Coordination of Alkenes at a Highly Electrophilic Site. New Dicationic Platinum(II) Complexes: Synthesis, Structure, and Reactions with Nucleophiles§

Christine Hahn,*,† Pasquale Morvillo,† Eberhardt Herdtweck,‡ and Aldo Vitagliano†

Dipartimento di Chimica, Università degli Studi di Napoli "Federico II", Complesso Universitario di Monte S. Angelo, Via Cinthia, I-80126 Napoli, Italy, and Anorganisch-Chemisches Institut, Technische Universität München, Lichtenbergstrasse 4, D-85747 Garching, Germany

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Dicationic platinum(II) alkene complexes $[Pt(PNP)(alkene)](BF_4)_2$ (alkene = ethylene, propene, 1-butene, *Z*- and *E*-2-butene, styrene, norbornene; PNP = 2,6-bis(diphenylphosphinomethyl)pyridine) have been prepared and characterized by ^1H and ^{13}C NMR spectroscopy, and the molecular structure of the ethylene complex has been determined by X-ray diffraction analysis. Nucleophilic attack at the coordinated double bond takes place more readily than for known neutral and monocationic species, and a variety of protic nucleophiles NuH (MeOH, H_2O, aromatic amines) give the corresponding β-functionalized σ-alkyl complexes $[Pt(PNP)(CHRCHR'Nu)]BF_4$ also in the absence of auxiliary bases. In the case of the styrene derivatives an unusual decomposition pathway gives the stable alkenyl complex $[Pt(PNP)(CH{=}CHPh)]BF_4$. A competitive equilibrium process between substitution and addition was revealed by reacting ethylene with the isolated aniline complex $[Pt(PNP)(PhNH_2)](BF_4)_2$. The nucleophilic addition product was found to be thermodynamically favored over the substitution product more than in the case of the analogous palladium complexes.

Introduction

The nucleophilic addition reaction at platinum(II) alkene complexes has been widely studied because of the great importance for introduction of functional groups in hydrocarbons.[1] In comparison to palladium(II) the analogous platinum(II) complexes usually exhibit a higher stability and were therefore used as model complexes for attaining mechanistic insights in Pd-catalyzed reactions.[2] Investigations of the reaction of π-alkene Pt(II) complexes with nucleophiles and the resulting σ-alkyl complexes revealed crucial and interesting mechanistic details such as the competition of nucleophilic addition and substitution reaction[3] or the reversal of the nucleophilic addition versus Pt−C bond cleavage in acidic medium.[4]

An important fact that has been revealed experimentally[5] and theoretically[2a,6] is that the electrophilic character of the coordinated alkene can be enhanced by increasing the positive charge on the metal ion. As was shown by Natile and co-workers, cationic alkene platinum(II) complexes react with a much wider variety of nucleophiles compared to the neutral complexes.[4b,7] Except for a couple of studies concerning dicationic diene complexes,[8] previous investigations were limited to species bearing a single positive charge on the metal center, and neither the reactivity nor the synthesis of dicationic Pt(II) complexes of simple monoalkenes has been described so far.

We have recently investigated novel dicationic palladium(II) alkene complexes[9] $[Pd(PNP)(alkene)](BF_4)_2$ stabilized by the tridentate ligand 2,6-bis(diphenylphos-

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* To whom correspondence should be addressed. Fax: +39 081 674090. E-mail: chahn@chemistry.unina.it.

† Dipartimento di Chimica, Università di Napoli.

‡ Anorganisch-Chemisches Institut, Technische Universität München.

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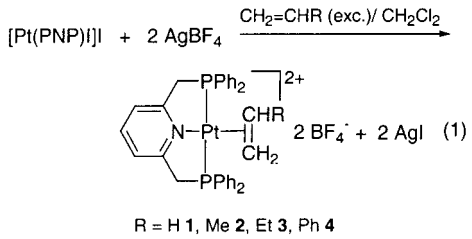
phinomethyl)pyridine[10] (PNP), in which the alkene is highly activated both kinetically and thermodynamically toward protic nucleophiles. The unusually high stability of those complexes and of their σ-alkyl derivatives allowed us to reveal a reversible overall equilibrium process and to estimate for the first time the thermodynamic constants for the competitive equilibria of nucleophilic addition and substitution reactions. In this paper we report on the synthesis and structural characterization of isostructural dicationic platinum(II) alkene complexes and on their reactions with protic nucleophiles. A comparison is given of their reactivities to those of the analogous palladium(II) complexes[9] as well as to those of neutral[3c] and monocationic[4b,7] platinum(II) species.

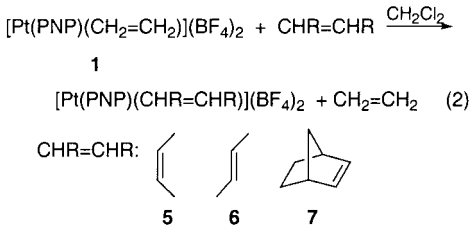
Results and Discussion

Synthesis and Characterization of [Pt(PNP)(alkene)](BF$_4$)$_2$. The dicationic alkene platinum(II) complexes [Pt(PNP)(CH_2=CHR)](BF$_4$)$_2$ (R = H **1**, Me **2**, Et **3**, Ph **4**) have been prepared similarly to the analogous palladium(II) alkene complexes[9] starting from the iodo complex [Pt(PNP)I]I,[11] by reaction with 2 equiv of silver tetrafluoroborate in the presence of an excess of the corresponding alkene, according to eq 1.



R = H **1**, Me **2**, Et **3**, Ph **4**

In contrast, the complexes with internal alkenes such as *Z*-, *E*-2-butene and norbornene could not be obtained by the silver salt method. Due perhaps to a stronger coordination tendency of these alkenes to silver rather than to platinum, the halide abstraction remained incomplete. However, these complexes (**5**−**7**) were alternatively accessible by substitution of ethylene from complex **1** with an excess of the corresponding alkene, cf. eq 2.



Compounds **1**−**7** were characterized by ^{1}H and ^{13}C NMR spectroscopy. They represent the first examples of dicationic monoalkene complexes of platinum(II) that have been isolated.[12] Compared to their analogous palladium(II) species,[9] the complexes **1**−**7** appear in general to be more stable as solids as well as in solution (CH_2Cl_2, CH_3NO_2), which is consistent with their higher inertness to the alkene substitution by potential donor molecules (e.g., H_2O, see later discussion).

Table 1. ^{13}C NMR Shifts δ (ppm) of the Coordinated Alkenes in [Pt(PNP)(alkene)](BF$_4$)$_2$, Coordination-Induced Upfield Shift $\Delta\delta = \delta_{coord} - \delta_{free}$ (ppm), and Coupling Constants to Platinum (Hz)

	=CH			=CH$_2$		
alkene	δ	$\Delta\delta$	J_{C-Pt}	δ	$\Delta\delta$	J_{C-Pt}
CH_2=CH_2				77.9	−45.4	116
CH_2=CHMe	103.5	−31.1	108	74.3	−41.7	138
CH_2=CHEt	107.7	−35.2	113	73.1	−42.7	131
CH_2=CHPh	108.2	−27.3	81	66.5	−45.5	137
E-MeCH=CHMe	96.9	−28.5	115			
Z-MeCH=CHMe	99.2	−26.7	118			
norbornene	91.9	−43.8	131			

The ^{31}P NMR signals of the complexes **1**−**4** and **7** appear as a singlet in the range δ 38−41, which are 6−10 ppm more upfield shifted than those of the corresponding Pd^{II} complexes. The ^{31}P−^{195}Pt coupling constants are observed around 2170−2330 Hz.

While the ^{1}H NMR data of the alkene protons (see Experimental Section) give little evidence for the influence of the high positive charge on the Pt−alkene bond, the ^{13}C NMR data (cf. Table 1) substantially reflect the bonding conditions of the coordinated alkenes. The coordination-induced upfield shift $\Delta\delta$ is about -31 ± 4 ppm for the methyne carbon atoms and about -43 ± 2 ppm for the methylene carbon atoms, which are slightly larger values than those of the analogous palladium(II) complexes ($\Delta\delta$(CH) ≈ -15 ppm and $\Delta\delta(CH_2) \approx -33$ ppm). However, compared to the upfield shifts found for monocationic platinum(II) alkene complexes[13] ($\Delta\delta$(CH) ≈ -40 ppm and $\Delta\delta(CH_2) \approx -50$ ppm), the $\Delta\delta$ values of the dicationic complexes are smaller. Similarly, carbon−platinum coupling constants $^1J_{C-Pt}$ are significantly smaller (81−138 Hz) than those in monocationic complexes (around 170−210 Hz).[13] This indicates the weakness of the Pt−alkene bond, which is consistent with the proposed decreased contribution of the π-backdonation.[14] Exceptionally higher values of both $\Delta\delta$ and J_{C-Pt} are found for the norbornene complex **7**, which can be explained by the pyramidalization effect occurring in a strained cyclic alkene, resulting in a stronger metal−alkene bond.[15]

The values of $\Delta\delta$ as well as of J_{C-Pt} are smaller for CH than for CH_2. The different extent of $\Delta\delta$ and J_{C-Pt} for the CH and CH_2 groups indicates an increased polarization of the C−C double bond in unsymmetrically substituted coordinated alkenes due to the different Pt−C bond strengths to CH and CH_2.[16] The resulting difference in electron density at the methyne and methylene carbon atoms could be the determining factor

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for the regioselectivity of the nucleophilic attack which would preferentially take place (at least kinetically[17]) at the methyne carbon (Markovnikov addition).

The ^{1}H NMR spectra show an average C_2 symmetry for the propene, 1-butene, and styrene complexes **2**−**4** and an average C_{2v} symmetry for the *Z*-2-butene and norbornene complexes **5** and **7**. This indicates a fast rotation around the Pt−(C═C) bond axis at room temperature.[18] The rotation is still fast at 203 K, as shown by the unchanged spectra of the propene and norbornene complexes **2** and **7** at this temperature. Compared to the analogous palladium(II) complexes,[9] no differences in the rotation behavior of the platinum complexes **1**−**7** can be noted.

Alkene Exchange. The intermolecular exchange between the coordinated and free alkene was found to be very slow for the platinum complexes **1**−**7** on the NMR time scale at room temperature. Even addition of a large excess of the corresponding free alkene did not affect the signal pattern of the coordinated alkene. Only a slight broadening was observed for the signal of the coordinated ethylene when about 5 equiv of free ethylene was added to a solution of complex **1**, the ^{195}Pt-satellites being still visible.

The exchange rate of the coordinated alkene in square planar platinum(II) complexes usually grows going from anionic to neutral[19] and is fast in monocationic[13] complexes. However, the exchange can be strongly retarded by steric hindrance of bulky substituents of adjacent ligands.[13,20] Presumably, the steric shielding by the phenyl groups of the PNP ligand is responsible for the slow alkene exchange in **1**−**7**, despite the 2-fold positive charge of the platinum center.

While the ethylene exchange in the dicationic palladium(II) complex with any other alkenes was equilibrated within a few minutes, in the case of the platinum(II) complexes the equilibration time was expectedly found to be longer and largely dependent on the structure of the individual alkene (eq 3).

$$[Pt(PNP)(CHR{=}CHR')](BF_4)_2 + C_2H_4 \xrightleftharpoons{K\,(CD_2Cl_2)} [Pt(PNP)(C_2H_4)](BF_4)_2 + CHR{=}CHR' \quad (3)$$

CHR=CHR'	*K*
norbornene	$6 \cdot 10^{-3}$
propene	2.1
E-2-butene	4
Z-2-butene	10
styrene	26

In complex **1** the displacement of the ethylene by α-alkenes CH_2═CHR was equilibrated within 15 min, whereas with internal alkenes RCH═CHR it needed ca. 3 h. Kinetic measurements of the substitution of *Z*-2-butene (complex **5**) by ethylene have shown clearly an approximately linear increase of the reaction rate upon increasing the ethylene concentration. These observations strongly support the associative mechanism for the alkene exchange,[19] which was also discussed elsewhere for square planar platinum(II) complexes[13] and was shown in the case of the isostructural rhodium(I) ethylene complex by freezing the five-coordinate species as the intermediate at low temperature.[21] The exchange rate also depends on the structural features of the leaving alkene. For example, the displacement of *Z*-2-butene by ethylene is faster than that of *E*-2-butene.[22]

By integration of the appropriate ^{1}H NMR signals of all the four species involved in eq 3, stability constants could be estimated relative to the ethylene complex **1**. Their order is the same as that found for the analogous palladium complexes. Interestingly, the relative stabilities of *E*- and *Z*-2-butene are reversed with respect to those of the square planar Pt(II) complexes described by Kurosawa.[23] Most likely as found also for the analogous palladium complexes,[9] the stability is affected by steric influence of the C_2-symmetrical ligand periphery of the PNP ligand, to which the *E*-2-butene fits better than *Z*-2-butene. Noteworthy is the relatively high stability of the norbornene complex **7**, consistent with the exceptionally larger values of $\Delta\delta$ and J_{C-Pt}, which suggests a stronger π-bond of this strained alkene to platinum.

Molecular Structure of [Pt(PNP)(CH_2═CH_2)]-(BF_4)$_2$·CH_2Cl_2, 1. Single crystals suitable for X-ray analysis were obtained from a saturated solution in dichloromethane after standing for a few days at room temperature. An ORTEP view of the complex dication is shown in Figure 1. Selected bond lengths and angles are collected in Table 2. The molecule displays the usual square planar coordination around the platinum center. The values of the structural parameters of the Pt(PNP) fragment like P−Pt−N angles and Pt−P and Pt−N distances are very similar to those of other square planar M(PNP) complexes (M = Rh,[21] Pd[9,24]), showing the rigidity of the coordinated PNP and its rather invariable structural feature when changing the metal or the other ligand. The ethylene molecule is symmetrically coordinated at the Pt(PNP) fragment: the Pt−C(3) and Pt−C(4) distances are identical [(2.181(8) and 2.180(6) Å, respectively], and the C−C double bond lies nearly ideally perpendicular to the coordination plane, whereas in the isostructural Rh^I complex the ethylene double bond is tilted by 6° from the normal of

(17) For the analogous dicationic palladium(II) a similar polarization of the C−C double bond is indicated by ^{13}C NMR data. As supposed, high Markovnikov regioselectivity was found for nucleophilic addition at unsymmetrically substituted alkenes. In the case of the styrene complex and dimethylamine the complex [(PNP)Pd(CH_2CHPhNMe$_2$)]$^+$ was observed as the kinetically controlled addition product; see ref 9.

(18) The methylene protons of the PNP ligand show a characteristic signal pattern in the ^{1}H NMR spectrum: for complexes with C_2 symmetry it appears as two doublets of virtual triplets due to AA′BB′XX′, whereas for those with C_{2v} symmetry as a simple virtual triplet due to an AA′XX′ spin system.

(19) Plutino, M. R.; Otto, S.; Roodt, A.; Elding, L. I. *Inorg. Chem.* **1999**, *38*, 1233−1238.

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(21) Hahn, C.; Sieler, J.; Taube, R. *Chem. Ber.* **1997**, *130*, 393−345.

(22) The following observation has been made monitoring by ^{1}H NMR in CD_3NO_2 solution: Addition of ca. 2 equiv of ethylene to complex **5** gives after 10 min ca. 10% of free *Z*-2-butene from **5** and after 1 h the ratio of **5**:free *Z*-2-butene is 1:4.5, which is close to the equilibrium. Addition of 2 equiv of ethylene to complex **6** gives after 10 min only traces of free *E*-2-butene and after 1 h 10% displacement, which is still very far from the equilibrium.

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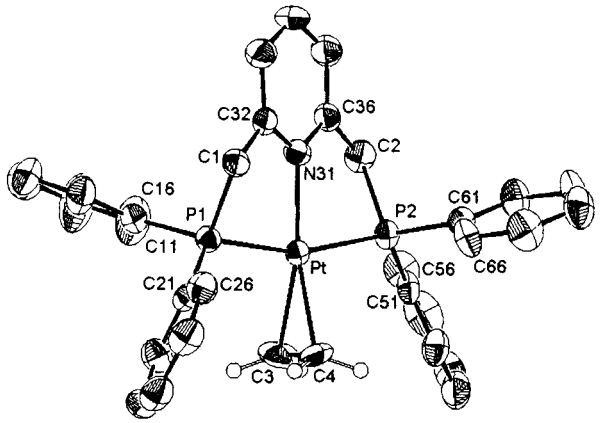

Figure 1. ORTEP representation of the dicationic part of compound **1**·CH_2Cl_2 in the solid state. Thermal ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Distances (Å) and Angles (deg) for [Pt(PNP)(CH_2=CH_2)](BF_4)$_2$·CH_2Cl_2 (1·CH_2Cl_2)

Pt−P1	2.3059(13)
Pt−P2	2.3063(13)
Pt−N31	2.051(4)
Pt−C3	2.181(8)
Pt−C4	2.180(6)
P1−C1	1.823(5)
P2−C2	1.827(6)
C3−C4	1.359(10)
P1−Pt−P2	163.57(5)
P1−Pt−N31	81.57(13)
P1−Pt−C3	98.1(2)
P1−Pt−C4	96.53(18)
P2−Pt−N31	82.00(13)
P2−Pt−C3	97.6(2)
P2−Pt−C4	99.05(18)
N31−Pt−C3	162.5(2)
N31−Pt−C4	161.1(2)
C3 −Pt −C4	36.3(3)

the coordination plane.[21] The C−C double bond length [1.359(10) Å] is similar to that found in the isostructural Rh^I complex [1.351(11) Å]. Compared to other square planar Pt^{II} alkene complexes, the Pt−C distances in complex **1** are significantly longer than those observed for the anionic complex $[Pt(C_2H_4)Cl_3]^-$ [2.128(3) and 2.135(3) Å],[25] but similar to the cationic complex $[Pt(C_2H_4)Cl(Me_2NCH_2CH_2NMe_2)]^+$ [2.184(5) and 2.166(5) Å].[26] While the high positive charge seems to affect significantly the Pt−C bond lengths, no particular influence is seen on the C−C double bond length, which was found to be around 1.37 Å for all the examples cited.

Reactions with Nucleophiles. I. Reaction with MeOH. Dissolution of the complexes **1**−**4** in CD_3OD led to the quantitative formation of the addition products **8**-d_3−**11**-d_3, producing a strongly acidic solution (cf. eq 4). The ^{1}H NMR spectra show exclusively signals of the β-methoxyalkyl complexes (see ExperimentalSection), and no signals of the substitution product were detectable. In contrast, in the case of the analogous palladium(II) complexes the substitution of the alkene by methanol was considerably competitive to the addition reaction and dominated with increasing steric hindrance of the substituents R/R′ at the alkene.[9]

$$\underset{\textbf{1-6}}{[Pt(PNP)(CHR{=}CHR')]^{2+}} + MeOH \rightleftharpoons [Pt(PNP)(CHRCHR'OMe)]^{+} + H^{+} \quad (4)$$

R/R′	
H/H	**8**
H/Me	**9**
H/Et	**10**
H/Ph	**11**
Me/Me	**12a**
Me/Me	**12b**

The formation of a small amount of the β-methoxyethyl complex **8** was even detectable when only 20 equiv of MeOH was added to a solution of complex **1** in CD_2Cl_2. This shows clearly the rather high reactivity to nucleophilic addition at the C−C double bond due to the higher electrophilicity of the dicationic complexes compared to monocationic alkene Pt^{II} complexes. Indeed, for the latter ones it was reported that they could be recrystallized even in hot methanol without showing any decomposition (or any other reaction).[5a] In that case the addition of methanol succeeded only in the presence of a strong base like KOH. The direct addition of alcohols at the C−C double bond has been reported only with dicationic platinum(II) diene complexes.[8] It was also promoted by a dimeric platinum(III) complex where a 4-fold positively charged alkene Pt^{III} complex was proposed as an intermediate.[27]

The ^{1}H NMR spectrum of *Z*- and *E*-2-butene complex **5** or **6** dissolved in CD_3OD shows a mixture of the addition product (**12a** or **12b**, respectively[28]) and unreacted starting complex in a ratio of ca. 2:1. By addition of 2 equiv of $NaHCO_3$ the equilibrium reaction (eq 4) could be immediately shifted quantitatively to the β-methoxyalkyl complex **12a** or **12b**. This demonstrates that the nucleophilic addition is a fast reaction. Thus, the complexes **8**−**11** could be readily obtained by reaction of the alkene complexes **1**−**4** in CH_2Cl_2 solution with 4 equiv of MeOH and addition of 2 equiv of $NaHCO_3$. For the complexes **2**−**4** a high regioselectivity (Markovnikov) of the methanol addition was observed, which was independently confirmed by reductive cleavage of the addition product with $NaBH_4$ in CD_3OD, producing $CH_3CHROMe$ (R = Me, Et, Ph).

The norbornene complex **7** dissolved in methanol gave a product mixture. In the ^{1}H NMR spectrum two new singlets appear at δ 2.63 and 2.82, which could be assigned to methoxy groups, suggesting the formation of two different addition products. Changes were also noted in the aliphatic region of the spectrum, but since the signals are relatively broad and overlapping, no efforts have been made for further structural identification of these products so far.

The treatment of the complex **8** with HBF_4 in methanol led to the reversal of the nucleophilic addition, and

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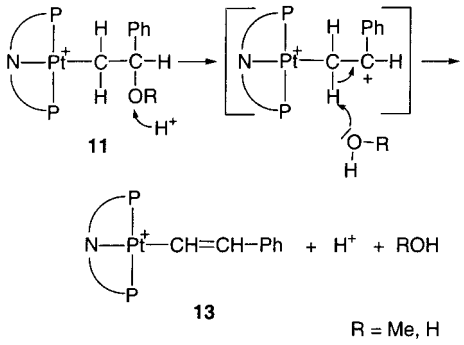
(28) The addition of methanol to *Z*- and *E*-2-butene complexes **5** and **6** gave the diastereomers **12a** and **12b** (see discussion for analogous Pd complexes in ref 9), which show slight but significant differences in their ^{1}H NMR spectrum; see Experimental Section.

Scheme 1



even in the absence of additional free ethylene to the regeneration of the complex **1**. This shows the high stability of the ethylene complex **1** toward substitution by methanol.

The β-methoxyalkyl complexes **8**−**12** are stable as solids as well as in solution. Although complex **11** is quite stable after isolation, it showed a decomposition in the solution in which it was formed in situ by dissolving **4** in CD_3OD, cf. eq 4. After standing for 2 h, complex **11** was completely converted to a new single species detected by ^1H NMR. A crystalline solid that precipitated from the methanol solution showed an identical ^1H NMR spectrum after dissolution in CD_2Cl_2. A doublet with ^{195}Pt satellites appearing at δ 6.12 ($^3J_{H-Pt}$ = 79 Hz), a partially hidden doublet of triplets at δ 7.84 assigned to the Pt−CH=CH moiety, and multiplets at δ 6.84 and 7.09 due to the phenyl group suggest the formation of the alkenyl complex [Pt(PNP)(CH=CHPh)]BF_4, **13**, cf. Scheme 1. The isolated alkenyl complex was also characterized by ^{13}C NMR spectroscopy, where signals for the alkenyl group were observed at δ 118.9 and 139.2, showing coupling to the phosphorus nuclei (J_{C-P} = 9.1 and 5.5 Hz, respectively). This interesting decomposition pathway does not seem to have been observed so far for a β-functionalized σ-alkyl complex.[29] A possible mechanism could involve initial protonation at the oxygen atom,[30] methanol removal from **11** (the reverse addition), and formation of a carbocation at the β-carbon atom followed by an α-proton loss (see Scheme 1). The additional stabilization in **13** due to the π-conjugation with the phenyl ring could explain why alkenyl complexes analogous to **13** were not formed starting from complexes **1** and **2**.

II. Reaction with H_2O. The ^1H NMR spectrum of a solution of the ethylene complex **1** in CD_2Cl_2 with ca. 4 equiv of H_2O did not show any detectable reaction. However, the addition of a larger excess of H_2O (resulting in a biphasic mixture) led to a complete disappearance of the signals of **1**, and the new signals observed in the ^1H NMR spectrum indicated a conversion to mono- and dialkylated addition products **14** and **15** in a ratio of 1:1 (cf. Scheme 2). The signal sets for the [$PtCH_2CH_2O$] have been assigned to **14** (δ 1.83 and 2.68) and to **15** (δ 2.05 and 3.62).[31] The dinuclear complex **15** is presumably formed by a further nucleophilic attack of **14** at remaining **1** or, as was supposed for [$PtCl(CH_2CH_2OH)(Me_2NCH_2CH_2NMe_2)$],[4b,32] by a spontaneous condensation reaction. In sharp contrast to the analogous palladium complex,[9] the ethylene displacement by water did not occur for complex **1** even in the absence of any free ethylene. Preparatively, the mixture of addition products **14**/**15** was obtained in a molar ratio of 1:4 by reaction of complex **1** with 4 equiv of H_2O and 2 equiv of $NaHCO_3$.

When aqueous HBF_4 was added to a solution of the isolated complex mixture **14**/**15**, the nucleophilic addition was reversed to the ethylene complex **1**, similar to the analogous reaction observed with the β-methoxyalkyl complex **8**. Although there was no free ethylene and a large excess of water was present in solution, no aqua complex was detected, which shows again the stability of the platinum(II) complex to alkene substitution by water.

The reactions of the propene, 1-butene, and styrene complexes (**2**, **3**, and **4**) with H_2O have been similarly investigated. They give only single addition products, likely due to the steric hindrance of the substituent R, and show exclusive Markovnikov regiochemistry [Pt(PNP)(CH_2CHROH)]BF_4 (R = Me **16**, Et **17**, Ph **18**). For the complex **18** (in situ formed from **4** and H_2O, cf. comment[30]) the same decomposition occurred in solution as observed for the methoxyalkyl complex **11**, resulting in the alkenyl complex **13** (cf. Scheme 1).

III. Reactions with Aromatic Amines. The nucleophilic addition of amines at platinum(II) alkene complexes has been the subject of investigation over several decades.[1] These studies have shown that the formation of the β-ammonioalkyl complex depends on several factors such as complex charge, basicity of the amine, and steric hindrance of substituents at the amine as well as at the alkene.[1d] Because of their weak basicity, the additions of aromatic amines at platinum(II) alkene complexes are rare[33] compared to those of aliphatic amines. While for neutral platinum(II) complexes no addition of aromatic amines was evident,[33] with a cationic complex a C−C bond formation in the *para* position of the aromatic amine occurred rather than N-addition to the C−C double bond.[35]

Since a high reactivity of the dicationic platinum(II) alkene complexes was observed with methanol and water as weakly basic nucleophiles, it was interesting to investigate the reactions with different weakly basic aromatic amines H_2NAr, also with the intention of comparing the actual reactivity with that of the isostructural palladium(II) complexes.

The reaction of the ethylene complex **1** in CD_2Cl_2 solution with only 1 equiv of aniline (pK_a = 4.6) at room

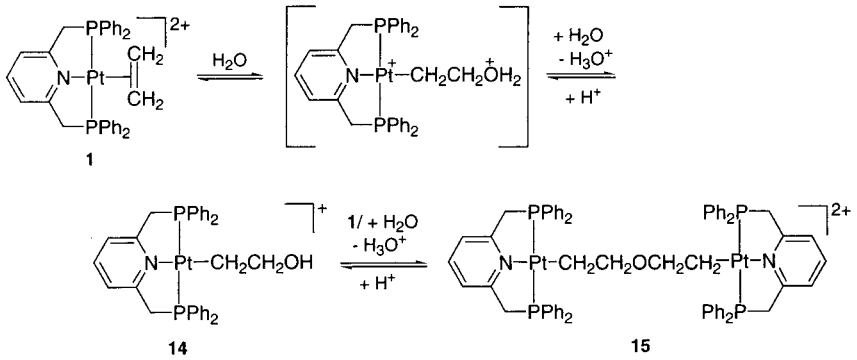
(29) Recently an interesting rearrangement of a Markovnikov addition product [$Pt(Me_2NCH_2CH_2NMe_2)Cl\{CH_2CHPh(CH(C(O)Me)_2\}$] into the anti-Markovnikov regioisomer was reported which is only observerd in solid state via detachment of the acetylacetonate, while in solution also an irreversible decompostion to other species takes place in a few days, for which unfortunately no further specification was given; see ref 32.

(30) It should be remembered that **11** here was formed in situ; therefore there was still a stoichiometric amount of H^+ in solution dissociated from the primarily formed addition product [$Pt(PNP)(CH_2CH(Ph)OHCH_3)]^{2+}$, which is considered also the intermediate species for the methanol dissociation (reverse addition) assuming the principle of the microscopic reversibility.

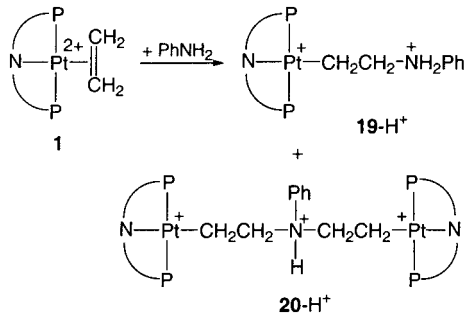
(31) The assignment of the signals for **14** and **15** has been done on the basis of the chemical shifts of the isostructural palladium complexes; see ref 9.

(32) Maresca, L.; Natile, G. *Inorg. Chim. Acta* **1999**, *285*, 301−304.
(33) Haszeldine, R. N.; Parish, R. V.; Robbins, D. W. *J. Chem. Soc., Dalton Trans.* **1976**, 2355−2363.
(34) Hollings, D.; Green, M.; Claridge, D. V. *J. Organomet. Chem.* **1973**, *54*, 399−402
(35) Maresca, L.; Natile, G.; Fanizzi, F. P. *J. Chem. Soc., Dalton Trans.* **1992**, 1867−1868.

Scheme 2



Scheme 3



temperature led immediately to a complete conversion to a mixture of β-ammonio mono- and dialkylated addition products **19**-H^+ and **20**-H^+ in a ratio of 1:1 (cf. Scheme 3). Also in this case no indication for the substitution of the ethylene could be detected by ^1H NMR spectroscopy.

Performing the reaction of complex **1** with 4 equiv of aniline and 2 equiv of $NaHCO_3$ at 0 °C, the β-aminoethyl complex $[Pt(PNP)(CH_2CH_2NHPh)]BF_4$, **19**, could be obtained as a single addition product. By further reaction of the isolated complex **19** with the ethylene complex **1**, the complex **20**-H^+ was independently prepared. Complex **20**-H^+ was isolated as a stable compound and characterized by ^1H NMR, confirming the dialkylated structure observed before. The proton of the ammonium group in **20**-H^+ was abstracted by reaction with 2 equiv of $NaHCO_3$, converting it into the corresponding amino derivative $[\{Pt(PNP)(CH_2CH_2)\}_2NPh](BF_4)_2$, **20**. Comparing the ^1H NMR spectra of corresponding ammonio and amino derivatives **19**-H^+/**19** or **20**-H^+/**20**, characteristic differences in chemical shifts of the NPh signals are notable. These signals of **19** and **20** appear significantly upfield shifted by $\Delta\delta$ 0.3−1.0 than those found correspondingly for **19**-H^+ and **20**-H^+, which is consistent with the loss of the positive charge at the N atom by abstracting a proton. Unfortunately, the ^1H NMR signals of NH_2 for **19**-H^+ and NH for **20**-H^+ are not detectable; either they might be hidden under the large signals of PPh in the region δ 7.4−7.8, or they might be very broad because of relatively fast intermoleculare H^+-exchange.

At this point it was difficult to decide whether the nucleophilic addition reaction is only kinetically controlled or also thermodynamically favored over the substitution reaction. Indeed, for the analogous palladium(II) complexes a thermodynamic equilibrium of substitution and addition reactions does exist.[9] The high inertness toward substitution of the platinum(II) complexes was shown by treatment of the aniline complex **21** (prepared independently, see Experimental Section) with a large excess of ethylene in the presence of $NaHCO_3$. Stirring the mixture overnight (in CD_2Cl_2/CD_3NO_2) no reaction was at all observed. By contrast, in the case of palladium(II) a complete equilibrium shift to the addition product was observed in a similar experiment.[9]

However, the kinetic inhibition of the substitution of aniline by ethylene could be overcome by addition of some acetonitrile (ca. 0.8 equiv) to the solution of the aniline complex **21** saturated with ethylene (in CD_2Cl_2/CD_3NO_2). In the ^1H NMR spectrum signals of the addition product **19**-H^+ became visible after 1 day, their intensity increased with time, and after ca. 10 days no further change was seen. In this way the existence of an equilibration process has been shown, which is quite slower than that revealed for the palladium(II) complexes. This allowed a rough estimation of the thermodynamic equilibrium constants for the formal "insertion" reaction, cf. eq 5.[36] The value $K_{ins} = 10^2$ L mol^{-1} indicates that the double positive charge on Pt does indeed *thermodynamically favor* the addition over the substitution reaction even more than in the case of palladium(II) ($K_{ins} = 1$ L mol^{-1}).[9] In comparison, for the neutral platinum(II) ethylene complexes it was found that the amine addition, although being kinetically favored, appears to be *thermodynamically disfavored* over the substitution.[3c]

$$[(PNP)Pt(PhNH_2)]^{2+} + CH_2{=}CH_2 \xrightleftharpoons[(MeCN)]{K_{ins'} = 10^2\ Lmol^{-1}} [(PNP)Pt(CH_2CH_2NH_2Ph)]^{2+} \quad (5)$$

21 **19**-H^+

The addition of ca. 0.8 equiv of acetonitrile is sufficient for a reasonable acceleration of the substitution of aniline by ethylene via the formation of acetonitrile complex **22**. Each individual auxiliary substitution

(36) The term "insertion" refers only to the formal outcome of the reaction and does not have any mechanistic implication. It is likely that the actual mechanism involves consecutive (bimolecular) substitutions of aniline by acetonitrile and then of acetonitrile by ethylene followed by external *trans* nucleophilic attack of aniline on the coordinated ethylene. In these considerations the equilibration to double addition product is completely neglected, although it was seen in the experiment described above. The equilibration constant K_{ins} however demonstrates clearly the higher preference for the nucleophilic addition (considering only the single addition).

reaction of complexes **21** and **1** with acetonitrile (cf. eqs 6 and 7) equilibrates within 10 h, allowing the evaluation of their equilibrium constants. Combining these values with that of the "insertion" equilibrium eq 5, the individual equilibrium constants for the ethylene substitution by aniline, $K_{sub} = 3 \times 10^4$, and nucleophilic addition, $K_{add} = 3 \times 10^6$ L mol^{-1} (cf. eq 8), were estimated. These values show that the relative stability of ethylene complexes **1** compared to the aniline complex **21** is somewhat higher than found for the analogous palladium(II) complexes ($K_{sub} = 2 \times 10^5$),[9] which seems to be consistent with the calculated overall metal−alkene bond energies decreasing in the order Pt > Pd.[37] However, the nucleophilic addition is more favored for the platinum(II) complexes than found for palladium(II) ($K_{add} = 2 \times 10^5$ L mol^{-1}). In contrast, neutral platinum(II) complexes do not undergo nucleophilic addition ($K_{add} < 0.1$ L mol^{-1}) with weak bases such as aniline (p$K_a < 5$).[3c]

$$[(PNP)Pt(MeCN)]^{2+} + PhNH_2 \underset{}{\overset{K = 10^2}{\rightleftharpoons}} [(PNP)Pt(PhNH_2)]^{2+} + MeCN \quad (6)$$

22 **21**

$$[(PNP)Pt(CH_2{=}CH_2)]^{2+} + MeCN \overset{K = 3\cdot10^2}{\rightleftharpoons} [(PNP)Pt(MeCN)]^{2+} + CH_2{=}CH_2 \quad (7)$$

1 **22**

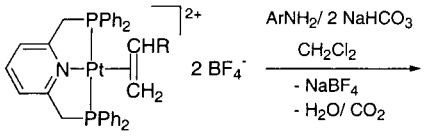
$$[(PNP)Pt(CH_2{=}CH_2)]^{2+} + PhNH_2 \overset{K_{add} = 3\cdot10^6\ Lmol^{-1}}{\rightleftharpoons} [(PNP)Pt(CH_2CH_2NH_2Ph)]^{2+} \quad (8)$$

1 **19**-H$^+$

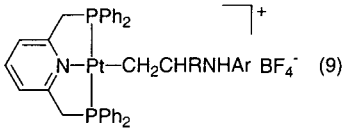
A solution of the propene complex **2** was treated with 1 equiv of aniline, giving the complete formation of the β-ammoniopropyl complex [Pt(PNP)(CHCHMeNH$_2$-Ph)](BF$_4$)$_2$, **23**-H$^+$ (Markovnikov addition), which was isolated as a stable compound. Upon proton abstraction by the auxiliary base $NaHCO_3$, the β-aminopropyl complex **23** could be obtained (cf. eq 9). As discussed above, the ^{1}H NMR signals of the NPh group in **23** show a characteristic upfield shift by $\Delta\delta$ 0.4−1.0, indicating the transformation of the ammonio into the amino derivatives. While the N*H* signal for **23** appears at δ 3.02, that of NH_2 for **23**-H$^+$ is not detectable for the same probable reasons described for **19**-H$^+$/**20**-H$^+$.

Furthermore the reaction of 1-butene and styrene complexes **3** and **4** with aniline/$NaHCO_3$ was investigated and gave also exclusively Markovnikov addition products **24** and **25**, cf. eq 9.

Even the addition of 1 equiv of the less basic 2-chloroaniline (p$K_a = 2.6$) to a solution of the ethylene complex **1** (CD_2Cl_2/CD_3NO_2) led to the complete conversion to the β-ammonioethyl complex **26**-H$^+$, and by treatment with $NaHCO_3$ the deprotonated complex **26** was obtained, whose ^{1}H NMR spectrum shows the characteristic upfield shift of the NPh signals by $\Delta\delta$ 0.2−1.0 compared to those of **26**-H$^+$. Likewise toluidine (p$K_a = 5.1$) and 4-methoxyaniline (p$K_a = 5.3$) readily gave with complex **1** and $NaHCO_3$ the β-aminoethyl complexes **27** and **28** (cf. eq 9), which could be isolated in good yields as quite stable solids.



1-4



(9)

R	Ar	
H	C_6H_5	**19**
Me	C_6H_5	**23**
Et	C_6H_5	**24**
Ph	C_6H_5	**25**
H	C_6H_4Cl-*o*	**26**
H	C_6H_4Me-*p*	**27**
H	C_6H_4OMe-*p*	**28**

As was seen for the treatment of the β-methoxy- and β-hydroxymethyl complexes with acid, the β-aminoalkyl complexes also gave rise to the reversal of the nucleophilic addition when gaseous HCl was bubbled in a CD_2-Cl_2 solution. In this case the chloro complex was formed and the alkene was liberated, cf. eq 10. Interestingly in β-ammonioethyl platinum(II) complexes (resulting from the addition of amines at the monocationic ethylene complex) the Pt−C σ bond can be cleaved with HCl.[4a,38] In the σ-alkyl complexes produced from the dicationic alkene complexes however, a positive charge remains at the platinum center, which presumably stabilizes the Pt−C σ bond, and this could be the reason the C−N bond dissociation is favored over the Pt−C cleavage.

$$[(PNP)Pt(CH_2CHRNHPh)]BF_4 \xrightarrow{+\ HCl\ (g)/\ CD_2Cl_2} [(PNP)PtCl]BF_4 + CH_2{=}CHR + PhNH_3Cl \quad (10)$$

R = H **19**, R = Me **23**

Conclusions

A novel class of dicationic platinum(II) monoalkene complexes has been obtained through the use of the tridentate "pincer" ligand PNP. Compared to their recently prepared palladium analogues,[9] these complexes appear to be thermodynamically more stable and kinetically less labile toward substitution by oxygen and nitrogen donors. The dicationic complexes display an exceptionally high reactivity toward nucleophilic attack on the coordinated alkene, as a consequence of the double positive charge on the metal ion (or, viewed from a thermodynamic perspective, the σ-alkyl derivatives resulting from the nucleophilic attack are strongly stabilized by the residual positive charge on the metal ion). This is exemplified by the "superacid" behavior in methanol solution, which leads to the protonation of the solvent and to the quantitative formation of the β-methoxyalkyl derivatives, in contrast to that of monocationic

(37) Hay, P. J. *J. Am. Chem. Soc.* **1981**, *103*, 1390−1393.

(38) De Renzi, A.; Paiaro, G.; Panunzi, A.; Paolillo, L. *Gazz. Chim. Ital.* **1972**, *102*, 281−287.

species, which require the presence of an auxiliary base to assist the same reaction.[4b] Aromatic amines (even those having very low basicity) also give the addition products quantitatively, and an approximate estimation of the equilibrium constants for the addition and substitution reactions has been obtained in the case of aniline and coordinated ethylene. The equilibrium constant for the addition reaction ($K_{add} = 3 \times 10^6$) is at least 7 orders of magnitude larger than in neutral complexes,[3c] and (again in contrast to the behavior of neutral species) the addition reaction proved to be thermodynamically favored over the substitution reaction ($K_{add}/K_{sub} = K_{ins} = 10^2$ L mol^{-1}). The electrophilicity of the coordinated alkene is also larger than that displayed by the isostructural palladium(II) complexes, which in methanol solution give only partial conversion to β-methoxyalkyl derivatives and which give lower values of K_{add} and K_{ins} for the reaction of aniline with coordinated ethylene.[9] In conclusion, dicationic platinum(II) alkene complexes appear to be ideal substrates for exploiting the electrophilic properties of coordinated alkenes and possibly give rise to new C−C and C−heteroatom bond formations, although the stability of the resulting σ-alkyl derivatives might be an obstacle to further useful transformations.

Experimental Section

General Procedures. All reactions were carried out under dry nitrogen. CH_2Cl_2 was refluxed over CaH_2, CH_3OH over Mg/$Mg(OCH_3)_2$, and diethyl ether over Na/benzophenone. The solvents were distilled before using. CD_2Cl_2, CD_3NO_3, and $CDCl_3$ were dried with 4 Å molecular sieves. $AgBF_4$ was obtained from ABCR and was used without further purification. The aromatic amines RNH_2 were obtained by Aldrich and were distilled before using. The NMR spectra were recorded on Varian Gemini 200 and 300, Bruker AC-250, and Bruker WH-400 instruments. The ^{1}H NMR shifts were referenced to the resonance of the residual protons of the solvents, the ^{13}C NMR shifts to the solvent resonance ($\delta = 53.8$, CD_2Cl_2; $\delta = 62.8$, CD_3NO_2; $\delta = 45.3$, CD_3OD_3), and the ^{13}P NMR shifts to the resonance of PPh_3 ($\delta = -3$, $CDCl_3$), the external standard. Abbreviations used in NMR data: s, singlet; d, doublet; t, triplet; ps.t, pseudo triplet; m, multiplet; br, broad.

X-ray Structure Determination of [Pt(PNP)(CH_2=CH_2)](BF_4)$_2$·CH_2Cl_2 (1·CH_2Cl_2). Details of the X-ray experiment, data reduction, and final structure refinement calculation are summarized in Table 3. A crystal of complex **1**·CH_2Cl_2 suitable for X-ray structure determination was grown from a saturated solution of complex **1** in dichloromethane, fixed with perfluorinated ether, and mounted in a glass capillary. Preliminary examination and data collection were carried out on a Stoe IPDS system attached to a rotating anode (NONIUS FR591; 50 kV; 60 mA; 3.0 kW) and graphite-monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Data collection was performed at 233 K with an exposure time of 600 s per image (φ-scans, oscillation modus, $\Delta\varphi = 1.2°$). A total number of 12 889 reflections were collected.[39a] After merging a sum of 6619 independent reflections remained and were used for all calculations. Data were corrected for Lorentz and polarization effects. A correction for absorption effects was applied using the program Difabs.[39b] The unit cell parameters were obtained by full-matrix least-squares refinements of 4965 reflections with the programs Select and Cell.[39a] The structure was solved by a combination of direct methods and difference Fourier syntheses.[39c] All non-hydrogen atoms of the asymmetric unit were refined with anisotropic thermal displacement parameters. All hydrogen atoms were calculated in ideal positions (riding model). Full-matrix least-squares refinements were carried out by minimizing $\sum w(F_o^2 - F_c^2)^2$ with the SHELXL-97 weighting scheme and stopped at maximum shift/err < 0.001.[39d] Neutral atom scattering factors for all atoms and anomalous dispersion corrections for the non-hydrogen atoms were taken from *International Tables for Crystallography*.[39e] All other calculations (including ORTEP graphics) were done with the program PLATON.[38b] Calculations were performed on a PC workstation (Intel Pentium II) running LINUX. The correct enantiomer is proved by Flack's parameter ($x = -0.026(6)$).

Table 3. Crystallographic Data for Compound 1·CH_2Cl_2

chem formula	$C_{34}H_{33}B_2Cl_2F_8NP_2Pt$
fw	957.15
color/shape	colorless/fragment
cryst size (mm)	0.34 × 0.28 × 0.12
cryst syst	monoclinic
space group	$P2_1$ (No. 4)
a (Å)	9.4350(9)
b (Å)	21.9467(10)
c (Å)	9.0662(8)
β (deg)	93.516(11)
V (Å^3)	1873.8(3)
Z	2
T (K)	233
ρ_{calcd} (g cm^{-3})	1.696
μ (mm^{-1})	4.038
F_{000}	936
θ-range (deg)	2.35−25.64
data collcd (h,k,l)	h: ±11, k: ±25, l: ±11
no. of rflns collcd	12 889
no. of indep rflns/R_{int}	6619/0.0409
no. of obsd rflns ($I > 2\sigma(I)$)	6244
no. of params refined	451
R1 (obsd/all)	0.0265/0.0287
wR2 (obsd/all)	0.0674/0.0690
GOF (obsd/all)	0.990/0.990
max/min $\Delta\rho$ (e Å^{-3})	0.95 /−0.65

Syntheses. The ligand PNP[10] and complex $Pt(SMe_2)_2I_2$[40] were prepared according to the procedures described in the literature.

[Pt(PNP)I]I. A solution of 1 g (2.10 mmol) of PNP in 10 mL of CH_2Cl_2 was added to a solution of 1.2 g (2.09 mmol) of $Pt(SMe_2)_2I_2$ in 60 mL of CH_2Cl_2. The volume of the solution was reduced to 15 mL by removing the solvent under reduced pressure. The product was precipitated by dropwise addition of ca. 40 mL of diethyl ether under stirring. The pale yellow solid was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 1.9 g (2.05 mmol, 98%). ^{1}H NMR (200 MHz, $CDCl_3$): 4.73 (ps.t, $^2J_{H-P} + {}^4J_{H-P} = 4.4$ Hz, 4H,CH_2), 7.56 (m, 12H, Ph), 7.88 (m, 8H, Ph), 8.17 (m, 3H, py).

[Pt(PNP)(CH_2=CHR)](BF_4)$_2$ 1−4. General Procedure. A mixture of 200 mg (0.216 mmol) of [Pt(PNP)I]I and 84 mg (0.432 mmol) of $AgBF_4$ in 8 mL of CH_2Cl_2 was cooled to 0 °C and saturated with the respective gaseous alkene; in the case of liquid alkenes 10 equiv was added. After stirring the mixture for 1 h the precipitate was filtered off. In the case of ethylene the precipitate (containing product) was washed with nitromethane (1 mL, free of any nitrile). The product was

(39) (a) *IPDS Operating System*, Version 2.8; Stoe&Cie, GmbH: Darmstadt, Germany, 1997. (b) Spek, A. L. *PLATON*, A Multipurpose Crystallographic Tool; Utrecht University: The Netherlands, 2001. (c) Altomare, A.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Burla, M. C.; Polidori, G.; Camalli, M. SIR92. *J. Appl. Crystallogr.* **1994**, *27*, 435. (d) Sheldrick, G. M. *SHELXL-97*, Program for Crystal Structure Refinement; University of Göttingen: Germany, 1998. (e) *International Tables for Crystallography*; Wilson, A. J. C., Ed., Kluwer Academic Publishers: Dordrecht, The Netherlands, 1992; Vol. C, Tables 6.1.1.4 (pp 500−502), 4.2.6.8 (pp 219−222), and 4.2.4.2 (pp 193−199).

(40) Roulet, R.; Barbey, C. *Helv. Chim. Acta* **1973**, *56*, 2179−2186.

precipitated respectively from the solution by dropwise addition of ca. 40 mL of diethyl ether. The solid was filtered off, washed with diethyl ether, and dried under vacuum.

[Pt(PNP)(CH_2=CH_2)](BF_4)$_2$ (1). Yield: 166 mg (0.191 mmol, 88%); white solid; dec pt 206 °C. Anal. Calcd for $C_{33}H_{31}B_2F_8NP_2Pt$: C, 45.44; H, 3.58; N, 1.61. Found: C, 45.23; H, 3.56; N, 1.70. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.35 (t, $^2J_{H-P}$ = 2.8 Hz, $^1J_{H-Pt}$ = 59 Hz, 4H, CH_2), 4.94 (ps.t, $^2J_{H-P}$ + $^4J_{H-P}$ = 5.0 Hz, 4H, PCH_2), 7.50−7.80 (m, 12H, Ph), 7.84−7.98 (m, 10H, Ph, py), 8.17 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py). ^{13}C NMR (100 MHz, CD_2Cl_2): δ 43.6 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 18.0 Hz, PCH_2), 77.9 (s, $^1J_{C-Pt}$ = 116.5 Hz, CH_2), 124.0 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.4 Hz, py-*3,5*), 130.4 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.3 Hz, Ph_m), 133.5 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.7 Hz, Ph_o), 134.0 (s, Ph_p), 144.0 (s, py-*4*), 161.6 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 41.7 (s, $^1J_{P-Pt}$ = 2174 Hz).

[Pt(PNP)(CH_2=$CHMe$)](BF_4)$_2$ (2). Yield: 159 mg (0.179 mmol, 83%); white solid; dec pt 185 °C. Anal. Calcd for $C_{34}H_{33}B_2F_8NP_2Pt$: C, 46.08; H, 3.75; N, 1.58. Found: C, 45.89; H, 3.84; N, 1.70. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.56 (d, $^3J_{H-H}$ = 5.8 Hz, $^3J_{H-Pt}$ = 44.0 Hz, 3H, CH_3), 4.31 (m, $^3J_{H-P}$ = 7.8 Hz, $^2J_{H-Pt}$ = 68 Hz, 1H, CH_2), 4.32 (m, $^3J_{H-P}$ = 14.8 Hz, 1H, CH_2), 4.69 (d ps.t, $^2J_{H-H}$ = 16.8 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 5.2 Hz, 2H, PCH_aH_b), 5.14 (d ps.t, $^2J_{H-H}$ = 16.8 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 5.4 Hz, 2H, PCH_aH_b), 5.47 (m, 1H, CH), 7.50−7.80 (m, 12H, Ph), 7.80−8.10 (m, 11H, Ph, py). ^{13}C NMR (100 MHz, CD_3NO_2): δ 21.2 (s, $^2J_{C-Pt}$ = 31 Hz, CH_3), 44.1 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 17.4 Hz, PCH_2), 74.3 (s, $^1J_{C-Pt}$ = 138 Hz, CH_2), 103.5 (s, $^1J_{C-Pt}$ = 108 Hz, CH), 124.0 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 36.8 Hz, Ph_i), 124.4 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 36.8 Hz, $Ph_{i'}$) 125.1 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 6.0 Hz, py-*3,5*), 131.0 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.7 Hz, $Ph_{m,m'}$), 133.6 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.7 Hz, Ph_o), 134.9 (s, Ph_p), 135.2 (s, $Ph_{p'}$), 135.3 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.7 Hz, $Ph_{o'}$), 145.5 (s, py-*4*), 162.6 (s, py-*2,6*). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 40.8 (s, $^1J_{PPt}$ = 2268 Hz).

[Pt(PNP)(CH_2=$CHEt$)](BF_4)$_2$ (3). Yield: 172 mg (0.191 mmol, 88%); white solid; dec pt 196 °C. ^{1}H NMR (200 MHz, CD_2Cl_2/CD_3NO_2): δ 0.71 (t, $^3J_{H-H}$ = 7.6 Hz, 3H, CH_3), 1.05 (m, 1H, CH_2), 1.92 (m, 1H, CH_2), 4.46 (m, 2H, CH_2), 4.81 (d ps.t, $^2J_{H-H}$ = 17.6 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 5.4 Hz, 2H, PCH_aH_b), 5.00 (d ps.t, $^2J_{H-H}$ = 17.6 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 4.8 Hz, 2H, PCH_aH_b), 5.52 (m, 1H, CH), 7.60−7.83 (m, 12H, Ph), 7.83−8.05 (m, 10H, Ph, py), 8.21 (t, $^3J_{H-H}$ = 8.4 Hz, 1H, py). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 14.9 (s, CH_3), 29.0 (s, CH_2), 44.2 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 16.3 Hz, PCH_2), 73.1 (s, $^1J_{C-Pt}$ = 131 Hz, CH_2), 107.7 (s, $^1J_{C-Pt}$ = 113.1 Hz, CH), 123.4 (m, Ph_i), 124.4 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.6 Hz, py-*3,5*), 131.2 (m, $Ph_{m,m'}$), 133.1 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.2 Hz, Ph_o), 134.3 (s, Ph_p), 134.6 (s, $Ph_{p'}$), 134.7 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.3 Hz, $Ph_{o'}$), 144.4 (s, py-*4*), 161.9 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2/CD_3NO_2): δ 39.3 (s, $^1J_{P-Pt}$ = 2236 Hz).

[Pt(PNP)(CH_2=$CHPh$)](BF_4)$_2$ (4). Yield: 167 mg (0.176 mmol, 82%); white solid; dec pt 210 °C. Anal. Calcd for $C_{39}H_{35}B_2F_8NP_2Pt$: C, 49.39; H, 3.72; N, 1.48. Found: C, 49.50; H, 3.87; N, 1.39. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.59 (d ps.t, $^2J_{H-H}$ = 16.0 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 6.0 Hz, 2H, PCH_aH_b), 4.71 (d ps.t, $^3J_{H-H}$ = 14.0 Hz, $^3J_{H-P}$ = 6.0 Hz, 1H, CH_2), 4.89 (d, $^3J_{H-H}$ = 10.0 Hz, $^2J_{H-Pt}$ = 72 Hz, 1H, CH_2), 5.24 (d ps.t, 2H, $^2J_{H-H}$ = 23.2 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 6.0 Hz, PCH_aH_b), 6.20 (m, 1H, $^2J_{H-Pt}$ = 56 Hz, CH), 6.91 (d, 2H, CPh), 7.19 (m, 3H, CPh), 7.50−7.80 (m, 23H, PPh, py). ^{13}C NMR (100 MHz, CD_3NO_2): δ 44.4 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 17.1 Hz, PCH_2), 66.5 (s, $^1J_{C-Pt}$ = 138 Hz, CH_2), 108.2 (s, $^1J_{C-Pt}$ = 81 Hz, CH), 123.4 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 30.8 Hz, PPh_i), 123.5 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 30.1 Hz, $PPh_{i'}$) 125.2 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 6.0 Hz, py-*3,5*), 129.5 (s, CPh), 130.7 (s, CPh), 130.8 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 6.2 Hz, PPh_m), 131.2 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 6.1 Hz, $PPh_{m'}$), 134.1 (s, Ph), 134.4 (s, PPh_p), 134.5 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.0 Hz, PPh_o), 134.8 (s, $PPh_{p'}$), 134.9 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.7 Hz, $PPh_{o'}$), 137.2 (s, CPh), 145.5 (s, py-*4*), 161.9 (s, py-*2,6*). ^{31}P NMR (81 MHz, CD_2Cl_2): δ 38.2 (s, $^1J_{P-Pt}$ = 2328 Hz).

[Pt(PNP)(MeCH=CHMe)](BF_4)$_2$ (5 and 6). General Procedure. To a solution of 200 mg of the ethylene complex **1** in 30 mL of CH_2Cl_2 was added ca. 20 equiv of *E*- or *Z*-2-butene as gas. The solution was stirred for 7 h at room temperature under refluxing the *E*- or *Z*-2-butene using a coil cooled with dry ice. The product was precipitated by dropwise addition of diethyl ether. The solid was filtered off, washed with diethyl ether, and dried under vacuum.

[Pt(PNP)(*Z*-MeCH=CHMe)](BF_4)$_2$ (5). Yield: 186 mg (0.206 mmol, 90%); white solid. Anal. Calcd for $C_{35}H_{35}B_2F_8NP_2Pt$: C, 46.69; H, 3.92; N, 1.56. Found: C, 46.58; H, 3.99; N, 1.63. ^{1}H NMR (200 MHz, CD_3NO_2): δ 1.88 (d, $^3J_{H-H}$ = 4.8 Hz, $^3J_{H-Pt}$ = 48 Hz, 6H, CH_3), 4.91 (ps.t, 4H, $^2J_{H-P}$ + $^4J_{H-P}$ = 5.0 Hz, PCH_2), 5.76 (br, $^2J_{H-Pt}$ = 72.0 Hz, 2H, CH), 7.60−8.02 (m, 22H, py, Ph), 8.17 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, py). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 17.7 (s, CH_3), 44.7 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 16.4 Hz, PCH_2), 99.2 (s, $^1J_{C-Pt}$ = 118 Hz, CH), 124.4 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 30.9 Hz, Ph_i), 125.7 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.3 Hz, py-*3,5*), 131.5 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.4 Hz, Ph_m), 133.5 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 7.2 Hz, Ph_o), 135.7 (s, Ph_p), 146.1 (s, py-*4*), 162.0 (s, py-*2,6*).

[Pt(PNP)(*E*-MeCH=CHMe)](BF_4)$_2$ (6). Yield: 172 mg (0.191 mmol, 88%); white solid. ^{1}H NMR (200 MHz, CD_3NO_2): δ 1.48 (d, $^3J_{H-H}$ = 4.0 Hz, $^3J_{H-Pt}$ = 44 Hz, 6H, CH_3), 4.85 (ps.t, $^2J_{H-H}$ = 17.6 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 5.1 Hz, 4H, PCH_aCH_b), 5.10 (ps.t, $^2J_{H-H}$ = 17.6 Hz, $^2J_{H-P}$ + $^4J_{H-P}$ = 4.6 Hz, 4H,PCH_aCH_b), 5.37 (br, 2H, J_{H-Pt} = 53 Hz, CH), 7.62−8.08 (m, 22H, Ph, py), 8.18 (t, 1H, $^3J_{H-H}$ = 8.2 Hz, py). ^{13}C NMR (50 MHz, CD_3NO_2): 20.9 (s, CH_3), 44.7 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 18.2 Hz, PCH_2), 96.9 (s, $^1J_{C-Pt}$ = 115 Hz, CH), 125.5 (m, Ph_i), 125.8 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.1 Hz, py-*3,5*), 131.6 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.5 Hz, $Ph_{m,m'}$), 134.4 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.5 Hz, Ph_o), 135.5 (s, Ph_p), 135.7 (s, $Ph_{p'}$), 135.8 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 6.8 Hz, $Ph_{o'}$), 146.1 (s, py-*4*), 162.0 (s, py-*2,6*).

[Pt(PNP)(norbornene)](BF_4)$_2$ (7). To a solution of 200 mg (0.229 mmol) of **1** in 30 mL of CH_2Cl_2 was added 10 equiv of norbornene. After 1 h of stirring at room temperature the volume of the solution was reduced to ca. 6 mL. A microcrystalline white solid precipitated. The precipitation was completed by addition of ca. 30 mL of diethyl ether. The solid was filtered off, washed three times with diethyl ether, and dried under vacuum. Yield: 162 mg (0.175 mmol, 81%); white solid; dec pt 160 °C. Anal. Calcd for $C_{38}H_{37}B_2F_8NP_2Pt\cdot0.5CH_2Cl_2$: C, 47.15; H, 3.90; N, 1.43. Found: C, 47.33; H, 3.98; N, 1.33. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.47 (d, J_{H-H} = 10.8 Hz, 1H,CH_2), 0.75 (d, J_{H-H} = 8.8 Hz, 3H,CH_2), 0.86 (d, J_{H-H} = 9.2 Hz, 2H,-CH_2), 1.32 (d, J_{H-H} = 8.7 Hz, 2H, CH_2), 1.80 (br, 2H, CH), 4.33 (t, $^3J_{H-P}$ = 6.0 Hz, $^2J_{H-Pt}$ = 54 Hz, 2H, CH), 4.92 (ps.t, $^2J_{H-P}$ + $^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 7.67−8.01 (m, 23H, Ph, py). ^{13}C NMR (50 MHz, CD_2Cl_2/CD_3NO_2): δ 25.1 (s, $^3J_{C-Pt}$ = 40 Hz, CH_2), 43.9 (s, CH), 46.2 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 16.3 Hz, PCH_2), 91.9 (s, $^1J_{C-Pt}$ = 131 Hz, CH), 124.5 (ps.t, $^1J_{C-P}$ + $^3J_{C-P}$ = 30.9 Hz, Ph_i), 125.1 (br, py-*3,5*), 131.3 (ps.t, $^3J_{C-P}$ + $^5J_{C-P}$ = 5.3 Hz, Ph_m), 134.8 (ps.t, $^2J_{C-P}$ + $^4J_{C-P}$ = 5.7 Hz, Ph_o), 135.2 (s, Ph_p), 144.4 (s, py-*4*), 160.1 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 40.7 (s, $^1J_{P-Pt}$ = 2177 Hz).

Reaction of [Pt(PNP)(CHR=CHR′)](BF_4)$_2$ (1−4) with MeOH. General Procedure. A 0.230 mmol portion of the alkene complex was dissolved in 2 mL of MeOH, and 2 equiv of $NaHCO_3$ was added. The mixture was stirred for 10 min. The gray precipitated $NaBF_4$ was filtered off. The solvent was removed under reduced pressure, and the crude product was dissolved in 2 mL of CH_2Cl_2 and crystallized by dropwise addition of diethyl ether. The product was filtered off, washed with diethyl ether, and dried under vacuum.

[Pt(PNP)(CH_2CH_2OMe)]BF_4 (8). Yield: 154 mg (0.188 mmol, 82%), white solid. Anal. Calcd for $C_{34}H_{34}BF_4NOP_2Pt$: C, 50.02; H, 4.20; N, 1.70. Found: C, 49.89; H, 4.10; N, 1.70. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.08 (m, $^2J_{H-Pt}$ = 88 Hz, 2H, $PtCH_2$), 2.82 (s, 3H, OCH_3), 3.02 (m, 2H, CH_2O), 4.46 (ps.t, $^2J_{H-P}$ + $^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 7.48−7.90 (m, 23H, Ph,

py). ^{13}C NMR (50 MHz, CD_3OD/CD_2Cl_2): δ 0.5 (s, $^1J_{C-Pt}$ = 651 Hz, $PtCH_2$), 46.5 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 16.4 Hz, PCH_2), 51.4 (s, OCH_3), 77.9 (s, CH_2), 124.0 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 4.3 Hz, py-*3,5*), 128.3 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 27.3 Hz, PPh_i), 130.6 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.5 Hz, Ph_m), 131.3 (s, Ph_p), 134.2 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.3 Hz, Ph_o), 140.2 (s, py-*4*), 160.8 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.9 (s, $^1J_{P-Pt}$ = 3020 Hz).

[Pt(PNP)(CH$_2$CH(Me)OMe)]BF$_4$ (9). Yield: 162 mg (0.195 mmol, 85%), white solid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.65 (d, $^3J_{H-H}$ = 6.0, 3H, CH_3), 1.79 (m, 1H, $PtCH_2$), 2.26 (m, 1H, $PtCH_2$), 2.72 (s, 3H, OCH_3), 2.97 (m, 1H, CHO), 4.42 (ps.t, 4H, $^2J_{H-P} + {}^4J_{H-P}$ = 4.6 Hz, PCH_2), 7.48−7.98 (m, 22H, Ph, py), 8.03 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py-*4*). ^{13}C NMR (50 MHz, CD_3OD): δ 4.6 (s, $^1J_{C-Pt}$ = 651 Hz, $PtCH_2$), 19.9 (s, CH_3), 42.3 (s, OCH_3), 42.8 (m, PCH_2), 79.3 (s, CH), 120.2 (br, py-*3,5*), 126.9 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.5 Hz, $Ph_{m,m'}$), 129.6 (s, Ph_p), 129.7 (s, $Ph_{p'}$), 130.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.1 Hz, Ph_o), 130.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.9 Hz, $Ph_{o'}$), 137.7 (s, py-*4*), 157.6 (s, py-*2,6*).

[Pt(PNP)(CH$_2$CH(Et)OMe)]BF$_4$ (10). Yield: 151 mg (0.179 mmol, 78%), white solid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.35 (t, $^3J_{H-H}$ = 7.4, 3H, CH_3), 0.98 (m, 1H, CH_2), 1.18 (m, 1H, CH_2), 1.80 (m, 1H, $PtCH_2$), 2.22 (m, 1H, $PtCH_2$), 2.64 (m, 1H, CHO), 2.73 (s, 3H, OCH_3), 4.42 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 7.48−7.98 (m, 22H, Ph, py), 8.03 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, py-*4*).

[Pt(PNP)(CH$_2$CH(Ph)OMe)]BF$_4$ (11). Yield: 181 mg (0.202 mmol, 88%), white solid. Anal. Calcd for $C_{40}H_{38}BF_4NOP_2Pt$: C, 53.83; H, 4.29; N, 1.57. Found: C, 53.71; H, 4.38; N, 1.56. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.02 (m, $^2J_{H-Pt}$ = 80 Hz, 2H, $PtCH_2$), 2.60 (s, 3H, OCH_3), 3.69 (m, 1H, CHO), 4.42 (m, 4H, PCH_2), 6.60 (m, 2H, Ph), 7.09 (m, 3H, CPh), 7.54−7.66 (m, 8H, PPh), 7.79−7.91 (m, 14H, PPh, py), 8.00 (t, 1H, $^3J_{H-H}$ = 7.4 Hz, py-*4*). ^{13}C NMR (75 MHz, CD_2Cl_2): δ 11.0 (t, $^2J_{C-P}$ = 4.4 Hz, $^1J_{C-Pt}$ = 658 Hz, $PtCH_2$), 46.2 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 17.3 Hz, PCH_2), 56.0 (s, OCH_3), 87.9 (s, $^2J_{C-Pt}$ = 26 Hz CH), 123.3 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.0 Hz, py-*3,5*), 125.9 (s, CPh), 127.0 (s, CPh), 127.4 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 28.1 Hz, PPh_i), 127.7 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 28.2 Hz, $PPh_{i'}$), 128.4 (s, CPh), 129.7 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.3 Hz, PPh_m), 129.8 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.8 Hz, $PPh_{m'}$), 132.5 (s, PPh_p), 132.6 (s, $PPh_{p'}$), 133.5 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.8 Hz, PPh_o), 134.1 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.8 Hz, $PPh_{o'}$), 140.4 (s, py-*4*), 145.8 (s, CPh), 159.6 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 30.3 (s, $^1J_{P-Pt}$ = 3110 Hz).

Reaction of 5 and 6 with CD$_3$OD. A 6 mg sample of complex **5** or **6** was dissolved in 0.5 mL of CD_3OD, and ca. 2 equiv of $NaHCO_3$ was added. After shaking the mixture in an NMR tube for 5 min a ^{1}H NMR spectrum was recorded.

[Pt(PNP)(CH(Me)CH(Me)OCD$_3$)]BF$_4$ (12a-*d*$_3$, from 5). ^{1}H NMR (200 MHz, CD_3OD): δ 0.78 (d, $^3J_{H-H}$ = 6.0 Hz, 3H, CH_3), 0.95 (d, $^3J_{H-H}$ = 7.0 Hz, $^3J_{H-Pt}$ = 58 Hz, 3H, CH_3), 2.34 (m, $^2J_{H-Pt}$ = 81 Hz, 1H, CH), 2.74 (m, 1H, CH) 4.58 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.7 Hz, 4H, PCH_2), 7.55−8.02 (m, 23H, Ph, py).

[Pt(PNP)(CH(Me)CH(Me)OCD$_3$)]BF$_4$ (12b-*d*$_3$, from 6). ^{1}H NMR (200 MHz, CD_3OD): δ 0.96 (d, $^3J_{H-H}$ = 6.2 Hz, 3H, CH_3), 1.06 (d, $^3J_{H-H}$ = 6.9 Hz, $^3J_{H-Pt}$ = 57 Hz, 3H, CH_3), 2.19 (m, $^2J_{H-Pt}$ = 85 Hz, 1H, CH), 2.56 (m, 1H, CH) 4.60 (m, 4H, PCH_2), 7.50−8.06 (m, 23H, Ph, py).

[Pt(PNP)(CH=CHPh)]BF$_4$ (13). Complex **11** was dissolved in MeOH. After 2 h a pale yellow crystalline solid precipitated, which was filtered off, washed with diethyl ether, and dried under vaccum. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.55 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 6.12 (d, 1H, $^3J_{H-H}$ = 16.6 Hz, $^2J_{H-Pt}$ = 78 Hz, CH), 6.84 (m, 2H, CPh), 7.09 (m, 2H, CPh), 7.56−7.84 (m, 23H, PPh, py), 7.84 (dt, 1H, $^3J_{H-P}$ = 6.0 Hz, PtCH), 8.08 (t, $^3J_{H-H}$ = 8.2 Hz). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 45.5 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 16.3 Hz, PCH_2), 118.9 (t, $^3J_{C-P}$ = 9.1 Hz, CH), 123.6 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.1 Hz, py-*3,5*), 125.3 (s, Ph), 126.2 (s, Ph), 127.4 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 29.1 Hz, PPh_i), 129.9 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.4 Hz, Ph_m), 132.7 (s, PPh_p), 133.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.3 Hz, PPh_o), 139.2 (t, $^4J_{C-P}$ = 5.5 Hz, CH), 140.8 (s, py-*4*), 160.5 (s, py-*2,6*).

Reaction of [Pt(PNP)(CH$_2$=CHR)](BF$_4$)$_2$ with H$_2$O. General Procedure. A mixture of 0.230 mmol of the alkene complex in 5 mL of CH_2Cl_2 with 4 equiv of H_2O and 2 equiv of $NaHCO_3$ was stirred for 1 h at 0 °C. The gray precipitated $NaBF_4$ was filtered off. The product was precipitated by dropwise addition of diethyl ether. The product was filtered off, washed with diethyl ether, and dried under vacuum.

[Pt(PNP)(CH$_2$CH$_2$OH)]BF$_4$ (14)/[{Pt(PNP)(CH$_2$CH$_2$)}$_2$O](BF$_4$)$_2$ (15). Yield: 160 mg (0.200 mmol, 87%, based on Pt), white solid. ^{1}H NMR (200 MHz, CD_2Cl_2): **14**: δ 2.08 (m, $^2J_{H-Pt}$ = 88 Hz, 2H, $PtCH_2$), 3.34 (m, 2H, CH_2O), 4.46 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 7.30−7.80 (m, 23H, Ph, py). **15**: δ 1.85 (m, $^2J_{H-Pt}$ = 93 Hz, 2H, $PtCH_2$), 2.66 (m, 2H, CH_2O), 4.39 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.6 Hz, 4H, PCH_2), 7.30−7.80 (m, 23H, Ph, py).

[Pt(PNP)(CH$_2$CH(Me)OH)]BF$_4$ (16). Yield: 150 mg (0.184 mmol, 80%), white solid. Anal. Calcd for $C_{34}H_{34}BF_4NOP_2Pt\cdot 2CH_2Cl_2$: C, 43.84; H, 3.88; N, 1.42. Found: C, 43.42; H, 3.81; N, 1.41. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.71 (d, $^3J_{H-H}$ = 6.0 Hz, 3H, CH_3), 0.96 (d, $^3J_{H-H}$ = 4.4 Hz, 1H, OH), 2.04 (m, $^2J_{H-Pt}$ = 79 Hz, 2H, $PtCH_2$), 3.55 (m, 1H, CHO), 4.43 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.6 Hz, 4H, PCH_2), 7.40−7.98 (m, 21H, Ph, py), 8.02 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, py-*4*). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 12.8 (s, $^1J_{C-Pt}$ = 666 Hz, $PtCH_2$), 26.8 (s, $^3J_{C-Pt}$ = 46 Hz, CH_3), 46.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 16.2 Hz, PCH_2), 71.9 (s, CH), 123.4 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 4.8 Hz, py-*3,5*), 130.0 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.1 Hz, Ph_m), 131.8 (s, Ph_p), 133.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.3 Hz, Ph_o), 139.7 (s, py-*4*), 159.0 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.4 (s, $^1J_{P-Pt}$ = 3033 Hz).

[Pt(PNP)(CH$_2$CH(Et)OH)]BF$_4$ (17). Yield: 152 mg (0.184 mmol, 80%), white solid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 0.40 (t, $^3J_{H-H}$ = 7.3 Hz, 3H, CH_3), 0.93 (d, $^3J_{H-H}$ = 4.4 Hz, 1H, OH), 0.93 (m, 1H, CH_2), 1.13 (m, 1H, CH_2), 2.06 (m, $^2J_{H-Pt}$ = 84 Hz, 2H, $PtCH_2$), 3.20 (br, 1H, CHO), 4.43 (m, 4H, PCH_2), 7.40−8.03 (m, 23H, Ph, py). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 9.5 (s, $PtCH_2$), 9.5 (s, CH_3), 33.0 (s, CH_2), 46.7 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 16.5 Hz, PCH_2), 77.2 (t, $^2J_{C-P}$ = 7.4 Hz, CH), 123.4 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 4.7 Hz, py-*3,5*), 130.0 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.4 Hz, Ph_m), 131.8 (s, Ph_p), 132.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.3 Hz, Ph_o), 139.7 (s, py-*4*), 159.0 (s, py-*2,6*).

[Pt(PNP)(CH$_2$CH(Ph)OH)]BF$_4$ (18). Yield: 151 mg (0.173 mmol, 75%), white solid. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 1.47 (d, $^3J_{H-H}$ = 2.8 Hz, 1H, OH), 2.05−2.18 (m, 2H, CH_2), 4.28−4.60 (m, 5H, CH, PCH_2), 6.70 (m, 2H, CPh), 7.04 (m, 3H, CPh), 7.50−8.05 (m, 23H, PPh, py). ^{13}C NMR (50 MHz, CD_2Cl_2/CD_3NO_2): δ 14.0 (s, $PtCH_2$), 46.1 (m, PCH_2), 78.9 (m, CH), 123.8 (br, py-*3,5*), 125.8 (s, CPh), 127.8 (s, CPh), 129.0 (s, CPh), 130.5 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.7 Hz, PPh_m), 133.3 (s, PPh_p), 134.3 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.8 Hz, PPh_o), 141.1 (s, py-*4*), 146.4 (s, CPh), 160.5 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 31.0 (s, $^1J_{P-Pt}$ = 3052 Hz).

[Pt(PNP)(MeCN)](BF$_4$)$_2$ (22). To a solution of 200 mg (0.228 mmol) of the ethylene complex **1** in 6 mL of CH_2Cl_2 was added ca. 20 equiv of MeCN. The mixture was stirred for 1 h at room temperature. The product was precipitated by dropwise addition of diethyl ether. The white solid was filtered off, washed two times with diethyl ether, and dried under vacuum. Yield: 198 mg (0.218 mmol, 95%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.42 (s, $^3J_{H-Pt}$ = 12 Hz, 3H, CH_3), 4.64 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.7 Hz, 4H, PCH_2), 7.60−7.97 (m, 22H, Ph, py), 8.17 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py).

[Pt(PNP)(PhNH$_2$)](BF$_4$)$_2$ (21). To a solution of 150 mg (0.165 mmol) of the acetonitrile complex **22** in 4 mL of CH_2Cl_2 was added ca. 10 equiv of $PhNH_2$. The mixture was stirred for 1 h at room temperature. The product was precipitated by dropwise addition of diethyl ether. The white solid was filtered off, washed three times with diethyl ether, and dried under vacuum. Yield: 141 mg (0.146 mmol, 89%). ^{1}H NMR (200 MHz, CD_2Cl_2): δ 4.64 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.7 Hz, 4H, PCH_2), 6.39 (br, $^3J_{H-Pt}$ = 68 Hz, 2H, NH_2), 6.40 (d, $^3J_{H-H}$ = 7.8 Hz, 2H,

NPh_o), 6.91−7.04 (m, 3H, $NPh_{m,p}$), 7.53−7.80 (m, 22H, PPh), 8.04 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, py).

Reaction of 1 with $PhNH_2$. A 0.008 mmol sample of complex **1** was dissolved in 0.5 mL of CD_2Cl_2, and after addition of 1 equiv of $PhNH_2$ a ^1H NMR spectrum was recorded.

[Pt(PNP)($CH_2CH_2NH_2Ph$)](BF_4)$_2$ (19-H$^+$). ^1H NMR (200 MHz, CD_2Cl_2): δ 2.18 (m, $^2J_{H-Pt}$ = 92 Hz, 2H, $PtCH_2$), 2.99 (m, 2H, CH_2), 4.39 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.6 Hz, 4H, PCH_2), 6.98 (d, $^3J_{H-H}$ = 8.0 Hz, 2H, NPh_o), 7.20 (m, 3H, NPh), 7.47−7.74 (m, 22H, PPh), 7.99 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py).

[{Pt(PNP)(CH_2CH_2)}$_2$NPh](BF_4)$_3$ (20-H$^+$). ^1H NMR (200 MHz, CD_2Cl_2): δ 1.22 (m, $^2J_{H-Pt}$ = 85 Hz, 2H, $PtCH_2$), 1.82 (m, $^2J_{H-Pt}$ = 92 Hz, 2H, $PtCH_2$), 2.78 (m, 4H, CH_2), 4.37 (m, 8H, PCH_2), 6.42 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, NPh_o), 6.84 (t, $^3J_{H-H}$ = 7.6 Hz, 2H, NPh_m), 7.05 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, NPh_p), 7.47−7.74 (m, 22H, PPh), 7.95 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py).

Reaction of 1 with 19. A mixture of 100 mg (0.115 mmol) of complex **1** and 100 mg of complex **19** in 5 mL of CH_2Cl_2 was stirred for 1 h at room temperature. The white product was preciptated by dropwise addition of diethyl ether. The product was filtered off, washed with diethyl ether, and dried under vacuum. Yield: 171 mg (0.098 mmol, 85%), pink solid. The product was identified as **20**-H$^+$ by ^1H NMR spectroscpoy (200 MHz, CD_2Cl_2). Anal. Calcd for $C_{72}H_{68}B_3F_{12}N_3P_4Pt_2 \cdot 0.5CH_2Cl_2$: C, 48.59; H, 3.88; N, 2.34. Found: C, 48.73; H, 4.11; N, 2.32. ^{13}C NMR (75 MHz, CD_2Cl_2): δ −9.7 (s, $PtCH_2$), 45.9 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 16.5 Hz, PCH_2), 64.0 (s, NCH_2), 122.2 (s, NPh), 123.3 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 4.3 Hz, py-*3,5*), 126.4 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 28.6 Hz, PPh_i), 126.5 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 28.6 Hz, $PPh_{i'}$), 129.3 (s, NPh), 130.2 (m, $Ph_{m,m'}$), 132.7 (s, Ph_p), 132.9 (s, $Ph_{p'}$), 133.2 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.9 Hz, Ph_o), 133.4 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.8 Hz, Ph_o), 136.7 (s, NPh), 140.6 (s, py-*4*), 160.0 (s, py-*2,6*).

[{Pt(PNP)(CH_2CH_2)}$_2$NPh](BF_4)$_2$ (20). A mixture of 70 mg (0.04 mmol) of complex **20**-H$^+$ in 4 mL of CH_2Cl_2 and 2 equiv of $NaHCO_3$ was stirred for 24 h at room temperature. The gray precipitated $NaBF_4$ was filtered off. The product was precipitated by dropwise addition of diethyl ether, filtered off, washed with diethyl ether, and dried under vacuum. Yield: 63 mg (96%, 0.038 mmol), pink solid. ^1H NMR spectroscpoy (200 MHz, CD_2Cl_2): δ 1.82 (m, $^2J_{H-Pt}$ = 90 Hz, 4H, $PtCH_2$), 2.75 (m, 4H, CH_2), 4.39 (m, 8H, PCH_2), 5.55 (d, $^3J_{H-H}$ = 8.2 Hz, 2H, NPh_o), 6.27 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, NPh_p), 6.58 (t, $^3J_{H-H}$ = 8.0 Hz, 2H, NPh_m), 7.41−7.76 (m, 22H, PPh), 8.04 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py).

Reaction of 2 with $PhNH_2$. To a solution of 69 mg (0.077 mmol) of complex **2** was added 1 equiv of $PhNH_2$ (7 μL), and after stirring for 5 min the product was precipitated by dropwise addition of diethyl ether. The product was filtered off, washed three times with diethyl ether, and dried under vacuum. Yield: 72 mg (0.073 mmol, 96%).

[Pt(PNP)($CH_2CH(Me)NH_2Ph$)](BF_4)$_2$ (23-H$^+$). Anal. Calcd for $C_{40}H_{40}B_2F_8N_2P_2Pt$: C, 49.05; H, 4.08; N, 2.86; F, 15.52. Found: C, 48.85; H, 4.21; N, 2.83; F, 15.36. ^1H NMR (300 MHz, CD_2Cl_2): δ 0.73 (d, $^3J_{H-H}$ = 6.0 Hz, 3H, CH_3), 1.92 (m, $^2J_{H-Pt}$ = 87 Hz, 1H, $PtCH_2$), 2.55 (m, $^2J_{H-Pt}$ = 95 Hz, 1H, $PtCH_2$), 3.14 (m, 1H, CH), 4.47 (m, 4H, PCH_2), 6.93 (d, $^3J_{H-H}$ = 7.5 Hz, 2H, NPh_o), 7.27 (t, $^3J_{H-H}$ = 7.8 Hz, 2H, NPh_m), 7.38 (t, $^3J_{H-H}$ = 7.5 Hz, NPh_p), 7.59−7.72 (m, 25H, NH_2, Ph, py), 8.07 (t, $^3J_{H-H}$ = 7.6 Hz, 1H, py-*4*).

Reaction of 1 with (2-$ClC_6H_4NH_2$). A 0.008 mmol sample of complex **1** was dissolved in 0.5 mL of CD_2Cl_2, and after addition of 1 equiv of 2-$ClC_6H_4NH_2$ a ^1H NMR spectrum was recorded.

[Pt(PNP)($CH_2CH_2NH_2C_6H_4Cl$)](BF_4)$_2$ (26-H$^+$). ^1H NMR (200 MHz, CD_2Cl_2/CD_3NO_2): δ 2.10 (m, $^2J_{H-Pt}$ = 99 Hz, 2H, $PtCH_2$), 3.17 (m, 2H, CH_2), 4.52 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.6 Hz, 4H, PCH_2), 6.77−7.39 (m, 4H, NC_6H_4), 7.57−7.77 (m, 22H, PPh), 8.04 (t, $^3J_{H-H}$ = 7.8 Hz, 1H, py).

Reaction of 1−4 with $ArNH_2$. General Procedure. A solution of 0.230 mmol of the alkene complex in 5 mL of CH_2Cl_2 was cooled to 0 °C, and 4 equiv of $ArNH_2$ and 2 equiv of $NaHCO_3$ were added. The mixture was stirred for 4 h at 0 °C. The gray precipitated $NaBF_4$ was filtered off. The white product was preciptated by dropwise addition of diethyl ether. The product was filtered off, washed three times with diethyl ether, and dried under vacuum.

[Pt(PNP)(CH_2CH_2NHPh)]BF_4 (19). Yield: 137 mg (0.156 mmol, 68%). ^1H NMR (200 MHz, CD_2Cl_2): δ 2.12 (m, $^2J_{H-Pt}$ = 87 Hz, 2H, $PtCH_2$), 2.85 (m, $^3J_{H-Pt}$ = 16 Hz, 2H, CH_2), 3.30 (br, 1H, NH), 4.46 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.7 Hz, 4H,), 5.92 (d, $^3J_{H-H}$ = 7.3 Hz, 2H, NPh_o), 6.50 (t, $^3J_{H-H}$ = 6.7 Hz, 1H, NPh_p), 6.90 (t, $^3J_{H-H}$ = 6.7 Hz, 2H, NPh_m), 7.20−7.95 (m, 22H, Ph, py), 8.05 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py-*4*).

[Pt(PNP)($CH_2CH(Me)NHPh$)]BF_4 (23). Yield: 162 mg (0.182 mmol, 79%). Anal. Calcd for $C_{40}H_{39}BF_4N_2P_2Pt$: C, 53.88; H, 4.41; N, 3.14; F, 8.52. Found: C, 53.62; H, 4.46; N, 3.08; F, 8.36. ^1H NMR (200 MHz, CD_2Cl_2): δ 0.70 (d, $^3J_{H-H}$ = 5.4 Hz, 3H, CH_3), 1.92 (m, 1H, $PtCH_2$), 2.21 (m, 1H, $PtCH_2$), 3.02 (s, 1H, NH), 3.15 (m, 1H, CH), 4.45 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 5.90 (d, J_{H-H} = 8.6 Hz, 2H, NPh_o), 6.56 (t, $^3J_{H-H}$ = 7.3 Hz, 1H, NPh_p), 6.93 (t, $^3J_{H-H}$ = 7.9 Hz, 2H, NPh_m), 7.48−7.93 (m, 22H, PPh, py), 8.05 (t, 1H, $^3J_{H-H}$ = 7.3 Hz, py-*4*). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 9.7 (s, $^1J_{C-Pt}$ = 657 Hz, $PtCH_2$), 24.7 (s, $^1J_{C-Pt}$ = 46 Hz, CH_3), 46.5 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 16.6 Hz, PCH_2), 52.6 (s, NCH), 113.2 (s, NPh_o), 117.6 (s, NPh_p), 124.3 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 4.2 Hz, py-*3,5*), 127.2 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 27.4 Hz, PPh_i), 127.8 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 28.3 Hz, $PPh_{i'}$), 129.1 (s, NPh_m), 129.9 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.8 Hz, $Ph_{m,m'}$), 132.6 (s, Ph_p), 132.7 (s, $Ph_{p'}$), 133.2 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.8 Hz, Ph_o), 133.7 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 6.8 Hz, Ph_o), 140.4 (s, py-*4*), 147.4 (s, NPh_i), 159.6 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.4 (s, $^1J_{P-Pt}$ = 3060 Hz).

[Pt(PNP)($CH_2CH(Et)NHPh$)]BF_4 (24). Yield: 170.8 mg (0.188 mmol, 82%). ^1H NMR (200 MHz, CD_2Cl_2): δ 0.32 (t, $^3J_{H-H}$ = 7.4 Hz, 3H, CH_3), 1.09 (m, 2H, CH_2), 2.00 (m, $^3J_{H-Pt}$ = 83.0 Hz, 1H, $PtCH_2$), 2.98 (m, 2H, CH, $PtCH_2$), 3.72 (br, 1H, NH), 4.43 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 5.89 (d, $^3J_{H-H}$ = 7.6 Hz, 2H, NPh_o), 6.50 (t, $^3J_{H-H}$ = 7.4 Hz, 1H, NPh_p), 6.90 (t, $^3J_{H-H}$ = 7.9 Hz, 2H, NPh_m), 7.48−7.83 (m, 22H, PPh, py), 8.05 (t, $^3J_{H-H}$ = 7.0 Hz, 1H, py-*4*).

[Pt(PNP)($CH_2CH(Ph)NHPh$)]BF_4 (25). Yield: 170 mg (0.179 mmol, 78%). ^1H NMR (200 MHz, CD_2Cl_2): δ 1.85 (m, 1H, $PtCH_2$), 2.30 (m, $^3J_{H-Pt}$ = 89 Hz, 1H, $PtCH_2$), 3.72 (m, 1H, NH), 3.83 (m, 1H, CH), 4.52 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.7 Hz, 4H, PCH_2), 5.82 (d, $^3J_{H-H}$ = 7.2 Hz, 2H, NPh_o), 6.50 (m, 3H, NPh_p, CPh), 6.87 (m, 2H, NPh_m), 7.02 (m, 3H, CPh), 7.34−7.82 (m, 22H, PPh, py), 8.02 (t, $^3J_{H-H}$ = 8.0 Hz, 1H, py-*4*). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 13.2 (s, $PtCH_2$), 46.0 (m, PCH_2), 63.6 (s, NCH), 113.2 (s, NPh), 116.9 (s, NPh), 123.5 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 4.2 Hz, py-*3,5*), 125.3 (s, CPh), 126.3 (s, CPh), 128.5 (s, CPh), 128.9 (s, NPh), 130.0 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.6 Hz, Ph_m), 130.3 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.4 Hz, $Ph_{m'}$), 132.6 (s, Ph_p), 132.7 (s, $Ph_{p'}$), 132.7 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.6 Hz, Ph_o), 132.7 (s, PPh_p), 133.0 (s, $PPh_{p'}$), 134.3 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 7.4 Hz, Ph_o), 140.5 (s, py-*4*), 147.0 (s, NPh), 159.8 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 32.8 (s, $^1J_{P-Pt}$ = 3003 Hz).

[Pt(PNP)($CH_2CH_2NHC_6H_4Cl$-*o*)]BF_4 (26). Yield: 151 mg (0.165 mmol, 72%). ^1H NMR (200 MHz, CD_2Cl_2): δ 2.24 (m, $^2J_{H-Pt}$ = 80 Hz, 2H, $PtCH_2$), 2.94 (m, $^3J_{H-Pt}$ = 41.3 Hz, 2H, CH_2), 3.99 (br, 1H, NH), 4.46 (ps.t, $^2J_{H-P} + {}^4J_{H-P}$ = 4.8 Hz, 4H, PCH_2), 5.75 (d, $^3J_{H-H}$ = 7.2 Hz, 1H, NC_6H_4-*o*), 6.48 (t, $^3J_{H-H}$ = 8.4 Hz, 1H, NC_6H_4-*p*), 6.81 (t, $^3J_{H-H}$ = 7.5 Hz, 1H, NC_6H_4-*m*), 7.10 (d, $^3J_{H-H}$ = 7.4 Hz, 1H,NC_6H_4-*m′*), 7.55−7.78 (m, 22H, PPh, py), 8.05 (t, $^3J_{H-H}$ = 8.1 Hz, 1H, py-*4*). ^{13}C NMR (50 MHz, CD_2Cl_2): δ −0.1 (s, $^1J_{C-Pt}$ = 645 Hz, $PtCH_2$), 46.1 (ps.t, $^2J_{C-P} + {}^4J_{C-P}$ = 16.4 Hz, PCH_2), 48.7 (s, NCH_2), 110.8 (s, NC_6H_4), 116.4 (s, NC_6H_4), 118.3 (s, NC_6H_4), 123.0 (ps.t, $^3J_{C-P} + {}^5J_{C-P}$ = 5.5 Hz, py-*3,5*), 126.1 (s, NC_6H_4-*p*), 126.9 (ps.t, $^1J_{C-P} + {}^3J_{C-P}$ = 29.9 Hz, PPh_i), 127.5 (s, NC_6H_4), 128.6 (s, NC_6H_4), 129.7

(ps.t, $^3J_{C-P} + {}^5J_{C-P} = 5.8$ Hz, Ph$_m$), 132.4 (s, Ph$_p$), 133.0 (ps.t, $^2J_{C-P} + {}^4J_{C-P} = 7.9$ Hz, Ph$_o$), 140.3 (s, py-*4*), 143.7 (s, NC_6H_4), 159.5 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.1 (s, $^1J_{P-Pt} = 2997$ Hz).

[Pt(PNP)(CH$_2$CH$_2$NHC$_6$H$_4$Me-*p*)]BF$_4$ (27). Yield: 147 mg (0.165 mmol, 72%). Anal. Calcd for $C_{40}H_{39}BF_4N_2P_2Pt$: C, 53.88; H, 4.41; N, 3.14. Found: C, 53.63; H, 4.31; N, 3.02. ^{1}H NMR (200 MHz, CD_2Cl_2): δ 2.14 (s, 3H, CH_3), 2.16 (br, $^2J_{H-Pt} = 103$ Hz, 2H, $PtCH_2$), 2.79 (m, $^3J_{H-Pt} = 35$ Hz, 2H, CH_2), 3.20 (br, 1H, NH), 4.45 (ps.t, $^2J_{H-P} + {}^4J_{H-P} = 4.6$ Hz, 4H, PCH_2), 5.85 (d, $^3J_{H-H} = 8.4$ Hz, 2H, NC_6H_4-*o*), 6.72 (d, $^3J_{H-H} = 8.4$ Hz, 2H, NC_6H_4-*m*), 7.54−7.83 (m, 22H, PPh, py), 8.03 (t, $^3J_{H-H} = 8.0$ Hz, 1H, py-*4*). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 1.6 (s, $^1J_{C-Pt} = 639$ Hz, $PtCH_2$), 36.5 (s, CH_3), 46.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P} = 17.5$ Hz, PCH_2), 49.9 (s, NCH_2), 111.3 (s, NC_6H_4-*o*), 123.5 (ps.t, $^3J_{C-P} + {}^5J_{C-P} = 4.3$ Hz, py-*3,5*), 126.1 (s, NC_6H_4-*p*), 126.6 (ps.t, $^1J_{C-P} + {}^3J_{C-P} = 27.6$ Hz, PPh$_i$), 128.8 (s, NC_6H_4-*m*), 129.1 (ps.t, $^3J_{C-P} + {}^5J_{C-P} = 5.4$ Hz, Ph$_m$), 131.8 (s, Ph$_p$), 132.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P} = 7.3$ Hz, Ph$_o$), 139.6 (s, py-*4*), 146.3 (s, NC_6H_4-*i*), 158.8 (s, py-*2,6*). ^{31}P NMR (162 MHz, CD_2Cl_2): δ 29.1 (s, $^1J_{P-Pt} = 3029$ Hz).

[Pt(PNP)(CH$_2$CH$_2$NHC$_6$H$_4$OMe-*p*)]BF$_4$ (28). Yield: 154 mg (0.170 mmol, 74%). ^{1}H NMR (200 MHz, $CDCl_3$): δ 2.14 (m, $^2J_{H-Pt} = 82$ Hz, 2H, $PtCH_2$), 2.78 (m, $^2J_{H-Pt} = 38$ Hz, 2H, CH_2), 3.68 (s, 3H, CH_3), 3.69 (br, 1H, NH), 4.45 (ps.t, $^2J_{H-P} + {}^4J_{H-P} = 4.7$ Hz, 4H, PCH_2), 5.89 (d, $^3J_{H-H} = 8.3$ Hz, 2H, NC_6H_4-*o*), 6.53 (d, $^3J_{H-H} = 8.4$ Hz, 2H, NC_6H_4-*m*), 7.54−7.83 (m, 23H, PPh, py). ^{13}C NMR (50 MHz, CD_2Cl_2): δ 0.9 (s, $^1J_{C-Pt} = 637$ Hz, $PtCH_2$), 46.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P} = 17.5$ Hz, PCH_2), 50.1 (s, NCH_2), 66.7 (s, CH_3), 113.8 (s, NC_6H_4), 114.7 (s, NC_6H_4), 123.5 (ps.t, $^3J_{C-P} + {}^5J_{C-P} = 4.3$ Hz, py-*3,5*), 130.1 (ps.t, $^3J_{C-P} + {}^5J_{C-P} = 5.5$ Hz, PPh$_m$), 132.7 (s, PPh$_p$), 133.6 (ps.t, $^2J_{C-P} + {}^4J_{C-P} = 7.3$ Hz, PPh$_o$), 140.5 (s, py-*4*), 140.7 (s, NC_6H_4), 159.6 (s, NC_6H_4), 159.7 (s, py-*2,6*).

Reductive Degradation with NaBH$_4$. For the reduction ca. 20 mg of the respective complexes was dissolved in 0.7 mL of the appropriate solvent. The solutions of complexes **9**−**11** in CD_3OD, complexes **16**−**18** in CD_2Cl_2/D_2O (10:1), and complexes **23**−**25** in CD_2Cl_2 (a drop of CD_3OD was added) were cooled to 0 °C and were treated with an excess of $NaBH_4$. After stirring the respective mixture for 1 h at 0 °C an ^{1}H NMR spectrum was recorded.

Equilibrium Constant Determinations. The equilibrium constants for the ligand exchange and addition reactions were determined by ^{1}H NMR analysis of equilibration mixtures at 298 K. The reported values are the average result of three measurements run at different concentrations of the olefin (eqs 3, 5, and 7) or acetonitrile (eq 6). The error of these values lies within ±15−20%. For the ligand exchange reactions (eq 3) solutions of the respective complexes in CD_2Cl_2/CD_3NO_2 (c = 7−15 mM) were treated with an excess of the appropriate substituting ligand. Very unbalanced equilibria like ethylene/norbornene exchange (eq 3), $PhNH_2$/MeCN (eq 6), and MeCN/ethylene (eq 7) were handled by treating a solution of the most stable complex with a large excess of the exchanging ligand. For the ethylene "insertion" reaction[36] to a solution of the isolated aniline complex **21** were added 0.8 equiv of MeCN and a large excess of ethylene. The reaction mixture was kept in a sealed NMR tube, which was monitored by ^{1}H NMR spectroscopy over a period of 14 days.

Kinetic Measurements. The olefin exchange reaction (eq 3) was monitored by ^{1}H NMR spectroscopy at T = 300 K on three samples containing 9 mg of complex **5** (0.01 mmol) in a mixture of 50 μL of CD_3NO_2/550 μL of CD_2Cl_2, after the addition of free excess ethylene to each sample (initial molar ratio 3.2, 4.5, and 8.0, respectively, for the three samples). The corresponding apparent rate constants were determined from pseudo-first-order plots (5×10^{-4}, 9×10^{-4}, 18×10^{-4} s^{-1}, respectively), showing a marked and approximately linear increase of the substitution rate with the concentration of free ethylene.

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Supporting Information Available: Full tables of crystal and data collection parameters, atomic coordinates, bond lengths, bond angles, and thermal displacement parameters for **1**·CH_2Cl_2. This material is available free of charge via the Internet at http://pubs.acs.org.

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