also recorded to get an insight into the emission behavior of agglomerated complexes. Neat emitter films of **4** and **22** could not be obtained due to rapid crystallization of the complexes during the film preparation. The absorption spectra of all complexes in a PMMA matrix (Fig. 5) display strong bands below 270 nm, which arise from spin allowed $^1\pi$–π transitions. In this region the absorption maximum of the complex with a 1-benzyl-4-phenyl triazol-5-ylidene unit and mesacac ancillary ligand **5** is located at around 230 nm, whereas the absorption maxima of all other complexes are detected at around 220 nm. Further bands of moderate intensity up to 350 nm arise from transitions involving the metal center, such as a metal-to-ligand charge transfer ^{1}MLCT transition. Here complex **5** exhibits another absorption maximum at around 310 nm.

All complexes are strongly emissive in a PMMA matrix at room temperature. The emission spectra (Fig. 6) and the PL data (Table 1) of **4** and **16** correspond well to those of analogous platinum(II) imidazol-2-ylidene complexes containing an acetylacetonato ancillary ligand and a methyl group instead of a benzyl group bound to the imidazol-N3 atom.[68] This clearly indicates that the emission behavior of these complexes is
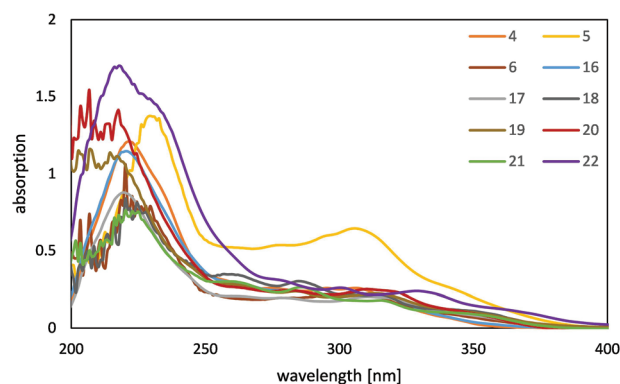

Fig. 5   Absorption spectra of the complexes **4–6** and **16–22** (2 wt% in PMMA).
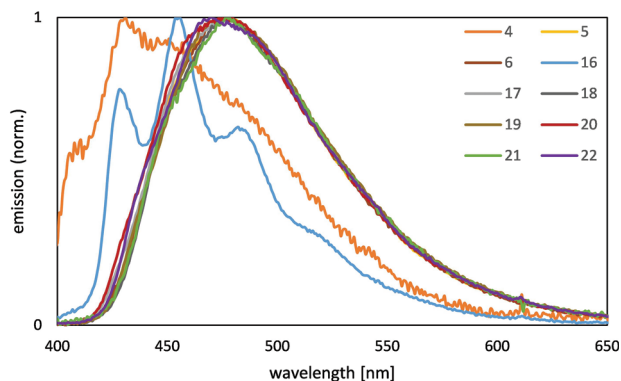
Fig. 6 Emission spectra of the complexes **4–6** and **16–22** (2 wt% in PMMA, rt).

Table 1 Photoluminescence data for complexes **4–6** and **16–22** (2% in PMMA, rt)

	λ_{exc} [a] [nm]	CIE x; y [b]	λ_{em} [c] [nm]	Φ [d]	τ_0 [e] [µs]
4	330	0.159; 0.157	455	0.35	15
5	345	0.183; 0.283	477	0.82	4
6	355	0.183; 0.287	477	0.83	4
16	330	0.166; 0.165	432	0.13	15
17	340	0.185; 0.284	478	0.82	4
18	355	0.185; 0.295	477	0.82	5
19	355	0.186; 0.294	475	0.82	3
20	370	0.182; 0.271	477	0.72	5
21	370	0.188; 0.304	478	0.70	7
22	340	0.184; 0.279	471	0.81	5

[a] Excitation wavelength. [b] CIE coordinates. [c] Max. emission wavelength. [d] Quantum yield at λ_{exc}, N$_2$ atmosphere. [e] Decay lifetimes (excited by laser pulses (355 nm, 1 ns)) given as $\tau_o = \tau_v/\phi$.

independent of the benzyl group (R^1). Both emitters display a structured emission band with the maximum located in the blue region of the spectrum, which indicates strong contributions of a ligand centered state (^{3}LC) to the emission process. The well-structured emission band of **16** reveals a vibronical progression of about 1300 cm^{-1} which corresponds to vibrations of the NHC ligand as determined by the frequency analysis from the density functional theory (DFT) calculations. However, complexes **5–6** and **17–22** reveal an essentially different emission behavior, which is caused by the mesacac ancillary ligand. In contrast to the vibronic structure of the ^{3}LC emission profiles of the emitters containing an acac ancillary ligand (**4** and **16**), the complexes **5–6** and **17–22** exhibit unstructured emission bands with only one maximum located between 471 and 478 nm. Therefore, another transition contributes essentially to the emission process of the complexes with a mesacac ligand. This transition is supposed to be a charge transfer transition involving the metal center, as the complexes with a mesacac ligand also show significantly enhanced quantum efficiencies (70–83%) and reduced decay

times below 8 µs (Table 1). Due to the change in the emission process to a transition with reduced ^{3}LC character, different substituents at the cyclometalated ligand do not significantly change the emission properties, like quantum yield and emission wavelength. All complexes, even the emitters based on 4-phenyl triazole **5** and **6** reveal high quantum yields, whereas very low efficiencies have been previously reported for several 4-phenyl triazole complexes with acac ancillary ligands in comparison to the 1-phenyl triazole complexes with acac ancillary ligands.[68] While in the case of 1-phenyl and 4-phenyl triazole complexes with acac ligands, substitution in 4-position of the phenyl ring of the cyclometalating ligand had a significant effect on the emission wavelengths, this was not observed for the complexes with mesacac ligands. Although the emissions of the respective acac complexes are shifted slightly to lower energies by several substituents, this effect is relatively small for the mesacac complexes **18**, **19**, **21** and **22**.

For the acac complexes **4** and **16** we could only get the neat film emission for **16** as **4** shows early crystallization. These are the only two complexes prone for stacking as the mesacac prevents short intermolecular contacts as shown in the solid state structure of **20**. The PL spectrum of the neat film of **16** (Fig. 7) reveals a low energy emission in the green region of the spectrum, similar to other acac complexes [Pt(C^C*)(acac)].[68] This emission is probably caused by a multi-molecular species, such as a stack of emitter molecules. The planar geometry of the complexes with acac ligands supports aggregation in the solid state with a short intermolecular separation and Pt–Pt distances lower than twice the van-der-Waals radius of platinum. The quantum efficiency of the neat film of **16** (Table 2) is significantly higher than that of the complex in a 2% PMMA matrix. In contrast to **16**, the emissions from the neat films of the mesacac complexes **5**, **6** and **17–21** correspond well to the results of the measurements of 2% complex in a PMMA matrix, although the emission maxima are slightly shifted to higher wavelengths by 7–22 nm. With respect to the results of the molecular structure determination, which shows no stacking behaviour of **20** in the solid state, the emissions from the neat films of **5–6** and **17–21** are expected to be mono-molecular emissions.
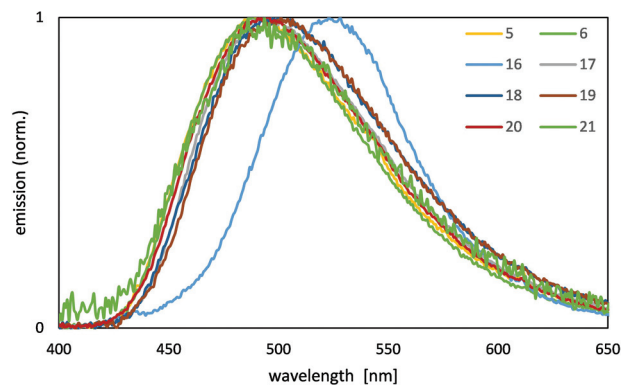

Fig. 7 Emission spectra of the neat complex films of **5–6** and **16–21** (rt).

Table 2 Photoluminescence data for complexes **5–6** and **16–21** (neat film, rt)

	$\lambda_{exc}{}^a$ [nm]	CIE x; y^b	$\lambda_{em}{}^c$ [nm]	Φ^d	$\tau_0{}^e$ [µs]
5	345	0.222; 0.385	489	0.28	5
6	355	0.215; 0.384	490	0.36	6
16	330	0.159; 0.157	523	0.23	4
17	340	0.232; 0.419	495	0.42	4
18	355	0.245; 0.433	499	0.23	5
19	355	0.247; 0.441	502	0.21	6
20	370	0.225; 0.398	494	0.46	4
21	370	0.233; 0.397	485	0.09	8

^{a} Excitation wavelength. ^{b} CIE coordinates. ^{c} Max. emission wavelength. ^{d} Quantum yield at λ_{exc}, N_2 atmosphere. ^{e} Decay lifetimes (excited by laser pulses (355 nm, 1 ns)) given as $\tau_o = \tau_v/\phi$.

DFT calculations

We recently published a methodology which allows us to predict the emission wavelengths of the platinum complexes.[73] Also for the new complexes reported in this study we could successfully use this methodology, where we optimize the singlet and triplet state geometries of all complexes in the gas phase using DFT methods, *e.g.* BP86 together with a 6-31G(d) basis set and Hay-Wadt-ECP for platinum. The difference between the calculated and the measured wavelength (see Table S2, ESI†) turned out to be ≤10 nm for all complexes reported here with the exception of **4** (21 nm).

The geometries of the optimized complexes **4** and **20** are also in good agreement with the data of the solid state structures obtained by X-ray diffraction analysis, which confirms that the DFT functionals used are capable of describing the bonding situation in these complexes.

Conclusion

We synthesized ten new platinum(II) complexes with C^C* cyclometalating ligands based on 1-phenyl-1,2,4-triazol-5-ylidene and 4-phenyl-1,2,4-triazol-5-ylidene, as well as acetylacetonato (O^O = acac) and 1,3-bis(2,4,6-trimethylphenyl) propan-1,3-dionato) (O^O = mesacac) ancillary ligands. The complexes were thoroughly characterized and investigated in terms of their photophysical properties for a potential application as emitter molecules for OLEDs. The solid-state structure determination of two complexes reveals the steric effect of the O^O ancillary ligands on the stacking behavior of the complexes, which consequently has an impact on the emissions of the neat emitter films. The emission properties of the complexes strongly depend on the O^O ligand, but less on the substituents in 4-position of the cyclometalating phenyl ring. All complexes containing 1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato as O^O ligand are strongly emissive at lower energies and reveal shorter decay times in comparison to the emitters with an acetylacetonato ancillary ligand.

Experimental details

The syntheses of the complexes were performed under an argon atmosphere, using common Schlenk techniques and dry solvents. DMF and 1,4-dioxane were dried according to standard techniques and stored over molecular sieve 4 Å. All other chemicals were used as purchased. 4-Phenyl-4*H*-1,2,4-triazole **1**,[74] 1-phenyl-1*H*-1,2,4-triazole **7**,[75] 1-(4-methoxyphenyl)-1*H*-1,2,4-triazole **8**, 1-(4-methylphenyl)-1*H*-1,2,4-triazole **9**, 1,3-bis-(2,4,6-trimethylphenyl)propan-1,3-dionato and dichloro(1,5-cyclooctadiene)platinum(II)[76] were synthesized according to published procedures.[66,68,77,78] Potassium tetrachloroplatinate (II) was purchased from Pressure Chemicals Co. NMR spectra were recorded on a Bruker NMR spectrometer and referenced to the internal resonances of the solvents (^{1}H: 7.26, ^{13}C: 77.0 for CDCl$_3$; ^{1}H: 2.50, ^{13}C: 39.43 for DMSO-d_6). ^{195}Pt spectra were referenced to potassium tetrachloroplatinate(II) in D$_2$O (-1617.2 (PtCl$_4{}^{2-}$), -2654.1 (PtCl$_2$)) as external standard. Shifts are given in ppm, coupling constants J in Hz.

Elemental analyses were performed by the analytical laboratory of the department using an Eurovektor Hekatech EA-3000 elemental analyzer. Melting points are not corrected. Photoluminescence measurements have been performed in thin PMMA films doped with 2 wt% of the emitter or from the neat emitter films. The films were prepared by doctor blading a solution of emitter (2 mg mL^{-1}) in a 10 wt% PMMA solution in dichloromethane on a substrate with a 60 µm doctor blade. The film was dried and the emission was measured under nitrogen. The excitation was carried out at a wavelength of 325–370 nm (Xe-lamp with monochromator) and the emission was detected with a calibrated quantum-yield detection system (Hamamatsu, model C9920-02). The phosphorescence decay was measured by excitation with pulses of a THG-NdYAG laser (355 nm, 1 ns) and time-resolved photon counting by multichannel scaling (MCS) technique.

General procedure for the synthesis of platinum(II) complexes

A flame-dried schlenk tube was charged with triazolium salt and silver(I) oxide. The reactants were dried *in vacuo* and the tube was refilled with argon. 1,4-Dioxane was added and the mixture was stirred for 21 h at room temperature under a positive pressure of argon. Afterwards, dichloro(1,5-cyclooctadiene) platinum(II) and butanone were added, and the mixture was slowly heated and stirred for 21 h at 115 °C. The solvent was removed under reduced pressure and the remaining solid was dissolved in DMF. Potassium *tert*-butoxide and β-diketone were added, and the mixture was stirred for 21 h at room temperature and another 6 h at 100 °C. Afterwards the solvent was removed under reduced pressure and the residue was washed with water and purified by flash chromatography.

Synthesis of 1-benzyl-4-phenyl-1,2,4-triazolium bromide 3

In a pressure tube 581 mg 4-phenyl-4*H*-1,2,4-triazole **1** (4 mmol) was dissolved in 3 mL of THF. 0.96 mL of benzyl bromide (8 mmol, 1.37 g, 2 eq.) were added, the pressure tube was sealed and the mixture was stirred for 22 h at 100 °C. After

cooling to room temperature, the solid was filtered, washed with THF, and dried *in vacuo* to yield a white powder (1.21 g, 3.81 mmol, 95%). Mp: 155 °C. ^{1}H-NMR (500.13 MHz, DMSO-d$_6$): δ 10.98 (s, 1 H, NCHN); 9.79 (s, 1 H, NCHN); 7.86 (d, $^3J_{HH}$ = 7.2 Hz, 2 H, C2H_{arom} and C6H_{arom} of phenyl ring); 7.71 (t, $^3J_{HH}$ = 7.7 Hz, 2 H, C3H_{arom} and C5H_{arom} of phenyl ring); 7.65 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, C4H_{arom} of phenyl ring); 7.55 (d, $^3J_{HH}$ = 7.7 Hz, 2 H, C2H_{arom} and C6H_{arom} of benzyl group); 7.50–7.36 (m, 3 H, C3H_{arom}–C5H_{arom} of benzyl group); 5.71 (s, 2 H, CH_2) ppm. ^{13}C-NMR (125.75 MHz, DMSO-d$_6$): δ 143.4 (NCHN); 141.9 (NCHN); 133.0 ($C1_{arom}$); 132.2 ($C1_{arom}$); 130.5 ($C4H_{arom}$ of phenyl ring); 130.2 ($C3H_{arom}$ and $C5H_{arom}$ of phenyl ring); 129.1 ($C2H_{arom}$ and $C6H_{arom}$ of benzyl group); 129.0 ($C4H_{arom}$ of benzyl group); 128.8 ($C3H_{arom}$ and $C5H_{arom}$ of benzyl group); 122.6 ($C2H_{arom}$ and $C6H_{arom}$ of phenyl ring); 55.0 (CH$_2$) ppm. Anal. Calcd for C$_{15}$H$_{14}$BrN$_3$: C, 56.98; H, 4.46; N, 13.29. Found: C, 57.15; H, 4.63; N, 13.26.

Synthesis of (pentan-2,4-dionato-κ^2O,O′)(1-benzyl-4-phenyl-κC^2-1,2,4-triazol-5-ylidene-κC^5)platinum(II) 4

253 mg triazolium bromide **3** (0.8 mmol), 93 mg silver(I) oxide (0.4 mmol, 0.5 eq.), 449 mg dichloro(1,5-cyclooctadiene)platinum(II) (1.2 mmol, 1.5 eq.), 359 mg potassium *tert*-butoxide (3.2 mmol, 4 eq.), and 0.33 mL of pentane-2,4-dione (3.2 mmol, 320 mg, 4 eq.) were reacted in 20 mL of 1,4-dioxane, 10 mL of butanone, and 20 mL of DMF according to the general procedure. The crude product was purified by flash chromatography (KG60, dichloromethane) to obtain a white powder (130 mg, 0.25 mmol, 31%). Mp: 211 °C. ^{1}H-NMR (300.13 MHz, CDCl$_3$) δ 8.22 (s, 1 H, NCHN); 7.84 (*pseudo*-t, d, $^3J_{PtH}$ = 26.3 Hz, $^3J_{HH}$ = 7.0 Hz, 1 H, C3H_{arom} of phenyl ring); 7.57 (d, $^3J_{HH}$ = 7.6 Hz, 2 H, C2H_{arom} and C6H_{arom} of benzyl group); 7.34 (m, 3 H, C3H_{arom}–C5H_{arom} of benzyl group); 7.08 (m, 3 H, C4H_{arom}–C6H_{arom} of phenyl ring); 5.85 (s, 2 H; CH_2); 5.57 (s, 1 H, CH); 2.11 (s, 3 H, CH_3) 1.97 (s, 3 H, CH_3) ppm. ^{13}C-NMR (75.48 MHz, CDCl$_3$) δ 185.4 (CO); 185.3 (CO); 143.3 ($C1_{arom}$ of phenyl ring); 136.3 (C_{ipso}); 135.8 (C_{ipso}); 132.4 ($C3H_{arom}$ of phenyl ring); 128.8 (CH$_{arom}$ of benzyl group); 128.7 (CH$_{arom}$ of benzyl group); 128.7 (CH$_{arom}$ of benzyl group); 128.3 (NCHN); 125.4 (CH$_{arom}$ of phenyl ring); 124.4 ($C1_{arom}$ of phenyl ring); 123.9 ($C5H_{arom}$ of phenyl ring); 110.8 (CH$_{arom}$ of phenyl ring); 102.3 (CH); 53.6 (CH$_2$); 28.0 (CH$_3$); 27.8 (CH$_3$) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3393.4 ppm. Anal. Calcd for C$_{20}$H$_{18}$N$_3$O$_2$Pt: C, 45.46; H, 3.62; N, 7.95. Found: C, 45.43; H, 3.53; N, 7.97.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ^2O,O′)(4-phenyl-κC^2-1-methyl-1,2,4-triazol-5-ylidene-κC^5)-platinum(II) 5

459 mg triazolium iodide **2** (1.6 mmol), 185 mg silver(I) oxide (0.8 mmol, 0.5 eq.), 898 mg dichloro(1,5-cyclooctadiene)platinum(II) (2.4 mmol, 1.5 eq.), 718 mg potassium *tert*-butoxide (6.4 mmol, 4 eq.), and 1970 mg 1,3-bis(2,4,6-trimethylphenyl)-propan-1,3-dione (6.4 mmol, 4 eq.) were reacted in 20 mL of 1,4-dioxane, 10 mL of butanone, and 20 mL of DMF according to the general procedure. The obtained solid was purified by

flash chromatography (KG60, dichloromethane/isohexanes solvent mixture (1 : 1)) and the crude product was recrystallized from isohexanes, which in the following turned out to be hard to remove. The product was obtained as a yellow powder (177 mg, 0.27 mmol, 17%). Mp: 79 °C. ^{1}H-NMR (600.16 MHz, CDCl$_3$) δ 8.25 (s, 1 H, NCHN); 7.74 (d, *pseudo*-t, $^3J_{HH}$ = 7.4 Hz, $^3J_{PtH}$ = 20.9 Hz, 1 H, C3H_{arom} of phenyl ring); 7.09 (d, $^3J_{HH}$ = 7.6 Hz, 1 H, C6H_{arom} of phenyl ring); 7.06 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, C5H_{arom} of phenyl ring); 7.01 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, C4H_{arom} of phenyl ring); 6.87 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.84 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 5.72 (s, 1 H, (CO)CH(CO)); 4.11 (s, 3 H, NCH_3); 2.35 (s, 6 H, *o*-CH_3 of mesityl group); 2.32 (s, 6 H, *o*-CH_3 of mesityl group); 2.31 (s, 3 H, *p*-CH_3 of mesityl group); 2.29 (s, 3 H, *p*-CH_3 of mesityl group) ppm. ^{13}C-NMR (150.93 MHz, CDCl$_3$) δ 185.4 (CO); 184.7 (CO); 152.5 (NCN); 143.4 ($C1_{arom}$ of phenyl ring); 139.4 ($C1_{arom}$ of mesityl group); 139.0 ($C1_{arom}$ of mesityl group); 137.8 ($C4_{arom}$ of mesityl group); 137.6 ($C4_{arom}$ of mesityl group); 135.8 (NCHN); 134.2 ($C2_{arom}$ and $C6_{arom}$ of mesityl group); 133.7 ($C2_{arom}$ and $C6_{arom}$ of mesityl group); 132.9 ($C3H_{arom}$ of phenyl ring); 128.2 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 128.1 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 125.5 ($C4H_{arom}$ of phenyl ring); 124.1 ($C5H_{arom}$ of phenyl ring); 123.9 ($C2_{arom}$ of phenyl ring); 110.8 ($C6H_{arom}$ of phenyl ring); 107.2 ((CO)CH(CO)); 37.5 (NCH$_3$); 21.1 (*p*-CH$_3$ of mesityl group); 21.1 (*p*-CH$_3$ of mesityl group); 19.9 (*o*-CH$_3$ of mesityl group); 19.6 (*o*-CH$_3$ of mesityl group) ppm. ^{195}Pt-NMR (128.56 MHz, CDCl$_3$) δ −3342.3 ppm. Anal Calcd for C$_{30}$H$_{31}$N$_3$O$_2$Pt · 0.7 C$_6$H$_{14}$: C, 57.08; H, 5.52; N, 5.84. Found: C, 57.24; H, 5.38; N, 5.90.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ^2O,O′)(1-benzyl-4-phenyl-κC^2-1,2,4-triazol-5-ylidene-κC^5)-platinum(II) 6

506 mg triazolium iodide **3** (1.6 mmol), 185 mg silver(I) oxide (0.8 mmol, 0.5 eq.), 599 mg dichloro(1,5-cyclooctadiene)platinum(II) (1.6 mmol, 1 eq.), 359 mg potassium *tert*-butoxide (3.2 mmol, 2 eq.), and 987 mg 1,3-bis(2,4,6-trimethylphenyl)-propan-1,3-dione (3.2 mmol, 2 eq.) were reacted in 20 mL of 1,4-dioxane, 10 mL of butanone, and 20 mL of DMF according to the general procedure. The remaining solid was purified by flash chromatography (KG60, dichloromethane/isohexanes solvent mixture (1 : 1)) and the crude product was washed with isohexanes, which in the following turned out to be hard to remove. The product was obtained as a white powder (440 mg, 0.60 mmol, 37%). Mp: 209 °C. ^{1}H-NMR (500.13 MHz, CDCl$_3$): δ 8.26 (s, 1 H, NCHN); 7.76 (d, *pseudo*-t, $^3J_{HH}$ = 7.7 Hz, $^3J_{PtH}$ = 24.1 Hz, 1 H, C3H_{arom} of phenyl ring); 7.29 (dd, $^3J_{HH}$ = 7.7 Hz, J_{HH} = 1.7 Hz, 2 H, C2H_{arom} and C6H_{arom} of benzyl group); 7.25–7.18 (m, 3 H, C3H_{arom}–C5H_{arom} of benzyl group); 7.08 (dt, J_{HH} = 1.6 Hz, $^3J_{HH}$ = 7.7 Hz, 1 H, C6H_{arom} of phenyl ring); 7.06 (dt, J_{HH} = 1.4 Hz, $^3J_{HH}$ = 7.4 Hz, 1 H, C5H_{arom} of phenyl ring); 7.01 (dt, $^3J_{HH}$ = 7.2 Hz, J_{HH} = 1.8 Hz, 1 H, C4H_{arom} of phenyl ring); 6.87 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.79 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 5.73 (s, 1 H, (CO)CH(CO)); 5.67 (s, 2 H, CH_2); 2.36 (s, 6 H,

o-CH_3 of mesityl group); 2.31 (s, 3 H, p-CH_3 of mesityl group); 2.26 (s, 3 H, p-CH_3 of mesityl group); 2.24 (s, 6 H, o-CH_3 of mesityl group) ppm. ^{13}C-NMR (125.77 MHz, CDCl$_3$): δ 185.7 (CO); 184.7 (CO); 152.4 (NCN); 143.3 ($C1_{\text{arom}}$ of phenyl ring); 139.3 ($C1_{\text{arom}}$ of mesityl group); 138.9 ($C1_{\text{arom}}$ of mesityl group); 137.8 ($C4_{\text{arom}}$ of mesityl group); 137.5 ($C4_{\text{arom}}$ of mesityl group); 134.2 ($C2_{\text{arom}}$ and $C6_{\text{arom}}$ of mesityl group); 133.4 ($C2_{\text{arom}}$ and $C6_{\text{arom}}$ of mesityl group); 132.8 ($C3H_{\text{arom}}$ of phenyl ring); 128.4 ($C4H_{\text{arom}}$ of benzyl group); 128.3 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 128.3 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of mesityl group); 128.0 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of benzyl group); 127.9 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of mesityl group); 125.5 ($C4H_{\text{arom}}$ of phenyl ring); 124.1 ($C2H_{\text{arom}}$ of phenyl ring); 124.0 ($C5H_{\text{arom}}$ of phenyl ring); 110.8 ($C6H_{\text{arom}}$ of phenyl ring); 107.2 ((CO)CH(CO)) 53.6 (CH_2), 21.1 (p-CH_3 of mesityl group); 21.1 (p-CH_3 of mesityl group); 20.0 (o-CH_3 of mesityl group); 19.3 (o-CH_3 of mesityl group) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3346.4 ppm. Anal. Calcd for $C_{36}H_{35}N_3O_2Pt\cdot0.5\ C_6H_{14}$: C, 60.06; H, 5.43; N, 5.39. Found: C, 60.25; H, 5.21; N, 5.34.

Synthesis of 4-benzyl-1-phenyl-1,2,4-triazolium bromide 13

In a pressure tube 653 mg 1-phenyl-1H-1,2,4-triazole 7 (4.5 mmol) was dissolved in 4 mL of THF. 1.08 mL of benzyl bromide (9 mmol, 1.54 g, 2 eq.) were added, the pressure tube was sealed and the mixture was stirred for 22 h at 110 °C. After cooling to room temperature, the solid was filtered, washed with THF, and dried *in vacuo* to yield a white powder (1.22 g, 3.87 mmol, 86%). Mp: 170 °C. ^{1}H-NMR (600.16 MHz, DMSO-d$_6$): δ 11.07 (s, 1 H, NCHN); 9.56 (s, 1 H, NCHN); 7.93 (d, $^{3}J_{HH}$ = 8.3 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl ring); 7.70 (t, $^{3}J_{HH}$ = 7.8 Hz; 2 H, $C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 7.65 (t, $^{3}J_{HH}$ = 7.4 Hz, 1 H, $C4H_{\text{arom}}$ of phenyl ring); 7.58 (d, $^{3}J_{HH}$ = 7.2 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 7.50–7.40 (m, 3 H, $C3H_{\text{arom}}$–$C5H_{\text{arom}}$ of benzyl group); 5.61 (s, 2 H, CH_2) ppm. ^{13}C-NMR (150.93 MHz, DMSO-d$_6$): δ 145.0 (NCHN); 141.8 (NCHN); 135.1 ($C1_{\text{arom}}$ of phenyl ring); 133.3 ($C1_{\text{arom}}$ of benzyl group); 130.6 ($C4H_{\text{arom}}$ of phenyl ring); 130.2 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 129.1 ($C4H_{\text{arom}}$ of benzyl group); 129.1 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of benzyl group); 128.9 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 120.9 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl ring); 51.0 (CH_2) ppm. Anal. Calcd for $C_{15}H_{14}BrN_3$: C, 56.98; H, 4.46; N, 13.29. Found: C, 57.09; H, 4.46; N, 13.41.

Synthesis of 4-benzyl-1-(4-methoxyphenyl)-1,2,4-triazolium bromide 14

In a pressure tube 526 mg 1-(4-methoxyphenyl)-1H-1,2,4-triazole 8 (3 mmol) was dissolved in 2 mL of THF. 0.72 mL of benzyl bromide (6 mmol, 1.03 g, 2 eq.) were added, the pressure tube was sealed and the mixture was stirred for 22 h at 100 °C. After cooling to room temperature, the solid was filtered, washed with THF, and dried *in vacuo* to yield a white powder (1.01 g, 2.91 mmol, 97%). Mp: 163 °C. ^{1}H-NMR (300.13 MHz, DMSO-d$_6$) δ 10.90 (NCHN); 9.49 (NCHN); 7.84 (d, $^{3}J_{HH}$ = 9.0 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl ring); 7.56 (d, $^{3}J_{HH}$ = 7.7 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl

ring); 7.51–7.42 (m, 3 H, $C3H_{\text{arom}}$–$C5H_{\text{arom}}$ of benzyl group); 7.23 (d, $^{3}J_{HH}$ = 9.1 Hz, 2 H, $C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 5.57 (s, 2 H, CH_2); 3.85 (s, 3 H, CH_3) ppm. ^{13}C-NMR (75.48 MHz, DMSO-d$_6$) δ 160.5 ($C4_{\text{arom}}$ of phenyl ring); 144.8 (NCHN); 141.0 (NCHN); 133.3 ($C1_{\text{arom}}$ of benzyl group); 129.0 ($C4H_{\text{arom}}$ of benzyl group); 129.0 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of benzyl group); 128.8 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 128.1 ($C1_{\text{arom}}$ of phenyl ring); 122.6 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl ring); 115.1 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 55.8 (CCH$_3$); 50.8 (CH_2) ppm. Anal. Calcd for $C_{16}H_{16}BrN_3O$: C, 55.51; H, 4.66; N, 12.14. Found: C, 55.55; H, 4.55; N, 12.01.

Synthesis of 4-benzyl-1-(4-methylphenyl)-1,2,4-triazolium bromide 15

In a pressure tube 653 mg 1-(4-methylphenyl)-1H-1,2,4-triazole 9 (3 mmol) was dissolved in 2 mL of THF. 0.72 mL of benzyl bromide (6 mmol, 1.03 g, 2 eq.) were added, the pressure tube was sealed and the mixture was stirred for 22 h at 100 °C. After cooling to room temperature, the solid was filtered, washed with THF, and dried *in vacuo* to yield a white powder (834 mg, 2.53 mmol, 84%). Mp: 162 °C. ^{1}H-NMR (300.13 MHz, DMSO-d$_6$) δ 10.96 (NCHN); 9.51 (NCHN); 7.81 (d, $^{3}J_{HH}$ = 8.6 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl ring); 7.56 (dd, J_{HH} = 1.8 Hz, $^{3}J_{HH}$ = 7.6 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 7.53–7.40 (m, 5 H, $C3H_{\text{arom}}$–$C5H_{\text{arom}}$ of benzyl group, $C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 5.58 (s, 2 H, CH_2); 2.41 (s, 3 H, CH_3) ppm. ^{13}C-NMR (75.48 MHz, DMSO-d$_6$) δ 144.9 (NCHN); 141.4 (NCHN); 140.5 ($C4_{\text{arom}}$ of phenyl ring); 133.3 ($C1_{\text{arom}}$ of benzyl group); 132.7 ($C1_{\text{arom}}$ of phenyl ring); 130.4 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of phenyl ring); 129.1 ($C4H_{\text{arom}}$ of benzyl ring); 129.0 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of benzyl group); 128.8 ($C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 120.6 ($C3H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 50.9 (CH_2); 20.7 (CCH$_3$) ppm. Anal. Calcd for $C_{16}H_{16}BrN_3$: C, 58.20; H, 4.88; N, 12.77. Found: C, 58.45; H, 4.70; N, 12.86.

Synthesis of (pentan-2,4-dionato-κ^2O,O')(4-benzyl-1-phenyl-κC^2-1,2,4-triazol-5-ylidene-κC^5)platinum(ɪɪ) 16

506 mg triazolium bromide 13 (1.6 mmol), 185 mg silver(ɪ) oxide (0.8 mmol, 0.5 eq.), 898 mg dichloro(1,5-cyclooctadiene)-platinum(ɪɪ) (2.4 mmol, 1.5 eq.), 718 mg potassium *tert*-butoxide (6.4 mmol, 4 eq.), and 0.66 mL of pentane-2,4-dione (6.4 mmol, 641 mg, 4 eq.) were reacted in 40 mL of 1,4-dioxane, 20 mL of butanone, and 40 mL of DMF according to the general procedure. The crude product was purified by flash chromatography (KG60, dichloromethane) to obtain a white powder (325 mg, 0.62 mmol 77%). Mp: 224 °C. ^{1}H-NMR (300.13 MHz, CDCl$_3$) δ 7.83 (*pseudo*-t, d, $^{3}J_{PtH}$ = 27.4 Hz, $^{3}J_{HH}$ = 5.4 Hz, 1 H, $C3H_{\text{arom}}$ of phenyl ring); 7.78 (s, 1 H, NCHN); 7.47 (d, $^{3}J_{HH}$ = 7.3 Hz, 2 H, $C2H_{\text{arom}}$ and $C6H_{\text{arom}}$ of benzyl group); 7.43–7.32 (m, 3 H, $C3H_{\text{arom}}$–$C5H_{\text{arom}}$ of benzyl group) 7.30–7.25 (m, 1 H, $C6H_{\text{arom}}$ of phenyl ring); 7.12–7.05 (m, 2 H, $C4H_{\text{arom}}$ and $C5H_{\text{arom}}$ of phenyl ring); 5.74 (s, 2 H, CH_2); 5.54 (s, 1 H, (CO)CH(CO)); 2.10 (s, 3 H, CH_3); 1.90 (s, 3 H, CH_3) ppm. ^{13}C-NMR (75.48 MHz, CDCl$_3$) δ 185.2 (CO); 185.1 (CO); 153.1 (NCN); 145.2 ($C1_{\text{arom}}$ of phenyl ring); 140.6 (NCHN);

135.4 ($C1_{arom}$ of benzyl group); 131.2 ($C3H_{arom}$ of phenyl ring); 129.4 ($C3H_{arom}$ and $C5H_{arom}$ of benzyl group); 128.8 ($C4H_{arom}$ of benzyl group); 128.2 ($C2H_{arom}$ and $C6H_{arom}$ of benzyl group); 125.3 ($C5H_{arom}$ of phenyl ring); 124.0 ($C4H_{arom}$ of phenyl ring); 121.6 ($C1_{arom}$ of phenyl ring); 111.6 ($C6H_{arom}$ of phenyl ring); 102.2 ((CO)CH(CO)); 49.5 (CH_2); 28.1 (CH_3); 27.9 (CH_3) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3450.2 ppm. Anal. Calcd for $C_{20}H_{19}N_3O_2Pt$: C, 45.46; H, 3.62; N, 7.95. Found: C, 45.21; H, 3.50; N, 7.94.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ²O,O′)(1-phenyl-κC²-4-methyl-1,2,4-triazol-5-ylidene-κC⁵)-platinum(ɪɪ) 17

Method A: 459 mg triazolium iodide **10** (1.6 mmol), 185 mg silver(ɪ) oxide (0.8 mmol, 0.5 eq.), 898 mg dichloro(1,5-cyclo-octadiene)platinum(ɪɪ) (2.4 mmol, 1.5 eq.), 718 mg potassium *tert*-butoxide (6.4 mmol, 4 eq.), and 1970 mg 1,3-bis(2,4,6-tri-methylphenyl)propan-1,3-dione (6.4 mmol, 4 eq.) were reacted in 40 mL of 1,4-dioxane, 20 mL of butanone, and 40 mL of DMF according to the general procedure. The obtained solid was purified by flash chromatography (KG60, dichloro-methane/isohexanes solvent mixture (1 : 1)) and the crude product was washed with isohexanes, which in the following turned out to be hard to remove. The product was obtained as a white powder (28 mg, 0.22 mmol, 13%). Mp: 135 °C. ^{1}H-NMR (300.13 MHz, CDCl$_3$) δ 7.48 (s, 1 H, NCHN); 7.73 (*pseudo*-t, d, $^3J_{PtH}$ = 28.0 Hz, $^3J_{HH}$ = 7.4 Hz, 1 H, C3H_{arom} of phenyl ring); 7.28 (d, $^3J_{HH}$ = 7.7 Hz, 1 H, C6H_{arom} of phenyl ring); 7.08 (t, $^3J_{HH}$ = 7.5 Hz, 1 H, C5H_{arom} of phenyl ring); 7.00 (t, $^3J_{HH}$ = 7.4 Hz, 1 H, C4H_{arom} of phenyl ring); 6.87 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.84 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 5.70 (s, 1 H, (CO)CH(CO)); 3.95 (s, 3 H, NCH_3); 2.35 (s, 6 H, *o*-CH_3 of mesityl group); 2.31 (s, 6 H, *o*-CH_3 of mesityl group); 2.30 (s, 3 H, *p*-CH_3 of mesityl group); 2.29 (s, 3 H, *p*-CH_3 of mesityl group) ppm. ^{13}C-NMR (125.77 MHz, CDCl$_3$) δ 187.2 (CO); 186.1 (CO); 143.6 (NCHN); 139.9 ($C1_{arom}$ of phenyl ring); 137.9 ($C1_{arom}$ of mesityl group); 137.0 ($C1_{arom}$ of mesityl group); 134.8 ($C2_{arom}$ and $C6_{arom}$ of mesityl group); 134.5 ($C2_{arom}$ and $C6_{arom}$ of mesityl group); 129.5 ($C3H_{arom}$ of phenyl ring); 128.2 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 128.1 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 127.9 ($C4H_{arom}$ of phenyl ring); 127.1 ($C5H_{arom}$ of phenyl ring); 116.09 ($C6H_{arom}$ of phenyl ring); 112.2 ((CO)CH(CO)); 33.8 (NCH_3); 21.2 (*p*-CH_3 of mesityl group); 21.1 (*p*-CH_3 of mesityl group); 19.9 (*o*-CH_3 of mesityl group); 19.5 (*o*-CH_3 of mesityl group) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3405.6 ppm. Anal. Calcd for $C_{30}H_{31}N_3O_2Pt \cdot 0.45\ C_6H_{14}$: C, 56.15; H, 5.37; N, 6.01. Found: C, 56.15; H, 5.36; N, 5.95.

Method B: A flame-dried schlenk tube was charged with 919 mg triazolium salt **10** (3.2 mmol) and 371 mg silver(ɪ) oxide (1.6 mmol, 0.5 eq.) and the tube was refilled with argon. 40 mL of DMF was added and the mixture was stirred for 21 h at 60 °C under a positive pressure of argon. Afterwards, 1197 mg dichloro(1,5-cyclooctadiene)platinum(ɪɪ) (3.2 mmol, 1 eq.) were added, and the mixture was stirred for 21 h at room temperature and another 48 h at 130 °C. After cooling to room

temperature 718 mg potassium *tert*-butoxide (6.4 mmol, 2 eq.) and 1974 mg 1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dione (6.4 mmol, 2 eq.) were added, and the mixture was stirred for 21 h at room temperature and another 6 h at 100 °C. Afterwards the solvent is removed under reduced pressure and the remaining residue was washed with water. The obtained solid was purified by flash chromatography (KG60, dichloromethane/ isohexanes solvent mixture (1 : 1)) and the crude product was washed with isohexanes, which in the following turned out to be hard to remove. The product was obtained as a white powder (638 mg, 0.97 mmol, 30%). Anal. Calcd for $C_{30}H_{31}N_3O_2Pt \cdot 0.35\ C_6H_{14}$: C, 55.81; H, 5.24; N, 6.08. Found: C, 55.62; H, 5.40; N, 5.82.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ²O,O′)(1-(4-methoxyphenyl-κC²)-4-methyl-1,2,4-triazol-5-ylidene-κC⁵)platinum(ɪɪ) 18

509 mg triazolium iodide **11** (1.6 mmol), 185 mg silver(ɪ) oxide (0.8 mmol, 0.5 eq.), 599 mg dichloro(1,5-cyclo-octadiene) plati-num(ɪɪ) (1.6 mmol, 1 eq.), 718 mg potassium *tert*-butoxide (6.4 mmol, 4 eq.), and 1970 mg 1,3-bis(2,4,6-tri-methylphenyl)-propan-1,3-dione (6.4 mmol, 4 eq.) were reacted in 20 mL of 1,4-dioxane, 10 mL of butanone, and 20 mL of DMF according to the general procedure. The obtained solid was purified by flash chromatography (KG60, dichloromethane/isohexanes solvent mixture (1 : 1)) and the crude product was washed with isohexanes to yield a white powder (188 mg, 0.27 mmol, 17%). Mp: 138 °C. ^{1}H-NMR (300.13 MHz, CDCl$_3$) δ 7.81 (s, 1 H, NCHN); 7.29 (d, *pseudo*-t, J_{HH} = 2.7 Hz, $^3J_{PtH}$ = 31.7 Hz, 1 H, C2H_{arom} of phenyl ring); 7.23 (d, $^3J_{HH}$ = 8.4 Hz, 1 H, C6H_{arom} of phenyl ring); 6.84 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.83 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.62 (d, $^3J_{HH}$ = 8.5 Hz, J_{HH} = 2.7 Hz, 1 H, C5H_{arom} of phenyl ring); 5.70 (s, 1 H, (CO)CH(CO)); 3.93 (s, 3 H, NCH_3); 3.76 (s, 3 H, OCH_3); 2.34 (s, 6 H, *o*-CH_3 of mesityl group); 2.31 (s, 6 H, *o*-CH_3 of mesityl group); 2.29 (s, 6 H, *p*-CH_3 of mesityl group) ppm. ^{13}C-NMR (125.77 MHz, CDCl$_3$) δ 185.0 (CO); 184.7 (CO); 157.1 ($C4_{arom}$ of phenyl ring); 151.7 (NCN); 141.2 (NCHN); 139.5 ($C1_{arom}$ of mesityl group); 139.1 ($C1_{arom}$ of phenyl ring); 138.8 ($C1_{arom}$ of mesityl group); 137.7 ($C4_{arom}$ of mesityl group); 137.5 ($C4_{arom}$ of mesityl group); 134.1 ($C2_{arom}$ and $C5_{arom}$ of mesityl group); 133.7 ($C2_{arom}$ and $C5_{arom}$ of mesityl group); 128.2 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 128.1 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 123.0 ($C2_{arom}$ of phenyl ring); 117.7 ($C3H_{arom}$ of phenyl ring); 112.2 ($C6H_{arom}$ of phenyl ring); 108.1 ($C5H_{arom}$ of phenyl ring); 107.2 ((CO)CH(CO)); 55.5 (OCH_3); 32.8 (NCH_3); 21.1 (*p*-CH_3 of mesityl group); 20.0 (*o*-CH_3 of mesityl group); 19.5 (*o*-CH_3 of mesityl group) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3375.8 ppm. Anal. Calcd for $C_{31}H_{33}N_3O_3Pt$: C, 53.91; H, 4.82; N, 6.08. Found: C, 54.05; H, 4.96; N, 6.03.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ²O,O′)(1-(4-methylphenyl-κC²)-4-methyl-1,2,4-triazol-5-ylidene-κC⁵)platinum(ɪɪ) 19

224 mg triazolium iodide **11** (0.74 mmol), 86 mg silver(ɪ) oxide (0.37 mmol, 0.5 eq.), 278 mg dichloro(1,5-cyclooctadiene)-plati-

num(II) (0.74 mmol, 1 eq.), 334 mg potassium *tert*-butoxide (2.98 mmol, 4 eq.), and 918 mg 1,3-bis(2,4,6-trimethylphenyl)-propan-1,3-dione (2.98 mmol, 4 eq.) were reacted in 20 mL of 1,4-dioxane, 10 mL of butanone, and 20 mL of DMF according to the general procedure. The obtained solid was purified by flash chromatography (KG60, dichloromethane/isohexanes solvent mixture (1:1)) and the crude product was washed with isohexanes, which in the following turned out to be hard to remove. The product was obtained as a white powder (133 mg, 0.20 mmol, 27%). Mp: 157 °C. ^{1}H-NMR (600.16 MHz, CDCl$_3$) δ 7.81 (s, 1 H, NCHN); 7.49 (pseudo-t, $^3J_{PtH}$ = 24.0 Hz, 1 H, C3H_{arom} of phenyl ring); 7.15 (d, $^3J_{HH}$ = 7.8 Hz, 1 H, C6H_{arom} of phenyl ring); 6.86 (s, 3 H, C3H_{arom} and C5H_{arom} of mesityl ring, and C5H_{arom} of phenyl ring); 6.82 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 5.87 (s, 1 H, (CO)CH(CO)); 3.92 (s, 3 H, NCH_3); 2.35 (s, 6 H, *o*-CH_3 of mesityl group); 2.30 (s, 12 H, *o*-CH_3 and *p*-CH_3 of mesityl group, and CH_3 of phenyl ring); 2.28 (s, 6 H, *p*-CH_3 of mesityl ring) ppm. ^{13}C-NMR (150.93 MHz, CDCl$_3$) δ 185.0 (CO); 184.6 (CO); 152.7 (NCN); 143.0 (C1$_{arom}$ of phenyl ring); 141.3 (NCHN); 139.5 (C1$_{arom}$ of mesityl group); 139.0 (C1$_{arom}$ of phenyl ring); 137.7 (C4$_{arom}$ of mesityl group); 137.5 (C4$_{arom}$ of mesityl group); 135.1 (C4$_{arom}$ of phenyl ring); 134.3 (C2$_{arom}$ and C6$_{arom}$ of mesityl group); 133.7 (C2$_{arom}$ and C6$_{arom}$ of mesityl group); 132.2 (C3H_{arom} of phenyl ring); 128.3 (C3H_{arom} and C5H_{arom} of mesityl group); 128.1 (C3H_{arom} and C5H_{arom} of mesityl group); 124.6 (C5H_{arom} of phenyl ring); 120.7 (C2$_{arom}$ of phenyl ring); 111.4 (C6H_{arom} of phenyl ring); 107.2 ((CO)CH(CO)); 32.8 (NCH$_3$); 21.6 (CH$_3$ of phenyl ring); 21.1 (*p*-CH$_3$ of mesityl group); 21.1 (*p*-CH$_3$ of mesityl group); 20.0 (*o*-CH$_3$ of mesityl group); 19.5 (*o*-CH$_3$ of mesityl group) ppm. ^{195}Pt-NMR (128.63 MHz, CDCl$_3$) δ = −3385.2 ppm. Anal. Calcd for C$_{31}$H$_{34}$N$_3$O$_2$Pt · 0.3 C$_6$H$_{14}$: C, 56.15; H, 5.49; N, 5.99. Found: C, 56.11; H, 5.46; N, 5.84.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ^{2}O,O′)(4-benzyl-1-phenyl-κC^2-1,2,4-triazol-5-ylidene-κC^5)-platinum(II) 20

506 mg triazolium bromide **13** (1.6 mmol), 185 mg silver(I) oxide (0.8 mmol, 0.5 eq.), 898 mg dichloro(1,5-cyclooctadiene)-platinum(II) (2.4 mmol, 1.5 eq.), 449 mg potassium *tert*-butoxide (4 mmol, 2.5 eq.), and 1230 mg 1,3-bis(2,4,6-trimethyl-phenyl)propan-1,3-dione (4 mmol, 2.5 eq.) were reacted in 40 mL of 1,4-dioxane, 20 mL of butanone, and 40 mL of DMF according to the general procedure. The crude product was purified by flash chromatography (KG60, dichloromethane/iso-hexanes solvent mixture (1:1)) to yield a yellow powder (227 mg, 31 mmol, 19%). Mp: 239 °C. ^{1}H-NMR (300.13 MHz, CDCl$_3$): δ 7.82 (s, 1 H, NCHN); 7.75 (*pseudo*-t, d, d, $^3J_{PtH}$ = 23.8 Hz, $^3J_{HH}$ = 7.4 Hz, J_{HH} = 1.3 Hz, 1 H, C3H_{arom} of phenyl ring); 7.32–7.22 (m, 4 H, C3H_{arom}–C5H_{arom} of benzyl group and C6H_{arom} of phenyl ring); 7.22–7.15 (m, 2 H, C2H_{arom} and C6H_{arom} of benzyl group); 7.08 (td, $^3J_{HH}$ = 7.6 Hz, J_{HH} = 1.5 Hz, 1 H, C5H_{arom} of phenyl ring); 7.00 (t, $^3J_{HH}$ = 7.4 Hz, J_{HH} = 1.5 Hz, 1 H, C4H_{arom} of phenyl ring); 6.87 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.76 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 5.70 (s, 1 H, (CO)CH(CO)); 5.57 (s, 2 H, CH_2);

2.35 (s, 6 H, *o*-CH_3 of mesityl group); 2.30 (s, 3 H, *p*-CH_3 of mesityl group); 2.24 (s, 3 H, *p*-CH_3 of mesityl group); 2.18 (s, 6 H, *o*-CH_3 of mesityl group) ppm. ^{13}C-NMR (150.93 MHz, CDCl$_3$): δ 185.4 (CO); 184.7 (CO); 153.1 (NCN); 145.2 (C1$_{arom}$ of phenyl ring); 140.9 (NCHN); 139.3 (C1$_{arom}$ of mesityl group); 138.9 (C1$_{arom}$ of mesityl group); 137.8 (C4$_{arom}$ of mesityl group); 137.4 (C4$_{arom}$ of mesityl group); 135.2 (C1$_{arom}$ of benzyl group); 134.2 (C2$_{arom}$ and C6$_{arom}$ of mesityl group); 133.4 (C2$_{arom}$ and C6$_{arom}$ of mesityl group); 131.6 (C3H_{arom} of phenyl ring); 128.9 (C3H_{arom} and C5H_{arom} of benzyl group); 128.4 (C4H_{arom} of benzyl group); 128.2 (C3H_{arom} and C5H_{arom} of mesityl group); 127.9 (C3H_{arom} and C5H_{arom} of mesityl group); 127.8 (C2H_{arom} and C6H_{arom} of benzyl group); 125.4 (C4H_{arom} of phenyl ring); 124.2 (C5H_{arom} of phenyl ring); 121.2 (C2$_{arom}$ of phenyl ring); 111.7 (C6H_{arom} of phenyl ring); 107.2 ((CO)CH(CO)); 49.4 (CH$_2$); 21.1 (*p*-CH$_3$ of mesityl group); 21.0 (*p*-CH$_3$ of mesityl group); 19.9 (*o*-CH$_3$ of mesityl group); 19.3 (*o*-CH$_3$ of mesityl group) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3405.0 ppm. Anal. Calcd for C$_{36}$H$_{35}$N$_3$O$_2$Pt: C, 58.69; H, 4.79; N, 5.70. Found: C, 58.53; H, 4.78; N, 5.65.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ^{2}O,O′)(4-benzyl-1-(4-methoxyphenyl-κC^2)-1,2,4-triazol-5-ylidene-κC^5)platinum(II) 21

277 mg triazolium bromide **14** (0.8 mmol), 93 mg silver(I) oxide (0.4 mmol, 0.5 eq.), 299 mg dichloro(1,5-cyclooctadiene)-platinum(II) (0.8 mmol, 1 eq.), 359 mg potassium *tert*-butoxide (3.2 mmol, 4 eq.), and 987 mg 1,3-bis(2,4,6-trimethylphenyl)-propan-1,3-dione (3.2 mmol, 4 eq.) were reacted in 20 mL of 1,4-dioxane, 10 mL of butanone, and 20 mL of DMF according to the general procedure. The remaining solid was purified by flash chromatography (KG60, dichloromethane) and the crude product was washed with isohexanes, which in the following turned out to be hard to remove. The product was obtained as a white powder (88 mg, 0.12 mmol, 14%). Mp: 238 °C. ^{1}H-NMR (500.13 MHz, CDCl$_3$) δ 7.80 (s, 1 H, NCHN); 7.31 (d, J_{HH} = 2.6 Hz, 1 H, C3H_{arom} of phenyl ring); 7.27–7.25 (s, 3 H, C3H_{arom}–C5H_{arom} of benzyl ring); 7.22 (d, $^3J_{HH}$ = 8.5 Hz, 1 H, C6H_{arom} of phenyl ring); 7.18 (dd, $^3J_{HH}$ = 7.6 Hz, J_{HH} = 1.7 Hz, 1 H, C2H_{arom} and C6H_{arom} of benzyl group); 6.84 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.76 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.63 (dd, $^3J_{HH}$ = 8.5 Hz, J_{HH} = 2.7 Hz, 1 H, C5H_{arom} of phenyl ring); 5.69 (s, 1 H, (CO)CH(CO)); 5.55 (s, 2 H, CH_2 of benzyl group); 3.76 (s, 3 H, NCH_3); 2.34 (s, 6 H, *o*-CH_3 of mesityl group); 2.29 (s, 3 H, *p*-CH_3 of mesityl group); 2.24 (s, 3 H, *p*-CH_3 of mesityl group); 2.17 (s, 6 H, *o*-CH_3 of mesityl group) ppm. ^{13}C-NMR (125.77 MHz, CDCl$_3$) δ 185.2 (CO); 184.7 (CO); 157.1 (C4$_{arom}$ of phenyl ring); 151.3 (NCN); 140.6 (NCHN); 139.3 (C1$_{arom}$ of mesityl group); 139.0 (C1$_{arom}$ of phenyl ring); 138.8 (C1$_{arom}$ of mesityl group); 137.7 (C4$_{arom}$ of mesityl group); 137.4 (C4$_{arom}$ of mesityl group); 135.3 (C1$_{arom}$ of benzyl group); 134.1 (C2$_{arom}$ and C6$_{arom}$ of mesityl group); 133.4 (C2$_{arom}$ and C6$_{arom}$ of mesityl group); 128.9 (C3H_{arom} and C5H_{arom} of benzyl group); 128.3 (C4H_{arom} of benzyl group); 128.2 (C3H_{arom} and C5H_{arom} of mesityl group); 127.9 (C3H_{arom} and C5H_{arom} of

mesityl group); 127.7 ($C2H_{arom}$ and $C6H_{arom}$ of benzyl group); 123.1 ($C2_{arom}$ of phenyl ring); 117.6 ($C3_{arom}$ of phenyl ring); 112.3 ($C6_{arom}$ of phenyl ring); 108.2 ($C5_{arom}$ of phenyl ring); 107.3 ((CO)CH(CO)); 55.5 (OCH_3); 49.4 (CH_2); 21.1 (p-CH_3 of mesityl group); 21.0 (p-CH_3 of mesityl group); 20.0 (o-CH_3 of mesityl group); 19.3 (o-CH_3 of mesityl group) ppm. ^{195}Pt-NMR (64.33 MHz, CDCl$_3$) δ −3374.3 ppm. Anal. Calcd for $C_{37}H_{37}N_3O_3Pt \cdot 0.4\ C_6H_{14}$: C, 59.06; H, 5.36; N, 5.24. Found: C, 59.16; H, 5.21; N, 5.29.

Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ^{2}O,O′)(4-benzyl-1-(4-methylphenyl-κC^2)-1,2,4-triazol-5-ylidene-κC^5)platinum(II) 22

528 mg triazolium bromide **15** (1.6 mmol), 185 mg silver(I) oxide (0.8 mmol, 0.5 eq.), 599 mg dichloro(1,5-cyclooctadiene)-platinum(II) (1.6 mmol, 1 eq.), 359 mg potassium *tert*-butoxide (3.2 mmol, 2 eq.), and 987 mg 1,3-bis(2,4,6-trimethylphenyl)-propan-1,3-dione (3.2 mmol, 2 eq.) were reacted in 40 mL of 1,4-dioxane, 20 mL of butanone, and 40 mL of DMF according to the general procedure. The remaining solid was purified by flash chromatography (KG60, dichloromethane/isohexanes solvent mixture (1 : 1)) and the crude product was washed with isohexanes, which in the following turned out to be hard to remove. The product was obtained as a white powder (329 mg, 0.44 mmol, 27%). Mp: 241 °C. ^{1}H-NMR (600.16 MHz, CDCl$_3$) δ 7.80 (s, 1 H, NCHN); 7.53 (*pseudo*-t, $^3J_{PtH}$ = 22.5 Hz, 1 H, C3H_{arom} of phenyl ring); 7.30–7.23 (m, 3 H, C3H_{arom}–C5H_{arom} of benzyl group); 7.19 (d, $^3J_{HH}$ = 5.9 Hz, 2 H, C2H_{arom} and C6H_{arom} of benzyl group); 7.17 (d, J_{HH} = 4.5 Hz, 1 H, C6H_{arom} of phenyl ring); 6.88 (d, $^3J_{HH}$ = 7.1 Hz, 1 H, C5H_{arom} of phenyl ring); 6.87 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 6.75 (s, 2 H, C3H_{arom} and C5H_{arom} of mesityl group); 5.67 (s, 1 H, (CO)CH(CO)); 5.57 (s, 2 H, CH_2 of benzyl group); 2.36 (s, 6 H, o-CH_3 of mesityl group); 2.32 (s, 3 H, CH_3 of phenyl ring); 2.31 (s, 3 H, p-CH_3 of mesityl group); 2.25 (s, 3 H, p-CH_3 of mesityl group); 2.17 (s, 6 H, o-CH_3 of mesityl group) ppm. ^{13}C-NMR (150.93 MHz, CDCl$_3$) δ 185.2 (CO); 184.6 (CO); 152.3 (NCN); 142.9 ($C1_{arom}$ of phenyl ring); 140.8 (NCHN); 139.3 ($C1_{arom}$ of mesityl group); 139.0 ($C1_{arom}$ of mesityl group); 137.7 ($C4_{arom}$ of mesityl group); 137.3 ($C4_{arom}$ of mesityl group); 135.3 ($C1_{arom}$ of benzyl group); 135.1 ($C4_{arom}$ of phenyl ring); 134.3 ($C2_{arom}$ and $C6_{arom}$ of mesityl group); 133.4 ($C2_{arom}$ and $C6_{arom}$ of mesityl group); 132.2 ($C3H_{arom}$ of phenyl ring); 128.9 ($C3H_{arom}$ and $C6H_{arom}$ of benzyl group); 128.3 ($C4H_{arom}$ of benzyl group); 128.3 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 127.9 ($C3H_{arom}$ and $C5H_{arom}$ of mesityl group); 127.7 ($C2H_{arom}$ and $C6H_{arom}$ of benzyl group); 124.7 ($C5H_{arom}$ of phenyl ring); 120.8 ($C2_{arom}$ of phenyl ring); 111.5 ($C6H_{arom}$ of phenyl ring); 107.2 ((CO)CH(CO)); 49.4 (CH_2 of benzyl group); 22.6 (CH_3 of phenyl ring); 21.6 (p-CH_3 of mesityl group); 21.0 (p-CH_3 of mesityl group); 20.0 (o-CH_3 of mesityl group); 19.3 (o-CH_3 of mesityl group) ppm. ^{195}Pt-NMR (128.56 MHz, CDCl$_3$) δ −3384.7 ppm. Anal. Calcd for $C_{37}H_{37}N_3O_2Pt \cdot 0.7\ C_6H_{14}$: C, 61.01; H, 5.82; N, 5.18. Found: C, 61.11; H, 5.69; N, 5.25.

Computational details

All calculations were performed with the Gaussian09 package.[79] The gradient-corrected density functional BP86[80–82] was used together with the 6-31G(d)[83–87] basis set. No symmetry or internal coordinate constraints were applied during optimizations. All reported structures were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. In all cases, platinum was described by using a decontracted Hay-Wadt(n + 1) ECP and basis set.[88,89] Approximate free energies were obtained through chemical 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 free energies at standard conditions (T = 298 K, p = 1 atm), using unscaled frequencies. For visualization CYLview[90] was used.

Acknowledgements

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