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Photoluminescence of a New Material: Cyclometalated C^C* Thiazole-2-ylidene Platinum(II) Complexes

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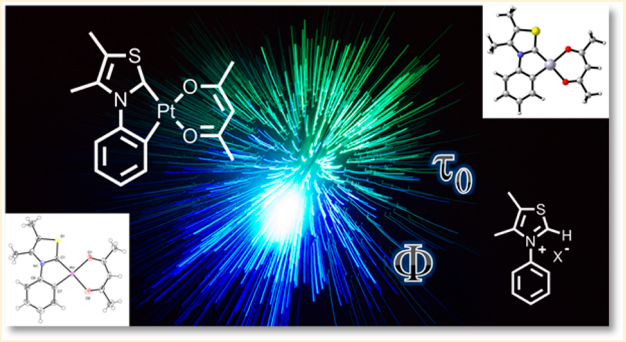
Supporting Information

ABSTRACT: A new class of platinum(II) compounds, the 4,5-dimethyl-3-aryl-thiazole-2-ylidene platinum(II) acetylacetonato complexes, are described. Their efficient phosphorescent emission at room temperature makes them suitable for potential applications in organic light-emitting diodes. A new synthetic pathway that allows the preparation of a broad range of different *N*-arylthiazole-2-thiones and their subsequent conversion into the corresponding *N*-arylthiazolium perchlorate and hexafluorophosphate salts has been developed. Not only electron-rich (4-OMe, 4-Me, 3-Me) *N*-arylthiazoles but also electron-deficient ligands with a cyano or an ester group could be synthesized. From commercially available anilines *N*-arylthiazolium perchlorate and hexafluorophosphate salts were synthesized via ring-closure of *in situ* generated *N*-aryldithiocarbamate salts followed by a sulfur-oxidation/-substitution protocol to the air-stable carbene precursors. All reactions were performed in multigram scale in good yields. The synthesis of the corresponding platinum(II) complexes involves generating the corresponding *N*-arylthiazole-silver(I)-carbene complexes, transmetalation to platinum, cyclometalation, and reaction with acetylacetonate (acac). Solid-state structures of two *N*-arylthiazole-2-thiones, one *N*-arylthiazolium salt, and three *N*-arylthiazole-2-ylidene-platinum(II) complexes complement the analytic characterization including ^{195}Pt NMR. The unsubstituted complex 4,5-dimethyl-3-phenylthiazole-2-ylidene-platinum(II)-acac was additionally characterized by 2D-NMR techniques (COSY, HSQC, HMBC, NOESY). Photoluminescence measurements were performed in amorphous poly(methyl methacrylate) films and revealed bluish-green emission maxima (~500 nm) independent of the electronic structure of the thiazoles, whereas the variation of the substitution pattern at the cyclometalating aryl system led to excellent quantum efficiencies and decay lifetimes of 8.1−21.4 μs.



INTRODUCTION

Sulfur-containing heterocycles have been an interesting and challenging motif in organic synthesis for more than a century.[1] From marine and terrestrial organisms, from simple industrial products to essential structures and building blocks in the human immune system, many different compounds have been isolated and thoroughly investigated.[2] Historically thiazole structures were early found to show interesting properties and have been studied up until today.[3] Structure−activity relationships of thiazole derivatives have been extensively investigated to explain their biological effects.[4] One is attributed to *in situ* generated carbene structures (Scheme 1, general structure **I**) followed by subsequent C2 substrate binding.[5] The most prominent example, the coenzyme thiamine (Scheme 1, **II**), itself represents a thiazole-2-ylidene precursor. Such *in situ* generated carbene structures[6] and respectively their ruthenium metal complexes[7] have been investigated in detail for their catalytic activities. Additionally, structurally diverse mesoionic 1,3-thiazole metal complexes were presented by Bertrand[8] and Shi.[9]

Sulfur-containing heterocycles and foremost their metal complexes are currently also of great interest because of their photophysical properties.[10] Compared to typical reoccurring motifs such as pyridine,[11] triazole,[12] and pyrazole structures,[13] only a small percentage of sulfur-containing heterocycles are found in emitter molecules.[14] The most commonly described structures contain C^N-coordinated 2-aryl-1,3-thiazoles (Scheme 1, **III**) at metals such as iridium[15] or platinum[16] and were shown to be interesting phosphorescent materials. To date phosphorescent complexes, used in organic light-emitting diodes (OLEDs), frequently rely on *N*-heterocyclic carbenes (NHCs)[17] derived from arylimidazole[18] and aryltriazole[19] structures to achieve defined emission wavelengths, high quantum yields, and short decay lifetimes. We could only find one report on the synthesis of cyclometalated ruthenium NHC complexes based on the *N*-aryl-1,3-thiazole-2-ylidene motif (Scheme 1, general motif **IV**) but without describing the photophysical properties.[20]

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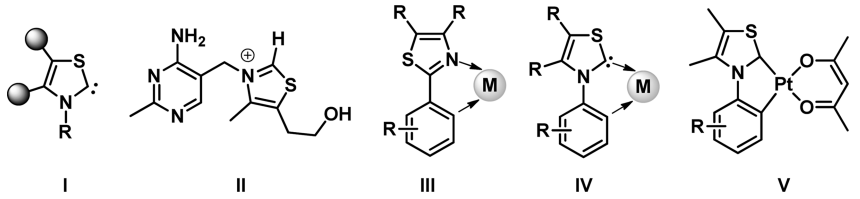
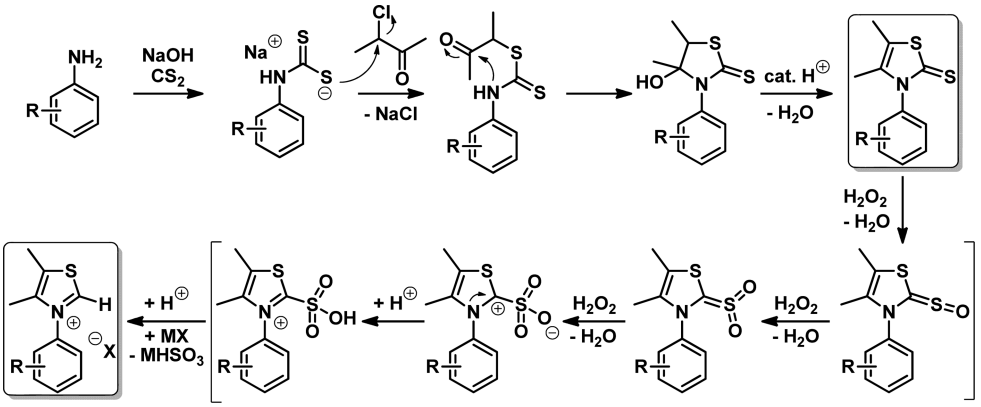
Scheme 1. Overview of 1,3-Thiazole Compounds I–V



Scheme 2. Postulated Mechanism for the Formation of *N*-Aryl-thiazolium Salts (MX = $NaClO_4$ or KPF_6) with Highlighted Isolated Compounds



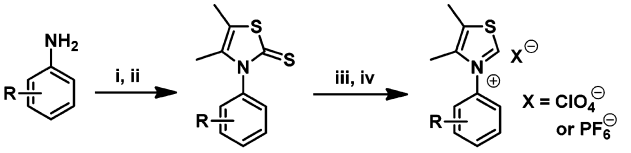
Herein we report the synthesis and the photophysical properties of a new class of C^C* cyclometalated platinum(II) *N*-arylthiazole-2-ylidene complexes with acetylacetonate ligands (Scheme 1, **V**). We developed and optimized a new synthetic route that allowed us to prepare structurally and electronically diverse *N*-arylthiazolium perchlorate and hexafluorophosphate salts starting from commercial anilines. The different electronic structure of the *N*-arylthiazole (compared to typical imidazole and triazole moieties) allowed us to develop a new type of efficient blue to green room-temperature emitter molecules. We studied the effect of electronically different substituents at the cyclometalating aryl ring on the photoluminescence properties.

RESULTS AND DISCUSSION

Synthesis. For the synthesis of the general motif of the *N*-arylthiazolium salts as carbene precursors there is recent literature precedent using different approaches.[7b,21] In particular the groups of Bach[22] and Glorius[23] used a two-step reaction sequence starting from commercially available anilines. The first step involves the reaction of different anilines with carbon disulfide in a basic medium and leads to the formation of the corresponding dithiocarbamate salts by a nucleophilic attack on the CS_2 carbon atom. The ring-closure is then achieved by adding an α-haloketone compound. Substitution of the chlorine atom by the nucleophilic sulfur atom is followed by another nucleophilic attack of the nitrogen atom onto the carbonyl function.[24] Treatment of the crude *N*-arylhydroxythiazolidine with hydrochloric acid finally yields the desired *N*-arylthiazole-2-thione structures (see Scheme 2 for a possible mechanism). Some *N*-arylthiazole structures with (sterically demanding) alkyl substituents[25] have been reported in the literature, but only a few examples of electronic variations of the phenyl ring can be found.[26]

Following the procedure reported by Bach[22] and Glorius[23] we were able to synthesize compound **8**, previously reported by different groups,[27] with a phenyl ring attached to the nitrogen atom and two methyl groups in the 4- and 5-position of the thiazole heterocycle by using 3-chloro-2-butanone (see Scheme 3). But unfortunately we found that the reported route does not allow the synthesis of new compounds with electron-donating or -withdrawing substituents. We therefore needed to change the procedure for the *N*-arylthiazole-2-thione synthesis. By using freshly ground sodium hydroxide, avoiding an aqueous solution, we were able to transform even electron-deficient anilines **2**, **4**, and **6** (Br, CN, CO_2Me) as well as electron-rich anilines **3**, **5**, and **7** (OMe, Me) into the desired thiazole structures **8**–**14** (see Scheme 3). After the reaction all *N*-arylthiazole-2-thiones **8**–**14** crystallized from the acidic solution. Filtration, washing with alcohol, and drying gave the

Scheme 3. Synthesis of *N*-Arylthiazole-2-thiones 8–14 and *N*-Arylthiazole-2-ium Salts 15–24[a]



1 R = H	**8** R = H	**15** R = H X = ClO_4
2 R = 4-Br	**9** R = 4-Br	**16** R = H X = PF_6
3 R = 4-OMe	**10** R = 4-OMe	**17** R = 4-Br X = ClO_4
4 R = 4-CN	**11** R = 4-CN	**18** R = 4-Br X = PF_6
5 R = 4-Me	**12** R = 4-Me	**19** R = 4-OMe X = PF_6
6 R = 4-CO_2Me	**13** R = 4-CO_2Me	**20** R = 4-CN X = PF_6
7 R = 3-Me	**14** R = 3-Me	**21** R = 4-Me X = PF_6
		22 R = 4-CO_2Me X = PF_6
		23 R = 3-Me X = ClO_4
		24 R = 3-Me X = PF_6

[a](i) NaOH, DMSO, then CS_2, 0 °C to rt, then 3-chloro-2-butanone, 0 °C to rt, aqueous workup; (ii) HCl, EtOH, reflux; (iii) 3 equiv of H_2O_2, AcOH, rt; (iv) $NaClO_4$ or KPF_6, $MeOH/H_2O$, rt.

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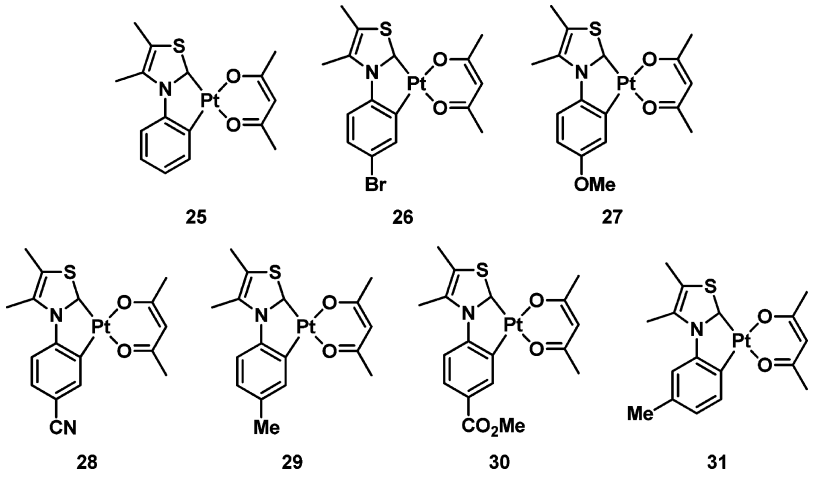
Scheme 4. Synthesized Platinum Complexes 25−31

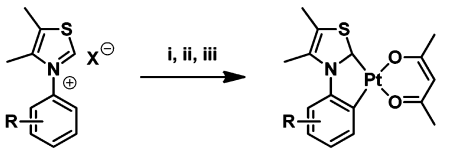


pure *N*-arylthiazole-2-thiones **8**−**14** in good yields from 30% to 68% even on a larger scale of 25 to 50 mmol.

The following generation of the *N*-arylthiazolium salts has been described by different groups[21−23] and involves an oxidation/substitution protocol in an acidic medium. Slow addition of H_2O_2 to an acetic acid solution of the *N*-arylthiazole-2-thiones **8**−**14** reliably removed the thione sulfur atom. As mentioned in the literature, this step includes the stepwise formation of a sulfonic acid derivative by oxidation of the thione sulfur atom.[28] The hydrogen atom at C2 is then introduced by a substitution/desulfonation process using a proton from the acidic solution as electrophile (see Scheme 2).[29] After evaporation of the solvent a salt metathesis yields the desired products. Either sodium perchlorate or potassium hexafluorophosphate was used to give the *N*-arylthiazolium perchlorate (ClO_4) or hexafluorophosphate (PF_6) salts **15**−**24** (see Scheme 3). After a washing and extraction procedure (see general procedure B in the Experimental Data section) all *N*-arylthiazolium salts were isolated by slow precipitation upon addition of diethyl ether to a concentrated dichloromethane solution. Only in the case of the perchlorate salt **23** was a further purification step using column chromatography necessary. Overall the hexafluorophosphate salts tend to be less hygroscopic compared to their perchlorate counterparts. Therefore, the hexafluorophosphate salts were preferably used for the complex synthesis, which is in need of dry reaction conditions. Moreover the advantage of using the *N*-arylthiazolium hexafluorophosphate salts over the perchlorate compounds is that the formation of potentially dangerous silver perchlorate in the drying process of the platinum(II) complex synthesis (see Experimental Data section, general procedures C and D) can be avoided. All *N*-arylthiazolium salts are obtained in yields from 10% to 72% on a scale of 5 to 10 mmol.

All complexes shown in Scheme 4 were prepared using an established one-pot synthesis developed in our group.[30] This procedure involves the deprotonation of the carbene precursor (here: *N*-arylthiazolium salts) in 1,4-dioxane using silver oxide (Ag_2O), transmetalation to dichloro(1,5-cyclooctadiene)-platinum(II) ($Pt(COD)Cl_2$), and cyclometalation by using a temperature gradient in a dioxane/butanone mixture. Afterward the acetylacetonate ligand is added under basic conditions in dimethylformamide (DMF) using KO^{t}Bu as the base (see Scheme 5, **A**). All complexes could be isolated by flash chromatography using dichloromethane as the solvent.

Scheme 5. Synthesis of the Cyclometalated Complexes 25−31[a]



15	R = H	X = ClO_4	**25** R = H	**A**
16	R = H	X = PF_6	**25** R = H	**B**
17	R = 4-Br	X = PF_6	**26** R = 4-Br	**A, B**
19	R = 4-OMe	X = PF_6	**27** R = 4-OMe	**A, B**
20	R = 4-CN	X = PF_6	**28** R = 4-CN	**A, B**
21	R = 4-Me	X = PF_6	**29** R = 4-Me	**B**
22	R = 4-CO_2Me	X = PF_6	**30** R = 4-CO_2Me	**B**
24	R = 3-Me	X = PF_6	**31** R = 5-Me	**B**

[a](i) 0.55 equiv of Ag_2O, rt to 50 °C, **A**: 1,4-dioxane (**B**: DMF) ; (ii) $Pt(COD)Cl_2$, rt to 115 °C, **A**: 1,4-dioxane/butanone (**B**: DMF); (iii) 4 equiv of Hacac, DMF, rt to 100 °C, **A**: 4 equiv of KO^{t}Bu (**B**: 4 equiv of K_2CO_3).

Washing the bright yellow compounds with diethyl ether and isohexanes yielded the pure complexes **25**−**31**. Over the course of this study we also focused on improving the yields and the general experimental procedure of the complex synthesis. We found DMF to be a superior solvent and lowered the basicity in the final step by employing K_2CO_3 as the base (Scheme 5, **B**). With this new protocol we were able to improve the yields of complexes **25**−**28** by more than 50% (e.g., for complex **26** we observed a 3-fold increase in comparison to the conventional synthesis). Complexes **29**−**31** were subsequently prepared using the new procedure. Noteworthy, even complex **31**, bearing an ester group, could be isolated analytically pure from the basic reaction conditions showing no signs of an ester hydrolysis. In conclusion seven new air-stable platinum(II) complexes with an acetylacetonate ligand[19a,31] based upon *N*-arylthiazolium salts as precursors were prepared in good yields of 24% up to 54% using the optimized one-pot procedure.

Characterization. All *N*-arylthiazole-2-thiones, *N*-arylthiazolium salts, and *N*-arylthiazole-2-ylidene platinum(II) complexes were investigated by standard techniques involving ^{1}H and ^{13}C NMR, as well as gas chromatography mass spectrometry (GCMS) for **8**−**14**, electron spray ionization mass spectrometry (ESI-MS) for **15**−**24**, and ^{195}Pt NMR for all complexes **25**−**31**. For complex **25** additional 2D-NMR spectra

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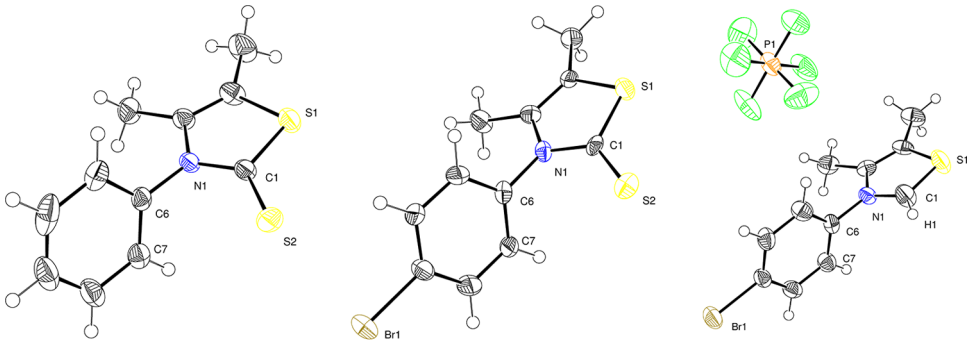

Figure 1. ORTEP representations of *N*-arylthiazole-2-thiones **8** and **9** and *N*-arylthiazolium salt **18**. Thermal ellipsoids are drawn at the 50% probability level.

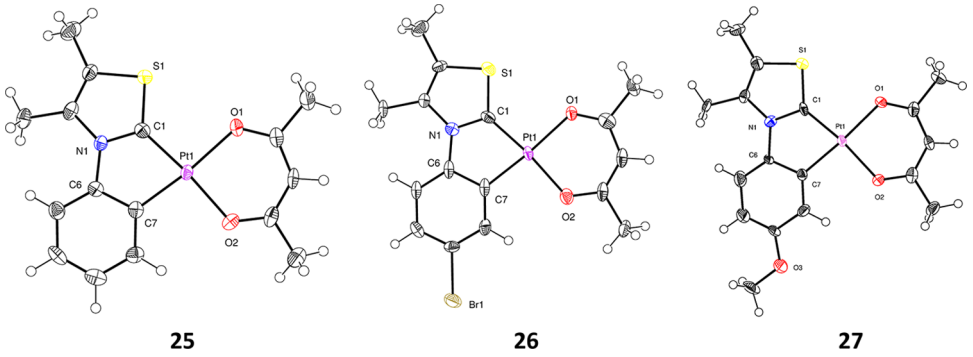

Figure 2. ORTEP representations of thiazole-2-ylidene platinum(II) complexes **25**–**27**. Thermal ellipsoids are drawn at the 50% probability level.

were recorded (COSY, HSQC, HMBC, and NOESY; see Supporting Information).

The ^{1}H chemical shifts for the proton at the C2 carbon atom of the *N*-arylthiazolium salts **15**–**24** were detected at 10.20–10.29 ppm. For those salts the resonance of the C2 carbon atom in the ^{13}C NMR spectra was found at chemical shifts between 157.04 and 157.86 ppm. The hexafluorophosphate salts show melting points between 86 and 166 °C. In comparison the perchlorate salts **15**, **17**, and **23** possess even lower melting points compared to the corresponding hexafluorophosphate salts. In addition to the cationic *N*-arylthiazolium fragment detected by ESI-MS, all *N*-arylthiazolium salts show higher *m*/*z* values that can be matched to the formation of charged pairs consisting of two positive *N*-arylthiazolium fragments and one counterion.

All complexes are bright yellow compounds and tend to decompose in the NMR solvent $CDCl_3$. As other typical NMR solvents (MeOD, d_3-MeCN, d_6-benzene, d_6-DMSO) could not sufficiently dissolve complexes **25**–**31**, all compounds were still measured in $CDCl_3$ but recorded as fast as possible to avoid decomposition before or during the acquisition of the spectra.

In addition to the 4-methyl-substituted complex **29**, the regioisomer **31** with the methyl group in the 5-position was synthesized to investigate the impact of the substitution pattern on the photoluminescence properties. In principle two different regioisomers regarding complex **31** could be formed (see DFT section), but only complex **31**, with the methyl group in the 5-position, was isolated according to the NMR data (see Experimental Data section).

We additionally recorded ^{195}Pt NMR spectra of all seven *N*-arylthiazol-2-ylidene platinum(II) complexes and compared the resonances with values reported in the literature. Complexes **25**–**31** show chemical shifts between −3346.21 and −3311.01 ppm in the ^{195}Pt NMR. These values are similar to those previously reported for imidazole- and triazole-based C^C* cyclometalated complexes with O^O ligands.[32]

Depending on the substitution pattern, the melting points of these novel platinum(II) complexes are quite different. Values between 264 and 265 °C for the methoxy-substituted complex **27** and 277–278 °C in case of the bromo-substituted complex **26** can be observed. Complexes **28** and **30** show decomposition at higher temperatures (>300 °C).

Solid-State Structure Determination. Single crystals of **8**, **9**, **18**, **26**, and **27** suitable for X-ray diffraction were obtained by slow evaporation of a saturated dichloromethane solution (Figures 1 and 2). Despite being bright yellow powders, complexes **26** and **27** crystallized as dark green crystals after evaporation. In the case of complex **25**, a concentrated dichloromethane solution was slowly infused with diethyl ether to yield bright yellow crystals. Details of the solid-state structure determination are given in the Supporting Information (Tables S1 and S2).

Both *N*-arylthiazole-2-thiones **8** and **9** as shown in Table 1 reveal similar S1–C1 bond distances of 1.718(6) Å for the unsubstituted thione **8** and of 1.726(10) Å for the bromo-substituted compound **9**. In addition the C1–N1 bond distances (1.357(7) Å for **8** and 1.363(12) Å in the case of compound **9**) and S(1)–C(1)–N(1) angles (108.5(4)° for compound **8** and 107.9(6)° for structure **9**) show only minor structural differences for the thiazole moiety. On the contrary compounds **8** (−74.1(7)°) and **9** (−79.3(12)°) reveal different C7–C6–N1–C1 torsions of the phenyl ring. Those values differ significantly (by more than 10 degrees) from the results of the DFT calculations, which show a nearly perpendicular

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Table 1. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles (deg) of the *N*-Arylthiazole-2-thiones 8 and 9 and the *N*-Arylthiazolium Salt 18

	8	9	18
S1−C1	1.718(6)	1.726(10)	1.657(8)
C1−N1	1.357(7)	1.363(12)	1.320(9)
N1−C6	1.434(7)	1.458(12)	1.446(9)
S1−C1−S2	124.2(4)	124.4(6)	(124.0)[a]
S1−C1−N1	108.5(4)	107.9(6)	112.2(5)
N1−C1−S2	127.3(4)	127.7(7)	−95.6(7)
C7−C6−N1−C1	−74.1(7)	−79.3(12)	178.3(4)

[a]In the case of compound **18** this refers to S1−C1−H1.

orientation of the phenyl ring to the thiazole moiety (see Supporting Information, Tables S5 and S6).

In comparison to the *N*-arylthiazole-2-thione structures **8** and **9** the *N*-arylthiazolium salt **18** shows shorter S1−C1 (1.657(8) Å) and C1−N1 (1.320(9) Å) bonds and a longer C1−N1 (1.446(9) Å) bond. Additionally the S1−C1−N1 angle (112.2(5)°) widens, whereas the N1−C1−S2 angle contracts (95.6(7)°). These structural changes in bond distances and angles further involve an almost perpendicular orientation (95.6(7)°) of the 4-bromophenyl ring to the N,S-heterocycle (for a comparison with DFT calculations see the Supporting Information, Table S7). Further investigations of the solid-state structure showed that no interactions of the ring structures (carbocycle or thiazole) with neighboring *N*-arylthiazolium molecules can be found due to the hexafluorophosphate anion, which is positioned in between the *N*-arylthiazolium structures (see Supporting Information, Figure S3).

Table 2. Selected Bond Lengths (Å), Angles (deg), and Dihedral Angles (deg) of Complexes 25−27

	25	26	27
C1−Pt	1.907(11)	1.907(5)	1.905(11)
C7−Pt	1.957(13)	1.967(4)	2.002(11)
Pt−O1	2.076(8)	2.082(3)	2.090(8)
Pt−O2	2.041(8)	2.052(3)	2.044(7)
C1−Pt−C7	79.9(5)	79.4(2)	79.9(5)
O1−Pt−O2	90.7(3)	90.61(13)	91.4(3)
C1−N1−C6−C7	1.5(14)	−2.7(5)	3.6(12)
O2−Pt−O1−C13	−3.7(10)	−1.2(4)	6.8(9)
Pt···Pt[a]	5.338	7.028	7.002

[a]Shortest intermolecular Pt−Pt distances.

All three complexes crystallize in a monoclinic crystal system and reveal a square planar coordination of the platinum(II) atom but with deviations from the ideal angles. While the O1−Pt−O2 angles are the closest to 90°, the C1−Pt−C7 angles (79.4(2)−79.9(5)°) show deviations of about 10 degrees as also observed for the imidazole- and triazol-based C^C* platinum(II) complexes.[19b,32a,33] The C1−Pt bond (1.905(11)−1.907(5) Å) is the shortest of all platinum−ligand bonds. The oxygen atom bond lengths show only minor differences (2.041(8)−2.090(8) Å), while the C7−Pt bonds are slightly shorter (1.957(13)−2.002)11) Å). Complex **25** forms molecular pairs (Pt···Pt distances 5.34 Å) in the solid state that are oriented at an angle of 49.19° toward the next molecular pair (both metallacycles were used for the calculation of the planes). Within two molecules $\pi-\pi$ interactions between the *N*-aryl-thiazol-2-ylidene moieties are found, revealing an interaction of the phenyl ring with a thiazole ring from the adjacent molecule (3.94 Å). Complex **26** shows a similar formation of molecular pairs and crystallizes in a zigzag pattern with an angle of about 53.1° between two molecular pairs. Pt···Pt distances of about 7.03 Å are revealed as well as $\pi-\pi$ interactions between two *N*-aryl-thiazol-2-ylidene moieties of 3.68 Å. For complex **27** no pairs are found but a zigzag layer of molecules with weak interactions between phenyl rings and thiazole moieties (4.53−5.02 Å) as well as interactions between the thiazole ring and the acetylacetonate ligand within 3.76 Å. All Pt···Pt distances of the three complexes exceed the sum of van der Waals radii for the platinum atom, indicating no interaction between two platinum metal atoms (see Supporting Information, Figures S4−S9).

In conclusion the *N*-arylthiazol-2-ylidene platinum(II) complexes show similar bond distances and angles regarding the central metal atom but provide a sterically less demanding environment at the heterocyclic ring compared to typical imidazole- and triazole-platinum(II) complexes with O^O ligands known from the literature.[18b,19a,31−33] This is a very promising result for the design of new emitter molecules.

Photoluminescence Properties. To investigate the photophysical behavior for this new class of complexes, the absorption and emission spectra at room temperature in doped poly(methyl acrylate) (PMMA) (2 wt % complex) were measured (see Supporting Information, Figures S12 and S13, for absorption and emission data for 100% emitter films). For all complexes a strong absorption between 250 and 280 nm is observed, and only minor absorptions appear in the region between 300 to 350 nm. Additionally local maxima in the low-energy region of 360 to 370 nm can be observed for all complexes (see Figure 3).

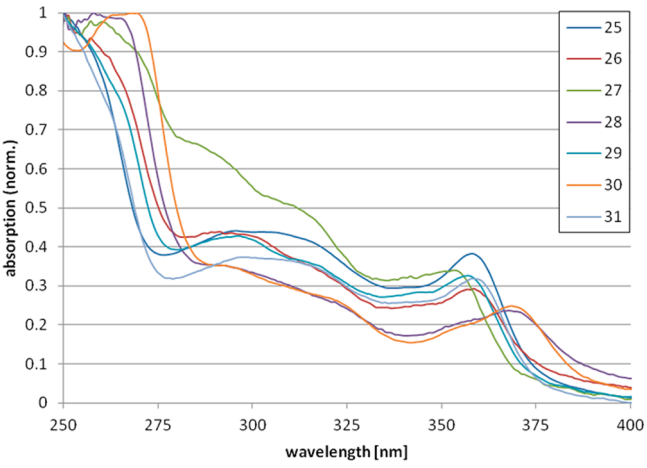

Figure 3. Absorption spectra of complexes **25−31** at room temperature (2 wt % in PMMA).

All new *N*-arylthiazole-2-ylidene platinum(II) complexes show interesting photoluminescence data (see Table 3), as they emit at room temperature and show high quantum yields, decay lifetimes of 8.1−21.4 μs, and remarkably stable emission maxima between 508 and 526 nm (see Figure 4). Interestingly all complexes emit in a very narrow range and retain their blue-green maximum emission wavelengths, almost independent from electron-donating or electron-withdrawing groups at the cyclometalating aryl ring, as only the shape of the emission spectra changed. Broad unstructured bands can be observed for

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Table 3. Photoluminescence Data (2 wt % in PMMA, rt) of the Cyclometalated Complexes 25−31

	λ_{exc} (nm)[a]	CIE $x;y$[b]	λ_{em} (nm)[c]	ϕ[d]	τ_0 (μs)[e]	k_r (10^3 s^{-1})[f]	k_{nr} (10^3 s^{-1})[g]
25	370	0.28;0.52	510	0.61	11.64	85.7	2776.8
26	360	0.32;0.50	508	0.67	9.30	107.0	2065.8
27	360	0.34;0.55	526	0.33	21.39	46.2	4790.5
28	370	0.39;0.49	515	0.72	10.93	92.0	2192.4
29	360	0.30;0.54	516	0.51	13.09	76.3	3273.2
30	370	0.31;0.55	520	0.79	8.11	97.4	1703.1
31	360	0.31;0.56	521	0.51	9.83	101.8	2454.9

[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 $\tau_0 = \tau_v/\phi$. [f]$k_r = \phi/\tau_v$. [g]$k_{nr} = (1 - \phi)/\tau_v$.

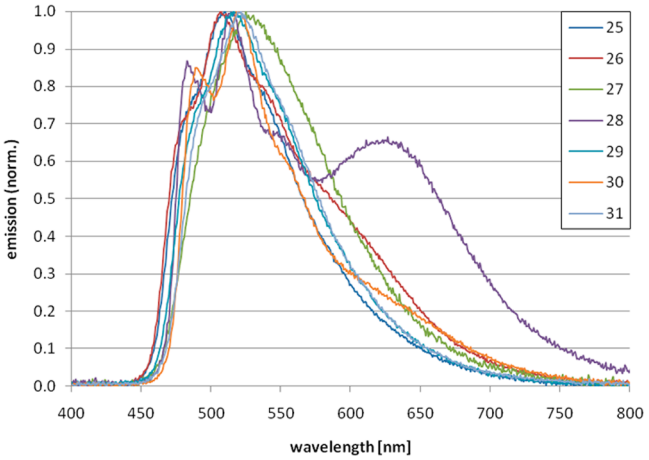

Figure 4. Emission spectra of complexes 25−31 at room temperature (2 wt % in PMMA).

compounds 25−27, 29, and 31, whereas complexes 28 and 30 show a spectrum with a vibronic coupling (progression distances of about 1120−1270 cm^{-1} for complex 28 and about 1070−1180 cm^{-1} for complex 30). In addition to the (global) maximum at 515 nm a second (local) maximum at about 640 nm can be observed for complex 28. These observations support a different emission process for complexes with electron-withdrawing substituents at the aryl system (28, 30) compared to the (mainly) electron-donating substituents present in complexes 25−27, 29, and 31.

While keeping stable blue-green emissions the substituents at the cyclometalating aryl ring furthermore enhance the quantum yields and the decay lifetimes. The unsubstituted complex 25 reveals quantum yields as high as 61%, a much higher intrinsic value when compared to the analogous triazole or imidazole complexes.[19b,30] Overall quantum yields from 33% up to 79% and decay lifetimes ranging from 8.1 to 21.4 μs were achieved by a variation of the substitution pattern at the cyclometalating aryl ring. We were pleased to find that the ester-substituted complex 30 not only showed the highest quantum yields and lowest τ_0 value but also retained high quantum yields of about 68% in the 100% film. All other complexes show lower quantum yields in the pure emitter film and a red-shift of the emission wavelength maxima (see Supporting Information Table S3).

In summary concerning the 2 wt % PMMA films, positive mesomeric or inductive effects originating from the methoxy and methyl substitution (complexes 27 and 29) decrease the overall quantum yield. In contrast negative mesomeric and inductive effects present in complexes 28 and 30 (CN and CO_2Me substituent) improve the quantum yields and lower the decay lifetimes. All comparisons are always related to the unsubstituted complex 25. The bromo-substituted compound 26 has a strong positive mesomeric effect and a small negative inductive effect showing a higher quantum yield than complex 25 and shorter decay lifetimes.

Comparing complexes 29 and 31, the decay lifetime of complex 31 could be lowered by 4 μs, but quantum yields and emission wavelengths are almost identical (see Supporting Information, Figures S10 and S11 for a direct comparison of absorption and emission spectra). In conclusion changing the position of the methyl substituent showed no significant improvement; hence no further variation was investigated.

Complexes 25−28 show remarkably better photoluminescence properties compared to their imidazole analogues.[30] Also complexes 25 and 28, when compared to their triazole-based equivalents,[19b] show enhanced quantum yields while maintaining good decay lifetimes. These data are very promising for developing new highly efficient emitters and their implementation in modern day phosphorescent OLEDs (PhOLEDs).

Quantum Chemical Calculations. All geometry optimizations including ground-state and triplet-state geometries were performed using DFT methods. As stated in the Characterization section complex 31 could possibly form two different regioisomers, but only the cyclometalated structure with the methyl group in the 5-position was isolated (see Figure 5).

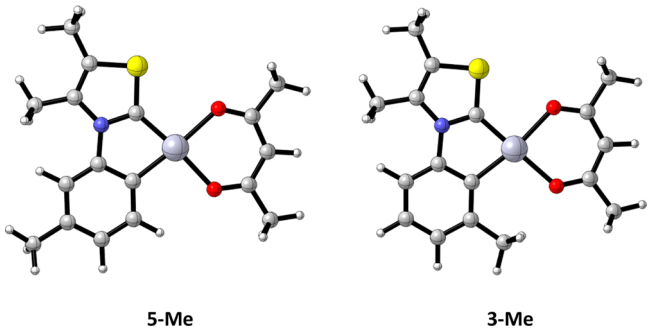

Figure 5. DFT (B3LYP/6-31G(d))-calculated geometries of possible isomers of complex 31.

Quantum chemical calculations support the formation of the 5-Me isomer, showing an energy difference of about 4 kcal/mol in favor of the sterically less hindered Pt environment (see Supporting Information, Table S4).

The calculated geometries and the solid-state structures are in very good agreement. Calculations on the triple-ζ level using B3LYP/6-311++G(d,p) show only minor geometrical changes for bond distances (up to 1%) and angles (up to 2%) compared to the structures obtained with B3LYP/6-31G(d) or BP86/6-31G(d). All three methods place the platinum atom in a perfectly planar environment, whereas the N1−C1−Pt−O1 dihedral angle in the solid-state structures shows a slight torsion of up to 2.8 degrees (see Supporting Information, Tables S8−S11, for a direct comparison).

The triplet-state geometries calculated by B3LYP/6-31G(d) show distortions of the thiazole ring system in comparison to the calculated singlet structures. Next to the distorted N1−C1−Pt−O1 dihedral angles, which slightly twist the NHC−ligand

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(171.1−175.0°), elongated C1−N1 bonds with differences of 0.98−1.17 Å and shortened N1−C6 distances with deviations of 0.65−0.82 Å are observed (see Supporting Information, Table S10). There is almost no change in the Pt−C and Pt−O bond distances, and no out-of-plane bending of the acetylacetonate ligand can be observed (also in the case of BP86). Spin densities based on B3LYP/6-31G(d) reveal a strong influence of the *N*-arylthiazole ligand and just a small contribution from the acetylacetonate (acac) system. This indicates that the main emission process is controlled by the thiazole-aryl moiety and therefore represents intraligand charge-transfer (ILCT) or metal-to-ligand charge-transfer (MLCT) character (see Supporting Information, Figure S15).

Using a previously described method developed in our group we could successfully predict the emission maxima by BP86/6-31G(d) and B3LYP/6-31G(d) calculations.[34] All complexes and their emission wavelengths could be well described and predicted.

CONCLUSION

The first seven C^C* cyclometalated Pt(II) acetylacetonate complexes with 1,3-thiazole-based NHC ligands could be synthesized, and their photophysical properties were investigated. A series of *N*-arylthiazole-2-thiones with electron-donating (OMe, Br, Me) as well as electron-withdrawing groups (CN, CO_2Me) could be synthesized. With overall yields of up to 48% air-stable *N*-arylthiazolium perchlorate and especially hexafluorophosphate salts were accessible in gram scale. They allowed controlling the electronic effect on the platinum atom and the overall absorption/emission process by variation of the substitution at the cyclometalating aryl ring. All complexes are efficiently emitting at room temperature with high quantum yields. These newly synthesized *N*-arylthiazol-2-ylidene platinum(II) complexes show remarkable stable emissions of about 508−526 nm independent from the substitution pattern. Quantum yields could be improved from 33% up to an excellent 79% with decay lifetimes between 8.1 and 21.4 μs in 2% PMMA films. The complex with methyl ester substituent not only showed the highest quantum yields of 79% but even retained excellent quantum yields of 68% in the concentrated film. The solid-state structures of two *N*-arylthiazol-2-thiones, one *N*-arylthiazolium hexafluorophosphate salt, and three *N*-arylthiazol-2-ylidene platinum(II) complexes provided structural information. In addition all solid-state structures are in good agreement compared to the results of quantum chemical DFT calculations. These new thiazole complexes are promising emitters for applications in OLEDs.

EXPERIMENTAL DATA

General Considerations. All complex syntheses were performed under an argon atmosphere and with exclusion of light, using flame-dried Schlenk tubes. Unless otherwise stated, all other syntheses were run without using an inert atmosphere. Solvents of at least 99.0% purity were used in this study. DMF and 1,4-dioxane were dried using standard techniques and stored under an argon atmosphere over molecular sieves (3 Å). Dichloro(1,5-cyclooctadiene)platinum(II) (Pt(COD)Cl_2)[35] was prepared following a modified literature procedure.[30] Compound **6**[36] was prepared according to the literature procedure. Compounds **8**,[27] **9**,[27c] and **12**[27c] have been synthesized following a modified procedure described below. Chemicals were obtained from common suppliers and used without further purification. ^{1}H, ^{13}C, and ^{195}Pt NMR spectra were recorded on Bruker NMR spectrometers. ^{1}H and ^{13}C NMR spectra were referenced internally by using the resonances of the solvent (^{1}H: 7.26 ppm, ^{13}C: 77.0 ppm for $CDCl_3$; ^{1}H: 2.50 ppm, ^{13}C: 39.43 ppm for DMSO-d_6). ^{195}Pt NMR spectra were referenced externally by using potassium tetrachloroplatinate(II) in D_2O (−1617.2 $PtCl_4^{2-}$, −2654.1 $PtCl_2$). Shifts are given in ppm; coupling constants *J* in Hz. Mass spectra of thiones **8**−**14** were recorded on an Agilent 6890N GC coupled with a 5973N MSD system using electron ionization (EI) as ionization method. Electrospray ionization (ESI) mass spectra of the *N*-arylthiazolium salts **15**−**24** were measured on a Bruker Esquire MS with an 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. The emitter films were prepared by doctor blading a solution of emitter in a 10 wt % PMMA solution in dichloromethane on a substrate with a 60 μm doctor blade.

X-ray Crystallography. Preliminary examination and data collection were carried out on a NONIUS κ-CCD diffraction system (FR590) equipped with an Oxford Cryosystem cooling system at the window of a fine-focus sealed tube using graphite-monochromated Mo Kα radiation (λ = 0.710 73 Å). The reflections were merged and corrected for Lorentz, polarization, and decay effects. An absorption correction was applied using SADABS.[37] The structures were solved by a combination of direct methods[38] with the aid of difference Fourier synthesis and were refined against all data using SHELXL-97.[39] 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 least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme. Details of the structure determinations are given in the Supporting Information. Neutral-atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from the International Tables for Crystallography.[40] All calculations were performed with the programs COLLECT,[41] DIRAX,[42] EVALCCD,[43] SIR92,[38a] SIR97,[38b] SADABS,[37] the SHELXL-97 package,[39,44] and PLATON.[45] Images of the solid-state structures were generated with ORTEP-3[46] and MERCURY.[47]

Computational Details. The Gaussian09 package[48] was used to perform all quantum chemical calculations employing the density functional hybrid model B3LYP[49] and gradient-corrected BP86.[50] Both functionals were combined with a 6-31G(d) basis set[51] further using a double valence basis set for bromine.[52] In addition B3LYP was combined with a 6-311++G(d,p) triple-ζ basis set.[53] In all calculations platinum was described with a decontracted Hay−Wadt(n+1) ECP and basis set.[54] 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 molecule orbitals (FMOs) and spin densities were visualized by GaussView.[55] Calculated geometries were visualized with CYLview.[56]

General Procedure A: *N*-Arylthiazole-2-thiones. According to a modified literature procedure,[22,23] 0.4 mL/mmol of DMSO and 1 equiv of the corresponding aniline (**1**−**7**) were mixed, and 1 equiv of freshly ground NaOH was added at room temperature in one portion. The solution immediately darkened. After 15 min of stirring at room temperature 1 equiv of CS_2 was added at 0 °C. A further 60 min of stirring at room temperature was followed by the slow addition of 1 equiv of 3-chloro-2-butanone at 0 °C. This led to another color change and slight evolution of HCl. The solution was diluted with 200 mL of distilled water after 60 min of stirring at room temperature and then vigorously stirred for another 30 min. A crude solid precipitated in the case of aniline **1** and **2**, whereas anilines **3**−**7** yielded a viscous oil. After 30 min of standing at 5 °C the water phase was decanted and the remaining oil or solid dissolved in 125 mL of EtOH. The concluding elimination was performed by refluxing the ethanolic solution with 1.5 mL of concentrated hydrochloric acid (37 wt %) for 1 h. The product

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crystallized after one night of standing at 5 °C. Filtration of the remaining solid, washing once with 0.4 mL/mmol of EtOH, and drying under high vacuum yielded pure 3-aryl-4,5-dimethylthiazole-2-thiones.

4,5-Dimethyl-3-phenyl-1,3-thiazole-2(3*H*)-thione (8). According to general procedure A 4.66 g (4.56 mL, 50 mmol) of aniline **1** and 2 g (50 mmol) of NaOH were added to 20 mL of DMSO followed by 3.02 mL of CS_2 (3.81 g, 1 equiv, 50 mmol) and 5.18 mL of 3-chloro-2-butanone (5.49 g, 1 equiv, 50 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A. The crystallized product was filtered, washed with 20 mL of EtOH, and dried under high vacuum to yield compound **8** as a pale brown solid (7.48 g, 67.6%). Mp: 87 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.80 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 7.30 (d, J = 6.8 Hz, 2H, CH_{arom}), 7.41−7.69 (m, 3H, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.23 (*C*S), 138.25 (C_i), 135.35 (C_i), 129.56 (2C, CH_{arom}), 129.18 (CH_{arom}), 128.28 (2C, CH_{arom}), 116.80 (C_i), 13.32 (CH_3), 11.18 (CH_3). GCMS (EI): m/z (fragment, %) 221 (M^+, 100). Anal. Calcd for $C_{11}H_{11}NS_2$: C, 59.69; H, 5.01; N, 6.33; S, 28.97. Found: C, 59.49; H 4.98; N, 6.25; S, 28.93.

3-(4-Bromophenyl)-4,5-dimethyl-1,3-thiazole-2(3*H*)-thione (9). According to general procedure A 4.39 g (25 mmol) of aniline **2** and 1 g (25 mmol) of NaOH were added to 10 mL of DMSO followed by 1.51 mL of CS_2 (1.90 g, 1 equiv, 25 mmol) and 2.59 mL of 3-chloro-2-butanone (2.75 g, 1 equiv, 25 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A. The crystallized product was filtered, washed with 10 mL of EtOH, and dried under high vacuum to yield compound **9** as a brown solid (4.62 g, 61.6%). Mp: 130 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.83 (s, 3H, CH_3), 2.19 (s, 3H, CH_3), 7.31 (d, J = 8.7 Hz, 2H, CH_{arom}), 7.77 (d, J = 8.7 Hz, 2H, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.34 (*C*S), 137.47 (C_i), 135.18 (C_i), 132.61 (2C, CH_{arom}), 130.67 (2C, CH_{arom}), 122.49 (C_i), 116.99 (C_i), 13.30 (CH_3), 11.17 (CH_3). GCMS (EI): m/z (fragment, %) 300 (M^+, 100), 220 (M^+ − Br, 31). Anal. Calcd for $C_{11}H_{10}BrNS_2$: C, 44.00; H, 3.36; N, 4.67; S, 21.36. Found: C, 44.02; H, 3.35; N, 4.69; S, 21.15.

3-(4-Methoxyphenyl)-4,5-dimethyl-1,3-thiazole-2(3*H*)-thione (10). According to general procedure A 6.22 g (50 mmol) of aniline **3** and 2 g (50 mmol) of NaOH were added to 20 mL of DMSO followed by 3.02 mL of CS_2 (3.81 g, 1 equiv, 50 mmol) and 5.18 mL of 3-chloro-2-butanone (5.49 g, 1 equiv, 50 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A. The crystallized product was filtered, washed with 20 mL of EtOH, and dried under high vacuum to yield compound **10** as a violet solid (6.06 g, 48.2%). Mp: 90−91 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.81 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 3.82 (s, 3H, CH_3), 7.08 (d, J = 9.0 Hz, 2H, CH_{arom}), 7.22 (d, J = 9.0 Hz, 2H, CH_{arom}). ^{13}C NMR (125 MHz, DMSO-d_6): δ 186.48 (*C*S), 159.33 (C_i), 135.73 (C_i), 130.81 (C_i), 129.42 (2C, CH_{arom}), 116.39 (C_i), 114.64 (2C, CH_{arom}), 55.33 (CH_3), 13.39 (CH_3), 11.23 (CH_3). GCMS (EI): m/z (fragment, %) 251 (M^+, 100), 236 (M^+ − Me, 33). Anal. Calcd for $C_{12}H_{13}NOS_2$: C, 57.34; H, 5.21; N, 5.57; S, 25.51. Found: C, 57.45; H, 5.24; N, 5.62; S, 25.74.

3-(4-Cyanophenyl)-4,5-dimethyl-1,3-thiazole-2(3*H*)-thione (11). According to general procedure A 5.91 g (50 mmol) of aniline **4** and 2 g (50 mmol) of NaOH were added to 20 mL of DMSO followed by 3.02 mL of CS_2 (3.81 g, 1 equiv, 50 mmol) and 5.18 mL of 3-chloro-2-butanone (5.49 g, 1 equiv, 50 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A. The crystallized product was filtered, washed with 20 mL of EtOH, and dried under high vacuum to yield compound **11** as an off-white solid (6.19 g, 50.3%). Mp: 211 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.82 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 7.61 (d, J = 8.4 Hz, 2H, CH_{arom}), 8.07 (d, J = 8.3 Hz, 2H, CH_{arom}). ^{13}C NMR (125 MHz, DMSO-d_6): δ 186.25 (*C*S), 142.09 (C_i), 134.85 (C_i), 133.69 (2C, CH_{arom}), 129.91 (2C, CH_{arom}), 117.93 (C_i), 117.39 (C_i), 112.11 (C_i), 13.16 (CH_3), 11.09 (CH_3). GCMS (EI): m/z (fragment, %) 246 (M^+, 100). Anal. Calcd for $C_{12}H_{10}N_2S_2$: C, 58.51; H, 4.09; N, 11.37; S, 26.03. Found: C, 58.31; H, 3.98; N, 11.41; S, 25.99.

3-(4-Methylphenyl)-4,5-dimethyl-1,3-thiazole-2(3*H*)-thione (12). According to general procedure A 5.34 g (50 mmol) of aniline **5** and 2 g (50 mmol) of NaOH were added to 20 mL of DMSO followed by 3.02 mL of CS_2 (3.81 g, 1 equiv, 50 mmol) and 5.18 mL of 3-chloro-2-butanone (5.49 g, 1 equiv, 50 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A. The crystallized product was filtered, washed with 20 mL of EtOH, and dried under high vacuum to yield compound **12** as a pale brown solid (5.44 g, 46.2%). Mp: 123−124 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.80 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.38 (s, 3H, CH_3), 7.17 (d, J = 8.3 Hz, 2H, CH_{arom}), 7.36 (d, J = 8.4 Hz, 2H, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.25 (*C*S), 138.73 (C_i), 135.68 (C_i), 135.46 (C_i), 130.03 (2C, CH_{arom}), 127.95 (2C, CH_{arom}), 116.61 (C_i), 20.67 (CH_3), 13.33 (CH_3), 11.18 (CH_3). GCMS (EI): m/z (fragment, %) 235 (M^+, 100), 220 (M^+ − Me, 10). Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95; S, 27.25. Found: C, 61.58; H, 5.66; N, 5.96; S, 27.12.

3-(4-Benzoic acid methyl ester)-4,5-dimethyl-1,3-thiazole-2(3*H*)-thione (13). According to general procedure A 3.78 g (25 mmol) of aniline **6** and 1 g (25 mmol) of NaOH were added to 10 mL of DMSO followed by 1.51 mL of CS_2 (1.90 g, 1 equiv, 25 mmol) and 2.59 mL of 3-chloro-2-butanone (2.75 g, 1 equiv, 25 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A but using MeOH instead of EtOH. The crystallized product was filtered, washed with 10 mL of MeOH, and dried under high vacuum to yield compound **13** as a brown solid (2.16 g, 30.9%). Mp: 150−151 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.82 (s, 3H, CH_3), 2.20 (s, 3H, CH_3), 3.90 (s, 3H, CH_3), 7.51 (d, J = 8.4 Hz, 2H, CH_{arom}), 8.12 (d, J = 8.4 Hz, 2H, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.24 (*C*S), 165.40 (C_i), 142.22 (C_i), 134.99 (C_i), 130.40 (2C, CH_{arom}), 130.29 (C_i), 129.28 (2C, CH_{arom}), 117.36 (C_i), 52.39 (CH_3), 13.23 (CH_3), 11.16 (CH_3). GCMS (EI): m/z (fragment, %) 279 (M^+, 100), 264 (M^+ − Me, 5). Anal. Calcd for $C_{13}H_{13}NO_2S_2$: C, 55.89; H, 5.01; N, 5.01; S, 22.95. Found: C, 55.92; H, 4.67; N, 5.09; S, 22.77.

3-(3-Methylphenyl)-4,5-dimethyl-1,3-thiazole-2(3*H*)-thione (14). According to general procedure A 5.36 g (50 mmol) of aniline **5** and 2 g (50 mmol) of NaOH were added to 20 mL of DMSO followed by 3.02 mL of CS_2 (3.81 g, 1 equiv, 50 mmol) and 5.18 mL of 3-chloro-2-butanone (5.49 g, 1 equiv, 50 mmol, 97 wt %). The next steps involving removal of the water phase and acidic elimination were conducted as described in general procedure A. The crystallized product was filtered, washed with 20 mL of EtOH, and dried under high vacuum to yield compound **14** as a pale brown solid (5.61 g, 47.7%). Mp: 118−119 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 1.81 (s, 3H, CH_3), 2.18 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 7.00−7.14 (m, 2H, CH_{arom}), 7.32 (d, J = 7.6 Hz, 1H, CH_{arom}), 7.45 (d, J = 7.8 Hz, 1H, CH_{arom}). ^{13}C NMR (75 MHz, DMSO-d_6): δ 186.14 (*C*S), 139.21 (C_i), 138.20 (C_i), 135.39 (C_i), 129.84 (CH_{arom}), 129.35 (CH_{arom}), 128.52 (CH_{arom}), 125.23 (CH_{arom}), 116.76 (C_i), 20.67 (CH_3), 13.32 (CH_3), 11.18 (CH_3). GCMS (EI): m/z (fragment, %) 235 (M^+, 98), 220 (M^+ − Me, 5). Anal. Calcd for $C_{12}H_{13}NS_2$: C, 61.24; H, 5.57; N, 5.95; S, 27.25. Found: C, 61.10; H, 5.56; N, 5.86; S, 27.54.

General Procedure B: *N*-Arylthiazolium Salts. According to a modified literature procedure,[22,23] a dispersion of the corresponding 3-aryl-4,5-dimethylthiazole-2-thione (**15**−**24**) and 2.5 mL/mmol of AcOH was slowly treated with 3 equiv of H_2O_2 (30 wt % in water; ***Warning!*** *Exothermic reaction!*). The solid dissolved, and the clear orange solution was stirred at room temperature for another 30 min. The solvent was removed *in vacuo*, and the remaining oil dissolved in 2 mL/mmol MeOH. A mixture of 4 mL/mmol MeOH/water (1:1) and 2 equiv KPF_6 or 2 equiv $NaClO_4$-monohydrate were added. A salt precipitated after the addition was completed, and the dispersion was stirred at room temperature for 16 h. The solids were filtered off, and the remaining solution was transferred to a separation funnel containing 100 mL of distilled water. The resulting water phase was extracted with 50 mL of dichloromethane first, followed by another extraction with 100 mL of dichloromethane. The combined organic

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phases were dried over Na_2SO_4, and the drying agent was filtered off. After evaporation of the solvent the resulting oil was dissolved in 2 mL of dichloromethane and the product was precipitated by slow addition of diethyl ether. The solid was filtered and washed with ether before drying under high vacuum.

4,5-Dimethyl-3-phenyl-1,3-thiazolium Perchlorate (15). According to general procedure B 1.99 g (9 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **8** in 23 mL of AcOH was treated with 2.75 mL of H_2O_2 (27 mmol). Following general procedure B the oil was dissolved in 18 mL of MeOH, and a mixture of 36 mL MeOH/water (1:1) and 2.53 g of $NaClO_4 \cdot H_2O$ (18 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **15** was obtained as a brown solid (1.87 g, 71.7%). Mp: 104−106 °C. NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 7.68−7.74 (m, 5H, CH_{arom}), 10.25 (s, 1H, N(C*H*)S). ^{13}C NMR (125 MHz, DMSO-d_6): δ 157.07 (N(*C*H)S), 142.05 (C_i), 137.01 (C_i), 132.69 (C_i), 131.27 (CH_{arom}), 129.96 (2C, CH_{arom}), 126.14 (2C, CH_{arom}), 12.01(CH_3), 11.94 (CH_3). MS (ESI): *m*/*z* (fragment) 190.0 (M^+), 479.0 (2[NHC]$^+$ + ClO_4^-). Anal. Calcd for $C_{11}H_{12}ClNO_4S$: C, 45.60; H, 4.17; N, 4.83; S, 11.07. Found: C, 45.87; H, 4.08; N, 4.56; S, 11.30.

4,5-Dimethyl-3-phenyl-1,3-thiazolium Hexafluorophosphate (16). According to general procedure B 2.21 g (10 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **8** in 25 mL of AcOH was treated with 3.06 mL of H_2O_2 (30 mmol). Following general procedure B the oil was dissolved in 20 mL of MeOH and a mixture of 40 mL of MeOH/water (1:1) and 3.68 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **16** was obtained as a brown solid (2.14 g, 63.9%). Mp: 115−120 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 7.66−7.80 (m, 5H, CH_{arom}) 10.26 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.12 (N(*C*H)S), 142.03 (C_i), 136.98 (C_i), 132.85 (C_i), 131.25 (CH_{arom}), 129.94 (2C, CH_{arom}), 126.13 (2C, CH_{arom}), 11.98 (CH_3), 11.92 (CH_3). MS (ESI): *m*/*z* (fragment) 190.0 (M^+), 525.0 (2[NHC]$^+$ + PF_6^-). Anal. Calcd for $C_{11}H_{12}F_6NPS$: C, 39.41; H, 3.61; N, 4.18; S, 9.56. Found: C, 39.67; H, 3.26; N, 4.22; S, 9.77.

3-(4-Bromophenyl)-4,5-dimethyl-1,3-thiazolium Perchlorate (17). According to general procedure B 2.99 g (10 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **9** in 25 mL of AcOH was treated with 3.06 mL of H_2O_2 (30 mmol). Following general procedure B the oil was dissolved in 20 mL of MeOH, and a mixture of 40 mL of MeOH/water (1:1) and 2.81 g of $NaClO_4 \cdot H_2O$ (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **17** was obtained as a brown solid (2.04 g, 55.4%). Mp: 131−134 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.22 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 7.69 (d, *J* = 8.7 Hz, 2H, CH_{arom}), 7.94 (d, *J* = 8.7 Hz, 2H, $CH_{arom.}$), 10.25 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.41 (N(*C*H)S), 142.01 (C_i), 136.15 (C_i), 132.86 (2C, CH_{arom}), 132.68 (C_i), 128.41 (2C, CH_{arom}), 124.69 (C_i), 11.96 (CH_3), 11.88 (CH_3). MS (ESI): *m*/*z* (fragment) 268.0 (M^+), 636.9 (2[NHC]$^+$ + ClO_4^-). Anal. Calcd for $C_{11}H_{11}BrClNO_4S$: C, 35.84; H, 3.01; N, 3.80; S, 8.70. Found: C, 36.23; H, 2.98; N, 3.70; S, 8.99.

3-(4-Bromophenyl)-4,5-dimethyl-1,3-thiazolium Hexafluorophosphate (18). According to general procedure B 1.49 g (5 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **9** in 13 mL of AcOH was treated with 1.53 mL of H_2O_2 (15 mmol). Following general procedure B the oil was dissolved in 10 mL of MeOH, and a mixture of 20 mL of MeOH/water (1:1) and 1.84 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **18** was obtained as a brown solid (631 mg, 30.5%). Mp: 162−166 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.68 (d, *J* = 8.6 Hz, 2H, CH_{arom}), 7.93 (d, *J* = 8.6 Hz, 2H, $CH_{arom.}$), 10.24 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.43 (N(*C*H)S), 142.00 (C_i), 136.15 (C_i), 132.85 (2C, CH_{arom}), 132.66 (C_i), 128.41 (2C, CH_{arom}), 124.69 (C_i), 11.95 (CH_3), 11.87 (CH_3). MS (ESI): *m*/*z* (fragment): 268.0 (M^+), 680.7 (2[NHC]$^+$ + PF_6^-). Anal. Calcd for $C_{11}H_{11}BrF_6NPS$: C, 31.90; H, 2.68; N, 3.38; S, 7.74. Found: C, 31.66; H, 2.48; N, 3.35; S, 7.88.

3-(4-Methoxyphenyl)-4,5-dimethyl-1,3-thiazolium Hexafluorophosphate (19). According to general procedure B, 1.26 g (5 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **10** in 13 mL of AcOH was treated with 1.53 mL of H_2O_2 (15 mmol). Following general procedure B the oil was dissolved in 10 mL of MeOH, and a mixture of 20 mL MeOH/water (1:1) and 1.84 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **19** was obtained as a brown solid (889 mg, 48.7%). Mp: 157−159 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (s, 3H, CH_3), 2.57 (s, 3H, CH_3), 3.87 (s, 3H, CH_3), 7.21 (d, *J* = 8.8 Hz, 2H, CH_{arom}), 7.63 (d, *J* = 8.8 Hz, 2H, CH_{arom}), 10.19 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 160.88 (C_i-OCH_3), 157.06 (N(*C*H)S), 142.28 (C_i), 132.36 (C_i), 129.70 (C_i), 127.49 (2C, CH_{arom}), 114.88 (2C, CH_{arom}), 55.71 (OCH_3), 12.02 (CH_3), 11.91(CH_3). MS (ESI): *m*/*z* (%) 220.0 ([NHC]$^+$), 585.0 (2[NHC]$^+$ + PF_6^-). Anal. Calcd for $C_{12}H_{14}F_6NOPS$: C, 39.46; H, 3.86; N, 3.83; S, 8.78. Found: C, 39.28; H, 3.73; N, 3.56; S, 8.97.

3-(4-Cyanophenyl)-4,5-dimethyl-1,3-thiazolium Hexafluorophosphate (20). According to general procedure B, 1.23 g (5 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **11** in 13 mL of AcOH was treated with 1.53 mL of H_2O_2 (15 mmol). Following general procedure B the oil was dissolved in 10 mL of MeOH, and a mixture of 20 mL of MeOH/water (1:1) and 1.84 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **20** was obtained as a brown solid (174 mg, 9.6%). Mp: 125−132 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 7.95 (d, *J* = 8.2 Hz, 2H, CH_{arom}), 8.24 (d, *J* = 8.3 Hz, 2H, $CH_{arom.}$), 10.29 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 157.77 (N(*C*H)S), 141.90 (C_i), 140.26 (C_i), 134.06 (2C, CH_{arom}), 132.88 (C_i), 127.68 (2C, CH_{arom}), 117.57 (CN), 114.10 (C_{arom}-CN), 11.92 (CH_3), 11.87 (CH_3). MS (ESI): *m*/*z* (fragment) 215.0 (M^+), 575.0 (2[NHC]$^+$ + PF_6^-). Anal. Calcd for $C_{12}H_{11}F_6N_2PS$: C, 40.01; H, 3.08; N, 7.78; S, 8.90. Found: C, 40.40; H, 2.97; N, 7.38; S, 9.23.

3-(4-Methylphenyl)-4,5-dimethyl-1,3-thiazolium Hexafluorophosphate (21). According to general procedure B, 2.35 g (10 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **9** in 25 mL of AcOH was treated with 3.06 mL of H_2O_2 (30 mmol). Following general procedure B the oil was dissolved in 20 mL of MeOH, and a mixture of 40 mL of MeOH/water (1:1) and 3.68 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **21** was obtained as a pale brown solid (1.74 g, 49.8%). Mp: 116−118 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.20 (s, 3H, CH_3), 2.44 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.50 (d, *J* = 8.5 Hz, 2H, CH_{arom}), 7.58 (d, *J* = 8.4 Hz, 2H, CH_{arom}), 10.21 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.97 (N(*C*H)S), 142.18 (C_i), 141.27 (C_i), 134.57 (C_i), 132.58 (C_i), 130.26 (2C, $CH_{arom.}$), 125.83 (2C, $CH_{arom.}$), 20.67 (CH_3), 11.99 (CH_3), 11.91 (CH_3). MS (ESI): *m*/*z* (fragment) 204.0 ([NHC]$^+$), 552.9 (2[NHC]$^+$ + PF_6^-). Anal. Calcd for $C_{12}H_{14}F_6NPS$: C 41.26; H 4.04; N 4.01; S 9.53. Found: C 41.33; H 4.11; N 4.00; S 9.52.

3-(4-Benzoic acid methyl ester)-4,5-dimethyl-1,3-thiazolium Hexafluorophosphate (22). According to general procedure B 2.79 g (10 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **9** in 25 mL of AcOH was treated with 3.06 mL of H_2O_2 (30 mmol). Following general procedure B the oil was dissolved in 20 mL of MeOH, and a mixture of 40 mL of MeOH/water (1:1) and 3.68 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **22** was obtained as a brown solid (1.01 g, 25.6%). Mp: 130−132 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.59 (s, 3H, CH_3), 3.93 (s, 3H, CH_3), 7.87 (d, *J* = 8.4 Hz, 2H, CH_{arom}), 8.24 (d, *J* = 8.4 Hz, 2H, CH_{arom}), 10.30 (s, 1H, N(C*H*)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 165.05 (CO), 157.44 (N(*C*H)S), 141.89 (C_i), 140.37 (C_i), 132.89 (C_i), 132.04 (C_i), 130.63 (2C, CH_{arom}), 126.94 (2C, CH_{arom}), 52.65 (CO_2CH_3), 11.94 (CH_3), 11.88

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(CH_3). MS (ESI): m/z (fragment) 248.1 ([NHC]$^+$). Anal. Calcd for $C_{13}H_{14}F_6NO_2PS$: C, 39.70; H, 3.59; N, 3.56; S, 8.15. Found: C, 39.77; H, 3.60; N, 3.57; S, 8.46.

3-(3-Methylphenyl)-4,5-dimethyl-1,3-thiazolium Perchlorate (23). According to general procedure B, 3.53 g (15 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **14** in 39 mL of AcOH was treated with 4.59 mL of H_2O_2 (45 mmol). Following general procedure B the oil was dissolved in 20 mL of MeOH, and a mixture of 60 mL of MeOH/water (1:1) and 4.21 g of $NaClO_4 \cdot H_2O$ (30 mmol, 2 equiv) was added. After extraction no solid could be precipitated. Further purification by column chromatography using a dichloromethane/methanol (10:1) mixture yielded a crude oil, which crystallized overnight. Further stirring of the crude solid in diethyl ether for 24 h and subsequent filtration gave compound **23** as a pale brown solid (1.31 g, 21.5%). Mp: 70−71 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.37−7.70 (m, 5H, CH_{arom}), 10.23 (s, 1H, N(CH)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.92 (N(CH)S), 142.00 (C_i), 139.90 (C_i), 136.92 (C_i), 132.66 (C_i), 131.80 (CH_{arom}), 129.71 (CH_{arom}), 126.40 (CH_{arom}), 123.10 (CH_{arom}), 20.66 (CH_3), 12.00 (CH_3), 11.92 (CH_3). MS (ESI): m/z (fragment) 204.0 ([NHC]$^+$), 507.0 (2[NHC]$^+$ + ClO_4^-). Anal. Calcd for $C_{12}H_{14}ClNO_4S$: C, 47.45; H, 4.65; N, 4.61; S, 10.56. Found: C, 47.82; H, 4.81; N, 4.65; S, 10.47.

3-(3-Methylphenyl)-4,5-dimethyl-1,3-thiazolium Hexafluorophosphate (24). According to general procedure B, 1.18 g (5 mmol) of 3-aryl-4,5-dimethylthiazole-2-thione **14** in 13 mL of AcOH was treated with 1.53 mL of H_2O_2 (15 mmol). Following general procedure B the oil was dissolved in 10 mL of MeOH, and a mixture of 20 mL of MeOH/water (1:1) and 1.84 g of KPF_6 (20 mmol, 2 equiv) was added. After extraction the precipitated solid was filtered and washed with ether before drying under high vacuum. Compound **23** was obtained as a pale brown solid (739 mg, 42.3%). Mp: 86−88 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ 2.21 (s, 3H, CH_3), 2.43 (s, 3H, CH_3), 2.58 (s, 3H, CH_3), 7.37−7.70 (m, 5H, CH_{arom}), 10.23 (s, 1H, N(CH)S). ^{13}C NMR (75 MHz, DMSO-d_6): δ 156.95 (N(CH)S), 141.99 (C_i), 139.89 (C_i), 136.92 (C_i), 132.64 (C_i), 131.79 ($CH_{arom.}$), 129.70 ($CH_{arom.}$), 126.39 ($CH_{arom.}$), 123.09 ($CH_{arom.}$), 20.65 (CH_3), 11.97 (CH_3), 11.90 (CH_3). MS (ESI): m/z (fragment) 204.0 ([NHC]$^+$), 553.0 (2[NHC]$^+$ + PF_6^-). Anal. Calcd for $C_{12}H_{14}F_6NPS$: C, 41.26; H, 4.04; N, 4.01; S, 9.18. Found: C, 41.46; H, 4.01; N, 4.23; S, 9.55.

General Procedures C and D: Thiazole-2-ylidene Pt(II) Complexes. The general procedure C employed in this study starts by adding 25 mL/mmol of dry 1,4-dioxane to a mixture of 3-aryl-4,5-dimethylthiazolium salt and 0.55 equiv of Ag_2O in a dry Schlenk tube. The resulting solution was stirred at room temperature for 2 h and for 22 h at 50 °C under the exclusion of light. After addition of 13 mL/mmol of 2-butanone and 1 equiv of Pt(COD)Cl_2 a further 2 h of stirring at room temperature was followed by 22 h of stirring at 115 °C. The solvent was removed *in vacuo*, and 25 mL/mmol of dry DMF, 4.0 equiv of acetylacetonate, and 4.0 equiv of KO^{t}Bu were added. Afterward the final mixture was stirred at room temperature for 24 h and then heated to 100 °C for 6 h. All volatiles were removed *in vacuo*, and the remaining solid was dispersed in 50 mL of distilled water and filtered. The solid residue was 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. The improved synthesis (general procedure D) followed the same time−temperature sequence but solely uses DMF as the solvent and K_2CO_3 as the base for deprotonation of the acetylacetonate ligand. Washing and purification remain the same as described above.

(SP-4-4)-Acetylacetonato-$\kappa O,\kappa O'$-[4,5-dimethyl-3-phenyl-$\kappa C'$-1,3-thiazole-2-ylidene-κC]platinum(II) (25). According to general procedure C 20 mL of dry 1,4-dioxane was added to a mixture of 268 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **15** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of Pt(COD)Cl_2 (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 370 mg of KO^{t}Bu (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **25** as a bright yellow powder (69 mg, 17.8%). The improved synthesis (general procedure D) using 536 mg (1.6 mmol) of 3-aryl-4,5-dimethylthiazolium salt **16**, 204 mg of Ag_2O (0.88 mmol, 0.55 equiv), 598 mg of Pt(COD)Cl_2 (1.6 mmol, 1 equiv), 640 mg of acetylacetonate (6.4 mmol, 4.0 equiv), and 884 mg of K_2CO_3 (6.4 mmol, 4.0 equiv) in 40 mL of dry DMF gave a bright yellow powder (260 mg, 33.7%). Mp: 294−295 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.06 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 5.49 (s, 1H, CH_{acac}), 6.97−7.16 (m, 2H, CH_{arom}), 7.32−7.48 (m, 1H, CH_{arom}), 7.73−8.02 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.30 (CO), 185.30 (CO), 178.00 (NCS), 151.35 (C_i-Pt), 136.96 (C_i), 132.53 ($CH_{arom.}$), 127.76 (C_i), 125.53 ($CH_{arom.}$), 123.60 (C_i), 123.37 ($CH_{arom.}$), 113.40 ($CH_{arom.}$), 102.39 ($CH_{arom;acac}$), 28.01 ($CH_{3;acac}$), 27.85 ($CH_{3;acac}$), 14.12 (CH_3), 12.67 (CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3346.22. Anal. Calcd for $C_{16}H_{17}NO_2PtS$: C, 39.83; H, 3.55; N, 2.90; S, 6.65. Found: C, 39.77; H, 3.70; N, 2.75; S, 6.63.

(SP-4-4)-Acetylacetonato-$\kappa O,\kappa O'$-[4,5-dimethyl-3-(4-bromophenyl)-$\kappa C'$-1,3-thiazole-2-ylidene-κC]platinum(II) (26). According to general procedure C 20 mL of dry 1,4-dioxane was added to a mixture of 331 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **18** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of Pt(COD)Cl_2 (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 370 mg of KO^{t}Bu (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **26** as a bright yellow powder (71 mg, 15.8%). The improved synthesis (general procedure D) using 166 mg (0.4 mmol) of 3-aryl-4,5-dimethylthiazolium salt **18**, 51 mg of Ag_2O (0.22 mmol, 0.55 equiv), 150 mg of Pt(COD)Cl_2 (0.8 mmol, 1 equiv), 160 mg of acetylacetonate (1.6 mmol, 4.0 equiv), and 221 mg of K_2CO_3 (1.6 mmol, 4.0 equiv) in 10 mL of dry DMF gave a bright yellow powder (122 mg, 54.3%). Mp: 277−279 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 5.50 (s, 1H, CH_{acac}), 7.16 (dd, J = 8.6, J = 2.2 Hz, 1H, CH_{arom}), 7.20−7.28 (*partially omitted by solvent signal*, m, 1H, CH_{arom}), 7.77−8.05 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.29 (CO), 185.51 (CO), 177.75 (NCS), 150.19 (C_i-Pt), 136.85 (C_i), 134.65 (CH_{arom}), 131.09 (C_i), 125.84 (CH_{arom}), 124.05 (C_i), 119.25 (C_i), 114.68 (CH_{arom}), 102.51 ($CH_{arom;acac}$), 27.93 ($CH_{3;acac}$), 27.88 ($CH_{3;acac}$), 14.01 (CH_3), 12.67 (CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3313.03. Anal. Calcd for $C_{16}H_{16}BrNO_2PtS$: C, 34.17; H, 3.05; N, 2.49; S, 5.70. Found: C, 34.42; H, 2.84; N, 2.56; S, 5.76.

(SP-4-4)-Acetylacetonato-$\kappa O,\kappa O'$-[4,5-dimethyl-3-(4-methoxyphenyl)-$\kappa C'$-1,3-thiazole-2-ylidene-κC]platinum(II) (27). According to general procedure C 20 mL of dry 1,4-dioxane was added to a mixture of 292 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **19** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of Pt(COD)Cl_2 (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 370 mg of KO^{t}Bu (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **27** as a bright yellow powder (85 mg, 20.7%). The improved synthesis (general procedure D) using 146 mg (0.4 mmol) of 3-aryl-4,5-dimethylthiazolium salt **19**, 51 mg of Ag_2O (0.22 mmol, 0.55 equiv), 150 mg of Pt(COD)Cl_2 (0.8 mmol, 1 equiv), 160 mg of acetylacetonate (1.6 mmol, 4.0 equiv), and 221 mg of K_2CO_3 (1.6 mmol, 4.0 equiv) in 10 mL of dry DMF gave a bright yellow powder (69 mg, 33.7%). Mp: 264−268 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.66 (s, 3H, CH_3), 3.86 (s, 3H, CH_3), 5.48 (s, 1H, CH_{acac}), 6.56 (dd, J = 8.8 Hz, J = 2.9 Hz, 1H, CH_{arom}), 7.31 (d, J = 8.8 Hz, 1H, CH_{arom}), 7.35−7.56 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.23 (CO), 185.25 (CO), 175.38 (NCS), 156.82 (C_i-Pt), 145.08 (C_i), 136.65 (C_i), 129.86 (C_i), 123.56 (C_i), 117.40 (CH_{arom}), 114.17 (CH_{arom}), 107.85 (CH_{arom}), 102.40 ($CH_{arom;acac}$), 55.32 (OCH_3), 27.99 ($CH_{3;acac}$), 27.86 ($CH_{3;acac}$), 13.94 (CH_3), 12.66 (CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3330.75. Anal. Calcd for $C_{17}H_{19}NO_3PtS$: C, 39.76; H, 3.93; N, 2.73; S, 6.24. Found: C, 39.90; H, 3.85; N, 2.74; S, 6.28.

(SP-4-4)-Acetylacetonato-$\kappa O,\kappa O'$-[4,5-dimethyl-3-(4-cyanophenyl)-$\kappa C'$-1,3-thiazole-2-ylidene-κC]platinum(II) (28). Accord-

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ing to general procedure C 20 mL of dry 1,4-dioxane was added to a mixture of 288 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **20** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of $Pt(COD)Cl_2$ (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 370 mg of KO^{t}Bu (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **28** as a bright yellow powder (86 mg, 20.7%). The improved synthesis (general procedure D) using 144 mg (0.4 mmol) of 3-aryl-4,5-dimethylthiazolium salt **20**, 51 mg of Ag_2O (0.22 mmol, 0.55 equiv), 150 mg of $Pt(COD)Cl_2$ (0.8 mmol, 1 equiv), 160 mg of acetylacetonate (1.6 mmol, 4.0 equiv), and 221 mg of K_2CO_3 (1.6 mmol, 4.0 equiv) in 10 mL of dry DMF gave a bright yellow powder (63 mg, 31.0%). Mp: 330 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.05 (s, 3H, CH_3), 2.10 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 5.53 (s, 1H, CH_{acac}), 7.35 (dd, J = 8.4 Hz, J = 1.9 Hz, 1H, CH_{arom}), 7.44 (d, J = 8.5 Hz, 1H, CH_{arom}), 7.99−8.26 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.54 (CO), 185.69 (CO), 176.72 (NCS), 136.92 (C_i), 135.51 (CH_{arom}), 129.69 (C_i), 128.04 (CH_{arom}), 124.59 (C_i), 119.61 (C_i), 113.22 (CH_{arom}), 108.49 (C_i), 102.66 ($CH_{arom;acac}$), 27.92 ($CH_{3;acac}$), 27.83 ($CH_{3;acac}$), 14.16 (CH_3), 12.70(CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3311.01. Anal. Calcd for $C_{17}H_{16}N_2O_2PtS$: C, 40.24; H, 3.18; N, 5.52; S, 6.32. Found: C, 40.15; H, 3.15; N, 5.50; S, 6.28.

(SP-4-4)-Acetylacetonato-κ*O*,κ*O*′-[4,5-dimethyl-3-(4-methylphenyl)-κ*C*′-1,3-thiazole-2-ylidene-κ*C*]platinum(II) (29). According to general procedure D, 20 mL of dry DMF was added to a mixture of 279 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **21** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of $Pt(COD)Cl_2$ (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 442 mg of K_2CO_3 (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **29** as a bright yellow powder (110 mg, 27.7%). Mp: 268−269 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H, CH_3), 2.08 (s, 3H, CH_3), 2.26 (s, 3H, CH_3), 2.37 (s, 3H, CH_3), 2.67 (s, 3H, CH_3), 5.48 (s, 1H, CH_{acac}), 6.83 (dd, J = 8.2 Hz, J = 1.3 Hz, 1H, CH_{arom}), 7.23−7.31 (*partially under solvent signal*, m, 1H, CH_{arom}), 7.52−7.80 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.25 (CO), 185.30 (CO), 177.05 (NCS), 149.09 (C_i-Pt), 136.84 (C_i), 135.30 (C_i), 133.09 (CH_{arom}), 127.37 (C_i), 123.68 (C_i), 123.49 (CH_{arom}), 113.31 (CH_{arom}), 102.39 ($CH_{arom;acac}$), 28.02 ($CH_{3;acac}$), 27.90 ($CH_{3;acac}$), 21.22 (CH_3), 14.05 (CH_3), 12.66 (CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3340.04. Anal. Calcd for $C_{17}H_{19}NO_2PtS$: C, 41.13; H, 3.86; N, 2.82; S, 6.46. Found: C, 40.73; H, 3.69; N, 2.87; S, 6.31.

(SP-4-4)-Acetylacetonato-κ*O*,κ*O*′-[4,5-dimethyl-3-(4-benzoic acid methyl ester)-κ*C*′-1,3-thiazole-2-ylidene-κ*C*]platinum(II) (30). According to general procedure D, 20 mL of dry DMF was added to a mixture of 315 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **22** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of $Pt(COD)Cl_2$ (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 442 mg of K_2CO_3 (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **30** as a bright yellow powder (202 mg, 46.7%). Mp: 276−278 °C. ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.03 (s, 3H, CH_3), 2.11 (s, 3H, CH_3), 2.24 (s, 3H, CH_3), 2.65 (s, 3H, CH_3), 3.92 (s, 3H, CH_3), 5.50 (s, 1H, CH_{acac}), 7.31−7.46 (m, 1H, CH_{arom}), 7.71 (dd, J = 8.5 Hz, J = 2.0 Hz, 1H, CH_{arom}), 8.31−8.60 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.24 (CO), 185.56 (CO), 179.67 (CO), 167.35 (C_i), 154.87 (C_i), 136.98 (C_i), 133.09 (CH_{arom}), 127.94 (C_i), 126.48 (C_i), 125.80 (CH_{arom}), 124.06 (C_i), 112.86 (CH_{arom}), 102.46 ($CH_{arom;acac}$), 51.90 (CO_2CH_3), 27.94 ($CH_{3;acac}$), 27.90 ($CH_{3;acac}$), 14.15 (CH_3), 12.63 (CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3320.80 (d, J = 49.0 Hz). Anal. Calcd for $C_{18}H_{19}NO_4PtS$: C, 40.00; H, 3.54; N, 2.59; S, 5.93. Found: C, 39.68; H, 3.47; N, 2.64; S, 6.31.

(SP-4-4)-Acetylacetonato-κ*O*,κ*O*′-[4,5-dimethyl-3-(5-methylphenyl)-κ*C*′-1,3-thiazole-2-ylidene-κ*C*]platinum(II) (31). According to general procedure D, 20 mL of dry DMF was added to a mixture of 279 mg (0.8 mmol) of 3-aryl-4,5-dimethylthiazolium salt **24** and 102 mg of Ag_2O (0.44 mmol, 0.55 equiv). Stepwise addition of 299 mg of $Pt(COD)Cl_2$ (0.8 mmol, 1 equiv), 320 mg of acetylacetonate (3.2 mmol, 4.0 equiv), and 442 mg of K_2CO_3 (3.2 mmol, 4.0 equiv) and following general procedure C in temperature and workup steps yielded complex **31** as a bright yellow powder (95 mg, 23.9%). Mp: 318 °C (dec). ^{1}H NMR (300 MHz, $CDCl_3$): δ 2.02 (s, 3H, CH_3), 2.05 (s, 3H, CH_3), 2.27 (s, 3H, CH_3), 2.35 (s, 3H, CH_3), 2.70 (s, 3H, CH_3), 5.48 (s, 1H, CH_{acac}), 6.94 (d, J = 6.8 Hz, 1H, CH_{arom}), 7.17−7.31 (*partially under solvent signal*, m, 1H, CH_{arom}), 7.58−7.86 (m, 1H, CH_{arom}). ^{13}C NMR (75 MHz, $CDCl_3$): δ 186.21 (CO), 185.26 (CO), 178.12 (C_i), 136.93 (C_i), 132.79 (CH_{arom}), 132.28 (C_i), 126.13 (CH_{arom}), 123.44 (C_i), 123.37 (C_i), 114.53 (CH_{arom}), 102.36 ($CH_{arom;acac}$), 28.03 ($CH_{3;acac}$), 27.85 ($CH_{3;acac}$), 21.72 (CH_3), 14.19 (CH_3), 12.70 (CH_3). ^{195}Pt NMR (64 MHz, $CDCl_3$): δ −3342.70. Anal. Calcd for $C_{17}H_{19}NO_2PtS$: C, 41.13; H, 3.86; N, 2.82; S, 6.46. Found: C, 40.91; H, 3.98; N, 2.78; S, 6.35.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.5b00991.

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

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Notes

The authors declare no competing financial interest.

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■ REFERENCES

(1) (a) Martin-Smith, M.; Reid, S. T. *J. Med. Pharm. Chem.* **1959**, *1*, 507−564. (b) Gibson, D. T. *Chem. Rev.* **1934**, *14*, 431−457. (c) Kausar, A.; Zulfiqar, S.; Sarwar, M. I. *Polym. Rev.* **2014**, *54*, 185−267.

(2) (a) Perepichka, I. F.; Perepichka, D. F. *Handbook of Thiophene-Based Materials*; John Wiley & Sons, Ltd: Chichester, UK, 2009. (b) Cinar, M. E.; Ozturk, T. *Chem. Rev.* **2015**, *115*, 3036−3140.

(3) (a) Jin, Z. *Nat. Prod. Rep.* **2011**, *28*, 1143−1191. (b) Davyt, D.; Serra, G. *Mar. Drugs* **2010**, *8*, 2755−2780.

(4) (a) Ayati, A.; Emami, S.; Asadipour, A.; Shafiee, A.; Foroumadi, A. *Eur. J. Med. Chem.* **2015**, *97*, 699−718. (b) Mishra, C. B.; Kumari, S.; Tiwari, M. *Eur. J. Med. Chem.* **2015**, *92*, 1−34.

(5) Malandrinos, G.; Louloudi, M.; Hadjiliadis, N. *Chem. Soc. Rev.* **2006**, *35*, 684−692.

(6) (a) Flanigan, D. M.; Romanov-Michailidis, F.; White, N. A.; Rovis, T. *Chem. Rev.* **2015**, *115*, 9307−9387. (b) Enders, D.; Niemeier, O.; Henseler, A. *Chem. Rev.* **2007**, *107*, 5606−5655. (c) Yetra, S. R.; Patra, A.; Biju, A. T. *Synthesis* **2015**, *47*, 1357−1378. (d) Benhamou, L.; Chardon, E.; Lavigne, G.; Bellemin-Laponnaz, S.; César, V. *Chem. Rev.* **2011**, *111*, 2705−2733. (e) Wang, G.; Chen, X.; Zhang, Y.; Yao, W.; Ma, C. *Org. Lett.* **2013**, *15*, 3066−3069. (f) Kuhl, N.; Glorius, F. *Chem. Commun.* **2011**, *47*, 573−575. (g) Ahire, M. M.; Mhaske, S. B. *Angew. Chem., Int. Ed.* **2014**, *53*, 7038−7042.

(7) (a) Vougioukalakis, G. C.; Grubbs, R. H. Olefin Metathesis initiators bearing thiazol-2-ylidene ligands. WO2008064223A1, 2008.

DOI: 10.1021/acs.organomet.5b00991
Organometallics XXXX, XXX, XXX−XXX

(b) Vougioukalakis, G. C.; Grubbs, R. H. *J. Am. Chem. Soc.* **2008**, *130*, 2234−2245.
(8) Mendoza-Espinosa, D.; Ung, G.; Donnadieu, B.; Bertrand, G. *Chem. Commun.* **2011**, *47*, 10614−10616.
(9) Zhang, J.; Fu, J.; Su, X.; Qin, X.; Zhao, M.; Shi, M. *Chem. Commun.* **2012**, *48*, 9625−9627.
(10) (a) Djurovich, P. I.; Murphy, D.; Thompson, M. E.; Hernandez, B.; Gao, R.; Hunt, P. L.; Selke, M. *Dalton Trans.* **2007**, 3763−3770. (b) Hui, H.; Wei, L.; Zhentao, L.; Xiangen, H. *Spectrochim. Acta, Part A* **2015**, *142*, 271−278.
(11) (a) Adamovich, V.; Brooks, J.; Tamayo, A.; Alexander, A. M.; Djurovich, P. I.; D'Andrade, B. W.; Adachi, C.; Forrest, S. R.; Thompson, M. E. *New J. Chem.* **2002**, *26*, 1171−1178. (b) Blight, B. A.; Ko, S.-B.; Lu, J.-S.; Smith, L. F.; Wang, S. *Dalton Trans.* **2013**, *42*, 10089−10092. (c) Bossi, A.; Rausch, A. F.; Leitl, M. J.; Czerwieniec, R.; Whited, M. T.; Djurovich, P. I.; Yersin, H.; Thompson, M. E. *Inorg. Chem.* **2013**, *52*, 12403−12415.
(12) (a) Fernández-Hernández, J. M.; Beltrán, J. I.; Lemaur, V.; Gálvez-López, M.-D.; Chien, C.-H.; Polo, F.; Orselli, E.; Fröhlich, R.; Cornil, J.; De Cola, L. *Inorg. Chem.* **2013**, *52*, 1812−1824. (b) Smith, A. R. G.; Riley, M. J.; Burn, P. L.; Gentle, I. R.; Lo, S. C.; Powell, B. J. *Inorg. Chem.* **2012**, *51*, 2821−2831.
(13) (a) Sajoto, T.; Djurovich, P. I.; Tamayo, A.; Yousufuddin, M.; Bau, R.; Thompson, M. E.; Holmes, R. J.; Forrest, S. R. *Inorg. Chem.* **2005**, *44*, 7992−8003. (b) Wu, W.; Guo, H.; Wu, W.; Ji, S.; Zhao, J. *Inorg. Chem.* **2011**, *50*, 11446−11460.
(14) (a) Kozhevnikov, D. N.; Kozhevnikov, V. N.; Shafikov, M. Z.; Prokhorov, A. M.; Bruce, D. W.; Williams, J. A. G. *Inorg. Chem.* **2011**, *50*, 3804−3815. (b) Fischer, T.; Czerwieniec, R.; Hofbeck, T.; Osminina, M. M.; Yersin, H. *Chem. Phys. Lett.* **2010**, *486*, 53−59. (c) Fan, C.; Yang, C. *Chem. Soc. Rev.* **2014**, *43*, 6439−6469.
(15) (a) Wang, R.; Liu, D.; Ren, H.; Zhang, T.; Wang, X.; Li, J. *J. Mater. Chem.* **2011**, *21*, 15494−15500. (b) Giridhar, T.; Cho, W.; Kim, Y.-H.; Han, T.-H.; Lee, T.-W.; Jin, S.-H. *J. Mater. Chem. C* **2014**, *2*, 9398−9405.
(16) (a) Mydlak, M.; Yang, C.-H.; Polo, F.; Galstyan, A.; Daniliuc, C. G.; Felicetti, M.; Leonhardt, J.; Strassert, C. A.; De Cola, L. *Chem. - Eur. J.* **2015**, *21*, 5161−5172. (b) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055−3066.
(17) Visbal, R.; Gimeno, M. C. *Chem. Soc. Rev.* **2014**, *43*, 3551−3574.
(18) (a) Haneder, S.; Da Como, E.; Feldmann, J.; Lupton, J. M.; Lennartz, C.; Erk, P.; Fuchs, E.; Molt, O.; Münster, I.; Schildknecht, C.; Wagenblast, G. *Adv. Mater.* **2008**, *20*, 3325−3330. (b) Hudson, Z. M.; Sun, C.; Helander, M. G.; Chang, Y.-L.; Lu, Z.-H.; Wang, S. *J. Am. Chem. Soc.* **2012**, *134*, 13930−13933.
(19) (a) Ko, S.-B.; Park, H.-J.; Gong, S.; Wang, X.; Lu, Z.-H.; Wang, S. *Dalton Trans.* **2015**, *44*, 8433−8443. (b) Tenne, M.; Metz, S.; Münster, I.; Wagenblast, G.; Strassner, T. *Organometallics* **2013**, *32*, 6257−6264.
(20) Tsai, J.-Y.; Elshenawy, Z. Thiazole and Oxozole Carbene Metal Complexes as Phosphorescent OLED Materials. WO2012116242A1, 2012.
(21) (a) Green, R. A.; Pletcher, D.; Leach, S. G.; Brown, R. C. D. *Org. Lett.* **2015**, *17*, 3290−3293. (b) Hovey, M. T.; Check, C. T.; Sipher, A. F.; Scheidt, K. A. *Angew. Chem., Int. Ed.* **2014**, *53*, 9603−9607.
(22) Pesch, J.; Harms, K.; Bach, T. *Eur. J. Org. Chem.* **2004**, *2004*, 2025−2035.
(23) (a) Piel, I.; Pawelczyk, M. D.; Hirano, K.; Fröhlich, R.; Glorius, F. *Eur. J. Org. Chem.* **2011**, *2011*, 5475−5484. (b) Schedler, M.; Fröhlich, R.; Daniliuc, C.-G.; Glorius, F. *Eur. J. Org. Chem.* **2012**, *2012*, 4164−4171.
(24) (a) Kharasch, N.; Meyers, C. Y. *The Chemistry of Organic Sulfur Compounds*; Wiley-Blackwell: Oxford, UK, 1966. (b) Vernin, G. General Synthetic Methods for Thiazole and Thiazolium Salts. In *Chemistry of Heterocyclic Compounds: Thiazole and Its Derivatives*; Hoboken, NJ, USA, 1979; Vol. 1979*1*, pp 165−335.
(25) (a) Djafri, A.; Roussel, C.; Sandström, J. *J. Chem. Soc., Perkin Trans. 2* **1985**, 273−277. (b) Roussel, C.; Popescu, C. *Chirality* **1994**, *6*, 251−260. (c) Vozka, J.; Kalíková, K.; Roussel, C.; Armstrong, D. W.; Tesařová, E. *J. Sep. Sci.* **2013**, *36*, 1711−1719. (d) Sattigeri, V. J.; Soni, A.; Singhal, S.; Khan, S.; Pandya, M.; Bhateja, P.; Mathur, T.; Rattan, A.; Khanna, J. M.; Mehta, A. *ARKIVOC* **2005**, *2*, 46−49. (e) Pirkle, W. H.; Brice, L. J.; Terfloth, G. J. *J. Chromatogr. A* **1996**, *753*, 109−119. (f) Wang, Z.; Yu, Z.; Wang, Y.; Shi, D. *Synthesis* **2012**, *44*, 1559−1568.
(26) (a) Pirkle, W. H.; Koscho, M. E.; Wu, Z. *J. Chromatogr. A* **1996**, *726*, 91−97. (b) Roussel, C.; Adjimi, M.; Chemlal, A.; Djafri, A. *J. Org. Chem.* **1988**, *53*, 5076−5080. (c) Roussel, C.; Favrou, A. *J. Inclusion Phenom. Mol. Recognit. Chem.* **1993**, *16*, 283−296. (d) Roussel, C.; Vanthuyne, N.; Bouchekara, M.; Djafri, A.; Elguero, J.; Alkorta, I. *J. Org. Chem.* **2008**, *73*, 403−411. (e) Roussel, C.; Rafii, E.; Del Rio, A.; Vanthuyne, N. *Biomed. Chromatogr.* **2005**, *19*, 434−438.
(27) (a) Bellec, N.; Guérin, D.; Lorcy, D.; Robert, A.; Carlier, R.; Tallec, A. *Acta Chem. Scand.* **1999**, *53*, 861−866. (b) Roussel, C.; Suteu, C. *J. Chromatogr. A* **1997**, *761*, 129−138. (c) Tripathy, H.; Das, M. K.; Sahu, B.; Dash, B. C.; Mahapatra, G. N. *J. Indian Chem. Soc.* **1973**, *1*, 417−419. (d) Rühlmann, K.; Grosalski, A.; Schräpler, U. *J. Prakt. Chem.* **1960**, *11*, 54−62.
(28) Opitz, G. *Angew. Chem.* **1967**, *79*, 161−177.
(29) Loosmore, S. M.; McKinnon, D. M. Oxidation Products of Cyclic Thiones. *Phosphorus Sulfur Relat. Elem.* **1976**, *1*, 185−209.
(30) Unger, Y.; Meyer, D.; Molt, O.; Schildknecht, C.; Münster, I.; Wagenblast, G.; Strassner, T. *Angew. Chem., Int. Ed.* **2010**, *49*, 10214−10216.
(31) Fuertes, S.; García, H.; Perálvarez, M.; Hertog, W.; Carreras, J.; Sicilia, V. *Chem. - Eur. J.* **2015**, *21*, 1620−1631.
(32) (a) Tronnier, A.; Metz, S.; Wagenblast, G.; Muenster, I.; Strassner, T. *Dalton Trans.* **2014**, *43*, 3297−3305. (b) Tronnier, A.; Nischan, N.; Metz, S.; Wagenblast, G.; Münster, I.; Strassner, T. *Eur. J. Inorg. Chem.* **2014**, *2014*, 256−264.
(33) Tronnier, A.; Poethig, A.; Herdtweck, E.; Strassner, T. *Organometallics* **2014**, *33*, 898−908.
(34) Unger, Y.; Strassner, T.; Lennartz, C. *J. Organomet. Chem.* **2013**, *748*, 63−67.
(35) Drew, D.; Doyle, J. R.; Shaver, A. G. Cyclic Diolefin Complexes of Platinum and Palladium. In *Inorganic Synthesis*; John Wiley & Sons, Inc.: New York, 2007; pp 346−349.
(36) Gansäuer, A.; Behlendorf, M.; von Laufenberg, D.; Fleckhaus, A.; Kube, C.; Sadasivam, D. V.; Flowers, R. A. *Angew. Chem., Int. Ed.* **2012**, *51*, 4739−4742.
(37) Sheldrick, G. M. *SADABS*, Version 2.10; University of Goettingen: Goettingen, Germany, 2002.
(38) (a) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. *J. Appl. Crystallogr.* **1994**, *27*, 435. (b) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G. L.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115−119.
(39) Sheldrick, G. M. *Acta Crystallogr., Sect. A: Found. Crystallogr.* **2008**, *64*, 112−122.
(40) Wilson, A. J. C. Ed. *Mathematical, Physical and Chemical Tables, International Tables for Crystallography*, Vol. C; Kluwer, 1992.
(41) Hooft, R. W. W. *Collect, Data Collection Software for Nonius-Kappa CCD*; Nonius B.V.: Delft, The Netherlands, 1999.
(42) Duisenberg, A. *J. Appl. Crystallogr.* **1992**, *25*, 92−96.
(43) Duisenberg, A. J. M.; Kroon-Batenburg, L. M. J.; Schreurs, A. M. M. *J. Appl. Crystallogr.* **2003**, *36*, 220−229.
(44) Sheldrick, G. M. *SHELXL-97, Program for the Refinement of Structures*; University of Goettingen: Goettingen, Germany, 1997.
(45) Spek, A. *Acta Crystallogr., Sect. D: Biol. Crystallogr.* **2009**, *65*, 148−155.
(46) (a) Farrugia, L. *J. Appl. Crystallogr.* **1997**, *30*, 565. (b) Burnett, M. N.; Johnson, C. K. *ORTEP-III*; Oak Ridge National Laboratory: Oak Ridge, TN, USA, 2000.
(47) Macrae, C. F.; Bruno, I. J.; Chisholm, J. A.; Edgington, P. R.; McCabe, P.; Pidcock, E.; Rodriguez-Monge, L.; Taylor, R.; van de Streek, J.; Wood, P. A. *J. Appl. Crystallogr.* **2008**, *41*, 466−470.

DOI: 10.1021/acs.organomet.5b00991
Organometallics XXXX, XXX, XXX−XXX

(48) Frisch, M. J.; Trucks, G. W.; Schlegel, H. B.; Scuseria, G. E.; Robb, M. A.; Cheeseman, J. R.; Scalmani, G.; Barone, V.; Mennucci, B.; Petersson, G. A.; Nakatsuji, H.; Caricato, M.; Li, X.; Hratchian, H. P.; Izmaylov, A. F.; Bloino, J.; Zheng, G.; Sonnenberg, J. L.; Hada, M.; Ehara, M.; Toyota, K.; Fukuda, R.; Hasegawa, J.; Ishida, M.; Nakajima, T.; Honda, Y.; Kitao, O.; Nakai, H.; Vreven, T., Jr.; Peralta, J. E.; Ogliaro, F.; Bearpark, M.; Heyd, J. J.; Brothers, E.; Kudin, K. N.; Staroverov, V. N.; Kobayashi, R.; Normand, J.; Raghavachari, K.; Rendell, A.; Burant, J. C.; Iyengar, S. S.; Tomasi, J.; Cossi, M.; Rega, N.; Millam, J. M.; Klene, M.; Knox, J. E.; Cross, J. B.; Bakken, V.; Adamo, C.; Jaramillo, J.; Gomperts, R.; Stratmann, R. E.; Yazyev, O.; Austin, A. J.; Cammi, R.; Pomelli, C.; Ochterski, J. W.; Martin, R. L.; Morokuma, K.; Zakrzewski, V. G.; Voth, G. A.; Salvador, P.; Dannenberg, J. J.; Dapprich, S.; Daniels, A. D.; Farkas, O.; Foresman, J. B.; Ortiz, J. V.; Cioslowski, J.; Fox, D. J. *Gaussian 09*, Rev. B 0.1; Gaussian, Inc.: Wallingford, CT, 2009.

(49) (a) Vosko, S. H.; Wilk, L.; Nusair, M. *Can. J. Phys.* **1980**, *58*, 1200−1211. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1988**, *37*, 785−789. (c) Miehlich, B.; Savin, A.; Stoll, H.; Preuss, H. *Chem. Phys. Lett.* **1989**, *157*, 200−206. (d) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (e) Stephens, P. J.; Devlin, F. J.; Chabalowski, C. F.; Frisch, M. J. *J. Phys. Chem.* **1994**, *98*, 11623−11627.

(50) (a) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *33*, 8822−8824. (b) Perdew, J. P. *Phys. Rev. B: Condens. Matter Mater. Phys.* **1986**, *34*, 7406. (c) Becke, A. D. *Phys. Rev. A: At., Mol., Opt. Phys.* **1988**, *38*, 3098−3100.

(51) (a) Ditchfield, R.; Hehre, W. J.; Pople, J. A. *J. Chem. Phys.* **1971**, *54*, 724−728. (b) Hehre, W. J.; Ditchfield, R.; Pople, J. A. *J. Chem. Phys.* **1972**, *56*, 2257−2261. (c) Hariharan, P. C.; Pople, J. A. *Chem. Phys. Lett.* **1972**, *16*, 217−219. (d) Hariharan, P. C.; Pople, J. A. *Theor. Chim. Acta* **1973**, *28*, 213−222. (e) Hariharan, P. C.; Pople, J. A. *Mol. Phys.* **1974**, *27*, 209−214. (f) Rassolov, V. A.; Ratner, M. A.; Pople, J. A.; Redfern, P. C.; Curtiss, L. A. *J. Comput. Chem.* **2001**, *22*, 976−984. (g) Rassolov, V. A.; Pople, J. A.; Ratner, M. A.; Windus, T. L. *J. Chem. Phys.* **1998**, *109*, 1223−1229.

(52) (a) Dunning, T. H. *J. Chem. Phys.* **1977**, *66*, 1382−1383. (b) Binning, R. C.; Curtiss, L. A. *J. Comput. Chem.* **1990**, *11*, 1206−1216.

(53) (a) Krishnan, R.; Binkley, J. S.; Seeger, R.; Pople, J. A. *J. Chem. Phys.* **1980**, *72*, 650−654. (b) McLean, A. D.; Chandler, G. S. *J. Chem. Phys.* **1980**, *72*, 5639−5648. (c) Clark, T.; Chandrasekhar, J.; Spitznagel, G. W.; von Ragué Schleyer, P. *J. Comput. Chem.* **1983**, *4*, 294−301. (d) Curtiss, L. A.; McGrath, M. P.; Blaudeau, J. P.; Davis, N. E.; Binning, R. C.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 6104−6113. (e) Glukhovtsev, M. N.; Pross, A.; McGrath, M. P.; Radom, L. *J. Chem. Phys.* **1995**, *103*, 1878−1885. (f) Blaudeau, J.-P.; McGrath, M. P.; Curtiss, L. A.; Radom, L. *J. Chem. Phys.* **1997**, *107*, 5016−5021.

(54) (a) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 299−310. (b) Hay, P. J.; Wadt, W. R. *J. Chem. Phys.* **1985**, *82*, 270−283. (c) Wadt, W. R.; Hay, P. J. *J. Chem. Phys.* **1985**, *82*, 284−298.

(55) Dennington, R., II; Keith, T.; Millam, J.; Eppinnett, K.; Hovell, W. L.; Gilliland, R. *GaussView*, 3.09; Semichem Inc.: Shawnee Mission, 2003.

(56) Legault, C. Y. *CYLview*, 1.0b; Université de Sherbrooke, 2009.

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