ORGANOMETALLICS

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Water Addition to Alkynes Promoted by a Dicationic Platinum(II) Complex†

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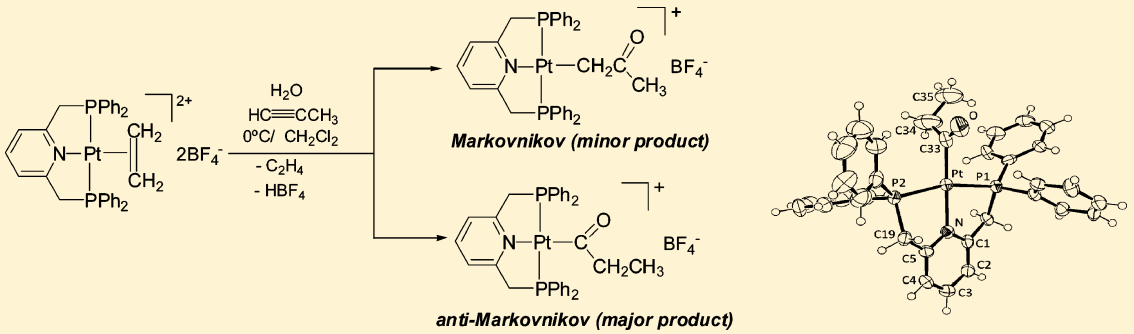
Supporting Information

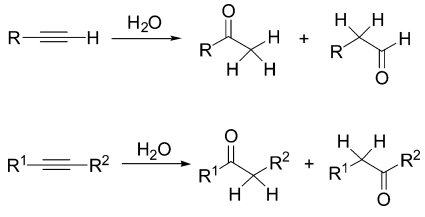


ABSTRACT: Dicationic platinum alkyne complexes were generated in situ by substitution of ethylene in $[Pt(PNP)(C_2H_4)](BF_4)_2$ (PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) with alkynes at low temperature. The dicationic acetylene complex readily adds water to form the platina-acetaldehyde complex $[Pt(PNP)(CH_2CHO)]BF_4$, which was analyzed by X-ray diffraction. ^1H and ^{31}P NMR studies were performed to elucidate the mechanism of formation of $[Pt(PNP)(CH_2CHO)]BF_4$. A reversible acid−base equilibrium between the platina-acetaldehyde and the corresponding η^2-vinyl alcohol complex $[Pt(PNP)(CH_2{=}CHOH)]^{2+}$ was observed. The complexes with terminal alkynes (propyne and 1-hexyne) gave with water a mixture of Markovnikov and anti-Markovnikov addition products $[Pt(PNP)\{CH_2C(O)R^1\}]BF_4$ and $[Pt(PNP)\{C(O)CH_2R^1\}]BF_4$ (R^1 = Me, *n*-Bu) in a ratio of 1:4. However, with *tert*-butyl- and phenylacetylene C−H bond activation occurred, yielding the σ-alkynyl complexes $[Pt(PNP)(C{\equiv}CR^2)]BF_4$ (R^2 = *t*-Bu, Ph). Complexes with internal alkynes $R^3C{\equiv}CR^4$ (R^3 = Me; R^4 = Me, *n*-Pr) react with water and form the corresponding β-ketonyl complexes $[Pt(PNP)\{CHR^3C(O)R^4\}]BF_4$. Moderate regioselectivity was observed for 2-hexyne.

INTRODUCTION

The hydration of alkynes is an important reaction to synthesize aldehydes or ketones, because it is atom-economical and inexpensive starting materials are used. With terminal alkynes either Markovnikov or anti-Markovnikov products can be formed, while with unsymmetrical alkynes two different regioisomers can be expected (Scheme 1).

Scheme 1. Hydration of Terminal and Internal Alkynes



In the last few decades increasing efforts have been made to develop new transition-metal catalysts for the hydration of alkynes in order to replace the traditional acid and the highly toxic mercury catalysts.[1] The first platinum(II)-catalyzed hydration of alkynes was reported by Chatt and Duncanson using $Na_2PtCl_4{\cdot}H_2O$ as catalyst.[2] Later, Jennings and co-workers found that Zeise's dimer and Pt^{II} halides efficiently catalyze the hydration of unactivated alkynes.[3] Terminal alkynes were hydrated with Markovnikov selectivity and unsymmetrical internal alkynes with moderate regioselectivity. Atwood and co-workers have synthesized water-soluble platinum(II) complexes containing sulfonated mono- and bidentate phosphine ligands.[4] Furthermore, platinum(IV) chloride was shown to catalyze the hydration of various alkynes at 1.38 MPa CO pressure.[5] Also, for the study of hydrative cyclizations of allenynes and trialkynes $PtCl_2$ has been frequently used as catalyst.[6]

While various new gold complexes were reported more recently as very efficient catalysts,[7] there seem to be currently

Received: August 23, 2011
Published: November 14, 2011

   dx.doi.org/10.1021/om2007908|*Organometallics* 2011, 30, 6446–6457

no further efforts to design structurally new complexes of platinum(II) and to study their catalytic activity, mechanistic details, or reaction intermediates. Many questions concerning transition-metal-catalyzed hydration of alkynes remain unanswered. For example, the regioselectivity of the hydration of unfunctionalized internal alkynes is still a challenge. The catalytic anti-Markovnikov addition of water to terminal alkynes to form aldehydes succeeded only with ruthenium catalysts.[8]

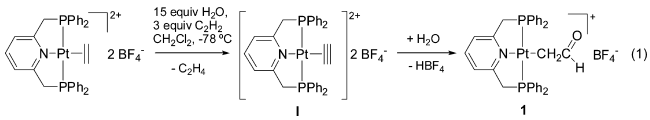
In analogy to our previous studies of electrophilic activation of alkenes by coordination in dicationic platinum(II) complexes of the type $[Pt(PNP)(CHR{=}CHR)](BF_4)_2$ (PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) and their reactions with water and other weakly basic nucleophiles,[9] we explored also the activation of alkynes at the $Pt(PNP)^{2+}$ complex fragment. Since water addition to the coordinated C−C double bond gave the stable β-hydroxyalkyl complexes $[Pt(PNP)(CH_2CHROH)]BF_4$ in a stoichiometric reaction, it was interesting to study similarly the products resulting from water addition to the coordinated C−C triple bond.

In this paper, we report the generation of dicationic platinum(II) alkyne complexes of the type $[Pt(PNP)(RC{\equiv}CR')](BF_4)_2$ with acetylene and terminal and internal alkynes. These complexes were reacted with water and gave platina-acetaldehyde, ketonyl, acyl, or alkynyl σ complexes, which were isolated and characterized by NMR, IR, and X-ray structure analysis and studied in solution. These results provide not only support for the relevant intermediates and reaction steps suggested by Jennings and co-workers[3] for the platinum(II)-catalyzed alkyne hydration but also demonstrate the possibility of the anti-Markovnikov addition of water to terminal alkynes using a platinum(II) complex.

RESULTS AND DISCUSSION

Reaction of $[Pt(PNP)(C_2H_4)](BF_4)_2$ with Acetylene and Water. A common method to generate platinum(II) alkyne complexes is the displacement of an alkene by the alkyne, since the alkyne is a stronger donor ligand.[10] When the ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$[9] was reacted with an excess of acetylene in CD_2Cl_2 at room temperature, the solution turned immediately dark brown, indicating fast acetylene oligo- or polymerization. The ^1H NMR spectra of the reaction solution showed a number of signals between 0 and 5 ppm, which can be assigned to oligomerization products. This is not unusual for platinum(II) complexes.[10] The formation of uncontrolled oligomerization byproduct could be strongly reduced by performing the reaction at lower temperature with only a slight excess of acetylene. When 3 equiv of acetylene was added to the ethylene complex in CH_2Cl_2 at −78 °C, the reaction solution turned only light brown. After 15 min the reaction mixture was warmed to room temperature and a light brown solid was precipitated by addition of diethyl ether. However, the ^1H and ^{31}P NMR spectra of the isolated product show the formation of a mixture of compounds. A dicationic acetylene complex could not be identified among them. This is not surprising, since it is expected to be extremely reactive and can easily undergo numerous side reactions. There are also no examples known for isolated platinum acetylene complexes.[11]

However, in the ^1H NMR spectrum of the compound mixture a characteristic set of signals could be identified. It suggests the formation of the platina-acetaldehyde complex $[Pt(PNP)(CH_2CHO)]BF_4$ (**1**) as a result of reaction of the coordinated acetylene with water which was adventitiously present in solution. The reaction was repeated under the same reaction conditions, but this time 15 equiv of water was added to the solution of the ethylene complex prior to the addition of acetylene. Water addition to the coordinated ethylene[9] is very slow at low temperature and is not a competing side reaction. In contrast, the far more reactive acetylene complex $[Pt(PNP)(C_2H_2)](BF_4)_2$ (**I**) (eq 1) immediately reacts upon its



(1)

formation with the excess water provided in advance.[12] This prevents practically all unwanted side reactions. Under these optimized conditions (eq 1) the platina-acetaldehyde complex $[Pt(PNP)(CH_2CHO)]BF_4$ (**1**) was isolated in analytically pure form.

The platina-acetaldehyde complex $[Pt(PNP)(CH_2CHO)]BF_4$ (**1**) was characterized by NMR and IR spectroscopy as well as by X-ray crystal structure analysis. The ^1H NMR spectrum shows a characteristic doublet of triplets for the $PtCH_2$ group at δ 2.94 with platinum satellites. The triplet at δ 8.95 is diagnostic for an aldehyde proton. In the ^{13}C NMR spectrum a signal at δ 201.7 is observed for the carbonyl carbon atom. The IR bands at $\tilde{\nu}$ 1673 and 2722 cm^{-1} are assigned to the C=O and C−H stretching frequencies of the aldehyde functional group. Similar IR bands were observed for the C=O group in other platina-acetaldehyde complexes.[13,14]

X-ray Structure Analysis of $[Pt(PNP)(CH_2CHO)]BF_4$ (1). Suitable crystals for X-ray structure analysis were obtained by overlayering a solution of complex **1** in CH_2Cl_2 with diethyl ether. An ORTEP drawing of the complex cation is shown in Figure 1. The complex cation **1** has a square-planar coordination

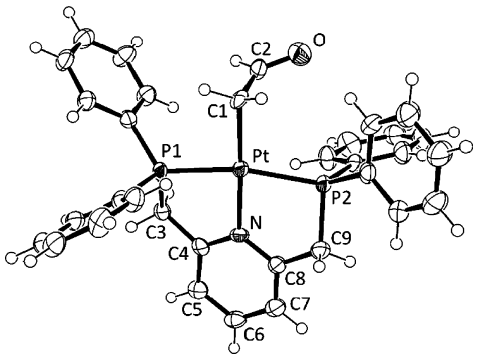


Figure 1. ORTEP drawing of the complex cation **1**. Selected bond lengths (Å) and angles (deg): Pt−P1 = 2.2693(9), Pt−P2 = 2.3033(10), Pt−N = 2.112(3), Pt−C1 = 2.132(3), C1−C2 = 1.410(6), C2−O = 1.218(5); P1−Pt−P2 = 165.90(3), N−Pt−P1 = 82.82(9), N−Pt−P2 = 83.15(9), N−Pt−C1 = 178.10(12), C1−Pt−P1 = 95.34(10), C1−Pt−P2 = 98.70(10), Pt−C1−C2 = 102.2(2), C1−C2−O = 126.7(4).

geometry with the η^1-acetaldehyde ligand in the fourth position. The Pt−C1 (2.132(3) Å) and C1−C2 (1.410(6) Å) bond lengths are similar to those found in $[Pt(PNP)\{CH_2CH_2C_6H_2(OCH_3)_3\}]SbF_6$[15] (2.157(9) and 1.421(16) Å; cf. Table 1), indicating a Pt−C σ bond and a C−C single bond type. The C2−O bond length of 1.218(5) Å is characteristic for a C−O double bond, and the C1−C2−O angle of 126.7° suggests the sp^2 character of the C2 atom. These structural features agree with the spectroscopic data.

dx.doi.org/10.1021/om2007908 | Organometallics 2011, 30, 6446−6457

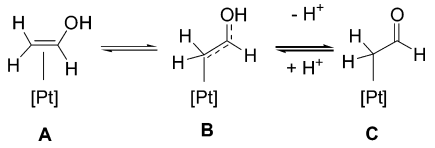
Table 1. Selected Bond Lengths (Å) and Angles (deg) of $[Pt(PNP)(CH_2CHO)]BF_4$ (1) and Those of Structurally Related Complexes[a]

	Pt−C1	Pt−C2	C1−C2	C2−O	Pt−C1−C2	C1−C2−O
$[Pt(PNP)(CH_2CHO)]BF_4$ (**1**)	2.132(3)	2.7937(3)	1.410(6)	1.218(5)	102.2(2)	126.7(4)
$[PtBr(CH_3)(dmphen)(CH_2{=}CHOH)]$[b]	2.081(9)	2.062(9)	1.45(1)	1.41(1)	70(1)	121(1)
$[PtCl(acac)(CH_2{=}CHOH)]$[c]	2.098(10)	2.222(9)	1.387(5)	1.297(12)	76.3	121.9(9)
$[Pt^{III}_2(NH_3)_4\{(CH_3)_3CCONH\}_2(CH_2CHO)](NO_3)_3{\cdot}H_2O$[d]	2.121(9)	2.93	1.35(2)	1.30(2)	113.5	n.a.
$[Pt(PNP)(CH_2{=}CH_2)](BF_4)_2$[e]	2.181(8)	2.180(6)	1.359(10)		71.8(4)	
$[Pt(PNP)\{CH_2CH_2C_6H_2(OCH_3)_3\}]SbF_6$[f]	2.157(9)	3.06(1)	1.421(16)		116.3(7)	

[a]For the sake of uniformity the atom labeling was adopted for all complexes to that of complex **1** and may not agree with the original labeling. [b]dmphen = 2,9-dimethyl-1,10-phenanthroline.[15] [c]Reference 17. [d]Reference 14. [e]Reference 9. [f]Reference 15.

It is interesting to compare the structure and bonding in complex **1** with those of the following platinum complexes: $[PtBr(CH_3)(dmphen)(CH_2{=}CHOH)]$,[16a] $[PtCl(acac)(CH_2{=}CHOH)]$,[17] and $[Pt^{III}_2(NH_3)_4\{(CH_3)_3CCONH\}_2(CH_2CHO)](NO_3)_3{\cdot}H_2O$[14] (cf. Table 1), which display structural features intermediate between vinyl alcohol π complex **A** and platina-acetaldehyde σ complex **C** (Scheme 2). Structures **A** and **C** are related through an acid−base equilibrium which was studied in solution,[13,14,16] while the intermediate structure **B** is considered to be important in the mechanism of the alkyne hydration (cf. Schemes 2 and 3; see discussion below).

Scheme 2. Structural Relationship between Vinyl Alcohol π Complex and Platina-Acetaldehyde σ Complex

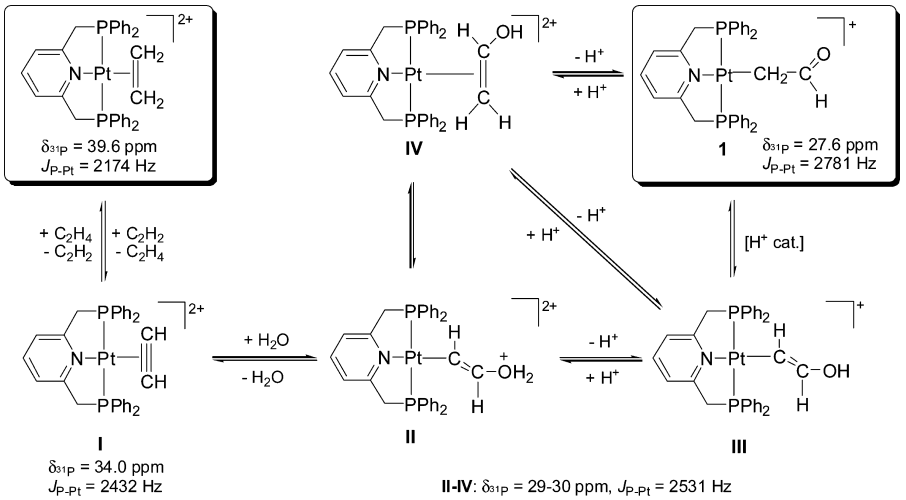


The five-coordinate complex $[PtBr(CH_3)(dmphen)(CH_2{=}CHOH)]$ is one of the few structurally characterized η^2-vinyl alcohol complexes of platinum[16] and provides an example for structure **A** (Scheme 2). The vinyl alcohol is coordinated with essentially equal Pt−C1 and Pt−C2 bond lengths, as similarly found for the π-coordinated ethylene in $[Pt(PNP)(C_2H_4)](BF_4)_2$ (cf. Table 1).[9] The C−C double bond (1.45(1) Å) of the coordinated vinyl alcohol in $[PtBr(CH_3)(dmphen)(CH_2{=}CHOH)]$ is lengthened due to the relatively strong π back-donation, which is expected for a relatively electron-rich five-coordinate platinum(II) complex.

In contrast, the solid-state structure of $[PtCl(acac)(CH_2{=}CHOH)]$ reported by Cotton et al.[17] displays a vinyl alcohol π complex with a strong geometric bias to the intermediate structure **B** (Scheme 2). In this structure the Pt−C2 bond (2.222(9) Å) is significantly longer than Pt−C1 (2.098(10) Å). The C2−O distance (1.29(12) Å) seems to be intermediate between C−O single- and a double-bond lengths.[18,19] The C−C bond length of 1.387(5) Å of the vinyl alcohol in $[PtCl(acac)(CH_2{=}CHOH)]$ lies between the lengths observed for the coordinated C−C double bonds in $[PtBr(CH_3)(dmphen)(CH_2{=}CHOH)]$[16a] and $[Pt(PNP)(C_2H_4)](BF_4)_2$[9] (cf. Table 1).

On the other hand, the platina-acetaldehyde σ complex $[Pt^{III}_2(NH_3)_4\{(CH_3)_3CCONH\}_2(CH_2CHO)](NO_3)_3{\cdot}H_2O$ reported by Matsumoto[14] represents essentially structure **C** but with a bias to structure **B**. The Pt−C1 and Pt−C2 distances (2.121(9) and 2.93 Å) are similar to those observed for complex **1**. The Pt−C1−C2 bond angle of 113.5° lies between the values found for η^1 complexes **1** and $[Pt(PNP)\{CH_2CH_2C_6H_2(OCH_3)_3\}]SbF_6$[15] (cf. Table 1) and indicates a σ-alkyl bond of the CH_2 group. However, the C1−C2 bond length in the Pt^{III} complex at 1.35(2) Å is shorter than a C−C single bond, while the C2−O distance (1.30(2) Å) appears somewhat longer than a C−O double-bond length.

Scheme 3. Proposed Mechanism for the Formation of Complex 1, Where All Nonhighlighted Species Are Proposed Intermediates



dx.doi.org/10.1021/om2007908|Organometallics 2011, 30, 6446−6457

A comparison of these structures may provide some insight into the progress of the acid−base equilibrium of the vinyl alcohol π complex and the platina-acetaldehyde σ-complex, where complex **1** represents "pure" structure **C**.

NMR Studies of Complex 1 in Solution. According to the mechanism for the alkyne hydration proposed by Jennings and co-workers,[3] it is suggested that the formation of complex **1** involves the nucleophilic addition of water to the in situ generated acetylene complex **I** (cf. Scheme 3). The β-hydroxonium vinyl species **II** is most likely the primary addition product from which the proton dissociates, and the η^1-enol species **III** is formed, which tautomerizes to the more stable platina-acetaldehyde complex **1**.

It was interesting to see if the proposed equilibrium reaction can be shifted back by addition of HBF_4 and if in this way the dicationic acetylene π complex **I** can be generated back and spectroscopically characterized. It should be noted that the methanol addition to $[Pt(PNP)(CH_2{=}CH_2)](BF_4)_2$ could be completely reversed by addition of HBF_4 to $[Pt(PNP)(CH_2CH_2OCH_3)]BF_4$.[9]

To a solution of complex **1** in CD_2Cl_2 were added 3 drops of $HBF_4{\cdot}Et_2O$. In the ^1H NMR spectrum the signal at δ 8.95 is no longer observed and the characteristic doublet of triplets for the $PtCH_2$ group has shifted downfield from δ 2.94 to δ 3.78 and the Pt−H coupling constant $^2J_{Pt-H}$ has decreased from 108 to 81 Hz (see Figure S2 in the Supporting Information). This indicates the formation of the η^2-enol complex **IV** rather than the acetylene complex **I**, because very similar ^1H NMR data were observed for $K[PtCl(acac)(CH_2CHO)]$ and the corresponding η^2-enol complex (cf. Table 2).[13b] All attempts to isolate the η^2-vinyl alcohol intermediate **IV**, however, failed.

Table 2. Characteristic ^1H NMR Data for Platina-Acetaldehyde and Vinyl Alcohol Complexes (δ in ppm, J in Hz)

	$\delta_{H_{ab}}$	$^3J_{H_{ab}-H_c}$	$^2J_{Pt\text{-}H_{ab}}$	δ_{H_c}
$[Pt(PNP)(CH_aH_bCH_cO)]^+$ (**1**)	2.94	5.5	108	8.95
$[Pt(PNP)(CH_aH_b{=}CH_cOH)]^{2+}$ (**IV**)	3.78	8.1	81	n.a.[b]
$K[PtCl(acac)(CH_aH_bCH_cO)]$[a]	3.28	5.5	113	9.16
$[PtCl(acac)(CH_aH_b{=}CH_cOH)]$[a]	3.89	8	76	7.27

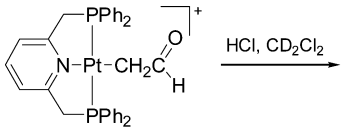
[a]Reference 13b. [b]Not observed or hidden under signals of aromatic protons.

When less $HBF_4{\cdot}Et_2O$ (1 drop) was added to complex **1**, the respective signals for the $CH_aH_bCH_cO$ moiety were shifted only slightly (δ_{H_c} 8.48, $\delta_{H_{ab}}$ 3.05) and the coupling constants also changed only slightly ($^2J_{Pt-H}$ = 97 Hz, $^2J_{H_{ab}-H_c}$ = 6.1 Hz; see Figure S3 in the Supporting Information). The same trend was also observed when $K[PtCl(acac)(CH_2CHO)]$ and the corresponding η^2-enol complex were mixed together in solution.[13b] This suggests that complex **1** and intermediate **IV** are involved in a similar dynamic acid−base equilibrium, where H_a and H_b scramble rapidly on the ^1H NMR time scale.

When the structural features of the different vinyl alcohol complexes and their acid−base properties in solution are compared, a trend of stability can be clearly seen. While the η^2-vinyl alcohol is stabilized in the five-coordinate Pt^{II} complex[16] by strong π back-donation, the neutral vinyl alcohol complex $[PtCl(acac)(CH_2{=}CHOH)]$ behaves as a weak Brønsted acid (pK_a = 3.5) in aqueous solution.[13] The dimeric platina-acetaldehyde Pt^{III} complex[14] (cf. Table 1) was isolated from strongly acidic solution. Therefore, even stronger Brønsted acidity of the corresponding vinyl alcohol Pt^{III} complex is expected. Similarly, intermediate **IV** should also display a relatively high acidity due to the high positive complex charge, and the equilibrium lies far on the side of complex **1**. This may explain the generally low stability of **IV** and the failure to isolate it.

By addition of Na_2CO_3 to the mixture of complex **1** and $HBF_4{\cdot}Et_2O$ the equilibrium was immediately shifted back to the pure form of complex **1**. The ^1H NMR spectrum of this solution showed the restored signals for complex **1**. The similar conversion of five-coordinate vinyl alcohol Pt^{II} π complexes to the corresponding square-planar platina-acetaldehyde σ complexes by addition of KOH was demonstrated by Panunzi[16a] and De Felice[16b] previously.

While the addition of HCl to those square-planar platina-acetaldehyde σ complexes regenerated the corresponding five-coordinate vinyl alcohol Pt^{II} π complexes,[15] the addition of HCl to complex **1** resulted in the formation of $[Pt(PNP)Cl]^+$ and acetaldehyde (eq 2). This reaction is fast and complete after



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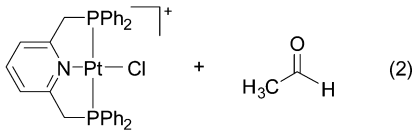


(2)

mixing (<1 min). In the ^{31}P NMR spectrum a signal appears at δ 21.5 which is similar to that of the iodo complex $[Pt(PNP)I]^+$ (cf. Table 3), and in the ^1H NMR spectrum a quartet at δ 9.73 and a doublet at δ 2.19 with $^3J_{H-H}$ = 2.7 Hz are observed, which are in agreement with the signals of free acetaldehyde.

Since the ^1H NMR spectra of the mixture of complex **1** with $HBF_4{\cdot}Et_2O$ are more or less obscured by large signals of the diethyl ether, we decided to study the acid−base equilibrium of complex **1** by ^{31}P NMR. This should better show how many different Pt(PNP) species are actually present in solution. ^{31}P NMR spectra were recorded upon subsequent addition of 5−200 μL of $HBF_4{\cdot}Et_2O$ to a solution of complex **1** in CD_2Cl_2 (see Figure S4 in the Supporting Information). After addition of 5 μL of $HBF_4{\cdot}Et_2O$ the signal of complex **1** at δ 27.6 disappeared and two new characteristic signals at δ 34.0 ($^1J_{P-Pt}$ = 2487 Hz) and δ 29.4 ($^1J_{P-Pt}$ = 2531 Hz) were observed in a ratio of 3:2. After addition of further portions of $HBF_4{\cdot}Et_2O$ the signal at δ 34.0 remained unchanged while the second signal shifted slightly downfield and changed its intensity relative to the first signal. At 35 μL of $HBF_4{\cdot}Et_2O$ the two species are almost equally abundant, and at 200 μL of $HBF_4{\cdot}Et_2O$ the second signal was observed at δ 30.2 with a decreased intensity. A third small signal at δ 21.3 ($^1J_{P-Pt}$ = 2554 Hz) appeared at 20 μL of $HBF_4{\cdot}Et_2O$ which increased in intensity with an increasing amount of $HBF_4{\cdot}Et_2O$. In order to attempt an assignment for the observed signals, the ^{31}P NMR data were compared with those of known Pt(PNP) complexes.[9,20] In Table 3 the ^{31}P NMR chemical shifts and corresponding $^{31}P-^{195}Pt$ coupling constants are given. A plot of these data is shown in Figure S5 (Supporting Information), visualizing the individual complex types.

dx.doi.org/10.1021/om2007908 | Organometallics 2011, 30, 6446−6457

Table 3. ^{31}P NMR Data for $[Pt(PNP)R]^{n+}$ Complexes (δ in ppm, J in Hz)

$[Pt(PNP)X]^{n+}$	δ	$^1J_{P-Pt}$	solvent	ref
$[Pt(PNP)(CH_2{=}CH_2)]^{2+}$	41.7	2174	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2{=}CHMe)]^{2+}$	40.8	2268	CD_2Cl_2	*b*
$[Pt(PNP)(norbornene)]^{2+}$	40.7	2177	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2{=}CHEt)]^{2+}$	39.3	2236	CD_2Cl_2/ CD_3NO_2	*b*
$[Pt(PNP)(CH_2{=}CHPh)]^{2+}$	38.2	2328	CD_2Cl_2	*c*
$[Pt(PNP)(CH_2{=}CHNaph)]^{2+}$	37.1	2330	CD_2Cl_2	
*$[Pt(PNP)(HC{\equiv}CH)]^{2+}$ (**I**)*[a]	*34.0*	*2432*	CD_2Cl_2	*d*
*Intermediates **II**–**IV***[a]	*29.4–30.2*	*2531*	CD_2Cl_2	*d*
$[Pt(PNP)(CH_2CHPhNHPh)]^+$	32.8	3003	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CHNaphOMe)]^+$	31.1	3055	CD_3OD	
$[Pt(PNP)(CH_2CHPhOH)]^+$	31.0	3052	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CHPhOMe)]^+$	30.3	3110	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CH_2OMe)]^+$	29.9	3020	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CHPhOEt)]^+$	29.7	3077	EtOH	*c*
$[Pt(PNP)(CH_2CHMeOH)]^+$	29.4	3033	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CHMeNHPh)]^+$	29.4	3060	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CH_2NHC_6H_4Cl\text{-}o)]^+$	29.1	2997	CD_2Cl_2	*b*
$[Pt(PNP)(CH_2CH_2NHC_6H_4Me\text{-}p)]^+$	29.1	3029	CD_2Cl_2	*b*
$[Pt(PNP)\{CH(CH_2CH_2CH_3)C(O)CH_3\}]^+$ (**7b**)	29.4	3026	CD_2Cl_2	*d*
$[Pt(PNP)\{CH(CH_3)C(O)CH_2CH_2CH_3\}]^+$ (**7a**)	28.9	3031	CD_2Cl_2	*d*
$[Pt(PNP)\{CH(CH_3)C(O)CH_3\}]^+$ (**6**)	28.7	3006	CD_2Cl_2	*d*
$[Pt(PNP)\{CH_2C(O)CH_2CH_2CH_2CH_3\}]^+$ (**3a**)	28.2	2866	CD_2Cl_2	*d*
$[Pt(PNP)\{CH_2C(O)CH_3\}]^+$ (**2a**)	28.1	2851	CD_2Cl_2	*d*
$[Pt(PNP)(CH_2CHO)]^+$ (**1**)	27.6	2781	CD_2Cl_2	*d*
$[Pt(PNP)(E\text{-}CH{=}CHPh)]^+$	27.1	2922	CD_3OD	*c*
$[Pt(PNP)(E\text{-}CH{=}CHNaph)]^+$	26.9	2929	CD_3OD	*c*
$[Pt(PNP)(C{\equiv}CPh)]^+$ (**4**)	22.5	2576	CD_2Cl_2	*d*
$[Pt(PNP)(C{\equiv}Ct\text{-}Bu)]^+$ (**5**)	20.2	2617	CD_2Cl_2	*d*
$[Pt(PNP)\{C(O)CH_2CH_3\}]^+$ (**2b**)	20.8	3252	CD_2Cl_2	*d*
$[Pt(PNP)\{C(O)CH_2CH_2CH_2CH_2CH_3\}]^+$ (**3b**)	20.5	3271	CD_2Cl_2	*d*
$[Pt(PNP)I]^+$	24.7	2487	$CDCl_3$	*e*
$[Pt(PNP)Cl]^+$	21.5	2554	CD_2Cl_2	*d*
$[Pt(PNP)(BF_4)]^+$	21.3	2554	CD_2Cl_2	*d*

[a]Assumed species, see text and Scheme 3. [b]Reference 9. [c]Reference 20. [d]This work. [e]^{31}P NMR data not given in ref 9, only here.

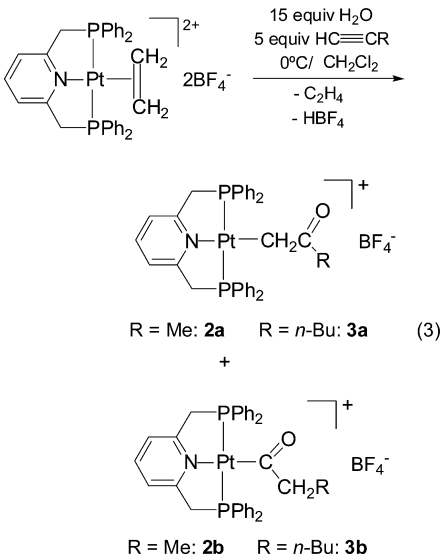
The first signal at δ 34.0 might be assigned to the dicationic acetylene complex **I**. The chemical shift and the ^{31}P–^{195}Pt coupling constant are similar to those observed for the dicationic alkene complexes (Table 3, Figure S5). Also the fact that the chemical shift of this signal is not affected by the concentration of HBF_4 in solution supports the assignment.

Instead, the second signal could be assigned to the blend of enol species **II**–**IV** being involved in the acid–base equilibrium with complex **1**. This is supported by the observed downfield shift upon addition of increasing amounts of HBF_4. It is also in agreement with the changes which could be observed in the ^{1}H NMR spectrum. The chemical shift and the ^{31}P–^{195}Pt coupling constant of this signal are between those for complex **1** and dicationic π complexes (cf. Table 3 and Figure S5).

The third signal at δ 21.3 which appeared only at higher concentrations of HBF_4 could be assigned to the tetrafluoroborato complex $[Pt(PNP)(BF_4)]^+$. Due to the relatively high concentration of BF_4^- ions in solution the otherwise only weakly coordinating anion may be able to bind at the platinum center in an equilibrium reaction. This ^{31}P NMR signal was also observed when a large excess of $HBF_4{\cdot}Et_2O$ was added to a dichloromethane solution of the ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$.

In another experiment ethylene was bubbled through a solution of complex **1** containing 200 equiv of $HBF_4{\cdot}Et_2O$ and a ^{31}P NMR spectrum was recorded (see Figure S4 in the Supporting Information). This spectrum showed a new signal at δ 39.6 ($^1J_{P-Pt}$ = 2174 Hz) which could be assigned to the ethylene complex $[Pt(PNP)(C_2H_4)]^{2+}$. While the signal at δ 34.0 strongly decreased in intensity, the signal at δ 30.2 was not visibly affected and became the most intense peak in the spectrum. This can be interpreted by the substitution of the acetylene by an ethylene molecule.

Reaction of $[Pt(PNP)(C_2H_4)](BF_4)_2$ with Terminal Alkynes and Water. The reaction of $[Pt(PNP)(C_2H_4)](BF_4)_2$ with terminal alkynes (propyne and 1-hexyne) and water gave mixtures of the ketonyl and acyl complexes $[Pt(PNP)\{CH_2C(O)R\}]BF_4$ (**2a**, **3a**) and $[Pt(PNP)\{C(O)CH_2R\}]BF_4$ (**2b**, **3b**) (R = Me, **2a**,**b**; R = *n*-Bu, **3a**,**b**); cf. eq 3.



The isomeric mixtures **2a**,**b** and **3a**,**b** were isolated in good yields with a ketonyl/acyl ratio of about 1/4, respectively. The terminal alkynes were somewhat less reactive than the acetylene. Therefore, the reaction was performed at 0 °C using 5 equiv of alkyne (cf. the Experimental Section).

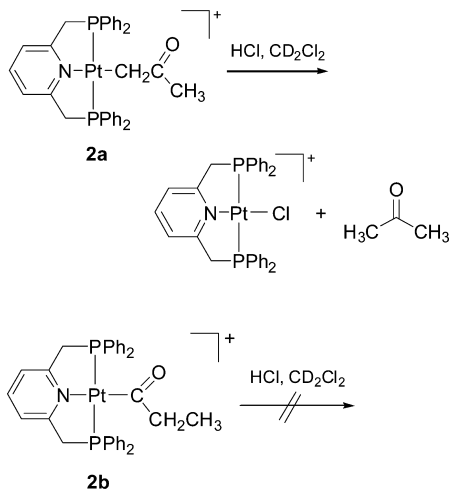
The respective complex mixtures **2a**,**b** and **3a**,**b** were characterized by IR and NMR spectroscopy. In the IR spectrum of **2a**,**b** two C=O stretching bands at $\tilde{\nu}$ 1626 and 1639 cm^{-1} were observed. Similar wavenumbers were reported for other ketonyl[21] and acyl[22] Pt^{II} complexes. The ^{1}H NMR spectrum of **2a**,**b** correspondingly showed two sets of signals. For the acetonyl complex **2a** a singlet for the methyl group appeared at δ 1.28, and the triplet at δ 2.94 with characteristic platinum satellites could be assigned to the $PtCH_2$ group. A triplet at δ 0.55 and a quartet at δ 2.09 were due to the ethyl group of the acyl complex **2b**. The ^{13}C NMR spectrum showed two signals at δ 214.6 and 219.1 for the two different carbonyl groups in **2a**,**b**, respectively. In the ^{31}P NMR spectrum two signals at δ 28.1 and δ 20.8 appeared in a ratio of 1:4. The first signal had a chemical shift and ^{31}P–^{195}Pt coupling constant similar to those observed for the platina-acetaldehyde complex **1** (cf. Table 3) and therefore could be assigned to the β-ketonyl complex **2a**. However, the signal for the acyl complex **2b** was

dx.doi.org/10.1021/om2007908|*Organometallics* 2011, 30, 6446–6457

shifted more upfield and displayed a considerably larger $^{31}P-^{195}Pt$ coupling constant (cf. Table 3 and Figure S5). For the complex mixture **3a,b** similar NMR data were obtained (see the Experimental Section).

Further structural evidence for the acetonyl complex **2a** was provided by protonolysis, whereby acetone was released upon addition of concentrated HCl (cf. Scheme 4). The ^1H NMR

Scheme 4. Protonolysis of the Complex Mixture 2a,b by HCl



spectrum of a solution of **2a,b** in CD_2Cl_2 with added HCl showed a singlet at δ 2.16 which can be assigned to acetone. However, all ^1H NMR signals of **2b** appeared the same as described above. The ^{31}P NMR spectrum showed the signal of $[Pt(PNP)Cl]^+$ at δ 21.4, while the second signal at δ 21.7 ($^1J_{P-Pt}$ = 3217 Hz) could be assigned to complex **2b** (cf. Table 3). The NMR signals of complex **2b** in the HCl-containing solution remained unchanged over at least 1 day. The inertness to protonolysis reflects the relatively strong Pt–C bond in **2b**, which is much less polar than that in **2a**.

The complex mixture **2a,b** was recrystallized, and single crystals suitable for X-ray structure analysis were obtained. The crystal that was picked up was the anti-Markovnikov product **2b**. An ORTEP drawing of the complex cation of **2b** is shown in Figure 2. The ethyl group of the acyl ligand is disordered, and only one of the most probable positions of C34 and C35 is depicted in Figure 2.[23] The Pt–C33 bond length of 2.002(10) Å is in the range (1.97–2.10 Å) found for other acyl complexes.[24]

In contrast to the terminal alkynes described above, phenyl- and *tert*-butylacetylene do not add water to the coordinated C–C triple bond under the same conditions. Instead, C–H bond activation occurred and the corresponding alkynyl complexes **4** and **5** were formed (eq 4), which were isolated in good yield as stable compounds. The IR spectrum showed a characteristic stretching band for the C–C triple bond at $\tilde{\nu}$ 2125 and 2123 cm^{-1} for the phenyl and *tert*-butyl derivatives **4** and **5**, respectively. Similar wavenumbers were reported for other platinum(II) alkynyl complexes.[22a,25] The ^1H NMR spectra of **4** and **5** showed the corresponding signals for the phenyl and the *tert*-butyl group (see the Experimental Section). The ^{13}C NMR signals for the alkynyl carbon atoms in complexes **4** and **5** are observed at δ 75.9 and 59.2 for C_α and δ 114.5 and 124.5 for C_β, respectively. The $^{13}C-^{195}Pt$ coupling constants are greater than those observed for the neutral bis-alkynyl platinum(II) complexes *trans*-$[Pt\{P(n\text{-}Bu)_3\}_2(C{\equiv}CAr)_2]$: $^1J_{C-Pt}$ by ~300 Hz

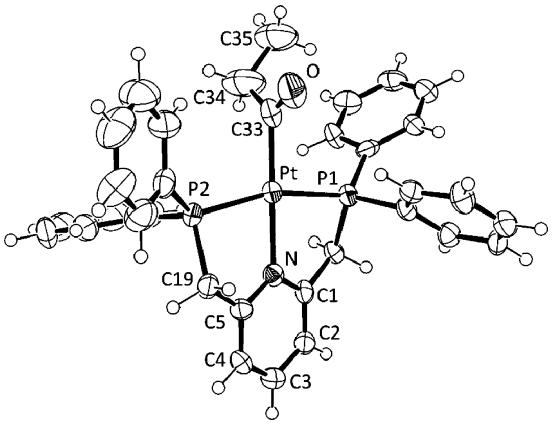
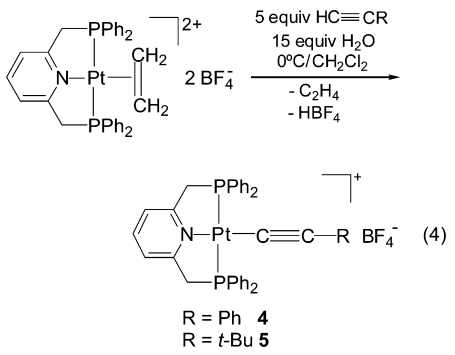


Figure 2. ORTEP drawing of the complex cation **2b**.[23] Selected bond lengths (Å) and angles (deg): Pt–P1 = 2.279(2), Pt–P2 = 2.284(3), Pt–N = 2.131(8), Pt–C33 = 2.002(10), C33–C34 = 1.5001(11), C34–C35 = 1.5000(11), C33–O = 1.200(15); P1–Pt–P2 = 163.61(9), N–Pt–P1 = 82.2(2), N–Pt–P2 = 81.4(2), N–Pt–C1 = 178.0(4), C1–Pt–P1 = 96.4(3), C1–Pt–P2 = 99.9(3), Pt–C33–C34 = 117.1(10), C34–C33–O = 121.6(13), C33–C34–C35 = 109.78(11).



and $^2J_{C-Pt}$ by ~100 Hz[26] (cf. the Experimental Section). For complex **4** a ^{31}P NMR signal is observed at δ 22.5 and for complex **5** at δ 20.2.

With these different terminal alkynes three possible reaction pathways in the presence of water have been demonstrated, which are summarized in Scheme 5. The reaction paths are very similar to those described earlier by Chisholm and Clark[27] and Belluco[28] for the reaction of monocationic Pt^{II} alkyne complexes with methanol. The way the coordinated terminal alkyne may react depends on several parameters, such as electronic conditions at the metal center, solvent, and the substituent at the alkyne.

In each case the dicationic alkyne complex **V** was generated in situ by substitution of ethylene (cf. Scheme 5). If the substituent at the terminal alkyne is small or less bulky (R = Me, *n*-Bu), the substituted carbon atom can be attacked by a water molecule, presumably giving the η^1-enol intermediate **VI**, which tautomerizes to the ketonyl complex (**2a**, **3a**: Markovnikov products).

However, in the case of propyne and 1-hexyne the 1,2-hydride shift is a more competitive path where either the carbocationic intermediate **VII** or the η^1-vinylidene species **VIII** is thought to be formed. In any resonance structure between **VII** and **VIII** the α-carbon atom is the electrophilic center and is attacked by the water molecule. This leads to the formation of an α-hydroxyalkenyl or an α-hydroxycarbene

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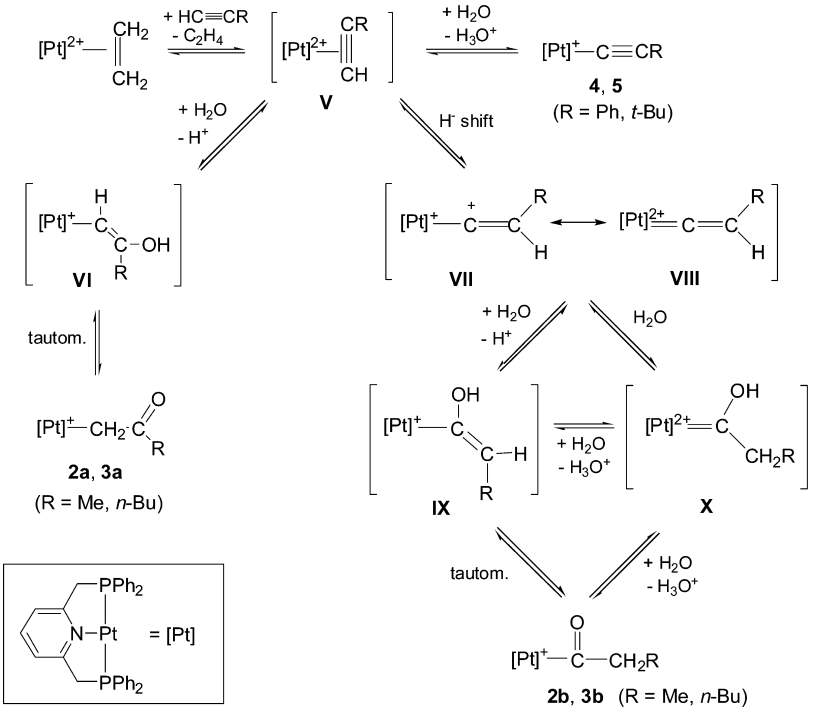
Scheme 5. Summary of the Reactions of $[Pt(PNP)(HC{\equiv}CR)]^{2+}$ with Water



complex (**IX** or **X**) which tautomerizes to the acyl complex (**2b**, **3b**: anti-Markovnikov products).

In the case of terminal alkynes with more bulky substituents (R = Ph, *t*-Bu) the rearrangement to alkynyl complexes (**4**, **5**) by proton dissociation is the preferred path, where water acts as a Brønsted base. Probably the water addition is kinetically inhibited due to steric hindrance. In addition, the alkynyl complexes **4** and **5** may be thermodynamically the most stable species in the equilibrium system. For the phenyl derivative **4** π conjugation may in addition contribute to the higher stability. This is similar to the case for the alkene complexes $[Pt(PNP)(CH_2{=}CHR)]^{2+}$ (R = Ar), where vinylic deprotonation is preferred over nucleophilic addition of water or alcohols, forming the very stable alkenyl complexes $[Pt(PNP)((E)\text{-}CH{=}CHR)]^{+}$.[20]

The suggested structures of the intermediates **V**–**X** are all supported by results reported for closely related reactions with platinum and other transition-metal complexes.[27−42] Isolated Pt^{II} complexes with terminal alkynes are extremely rare.[29,30] The coordinated terminal alkyne is only reasonably stabilized in electron-rich complexes, which are either anionic[29] or five-coordinate.[30] In contrast, the dicationic alkyne complex **V** cannot be easily trapped or detected, due to its high electrophilicity, and reacts instantly either with a nucleophile or rearranges upon its formation. Chisholm and Clark noted that they were also not able to isolate monocationic Pt^{II} complexes of terminal alkynes but have suggested them as reactive intermediates.[27]

Similar to the first path (cf. Scheme 5), Markovnikov addition of water to a series of terminal alkynes was observed with the dimeric Pt^{III} complex $[Pt^{III}_2(NH_3)_4\{(CH_3)_3CCONH\}_2(NO_3)_2](NO_3)_2$, and the corresponding ketonyl complexes were formed.[31] In analogy to the η^1-enol intermediate **VI**, η^1-vinyl ether complexes $[(CO)(PPh_3)_2Pt\{CH{=}CR(OR')\}]BF_4$ were isolated as a result of alcohol addition to the coordinated alkyne which, in contrast to the enol **VI**, cannot further tautomerize.[32]

The acyl complexes **2b** and **3b** seem to represent the first examples for anti-Markovnikov addition of water to terminal alkynes promoted by platinum(II). Although no catalytic anti-Markovnikov hydration of terminal alkynes has been observed with any platinum catalyst, the formation of **2b** and **3b** is not so unusual with respect to earlier studies with monocationic Pt^{II} alkyne complexes.[27,28,32−35] Chisholm and Clark have suggested a 1,2-hydride shift of terminal alkynes giving an α-carbocationic intermediate such as **VII** to explain the methanol addition at the α-carbon atom.[27] Later Belluco et al.[35] were able to detect the η^1-vinylidene complexes $[(CH_3)(PPh_3)_2Pt(=C{=}CHR)]X$ in solution by NMR spectroscopy at low temperature; these were generated by protonation of the corresponding alkynyl complexes. This may support the proposed η^1-vinylidene species **VIII**. Whether the α-hydroxyalkenyl species **IX** or the α-hydroxycarbene complex **X** is formed is unknown. Analogous monocationic α-alkoxycarbene Pt^{II} complexes were prepared by alcohol addition to a coordinated terminal alkyne and were isolated and structurally characterized.[33,34,36] The β-proton in the monocationic α-alkoxycarbene Pt^{II} complexes is found to be relatively acidic and can be removed by a base.[34] In the proposed dicationic α-hydroxycarbene complex **X** the acidity of the β-proton might be enhanced due to the higher positive complex charge and the equilibrium may probably be shifted more to the side of the α-hydroxyalkenyl species **IX**. While no stable α-hydroxycarbene complexes of platinum(II) have been isolated (with the exception of dimeric acyl hydroxycarbene Pt^{II} complexes reported by Steinborn and co-workers),[37] those of rhenium[38] and other transition metals[39] are well-known, which can be generated by protonation of corresponding acyl complexes. The latter reaction would exhibit the reverse reaction to the formation of acyl complexes **2b** and **3b** from intermediate **X**.

dx.doi.org/10.1021/om2007908|*Organometallics* 2011, 30, 6446−6457

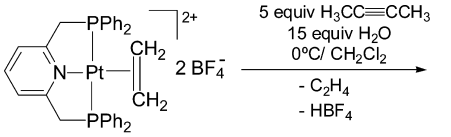
Studies by Michelin and co-workers have demonstrated the addition of water to a cationic η^1-vinylidene complex, forming the α-hydroxycarbene Pt^{II} complex $[(CH_3)Pt(PPh_3)_2\{=C(OH)\text{-}CH_2R\}]^+$, which was spectroscopically observed only in solution.[35] The α-hydroxycarbene Pt^{II} complex was found to be unstable, and one of the decomposition paths is C−C bond cleavage resulting in the corresponding carbonyl complex and a hydrocarbon due to the highly polarized C_α−C_β bond. A similar reaction path was observed by Bianchini et al., studying the mechanism of the ruthenium-catalyzed anti-Markovnikov addition of water to terminal alkynes in detail.[40] However, the acyl complexes **2b** and **3b** are stable even under acidic conditions (see above) and do not decompose at room temperature.

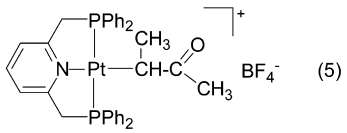
Further examples for simultaneous Markovnikov and anti-Markovnikov addition of water to ruthenium alkynyl complexes yielding a mixture of both ketonyl and acyl complexes were reported by Onishi and co-workers.[41]

The conditions for a 1,2-hydride shift vs the formation of alkynyl complexes from Pt^{II} complexes with terminal alkynes vary, depending on the particular nature of the respective complexes. For monocationic Pt^{II} alkyne complexes proton dissociation is preferred over a 1,2-hydride shift when a polar aprotic solvent instead of a protic solvent is used.[27] In the case of five-coordinate Pt^{II} complexes oxidative addition of the terminal alkyne is observed upon heating, giving the corresponding hydrido alkynyl Pt^{IV} complexes.[30] So far it is known for the dicationic Pt^{II} alkyne complexes **V** that the nature of the substituent at the terminal alkyne determines whether the proton dissociation or 1,2-hydride shift reaction path is preferred. Other conditions remain to be explored.

Notable are the studies by Ogo and Fukuzumi where it was shown that with a water-soluble iridium(III) complex all three pathways can be tuned by adjustment of the pH of the aqueous solution. Depending on the pH alkynyl, ketonyl, or acyl complexes could be generated from a phenylacetylene Ir^{III} complex.[42]

Reaction of $[Pt(PNP)(C_2H_4)](BF_4)_2$ with Internal Alkynes and Water. Furthermore, internal alkynes (2-butyne and 2-hexyne) were reacted with $[Pt(PNP)(C_2H_4)](BF_4)_2$ in the presence of 15 equiv of water under conditions similar to those described above for the reactions with the terminal alkynes (eqs 5 and 6). The reaction with 2-butyne gave the

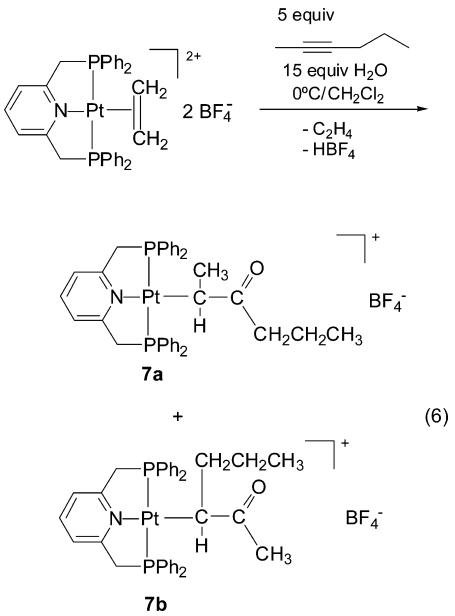




(5)

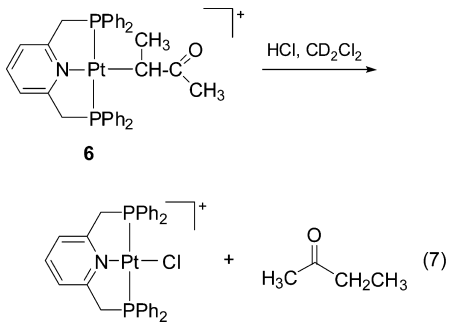
6

corresponding ketonyl complex **6**, which was isolated in 85% yield. With 2-hexyne the two regioisomers **7a**,**b** in a ratio of 4/1 were formed, and the isomeric mixture was isolated in 89% yield. The isomer **7a** is more abundant due to less steric interaction of the α-methyl group with the phenyl groups of the PNP ligand in comparison to the other isomer **7b**, having a longer substituent at the α-carbon atom.



The ketonyl complexes **6** and **7a**,**b** were analyzed by ^1H, ^{13}C, and ^{31}P NMR spectroscopy.

The ^1H NMR spectrum of **6** shows the characteristic signals for the butanonyl group: a doublet at δ 0.85 and a singlet at δ 1.48 for the two different methyl groups with platinum satellites of 50.5 and 11.0 Hz, respectively. A quartet for the α-proton at δ 3.28 appears with platinum satellites of 117 Hz. In the ^{13}C NMR spectrum the signal at δ 212.1 can be assigned to the carbonyl group. The ^{31}P NMR spectrum shows a signal at δ 28.7. Further structural evidence for the ketonyl complex **6** is provided by treatment of a solution of this complex in CD_2Cl_2 with concentrated HCl (eq 7). In the ^1H NMR spectrum the



signals at δ 1.05 (triplet), 2.14 (singlet), and 2.46 (quartet) are in agreement with 2-butanone. In the ^{31}P NMR a signal appears for $[Pt(PNP)Cl]^+$ at δ 21.4.

The isolated ketonyl complexes **7a**,**b** were characterized as a product mixture. The presence of two different isomers can be easily identified in the ^{31}P NMR spectrum, where two signals at δ 28.9 (**7a**) and δ 29.4 (**7b**) appear in a ratio of 4:1. In the ^1H NMR spectrum a set of signals can be unambiguously assigned to the major isomer **7a**, while the signals for the minor isomer **7b** are partially overlapped by those of **7a** (see the Experimental Section). The signal set for the organic moiety of **7a** consists of a multiplet at δ 3.35 with platinum satellites of 148 Hz for the PtCH group and a doublet at δ 0.88 for the α-methyl group. Further signals in the region δ 0.5−2.0 belong to the *n*-propyl group in **7a**. In the ^{13}C NMR spectrum for each isomer a set of signals could be assigned (see the Experimental Section).

dx.doi.org/10.1021/om2007908 | *Organometallics* 2011, 30, 6446−6457

The signals for the carbonyl groups appear at δ 215.5 for **7a** and at δ 212.0 for **7b**.

Most likely as a result of steric interaction with the PNP ligand the regioselectivity of the water addition to 2-hexyne is slightly improved in favor of the 3-hexanonyl derivative **7a** in comparison to the catalytic hydration of 2-hexyne by Zeise's dimer or other Pt^{II} salts, where 3-hexanone and 2-hexanone were obtained in a ratio of about 2/1.[3]

CONCLUSION

With these studies it has been shown that dicationic Pt^{II} alkyne complexes can be generated by facile displacement of the ethylene ligand in $[Pt(PNP)(C_2H_4)]^{2+}$(cf. eq 1 and Scheme 5). However, the dicationic alkyne complexes are too reactive and therefore could not be isolated. The alkyne complexes readily add water under very mild conditions in a relatively short reaction time (eqs 1, 3, 5, and 6). In the case of terminal alkynes three different reaction paths were observed, depending on the substituent at the alkyne (cf. Scheme 5). With less bulky substituents ketonyl and acyl complexes were obtained (i.e., Markovnikov and anti-Markovnikov products) in a ratio of 1/4 (eq 3), while for terminal alkynes with more bulky substituents no water addition was observed. Instead alkynyl complexes were formed by proton dissociation (eq 4). Internal alkynes reacted by water addition and formation of the corresponding ketonyl complexes (eqs 5 and 6). In the case of an unsymmetrical alkyne moderate regioselectivity was observed in favor of the isomer where the carbonyl function is located at the carbon atom bearing the longer substituent (eq 6).

Studies are in progress addressing the isolation or detection of dicationic alkyne and vinylidene Pt(PNP) complexes. Also, other parameters such as solvent effects influencing the anti-Markovnikov selectivity as well as conditions for a catalytic alkyne hydration are of further interest.

EXPERIMENTAL SECTION

General Considerations. The ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$ was prepared as described previsously.[9] All reactions were performed under an argon atmosphere. Atomic absorption grade acetylene (dissolved) was used. The other alkynes were received from Aldrich and were 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 were distilled before use. The IR spectra were recorded as neat solids on an FT Perkin-Elmer instrument. The elemental analyses were performed by Columbia Analytical Services, Tuscon, AZ. The NMR spectra were recorded on Bruker 250, 400, and 500 MHz (cryoprobe) instruments. The ^{1}H NMR shifts were referenced to the resonance of the residual protons. The ^{31}P NMR shifts were referenced to an external 85% H_3PO_4 standard. The following abbreviations were used for NMR signals: s, singlet; d, doublet; t, triplet; ps t, pseudotriplet; q, quartet, m, multiplet.

X-ray Structure Determination of $[Pt(PNP)(CH_2CHO)]BF_4$ (1) and $[Pt(PNP)\{C(O)CH_2CH_3\}]BF_4\cdot 0.5CH_2Cl_2$ (2b)[43−45]. Details of the X-ray experiments, data collection and reduction, and final structure refinement calculations for complexes **1** and **2b** are summarized in Table S8 (Supporting Information). Crystals of complexes **1** and **2b** were grown from CH_2Cl_2 solution by diffusion with diethyl ether over several days at room temperature. Suitable crystals were respectively selected and fixed to a nylon loop or a cactus needle, which in turn was attached to a copper mounting pin. The mounted crystals were then placed under a cold nitrogen stream (Oxford) maintained at 110 K. A Bruker SMART 1000 three-circle X-ray diffractometer with graphite-monochromated Cu Kα (λ = 1.541 84 Å, 40 kV, 40 mA) and Mo Kα radiation (λ = 0.70173 Å, 50 kV, 40 mA) were employed for sample screening and data collection, respectively, for complexes **1** and **2b**. 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. Suitable cells were found and refined by nonlinear least-squares and Bravais lattice procedures and are reported in Table S8 (Supporting Information). The standard data collection procedure consists of the collection of one hemisphere of data collected using ω scans, involving 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 for a duration of approximately 25 h at 110 K. All non-hydrogen atoms of the asymmetric unit were refined with anisotropic displacement parameters. All hydrogen atoms were calculated in ideal positions. In the structure of complex **2b** disorder was found for the ethyl group in the acyl ligand and the solvent molecule (CH_2Cl_2). The ethyl group is disordered over the two most probable positions C34−C35 and C34′−C35′ with relative occupancies of 76.1 and 23.9%, respectively. The molecule of CH_2Cl_2 has full occupancy of 50%. In that molecule one of the chlorine atoms is disordered over the two most probable positions Cl(2) and Cl(2′) with occupancies of 31.7 and 18.3%. Bond restraints and distances were applied to model the disorder.

General Procedure for the Synthesis of Complexes 1−7. The ethylene complex $[Pt(PNP)(C_2H_4)](BF_4)_2$ (300 mg, 0.344 mmol) was dissolved in 100 mL of CH_2Cl_2, and the solution was cooled to −78 °C (when reacted with acetylene) or 0 °C (for all other alkynes). Fifteen equivalents of water (93 μL, 5.2 mmol) was added to the cold solution. Then, 3 equiv of acetylene (24 mL, 1.0 mmol) or 5 equiv of the substituted alkyne was added. The mixture was stirred for 15 min at the respective temperature. The cooling bath was removed, and the reaction solution was warmed to room temperature. The volume of the solution was reduced to 10 mL, and the product was precipitated with 100 mL of diethyl ether. The product was filtered off, washed with diethyl ether, and dried under vacuum. For further purification the product was recrystallized by dissolution in CH_2Cl_2 and precipitation with diethyl ether.

$[Pt(PNP)(CH_2CHO)]BF_4$ (1). Yield: 226 mg (0.282 mmol, 82%). Mp: 239 °C dec. Anal. Calcd for $C_{33}H_{30}BF_4NOP_2Pt$: C, 49.52; H, 3.78; N, 1.75. Found: C, 49.11; H, 3.37; N, 1.72. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 2.94 (dt, 2H, $^3J_{H-H}$ = 5.5 Hz, $^3J_{H-P}$ = 5.5 Hz, $^2J_{H-Pt}$ = 108 Hz, $PtCH_2$), 4.49 (ps t, 4H, $^{2+4}J_{H-P}$ = 4.7 Hz, PCH_2), 7.45−8.21 (m, 23H, Ph, py), 8.95 (t, 1H, $^3J_{H-H}$ = 5.5 Hz, CHO). ^{13}C NMR (62.89 MHz, CD_2Cl_2): δ 16.9 (t, $^2J_{C-P}$ < 3 Hz, $^1J_{C-Pt}$ = 530 Hz, $PtCH_2$), 45.5 (ps t, $^{1+3}J_{C-P}$ = 16.9 Hz, PCH_2), 123.3 (ps t, $^{3+5}J_{C-P}$ = 5.5 Hz, 3,5-py), 126.2 (ps t, $^{1+3}J_{C-P}$ = 29.0 Hz, Ph_i), 129.7 (ps t, $^{3+5}J_{C-P}$ = 5.7 Hz, Ph_m), 132.6 (s, Ph_p), 133.2 (ps t, $^{2+4}J_{C-P}$ = 6.9 Hz, Ph_o), 140.9 (s, 4-py), 160.0 (ps t, $^{2+4}J_{C-P}$ = 3.1 Hz, 2,6-py), 201.7 (t, $^3J_{C-P}$ = 3.0 Hz, $^2J_{C-Pt}$ = 54 Hz, CHO). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 27.6 ($^1J_{P-Pt}$ = 2781 Hz). IR $\tilde{\nu}$ (cm^{-1}): 1052 (vs, BF_4), 1671 (m, C═O), 2721 (w, CHO).

$[Pt(PNP)\{CH_2C(O)CH_3\}]BF_4$ (2a) and $[Pt(PNP)\{C(O)CH_2CH_3\}]BF_4$ (2b). Yield (combined): 220 mg (0.270 mmol, 78%). Anal. Calcd for $C_{34}H_{32}BF_4NOP_2Pt\cdot(CH_3CH_2)_2O$: C, 51.36; H, 4.76; N, 1.58. Found: C, 51.13; H, 5.10; N, 1.76. ^{1}H NMR (250 MHz, CD_2Cl_2): **2a**, δ 1.28 (s, 3H, $^4J_{H-Pt}$ = 7.0 Hz, CH_3), 2.94 (t, 2H, $^3J_{H-P}$ = 6.2 Hz, $^2J_{H-Pt}$ = 109 Hz, $PtCH_2$), 4.48 (ps t, 4H, $^{2+4}J_{H-P}$ = 4.7 Hz, PCH_2), 7.55−7.66 (m, 12H, Ph), 7.69−7.81 (m, 10H, Ph, 3,5-py), 8.06 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, 4-py); **2b**, δ 0.55 (t, 3H, $^3J_{H-H}$ = 7.4 Hz, CH_3), 2.09 (q, 2H, $^3J_{H-H}$ = 7.3 Hz, CH_2), 4.54 (ps t, 4H, $^{2+4}J_{H-P}$ = 5.0 Hz, PCH_2), 7.55−7.66 (m, 12H, Ph), 7.69−7.81 (m, 10H, Ph, 3,5-py), 8.06 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, 4-py). ^{13}C NMR (100.61 MHz, CD_2Cl_2): **2a**, δ 14.8 (t, $^2J_{C-P}$ = 4.0 Hz, $PtCH_2$), 29.9 (s, CH_3), 45.8 (ps t, $^{1+3}J_{C-P}$ = 17.2 Hz, PCH_2), 123.2 (ps t, $^{3+5}J_{C-P}$ = 5.5 Hz, 3,5-py), 126.2 (ps t, $^{1+3}J_{C-P}$ = 29.5 Hz, Ph_i), 129.5 (ps t, $^{3+5}J_{C-P}$ = 5.6 Hz, Ph_m), 132.5 (s, Ph_p), 133.3 (ps t, $^{2+4}J_{C-P}$ = 6.7 Hz, Ph_o), 140.7 (s, 4-py), 160.2 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, 2,6-py), 214.6 (s, C═O); **2b**, δ 7.9 (s, $^3J_{C-Pt}$ = 18 Hz, CH_3), 44.9 (pst, $^{1+3}J_{C-P}$ = 17.7 Hz, PCH_2), 51.3 (t, $^3J_{C-P}$ = 4.0 Hz, $^2J_{C-Pt}$ = 205 Hz, CH_2), 123.0 (ps t, $^{3+5}J_{C-P}$ = 5.6 Hz, 3,5-py), 127.7 (ps t, $^{1+3}J_{C-P}$ = 29.3 Hz, Ph_i), 129.5 (ps t, $^{3+5}J_{C-P}$ = 5.8 Hz, Ph_m), 132.4 (s, Ph_p), 132.9 (ps t, $^{2+4}J_{C-P}$ = 6.8 Hz, Ph_o), 141.0 (s, 4-py),

159.4 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, 2,6-py), 219.1 (t, $^{2}J_{C-P}$ = 5 Hz, C=O). ^{31}P NMR (101.25 MHz, CD_2Cl_2): **2a**, δ 28.1 (s, $^{1}J_{P-Pt}$ = 2851 Hz); **2b**, δ 20.8 (s, $^{1}J_{P-Pt}$ = 3252 Hz). IR $\tilde{\nu}$ (cm^{-1}): **2a,b**, 1626 (m, C=O), 1639 (m, C=O).

*[Pt(PNP){CH$_2$C(O)(CH$_2$)$_3$CH$_3$}]BF$_4$ (**3a**) and [Pt(PNP){C(O)-(CH$_2$)$_4$CH$_3$}]BF$_4$ (**3b**).* Yield (combined): 268 mg (0.313 mmol, 91%). Anal. Calcd for $C_{37}H_{38}BF_4NOP_2Pt\cdot(CH_3CH_2)_2O$: C, 52.91; H, 5.20; N, 1.51. Found: C, 52.52; H, 5.29; N, 1.71. ^{1}H NMR (500 MHz, CD_3NO_2): **3a**, δ ($CH_2CH_2CH_2CH_3$ are hidden under the signals of **3b**) 2.94 (t, 2H, $^{3}J_{H-P}$ = 6.3 Hz, $^{2}J_{H-Pt}$ = 110 Hz, PtCH$_2$), 4.64 (ps t, 4H, $^{2+4}J_{H-P}$ = 4.6 Hz, PCH$_2$), 7.59−7.68 (m, 12H, Ph), 7.74 (d, 2H, $^{3}J_{H-H}$ = 7.5 Hz, 3,5-py), 7.86−7.90 (m, 8H, Ph), 8.06 (t, 1H, $^{3}J_{H-H}$ = 7.5 Hz, 4-py); **3b**, δ 0.63 (t, 3H, $^{3}J_{H-H}$ = 7.3 Hz, CH$_3$), 0.76 (m, 2H, CH$_2$), 0.93 (m, 2H, CH$_2$), 1.09 (m, 2H, CH$_2$), 2.16 (t, 2H, $^{3}J_{H-H}$ = 7.5 Hz, COCH$_2$), 4.70 (ps t, 4H, $^{2+4}J_{H-P}$ = 4.8 Hz, PCH$_2$), 7.59−7.68 (m, 12H, Ph), 7.74 (d, 2H, $^{3}J_{H-H}$ = 7.5 Hz, 3,5-py), 7.86−7.90 (m, 8H, Ph), 8.06 (t, 1H, $^{3}J_{H-H}$ = 7.5 Hz, 4-py). ^{13}C NMR (100.61 MHz, CD_2Cl_2): **3a**, δ (CH$_3$ not observed or overlapped by **3b** signal at 13.6), 14.2 (s, PtCH$_2$), 22.1 (s, CH$_2$), 26.1 (s, CH$_2$), 43.1 (s, CH$_2$), 45.9 (ps t, $^{1+3}J_{C-P}$ = 16.9 Hz, PCH$_2$), 123.1 (ps t, $^{3+5}J_{C-P}$ = 5.5 Hz, 3,5-py), 126.6 (ps t, $^{2+4}J_{C-P}$ = 29.7 Hz, Ph$_i$), 129.5 (ps t, $^{3+5}J_{C-P}$ = 5.5 Hz, Ph$_m$), 132.6 (s, Ph$_p$), 133.3 (ps t, $^{2+4}J_{C-P}$ = 6.8 Hz, Ph$_o$), 140.5 (s, 4-py), 160.2 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, 2,6-py), 214.9 (s, C=O); **3b**, δ 13.6 (s, CH$_3$), 22.2 (s, CH$_2$), 23.5 (s, $^{4}J_{C-Pt}$ = 18 Hz, CH$_2$), 31.1 (s, CH$_2$), 45.1 (ps t, $^{1+3}J_{C-P}$ = 17.3 Hz, PCH$_2$), 58.3 (t, $^{3}J_{C-P}$ = 3.8 Hz, $^{2}J_{C-Pt}$ = 188 Hz, COCH$_2$), 123.0 (ps t, J_{C-P} = 5.3 Hz, 3,5-py), 127.7 (ps t, J_{C-P} = 29.0 Hz, Ph$_i$), 129.6 (ps t, $^{3+5}J_{C-P}$ = 5.7 Hz, Ph$_m$), 132.4 (s, Ph$_p$), 133.0 (ps t, $^{2+4}J_{C-P}$ = 6.8 Hz, Ph$_o$), 140.9 (s, 4-py), 159.4 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, $^{4}J_{C-Pt}$ = 33 Hz, 2,6-py), 218.1 (t, $^{2}J_{C-P}$ = 5.0 Hz, C=O). ^{31}P NMR (161.92 MHz, CD_2Cl_2): **3a**, δ 28.2 (s, $^{1}J_{P-Pt}$ = 2866 Hz); **3b**, δ 20.5 (s, $^{1}J_{P-Pt}$ = 3271 Hz).

*[Pt(PNP)(C≡CC$_6$H$_5$)]BF$_4$ (**4**).* Yield: 230 mg (0.268 mmol, 78%). Mp: 277 °C dec. Anal. Calcd for $C_{39}H_{32}BF_4NP_2Pt$: C, 54.56; H, 3.76; N, 1.63. Found: C, 53.77; H, 4.16; N, 1.65.[46] ^{1}H NMR (250 MHz, CD_2Cl_2): δ 4.63 (ps t, 4H, $^{2+4}J_{H-P}$ = 5.0 Hz, PCH$_2$), 7.08−7.23 (m, 5H, CPh), 7.54−7.63 (m, 12H, Ph), 7.84 (d, 2H, $^{3}J_{H-H}$ = 7.6 Hz, 3,5-py), 7.98−8.07 (m, 8H, Ph), 8.13 (t, 1H, $^{3}J_{H-H}$ = 7.6 Hz, 4-py). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 43.9 (ps t, $^{1+3}J_{C-P}$ = 16.9 Hz, PCH$_2$), 75.9 (t, $^{2}J_{C-P}$ = 13.5 Hz, $^{1}J_{C-Pt}$ = 1325 Hz, PtC≡C), 114.5 (t, $^{3}J_{C-P}$ = 3.0 Hz, $^{2}J_{C-Pt}$ = 372 Hz, PtC≡*C*), 123.5 (ps t, $^{3+5}J_{C-P}$ = 5.8 Hz, 3,5-py), 126.6 (s, C_6H_5), 126.9 (s, C_6H_5), 127.5 (ps t, $^{1+3}J_{C-P}$ = 30.0 Hz, Ph$_i$), 128.0 (s, C_6H_5), 129.5 (ps t, $^{3+5}J_{C-P}$ = 5.8 Hz, Ph$_m$), 131.1 (s, C_6H_5), 132.4 (s, Ph$_p$), 133.1 (ps t, $^{2+4}J_{C-P}$ = 7.0 Hz, Ph$_o$), 141.1 (s, 4-py), 161.8 (ps t, $^{2+4}J_{C-P}$ = 3.8 Hz, $^{2}J_{C-Pt}$ = 34 Hz, 2,6-py). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 22.5 (s, $^{1}J_{P-Pt}$ = 2576 Hz). IR $\tilde{\nu}$ (cm^{-1}): 1055 (vs, BF_4), 2125 (m, C≡C).

*[Pt(PNP){C≡CC(CH$_3$)$_3$}]BF$_4$ (**5**).* Yield: 222 mg (0.265 mmol, 77%). Mp 238 °C (decomposition). Anal. Calcd for $C_{37}H_{36}BF_4NP_2Pt$: C, 53.00; H, 4.33; N, 1.67. Found: C, 51.63; H, 4.28; N, 1.67.[46] ^{1}H NMR (250 MHz, CD_2Cl_2): δ 1.16 (s, 9H, C_4H_9), 4.56 (ps t, 4H, $^{2+4}J_{H-P}$ = 5.0 Hz, PCH$_2$), 7.54−7.61 (m, 12H, Ph), 7.80 (d, 2H, $^{3}J_{H-H}$ = 7.7 Hz, 3,5-py), 7.95−8.04 (m, 8H, Ph), 8.11 (t, 1H, $^{3}J_{H-H}$ = 7.7 Hz, 4-py). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 29.6 (s, $^{3}J_{C-Pt}$ = 18 Hz, *C*(CH$_3$)$_3$), 31.9 (s, C(*C*H$_3$)$_3$), 43.81 (ps t, $^{1+3}J_{C-P}$ = 16.8 Hz, PCH$_2$), 59.2 (t, $^{2}J_{C-P}$ = 16.8 Hz, $^{1}J_{C-Pt}$ = 1299 Hz, PtC≡C), 123.4 (ps t, $^{3+5}J_{C-P}$ = 5.7 Hz, 3,5-py), 124.5 (t, $^{3}J_{C-P}$ < 3 Hz, $^{2}J_{C-Pt}$ = 363 Hz, PtC≡*C*), 128.0 (ps t, $^{2+4}J_{C-P}$ = 30.0 Hz, Ph$_i$), 129.3 (ps t, $^{3+5}J_{C-P}$ = 5.8 Hz, Ph$_m$), 132.2 (s, Ph$_p$), 133.2 (ps t, J_{C-P} = 6.9 Hz, Ph$_o$), 140.8 (s, 4-py), 161.7 (ps t, $^{2+4}J_{C-P}$ = 3.7 Hz, $^{2}J_{C-Pt}$ = 38 Hz, 2,6-py). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 20.2 (s, $^{1}J_{P-Pt}$ = 2617 Hz). IR $\tilde{\nu}$ (cm^{-1}): 1051 (vs, BF_4), 2123 (w, C≡C).

*[Pt(PNP){CH(CH$_3$)C(O)CH$_3$}]BF$_4$ (**6**).* Yield: 242 mg (0.292 mmol, 85%). Mp: 244 °C dec. Anal. Calcd for $C_{35}H_{34}BF_4NOP_2Pt\cdot0.5(CH_3CH_2)_2O$: C, 51.34; H, 4.54; N, 1.62. Found: C, 51.31; H, 4.81; N, 1.72. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 0.85 (d, 3H, $^{3}J_{H-H}$ = 6.6 Hz, $^{3}J_{H-Pt}$ = 50.5 Hz, CH$_3$), 1.48 (s, 3H, $^{4}J_{H-Pt}$ = 11.0 Hz, CH$_3$), 3.28 (q, 1H, $^{3}J_{H-H}$ = 6.8 Hz, $^{2}J_{H-Pt}$ = 117 Hz, PtCH), 4.47 (m, 4H, PCH$_2$), 7.53−8.04 (m, 23H, Ph, py). ^{13}C NMR (100.62 MHz, CD_2Cl_2): δ 17.1 (s, $^{3}J_{C-Pt}$ = 34 Hz, PtCHCH$_3$), 23.1 (t, $^{2}J_{C-P}$ = 3.0 Hz, $^{1}J_{C-Pt}$ = 578 Hz, PtCH), 30.0 (s, CH$_3$), 45.8 (ps t, $^{1+3}J_{C-P}$ = 16.9 Hz, PCH$_2$), 123.2 (ps t, $^{3+5}J_{C-P}$ = 5.1 Hz, 3,5-py), 126.5 (ps t, $^{1+3}J_{C-P}$ = 28.8 Hz, Ph$_i$), 126.8 (ps t, $^{1+3}J_{C-P}$ = 28.5 Hz, Ph$_{i'}$), 129.4 (ps t, $^{3+5}J_{C-P}$ = 5.6 Hz, Ph$_m$), 129.5 (ps t, $^{3+5}J_{C-P}$ = 5.6 Hz, Ph$_{m'}$), 132.3 (s, Ph$_p$), 132.6 (s, Ph$_{p'}$), 133.2 (ps t, $^{2+4}J_{C-P}$ = 6.1 Hz, Ph$_o$), 133.9 (ps t, $^{2+4}J_{C-P}$ = 7.1 Hz, Ph$_{o'}$), 140.6 (s, 4-py), 159.5 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, $^{2}J_{C-Pt}$ = 33 Hz, 2,6-py), 212.1 (s, C=O). ^{31}P NMR (101.25 MHz, CD_2Cl_2): δ 28.7 (s, $^{1}J_{P-Pt}$ = 3006 Hz).

*[Pt(PNP){CH(CH$_3$)C(O)CH$_2$CH$_2$CH$_3$}]BF$_4$ (**7a**) and [Pt(PNP){CH-(CH$_2$CH$_2$CH$_3$)C(O)CH$_3$}]BF$_4$ (**7b**).* Yield (combined): 262 mg (0.306 mmol, 89%). Mp: 251 °C dec. Anal. Calcd for $C_{37}H_{38}BF_4NOP_2Pt\cdot(CH_3CH_2)_2O$: C, 52.91; H, 5.20; N, 1.51. Found: C, 52.90; H, 5.30; N, 1.66. ^{1}H NMR (500 MHz, CD_3NO_2): **7a**, δ 0.57 (t, 3H, $^{3}J_{H-H}$ = 9.1 Hz, CH$_3$), 0.88 (d, 3H, $^{3}J_{H-H}$ = 8.2 Hz, $^{3}J_{H-Pt}$ = 57 Hz, PtCCH$_3$), 1.05 (m, 2H, CH$_2$), 1.71 (m, 1H, O=CC*H$_a$*H$_b$), 1.93 (m, 1H, O=CCH$_a$*H$_b$*), 3.35 (m, 1H, $^{3}J_{H-H}$ = 8.2 Hz, $^{3}J_{H-Pt}$ = 148 Hz, PtCH), 4.56 (d ps t, 2H, $^{3}J_{H-H}$ = 22.1 Hz, $^{2+4}J_{H-P}$ = 5.8 Hz, PC*H$_a$*H$_b$), 4.71 (d ps t, 2H, $^{3}J_{H-H}$ = 22.1 Hz, $^{2+4}J_{H-P}$ = 5.6 Hz, PCH$_a$*H$_b$*),7.59−7.72 (m, 14H, Ph, 3,5-py), 7.85−8.25 (m, 9H, Ph, 4-py); **7b**, δ 0.48 (t, 3H, $^{3}J_{H-H}$ = 9.1 Hz, CH$_3$), 0.55−2.50 (signals for CH$_2$CH$_2$ and O=CCH$_3$ overlapped by signals of **7a**), 3.31 (m, 1H, PtCH), 4.52−4.76 (signals for 4H of PCH$_a$H$_b$ overlapped by signals of **7a**), 7.59−7.72 (m, 14H, Ph, 3,5-py), 7.85−8.25 (m, 9H, Ph, 4-py). ^{13}C NMR (100.62 MHz, CD_2Cl_2): **7a**, δ 13.2 (s, CH$_3$), 18.2 (s, CH$_2$), 16.8 (t, $^{3}J_{C-P}$ = 2 Hz, $^{3}J_{C-Pt}$ = 33 Hz, PtCHCH$_3$), 22.5 (t, $^{2}J_{C-P}$ = 3 Hz, $^{1}J_{C-P}$ = 579 Hz, PtCH), 45.2 (ps t, $^{1+3}J_{C-P}$ = 17.1 Hz, PCH$_2$), 45.4 s (s, CH$_2$), 123.1 (ps t, $^{3+5}J_{C-P}$ = 4.8 Hz, 3,5-py), 127.5 (ps t, $^{1+3}J_{C-P}$ = 28.7 Hz, Ph$_i$), 127.8 (ps t, $^{1+3}J_{C-P}$ = 28.5 Hz, Ph$_{i'}$), 129.5 (ps t, $^{3+5}J_{C-P}$ = 5.5 Hz, Ph$_m$), 129.6 (ps t, $^{3+5}J_{C-P}$ = 5.5 Hz, Ph$_{m'}$), 132.4 (s, Ph$_p$), 132.9 (s, Ph$_{p'}$), 133.5 (ps t, $^{2+4}J_{C-P}$ = 6.1 Hz, Ph$_o$), 134.7 (ps t, $^{2+4}J_{C-P}$ = 7.2 Hz, Ph$_{o'}$), 140.7 (s, 4-py), 160.2 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, $^{2}J_{C-Pt}$ = 33 Hz, 2,6-py), 215.2 (s, C=O); **7b**, δ 13.5 (s, CH$_3$), 22.7 (s, PtCH), 24.3 (s, CH$_2$), 30.1 (s, CH$_3$), 34.5 (s, CH$_2$), 45.1 (ps t, $^{1+3}J_{C-P}$ = 17.0 Hz, PCH$_2$), 123.2 (ps t, $^{3+5}J_{C-P}$ = 4.8 Hz, 3,5-py), 127.3 (ps t, $^{1+3}J_{C-P}$ = 28.8 Hz, Ph$_i$), 127.7 (ps t, $^{1+3}J_{C-P}$ = 28.4 Hz, Ph$_{i'}$), 129.3 (ps t, $^{3+5}J_{C-P}$ = 5.4 Hz, Ph$_m$), 129.8 (ps t, $^{3+5}J_{C-P}$ = 5.3 Hz, Ph$_{m'}$), 132.5 (s, Ph$_p$), 132.8 (s, Ph$_{p'}$), 133.6 (ps t, $^{2+4}J_{C-P}$ = 6.2 Hz, Ph$_o$), 134.6 (ps t, $^{2+4}J_{C-P}$ = 7.1 Hz, Ph$_{o'}$), 140.8 (s, 4-py), 160.1 (ps t, $^{2+4}J_{C-P}$ = 3.0 Hz, 2,6-py), 212.0 (s, C=O). ^{31}P NMR (161.92 MHz, CD_2Cl_2): **7a**, δ 28.9 (s, $^{1}J_{P-Pt}$ = 3031 Hz); **7b**, 29.4 (s, $^{1}J_{P-Pt}$ = 3026 Hz).

NMR Studies of Complexes 1, 2a,b, and 6 in Solution. To a solution of 10 mg (0.011 mmol) of complex **1** in 0.5 mL of CD_2Cl_2 (a) 3 drops (~ 30 mg, ~ 0.18 mmol) and (b) 1 drop (~ 10 mg, ~ 0.062 mmol) of $HBF_4\cdot Et_2O$ (54% HBF_4 in Et_2O) were added. A ^{1}H NMR spectrum was recorded of each respective solution.

To a solution of 10 mg of complex **1** in 0.5 mL of CD_2Cl_2 successively 5−200 μL portions (3−600 equiv) of $HBF_4\cdot Et_2O$ were added. After each 5 μL (for the first 50 μL) and after 100, 150, and 200 μL were added to the solution, a ^{31}P NMR spectrum was recorded.

To the respective solutions of 10 mg of complexes **1**, **2a,b**, and **6** in 0.5 mL of CD_2Cl_2 a few drops of concentrated HCl were added. ^{1}H and ^{31}P NMR spectra were recorded of each solution.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Figures giving the ^{1}H,^{1}H COSY NMR spectrum of complex **1**, ^{1}H and ^{31}P NMR spectra of complex **1** and $HBF_4\cdot Et_2O$ added, a ^{31}P NMR data plot of Table 3, and ^{1}H, ^{13}C, and ^{31}P NMR spectra of complexes **4** and **5**, and a CIF file and table giving crystallographic data and refinement details for complexes **1** and **2b**. This material is available free of charge via the Internet at http://pubs.acs.org.

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■ ACKNOWLEDGMENTS

This work was supported by the donors of the Petroleum Research Fund, administered by the American Chemical Society (No. 48223-GB3), the Welch Foundation (No. AW-0013), and the NSF-LSAMP program of the UT system. Dr. Joseph H. Reibenspies, Dr. Christian Hilty, and Dr. Howard Williams (Texas A&M University, College Station) are acknowledged for the X-ray structure analyses and NMR spectroscopy. Furthermore, we thank Dr. Thomas Ready (Midland College) for his support.

■ DEDICATION

†Dedicated to Professor Rudolf Taube on the occasion of his 80th birthday.

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