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C^C* Cyclometalated Platinum(II) NHC Complexes with β-Ketoimine Ligands

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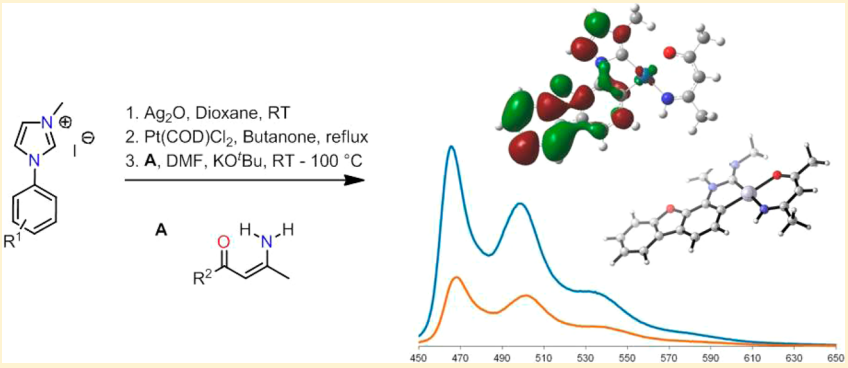
Supporting Information



ABSTRACT: C^C* cyclometalated platinum(II) NHC complexes with chelating acetylacetonate ligands have been recently shown to be an interesting class of phosphorescent emitters. We sought to clarify the role of the acetylacetonate ligand by replacing one of the coordinating oxygen atoms in the auxiliary ligand with an NH group. This allowed us to study the effect on the emission, and we found that the nature of the emission process changes significantly. We herein report the synthesis of novel cyclometalated platinum(II) NHC complexes with the chelating β-ketoimine ligands (3*Z*)-4-amino-3-penten-2-one and (2*Z*)-3-amino-1-phenyl-2-buten-1-one. Due to the unsymmetrical nature of the auxiliary ligands, two isomers were always formed, which could be separated and characterized. Their photophysical properties as well as solid-state structures of representative members of this new class of compounds are given. All new complexes emit in the blue to green region of the visible spectrum with quantum yields as high as 74% at room temperature. The photophysical data of the isomers show significant differences. The new compounds have been fully characterized by ^{1}H and ^{13}C as well as 2D NMR (COSY, HSQC, HMBC, NOESY) spectroscopy. DFT calculations were used to determine differences between the respective isomers and to predict the emission wavelengths of the synthesized complexes. We found the reason for the different properties in comparison to the acetylacetonate complexes to be the smaller HOMO−LUMO gap.

INTRODUCTION

Development over the past decade in organic light-emitting diodes (OLEDs) has brought about considerable progress in electrooptical applications such as true-color flat-panel displays and illumination devices with remarkably low energy consumption.[1−4] The previously used purely organic lumophores have been replaced more and more by organometallic compounds. Organometallic chemistry is taking a leading role in the development of this technology, which has the potential to save vast amounts of global energy in the field of domestic lighting.[5] With the utilization of organometallic phosphorescent emitters the limit of quantum efficiency in classical fluorescent devices (25%) can be overcome. Due to greater heavy-metal-induced spin−orbit coupling (SOC) and the resulting admixture of metal d orbitals to the frontier orbitals of the complexes, intersystem crossing from the excited singlet state to the phosphorescent triplet states is enhanced in most cases.[6] Therefore, transition-metal complexes have become increasingly important over the past years, showing promising quantum efficiencies of up to 100%.[7−10] Especially, cyclometalated heteroleptic Ir(III)[11−13] and Pt(II)[14,15] complexes of the type $[(C^N)_{1-2}M(O^O)]$ (C^N, 2-arylpyridinate or a related ligand; O^O, a β-diketonate ligand) have been studied in detail due to their exceptional luminescence properties.[16,17] In most cases the photophysical properties were improved by changing the cyclometalating ligands. These cyclometalating bidentate ligands are often derived from biphenyl,[16,18,19] 2-phenylpyridine,[16,17,20] a phenylazole such as phenylpyrazole (ppz),[9,17] or 2-phenylbenzimidazole,[21] generating a five-membered metallacycle.

N-heterocyclic carbene (NHC) ligands are versatile ligands that today often replace the more traditional phosphines.[22] Although their development as an important class of ligands in

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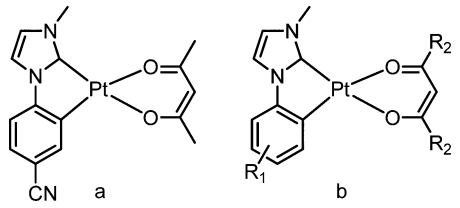
organometallic chemistry is quite considerable, their application in emissive transition-metal complexes has been far less investigated in comparison to arylpyridines. Cyclometalated heteroleptic NHC platinum complexes of the general structure [(C^C*)Pt(O^O)] were first mentioned in patents in 2006[23−25] and have been investigated since in more detail by our group and others (Chart 1).[26−30] As recently shown by us

Chart 1. The Very First (a) and General Motif (b) of C^C* Cyclometalated Platinum(II) NHC (Imidazole) Complexes[a]



[a] R_1 = 4-Me, OMe, Br, NO_2, $BMes_2$, H, 2,3-OC_6H_4, 5-$BMes_2$; R_2 = CH_3, CF_3.

and described in the literature for cyclometalated platinum(II) β-diketonate complexes of the type [(C^N)Pt(O^O)], the photophysical properties of these complexes depend strongly on the substitution pattern of the cyclometalating ligands.[15,26,31] The ongoing investigations of ligand effects have quite recently also included the auxiliary ligand. Therein different β-diketones[32,33] as well as β-ketoimines[34−36] derived from the common acetylacetonate have had a significant impact on the photophysical behavior. The latter have also attracted considerable interest in other research fields as ligands in numerous metal complexes.[37−39]

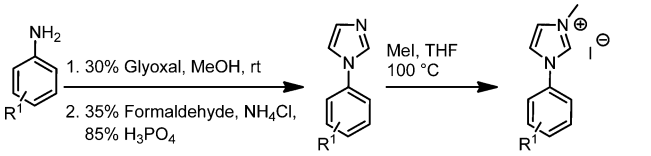
We set out to combine another auxiliary ligand with C^C* cyclometalated NHC platinum(II) complexes. Our goal was to investigate the influence of β-ketoimine ligands in lieu of acetylacetonate on the photoluminescence properties of cyclometalated Pt(II) complexes in combination with known NHC ligands. The focus was on stable emitters for the (deep) blue region of the visible spectrum. Here we present the synthesis and photophysical properties of a new class of temperature- and air-stable Pt(II) complexes bearing N-heterocyclic carbenes as cyclometalating C^C* ligands and β-ketoimines as auxiliary ligands. Density functional theory (DFT) calculations have been used to investigate the frontier molecular orbitals, energies, and geometries of the complexes.

RESULTS AND DISCUSSION

Synthesis. The preparation of aryl- and methyl-functionalized imidazolium salts as ligand precursors is well established (Scheme 1).[40] Imidazoles **1**−**5** were prepared in good yields via Radziszewski ring closure synthesis from commercially available substituted anilines. Imidazole **6** was prepared via a different route:[26] the bromination of dibenzofuran followed by an Ullmann-type reaction with copper(I) oxide and imidazole. The iodide salts **7**−**12** were obtained in very good yields after reaction with methyl iodide in THF at elevated temperatures.

The β-ketoimine ligands **13** and **14** were readily obtained by a condensation reaction of the corresponding commercially available β-diketones acetylacetone and 1-phenyl-1,3-butanedione with ammonium carbamate (Scheme 2). These reaction conditions were found to be superior to those for other reactions such as the silica gel[41] or K-10 montmorillonite[42] catalyzed enamination of β-dicarbonyl compounds. These

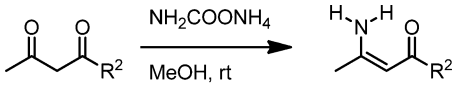
Scheme 1. Synthesis of the NHC Precursors: Imidazoles 1−6 and the Corresponding Imidazolium Salts 7−12



1 R^1 = 4-F
2 R^1 = 4-Cl
3 R^1 = 4-Br
4 R^1 = 4-NO_2
5 R^1 = 4-OMe
6 R^1 = 2,3-OC_6H_4

7 R^1 = 4-F
8 R^1 = 4-Cl
9 R^1 = 4-Br
10 R^1 = 4-NO_2
11 R^1 = 4-OMe
12 R^1 = 2,3-OC_6H_4

Scheme 2. Synthesis of the β-Ketoimine Ligands 13 and 14



13 R^2 = Me
14 R^2 = Ph

suffer from one or more disadvantages such as unsatisfactory yields, usage of ammonium salts, and the necessity of extractive workups or distillation of the reaction mixture.[43] Both ligands exist in their ketoenamine form in solution, as determined by ^{1}H NMR (9.70 and 10.23 ppm for HN*H*O, 5.24 ppm for N*H*), as well as in the solid state (Figure 1). For **13** our results are in agreement with previous reports.[44]

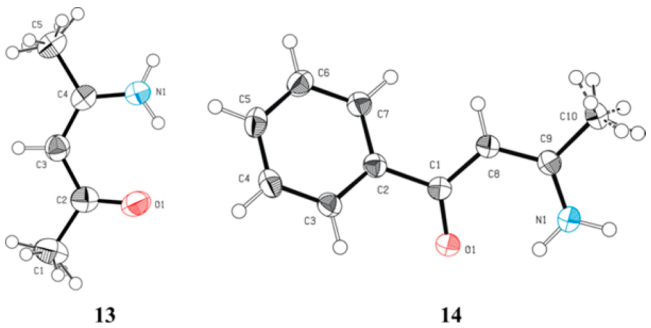


Figure 1. ORTEP representations of the β-ketoimine ligands **13** and **14** in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) for **13**: O(1)−C(2), 1.253(2); N(1)−C(4), 1.321(2); C(2)−C(3), 1.418(3); C(3)−C(4), 1.379(3). Selected bond lengths (Å) and angles (deg) for **14**: O(1)−C(1), 1.2582(12); C(1)−C(8), 1.4107(15); C(8)−C(9), 1.3866(14); N(1)−C(9), 1.3203(14); O(1)−C(1)−C(8), 123.50(9); C(8)−C(9)−N(1), 123.03(10).

Dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl_2, **15**) was chosen as the platinum(II) precursor to introduce one NHC ligand after deprotonation with silver(I) oxide via transmetalation at the metal center, blocking two coordination sites.[26] The intermediate, most probably a chloro-bridged binuclear complex, was then reacted with the bidentate auxiliary ligand in DMF in the next step without isolation, leading to a mixture of the two possible isomers. We were able to separate and purify them by column chromatography, albeit in quite different yields. Complexes of the **a** type (**16a**−**22a**) with the imine group opposite the carbene carbon atom (trans) were obtained more readily, with yields ranging from 22 to 44%

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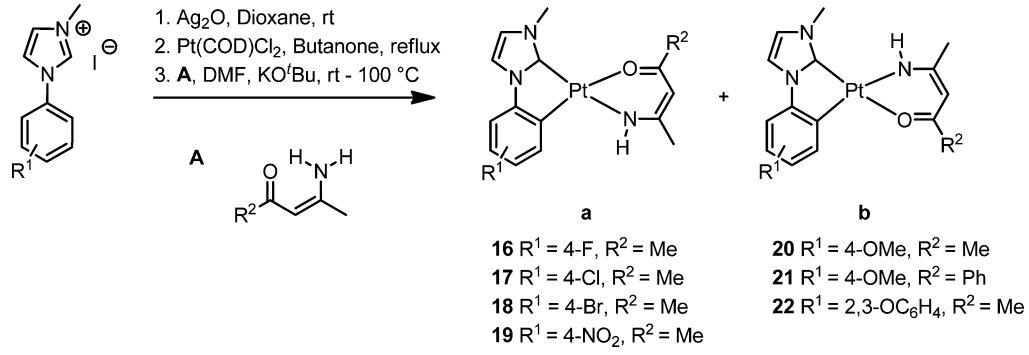
Scheme 3. Synthesis of the Cyclometalated NHC Complexes 16−22



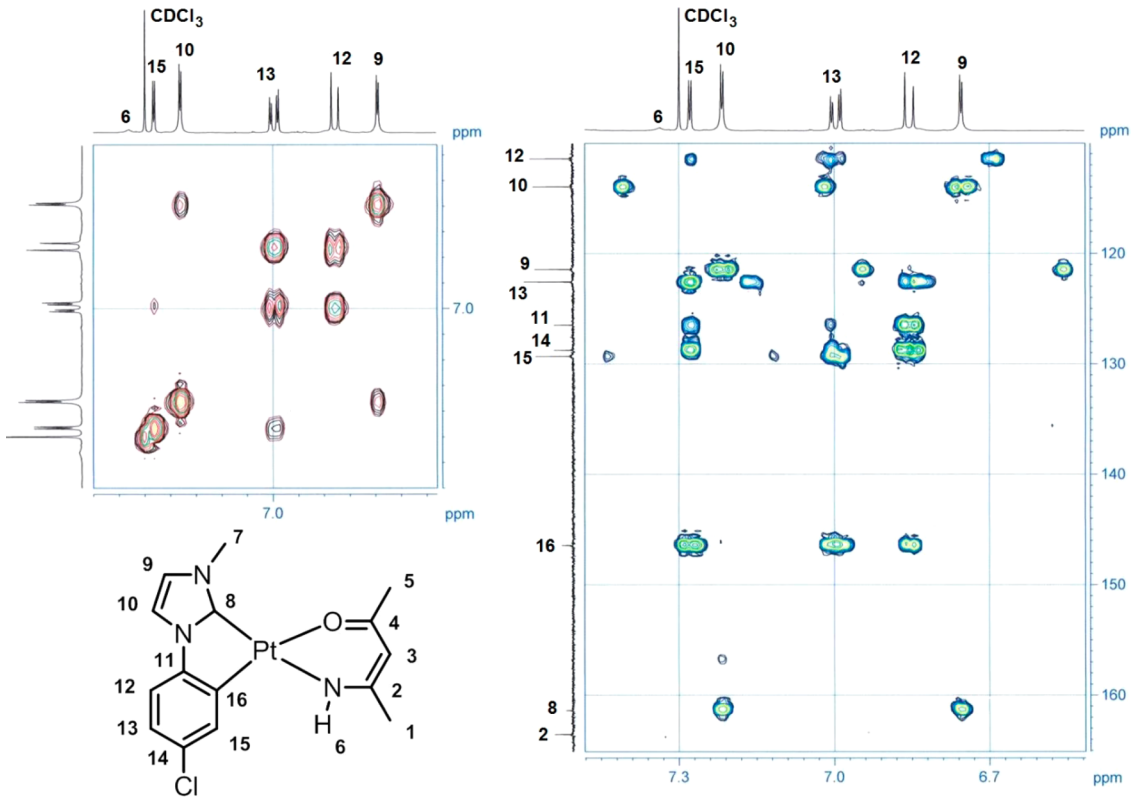


Figure 2. COSY (left) and HMBC (right) spectra of **17a** in $CDCl_3$ at room temperature.

(Scheme 3). This is in agreement with quantum chemical DFT calculations, which showed a thermodynamic preference of 4.8−6.7 kcal/mol in favor of the **a** isomers (see the Supporting Information). The **b** isomers were obtained in yields of 5−16%, with the exception of **22**, where only traces of the second isomer were observed in the ^{1}H NMR. All complexes are stable toward air and moisture at elevated temperatures and have melting points higher than 170 °C.

The two *β*-ketoimines 4-amino-3-penten-2-one (**13**) and 3-amino-1-phenyl-2-buten-1-one (**14**) were chosen as auxiliary ligands. The former has a close resemblance to the acetylacetonate ligand and allows a direct comparison with complexes bearing the same NHC ligand.[26] In the case of **14** a phenyl group was incorporated into the ligand backbone. An expansion of the *π* system normally leads to a red shift of the emission and in some cases to increased quantum yields. For platinum complexes it was furthermore reported that *π*-conjugated chromophoric ligands with their *π* systems somewhat remote from the metal center could exhibit fluorescence. Because of its good solubility, we reacted the imidazolium salt **11** with both auxiliary ligands, yielding complexes **20a** and **21a** and the corresponding **b** isomers, to study these effects in more detail.

NMR Characterization. The ketoenamine form of the two free ligands **13** and **14** in solution was proven by ^{1}H NMR spectroscopy. In both cases two separate proton resonances for a NH group were detected with the signal for the N*H*O proton at lower field (9.70 and 10.23 ppm). The other resonance was measured in a region typical for amines: 5.24 ppm for both **13** and **14**.

The successful deprotonation of the NHC precursor and the subsequent formation of a silver(I) complex intermediate was verified by the disappearance of the imidazolium C*H* signal, whereas during the formation of the cyclometalated platinum complexes one doublet of the NHC aryl ring disappeared. The

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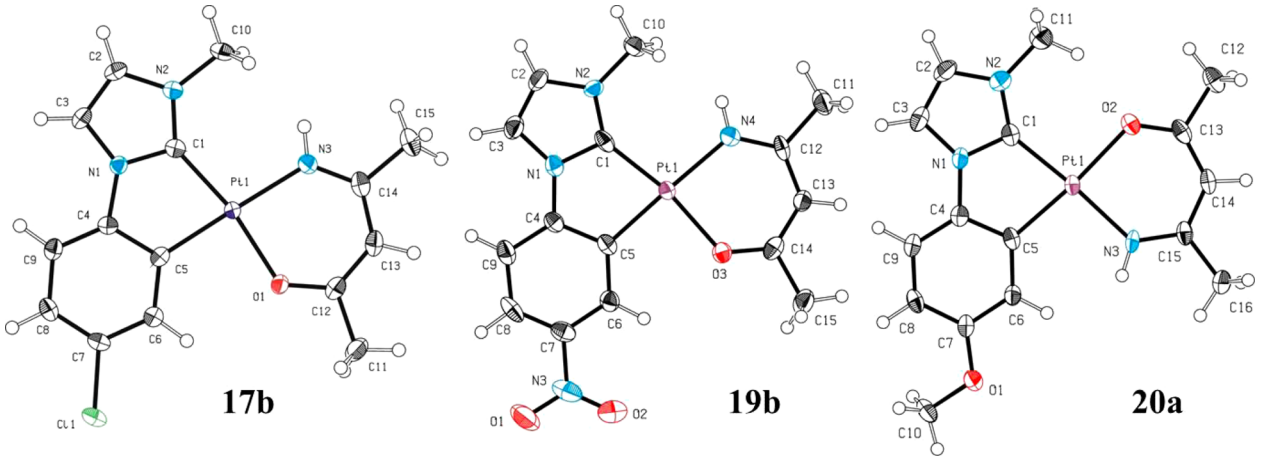

Figure 3. ORTEP representation of complexes **17b**, **19b**, and **20a**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **17b**: Pt(1)−C(1), 1.956(3); Pt(1)−C(5), 1.995(2); Pt(1)−O(1), 2.0415(17); Pt(1)−N(3), 2.049(2); O(1)−Pt(1)−N(3), 88.97(8); C(1)−Pt(1)−C(5), 80.00(10); C(4)−N(1)−C(1)−Pt(1), −1.72(3). Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **19b**: Pt(1)−C(1), 1.961(10); Pt(1)−C(5), 1.991(8); Pt(1)−O(3), 2.048(6); Pt(1)−N(4), 2.051(6); O(3)−Pt(1)−N(4), 89.0(3); C(1)−Pt(1)−C(5), 80.6(4); C(4)−N(1)−C(1)−Pt(1), 0.7(9). Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **20a**: Pt(1)−C(1), 1.973(4); Pt(1)−C(5), 1.997(4); Pt(1)−O(2) 2.072(3); Pt(1)−N(3), 2.026(4); O(2)−Pt(1)−N(3), 89.13(13); C(1)−Pt(1)−C(5), 80.34(17); C(4)−N(1)−C(1)−Pt(1), 0.3(4).

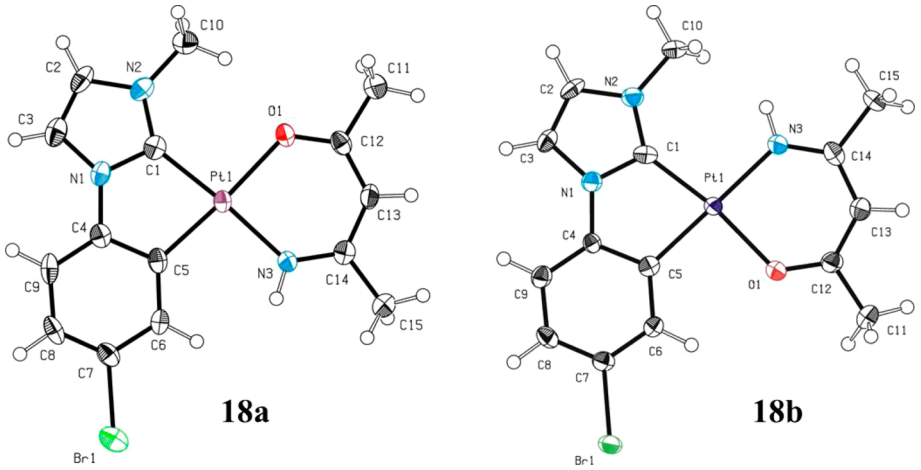

Figure 4. ORTEP representation of complexes **18a**,**b**. Thermal ellipsoids are drawn at the 50% probability level, and solvent molecules are omitted for clarity. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **18a**: Pt(1)−C(1), 1.964(5); Pt(1)−C(5), 2.000(4); Pt(1)−O(1), 2.077(2); Pt(1)−N(3), 2.013(3); O(1)−Pt(1)−N(3), 89.20(12); C(1)−Pt(1)−C(5), 80.79(19); C(4)−N(1)−C(1)−Pt(1), −1.0(5). Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **18b**: Pt(1)−C(1), 1.929(6); Pt(1)−C(5), 1.987(6); Pt(1)−O(1), 2.037(4); Pt(1)−N(3), 2.022(5); O(1)−Pt(1)−N(3), 89.42(19); C(1)−Pt(1)−C(5), 80.3(3); C(4)−N(1)−C(1)−Pt(1), −1.12(10).

signal for its neighboring hydrogen atom changed into a characteristic PtCC*H* signal (pseudo-triplet).

All complexes were fully characterized by two-dimensional ^{1}H and ^{13}C NMR (COSY, HSQC, HMBC and NOESY) spectroscopy to unambiguously assign all signals. Generally, significant differences between the two isomers were found (see the Supporting Information, Figures S1−S7). A characteristic long-range ^{1}H−^{195}Pt coupling, resulting in the formation of a pseudo-triplet ($J_{H,Pt}$ = 21.0−31.3 Hz), was observed (signal 15, Figure 2). For the **b** isomers this coupling constant is on average 6 Hz smaller. The ^{13}C carbene signal (NCN) was observed at 160.6−162.9 ppm for the **a** isomers and at the higher field of 150.0−152.8 ppm for the **b** isomers, indicating a greater electron density at the carbene carbon atom with an oxygen atom at the opposite coordination site. As an example, the COSY and HMBC spectra of **17a** are given in Figure 2.

To distinguish between the two isomers, NOESY experiments were conducted for all **a** and **b** isomers. Using the very characteristic signals of the NCH_3 group and the pseudo-triplet adjacent to the Pt−C bond (PtCC*H*), a coupling with the proton of the N*H* group of the auxiliary ligand could be observed. The **a** isomers were identified as the complexes with the NH group directly opposite the PtCCH group, where no coupling is observed for the NCH$_3$ group.

Solid-State Structure Determination. To unambiguously assign the three-dimensional structure of the two isomers and to verify the expected square-planar coordination of the platinum atom, single crystals suitable for X-ray diffraction were obtained by slow evaporation of solvent from a saturated dichloromethane solution of the complexes **17b**, **18a**,**b**, **19b**, **20a**, and **21a**,**b** (Figures 3−5) and the *β*-ketoimine ligands **13** and **14** (Figure 1). Details of the solid-state structure

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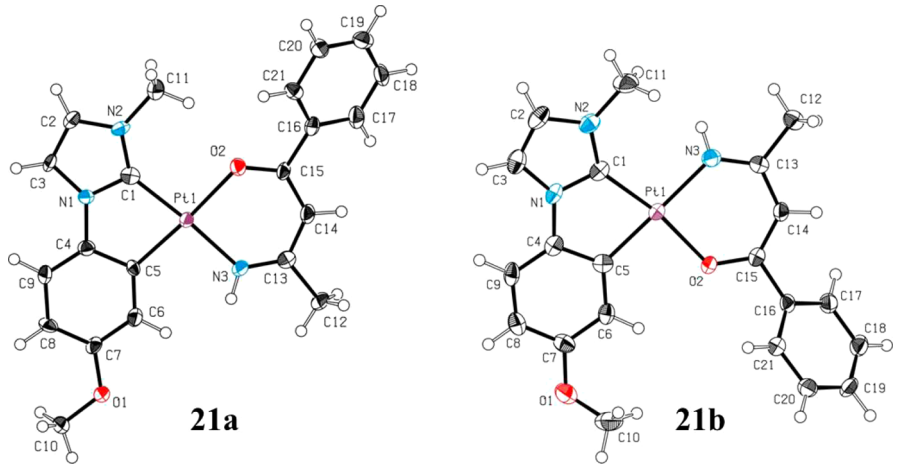

Figure 5. ORTEP representation of complexes **21a** and **21b**. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **21a**: Pt(1)−C(1), 1.980(7); Pt(1)−C(5), 1.998(7); Pt(1)−O(2) 2.058(4); Pt(1)−N(3), 2.023(5); O(2)−Pt(1)−N(3), 89.3(2); C(1)−Pt(1)−C(5), 80.6(3); C(4)−N(1)−C(1)−Pt(1), 4.2(8); O(2)−C(15)−C(16)−C(17) −154.8(6). Selected bond lengths (Å), angles (deg), and dihedral angles (deg) for **21b**: Pt(1)−C(1), 1.951(4); Pt(1)−C(5), 2.000(4); Pt(1)−O(2) 2.049(2); Pt(1)−N(3), 2.049(3); O(2)−Pt(1)−N(3), 89.70(11); C(1)−Pt(1)−C(5), 80.22(15); C(4)−N(1)−C(1)−Pt(1), 0.3(4); O(2)−C(15)−C(16)−C(17), 140.9(3).

determination are given in the Supporting Information (Tables S1 and S2).

All solid-state structures show an almost perfectly square-planar coordinated metal ion. The Pt−C bond lengths are different, and the distance between the metal and the carbene carbon atom C1 (1.93−1.98 Å) is shorter than the distance to the cyclometalated carbon atom C5 (1.99−2.00 Å). The planarity becomes even more obvious from the small dihedral angles in the central five-membered ring with the platinum(II) center. The C1−Pt1−C5 angle (about 80°) deviates significantly from the perfect 90° angle, whereas the O−Pt1−N angle of the ketoimine ligand (about 88°) is nearly ideal for a square-planar coordination geometry. Similar angles and bond lengths have been described before for other cyclometalated platinum(II) NHC complexes with β-diketonates.[26,28−30,45]

For all solid-state structures the platinum−carbene bond as well as the platinum−oxygen bond is always slightly shorter for the **b** isomers, while the Pt−N contact is longer in comparison to the **a** isomers (Figures 4 and 5). All complexes form zigzag patterns throughout the crystal with intermolecular Pt−Pt distances ranging from 3.33 to 7.07 Å (see the Supporting Information, Figures S8−S11).

Photoluminescence Properties. To investigate the potential application of the synthesized compounds as emitters in phosphorescent organic light-emitting devices (PhOLEDs) and to compare them to their acetylacetonate analogues,[26] the absorption and emission behavior of complexes **16**−**22** was investigated (see the Supporting Information, Figures S12−S18).[46] To determine intermolecular interactions of the square-planar Pt(II) compounds during the photoluminescence process, efforts were made to create pure emitter films. In some cases this was not successful due to early crystallization. Figure 6 shows the absorption spectra of the 100% film measurements.

The strongest absorption peak is found below 250 nm for all complexes. The transition with the highest energy can be attributed to the $^1\pi-\pi^*$ transition of the NHC ligand. Further MLCT d−π^* transitions are found at around 300 and 350 nm. For complexes **21a,b** these are found at even lower energies at about 370 nm. All pure film samples showed very low quantum

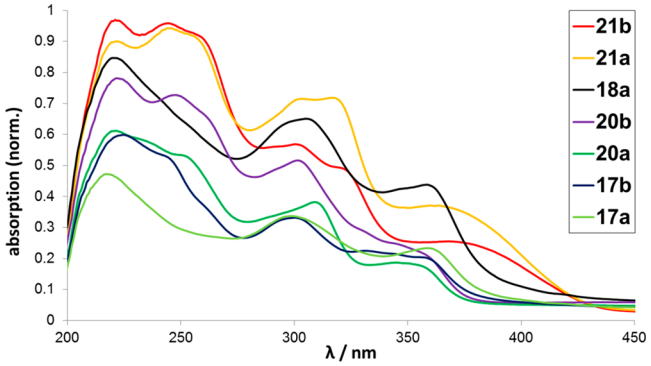

Figure 6. Absorption spectra of selected complexes in 100% films at room temperature. Annotations in the legend are given in the same order as the traces at 220 nm.

yields and broad unstructured emission bands (see the Supporting Information, Figure S19). The chloro-substituted complexes **17a,b** showed even higher quantum yields and a red-shifted emission in comparison to the diluted samples in poly(methyl methacrylate) (PMMA).

The absorption spectra were also measured in doped PMMA films (2 wt % complex). The spectra for the **a** isomers are given in Figure 7. They display a different number of peaks starting from the high-energy absorption below 250 nm and additional peaks around 300 and 350 nm. Most complexes show the same absorption behavior, where the high-energy peak can be assigned to a spin-allowed $^1\pi-\pi^*$ transition within the cyclometalated ligand, while the transitions at higher wavelengths can be attributed to d−π^* metal to ligand charge-transfer (MLCT) processes between the platinum metal atom and the cyclometalated ligand. The **b** isomers show very similar behavior, with only minor deviations in the low-energy region (see the Supporting Information).

All complexes emit in the blue to green region of the visible spectrum (Table 1, Figure 8) with maxima red-shifted by up to 33 nm (for the **a** isomers) in comparison to their acac analogues[26] (see the Supporting Information, Figure S20). A comparison of the respective isomers reveals a good agreement,

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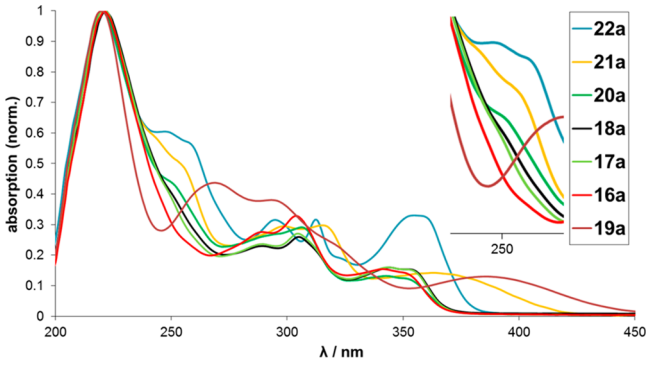

Figure 7. Normalized absorption spectra of complexes **16a**–**22a** at room temperature (2 wt % in PMMA). Annotations in the legend are given in the same order as the traces in the insert.

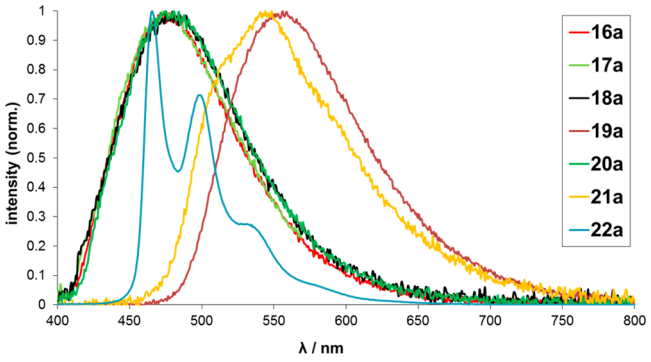

Figure 8. Normalized emission spectra of complexes **16a**–**22a** at room temperature (2 wt % in PMMA).

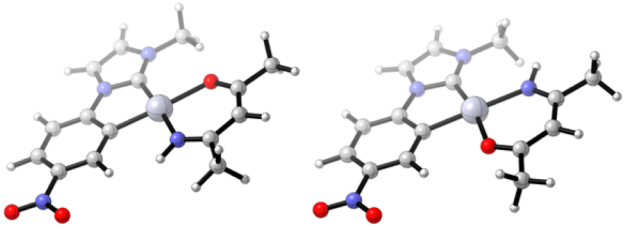

Figure 9. Optimized structures of **19a** (left) and **19b** (right) in the singlet ground state (B3LYP/6-31G(d)).

although some **b** isomers are slightly red-shifted to higher wavelengths. Generally the obtained **b** isomers show significantly lower quantum yields than the corresponding **a** isomers (Table 1).

Quantum Chemical Calculations. For geometry optimization of the singlet ground states and triplet states of all complexes the B3LYP functional was used together with a 6-31G(d) basis set and an ECP for platinum. BP86/6-31G(d) was used for the prediction of the emission wavelengths.

All complexes show a square-planar coordination and no twisting of the ligands in the singlet ground state (see Figure 9). Substitution at the cyclometalated phenyl ring has no significant impact on the bonding situation around the metal center. For both isomers the carbene–platinum bond is the shortest contact and the bond trans to the cyclometalated ring is always the longest. Both isomers show similar features at first glance, but the H–N–C angle in the *β*-ketoimine is always smaller for the **b** isomers (about 112°, vs >113° for **a** isomers), hinting at a slightly stronger steric interaction with the methyl group of the NHC ligand on the opposite side. Indeed, all **a** isomers are calculated to be thermodynamically favored by about 5 kcal/mol (Table S3, Supporting Information). This preference may also result from an O–H interaction between the oxygen of the auxiliary ligand and a hydrogen atom from the NHC ligand. While the O–H distance in the **a** isomers (O–*H*CH$_2$N) is found to be about 2.10 Å, for the **b** isomers (O–*H*C$_{arom}$) it increases to 2.47 Å. Experimentally, the ^{1}H NMR spectra confirm this observation, since the resonance of the NMe group is shifted to lower field because of the O–H interaction for the **a** isomers (see the Supporting Information, Figure S1). However, the signal of the hydrogen atom next to the C–Pt bond is significantly shifted to lower field for the **b** isomers. Again no substantial influence of the substituents at

Table 1. Photoluminescence Data (2 wt % in PMMA, Room Temperature) of the Cyclometalated Complexes

	λ_{exc} (nm)[a]	CIE *x*;*y*[b]	λ_{em} (nm)[c]	ϕ[d]	τ_o (μs)[e]	k_r (10^3 s^{-1})[f]	k_{nr} (10^3 s^{-1})[g]
16a	350	0.185;0.269	476	0.12	19.4	51.4	363.5
16b	355	0.203;0.319	483	0.05			
17a	355	0.185;0.267	476	0.15	3.1	322.2	1900.0
17b	355	0.199;0.307	480	0.06			
18a	370	0.193;0.287	479	0.05			
18b	350	0.209;0.344	493	0.03			
18(acac)[h]	310	0.171;0.163	446	0.05	85.1	11.7	248.7
19a	355	0.430;0.547	555	0.31	23.1	43.2	96.2
19b	355	0.424;0.547	553	0.20	37.3	26.8	105.3
19(acac)[h]	355	0.362;0.469	546	0.11	91	9.0	70.6
20a	355	0.193;0.291	478	0.15	51.2	19.5	111.7
20b	355	0.215;0.337	491	0.05			
20(acac)[h]	355	0.167;0.157	456	0.32	24	26.9	56.5
21a	350	0.383;0.554	544	0.14	25.9	38.6	243.1
21b	350	0.411;0.536	553	0.07			
22a	355	0.156;0.297	464, 498	0.74	19.3	51.9	18.4
22(acac)[h]	355	0.162;0.314	463, 497	0.90	23	39.9	4.7

[a]Excitation wavelength. [b]CIE coordinates at room temperature. [c]Maximum emission wavelength. [d]Quantum yield at λ_{exc}; N_2 atmosphere. [e]Decay lifetimes (excited by laser pulses (355 nm, 1 ns)) given as $\tau_o = \tau_v/\phi$. [f]$k_r = \phi/\tau_v$. [g]$k_{nr} = (1 - \phi)/\tau_v$. [h]Complexes with the same NHC ligand but with an acac auxiliary ligand.[26]

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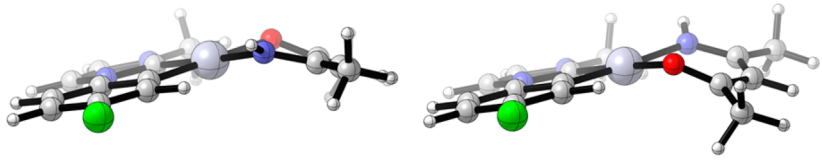

Figure 10. Optimized structures for **17a** (left) and **17b** (right) in the lowest triplet state as examples of changes in the ligand backbone upon excitation (B3LYP/6-31G(d)).

the phenyl ring was found with complexes **19** (electron withdrawing) and **20** (electron donating), showing almost the same energy difference for the isomers.

A recently developed method[47] using BP86 to reliably predict the emission wavelength of transition-metal complexes allowed us to predict the emission maxima with good accuracy (Table S4, Supporting Information). The largest deviation between predicted and experimentally determined wavelength was found for **20a** at 34 nm. On average the deviation for all complexes was found to be 9 nm.

Additionally, the frontier molecular orbitals and spin densities were calculated for the **a** isomers (Figures S21 and S22, Supporting Information). These calculations reveal that the density for the excited state lies on the auxiliary ligands, with the exception of complexes **19** and **22**, which clearly show NHC-centered emission properties.

Geometry optimizations for the T_1 state showed significant reorganization effects upon excitation for most complexes. As expected, the optimized bond distances around the Pt center increase slightly. With the exception of **19a,b** and **22a,b** this was also accompanied by large changes in the angle of the NHC−Pt−ketoimine backbone of up to 40° (Figure 10). This twisting of the auxiliary ligand is not uncommon for planar Pt(II) complexes with low to moderate quantum yields and is often encountered with halide ligands[48] as well as with acac analogues with bromo and methoxy and without a substituent at the cyclometalating ring.[26] It is interesting to note that the compounds with the least changes have shown the best quantum yields in the photophysical experiments.

CONCLUSION

We synthesized the first C^C*-cyclometalated heteroleptic platinum(II) complexes with different aryl-substituted NHC ligands and β-ketoimine ligands. Only a small number of examples of the recently introduced new class of platinum(II) compounds with cyclometalated carbenes have previously been reported, in general with symmetrical counter ligands such as acetylacetonate (acac). These had the advantage that no isomers were formed during the synthesis. Changing one of the oxygens of the acac ligand to a NH group allowed us to study the influence on the emission process. We therefore had to accept that isomers are formed but succeeded in separating and characterizing them individually. Solid-state structures of seven complexes could be obtained, confirming a square-planar geometry of the heteroleptic complexes. In comparison to the corresponding acac complexes the quantum yields are lower, but other photophysical properties such as the color coordinates or especially the short decay lifetimes make them very interesting compounds. Additionally a quantum yield of 74% for the dibenzofuran complex **22a** is still impressive and indicates that the complexes are a promising class of triplet emitters for PhOLEDs. Experimentally determined photophysical data and the measured emission behavior agree very well with predicted values obtained by DFT calculations.

EXPERIMENTAL SECTION

General Comments. Solvents of at least 99.5% purity were used throughout this study. Dry solvents were obtained through standard procedures and stored under argon over molecular sieves 4 Å. Imidazoles **2**−**5** were prepared according to literature procedures.[40,49] Imidazole **6** was not isolated and was used without further purification for the synthesis of the imidazolium salt. The corresponding imidazolium iodides **8**−**12** were prepared according to a previously described procedure.[26] The β-ketoimine ligands **13** and **14** were prepared by a modified method derived from a known literature procedure.[43] Potassium tetrachloroplatinate(II) was obtained from Pressure Chemicals Co. All other chemicals were obtained from common suppliers and used without further purification. ^{1}H NMR, ^{13}C NMR, and ^{19}F NMR spectra were recorded at 298 K. ^{1}H NMR and ^{13}C NMR spectra were referenced internally using the resonances of the solvent (^{1}H 7.26 ppm and ^{13}C 77.0 ppm for $CDCl_3$; ^{1}H 2.50 ppm and ^{13}C 39.43 ppm for DMSO-d_6). ^{19}F NMR spectra were referenced externally against trifluoromethylbenzene ($F_3CC_6H_5$). Shifts are given in ppm and coupling constants J in Hz. Elemental analyses were performed by the microanalytical laboratory of our institute. Some of the microanalytical data deviate, as the isomers were hard to separate and purify (extensive flash chromatography), but we succeeded and even got solid-state structures from some of the separated compounds. The problem with these particular compounds was that methylene chloride from the flash chromatography could not be removed efficiently in vacuo (see the Supporting Information Figures S3−S7). Even under high vacuum (10^{-5} mbar) not all traces of the solvent could be removed. Heating of the colorful solids under reduced pressure led to a color change and degradation (validated by ^{1}H NMR).

The melting points have been determined using a standard system and are not corrected. The photoluminescence of the complexes was measured in thin PMMA films doped with 2 wt % emitter or in 100% emitter films. The 2 wt % films were prepared by doctor-blading a solution of emitter (2 mg/mL) 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 355−370 nm (Xe lamp with monochromator), and emission was detected with a calibrated CCD spectrometer. 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 (MCS) technique.

1-(4-Fluorophenyl)imidazole (1). An 11.1 g portion (0.1 mol) of 4-fluoroaniline in 50.0 mL of methanol was treated with 16.2 mL (0.1 mol) of glyoxal (30% aqueous) for 16 h at room temperature. After this period a yellowish mixture was formed. Then 10.7 g (0.2 mol) of ammonium chloride was added followed by 37% aqueous formaldehyde (16.0 mL, 0.2 mol). The mixture was diluted with methanol (400.0 mL) and refluxed for 1 h before H_3PO_4 (14.0 mL, 85%) was slowly added. The resulting mixture was then stirred at reflux for another 8 h. After removal of the solvent, the dark residue was poured onto ice (300 g). KOH solution (1 N) was used to adjust the pH value to pH 9. The crude product was extracted with CH_2Cl_2, the combined organic layers were dried over $MgSO_4$ and filtered, and the solvent was removed in vacuo. The product was subsequently purified by distillation and obtained as a colorless oil (12.1 g, 75%). ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 7.11 (s, 1H, NC*H*CHN), 7.18 (s, 1H, NCHC*H*N), 7.25 (m, 2H, CH_{arom}), 7.38 (m, 2H, CH_{arom}), 7.79 (s, 1H,

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NC*H*N). ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ 116.6 (d, $J_{F,C}$ = 23.0 Hz, CH_{arom}), 118.5 (NCHCHN), 123.4 (d, $J_{F,C}$ = 8.6 Hz, CH_{arom}), 130.5 (NCHCHN), 133.5 (d, $J_{F,C}$ = 2.8 Hz, NC_{arom}), 135.7 (NCHN), 161.0 (d, $J_{F,C}$ = 247.2 Hz, FC_{arom}). ^{19}F NMR ($CDCl_3$, 282.4 MHz): δ −114.0. Anal. Calcd for $C_9H_7FN_2$: C, 66.66; H, 4.35; N, 17.27. Found: C, 66.61; H, 4.34; N, 17.51.

1-(4-Fluorophenyl)-3-methylimidazolium Iodide (7). A sealed tube was charged with 811 mg (5.0 mmol) of 1-(4-fluorophenyl)-imidazole and 5 mL of THF. A 781 mg portion (5.5 mmol) of methyl iodide was added, and the reaction mixture was stirred for 17 h at 100 °C. A yellowish precipitate formed, which was separated and washed with THF and diethyl ether. Drying in vacuo gave a white solid as the product (1.38 g, 91%). Mp: 168−170 °C. ^{1}H NMR (DMSO-d_6, 300.13 MHz): δ 3.95 (s, 3H, NCH_3), 7.55 (t, J = 8.8 Hz, 2H, CH_{arom}), 7.84 (dd, J_1 = 4.6 Hz, J_2 = 9.0 Hz, 2H, CH_{arom}), 7.95 (s, 1H, NCHC*H*N), 8.26 (s, 1H, NC*H*CHN), 9.73 (s, 1H, NC*H*N). ^{13}C NMR (DMSO-d_6, 75.475 MHz): δ 36.1 (NCH_3), 117.0 (d, $J_{F,C}$ = 23.6 Hz, CH_{arom}), 121.3 (NCHCHN), 124.2 (NCHCHN), 124.4 (d, $J_{F,C}$ = 9.1 Hz, $NCCH_{arom}$), 131.2 (d, $J_{F,C}$ = 3.0 Hz, NC_{arom}), 136.1 (NCHN), 162.1 (d, $J_{F,C}$ = 247.1 Hz, FC_{arom}). Anal. Calcd for $C_{10}H_{10}FIN_2$: C, 39.50; H, 3.31; N, 9.21. Found: C, 39.75; H, 3.21; N, 9.20.

4-Amino-3-penten-2-one (13). The β-ketoimine ligand was obtained by the modification of a known literature procedure.[43] A 10.02 g amount (100 mmol) of acetylacetone was dissolved in 100 mL of methanol, and 7.81 g (100 mmol) of ammonium carbamate was added at room temperature. The solution was stirred for 2 h before evaporation of the solvent at reduced pressure. Further drying in vacuo gave the colorless crystalline product (9.25 g, 93%). Mp: 31 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 1.90 (s, 3H, $NCCH_3$), 2.02 (s, 3H, $OCCH_3$), 5.02 (s, 1H, C*H*), 5.24 (s, 1H, O-HN*H*), 9.70 (s, 1H, O-*H*NH). ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ 22.2 ($NCCH_3$), 29.2 ($OCCH_3$), 95.7 (CH), 160.8 (CH_3CNH_2), 196.7 (CH_3CO). Anal. Calcd for C_5H_9NO: C, 60.58; H, 9.15; N, 14.13. Found: C, 60.35; H, 9.35; N, 13.95.

3-Amino-1-phenyl-2-buten-1-one (14). For the synthesis of the second β-ketoimine ligand we also used the procedure described above. To 10 mL of methanol were added in succession a 1.62 g (10 mmol) portion of 1-benzoylacetone and 0.78 g (10 mmol) of ammonium carbamate, and the suspension was stirred for 24 h at room temperature. The solvent was removed in vacuo and the residue washed with diethyl ether to give the product as a white solid (1.21 g, 75%). Mp: 132−134 °C. ^{1}H NMR ($CDCl_3$, 300.13 MHz): δ 2.06 (s, 3H, $NCCH_3$), 5.24 (s, 1H, O-HN*H*), 5.74 (s, 1H, C*H*), 7.42 (m, 3H, CH_{arom}), 7.88 (dd, J_1 = 1.8 Hz, J_2 = 7.8 Hz, 2H, CH_{arom}), 10.23 (s, 1H, O-*H*NH). ^{13}C NMR ($CDCl_3$, 75.475 MHz): δ 22.9 ($NCCH_3$), 92.3 (CH), 127.1 (CH_{arom}), 128.2 (CH_{arom}), 130.8 (CH_{arom}), 104.2 ($C_{arom}CO$), 162.8 (CH_3CNH_2), 189.5 (PhCO). Anal. Calcd for $C_{10}H_{11}NO$: C, 74.51; H, 6.88; N, 8.69. Found: C, 74.36; H, 7.22; N, 8.65.

Dichloro(1,5-cyclooctadiene)platinum (Pt(COD)Cl_2, 15). The published synthesis of dichloro(1,5-cyclooctadiene)platinum(II)[50] was modified in the following way: potassium tetrachloroplatinate (K_2PtCl_4, 2.00 g, 4.8 mmol) was dissolved in a solution of 53.0 mL of water and 63.0 mL of acetic acid. To the light red solution was added 1.6 mL (1.36 g, 12.6 mmol) of 1,5-cyclooctadiene. The reaction mixture was stirred rapidly and heated to 110 °C. Over 3 h the solution became pale yellow and a white precipitate was formed. The volume of the solution was reduced to about 20 mL by evaporation under reduced pressure. The precipitate was collected and washed in succession with small portions of water, ethanol, and diethyl ether. The product was dried in vacuo to give white needles (1.71 g, 95%). Dec pt: >230 °C. ^{1}H NMR (DMSO-d_6, 300.13 MHz): δ 2.25 (m, 4H, CH_2), 2.60 (m, 4H, CH_2), 5.50 (t, $J_{H,Pt}$ = 33.0 Hz, 4H, C*H*). ^{13}C NMR (DMSO-d_6, 75.475 MHz): δ 30.3 (CH_2), 100.2 (t, $J_{C,Pt}$ = 76.0 Hz, *C*H). Anal. Calcd for $C_8H_{12}Cl_2Pt$: C, 25.68; H, 3.23. Found: C, 25.68; H, 3.18.

Preparation of Platinum(II) Complexes. General Procedure. A 0.8 mmol portion of the imidazolium salt and 93 mg (0.4 mmol) of silver(I) oxide were dissolved in 20 mL of dry 1,4-dioxane, and the mixture was stirred for 16 h at room temperature under an argon atmosphere. After addition of 10 mL of 2-butanone and 299 mg (0.8 mmol) of dichloro(1,5-cyclooctadiene)platinum(II) the reaction mixture was heated and refluxed for 16 h. The solvent was removed and the residue dissolved in 20 mL of DMF. A 3.2 mmol portion of the β-ketoimine and 359 mg (3.2 mmol) of potassium-*tert*-butanolate were added. The mixture was then stirred for 16 h at room temperature and for another 6 h at 100 °C under argon. After filtration all volatiles were removed under reduced pressure and the residue washed with water, followed by column chromatography with dichloromethane as eluent, yielding the two separated isomers **a** and **b** (silica gel KG60).

(SP-4-4)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-fluorophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) ***(16a)***. A 243 mg (0.8 mmol) portion of 1-(4-fluorophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **a** was obtained as a light green solid (115 mg, 31%). Mp: 215−218 °C. ^{1}H NMR ($CDCl_3$, 600.16 MHz): δ 1.97 (s, 3H, $OCCH_3$), 2.07 (s, 3H, $NCCH_3$), 4.13 (s, 3H, NCH_3), 5.09 (d, J = 2.3 Hz, 1H, C*H*), 6.71 (dt, J = 2.6 Hz, J = 8.5 Hz, 1H, CH_{arom}), 6.78 (d, J = 1.8 Hz, 1H, NCHC*H*NCH_3), 6.91 (dd, $J_{H,H}$ = 8.4 Hz, $J_{H,F}$ = 4.8 Hz, 1H, CH_{arom}), 7.00 (ddt, $J_{H,H}$ = 2.6 Hz, $J_{H,F}$ = 9.7 Hz, $J_{H,Pt}$ = 31.8 Hz, 1H, $PtCCH_{arom}$), 7.18 (d, J = 1.9 Hz, 1H, NC*H*$CHNCH_3$), 7.42 (s, 1H, PtN*H*). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 26.9 ($OCCH_3$), 28.3 ($NCCH_3$), 34.7 (NCH_3), 98.4 (CH), 108.6 (d, $J_{C,F}$ = 23.8 Hz, $FCCH_{arom}$), 111.1 (d, $J_{C,F}$ = 8.9 Hz, $NCCH_{arom}$), 113.9 ($NCHCHNCH_3$), 116.2 (d, $J_{C,F}$ = 19.9 Hz, $PtCCH_{arom}$), 121.2 ($NCHCHNCH_3$), 126.9 (d, $J_{C,F}$ = 4.8 Hz, NC_{arom}), 143.9 (PtC_{arom}), 159.2 (d, $J_{C,F}$ = 244.1 Hz, FC_{arom}), 160.8 (NCN), 163.4 ($NCCH_3$), 176.9 ($OCCH_3$). Anal. Calcd for $C_{15}H_{16}FN_3OPt$: C, 38.46; H, 3.44; N, 8.97. Found: C, 38.57; H, 3.15; N, 8.63.

(SP-4-3)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-fluorophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) ***(16b)***. A 243 mg (0.8 mmol) portion of 1-(4-fluorophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **b** was obtained as a light green solid (20 mg, 5%). Mp: 241−244 °C. ^{1}H NMR ($CDCl_3$, 600.16 MHz): δ 2.00 (s, 3H, $NCCH_3$), 2.09 (s, 3H, $OCCH_3$), 3.83 (s, 3H, NCH_3), 5.10 (d, J = 2.3 Hz, 1H, C*H*), 6.70 (m, 2H, CH_{arom}, NCHC*H*NCH_3), 6.88 (dd, $J_{H,H}$ = 8.4 Hz, $J_{H,F}$ = 4.5 Hz, 1H, CH_{arom}), 7.15 (d, J = 2.1 Hz, 1H, NC*H*$CHNCH_3$), 7.68 (m, $J_{H,H}$ = 2.8 Hz, $J_{H,F}$ = 9.4 Hz, $J_{H,Pt}$ = 24.0 Hz, 2H, PtN*H*, $PtCCH_{arom}$). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 27.1 ($OCCH_3$), 28.8 ($NCCH_3$), 35.9 (NCH_3), 98.3 (CH), 108.8 (d, $J_{C,F}$ = 25.1 Hz, $FCCH_{arom}$), 110.3 (d, $J_{C,F}$ = 8.3 Hz, $NCCH_{arom}$), 114.1 ($NCHCHNCH_3$), 117.9 (d, $J_{C,F}$ = 19.9 Hz, $PtCCH_{arom}$), 121.1 ($NCHCHNCH_3$), 139.8 (d, $J_{C,F}$ = 5.3 Hz, NC_{arom}), 142.8 (PtC_{arom}), 150.3 (NCN), 160.2 (d, $J_{C,F}$ = 244.2 Hz, FC_{arom}), 163.5 ($NCCH_3$), 177.3 ($OCCH_3$).

(SP-4-4)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-chlorophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) ***(17a)***. A 257 mg (0.8 mmol) portion of 1-(4-chlorophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **a** was obtained as a light green solid (170 mg, 44%). Mp: 195−200 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 1.97 (s, 3H, $OCCH_3$), 2.09 (s, 3H, $NCCH_3$), 4.14 (s, 3H, NCH_3), 5.10 (d, J = 2.3 Hz, 1H, C*H*), 6.81 (d, J = 2.0 Hz, 1H, NCHC*H*NCH_3), 6.89 (d, J = 8.2 Hz, 1H, CH_{arom}), 7.01 (dd, J_1 = 2.1 Hz, J_2 = 8.2 Hz, 1H, CH_{arom}), 7.19 (d, J = 2.0 Hz, 1H, NC*H*$CHNCH_3$), 7.24 (dt, $J_{H,H}$ = 2.1 Hz, $J_{H,Pt}$ = 30.8 Hz, 1H, $PtCCH_{arom}$), 7.46 (s, 1H, PtN*H*). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 26.9 ($OCCH_3$), 28.3 ($NCCH_3$), 34.8 (NCH_3), 98.5 (CH), 111.4 ($NCCH_{arom}$), 114.0 ($NCHCHNCH_3$), 121.4 ($NCHCHNCH_3$), 122.6 ($ClCCH_{arom}$), 126.5 (NC_{arom}), 128.8 (ClC_{arom}), 129.3 ($PtCCH_{arom}$), 146.4 (PtC_{arom}), 161.4 (NCN), 163.5 ($NCCH_3$), 176.9 ($OCCH_3$). Anal. Calcd for $C_{15}H_{16}ClN_3OPt$: C, 37.16; H, 3.33; N, 8.67. Found: C, 37.30; H, 3.17; N, 8.65.

(SP-4-3)-(4-aminopent-3-en-2-one-κN,κO)[1-(4-chlorophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) ***(17b)***. A 257 mg (0.8 mmol) portion of 1-(4-chlorophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **b** was obtained as a light green

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solid (60 mg, 15%). Mp: 210−215 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 2.00 (s, 3H, NCCH_3), 2.10 (s, 3H, OCCH_3), 3.83 (s, 3H, NCH_3), 5.10 (d, J = 2.3 Hz, 1H, CH), 6.72 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 6.85 (d, J = 8.2 Hz, 1H, CH_{arom}), 7.00 (dd, J_1 = 2.3 Hz, J_2 = 8.2 Hz, 1H, CH_{arom}), 7.15 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 7.68 (s, 1H, PtNH), 7.91 (dt, $J_{H,H}$ = 2.3 Hz, $J_{H,Pt}$ = 24.0 Hz, 1H, PtCCH_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 27.1 (OCCH_3), 28.8 (NCCH_3), 35.9 (NCH_3), 98.3 (CH), 110.6 (NCCH_{arom}), 114.1 (NCHCHNCH$_3$), 121.3 (NCHCHNCH$_3$), 122.6 (ClCCH_{arom}), 129.7 (NC$_{arom}$), 131.1 (PtCCH_{arom}), 138.9 (PtC$_{arom}$), 145.2 (ClC$_{arom}$), 150.9 (NCN), 163.4 (NCCH_3), 177.3 (OCCH_3). Anal. Calcd for $C_{15}H_{16}ClN_3OPt$: C, 37.16; H, 3.33; N, 8.67. Found: C, 37.06; H, 3.04; N, 8.83.

(SP-4-4)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-bromophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**18a**). A 292 mg (0.8 mmol) portion of 1-(4-bromophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **a** was obtained as a light orange solid (172 mg, 41%). Mp: 208−211 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 1.97 (s, 3H, OCCH_3), 2.09 (s, 3H, NCCH_3), 4.14 (s, 3H, NCH_3), 5.10 (d, J = 2.3 Hz, 1H, CH), 6.81 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 6.85 (d, J = 8.2 Hz, 1H, CH_{arom}), 7.16 (dd, J_1 = 2.0 Hz, J_2 = 8.2 Hz, 1H, CH_{arom}), 7.19 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 7.39 (dt, $J_{H,H}$ = 2.0 Hz, $J_{H,Pt}$ = 30.3 Hz, 1H, PtCCH_{arom}), 7.44 (s, 1H, PtNH). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 26.9 (OCCH_3), 28.3 (NCCH_3), 34.7 (NCH_3), 98.4 (CH), 111.9 (NCCH_{arom}), 113.9 (NCHCHNCH$_3$), 117.1 (NC$_{arom}$), 121.4 (NCHCHNCH$_3$), 125.5 (BrCCH_{arom}), 127.1 (PtC$_{arom}$), 132.0 (PtCCH_{arom}), 146.8 (BrC$_{arom}$), 161.4 (NCN), 163.5 (NCCH_3), 176.8 (OCCH_3). Anal. Calcd for $C_{15}H_{16}BrN_3OPt$: C, 34.04; H, 3.05; N, 7.94. Found: C, 34.35; H, 3.35; N, 7.64.

(SP-4-3)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-bromophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**18b**). A 292 mg (0.8 mmol) portion of 1-(4-bromophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **b** was obtained as a light orange solid (61 mg, 14%). Mp: 217−220 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 2.00 (s, 3H, NCCH_3), 2.10 (s, 3H, OCCH_3), 3.82 (s, 3H, NCH_3), 5.10 (d, J = 2.3 Hz, 1H, CH), 6.71 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 6.80 (d, J = 8.2 Hz, 1H, CH_{arom}), 7.17−7.14 (m, 2H, NCHCHNCH$_3$, CH_{arom}), 7.67 (s, 1H, PtNH), 8.06 (dt, $J_{H,H}$ = 2.2 Hz, $J_{H,Pt}$ = 23.8 Hz, 1H, PtCCH_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 27.2 (OCCH_3), 28.8 (NCCH_3), 35.9 (NCH_3), 98.3 (CH), 111.2 (NCCH_{arom}), 114.1 (NCHCHNCH$_3$), 118.3 (NC$_{arom}$), 121.3 (NCHCHNCH$_3$), 125.5 (BrCCH_{arom}), 133.9 (PtCCH_{arom}), 139.6 (PtC$_{arom}$), 145.6 (BrC$_{arom}$), 151.0 (NCN), 163.4 (NCCH_3), 177.3 (OCCH_3). Anal. Calcd for $C_{15}H_{16}BrN_3OPt$: C, 34.04; H, 3.05; N, 7.94. Found: C, 33.93; H, 2.87; N, 7.67.

(SP-4-4)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-nitrophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**19a**). A 265 mg (0.8 mmol) portion of 1-(4-nitrophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **a** was obtained as a red-orange solid (151 mg, 38%). Dec pt: >275 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 2.01 (s, 3H, OCCH_3), 2.15 (s, 3H, NCCH_3), 4.18 (s, 3H, NCH_3), 5.15 (d, J = 2.3 Hz, 1H, CH), 6.88 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 7.04 (d, J = 8.6 Hz, 1H, CH_{arom}), 7.29 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 7.55 (s, 1H, PtNH), 7.98 (dd, J_1 = 2.3 Hz, J_2 = 8.6 Hz, 1H, CH_{arom}), 8.20 (dt, $J_{H,H}$ = 2.3 Hz, $J_{H,Pt}$ = 31.1 Hz, 1H, PtCCH_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 26.8 (OCCH_3), 28.3 (NCCH_3), 34.9 (NCH_3), 98.7 (CH), 110.2 (NCCH_{arom}), 114.3 (NCHCHNCH$_3$), 120.1 (O$_2$NCCH_{arom}), 122.4 (NCHCHNCH$_3$), 124.2 (PtCCH_{arom}), 126.1 (NC$_{arom}$), 143.8 (PtC$_{arom}$), 153.3 (NO$_2$C$_{arom}$), 162.9 (NCN), 164.0 (NCCH_3), 177.0 (OCCH_3). Anal. Calcd for $C_{15}H_{16}N_4O_3Pt$: C, 36.37; H, 3.26; N, 11.31. Found: C, 36.48; H, 3.05; N, 11.01.

(SP-4-3)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-nitrophenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**19b**). A 265 mg (0.8 mmol) portion of 1-(4-nitrophenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **b** was obtained as an orange solid (35 mg, 8.5%). Dec pt: >230 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 2.06 (s, 3H, NCCH_3), 2.17 (s, 3H, OCCH_3), 3.90 (s, 3H, NCH_3), 5.17 (d, J = 2.2 Hz, 1H, CH), 6.83 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 7.01 (d, J = 8.5 Hz, 1H, CH_{arom}), 7.27 (s, 1H, NCHCHNCH$_3$), 7.71 (s, 1H, PtNH), 7.96 (dd, J_1 = 2.5 Hz, J_2 = 8.5 Hz, 1H, CH_{arom}), 8.84 (dt, $J_{H,H}$ = 2.5 Hz, $J_{H,Pt}$ = 24.2 Hz, 1H, PtCCH_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 27.1 (OCCH_3), 28.9 (NCCH_3), 36.1 (NCH_3), 98.5 (CH), 109.5 (NCCH_{arom}), 114.6 (NCHCHNCH$_3$), 120.1 (O$_2$NCCH_{arom}), 122.2 (NCHCHNCH$_3$), 126.3 (PtCCH_{arom}), 138.5 (NC$_{arom}$), 144.5 (PtC$_{arom}$), 152.8 (NCN), 164.5 (NCCH_3), 177.8 (OCCH_3). Anal. Calcd for $C_{15}H_{16}N_4O_3Pt{\cdot}0.2CH_2Cl_2$: C, 35.63; H, 3.23; N, 10.93. Found: C, 35.95; H, 2.74; N, 10.87.

(SP-4-4)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-methoxyphenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**20a**). A 253 mg (0.8 mmol) portion of 1-(4-methoxyphenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **a** was obtained as a yellow solid (148 mg, 37%). Mp: 171−173 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 1.95 (s, 3H, OCCH_3), 2.02 (s, 3H, NCCH_3), 3.81 (s, 3H, OCH_3), 4.09 (s, 3H, NCH_3), 5.06 (d, J = 2.3 Hz, 1H, CH), 6.53 (dd, J_1 = 2.6 Hz, J_2 = 8.4 Hz, 1H, CH_{arom}), 6.74 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 6.87 (dt, $J_{H,H}$ = 3.5 Hz, $J_{H,Pt}$ = 31.3 Hz, 1H, PtCCH_{arom}), 6.89 (d, J = 6.7 Hz, 1H, CH_{arom}), 7.14 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 7.48 (s, 1H, PtNH). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 26.9 (OCCH_3), 28.2 (NCCH_3), 34.6 (NCH_3), 55.5 (OCH_3), 98.2 (CH), 105.7 (OCCH_{arom}), 110.7 (NCCH_{arom}), 113.8 (NCHCHNCH$_3$), 116.9 (PtCCH_{arom}), 120.9 (NCHCHNCH$_3$), 125.5 (NC$_{arom}$), 141.9 (PtC$_{arom}$), 155.8 (C$_{arom}$OCH$_3$), 160.6 (NCN), 163.1 (NCCH_3), 176.8 (OCCH_3). Anal. Calcd for $C_{16}H_{19}N_3O_2Pt{\cdot}0.2CH_2Cl_2$: C, 39.12; H, 3.93; N, 8.45. Found: C, 39.43; H, 3.52; N, 8.26.

(SP-4-3)-(4-Aminopent-3-en-2-one-κN,κO)[1-(4-methoxyphenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**20b**). A 253 mg (0.8 mmol) portion of 1-(4-methoxyphenyl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Isomer **b** was obtained as a yellow solid (63 mg, 16%). Mp: 185−188 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 1.99 (s, 3H, NCCH_3), 2.08 (s, 3H, OCCH_3), 3.83 (s, 3H, NCH_3), 3.87 (s, 3H, OCH_3), 5.09 (d, J = 2.1 Hz, 1H, CH), 6.57 (dd, J_1 = 2.7 Hz, J_2 = 8.4 Hz, 1H, CH_{arom}), 6.70 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 6.87 (d, J = 8.3 Hz, 1H, CH_{arom}), 7.15 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 7.61 (dt, $J_{H,H}$ = 2.7 Hz, $J_{H,Pt}$ = 23.0 Hz, 1H, PtCCH_{arom}), 7.69 (s, 1H, PtNH). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 27.1 (OCCH_3), 28.9 (NCCH_3), 35.9 (NCH_3), 55.4 (OCH_3), 98.2 (CH), 108.0 (OCCH_{arom}), 110.2 (NCCH_{arom}), 113.9 (NCHCHNCH$_3$), 116.6 (PtCCH_{arom}), 120.8 (NCHCHNCH$_3$), 138.0 (NC$_{arom}$), 140.6 (PtC$_{arom}$), 150.0 (NCN), 156.6 (C$_{arom}$OCH$_3$), 163.3 (NCCH_3), 177.1 (OCCH_3). Anal. Calcd for $C_{16}H_{19}N_3O_2Pt{\cdot}0.2CH_2Cl_2$: C, 39.12; H, 3.93; N, 8.45. Found: C 39.24, H 3.79; N, 8.15.

(SP-4-4)-(3-Amino-1-phenylbut-2-en-1-one-κN,κO)[1-(4-methoxyphenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**21a**). A 253 mg (0.8 mmol) portion of 1-(4-methoxyphenyl)-3-methylimidazolium iodide and 516 mg of 3-amino-1-phenyl-2-buten-1-one were reacted, following the general procedure described above. Isomer **a** was obtained as an orange solid (159 mg, 37%). Mp: 207−209 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 2.16 (s, 3H, NCCH_3), 3.85 (s, 3H, OCH_3), 4.21 (s, 3H, NCH_3), 5.68 (d, J = 2.2 Hz, 1H, CH), 6.57 (dd, J_1 = 2.5 Hz, J_2 = 8.4 Hz, 1H, CH_{arom}), 6.80 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 6.92 (t, $J_{H,Pt}$ = 29.7 Hz, 1H, PtCCH_{arom}), 6.93 (d, J = 10.5 Hz, 1H, NCCH_{arom}), 7.20 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 7.41−7.34 (m, 3H, CH_{arom}), 7.73 (s, 1H, PtNH), 7.83 (dd, J_1 = 1.7 Hz, J_2 = 7.8 Hz, 2H, OCCCH_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 28.8 (NCCH_3), 35.1 (NCH_3), 55.5 (OCH_3), 97.3 (CH), 105.8 (OCCH_{arom}), 110.8 (NCCH_{arom}), 113.8 (NCHCHNCH$_3$), 117.0 (PtCCH_{arom}), 120.9 (NCHCHNCH$_3$), 125.0 (NC$_{arom}$), 126.6 (CH_{arom}), 128.1 (CH_{arom}), 129.0 (CH_{arom}), 141.8 (PtC$_{arom}$), 142.1 (OCC$_{arom}$), 155.8 (C$_{arom}$OCH$_3$), 160.6 (NCN), 163.9 (NCCH_3), 172.7 (OCC$_{arom}$). Anal. Calcd for $C_{21}H_{21}N_3O_2Pt$: C, 46.49; H, 3.90; N, 7.75. Found: C, 46.36; H, 3.79; N, 7.47.

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*(SP-4-3)-(3-Amino-1-phenylbut-2-en-1-one-κN,κO)[1-(4-methoxyphenyl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**21b**).* A 253 mg (0.8 mmol) portion of 1-(4-methoxyphenyl)-3-methylimidazolium iodide and 516 mg of 3-amino-1-phenyl-2-buten-1-one were reacted, following the general procedure described above. Isomer **b** was obtained as an orange solid (58 mg, 13%). Mp: 193−195 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 2.11 (s, 3H, NCCH_3), 3.86 (s, 3H, NCH_3), 3.91 (s, 3H, OCH_3), 5.77 (d, J = 2.1 Hz, 1H, CH), 6.60 (dd, J_1 = 2.7 Hz, J_2 = 8.4 Hz, 1H, CH_{arom}), 6.71 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 6.90 (d, J = 8.4 Hz, 1H, CH_{arom}), 7.17 (d, J = 2.1 Hz, 1H, NCHCHNCH$_3$), 7.46−7.37 (m, 3H, CH_{arom}), 7.79 (dt, $J_{H,H}$ = 2.7 Hz, $J_{H,Pt}$ = 23.7 Hz, 1H, PtCCH_{arom}), 7.96 (s, 1H, PtNH), 8.06 (dd, J_1 = 2.1 Hz, J_2 = 7.5 Hz, 2H, OCCCH_{arom}). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 29.5 (NCCH$_3$) 35.9 (NCH$_3$), 55.4 (OCH$_3$), 96.5 (CH), 109.1 (OCCH$_{arom}$), 110.5 (NCCH$_{arom}$), 114.0 (NCHCHNCH$_3$), 116.2 (PtCCH$_{arom}$), 120.9 (NCHCHNCH$_3$), 126.9 (CH$_{arom}$), 128.2 (CH$_{arom}$), 129.3 (CH$_{arom}$), 138.1 (NC$_{arom}$), 140.6 (PtC$_{arom}$), 140.8 (OCC$_{arom}$), 149.6 (NCN), 156.6 (C$_{arom}$OCH$_3$), 164.2 (NCCH$_3$), 171.6 (OCC$_{arom}$). Anal. Calcd for $C_{21}H_{21}N_3O_2Pt{\cdot}0.15CH_2Cl_2$: C, 45.75; H, 3.87; N, 7.57. Found: C, 45.84; H, 3.95; N, 7.24.

*(SP-4-4)-(4-Aminopent-3-en-2-one-κN,κO)[1-(dibenzo[b,d]furan-4-yl)-3-methylimidazol-2-ylidene-κC,κC′]platinum(II) (**22a**).* A 301 mg (0.8 mmol) portion of 1-(dibenzo[*b*,*d*]furan-4-yl)-3-methylimidazolium iodide and 317 mg of 4-amino-3-penten-2-one were reacted, following the general procedure described above. Only isomer **a** was isolated as a yellow powder (109 mg, 25%). Dec pt: >260 °C. ^{1}H NMR ($CDCl_3$, 500.1 MHz): δ 1.99 (s, 3H, OCCH_3), 2.10 (NCCH_3), 4.21 (NCH_3), 5.12 (d, J = 2.2 Hz, 1H, CH), 6.89 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$), 7.31 (m, 2H, CH_{arom}), 7.41 (m, 1H, CH_{arom}), 7.60−7.52 (m, 2H, CH_{arom}), 7.67 (s, 1H, PtNH), 7.90 (d, J = 7.0 Hz, 1H, CH_{arom}), 8.06 (d, J = 2.0 Hz, 1H, NCHCHNCH$_3$). ^{13}C NMR ($CDCl_3$, 125.8 MHz): δ 26.9 (OCCH$_3$), 28.4 (NCCH$_3$), 34.6 (NCH$_3$), 98.3 (CH), 111.3 (CH$_{arom}$), 115.3 (CH$_{arom}$), 117.6 (NCHCHNCH$_3$), 120.2 (CH$_{arom}$), 120.7 (NCHCHNCH$_3$), 121.9 (C$_{arom}$), 122.8 (CH$_{arom}$), 123.7 (CH$_{arom}$), 124.9 (C$_{arom}$), 126.2 (CH$_{arom}$), 131.7 (C$_{arom}$), 143.1 (C$_{arom}$), 155.7 (C$_{arom}$), 161.7 (NCN), 163.2 (NCCH$_3$), 176.8 (OCCH$_3$). Anal. Calcd for $C_{21}H_{19}N_3O_2Pt$: C, 46.67; H, 3.54; N, 7.77. Found: C, 46.62; H, 3.22; N, 7.72.

Computational Details. All calculations were performed with the Gaussian09 package.[51] The density functional hybrid model B3LYP[52−56] and the gradient-corrected density functional BP86[53,57,58] were used together with the 6-31G(d)[59−64] basis set. No symmetry or internal coordinate constraints were applied during optimizations. All reported intermediates were verified as true minima by the absence of negative eigenvalues in the vibrational frequency analysis. In all cases platinum was described using a decontracted Hay−Wadt(n+1) ECP and basis set.[65,66]

Approximate free energies were obtained through thermochemical 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 under standard conditions (T = 298 K, p = 1 atm), using unscaled frequencies. For visualization GaussView[67] and CYLview[68] were used.

■ ASSOCIATED CONTENT

Supporting Information

CIF files, text, tables, and figures giving experimental details, crystallographic data, detailed spectra, and Cartesian coordinates for the optimized structures. This material is available free of charge via the Internet at http://pubs.acs.org. Crystallographic data are also available from the CCDC, under reference numbers 967277−967285.

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Notes

The authors declare no competing financial interest.

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