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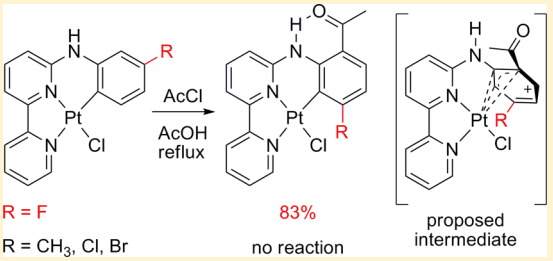
Regiospecific Acylation of Cycloplatinated Complexes: Scope, Limitations, and Mechanistic Implications

Jeffrey Carroll, Hannah G. Woolard, Robert Mroz, Charles A. Nason, and Shouquan Huo*

Department of Chemistry, East Carolina University, Greenville, North Carolina 27858, United States

Supporting Information

ABSTRACT: A series of platinum complexes based on the tridentate cyclometalating ligand derivatives 6-arylamino-2,2′-bipyridine, 6-phenoxy-2,2′-bipyridine, 6-phenylthio-2,2′-bipyridine, 6-benzyl-2,2′-bipyridine, and 6-benzoyl-2,2′-bipyridine were synthesized, and their acylation reactions were studied. Acylation of platinum complexes based on 6-(4-R-phenylamino)-2,2′-bipyridine derivatives (R = CH_3O, CH_3, Cl, COOEt) tolerates both electron-donating and electron-withdrawing substituents on the aryl ring that are para to the amino group. However, platinum complexes based on 6-(3-R′-phenylamino)-2,2′-bipyridine (R′ = CH_3, Cl, Br) did not undergo the acylation reaction under the same conditions. Interestingly, the acylation of the platinum complexes based on 6-(3-fluorophenylamino)-2,2′-bipyridine proceeded smoothly, and the results indicate that the acylation is regiospecific and occurs at the metalated carbon. Complexes based on 6-phenoxy-2,2′-bipyridine, 6-phenylthio-2,2′-bipyridine, and 6-benzyl-2,2′-bipyridine are also regioselectively acylated. A cyclometalated platinum complex based on 6-benzoyl-2,2′-bipyridine, where the benzene is more electron deficient than those in other cyclometalated platinum complexes, failed to undergo the acylation reaction. The acylation can be carried out in acetic acid, 1,2-dichloroethane, benzonitrile, and acetonitrile. Other acyl halides such as benzoyl chloride and crotonyl chloride are also effective acylating reagents. On the basis of the fact that the reaction is discouraged by the electron deficiency of the phenyl ring and contrasting results of the acylation of platinum complexes based on 6-(3-R′-phenylamino)-2,2′-bipyridine (R′ = CH_3, F, Cl, Br), an unprecedented electrophilic addition−platinum migration−rearomatization cascade mechanism is proposed for the regiospecific acylation reaction.



INTRODUCTION

Cyclometalated complexes constitute an important family of organometallic compounds and have been rigorously studied over the last five decades in terms of their formation, reactivity, and various applications.[1−3] Cyclometalated complexes based on group 10 metals, especially palladium and platinum, are among the earliest reported and most extensively studied species. In comparison to cyclometalated palladium complexes, which show a wide range of reactivity of the carbon−palladium bonds such as carbonylation, insertion of alkenes and alkynes, and insertion of isocyanates,[4] the platinum counterparts are relatively less reactive.[5] Therefore, cycloplatinated complexes are frequently studied as functional materials in a variety of applications in chemical, biological, and organic optoelectronic fields.[6] Recently, we discovered that regioselective acylation of complex **1a**, prepared from the cycloplatination of ligand **L1**, produced **1b** in high yield (Scheme 1).[7] There is strong intramolecular hydrogen bonding in the acylated product with an H−O bond length of 1.8 Å revealed by the X-ray crystal structure of the alkynyl-substituted derivative **1c**. The acylation of cyclometalated complexes has been scarcely reported.[4] Only in two papers were acylations of palladacycles derived from substituted benzylamine derivatives reported, but the products did not preserve a carbon−palladium bond.[8,9] The reaction only worked when the phenyl ring was unsubstituted or substituted with a strongly electron donating alkoxy group(s). Further experiments showed that the reaction of **L1** with K_2PtCl_4 in acetic acid and acetic anhydride can directly produce **1b** in moderate yield.[7] This reaction also represents a rare case of the cyclometalation of a ligand accompanied by functionalization of the cyclometalated complex.[10] In order to further understand the regioselective acylation of cyclometalated platinum complexes, the scope and limitations of this reaction have been investigated, particularly regarding the role of the hydrogen bonding, substituent effects, and mechanistic aspects.

RESULTS AND DISCUSSION

Role of Hydrogen Bonding. Since there is strong hydrogen bonding in the acylated product **1b**, it is necessary to examine whether the hydrogen bonding plays a role in directing the regioselective acylation. The ligands **L2**−**L5** were designed and prepared as shown in Scheme 2, and the corresponding complexes **2a**−**5a** were synthesized, where the atom or group that links the bipyridyl and the phenyl rings does not offer an acidic proton for hydrogen bonding with the incoming carbonyl group. For ligands with oxygen (**L2**) and sulfur (**L3**) linker atoms, the synthesis was accomplished by

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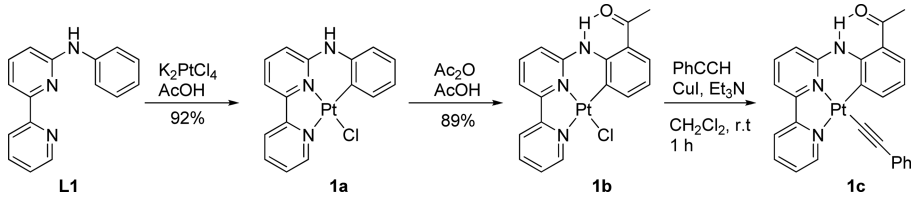
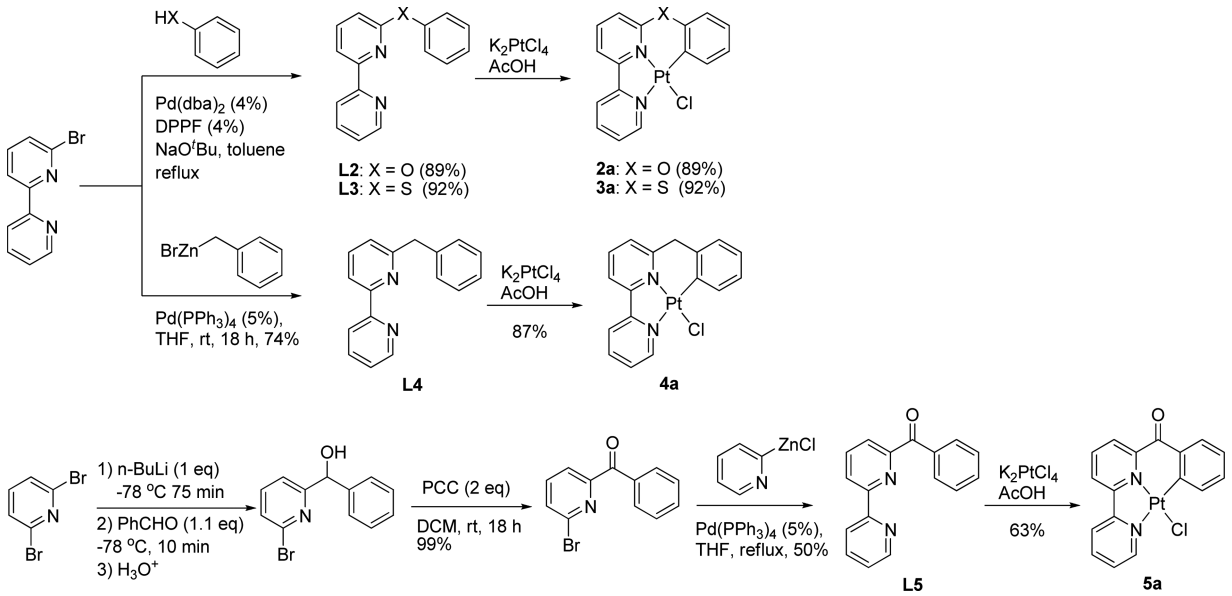
Scheme 1. Preparation and Regioselective Acylation of Complex 1a



Scheme 2. Synthesis of Ligands L2−L5 and Complexes 2a−5a



Buchwald−Hartwig cross-coupling of 6-bromo-2,2′-bipyridine with phenol and thiophenol, respectively.[11] The synthesis of ligands with methylene (**L4**) and carbonyl (**L5**) linker groups was accomplished by different synthetic strategies. Ligand **L4** was synthesized by the Negishi coupling of 6-bromo-2,2′-bipyridine with a benzyl zinc reagent[12] in 74% yield. Ligand **L5** was synthesized by a multistep synthesis. Lithium−bromine exchange of 2,6-dibromopyridine with *n*-BuLi[13] followed by treatment of the lithiated intermediate with benzaldehyde produced, after aqueous workup, the corresponding secondary alcohol in 72% yield. Oxidation of the secondary alcohol with pyridinium chlorochromate (PCC)[14] gave the corresponding ketone, which was cross-coupled with 2-pyridylzinc chloride[15] to form ligand **L5** in 50% yield. The cycloplatination of these ligands with K_2PtCl_4 proceeds smoothly in acetic acid to give the desired complexes **2a−5a** in good to high yields (Scheme 2).

Acylation of Complexes 2a−5a. Acylation of complexes **2a−5a** would allow assessment of the role of hydrogen bonding in the regioselectivity. For example, if the acylation of **1a** were directed to the position ortho to the amino linker group by hydrogen bonding, in the absence of hydrogen bonding, acylation of **2a** should occur, at least to some degree, at the position para to the oxygen linker atom. In addition to the absence of hydrogen bonding in their potential regioselective acylation products, complexes **2a−5a** also differ in electronic richness of the phenyl groups because of the different electronic effects of the linker atoms or groups. The electron richness of the phenyl ring may have an effect on the acylation of the complexes. An electron-rich phenyl ring is more susceptible to electrophilic attack by the acylium ion, a possible step involved in the mechanism of the reaction.

The acylation of cycloplatinated complex **1a** was previously carried out by refluxing it in a 1/1 mixture of acetic acid and acetic anhydride.[7] A long reaction time is required for complete conversion. Cyclometalated platinum complexes generally tend to decompose if they are heated for a prolonged period of time. When **2a** was refluxed in a 1/1 mixture of acetic acid and acetic anhydride for 3 days, the desired compound **2b** was only isolated in 34% yield along with unreacted starting materials (entry 1, Table 1). Considering the higher reactivity of acetyl chloride, we decided to use an excess amount of acetyl chloride (40 equiv) instead of acetic anhydride as the acylating reagent. Even though acetyl chloride may react with acetic acid to form acetic anhydride, hydrogen chloride generated in the reaction should promote the formation of active acylium ion. Indeed, the acylation of **2a** was complete within 1 h to afford **2b** in 84% isolated yield. Since the use of acetic acid as the solvent limits the use of acylating reagents other than acetyl halides, a series of other solvents were screened in the reaction of **2a** with acetyl chloride. The reaction in acetonitrile with 40 equiv of acetyl chloride was slow and black precipitates formed, likely platinum metal, due to the decomposition of platinum complexes. The yield of **2b** was low (entry 3). The reaction in benzonitrile with 20 equiv of acetyl chloride proceeded cleanly at 150 °C and was complete in 3 h to give **2b** in 75% isolated yield. Using 1,2-dichloroethane as the solvent afforded a 75% yield of complex **2b**. When chlorobenzene and 1,2-dichlorobenzene were used, the reaction proceeded initially but did not go to completion even with an excess amount of the acetyl chloride. The acylation reaction in THF and DMF did not proceed. Acetic

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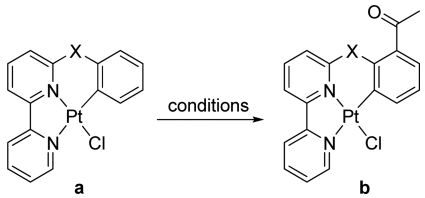
Table 1. Acylation of 2a−5a under Various Conditions



entry	X (a)	conditions	time (h)	b, yield (%)
1	O (**2a**)	$AcOH/Ac_2O$	72	**2b**, 34
2	O (**2a**)	AcOH/AcCl	1	**2b**, 84
3	O (**2a**)	MeCN/AcCl	6	**2b**, 35
4	O (**2a**)	PhCN/AcCl	3	**2b**, 75
5	O (**2a**)	DCE[a]/AcCl	1	**2b**, 75
6	S (**3a**)	AcOH/AcCl	3	**3b**, 40[b]
7	S (**3a**)	$AcOH/Ac_2O$	48	**3b**, 54[c]
8	CH_2 (**4a**)	AcOH/AcCl	6	**4b**, 62
9	CO (**5a**)	AcOH/AcCl	12	**5b**, NR[d]

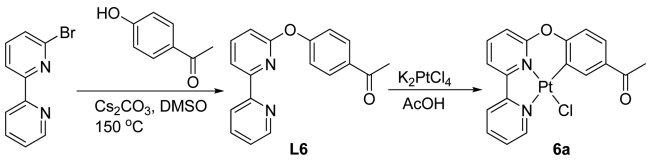
[a]1,2-Dichloroethane. [b]12% of **3a** was recovered. [c]24% of **3a** was recovered. [d]No reaction.

acid, 1,2-dichloroethane, and benzonitrile turned out to be the most effective solvents.

The reactions of complexes **3a** and **4a** with acetyl chloride in acetic acid gave **3b** and **4b** in 40% and 62% yields, respectively. In the reaction of **3a**, the starting material did not decompose and 12% of this was collected after column chromatography. When 1/1 acetic acid/acetic anhydride was used as the solvent, the reaction of **3a** also proceeded, but not to completion. Some of the starting material remained unreacted even after 2 days of refluxing. A 54% yield of **3b** was isolated and 24% of the starting material **3a** was recovered after column chromatography. There was no reaction observed for complex **5a**, and 93% of the starting material was recovered. This is probably due to the electron-withdrawing effect of the carbonyl group, which deactivates the metalated phenyl ring toward the acylation reaction.

The acylated products **2b−4b** were characterized by ^{1}H NMR and elemental analysis. The ^{1}H NMR spectra of **2b−4b** are consistent with the proposed structure resulting from an acylation at the position ortho rather than para to the linker atoms O, S, and C. In order to evaluate the degree of regioselectivity, complex **6a** was synthesized. Ligand **L6** was synthesized by reacting 6-bromo-2,2′-bipyridine with 4-hydroxyacetophenone in the presence of cesium carbonate.[16] Ligand **L6** was then reacted with K_2PtCl_4 at reflux in acetic acid to yield complex **6a** (Scheme 3). This complex has an acetyl

Scheme 3. Synthesis of L6 and 6a

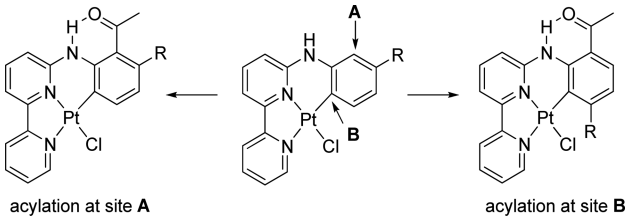


group para to the oxygen linker, making it a structural isomer of **2b**. The ^{1}H NMR spectra of complexes **6a** and **2b** show different splitting patterns due to different positions of the acetyl group. Whereas the spectrum of **2b** consists of only doublets and triplets, **6a** shows a downfield singlet at 9.12 ppm with platinum satellites, which can be assigned to the H ortho to the platinum. On the other hand, in the spectrum of **2b**, the doublet of doublets at 8.6 ppm, having the platinum satellites overlapping with adjacent signals, can be assigned to the H ortho to the platinum in **2b**. Complexes **6a** and **2b** showed different affinities on TLC: **6a** moved slightly faster than **2b**. TLC analysis of the crude products from the acylation of **2a** showed that there was no formation of **6a**.

The fact that acylation of complexes **2a−4a** occurs at the position ortho to the linker atom/group suggests that the hydrogen bonding is not a necessary factor in the regiocontrol of the acylation.

Substituent Effect on the Acylation Reaction. Introduction of a substituent to the phenyl ring in **L1** would allow us to examine the substituent effect on the acylation reaction. Since the acylation occurs at the position ortho to the amino linker, the electronic effect on the acylation can be elucidated without interference of steric effects by introducing electron-donating and electron-withdrawing groups at the position para to the amino linker. Although the acylation of **1a** occurs regioselectively at the position ortho to the amino linker group, which of the two ortho carbons of the phenyl ring is acylated is unclear: namely the metalated carbon or the unmetalated carbon (Scheme 4, R = H). By introduction of a substituent to

Scheme 4. Possible Outcomes of Acylation of Complexes with a Substituent at the Position Meta to the Amino Linker Group



the position *meta* to the amino linker, the acylated complex can then be characterized by NMR experiments or other tools if necessary, which allows for determination of the site of acylation: site **A** or site **B** (Scheme 4). To this end, ligands **L7−L16** were synthesized by Buchwald−Hartwig cross-coupling of 6-bromo-2,2′-bipyridine with an aniline or phenol derivative with a substituent on the phenyl ring. Their cycloplatination and subsequent acylation of the formed cycloplatinated complexes were studied. The results are summarized in Table 2.

Cycloplatination of **L7−L16** proceeds smoothly to produce **7a−16a** in high yields. The complexes formed cleanly as precipitates with little to no reduction of the Pt(II) to platinum metal, which can be easily isolated by filtration and washing sequentially with methanol, water, and methanol. The crude products were used directly for the subsequent acylation study. Cyclometalation occurred at the position ortho to the linker group. In the case of meta-substituted ligands **L11−L14**, the metalation occurs at the position para to the methyl or halogen substituent, presumably because of the steric effect of the substituent.

The reaction of complexes **7a−10a** with acetyl chloride (20 equiv) in acetic acid proceeded cleanly to form the acylated complexes **7b−10b** in high yields (entries 1−4, Table 2). Although the acylation reaction was not significantly affected by the difference in electron richness of the phenyl ring due to the electron-withdrawing or electron-donating effect of the substituents, the reaction of **10a** required a longer reaction

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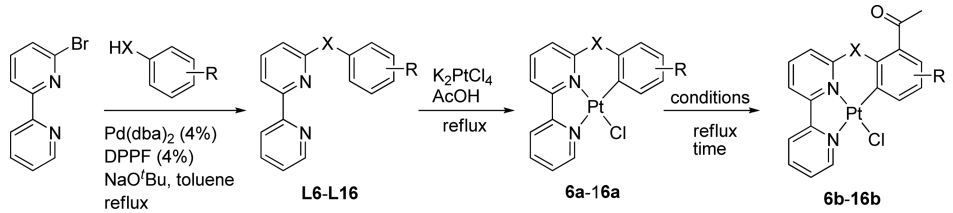
Table 2. Synthesis of Ligands L6−L16 and Complexes 6a−16a and Acylation of 6a−16a



entry	X	R	L, yield (%)	a, yield (%)	acylation conditions	time (h)	b, yield (%)
1	NH	4-OMe	**L7**, 51	**7a**, 76	AcOH/AcCl	1	**7b**, 69
2	NH	4-Me	**L8**, 73	**8a**, 91	AcOH/AcCl	1	**8b**, 91
3	NH	4-Cl	**L9**, 66	**9a**, 82	AcOH/AcCl	1	**9b**, 94
4	NH	4-COOEt	**L10**, 15	**10a**, 89	AcOH/Ac_2O	21	**10b**, 75
5	NH	3-Me	**L11**, 63	**11a**, 89	AcOH/AcCl	12	**11b**, NR[a]
6	NH	3-F	**L12**, 62	**12a**, 89	AcOH/AcCl	1	**12b**, 83
7	NH	3-Cl	**L13**, 21	**13a**, 97	AcOH/AcCl	12	**13b**, NR
8	NH	3-Br	**L14**, 25	**14a**, 99	AcOH/AcCl	12	**14b**, NR
10	O	4-OMe	**L15**, 81	**15a**, 74	AcOH/AcCl	24	**15b**, 61
11	O	4-Me	**L16**, 99	**16a**, 67	AcOH/AcCl	1	**16b**, 90
12	O	4-COMe	**L6**,[b] 43	**6a**, 51	AcOH/AcCl	12	**6b**, NR

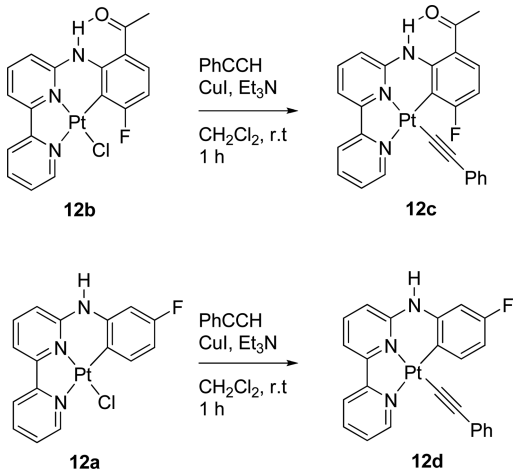
[a]No reaction. [b]**L6** was synthesized according to a literature procedure.[16]

time. The regioselectivity can be easily established by the characteristic downfield N−*H* signal in the ^{1}H NMR spectra of the acylated products, which appear in the region of 13−14 ppm due to the hydrogen bonding, while the N−*H* signals of the unacylated compounds **7a−10a** appear in the region of 10.5−11 ppm.

Complexes **11a**, **13a**, and **14a** were initially prepared to examine the site of acylation; however, no reaction was observed when these complexes reacted with 20 equiv of acetyl chloride at reflux in acetic acid. The starting materials essentially remained unreacted, although some decomposition and formation of a black precipitate was observed in the reaction of **13a** after prolonged heating. These results were initially thought to be quite disappointing, because the acylation of these complexes would provide information on the specific site of the regioselective reaction and should shed light on the reaction mechanism. It is obvious that the lack of reactivity is not due to the electronic effect of the substituents. Presumably, the steric effect may be the factor that restricts the regioselective acylation of complexes **11a**, **13a**, and **14a**. Therefore, we turned our attention to complex **12a**, bearing a fluoro substituent, because fluorine is a smaller group and the C−F bond is shorter. To our delight, acylation of **12a** with acetyl chloride in acetic acid was completed in 1 h, and the acylated product was isolated in 83% yield.

As mentioned above, the characterization of the acylated cycloplatinated complex **12b** is the key to understanding the regioselective acylation, but the poor solubility of complex **12b** makes it difficult to grow a crystal for X-ray structural determination. Therefore, the chloride ligand was replaced by a phenylacetylide to yield **12c** (Scheme 5) to increase the solubility. Although attempts to grow crystals of **12c** for X-ray structural determination have been unsuccessful, ^{1}H NMR spectra with reasonable quality have been obtained and used to characterize the structure of **12c** (Figure 1, middle). All signals have been assigned on the basis of its ^{1}H-^{1}H COSY spectrum, as shown in Figure 1. The protons of the phenylacetylide were not labeled because their resonances can be easily identified in the spectrum. The ortho acylation is confirmed by the

Scheme 5. Synthesis of 12c,d



downfield shift of the N−*H* signal from 10.80 ppm in **12a** ppm to 14.01 ppm (not displayed in Figure 1) in **12c** because of the hydrogen bonding. To further establish the location of the fluorine substituent, the ^{1}H NMR spectrum of complex **1c** is shown in Figure 1 (top) as a comparison. The structure of **1c** has been determined by X-ray crystallography.[7] The most striking difference between the two spectra is the doublet centered at 9.35 ppm with typical Pt satellite peaks ($^3J_{PtH}$ = 41.3 Hz) in the spectrum of complex **1c**, which is assigned to the hydrogen proximal to the metalated carbon. The significant downfield shift of the signal in comparison with the rest of hydrogens on the phenyl ring is due to the deshielding effect of the alkynyl group. The absence of such a signal with platinum satellite peaks in a similar region of the spectrum of **12c** suggests that the fluorine group is bonded to the carbon adjacent to the metalated carbon. In addition, the ^{19}F NMR of **12c** shows a doublet of doublets ($^3J_{FH}$ = 8.5 Hz, $^4J_{FH}$ = 5.8 Hz) at −63.04 ppm (DMSO-d_6, TFA as reference at −76.55 ppm), displaying platinum satellites with an F−Pt coupling constant of 337.7 Hz. Thus, the acylation of **12a** is regiospecific and occurs at the metalated carbon. For further comparison, phenyl-

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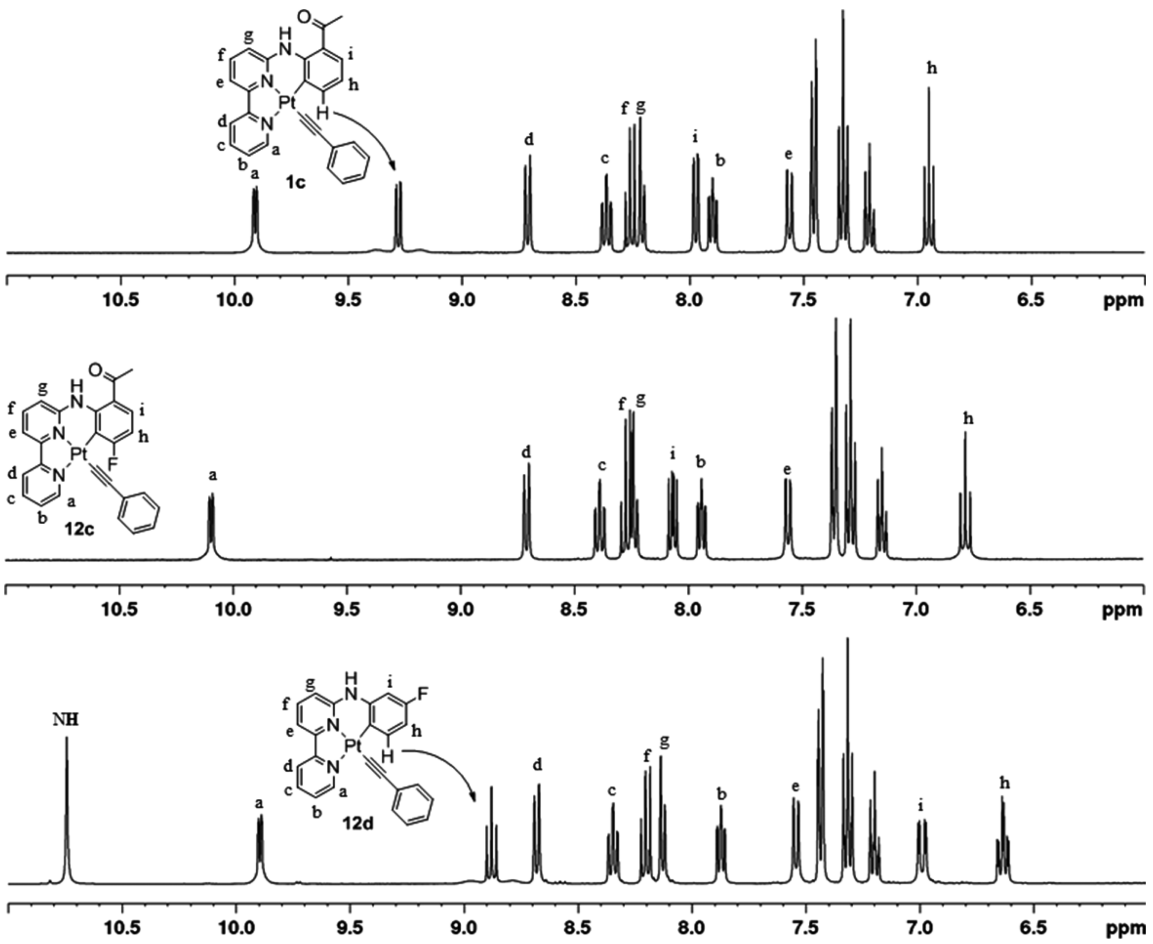


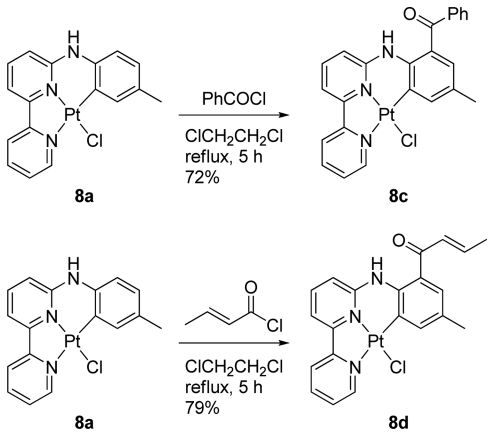
Figure 1. ^{1}H NMR spectra of **1c** (top, N*H* at 13.8 ppm), **12c** (middle, N*H* at 14.01 ppm), and **12d** (bottom).

acetylide complex **12d** was prepared from **12a**, and the ^{1}H NMR spectrum of **12d** is also displayed in Figure 1 (bottom). The triplet at 8.88 ppm with platinum satellite peaks can be assigned to the hydrogen proximal to the metalated carbon. The triplet splitting is due to the three-bond coupling with the adjacent hydrogen and the four-bond coupling with the fluorine, which display very similar coupling constants.[17] This spectroscopic feature also clearly indicates that the cycloplatination of **L12** occurs regioselectively at the carbon para to the fluorine to produce **12a**. The varied results of the acylation reactions of complexes **11a**−**14a** suggest that the acylation of cycloplatinated complexes may be hindered by larger substituents on the phenyl ring at the position *meta* to the linker group.

The acylation of **15a** and **16a** produced **15b** and **16b** in 61% and 79% yields, respectively. However, the reaction of **6a** did not proceed, indicating that the electron-withdrawing acetyl group in **6a** inhibited the acylation reaction.

Use of Alternate Electrophiles. The successful use of organic solvents such as 1,2-dichloroethane and benzonitrile allows for electrophiles other than acetyl chloride to be used in the reaction. Benzoyl chloride and crotonyl chloride successfully participated in the regioselective acylation reaction of complex **8a** to give the acylated products **8c**,**d** in good yields (Scheme 6). Both 1,2-dichloroethane and benzonitrile could be used as solvents and gave comparable yields. No reaction was observed when **2a** was refluxed in 1,2-dichloroethane or benzonitrile with 10 equiv of benzoyl chloride for 5 h. All of the starting material was recovered. These results indicate that the complex based on 6-phenoxy-2,2′-bipyridine is less reactive than those based on 6-arylamino-2,2′-bipyridine and benzoyl chloride is less reactive than acetyl chloride.

Scheme 6. Acylation of Cyclometalated Platinum Complexes with Benzoyl Chloride and Crotonyl Chloride



Tandem Cyclometalation−Acylation Process. As an alternative to the two-step synthetic route of ligand complexation followed by acylation, the cycloplatinated acylated complexes can also be synthesized in a cascade cycloplatination−acylation reaction (Scheme 7). At reflux in acetic acid for 18 h, ligand **L2** also reacted with 1 equiv of K_2PtCl_4

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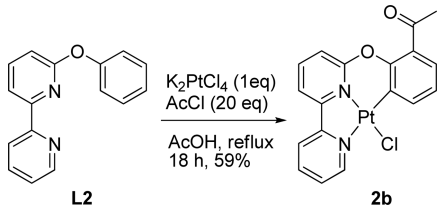
Scheme 7. Cascade Cycloplatination−Acylation of L2



and 20 equiv of acetyl chloride to give **2b** in 59% yield. After 1 h of the reaction, TLC analysis of the reaction mixture indicated that **L2** and **2a,b** were all present in the reaction mixture. After 18 h, there was only a small amount of the unacylated complex **2a** present, and the ligand **L2** was consumed. It should be pointed out that, in the absence of the platinum salt, there was no acylation at the phenyl ring of **L2** under otherwise identical conditions. When the NH-bridged ligand **L1** was used, only N-acylation was detected in the absence of the platinum salt.

Mechanisms of Acylation−Cyclometalation Reaction. In our previous paper,[7] two possible mechanisms were proposed for the acylation of **1a**. One involves a classical Friedel−Crafts acylation at the unmetalated carbon, and the other involves oxidative addition−reductive elimination followed by recyclometalation. As the site of acylation has been identified as the metalated carbon in the acylation of **12a**, the Friedel−Crafts reaction at the unmetalated carbon can be ruled out. The oxidative addition−reductive elimination[8] and insertion−elimination[9] mechanisms have been suggested for the regioselective acylation of palladacycles; however, these mechanisms fail to explain the fact that complexes **11a**, **13a**, and **14a** are not reactive toward acylation. If either of the mechanisms were operating, for example, in the acylation of **11a**, N,N-coordinated platinum complexes **11c** should be formed initially (Scheme 8), even though the steric hindrance of the bromo group in **11a** may prohibit the recyclometalation of **11c** to give **11b**. Instead, the starting material **11a** remained unreacted. Electronic effects should not play a role here because the methyl group is electron-donating.

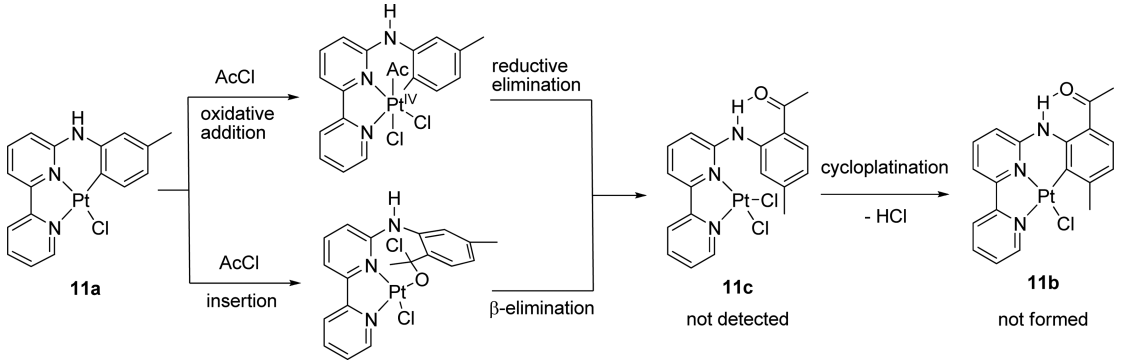
A plausible mechanism involves electrophilic attack by the acylium ion at the metalated carbon, followed by allylic 1,3-rearrangement (platinum migration), and finally rearomatization with the removal of a proton, as illustrated in Scheme 9. In this proposed mechanism, complex **1a** undergoes electrophilic attack by the acylium ion at the metalated carbon to form intermediate **1d**. Platinum may bond to the benzene ring through a π-allyl system (**1e**). The benzene ring would adopt a perpendicular orientation to the coordination plane of the complex. Following allylic 1,3-rearrangement to form intermediate **1f**, the newly metalated carbon is deprotonated and the aromaticity of the benzene ring is restored, affording the planar complex **1b**.

The electrophilic attack−platinum migration−rearomatization mechanism is also consistent with the experimental observations in this work. Most importantly, the unsuccessful acylation of complexes **11a**, **13a**, and **14a** with bulky groups meta to the linker group can be explained in the context of this mechanism. First of all, the electronic effect of the substituents on **11a**, **13a**, and **14a** should not be a factor because similar complexes **7a−10a** bearing either electron-donating or electron-withdrawing groups were successfully acylated. Most likely, the steric effect plays a role. The rearomatization requires the rotation of the phenyl ring to restore the coplanar geometry of the complex, but the rotation would suffer from unfavorable steric effects between the platinum and the substituent, and probably more so between the chloride ligand and the substituent as the rotation is approaching the coplanar geometry. Significant steric interactions caused by the methyl, chloro, and bromo groups in **11a**, **13a**, and **14a** prohibit the rearomatization (Scheme 10). Therefore, the intermediate would fall back to the starting material and the reaction favors the more stable reactants. The cleavage of a chelating C−Pt bond may be less favorable than deacylation. In the case of **12a**, the fluoro group is much smaller so that its steric interaction with the chloride ligand is not significant enough to block the rotation of phenyl ring for rearomatization. The aryl C−F bond (1.363 Å) is slightly longer than the C−H bond (1.083 Å), but much shorter than the aryl C−Cl (1.739 Å) and C−Br bonds (1.899 Å).[18]

CONCLUSIONS

The acylation of cyclometalated platinum complexes based on 6-substituted 2,2′-bipyridine derivatives has been investigated. The acylation reaction is regiospecific and occurs at the metalated carbon. The results indicate that the reaction likely proceeds via an unprecedented electrophilic addition−platinum migration−rearomatization cascade mechanism. The acylation reaction of cyclometalated platinum complexes based on 6-arylamino-2,2′-bipyridines tolerates both electron-donating and electron-withdrawing substituents on the phenyl ring but is affected by the steric hindrance of a substituent that is meta to

Scheme 8. Possible Oxidative Addition−Reductive Elimination and Insertion−Elimination Pathways for the Acylation Reaction of 11b



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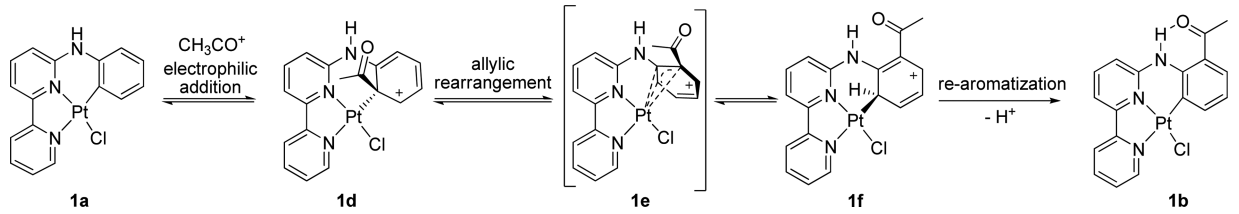
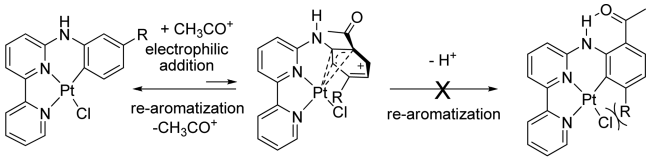
Organometallics XXXX, XXX, XXX−XXX

Scheme 9. Proposed Mechanism: Electrophilic Attack−Platinum Migration−Rearomatization



Scheme 10. Steric Effects in the Acylation of 11a, 13a, and 14a



R = CH_3 (**11a**), Cl (**13a**), Br (**14a**)

the amino group, which prohibits the rearomatization to form the new carbon−platinum bond. The acylation did not proceed when the metalated phenyl ring was sufficiently electron deficient, which is consistent with the mechanism involving an electrophilic addition of an acylium ion. Intramolecular hydrogen bonding is not a required factor in the regiocontrol of the acylation reaction. The acylation can be carried out in several different solvents, such as acetic acid, 1,2-dichloroethane, benzonitrile, and acetonitrile, and other acylating reagents such as benzoyl chloride and crotonyl chloride have also been used successfully.

EXPERIMENTAL SECTION

All reactions involving moisture- and/or oxygen-sensitive organometallic complexes were carried out under nitrogen or argon atmosphere and anhydrous conditions. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium and benzophenone under nitrogen before use. All other anhydrous solvents were purchased from Aldrich Chemical Co. and were used as received. All other reagents were purchased from chemical companies and were used as received. NMR spectra were measured on a Bruker 400 or a Varian 500 spectrometer. Spectra were taken in $CDCl_3$ or DMSO-d_6 using tetramethylsilane as the standard for ^{1}H NMR chemical shifts and the solvent peak ($CDCl_3$, 77.0 ppm; DMSO, 39.5 ppm) as the standard for ^{13}C NMR chemical shifts. ^{19}F NMR spectra were measured on a Bruker 400 using DMSO-d_6 as the solvent and TFA (trifluoroacetic acid) as the internal standard (−76.55 ppm). Coupling constants (J) are reported in Hz. Mass spectra were measured on a Waters ESI-Q-TOF mass spectrometer. Elemental analyses were performed at Atlantic Microlab, Inc. Norcross, GA. Synthesis details and characterization data of ligands **L1**−**L16** are provided in the Supporting Information.

Cycloplatination of L1−16. *Synthesis of Complex* ***1a***.[7] In a 50 mL, dry, three-necked round-bottom flask with condenser and drying tube were placed ligand **L1** (40 mg, 0.25 mmol), K_2PtCl_4 (66 mg, 0.25 mmol), and acetic acid (6 mL). The mixture was heated at reflux for 24 h. After the mixture was cooled to room temperature, the precipitates were collected by filtration, washed with acetic acid, water, methanol, and ethyl acetate: yellow solid, 67 mg, 89%. Complexes **2a**−**16a** were synthesized using the same procedure.

Complex ***2a***. Yellow solid, 52%. ^{1}H NMR (400 MHz, DMSO): δ 9.61 (d, $^3J_{HH}$ = 5.5, 1H), 8.72 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.57−8.32 (m, 4H), 7.93 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.67 (m, 1H), 7.22−7.07 (m, 2H), 6.97 (t, $^3J_{HH}$ = 7.4 Hz, 1H). MS: calcd for $C_{16}H_{11}N_2OPt$ (M − Cl)$^+$ 442.1; found 441.9.

Complex ***3a***. Yellow solid, 93%. ^{1}H NMR (400 MHz, DMSO): δ 9.57 (d, $^3J_{HH}$ = 5.6, 1H), 8.68 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.52 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 8.40 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.29 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 8.13 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 8.02 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 7.94 (t, $^3J_{HH}$ = 6.5 Hz, 1H), 7.41 (dd, $^3J_{HH}$ = 7.5 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 7.00 (td, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 6.94 (td, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.6 Hz, 1H). MS: calcd for $C_{16}H_{11}N_2PtS$ (M−Cl)$^+$ 458.0; found 457.9.

Complex ***4a***. Brownish yellow solid, 87%. ^{1}H NMR (400 MHz, DMSO): δ 9.40 (d, $^3J_{HH}$ = 5.2, 1H), 8.62 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.47 (d, $^3J_{HH}$ = 7.9 Hz, 1H), 8.37 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 8.28 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 8.02−7.64 (m, 3H), 7.06 (d, $^3J_{HH}$ = 6.8 Hz, 1H), 6.94−6.77 (m, 2H), 4.37 (s, 2H). MS: calcd for $C_{17}H_{13}N_2Pt$ (M−Cl)$^+$ 440.1; found 440.0.

Complex ***5a***. Brown solid, 63%. ^{1}H NMR (400 MHz, DMSO): δ 9.56 (d, $^3J_{HH}$ = 5.4 Hz, 1H), 8.82 (d, $^3J_{HH}$ = 8.0 Hz; Pt satellites, $^3J_{PtH}$ = 88.2 Hz, 1H), 8.72 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.58 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 8.43 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 8.31 (d, $^3J_{HH}$ = 8.0 Hz, $^3J_{PtH}$ = 46.0 Hz, 1H), 7.99 (t, $^3J_{HH}$ = 6.5 Hz, 1H), 7.84 (dd, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 7.26 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 7.18 (t, $^3J_{HH}$ = 7.4 Hz, 1H). MS: calcd for $C_{17}H_{11}N_2OPt$ (M − Cl)$^+$ 454.1; found 454.0.

Complex ***6a***. Yellow solid, 27 mg, 51%. ^{1}H NMR (400 MHz, DMSO): δ 9.62 (d, $^3J_{HH}$ = 5.6 Hz, 1H), 9.12 (s, Pt satellites, $^3J_{PtH}$ = 53.6 Hz, 1H), 8.74 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.59−8.46 (m, 2H), 8.41 (td, $^3J_{HH}$ = 7.8 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 7.96 (t, $^3J_{HH}$ = 6.8 Hz, 1H), 7.78−7.65 (m, 2H), 7.26 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 2.55 (s, 3H). MS: calcd for $C_{18}H_{13}N_2O_2Pt$ (M − Cl)$^+$ 484.1; found 484.0.

Complex ***7a***. Red solid, 76%. ^{1}H NMR (400 MHz, DMSO): δ 10.80 (s, 1H), 9.73 (d, $^3J_{HH}$ = 5.2 Hz, 1H), 8.63 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 8.31 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 8.25 (s, Pt satellites, $^3J_{PtH}$ = 36.2 Hz, 1H), 8.07 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 7.99 (d, $^3J_{HH}$ = 7.1 Hz, 1H), 7.85 (t, $^3J_{HH}$ = 6.8 Hz, 1H), 7.51 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 7.13 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 6.68 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.9 Hz, 1H), 3.70 (s, 3H). MS: calcd for $C_{17}H_{14}N_3OPt$ (M − Cl)$^+$ 471.1; found 471.0.

Complex ***8a***. Bright orange solid, 91%. ^{1}H NMR (400 MHz, DMSO): δ 10.62 (s, 1H), 9.75 (d, $^3J_{HH}$ = 5.4 Hz, 1H), 8.63 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.41 (s, Pt satellites, $^3J_{PtH}$ = 33.2 Hz, 1H), 8.31 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 8.11 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 8.02 (d, $^3J_{HH}$ = 7.0 Hz, 1H), 7.85 (t, $^3J_{HH}$ = 6.7 Hz, 1H), 7.45 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.00 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 6.87 (dd, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.9 Hz, 1H), 2.21 (s, 3H). MS: calcd for $C_{17}H_{14}N_3Pt$ (M − Cl)$^+$ 455.1; found 455.0.

Complex ***9a***. Bright orange solid, 82%. ^{1}H NMR (400 MHz, DMSO): δ 10.81 (s, 1H), 9.71 (d, $^3J_{HH}$ = 5.3 Hz, 1H), 8.66 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.59 (s, Pt satellites, $^3J_{PtH}$ = 44.0 Hz, 1H), 8.33 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 8.16 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 8.08 (d, $^3J_{HH}$ = 7.3 Hz, 1H), 7.87 (t, $^3J_{HH}$ = 6.5 Hz, 1H), 7.47 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.18−7.04 (m, 2H). MS: calcd for $C_{16}H_{11}ClN_3Pt$ (M − Cl)$^+$ 475.0; found 474.9.

Complex ***10a***. Orange solid, 89%. ^{1}H NMR (400 MHz, DMSO): δ 10.95 (s, 1H), 9.73 (d, $^3J_{HH}$ = 5.3 Hz, 1H), 9.28 (s, 1H), 8.65 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.33 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 8.20 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 8.11 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.88 (t, $^3J_{HH}$ = 6.7 Hz, 1H), 7.70 (dd, $^3J_{HH}$ = 8.4 Hz, $^3J_{HH}$ = 2.0 Hz, 1H), 7.52 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.15 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 4.28 (q, $^3J_{HH}$ = 7.1 Hz, 2H), 1.33 (t, $^3J_{HH}$ = 7.1 Hz, 3H). MS: calcd for $C_{19}H_{16}N_3O_2Pt$ (M − Cl)$^+$ 513.1; found 513.0.

Complex ***11a***. Red solid, 89%. ^{1}H NMR (400 MHz, DMSO): δ 10.62 (s, 1H), 9.74 (d, $^3J_{HH}$ = 5.8 Hz, 1H), 8.65 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.45 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.32 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 8.14 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 8.05 (d, $^3J_{HH}$ = 7.4 Hz, 1H), 7.86 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.49 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 6.94 (s, 1H), 6.62 (d, $^3J_{HH}$ = 8.2 Hz,

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Organometallics XXXX, XXX, XXX−XXX

1H), 2.27 (s, 3H). MS: calcd for $C_{17}H_{14}N_3Pt$ $(M - Cl)^+$ 455.1; found 455.0.

Complex ***12a***. Orange solid, 89%. ^{1}H NMR (400 MHz, DMSO): δ 10.80 (s, 1H), 9.73 (d, $^3J_{HH}$ = 5.6 Hz, 1H), 8.66 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.58 (t, $^3J_{HH}$ = 8.4 Hz, 1H), 8.34 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 8.19 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 8.11 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.88 (t, $^3J_{HH}$ = 6.5 Hz, 1H), 7.46 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 6.93 (dd, $^3J_{FH}$ = 11.4 Hz, $^4J_{HH}$ = 2.8 Hz, 1H), 6.63 (td, $^3J_{HH}$ = $^3J_{FH}$ = 8.8 Hz, $^4J_{HH}$ = 2.8 Hz, 1H). MS: calcd for $C_{16}H_{11}FN_3Pt$ $(M - Cl)^+$ 459.1; found 459.0.

Complex ***13a***. Orange solid, 82%. ^{1}H NMR (400 MHz, DMSO): δ 10.79 (s, 1H), 9.70 (d, $^3J_{HH}$ = 5.7 Hz, 1H), 8.65 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.57 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 8.33 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 8.18 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 8.09 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.87 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.45 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 7.16 (d, $^3J_{HH}$ = 2.3 Hz, 1H), 6.79 (dd, $^3J_{HH}$ = 8.7 Hz, $^4J_{HH}$ = 2.4 Hz, 1H). MS: calcd for $C_{16}H_{11}ClN_3Pt$ $(M - Cl)^+$ 475.0; found 474.9.

Complex ***14a***. Orange solid, 99%. ^{1}H NMR (400 MHz, DMSO): δ 10.78 (s, 1H), 9.71 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 8.66 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.52 (d, $^3J_{HH}$ = 8.6 Hz, 1H), 8.33 (t, $^3J_{HH}$ = 7.5 Hz, 1H), 8.19 (t, $^3J_{HH}$ = 8.1 Hz, 1H), 8.10 (d, $^3J_{HH}$ = 7.2 Hz, 1H), 7.87 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.45 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 7.30 (d, $^3J_{HH}$ = 2.1 Hz, 1H), 6.91 (dd, $^3J_{HH}$ = 8.5 Hz, $^3J_{HH}$ = 2.1 Hz, 1H). MS: calcd for $C_{16}H_{11}BrN_3Pt$ $(M - Cl)^+$ 519.0; found 518.9.

Complex ***15a***. Orange solid, 74%. ^{1}H NMR (400 MHz, DMSO): δ 9.60 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 8.70 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.57−8.31 (m, 3H), 8.00 (d, $^4J_{HH}$ = 3.1 Hz, 1H), 7.92 (t, $^3J_{HH}$ = 6.9 Hz, 1H), 7.62 (t, $^3J_{HH}$ = 4.8 Hz, 1H), 7.12 (d, $^3J_{HH}$ = 8.8 Hz, 1H), 6.70 (dd, $^3J_{HH}$ = 8.9 Hz, $^4J_{HH}$ = 3.1 Hz, 1H), 3.72 (s, 3H). MS: calcd for $C_{17}H_{13}N_2O_2Pt$ $(M - Cl)^+$ 472.1; found 472.0.

Complex ***16a***. Yellow-orange solid, 67%. ^{1}H NMR (400 MHz, DMSO): δ 9.60 (d, $^3J_{HH}$ = 5.1 Hz, 1H), 8.89 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.51−8.33 (m, 3H), 8.21 (s, Pt satellites, $^3J_{PtH}$ = 54.6 Hz, 1H), 7.91 (t, $^3J_{HH}$ = 6.9 Hz, 1H), 7.61 (dd, $^3J_{HH}$ = 6.9 Hz, $^4J_{HH}$ = 2.8 Hz, 1H), 7.04 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.92 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 2.24 (s, 3H). MS: calcd for $C_{17}H_{13}N_2OPt$ $(M - Cl)^+$ 456.1; found 456.0.

Acylation Reactions. *Preparation of* ***2b****: General Procedure*. In a 25 mL three-necked round-bottom flask with condenser and drying tube were placed **2a** (50 mg, 0.1 mmol), acetic acid (5 mL), and acetyl chloride (1 mL). The mixture was stirred and heated at reflux for 1 h. The mixture was stirred and heated at reflux for 1 h. After the solvent was evaporated, the crude product was dissolved in dichloromethane and purified by column chromatography on silica gel first with dichloromethane and then with dichloromethane and ethyl acetate (v/v 1/1): **2b**, yellow solid, 45.4 mg, 84%. ^{1}H NMR (400 MHz, DMSO): δ 9.61 (d, $^3J_{HH}$ = 5.1 Hz, 1H), 8.75 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.59 (dd, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 8.50 (d, $^3J_{HH}$ = 5.1 Hz, 2H), 8.41 (td, $^3J_{HH}$ = 8.0 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 7.96 (t, $^3J_{HH}$ = 6.7 Hz, 1H), 7.74 (t, $^3J_{HH}$ = 4.8 Hz, 1H), 7.33 (dd, $^3J_{HH}$ = 7.3 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 7.05 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 2.73 (s, 3H). Anal. Calcd for $C_{18}H_{13}ClN_2O_2Pt$: C, 41.59; H, 2.52; N, 5.39. Found: C, 41.59; H, 2.45; N, 5.45. Following the general procedure, acylation of **2a** with acetic acid/acetic anhydride, AcCl (20 equiv) in acetic acid, acetonitrile, benzonitrile, and 1,2-dichloroethane gave **2b** in 34%, 77%, 35%, 75%, and 75% yields, respectively.

The following compounds were prepared following the general procedure by using acetyl chloride and with acetic acid as the solvent unless specified otherwise.

Complex ***3b***. Orange solid, 40%. ^{1}H NMR (400 MHz, DMSO): δ 9.49 (d, $^3J_{HH}$ = 5.6 Hz, 1H), 8.67 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.50 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.40 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.24 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 8.17−8.00 (m, 2H), 7.94 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.60 (dd, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.5 Hz, 1H), 7.00 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 2.63 (s, 3H). Anal. Calcd for $C_{18}H_{13}ClN_2OPtS$: C, 40.34; H, 2.45; N, 5.23. Found: C, 39.94; H, 2.56; N, 5.25.

Complex ***4b***. Brownish yellow solid, 68%. ^{1}H NMR (400 MHz, DMSO): δ 9.37 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 8.62 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 8.46 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.38 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.27 (t, $^3J_{HH}$ = 7.8 Hz, 1H), 8.03−7.86 (m, 2H), 7.79 (d, $^3J_{HH}$ = 7.8 Hz, 1H), 7.29 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 6.93 (t, $^3J_{HH}$ = 7.6 Hz, 1H), 4.47 (s, 2H), 2.60 (s, 3H). Anal. Calcd for $C_{19}H_{15}ClN_2OPt$: C, 44.07; H, 2.92; N, 5.41. Found: C, 43.88; H, 2.97; N, 5.46.

Complex ***7b***. Dark red solid, 69%. ^{1}H NMR (400 MHz, DMSO): δ 13.49 (s, 1H), 9.72 (d, $^3J_{HH}$ = 5.6 Hz, 1H), 8.67 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 8.65 (d, $^4J_{HH}$ = 3.1 Hz, 1H), 8.35 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 8.19 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 8.12 (d, $^3J_{HH}$ = 7.6 Hz, 1H), 7.89 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.45 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 7.42 (d, $^4J_{HH}$ = 3.0 Hz, 1H), 3.80 (s, 3H), 2.77 (s, 3H). Anal. Calcd for $C_{19}H_{16}ClN_3O_2Pt.0.5CH_2Cl_2$: C, 39.61; H, 2.90; N, 7.11. Found: C, 39.33; H, 2.81; N, 7.12.

Complex ***8b***. Red solid, 91%. ^{1}H NMR (400 MHz, DMSO): δ 13.63 (s, 1H), 9.74 (d, $^3J_{HH}$ = 5.7 Hz, 1H), 8.77 (d, $^4J_{HH}$ = 1.6 Hz, 1H), 8.68 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.35 (td, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.22 (t, $^3J_{HH}$ = 8.3 Hz, 1H), 8.15 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.90 (t, $^3J_{HH}$ = 6.7 Hz, 1H), 7.75 (d, $^4J_{HH}$ = 1.2 Hz 1H), 7.46 (d, $^3J_{HH}$ = 8.5 Hz, 1H), 2.76 (s, 3H), 2.30 (s, 3H). Anal. Calcd for $C_{19}H_{16}ClN_3OPt$: C, 42.82; H, 3.03; N, 7.89. Found: C, 42.65; H, 2.97; N, 7.82.

Complex ***8c***. In a 25 mL three-necked round-bottom flask with condenser and drying tube were placed **8a** (40 mg, 0.081 mmol), benzoyl chloride (47 μL, 0.41 mmol), and 1,2-dichloroethane (5 mL). The mixture was stirred and heated at reflux for 24 h. After the mixture was cooled to room temperature, the solvent was evaporated and the product was collected by suction filtration and washed with hexane, water, and methanol: **8c**, yellow solid, 35.2 mg, 72%. ^{1}H NMR (400 MHz, DMSO): δ 12.58 (s, 1H), 9.76 (d, $^3J_{HH}$ = 5.6 Hz, 1H), 8.81 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 8.71 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.37 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 8.24 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 8.19 (d, $^3J_{HH}$ = 8.0 Hz, 1H), 7.91 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.73−7.50 (m, 6H), 7.14 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 2.20 (s, 3H). Anal. Calcd for $C_{24}H_{18}ClN_3OPt$: C, 48.45; H, 3.05; N, 7.06. Found: C, 48.38; H, 2.96; N, 7.18.

Complex ***8d***. In a 50 mL three-necked round-bottom flask fitted with a condenser and drying tube were placed **8a** (50 mg, 0.1 mmol), crotonyl chloride (100 μL, 1.0 mmol), and benzonitrile (5 mL). The reaction mixture was stirred and heated at 150 °C for 1 h. After cooling, the product was precipitated from the reaction mixture with 5 mL of hexane and collected by filtration. The product was purified by column chromatography on silica gel with dichloromethane and then dichloromethane and ethyl acetate (v/v 40/1): bright orange solid, 40 mg, 72%. ^{1}H NMR (400 MHz, DMSO): δ 13.77 (s, 1H), 9.74 (d, $^3J_{HH}$ = 5.7 Hz, 1H), 8.77 (d, $^4J_{HH}$ = 1.6 Hz, 1H), 8.67 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.34 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.7 Hz, 1H), 8.22 (t, $^3J_{HH}$ = 7.9 Hz, 1H), 8.15 (dd, $^3J_{HH}$ = 7.6 Hz, $^4J_{HH}$ = 1.1 Hz, 1H), 7.89 (td, $^3J_{HH}$ = 6.8 Hz, $^4J_{HH}$ = 1.2 Hz, 1H), 7.82 (d, $^4J_{HH}$ = 1.9 Hz, 1H), 7.50−7.43 (m, 2H), 7.09 (m, 1H), 2.30 (s, 3H), 2.03 (d, $^3J_{HH}$ = 7.0 Hz, 3H). Anal. Calcd for $C_{21}H_{18}ClN_3OPt$: C, 45.13; H, 3.25; N, 7.52. Found: C, 44.99; H, 3.07; N, 7.55.

In a 50 mL three-necked round-bottom flask fitted with a condenser and drying tube were placed **8a** (50 mg, 0.1 mmol), crotonoyl chloride (100 μL, 1.0 mmol), and 1,2-dichloroethane (5 mL). The reaction mixture was stirred and heated to reflux for 5 h. After cooling, the product was precipitated from the reaction mixture with 5 mL of hexane and collected by filtration. The product was purified by column chromatography on silica gel with dichloromethane and then dichloromethane and ethyl acetate (v/v 40/1): bright orange solid, 45 mg, 79%.

Complex ***9b***. Red solid, 94%. ^{1}H NMR (400 MHz, DMSO): δ 13.50 (s, 1H), 9.68 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 8.88 (s, Pt satellites, $^3J_{PtH}$ = 48.0 Hz, 1H), 8.69 (d, $^3J_{HH}$ = 8.3 Hz, 1H), 8.37 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.26 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 8.19 (d, $^3J_{HH}$ = 7.5 Hz, 1H), 7.94 (d, $^4J_{HH}$ = 2.4 Hz, 1H), 7.90 (t, $^3J_{HH}$ = 6.8 Hz, 1H), 7.49 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 2.78 (s, 3H). Anal. Calcd for $C_{18}H_{13}Cl_2N_3OPt$: C, 39.07; H, 2.37; N, 7.59. Found: C, 39.23; H, 2.22; N, 7.62.

Complex ***10b***. In a 25 mL three-necked round-bottom flask with condenser and drying tube were placed **10a** (40 mg, 0.072 mmol), acetic acid (3 mL), and acetic anhydride (3 mL). The mixture was stirred and heated at reflux for 21 h. After cooling to room temperature, water (3 mL) was added and the precipitate was filtered and washed with hexane, methanol, water, and ethyl acetate: **10b**,

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Organometallics XXXX, XXX, XXX−XXX

orange solid, 35.4 mg, 75%. ^{1}H NMR (400 MHz, DMSO): δ 13.76 (s, 1H), 9.72 (d, $^3J_{HH}$ = 5.7 Hz, 1H), 9.52 (d, $^4J_{HH}$ = 2.0 Hz; Pt satellites, $^3J_{PtH}$ = 36.2 Hz, 1H), 8.71 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.47 (d, $^4J_{HH}$ = 2.0 Hz, 1H), 8.37 (t, $^3J_{HH}$ = 8.0 Hz, 1H), 8.31 (t, $^3J_{HH}$ = 8.2 Hz, 1H), 8.28−8.22 (m, 1H), 7.92 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.56 (d, $^3J_{HH}$ = 8.4 Hz, 1H), 4.35 (q, $^3J_{HH}$ = 7.2 Hz, 2 H), 2.81 (s, 3H), 1.36 (t, $^3J_{HH}$ = 7.1 Hz, 3H). Anal. Calcd for $C_{21}H_{18}ClN_3O_3Pt$: C, 42.68; H, 3.07; N, 7.11. Found: C, 42.79; H, 3.16; N, 6.81.

Complex ***12b***. Orange solid, 94%. ^{1}H NMR (400 MHz, DMSO): δ 13.64 (s, 1H), 9.67 (d, $^3J_{HH}$ = 5.6 Hz, 1H), 8.66 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.38 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 8.27−8.16 (m, 2H), 8.04−7.91 (m, 2H), 7.49 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 6.69 (t, $^3J_{FH}$ = $^3J_{HH}$ = 8.8 Hz, 1H), 2.73 (s, 3H). Anal. Calcd for $C_{18}H_{13}ClFN_3OPt$: C, 40.27; H, 2.44; N, 7.83. Found: C, 40.28; H, 2.32; N, 7.78.

Complex ***15b***. Orange solid, 16% recovered. The second band gave **15b**, orange solid, 61%. ^{1}H NMR (400 MHz, DMSO): δ 9.58 (d, $^3J_{HH}$ = 5.4 Hz, 1H), 8.72 (d, $^3J_{HH}$ = 8.1 Hz, 1H), 8.46 (d, $^3J_{HH}$ = 4.8 Hz, 2H), 8.40 (t, $^3J_{HH}$ = 7.7 Hz, 1H), 8.16 (d, $^4J_{HH}$ = 3.2 Hz; Pt satellites, $^3J_{PtH}$ = 52 Hz, 1H), 7.94 (t, $^3J_{HH}$ = 6.5 Hz, 1H), 7.69 (t, $^3J_{HH}$ = 4.8 Hz, 1H), 6.85 (d, $^4J_{HH}$ = 3.2 Hz, 1H), 3.75 (s, 3H), 2.73 (s, 3H). Anal. Calcd for $C_{19}H_{15}ClN_2O_3Pt$: C, 41.50; H, 2.75; N, 5.09. Found: C, 41.73; H, 2.60; N, 5.25.

Complex ***16b***. Yellow solid, 90%. ^{1}H NMR (400 MHz, DMSO): δ 9.59 (d, $^3J_{HH}$ = 5.7 Hz, 1H), 8.72 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.52−8.28 (m, 4H), 7.93 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.69 (t, $^3J_{HH}$ = 4.8 Hz, 1H), 7.11 (d, $^4J_{HH}$ = 2.1 Hz, 1H), 2.70 (s, 3H), 2.25 (s, 3H). Anal. Calcd for $C_{19}H_{15}ClN_2O_2Pt{\cdot}0.25\ CH_2Cl_2$: C, 41.65; H, 2.81; N, 5.05. Found: C, 41.46; H, 2.73; N, 5.17.

Preparation of Phenylacetylide Complexes. *Preparation of Complex* ***12c***. In a 50 mL three-necked round-bottom flask under argon were placed complex **12b** (100 mg, 0.19 mmol), phenylacetylene (61 μL, 0.66 mmol), copper iodide (2.8 mg, 0.015 mmol), triethylamine (1.7 mL, 12.1 mmol), and anhydrous dichloromethane (15 mL). The reaction mixture was stirred at room temperature for 1 h and then quenched with water (15 mL) and extracted with dichloromethane. The organic phase was washed with brine and dried over $MgSO_4$. After filtration, the solvent was removed and the crude product was purified by column chromatography on silica gel with dichloromethane and ethyl acetate (v/v 3/1): red solid, 80 mg, 71%. ^{1}H NMR (400 MHz, DMSO): δ 14.01 (s, 1H), 10.10 (d, $^3J_{HH}$ = 5.5 Hz, 1H), 8.71 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.39 (td, $^3J_{HH}$ = 7.9, $^4J_{HH}$ = 1.5 Hz, 1H), 8.31−8.20 (m, 2H), 8.07 (dd, $^3J_{FH}$ = 8.7 Hz, $^3J_{HH}$ = 5.7 Hz, 1H), 7.95 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.56 (d, $^3J_{HH}$ = 8.3, 1H), 7.40−7.26 (m, 4H), 7.16 (t, $^3J_{HH}$ = 7.3 Hz, 1H), 6.78 (t, $^3J_{FH}$ = $^3J_{HH}$ = 8.7 Hz, 1H), 2.77 (s, 3H). ^{19}F NMR (376.46 Hz, DMSO): δ − 63.04 (dd, $^3J_{FH}$ = 8.5, $^4J_{FH}$ = 5.8 Hz; Pt satellites, $^3J_{PtF}$ = 337.7 Hz). Anal. Calcd for $C_{26}H_{18}FN_3OPt{\cdot}0.25CH_2Cl_2$: C, 50.55; H, 2.99; N, 6.74. Found: C, 50.45; H, 3.26; N, 6.57.

Preparation of ***12d***. This compound was prepared from **12a** using the same procedure described above for **12c**: red solid, 76%. ^{1}H NMR (400 MHz, DMSO): δ 10.74 (s, 1H), 9.89 (dd, $^3J_{HH}$ = 5.7 Hz, $^4J_{HH}$ = 0.9 Hz, 1H), 8.88 (t, $^3J_{HH}$ = 8.4 Hz; Pt satellites, $^3J_{PtH}$ = 72.3 Hz, 1H), 8.60 (d, $^3J_{HH}$ = 8.2 Hz, 1H), 8.35 (td, $^3J_{HH}$ = 7.9 Hz, $^4J_{HH}$ = 1.6 Hz, 1H), 8.16 (m, 2H), 7.87 (t, $^3J_{HH}$ = 6.6 Hz, 1H), 7.54 (dd, $^3J_{HH}$ = 8.8 Hz, $^4J_{HH}$ = 0.8 Hz, 1H), 7.43 (dd, $^3J_{HH}$ = 6.8 Hz, $^3J_{HH}$ = 1.2 Hz, 2H), 7.31 (t, $^3J_{HH}$ = 7.8 Hz, 2H), 7.20 (tt, $^3J_{HH}$ = 7.4 Hz, $^4J_{HH}$ = 1.3 Hz, 1H), 6.99 (dd, $^3J_{FH}$ = 11.6 Hz, $^4J_{HH}$ = 2.7 Hz, 1H), 6.63 (td, $^3J_{FH}$ = $^3J_{HH}$ = 8.6 Hz, $^4J_{HH}$ = 2.8 Hz, 1H). Anal. Calcd for $C_{24}H_{16}FN_3Pt{\cdot}0.25CH_2Cl_2$: C, 50.07; H, 2.86; N, 7.22. Found: C, 50.07; H, 2.84; N, 7.51.

■ ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.organomet.6b00174.

Synthesis and characterization data of **L1**−**L16**, ^{1}H and ^{13}C NMR spectra of the ligands **L2**−**L16**, and ^{1}H NMR spectra of complexes **2a**−**16a**, **2b**−**4b**, **7b**−**10b**, **8c,d**, **12b**, **15b**, and **16b** (PDF)

■ AUTHOR INFORMATION

Corresponding Author

*E-mail for S.H.: huos@ecu.edu.

Notes

The authors declare no competing financial interest.

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