# **ORGANOMETALLICS**

# Phosphorescent Thiazol-2-ylidene Platinum(II) Complexes with $\beta$ -Ketoiminates: Single Isomer Formation by Ligand Architecture

Hendrik Leopold and Thomas Strassner\*

Physikalische Organische Chemie, Technische Universität Dresden, Bergstrasse 66, 01069 Dresden, Germany

# **Supporting Information**

**ABSTRACT:** We present the synthesis and photophysical properties of six novel *N*-phenyl-1,3-thiazol-2-ylidene platinum(II) complexes with sterically demanding *N*-aryl- $\beta$ -ketoiminate ligands. Diverse aryl substituents at the coordinating nitrogen atom (phenyl, mesityl, 2,6-diisopropylphenyl, 4-cyanophenyl, 1-naphthyl, and 2,4-difluorophenyl) of the *N*-aryl-(3Z)-4-amino-3-penten-2-ones exclusively yielded the SP-4-3 coordinated C<sup>C</sup>C<sup>\*</sup> cyclometalated platinum(II) complexes as single isomers as a consequence of the low steric demand of the C<sup>C</sup>C<sup>\*</sup> cyclometalating thiazole ligand and the bulkiness of the  $\beta$ -ketoiminate ligands. The formation of this isomer was



confirmed by <sup>195</sup>Pt NMR and extensive 2D NMR experiments, two solid-state structures, and the results of DFT calculations. As a proof of principle, two complexes with the sterically less demanding  $\beta$ -ketoiminate ligands (3Z)-4-amino-3-penten-2-onato and (2Z)-3-amino-1-phenyl-2-buten-1-onato were synthesized and isolated as an isomeric mixture.

# ■ INTRODUCTION

Photoluminescent, organometallic compounds attract great interest due to their interesting properties and numerous applications.<sup>1</sup> In particular, transition metal complexes are used as high-performance materials for the fabrication of photoelectronic devices such as dye-sensitized solar cells<sup>2</sup> and organic light-emitting diodes (OLEDs),<sup>3</sup> next to being valuable synthetic tools in photocatalysis.<sup>4</sup> The use of diverse ligand architectures to modify different electronic effects onto the metal atom and to establish defined steric environments has emerged into a widespread research area in photophysics and photochemistry.<sup>5</sup>

With the development of OLEDs based on phosphorescent transition metal complexes,<sup>6</sup> the need to achieve defined excited states is met by using specifically designed ligands.<sup>7</sup> In particular, cyclometalated complexes with phenylpyridines<sup>8</sup> or arylimidazole-based N-heterocyclic carbenes (NHCs)<sup>9</sup> show an excellent photophysical performance. Among the auxiliary ligands used in combination with bidentate C^N or C^C\* cyclometalating ligands, the monoanionic, bidentate acetyl-acetonate (acac) and its derivatives were investigated in several studies, and different highly phosphorescent emitters with O<sup>^</sup>O coordinating ligands have been presented.<sup>5d,e,10</sup>

Compared to typical acac ligand systems,  $\beta$ -ketoimines (acnac) have the advantage of applying electronic and steric effects via the (substituted) nitrogen atom while still keeping the monoanionic, bidentate ligand structure. *N*-Aryl- $\beta$ -ketoiminates have previously been used as coordination compounds for different photoluminescent complexes with gallium (Scheme 1, I)<sup>11</sup> and aluminum (Scheme 1, II)<sup>12</sup> and in phosphorescent iridium(III) emitters (Scheme 1, III and IV).<sup>13</sup> In addition, coordination compounds of platinum(II) with similar  $\beta$ -ketoiminate structures have been presented with interesting photophysical properties,<sup>14</sup> but problems of isomer formation and subsequent separation, due to the unsymmetrical nature of the  $\beta$ -ketoiminate ligand, were reported.<sup>15</sup>

Recently, cyclometalated 1,3-thiazol-2-ylidene-based NHC platinum(II) complexes with acetylacetonate ligands were reported as phosphorescent emitters.<sup>16</sup> The 1,3-thiazole motif provides variable electronic effects and a different steric environment compared to typical imidazole- and triazolebased heterocycles and their complexes. By using the C^C\* cyclometalating N-aryl-1,3-thiazol-2-ylidene motif we wanted to take advantage of the reduced steric demand to exclusively yield single isomers from the complex synthesis even with unsymmetrical  $\beta$ -ketoiminate ligands. We therefore studied the steric effect of bulky groups attached to the nitrogen atom of the  $\beta$ ketomine ligand on the complex formation and the photophysical properties. We herein present the synthesis of six novel N-phenyl-1,3-thiazol-2-ylidene platinum(II) complexes with sterically demanding N-aryl-(3Z)-4-amino-3-penten-2-onato ligands. In addition, the corresponding complexes based on the (3Z)-4-amino-3-penten-2-one motif, with no further steric demand at the nitrogen atom, were synthesized. Two solid-state structures unambiguously confirm the formation of the proposed isomers. Density functional theory (DFT) calculations using different functionals (B3LYP, BP86, B97D) agree with the experimental results.

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# RESULTS AND DISCUSSION

Synthesis and Characterization. The *N*-phenyl-4,5dimethyl-1,3-thiazol-2-ylidene motif was chosen as the  $C^{C*}$ cyclometalating NHC ligand in the platinum(II) complex synthesis because of the lower steric demand next to the sulfur atom in comparison to imidazole or triazole compounds (see Scheme 2). NHC precursor 1 was prepared starting from the

Scheme 2. Synthesis of Complexes 8-13<sup>a</sup>



<sup>*a*</sup>Conditions: (i) Ag<sub>2</sub>O, rt to 50 °C, DMF; (ii) Pt(COD)Cl<sub>2</sub>, rt to 115 °C, DMF; (iii) KO<sup>t</sup>Bu, *N*-arylketoimine **2**–7, rt to 100 °C, DMF.

aniline, by synthesis of the *N*-phenyl-1,3-thiazol-2-thione and the oxidation to the corresponding 1,3-thiazolium salt followed by a salt metathesis.<sup>16</sup>

The synthesis of the sterically and electronically different *N*-aryl-substituted  $\beta$ -ketoimine compounds 2–7 was accomplished by reaction of Hacac with the corresponding aniline derivatives using a Dean–Stark trap for the azeotropic removal of water.<sup>17</sup>

The synthesis of the platinum(II) complexes followed a modified literature procedure.<sup>10c,16</sup> The *N*-phenyl-1,3-thiazolium salt 1 was reacted with silver(I) oxide (Ag<sub>2</sub>O) in dry dimethylformamide (DMF) to *in situ* generate the silver(I)carbene complex, which was transmetalated to dichloro(1,5cyclooctadiene)platinum(II) (Pt(COD)Cl<sub>2</sub>). Cyclometalation at elevated temperatures and reaction with the  $\beta$ -ketoimine auxiliary ligands under basic conditions using potassium *tert*butanolate (KO<sup>t</sup>Bu) as the base (Scheme 2) led to complexes 8–13.

We were pleased to find that the use of the sterically demanding *N*-aryl-substituted  $\beta$ -ketoimine ligands 2–7 led to the exclusive formation of single isomers of 8–13. In detail, the SP-4-3 coordinated isomers with the *N*-aryl substituents of the  $\beta$ -ketoiminate ligand oriented to the 1,3-thiazole moiety were isolated (see the characterization *vide infra* for further details). Overall, complexes 8–13 were obtained in analytically pure form, after further washing with isohexanes and diethyl ether, in yields of 18% to 40%. All complexes have been characterized by standard techniques including <sup>19</sup>F (for 13) and <sup>195</sup>Pt NMR, as well as extensive 2D NMR investigations to confirm the identity of the expected preferred isomers (see Figure 1 for the structures of the synthesized complexes).





<sup>1</sup>H and <sup>195</sup>Pt NMR spectra of compounds **8–13** reveal the exclusive formation of only a single isomer. All complexes show a single <sup>195</sup>Pt NMR resonance with a chemical shift of -3394 (8) to -3417 (11) ppm, which is in the typical range of similar C<sup>^</sup>C\* cyclometalated platinum(II) complexes.<sup>10b,f</sup> We measured additional 2D NMR spectra for **8–13** and focused on the NOESY experiments. As an example we will discuss the determination of the isolated SP-4-3 isomer for complex 8 (Figure 2, for additional NMR spectra see the Supporting Information, Figures S1–S31).

The most defining interaction in the NOESY spectrum consists of a coupling of the auxiliary ligand's methyl group at 2.14 ppm with the characteristic, most deshielded proton of the cyclometalating aryl system at 8.27 ppm (Figure 2, red). In addition, a coupling of said methyl group at 2.14 ppm with the single proton of the  $\beta$ -ketoiminate ligand at 5.18 ppm is observed (Figure 2, orange). In agreement with this orientation of the  $\beta$ -ketoiminate ligand, we see the coupling of the second  $\beta$ -ketoiminate's methyl group at 1.63 ppm, not only with the single proton of the  $\beta$ -ketoiminate ligand at 5.18 ppm (Figure 2, green) but also with the nitrogen-bound phenyl ring of the  $\beta$ -ketoiminate at 7.13 ppm (Figure 2, blue).

With this, we can conclude that the synthesized and isolated isomer is indeed the SP-4-3 coordinated platinum(II) complex 8. The formation of only this isomer is a result of the steric



Figure 2. NOESY spectrum of compound 8 with highlighted CH<sub>3</sub>-H<sub>arvl</sub> interactions.

demand of the nitrogen-bound aryl ring of the  $\beta$ -ketoiminate ligand in combination with the steric demand of the thiazole heterocycle. For complexes 9–13 the same characteristic NOESY couplings are observed (see Supporting Information, Figures S26–S31), supporting the preferred formation of the SP-4-3 isomers for this new class of complexes.

We additionally calculated the ground-state geometries of both isomers of complex 8 with DFT methods to investigate the distances of defining hydrogen-hydrogen through-space interactions in both isomers (see Supporting Information, Figure S32). For the SP-4-3 coordinated isomer 8 short distances and therefore possible interactions of the protons at the  $\beta$ -ketoiminate methyl group with the proton adjacent to the cyclometalating carbon atom are found. In addition, interactions between the second methyl group and the protons at the nitrogen-bound phenyl ring of the  $\beta$ -ketoiminate ligand are observed. These results agree well with the observed couplings from the NOESY experiment for compound 8 (Figure 2). The corresponding signals can also be observed for complexes 9–13.

We then chose to calculate the free energy differences of the isomers with different functionals (BP86, B3LYP, B97D) together with the 6-31G(d) basis set. For a summary of the results and selected structural data see the Supporting Information, Figures S33 and S34 and Tables S1–S6. For complexes 8–13 the SP-4-3 coordinated isomers are generally favored, with average energy differences of -1.9 to -2.3 kcal/

mol, which is in good agreement with the experimental results from the NMR studies.

Additionally, we were able to obtain single crystals of complexes 8 and 12 (Figures 3 and 4). Both structures unambiguously confirm the expected orientation of the  $\beta$ ketoiminate ligand. Selected bond lengths and angles are given in the figure legends; for further information refer to the Supporting Information Tables S7 and S8 and Figure S35. The solid-state structures of complexes 8 and 12 show a squareplanar coordination environment for the platinum(II) center. The C1-Pt1-C7 angle in the five-membered ring is smaller at  $79.0(3)^{\circ}$  for 8 and  $78.9(5)^{\circ}$  for 12 compared to the nearly rectangular N1-Pt1-O1 angle of 88.9(2)° for 8 and 89.3(4)° for 12 in the six-membered ring. The bond length between the platinum atom and the electronically different coordinating atoms follow the expectation: the Pt1-N2 distances are the longest platinum contacts (2.112(5) Å for 8 and 2.109(9) Å for 12), whereas those to the carbon carbon atom (Pt1-C1) are the shortest (1.944(7) Å for 8 and 1.959(12) Å for 12). Compared to other solid-state structures of C<sup>A</sup>C\* cyclometalated complexes from the literature, the observed bond lengths and angles in this study are in very good agreement with previously reported data. Additionally, the N-bound aryl systems of the  $\beta$ -ketoiminate ligand are almost orthogonally oriented to the coordination plane, with  $70.8(7)^{\circ}$  for 8 and  $83.0(1)^{\circ}$  for 12, preventing molecular aggregation. In agreement with the higher steric demand of the aryl substituents,



Figure 3. ORTEP representation of complex 8. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): C1-Pt1 1.944(7); C7-Pt1 1.986(7); Pt1-N2 2.112(5); Pt1-O1 2.041(5); N2-C17 1.441(9); C1-Pt1-C7 79.0(3); N1-Pt1-O1 88.9(2); C1-N1-C6-C7-2.3(8).



Figure 4. ORTEP representation of complex 12. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å), angles (deg), and dihedral angles (deg): C1-Pt1 1.959(12); C7-Pt1 1.991(12); Pt1-N2 2.109(9); Pt1-O1 2.033(10); N2-C17 1.433(16); C1-Pt1-C7 78.9(5); N1-Pt1-O1 89.3(4); C1-N1-C6-C7 1.9(14).

large intermolecular Pt…Pt-distances of 7.895(2) Å for **8** and 7.833(2) Å for **12** (above the sum of their van der Waals radii) are observed, indicating no Pt…Pt interaction in the solid state.

In summary, the NOESY spectra and the calculated structures support the formation of the SP-4-3 isomers (8–13) over the SP-4-4 isomers. This fact was unambiguously proven by the solid-state structures of complexes 8 and 12. The formation of the SP-4-3 isomers can be explained by the low steric demand of the 1,3-thiazole moiety of the C<sup>^</sup>C\* cyclometalating ligand and the high steric demand of the N<sup>^</sup>O coordinating  $\beta$ -ketoiminate ligand. These findings can also be confirmed by DFT calculations, which show an average

free energy difference that is >1.9 kcal/mol in favor of the SP-4-3 isomers.

To test the hypothesis, we also synthesized the sterically less demanding  $\beta$ -ketoimines (3Z)-4-amino-3-penten-2-one (14) and (2Z)-3-amino-1-phenyl-2-buten-1-one (15)<sup>15,18</sup> by reaction of Hacac (for 14) or respectively of 1-phenyl-1,3-butandione (for 15) with ammonium carbamate.<sup>33,35</sup> Synthesis and isolation of the complexes followed the same route as described for complexes 8–13. As anticipated, both complexes (16 and 17) were isolated as a mixture of two isomers (see Scheme 3 and the Experimental Section for further details).



<sup>*a*</sup>Conditions: (i) Ag<sub>2</sub>O, rt to 50 °C, DMF; (ii) Pt(COD)Cl<sub>2</sub>, rt to 115 °C, DMF; (iii) KO'Bu, ketoimine 14 or 15, rt to 100 °C, DMF.

Next to an additional second signal set in the <sup>1</sup>H and <sup>13</sup>C NMR spectra, the isomeric mixture of compound **16** shows two separate <sup>195</sup>Pt resonances at -3351 and -3375 ppm, which reveals the formation of two isomers. Even the use of an additional phenyl group at the C1 position of the  $\beta$ -ketoiminate ligand, as in complex **17** with an (2Z)-3-amino-1-phenyl-2-buten-1-onato ligand, leads to two signal sets and two <sup>195</sup>Pt NMR signals at -3322 and -3349 ppm. DFT calculations show smaller free energy differences for the isomers, with the SP-4-3 coordinated complex disfavored over its SP-4-4 coordinated isomer.

By using sterically demanding *N*-aryl- $\beta$ -ketoiminates as ligands, the formation of isomerically pure C<sup>C</sup>C<sup>\*</sup> cyclometalated complexes can be controlled, even with unsymmetrical ligands.

**Photophysical Properties.** Frequently photophysical data in the literature report the absorption and emission spectra of mixtures when the isomers are difficult to separate. In our case the synthesis and isolation of only one isomer of 8-13 allowed for a detailed investigation of the photophysical properties of this novel class of (SP-4-3)-1,3-thiazol-2-ylidene platinum(II) complexes with *N*-aryl-substituted  $\beta$ -ketoiminate auxiliary ligands. We first recorded the absorption spectra in diluted dichloromethane (DCM) solutions, which are shown in Figure 5.

For complexes 8–13 strong absorptions in the high-energy region below 275 nm can be observed, which are typically attributed to  $\pi - \pi^*$  transitions for this class of C<sup>C</sup>\* cyclometalated platinum(II) complexes.<sup>10g</sup> Small maxima at about 340 nm together with stronger absorptions at about 370 nm are found for all complexes. These absorptions are referred to as metal-to-ligand charge transfer (<sup>1</sup>MLCT) states in the literature.<sup>10g</sup> Interestingly, despite the electronically and sterically diverse substituents present at the coordinating nitrogen atom of the platinum(II) environment, almost no change in their absorption behavior is observed.

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Figure 5. Absorption spectra of complexes 8-13 at room temperature ( $10^{-4}$  mol L<sup>-1</sup> in DCM).

In addition, we measured the emission spectra of amorphous 2 wt % emitter films of the corresponding complexes 8-13 in poly(methyl methacrylate) (PMMA) at room temperature (Figure 6). All complexes show broad, unstructured emission



Figure 6. Emission spectra of complexes 8-13 at room temperature (2 wt % in PMMA).

bands with a stable maximum emission wavelength of about 500 nm (see Table 1). The use of different aryl systems at the coordinating nitrogen atom does not change the band form or the maximum emission wavelength, showing an interesting dominant electronic effect of the 1,3-thiazole NHC ligand over

Table 1. Photoluminescence Data (2 wt % in PMMA, Room Temperature) of Complexes 8–13

no.	$\lambda_{\rm exc} [nm]^a$	CIE $x; y^b$	$\lambda_{em} \ [nm]^{c}$	$\phi$ [%] <sup>d</sup>	$[\mu s]^e$	$\begin{array}{c} k_{\rm r} \left[ 10^3 \\ {\rm s}^{-1} \right]^f \end{array}$	$\begin{array}{c} k_{\rm nr} \begin{bmatrix} 10^3 \\ {\rm s}^{-1} \end{bmatrix}^g \end{array}$
8	370	0.24;0.45	503	7	71.9	13.9	4681.2
9	370	0.24;0.47	506	23	25.3	39.6	4477.2
10	370	0.25;0.49	509	26	22.5	44.4	4334.8
11	370	0.26;0.50	507	19	29.2	34.2	4494.9
12	370	0.25;0.47	504	14	_h	h	_h
13	370	0.26;0.50	509	23	23.1	43.4	4084.0

<sup>*a*</sup>Excitation wavelength. <sup>*b*</sup>CIE coordinates at room temperature. <sup>*c*</sup>Maximum emission wavelength. <sup>*d*</sup>Quantum yield at  $\lambda_{exc}$ ; N<sub>2</sub> atmosphere. <sup>*e*</sup>Decay lifetimes (excited by laser pulses (360 nm, 20 kHz)) given as  $\tau_o = \tau_v/\phi$ . <sup>*f*</sup> $k_r = \phi/\tau_v$ . <sup>*s*</sup> $k_{nr} = (1 - \phi)/\tau_v$ . <sup>*h*</sup>Decay lifetime above detection limit. the different  $\beta$ -ketoiminate ligands (for the individual spectra of compounds 8–13 refer to the Supporting Information, Figures S36–S41).

The photoluminescence data for complexes 8-13 are summarized in Table 1 and reveal quantum yields (QY) from 7% (8) up to 26% (10) with decay lifetimes between 22.5  $\mu$ s (10) and 71.9  $\mu$ s (8). The decay lifetime of complex 12 could not be determined because of the detection limit of the instrumental setup ( $\tau_0 > 350 \ \mu$ s). The complex with the 2,6diisopropylphenyl-substituted  $\beta$ -ketoimine ligand 10 shows the highest quantum yield. The lowest quantum yield is observed for the unsubstituted phenyl ring (8), while ortho-substituents (9, methyl; 10, isopropyl), which due to steric requirements reduce the conjugation between the plane of the acnac system and the substituent, lead to a higher quantum yield. Electronwithdrawing substituents (11, cyano; 13, fluoro) also improve the quantum yields (11, 19%; 13, 23%) and are beneficial for shorter decay lifetimes.

For photophysical data for the isomeric mixtures of complexes 16 and 17 refer to the Supporting Information, Figures S42 and S43 and Table S9.

To further investigate the emission process, we calculated the Kohn–Sham orbitals of the singlet-state geometries and spin densities of the triplet-state geometries using DFT methods (see Supporting Information, Figure S44). All calculated triplet-state geometries show strong distortions of the  $\beta$ -ketoimine auxiliary ligand at the platinum(II) complexes. The relatively low quantum yields of the complexes can therefore be attributed to thermal quenching effects that result from geometrical changes in the excited states.<sup>15</sup>

# CONCLUSIONS

We present the synthesis of the first bidentate C<sup>^</sup>C\* cyclometalated platinum(II) complexes based on 1,3-thiazol-2-ylidene ligands with unsymmetrical N-aryl-functionalized  $\beta$ ketoiminate ligands. All six complexes were exclusively obtained as the SP-4-3 coordinated isomers due to the high steric demand of the N-aryl- $\beta$ -ketoiminate ligand and the use of Naryl-1,3-thiazol-2-ylidenes as the C<sup>C</sup>\* cyclometalating ligands. 2D NOESY spectra show long-range couplings between the methyl group proton of the  $\beta$ -ketoiminate and the proton of the cyclometalating aryl system. The N-aryl moiety of the  $\beta$ ketoiminate is oriented to the 1,3-thiazole heterocycle of the NHC ligand, which was additionally proven by two solid-state structures. For comparison, systems with no steric demand at the coordinating nitrogen atom were synthesized, which as expected yielded only an isomeric mixture. Their photophysical properties were measured and revealed bluish-green phosphorescence with emission maxima of about 500 nm at room temperature in 2 wt % PMMA films. DFT calculations support the formation of the isolated SP-4-3 isomers.

# EXPERIMENTAL SECTION

**General Experimental Procedures.** All syntheses of the platinum(II) complexes were performed under an argon atmosphere and the exclusion of light, using flame-dried Schlenk tubes. Solvents of at least 99.0% purity were used in this study. DMF was dried using standard techniques and stored under an argon atmosphere over molecular sieves (3 Å). Dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl<sub>2</sub>)<sup>19</sup> was prepared according to a modified literature procedure.<sup>10c</sup> Compound **1** was synthesized according to a previously described literature procedure.<sup>16</sup> Compounds 4-(phenylamino)pent-3-en-2-one (3),<sup>17b</sup> and 4-(2,6-diisopropylphenylamino)pent-3-en-2-one (4)<sup>17b</sup>

were prepared according to the literature procedures. Compounds 4-(N-(4-cyanophenyl)amino)pent-3-en-2-one (5), 4-(N-(naphthyl)amino)pent-3-en-2-one (6), and 4-(N-(2,4-difluorphenyl)amino)pent-3-en-2-one (7) were prepared following a modified literature procedure as described below.<sup>17b</sup> Compounds 4-aminopent-3-en-2one  $(14)^{15,18}$  and 3-amino-1-phenylbut-2-en-1-one  $(15)^{15,18}$  were prepared according to the literature procedures. Chemicals were obtained from common suppliers and used without further purification. <sup>1</sup>H, <sup>13</sup>C, <sup>19</sup>F, and <sup>195</sup>Pt NMR spectra were recorded on Bruker NMR spectrometers. <sup>1</sup>H and <sup>13</sup>C NMR spectra were referenced internally by using the resonances of the solvent (<sup>1</sup>H, 7.26 ppm; <sup>13</sup>C, 77.0 ppm for CDCl<sub>3</sub>). <sup>19</sup>F NMR spectra are referenced externally against trifluoromethylbenzene as the standard signal. <sup>195</sup>Pt NMR spectra were referenced externally by using potassium tetrachloroplatinate(II) in  $D_2O$  (-1617.2 ppm (PtCl<sub>4</sub><sup>2-</sup>), -2654.1 ppm (PtCl<sub>2</sub>)). Shifts are given in ppm; coupling constants J in Hz. Mass spectra of ligands 5-7 were recorded on an Agilent 6890N GC coupled with a 5973N MSD system using electron ionization (EI) as the ionization method. The reported masses are assigned to the matching fragments and referenced to the basis peak. Electrospray ionization mass spectra of compounds 8-13, 16, and 17 were measured on a Bruker Esquire MS with ion trap detector. Elemental analyses were performed on a Hekatech elemental analyzer by the microanalytical laboratory of our institute. Uncorrected melting points have been determined using a Wagner and Munz Poly Therm A system. Photoluminescence measurements were performed in thin PMMA films doped with 2 wt % emitter. The emitter films were prepared by doctor blading a solution of emitter in a 10 wt % PMMA solution in dichloromethane on a quartz substrate with a 60  $\mu$ m doctor blade. The film was dried, and the emission was measured under nitrogen. Excitation was conducted at wavelengths of 370 nm (Xe lamp with a monochromator), and the emission was detected with a calibrated quantum yield detection system (Hamamatsu, model C9920-02). The uncertainty of the quantum yield is  $\pm 2\%$  for quantum yields of >10%. The phosphorescence decay was measured with an Edinburgh Instruments Mini- $\tau$  by excitation with pulses of an EPLED (360 nm, 20 kHz) and time-resolved photon counting. Absorption spectra were measured on a PerkinElmer Lambda 25 UV-VIS spectrometer.

**Computational Details.** The Gaussian09 package<sup>20</sup> was used to perform all quantum chemical calculations employing the density functional hybrid model B3LYP,<sup>21</sup> gradient-corrected BP86,<sup>22</sup> and dispersion-corrected B97D.<sup>23</sup> All functionals were combined with a 6-31G(d) basis set.<sup>24</sup> In all calculations platinum was described with a decontracted Hay-Wadt(*n*+1) ECP and basis set.<sup>25</sup> All given structures were verified as true minima by vibrational frequency analysis and the absence of negative eigenvalues. By applying thermochemical analysis approximate free energies could be obtained. Thermal corrections to Gibbs free energy, as reported by Gaussian09, were taken into account including zero-point effects, thermal enthalpy corrections, and entropy. All presented energies, unless otherwise stated, are free energies at standard conditions (T = 298 K, p = 1 atm) using unscaled frequencies. Frontier molecular orbitals and spin densities were visualized by GaussView.<sup>26</sup> Calculated geometries were visualized with CYLview.<sup>27</sup>

X-ray Crystallography. Yellow single crystals of compound 8 were grown by slow evaporation of a saturated dichloromethane solution. Slow infusion of a saturated dichloromethane solution of complex 12 with diethyl ether yielded the corresponding yellow single crystals.

Preliminary examination and data collection were carried out on a Nonius  $\kappa$ -CCD diffraction system (FR590) equipped with an Oxford Cryosystem cooling system at the window of a fine-focus sealed tube using graphite-monochromated Mo K $\alpha$  radiation ( $\lambda = 0.71073$  Å). The reflections were merged and corrected for Lorentz, polarization, and decay effects. Absorption correction was applied using SADABS.<sup>28</sup> The structures were solved by a combination of direct methods<sup>29</sup> with the aid of difference Fourier synthesis and were refined against all data using SHELXL-97.<sup>30</sup> Hydrogen atoms were assigned to ideal positions using the SHELXL-97 riding model. All non-hydrogen atoms were

refined with anisotropic displacement parameters. Full-matrix leastsquares refinements were carried out by minimizing  $\sum w(F_o^2 - F_c^2)^2$  with the SHELXL-97 weighting scheme. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the nonhydrogen atoms were taken from the International Tables for Crystallography.<sup>31</sup> All calculations were performed with the programs COLLECT,<sup>32</sup> DIRAX,<sup>33</sup> EVALCCD,<sup>34</sup> SIR92,<sup>29b</sup> SIR97,<sup>29a</sup> SADABS,<sup>28</sup> the SHELXL-97 package,<sup>35</sup> and PLATON.<sup>36</sup> Images of the solid-state structures were generated with ORTEP-3<sup>37</sup> and Mercury.<sup>38</sup>

Synthesis of Ligands 5–7. 4-(N-(4-Cyanophenyl)amino)pent-3en-2-one (5). In a 50 mL round-bottom flask with a Dean-Stark apparatus 5.01 g (50 mmol) of acetylacetone and 6.63 g (55 mmol, 1.1 equiv) of 4-aminobenzonitrile in 30 mL of benzene are combined, before 15 drops of concentrated hydrochloric acid (37 wt %) are added. The reaction mixture is stirred at 110 °C for 24 h. The resulting black suspension is filtered, and the remaining solid is washed with 10 mL of isohexanes. The filtrate is collected and treated with 100 mL of diethyl ether. After 4 h at room temperature a yellow solid precipitates. The solid is filtered, washed with 50 mL of diethyl ether, and dried under high vacuum (3.71 g, 37.0%). Mp: 94-95 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 300 MHz, tautomer A): δ 12.67 (s, 1H, NH), 7.59  $(dd, J = 8.3 Hz, 2H, CH_{arom}), 7.14 (d, J = 8.4 Hz, 2H, CH_{arom}), 5.27 (s, J)$ 1H, CH<sub>acnac</sub>), 2.11 (2 s, 6H, CH<sub>3</sub>) ppm. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 300 MHz, tautomer B):  $\delta$  15.45 (s, 1H, OH), 7.39 (dd, J = 8.7, 1.1 Hz, 2H,  $CH_{arom}$ ), 6.63 (d, J = 8.7 Hz, 2H,  $CH_{arom}$ ), 5.48 (s, 1H,  $CH_{acnac}$ ), 2.02 (2 s, 6H, CH<sub>3</sub>) ppm. The tautomeric ratio of 20:1 (A:B) was determined based on the <sup>1</sup>H NMR integrations for the NH-proton resonance at 12.67 ppm and the OH-proton resonance at 15.45 ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 <sup>o</sup>C, 75 MHz, tautomeric mixture):  $\delta$  202.0 (CO/CN), 197.5 (CO/ CN), 191.2 (CO/CN), 157.5 (C<sub>i</sub>), 150.4 (C<sub>i</sub>), 143.3 (C<sub>i</sub>), 133.7 (CH<sub>arom</sub>), 133.2 (CH<sub>arom</sub>), 122.8 (CH<sub>arom</sub>), 120.1 (C<sub>i</sub>), 118.6 (C<sub>i</sub>), 114.4 (CH<sub>arom</sub>), 107.3 (C<sub>i</sub>), 100.4 (CH<sub>arom</sub>), 100.4 (CH<sub>arom</sub>), 100.1 (C<sub>i</sub>), 58.5 (CH<sub>2</sub>), 30.8 (CH<sub>3</sub>), 29.5 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 20.3 (CH<sub>3</sub>) ppm. GC-MS (EI, m/z, fragment, %): 200 (M<sup>+</sup>, 32), 185 (M<sup>+</sup> - Me, 100). Anal. Calcd for C<sub>12</sub>H<sub>12</sub>N<sub>2</sub>O: C, 71.98; H, 6.04; N, 13.99. Found: C, 72.35; H, 6.25; N, 14.04.

4-(N-Naphthylamino)pent-3-en-2-one (6). In a 50 mL roundbottom flask with a Dean-Stark apparatus 2.50 g (25 mmol) of acetylacetone and 3.53 g (28 mmol, 1.1 equiv) of 1-naphthylamine in 30 mL of toluene are combined, before 15 drops of concentrated hydrochloric acid (37 wt %) are added. The reaction mixture is stirred at 130  $^{\circ}\mathrm{C}$  for 24 h. The resulting black solid is filtered off, and the filtrate is treated with 100 mL of diethyl ether. Again a dark solid is formed and filtered off to remove side products. The remaining diethyl ether-benzene mixture is evaporated using a rotary evaporator. The product is then isolated via flash column chromatography using an ethyl acetate-isohexanes mixture (1:3) and obtained as a red-orange oil (2.58 g, 22.9%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 300 MHz):  $\delta$  12.75 (s, 1H, NH), 8.07-7.98 (m, 1H, CH<sub>arom</sub>), 7.91-7.83 (m, 1H, CH<sub>arom</sub>), 7.77 (d, J = 8.3 Hz, 1H, CH<sub>arom</sub>), 7.58–7.49 (m, 2H, CH<sub>arom</sub>), 7.48– 7.41 (m, 1H,  $CH_{arom}$ ), 7.28 (dd, J = 7.3 Hz, J = 0.7 Hz, 1H,  $CH_{arom}$ ), 5.31 (s, 1H, CH<sub>acnac</sub>), 2.18 (s, 3H, CH<sub>3</sub>), 1.88 (s, 3H, CH<sub>3</sub>) ppm. NMR (CDCl<sub>3</sub>, 25 °C, 75 MHz): δ 196.5 (CO/CN), 161.8 (C<sub>i</sub>), 134.8 (C<sub>i</sub>), 134.2 (C<sub>i</sub>), 130.0 (C<sub>i</sub>), 128.2 (CH<sub>arom</sub>), 126.9 (2C, CH<sub>arom</sub>), 126.5 (CH<sub>arom</sub>), 125.2 (CH<sub>arom</sub>), 123.4 (CH<sub>arom</sub>), 122.8 (CH<sub>arom</sub>), 97.4 (CH<sub>arom</sub>), 29.2 (CH<sub>3</sub>), 19.6 (CH<sub>3</sub>) ppm. GC-MS (EI, *m/z*, fragment, %): 225 (M<sup>+</sup>, 100), 210 (M<sup>+</sup> – Me, 81). Anal. Calcd for C<sub>15</sub>H<sub>15</sub>NO: C, 79.97; H, 6.71; N, 6.22. Found: C, 79.88; H, 6.76; N, 6.46.

4-(N-(2,4-Difluoroyphenyl)amino)pent-3-en-2-one (7). In a 50 mL round-bottom flask with a Dean–Stark apparatus 2.50 g (25 mmol) of acetylacetone and 3.55 g (28 mmol, 1.1 equiv) of 2,4-difluoroaniline in 30 mL of toluene are combined, before 15 drops of concentrated hydrochloric acid (37 wt %) are added. The reaction mixture is stirred at 130 °C for 24 h. The resulting black solid is filtered off, and the filtrate is treated with 100 mL of diethyl ether. Again a dark solid is formed and filtered off to remove side products. The remaining diethyl ether–benzene mixture is evaporated using a rotary evaporator. The product is then isolated via flash column chromatography using an ethyl acetate–isohexanes mixture (1:3) and obtained as a light yellow

solid (1.77 g, 16.8%). Mp: 36–39 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 300 MHz): δ 12.07 (s, 1H, NH), 7.21–7.08 (m, 1H, CH<sub>aron</sub>), 6.96–6.76  $(m, 2H, CH_{arom}), 5.26 (s, 1H, CH_{acnac}), 2.11 (s, 3H, CH_3), 1.88 (d, J =$ 0.6 Hz, 3H, CH<sub>3</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 75 MHz, tautomeric mixture): § 196.9 (CO/CN), 191.2 (CO/CN), 160.8 (dd, J = 248.8 Hz, J = 11.0 Hz, CF), 160.7 (C<sub>i</sub>), 157.1 (dd, J = 250.7 Hz, J =12.4 Hz, CF), 128.5 (dd, J = 9.6 Hz, J = 1.8 Hz, CH<sub>arom</sub>), 123.0 (dd, J = 12.9 Hz, J = 4.0 Hz,  $C_i$ ), 116.9 (dd, J = 9.0 Hz, J = 4.7 Hz,  $CH_{arom}$ ), 111.3 (dd, J = 22.2 Hz, J = 4.0 Hz,  $CH_{arom}$ ), 110.8 (dd, J = 22.0 Hz, J =3.8 Hz, CH<sub>arom</sub>), 104.7 (dd, J = 26.2 Hz, J = 24.3 Hz, CH<sub>arom</sub>), 103.7 (dd, J = 26.4 Hz, J = 22.7 Hz, CH<sub>arom</sub>), 100.4 (CH<sub>arom</sub>), 98.0 (CH<sub>arom</sub>), 29.2 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 19.3 (CH<sub>3</sub>), 19.2 (CH<sub>3</sub>) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 25 °C, 75 MHz, tautomeric mixture):  $\delta$  –131.26 (s, CF), -124.39 (s, CF), -117.7 (d, J = 6.4 Hz, CF), -112.1 (d, J = 6.7 Hz, CF) ppm. GC-MS (EI, m/z, fragment, %): 211 (M<sup>+</sup>, 44), 196 (M<sup>+</sup> -Me, 100). Anal. Calcd for C<sub>11</sub>H<sub>11</sub>F<sub>2</sub>NO: C, 62.55; H, 5.25; N, 6.63. Found: C, 62.44; H, 5.23; N, 6.66.

Synthesis of Complexes 8–13, 16, and 17. General Procedure A. Dry DMF is added to a mixture of the N-phenyl-4,5-dimethyl-1,3thiazolium hexafluorophosphate salt 1 and 0.55 equiv of Ag<sub>2</sub>O in a dry Schlenk tube. The resulting solution is stirred at room temperature for 2 h and for 22 h at 50 °C under the exclusion of light. After addition of 1 equiv of  $Pt(COD)Cl_2$  stirring is continued for another 2 h at room temperature and 22 h at 115 °C, followed by addition of the described equivalents of the corresponding N-aryliminopentan-2-one and the base (KO<sup>t</sup>Bu). Afterward the mixture is stirred at room temperature for another 24 h and then heated to 100 °C for 6 h. All volatiles are removed in vacuo, and the remaining solid is dispersed in 50 mL of distilled water and filtered. The solid residue is dissolved in dichloromethane, and the complex isolated by flash column chromatography using pure dichloromethane as the eluent. Subsequent washing with isohexanes and diethyl ether yielded the pure complexes.

 $[4, 5-Dimethy]-3-pheny]-\kappa C'-1, 3-thiazol-2-ylidene-\kappa C]-[N-pheny]-$ 4-aminopent-3-en-2-onato-κN,κO]platinum(II) (8). According to the general procedure A 20 mL of dry DMF is added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5-dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1.0 equiv) of Pt(COD)Cl<sub>2</sub>, 280 mg (1.6 mmol, 2.0 equiv) of 4-(N-phenylamino)pent-3-en-2-one (2), and 180 mg (1.6 mmol, 2.0 equiv) of  $KO^tBu$  while following the general procedure A yielded complex 8 as a yellow powder (100 mg, 22.3%). Mp: 257-260 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz): δ 8.29-8.15 (m, 1H, CH<sub>arom</sub>), 7.42-7.31 (m, 3H, CH<sub>arom</sub>), 7.30-7.23 (partially omitted by solvent signal, m, 1H,  $CH_{arom}$ ), 7.13 (td, J = 7.4 Hz, J = 0.9 Hz, 1H, CH<sub>arom</sub>), 7.10–7.03 (m, 2H, CH<sub>arom</sub>), 7.03–6.98 (m, 1H, CH<sub>arom</sub>), 5.18 (s, 1H, CH<sub>acnac</sub>), 2.58 (s, 3H, CH<sub>3;NHC</sub>), 2.14 (s, 3H, CH<sub>3;acnac</sub>), 2.00 (s, 3H, CH<sub>3;NHC</sub>), 1.63 (s, 3H, CH<sub>3;acnac</sub>) ppm. NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz): δ 179.4 (CN), 176.3 (CO), 162.7 (NCS), 153.5 (C<sub>i</sub>-Pt), 150.7 (C<sub>i</sub>), 136.3 (C<sub>i</sub>), 134.2 (C<sub>i</sub>), 131.8 (CH<sub>arom</sub>), 129.6 (2C, CH<sub>arom</sub>), 126.0 (2C, CH<sub>arom</sub>), 125.7 (CH<sub>arom</sub>), 125.1 (CH<sub>arom</sub>), 123.8 (C<sub>i</sub>), 123.2 (CH<sub>arom</sub>), 113.0 (CH<sub>arom</sub>), 100.5 (CH<sub>arom</sub>), 26.7 (CH<sub>3</sub>), 24.7 (CH<sub>3</sub>), 14.6 (CH<sub>3</sub>), 12.5 (CH<sub>3</sub>) ppm. <sup>195</sup>Pt NMR (65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3394 ppm. MS (ESI<sup>+</sup>, m/z, fragment): 558.3 (M + H)<sup>+</sup>. Anal. Calcd for C<sub>22</sub>H<sub>22</sub>N<sub>2</sub>OPtS: C, 47.39; H, 3.98; N, 5.02; S, 5.75. Found: C, 47.06; H, 3.97; N, 4.96; S, 5.74.

[4,5-Dimethyl-3-phenyl- $\kappa$ C'-1,3-thiazol-2-ylidene- $\kappa$ C]-[N-(2,4,6-trimethylphenyl)-4-aminopent-3-en-2-onato- $\kappa$ N, $\kappa$ O]platinum(II) (9). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5-dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1 equiv) of Pt(COD)Cl<sub>2</sub>, 348 mg (1.6 mmol, 2 equiv) of 4-(N-(2,4,6-trimethylphenyl)amino)pent-3-en-2-one (3), and 180 mg (1.6 mmol, 2 equiv) of KO'Bu (1.6 mmol, 2.0 equiv) while following the general procedure A yielded complex 9 as a yellow powder (159 mg, 33.1%). Mp: >318 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz): δ 8.35–8.18 (m, 1H, CH<sub>arom</sub>), 7.05–6.96 (m, 3H, CH<sub>arom</sub>), 5.22 (s, 1H, CH<sub>arom</sub>), 2.58 (s, 3H, CH<sub>3;NHC</sub>), 2.41 (s, 3H, CH<sub>3;mesityl</sub>), 2.15 (s, 3H, CH<sub>3;acnac</sub>), 2.11 (s, 6H, CH<sub>3;mesityl</sub>), 2.00 (s, 3H, CH<sub>3;NHC</sub>), 1.47 (s, 3H, CH<sub>3;acnac</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz):  $\delta$  179.2 (CO/CN), 175.9 (CO/CN), 162.5 (NCS), 150.9 (C<sub>i</sub>-Pt), 148.0 (C<sub>i</sub>), 136.6 (C<sub>i</sub>), 135.3 (C<sub>i</sub>), 134.7 (C<sub>i</sub>), 131.6 (2C, CH<sub>arom</sub>), 130.3 (2C, CH<sub>arom</sub>), 125.2 (CH<sub>arom</sub>), 123.6 (C<sub>i</sub>), 123.1 (CH<sub>arom</sub>), 113.0 (CH<sub>arom</sub>), 100.4 (CH<sub>arom</sub>), 26.7 (CH<sub>3</sub>), 23.4 (CH<sub>3</sub>), 20.9 (CH<sub>3</sub>), 18.1 (2C, CH<sub>3</sub>), 14.7 (CH<sub>3</sub>), 12.5 (CH<sub>3</sub>) ppm. <sup>195</sup>Pt NMR (65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3390 ppm. MS (ESI<sup>+</sup>, *m*/*z*, fragment): 600.3 (M + H)<sup>+</sup>. Anal. Calcd for C<sub>25</sub>H<sub>28</sub>N<sub>2</sub>OPtS: C, 50.07; H, 4.71; N, 4.67; S, 5.35. Found: C, 49.76; H, 4.69; N, 4.61; S, 5.13.

[4,5-Dimethyl-3-phenyl- $\kappa$ C'-1,3-thiazol-2-ylidene- $\kappa$ C]-[N-(2,6-bis-(methylethyl)phenyl)-4-aminopent-3-en-2-onato- $\kappa N,\kappa O$ ]platinum-(II) (10). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1.0 equiv) of Pt(COD)Cl<sub>2</sub>, 415 mg (1.6 mmol, 2.0 equiv) of 4-(N-(2,6-diisopropylphenyl)amino)pent-3-en-2-one (4), and 180 mg (1.6 mmol, 2.0 equiv) of KO<sup>t</sup>Bu while following the general procedure A yielded complex 10 as a yellow powder (203 mg, 39.5%). Mp: >330 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz):  $\delta$  8.36–8.20 (m, 1H,  $CH_{arom}$ ), 7.39 (d, J = 8.1 Hz, 1H,  $CH_{arom}$ ), 7.35–7.28 (m, 1H,  $CH_{arom}$ ), 7.28–7.25 (partially omitted by solvent signal, m, 1H,  $CH_{arom}$ ), 7.24 (d, J = 1.0 Hz, 1H,  $CH_{arom}$ ), 7.16 (td, J = 7.4, 0.8 Hz, 1H, CH<sub>arom</sub>), 7.05-7.00 (m, 1H, CH<sub>arom</sub>), 5.26 (s, 1H, CH<sub>arom</sub>), 3.31 (hept, J = 6.8 Hz, 2H,  $CH(CH_3)_2$ ), 2.60 (s, 3H,  $CH_{3,NHC}$ ), 2.19 (s, 3H,  $CH_{3;acnac}$ ), 2.02 (s, 3H,  $CH_{3;NHC}$ ), 1.57 (s, 3H,  $CH_{3;acnac}$ ), 1.12 (d, J = 6.9 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>), 1.02 (d, J = 6.8 Hz, 6H, CH(CH<sub>3</sub>)<sub>2</sub>) ppm.  $^{13}\text{C}$  NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz):  $\delta$  180.4 (CO/CN), 175.7 (CO/ CN), 163.1 (NCS), 150.9 (C<sub>i</sub>-Pt), 148.3 (C<sub>i</sub>), 141.3 (C<sub>i</sub>), 136.2 (C<sub>i</sub>), 134.0 (C<sub>i</sub>), 131.5 (CH<sub>arom</sub>), 126.5 (CH<sub>arom</sub>), 125.2 (2C, CH<sub>arom</sub>), 125.1 (CH<sub>arom</sub>), 123.5 (C<sub>i</sub>), 123.2 (CH<sub>arom</sub>), 113.0 (CH<sub>arom</sub>), 100.1 (CH<sub>arom</sub>), 27.3 (2C, CH), 26.7 (2C, CH<sub>3</sub>), 24.5 (2C, CH<sub>3</sub>), 23.9 (2C, CH<sub>3</sub>), 14.7 (CH<sub>3</sub>), 12.6 (CH<sub>3</sub>) ppm. <sup>195</sup>Pt NMR (65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$ -3412 ppm. MS (ESI<sup>+</sup>, m/z, fragment): 642.3 (M + H)<sup>+</sup>. Anal. Calcd for C28H34N2OPtS: C, 52.41; H, 5.34; N, 4.37; S, 5.00. Found: C, 52.43; H, 5.08; N, 4.35; S, 4.74.

[4,5-Dimethyl-3-phenyl-κC'-1,3-thiazol-2-ylidene-κC]-[N-(4-cvanophenyl)-4-aminopent-3-en-2-onato-κN,κO]platinum(II) (11). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5-dimethyl-1,3thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1 equiv) of Pt(COD)Cl<sub>2</sub>, 641 mg (3.2 mmol, 4.0 equiv) of 4-(N-(4-cyanophenyl)amino)pent-3-en-2-one (5), and 359 mg (3.2 mmol, 4.0 equiv) of KO<sup>t</sup>Bu while following the general procedure A yielded complex 11 as a yellow powder (85 mg, 18.2%). Mp: 286-288 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz):  $\delta$  8.32–8.07 (m, 1H, CH<sub>arom</sub>), 7.73 (d, J = 8.4 Hz, 2H, CH<sub>arom</sub>), 7.46-7.32 (m, 1H, CH<sub>arom</sub>), 7.23 (partially omitted by solvent signal, d, J = 8.5 Hz, 2H,  $CH_{arom}$ ), 7.15 (td, J = 7.4 Hz, J = 0.9Hz, 1H, CH<sub>arom</sub>), 7.03 (td, J = 8.1 Hz, J = 1.5 Hz, 1H, CH<sub>arom</sub>), 5.22 (s, 1H, CH<sub>arom:acac</sub>), 2.61 (s, 3H, CH<sub>3:NHC</sub>), 2.16 (s, 3H, CH<sub>3:acnac</sub>), 2.06 (s, 3H, CH<sub>3;NHC</sub>), 1.63 (s, 3H, CH<sub>3;acnac</sub>) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz): δ 178.1 (CO/CN), 177.5 (CO/CN), 161.9 (NCS), 157.8 (C $\equiv$ N), 150.3 (C<sub>i</sub>-Pt), 136.8 (C<sub>i</sub>), 133.7 (2C, CH<sub>arom</sub>), 133.3 (C<sub>i</sub>), 131.7 (CH<sub>arom</sub>), 127.4 (CH<sub>arom</sub>), 125.3 (CH<sub>arom</sub>), 123.7 (C<sub>i</sub>), 123.5 ( $CH_{arom}$ ), 122.9 ( $C_i$ ), 118.8 ( $C_i$ ), 113.2 ( $CH_{arom}$ ), 109.3 ( $C_i$ ), 100.9 (CH<sub>arom</sub>), 26.9 (CH<sub>3</sub>), 24.8 (CH<sub>3</sub>), 14.6 (CH<sub>3</sub>), 12.5 (CH<sub>3</sub>) ppm. <sup>195</sup>Pt NMR (65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3417 ppm. MS (ESI<sup>+</sup>, m/z, fragment): 583.2 (M + H)<sup>+</sup>. Anal. Calcd for C<sub>23</sub>H<sub>21</sub>N<sub>3</sub>OPtS: C, 47.42; H, 3.63; N, 7.21; S, 5.50. Found: C, 47.13; H, 3.33; N, 7.03; S, 5.50

[4,5-Dimethyl-3-phenyl- $\kappa$ C'-1,3-thiazol-2-ylidene- $\kappa$ C]-[N-(4naphthylphenyl)-4-aminopent-3-en-2-onato- $\kappa$ N, $\kappa$ O]platinum(II) (12). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1 equiv) of Pt(COD)Cl<sub>2</sub>, 721 mg (3.2 mmol, 4 equiv) of 4-(N-(naphthyl)amino)pent-3-en-2-one (6), and 359 mg (3.2 mmol, 4.0 equiv) of KO'Bu while following the general procedure A yielded complex 12 as a yellow powder (93 mg, 19.1%). Mp: >325 °C (dec). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz): δ 8.40–8.15 (m, 1H, CH<sub>arom</sub>), 8.09 (d, J = 8.4 Hz, 1H, CH<sub>arom</sub>), 7.86 (dd, J = 13.5 Hz, J = 8.0 Hz, 2H,  $CH_{arom}$ ), 7.53 (t, J = 7.8 Hz, 1H,  $CH_{arom}$ ), 7.45 (dd, J = 10.9 Hz, J = 4.0 Hz, 1H, CH<sub>arom</sub>), 7.37 (ddd, J = 6.8 Hz, J = 4.9 Hz, J = 1.0 Hz, 1H,  $CH_{arom}$ ), 7.30 (d, J = 8.1 Hz, 1H,  $CH_{arom}$ ), 7.20 (d, J = 7.2 Hz, 1H, CH<sub>arom</sub>), 7.17-7.11 (m, 1H, CH<sub>arom</sub>), 6.99 (m, 1H, CH<sub>arom</sub>), 5.30 (s, 1H,  $CH_{acnac}$ ), 2.48 (s, 3H,  $CH_{3;NHC}$ ), 2.22 (s, 3H,  $CH_{3;acnac}$ ), 1.82 (s, 3H,  $CH_{3;NHC}$ ), 1.52 (s, 3H,  $CH_{3;acnac}$ ) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz):  $\delta$  179.1 (CO/CN), 176.9 (CO/CN), 163.7 (NCS), 150.7 (C<sub>i</sub>-Pt), 149.7 (C<sub>i</sub>), 136.1 (C<sub>i</sub>), 135.1 (C<sub>i</sub>), 133.9 (C<sub>i</sub>), 131.7 (CH<sub>arom</sub>), 129.7 (C<sub>i</sub>), 127.7 (CH<sub>arom</sub>), 126.5 (CH<sub>arom</sub>), 126.4 (CH<sub>arom</sub>), 126.2 (CH<sub>arom</sub>), 126.0 (CH<sub>arom</sub>), 125.2 (CH<sub>arom</sub>), 123.5 (2C, CH<sub>arom</sub>), 123.2  $(CH_{arom})$ , 122.2  $(CH_{arom})$ , 113.0  $(CH_{arom})$ , 100.6  $(CH_{arom})$ , 26.9  $(CH_{3})$ , 24.3  $(CH_{3})$ , 14.5  $(CH_{3})$ , 12.3  $(CH_{3})$  ppm. <sup>195</sup>Pt NMR (65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3397 ppm. MS (ESI<sup>+</sup>, m/z, fragment): 608.3 (M + H)<sup>+</sup>. Anal. Calcd for C<sub>26</sub>H<sub>24</sub>N<sub>2</sub>OPtS: C, 51.39; H, 3.98; N, 4.61; S, 5.28. Found: C, 51.03; H, 3.90; N, 4.46; S, 5.07.

[4,5-Dimethyl-3-phenyl- $\kappa$ C'-1,3-thiazol-2-ylidene- $\kappa$ C]-[N-(2,4-difluorophenyl)-4-aminopent-3-en-2-onato- $\kappa N, \kappa O$ ]platinum(II) (13). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1 equiv) of Pt(COD)Cl<sub>2</sub>, 676 mg (3.2 mmol, 4 equiv) of 4-(N-(2,4difluorphenyl)amino)pent-3-en-2-one (7), and 59 mg (3.2 mmol, 4 equiv) of KO<sup>t</sup>Bu while following the general procedure A yielded complex 13 as a yellow powder (85 mg, 17.9%). Mp: 274–276 °C. <sup>1</sup>H NMR (CDCl<sub>3</sub>, 25 °C, 500 MHz): δ 8.34–8.05 (m, 1H, CH<sub>arom</sub>), 7.38 (d, J = 8.0 Hz, 1H,  $CH_{arom}$ ), 7.14 (tt, J = 14.4 Hz, J = 7.2 Hz, 1H), 7.10-6.83 (m, 4H, CH<sub>arom</sub>), 5.25 (s, 1H, CH<sub>acnac</sub>), 2.61 (s, 3H,  $CH_{3;NHC}$ ), 2.15 (s, 3H,  $CH_{3;acnac}$ ), 2.07 (s, 3H,  $CH_{3;NHC}$ ), 1.67 (s, 3H,  $CH_{3;acnac}$ ) ppm. <sup>13</sup>C NMR (CDCl<sub>3</sub>, 25 °C, 125 MHz):  $\delta$  178.4 (CO/ CN), 178.0 (CO/CN), 164.3 (NCS), 161.2 (dd, J = 248.3 Hz, J = 10.8 Hz, C<sub>i</sub>), 155.8 (dd, J = 248.3 Hz, J = 10.9 Hz, C<sub>i</sub>), 150.6 (C<sub>i</sub>-Pt), 137.3 (dd, J = 13.3 Hz, J = 3.8 Hz,  $CH_{arom}$ ), 136.9 (C<sub>i</sub>), 133.8 (C<sub>i</sub>), 131.7  $(CH_{arom})$ , 129.0 (dd, J = 10.9 Hz, J = 2.4 Hz,  $CH_{arom}$ ), 125.6 ( $CH_{arom}$ ), 123.5 ( $C_i$ ), 123.3 ( $CH_{arom}$ ), 113.2 ( $CH_{arom}$ ), 112.1 (dd, J = 21.8 Hz, J = 21.8 H 3.8 Hz,  $CH_{arom}$ ) 105.1 (dd, J = 25.8 Hz, J = 24.4 Hz,  $CH_{arom}$ ) 100.9 (CH<sub>arom</sub>), 26.9 (CH<sub>3</sub>), 24.1 (CH<sub>3</sub>), 14.6 (CH<sub>3</sub>), 12.5 (CH<sub>3</sub>) ppm. <sup>19</sup>F NMR (CDCl<sub>3</sub>, 25 °C, 75 MHz):  $\delta$  –118.1 (d, J = 6.1 Hz, CF), –114.3 (d, J = 6.1 Hz, CF) ppm. <sup>195</sup>Pt NMR (65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3395 ppm. MS (ESI<sup>+</sup>, m/z, fragment): 594.2 (M + H)<sup>+</sup>. Anal. Calcd for C222H20F2N2OPtS: C, 44.52; H, 3.37; N, 4.72; S, 5.40. Found: C, 44.88; H, 3.33; N, 4.59; S, 5.31.

[4,5-Dimethyl-3-phenyl-κC'-1,3-thiazol-2-ylidene-κC]-[4-aminopent-3-en-2-onato-KN,KO]platinum(II) (16). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5-dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1.0 equiv) of Pt(COD)Cl<sub>2</sub>, 317 mg (3.2 mmol, 4 equiv) of 4-aminopent-3-en-2-one (14), and 359 mg (3.2 mmol, 4.0 equiv) of KO'Bu while following the general procedure A yielded complex 16 as a mixture of two regioisomers as a green powder (141 mg, 36.6%). Mp: 252-254 °C. <sup>1</sup>H NMR (isomeric mixture, CDCl<sub>3</sub>, 25 °C, 300 MHz): δ 8.19-7.94 (m, 1H, CH<sub>arom</sub>), 7.72-7.29 (m, 5.6H, CH<sub>arom</sub>), 7.22-7.11 (m, 1H, CH<sub>arom</sub>), 7.11-6.94 (m, 1H, 3.4H,  $CH_{arom}$ ), 5.07 (s, 2.2H,  $CH_{acnac}$ ), 2.68 (s, 6.6H,  $CH_3$ ), 2.26 (s, 3H,  $CH_3$ ), 2.24 (s, 3H,  $CH_3$ ), 2.07 (s, 7.2H,  $CH_3$ ), 2.04 (s, 3.6H, CH<sub>3</sub>), 2.01 (s, 3H, CH<sub>3</sub>) ppm. The isomeric ratio was determined to be 1:1.2 after investigation of the <sup>1</sup>H NMR integral for the CH<sub>acnac</sub>proton signal at 5.07 ppm and the  $CH_{arom}$ -proton signal at about 8.07 *ppm.* <sup>13</sup>C NMR (isomeric mixture, CDCl<sub>3</sub>, 25 °C, 75 MHz):  $\delta$  190.3 (CN), 178.7 (CO), 177.4 (CO), 176.5 (CO), 164.4 (NCS), 164.1 (NCS), 152.4 (C<sub>i</sub>-Pt), 150.9 (C<sub>i</sub>-Pt), 138.7 (C<sub>i</sub>), 137.4 (C<sub>i</sub>), 136.8 (C<sub>i</sub>), 132.4 ( $CH_{arom}$ ), 130.8 ( $CH_{arom}$ ), 126.8 ( $C_i$ ), 125.7 ( $CH_{arom}$ ), 125.1 (CH<sub>arom</sub>), 123.8 (C<sub>i</sub>), 122.9 (CH<sub>arom</sub>), 122.8 (C<sub>i</sub>), 122.5 (C<sub>i</sub>), 114.1 (CH<sub>arom</sub>), 113.1 (CH<sub>arom</sub>), 98.9 (CH<sub>arom</sub>), 28.5 (CH<sub>arom</sub>), 28.3 (CH<sub>3</sub>), 27.2 (2C, CH<sub>3</sub>), 14.4 (CH<sub>3</sub>), 14.3 (CH<sub>3</sub>), 12.7 (2C, CH<sub>3</sub>) ppm. <sup>195</sup>Pt

NMR (isomeric mixture, 65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3351, –3375 ppm. MS (ESI<sup>+</sup>, *m/z*, fragment): 482.3 (M + H)<sup>+</sup>. Anal. Calcd for C<sub>16</sub>H<sub>18</sub>N<sub>2</sub>OPtS: C, 39.91; H, 3.77; N, 5.82; S, 6.66. Found: C, 39.91; H, 3.78; N, 5.80; S, 6.46.

[4,5-Dimethyl-3-phenyl- $\kappa$ C'-1,3-thiazol-2-ylidene- $\kappa$ C]-[3-amino-1-phenyl-but-2-en-1-onato-κN,κO]platinum(II) (17). According to the general procedure A 20 mL of dry DMF was added to a mixture of 268 mg (0.8 mmol) of the N-phenyl-4,5-dimethyl-1,3-thiazolium hexafluorophosphate salt 1 and 102 mg (0.44 mmol, 0.55 equiv) of Ag<sub>2</sub>O. Stepwise addition of 299 mg (0.8 mmol, 1.0 equiv) of Pt(COD)Cl<sub>2</sub>, 516 mg (3.2 mmol, 4 equiv) of 3-amino-1-phenylbut-2en-1-one (15), and 359 mg (3.2 mmol, 4.0 equiv) of KO'Bu while following the general procedure A yielded complex 17 as a mixture of two regioisomers as a yellow powder (124 mg, 28.4%). Mp: >317 °C (dec). <sup>1</sup>H NMR (isomeric mixture, CDCl<sub>3</sub>, 25 °C, 300 MHz): δ 8.28– 8.15 (m, 0.3H, CH<sub>arom</sub>), 8.06-8.00 (m, 2.6H, CH<sub>arom</sub>), 7.51-7.46 (m, 2H, CH<sub>arom</sub>), 7.44–7.38 (m, 4.2H, CH<sub>arom</sub>), 7.11–7.01 (m, 2.6H,  $CH_{arom}$ ), 5.79 (d, J = 2.1 Hz, 1H,  $CH_{arom}$ ), 5.76 (d, J = 2.2 Hz, 0.3H, CH<sub>arom</sub>), 2.70 (s, 3.9H, CH<sub>3</sub>), 2.30 (s, 3H, CH<sub>3</sub>), 2.26 (s, 0.9H, CH<sub>3</sub>), 2.20 (s, 0.9H, CH<sub>3</sub>) ppm. The isomeric ratio was determined to be 1:0.3 after investigation of the <sup>1</sup>H NMR integrals for the CH<sub>acnac</sub>-proton signals at 5.79 and 5.78 ppm. <sup>13</sup>C NMR (isomeric mixture, CDCl<sub>3</sub>, 25 °C, 75 MHz): δ 190.3 (CN), 172.4 (CO), 165.4 (NCS), 152.5 (C<sub>i</sub>-Pt), 140.6 (C<sub>i</sub>), 136.9 (C<sub>i</sub>), 130.9 (CH<sub>arom</sub>), 129.4 (CH<sub>arom</sub>), 128.2 (CH<sub>arom</sub>), 126.9 (CH<sub>arom</sub>), 125.2 (CH<sub>arom</sub>), 124.0 (C<sub>i</sub>), 122.9 (CH<sub>arom</sub>), 114.2 (CH<sub>arom</sub>), 96.6 (CH<sub>arom</sub>), 29.0 (CH<sub>3</sub>), 14.4 (CH<sub>3</sub>), 12.8 (CH<sub>3</sub>) ppm.  $^{195}$  Pt NMR (isomeric mixture, 65 MHz, 25 °C, CDCl<sub>3</sub>):  $\delta$  –3322, -3349 ppm. MS (ESI<sup>+</sup>, m/z, fragment): 544.3 (M + H)<sup>+</sup>. Anal. Calcd for C<sub>21</sub>H<sub>20</sub>N<sub>2</sub>OPtS: C, 46.32; H, 3.71; N, 5.15; S, 5.90. Found: C, 46.37; H, 3.66; N, 5.17; S, 5.92.

# ASSOCIATED CONTENT

#### **S** Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organo-met.6b00710.

List of abbreviations, 1D and detailed 2D NMR spectra, photoluminescence data, crystallographic data, and details of the quantum chemical calculations (PDF) Crystallographic data (CIF) Optimized *xyz*-coordinates data (XYZ)

#### AUTHOR INFORMATION

#### **Corresponding Author**

\*Fax: +49 351-463-39679. Tel: +49 351-463-38571. E-mail: thomas.strassner@chemie.tu-dresden.de.

#### ORCID 🔍

Thomas Strassner: 0000-0002-7648-457X

#### Notes

The authors declare no competing financial interest.

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