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

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Neutral cyclometalated platinum(II) N-heterocyclic carbene complexes \([\text{Pt}(\text{C}^\text{C*})(\text{O}^\text{O})]\) with C\(^{\text{C*}}\) 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\(^{\text{O}}\) = acac) and 1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato (O\(^{\text{O}}\) = 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).\(^18\),\(^19\)–35 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.\(^18\) 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\(^{\text{C*}}\) ligands attract a lot of scientific interest. Especially those with the general structure \([\text{Pt}(\text{C}^\text{C*})(\text{O}^\text{O})]\) (O\(^{\text{O}}\) = \(\beta\)-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\(^{\text{C*}}\) cyclometalating ligands and \(\beta\)-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 \(\pi\)–\(\pi\) 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.\(^19\),\(^34\),\(^38\),\(^41\)–61

After the first report of a C\(^{\text{C*}}\) cyclometalated platinum(II) complex in 2006,\(^62\) C\(^{\text{C*}}\) cyclometalating ligands have also been used for the development of new phosphorescent platinum(II) emitters of the general structure \([\text{Pt}(\text{C}^\text{C*})(\text{O}^\text{O})]\) (O\(^{\text{O}}\) = \(\beta\)-diketonato).\(^63\)–68 This class of complexes reveals an extraordinary photoluminescent behavior, which strongly depends on the structure of the C\(^{\text{C*}}\) cyclometalating ligand (C: carbene carbon atom; C\(^{\text{C*}}\): cyclometalated carbon atom), as well as on the O\(^{\text{O}}\) chelating ligand. Recently, several promising \([\text{Pt}(\text{C}^\text{C*})(\text{O}^\text{O})]\) 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...
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* cyclo-metating 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.66 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 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(0) (Pt(COD)Cl2) 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 (KOTBu) in dimethylformamide (DMF).

Although this method was successful with imidazolium-based ligand precursors, the synthesis of platinum(0) 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 ESL†. The complexes 4 (Fig. 1 and 2) and 20 (Fig. 3 and 4) crystallize in the monoclinic space group P21/c and are devoid of any solvent molecules. X-ray diffraction analysis confirms a quasi-square planar coordination environment of the platinum(0) center with bond lengths of the

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**Scheme 1** Synthesis of the ligand precursors 2, 3 and complexes 4–6.

1. Methyl iodide/benzyl bromide, THF, 100–110 °C; (ii) Ag2O, 1,4-dioxane; (iii) Pt(COD)Cl2, 1,4-dioxane/butanone solvent mixture (2:1), 115 °C; (iv) β-diketone, KOtBu, DMF, room temperature to 100 °C.

**Scheme 2** Synthesis of the ligand precursors 10–15 and complexes 16–22.

7. Methyl iodide/benzyl bromide, THF, 100–110 °C; (ii) Ag2O, 1,4-dioxane; (iii) Pt(COD)Cl2, 1,4-dioxane/butanone solvent mixture (2:1), 115 °C; (iv) β-diketone, KOtBu, DMF, room temperature to 100 °C.

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**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(11) 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(11)–Pt(1)–C(1) 80.4(2), C(11)–Pt(1)–O(1) 91.7(2), C(1)–Pt(1)–O(2) 97.9(2), O(1)–Pt(1)–O(2) 90.2(2), C(11)–Pt(1)–O(2)–C(17) 176.6(6), O(2)–Pt(1)–C(1)–N(1) 176.6(6), O(1)–Pt(1)–O(2)–C(17) 176.6(6).
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 π–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 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(n) imidazol-2-ylidene complexes containing an acetylacetono 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...
mesacac ancillary ligand. In contrast to the vibronic structure essentially di
16 process. The well-structured emission band of calculations. However, complexes with a mesacac ligand also show significantly contributions of a ligand centered state (3LC) to the emission process of the complexes with mesacac ligands. This transition is supposed to be located between 471 and 478 nm. Therefore, another transition contributions of a ligand centered state (3LC) reveal 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.

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

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<tr>
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<th>λexc [nm]</th>
<th>CIE x</th>
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<td>5</td>
<td>345</td>
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<td>0.183; 0.287</td>
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<td>17</td>
<td>340</td>
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Excitation wavelength. CIE coordinates. Maximum emission wavelength. Quantum yield at λexc, N2 atmosphere. Decay lifetimes (excited by laser pulses (355 nm, 1 ns)) given as t0 = τ/Φ.

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

Fig. 7 Emission spectra of the neat complex films of 5–6 and 16–21 (rt).
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 sieves 4 Å. All other chemicals were used as purchased. 4-Phenyl-4H-1,2,4-triazole 1,74 1-phenyl-1H-1,2,4-triazole 7,75 1-(4-methoxyphenyl)-1H-1,2,4-triazole 8, 1-(4-methylphenyl)-1H-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 (1H: 7.26, 13C: 77.0 for CDCl3; 1H: 2.50, 13C: 39.43 for DMSO-d6).195Pt spectra were referenced to potassium tetrachloroplatinate(ii) in D2O (−1617.2 (PtCl4−), −2654.1 (PtCl3)) 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 Eurovector 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-4H-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. 1H-NMR (500.13 MHz, DMSO-d6): δ 10.98 (s, 1 H, NCHN); 9.79 (s, 1 H, NCHN); 7.86 (d, 3JHH = 7.2 Hz, 2 H, C2H2arom and C6H4arom of phenyl ring); 7.71 (t, 3JHH = 7.7 Hz, 2 H, C3H3arom and C5H3arom of phenyl ring); 7.65 (t, 3JHH = 7.4 Hz, 1 H, C4H4arom of phenyl ring); 7.55 (d, 3JHH = 7.7 Hz, 2 H, C2H2arom and C6H4arom of benzyl group); 7.30–7.36 (m, 3 H, C3H3arom–C5H3arom of benzyl group); 5.71 (s, 2 H, CH2) ppm. 13C-NMR (125.75 MHz, DMSO-d6): δ 143.4 (NCHN); 141.9 (NCHN); 133.0 (C1arom); 132.2 (C2arom); 130.5 (C4H4arom of phenyl ring); 130.2 (C3H3arom and C5H3arom of phenyl ring); 129.1 (C2H2arom and C6H4arom of benzyl group); 129.0 (C4H4arom of benzyl group); 128.8 (C3H3arom and C5H3arom of benzyl group); 122.6 (C2H2arom and C6H4arom of phenyl ring); 55.0 (CH2) ppm. Anal. Calcd for C15H14BrN3: 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-κ⁶O⁶O⁶)(1-benzyl-4-phenyl-k⁴C⁴)-[1,4-triazol-5-ylidine-k²C²] platinum(u) 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(u) (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/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. 1H-NMR (600.16 MHz, CDCl3) δ 8.25 (s, 1 H, NCHN); 7.74 (d, pseudo-t, 3JHH = 7.4 Hz, 3JPH = 20.9 Hz, 1 H, C3H3arom of phenyl ring); 7.09 (d, 3JHH = 7.6 Hz, 1 H, C6H4arom of phenyl ring); 7.06 (t, 3JHH = 7.5 Hz, 1 H, C5H3arom of phenyl ring); 7.01 (t, 3JHH = 7.4 Hz, 1 H, C4H4arom of phenyl ring); 6.87 (s, 2 H, C3H3arom and C5H3arom of mesityl group); 6.84 (s, 2 H, C2H2arom and C6H4arom of mesityl group); 5.72 (s, 1 H, (CO)CH(CO)); 4.11 (s, 3 H, NCH3); 2.35 (s, 6 H, o-CH3 of mesityl group); 2.32 (s, 6 H, o-CH3 of mesityl group); 2.29 (s, 3 H, p-CH3 of mesityl group) ppm. 13C-NMR (150.93 MHz, CDCl3) δ 185.4 (CO); 184.7 (CO); 152.5 (NCH3); 143.4 (C1arom of phenyl ring); 139.4 (C3arom of mesityl group); 137.8 (C4arom of mesityl group); 135.8 (NCH3); 134.2 (C2arom and C6arom of mesityl group); 133.7 (C7arom and C8arom of mesityl group); 132.9 (C9arom of phenyl ring); 128.2 (C3arom and C5arom of mesityl group); 128.1 (C3arom and C5arom of mesityl group); 125.5 (C4H4arom of phenyl ring); 124.1 (C3H3arom of phenyl ring); 123.9 (C2arom of phenyl ring); 110.8 (C6H4arom of phenyl ring); 107.2 ((CO)CH(CO)); 37.5 (NCH3); 21.1 (p-CH3 of mesityl group); 21.1 (p-CH3 of mesityl group); 19.9 (o-CH3 of mesityl group); 19.6 (o-CH3 of mesityl group) ppm. 195Pt-NMR (128.56 MHz, CDCl3) δ −3342.3 ppm. Anal Calcd for C39H31N3Pt0.7-O2 · 0.7 CH4; 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-κ⁶O⁶O⁶)(1-benzyl-4-phenyl-k⁴C⁴)-[1,4-triazol-5-ylidine-k²C²] platinum(u) 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(u) (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. 1H-NMR (500.13 MHz, CDCl3): δ 8.26 (s, 1 H, NCHN); 7.76 (d, pseudo-t, 3JHH = 7.7 Hz, 3JPH = 24.1 Hz, 1 H, C3H3arom of phenyl ring); 7.29 (dd, 4JHH = 7.7 Hz, 4JPH = 1.7 Hz, 2 H, C2H2arom and C6H4arom of benzyl group); 7.25–7.18 (m, 3 H, C3H3arom–C5H3arom of benzyl group); 7.08 (dt, 4JHH = 1.6 Hz, 4JPH = 7.7 Hz, 1 H, C4H4arom of phenyl ring); 7.06 (dt, 4JHH = 1.4 Hz, 4JPH = 7.2 Hz, 1 H, C6H4arom of phenyl ring); 7.01 (dt, 4JHH = 1.4 Hz, 4JPH = 7.2 Hz, 1 H, C4H4arom of phenyl ring); 6.87 (s, 2 H, C3H3arom and C5H3arom of mesityl group); 6.79 (s, 2 H, C3H3arom and C5H3arom of mesityl group); 5.73 (s, 1 H, (CO)CH(CO)); 5.67 (s, 2 H, CH2); 2.36 (s, 6 H,
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 (834 mg, 2.53 mmol, 84%). Mp: 162°C. 1 H-NMR (300.13 MHz, DMSO-d6) δ 10.96 (NCH; 9.51 (NCHN); 7.81 (d, JHH = 8.6 Hz, 2 H, C2H2arom and C6H5arom of phenyl ring); 7.56 (dd, JHH = 1.8 Hz, JH2H = 7.6 Hz, 2 H, C2H2arom and C6H5arom of benzyl group); 7.53–7.40 (m, 5 H, C3H4arom–C5H4arom of benzyl group, C7H4arom and C5H4arom of phenyl ring); 5.58 (s, 2 H, CH2); 2.41 (s, 3 H, C3H3) ppm. 13C-NMR (75.48 MHz, DMSO-d6) δ 144.9 (NCHN); 141.4 (NCHN); 140.5 (C4 of phenyl ring); 133.3 (C1 of benzyl group); 132.7 (C1 of phenyl ring); 130.4 (C2H2arom and C6H5arom of phenyl ring); 129.1 (C4H4arom of benzyl ring); 129.0 (C3H4arom and C5H4arom of benzyl group); 128.8 (C2H2arom and C6H5arom of benzyl group); 120.6 (C3H4arom and C5H4arom of phenyl group); 50.9 (CH3); 20.7 (CCH3) ppm. Anal. Calcd for C15H14BrN3: C, 58.20; H, 4.88; N, 12.77. Found: C, 58.45; H, 4.70; N, 12.86.

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. 1H-NMR (300.13 MHz, CDCl3) δ 10.90 (NCHN); 9.49 (NCHN); 7.84 (d, JHH = 9.0 Hz, 2 H, C2H2arom and C6H5arom of phenyl ring); 7.56 (d, JHH = 7.7 Hz, 2 H, C2H2arom and C6H5arom of phenyl ring); 7.51–7.42 (m, 3 H, C3H4arom–C5H4arom of benzyl group); 7.23 (d, JHH = 9.1 Hz, 2 H, C3H4arom and C5H4arom of phenyl ring); 5.57 (s, 2 H, CH2); 3.85 (s, 3 H, CH3) ppm. 13C-NMR (75.48 MHz, DMSO-d6) δ 160.5 (C4 of phenyl ring); 144.8 (NCHN); 141.0 (NCHN); 133.3 (C1 of benzyl group); 129.0 (C4H4arom of benzyl group); 128.8 (C2H2arom and C6H5arom of benzyl group); 128.1 (C1 of phenyl ring); 122.6 (C2H2arom and C6H5arom of phenyl ring); 115.1 (C3H4arom and C5H4arom of phenyl ring); 55.8 (CCH3); 50.8 (CH3) ppm. Anal. Calcd for C16H13BrN3O: 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. 1H-NMR (300.13 MHz, DMSO-d6) δ 10.96 (NCHN); 9.51 (NCHN); 7.81 (d, JHH = 8.6 Hz, 2 H, C2H2arom and C6H5arom of phenyl ring); 7.56 (dd, JHH = 1.8 Hz, JH2H = 7.6 Hz, 2 H, C2H2arom and C6H5arom of benzyl group); 7.53–7.40 (m, 5 H, C3H4arom–C5H4arom of benzyl group, C7H4arom and C5H4arom of phenyl ring); 5.58 (s, 2 H, CH2); 2.41 (s, 3 H, C3H3) ppm. 13C-NMR (75.48 MHz, DMSO-d6) δ 144.9 (NCHN); 141.4 (NCHN); 140.5 (C4 of phenyl ring); 133.3 (C1 of benzyl group); 132.7 (C1 of phenyl ring); 130.4 (C2H2arom and C6H5arom of phenyl ring); 129.1 (C4H4arom of benzyl ring); 129.0 (C3H4arom and C5H4arom of benzyl group); 128.8 (C2H2arom and C6H5arom of benzyl group); 120.6 (C3H4arom and C5H4arom of phenyl group); 50.9 (CH3); 20.7 (CCH3) ppm. Anal. Calcd for C15H14BrN3: 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-k2O)(4-benzyl-1-phenyl-kC32-1,2,4-triazol-5-ylidene-kC5)platinum(ii) 16

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.), 718 mg potassium tert-butylate (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. 1H-NMR (300.13 MHz, CDCl3) δ 7.83 (pseudot-d, JHH = 27.4 Hz, JHH = 5.4 Hz, 1 H, C3H4arom of phenyl ring); 7.78 (s, 1 H, NCHN); 7.47 (d, JHH = 7.3 Hz, 2 H, C2H2arom and C6H5arom of benzyl group); 7.43–7.32 (m, 3 H, C3H4arom–C5H4arom of benzyl group) 7.30–7.25 (m, 1 H, C6H6arom of phenyl ring); 7.12–7.05 (m, 2 H, C4H4arom and C5H4arom of phenyl ring); 5.74 (s, 2 H, CH2); 5.54 (s, 1 H, (CO)CH(CO)); 2.10 (s, 3 H, CH2); 1.90 (s, 3 H, CH2) ppm. 13C-NMR (75.48 MHz, CDCl3) δ 185.2 (CO); 185.1 (CO); 153.1 (NCHN); 145.2 (C1 of phenyl ring); 140.6 (NCHN);
135.4 (C\textsubscript{1} of benzyl group); 131.2 (C\textsubscript{3} of phenyl ring); 129.4 (C\textsubscript{3} of benzyl and C\textsubscript{5} of benzyl group); 128.8 (C\textsubscript{4} of benzyl group); 128.2 (C\textsubscript{2} of benzyl and C\textsubscript{6} of benzyl group); 125.3 (C\textsubscript{4} of phenyl ring); 124.0 (C\textsubscript{4} of benzyl and C\textsubscript{5} of benzyl group); 121.6 (C\textsubscript{1} of phenyl ring); 111.6 (C\textsubscript{6} of phenyl ring); 102.2 ((CO)CH(CO)); 49.5 (CH\textsubscript{2}); 28.1 (CH\textsubscript{2}); 27.9 (CH\textsubscript{3}) ppm. \textsuperscript{195}Pt-NMR (64.33 MHz, CDCl\textsubscript{3}) δ -3450.2 ppm. Anal. Calcd for C\textsubscript{20}H\textsubscript{19}N\textsubscript{3}O\textsubscript{2}Pt: C, 56.15; H, 5.36; N, 5.95. Found: C, 55.62; H, 5.40; N, 5.82.

**Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ\textsuperscript{2}O\textsubscript{2}O\textsubscript{2})(1-phenyl-κ\textsuperscript{3}C\textsubscript{4}-4-methyl-1,2,4-triazol-5-ylidene-κ\textsuperscript{5})platinum(II)**

Method A: 459 mg triazolium iodide \textbf{10} (1.6 mmol), 185 mg silver(i) oxide (0.8 mmol, 0.5 eq.), 898 mg dichloro(1,5-cyclooctadiene)platinum(ii) (1.4 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 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, 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\textsubscript{20}H\textsubscript{19}N\textsubscript{3}O\textsubscript{2}Pt·0.35 C\textsubscript{6}H\textsubscript{14}: C, 58.61; H, 5.24; N, 6.08. Found: C, 58.62; H, 5.40; N, 5.82.

**Synthesis of (1,3-bis(2,4,6-trimethylphenyl)propan-1,3-dionato-κ\textsuperscript{2}O\textsubscript{2}O\textsubscript{2})(1-(4-methoxyphenyl-κ\textsuperscript{2}C\textsubscript{3})-4-methyl-1,2,4-triazol-5-ylidene-κ\textsuperscript{5})platinum(II)**

509 mg triazolium iodide \textbf{11} (1.6 mmol), 185 mg silver(i) oxide (0.8 mmol, 0.5 eq.), 599 mg dichloro(1,5-cyclooctadiene)platinum(ii) (1.4 mmol, 1 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 washed with isohexanes to yield a white powder (188 mg, 0.27 mmol, 17%).

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num (n) (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. 1H-NMR (600.16 MHz, CDCl3) δ 7.81 (s, 1 H, NCHN); 7.49 (pseudo-τ, 3JHH = 24.0 Hz, 1 H, C3H40m of phenyl ring); 7.15 (d, 3JHH = 7.8 Hz, 1 H, C6H40m of phenyl ring); 6.86 (s, 3 H, C3H40m and C5H40m of mesityl ring, and C5H40m of phenyl ring); 6.82 (s, 2 H, C3H40m and C5H40m of mesityl group); 5.87 (s, 1 H, (CO)CH(CO)); 3.92 (s, 3 H, NCH3); 2.35 (s, 6 H, o-CH3 of mesityl group); 2.24 (s, 3 H, p-CH3 of mesityl group); 2.18 (s, 6 H, o-CH3 of mesityl group) ppm. 13C-NMR (150.93 MHz, CDCl3) δ 185.4 (CO); 184.7 (CO); 153.1 (NCH); 145.2 (C1arom of phenyl ring); 140.9 [NCHN]; 139.3 (C1arom of mesityl group); 138.9 [C1arom of mesityl group]; 137.8 (C4arom of mesityl group); 137.4 (C4arom of mesityl group); 135.2 (C1arom of benzyl group); 134.2 (C2arom and C6arom of mesityl group); 133.4 (C2arom and C6arom of mesityl group); 131.6 (C6H40m of phenyl ring); 128.9 (C3H40m and C5H40m of benzyl group); 128.4 (C3H40m of benzyl group); 128.2 (C3H40m and C5H40m of mesityl group); 127.9 (C3H40m and C5H40m of mesityl group); 127.8 (C2H40m and C6H40m of benzyl group); 125.4 (C4H40m of phenyl ring); 124.2 (C5H40m of phenyl ring); 121.2 (C2arom of phenyl ring); 111.7 (C6H40m of phenyl ring); 107.2 ((CO)CH(CO)); 49.4 (CH3); 21.1 (p-CH3 of mesityl group); 21.0 (p-CH3 of mesityl group); 19.9 (o-CH3 of mesityl group); 19.3 (o-CH3 of mesityl group) ppm. 195Pt-NMR (64.33 MHz, CDCl3) δ −3405.0 ppm. Anal. Calcd for C36H35N3O2Pt: 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-diono-κ5O,O')(4-benzyl-1-(4-methoxyphenyl)-κ2)-2,4-triazol-5-ylidene-κ5)platinum(n) 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(n) (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. 1H-NMR (500.13 MHz, CDCl3) δ 7.80 (s, 1 H, NCHN); 7.31 (d, δJHH = 2.6 Hz, 1 H, C3H40m of phenyl ring); 7.27–7.25 (s, 3 H, C3H40m–C5H40m of benzyl ring); 7.22 (d, δJHH = 8.5 Hz, 1 H, C6H40m of phenyl ring); 7.18 (dd, 3JHH = 7.6 Hz, JHH = 1.7 Hz, 1 H, C2H40m and C6H40m of benzyl group); 6.84 (d, 2 H, C3H40m and C5H40m of mesityl group); 6.76 (s, 2 H, C3H40m and C5H40m of mesityl group); 6.63 (dd, δJHH = 8.5 Hz, JHH = 2.7 Hz, 1 H, C5H40m of phenyl ring); 5.69 (s, 1 H, (CO)CH(CO)); 5.55 (s, 2 H, CH3 of benzyl group); 3.76 (s, 3 H, NCH3); 2.34 (s, 6 H, o-CH3 of mesityl group); 2.29 (s, 3 H, p-CH3 of mesityl group); 2.24 (s, 3 H, p-CH3 of mesityl group); 2.17 (s, 6 H, o-CH3 of mesityl group) ppm. 11C-NMR (125.77 MHz, CDCl3) δ 185.2 (CO); 184.7 (CO); 157.1 (C4arom of phenyl ring); 151.3 (NCH); 140.6 (NCHN); 139.3 (C1arom of mesityl group); 139.0 (C1arom of phenyl ring); 138.8 (C4arom of mesityl group); 137.7 (C4arom of mesityl group); 137.4 (C4arom of mesityl group); 135.3 (C1arom of benzyl group); 134.1 (C2arom and C6arom of mesityl group); 128.9 (C3H40m and C5H40m of benzyl group); 128.3 (C4H40m of benzyl group); 128.2 (C3H40m and C5H40m of mesityl group); 127.9 (C3H40m and C5H40m of mesityl group).
mesityl group); 127.7 (C2H arom and C6H arom of benzyl group); 123.1 (C2 arom of phenyl ring); 117.6 (C3H arom of phenyl ring); 112.3 (C6H arom of phenyl ring); 108.2 (C7H arom of phenyl ring); 107.3 ((CO)CH(CO)); 55.5 (OCH3); 49.4 (CH2); 21.1 (p-CH3 of mesityl group); 21.0 (p-CH3 of mesityl group); 20.0 (o-CH3 of mesityl group); 19.3 (o-CH3 of mesityl group) ppm. 195Pt-NMR (64.33 MHz, CDCl3) δ = -3374.3 ppm. Anal. Calcd for C37H37N3O3Pt · 0.4 C6H14: 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-kO,0)[4-benzyl(1-methylphenyl-kC2)-2,4-triazol-5-ylidene-kC5]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: 214 °C. 1H-NMR (600.16 MHz, CDCl3) δ 7.80 (s, 1 H, NCHN); 7.53 (pseudo-t, JPH = 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, JHH = 5.9 Hz, 2 H, C2H arom and C6H arom of benzyl group); 7.17 (d, JHH = 4.5 Hz, 1 H, C6H arom of phenyl ring); 6.88 (d, JHH = 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, C2H arom and C5H arom of mesityl group); 5.67 (s, 1 H, CH3 of benzyl group); 5.67 (s, 1 H, CO(CH3)); 5.57 (s, 2 H, CH2 of benzyl group); 2.26 (s, 6 H, o-CH3 of mesityl group); 2.23 (s, 2 H, CH2 of phenyl ring); 2.21 (s, 3 H, p-CH3 of mesityl group); 2.25 (s, 3 H, p-CH3 of mesityl group); 2.17 (s, 6 H, o-CH3 of mesityl group) ppm. 13C-NMR (159.93 MHz, CDCl3) δ 185.2 (CO); 184.6 (CO); 152.3 (NCN); 142.9 (CI arom of phenyl ring); 140.8 (NCHN); 139.3 (CI arom of mesityl group); 139.0 (CI arom of mesityl group); 137.7 (CI arom of mesityl group); 137.3 (CI arom of mesityl group); 135.3 (CI arom of benzyl group); 135.1 (CI arom of phenyl ring); 134.3 (CI arom and C6 arom of mesityl group); 133.4 (C2 arom and C6 arom of mesityl group); 132.2 (C6H 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 C6H arom of mesityl group); 127.7 (C2H arom and C6H arom of benzyl group); 124.7 (C5H arom of phenyl ring); 120.2 (C2 arom of phenyl ring); 111.5 (C6H arom of benzyl group); 107.2 ((CO)CH(CO)); 49.4 (CH2 of benzyl group); 22.6 (CH2 of phenyl ring); 21.6 (p-CH3 of mesityl group); 21.0 (p-CH3 of mesityl group); 20.0 (o-CH3 of mesityl group); 19.3 (o-CH3 of mesityl group) ppm. 195Pt-NMR (128.56 MHz, CDCl3) δ = -3384.7 ppm. Anal. Calcd for C17H27N3O2Pt · 0.7 C6H14: 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 BP8680 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 CYLview80 was used.

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Notes and references


