ORGANOMETALLICS

Article

pubs.acs.org/Organometallics

Mechanistic Studies on Platinum(II) Catalyzed Hydroarylation of Alkynes

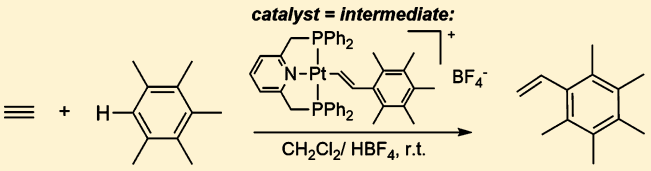
Christine Hahn,*[,†] Mayra Miranda,[‡] Nagendra P. B. Chittineni,[†] Trent A. Pinion,[†] and Ricardo Perez[†]

[†]Department of Chemistry, Texas A&M University—Kingsville, 700 University Blvd., Kingsville, Texas 78363, United States

[‡]Department of Physical Sciences, University of Texas of the Permian Basin, 4901 East University Boulevard, Odessa, Texas 79762, United States

Supporting Information

ABSTRACT: The dicationic acetylene platinum(II) complex $[Pt(PNP)(C_2H_2)](BF_4)_2$ (PNP = 2,6-bis-(diphenylphosphinomethyl)pyridine) was generated in situ by ligand substitution from the ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$ and was reacted with a series of arenes at low temperature. Only electron-rich arenes added across the coordinated C−C triple bond and gave the corresponding arylalkenyl complexes (*E*)-$[Pt(PNP)(CH{=}CHAr)]BF_4$ (Ar = C_6Me_5, $C_6H_2Me_3$-2,4,6, $C_6H_3Me_2$-2,6, $C_6H_3Me_2$-2,4). A slow *E*−*Z* isomerization of the arylalkenyl complexes was observed. Single-crystal X-ray structure analyses were obtained for both *E* and *Z* isomers of the pentamethylbenzene derivative. The *E* isomers of $[Pt(PNP)(CH{=}CHAr)]BF_4$ (Ar = C_6Me_5, $C_6H_2Me_3$-2,4,6) reacted with excess $HBF_4{\cdot}Et_2O$ to give the corresponding arylalkene complexes $[Pt(PNP)(CH_2{=}CHAr)](BF_4)_2$, whereas the *Z* isomers did not undergo immediate protonolysis. Using (*E*)-$[Pt(PNP)(CD{=}CDC_6Me_5)]BF_4$ it was shown that the stereochemistry of the C−C double bond in the protonolysis product depends on the nature of the acid anion HX (X^- = Cl^-, BF_4^-). The catalytic hydroarylation was studied in solution by NMR spectroscopy. The reaction studies provide a more refined view of the individual steps proposed for the Friedel−Crafts type mechanism of the Pt^{II}-catalyzed intermolecular hydroarylation of alkynes.



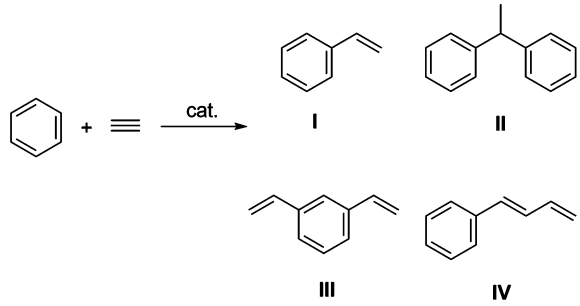
INTRODUCTION

The hydroarylation of alkynes is a C−C bond formation reaction that generates aryl alkenes from simple substrates, which is of considerable interest in organic synthesis. Particularly during the past decade, increasing efforts have been made to develop catalytic systems for the direct C−H addition of aromatic compounds to alkynes without using prefunctionalized substrates.[1] In contrast to the intramolecular hydroarylation, which is relatively easy to realize,[2] the intermolecular version still needs to be developed to make it more efficient and applicable to a broader substrate scope. The particular challenge of the intermolecular reaction is the control of the chemo-, regio-, and stereoselectivity. In addition to the aryl alkene **I**, other products can be formed: diaryl alkanes **II**, dialkenyl arenes **III**, and aryl dienes **IV** (cf. Scheme 1). In addition, alkyne oligo- or polymerization may occur as an undesired side reaction.

Regioselectivity needs to be considered not only for terminal or unsymmetrical internal alkynes but also for arenes with one or more substituent. The preferred formation of either the *Z* or *E* aryl alkene depends mostly on the type of catalyst and its specific reaction mechanism but may also be influenced by the nature of the substrate.

Compounds of different metals such as iron,[3] cobalt,[4] nickel,[5] ruthenium,[6] rhodium,[7] gold,[8] and indium[9] were found to catalyze the intermolecular hydroarylation of alkynes. Fujiwara reported a comprehensive study on hydroarylation reactions of terminal and internal alkynes under mild conditions using $Pd(OAc)_2$ and $PtCl_2$/2AgOAc as catalysts in TFA/CH_2Cl_2.[10] The best results were achieved with activated alkynes such as ethyl propiolate and electron-rich arenes. The platinum(II) catalyst was found to be less active but more selective than $Pd(OAc)_2$. Modifications of the platinum(II) catalyst, i.e. using $PtCl_2$/2AgOTf[11] and K_2PtCl_4/AgOTf,[12] led to an enhanced catalytic activity. The K_2PtCl_4/AgOTf system proved to be an efficient catalyst for a broader range of aromatic and

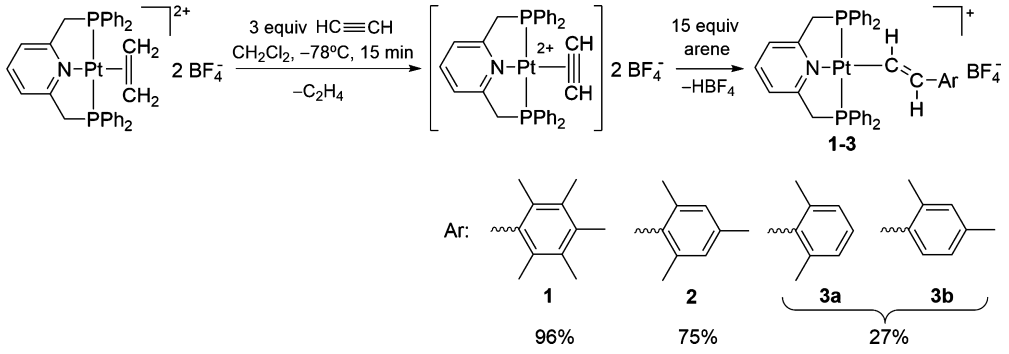
Scheme 1. Possible Products for the Intermolecular Hydroarylation of Alkynes



Received: March 23, 2014
Published: June 11, 2014

   dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040−3050

Scheme 2



heteroaromatic compounds, including benzene, pyrroles,[13] thiophenes,[14] and polystyrene.[15]

The original palladium(II) catalyst, $Pd(OAc)_2$, has been modified as well. With the introduction of a bidentate phosphine ligand the selectivity was improved, and aryl dienes of type **IV** (Scheme 1) were formed with preference.[16] Palladium(II) complexes with mono- and polydentate N-heterocyclic carbene ligands have been studied by the groups of Nolan[17] and Biffis[18] and other groups.[19] Dinuclear palladium(II) complexes with a phosphine ligand developed by Tsukada and co-workers show good catalytic activity in the presence of alkylboranes for both electron-rich and electron-poor arenes reacting with internal alkynes.[20]

The development of Pd^{II} and Pt^{II} hydroarylation catalysts seems to be a very promising field of current research; however, the reaction mechanism is not completely understood. It has been suggested that Pd^{II}- and Pt^{II}-catalyzed hydroarylation proceeds by the same machanism.[11b,21] Tunge and Foresee undertook more detailed mechanistic studies with $Pd(OAc)_2$/TFA and [(4,4′-di-*tert*-butyl-2,2′-bipyridyl)$PtMe_2$]/TFA and found for both catalysts a similar inverse kinetic isotope effect.[22]

A Friedel–Crafts type mechanism is suggested which starts with the electrophilic activation of the alkyne by coordination at the metal center, followed by nucleophilic addition of the arene across the C–C triple bond (i.e., electrophilic aromatic substitution). Although strong evidence for the formation of an arylalkenyl palladium(II) σ complex was reported,[10b] those species have so far not been isolated or directly characterized as reaction intermediates.[23]

For a rational design of more efficient palladium(II) or platinum(II) catalysts, more structural details of reaction intermediates are needed. The original Fujiwara system is too difficult to study due to the lack of stabilizing coligands. Nonetheless, one important aspect has been recognized in this system's development, that "a more strong cationic Pt catalyst is required to improve the activity...".[11b] In fact, it has also been observed for other transition-metal-catalyzed functionalization reactions of unsaturated hydrocarbons that the efficiency can be enhanced by increasing the positive complex charge.[24] However, it is unknown what degree of cationic character the Pt^{II} complex should exactly have in order to provide a higher catalytic efficiency for the alkyne hydroarylation. The closely related hydroarylation of alkenes, studied by Vitagliano and co-workers using the highly electrophilic $M(PNP)^{2+}$ complexes (M = Pd, Pt; PNP = 2,6-bis(diphenylphosphinomethyl)-pyridine), provides an example which illustrates the inherent problem.[25] The high positive complex charge strongly activates the coordinated alkene and thus facilitates the nucleophilic addition of arenes across the C–C double bond but at the same time stabilizes the M–C σ bond of the arylalkyl intermediate and impedes its protonolysis: i.e., the product-releasing step. On the other hand, dicationic Pd^{II} and Pt^{II} PNP complexes are very useful to prepare stable model compounds for those reaction intermediates, which are otherwise inaccessible.[26] Individual reaction steps of the catalytic cycle can be performed stoichiometrically and studied in more subtle detail.

More recently we have explored the electrophilic activation of alkynes at the $Pt(PNP)^{2+}$ complex fragment and the stoichiometric addition of water across the C–C triple bond.[27] It was interesting to extend these studies to arene addition and to characterize the corresponding reaction products. Here, we report the first structural evidence for arylalkenyl platinum(II) complexes resulting from the addition of arenes across the coordinated C–C triple bond. These results further support the Friedel–Crafts type mechanism proposed for the Pd^{II}- and Pt^{II}-catalyzed alkyne hydroarylation, and a more refined reaction mechanism will be discussed.

RESULTS AND DISCUSSION

Reaction of $[Pt(PNP)(C_2H_4)](BF_4)_2$ with Acetylene and Arenes. The previously developed method for water addition to Pt(PNP) alkyne complexes[27] was directly applied to the study of arene addition to acetylene. In this procedure a solution of the ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$[26c] in dichloromethane was cooled to −78 °C. To the solution first the arene (15 equiv) and then acetylene (3 equiv) were added. After 15 min of reaction at −78 °C and warming to room temperature the product was isolated by precipitation with diethyl ether. At this low temperature the arene does not react with the ethylene complex, as it might do at room temperature.[25] However, acetylene first substitutes the ethylene (Scheme 2). Since the formed dicationic acetylene complex is highly reactive,[27] it is critical that the arene is present in solution prior to the acetylene. In this way the arene can undergo nucleophilic addition at the coordinated C–C triple bond immediately after the acetylene complex has formed in situ (Scheme 2). In the absence of any nucleophile the acetylene complex would undergo undesired side reactions.

A series of arenes were screened; however, only those which were sufficiently electron-rich (pentamethylbenzene, mesitylene, and *m*-xylene) gave arylalkenyl σ complexes with an *E* configuration as the corresponding addition products **1**–**3** (Scheme 2). With a decreasing number of electron-donating substituents at the arene the yield decreases and more side products were formed (**1**, 96%; **2**, 75%; **3a**,**b**, 27%). No addition products were obtained under the same reaction

dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040–3050

conditions with *o*- and *p*-xylene and other arenes such as benzene, toluene, and anisole. A similar trend in reactivity was observed by Fujiwara for the Pd^{II}- and Pt^{II}-catalyzed intermolecular hydroarylation reaction,[10b] and it is also in agreement with general features of electrophilic aromatic substitution.[28] The fact that pentamethylbenzene as the bulkiest arene displayed the highest reactivity shows that the addition reaction is only controlled by electronic properties and not by steric factors. This is in agreement with the trans addition. For the aproach of the arene to the coordinated acetylene, there is enough space between the phenyl groups of the PNP ligand (cf. the X-ray structure analysis of complex **1** below).

In the case of 1,3,5-trimethoxybenzene the protocol described above could not be applied to generate a corresponding arylalkenyl complex. This arene is a stronger nucleophile than pentamethylbenzene; therefore, addition to the coordinated ethylene proceeded faster than the alkene/alkyne ligand substitution, and the arylethyl σ complex $[Pt(PNP)CH_2CH_2C_6H_2(OCH_3)_3]BF_4$ was obtained.

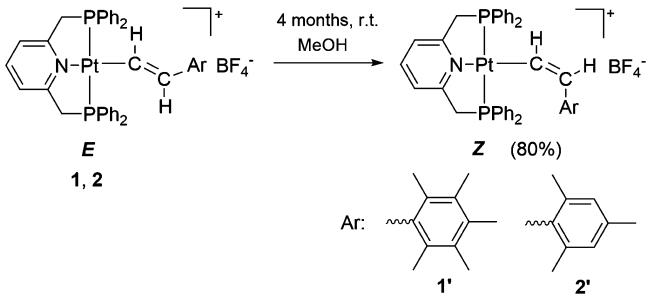
The addition products **1**−**3** were characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy, including 2D NMR methods (cf. the Experimental Section and S1−S3 in the Supporting Information). In the ^1H NMR spectra of the arylalkenyl complexes **1** and **2**, two signals characteristic for the vinylic protons appear in the region δ 6.2−7.1. The $^1H-^1H$ coupling constant J of 17 Hz suggests an *E* configuration of the vinylic protons. An unambiguous assignment of the signals for H_α and H_β could be made by a $^1H,^{13}C$ COSY experiment (S1, Supporting Information) and by comparison with respective NMR spectra reported for structurally related complexes.[23e,29]

From the reaction with *m*-xylene a more complex product mixture was isolated. The 1D and 2D ^1H NMR spectra (S2 and S3, Supporting Information) show three sets of signals for the three major products as well as a number of small signals for impurities or minor, unidentified side products. Two of the major products are the regioisomers **3a**,**b** resulting from addition of the *m*-xylene at different sites relative to the two methyl groups (cf. Scheme 2), while the third product is the platina-acetaldehyde complex $[Pt(PNP)CH_2CHO]BF_4$ (**4**)[27] due to water addition to the coordinated acetylene. The three complexes **3a**,**b** and **4** were formed in about a 3/2/5 ratio. This shows that traces of water were in the system which were competing with the arene addition; however, this was observed only in the case of the less reactive *m*-xylene. Alkyne hydration caused by traces of water has also been reported elsewhere for catalytic systems as a highly competitive side reaction to the intermolecular alkyne hydroarylation.[18a,19b]

The reaction of pentamethylbenzene with terminal alkynes such as propyne or 1-hexyne in the presence of $[Pt(PNP)(C_2H_4)](BF_4)_2$ was unsuccessful. A similar trend was observed for the arylation of alkenes using $M(PNP)^{2+}$ complexes, where propene reacted more sluggishly than ethylene with electron-rich arenes.[25]

***E*−*Z* Isomerization of (*E*)-[Pt(PNP)(CH═CHAr)]BF_4 (1 and 2).** A solution of the pentamethylbenzene addition product **1** in CD_2Cl_2 was reinvestigated by NMR spectroscopy after a storage period of 3 weeks at room temperature (S4 and S5, Supporting Information). In addition to the signals for complex **1**, the ^1H NMR spectrum showed a new set of signals which consists of two doublets at δ 7.19 and 8.27 characteristic for the vinylic protons and the respective signals for the pentamethylphenyl and PNP moieties (see the Experimental Section). The $^1H-^1H$ coupling constant J of those new doublets was found to be 11.8 Hz, suggesting the formation of the corresponding *Z* isomer **1′** (cf. Scheme 3). With complex **2** a similar *E*−*Z* rearrangement was observed (S6, Supporting Information). In order to monitor the progress of the *E*−*Z* isomerization by NMR spectroscopy over an extended period of time, solutions of complexes **1** and **2** in CD_3OD were stored at room temperature and ^1H NMR spectra were recorded (cf. Scheme 3, Figure 1, and S8 (Supporting Information)). After 4 months an *E*/*Z* ratio of about 20/80 was observed for both complexes.

Scheme 3. *E*−*Z* Isomerization of [Pt(PNP)(CH═CHAr)]BF_4 (1, 2)



A very similar *E*−*Z* isomerization of arylalkenyl Pt^{II} complexes of the type [PtCl(CH═CHAr)(tmeda)] (Ar = Ph, *p*-C_6H_4OMe) has been observed by Maresca and Natile.[23e] Amatore et al. reported a *Z*−*E* isomerization of *trans*-$[PdI(PPh_3)_2(EtO_2CC{=}CHPh)]$ which equilibrated at a 64/36 *E*/*Z* ratio.[31a] The isomerization was suggested to proceed via a zwitterionic carbene species with a carbocation located at the benzylic carbon atom.[31] The similar carbocationic carbene intermediate **I** is proposed for the *E*−*Z* isomerization of the arylalkenyl Pt(PNP) complexes **1** and **2** (Scheme 4). Presumably it is present in solution only in small concentration and therefore could not be detected under ordinary conditions. The rotation of the C−C bond in intermediate **I** is strongly sterically hindered due the bulkiness of the PPh_2 and arene groups (see X-ray structure analysis below, Figure 2). This would explain the very slow rate of the *E*−*Z* rearrangement. Although the isomerization process has a high activation barrier, the *Z* isomer is the thermodamically more stable form of the arylalkenyl Pt(PNP) complexes.

X-ray Crystal Structure Analysis of (*E*)- and (*Z*)-[Pt(PNP)(CH═CHC$_6$Me$_5$)]BF_4 (1 and 1′). The X-ray structure analysis of the two isomeric forms of the arylalkenyl complex (*E*-**1** and *Z*-**1′**) were sought to provide important structural details and to help explain their specific reactivities. Suitable crystals of complex **1** were grown from a solution in dichloromethane overlayered with diethyl ether. In order to obtain single crystals of the *Z* isomer **1′**, a solution of the *E* isomer **1** in methanol was stored for 4 months at room temperature. After this period of time the solution containing about 80% *Z* isomer was concentrated by evaporation of the solvent. The molecular structures of the complex cations of *E* and *Z* isomers **1** and **1′** are shown in Figure 2, and selected structural parameters are given in Table 1.

The overall structure of *E*-**1** is closely related to that of the previously studied styryl complex (*E*)-[Pt(PNP)(CH═CHPh)]BF_4[23f] and displays similar bonding parameters. The crystal structure of *Z*-**1′** contains a disordered methanol

dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040−3050

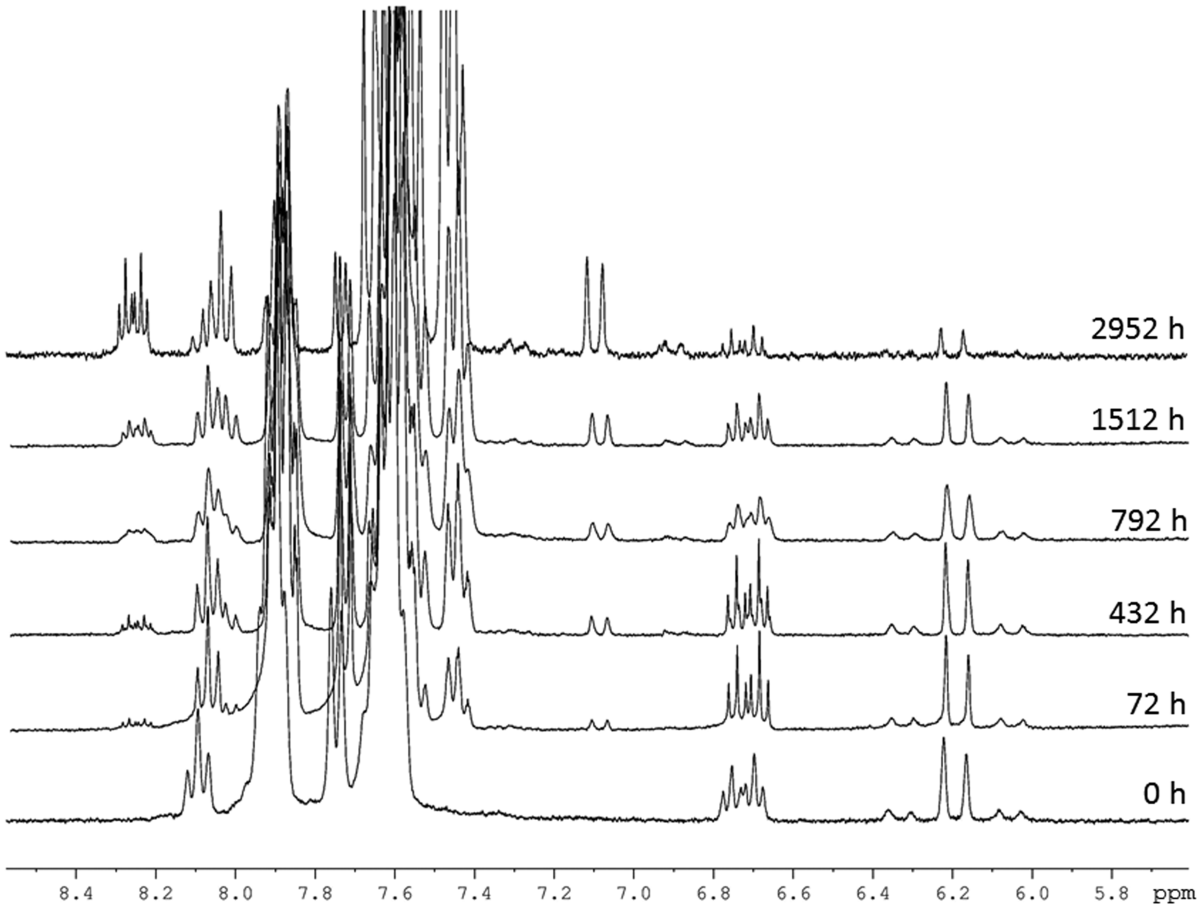
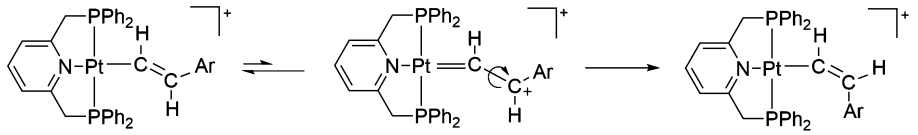


Figure 1. Time-dependent ^{1}H NMR spectra of *E*−*Z* isomerization of [Pt(PNP)(CH═CHC$_6$Me$_5$)]BF$_4$ (**1** → **1′**) in CD$_3$OD.

Scheme 4. Carbocationic Carbene Intermediate I Suggested for *E*−*Z* Isomerization of [Pt(PNP)(CH═CHAr)]$^+$ (1, 2)



molecule with a partial occupancy of 0.375 per formula unit of **1′**. The Pt−C σ-bond lengths in the *E* and *Z* isomers are very similar (2.017(2) Å, **1**; 2.019(4) Å, **1′**), and the C1−C2 double-bond lengths are identical (1.339(3) Å, **1**; 1.337(6) Å, **1′**). The angle between the C1−C2 double bond and the normal plane[30] in the *E* isomer **1** is found to be 23°, while in the Z isomer **1′** this angle is 32°. The pentamethylphenyl group in **1** is tilted by 25° from the plane of the C−C double bond. This angle is larger in **1′** (34°). These two bond angles of the arylalkenyl ligand in the *Z* isomer **1′** bring the pentamethylphenyl group in close proximity to one of the phenyl groups of the PNP ligand. Probably the steric hindrance of the aryl groups in **1′** is responsible for the relatively large bond angles of ∼133° for the sp^2-hybridized carbon atoms C1 and C2. These angles are ∼7° larger in comparison to those in **1** (cf. Table 1). This may cause considerable constraints in the *Z* arylalkenyl moiety. Also notable in ***Z*-1′** is the smaller P1−Pt−P2 angle of 163° and the larger C1−Pt−P1 angle of 100°, in comparison to those in ***E*-1** (166° and 95°, respectively). These angles help to offset the steric congestion in ***Z*-1′**. However, the short distance of 3.289(5) Å, observed in ***Z*-1′** between the carbon atom C25 of the PNP phenyl group and the centroid of the pentamethylphenyl ring (Figure 2D), can be considered a C−H$\cdots\pi$ interaction.[32] In addition, the C13−Pt distance of 3.496(6) Å could be an indication for an interaction between the ortho methyl group and the platinum center (cf. Figure 2F), which may contribute to stabilize the *Z* configuration. These nonbonding interactions combined are probably strong enough that they energetically outweigh all of the steric constraints and may explain the higher thermodynamic stability of the *Z* isomer over the *E* isomer.

Study of the Protonolysis Equilibrium. The protonolysis of the Pt−C σ bond in the arylalkenyl complex is the product-forming step in the catalytic cycle of alkyne hydroarylation. Therefore, it was interesting to study this reaction in more detail. The *E*−*Z* isomeric mixtures of complexes **1**/**1′** and **2**/**2′** (3 week old solutions of **1** and **2** in CD$_2$Cl$_2$, *E*/*Z* ≈ 80/20) were treated with excess HBF$_4$·Et$_2$O. A ^{1}H NMR spectrum was recorded after mixing. The signals of the *E* isomers **1** and **2** disappeared and new signals indicating the formation of the arylalkene π complexes **5** and **6** were observed, respectively (cf. Scheme 5, the Experimental Section, and S9−S12 in the

dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040−3050

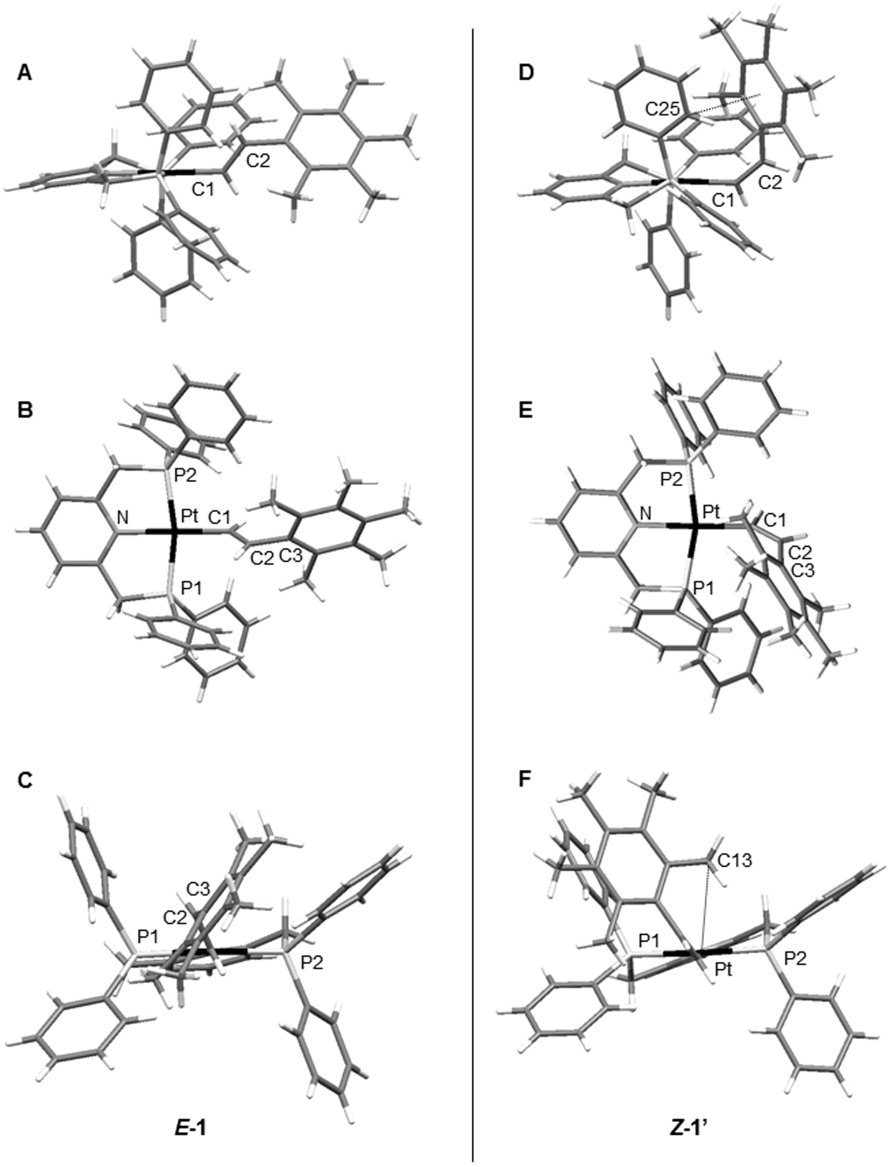


Figure 2. Molecular structures of (*E*)- and (*Z*)-[Pt(PNP)(CH═CHC$_6$Me$_5$)]$^+$ (**1** and **1′**). Complex cations of ***E*-1** and ***Z*-1′** are shown from different views: side (A and D), top (B and E), and front (C and F).

Table 1. Selected Bond Lengths (Å) and Angles (deg) for Complexes 1 and 1′:

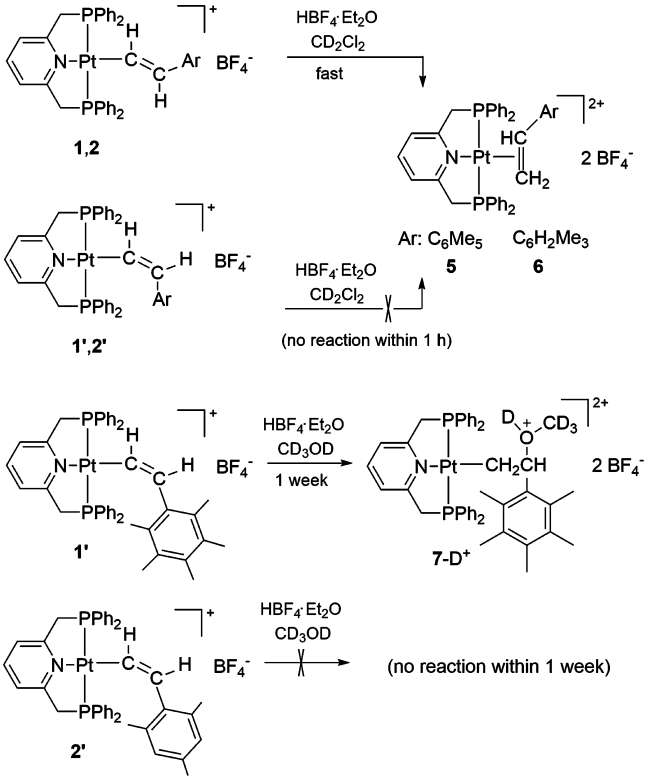
	1	1′
C1−C2	1.339(3)	1.337(6)
Pt−C1	2.017(2)	2.019(4)
Pt−P1	2.2557(6)	2.2844(10)
Pt−P2	2.2974(6)	2.2967(10)
Pt−N	2.1154(19)	2.124(3)
C2−C1−Pt	126.85(19)	134.2(3)
C1−C2−C3	124.2(2)	131.6(4)
C1−Pt−P1	95.93(7)	100.01(11)
C1−Pt−P2	97.67(7)	96.96(11)
P1−Pt−P2	166.18(2)	163.02(3)
C1−Pt−N	178.74(9)	174.80(14)
N−Pt−P1	83.68(6)	81.48(8)
N−Pt−P2	82.76(5)	81.67(8)

Supporting Information). The signals of the *Z* isomers, however, remained unchanged over at least 1 h. In order to monitor the protonolysis of the *Z* isomers by ^{1}H and ^{31}P NMR spectroscopy over an extended period of time, excess HBF$_4$·Et$_2$O was added to the 4 month old solutions of isomeric mixtures **1**/**1′** and **2**/**2′** in CD$_3$OD (with a *Z*/*E* ratio of ∼80/20). In contrast to the *E* isomers **1** and **2**, the protonolysis of the *Z* isomers **1′** and **2′** was found to occur at considerably different reaction rates. While the protonolysis of **1′** was complete within about 1 week, complex **2′** did not show any reaction over the same period of time (cf. Scheme 5). For the protonolysis of **1**/**1′** in CD$_3$OD a signal in the ^{31}P NMR spectrum at 31.7 ppm indicates the formation of the methanol-d_4 addition product 7-D$^+$.

These results demonstrate clearly that the protonolysis reaction strongly depends on the stereochemistry of the arylalkenyl moiety. The transformation implies a molecular rearrangement of the arylalkenyl moiety from a σ to π coordination mode. This process is sterically demanding to a different degree with respect to each isomer (cf. Figure 2).[33] The protonolysis is fast for the *E* isomer because there is enough space for the pentamethylphenyl ring to turn over

dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040−3050

Scheme 5. Protonolysis of *E*/*Z* Arylalkenyl Pt(PNP) Complexes 1/1′ and 2/2′



during the $\sigma-\pi$ rearrangement (cf. Figure 2A–C). In the case of the *Z* isomer the pentamethylphenyl ring has to move around or push back one of the phenyl groups of the PNP ligand (cf. Figure 2D–F). This steric obstacle strongly slows down the reaction rate of the protonolysis for the *Z* isomer **1′**. Moreover, as mentioned above, thermodynamic stabilization through C–H$\cdots\pi$ interactions might additionally contribute to an increased activation barrier for the protonolysis of the *Z* isomer.

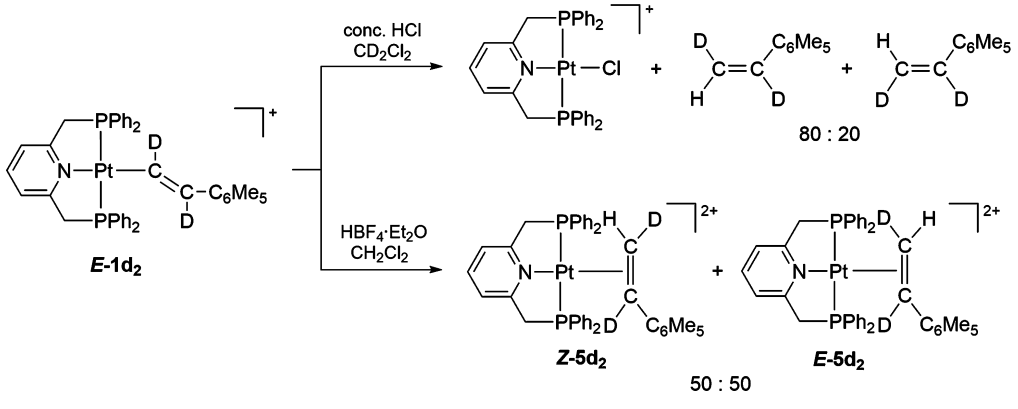
Provided that the *E*–*Z* isomerization of the arylalkenyl intermediate is not faster than protonolysis, the stereochemistry is assumed to be retained during the protonolysis step. However, this has not been experimentally verified so far. For this purpose the deuterium-labeled arylalkenyl complex (*E*)-[Pt(PNP)(CD=CDC_6Me_5)]BF_4 (***E*-1d$_2$**) was synthesized (cf. the Experimental Section and S13 and S14 (Supporting Information)).

Treatment of ***E*-1d$_2$** with concentrated HCl in CD_2Cl_2 gave the chloroplatinum complex and a mixture of free CHD=CDC_6Me_5 with a *Z*/*E* ratio of 80/20 (Scheme 6 and S15 (Supporting Information)), which was directly detected in solution by ^{1}H NMR spectroscopy (S15 (Supporting Information)). In contrast, the protonolysis of ***E*-1d$_2$** with $HBF_4{\cdot}Et_2O$ in CH_2Cl_2 resulted in a 50/50 mixture of arylalkene complexes ***Z*-5d$_2$** and ***E*-5d$_2$** (Scheme 6). The complex mixture was isolated and analyzed by ^{1}H NMR spectroscopy (S16 (Supporting Information)).

These experiments show that the stereochemistry of the arylalkenyl moiety certainly can change during the protonolysis step. The *Z*/*E* ratio depends on the nature of the respective acid anion. The chloride is a stronger nucleophile than the tetrafluoroborate and probably reacts preferably with the platinum center by substitution of the arylalkenyl ligand, which then is immediately protonated with major but not complete retention of the stereochemistry. In the case of $HBF_4{\cdot}Et_2O$ it is suggested that the proton is first transferred to the α carbon atom in ***E*-1d$_2$** with equal probability to the *Re* and *Si* sides (cf. Scheme 7). When the protonolysis is performed in the absence of any donor molecule (i.e., dichloromethane), the resulting carbocationic intermediates **IIa**,**b** would immediately rearrange to the isomeric π complex mixture ***Z*-/*E*-5d$_2$**. In methanol, however, the carbocations **IIa**,**b** are trapped to give the β-methoxoniumalkyl species **IV** (cf. also **7-D$^+$**, Scheme 5), which is in equilibrium with the β-methoxyalkyl complex **V**. The formation and "decomposition" of the methanol addition products of type **V**, i.e. vinylic deprotonation of the coordinated arylalkene, have been studied earlier with other arylalkene derivatives [Pt(PNP)(CH_2=CHR)]$(BF_4)_2$ (R = Ph, naphthyl).[23f]

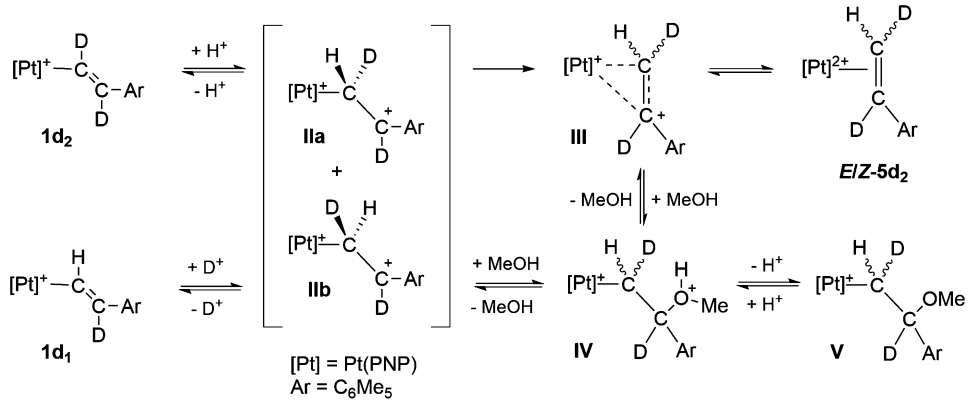
The reaction of the isomeric π complex mixture ***Z*-/*E*-5d$_2$** with methanol gave a 1/1 mixture of arylalkenyl complexes **1-d$_2$** and **1-d$_1$** (cf. Scheme 7, and S17 (Supporting Information)). Although the complete reversibility of the protonolysis step is shown herewith, the vinylic deprotonation would not occur spontaneously in absence of a donor molecule.[23f] It is unlikely that intermediate **III** ("slipped" form of ***Z*-/*E*-5d$_2$**) would rearrange to intermediate **II** by itself. However, in the presence of a donor molecule such as methanol, another mechanistic path will be opened, allowing the alkenyl moiety to rearrange from π to σ coordination mode by nucleophilic attack at the substituted carbon atom. Dissociation of the methanol from **IV**

Scheme 6. Protonolysis of Arylalkenyl-d_2 Complex (*E*-1d$_2$) with HCl and $HBF_4{\cdot}Et_2O$



dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040–3050

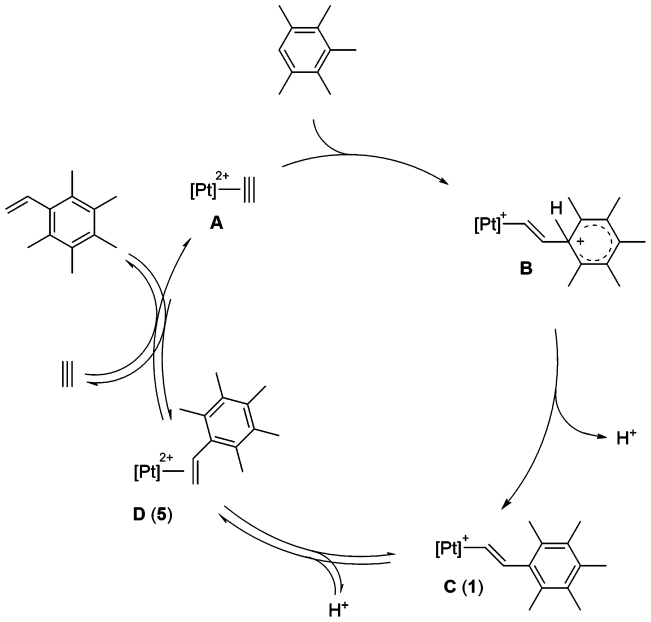
Scheme 7. Mechanistic Study of the Protonolysis/Vinylic Deprotonation Equilibrium System



gives the carbocationic intermediates **IIa,b**, from which H^+ (or D^+) dissociates to afford the mixture of **1-d$_2$** and **1-d$_1$** (cf. Scheme 7).

Study of the Catalytic Cycle in Solution. It was then of interest to demonstrate a complete catalytic cycle of the hydroarylation, as proposed in Scheme 8 starting from intermediate **C** by using the arylalkenyl complex **1**. From the reaction studies described above it is obvious that excess Brønsted acid helps to shift the protonolysis equilibrium forward (**C** → **D**, Scheme 8). The stoichiometric proton dissociated from intermediate **B** alone is not sufficient enough to cleave the Pt−C σ bond in the alkenyl complex **C** (Scheme 8). This observation is quite consistent with previously reported experimental findings for all palladium(II)- and platinum(II)-catalyzed hydroarylation reactions where a Brønsted acid (typically CF_3COOH) is required as a cocatalyst.[10−19] Labeling studies with d_1-TFA showed the incorporation of deuterium in the product, indicating that the acid is actually consumed for the protolytic cleavage.[10b,22]

Scheme 8. Proposed Mechanism for the Pt^{II}-Catalyzed Alkyne Hydroarylation



For the stepwise study of the catalytic cycle at room temperature, a CD_2Cl_2 solution containing complex **1** and 8 equiv of pentamethylbenzene was prepared. Upon addition of 4 equiv of $HBF_4{\cdot}Et_2O$ ^{1}H and ^{31}P NMR spectra were recorded, confirming the expected formation of complex **5** (intermediate **D**, S18 (Supporting Information)). Then 9 equiv of acetylene was added, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy (S19 and S20 (Supporting Information)). After 10 min 33% of the pentamethylbenzene was converted into pentamethylphenylethene, and within 1.5 h the reaction was practically complete.

In a second experiment it was tested whether or not catalytic turnovers are observed without addition of acid cocatalyst. The catalytic cycle was started with the product complex **5** (intermediate **D**, Scheme 8). The substrates were added in a manner similar to that described in the previous experiment, and the reaction was monitored by ^{1}H and ^{31}P NMR spectroscopy. A catalytic reaction with 8 turnovers was observed within 10 h (S20 (Supporting Information)). This demonstrates that the stoichiometric proton present in the system (**B** → **C**) *is* sufficient enough to cleave the Pt−C σ bond and thus afford catalytic turnovers at the $[Pt(PNP)]^{2+}$ complex at room temperature.

From these experimental findings the following details can be rationalized for the individual reaction steps of the catalytic alkyne hydroarylation, as shown in Scheme 8. The catalytic cycle can be started either with intermediate **C** and acid cocatalyst, generating intermediate **D** in situ, or directly with **D** without added acid (Scheme 8). The π-coordinated pentamethylphenylethylene in **5** is immediately substituted by the excess acetylene. This generates the highly reactive acetylene complex **A**, which instantly reacts further with excess arene to form the arylalkenyl complex **1** (intermediate **C**, Scheme 8) via intermediate **B** and proton dissociation. The ^{13}P NMR spectra recorded during the catalytic reactions show the signals of complexes **1** (**C**) and **5** (**D**) with a practically constant **C**/**D** ratio of 3/1 in the case of 4 equiv of acid cocatalyst and 9/1 in the absence of acid cocatalyst. Thus, an equilibrium constant of $K \approx 0.2$ can be estimated for the Pt−C protonolysis step, and complex **1** (**C**) can be considered the most stable species in the catalytic cycle.

While the protonolysis (**C** → **D**) is the rate-determining step and depends on acid concentration, the product-releasing step (**D** → **A**) proceeds relatively easily. It is notable that product complex **5** is still observable in a significant amount even in the absence of acid cocatalyst. The alkene/alkyne substitution is assumed to be a thermodynamically downhill process for cationic Pt^{II} species. Alkynes are usually stronger donor ligands than alkenes, and substitution reactions with alkene complexes

dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040−3050

have been commonly applied to prepare Pt^{II} alkyne complexes.[34] The substitution of ethylene by acetylene at the dicationic Pt(PNP) fragment was found to be very fast and proceeded even at low temperature.[35] Theoretical studies by Sakaki suggest for Zeise's salt type complexes $[PtX_3(L)]^-$ (L = C_2H_4, C_2H_2) that acetylene forms a stronger π bond to the Pt^{II} center than ethylene does.[36] However, more recently Steinborn et al. found for internal alkynes in experimental and theoretical studies that the Pt^{II}–alkyne bond in Zeise's salt type complexes tends to be slightly less stable than the Pt^{II}–alkene bond.[37]

From the ratio of intermediates **C** and **D** observed during the catalytic reaction the following relative reaction rates can be estimated for the individual steps of the proposed mechanism (Scheme 8): $k_{C\rightarrow D} < k_{D\rightarrow A} \ll k_{A\rightarrow B} \approx k_{B\rightarrow C}$.

CONCLUSION

Using the dicationic Pt(PNP) complex fragment, the complete catalytic cycle of the alkyne hydroarylation has been studied. Each of the individual reaction steps of the proposed reaction mechanism (Scheme 8) has been demonstrated in a stoichiometric reaction: (i) generation of the alkyne complex (**A**), (ii) nucleophilic arene addition (**A** → [**B**] → **C**), (iii) Pt–C protonolysis (**C** → **D**), and (iv) product displacement/regeneration of alkyne complex (**D** → **A**).

The first structural evidence for the proposed arylalkenyl intermediate (**C**; Scheme 8) was provided by intermolecular arene addition to the activated alkyne in complex **A**.

Although the arene addition proceeds trans to the metal center, resulting in (*E*)-arylalkenyl complexes, the overall stereoselectivity of a catalytic alkyne hydroarylation would be determined by the *E*–*Z* isomerization rate of intermediate **C**, by the individual protonolysis rates of *E* and *Z* isomers of **C**, and by the stereochemistry of the protonolysis itself. In case of the Pt(PNP) model complexes the *E*–*Z* isomerization of the arylalkenyl intermediate **C** (Scheme 3) occurs at such a slow rate that it is negligible for a catalytic reaction. In addition *Z* arylalkenyl complexes did not easily undergo protonolysis. However, stereoselectivity of the protonolysis of the *E* isomer depended on the nature of the counteranion, which requires further study. The solid-state structures of the *E* and *Z* isomers of $[Pt(PNP)(CH{=}CHC_6Me_5)]BF_4$ (**1** and **1′**) show the spatial orientation of the arylalkenyl moiety relative to the PNP ligand periphery and explain the individual reaction rates of *E*–*Z* isomerization and protonolysis.

Herewith it has been confirmed that the protonolysis is the rate-determining step and it has been determined how the proton concentration affects the overall reaction rate. The high positive complex charge of the catalyst complex can be considered favorable for the overall reaction. This is supported by the fact that the catalytic reaction is observed even in absence of acid cocatalyst under mild conditions.

Further experiments are in progress to explore more aspects of the catalytic intermolecular alkyne hydroarylation. The present results are very encouraging to develop new platinum hydroarylation catalysts with no need of acid cocatalyst, which would be very beneficial for industrial-scale applications.

EXPERIMENTAL SECTION

General Considerations. The ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$ was prepared according to a procedure reported previously.[26c] All reactions were performed under a dry argon atmosphere. Atomic absorption grade acetylene (dissolved) was used. D_2O was received from Aldrich and used without purification. CD_2Cl_2 and CD_3NO_2 were received from Aldrich and dried over 3 Å molecular sieves. CH_2Cl_2 was dried over CaH_2 and diethyl ether over sodium/benzophenone. The solvents and the liquid arenes were distilled immediately before use. Solid arenes were recrystallized before use. NMR spectra were recorded on 250, 300, 400, and 500 MHz instruments. Elemental analyses were performed by Columbia Analytical Services, Tucson, AZ. The ^{1}H NMR shifts were referenced to the resonance of the residual protons of the solvent. The ^{31}P NMR shifts were referenced to external 85% H_3PO_4 standard. The following abbreviations were used for NMR signals: s, singlet; d, doublet; t, triplet; pst, pseudotriplet; q, quartet, m, multiplet.

X-ray Structure Determination of (*E*)- and (*Z*)-[Pt(PNP)(CH=CHC$_6$Me$_5$)]BF$_4$ (1 and 1′).[38−40] Details of the X-ray experiment, data collection and reduction, and final structure refinement calculations for complexes **1** and **1′** are summarized in the table given in S21 (Supporting Information). Crystals of complex **1** were grown from CH_2Cl_2 solution by slow diffusion with diethyl ether over several days at room temperature. Crystals of complex **1′** were obtained from a concentrated solution in methanol. Suitable crystals of **1** and **1′** were selected and fixed respectively to a nylon loop, which in turn was attached to a copper mounting pin. A Bruker SMART 1000 X-ray three-circle diffractometer and graphite-monochromated Mo Kα radiation (λ = 0.71073 Å, 50 kV, 40 mA) were employed for sample screening and data collection. A total of 45 data frames were taken at a width of 0.3° with an exposure time of 20 s. Over 200 reflections were centered, and their positions were determined. These reflections were used in the autoindexing procedure to determine the unit cell. A suitable cell was found and refined respectively by nonlinear least-squares and Bravais lattice procedures and reported in S21 (Supporting Information). The standard data collection procedure consists of the collection of one hemisphere of data collectd using ω scans, involving the collection over 1400 0.3° frames at fixed angles for ϕ, 2θ, and χ (2θ = 28, 54.73°), while ω was varied. The total data collection was performed at 293 K for complex **1** and at 110 K for **1′**. All non-hydrogen atoms of the asymmetric unit were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions. In case of complex **1′** completeness to θ (30.8°) is only 88.1% due to crystal loss during data collection. In the crystal lattice of **1′** a disordered methanol molecule was determined with a partial occupancy of 37.5%. The tetrafluoroborate anion was found disordered as well; however, bond restraints and distances were applied to model the disorder only for the solvent molecule.

General Procedure for the Synthesis of (*E*)-[Pt(PNP)(CH=CHAr)]BF$_4$ (1−3). The ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$ (300 mg, 0.344 mmol) was dissolved in 60 mL of dichloromethane. The solution was cooled to −78 °C, and 15 equiv of the respective arene (5.26 mmol) was added. To the cold solution was added 3 equiv of acetylene (24 mL, 1.0 mmol). After the mixture was stirred at −78 °C for 15 min, the cold bath was removed to allow the reaction mixture to reach room temperature. The volume of the solution was reduced to 10 mL under reduced pressure. The product was precipitated by dropwise addition of diethyl ether. The product was filtered off, washed several times with diethyl ether, and dried under vacuum. For purification the product was dissolved in dichloromethane and the product was precipitated by addition of diethyl ether. The products were isolated as colorless microcrystalline solids.

(*E*)-[Pt(PNP)(CH=CHC$_6$Me$_5$)]BF$_4$ (1). Yield: 307 mg (96%, 0.330 mmol). Mp: 249 °C dec. Anal. Calcd for $C_{44}H_{44}BF_4NP_2Pt$: C, 56.78; H, 4.77; N, 1.50. Found: C, 49.47;[41] H, 4.42; N, 1.33. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.69 (s, 6H, CH_3), 2.06 (s, 6H, CH_3), 2.13 (s, 3H, CH_3), 4.56 (pst, 4H, $^{2+4}J_{H-P}$ = 4.9 Hz, PCH_2), 6.27 (d, 1H, $^3J_{H-H}$ = 17.0 Hz, $^3J_{H-Pt}$ = 84 Hz, =CH), 6.80 (dt, 1H, $^3J_{H-H}$ = 17.0 Hz, $^3J_{H-P}$ = 6.6 Hz, PtCH=), 7.58−7.67 (m, 12H, Ph), 7.76 (d, 2H, $^3J_{H-H}$ = 7.7 Hz, py-3,5), 7.86−7.92 (m, 8H, Ph), 8.08 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, py-4). ^{13}C NMR (100.61 MHz, CD_2Cl_2): δ 16.2 (s, *m*-CH_3), 16.3 (s, *p*-CH_3), 17.5 (s, *o*-CH_3), 46.2 (pst, J_{C-P} = 16.9 Hz, PCH_2), 119.2 (s, $^2J_{C-P}$ = 7.9 Hz, $^1J_{C-Pt}$ = 869 Hz, PtCH=), 123.0 (pst, J_{C-P} = 5.0 Hz, py-3,5), 126.8 (pst, J_{C-P} = 29.2 Hz, Ph_i), 129.6 (pst, J_{C-P} = 5.8 Hz, Ph_m), 130.6 (s, C_6Me_5), 131.7 (s, C_6Me_5), 132.3 (s, C_6Me_5), 132.4 (s,

dx.doi.org/10.1021/om5003123 | Organometallics 2014, 33, 3040−3050

Ph_p), 133.4 (pst, J_{C-P} = 6.8 Hz, Ph_o), 139.5 (s, C_6Me_5), 140.3 (s, py-4), 140.4 (t, $^3J_{C-P}$ = 7.9 Hz, $^2J_{C-Pt}$ = 331 Hz, =CH), 160.2 (pst, J_{C-P} = 3.5 Hz, $^2J_{C-Pt}$ = 35 Hz, py-2,6). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 26.4 (s, $^1J_{P-Pt}$ = 2998 Hz). MS (ESI): m/z 843 (M^+).

(*E*)-[Pt(PNP)(CH=CHC$_6$H$_2$Me$_3$-2,4,6)]BF$_4$ (2). Yield: 233 mg (75%, 0.258 mmol) Mp: 239 °C dec. Anal. Calcd for $C_{42}H_{40}BF_4NP_2Pt$: C, 55.89; H, 4.47; N, 1.55. Found: C, 51.33;[41] H, 4.42; N, 1.45. ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.68 (s, 6H, CH_3), 2.14 (s, 3H, CH_3), 4.56 (pst, 4H, $^{2+4}J_{H-P}$ = 4.8 Hz, PCH_2), 6.23 (d, 1H, $^3J_{H-H}$ = 16.9 Hz, $^3J_{H-Pt}$ = 84 Hz, =CH), 6.64 (s, 2H, $C_6H_2Me_3$), 7.04 (dt, 1H, $^3J_{H-H}$ = 16.9 Hz, $^3J_{H-P}$ = 6.8 Hz, PtCH=), 7.58−7.69 (m, 12H, Ph), 7.76 (d, 2H, $^3J_{H-H}$ = 7.8 Hz, py-3,5), 7.86−7.92 (m, 8H, Ph), 8.07 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, py-4). ^{13}C NMR (100.61 MHz, CD_2Cl_2): δ 20.4 (s, *p*-CH_3), 20.5 (s, *o*-CH_3), 45.9 (pst, J_{C-P} = 16.9 Hz, PCH_2), 120.5 (s, $^2J_{C-P}$ = 8.0 Hz, $^1J_{C-Pt}$ = 873 Hz, PtCH=), 123.0 (pst, J_{C-P} = 5.0 Hz, py-3,5), 126.8 (pst, J_{C-P} = 29.2 Hz, Ph_i), 128.1 (s, $C_6H_2Me_3$), 129.6 (pst, J_{C-P} = 5.6 Hz, Ph_m), 132.4 (s, Ph_p), 133.5 (pst, J_{C-P} = 6.9 Hz, Ph_o), 134.7 (s, $C_6H_2Me_3$), 134.9 (s, $C_6H_2Me_3$), 137.7 (t, $^3J_{C-P}$ = 6.0 Hz, $^2J_{C-Pt}$ = 250 Hz, =CH), 138.1 (s, $C_6H_2Me_3$), 140.4 (s, py-4), 160.2 (pst, J_{C-P} = 3.0 Hz, $^2J_{C-Pt}$ = 32 Hz, py-2,6). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 26.6 (s, $^1J_{P-Pt}$ = 2970 Hz). MS (ESI): m/z 815 (M^+).

(*E*)-[Pt(PNP)(CH=CHC$_6$H$_3$Me$_2$-2,6)]BF$_4$ (3a) and (*E*)-[Pt(PNP)-(CH=CHC$_6$H$_3$Me$_2$-2,4)]BF$_4$ (3b). Complexes **3a,b** were isolated as a 3/2 mixture containing 50% [Pt(PNP)(CH_2CHO)]BF_4 (**4**).[27] Combined yield **3a,b**: 83 mg (27%, 0.093 mmol).

(*E*)-[Pt(PNP)(CH=CHC$_6$H$_3$Me$_2$-2,6)]BF$_4$ (3a). ^{1}H NMR (400 MHz, CD_3NO_2): δ 1.71 (s, 6H, CH_3), 4.55 (pst, 4H, $^{2+4}J_{H-P}$ = 4.9 Hz, PCH_2), 6.24 (d, 1H, $^3J_{H-H}$ = 17.1 Hz, $^3J_{H-Pt}$ = 81 Hz, =CH), 6.80 (m, 3H, $C_6H_3Me_2$), 7.13 (dt, 1H, $^3J_{H-H}$ = 17.1 Hz, $^3J_{H-P}$ = 7.2 Hz, PtCH=), 7.59−7.70 (m, 12H, Ph), 7.75 (d, 2H, $^3J_{H-H}$ = 7.7 Hz, py-3,5), 7.88−7.93 (m, 8H, Ph), 8.05 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, py-4). ^{13}C NMR (100.61 MHz, CD_2Cl_2): δ 20.5 (s, CH_3), 45.9 (pst, J_{C-P} = 16.6 Hz, PCH_2), 120.5 (s, $^2J_{C-P}$ = 8.0 Hz, PtCH=), 123.0 (pst, J_{C-P} = 5.0 Hz, py-3,5), 125.3 (s, $C_6H_3Me_2$), 126.7 (pst, J_{C-P} = 29.1 Hz, Ph_i), 127.4 (s, $C_6H_3Me_2$), 129.6 (pst, J_{C-P} = 5.5 Hz, Ph_m), 132.4 (s, Ph_p), 132.5 (s, $C_6H_3Me_2$), 133.4 (pst, J_{C-P} = 6.8 Hz, Ph_o), 135.1 (s, $C_6H_3Me_2$), 137.6 (t, $^3J_{C-P}$ = 5.8 Hz, =CH), 140.4 (s, py-4), 140.6 (s, $C_6H_3Me_2$), 160.2 (pst, J_{C-P} = 3.0 Hz, py-2,6). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 26.4 (s, $^1J_{P-Pt}$ = 2984 Hz).

(*E*)-[Pt(PNP)(CH=CHC$_6$H$_3$Me$_2$-2,4)]BF$_4$ (3b). ^{1}H NMR (400 MHz, CD_3NO_2): δ 1.69 (s, 3H, CH_3), 2.17 (s, 3H, CH_3), 4.66 (pst, 4H, $^{2+4}J_{H-P}$ = 5.0 Hz, PCH_2), 6.64 (d, 1H, $^3J_{H-H}$ = 16.7 Hz, $^3J_{H-Pt}$ = 75 Hz, =CH), 6.80 (m, 3H, $C_6H_3Me_2$), 7.55−7.70 (m, 12H, Ph), 7.60 (dt, 1H, PtCH=), 7.75 (d, 2H, $^3J_{H-H}$ = 7.7 Hz, py-3,5), 7.88−7.93 (m, 8H, Ph), 8.05 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, py-4).

Generation of (*Z*)-[Pt(PNP)(CH=CHAr)]BF$_4$ (1′ and 2′). Solutions of complex **1** and complex **2** in CD_3OD, respectively, were stored over 4 months at room temperature. ^{1}H and ^{31}P NMR spectra were recorded at least 2−3 times per week over a period of 4 months.

(*Z*)-[Pt(PNP)(CH=CHC$_6$Me$_5$)]BF$_4$ (1′). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.72 (s, 6H, CH_3), 1.81 (s, 6H, CH_3), 1.94 (s, 3H, CH_3), 4.39 (pst, 4H, $^{2+4}J_{H-P}$ = 4.6 Hz, PCH_2), 7.19 (d, 1H, $^3J_{H-H}$ = 11.8 Hz, $^3J_{H-Pt}$ = 116 Hz, =CH), 7.45−7.92 (m, 22H, Ph, py-3,5), 8.05 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, py-4), 8.27 (dt, 1H, $^3J_{H-H}$ = 11.8 Hz, $^3J_{H-P}$ = 5.0 Hz, PtCH=). ^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 23.4 (s, $^1J_{P-Pt}$ = 3038 Hz).

(*Z*)-[Pt(PNP)(CH=CHC$_6$H$_2$Me$_3$-2,4,6)]BF$_4$ (2′). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.79 (s, 6H, CH_3), 2.04 (s, 3H, CH_3), 4.42 (pst, 4H, $^{2+4}J_{H-P}$ = 5.0 Hz, PCH_2), 6.28 (s, 2H, $C_6H_2Me_3$), 7.11 (d, 1H, $^3J_{H-H}$ = 11.9 Hz, $^3J_{H-Pt}$ = 119 Hz, =CH), 7.72−7.95 (m, 22H, Ph, py-3,5), 8.19 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, py-4), 8.30 (dt, 1H, $^3J_{H-H}$ = 11.9 Hz, $^3J_{H-P}$ = 5.1 Hz, PtCH=). ^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 23.3 (s, $^1J_{P-Pt}$ = 3023 Hz).

Generation of [Pt(PNP)(CH_2=CHAr)](BF$_4$)$_2$ (5 and 6). To 0.5 mL 0.01 M solutions of the complex mixtures **1**/**1**′ and **2**/**2**′ in CD_2Cl_2, respectively, was added 1 drop (~10 mg, ~0.062 mmol) of HBF_4·Et_2O (54% HBF_4 in Et_2O). ^{1}H and ^{31}P NMR spectra were recorded immediately after mixing (S5, Supporting Information).

[Pt(PNP)(CH_2=CHC$_6$Me$_5$)](BF$_4$)$_2$ (5). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 2.01 (s, 6H, CH_3), 2.04 (s, 6H, CH_3), 2.07 (s, 3H, CH_3), 4.50 (d pst, 2H, $^2J_{H-H}$ = 17.2 Hz, $^{2+4}J_{H-P}$ = 4.6 Hz, PCH_aH_b), 5.05 (dt 1H, $^3J_{H-H}$ = 15.9 Hz, $^3J_{H-P}$ = 4.8 Hz, $=CH_aH_b$), 5.23 (d pst, 2H, $^2J_{H-H}$ = 17.2 Hz, $^{2+4}J_{H-P}$ = 4.2 Hz, PCH_aH_b), 5.55 (dt, 1H, $^2J_{H-H}$ = 7.9 Hz, $^3J_{H-P}$ < 2 Hz, $^2J_{H-Pt}$ = 73 Hz, $=CH_aH_b$), 6.54 (dd, 1H, $^3J_{H-H}$ = 7.8 Hz, $^3J_{H-H}$ = 15.9 Hz, $^3J_{H-Pt}$ = 60 Hz, =CH), 7.44−7.85 (m, 22H, Ph, py-3,5), 8.05 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, py-4). ^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 34.5 (s, $^1J_{P-Pt}$ = 2350 Hz).

[Pt(PNP)(CH_2=CHC$_6$H$_2$Me$_3$-2,4,6)](BF$_4$)$_2$ (6). ^{1}H NMR (400 MHz, CD_2Cl_2): δ 1.99 (s, 6H, CH_3), 2.17 (s, 3H, CH_3), 4.55 (d pst, 2H, $^2J_{H-H}$ = 17.2 Hz, $^{2+4}J_{H-P}$ = 4.6 Hz, PCH_aH_b), 5.22 (dt 1H, $^3J_{H-H}$ = 16.5 Hz, $^3J_{H-P}$ = 4.5 Hz, $=CH_aH_b$), 5.26 (d pst, 2H, $^2J_{H-H}$ = 17.4 Hz, $^{2+4}J_{H-P}$ = 4.4 Hz, PCH_aH_b), 5.56 (dt, 1H, $^2J_{H-H}$ = 8.0 Hz, $^3J_{H-P}$ < 2 Hz, $^2J_{H-Pt}$ = 70 Hz, $=CH_aH_b$), 6.41 (dd, 1H, $^3J_{H-H}$ = 8.1 Hz, $^3J_{H-H}$ = 15.9 Hz, $^3J_{H-Pt}$ = 53 Hz, =CH), 7.50−7.75 (m, 22H, Ph, py-3,5), 8.04 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, py-4). ^{31}P NMR (161.98 MHz, CD_2Cl_2): δ 34.7 (s, $^1J_{P-Pt}$ = 2339 Hz).

Preparation of (*E*)-[Pt(PNP)(CD=CDC$_6$Me$_5$)]BF$_4$ (*E*-1d$_2$). Complex ***E*-1d$_2$** was prepared according to the procedure as described above using C_2D_2. Acetylene-d_2 was generated by the reaction of CaC_2 and D_2O. ^{1}H NMR (300 MHz, CD_2Cl_2): δ 1.62 (s, 6H, CH_3), 2.02 (s, 6H, CH_3), 2.15 (s, 3H, CH_3), 4.53 (pst, 4H, $^{2+4}J_{H-P}$ = 5.0 Hz, PCH_2), 7.55−7.90 (m, 22H, Ph, py-3,5), 8.07 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, py-4). ^{31}P NMR (121.49 MHz, CD_2Cl_2): δ 27.6 (s, $^1J_{P-Pt}$ = 2974 Hz).

Protonolysis of (*E*)-[Pt(PNP)(CD=CDC$_6$Me$_5$)]BF$_4$ (*E*-1d$_2$). *With HCl.* Complex ***E*-1d$_2$** (10 mg, 0.011 mmol) was dissolved in 0.5 mL of CD_2Cl_2. To the solution was added 1 drop of concentrated HCl. After mixing a ^{1}H NMR spectrum was recorded.

With HBF_4·Et_2O. Complex ***E*-1d$_2$** (100 mg, 0.107 mmol) was dissolved in 5 mL of CH_2Cl_2. To the solution was added 0.1 mL (0.7 mmol) of HBF_4·Et_2O. The mixture was stirred overnight. The solid products were precipitated by addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and dried under vacuum. The solid was analyzed by ^{1}H NMR spectroscopy (cf. S16 (Supporting Information)), showing the formation of a 1/1 ratio of (*E*)-/(*Z*)-[Pt(PNP)(CDH=CDC$_6$Me$_5$)](BF$_4$)$_2$ (***E*/*Z*-5d$_2$**): ^{1}H NMR (500 MHz, CD_2Cl_2): δ 1.98 (s, 6H, CH_3), 2.00 (s, 6H, CH_3), 2.05 (s, 3H, CH_3), 4.37 (d pst, 2H, $^2J_{H-H}$ = 17.6 Hz, $^{2+4}J_{H-P}$ = 4.5 Hz, PCH_aH_b), 4.95 (t 0.5H, $^3J_{H-P}$ = 4.6 Hz, =CHD), 5.23 (d pst, 2H, $^2J_{H-H}$ = 17.6 Hz, $^{2+4}J_{H-P}$ = 4.2 Hz, PCH_aH_b), 5.47 (dt, 0.5H, $^3J_{H-P}$ < 2 Hz, $^2J_{H-Pt}$ = 68 Hz, =CHD), 7.44−7.85 (m, 22H, Ph, py-3,5), 8.05 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, py-4).

Catalytic Hydroarylation Reaction. (a) A solution of 10 mg (0.01 mmol) of complex **1** and 12 mg (0.08 mmol) of pentamethylbenzene in CD_2Cl_2 were placed in an NMR tube. After addition of HBF_4·Et_2O (6 μL, 0.04 mmol) ^{1}H and ^{31}P NMR spectra were recorded (S18 (Supporting Information)). To the solution was added 2.2 mL (0.09 mmol) of acetylene at 25 °C, and the progress of catalytic conversions was monitored by NMR spectroscopy (S19 and S20 (Supporting Information)).

(b) The experiment described in (a) was repeated using complex **5**, but this time no acid cocatalyst was added. The progress of the catalytic reaction was followed by NMR spectroscopy (S20 (Supporting Information)).

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving the ^{1}H,^{13}C COSY NMR spectrum of complex **1**, ^{1}H and ^{1}H,^{1}H COSY NMR spectra of the complex mixture **3a,b**, ^{1}H and ^{31}P NMR spectra of the *E*−*Z* rearrangement of complexes **1** and **2**, time-dependent ^{1}H NMR spectra of *E*−*Z* isomerization of complex **2**, ^{1}H and ^{31}P NMR spectra of protonolysis of complexes **1** and **2**, ^{1}H and ^{31}P NMR spectra of reaction studies with ***E*-1d$_2$**, time-dependent ^{1}H NMR spectra for catalytic hydroarylation, conversion curves of catalytic reactions, and mass spectra of **1** and **2**, and a CIF file and table giving crystallographic data and refinement details for

dx.doi.org/10.1021/om5003123 | *Organometallics* 2014, 33, 3040−3050

complexes **1** and **1′**. This material is available free of charge via Internet at http://pubs.acs.org.

AUTHOR INFORMATION

Corresponding Author

*E-mail for C.H.: christine.hahn@tamuk.edu.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

This article is dedicated to Professor Helmut Werner on the occasion of his 80th birthday. This work has been supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society (No. 48223-GB3), the Robert A. Welch Foundation (AW-0013 and AC-006), and the Texas A&M University—Kingsville. Dr. Joseph H. Reibenspies, Dr. Christian Hilty, and Dr. Howard Williams (Texas A&M University, College Station, TX) are acknowledged for the X-ray structure analyses and NMR spectroscopy. Dr. Yohannes Rezenom (LBMS, Texas A&M University, College Station, TX) is acknowledged for the ESI MS analyses.

REFERENCES

(1) (a) Jia, C.; Kitamura, F.; Fujiwara, Y. *J. Synth. Org. Chem. Jpn.* **2001**, *59*, 1052−1061. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633−639. (c) Nevado, C.; Echavarren, A. M. *Synthesis* **2005**, 167−182. (d) Kitamura, T. *Eur. J. Org. Chem.* **2009**, 1111−1125. (e) Vasil'ev, A. V. *Russ. J. Org. Chem.* **2009**, *45*, 1−17. (f) Wang, X.; Zhou, L.; Lu, W. *Curr. Org. Chem.* **2010**, *14*, 289−307. (g) de Mendoza, P.; Echavarren, A. M. *Pur. Appl. Chem.* **2010**, *82*, 801−820.

(2) For example: (a) Goldfinger, M. B.; Crawford, K. B.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 4578−4593. (b) Pastine, S. J.; Youn, S. W.; Sames. *Org. Lett.* **2003**, *5*, 1055−1058. (c) Nevado, C.; Echavarren, A. M. *Chem. Eur. J.* **2005**, *11*, 3155−3164. (d) Ferrer, C.; Amijs, C. H. M.; Echavarren, A. M. *Chem. Eur. J.* **2007**, *13*, 1358−1373. (e) Dal Zotto, C.; Wehbe, J.; Virieux, D.; Campagne, J.-M. *Synlett* **2008**, 2033−2035. (f) Kitamura, T.; Otsubo, K. *J. Org. Chem.* **2012**, *77*, 2978−2982.

(3) Hashimoto, T.; Kutubi, S.; Izumi, T.; Rahman, A.; Kitamura, T. *J. Organomet. Chem.* **2011**, *696*, 99−105.

(4) (a) Gau, K.; Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2010**, *132*, 12249−12251. (b) Lee, P.-S.; Fujita, T.; Yoshikai, N. *J. Am. Chem. Soc.* **2011**, *133*, 17283−17295. (c) Ding, Z.; Yoshikai, N. *Angew. Chem., Int. Ed.* **2012**, *51*, 4698−4701.

(5) (a) Nakao, Y.; Kanyiva, K. S.; Oda, S.; Hiyama, T. *J. Am. Chem. Soc.* **2006**, *128*, 8146−8147. (b) Nakao, Y.; Kashihara, N.; Kanyiva, K. S.; Hiyama, T. *J. Am. Chem. Soc.* **2008**, *130*, 16170−16171. (c) Nakao, Y. *Chem. Rec.* **2011**, *11* (5), 242−251.

(6) (a) Hashimoto, Y.; Hirano, K.; Satoh, T.; Kakiuchi, F.; Miura, M. *Org. Lett.* **2012**, *14*, 2058−2061. (b) Tan, S. T.; Teo, Y. C.; Fan, W. Y. *J. Organomet. Chem.* **2012**, *708*−*709*, 58−64.

(7) (a) Schipper, D. J.; Hutchinson, M.; Fagnou, K. *J. Am. Chem. Soc.* **2010**, *132*, 6910−6911. (b) Ryu, J.; Cho, S. H.; Chang, S. *Angew. Chem., Int. Ed.* **2012**, *51*, 3677−3681.

(8) (a) Reetz, M. T.; Sommer, K. *Eur. J. Org. Chem.* **2003**, 3485−3496. (b) Shi, Z.; He, C. *J. Org. Chem.* **2004**, *69*, 3669−3671. (c) Li, Z.; Shi, Z.; He, C. *J. Organomet. Chem.* **2005**, *690*, 5049−5054. (d) Barluenga, J.; Fernández, A.; Rodríguez, F.; Fañanás, F. J. *J. Organomet. Chem.* **2009**, *694*, 546−550. (e) Tubari, C.; Baron, M.; Biffis, A.; Basato, M. *Beilstein J. Org. Chem.* **2013**, *9*, 246−253.

(9) (a) Tsuchimoto, T.; Hatanaka, K.; Shirakawa, E.; Kawakami, Y. *Chem. Commun.* **2003**, 2454−2455. (b) Bhaskar, G.; Saikumar, C.; Perumal, P. T. *Tetrahedron Lett.* **2010**, *51*, 3141−3145.

(10) (a) Jia, C.; Piao, D.; Oyamada, J.; Lu, W.; Kitamura, T.; Fujiwara, Y. *Science* **2000**, *287*, 1992−1995. (b) Jia, C.; Lu, W.; Oyamada, J.; Kitamura, T.; Matsuda, K.; Irie, M.; Fuijiwara, Y. *J. Am. Chem. Soc.* **2000**, *122*, 7252−7263.

(11) (a) Oyamada, J.; Kitamura, T. *Tetrahedron Lett.* **2005**, *46*, 3823−3827. (b) Oyamada, J.; Kitamura, T. *Tetrahedron* **2007**, *63*, 12754−12762.

(12) (a) Oyamada, J.; Kitamura, T. *Chem. Lett.* **2005**, *34*, 1430−1431. (b) Oyamada, J.; Hashimoto, T.; Kitamura, T. *J. Organomet. Chem.* **2009**, *694*, 3626−3632.

(13) Oyamada, J.; Kitamura, T. *Tetrahedron* **2009**, *65*, 3842−3847.

(14) Oyamada, J.; Kitamura, T. *Chem. Lett.* **2007**, *36*, 1150−1151.

(15) Oyamada, J.; Kitamura, T. *Chem. Lett.* **2008**, *37*, 910−911.

(16) Oyamada, J.; Kitamura, T. *Chem. Commun.* **2008**, 4992−4994.

(17) Viciu, M. S.; Stevens, E. D.; Petersen, J. L.; Nolan, S. P. *Organometallics* **2004**, *23*, 3752−3755.

(18) (a) Biffis, A.; Tubaro, C.; Buscemi, G.; Basato, M. *Adv. Synth. Catal.* **2008**, *350*, 189−196. (b) Buscemi, G.; Biffis, A.; Tubaro, C.; Basato, M. *Catal. Today* **2009**, *140*, 84−89. (c) Biffis, A.; Gazzola, L.; Gobbo, P.; Buscemi, G.; Tubaro, C.; Basato, M. *Eur. J. Org. Chem.* **2009**, 3189−3198. (d) Buscemi, G.; Biffis, A.; Tubaro, C.; Basato, M.; Graiff, C.; Tiripicchio, A. *Appl. Organomet. Chem.* **2010**, *24*, 285−290. (e) Gazzola, L.; Tubaro, C.; Biffis, A.; Basato, M. *New J. Chem.* **2010**, *34*, 482−486.

(19) (a) Saravanakumar, R.; Ramkumar, V.; Sankararaman, S. *Organometallics* **2011**, *30*, 1689−1694. (b) Gonell, S.; Poyatos, M.; Mata, J. A.; Peris, E. *Organometallics* **2011**, *30*, 5985−5990.

(20) Tsukada, N.; Mitsuboshi, T.; Setoguchi, H.; Inoue, Y. *J. Am. Chem. Soc.* **2003**, *125*, 12102−12103.

(21) In the case of dinuclear Pd^{II} complexes the mechanism may be very different, as pointed out in ref 20.

(22) Tunge, J. A.; Foresee, L. N. *Organometallics* **2005**, *24*, 6440−6444.

(23) Arylalkenyl Pd^{II} and Pt^{II} complexes are known, but they were obtained by other routes. Alkyne insertion into Pd^{II}−aryl bond: (a) Vicente, J.; Abad, J.-A.; Förtsch, W.; López-Sáez, M.-J. *Organometallics* **2004**, *23*, 4414−4429. Insertion of phenylacetylene into Pt^{II}−H bond: (b) Ohtaka, A.; Kuniyasu, H.; Kinomoto, M.; Kurosawa, H. *J. Am. Chem. Soc.* **2002**, *124*, 14324−14325. Oxidative addition of arylvinyl halides to a Pt^{0} complex: (c) Cook, C. D.; Jauhal, G. S. *Can. J. Chem.* **1967**, *45*, 301−304. Use of Grignard reagent: (d) Cardin, C. J.; Cardin, D.; Parge, H. E.; Sullivan, A. C. *J. Chem. Soc., Dalton Trans.* **1986**, 2315−2320. Vinylic deprotonation of styrene Pt^{II} complexes: (e) Lorusso, G.; Boccaletti, G.; Di Masi, N. G.; Fanizzi, F. P.; Maresca, L.; Natile, G. *Eur. J. Chem.* **2004**, 4751−4754. (f) Hahn, C. *Organometallics* **2010**, *29*, 1331−1338.

(24) Hahn, C. *Chem. Eur. J.* **2004**, *10*, 5888−5899.

(25) Cucciolito, M. E.; D'Amora, A.; Tuzi, A.; Vitagliano, A. *Organometallics* **2007**, *26*, 5216−5223.

(26) (a) Hahn, C.; Vitagliano, A.; Giordano, F.; Taube, R. *Organometallics* **1998**, *17*, 2060−2066. (b) Hahn, C.; Morvillo, P.; Vitagliano, A. *Eur. J. Inorg. Chem.* **2001**, 419−429. (c) Hahn, C.; Morvillo, P.; Herdtweck, E.; Vitagliano, A. *Organometallics* **2002**, *21*, 1807−1818. (d) Hahn, C.; Cucciolito, M. E.; Vitagliano, A. *J. Am. Chem. Soc.* **2002**, *124*, 9038−9039. (e) Cucciolito, M. E.; D'Amora, A.; Vitagliano, A. *Organometallics* **2010**, *29*, 5878−5884.

(27) Carlisle, S.; Matta, A.; Valles, H.; Bracken, J. B.; Miranda, M.; Yoo, J.; Hahn, C. *Organometallics* **2011**, *30*, 6446−6457.

(28) Smith, M. B.; March, J. *Advanced Organic Chemistry*, 5th ed.; Wiley: New York, 2001; pp 675−758.

(29) (a) Shubin, A. A.; Mitchenko, R. S.; Bezbozhnaya, T. V.; Vdovichenko, A. N. *Russ. Chem. Bull., Int. Ed.* **2005**, *54*, 2456−2459. (b) Steinborn, D.; Hoffmann, T.; Gerisch, M.; Bruhn, C.; Schmidt, H.; Nordhoff, K. *Z. Anorg. Allg. Chem.* **2000**, *626*, 661−666.

(30) Plane perpendicular to the best plane defined by P1, P2, N, and Pt.

(31) (a) Amatore, C.; Bensalem, S.; Ghalem, S.; Jutand, A. *J. Organomet. Chem.* **2004**, *689*, 4642−4646. (b) Zargarrian, D.; Alper, H. *Organometallics* **1993**, *12*, 712−724.

(32) (a) Yoon, M. Y.; Kim, J. H.; Choi, D. S.; Shin, U. S.; Lee, J. Y.; Song, C. E. *Adv. Synth. Catal.* **2007**, *349*, 1725−1737. (b) Kim, K. S.;

Tarakeshwar, P.; Lee, J. Y. *Chem. Rev.* **2000**, *100*, 4145−4185. (c) Hobza, P.; Havlas, Z. *Chem. Rev.* **2000**, *100*, 4253−4264.

(33) To trace the structural movements during protonolysis reactions **1** → **5** (or **2** → **6**) vs **1′** → **5** (or **2′** → **6**) the molecular structures of **1** and **1′** should be compared with the X-ray crystal structure analysis of the related styrene π complex $[Pt(PNP)(CH_2{=}CHPh)](BF_4)_2$ in ref 23f.

(34) Hartley, F. R. Platinum. In *Comprehensive Organometallic Chemistry*; Wilkinson, G., Stone, F. G. A., Abel, E. W., Eds.; Pergamon Press: Oxford, U.K., 1982; Vol. *6*, pp 691−713.

(35) The substitution equilibrium between platinum(II) alkene and alkyne complexes is difficult to study experimentally, due to the high reactivity of the alkyne complexes which is usually accompanied by alkyne oligo- or polymerization. Dicationic platinum alkyne complexes of the type $[Pt(PNP)(alkyne)]^{2+}$ could not be directly detected; cf. ref 27.

(36) Sakaki, S.; Kato, H.; Kawamura, T. *Bull. Chem. Soc. Jpn.* **1975**, *48*, 195−200.

(37) König, A.; Bette, M.; Wagner, C.; Lindner, R.; Steinborn, D. *Organometallics* **2011**, *30*, 5919−5927.

(38) Sheldrick, G. M. *Acta Crystallogr.* **2008**, *A64*, 112−122.

(39) Barbour, L. J. *J. Supramol. Chem. 1* **2001**, 189−191.

(40) (a) *SMART (5.632)*; Bruker Analytical X-ray Instruments Inc., Madison WI, USA, 2000. (b) *SAINT (6.45)*; Bruker Analytical X-ray Instruments Inc., Madison WI, USA, 2003.

(41) For the arylalkenyl complexes **1** and **2** low values for C were found. Most likely the combustion was incomplete during the analysis due to carbide formation. Similarly low C values were found for the structurally related alkynyl complexes $[Pt(PNP)(C{\equiv}CR)]BF_4$ (R = ^{t}Bu, Ph); cf. ref 27.