Amine Attack on Coordinated Alkenes: An Interconversion from Anti-Markovnikoff to Markovnikoff Products

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Abstract: A sequence of alkene complexes of platinum, $PtCl_2(PPh_3)$(alkene) (alkene = ethylene, propene, 1-butene, *cis*-2-butene, 1-hexene, 1-octene, and 1-decene), has been prepared. These complexes are characterized by NMR spectroscopy, including assignment of each proton, and X-ray crystal structures of the 1-propene and 1-hexene complexes. Each complex was reacted with diethylamine. For the 1-hexene, 1-octene, and 1-decene complexes, the amine displaces the alkene. For the smaller alkenes, the diethylamine nucleophilically attacks the coordinated alkene. For propene and 1-butene, the low-temperature addition leads to the anti-Markovnikoff nucleophilic attack, which slowly converts at room temperature to the Markovnikoff product. The transformation from anti-Markovnikoff to Markovnikoff addition occurs without diethylamine dissociation.
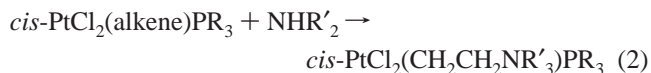
Nucleophilic attack on an alkene coordinated to a transition metal is arguably the most important application of organometallic chemistry. Theoretical studies[1,2] and reviews[3] summarize the basics of coordination and activation. Depending on the attack site, Markovnikoff or anti-Markovnikoff products may result.

An often-studied nucleophilic attack involves amines and palladium or platinum alkene complexes.[4–10] Among the earliest accounts of amine attack on a simple alkene were those of Orchin et al.,[4]

$$trans\text{-}PtCl_2(C_2H_4)(Py) + C_5D_5N \rightarrow$$
$$trans\text{-}PtCl_2(C_2H_4C_5D_5N)(py) \quad (1)$$
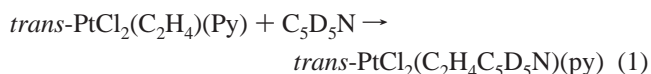
(py = C_5H_5N), and Panunzi et al.,[5]

$$cis\text{-}PtCl_2(alkene)PR_3 + NHR'_2 \rightarrow$$
$$cis\text{-}PtCl_2(CH_2CH_2NR'_3)PR_3 \quad (2)$$

(alkene = C_2H_4, C_3H_6, 1-C_4H_8; PR_3 = PPh_3, PnBu_3; NHR'_2 = $NHMe_2$, $NHEt_2$, $NHBu_2$). The Panunzi group published extensively on related reactions around 1970.[6]

Green and colleagues published a series of manuscripts around 1980, further describing the electronic and steric effects involved in amine attack on coordinated alkenes, *cis*-PtCl_2-(alkene)L, with L = a variety of amine ligands, DMSO, etc.[7] In a number of cases, azaplatinacyclobutane complexes were formed, and their stability was evaluated.[7c,f–i] In only one case, *cis*-PtCl_2(3-methylbut-1-ene)(P(OMe)_3), was anti-Markovnikoff addition reported.[7i]

Interest in such nucleophilic attack on coordinated alkenes revived around 2000, primarily as a result of Hartwig's work on palladium-catalyzed hydroaminations of vinylarenes.[8] These proceed through an η^3-arylethyl complex and give Markovnikoff products. However, a rhodium complex provided anti-Markovnikoff hydroamination through a metallacyclic intermediate.[9] Markovnikoff addition of amines to alkenes coordinated to a dicationic platinum complex was reported to be facile.[10] A summary of recent developments emphasizing the importance of hydroamination was published.[11] A DFT theoretical study

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of complexes M(Cl)(PH₃)₂ evaluated the hydroamination process for different metals, concluding that nucleophilic attack of amine is thermodynamically and kinetically favorable for Group 10 metals.[12] A review of aminations summarizes the research prior to 1998.[13]

In re-examining reactions of *cis*-PtCl₂(alkene)(PPh₃), we have discovered that anti-Markovnikoff addition is kinetically controlled, but Markovnikoff addition is thermodynamically controlled. Herein, we report the synthesis of seven alkene complexes and reactions with NHEt₂.

Results and Discussion

Synthesis. Simple alkenes coordinate to platinum(II), yielding stable species not prone to air oxidation. However, the synthetic procedures documented for syntheses of such alkene complexes are quite complex and require long incubation times,[5,14] which result in both time dependency and overall decrease in yield. We have established a new synthetic procedure for the synthesis of *cis*-PtCl₂PPh₃(alkene) (alkene = ethylene, propylene, 1-butene, *cis*-butene 1-hexene, 1-octene and 1-decene) with an overall yield >80% based on the starting platinum complex. PtCl₂,[15]
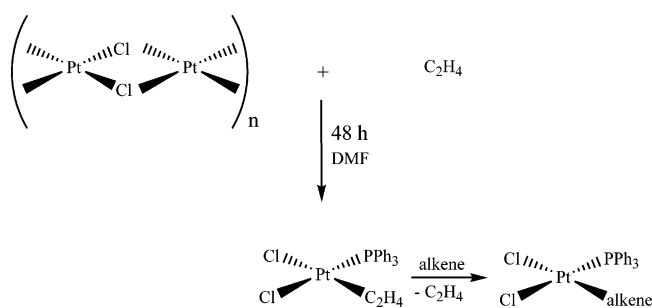
dissolved in DMF, was reacted with ethylene in the presence of triphenylphosphine. The product was precipitated from DMF by addition of triply distilled water, and the white solid was recrystallized from chloroform. To obtain species with higher olefins, the ethylene complex was dissolved in chloroform and placed in the presence of the desired alkene. The solubility of *cis*-PtCl₂PPh₃(alkene) complexes in chloroform decreases significantly with increase in the hydrocarbon chain length of the bound alkene.

Based on the results of our investigation, alkene addition to PtCl₂PPh₃ takes place cis to triphenylphosphine. These results are supported by the body of work reported in the literature, especially that by Green et al.[7] and Panunzi et al.[5,6] and our own X-ray crystal structures (reported herein). Coordination cis to triphenylphosphine is not expected based on steric factors. Whereas coordination of smaller alkenes does not sterically hinder rotation of triphenylphosphine, coordination of 1-hexene and larger olefins can, in theory, pose some steric hindrance between the alkyl chains and phenyl rings, thereby lowering the E_{act} barrier for dissociation of the respective alkene, and thus the larger alkene complexes are less stable.[16]

A kinetic preference for trans geometry might be expected, given the strong trans effect of PPh₃ and alkene.[17a] However,

given the synthesis from a mixture of PtCl₂, alkene, and PPh₃, *cis*-PtCl₂(alkene)(PPh₃) appears to be thermodynamically favored, maximizing the bonding by placing the strong trans-influence ligands cis.[17b]

The new procedure for synthesizing the ethylene complex has proven to be invaluable, because synthetic methods described in the literature require several steps and long times,[14] resulting in both smaller yields and decreased purity of the product. Utilizing DMF in a "one-pot" synthesis allowed easy separation of the product and a significant increase in yield (from 40% to 95%) based on the starting Pt(II) complex. The success of the procedure may arise from the reaction conditions, in which bridged platinum species were broken into monomers by association with triphenylphosphine, yielding an open coordination site blocked by DMF long enough to not coordinate another phosphine ligand but to allow coordination of ethylene. Therefore, DMF played a crucial role in formation of the product. A similar reaction run in dichloromethane resulted in formation of the bistriphenylphosphine complex, indicating that the solvent was not coordinating enough. However, when DMSO was used, solvent complex, PtCl₂(DMSO)(PPh₃), was produced, presumably due to greater coordinating power of the solvent over ethylene. These results were also confirmed by an independent experiment in which ethylene-bound complex was dissolved in DMSO-d₆; evolution of the gas was immediate and PtCl₂(DMSO-d₆)(PPh₃) was formed. Therefore, the choice of solvent plays an important role in the synthesis, yield, and purity of the ethylene complex. The ethylene complex *cis*-PtCl₂(C₂H₄)-(PPh₃) provides an excellent precursor to the other alkene complexes.

Amine Addition. The alkene complexes were reacted independently with diethylamine. Each reaction was performed at −75 °C, since the addition is exothermic and the lower temperature should shift the equilibrium toward formation of the products.[5−7] To achieve greater yields, excess amine was used. In the case of the ethylene adduct, only a stoichiometric amount of amine was required for reaction. However, with the longer chain alkene adducts, no reaction was observed with 1 equiv of diethylamine, possibly due to increased steric hindrance about the olefin. Temperature control has proven to be essential for obtaining alkyl derivatives, and experiments resulted in failure when the reaction mixture was brought to room temperature too rapidly, causing ligand substitution rather than nucleophilic attack. Even at low temperatures, the alkene was displaced if it was larger than four carbons.

Alkyl species resulting from the addition of diethylamine onto a bound alkene are shown in Figure 1. For propylene and 1-butene, Markovnikoff or anti-Markovnikoff addition is possible. Due to some discrepancies in the literature with regard to the latter and former conventions, we consider a Markovnikoff species to result from attack of a nucleophile onto an internal carbon of the bound alkene, thus resulting in a bond between a metal and a carbon carrying two hydrogens.

***cis*-PtCl₂(PPh₃)C₂H₄NHEt₂.** The ¹H NMR spectrum (Figure 2) of product **I** shows a triplet of doublets in the region of δ 0.47 ppm and a triplet around δ 4.2 ppm, corresponding to **a** and **b** protons, respectively. The phosphorus atom caused an unexpected splitting of the triplet at 0.47 ppm; cis-coupling is

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Anti - Markovnikoff   Markovnikoff
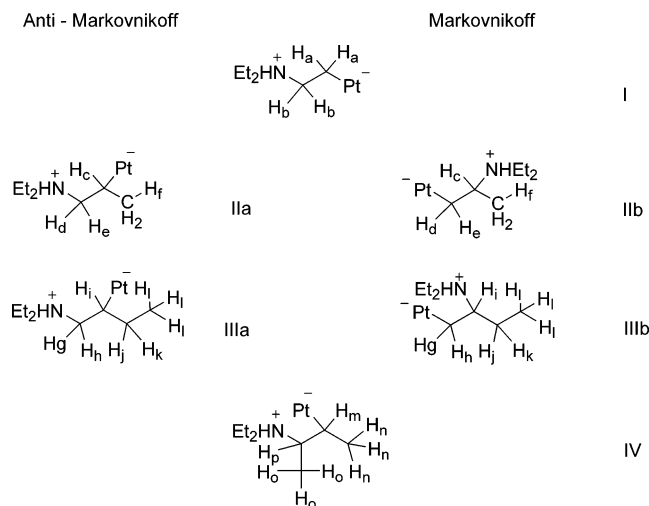
**Figure 1.** Proton assignments for the platinum alkyl complex resulting from diethylamine attack on coordinated alkene.

usually too small to be observed. Upon decoupling phosphorus ($^1H\{^{31}P\}$ NMR), the triplet of doublets was transformed into a triplet resulting from splitting by adjacent **b** protons, as shown in Figure 3. The broad satellites arise from coupling of the methylene protons to the ^{195}Pt nucleus (33% abundant), which possesses a spin of $^1/_2$. The coupling $^2J_{^{195}Pt-CH_2}$ has a magnitude of 80 Hz. The **b** protons are significantly more downfield, around δ 4.1 ppm, due to the deshielding effects of the nitrogen atom. The decrease in $^3J_{^{195}Pt-CH_2}$ coupling of the 4.1 ppm resonance is attributed to an increase in spatial separation between interacting nuclei. Methyl and methylene hydrogens of the ethyl groups on nitrogens showed complex splitting patterns due to overlap of the bound and unbound diethylamine. Therefore, no precise assignments in those regions were made for this and the other alkyl derivatives.

cis-PtCl$_2$(PPh$_3$)C$_3$H$_6$NHEt$_2$. The ^1H NMR spectrum of complex **II** is characterized by the presence of several multiplets in the aliphatic region of the spectrum. No coherent assignment for the protons of the aliphatic region is present in the literature due to the complexity of the ^1H spectrum (Figure 4). To establish the connectivity within the alkyl chain, a TOCSY was performed

with original selection of the doublet at δ 0.11 ppm, corresponding to the methyl group. Results of the experiment (Figure 5) showed that four separate resonances in the ^1H NMR correspond to the protons on the propyl chain. Integration of the peaks establishes the pattern of 1:1:1:3. However, unprecedented $^2J_{^{195}Pt-CH_2}$ coupling of 70 Hz is difficult to explain. A platinum decoupling experiment (Figure 6) shows the disappearance of the platinum satellites. Two-dimensional $^{195}Pt-^1H$ HSQC (Figure S1) shows a definitive coupling interaction between the ^{195}Pt and the methyl group. Both **e** and **d** protons are coupled to the same carbon, as shown in $^1H-^{13}C$ HSQC (Figure S2). The chemical shift of the carbon atom carrying those protons is indicative of the presence of bound nitrogen. Moreover, an upfield shift of the carbon bonded to the metal can be rationalized in terms of shielding effects imposed by the presence of the metal nucleus.

Contrary to the literature precedent,[5-7] we found that the anti-Markovnikoff adduct, initially formed, rearranges in chloroform at room temperature to form the Markovnikoff addition species. The appearance of the doublet at δ 1.11 ppm and disappearance of the doublet at δ 0.11 ppm in the ^1H NMR spectrum (Figure S3) indicated formation of the new species. The progress can be monitored by ^1H NMR spectroscopy. However, the time frame required for complete rearrangement is measured in months. Slow emergence of new resonances was accompanied by a decrease in the intensity of the resonances, corresponding to the anti-Markovnikoff species. A striking feature in the spectral characterization of the new alkyl derivative was the absence of platinum satellites and significant shift on the NMR scale of 1 ppm for **f** protons. Methylene protons **e** and **d** were also shifted upfield due to shielding effects caused by the presence of an electropositive nucleus. Methyne proton **c** was shifted upfield, and the connectivity of the alkyl chain was established through TOCSY NMR (Figure S4) and 2D $^1H-$ ^{13}C HSQC (Figure S2). Changes in the relative positions of the carbon atoms in the ^{13}C NMR are also indicative of the rearrangement and provide further support for the presence of a σ bond between the primary carbon and platinum.
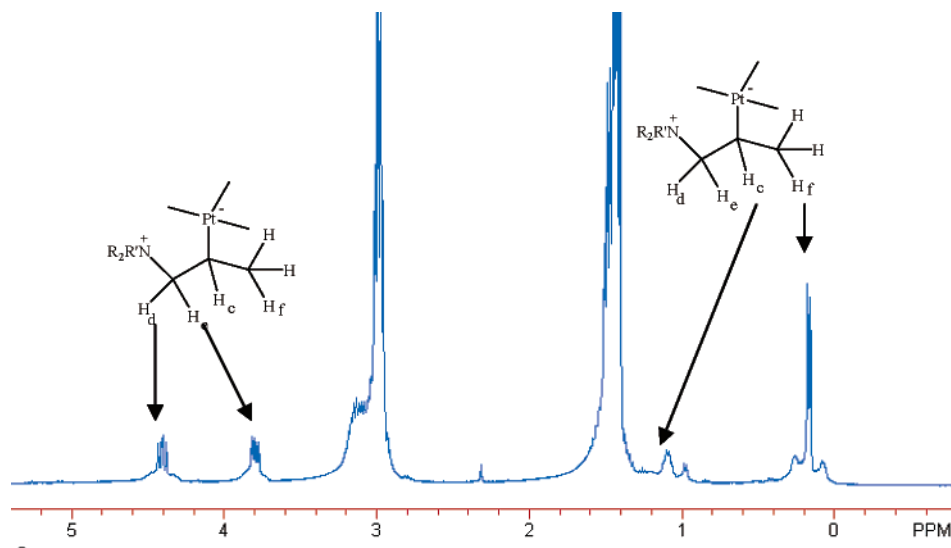
cis-PtCl$_2$(PPh$_3$)C$_4$H$_8$NHEt$_2$. Synthesis of alkyl derivative **IV** was challenging due to rapid dissociation of the *cis*-2-butene
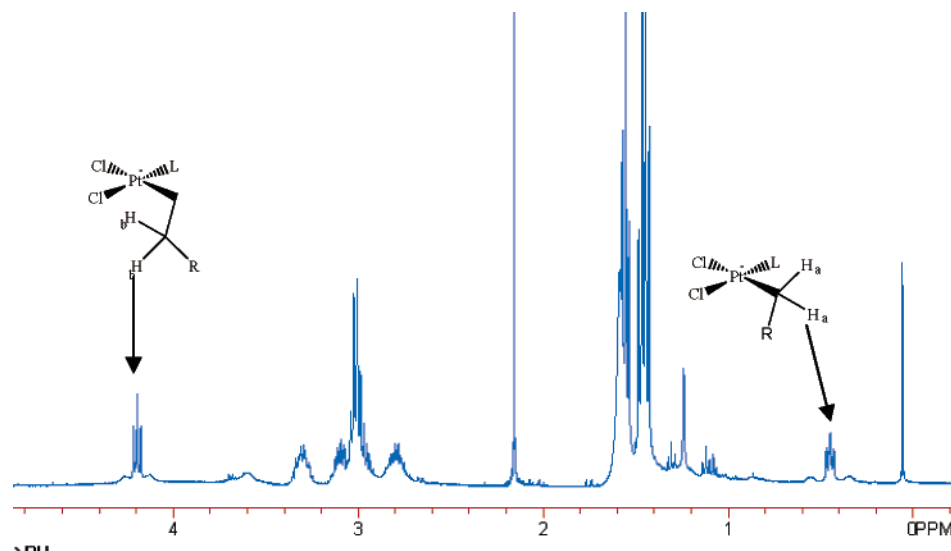
Figure 2. Partial ^1H spectrum of *cis*-PtCl$_2$(PPh$_3$)C$_2$H$_4$NHEt$_2$ in CDCl$_3$.
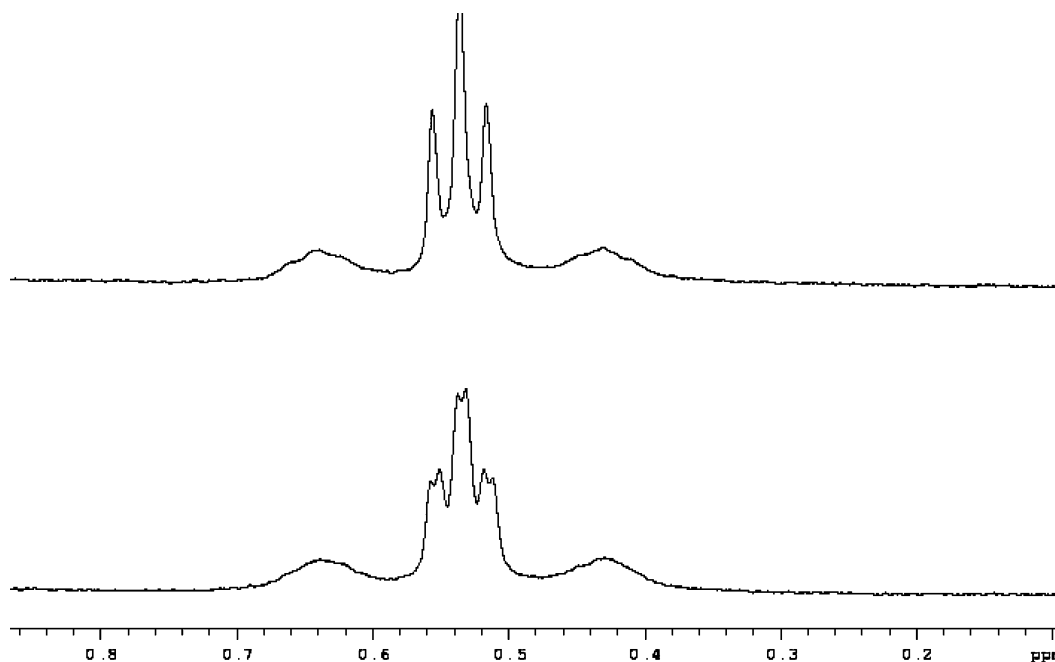
Figure 3. Partial $^1H\{^{31}P\}$ NMR spectrum of *cis*-PtCl$_2$(PPh$_3$)C$_2$H$_4$NHEt$_2$ in CDCl$_3$. (bottom, ^{1}H NMR spectrum; top, $^1H\{^{31}P\}$ NMR spectrum).

Figure 4. Partial ^{1}H spectrum of *cis*-PtCl$_2$(PPh$_3$)C$_3$H$_6$NHEt$_2$ in CDCl$_3$.

and formation of the dimeric platinum species. The coupling pattern within the alkyl chain of **IV** was established by TOCSY NMR with selective mixing times (Figure S5). A doublet at δ 0.11 ppm in the ^{1}H NMR spectrum showed platinum satellites (Figure S6), and a multiplet at δ 3.95 ppm exhibited numerous couplings. Based on the chemical shift in the ^{1}H NMR, the multiplet at δ 3.95 ppm is most likely from carbon coordinated to diethylamine. A multiplet at δ 0.9 ppm is consistent with **m**, and the doublet (1.05 ppm) results from coupling of **p** with **o**. Satellites for **n** are a result of interaction with platinum ($^3J_{Pt-H}$).[18] To confirm the preliminary assignment of resonances in the ^{1}H NMR spectrum, a 2D $^1H-^{13}C$ HSQC was taken (Figure S7). The carbon atom bonded to **p** is shifted downfield to around δ 70 ppm, indicative of the bond to nitrogen. The **m** proton is bonded to the carbon shifted upfield above δ 0 ppm due to coordination to platinum. The carbon at δ 20 ppm carries **n**, while that at δ 18 ppm is bonded to **o**. One would expect an

activated methyl group to be shifted upfield of an inactivated methyl carbon due to formation of the partial three-center, four-electron bond in a fluxional manner with **n** hydrogens.[19] A TOCSY experiment confirmed the connectivity within the carbon chain.

cis-**PtCl$_2$(PPh$_3$)-1-C$_4$H$_8$NHEt$_2$.** Complex **III** was characterized in the same way as the other alkyl derivatives. The ^{1}H NMR analysis (Figure S8) allowed distinguishing between several possible isomers. Multiplets around δ 3.9 ppm and δ 4.4 ppm are similar to those observed in the propyl complex and may be assigned to **g** and **h** from both chemical shift and 2D $^1H-^{13}C$ HSQC (Figure S9), which shows that both are coupled to the same carbon. However, it is difficult to distinguish **g** from **h** without quantum mechanical calculations. The identification of the resonances corresponding to the anti-Markovnikoff species **IIIa** was complicated by significant overlap in the ^{1}H NMR. Thus, a TOCSY NMR with selective
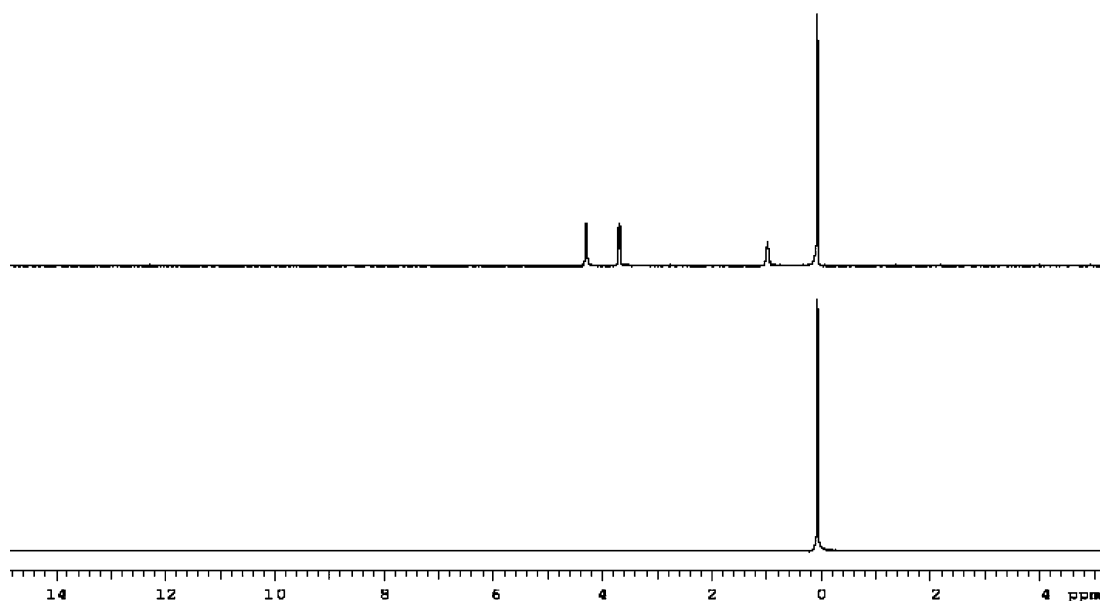
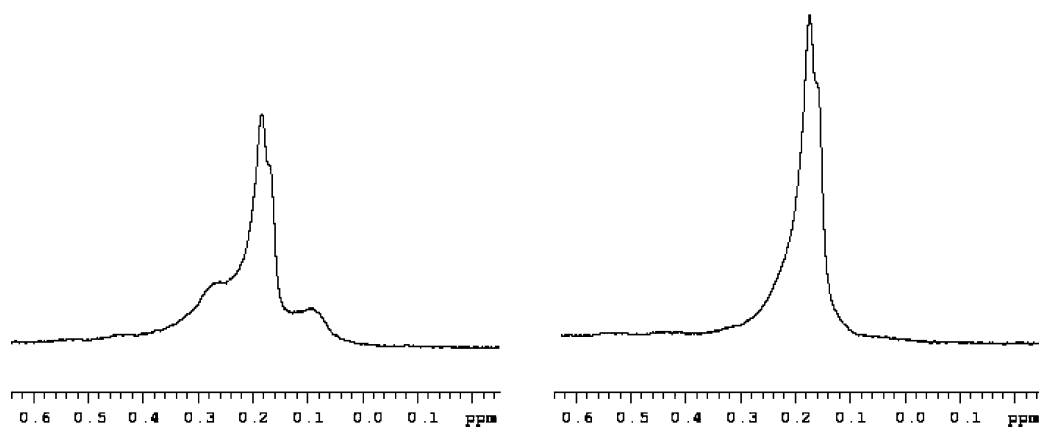**Figure 5.** TOCSY 1D NMR spectrum of *cis*-PtCl$_2$(PPh$_3$)C$_3$H$_6$NHEt$_2$ in CDCl$_3$.

Figure 6. Partial ^{1}H{^{195}Pt} NMR spectrum of *cis*-PtCl$_2$(PPh$_3$)C$_3$H$_6$NHEt$_2$ in CDCl$_3$.

mixing was taken (Figure S10), and **j** and **k** were separated and identified at δ 1.3 ppm and δ 1.5 ppm, an area obscured by methyl protons of bound and unbound diethylamine. Methyl protons in both **IIIa** and **IIIb** were located at 0.3 and 0.7 ppm, respectively, and showed a peculiar coupling pattern: both appear as triplets, although methylene protons **j** and **k** are inequivalent. A series of irradiation experiments resulted in disappearance of the triplets and appearance of broad doublets. It is possible that the J_{j-n} and J_{k-n} are of a similar magnitude, giving the observed splitting pattern. The **i** proton was determined to be underneath the resonances of **j** and **k**.

Multiple studies on addition of a nucleophile to a Pt(II)-bound alkene have been performed, but few dealt with precise assignment of the stereochemistry of addition.[6a−d] It is very difficult to unequivocally conclude which type of addition is more favorable, because many factors come into play, such as the nature of the amine, cone angle of the phosphine ligand, temperature of addition, and subtle electronic effects.[5,7b,16,20] Azaplatinacyclobutane has been suggested[7] from reaction

between secondary amine and Pt(II)-bound alkenes. Our NMR analyses, detailed above, show no evidence for formation of azaplatinacyclobutanes for our reactions. Microanalyses indicate two Cl$^-$ for each platinum, consistent with the NMR results.

An amine can displace the alkene or attack the alkene inter- or intramolecularly. Based on calculations by Sieghban,[20] intermolecular attack provides a lower energy barrier for an OH$^-$ attack onto a bound ethylene of PdCl$_2$(C$_2$H$_4$). Dewar and Ford[21] calculated the lowest energy pathway for addition of an amine to a bound olefin. Their conclusions indicate that there is a significant difference in energy between intermolecular and intramolecular modes of attack. Nucleophilic addition can be established either with the terminal, least hindered, or with the internal, most hindered, carbon of the alkene. Since the temperature of the addition was low, the product with the lowest activation energy should be favored. The presence of anti-Markovnikoff product exclusively for **II** and **III** at low temperature indicates the preference for attack on the least substituted carbon.

If **II** and **III** are left in solution for an extended period of time, they rearrange to form the Markovnikoff addition products.

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All attempts at making Markovnikoff species by direct addition have failed, because when amine addition takes place at temperatures above −30 °C, olefin displacement takes precedent over amine addition and no alkyl derivatives could be isolated for either **II** or **III**. The rearrangement from the anti-Markovnikoff product to the Markovnikoff takes place quantitatively with no loss of alkene. Given the ready displacement of alkene under the conditions where the rearrangement occurs, any mechanism involving a free alkene complex would be precluded. Allyl complexes could form[22] and have been suggested for isomerization reactions; however, those involve 1,3 shifts,[23] not the 1,2 shift observed here. A synchronous formation of Pt−C and C−N bonds, while weakening of the existing Pt−C and C−N bonds, seems most consistent with the observations. Calculations may clarify this unusual rearrangement.

After the rearrangement takes place, a doublet corresponding to **f** along with the satellites disappears, and emergence of the Markovnikoff product **IIb** is accompanied by the appearance of a sharp doublet at δ 1.11 ppm, indicative of the **f** protons. A ^{1}H NMR shift of 1 ppm indicates a decrease in electron density surrounding the **f** protons. Disappearance of platinum satellites signifies the absence of interaction between methyl protons and the metal ion. It is very peculiar that the platinum interaction takes place only when **f** protons are on the carbon adjacent to the carbon bonded to platinum. Thus, the distance between the methyl protons must be significant. A ^{13}C decoupled spectrum shows $J_{^{13}C-^{1}H}$ coupling close to normal, but the platinum satellites in the ^{1}H spectrum of **IIa** indicate interactions between the metal ion and **f** protons, with interaction ceasing to exist after the rearrangement to **IIb**. Species **III** exhibits the same type of rearrangement, although no platinum satellites were observed for either Markovnikoff or anti-Markovnikoff products, confirming that the methyl group has to be adjacent to the carbon bonded to the metal.

Structures. Crystals of *cis*-PtCl$_2$(PPh$_3$)C$_3$H$_6$ (Figure 7) and *cis*-PtCl$_2$(PPh$_3$)C$_6$H$_{12}$ (Figure 8) were grown in an H tube by slow diffusion of pentane into 1,1,2,2-tetrachloroethane. X-ray crystal structure analysis showed cis coordination of the olefin relative to the triphenylphosphine. Selected bond distances and angles are given in Tables 1 and 2. The geometry of both is a distorted square-planar complex with the alkene perpendicular to the plane. The distances and angles are about the same, although the average Pt−C(alkene) bond distance is slightly longer for 1-hexene, consistent with the decreased stability. The rest of the olefin-bound complexes also showed cis coordination, based on the inequivalency of the respective protons stemming from the perpendicular and parallel modes of coordination relative to the square-planar geometry of the molecule. Complexes of 1-butene and *cis*-butene readily decomposed in solution to form platinum dimer and respective gases.

Orchin et al.[24] implied that the magnitude of J_{Pt-CH_2} is representative of the distance between the metal ion and the respective protons. Coupling with a magnitude of 70 Hz, as observed for **II** and **IV**, is quite large and unprecedented for a three-bond separation. Based on the 2D ^{1}H−^{195}Pt spectrum

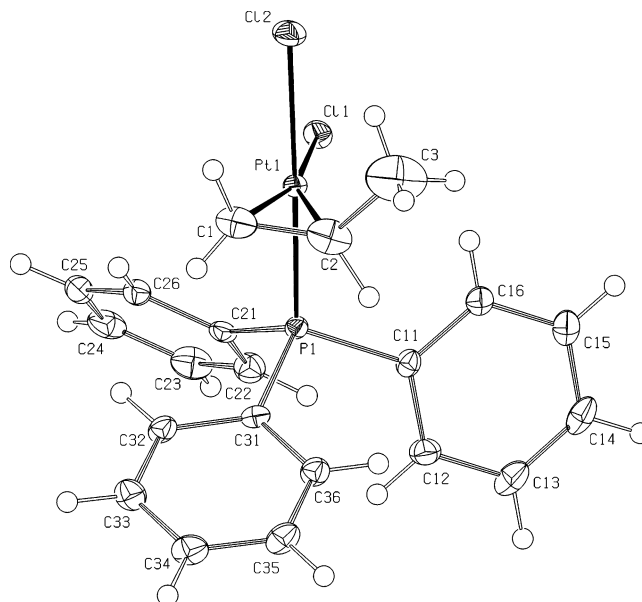(22) Collman, J. P.; Hegedus, L. S.; Norton, J. R.; Finke, R. G. *Principles and Applications of Organotransition Metal Chemistry*; University Science Books: Mill Valley, CA, 1987; pp 175−180.

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Figure 7. ORTEP diagram of PtCl$_2$(PPh$_3$)C$_3$H$_6$ (50% thermal ellipsoids).
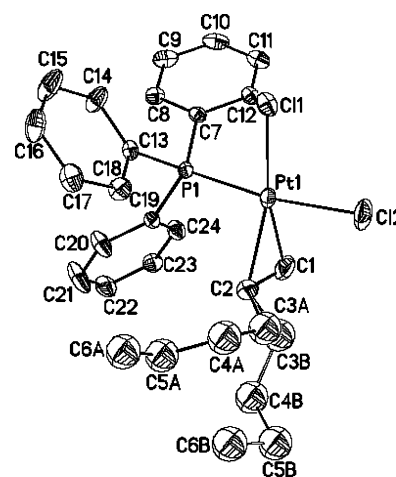

Figure 8. ORTEP diagram of *cis*-PtCl$_2$(PPh$_3$)(1-hexene) (50% thermal ellipsoids).

Table 1. Selected Bond Lengths (Å) and Angles (°) for PtCl$_2$(PPh$_3$)C$_3$H$_6$

Pt(1)−C(1)	2.146(3)	Pt(1)−Cl(2)	2.3623(8)
Pt(1)−C(2)	2.188(3)	C(1)−C(2)	1.394(5)
Pt(1)−P(1)	2.2610(7)	C(2)−C(3)	1.497(6)
Pt(1)−Cl(1)	2.3195(8)		
C(1)−Pt(1)-C(2)	37.52(14)	C(2)−Pt(1)−Cl(2)	93.87(10)
C(1)−Pt(1)−P(1)	95.58(10)	P(1)−Pt(1)−Cl(2)	175.05(3)
C(2)−Pt(1)−P(1)	91.06(10)	Cl(1)−Pt(1)−Cl(2)	88.21(3)
C(1)−Pt(1)−Cl(1)	164.29(11)	C(2)−C(1)−Pt(1)	72.9(2)
C(2)−Pt(1)−Cl(1)	158.11(11)	C(1)−C(2)−C(3)	127.1(4)
P(1)−Pt(1)−Cl(1)	87.35(3)	C(1)−C(2)−Pt(1)	69.6(2)
C(1)−Pt(1)−Cl(2)	88.13(10)	C(3)−C(2)−Pt(1)	113.2(3)

(location of the resonance for **f** protons in the ^{1}H NMR spectrum and location of the respective carbon atom in 2D ^{1}H−^{13}C HSQC), we believe that direct interaction takes place between the methyl protons and the Pt center. This interaction can take place due to proximity of the methyl group in both **II** and **IV** and results in direct spin−spin coupling between the **f** and **o** or **n** protons with the platinum atom. If C−H activation takes place, it occurs in a fluxional manner in which all methyl protons become equivalent on the NMR time scale due to the rapid

Table 2. Selected Bond Lengths (Å) and Angles (°) for PtCl$_2$(PPh$_3$)(1-hexene)

Pt(1)−C(1)	2.144(5)	Pt(1)−Cl(1)	2.3149(9)
Pt(1)−C(2)	2.204(5)	Pt(1)−Cl(2)	2.3514(9)
Pt(1)−P(1)	2.2517(8)	C(1)−C(2)	1.405(8)
C(1)−Pt(1)−C(2)	37.7(2)	C(1)−Pt(1)−Cl(2)	87.8(2)
C(1)−Pt(1)−P(1)	98.0(2)	C(2)−Pt(1)−Cl(2)	95.5(1)
C(2)−Pt(1)−P(1)	92.3(1)	P(1)−Pt(1)−Cl(2)	172.1(4)
C(1)−Pt(1)−Cl(1)	164.6(2)	Cl(1)−Pt(1)−Cl(2)	88.27(4)
C(2)−Pt(1)−Cl(1)	157.7(2)	Cl(2)−C(1)−Pt(1)	73.4(3)
P(1)−Pt(1)−Cl(1)	84.77(3)	Cl(1)−C(2)−Pt(1)	68.9(3)

rotation around the C−C σ bond. Based on the results by Eisenstein et al.,[25] if C−H activation takes place, the J_{C-H} should have a magnitude of 100 Hz or below, whereas in all other cases it is around 125 Hz for a methyl group. The ^{13}C spectrum showed a coupling constant of 123 Hz for the carbon carrying **f** and **n** or **o** protons, which is normal for methyl carbon. Thus, while the ^{1}H chemical shift and J_{Pt-H} indicate significant interactions of the methyl of **II** and one methyl of **IV** with platinum, the J_{C-H} does not indicate C−H activation. Therefore, the Pt−H interaction must not cause significant C−H elongation, consistent with the equivalency of the three hydrogens of the methyl. The carbon carrying **f** protons in **IIb** has an almost identical chemical shift and J_{C-H} coupling constant. Although **e** and **d** of **IIb** are inequivalent in the ^{1}H spectrum, they split carbon carrying them into a triplet in the ^{1}H-coupled ^{13}C NMR (Figure S11). Thus, the J_{C-H} coupling constant of each of the protons is similar enough to provide the appearance of a triplet. Moreover, the C−H coupling constant of 139 Hz for both Markovnikoff and anti-Markovnikoff species indicates partial sp^2 hybridization[26] on the carbon attached to the metal, which is peculiar because the former is primary and the latter is secondary.

Concluding Remarks

To the best of our knowledge, we report the first example of facile synthesis for PtCl$_2$PPh$_3$(alkene). Complexes were thoroughly characterized, and crystal structures indicate cis coordination with respect to triphenylphosphine. Each species was reacted with diethylamine, and alkenes with a hydrocarbon chain longer than four carbons were displaced rather than undergoing nucleophilic addition. All alkyl derivatives were extensively characterized by NMR, and each proton was assigned on the alkyl chain. Unprecedented coupling was shown to take place between the methyl protons of the carbon adjacent to the carbon bonded to platinum and the metal nucleus.

Diethylamine addition to the 1-propene and 1-butene complexes at low temperature leads to the anti-Markovnikoff product, which slowly rearranges at room temperature to the Markovnikoff product. The mechanism for this rearrangement is not established, but probably does not involve amine loss to give the platinum−alkene complex. This rearrangement could be very important in catalysis directed toward anti-Markovnikoff products.

Supporting Information Available: Experimental Section, additional NMR data, further X-ray crystallographic data, and CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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