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Phosphorescent Platinum(II) Complexes Based on C^C* Cyclometalating Aryltriazol-5-ylidenes

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Supporting Information

ABSTRACT: Two series of heteroleptic platinum(II) carbene compexes of the type $[Pt(C^C^*)(O^O)]$ (O^O = acetylacetonate) with C^C* cyclometalated 4-phenyl-1,2,4-triazol-5-ylidene as well as 1phenyl-1,2,4-triazol-5-ylidene ligands were prepared. The effect of various substituents in the 4-position of the phenyl ring (4phenyltriazole: H, Cl, OCH₃, NO₂; 1-phenyltriazole: H, Cl, OCH₃, CH₃) was studied. The ligand precursors were obtained by quaternization of the corresponding aryl-1,2,4-triazoles with iodomethane. The complexes were synthesized by a reaction sequence starting from the triazolium precursors via the silver(I) carbenes, transmetalation with dichloro(1,5-cyclooctadiene)platinum(II), cyclo-



metalation reaction, and finally addition of acetylacetonate. All complexes have been characterized by standard techniques such as ¹H NMR, ¹³C NMR, and elemental analysis. Additionally, solid-state structures of seven complexes could be obtained by singlecrystal X-ray diffraction. According to absorption and emission spectra, the complexes reveal interesting photophysical properties with strong emissions in the blue region of the visible spectrum at room temperature, which are sensitive to the donor and acceptor properties of the substituents at the cyclometalating ligand.

INTRODUCTION

Cyclometalated platinum(II) complexes attract a lot of interest due to their extraordinary photoluminescence properties and potential applications as photocatalysts,¹ chemical sensors,² and chromophors in organic light-emitting diodes (OLEDs).³ The platinum(II) ion induces spin-orbit coupling (SOC) leading to triplet harvesting and allows electroluminescence quantum yields of up to 100%, four times larger than those of common fluorescent chromophores, which are limited to 25%.⁴ Furthermore, cyclometalation with aromatic systems affords strong metal-ligand bonding, which increases the metalcentered d-d energy gap and prevents population of the d-d excited state, often responsible for radiationless desactivation. In the last years the luminescence properties of heteroleptic C^N cyclometalated complexes with the general formula $[Pt(C^N)(O^O)]$ have been studied,⁵ and some of these promising emitter molecules were used in OLEDs.^{5a,g,m,p,x,aa} Ancillary O^O ligands derived from β -diketones coordinated to the platinum center ensure solubility, stability, and high quantum efficiency of the complexes.^{5k}

However, irrespective of the multitude of new highly efficient platinum(II) emitters containing C^N chelates, the development of blue-light-emitting phosphors with long-term stability remains a real challenge. In this context, C^C^* cyclometalated ligands based on N-heterocyclic carbenes (NHCs) may remedy the deficiencies. The carbene increases the ligand field of the cyclometalated complexes, which is associated with short metal–carbene carbon atom bond lengths. Consequently, the

stability of $[Pt(C^C^*)(O^O)]$ complexes might be improved in order to achieve longer lifetimes in lighting devices. The strong ligand field also supports high-energy emissions due to an increase of the LUMO energy level and raises the d–d level of the excited state to effectively suppress thermal quenching.⁶

Although not many examples of platinum(II) complexes of the general structure $[Pt(C^{C*})(O^{O})]$ have been published yet, most complexes (with the exception of one complex containing a trifluoromethyl-acetylacetonato ligand⁷) showed interesting photophysical properties. The known compounds of this class are based on different 1-arylimidazol-2-ylidene ligands.⁸ The first example was based on the 1-(4cyanophenyl)imidazol-2-ylidene and revealed strong phosphorescence in the deep-blue region at room temperature.^{8a} Substitution at the phenyl ring and extension of the π -system alter the emission wavelength and may significantly increase the phosphorescence quantum yields (PQYs).^{8b-d} Modification of the NHC moiety may offer another approach to improve the photophysical properties and stability. We describe the synthesis and characterization of a series of blue-phosphorescent $[Pt(C^C^*)(O^O)]$ complexes containing C^C^* cyclometalating 1-aryl-1,2,4-triazol-5-ylidenes as well as 4-aryl-1,2,4triazol-5-ylidenes and their photophysical properties.

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RESULTS AND DISCUSSION

Synthesis and Characterization. The synthetic route to all platinum(II) complexes described here starts with the preparation of the corresponding aryl-substituted triazoles. Depending on the orientation of the triazol-5-ylidene unit in the final complexes, synthesis of either a 4-aryl-4H-1,2,4-triazole (1–4) (Scheme 1) or a 1-aryl-1H-1,2,4-triazole (13–16)

Scheme 1. Formation of Cyclometalated Complexes $9-12^{a}$



^{*a*}(i) CH₃I, THF, 100–110 °C; (ii) Ag₂O, 1,4-dioxane; (iii) Pt(COD)Cl₂, 1,4-dioxane/butanone solvent mixture, 115 °C; (iv) Hacac, KO^tBu, DMF, room temperature to 100 °C.

Scheme 2. Formation of Cyclometalated Complexes 21–24^a



^{*a*}(i) CH₃I, THF, 100–110 °C; (ii) Ag₂O, 1,4-dioxane; (iii) Pt(COD)Cl₂, 1,4-dioxane/butanone solvent mixture, 115 °C; (iv) Hacac, KO^tBu, DMF, room temperature to 100 °C.

(Scheme 2) is required at the beginning of the synthetic route. The 4-aryl triazoles 1-4 have been synthesized by reaction of 4-substituted anilines with diformyl hydrazine according to a literature procedure,⁹ and the 1-aryl triazoles 13–16 have been prepared by a well-established Ullmann reaction protocol¹⁰ from 1H-1,2,4-triazole and aryl halides functionalized in the 4position. Quaternization with methyl iodide then leads to the 1,2,4-triazolium salts 5-8 (Scheme 1) and 17-20 (Scheme 2) in high yields. The platinum(II) complexes 9-12 and 21-24 have been synthesized according to a modified procedure, originally developed for the preparation of the analogous imidazolylidene complexes.^{8b} A silver(I) carbene complex, formed by reaction with silver(I) oxide, is transmetalated with dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl₂) followed by cyclometalation at the C2 carbon atom of the phenyl ring. Addition of acetylacetone together with potassium tertbutoxide then yielded the complexes, which were purified by column chromatography. The complexes were fully characterized by ¹H NMR and ¹³C NMR spectroscopy as well as elemental analysis.

The NMR spectra reveal one set of signals with chemical shifts characteristic for both the cyclometalating ligand and the acetylacetonate spectator ligand. The absence of a proton signal above 9 ppm indicates deprotonation on the C2 carbon atom of the triazole and thus formation of the carbene. Cyclometalation of the phenyl ring to platinum is confirmed by a Pt–H coupling constant observed for the proton at the C3 carbon atom of the phenyl ring. Additionally, ¹⁹⁵Pt NMR spectra measured for **10–12** and **21–24** exhibit signals in the range -3447.9 to -3358.7 ppm, which are characteristic for [Pt(C^C*)(O^O)]-type complexes.^{8c}

Details of the Molecular Structure Determination. Single crystals of 9 suitable for X-ray diffraction could be obtained by slow diffusion of diethyl ether into a highly concentrated solution of the complex in dichloromethane. Those of 10–12, 21, 23, and 24 were obtained by slow solvent evaporation from their saturated solution in dichloromethane. Selected bond lengths, angles, and intermolecular Pt–Pt distances are given in Table 1. All compounds (with the exception of 11) crystallize in the monoclinic space group $P2_1/c$. Their asymmetric units contain only one molecule and are devoid of solvent molecules. Compound 11 crystallizes in the triclinic space group $P\overline{1}$, and the asymmetric unit contains two molecules. The overall structure is similarly arranged when

Table 1. Selected Bond Lengths (Å), Bond Angles (deg), and Dihedral Angles (deg), as well as Intermolecular Pt–Pt Distances (Å) of Complexes 9–12, 21, 23, and 24

	9	10	11	12	21	23	24
Pt-C1	1.928(6)	1.932(8)	1.901(10)	1.932(5)	1.930(4)	1.937(5)	1.933(5)
Pt-C5	1.994(5)	1.987(7)	1.999(10)	1.983(4)	1.996(4)	1.995(5)	1.993(5)
Pt-O1	2.068(4)	2.084(4)	2.086(6)	2.066(3)	2.082(3)	2.071(4)	2.075(3)
Pt-O2	2.032(4)	2.042(5)	2.028(7)	2.044(3)	2.039(2)	2.045(4)	2.057(3)
C1-Pt1-C5	80.1(2)	80.0(3)	80.0(4)	80.43(19)	80.33(15)	79.9(2)	79.82(19)
C1-Pt1-O1	96.6(2)	96.8(2)	97.9(3)	96.45(17)	97.24(14)	96.29(19)	96.20(17)
C5-Pt1-O2	92.6(2)	92.6(2)	91.7(4)	92.44(16)	91.41(12)	92.82(18)	93.33(15)
O1-Pt1-O2	90.59(16)	90.58(19)	90.4(3)	90.65(13)	90.90(10)	90.94(14)	90.70(12)
C11-C12-C13	127.3(7)	127.7(7)	126.8(10)	127.2(5)	127.2(4)	127.3(5)	127.4(5)
C1-N1-C4-C5	1.3(7)	0.1(8)	-2.6(12)	1.8(5)	0.5(4)	1.9(6)	0.8(6)
O2-Pt1-O1-C11	5.9(5)	0.0(6)	0.8(8)	-5.8(4)	8.8(3)	2.8(4)	-0.1(4)
Pt-Pt ^a	3.386	3.707	3.190	3.592	3.352	5.072	3.937

^aIntermolecular Pt-Pt distances.







Figure 2. Molecular structure of complexes 21 and 23, and 24. Thermal ellipsoids are drawn at the 50% probability level.

compared to the previously reported imidazolylidene complexes. $^{8b,11}_{\mbox{ }}$

The molecular structures of 9–12 (Figure 1), 21, 23, and 24 (Figure 2) are planar with a platinum center that is coordinated by one cyclometalated aryltriazolylidene ligand on one side and one acetylacetonato ligand on the other side. The square-planar coordination environment of the metal atom reveals deviations from 90°, observed for the C1-Pt1-C5, C1-Pt1-O1, and C5-Pt1-O2 angles. The smallest values have been observed for the C1-Pt1-C5 angle of the cyclometalated ring $(79.82(19)-80.43(19)^\circ)$. This distortion is similar to those found for related (C[^]C^{*})Pt-type complexes^{7,8b,11} and causes a widening of the C1-Pt1-O1 and C5-Pt1-O2 angles. However, the almost ideal value is preserved for the O1-Pt1-O2 angle $(90.4(3)-90.94(14)^\circ)$ due to the widening of the acetylacetonate moiety, as shown for C11-C12-C13. The Pt1-C1 bond lengths lie in a characteristic range also found in other platinum(II) NHC complexes.¹² The strong trans influence of the phenyl C2 carbon atom leads to an elongation of the Pt1-O1 bond lengths in comparison to the Pt1-O2 bond lengths opposite the carbone carbon donor atom. In the solid state the planar complexes are arranged in molecular stacks so that short Pt-Pt contacts can be formed. Crystal packing diagrams (Figures S1-S7) as well as details of the structure determination and the software¹³ used can be found in the SI. The Pt-Pt distances of all complexes (with the exception of complex 23) are about twice the van der Waals radius of platinum (Table 1). In the solid-state structure of 23 the complexes are shifted in the plane, which significantly increases the Pt-Pt distance (Figure S6).

Photoluminescence Measurements. The absorption spectra of the poly(methyl methacrylate) (PMMA) films of 9-11 and 21-24 are shown in Figure 3. All spectra reveal weak



Figure 3. UV-vis absorption spectra of complexes 9–11 and 21–24 (2% in PMMA).

absorptions of the complexes in the range between 220 and 340 nm. Complex **12** did not show a significant emission and was therefore not included in Figure 4. All other complexes emit in the blue or blue-green region of the visible spectrum with maxima at wavelengths between 420 and 493 nm. Lifetimes of the excited states in the microsecond range and large Stokes shifts identify the complexes as phosphorescent emitters.

The emission spectra given in Figures 4 and 5 exhibit different line shapes due to the normalization, and the quantum yields of complexes 9-11 are significantly lower compared to complexes 21-24. They all possess a vibronic-like progression

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Figure 4. Normalized emission spectra of complexes 9-11, 2% in PMMA (excitation wavelengths: 330 nm (9), 325 nm (10), 340 nm (11)).



Figure 5. Normalized emission spectra of complexes 21-24, 2% in PMMA (excitation wavelengths: 335 nm (21), 325 nm (22), 330 nm (23, 24)).

of ca. 1100 to 1500 cm⁻¹ (Figures 4 and 5). This is a common feature for phosphorescent platinum(II) complexes where the emission process involves an intraligand (³IL) charge transfer transition and suggests a strong participation of the C[^]C* cyclometalating ligand in the emission process.^{5g,k,l,u,14}

As shown in Figures 4 and 5 the C^{\land}C^{*} cyclometalated ligand significantly influences the emission process. Therefore modifications of this ligand show an effect on the emission as seen for complexes 10, 11, and 22–24. Substitution at the 4-position of the phenyl unit shifts the emission slightly to lower energies and therefore allows a fine-tuning of the emission wavelength. The electron-donating methoxy group causes the largest shifts (11: 14 nm; 23: 15 nm).

The structural effects on the phosphorescence quantum yield are more pronounced (Table 3). For the 1-aryl triazole complexes 22-24 quantum yields of up to 40% could be observed, while the PQY of the corresponding 4-aryl triazole complexes is found to be only 11–14%. Also the substituent effects on the 4-aryl triazoles is negligible, as can be seen from the barely enhanced PQYs of 10 and 11. The 4-aryl triazole complexes 9–11 reveal quantum yields in a range comparable to those of the corresponding imidazole complexes reported previously.^{8b} However, remarkably higher quantum efficiencies have been detected for 21–24. With a PQY of 41%, the chlorosubstituted 1-aryl triazole complex 22 represents the most efficient emitter of these examples.

Moreover, the additional nitrogen atom in the carbene unit leads to shorter decay times of the excited state (11: 18 μ s; 23:

Table 3. Photoluminescence Data for Complexes 9-11 and 21-24 (2% in PMMA)

	$\lambda_{ m exc} \ [m nm]^a$	CIE $x; y^b$	$\lambda_{ m em} \ [m nm]^c$	Φ^d	$ au_0 \ [\mu s]^e$
9	330	0.169; 0.194	405, 431, 456	0.11	15
10	325	0.192; 0.272	411, 436, 465, 493	0.12	9
11	340	0.174; 0.200	421, 445, 468	0.14	18
21	335	0.166; 0.180	428, 455, 483	0.30	13
22	325	0.193; 0.261	432, 459, 488	0.41	11
23	330	0.169; 0.227	470	0.38	16
24	330	0.165; 0.201	435, 462, 489	0.38	14
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^{*a*}Excitation wavelength. ^{*b*}CIE coordinates at rt. ^{*c*}Max. emission wavelength. ^{*d*}Quantum yield at λ_{exc} , N₂ atmosphere. ^{*e*}Decay lifetimes (excited by laser pulses (355 nm, 1 ns)) given as $\tau_{o} = \tau_{v}/\phi$.

16 μ s; 24: 14 μ s), when compared to the corresponding imidazole complexes (24–25 μ s).

The complexes are also strongly emissive in neat films, as shown for 9, 21-22, and 24 (Figure 6, Table 4). For 10, 11,



Figure 6. Emission spectra of complexes 9, 21, 22, and 24 (neat films).

Table 4. Photoluminescence Data for Complexes 9, 21, 22, and 24 (Neat Films)

	$\lambda_{ m exc} [m nm]^a$	CIE $x; y^b$	$\lambda_{\rm em} \; [{\rm nm}]^c$	Φ^d	$ au_0 \ [\mu s]^e$
9	330	0.151; 0.290	487	0.45	2
21	355	0.178; 0.395	499	0.39	2
22	330	0.495; 0.487	584	0.23	4
24	330	0.404; 0.529	551	0.23	4
^a Excitati	ion waveleng	gth. ^b CIE coor	dinates at rt	. <i>°</i> Max.	emission
wavelen	gth. ^d Quantu	m yield at λ_{exc} , 1	N ₂ atmosphere	e. ^e Decay	v lifetimes
(excited	by laser puls	es (355 nm, 1 r	ns)) given as 1	$\tau_{a} = \tau_{u}/dt$	

and 23 we were not able to measure neat amorphous emitter films, as these films rapidly crystallize during preparation. In contrast to the emission spectra measured from PMMA, neat films of complexes 9, 21-22, and 24 emit at higher wavelengths with only one maximum. To shed light on the origin of the emissions in neat film and the additional lowenergy emission in the spectrum of 10 (Figure 4), the emission spectra of 9, 10, 21, and 23 in PMMA films at different concentrations from 0.5 to 4 wt % were measured (Figures S8-S11). At least for compounds 9 and 10 at higher concentrations the emission is shifted toward longer wavelengths. The lowenergy emission observed for 9 in the neat film corresponds nicely to the new maximum found already in the 4 wt % PMMA film (Figure S8). The low-energy emission of 10 in 2 wt % PMMA (493 nm, Figure 4) becomes more pronounced in the 4 wt % PMMA film, and we expect that a neat film of 10 would show a similar emission around 503 nm. Additionally it is already known that platinum(II) complexes tend to form aggregated species, which emit at lower energies compared to the monomers.^{5a,15} Especially the phenyl triazole complexes **9** and **21** are strongly emissive in neat film with quantum yields of 45% and 39%, respectively. In contrast to **21**, complexes **22** and **24** emit with lower PQYs of 23%. The significant red-shift and the broadened line shape of the emissions suggest that the emission process in neat film reflects a broad density of states for the emitter molecules.

CONCLUSION

We were able to synthesize and fully characterize new C^C* cyclometalated platinum(II) complexes with aryl triazole ligands. The 4-aryl-1,2,4-triazol-5-ylidenes 9-11 and 1-aryl-1,2,4-triazol-5-ylidenes 21-24 are emissive at room temperature (measured in PMMA) with emission wavelengths in the blue and blue-green region of the visible spectrum. The emission data reveal that cyclometalated 1-aryl-1,2,4-triazol-5-ylidenes lead to significantly higher quantum yields. Compared to the respective 4-aryl-1,2,4-triazol-5-ylidenes, substitution at the phenyl ring leads to a red-shifted emission. X-ray diffraction analysis of seven compounds confirms the planar structure of the platinum(II) complexes, leading to molecular stacking in the solid state.

EXPERIMENTAL SECTION

General Experimental Methods. Dimethylformamide (DMF) and 1,4-dioxane were dried according to standard methods and stored over 4 Å molecular sieves under an argon atmosphere. Dichloro(1,5-cyclooctadiene)platinum(II), 4-aryl-4H-1,2,4-triazoles 1¹⁶ and 2–4,¹⁷ and 1-phenyl-1H-1,2,4-triazole 13¹⁸ were synthesized according to literature procedures.^{8b,9,10} Potassium tetrachloroplatinate(II) was purchased from Pressure Chemicals Co. and was used as received. Other chemicals were obtained from common suppliers and were used without further purification. ¹H NMR, ¹³C NMR, and ¹⁹⁵Pt NMR spectra were referenced internally using the resonances of the solvent (¹H: 7.26, ¹³C: 77.0 for CDCl₃; ¹H: 2.50, ¹³C: 39.43 for DMSO-*d*₆). ¹⁹⁵Pt NMR spectra were referenced externally using potassium tetrachloroplatinate(II) in D₂O (-1617.2 (PtCl₄²⁻), -2654.1 (PtCl₂)). Shifts are given in ppm; coupling constants *J* in Hz.

Elemental analyses were performed by the analytical laboratory of the department using a Eurovektor Hekatech EA-3000 elemental analyzer. Melting points are not corrected. Photoluminescence measurements have been performed in thin PMMA films doped with 0.5 wt %, 2 wt %, and 4 wt % of the emitter or from neat emitter films. The films were prepared by doctor blading a solution of emitter in a 10 wt % PMMA solution in dichloromethane on a substrate with a 60 μ m doctor blade. The film was dried, and the emission was measured under nitrogen. The excitation was carried out at a wavelength of 325–340 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 the multichannel scaling technique.

General Procedure A. According to a modified literature procedure, ¹⁰ a dry and argon-flushed Schlenk tube was charged with Cu_2O , 1,10-phenanthroline, triazole, and K_2CO_3 . The reactants were dried *in vacuo* at room temperature before the Schlenk tube was refilled with argon. Dry DMF was added, followed by the respective aryl halide. The mixture was stirred for 48 h at 120 °C under a positive pressure of argon. The reaction mixture was cooled to room temperature before 20 mL of dichloromethane was added. The suspension was filtered through a plug of Celite and rinsed with

dichloromethane. The organic layer was washed with water and brine and dried over Na_2SO_4 . The solvent was removed under reduced pressure, and the crude product was purified by flash column chromatography or recrystallization.

General Procedure B. In a pressure tube iodomethane was added to a solution of the respective triazole in THF. The mixture was stirred at 100–110 °C for 17–22 h. After cooling to ambient temperature, the precipitate was filtered, washed with THF, and dried *in vacuo*.

General Procedure C. A dry Schlenk tube was charged with triazolium iodide and silver(I) oxide. The reactants were dried *in vacuo*, and the Schlenk tube was refilled with argon. After addition of 20 mL of 1,4-dioxane the mixture was stirred at room temperature in the dark for 21 h under a positive pressure of argon. Afterward, dichloro(1,5-cyclooctadiene)platinum(II)^{8b} and 10 mL of butanone were added, and the mixture was heated and stirred at 115 °C for 21 h. The solvents were removed under reduced pressure, and the resulting solid was dissolved in 20 mL of anhydrous DMF. Potassium *tert*-butoxide and acetylacetone were added, and the mixture was stirred for 21 h at room temperature and another 6 h at 100 °C. After removing the DMF under reduced pressure the residue was washed with water and the crude product was purified by flash column chromatography.

1-Methyl-4-phenyl-1,2,4-triazolium lodide (5). 4-Phenyl-4*H*-1,2,4-triazole 1¹⁶ (290 mg, 2.00 mmol) was reacted with iodomethane (573 mg, 0.25 mL, 4.00 mmol) in 2 mL of THF for 17 h at 110 °C according to general procedure B. Compound **5** was isolated as a white powder (470 mg, 1.64 mmol, 82%). Mp: 208 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 10.71 (s, 1 H, NC<u>H</u>N), 9.74 (s, 1 H, NC<u>H</u>N), 7.80 (d, ³*J*_{HH} = 7.4 Hz, 2 H, C2<u>H</u>_{arom} and C6<u>H</u>_{arom}), 7.75–7.60 (m, 3 H, C3<u>H</u>_{arom}–C5<u>H</u>_{arom}), 4.15 (s, 3 H, CH₃). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 142.8 (N<u>C</u>HN), 142.1 (N<u>C</u>HN), 132.1 (<u>C1</u>_{arom}), 130.5 (<u>C4</u>H_{arom}), 38.9 (<u>CH</u>₃). Anal. Calcd for C₉H₁₀IN₃: C, 37.65; H, 3.51; N, 14.64. Found: C, 37.77; H, 3.46; N, 14.61.

4-(4-Chlorophenyl)-1-methyl-1,2,4-triazolium lodide (6). 4-(4-Chlorophenyl)-4*H*-1,2,4-triazole **2**¹⁷ (205 mg, 1.14 mmol) was reacted with iodomethane (327 mg, 0.14 mL, 2.28 mmol) in 3 mL of THF for 22 h at 110 °C according to general procedure B. Compound **6** was isolated in the form of brown crystals (258 mg, 0.89 mmol, 78%). Mp: 247 °C. ¹H NMR DMSO-*d*₆ (300.13 MHz, DMSO-*d*₆): *δ* 10.70 (s, 1 H, CH₃NC<u>H</u>N), 9.72 (s, 1 H, NC<u>H</u>N), 7.83 (s, 4 H, C<u>H_{arom}), 4.15 (s, 3 H, CH₃). ¹³C NMR (125.75 MHz, DMSO-*d*₆): *δ* 142.9 (N<u>C</u>HN), 142.2 (N<u>C</u>HN), 135.1 (<u>C_{ipso}</u>), 131.0 (<u>C_{ipso}</u>), 130.2 (<u>C</u>H_{arom}), 124.5 (<u>C</u>H_{arom}), 38.8 (<u>C</u>H₃). Anal. Calcd for C₉H₉CIIN₃: C, 33.62; H, 2.82; N, 13.07. Found: C, 33.22; H, 2.46; N, 13.05.</u>

4-(4-Methoxyphenyl)-1-methyl-1,2,4-triazolium lodide (7). 4-(4-Methoxyphenyl)-4*H*-1,2,4-triazole 3¹⁷ (701 mg, 4.00 mmol) was reacted with iodomethane (1136 mg, 0.50 mL, 8.00 mmol) in 3 mL of THF for 19 h at 100 °C according to general procedure B. Compound 7 was isolated as a white powder (1120 mg, 3.53 mmol, 88%). Mp: 227 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 10.61 (s, 1 H, NC<u>H</u>N), 9.65 (s, 1 H, NC<u>H</u>N), 7.73 (d, ³*J*_{HH} = 9.0 Hz, 2 H, C<u>H</u>_{arom}), 7.25 (d, ³*J*_{HH} = 9.0 Hz, 2 H, C<u>H</u>_{arom}), 4.14 (s, 3 H, C<u>H</u>₃), 3.86 (s, 3 H, C<u>H</u>₃). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 160.5 (C1_{arom}), 143.0 (NCHN), 142.0 (NCHN), 124.9 (C4_{arom}), 124.2 (C2H_{arom} and C6H_{arom}), 123.6 (C3H_{arom} and C5H_{arom}), 55.8 (CH₃), 38.7 (CH₃). Anal. Calcd for C₁₀H₁₂IN₃O: C, 37.87; H, 3.81; N, 13.25. Found: C, 37.96; H, 3.80; N, 13.30.

1-Methyl-4-(4-nitrophenyl)-1,2,4-triazolium lodide (8). 4-(4-Nitrophenyl)-4*H*-1,2,4-triazole 4¹⁷ (380 mg, 2.00 mmol) was reacted with iodomethane (341 mg, 0.37 mL, 2.40 mmol) in 3 mL of THF for 22 h at 100 °C according to general procedure B. Compound **8** was isolated as a white powder (364 mg, 1.1 mmol, 55%). Mp: 242 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 10.89 (s, 1 H, NC<u>H</u>N), 9.88 (s, 1 H, NC<u>H</u>N), 8.59 (d, ³*J*_{HH} = 8.9 Hz, 2 H, C3<u>H</u>_{arom} and C5<u>H</u>_{arom}), 8.11 (d, ³*J*_{HH} = 8.9 Hz, 2 H, C2<u>H</u>_{arom} and C6<u>H</u>_{arom}), 4.19 (s, 3 H, C<u>H</u>3). ¹³C NMR (150.93 MHz, DMSO-*d*₆): δ 148.0 (<u>C4</u>_{arom}), 142.7 (N<u>C</u>HN), 142.3 (N<u>C</u>HN), 136.5 (<u>C1</u>_{arom}), 125.5 (<u>C3</u>H_{arom} and <u>C5</u>H_{arom}), 123.6 (<u>C2</u>H_{arom} and <u>C6</u>H_{arom}), 38.9 (<u>C</u>H₃). Anal. Calcd for C₉H₉IN₄O₂: C, 32.55; H, 2.73; N, 16.87. Found: C, 32.23; H, 2.53; N, 16.71.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)(4-phenyl- κC^2 -1-methyl-1,2,4triazol-5-ylidene-kC⁵)platinum(II) (9). Triazolium iodide 5 (230 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5cyclooctadiene)platinum(II) (299 mg, 0.8 mmol), potassium tertbutoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. Compound 9 was isolated as a white powder (106 mg, 0.234 mmol, 29%). Mp: 248 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 8.22 (s, 1 H, NC<u>H</u>N), 7.81 (t, ${}^{3}J_{PtH}$ = 26.8 Hz, 1 H, C3<u>H</u>_{arom}), 7.10–6.95 (m, 3 H, C4Harom - C6Harom), 5.53 (s, 1 H, CCHC), 4.23 (s, 3 H, NCH3), 2.08 (s, 3 H, CCH₃), 2.00 (s, 3 H, CCH₃). ¹³C NMR (75.48 MHz, CDCl₃): δ 185.3 (CO), 185.1 (CO), 152.7 (NCN), 143.4 (Cl_{arom}), 135.8 (N<u>C</u>HN), 132.4 (<u>C3</u>H_{arom}), 125.4 (<u>C</u>H_{arom}), 124.3 (<u>C2</u>_{arom}), 123.8 (<u>C5Harom</u>), 110.8 (<u>CHarom</u>), 102.1 (<u>CH</u>), 37.4 (N<u>CH</u>₃), 27.9 (C<u>C</u>H₃), 27.8 (C<u>C</u>H₃). Anal. Calcd for C₁₄H₁₅N₃O₂Pt H₂O: C, 35.75; H, 3.64; N, 8.93. Found: C, 35.65; H, 3.32; N, 8.95.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)[4-(4-chlorophenyl- κC^2)-1-methyl-1,2,4-triazol-5-ylidene-κC⁵]platinum(II) (10). Triazolium iodide 6 (257 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5-cyclooctadiene)platinum(II) (299 mg, 0.8 mmol), potassium tert-butoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The resulting solid was washed with diethyl ether and dried in vacuo to yield compound 10 in the form of white crystals (106 mg, 0.218 mmol, 27%). Mp: 231 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 8.20 (s, 1 H, NC<u>H</u>N), 7.73 (t, ³J_{PtH} = 29.5 Hz, 1 H, C3<u>H</u>_{arom}), 7.07 (d, ${}^{3}J_{HH} = 8.2$ Hz, 1 H, C5<u>H</u>_{arom}), 7.00 (d, ${}^{3}J_{HH} = 8.2$ Hz, 1 H, C6H_{arom}), 5.55 (s, 1 H, CH), 4.23 (s, 3 H, NCH₃), 2.11 (s, 3 H, CCH_3 , 2.02 (s, 3 H, CCH_3). ¹³C NMR (150.93 MHz, $CDCl_3$): δ 185.4 (<u>C</u>O), 135.8 (N<u>C</u>HN), 132.0 (<u>C3</u>H_{arom}), 130.5 (<u>C4</u>_{arom}), 127.0 $(\underline{C2}_{arom}), 123.5 (\underline{C5}H_{arom}), 111.7 (\underline{C6}H_{arom}), 102.3 (\underline{CH}), 37.5 (\underline{NCH}_3), 27.9 (\underline{CCH}_3), 27.8 (\underline{CCH}_3). ^{195}Pt NMR (129.01 MHz, 129.01 MHz)$ CDCl₃): δ -3359.7. Anal. Calcd for C₁₄H₁₄ClN₃O₂Pt: C, 34.54; H, 2.90; N, 8.63. Found: C, 34.21; H, 2.64; N, 8.50.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)[4-(4-methoxyphenyl- κC^2)-1methyl-1,2,4-triazol-5-ylidene- κC^{3}]platinum(II) (11). Triazolium iodide 7 (254 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5-cyclooctadiene)platinum(II) (449 mg, 1.2 mmol), potassium tert-butoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The resulting solid was washed with diethyl ether and isohexane and dried in vacuo to yield compound 11 in the form of white crystals (72 mg, 0.149 mmol, 19%). Mp: 162 °C. ¹H NMR CDCl₃ (300.13 MHz, CDCl₃): δ 8.16 (s, 1 H, NC<u>H</u>N), 7.38 (td, ³J_{PtH} = 30.1 Hz, ${}^{3}J_{HH}$ = 2.7 Hz, 1 H, C3<u>H</u>_{arom}), 7.01 (dd, ${}^{3}J_{HH}$ = 8.5 Hz, ${}^{3}J_{HH}$ = 2.7 Hz, 1 H, C6<u>H</u>_{arom}), 6.62 (d, ${}^{3}J_{HH}$ = 8.5 Hz, 1 H, C5<u>H</u>_{arom}), 5.53 (s, 1 H, CH), 4.23 (s, 3 H, NCH₃), 3.86 (s, 3 H, OCH₃), 2.09 (s, 3 H, CCH_3), 2.01 (s, 3 H, CCH_3). ¹³C NMR (75.48 MHz, $CDCl_3$): δ 185.3 (<u>C</u>O), 185.1 (<u>C</u>O), 156.9 (<u>C4</u>arom), 151.7 (N<u>C</u>N), 137.2 (<u>C1</u>arom), 135.4 (N<u>C</u>HN), 126.2 (<u>C2</u>_{arom}), 117.5 (<u>C3</u>H_{arom}), 111.4 (<u>C6</u>H_{arom}), 108.6 (<u>C5</u>H_{arom}), 102.1 (<u>C</u>H), 55.4 (O<u>C</u>H₃), 37.4 (N<u>C</u>H₃), 27.9 (C<u>C</u>H₃), 27.8 (C<u>C</u>H₃). ¹⁹⁵Pt NMR (129.01 MHz, CDCl₃): δ -3368.2. Anal. Calcd for C₁₅H₁₇N₃O₃Pt: C, 37.35; H, 3.55; N, 8.71. Found: C, 37.66; H, 3.40; N, 8.78.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)[4-(4-nitrophenyl- κC^2)-1-methyl-1,2,4-triazol-5-ylidene-*kC*⁵]platinum(II) (12). Triazolium iodide 8 (266 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5-cyclooctadiene)platinum(II) (449 mg, 1.2 mmol), potassium tert-butoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The resulting solid was washed with isohexane and dried in vacuo to yield compound 12 as a green powder (71 mg, 0.143 mmol, 18%). Mp: 260 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 8.63 (td, ${}^{3}J_{PtH} = 29.8$ Hz, ${}^{3}J_{HH} = 2.5$ Hz, 1 H, C3<u>H</u>_{arom}), 8.02 (dd, ${}^{3}J_{HH} = 8.6$ Hz, ${}^{3}J_{HH} = 2.5$ Hz 1 H, C<u>H</u>_{arom}), 7.18 (d, ${}^{3}J_{HH} = 8.5$ Hz, 1 H, C<u>H</u>_{arom}), 5.59 (s, 1 H, C<u>H</u>), 4.27 (s, 3 H, C<u>H</u>₃), 2.16 (s, 3 H, C<u>H</u>₃), 2.05 (s, 3 H, <u>CH₃</u>). ¹³C NMR (150.93 MHz, CDCl₃): δ 185.7 (<u>C</u>O), 185.5 (<u>C</u>O), 136.2 (N<u>C</u>HN), 127.1 (<u>C3</u>H_{arom}), 120.4 (<u>C5</u>H_{arom}), 110.7 (<u>C6</u>H_{arom}), 102.4 (<u>C</u>H), 37.6 (N<u>C</u>H₃), 27.9 (C<u>C</u>H₃), 27.8 (C<u>C</u>H₃). ¹⁹⁵Pt NMR (129.01 MHz, CDCl₃): δ -3358.7. Anal. Calcd for C₁₄H₁₄N₄O₄Pt·0.5

CH₂Cl₂: C, 32.26; H, 2.80; N, 10.38. Found: C, 32.46; H, 2.53; N, 10.51.

1-(4-Chlorophenyl)-1*H***-1,2,4-triazole (14).** 1*H*-1,2,4-Triazole (2.00 g, 29 mmol), 1-chloro-4-iodobenzene (10.50 g, 44 mmol), 1,10-phenanthroline (1.06 g, 5.8 mmol), copper(I) oxide (0.43 g, 3 mmol), and potassium carbonate (12.20 g, 88 mmol) were reacted in 20 mL of DMF according to general procedure A. The product was washed with diethyl ether and dried *in vacuo*. Compound **14** was obtained in the form of colorless needles (489 mg, 2.72 mmol, 9%). Mp: 98 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 8.55 (s, 1 H, NC<u>H</u>N), 8.12 (s, 1 H, NC<u>H</u>N), 7.65 (d, ³*J*_{HH} = 8.9 Hz, 2 H, C<u>H</u>_{arom}), 7.50 (d, ³*J*_{HH} = 8.9 Hz, 2 H, C<u>H</u>_{arom}). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 152.7 (N<u>C</u>HN), 140.9 (N<u>C</u>HN), 135.4 (<u>C</u>_{ipso}), 133.8 (<u>C</u>_{ipso}), 129.9 (<u>C</u>H_{arom}), 121.1 (<u>C</u>H_{arom}). Anal. Calcd for C₈H₆ClN₃: C, 53.50; H, 3.37; N, 23.40. Found: C, 53.36; H, 3.40; N, 23.30.

1-(4-Methoxyphenyl)-1*H***-1,2,4-triazole (15).** 1*H*-1,2,4-Triazole (1.00 g, 14.5 mmol), 4-iodoanisole (5.15 g, 22.0 mmol), 1,10-phenanthroline (0.53 g, 2.9 mmol), copper(I) oxide (0.22 g, 1.5 mmol), and potassium carbonate (6.08 g, 44 mmol) were reacted in 10 mL of DMF according to general procedure A. After flash chromatography with ethyl acetate (silica gel KG60) **15** was obtained as a white powder (1.39 g, 7.92 mmol, 55%). Mp: 71 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 8.62 (s, 1 H, NC<u>H</u>N), 8.13 (s, 1 H, NC<u>H</u>N), 7.60 (d, ³*J*_{HH} = 8.9 Hz, 2 H, C2<u>H</u>_{arom} and C6<u>H</u>_{arom}), 7.03 (d, ³*J*_{HH} = 8.9 Hz, 2 H, C3<u>H</u>_{arom} and C5<u>H</u>_{arom}), 151.7 (N<u>C</u>HN), 140.6 (N<u>C</u>HN), 130.3 (<u>C</u>_{ipso}), 121.9 (<u>C2</u>H_{arom} and <u>C6</u>H_{arom}), 114.9 (<u>C3</u>H_{arom} and <u>C5</u>H_{arom}), 55.6 (O<u>C</u>H₃). Anal. Calcd for C₉H₉N₃O: C, 61.70; H, 5.18; N, 23.99. Found: C, 61.48; H, 5.31; N, 24.24.

1-(4-Methylphenyl)-1*H***-1,2,4-triazole (16). 1***H***-1,2,4-Triazole (2.00 g, 29 mmol), 1-bromotoluene (7.53 g, 44 mmol), 1,10-phenanthroline (1.06 g, 5.8 mmol), copper(I) oxide (0.43 g, 3 mmol), and potassium carbonate (12.20 g, 88 mmol) were reacted in 20 mL of DMF according to general procedure A. After flash chromatography with ethyl acetate (silica gel KG60) 16** was obtained as a white powder (1.94 g, 12.20 mmol, 42%). Mp: 62 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 8.51 (s, 1 H, NC<u>H</u>N), 8.09 (s, 1 H, NC<u>H</u>N), 7.55 (d, ³*J*_{HH} = 8.5 Hz, 2 H, C2<u>H</u>_{arom} and C6<u>H</u>_{arom}), 7.31 (d, ³*J*_{HH} = 8.4 Hz, 2 H, C<u>H</u>_{arom}), 2.41 (s, 3 H, C<u>H</u>₃). ¹³C NMR (125.75 MHz, DMSO-*d*₆): δ 152.4 (N<u>C</u>HN), 140.7 (N<u>C</u>HN), 138.3 (<u>C4</u>_{arom}), 134.7 (<u>C1</u>_{arom}), 130.3 (<u>C3</u>H_{arom} and <u>C5</u>H_{arom}), 120.0 (<u>C2</u>H_{arom} and <u>C6</u>H_{arom}), 21.0 (<u>CH</u>₃). Anal. Calcd for C₉H₉N₃:C, 67.91; H, 5.70; N, 26.40. Found: C, 67.74; H, 5.70; N, 26.42.

4-Methyl-1-phenyl-1,2,4-triazolium lodide (17). 1-Phenyl-1*H*-1,2,4-triazole 13¹⁸ (581 mg, 4.00 mmol) was reacted with iodomethane (1136 mg, 0.50 mL, 8.00 mmol) in 3 mL of THF for 17 h at 110 °C according to general procedure B. Compound 17 was isolated as a white powder (1000 mg, 3.49 mmol, 87%). Mp: 127 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 10.82 (s, 1 H, NC<u>H</u>N), 9.36 (s, 1 H, NC<u>H</u>N), 7.90 (d, ²*J*_{HH} = 7.9 Hz, 2 H, C2<u>H</u>_{arom} and C6<u>H</u>_{arom}), 7.78–7.60 (m, 3 H, C3<u>H</u>_{arom}-C5<u>H</u>_{arom}), 3.98 (s, 3 H, C<u>H</u>₃). ¹³C NMR (125.75 MHz, DMSO-*d*₆): δ 145.8 (N<u>C</u>HN), 142.2 (N<u>C</u>HN), 134.9 (<u>C1</u>_{arom}), 130.5 (<u>C4</u>H_{arom}), 130.3 (<u>C3</u>H_{arom} and <u>C5</u>H_{arom}), 120.6 (<u>C2</u>H_{arom} and <u>C6</u>H_{arom}), 34.4 (<u>C</u>H₃). Anal. Calcd for C₉H₁₀IN₃: C, 37.65; H, 3.51; N, 14.64. Found: C, 37.43; H, 3.40; N, 14.66.

1-(4-Chlorophenyl)-4-methyl-1,2,4-triazolium lodide (18). 1-(4-Chlorophenyl)-1*H*-1,2,4-triazole 14¹⁷ (359 mg, 2.00 mmol) was reacted with iodomethane (568 mg, 0.25 mL, 4.00 mmol) in 3 mL of THF for 22 h at 100 °C according to general procedure B. Compound **18** was isolated as a white powder (555 mg, 1.73 mmol, 86%). Mp: 248 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 10.87 (s, 1 H, NC<u>H</u>N), 9.38 (s, 1 H, NC<u>H</u>N), 7.88–7.98 (d, ³J_{HH} = 8.9 Hz, 2 H, C<u>H_{arom}</u>), 7.74–7.85 (d, ³J_{HH} = 8.9 Hz, 2 H, C<u>H_{arom}</u>), 3.98 (s, 3 H, C<u>H₃</u>). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 145.9 (N<u>C</u>HN), 142.5 (N<u>C</u>HN), 134.9 (<u>C_{ipso}</u>), 133.8 (<u>C_{ipso}</u>), 130.3 (<u>C</u>H_{arom}), 122.5 (<u>C</u>H_{arom}), 34.4 (<u>C</u>H₃). Anal. Calcd for C₉H₉N₃CII: C, 33.62; H, 2.82; N, 13.07. Found: C, 33.81; H, 2.76; N, 13.13.

1-(4-Methoxyphenyl)-4-methyl-1,2,4-triazolium lodide (19). 1-(4-Methoxyphenyl)-1*H*-1,2,4-triazole **15**¹⁹ (526 mg, 3.00 mmol) was reacted with iodomethane (639 mg, 0.28 mL, 4.50 mmol) in 3 mL of THF for 22 h at 110 °C according to general procedure B. Compound **19** was isolated as a white powder (812 mg, 2.56 mmol, 85%). Mp: 212 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 10.72 (s, 1 H, NC<u>H</u>N), 9.33 (s, 1 H, NC<u>H</u>N), 7.81 (d, ³J_{HH} = 9.0 Hz, 2 H, C2<u>H_{arom}</u> and C6<u>H_{arom}</u>), 7.24 (d, ³J_{HH} = 9.0 Hz, 2 H, C3<u>H_{arom}</u> and C5<u>H_{arom}</u>), 3.97 (s, 3 H, NC<u>H</u>₃), 3.86 (s, 3 H, OC<u>H</u>₃). ¹³C NMR (150.93 MHz, DMSOd₆): δ 160.5 (<u>C1_{arom}</u>), 145.6 (N<u>C</u>HN), 141.6 (N<u>C</u>HN), 128.1 (<u>C4_{arom}</u>), 122.4 (<u>C2</u>H_{arom} and <u>C6</u>H_{arom}), 115.2 (<u>C3</u>H_{arom} and <u>C5</u>H_{arom}), 55.8 (O<u>C</u>H₃), 34.3 (N<u>C</u>H₃). Anal. Calcd for C₁₀H₁₂IN₃O: C, 37.87; H, 3.81; N, 13.25. Found: C, 38.15; H, 3.84; N, 13.35.

4-Methyl-1-(4-methylphenyl)-1,2,4-triazolium lodide (20). 1-(4-Methylphenyl)-1*H*-1,2,4-triazole **16**²⁰ (637 mg, 4.00 mmol) was reacted with iodomethane (1136 mg, 0.50 mL, 8.00 mmol) in 3 mL of THF for 22 h at 100 °C according to general procedure B. Compound **20** was isolated as a white powder (1121 mg, 3.72 mmol, 93%). Mp: 169 °C. ¹H NMR (300.13 MHz, DMSO-*d*₆): δ 10.77 (s, 1 H, NC<u>H</u>N), 9.34 (s, 1 H, NC<u>H</u>N), 7.78 (d, ³*J*_{HH} = 8.4 Hz, 2 H, C<u>H</u>_{arom}), 7.51 (d, ³*J*_{HH} = 8.6 Hz, 2 H, C<u>H</u>_{arom}), 3.97 (s, 3 H, CC<u>H</u>₃). ¹³C NMR (75.48 MHz, DMSO-*d*₆): δ 145.7 (NCHN), 141.8 (NCHN), 140.5 (C_{ipso}), 132.7 (C_{ipso}), 130.6 (CH_{arom}), 120.4 (CH_{arom}), 34.3 (NCH₃), 20.65 (CC<u>H</u>₃). Anal. Calcd for C₁₀H₁₂IN₃: C, 39.89; H, 4.02; N, 13.95. Found: C, 40.09; H, 4.05; N, 14.05.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)(1-phenyl- κC^2 -4-methyl-1,2,4triazol-5-ylidene-xC5)platinum(II) (21). Triazolium iodide 17 (230 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5cyclooctadiene)platinum(II) (449 mg, 1.2 mmol), potassium tertbutoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The solid was washed with diethyl ether and isohexane and dried in vacuo to yield compound 21 as a white powder (160 mg, 0.354 mmol, 44%). Mp: 235 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 7.85 (s, 1 H, NCHN), 7.79 (t, ${}^{3}J_{PtH}$ = 27.2 Hz, 1 H, $C3H_{arom}$), 7.35–7.25 (m, 1 H, C6 \underline{H}_{arom}), 7.14–7.03 (m, 2 H, C4 \underline{H}_{arom} and C5 \underline{H}_{arom}), 5.52 (s, 1 H, C<u>H</u>), 4.09 (s, 3 H, NC<u>H</u>₃), 2.08 (s, 3 H, CC<u>H</u>₃), 1.98 (s, 3 H, CC<u>H</u>₃). ¹³C NMR (125.75 MHz, CDCl₃): δ 185.1 (<u>C</u>O), 185.0 (<u>C</u>O), 153.7 (N<u>C</u>N), 145.2 (<u>C1</u>_{arom}), 141.5 (N<u>C</u>HN), 131.1 (<u>C3</u>H_{arom}), 125.2 (\underline{CH}_{arom}) ,123.9 (\underline{CH}_{arom}) ,121.6 $(\underline{C2}_{arom})$, 111.5 $(\underline{C6H}_{arom})$, 102.1 (\underline{CH}) , 32.7 $(N\underline{CH}_{3})$, 27.9 $(C\underline{CH}_{3})$, 27.8 $(C\underline{CH}_{3})$. ¹⁹⁵Pt NMR (129.01 MHz, CDCl₃): δ -3447.9. Anal. Calcd for C₁₄H₁₅N₃O₂Pt: C₁ 37.17; H, 3.34; N, 9.29. Found: C, 36.86; H, 3.28; N, 9.11.

(Pentan-2,4-dionato- $\kappa^2 0,0'$)[1-(4-chlorophenyl- κC^2)-4-methyl-1,2,4-triazol-5-ylidene-kC5]platinum(II) (22). Triazolium iodide 18 (257 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5-cyclooctadiene)platinum(II) (449 mg, 1.2 mmol), potassium tert-butoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The solid was washed with diethyl ether and isohexane and dried in vacuo to yield compound 22 as a white powder (90 mg, 0.19 mmol, 23%). Mp: 163 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 7.81 (s, 1 H, NC<u>H</u>N), 7.70 (td, ${}^{3}J_{PtH}$ = 30.2 Hz, ${}^{3}J_{HH}$ = 2.2 Hz, 1 H, $C3H_{arom}$). 7.18 (d, ${}^{3}J_{HH}$ = 8.2 Hz, 1 H, C6 H_{arom}), 7.07 (dd, ${}^{3}J_{PtH}$ = 8.2 Hz, ${}^{3}J_{HH} = 2.2$ Hz, 1 H, $C5\underline{H}_{arom}$), 5.52 (s, 1 H, C<u>H</u>), 4.05 (s, 3 H, NCH₃), 2.10 (s, 3 H, CCH₃), 1.98 (s, 3 H, CCH₃). ¹³C NMR (150.93 MHz, CDCl₃): δ 185.2 (<u>C</u>O), 185.1 (<u>C</u>O), 153.2 (N<u>C</u>N), 143.8 (<u>C1</u>_{arom}), 141.6 (N<u>C</u>HN), 130.7 (<u>C3</u>H_{arom}), 130.2 (<u>C4</u>_{arom}), 124.2 $(\underline{C2}_{arom})$, 123.6 $(\underline{C5}H_{arom})$, 112.4 $(\underline{C6}H_{arom})$, 102.2 (\underline{CH}) , 32.7 (\underline{NCH}_3) , 27.8 (\underline{CCH}_3) , 27.8 (\underline{CCH}_3) , 27.8 (\underline{CCH}_3) . ¹⁹⁵Pt NMR (129.01 MHz, CDCl₃): δ -3397.8. Anal. Calcd for C₁₄H₁₄ClN₃O₂Pt: C, 34.54; H, 2.90; N, 8.63. Found: C, 34.71; H, 2.90; N, 8.50.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)[1-(4-methoxyphenyl- κC^2)-4-methyl-1,2,4-triazol-5-ylidene- κC^5]platinum(II) (23). Triazolium iodide 19 (254 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5-cyclooctadiene)platinum(II) (449 mg, 1.2 mmol), potassium *tert*-butoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The solid was washed with diethyl ether and isohexane and dried *in vacuo* to yield compound 23 as a white powder (113 mg, 0.234 mmol, 29%). Mp: 245 °C. ¹H NMR (300.13 MHz, CDCl₃): δ 7.80 (s, 1 H, NC<u>H</u>N), 7.37 (td, ³J_{PtH} = 30.3 Hz, ³J_{HH} = 2.7 Hz, 1 H,

C3<u>H</u>_{arom}), 7.19 (d, 1 H, ³*J*_{IH} = 8.4 Hz, C6<u>H</u>_{arom}), 6.63 (dd, 1 H, ³*J*_{IH} = 8.4 Hz, ³*J*_{HH} = 2.7 Hz, C5<u>H</u>_{arom}), 5.51 (s, 1 H, C<u>H</u>), 4.05 (s, 1 H, NC<u>H</u>₃), 3.86 (s, 3 H, OC<u>H</u>₃), 2.07 (s, 3 H, CC<u>H</u>₃), 1.97 (s, 3 H, CC<u>H</u>₃). ¹³C NMR (150.93 MHz, CDCl₃): δ 185.0 (<u>C</u>O), 185.0 (<u>C</u>O), 157.0 (<u>C</u>4_{arom}), 152.0 (N<u>C</u>N), 141.2 (N<u>C</u>HN), 139.1 (<u>C</u>1_{arom}), 123.4 (<u>C</u>2_{arom}), 116.9 (<u>C</u>3H_{arom}), 112.1 (<u>C</u>6H_{arom}), 108.2, (<u>C</u>5H_{arom}), 102.1 (<u>C</u>H), 55.5 (O<u>C</u>H₃), 32.7 (N<u>C</u>H₃), 27.9 (C<u>C</u>H₃), 27.8 (C<u>C</u>H₃). ¹⁹⁵Pt NMR (129.01 MHz, CDCl₃): δ -3421.4. Anal. Calcd for C₁₅H₁₇N₃O₃Pt: C 37.35; H, 3.55; N, 8.71. Found: C, 37.44; H, 3.50; N, 8.69.

(Pentan-2,4-dionato- $\kappa^2 O, O'$)[1-(4-methylphenyl- κC^2)-4methyl-1,2,4-triazol-5-ylidene- κC^5]platinum(ll) (24). Triazolium iodide 20 (241 mg, 0.8 mmol), silver(I) oxide (93 mg, 0.4 mmol), dichloro(1,5-cyclooctadiene)platinum(II) (449 mg, 1.2 mmol), potassium tert-butoxide (359 mg, 3.2 mmol), and pentane-2,4-dione (0.33 mL, 320 mg, 3.2 mmol) were reacted according to general procedure C. The solid was washed with isohexane and diethyl ether and dried in vacuo to yield compound 24 as a white powder (108 mg, 0.232 mmol, 29%). Mp: 206 °C. ¹H NMR (300.13 MHz, CDCl₂): δ 7.82 (s, 1 H, NC<u>H</u>N), 7.58 (t, ${}^{3}J_{PtH}$ = 28.4 Hz, 1 H, C3<u>H</u>_{arom}), 7.15 (d, ${}^{3}J_{\text{HH}} = 7.8 \text{ Hz}, 1 \text{ H}, \text{ C6}\underline{\text{H}}_{\text{arom}}), 6.88 \text{ (d, } {}^{3}J_{\text{HH}} = 7.8 \text{ Hz}, 1 \text{ H}, \text{ C5}\underline{\text{H}}_{\text{arom}}),$ 5.52 (s, 1 H, C<u>H</u>), 4.07 (s, 3 H, NC<u>H</u>₃), 2.39 (s, 3 H, C<u>H</u>₃), 2.10 (s, 3 H, CC<u>H₃</u>), 1.98 (s, 3 H, CC<u>H₃</u>). ¹³C NMR (150.93 MHz, CDCl₃): δ 185.0 (<u>C</u>O), 153.0 (N<u>C</u>N), 143.0 (<u>C1_{arom}</u>), 141.3 (N<u>C</u>HN), 134.9 (<u>C4</u>_{arom}), 131.8 (<u>C3</u>H_{arom}), 124.3 (<u>C5</u>H_{arom}), 121.2 (<u>C2</u>_{arom}), 110.9 (<u>C6</u>H_{arom}), 102.1 (<u>C</u>H), 32.7 (N<u>C</u>H₃), 28.5 (C<u>C</u>H₃), 28.3 (C<u>C</u>H₃), 21.7 (CCH₃). ¹⁹⁵Pt NMR (129.01 MHz, CDCl₃): δ –3436.3. Anal. Calcd for C₁₅H₁₇N₃O₂Pt: C, 38.63; H, 3.67; N, 9.01. Found: C, 38.37; H, 3.59; N, 8.92.

ASSOCIATED CONTENT

S Supporting Information

CIF files, text, tables, and figures giving experimental details, crystallographic data, and detailed spectra. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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