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Structural Investigations of Platinum(II) Styrene and Styryl Complexes and Mechanistic Study of Vinylic Deprotonation

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The X-ray structures of the π-complex [Pt(PNP)(CH_2=CHPh)]$(BF_4)_2$ and the σ-complex [Pt(PNP)-((*E*)-CH=CHPh)]BF_4 are reported (PNP = 2,6-bis(diphenylphosphinomethyl)pyridine). The styrene complex undergoes vinylic deprotonation by reaction with the weakly basic nucleophiles ROH (R = Me, Et, H), which was monitored by ^{1}H and ^{31}P NMR. The mechanistic pathway includes nucleophilic addition of the oxygen donor nucleophiles to the coordinated styrene. The resulting addition products [Pt(PNP)(CH_2CHPhOR)]BF_4 transformed to the styryl complex only when protons are present. Similarly, the related 1-vinylnaphthalene complex [Pt(PNP)(CH_2=C$HC_{10}H_7$)]$(BF_4)_2$ undergoes vinylic deprotonation in the presence of methanol, forming the corresponding σ-complex [Pt(PNP)((*E*)-CH=C$HC_{10}H_7$)]BF_4.

Introduction

Dicationic palladium(II) and platinum(II) monoalkene complexes[1,2] have recently gained increasing interest in C−C, C−N, and C−O bond formations.[3−6] Due to the high positive complex charge, the coordinated C−C double bond in these complexes is highly activated, and the complexes add readily even very weak nucleophiles such as internal alkenes and activated arenes. These C−C bond formations were observed in stoichiometric and catalytic reactions.[4]

Equilibrium studies of dicationic Pd^{II} and Pt^{II} alkene complexes [M(PNP)(CHR=CHR′)]$(BF_4)_2$ (PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) with protic nucleophiles (HNR_2, HOR) showed that the nucleophilic addition is thermodynamically highly favored compared to neutral or cationic complexes, while substitution of the alkene by the nucleophile is less competitive.[1b,2] Although the dicationic Pd^{II} and Pt^{II} alkene complexes are highly reactive they are stable enough for complete characterization in solution and in solid state. [Pd(PNP)(CH_2=CHPh)]$(BF_4)_2$ and [Pt(PNP)(CH_2=CH_2)]$(BF_4)_2$ are the first dicationic monoalkene complexes of Pd^{II} and Pt^{II} being investigated by X-ray structure analysis.[1a,2]

In the course of the investigation of nucleophilic addition of dicationic platinum alkene complexes [Pt(PNP)(CHR=CHR′)]$(BF_4)_2$ (R/R′ = H/H, H/Me, H/Et, H/Ph (**1**), (*E*)-/(*Z*)-Me/Me) with nitrogen and oxygen donor molecules, it was observed that only in the case of the styrene derivatives [Pt(PNP)(CH_2CHPhOR)]BF_4 (R = H (**2a**), Me (**2b**)) did spontaneous decomposition occur at room temperature.[2] The resulting product was identified as [Pt(PNP)((*E*)-CH=CHPh)]BF_4 (**3**) by ^{1}H and ^{13}C NMR spectroscopy. It was found that the platinum(II) styrene complex **1** underwent in the presence of weakly basic nucleophiles such as methanol and water a vinylic deprotonation. Complex **1** displays the most reactive alkene complex known, with regard to olefinic C−H bond activation.

Vinylic deprotonation has been studied for a few alkene complexes of other transition metals.[7,8] The only platinum(II) alkene complex from which a vinylic proton could be removed, [PtCl(CH_2=CHPh)(tmeda)]ClO_4 (tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine), was reported recently.[9] The activation of an olefinic C−H bond by transition metals not only is a useful method to prepare σ-vinyl complexes

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from parent alkene complexes but also has considerable importance for organic synthesis.[10] Platinum vinyl complexes are relevant intermediates in catalytic processes, e.g. hydrosilylation of alkynes,[11] and are commonly prepared by oxidative addition of the vinyl halide X−CH=CHR to a Pt^0 center,[12] from Grignard or lithium reagents,[13] or by insertion of an alkyne into Pt−H bond.[14]

In this paper the X-ray structure analysis of $[Pt(PNP)(CH_2{=}CHPh)](BF_4)_2$ (**1**) is reported. An overview of the characteristic structural parameters of all isostructural complexes[15] $[M(PNP)(CH_2{=}CHR)]^{n+}$ (M = Rh^I, Pd^{II}, Pt^{II}; R = H, Ph) will be given and discussed. The process of vinylic deprotonation of complex **1** which was observed with oxygen donor nucleophiles[2] has been reinvestigated, and the results of more detailed ^1H NMR studies as well as the solid-state structure of the styryl complex [Pt(PNP)((*E*)-CH=CHPh)]BF_4 (**3**) are reported in this paper.

Results and Discussion

Molecular Structure of $[Pt(PNP)(CH_2{=}CHPh)](BF_4)_2$ (1). Single crystals of the dicationic platinum styrene complex **1**, suitable for X-ray analysis, were obtained from a solution in dichloromethane after slow evaporation of the solvent at room temperature over a period of several days. No additional free styrene was added for stabilization which was otherwise necessary for crystal growth of the isostructural palladium complex.[1a] An ORTEP view of the dication of **1**, $[Pt(PNP)(CH_2{=}CHPh)]^{2+}$, is shown in Figure 1. The overall geometry of complex **1** is quite similar to that of $[Pt(PNP)(CH_2{=}CH_2)]^{2+}$ and related alkene PNP complexes of Rh^I and Pd^{II}.[1a,2,15] Characteristic structural parameters for all PNP alkene complexes of Rh^I, Pd^{II}, and Pt^{II} are summarized in Table 1. The P(1)−Pt−P(2) angle in complex **1** is found to be 162.8°, which is within the range observed in the other M(PNP) complexes. The two five-membered rings are very constrained, which forces an inclination of the pyridine ring from the coordination plane by 21°. Similar values were observed for the isostructural Rh^I and Pd^{II} complexes.[1a,15]

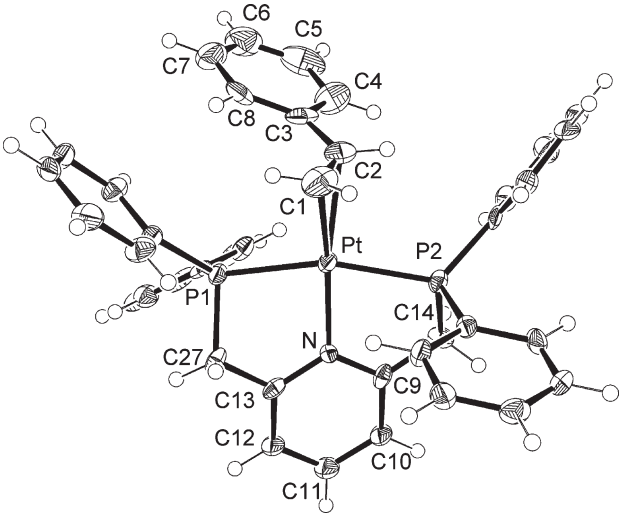

Figure 1. ORTEP view of the complex dication of **1**, $[Pt(PNP)(CH_2{=}CHPh)]^{2+}$. Thermal ellipsoids are drawn at the 50% probability level. Selected bond lengths (Å) and angles (deg): Pt−P(1) = 2.3309(15), Pt−P(2) = 2.3105(14), Pt−N = 2.076(4), Pt−C(1) = 2.188(6), Pt−C(2) = 2.282(6), C(1)−C(2) = 1.350(10), P(1)−C(27) = 1.811(6), P(2)−C(14) = 1.842(6); P(1)−Pt−P(2) = 162.79(5), P(1)−Pt−N = 81.15(12), P(2)−Pt−N = 81.64(12), N−Pt−C(1) = 159.7(2), N−Pt−C(2) = 164.7(2), C(1)−Pt−C(2) = 35.1(3), C(1)−C(2)−C(3) = 127.6(7), Pt−C(2)−C(3) = 112.5(5).

The C−C double bond of the coordinated styrene is tilted by 11° from the normal plane in complex **1**. This angle is somewhat smaller than that in the isostructural styrene complexes (Rh^I, 15°; Pd^{II}, 16°).[15,1a] This trend was also noted for the Pt^{II} and Rh^I ethylene complexes (cf. Table 1).[2,15] However, the coordinated ethylene in these complexes is overall less tilted than the styrene due to fewer steric interactions with the phenyl groups of the PNP ligand.

The C−C double-bond length in complex **1** (C(1)−C(2) = 1.350(10) Å) is somewhat longer than that found in the isostructural Pd^{II} styrene complex[1a] (1.292(10) Å) and is not significantly shorter than that in the monocationic Rh^I styrene complex[15] (1.383(7) Å) (cf. Table 1). While the Pt−CH_2 bond length (Pt−C(1) = 2.188(6) Å) is the same as the Pt−C distances in the analogous Pt^{II} ethylene complex,[2] the Pt−*C*HPh bond (Pt−C(2) = 2.282(6) Å) is significantly longer. The same strong elongation of the M−*C*HPh bond by 0.1 Å was also observed in the dicationic Pd^{II} styrene complex,[1a] whereas in the monocationic Rh^I styrene complex this elongation is much less pronounced.[15] In comparison to other Pt^{II} styrene complexes, similar differences between the two Pt−C bond lengths of about 0.1 Å and similar C−C double-bond lengths were reported for $[Pt(\eta^3\text{-}CH_2CMeCH_2)(PPh_3)(CH_2{=}CHPh)]PF_6$ (Pt−C = 2.203(12) Å, 2.301(12) Å; C−C = 1.341(17) Å)[16] and $[PtCl_2(CH_2{=}CHPh)_2]$ (Pt−C = 2.156(7), 2.2705(5) Å; C−C = 1.382(9) Å).[17] In a monocationic Pt^{II} styrene complex containing an anionic chelating ligand with relatively strong C and N donor functions[18] the Pt−C distances (2.160(5), 2.218(5) Å) have a difference of about 0.06 Å while the C−C double-bond

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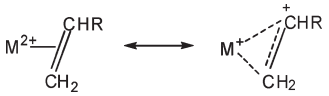
Table 1. Structural Parameters of Related Alkene Complexes $[M(PNP)(CH_2{=}CHR)]^{n+}$ (M = Rh^I, Pd^{II}, Pt^{II}; R = H, Ph)

complex	C=C, Å	M−CH_2, Å	M−CHR, Å	M−N, Å	M−P(1), Å	M−P(2), Å	P(1)−M−P(2), deg	∠C=C, deg[a]
$[Rh(PNP)(CH_2{=}CH_2)]^{+}$[b]	1.351(11)	2.132(6)	2.157(6)	2.092(4)	2.2690(13)	2.3001(13)	161.39(5)	6
$[Rh(PNP)(CH_2{=}CHPh)]^{+}$[b]	1.383(7)	2.144(5)	2.201(4)	2.102(3)	2.2916(10)	2.3004(11)	161.96(4)	16
$[Pd(PNP)(CH_2{=}CHPh)]^{2+}$[c]	1.292(10)	2.165(7)	2.273(7)	2.058(4)	2.314(1)	2.330(2)	162.4(1)	15
$[Pt(PNP)(CH_2{=}CH_2)]^{2+}$[d]	1.359(10)	2.180(6)	2.181(8)	2.051(4)	2.3059(13)	2.3063(13)	163.57(5)	2
$[Pt(PNP)(CH_2{=}CHPh)]^{2+}$ (cation of **1**)	1.350(10)	2.188(6)	2.282(6)	2.076(4)	2.3105(14)	2.3309(14)	162.79(5)	11

[a] Angle between the coordinated C−C double bond and the normal to the complex plane, which is the best plane of P(1), N, Pt, and P(2). [b] See ref 15. [c] See ref 1a. [d] See ref 2.

Scheme 1. Formation of an Incipient Carbocation by Slipping of the Alkene from η^2 to η^1 Coordination Mode



length (1.380(8) Å) falls within the range of the Pt^{II} styrene complexes mentioned above. These complexes seem to have a relatively moderate degree of π-back-donation in their Pt−(C=C) bond. Strong π-back-donation in the neutral four- and five-coordinate Pt^{II} styrene complexes $[PtCl_2(NC_5H_4Me)(CH_2{=}CHPh)]$[19] and $[PtCl_2(diimine)(CH_2{=}CHPh)]$[20] is suggested by the relatively long C−C double-bond length (1.454(17) Å and 1.53(5) Å, respectively). The Pt−C distances are only different by about 0.05 Å.

From the structural parameters of the coordinated styrene and ethylene at the $Pt(PNP)^{2+}$ fragment it can be seen in comparison to the isostructural Pd^{II} and Rh^I alkene complexes that the Pt^{2+} center has no particular influence on the C−C double-bond length. While the C−C double-bond length is commonly sought to estimate the degree of π-back-donation contribution in the metal−alkene bond,[21] it does not appear to be very diagnostic for the dicationic Pt^{II} alkene complexes. As pointed out earlier, the high positive charge in the dicationic complexes rather affects the M−C bond lengths.[22] In particular, in the case of monosubstituted alkenes such as styrene, the *unequally* stronger lengthening of the M−*C*HR bond may indicate the degree of activation by increasing the positive net charge. These structural features are supported by ^{13}C NMR spectroscopic data: (i) the signal for M−*C*HPh is shifted less upfield than that for M−*C*H_2 in comparison to the signals of the free styrene and (ii) J_{C-Pt}(Pt−*C*HPh) < J_{C-Pt}(Pt−*C*H_2).[2] These data indicate a greater weakening of the M−CHR bond. Overall, the structural parameters observed for the dicationic Pt^{II} styrene complex confirm the general picture of the enhanced "slipping" of the alkene with higher positive complex charge, thus promoting the formation of an incipient carbocation preferably located at the substituted carbon atom (cf. Scheme 1).

Vinylic Deprotonation. When styrene complex **1** was dissolved in methanol, the addition product $[Pt(PNP)(CH_2CHPhOCH_3)]BF_4$ (**2b**) was formed immediately and quantitatively (cf. Scheme 2) and could be isolated in high yield and analytically pure form.[2] However, if the methoxyalkyl complex **2b** was not isolated within 10 min from the solution, it started transforming to the styryl complex $[Pt(PNP)((E)\text{-}CH{=}CHPh)]BF_4$ (**3**). Similarly, the addition products $[Pt(PNP)(CH_2CHPhOR)]BF_4$ (R = H (**2a**), Et (**2c**)), formed in situ by treatment of the styrene complex **1** with water and ethanol, respectively, also transformed slowly to complex **3**. In each case the *E* isomer was formed, which is stable as a solid and in solution without showing any indication for isomerization to the *Z* form.

This process was monitored by ^1H and ^{13}P NMR spectroscopy. For this purpose a solution of 20 mM of the styrene complex **1** in CD_3OD was prepared, generating complex **2b**-d_3 in situ (cf. Scheme 2). The change of concentrations of **2b**-d_3 and **3** over time, which is shown in Figure 2, was determined by integration of ^1H NMR signals in the respective spectra. The graph in Figure 3 shows a plot of pseudo-first-order kinetics of the transformation of **2b**-d_3 to **3**. The observed rate constant was determined as $k_{obs} = 1.25 \times 10^{-4}\ s^{-1}$, and the half-life of **2b**-d_3 is $t_{1/2} = 90 \pm 3$ min. In Figure 4, selected ^1H NMR spectra recorded over the course of the reaction show the slow transformation of **2b**-d_3 to **3**. Notable in these spectra, the signals at δ 2.02 and 2.17 (PtCH_aH_b), 3.71 (C*H*Ph), 4.56 (PCH_2), and 6.62 (CPh-*o*) of complex **2b**-d_3 appear relatively broad. A similar broadening of the ^{31}P NMR signal at δ 30.5 was also observed for **2b**-d_3 in this reaction mixture ($w_{1/2}$ = 13 Hz). In contrast, all signals in the ^1H NMR spectrum of a solution of isolated **2b** dissolved in CD_3OD are sharp and show complex H−H, H−P, and H−Pt coupling patterns, respectively (see the Experimental Section). The isolated methoxyalkyl complex **2b** is completely stable in CD_3OD solution over several days. No indication for any decomposition or transformation to the styryl complex **3** was noted.

Another kinetic experiment was performed with the in situ prepared ethoxyalkyl complex $[Pt(PNP)(CH_2CHPhOCH_2CH_3)]BF_4$ (**2c**) (from 20 mM complex **1** in ethanol), where $k_{obs} = 1.00 \times 10^{-5}\ s^{-1}$ and $t_{1/2} = 1155 \pm 150$ min were observed for the transformation to complex **3**. The change of concentrations of **2c** and **3** was recorded by integration of the respective ^{31}P NMR signals at δ 29.7 (J_{P-Pt} = 3077 Hz) and 27.0 (J_{P-Pt} = 2922 Hz), respectively.

When complex $[Pt(PNP)(CH_2CHPhOR)]BF_4$ (**2**) is generated in situ, it always forms a stoichiometric amount of protons by instant dissociation from the primarily formed addition product **I** (cf. Scheme 2). The equilibrium between **I** and **2** lies on the very right side; however, the broad NMR signals observed for **2b**-d_3 suggest a dynamic interaction between the methoxy group of **2b**-d_3 and the stoichiometric proton on the NMR time scale. This suggests that only the presence of additional protons in solution allows the transformation of **2** to the styryl complex **3**, which involves the reassociation of the proton at the hydroxy or alkoxy group and dissociation of ROH from intermediate **I**. In other words, the transformation from **2** to **3** is a proton-catalyzed process, and its rate depends on the proton concentration.

Upon treatment of the styryl complex **3** with an excess of $HBF_4 \cdot Et_2O$ in CD_3OD, the styrene complex **1** was re-formed in an equilibrium reaction (cf. Scheme 2). The reaction of the

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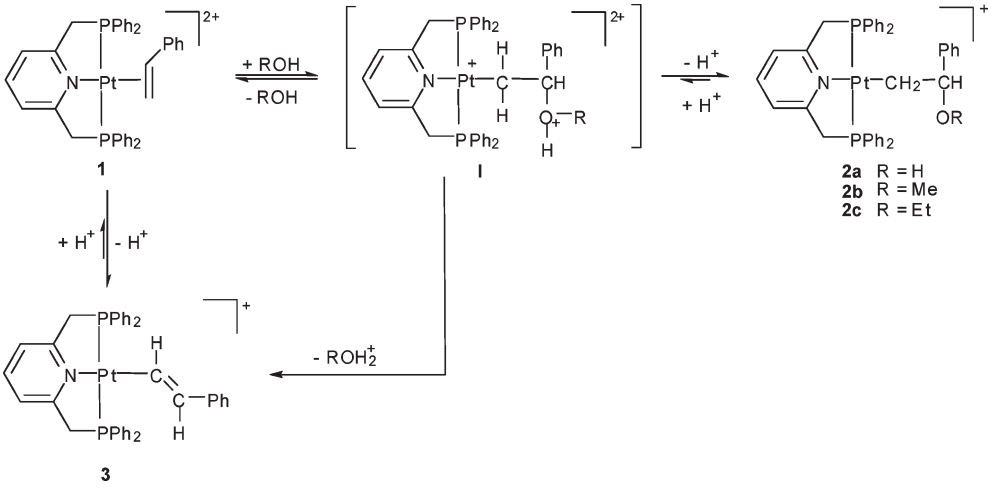
Scheme 2. Mechanistic View of the Vinylic Deprotonation of Styrene Complex 1



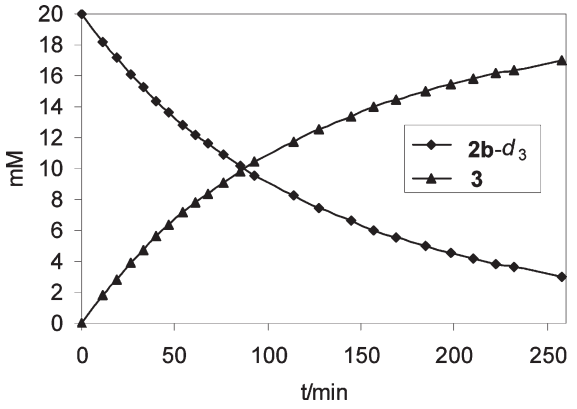


Figure 2. Plot of the concentrations [**2b**-d_3] and [**3**] against time.

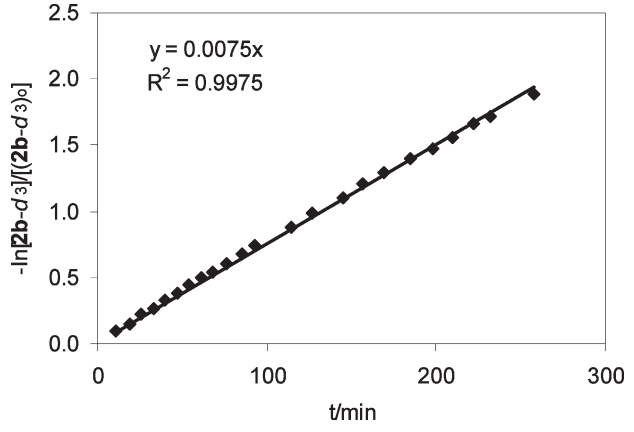


Figure 3. Pseudo-first-order plot for the transformation of **2b**-d_3 to **3**.

methoxyalkyl complex **2b** with an excess of $HBF_4 \cdot Et_2O$ in CD_3OD led first to the formation of the styryl complex **3** as the kinetic product, which then slowly transformed to the styrene complex **1** as the thermodynamic product. The formation of the styryl complex **3** even in the presence of a large excess of the acid indicates that the vinylic deprotonation must be a very fast intramolecular process, whereas the protonation of the styryl complex **3** is a much slower equilibrium.

Thermodynamically, the formation of the σ-vinyl complex **3** is thought to be considerably facilitated due to the phenyl

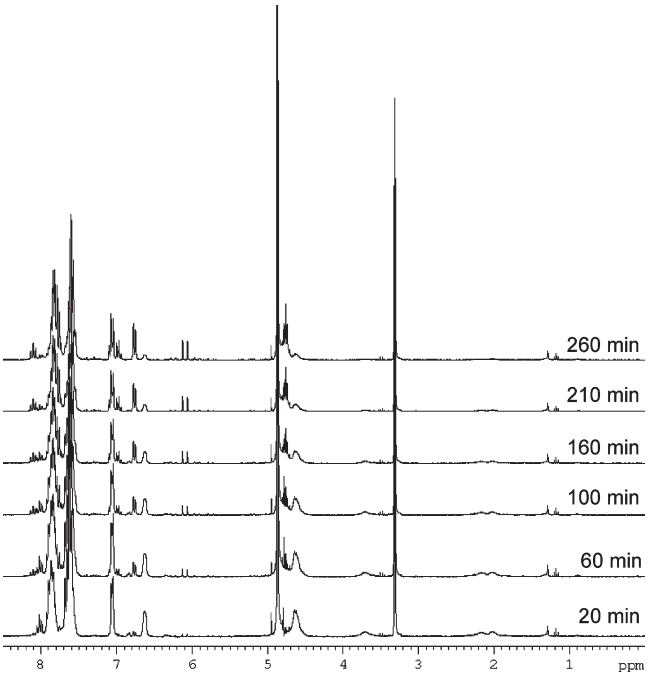


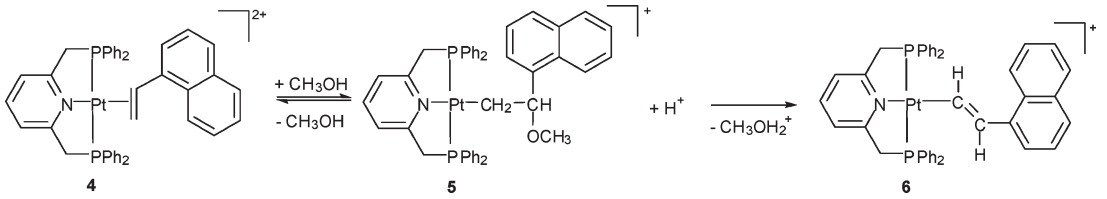
Figure 4. Time-dependent ^1H NMR spectra showing the transformation of **2b**-d_3 to **3** in CD_3OD.

substituent at the β-carbon atom, providing an extended π-conjugation. Notably, no spontaneous vinylic deprotonation was observed for the analogous ethylene and alkyl alkene derivatives $[Pt(PNP)(CH_2CHROCH_3)]BF_4$ (R = H, Me, Et) in the presence of a stoichiometric amount of protons.[2]

In order to broaden the scope of the vinylic deprotonation, the 1-vinylnaphthalene complex $[Pt(PNP)(CH_2{=}CHC_{10}H_7)](BF_4)_2$ (**4**) was investigated. Complex **4** was prepared from $[Pt(PNP)(CH_2{=}CH_2)](BF_4)_2$ by substitution of ethylene[2] by 1-vinylnaphthalene and characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (see the Experimental Section).[23] When complex

(23) Compounds **4**−**6** seem to be slightly unstable in solution and form some black platinum precipitate. The platinum metal impurities are most likely the reason for the light gray-brownish color of the isolated compounds **4**−**6**, which were difficult to remove. This also may explain the lower values of the elemental analyses (C, H, N) by 4−11% found for these compounds. In case of compound **6** no sufficient amount was available for analysis, due to strong electrostatic problems during weighing.

Scheme 3. Vinylic Deprotonation of 1-Vinylnaphthalene Complex 4



4 was dissolved in methanol, its characteristic yellow color disappeared immediately, giving a colorless solution. This indicates the immediate addition of methanol at the C−C double bond, forming the corresponding methoxyalkyl complex **5** (see Scheme 3), which could be trapped by addition of $NaHCO_3$ to remove the stoichiometric proton. The isolated complex **5** was characterized by ^1H, ^{13}C, and ^{31}P NMR spectroscopy (see the Experimental Section).[23] In the ^{31}P NMR spectrum a characteristic signal at δ 31.2 (J_{P-Pt} = 3057 Hz) was observed. Very similar to the case for the in situ generated complex **2b**-d_3, the methoxyalkyl complex **5**-d_3 prepared by dissolution of the π-complex **4** in CD_3OD also transformed slowly to the corresponding σ-vinyl complex **6** [Pt(PNP)(CH=CHC$_{10}$H$_7$)]BF_4 (cf. Scheme 3).[23] The process was monitored by ^{31}P NMR spectroscopy, showing a new signal at δ 27.1 (J_{P-Pt} = 2931 Hz) which is similar in chemical shift and P−Pt coupling constant to those of the styryl complex **3**. In the ^1H NMR spectrum a doublet at δ 6.97 with characteristic platinum satellites ($^2J_{H-Pt}$ = 79 Hz) and a H−H coupling constant of 16.6 Hz appears for the α-vinyl proton, which indicates the formation of the *E* isomer. The observed rate constant of the transformation of **5**-d_3 to **6** with an initial concentration of 15 mM of **5**-d_3 in CD_3OD was determined as $k_{obs} = 9.67 \times 10^{-5}\ s^{-1}$, and the half-life of **5**-d_3 was found to be $t_{1/2}$ = 120 ± 10 min. Considering the somewhat lower initial concentration of **5**-d_3 due to the limited solubility in methanol, the rate constant of transformation of **5**-d_3 to **6** can be estimated to be practically the same as that observed for the vinylic deprotonation of the styrene derivative. This experiment demonstrates that the extended π-conjugation of the alkene through an aromatic group is crucial to observe the loss of the vinylic proton, while the naphthyl group does not seem to have much influence on the rate. Similarly, treatment of complex **5** with a large excess of $HBF_4 \cdot Et_2O$ led to the instant formation of complex **6**.

The mechanistic pathway of the vinylic deprotonation of the dicationic alkene complexes complex **1** and **4** can be described as follows. Although the styrene and 1-vinylnaphthalene molecules are highly activated in the dicationic platinum(II) complexes **1** and **4** in terms of a promoted slipping from the η^2 to η^1 coordination mode, no direct spontaneous dissociation of the vinylic proton has been observed in acceptor solvents such as CH_2Cl_2 and CH_3NO_2. However, alcohols or water, which may actually act as Brønsted bases for a direct vinylic deprotonation, add preferably at the C−C double bond. Thus, the oxygen donor nucleophile helps first to unfold the styrene molecule from the η^2 to η^1 coordination mode by formation of the thermodynamically labile oxonium intermediate **I**. The alcohol or water molecules are, on the other hand, also good leaving groups. As the kinetic studies showed, they display individual rates: methanol dissociates somewhat faster than ethanol. The leaving ROH molecule acts probably as the closest and most efficient base to promote a very fast intramolecular, vicinal deprotonation. That this deprotonation occurs even in the presence of *excess* $HBF_4 \cdot Et_2O$ ($pK_a = -5$) demonstrates the high thermodynamic stability of the σ-vinyl complexes [Pt(PNP)(CH=CHAr)]BF_4 (Ar = Ph (**3**), $C_{10}H_7$ (**6**)). In contrast, treatment of the methoxyethyl complex [Pt(PNP)($CH_2CH_2OCH_3$)]BF_4 with excess HBF_4 in methanol led directly to the formation of the ethylene complex [Pt(PNP)(CH_2=CH_2)]$(BF_4)_2$, while the corresponding vinyl complex was not observed.[2]

These results suggest that at the stage of intermediate **I** (or complexes **2** + H^+ and **5** + H^+; cf. Schemes 2 and 3) there exist two pathways in the reverse direction: (i) reverse nucleophilic addition (according to the principle of microscopic reversibility) and (ii) the formation of complexes **3** and **6** by simultaneous dissociation of ROH_2^+. In the case of ethylene and alkenes with aliphatic substituents the activation barrier of path ii is presumably so high that no indication for vinylic deprotonation has been observed. However, if extended π-conjugation is introduced in the alkene, then the activation barrier of path ii decreases considerably so that it becomes readily available. In the reaction of complexes **1** and **4** with ROH overall, the species [**2** + H^+] and [**5** + H^+] represent kinetic products, while the σ-vinyl complexes **3** and **6** are the thermodynamic products, respectively. The kinetic products can be trapped simply by proton removal with $NaHCO_3$ but react further in the presence of protons.

Despite their mechanistic implications as nucleophiles with formation of intermediates [**2** + H^+] or [**5** + H^+], alcohols or water can be seen as efficient enough Brønsted bases in the overall reaction of the vinylic deprotonation. Considering their low basicity, for example for methanol with $pK_a(MeOH_2^+) = -2.2$, and the low acidity of the free styrene (pK_a = 40), it can be concluded that the coordination of the styrene at the Pt^{2+} center allows an extreme enhancement of the acidity of the vinylic proton by about 43 orders of magnitude.

Vinylic deprotonation of alkenes in transition-metal complexes can occur by different pathways, depending on electronic conditions at the metal center. Monocationic Pt^{II} alkene complexes, in comparison, are quite inert toward methanol and react only with stronger basic nucleophiles (e.g., OH^-, MeO^-) to form the corresponding addition products.[24] Vinylic deprotonation of [PtCl(CH_2=CHPh)(tmeda)]ClO_4 occurred with NEt_3 and anhydrous Na_2CO_3 by external proton abstraction.[9] The resulting styryl complex which forms *E* and *Z* isomers can be also reversibly reprotonated, showing an overall Brønsted acid−base equilibrium similar to that observed between complexes **1** and **3**.

Vinylic deprotonation of coordinated alkenes in cationic Re^{II} complexes of the type [Re(η^5-C_5H_5)(NO)(PPh_3)(CH_2=CHR)]BF_4 has been studied in detail using *t*-BuO^-K^+ as the Brønsted base (pK_a(*t*-BuOH) = 19).[7] In this case protonation of the resulting vinyl complex with $HBF_4 \cdot Et_2O$ did not give back the parent stryene complex, but a cationic alkylidene rhenium complex was formed.

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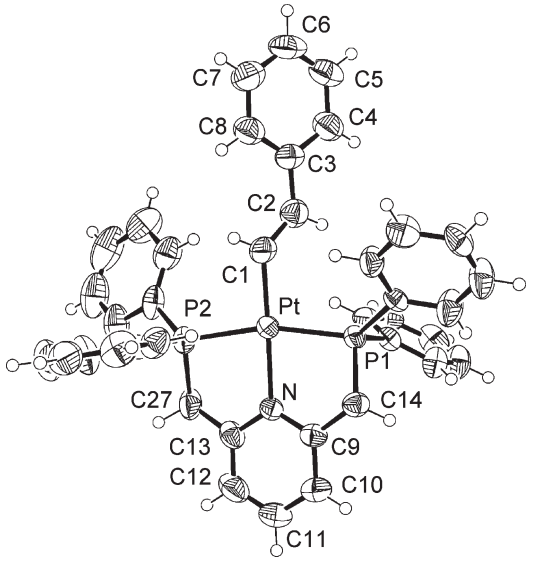

Figure 5. ORTEP view of the complex cation $[Pt(PNP)(CH{=}CHPh)]^+$ (**3A**).

A spontaneous vinylic C−H bond activation occurred when the iridium(I) cyclooctene complex $[\{Ir(COE)_2Cl\}_2]$ was reacted with the tridentate PNP ligand 2,6-bis((di-*tert*-butylphosphino)methyl)pyridine.[8a] An iridium(III) hydrido vinyl complex formed by oxidative addition of the vinylic C−H bond. In contrast, the analogous rhodium(I) complex $[\{Rh(COE)_2Cl\}_2]$ did not undergo vinylic C−H bond activation. This is analogous to the case for the "active" platinum complex $[Pt(PNP)(CH_2{=}CHPh)]^{2+}$ (**1**), while no indication of a vinylic deprotonation was observed with the isostructural palladium complex $[Pd(PNP)(CH_2{=}CHPh)]^{2+}$ under similar conditions (see above).

Molecular Structure of the Platinum(II) *σ*-Styryl Complex $[Pt(PNP)(CH{=}CHPh)]BF_4$ (3). Single crystals of the styryl complex **3** were grown from a reaction solution of styrene complex **1** in methanol at room temperature over the course of 3 days. The unit cell contains two independent molecules of the styryl complex **3**, which display a nearly square-planar geometry around the metal center. In both molecules the styryl moiety is in the *E* configuration, confirming the NMR spectroscopic data. The structure of the cation **3A** is shown in Figure 5. Selected structural parameters of **3A** and **3B** are summarized in Table 2. The average Pt−C bond length in complex **3** is comparable with Pt−C *σ*-bonds in other platinum(II) vinyl complexes (e.g., 2.022 Å in *trans*-$[PtBr((Z)\text{-}CH{=}CHPh)(PPh_3)_2]$[12a] and 2.032 Å in *trans*-$[PtCl(CH{=}CH_2)(PMe_2Ph)_2]$[25]). In both molecules (**3A** and **3B**) the C−C double bond has the same length of 1.322 Å, which falls in the range of bond lengths (1.31−1.34 Å) found in vinyl ligands coordinated in other metal complexes. The C(2)−C(3) bond length (**3A**, 1.478(9) Å; **3B**, 1.458(9) Å) is typical for a single bond between two sp^2 carbon atoms. The vinylic double bond in molecule **3A** is tilted 47° from the normal plane of the complex, and the phenyl group lies practically in plane with the double bond. In contrast, in molecule **3B** the angle between the double bond and the normal plane of the complex is observed to be only 27°, whereas the phenyl group lies 15° out of the plane of the double bond. Packing forces may be likely responsible for the respective distortions.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for $[Pt(PNP)(CH{=}CHPh)]BF_4$ (3; Molecules 3A and 3B)

	molecule **3A**	molecule **3B**
Pt−P(1)	2.2896(18)	2.2775(19)
Pt−P(2)	2.2893(18)	2.2840(18)
Pt−N	2.125(4)	2.110(4)
Pt−C(1)	2.005(6)	2.012(6)
C(1)−C(2)	1.322(9)	1.322(8)
C(2)−C(3)	1.478(9)	1.458(9)
P(1)−C(14)	1.824(6)	1.836(6)
P(2)−C(27)	1.854(6)	1.844(6)
P(1)−Pt−P(2)	164.36(6)	165.12(5)
P(1)−Pt−N	81.81(13)	83.00(13)
P(2)−Pt−N	82.91(13)	82.27(13)
P(1)−Pt−C(1)	98.56(18)	96.21(17)
P(2)−Pt−C(1)	96.89(18)	98.53(17)
N−Pt−C(1)	176.6(2)	179.1(2)
C(1)−C(2)−C(3)	128.0(7)	128.5(7)
Pt−C(1)−C(2)	130.3(6)	127.9(5)

Conclusion

The X-ray structure analysis of the platinum styrene complex $[Pt(PNP)(CH_2{=}CHPh)]^{2+}$ shows close structural similarities to that of the analogous palladium styrene complex, in particular the significantly different metal−carbon bond lengths of $M{-}CH_2$ and M−CHPh. This feature indicates an incipient slipping of the C−C double bond and carbocationic character at the substituted carbon atom.

Vinylic deprotonation was observed, however, only with the platinum styrene complex. Platinum may probably form a stronger M−C *σ*-bond in the resulting styryl complex than palladium does. The spontaneous vinylic deprotonation is also limited to the complexes of aromatic alkenes. It did not occur with the analogous ethylene or other alkyl alkene complexes. The aryl group has a strong stabilizing effect in the vinyl complex through extended *π*-conjugation and provides the main thermodynamic driving force of the equilibrium system. A further factor, which opens this particular reaction path, is the use of water or alkohols (MeOH, EtOH) as weakly basic nucleophiles. The rate-limiting factor in this process seems to be the ease of the reversible dissociation of the nucleophile from the former olefinic carbon atom. The rate of the process is determined by the type of nucleophile and even the proton concentration: the higher the proton concentration, the faster the reversible nucleophilic addition *and* hence the faster the vinylic *de*protonation! Although amines are stronger bases than water or alcohols, they are much poorer leaving groups, and thus the addition products are quite stable and do not undergo vinylic deprotonation. Overall it can be concluded that the vinylic C−H bond is highly activated in the dicationic platinum(II) complex. The proton release depends just on a very subtle interplay of thermodynamic and kinetic factors. NMR spectroscopy and X-ray crystal structure analysis confirm the formation of exclusively the *E* isomer in each case.

These studies furthermore demonstrate a facile way to prepare cationic platinum(II) aryl vinyl complexes using alcohols or water for effective deprotonation of the dicationic Pt^{II} aryl alkene complexes. The Pt^{II} complexes **3** and **5** can be used for further reaction studies representing key intermediates in catalytic cycles.

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Experimental Section

General Consideration. Complexes **1**, **2b**, **3**, and [Pt(PNP)-(CH_2=CH_2)](BF_4)$_2$ were prepared and isolated under conditions described previously.[2] The NMR studies were performed on a Bruker 250 MHz instrument. CD_2Cl_2 and CD_3OD were received from Aldrich and dried over 3 Å molecular sieves. 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, pseudo triplet; m, multiplet; br, broad.

X-ray Structure Determination of [Pt(PNP)(CH_2=CHPh)](BF_4)$_2$ (1) and [Pt(PNP)(CH=CHPh)]BF_4 (3).[26−28] Details of the X-ray experiment, data collection and reduction, and final structure refinement calculation for complexes **1** and **3** are summarized in Table 3. Suitable crystals of complexes **1** and **3** were selected and fixed to a nylon loop, which in turn was attached to a copper mounting pin. The crystal of complex **1** was coated in a cryogenic protectant (Paratone) and was placed in a cold nitrogen stream maintained at 110 K. Bruker D8 GADDS and SMART 1000 three-circle X-ray diffractometers and graphite-monochromated Cu Kα (λ = 1.541 84 Å, 40 kV, 40 mA) and Mo Kα radiation (λ = 0.701 73 Å, 50 kV, 40 mA) were employed for sample screening and data collection, respectively, for complexes **1** and **3**. Sixty data frames were taken at widths of 0.5° (**1**) and 0.3° (**3**) with an exposure time of 10 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 by nonlinear least-squares and Bravais lattice procedures and reported in Table 3. The standard data collection consisted of collection of one hemisphere of data collected using ω scans, involving the collection of 2520 0.5° (**1**) and 2400 0.3° (**3**) frames at fixed angles for ϕ, 2θ, and χ (2θ = −28°, χ = 54.73°), while varying ω. Each frame was exposed for 10 s (**1**) or 30 s (**3**). The total data collection was performed for a duration of approximately 24 h at 110 K (**1**) and 293 K (**3**). All non-hydrogen atoms were calculated in ideal positions. The tetrafluoroborate anions in complex **3** were found disordered over several positions, which is a common feature for this anion.[29] Bond restraints and distances were applied to model the disorder.

Synthesis and NMR Studies. Synthesis of [Pt(PNP)(CH_2-CHPhOR)]BF_4 (R = Me (2b), Et (2c)). The styrene complex **1** (112 mg, 0.118 mmol) was dissolved in 3 mL of methanol (for **2b**) or ethanol (for **2c**), and the mixture was stirred for 10 min in the presence of 3 equiv of $NaHCO_3$. The solution was filtered. The white product was precipitated by dropwise addition of diethyl ether to the filtrate. The product was filtered off, washed twice with 3 mL of diethyl ether, and dried under vacuum.

[Pt(PNP)(CH_2CHPhOCH$_3$)]BF_4 (2b). Yield: 91% (88 mg, 0.107 mmol). ^{1}H NMR (250 MHz, CD_3OD): δ 2.01 (m, $^2J_{H-Pt}$ = 88 Hz, 1H, PtCH_aH_b), 2.16 (m, $^2J_{H-Pt}$ = 85 Hz, 1H, PtCH$_a$$H_b$), 2.61 (s, 3H, OCH_3), 3.69 (m, $^2J_{H-Pt}$ = 39 Hz, 1H, CHPhO), 4.62 (m, 4H, PCH_2), 6.61 (m, 2H, CPh), 7.05 (m, 3H, CPh), 7.54−7.68 (m, 8H, PPh_2), 7.80−7.93 (m, 14H, PPh_2, 3,5-py), 8.02 (t, 1H, $^3J_{H-H}$ = 8 Hz, 4-py). ^{31}P NMR (101.25 MHz, CD_3OD): δ 30.5 (s, J_{P-Pt} = 3054 Hz).

[Pt(PNP)(CH_2CHPhOCH$_2$CH$_3$)]BF_4 (2c). Yield: 95% (102 mg, 0.112 mmol). Anal. Calcd for $C_{41}H_{40}BF_4NOP_2Pt$: C, 54.32; H, 4.45; N, 1.54. Found: C, 53.77; H, 4.38; N, 1.57. ^{1}H NMR (250 MHz, CD_2Cl_2): δ 0.96 (t, $^2J_{H-H}$ = 6.5 Hz, 3H, CH_3), 2.09 (m, 1H, PtCH_aH_b), 2.12 (m, 1H, PtCH$_a$$H_b$), 2.77 (t, $^2J_{H-H}$ = 6.5 Hz, 1H, OCH_aH_b), 2.93 (t, $^2J_{H-H}$ = 6.5 Hz, 1H, OCH$_a$$H_b$), 3.89 (m, $^2J_{H-Pt}$ = 49 Hz, 1H, CHPhO), 4.21 (m, 2H, PCH_aH_b), 4.66 (m, 2H, PCH$_a$$H_b$), 6.61 (m, 2H, CPh), 7.08 (m, 3H, CPh), 7.52−8.06 (m, 23H, PPh_2, py). ^{31}P NMR (101.25 MHz, EtOH): δ 29.7 (s, J_{P-Pt} = 3077 Hz).

In Situ Preparation of [Pt(PNP)(CH_2CHPhOCD$_3$)]BF_4·$D^+BF_4^-$ (2b-d_3). A 20 mM solution of styrene complex **1** in CD_3OD was prepared which produces quantitatively **2a**-d_3 and 1 equiv of $D^+BF_4^-$. NMR spectra were recorded upon mixing. ^{1}H NMR (250 MHz, CD_3OD): δ 2.01 (br, 1H, PtCH_aH_b), 2.16 (br, 1H, PtCH$_a$$H_b$), 3.69 (br, 1H, PtCH$_a$$H_b$, CHO), 4.62 (m, 4H, PCH_2), 6.63 (br, 2H, Ph), 7.05 (m, 3H, Ph), 7.54−7.68 (m, 8H, PPh_2), 7.80−7.93 (m, 14H, PPh_2, py), 8.02 (t, 1H, $^3J_{H-H}$ = 8 Hz, py). ^{31}P NMR (101.25 MHz, CD_3OD): δ 30.5 (s br, $w_{1/2}$ = 13 Hz, J_{P-Pt} = 3048 Hz).

[Pt(PNP)(CH=CHPh)]BF_4 (3). Complex **3** was formed in situ from a solution of **2b**-d_3·$D^+BF_4^-$ and analyzed after 24 h by NMR spectroscopy. ^{1}H NMR (250 MHz, CD_3OD): δ 4.76 (ps t, $^{2+4}J_{H-P}$ = 5 Hz, 4H, PCH_2), 6.08 (d, $^2J_{H-Pt}$ = 78 Hz, J_{H-H} = 17 Hz, 1H, PtCH=), 6.78 (m, 2H, Ph), 7.04−7.10 (m, 3H, Ph), 7.53−7.87 (m, 22H, PPh_2, 3,5-py), 8.01 (t, 1H, $^3J_{H-H}$ = 8 Hz, 4-py). ^{31}P NMR (101.25 MHz, CD_3OD): δ 27.0 (s, J_{P-Pt} = 2922 Hz).

[Pt(PNP)(CH_2=CHC$_{10}$H$_7$)](BF_4)$_2$ (4). To a solution of 480 mg (0.550 mmol) of [Pt(PNP)(CH_2=CH_2)](BF_4)$_2$ in 50 mL of dichloromethane was added 3 equiv of 1-vinylnaphthalene (245 μL, 1.65 mmol). Argon was gently bubbled through the reaction mixture for 1 h with stirring. The yellow reaction solution was filtered, and the volume of the filtrate was reduced to 10 mL. The product was precipitated by dropwise addition of diethyl ether. The product was filtered off, washed three times with 5 mL of diethyl ether, and dried under vacuum. The product was obtained as a yellow solid. Yield: 503 mg (0.504 mmol, 92%). Anal.

Table 3. Crystal Data and Structure Refinement Details for [Pt(PNP)(CH_2=CHPh)](BF_4)$_2$ (1) and [Pt(PNP)(CH=CHPh)]BF_4 (3)

	1	3
empirical formula	$C_{39}H_{35}B_2F_8NP_2Pt$	$C_{39}H_{34}BF_4NP_2Pt$
formula wt	948.33	860.51
temp (K)	110(2)	293(2)
wavelength (Å)	1.541 84	0.710 73
cryst syst	monoclinic	triclinic
space group	$P2_1/c$	$P\bar{1}$
a (Å)	13.684(3)	12.534(6)
b (Å)	11.966(3)	17.101(8)
c (Å)	22.420(6)	17.919(8)
α (deg)	90	70.036(8)
β (deg)	96.020(15)	82.643(8)
γ (deg)	90	78.659(8)
V (Å^3)	3651.0(15)	3532(3)
Z	4	4
ρ_{calcd} (g cm^{-3})	1.725	1.618
μ (mm^{-1})	8.647	4.114
F_{000}	1864	1696
cryst size (mm)	0.09 × 0.09 × 0.01	0.40 × 0.30 × 0.20
θ range for data collecn (deg)	3.97−59.99	2.03−25.00
index ranges (h, k, l)	h, ±15; k, ±13; l, ±25	h, ±14; k, ±20; l, ±25
no. of rflns collected	27 490	32 873
no. of indep rflns/R_{int}	5335/0.1084	12 170/0.0524
completeness to θ = 59.99° (%)	98.4	97.7
abs cor	semiempirical from equivalents	
max/min transmissn	0.9185/0.5100	0.4934/0.2899
refinement method	full-matrix least squares on F^2	
no. of data/restraints/params	5335/0/481	12 170/196/957
goodness of fit on F^2	1.008	1.000
R1 (obsd, I > 2σ(I)/all)	0.0348/0.0499	0.0342/0.0609
wR2 (obsd, I > 2σ(I)/all)	0.0672/0.0694	0.0725/0.0867
max/min $\Delta\rho$ (e Å^{-3})	0.846/−1.318	1.145/−0.611

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Calcd for $C_{43}H_{37}B_2F_8NP_2Pt \cdot CH_2Cl_2$: C, 50.90; H, 3.78; N, 1.34. Found: C, 49.09; H, 3.38; N, 1.35. ^{1}H NMR (250 MHz, CD_3NO_2): δ 4.89 (d ps t, 2H, $^2J_{H-H}$ = 17.6 Hz, $^{2+4}J_{H-P}$ = 4.8 Hz, PCH_aH$_b$), 4.95 (m, 1H, =CH), 5.31 (d ps t, 2H, $^2J_{H-H}$ = 17.6 Hz, $^{2+4}J_{H-P}$ = 4.8 Hz, PCH$_a$$H_b$), 5.36 (dt, 1H, $^3J_{H-H}$ = 15.2 Hz, $^3J_{H-P}$ = 4.7 Hz, =CH$_2$), 5.53 (d, 1H, $^3J_{H-H}$ = 8.7 Hz, =CH$_2$), 7.03 (d, 1H, $^3J_{H-H}$ = 7.1 Hz, $C_{10}H_7$), 7.21 (t, 1H, $^3J_{H-H}$ = 7.6 Hz, $C_{10}H_7$), 7.36−8.14 (m, 27H, $C_{10}H_7$, Ph, 3,5-py), 8.27 (t, 1H, $^3J_{H-H}$ = 7.7 Hz, 4-py). ^{13}C NMR (62.89 MHz, CD_3NO_2): δ 45.2 (ps t, $^{1+3}J_{C-P}$ = 17.3 Hz, PCH$_2$), 69.6 (s, =CH$_2$), 108.6 (s, =CH), 123.6 (ps.t, $^1J_{C-P}$ = 30.8 Hz, PPh$_i$), 124.1 (ps t, $^1J_{C-P}$ = 30.8 Hz, PPh$_{i'}$), 124.4 (s, $C_{10}H_7$), 126.4 (ps.t, $^{3+5}J_{C-P}$ = 5.5 Hz, 3,5-py), 127.3 (s, $C_{10}H_7$), 127.4 (s, $C_{10}H_7$), 129.2 (s, $C_{10}H_7$), 130.3 (s, $C_{10}H_7$), 131.5 (s, $C_{10}H_7$), 131.5 (ps t, $^{3+5}J_{C-P}$ = 6.1 Hz, PPh$_m$), 132.1 (s, $C_{10}H_7$), 132.4 (ps.t, $^{3+5}J_{C-P}$ = 5.6 Hz, PPh$_{m'}$), 134.0 (s, $C_{10}H_7$), 135.7 (s, PPh$_p$), 134.9 (ps t, $^{2+4}J_{C-P}$ = 6.0 Hz, PPh$_o$), 135.9 (s, $C_{10}H_7$), 135.9 (ps.t, $^{2+4}J_{C-P}$ = 7.0 Hz, PPh$_{o'}$), 136.2 (s, $C_{10}H_7$), 136.4 (s, PPh$_{p'}$), 146.7 (s, 4-py), 162.9 (ps t, $^3J_{C-P}$ < 3 Hz, 2,6-py). ^{31}P (101.25 MHz, CD_2Cl_2): δ 37.0 (s, J_{P-Pt} = 2329 Hz).

[Pt(PNP){CH$_2$CH(C$_{10}$H$_7$)(OCH$_3$)}]BF$_4$ (5). The 1-vinylnaphthalene complex **4** (106 mg (0.106 mmol) was dissolved in 2 mL of methanol, and 3 equiv of $NaHCO_3$ was added. After it was stirred for 5 min, the mixture was filtered through Celite. The solvent was removed under vacuum. The light brown solid residue was washed twice with 2 mL of diethyl ether and dried under vacuum. Yield: 82 mg (0.092 mmol, 87%). Anal. Calcd for $C_{44}H_{40}BF_4NOP_2Pt$: C, 56.06; H, 4.28; N, 1.49. Found: C, 52.79; H, 4.06; N, 1.43. ^{1}H NMR (250 MHz, CD_3OD): δ 2.33 (m, $^2J_{H-Pt}$ = 78.9 Hz, 2H, PtCH$_2$), 2.71 (s, 3H, OCH$_3$), 3.82 (m, 1H, CH), 4.43 (m, 4H, PCH$_2$), 6.79 (d, 1H, J_{H-H} = 6.8 Hz, $C_{10}H_7$), 6.98 (dt, 1H, J_{H-H} = 6.7 Hz, $C_{10}H_7$), 7.22 (t, 1H, J_{H-H} = 7.3 Hz, $C_{10}H_7$), 7.31 (t, 1H, J_{H-H} = 7.0 Hz, $C_{10}H_7$), 7.53−7.75 (m, 14H, PPh$_2$, 3,5-py), 7.83−7.97 (m, 8H, PPh$_2$), 8.00 (t, 1H, $^3J_{H-H}$ = 7.8 Hz, 4-py). ^{31}P (101.25 MHz, CD_2Cl_2): δ 31.2 (s, J_{P-Pt} = 3057 Hz).

[Pt(PNP)(CH=CHC$_{10}$H$_7$)]BF$_4$ (6). The vinylnaphthalene complex **4** (53 mg, 0.053 mmol) was dissolved in 2 mL of CH_3OH. After the solution was stirred for 24 h at room temperature, the solvent was removed under reduced pressure. The residue was dissolved in 2 mL of CH_2Cl_2, and the solution was filtered through Celite. Diethyl ether (6 mL) was added to the filtrate, and the product precipitated as a light gray solid. Yield: 37 mg (0.041 mmol, 78%). Anal. Calcd for $C_{43}H_{36}BF_4NOP_2Pt$: C, 56.72; H, 3.98; N, 1.54. Found: C, 50.5; H, 3.5; N, 1.3. ^{1}H NMR (250 MHz, CD_3OD): δ 4.76 (ps t, 4H, $^{2+4}J_{H-P}$ = 4.0 Hz, PCH$_2$), 6.97 (d, 1H, $^3J_{H-H}$ = 16.6 Hz, $^2J_{H-Pt}$ = 79 Hz, PtCH=), 6.99 (d, 1H, $^3J_{H-H}$ = 8.2 Hz, $C_{10}H_7$), 7.04 (d, 1H, $^3J_{H-H}$ = 7.3 Hz, $C_{10}H_7$), 7.11 (dt, 1H, J_{H-H} = 1.3 Hz, $^3J_{H-H}$ = 8.5 Hz, $C_{10}H_7$), 7.21 (t, 1H, $^3J_{H-H}$ = 7.5 Hz, $C_{10}H_7$), 7.31 (dt, 1H, J_{H-H} = 1.2 Hz, $^3J_{H-H}$ = 8.1 Hz, $C_{10}H_7$), 7.41−8.04 (m, 25H, $C_{10}H_7$, =CH, Ph, 3,5-py), 8.11 (t, 1H, $^3J_{H-H}$ = 8.0 Hz, 4-py). ^{13}C NMR (62.89 MHz, CD_3OD): δ 45.4 (ps.t, $^{1+3}J_{C-P}$ = 17.2 Hz, PCH$_2$), 123.4 (s, $C_{10}H_7$), 123.9 (t, $^2J_{C-P}$ = 8.6 Hz, PtCH=), 124.0 (ps t, $^4J_{C-P}$ = 5.5 Hz, 3,5-py), 124.7 (s, $C_{10}H_7$), 126.2 (s, $C_{10}H_7$), 126.3 (s, $C_{10}H_7$), 126.6 (s, $C_{10}H_7$), 127.2 (s, $C_{10}H_7$), 128.7 (s, $C_{10}H_7$), 129.1 (s, $C_{10}H_7$), 130.8 (ps t, $^{3+5}J_{C-P}$ = 5.6 Hz, PPh$_m$), 133.5 (s, PPh$_p$), 134.5 (ps.t, $^{2+4}J_{C-P}$ = 6.8 Hz, PPh$_o$), 135.0 (s, $C_{10}H_7$), 137.4 (t, $^3J_{C-P}$ = 5.2 Hz, =CH), 140.1 (s, 4-py), 141.6 (s, $C_{10}H_7$), 162.1 (t, $^3J_{C-P}$ = 3.6 Hz, 2,6-py). ^{31}P (101.25 MHz, CD_3OD): δ 27.1 (s, J_{P-Pt} = 2931 Hz).

NMR Studies. The progressive formation of complex **3** from in situ prepared solutions of 20 mM **2b**-d_3 in CD_3OD and 20 mM **2c** in EtOH was monitored over time by ^{1}H and ^{31}P NMR spectroscopy at T = 298 K. In case of the conversion of **2c** only ^{31}P NMR spectra were recorded. Similarly, the progressive formation of complex **6** starting from a 15 mM solution of **5**-d_3 in CD_3OD was monitored by ^{31}P NMR spectroscopy. The error of the obtained kinetic data is ±10%. For monitoring of the equilibrium of the back-formation of complex **1**, a 20-fold excess of $HBF_4 \cdot Et_2O$ was added to (i) complex **2b** and (ii) complex **3**, respectively, in CD_3OD.

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Supporting Information Available: CIF files giving all crystal data and refinement parameters, atomic coordinates, bond length, bond angles, and thermal displacement parameters for complexes **1** and **3** and figures giving NMR spectra of compounds **4**−**6**. This material is available free of charge via the Internet at http://pubs.acs.org.