ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Reaction of *N*-Isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine with K_2PtCl_4: Selective C−H Bond Activation, C−N Bond Cleavage, and Selective Acylation

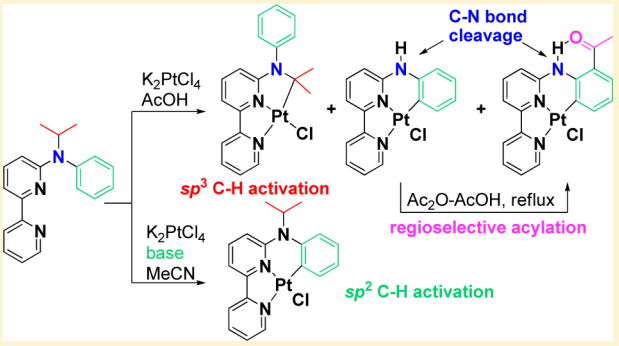
Jeffrey Carroll,[†] Joshua P. Gagnier,[†] Alexander W. Garner,[†,§] Justin G. Moots,[†,∥] Robert D. Pike,[‡] Yumin Li,[†] and Shouquan Huo*[,†]

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

[‡]Department of Chemistry, College of William and Mary, Williamsburg, Virginia 23185, United States

Supporting Information

ABSTRACT: The selective C−H bond activation of *N*-isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine promoted by Pt(II) was complicated by the low selectivity of sp^2 C−H bond activation in acetonitrile and low yield of sp^3 C−H activation in acetic acid. The use of a base was found to effectively suppress the competing sp^3 C−H bond activation in acetonitrile, improving the selectivity of sp^2 C−H bond activation from 70% to 99%. In the reaction in acetic acid, the low yield was due to the competing C−N bond cleavage. The use of a base reduced the C−N bond cleavage, but not completely. The reaction of *N*-*tert*-butyl-*N*-phenyl-2,2′-bipyridin-6-amine with K_2PtCl_4 in acetic acid produced the cyclometalated complex with complete C−N bond cleavage and its acylated derivative. These results indicated that the C−N bond cleavage might proceed via heterolytic C−N bond dissociation. The acylation following the C−N cleavage in the reaction in acetic acid is regioselective. Further experiments showed that the reaction of *N*-phenyl-2,2′-bipyridin-6-amine with K_2PtCl_4 in acetic acid produced the cyclometalated complex, while the reaction in a mixture of acetic anhydride and acetic acid produced the acylated cyclometalated complex. An X-ray crystal structure study revealed strong intramolecular H bonding in the acylated complexes. The regioselectivity was explained in terms of H bonding and the electron distribution predicted by the DFT calculations.



INTRODUCTION

Cyclometalation is an important process in organometallic chemistry, which involves chelation-assisted carbon−metal bond formation.[1] Cyclometalation via the cleavage of a C−H bond to form the metallacycle is the intramolecular version of organometallic C−H bond activation.[2] Since the chelation can significantly improve the thermal stability of organometallic compounds, many of the cyclometalated complexes are very stable and can be isolated and fully characterized. This makes them extremely important in studying fundamental mechanistic issues associated with C−H bond activation.[1,2] Some key active intermediates involved in or proposed for the C−H bond activation may be stabilized by the chelation so that they can be fully studied. For example, an agostic interaction is conceived to be an important process in intermolecular C−H bond activation but could not be fully characterized. With chelation stabilization, complexes displaying an agostic interaction have been isolated and fully characterized.[3,4] On the other hand, cyclometalated complexes have found applications in a wide range of areas, from catalysis[5,6] to advanced materials.[7]

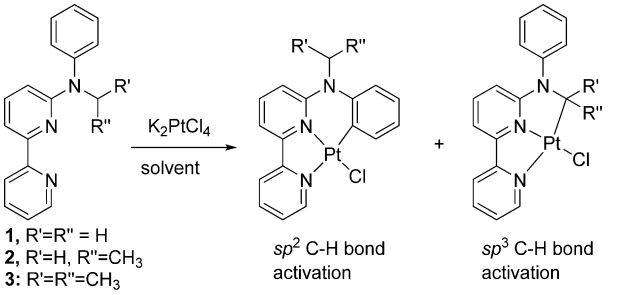
One of the fundamental issues in chemical transformations is the selectivity. A selective reaction allows the formation of one compound out of two or more possibilities. For cyclopalladation and cycloplatination, it is generally observed that the activation of an sp^2 C−H bond is preferred over the activation of an sp^3 C−H bond; however, there have been many reports on the competing sp^2/sp^3 C−H activation in cyclopalladation.[8] Remarkably, in some cases either of the two C−H activations can be achieved through a switch of the selectivity. One of the earliest examples of the selectivity switch was reported by Yoshida et al.,[8a] who observed that the cyclopalladation of *N*-thiobenzoylpyrrolidine with $PdCl_2$ in methanol occurred at the phenyl ring while a similar reaction in hexamethylphosphoramide (HMPA) resulted in metalation at the CH_2 group next to the nitrogen of the pyrrolidine ring. The preference in the competing sp^2/sp^3 C−H bond activation can also be influenced by other factors such as the ring size of the metallacycle,[8b,f,i] metal precursors,[8d,f−h] and the reaction temperature.[8b,f] In contrast, reports on the competing sp^2/sp^3 C−H bond activation via cycloplatination are very rare.[3] In the cycloplatination of 6-(1-methylbenzyl)-2,2′-bipyridine and 6-

Received: June 11, 2013
Published: August 26, 2013

   dx.doi.org/10.1021/om400540y | *Organometallics* 2013, 32, 4828−4836

(1,1-dimethylbenzyl)-2,2′-bipyridine, metalation was reported to occur at the phenyl ring rather than the methyl groups,[9a,b] although forced sp^3 C−H bond activation in cycloplatination of 6-alkyl-2,2′-bipyridine is known.[9c,d] Recently, we have discovered a solvent-controlled switch of selectivity between intramolecular sp^2 and sp^3 C−H bond activation mediated by platinum,[10] in which the reaction of *N*-alkyl-*N*-phenyl-2,2′-bipyridin-6-amine (alkyl = Me (**1**), Et (**2**), *i*-Pr (**3**)) with K_2PtCl_4 in acetic acid produced predominantly sp^3 C−H activation products, while interestingly, the reaction in acetonitrile gave selectively sp^2 C−H activation products (Scheme 1). Further experiments suggested that the switch of

Scheme 1. Reaction of *N*-Alkyl-*N*-phenyl-2,2′-bipyridin-6-amine with K_2PtCl_4



selectivity could be attributed to kinetic or thermodynamic control under different conditions. The degree of the selectivity control is quite remarkable except for the reaction of *N*-isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine (**3**), which produced a 70:30 mixture of both sp^2 and sp^3 activation products **4** and **5** in acetonitrile (Table 1). In addition, the reaction in acetic acid gave the product **5** resulted from exclusive sp^3 C−H bond activation, but only in 38% yield. In this paper, we report our effort to improve the control of the selectivity of this reaction and to gain an insight into the competing side reactions associated with the C−N bond cleavage.

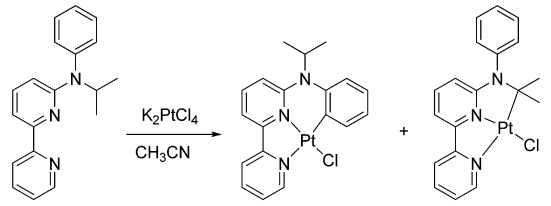
RESULTS AND DISCUSSION

There are two issues with the C−H bond activation of *N*-isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine (**3**) by platinum: namely the low selectivity of **4** formation in the reaction in acetonitrile and the low yield of **5** in the reaction in acetic acid. This is in sharp contrast with the reaction of *N*-methyl-*N*-phenyl-2,2′-bipyridin-6-amine (**1**), which exhibited both high selectivity and high yield of sp^2 C−H bond activation in acetonitrile and sp^3 C−H bond activation in acetic acid.[10]

Selectivity of sp^2 C−H Bond Activation. The cause of the lower selectivity may be complicated; however, two factors may be significant. First of all, the intrinsic reactivity of different types of sp^3 C−H bonds is different. Generally, the bond strength decreases in the order methane, primary, secondary, and tertiary C−H bonds,[11] which indicates that the secondary C−H bond in *N*-isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine (**3**) may be more reactive than the methyl C−H bond in *N*-methyl-*N*-phenyl-2,2′-bipyridin-6-amine. Therefore, the sp^3 C−H activation becomes relatively more competitive under kinetically controlled conditions of the reaction of **3** in acetonitrile, resulting in lower selectivity of **4**. It should be mentioned that the relative reactivity of primary, secondary, and tertiary C−H bonds depends on the nature of the reactions and other factors and a reverse order is known in cyclometalation chemistry.[1a]

On the other hand, since the formation of **4** was considered to be kinetically controlled,[10] the isomerization of **4** to **5** is at least one major contributor to the poor selectivity. The isomerization likely proceeds via the cleavage of the sp^2 C−Pt bond of **4** by the HCl generated from the cyclometalation reaction; therefore, the use of a base may terminate this pathway by neutralizing the HCl. We may not be able to alter the intrinsic reactivity of the C−H bond but certainly can use an HCl scavenger in the reaction. The choice of the HCl scavenger could be critical; a strong base may coordinate strongly to the platinum and inhibit the reaction, while a weak base may not bind to the proton strongly enough to block the protonolysis of the sp^2 C−Pt bond. A strong but bulky base may be the best choice. Nonetheless, a few different bases were examined in the reaction of **3** with K_2PtCl_4 in acetonitrile, and the results are summarized in Table 1.

Table 1. Effect of Bases on the Selectivity of Reaction of 3 with K_2PtCl_4 in Acetonitrile[a]



3 4 5

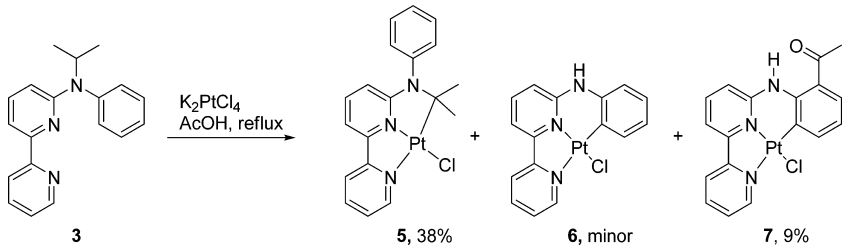
entry	base	amt, equiv	time (days)	yield (%)[b]	selectivity (4:5)
1	none		3	36[c]	70:30
2	sodium acetate	1	10	64	99:1
3	triethylamine	1	5	52	98:2
4	triethylamine	1	10	91	94:6
5	DABCO[e]	1	10	58	98:2
6	TMP[d]	1	2	41	97:3
7	TMP	2	3	34	90:10
8	Na_2CO_3	1	5	trace	
9	NaOH	1	5	trace	
10	**3**	1	1	83	99:1

[a]Reactions were run with equimolar amounts of the ligand **3** and K_2PtCl_4 in acetonitrile at reflux. [b]Isolated yield of the mixture of **4** and **5** by flash column chromatography. [c]Isolated yield of pure **4** by recrystallization.[10] [d]2,2′-6,6′-Tetramethylpiperidine. [e]1,4-Diazabicyclo-[2.2.2]octane.

It can be seen from Table 1 that the effect of the bases is quite remarkable. Excellent to perfect selectivity was achieved with the use of a proper base. When sodium acetate was used, the reaction appeared to be much slower in comparison with the reaction in the absence of a base. A reasonable conversion could be attained after 10 days of reaction at reflux; however, a nearly perfect control of selective sp^2 C−H bond activation (99%) was achieved. The slower reaction rate may be attributed to the acetate ion, which may bind to the platinum and deactivate the platinum complex toward C−H bond activation. When triethylamine was used, again, the reaction was slow but the selectivity was high. It was also found that the selectivity decreased slightly as the conversion increased with prolonged heating (entry 4). 1,4-Diazabicyclo[2.2.2]octane (DABCO) displayed a similar effect (entry 5). For comparison, a sterically hindered secondary amine, 2,2,6,6-tetramethylpiperidine (TMP), was tested. When 1 equiv of TMP was used, after 2

dx.doi.org/10.1021/om400540y | *Organometallics* 2013, 32, 4828−4836

Scheme 2. Reaction of 3 with K_2PtCl_4 in Acetic Acid[10]



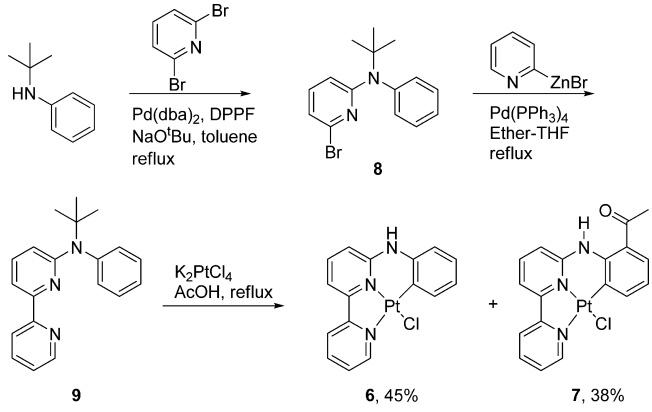
days, the product **4** was isolated in moderate yield (41%) with high selectivity (97%). When 2 equiv of TMP was used, the reaction was much slower. After 3 days of reaction, a mixture of **4** and **5** was isolated in 34% yield with a ratio of 90:10. It appears that the tertiary amines are a better choice, perhaps because of the stronger basicity and greater bulkiness of the tertiary amine. It should be pointed out that when the amount of other bases used in the reaction was increased, the reaction became very sluggish. When sodium carbonate and sodium hydroxide were used, only a trace of cyclometalation product(s) could be detected by the TLC analysis and the reaction did not proceed further to produce more of the product(s) after the first day of the reaction. The formation of black precipitates was observed, likely due to the reduction of platinum(II) to platinum(0). Finally, the use of another 1 equiv of the ligand **3** resulted in nearly exclusive formation of **4** without a low reaction rate (entry 10).

C−N Bond Cleavage. The second issue with the C−H bond activation of *N*-isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine (**3**) by platinum is the low yield of **5**, although there was no presence of **4** in the products of the reaction.[10] A careful analysis of the reaction mixture by TLC showed that there were two other compounds accompanying the major desired product **5**. The two byproducts are more polar and moved much more slowly than **5** on TLC. The proton NMR spectra of the two compounds did not show any signals that could be assigned to the isopropyl group, suggesting that the C−N bond was cleaved. In particular, one of the two byproducts, which is less polar and moved more quickly on TLC, showed a singlet proton signal appearing at significantly low field (DMSO-d_6, 13.70 ppm) and a singlet at 2.76 ppm, which could be assigned to a methyl group according to the integration. We proposed that the two byproducts were the cyclometalated compound **6** with the C−N bond cleavage and its acylated derivatives **7**, as shown in Scheme 2. Complex **6** was formed in a very small amount and could not be recovered from column chromatographic separation.

To gain further information on the C−N bond cleavage, the ligand *N*-*tert*-butyl-*N*-phenyl-2,2′-bipyridin-6-amine (**9**) with a *tert*-butyl group was prepared by consecutive palladium-catalyzed C−N[12] and C−C[7b,13] bond cross-coupling reactions, as shown in Scheme 3. The cross coupling of *N*-*tert*-butylaniline with an excess amount of 2,6-dibromopyridine produced intermediate **8**. Palladium-catalyzed Negishi coupling of **8** with 2-pyridylzinc bromide produced the ligand **9**. The reaction of **9** with K_2PtCl_4 in acetic acid resulted in exclusive C−N bond cleavage, producing **6** and **7** in 45% and 38% isolated yields, respectively (Scheme 3).

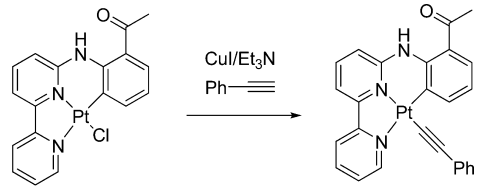
Compounds **6** and **7** have very poor solubility. An attempt to grow suitable crystals of compound **7** for an X-ray structure determination was unsuccessful. Therefore, compound **7** was converted into its phenylacetylide derivative **10** by treating **7**

Scheme 3. Preparation of 9 and Its Reaction with K_2PtCl_4 in Acetic Acid



with phenylacetylene in the presence of CuI and triethylamine[14] (Scheme 4). A crystal suitable for X-ray crystallographic analysis was obtained by diffusing hexanes into a solution of **10** in dichloromethane.

Scheme 4. Reaction of 7 with Phenylacetylene



The crystal data are summarized in Table S1 (Supporting Information), and the molecular structure is depicted in Figure 1. The results confirmed the proposed structure of **10**, which also substantiates the structure of **7** as well as the C−N bond cleavage in the reaction of **3** and **9** with K_2PtCl_4 in acetic acid. The platinum complex adopts a square-planar geometry with a C(16)−Pt(1)−N(1) bite angle of 173.76°, being close to 180°, similar to those for cyclometalated platinum complexes with a 5−6-fused metallacycle reported previously.[7b,13,14b] The Pt−C(sp) bond is shorter than the Pt−C(sp^2) bond, as expected. The Pt−N bond *trans* to the Pt−C(sp^2) bond is slightly longer than the other Pt−N bond that is *trans* to the Pt−C(sp) bond, indicating a stronger structural *trans* effect[15] induced by an sp^2 carbon donor. The phenyl ring of the phenylacetylide is slightly twisted from the coordination plane with a dihedral angle of 24.7°. It is noteworthy that there exists a strong intramolecular hydrogen bond between the carbonyl oxygen and the hydrogen attached to the amino nitrogen. The hydrogen bond length is 1.81 Å, well within the range of a typical hydrogen bond of

dx.doi.org/10.1021/om400540y | *Organometallics* 2013, 32, 4828−4836

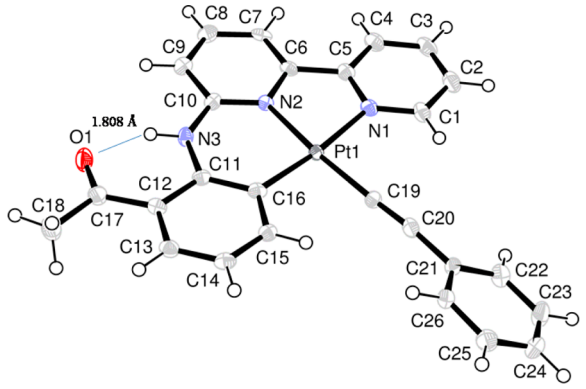


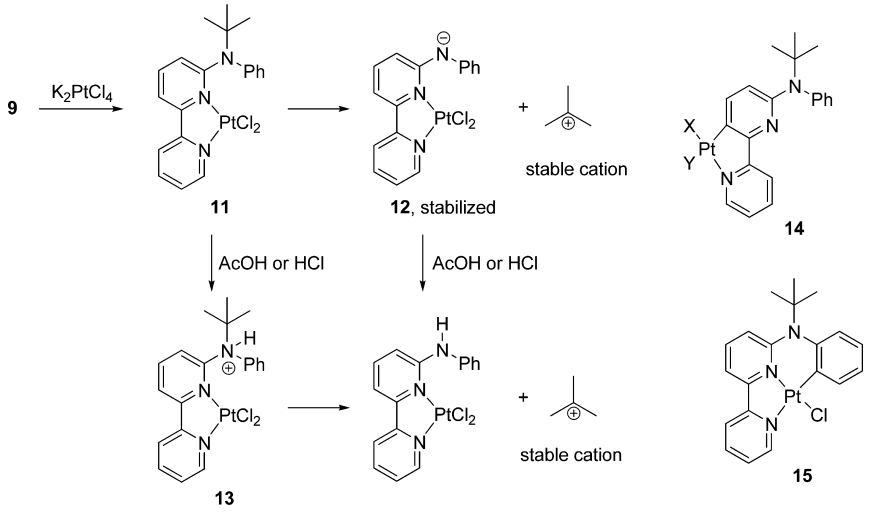
Figure 1. Perspective drawing of the molecular structure of **10**. Selected bond lengths (Å): Pt(1)−C(19) = 1.961(4), Pt(1)−C(16) = 2.006(4), Pt(1)−N(2) = 2.029(3), Pt(1)−N(1) = 2.084(3). Selected bond angles (deg): C(19)−Pt(1)−C(16) = 92.08(16), C(19)−Pt(1)−N(2) = 173.38(15), C(16)−Pt(1)−N(2) = 94.32(14), C(19)−Pt(1)−N(1) = 93.89(15), C(16)−Pt(1)−N(1) = 173.76(14), N(2)−Pt(1)−N(1) = 79.77(13).

1.6−2.0 Å. This intramolecular hydrogen bond may explain the unusual downfield proton signal observed in the NMR spectrum of **7**. This proton in **10** appeared at 13.89 ppm ($CDCl_3$). In contrast, the NH proton in **6** appeared at 10.69 ppm (DMSO-d_6).

The C−N cleavage may be attributed to the heterolytic dissociation of the alkyl C−N bond. In general, C−N bond dissociation is an unfavorable process, because the amide is a strong base and thus a poor leaving group. However, with stabilization of the anion and the cation, C−N bond dissociation is possible. In a classical Hoffman elimination, a quaternary ammonium salt has to be formed to create a reasonably good leaving group. Under strongly acidic conditions, elimination of tertiary alkyl groups from alkylanilines by hydrolysis was reported.[16] Therefore, the C−N cleavage in the reaction of **3** and **9** may benefit from several factors, including stabilization of the amide anion by the bipyridyl ring, the increasing stability of the isopropyl and *tert*-butyl carbocation, and the protonation of the amino nitrogen by the HCl generated from the C−H bond activation. The complete C−N bond cleavage in the reaction of **9** is consistent with the extraordinary stability of the *tert*-butyl cation. The fact that the reactions of **1** and **2** with K_2PtCl_4 in acetic acid were not accompanied by C−N bond cleavage is also supportive of a heterolytic cleavage of the C−N bond in the reactions of **3** and **9** with K_2PtCl_4, because the methyl and ethyl cations that would be formed from the heterolytic C−N dissociation of **1** and **2**, respectively, are too unstable to be formed. Another fact that the C−N cleavage occurred readily in acetic acid but not in acetonitrile provides additional support of the heterolytic C−N bond dissociation process, which is favored in protic solvents. It should be noted that transition-metal-assisted C−N bond cleavage through oxidative addition[17] and *β*-hydrogen abstraction[18] has been proposed. In the former case, the cleavage of the methyl C−N bond,[17d,e] allyllic C−N bonds,[17a] benzylic C−N bonds,[17b] and strained aziridines[17c] appears more common. A *β*-hydrogen is required in the latter case.[18]

The role of acid in the C−N bond cleavage has also been examined. When ligand **3** alone was heated at reflux in acetic acid, no C−N bond cleavage was observed. The cyclometalation produced HCl as the side product, thus, the HCl might facilitate the C−N bond dissociation. However, even with addition of a few drops of concentrated hydrochloric acid to the reaction of **3** in acetic acid, C−N bond cleavage was not observed. These results indicated that the presence of the platinum salt and/or the cyclometalation process may play a role in the C−N bond cleavage. Complexation of platinum to the bipyridyl motif would further stabilize the amide anion, thus promoting the C−N dissociation as shown in Scheme 5. Complexation of **9** with the platinum (**9** to **11**) not only improves the planar geometry of the bipyridine for better electron delocalization of the amide anion **12** but also makes the bipyridine more electron deficient, both of which would lead to the stabilization of **12**. The protonation of the amino nitrogen could also precede the C−N bond cleavage to form **13** and the heterolytic C−N bond cleavage of **13** would be facilitated by the electron delocalization of the developing lone pair at the nitrogen. C−N bond cleavage may also occur following the cycloplatination, producing the intermediates **14** and **15** rather than the coordination giving **11**. The C−N bond cleavage likely results from a cooperative action of stabilization of the amide anion or delocalization of the lone pair at the

Scheme 5. Proposed Pathways for C−N Bond Cleavage in the Reaction of 9 with K_2PtCl_4 in Acetic Acid



dx.doi.org/10.1021/om400540y | *Organometallics* 2013, 32, 4828−4836

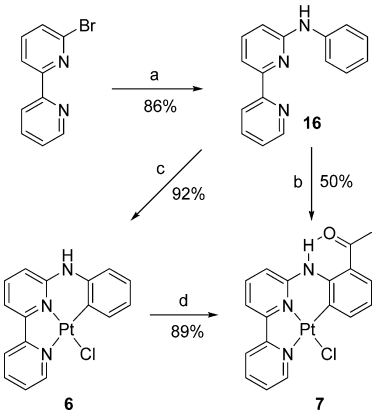
nitrogen, protonation of the amino nitrogen, and stabilization of the carbocation (Scheme 5).

To suppress this unwanted process in the formation of **5**, the use of a base to neutralize the HCl generated from the C−H bond activation may be necessary. Therefore, the use of NaOAc in the reaction of **3** with K_2PtCl_4 in acetic acid was examined. It turned out that the addition of 1 equiv of NaOAc slowed the reaction and suppressed the C−N bond cleavage to some extent, and an isolated yield of 50% for **5** was achieved. When an extra 1 equiv of NaOAc was used, the reaction was even slower, and the C−N bond cleavage still could not be suppressed completely. Apparently the presence of HCl was not a necessary factor in the C−N bond cleavage but might accelerate the process. Furthermore, the use of excess base led to the decomposition of the platinum complexes, as a black precipitate was observed. An attempt to use 2-ethoxyethanol as the solvent and sodium bicarbonate as the base for the reaction resulted in mainly decomposition of the complexes to black precipitates, which is likely the reduced platinum metal. Finally, **4** was completely isomerized to **5** when it was heated in acetic acid at reflux for 3 h, producing **5** in 72% isolated yield, but was accompanied by the decomposition to black platinum metal. The formation of **6** was also detected by TLC, and the ratio of **6** and **5** was determined to be 5:95 from the ^{1}H NMR spectrum of the reaction mixture, which further indicates that C−N bond cleavage could be effected under the reaction conditions without the presence of HCl. The isomerization of **4** to **5** is an intramolecular process. It should be noted that the proton-assisted intermolecular ligand exchange in cyclopalladation and cycloplatination has been reported.[19]

Regioselective Acylation. It was also found that the presence of HCl is responsible for the formation of the acylation product **7** in the reaction of **3** with K_2PtCl_4 in acetic acid, because there was no acylation detected when NaOAc was used in the reaction to neutralize the HCl and the isomerization of **4** to **5** in acetic acid was accompanied by **6** but not **7**. We speculate that a classical Friedel−Crafts acylation might be the mechanism of this reaction, because hydrogen chloride generated in the cyclometalation can catalyze the Friedel−Crafts acylation by promoting the formation of the acyl cation from acetic acid. To gain more information on the acylation reaction, compound **16** was synthesized and subject to a series of reactions as shown in Scheme 6. The reaction of **16** with K_2PtCl_4 in acetic acid produced cyclometalation product **6** in 89% yield. As acetic anhydride is a good reagent for the Friedel−Crafts reaction, the cyclometalation of **16** with K_2PtCl_4 in pure acetic anhydride was attempted. However, no reaction proceeded, as the platinum salt remained undissolved in the solvent even after 24 h of refluxing. Surprisingly, when water was added to the reaction mixture, the reaction proceeded to form **7** cleanly, which suggests that acetic acid is needed for this reaction. Indeed, when a mixture of acetic acid and acetic anhydride was used as the solvent, the acylation product **7** was the only product detected by TLC and there was no **6** present. Furthermore, when **6** was heated in the mixed solvent of acetic acid and acetic anhydride, complete acylation of **6** was observed. The lack of **7** in the reaction of **16** in acetic acid may be attributed to the poor solubility of **6** in acetic acid. Once precipitated, **6** was essentially insoluble in acetic acid.

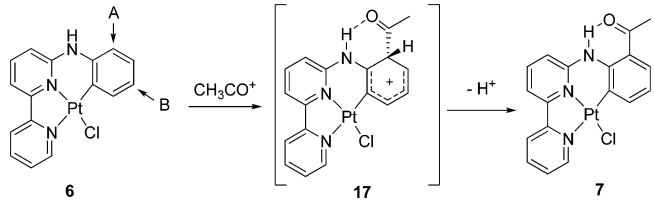
It is also noteworthy that the acylation is regioselective. There are two competitive sites on the phenyl ring of **6** that could be acylated, labeled A and B, as shown in Scheme 7. The electronic effects of the substituents are expected to be similar

Scheme 6. Cycloplatination of 16 and Related Reactions[a]



[a]Reagents and conditions: (a) aniline (2 equiv), $Pd(dba)_2$ (2%), DPPF (2%), NaO^tBu (1.2 equiv), toluene, reflux; (b) K_2PtCl_4 (1 equiv), $AcOH/Ac_2O$ (1/1), reflux.; (c) K_2PtCl_4 (1 equiv), AcOH, reflux; (d) $AcOH/Ac_2O$ (1/1), reflux.

Scheme 7. Proposed Mechanism for the Selective Acylation of 6



for both positions, so why did the acylation occur exclusively at the position A that is *ortho* to the amino nitrogen? A possible explanation could be that the regioselective acylation is directed by the hydrogen bond between the incoming carbonyl oxygen and the proton attached to the nitrogen (Scheme 7). The hydrogen bond not only stabilizes the product **7** and proposed intermediate **17** but may also stabilize the transition state leading to the intermediate in the rate-determining step.

To gain information on the electron distribution of the compound **6**, particularly in the phenyl ring, DFT (density functional theory) calculations were performed on **6** and the optimized geometry is depicted in Figure 2. The optimized structure of **6** displays a nearly perfect square-planar geometry, similar to that of **7** revealed by X-ray crystallography (Figure 1). Notably, all atoms of the molecule are coplanar. The C−Pt bond is 2.015 Å. The Pt−N(1) bond (2.132 Å), which is *trans* to the carbon donor, is significantly longer than the Pt−N(2) bond (2.038 Å) *trans* to the chlorine, indicating a much stronger structural *trans* effect induced by a carbon donor.[15] The valence angle is 174.32°. At the optimized geometry, the atomic charges were calculated at the CCSD level of theory. Net charges on the carbons of the metalated phenyl ring are shown in Figure 2. There is net negative charge on both A and B carbons, indicating that both sites are activated toward the electrophilic aromatic substitution reaction; however, the negative charge on carbon A (−0.056) *ortho* to N3 is much larger than that on carbon B (−0.025) *para* to the N3, which further explains the preferential substitution at the A carbon. It should be mentioned that regioselective aromatic substitution of cyclometalated iridium(III) complexes has been reported,[20,21] but the carbon of the cyclometalated phenyl ring that was substituted is *para* to the iridium.

dx.doi.org/10.1021/om400540y | *Organometallics* 2013, 32, 4828−4836

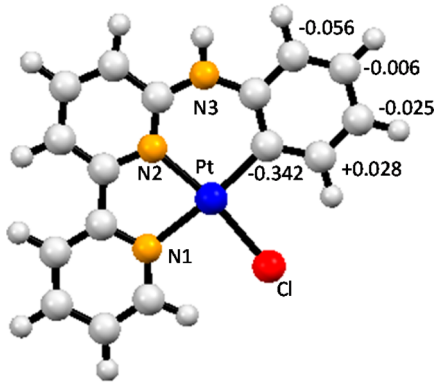


Figure 2. Optimized geometry of **6** in the ground state and net charges on the carbons of the phenyl ring. Selected bond lengths (Å): Pt−Cl = 2.345, Pt(1)−C = 2.015, Pt−N(1) = 2.132, Pt−N(2) = 2.038. Selected bond angles (deg): Cl−Pt−C = 94.04, Cl−Pt−N(2) = 170.76, C−Pt−N(2) = 95.2, Cl−Pt−N(1) = 91.64, C−Pt−N(1) = 174.32, N(2)−Pt(1)−N(1) = 79.12.

An alternative mechanism involving oxidative addition of acetic anhydride to the platinacycle **6** could also be proposed for the selective acylation, as shown in Scheme 8. Reductive elimination of the intermediate **18**, which is a Pt(IV) species, would be expected to proceed readily, leading to the acylated intermediate **19**. A subsequent cycloplatination of **19** would occur to produce **7**. Although not reported in the cycloplatinated complexes, regioselective acylation[22] and acetoxylation[8f] of palladacycles have been observed and an oxidative addition mechanism was proposed for the reactions.[22a] Since the selective acylation of **6** is an isolated special case, further investigations would be necessary to gain a deeper understanding of the reaction mechanism.

CONCLUSION

The use of a proper base was found to improve the selectivity of the sp^2 C−H bond activation of *N*-isopropyl-*N*-phenyl-2,2′-bipyridin-6-amine by platinum(II) in acetonitrile, from 70% up to 99%. However, the selective sp^3 C−H bond activation in acetic acid was complicated by the cleavage of the C(isopropyl)−N bond. The use of a base retarded the C−N bond cleavage but did not block it completely. The fact that the reaction of *N*-*tert*-butyl-*N*-phenyl-2,2′-bipyridin-6-amine with K_2PtCl_4 in acetic acid resulted in completely C−N bond cleavage suggested that the C−N bond cleavage proceeded via heterolytic C−N bond dissociation. Further investigations showed that the acylation of platinacycle **6** occurred regioselectively at the *N*-phenyl ring to form complex **7**, possibly via a Friedel−Crafts reaction facilitated by intramolecular H bonding, although other mechanisms are also possible.

EXPERIMENTAL SECTION

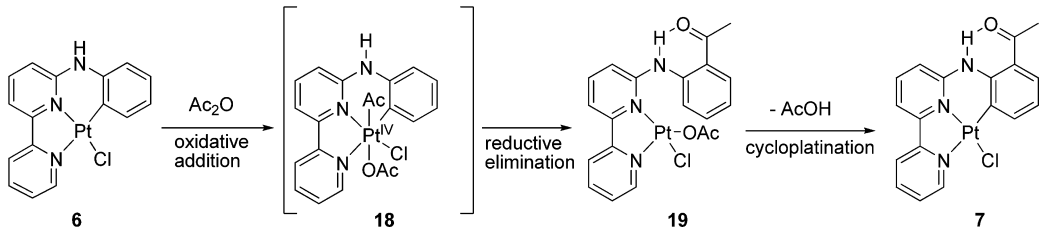
Synthesis. All reactions involving moisture- and/or oxygen-sensitive organometallic complexes were carried out under a nitrogen or argon atmosphere and anhydrous conditions. Tetrahydrofuran (THF) and diethyl ether were distilled from sodium and benzophenone under nitrogen before use. All other anhydrous solvents were purchased from Aldrich Chemical Co. and were used as received. *N*-*tert*-Butylaniline[23] and 6-bromo-2,2′-bipyridine[24] were prepared according to the literature procedures. 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 CD_2Cl_2 using tetramethylsilane as the standard for ^{1}H NMR chemical shifts and the solvent peak ($CDCl_3$, 77.0 ppm; CD_2Cl_2, 53.8 ppm) as the standard for ^{13}C NMR chemical shifts. Coupling constants (*J*) are reported in Hz. Elemental analyses were performed at Atlantic Microlab, Inc., Norcross, GA.

Reaction of 3 with K_2PtCl_4 in the Presence of a Base. General Procedure. In a dry 50 mL three-necked flask were added **3** (36 mg, 0.125 mmol), K_2PtCl_4 (52 mg, 0.125 mmol), and acetonitrile (5 mL). A few crystals of tetrabutylammonium chloride were added to the mixture. The reaction mixture was refluxed for 10 days and then cooled to room temperature. The solvent was removed by rotary evaporation. The crude product was analyzed by ^{1}H NMR spectroscopy, which showed that the ratio of **4** and **5** was 99:1. The crude product was purified by flash column chromatography on silica gel first with dichloromethane then with a mixture of dichloromethane and ethyl acetate (v/v, 50/1) to give **4**: orange solid, 38 mg, 64%. It should be mentioned that, under the column chromatographic conditions, there was no enrichment in either **4** or **5**.

Preparation of 6-Bromo-*N*-*tert*-butyl-*N*-phenylpyridin-2-amine (8). In a dry, nitrogen-flushed, 100 mL three-necked round-bottom flask were charged 2,6-dibromopyridine (2.49 g, 10.5 mmol), *N*-*tert*-butylaniline (1.05 g, 7 mmol), NaOtBu (0.81 g, 8.4 mmol), toluene (14 mL), bis(dibenzylideneacetone)palladium ($Pd(dba)_2$, 0.16 g, 0.28 mmol), and 1,1′-bis(diphenylphosphino)ferrocene (DPPF, 0.16 g, 0.28 mmol). The mixture was stirred and heated at reflux for 26 h. After it was cooled to room temperature, the mixture was diluted with 10 mL of ethyl acetate. The organic layer was washed with 20 mL of water and dried over $MgSO_4$. After filtration, the organic solvents were removed by rotary evaporation and the crude product was purified by column chromatography on silica gel with hexanes and dichloromethane (v/v 1/1) as the mobile phase: colorless crystalline solid, 0.66 g, 31%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 7.35 (t, J = 7.2, 2 H), 7.27 (t, J = 7.3, 1 H), 7.04 (d, J = 7.1, 2 H), 6.86 (t, J = 7.9, 1 H), 6.55 (d, J = 7.4, 1 H), 5.59 (d, J = 8.4, 1 H), 1.43 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.4, 144.0, 138.3, 137.7, 131.2 (2C), 129.7 (2C), 127.5, 114.4, 109.6, 57.9, 31.0 (3C). Anal. Calcd for $C_{15}H_{17}BrN_2$: C, 59.03; H, 5.61; N, 9.18. Found: C, 58.54; H, 5.71; N, 8.77.

Preparation of *N*-*tert*-butyl-*N*-phenyl-2,2′-bipyridin-6-amine (9). Under nitrogen flushing, a 100 mL three-necked round-bottom flask equipped with a condenser was dried with a heat gun. A solution of nBuLi in hexanes (1.6 M, 3 mL, 3.8 mmol) was added to the flask via a syringe, and the flask was cooled to −78 °C with a dry ice/acetone bath. Under nitrogen, in a 25 mL dried flask was prepared a solution of 2-bromopyridine (0.58 g, 4 mmol) in diethyl ether (5 mL).

Scheme 8. Alternative Mechanism for the Selective Acylation of 6



dx.doi.org/10.1021/om400540y | Organometallics 2013, 32, 4828−4836

The solution was cooled with a dry ice/acetone bath. The cold solution was added dropwise into the solution of nBuLi with stirring. After 10 min, the reaction mixture was warmed to 0 °C, and then a solution of $ZnCl_2$ in diethyl ether (1 M, 4 mL) was added and the mixture was warmed to room temperature. To the in situ generated 2-pyridylzinc reagent were added 6-bromo-*N*-*tert*-butyl-*N*-phenylpyridin-2-amine (0.59 g, 2 mmol), $Pd(PPh_3)_4$ (119 mg, 0.1 mmol), and THF (15 mL). The mixture was stirred at reflux for 20 h and then cooled to room temperature. Ethylenediaminetetraacetic acid (EDTA, 2.3 g) was used to facilitate aqueous workup. The crude product was purified on a silica gel packed column with dichloromethane and ethyl acetate (v/v 30/1) as eluting solvents: colorless crystalline solid, 0.51 g, 84%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.58 (d, J = 4.8, 1 H), 8.35 (d, J = 8.0, 1 H), 7.75 (td, J = 7.7, 1.8, 1 H), 7.61 (d, J = 7.4, 1 H), 7.35 (t, J = 7.3, 2 H), 7.27 (t, J = 7.4, 1 H), 7.20 (t, J = 8.5, 1 H), 7.19 (t, J = 7.5, 1 H), 7.11 (d, J = 8.3, 2 H), 5.80 (d, J = 8.5, 1 H), 1.54 (s, 9H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 159.6, 157.4, 152.7, 148.9, 145.2, 136.8, 131.8 (2C), 129.6 (2C), 127.1, 123.0, 120.9, 109.2, 57.3, 29.6 (3C). Anal. Calcd for $C_{20}H_{21}N_3$: C, 79.17; H, 6.98; N, 13.85. Found: C, 78.72; H, 6.98; N, 13.51.

Reaction of 9 with K_2PtCl_4 in Acetic Acid. A mixture of **9** (153 mg, 0.5 mmol) and K_2PtCl_4 (207 mg, 0.5 mmol) in acetic acid (20 mL) was refluxed for 22 h. The solvent was removed by rotary evaporation, and the residue was dissolved in dichloromethane. The solution was run through a silica gel column with dichloromethane and ethyl acetate (v/v 15/1) as eluting solvents. Two major bands were resolved and collected. After removal of the solvents, the first band gave 0.1 g of **7** (38%). ^{1}H NMR (400 MHz, DMSO): δ 13.70 (s, 1 H), 9.71 (d, J = 5.6, 1 H), 8.91 (d, J = 7.9, 1 H), 8.67 (d, J = 8.2, 1 H), 8.33 (t, J = 8.0, 1 H), 8.24 (t, J = 7.5, 1 H), 8.17 (d, J = 7.7, 1 H), 7.93 (d, J = 7.8, 1 H), 7.88 (t, J = 6.4, 1 H), 7.49 (t, J = 8.3, 1 H), 6.93 (t, J = 7.7, 1H), 2.73 (s, 3 H). Anal. Calcd for $C_{18}H_{14}ClN_3OPt$: C, 41.67; H, 2.72; N, 8.10. Found: C, 41.46; H, 2.78; N, 7.94. The second band produced 0.12 g of **6** (45%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 10.69 (s, 1 H), 9.74 (d, J = 5.5, 1 H), 8.64 (d, J = 8.3, 1 H), 8.60 (d, J = 7.7, 1 H), 8.32 (t, J = 7.3, 1 H), 8.14 (t, J = 7.4, 1 H), 8.05 (d, J = 7.4, 1 H), 7.86 (t, J = 6.9, 1 H), 7.49 (d, J = 8.5, 1 H), 7.09 (t, J = 12.4, 1 H), 6.78 (t, J = 7.2, 1 H). ^{13}C NMR (75 MHz, DMSO-d_6): δ 155.4, 152.5, 147.8, 144.7, 139.6, 139.2, 135.6, 134.9, 126.5, 124.5, 123.0, 120.3, 118.2, 115.2, 115.0, 113.6. Anal. Calcd for $C_{16}H_{12}ClN_3Pt$: C, 40.30; H, 2.54; N, 8.81. Found: C, 40.49; H, 2.52; N, 8.79.

Preparation of Platinum Complex 10. In a 25 mL dry, argon-flushed flask was charged complex **7** (40 mg, 0.08 mmol), phenylacetylene (25 mg, 0.24 mmol), CuI (1.2 mg, 0.006 mmol), Et_3N (0.7 mL), and dichloromethane (20 mL). The mixture was stirred under argon at room temperature for 24 h. After removal of the solvents, the crude material was purified by flash chromatography on silica gel with dichloromethane and ethyl acetate (v/v 50/1) to give a bright orange solid: 32 mg, 70%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 13.89 (s, 1H), 10.01 (d, J = 5.6, 1 H), 9.35 (dd, J = 3.8, 1.5, $^3J_{Pt-H}$ = 41.3, 1 H), 8.03 (d, J = 8.03, 1 H), 7.97 (t, J = 7.4, 1 H), 7.87 (t, J = 8.0, 1 H), 7.79 (d, J = 7.8, 1 H), 7.56–7.42 (m, 3 H), 7.47 (t, J = 6.4, 1 H), 7.29–7.21 (m, 3 H), 7.14 (t, J = 7.5, 1 H), 6.90 (t, J = 7.7, 1 H), 2.70 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 204.4, 155.5, 153.1, 153.0, 151.3, 145.0, 137.2, 136.8, 135.1, 131.6 (2 C), 129.6, 129.0, 128.0 (2 C). 125.9, 125.2, 121.5, 120.4, 120.2, 118.5, 118.2, 113.6, 103.8, 100.7, 28.7. Anal. Calcd for $C_{26}H_{19}N_3OPt$: C, 53.42; H, 3.28; N, 7.19. Found: C, 53.13; H, 3.26; N, 7.24.

Isomerization of 4 in Acetic Acid. A mixture of **4** (92 mg, 0.18 mmol) in acetic acid (8 mL) was refluxed for 3 h. ^{1}H NMR analysis of the reaction mixture showed that **4** was completely isomerized to **5** with the presence of a small amount of **6**. The ratio of **5** and **6** was determined to be 95:5. After removal of acetic acid by rotary evaporation, the residue was dissolved in dichloromethane (30 mL) and the solution was washed with water and brine, dried over Na_2SO_4, and filtered. The filtrate was concentrated, and the crude product was purified by flash column chromatography on silica gel with dichloromethane and ethyl acetate (v/v 80/1) to give **5** as an orange solid: 66 mg, 72%.

Preparation of *N*-Phenyl-2,2′-bipyridin-6-amine (16). In a dry, argon-flushed, 50 mL three-necked round-bottom flask were charged 6-bromo-2,2′-bipyridine (0.94 g, 4 mmol), aniline (0.73 mL, 8 mmol), NaO^{t}Bu (0.46 g, 4.8 mmol), toluene (15 mL), $Pd(dba)_2$ (92 mg, 0.16 mmol), and DPPF (89 mg, 0.16 mmol). The mixture was stirred and heated at reflux for 19 h. After it was cooled to room temperature, the mixture was diluted with 10 mL of ethyl acetate and filtered through a disk of Celite. The filtrate was extracted with ethyl acetate, and the organic phase was washed with brine and dried over $MgSO_4$. After filtration, the organic solvents were removed and the crude product was purified by column chromatography on silica gel first with dichloromethane and hexanes (v/v 5/1) then with hexanes and ethyl acetate (v/v 3/1): off-white crystalline solid, 0.83 g, 85%. ^{1}H NMR (400 MHz, $CDCl_3$): δ 8.60 (d, J = 4.8, 1 H), 8.26 (d, J = 8.0, 1 H), 7.77 (d, J = 7.5, 1 H), 7.74 (td, J = 7.7, 1.8, 1 H), 7.57 (t, J = 8.0, 1 H), 7.37 (d, J = 8.5, 2 H), 7.29 (t, J = 7.4, 2 H), 7.22 (t, J = 6.2, 1 H), 6.99 (t, J = 7.3, 1 H), 6.81 (d, J = 8.2, 1 H), 6.59 (s, 1 H). ^{13}C NMR (75 MHz, $CDCl_3$): δ 156.3, 155.4, 154.7, 149.1, 140.6, 138.6, 136.9, 129.2 (2 C), 123.5, 122.6, 121.0, 120.1 (2 C), 112.6, 108.9. Anal. Calcd for $C_{16}H_{13}N_3$: C, 77.71; H, 5.30; N, 16.99. Found: C, 77.47; H, 5.31; N, 16.86.

Reaction of 16 with K_2PtCl_4 in Acetic Anhydride–Acetic Acid. A mixture of **16** (62 mg, 0.25 mmol) and K_2PtCl_4 (104 mg, 0.25 mmol) in acetic anhydride (5 mL) and acetic acid (5 mL) was refluxed for 24 h. After removal of the solvents, the residue was dissolved in dichloromethane and purified by flash column chromatography on silica gel with dichloromethane and ethyl acetate (v/v 5/1) to give **7**: bright orange solid, 60 mg, 50%.

Reaction of 16 with K_2PtCl_4 in Acetic Acid. A mixture of **16** (40 mg, 0.16 mmol) and K_2PtCl_4 (66 mg, 0.16 mmol) in acetic acid (6 mL) was refluxed 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, and dried in air to give a yellow solid of **6**: 67 mg, 89%.

Reaction of 6 with Acetic Anhydride in Acetic Acid. Complex **6** (30 mg, 0.063 mmol) was suspended in a mixture of acetic anhydride (4 mL) and acetic acid (4 mL). The mixture was heated at reflux for 24 h, and then the solvents were removed by rotary evaporation. The residue was dissolved in dichloromethane and purified by flash column chromatography on silica gel with dichloromethane and ethyl acetate (v/v 5/1) to give **7**: bright orange solid, 30 mg, 92%.

X-ray Crystallography. All crystals were grown by diffusing hexanes into dichloromethane solutions of the complexes. A suitable crystal was selected and mounted on a glass fiber. All measurements were made using graphite-monochromated Cu Kα radiation (1.54178 Å) on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. In each case, initial space group determination was based on a matrix consisting of 120 frames. The data were reduced using SAINT+,[25] and empirical absorption correction was applied using SADABS.[26] Structures were solved using direct methods. Least-squares refinement for all structures was carried out on F^2. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in calculated positions and allowed to be refined isotropically as riding models. Structure solution, refinement, and calculation of derived results were performed using the SHELXTL package of computer programs.[27]

DFT and CCSD Calculations. Geometry optimizations were performed for the ground state using density functional theory (DFT) with Gaussian 03[28] and the B3LYP exchange-correlation functional.[29] The DEF2_TZVP basis set[30] was used for platinum, while the cc-pvdz basis set[31] was used for all other atoms. At the optimized geometry with the same basis sets, the atomic charges were calculated at the CCSD (coupled-cluster with single and double excitations) level of theory.[32]

dx.doi.org/10.1021/om400540y | *Organometallics* 2013, 32, 4828–4836

■ ASSOCIATED CONTENT

Supporting Information

A CIF file giving crystallographic data for complex **10**, tables giving crystal data and refinement details for **10** and Cartesian coordinates of the optimized geometry of complex **6**, and figures giving an ^{1}H NMR analysis of ratio of **4** and **5** formed in the reaction of **3** with K_2PtCl_4 in acetonitrile in the presence of a base and NMR spectra of new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Author

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

Present Addresses

[§]Metrics Inc., Greenville, NC 27834.

[∥]Campbell University, Buies Creek, NC 27506.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

This work was supported by the ACS Petroleum Research Fund (PRF# 51147-UR3). RDP acknowledges NSF (CHE-0443345) and the College of William and Mary for the purchase of the X-ray equipment.

■ REFERENCES

(1) (a) Dunina, V. V.; Zalevskaya, O. A.; Potapov, V. M. *Russ. Chem. Rev.* **1988**, *57*, 434−473. (b) Ryabov, A. D. *Chem. Rev.* **1990**, *90*, 403−424. For a recent review, see (c) Albrecht, M. *Chem. Rev.* **2010**, *110*, 576−623. For a recent book on cyclopalladation, see: (d) *Palladacycles: Synthesis, Characterization and Applications*; Dupont, J., Pfeffer, M.,, Eds.; Wiley-VCH: Weinheim, Germany, 2008.

(2) (a) Labinger, J. A.; Bercaw, J. E. *Nature* **2002**, *417*, 507−514. (b) Bergman, R. G. *Nature* **2007**, *446*, 391−393.

(3) (a) Crosby, S. H.; Clarkson, G. J.; Rourke, J. P. *J. Am. Chem. Soc.* **2009**, *131*, 14142−14143. (b) Thomas, H. R.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2011**, *30*, 5641−5648. (c) Crosby, S. H.; Clarkson, G. J.; Rourke, J. P. *Organometallics* **2011**, *30*, 3603−3609. (d) Crosby, S. H.; Deeth, R. J.; Clarkson, G. J.; Rourke, J. P. *Dalton Trans.* **2011**, *40*, 1227−1229.

(4) Campora, J.; Lopez, J. A.; Palma, P.; Valerga, P.; Spillner, E.; Carmona, E. H.; Peters, R. *Angew. Chem., Int. Ed.* **1999**, *38*, 147−151.

(5) (a) Dupont, J.; Consorti, C. S.; Spencer, J. *Chem. Rev.* **2005**, *105*, 2527. (b) Bedford, R. B. In *Palladacycles: Synthesis, Characterization and Applications*, Dupont, J.; Pfeffer, M., Eds, Wiley-VCH, Weinheim, 2008, pp 209−225. (c) Nájera, C.; Alonso, D. A. in Palladacycles: Synthesis, *Characterization and Applications*; Dupont, J., Pfeffer, M., Eds.; Wiley-VCH: Weinheim, Germany; pp 155−207. (d) Kisala, J.; Ruman, T. *Curr. Org. Chem.* **2011**, *15*, 3486−3502. (e) Dunina, V. V.; Gorunova, O. N.; Zykov, P. A.; Kochetkov, K. A. *Russ. Chem. Rev.* **2011**, *80*, 51−74.

(6) (a) Goldman, A. S.; Roy, A. H.; Huang, Z.; Ahuja, R.; Schinski, W.; Brookhart, M. *Science* **2006**, *312*, 257−261. (b) Huang, H.; Peters, R. *Angew. Chem., Int. Ed.* **2009**, *48*, 604−606.

(7) (a) Williams, J. A. G.; Develay, S. D.; Rochester, D. L.; Murhy, L. *Coord. Chem. Rev.* **2008**, *252*, 2596−2611. (b) Vezzu, D. A. K.; Deaton, J. C.; Jones, J. S.; Bartolotti, L.; Harris, C. F.; Marchetti, A. P.; Kondakova, M.; Pike, R. D.; Huo, S. *Inorg. Chem.* **2010**, *49*, 5107−5119. (c) Deaton, J. C.; Young, R. H.; Lenhard, J. R.; Rajeswaran, M.; Huo, S. *Inorg. Chem.* **2010**, *49*, 9151−9161. (d) Kalinowski, J.; Fattori, V.; Cocci, M.; Williams, J. A. G. *Coord. Chem. Rev.* **2011**, *255*, 2401−2425. (e) Wang, Y.; Liu, Y.; Luo, J.; Qi, H.; Li, X.; Nin, M.; Liu, M.; Shi, D.; Zhu, W.; Cao, Y. *Dalton Trans.* **2011**, *40*, 5046−5051.

(8) (a) Tamaru, Y.; Kagotani, M.; Yoshida, Z.-i. *Angew. Chem., Int. Ed.* **1981**, *20*, 980−981. (b) Albert, J.; Ceder, R. M.; Gomez, M.; Granell, J.; Sales, J. *Organometallics* **1992**, *11*, 1536−1541. (c) Alsters, P. L.; Engel, P. F.; Hogerheide, M. P.; Copijn, M.; Spek, A. L.; van Koten, G. *Organometallics* **1993**, *12*, 1831−1844. (d) Cardenas, D. J.; Echavarren, A. M.; Vegas, A. *Organometallics* **1994**, *13*, 882−889. (e) Dunina, V. V.; Golovan', E. B. *Inorg. Chem. Commun.* **1998**, *1*, 12−14. (f) Zucca, A.; Cinellu, M. A.; Pinna, M. V.; Stoccoro, S.; Minghetti, G.; Manassero, M.; Sansoni, M. *Organometallics* **2000**, *19*, 4295−4303. (g) Dunina, V. V.; Gorunova, O. N.; Averina, E. B.; Grishin, Y. K.; Kuz'mina, L. G.; Howard, J. A. K. *J. Organomet. Chem.* **2000**, *603*, 138−151. (h) Stoccoro, S.; Soro, B.; Minghetti, G.; Zucca, A.; Cinellu, M. A. *J. Organomet. Chem.* **2003**, *679*, 1−9. (i) Vazquez-Garcia, D.; Fernandez, A.; Lopez-Torres, M.; Rodriguez, A.; Gomez-Blanco, N.; Viader, C.; Vila, J. M.; Fernandez, J. J. *Organometallics* **2010**, *29*, 3303−3307.

(9) (a) Minghetti, G.; Cinellu, M. A.; Chelucci, G.; Gladiali, S. *J. Organomet. Chem.* **1986**, *307*, 107−114. (b) Sana, G.; Minghetti, G.; Zucca, A.; Pilo, L. I.; Seeber, R.; Laschi, F. *Inorg. Chim. Acta* **2000**, *305*, 189−205. (c) Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.; Manassero, M. *J. Chem. Soc., Dalton Trans.* **1995**, 777−781. (d) Wong-Foy, A. G.; Henling, L. M.; Day, M.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Catal. A: Chem.* **2002**, *189*, 3−16.

(10) Garner, A. W.; Harris, C. F.; Vezzu, D. A. K.; Pike, R. D.; Huo, S. *Chem. Commun.* **2011**, *47*, 1902−1904.

(11) Carey, F. A.; Sundberg, R. J. *Advanced Organic Chemistry: Part A: Structure and Mechanism*, 5th ed.; Springer: New York, 2007; p 258.

(12) Yang, J.-S.; Lin, Y.-H.; Yang, C.-S. *Org. Lett.* **2002**, *4*, 777−780.

(13) (a) Vezzu, D. A. K.; Ravindranathan, D.; Garner, A. W.; Bartolotti, L.; Smith, M. E.; Boyle, P. D.; Huo, S. *Inorg. Chem.* **2011**, *50*, 8261−8273. (b) Huo, S.; Harris, C. F.; Vezzu, D. A. K.; Gagnier, J.; Smith, M. E.; Pike, R.; Li, Y. *Polyhedron* **2013**, *52*, 1030−1040.

(14) (a) Lu, W.; Mi, B.-X.; Chan, M. C. W.; Hui, Z.; Che, C.-M.; Zhu, N.; Lee, S. T. *J. Am. Chem. Soc.* **2004**, *126*, 4958−4971. (b) Ravindranathan, D.; Vezzu, D. A. K.; Bartolotti, L.; Boyle, P. D.; Huo, S. *Inorg. Chem.* **2010**, *49*, 8922−8928.

(15) (a) Dunina, V. V.; Gorunova, O. N. *Russ. Chem. Rev.* **2005**, *74*, 871−913. (b) Sajith, P. K.; Suresh, C. H. *Dalton Trans.* **2010**, *39*, 815−822.

(16) Hickinbottom, W. J. *J. Chem. Soc.* **1933**, 1070−1073.

(17) (a) Guibe, F. *Tetrahedron* **1998**, *54*, 2967−3320. (b) Gandelman, M.; Milstein, D. *Chem. Commun.* **2000**, 1603−1604. (c) Lin, B. L.; Clough, C. R.; Hillhouse, G. L. *J. Am. Chem. Soc.* **2002**, *124*, 2890−2891. (d) Ozerov, O. V.; Guo, C.; Papkov, V. A.; Foxman, B. M. *J. Am. Chem. Soc.* **2004**, *126*, 4792−4793. (e) Weng, W.; Guo, C.; Moura, C.; Yang, L.; Foxman, B. W.; Ozerov, O. V. *Organometallics* **2005**, *24*, 3487−3499 and references cited therein.

(18) Collman, J. P.; Wang, H. J. H.; Decreau, R. A.; Eberspacher, T. A.; Sunderland, C. J. *Chem. Commun.* **2005**, 2497−2499.

(19) (a) Ryabov, A. D. *Inorg. Chem.* **1987**, *26*, 1252−1260. (b) Ryabov, A. D.; van Eldik, R. *Angew. Chem., Int. Ed.* **1994**, *33*, 783−784.

(20) Aoki, S.; Matsuo, Y.; Ogura, S.; Ohwada, H.; Hisamatsu, Y.; Moromizato, S.; Shiro, M.; Kitamura, M. *Inorg. Chem.* **2011**, *50*, 806−818.

(21) Arm, K. J.; Williams, J. A. G. *Chem. Commun.* **2005**, 230−232.

(22) (a) Holton, R. A.; Natalie, K. J., Jr. *Tetrahedron Lett.* **1981**, *22*, 267−270. (b) Clark, P. W.; Dyke, H. J.; Dyke, S. F.; Perry, G. *J. Organomet. Chem.* **1983**, *253*, 399−413.

(23) Lundgren, R. J.; Sappong-Kumankumah, A.; Stradiotto, M. *Chem. Eur. J* **2010**, *16*, 1983−1991.

(24) Fang, Y.-Q.; Hanan, G. S. *Synlett* **2003**, 852−854.

(25) *SAINT PLUS*; Bruker Analytical X-ray Systems, Madison, WI, 2001.

(26) *SADABS*: Bruker Analytical X-ray Systems, Madison, WI, 2001.

(27) Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112−122.

(28) *Gaussian 03, Revision C.02*; Gaussian, Inc., Wallingford, CT, 2004.

(29) (a) Becke, A. D. *J. Chem. Phys.* **1993**, *98*, 5648−5652. (b) Lee, C.; Yang, W.; Parr, R. G. *Phys. Rev. B* **1988**, *37*, 785−789.

(30) Weigend, F.; Ahlrichs, R. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3297−3305.
(31) Dunning, T. H. *J. Chem. Phys.* **1989**, *90*, 1007−1023.
(32) (a) Scuseria, G. E.; Janssen, C. L.; Schaefer, H. F., III *J. Chem. Phys.* **1988**, *89*, 7382−7387. (b) Scuseria, G. E.; Schaefer, H. F., III *J. Chem. Phys.* **1989**, *90*, 3700−3703.