Sequential Deprotonation of Olefins in the Coordination Sphere of Platinum(II): Occurrence and Synthetic Aspects

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The cationic platinum complexes [Pt(η^2-alkene)X(tmeda)](ClO_4) (**1**: X = Cl, alkene = propene, 1-butene, 1-hexene; X = NO_2, alkene = (*E*)-2-butene, (*Z*)-2-butene; tmeda = *N*,*N*,*N*′,*N*′-tetramethylethylenediamine) smoothly react with triethylamine to undergo loss of one allylic proton of the alkene ligand and formation of the η^1-allyl species [Pt(η^1-allyl)X(tmeda)] (**2**). In the case of 1-butene and 1-hexene, the η^1-allyl species containing a nonterminal olefinic function (X(tmeda)PtCH_2CH=CHR, R = Me, Pr) undergoes release of the X ligand and $\eta^1 \rightarrow \eta^3$ rearrangement of the allyl to form [Pt(η^3-allyl)(tmeda)]$^+$ (**3**). The reaction is stereoselective, and the R substituent is always found syn to the central hydrogen of the allyl group; however, in solution, a partial isomerization of the syn into the anti form slowly takes place. In the case of propene and (*E*)- and (*Z*)-2-butene the terminal olefinic function of **2**, [X(tmeda)PtCHRCH=CH_2], can displace the η^2-alkene from a second molecule of **1** to form the η^1:η^2-allyl-bridged dinuclear complex [{PtX(tmeda)}$_2$(μ-η^1:η^2-CH_2−CH=CHR)]$^+$ (**4**). Further deprotonation of the η^1-bonded methylene of **4** and simultaneous release of the X ligand by one platinum unit leads to formation of the η^1:η^3-allyl-bridged platinum dimer [{PtX(tmeda)}(μ-η^1:η^3-CHCHCHR){Pt(tmeda)}]$^+$ (**5**). In the case of (*E*)- and (*Z*)-2-butene **3** and **5** are formed in comparable yield, while in the case of propene **5** is by far the major product. The structure of **5a** (R = H) has been confirmed by single-crystal X-ray diffraction. The two platinum subunits are nearly perpendicular (dihedral angle between the two PtN_2 planes of 77.0°). The allyl plane (C(7)C(8)C(9)) forms a dihedral angle of 60.6° with the coordination plane of the η^3-bonded platinum (Pt(2)N(3)N(4)). The Pt−C distances are shorter for the η^1-bound platinum (Pt(1)−C(7) = 2.00(1) Å) than for the η^3-bound platinum (Pt(2)−C(7) = 2.24, Pt(2)−C(8) = 2.15, and Pt(2)−C(9) = 2.07 Å).

Introduction

The activation of unsaturated molecules, promoted by coordination to a metal center, is a topic of great interest in organometallic chemistry and is involved in the catalysis of several reactions. Metal-coordinated alkenes reverse their polarity and become susceptible to attack by nucleophiles, leading to the formation of new synthons; furthermore, they can insert into adjacent metal−carbon or metal−hydrogen bonds.[1]

Increased Brønsted acidity of metal-coordinated olefins has sometimes been reported. Deprotonation of cationic iron complexes of the formula [Fe^{II}(η^5-cyclopentadienyl)$(CO)_2$(olefin)]$^+$, promoted by trialkylamines, was reported for the first time by Rosenblum et al. in the 1970s. The removal of an allylic proton led to the formation of (η^1-allyl)iron species that easily got involved in cycloaddition reactions.[2] A stronger base (*tert*-butyloxy anion) was required for deprotonation of olefins in the rhenium complexes [Re^{II}(η^5-cyclopentadienyl)(PPh_3)(NO)(olefin)]$^+$.[3] In the latter case it was possible to promote the abstraction of the vinylic proton, instead of the allylic proton, by increasing the steric hindrance on the allylic carbon. Finally, a recent report described a series of reactions initiated by deprotonation of the olefin in the tungsten calix[4]arene complex [W^{IV}{*p*-Bu^t-

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calix[4]-O_4}(η^2-olefin)]. Also in this case the abstracted proton could be either allylic or vinylic and a strong base, such as LiBu, was required.[4] In addition to monoalkenes, also conjugated dienes in cationic molybdenum(II)[5] and iridium(I)[6] complexes can undergo abstraction of either an allylic or a vinylic proton (the abstraction of a vinylic proton usually requiring more drastic reaction conditions).[5]

It has to be noted, however, that very electrophilic metal complexes can promote C−H allylic activation of terminal olefins, leading to η^3-allyl species, without the assistance of a base. This interesting behavior has been observed, apart from palladium chemistry,[7] in the case of dicationic rhodium,[8] iridium,[8,9] and ruthenium[10] complexes.

Differently from palladium, platinum−olefin complexes were considered end products and, up to now, C−H allylic activation or base-promoted olefin deprotonation did not appear to be pertinent to platinum(II) chemistry. In the literature there is only one report concerning the loss of an HCl molecule from [PtCl(η^5-C_5H_5)(η^2-alkene)] complexes, leading to formation of the corresponding [PtCl(η^5-C_5H_5)(η^3-allyl)] species. The reaction occurs under rather drastic conditions, in small yield, and the proton was only removed from a tertiary vinylic carbon.[11]

However, the reactivity of olefin platinum species could be greater in cationic complexes. Unfortunately, cationic olefin complexes of platinum[12−17] often undergo loss of the unsaturated ligand, preventing the full exploitation of this reactivity. In contrast with the general behavior, a class of stable cationic species is represented by complexes of the formula [PtX(η^2-olefin)(tmeda)](ClO_4) (**1**: X = Cl, NO_2, tmeda = *N*,*N*′,*N*′,*N*′-tetramethylethylenediamine), isolated and investigated by some of us over several years.[14,18] In these complexes the presence of a fully substituted diamine ligand (such as tmeda) renders the chelate ring particularly stable and able to counterbalance the strong trans effect of the olefin. The stability of complexes of type **1** is demonstrated by the presence, at room temperature, of sharp ^{1}H NMR signals with well-defined ^{195}Pt satellites. Moreover, a recent theoretical investigation by Strømberg and Svensson has come to the conclusion that a *cis*-Pt(NH_3)$_2$Cl$^+$ fragment should form, with olefins, a more stable η^2 complex than neutral Pt(NH_3)Cl_2 or anionic $PtCl_3^-$ moieties.[19]

In compounds **1** the coordinated η^2-olefin is highly electrophilic and undergoes addition of various oxygen, nitrogen, and carbon donors.[10c,14] The reactivity is particularly high in the case of ethene, which is able to add also tertiary amines,[14a,c] inorganic anions,[14d,e] and 1,8-bis(dimethylamino)naphthalene (in the last case displacing a proton in the para position of the ring system).[14h] Interestingly, in the case of olefins higher than ethene the reaction of compounds **1** with tertiary amines does not lead to addition products but, instead, to proton abstraction and formation of allyl complexes. A preliminary account of this research has been published.[20]

Results and Discussion

All investigated complexes have the general formula [PtX(η^2-alkene)(tmeda)](ClO_4) (**1**: X = Cl, alkene = propene (**1a**), 1-butene (**1b**), 1-hexene (**1c**); X = NO_2, olefin = (*E*)-2-butene (**1d**), (*Z*)-2-butene (**1e**)). All complexes were reacted with triethylamine at room temperature and in chlorinated solvents.

Propene Complex. The propene complex **1a** reacts with triethylamine to give a cascade of three subsequent reactions (Figure 1). The first reaction is deprotonation of the propene methyl and formation of the neutral η^1-allyl complex **2a**. This first reaction step is similar to that observed by Rosenblum et al. for cationic alkene complexes of iron(II).[2] In the second reaction step complex **2a** (R = R′ = H in Figure 1), which contains a reactive terminal olefinic function, displaces the propene ligand from another molecule of **1a** to form the monocationic dinuclear complex **4a**, in which the allyl group is η^1-bound to one platinum atom and η^2-bound to the second platinum atom. In the third step **4a** undergoes further deprotonation of the bridging allyl moiety, converting the η^1:η^2-bridging allyl ligand into a η^1:η^3 form (compound **5a**). The last transformation requires the simultaneous loss of the anionic ligand (Cl^-) from one of the two platinum units and completes the reaction sequence.

Complex **2a** was not directly detected in the reaction mixture, but it was hypothesized as being a reactive intermediate in order to account for the formation of **4a**. The latter compound (together with free propene)

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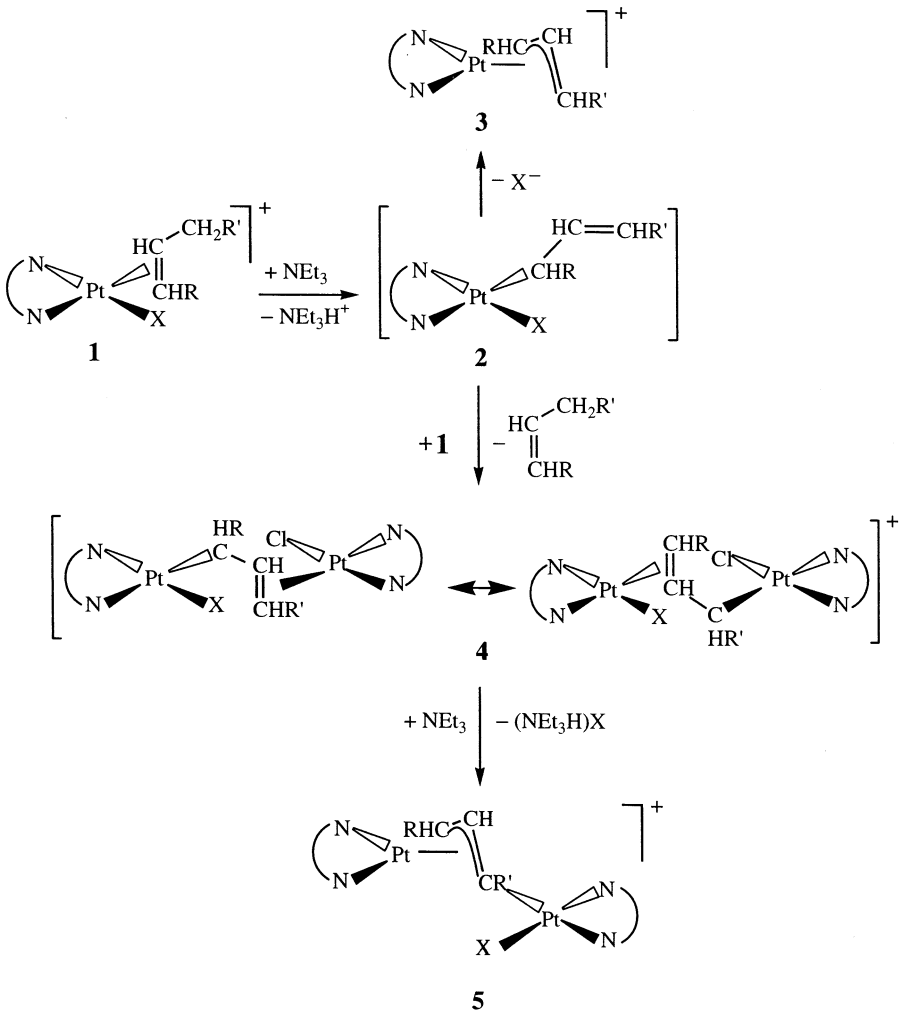

Figure 1. Reaction pathway for sequential deprotonation of platinum-bound olefins. For the olefin RHC=CHCH$_2$R′: R = R′ = H, **a**; R = H, R′ = Me, **b**; R = H, R′ = *n*-Pr, **c**; R = Me, R′ = H, **d**, **e**; X = Cl, **a**−**c**; X = NO_2, **d, e**.

could be clearly identified by ^{1}H NMR. It was sufficient to perform the reaction in the presence of a substoichiometric amount of triethylamine for preventing the further transformation of **4a** into **5a**. At ambient temperature the two metal units of **4a** are equivalent on the NMR time scale and the protons of the bridging allyl group exhibit an AX_4 pattern, in accord with rapid interchange of the η^1 and η^2 bonding modes.[21] Under the experimental conditions of a substoichiometric amount of triethylamine used to stabilize **4a**, a monomeric allyl complex [Pt(η^3-C_3H_5)(tmeda)]$^+$ (**3a**), which most likely is derived from **2a** by dissociation of the anionic ligand (Cl^-) and $\eta^1 \rightarrow \eta^3$ rearrangement of the allyl ligand, was also detected in solution. Compound **3a** shows the signals characteristic of a symmetrical η^3-C_3H_5 system and two NMe resonances for the tmeda ligand arising from inequivalence of the two methyls within each $-NMe_2$ unit (^{1}H NMR). When a moderate excess of NEt_3 (NEt_3/Pt = 3) was used, compound **5a** was formed in almost quantitative yield. **5a**, which contains an unusual μ-η^1:η^3-allyl group bridging two platinum atoms, was characterized by NMR (^{1}H, ^{195}Pt, ^{1}H/^{13}C (normal and long range), and ^{1}H/^{195}Pt correlation spectra) and X-ray analysis performed on its perchlorate salt.

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NMR Characterization of 5a. Long-range ^{1}H/^{13}C inverse HETCOR (Figure S1; Supporting Information) and ^{1}H/^{13}C inverse HETCOR (Figure S2; Supporting Information) spectra allowed unambiguous assignment of chemical shifts within each diamine moiety. Moreover, the ^{1}H/^{195}Pt inverse HETCOR spectra allowed unambiguous identification of signals belonging to each platinum subunit (Figure 2). The tmeda ligand of the platinum at lower field, Pt(1), had $^3J_{Pt,H}$ couplings of ca. 15 Hz for one pair of methyls (A′$_1$) and of ca. 40 Hz for the second pair of methyls (A″$_1$). In contrast, the tmeda ligand of the platinum at higher field, Pt(2), had a $^3J_{Pt,H}$ value in the range 30−40 Hz for all methyls and a remarkable diastereotopic splitting of one NMe_2 group (chemical shifts of 3.82 and 3.12 ppm).

We identify the low-field platinum, Pt(1), as the η^1-bound platinum having the two ends of tmeda trans to ligands of very different trans influence (η^1 carbon and chloro ligand, respectively), while the high-field platinum is identified as the Pt(2) subunit having the two coordinated nitrogen atoms trans to ligands of comparable trans influence and therefore exhibiting very similar $^3J_{Pt,H}$ couplings for the *N*-methyls. (As quoted above, one methyl of the latter subunit suffers a considerable deshielding effect; this is probably caused by the metal center of the second subunit, which comes close to it.) The ^{1}H/^{195}Pt inverse HETCOR spectra

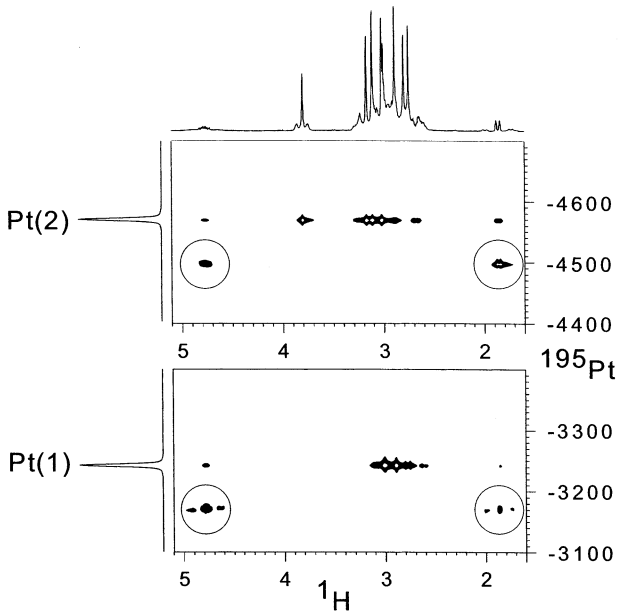

Figure 2. [^{1}H/^{195}Pt] HETCOR spectra ($CDCl_3$) of compound **5a** obtained in Pt(1) and Pt(2) excitation windows.

(Figure 2) also show how the central allylic proton has a larger coupling with Pt(2) than with Pt(1). Moreover, the observed field of the η^3-allyl platinum, Pt(2), is in agreement with observed trends in ^{195}Pt resonances.[22] The X-ray data of this compound will be discussed in detail at the end of this section.

Derivatives with Higher Olefins: 1-Butene and 1-Hexene. The cationic complexes containing the higher terminal olefins 1-butene (**1b**) and 1-hexene (**1c**), similarly to **1a**, undergo loss of an allylic proton by treatment with NEt_3 (at room temperature and in chlorinated solvents). Differently from the propene case, the η^1-allyl species (**2b**,**c**, respectively) could be detected in solution (^{1}H NMR) in the early stages of the reaction. Moreover, the reaction is stereoselective and leads exclusively to the formation of the *E* isomer (R′ and CH_2-Pt in trans positions with respect to the double bond; Figure 3), as can be deduced from the $^3J_{HH}$ coupling between vinyl protons (15 Hz), which is characteristic of protons in trans positions.

The stereoselectivity of this reaction step can be reasonably understood, according to Rosenblum's findings, as being a consequence of the greater reactivity of the conformer having the allylic proton anti to the metal−olefin bond.[2a] Possible conformers for complexes **1b**,**c** are shown in Figure 4. The interconversion among conformers must be rather hindered, as shown by the large dispersion of the allylic protons ($\Delta\delta$ = 0.47 and 0.41 ppm for **1b**,**c**, respectively). Of the three conformers only **A** is expected to be a reactive species, since **B** has no hydrogens anti to the metal−olefin bond and **C** is highly disfavored for steric reasons. Since **2** is generated by rotamer **A**, the double-bond formation between C(2) and C(3) sets the vinyl protons trans to each other. However, stereo random activation followed by rapid equilibration via 1,3-shifts in allyl bonding cannot be in principle ruled out.

The trans arrangement of the two vinyl protons is kept in the subsequent $\eta^1 \rightarrow \eta^3$ transformation leading to **3** (^{1}H NMR data). Therefore, the R′ substituent is found always syn to the central allyl hydrogen (Figure 3). The proton on the central carbon of the allyl ligand appears as a triplet of doublets with the $^3J_{HH}$ value within the triplet (11 Hz) greater than the $^3J_{HH}$ value within the doublets (6 Hz). The **2** → **3** transformation, which requires the loss of the chloro ligand, occurs smoothly and quantitatively under our experimental conditions.

Compounds **2b**,**c** do not give the series of reactions leading to formation of compounds **4** and **5** (see Figure 1). The reason is that **2b**,**c**, containing a nonterminal olefinic function (R′ = Me, Pr^n, respectively), are unable to displace the terminal olefin from a second molecule of **1** to form **4**. Therefore, since the evolution to **4** is precluded, the only alternative for **2b**,**c** is the $\eta^1 \rightarrow \eta^3$ rearrangement of the allyl moiety with release of the chloro ligand and formation of **3b**,**c**, respectively. The conversion of **2b**,**c** into the corresponding species **3b**,**c** is, therefore, quantitative.

In solution **3b**,**c** undergo a slow isomerization to the form having the R substituent anti with respect to the central allyl hydrogen. The ^{1}H NMR spectra are very diagnostic. In the newly formed isomer the doublet of triplets, belonging to the central allyl hydrogen, has a $^3J_{HH}$ value within the triplets (ca. 7 Hz) which is smaller than the $^3J_{HH}$ value within the doublet (ca. 12 Hz) (Figure 5). The syn/anti equilibration of allylic species is reported to be catalyzed by acids;[23] accordingly, a slower isomerization rate was observed in chloroform treated with sodium carbonate (traces of HCl can be present in chloroform, and they are removed by sodium carbonate). This type of isomerization is well-documented in platinum chemistry and takes place through a $\eta^3 \rightarrow \eta^1$:$\eta^2$ rearrangement with terminal allyl carbons exchanging their bonding mode (η^1 or η^2).[23] A 4/1 ratio, in favor of the syn form, is attained at equilibrium.

Derivatives with (*E*)- and (*Z*)-2-Butene. The cationic complexes containing (*E*)- and (*Z*)-2-butene (**1d**,**e**) react with triethylamine to give a mixture of essentially four different reaction products (two major and two minor species). The reaction products are the same for the two substrates. The four species have not been separated; however, they have been clearly identified by NMR spectroscopy (1D, 2D, and *J*-resolved ^{1}H spectra and ^{1}H/^{195}Pt inverse HETCOR). ^{1}H *J*-resolved spectra show the presence of two major (**A** and **B**) and two minor (**C** and **D**) species. In Figure 6 the four signals belonging to central allylic protons are shown. Two of them (**A** and **B**, one major and one minor component) have a rather complex coupling pattern (more than two major coupling constants) and can be identified as central allylic protons of monomeric η^3-allyl species coincident with the syn and anti forms of complex **3b** obtained starting from 1-butene and already described (Figure 3). The other two species (**C** and **D** in Figure 6,

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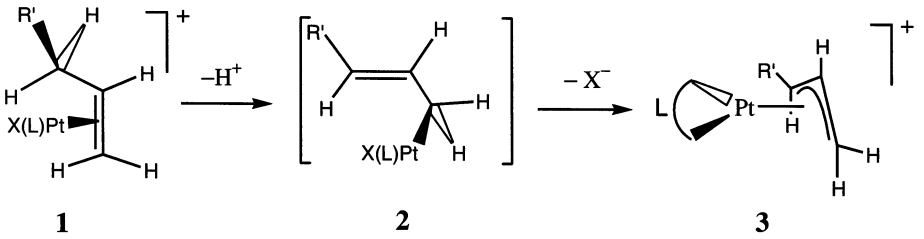

Figure 3. Stereoselective pathway showing how preferential dissociation of the allylic proton, in a position anti to the metal−olefin bond, leads to the exclusive formation of the η^3-allyl species with the R substituent syn to the central allylic proton (**3** syn).

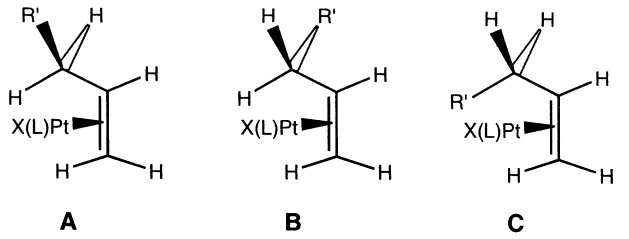

Figure 4. Different rotameric conformers for a platinum-coordinated terminal olefin (R′ = Me, *n*-Pr for **1b**,**c**, respectively).

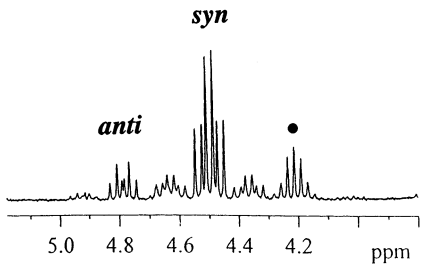

Figure 5. ^{1}H NMR spectrum ($CDCl_3$, region of allylic $C_{central}H$) of an equilibrated solution of syn and anti forms of $[Pt\{\eta^3\text{-}CH_2CHCH(CH_3)\}(tmeda)]^+$ (**3b**). Side multiplets are due to coupling with ^{195}Pt, and the high-field multiplet (●) belongs to a terminal allylic proton, $CH_2CHCH(CH_3)$, of the anti isomer.

again one major and one minor component) have the central allyl proton coupled with only two other protons (doublet of doublets). The two $^3J_{H-H}$ coupling constants are similar in the major component (10 and 12 Hz, respectively) and quite different in the minor species (7 and 12 Hz, respectively). These latter species correspond to dinuclear platinum complexes (**5d**,**e**), analogous to **5a** obtained in the case of propene, but having a methyl substituent on the bridging allyl ligand, which can be either syn or anti to the central allyl proton (Figure 7). NMR data indicated that the major form has the syn configuration and the minor form the anti configuration. The coupling of the central allyl proton with three other protons in species **A** and **B**, and with other two protons in species **C** and **D**, is clearly shown in the ^{1}H COSY spectrum reported in Figure S3 of Supporting Information. The methyl group on the bridging η^1:η^3-allyl moiety is always a doublet; therefore, **5d**,**e** species have the η^1-bound platinum and the methyl substituent on different carbons of the η^3-allyl ($^3J_{H-H}$ coupling for the methyl of 6 Hz).

In some preparative runs there was also evidence for a third species formed in very low concentration. Its proton resonances were nearly undetectable in the 1D ^{1}H NMR spectrum but were clearly observed as cross-peaks in the ^{1}H/^{195}Pt inverse HETCOR spectrum (Figure S4, Supporting Information). This species could be a variant of the **5d,e** syn form having the η^1-bound platinum anti to the central allylic proton.

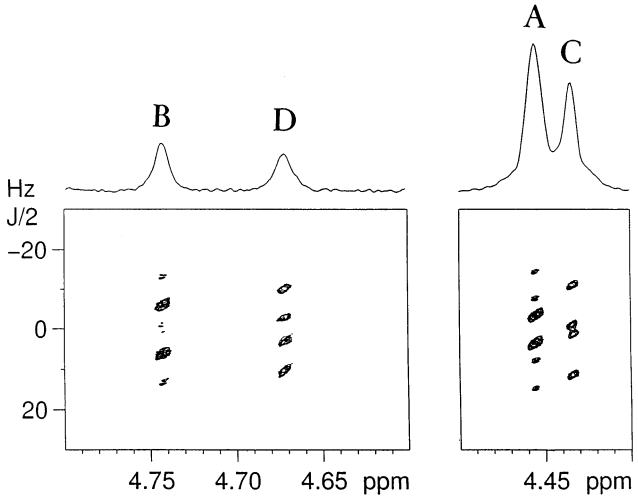

Figure 6. *J*-Resolved ^{1}H NMR spectrum ($CDCl_3$) showing the region for $C_{central}H$ of the allyl group for the compounds obtained in the deprotonation reaction of **1e** with NEt_3: (A) **3e** syn (coincident with **3b** syn); (B) **3e** anti (coincident with **3b** anti); (C) **5e** syn (major isomer); (D) **5e** anti (minor isomer).

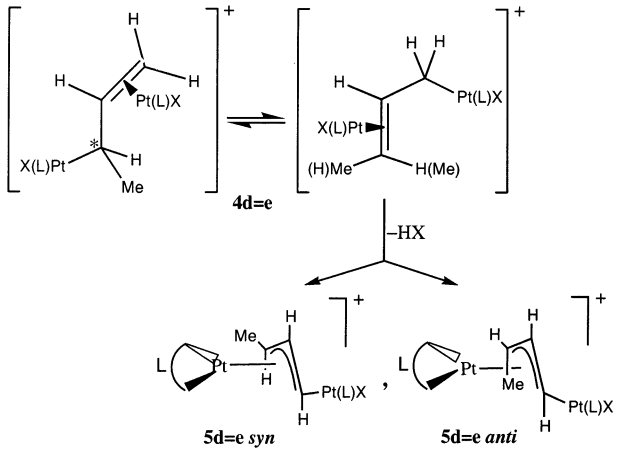

Figure 7. Formation pattern of different isomers of compounds **5d**,**e** after the deprotonation of the precursors, compounds **4d**,**e**.

The obtainment of identical products, starting with (*E*)- or (*Z*)-2-butene, can be explained by the fact that, once coordinated to a metal, the olefinic carbons of (*E*)- and (*Z*)-2-butene become asymmetric centers.[24] The two

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carbons have equal absolute configurations (either *R*,*R* or *S*,*S*) in the case of (*E*)-2-butene (**1d**) and opposite absolute configurations (*R*,*S*) in the case of (*Z*)-2-butene (**1e**).[25] The loss of an allylic proton leads to the formation of the same η^1-allyl complex [PtCl{η^1-C*H(CH_3)CH=CH_2}(tmeda)}] (**2d**,**e**) (the asymmetric carbon, labeled with an asterisk, can have either an *R* or an *S* configuration). The η^1-allyl complex can be detected in solution by ^{1}H NMR. The evolution of **2d**,**e** into the corresponding η^3-allyl complex generates a mixture of the syn and anti isomers coincident with those of **3b**. The syn and anti isomers are formed in a 4:1 molar ratio. Compounds **2d**,**e**, differently from **2b**, contain a terminal olefinic function; therefore, in addition to the $\eta^1 \rightarrow \eta^3$ allyl rearrangement, they can easily displace the olefin from a second molecule of **1d**,**e**, forming a dimeric species (**4d**,**e**) analogous to **4a** obtained in the case of propene. Compounds **4d**,**e** can be further deprotonated to give the η^1:η^3-allyl dimers **5d**,**e** analogous to **5a**. The **4d**,**e** species could not be detected by NMR; however, they are a necessary precursors for the formation of **5d**,**e**.

The reaction intermediate [Fe(η^5-cyclopentadienyl)-$(CO)_2$(η^1-CHMeCH=CH_2)]$^+$, analogous to **2d**,**e**, was obtained by Rosenblum through deprotonation of the (*Z*)-2-butene complex [Fe(η^5-cyclopentadienyl)$(CO)_2$((*Z*)-2-butene)]$^+$.[2c] However, the initially formed species rapidly isomerized into the corresponding butenyl complex [Fe(η^5-cyclopentadienyl)$(CO)_2$(η^1-CH_2CH=CHMe)], which was formed as a mixture of cis and trans isomers. The different evolution of the first formed η^1-allyl species in the platinum and iron cases is a consequence of the different stabilities of η^1- versus η^3-bonding modes of the allyl ligand for the two metals. η^3-Allyl complexes of iron(II) cannot be prepared by deprotonation of η^2-olefins (as shown for platinum in the present paper), but they can be prepared by different routes such as protonation of (diene)iron(0) complexes,[26] oxidative addition of allyl halides to iron carbonyls,[27] and reaction of highly nucleophilic iron anions with allylic substrates.[28]

X-ray Structure of 5a. Molecular structure and atomic numbering scheme are reported in Figure 8. Each platinum carries a tmeda chelate ligand, and the PtN_2 atoms have been used to define the coordination planes. Bond distances within the tmeda moiety bound to Pt(2) are very close to those found for [PtCl(η^2-ethene)(tmeda)]$^+$.[14b] In contrast, interatomic distances

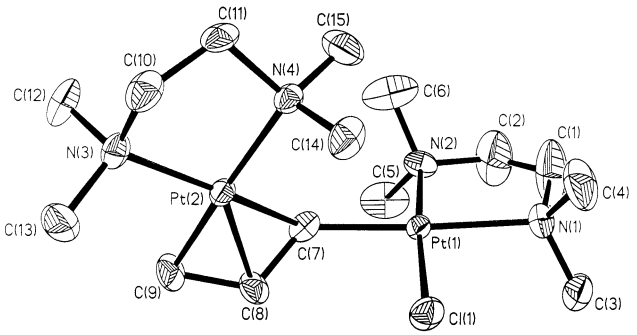

Figure 8. View of the molecular structure of the complex cation **5a** with the atomic numbering scheme. Ellipsoids include 40% probability.

within the tmeda ligand coordinated to Pt(1) are found to be shorter by ca. 0.09 Å; however, we do not believe that the observed differences have a real significance. The two five-membered Pt−tmeda rings have a "twisted-envelope" shape which is more pronounced in the case of Pt(2) than in the case of Pt(1) (C(1) and C(2) are displaced by only 0.12 Å above and below the Pt(1)N-(1)N(2) coordination plane, while C(10) and C(11) are displaced from the Pt(2)N(3)N(4) coordination plane by +0.30 and −0.40 Å, respectively).

The two platinum coordination planes are nearly perpendicular (dihedral angle between the two PtN_2 planes of 77.0°) in order to reduce steric interactions between the two subunits.

In the Pt(1) subunit the two Pt−N distances are significantly different (2.167(12) and 2.089(12) Å, respectively), reflecting the very different labilizing influences of the two trans ligands (η^1-carbon and chloro ligand, respectively). The Cl ligand is displaced from the Pt(1)N(1)N(2) plane by +0.15 Å, and the Pt(1)−Cl distance (2.308(4) Å) is that expected for a chlorine ligand trans to an amine ligand in a platinum(II) substrate.[29] The η^1-bonded carbon, C(7), which completes the coordination sphere, is very close to the Pt-(1)N(1)N(2) coordination plane (displacement of only −0.05 Å). The Pt(1)−C(7) distance is rather short (2.00-(1) Å), and its value is in the range of those observed for the platinum(IV) complex [$PtMe_2$(η^1-C_3H_5)(BPMA)]$^+$ (1.92 Å; BPMA = bis(2-pyridylmethyl)amine)[30] and for some η^1-allyl complexes of platinum(II) such as *trans*-[Pt(η^1-C_3H_5)Br(PEt_3)$_2$][31a] and *trans*-[Pt(η^1-C_3H_5)Cl(P-Ph_3)$_2$][31b] (2.086(7) and 2.090(4) Å, respectively).

In the Pt(2) subunit the two Pt−N distances are practically identical (2.139(12) and 2.145(12) Å), and their values are close to the longer distance observed in the Pt(1) subunit. The Pt(2)−C distances involving the η^3-allyl ligand (Pt(2)−C(7), Pt(2)−C(8), and Pt(2)−C(9)) are in the range of 2.07−2.24 Å. The Pt(2)−C(7) distance involving the carbon atom already engaged in the η^1-bond with Pt(1) is very long (2.24(1) Å) and gives an indication of the steric repulsion between the two platinum subunits. The Pt(2)−C(8) distance (2.15(2) Å)

(25) In the ^{1}H NMR spectrum (CD_2Cl_2, room temperature) of **1e**, only one methyl signal for the coordinated olefin was observed.[14c] In a regime of fast inversion of the coordinated tmeda ring (which renders the coordination plane a mirror plane) the presence of only one methyl resonance accounts either for fast rotation of the olefin or, if the rotation is blocked, for the overwhelming presence of one of the two possible rotamers. In **1e** the unique methyl signal splits only below 200 K when the inversion of the tmeda ligand becomes slow on the NMR time scale. The ^{1}H NMR spectrum (CD_2Cl_2, room temperature) of **1d** is complicated by the presence of an equilibrium between the η^2 form and a cyclization product, caused by intramolecular nucleophilic attack of one oxygen of coordinated NO_2 onto an olefinic carbon.[9c] In this case, however, the magnetic environments of the two methyl substituents are different in any possible situation of the coordinated olefin.

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is in the range of those observed for η^3-allyl and η^3-methylallyl platinum complexes,[32] while the Pt(2)−C(9) distance (2.07(2) Å) is rather short. The shortening of the Pt(2)−C(9) distance could be a consequence of the lengthening of the Pt(2)−C(7) distance. The allyl plane (C(7)C(8)C(9)) forms a dihedral angle of 60.6° with the Pt(2)N(3)N(4) plane. The terminal allylic carbons C(7) and C(9) are displaced from the Pt(2)N(3)N(4) plane by +0.39 and +0.12 Å, respectively, and the central carbon atom, C(8), is displaced from the same plane by −0.38 Å.

Conclusions

The reaction sequence described in this paper is unprecedented in platinum chemistry. The [PtCl(tmeda)]$^+$ fragment has proven to be very effective in conferring acidic character to allylic protons of coordinated alkenes of any type.

The ready dissociation of the metal-bound X^- anion (Cl^- or NO_2^-) is another peculiarity of this system, favoring the $\eta^1 \rightarrow \eta^3$ rearrangement of the η^1-allyl species. In other substrates a strong precipitating agent for the halide ion was required to warrant a complete shift in favor of the η^3-allyl species.[33]

Finally, the stereoselectivity in proton abstraction (Figure 3) and the slow isomerization of the kinetically favored isomer are important features, which can be further exploited for the regiospecific preparation of η^3-allyl species having syn configurations.

Experimental Section

Starting Complexes. Cationic complexes **1a**−**e** were prepared by exchange of the coordinated olefin in the parent ethene complex as described in ref 14c. **1b**,**c** are reported for the first time.

[PtCl(η^2-1-butene)(tmeda)](ClO$_4$) (1b). In a typical experiment 237 mg (0.5 mmol) of [PtCl(η^2-ethene)(tmeda)](ClO$_4$), treated with 1-butene as described in ref 14c, afforded after evaporation of the reaction solution 250 mg of **1b**; the yield, referenced to platinum, was quantitative. Anal. Calcd for $C_{10}H_{24}N_2Cl_2O_4Pt$: C, 23.91; H, 4.82; N, 5.58. Found: C, 24.09; H, 4.65; N, 5.64. NMR data in $CDCl_3$ (tmeda signals are given first) are as follows. ^{1}H NMR: δ(^{1}H) 2.70 (s, 3H, $^3J_{Pt-H}$ = 35 Hz), 2.95 (s, 3H), 3.01 (s, 3H), and 3.02 (s, 3H) CH_3N; 2.90 (d, 1H), 3.10 (d, 1H), and 3.32 (d, 2H, $^3J_{H-H}$ = 10 Hz), $-CH_2N$; 1.36 (t, 3H, $^3J_{H-H}$ = 7 Hz), CH_2=CHCH$_2$C*H*$_3$; 1.92 (m, 1H) and 2.33 (m, 1H), CH_2=CHC*H*$_2$CH$_3$; 4.58 (d, 1H, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 66 Hz) and 4.85 (d, 1H, $^3J_{H-H}$ = 16 Hz, $^2J_{Pt-H}$ = 41 Hz), C*H*$_2$=CHCH$_2$CH$_3$; 5.01 (m, 1H), CH_2=C*H*CH$_2$CH$_3$. ^{13}C NMR: δ(^{13}C) 50.3, 50.7, 51.9, and 52.5, *C*H$_3$N; 62.9 and 66.0, −*C*H$_2$N; 14.1, CH_2=CHCH$_2$*C*H$_3$; 28.3, *C*H$_2$=CH*C*H$_2$CH$_3$; 75.8, *C*H$_2$=CHCH$_2$CH$_3$; 110.5, CH_2=*C*HCH$_2$CH$_3$.

[PtCl(η^2-1-hexene)(tmeda)](ClO$_4$) (1c). In a typical experiment 237 mg (0.5 mmol) of [PtCl(η^2-ethene)(tmeda)](ClO$_4$), treated with 1-hexene as described in ref 14c, afforded after evaporation of the reaction solution 264 mg of **1c**; the yield, referenced to platinum, was quantitative. Anal. Calcd for $C_{12}H_{28}N_2Cl_2O_4Pt$: C, 27.18; H, 5.32; N, 5.28. Found: C, 27.15; H, 5.57; N, 5.29. NMR data in $CDCl_3$ (signals are given in the same order as for **1b**) are as follows. ^{1}H NMR: δ(^{1}H) 2.74 (s, 3H, $^3J_{Pt-H}$ = 34 Hz), 2.99 (s, 3H), and 3.05 (s, 6H), CH_3N; 2.88 (1H), 3.10 (1H), and 3.36 (d, 2H, $^3J_{H-H}$) = 10 Hz), $-CH_2N$; 0.97 (t, 3H, $^3J_{H-H}$ = 7 Hz), CH_2=CHCH$_2$CH$_2$CH$_2$C*H*$_3$; 1.47 (m, 2H), CH_2=CHCH$_2$CH$_2$C*H*$_2$CH$_3$; 1.63 (m, 1H) and 1.89 (m, 1H), CH_2=CHCH$_2$C*H*$_2$CH$_2$CH$_3$; 1.95 (m, 1H) and 2.42 (m, 1H), CH_2=CHC*H*$_2$CH$_2$CH$_2$CH$_3$; 4.63 (d, 1H, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 63 Hz) and 4.88 (d, 1H, $^3J_{H-H}$ = 15 Hz, $^2J_{Pt-H}$ = 55 Hz), C*H*$_2$=CHCH$_2$CH$_2$CH$_2$CH$_3$; 5.05 (m, 1H), CH_2=C*H*CH$_2$CH$_2$CH$_2$-CH$_3$. ^{13}C NMR: δ(^{13}C) 50.7, 51.1, 52.3, and 53.0, *C*H$_3$N; 63.3 and 67.4, −*C*H$_2$N; 14.2, CH_2=CHCH$_2$CH$_2$CH$_2$*C*H$_3$; 22.9, CH_2=CHCH$_2$CH$_2$*C*H$_2$CH$_3$; 32.1, CH_2=CHCH$_2$*C*H$_2$CH$_2$CH$_3$; 35.1, CH_2=CH*C*H$_2$CH$_2$CH$_2$CH$_3$; 76.5, *C*H$_2$=CHCH$_2$CH$_2$CH$_2$CH$_3$; 109.3, CH_2=*C*HCH$_2$CH$_2$CH$_2$ CH$_3$.

Deprotonation Reactions. [PtCl(η^2-propene)(tmeda)](ClO$_4$) (1a). In a typical experiment **1a** (244 mg, 0.5 mmol) was suspended in dichloromethane (8 mL) and triethylamine was added with stirring at room temperature (2.5 times the stoichiometric amount). The mixture was stirred for several hours, while dissolution of the solid residue was observed. The final colorless solution was extracted with small volumes of water (5 × 1 mL) to remove the triethylammonium salt; the mother solution was dried over anhydrous sodium sulfate and filtered and the solvent evaporated under vacuum. Trituration with diethyl ether of the sticky solid afforded 137 mg of a white compound, which was identified as [{PtCl(tmeda)}(μ-η^1:η^3-CHCHCH$_2$){Pt(tmeda)}](ClO$_4$)] (**5a**). The isolated yield, referenced to platinum, was 69%. Compound **5a** is partly soluble in water, and colorless crystals of **5a** were obtained by concentration of the aqueous extract. Anal. Calcd for $C_{15}H_{36}N_4Cl_2O_4Pt_2$: C, 22.59; H, 4.55; N, 7.02. Found: C, 22.45; H, 4.57; N, 6.99. NMR data in $CDCl_3$ (numbering of atoms as in Figure 8, listed data are grouped according to subunits in the order Pt(1), Pt(2), and μ-allyl) are as follows. ^{1}H NMR: δ(^{1}H) 2.76 (s, 3H) and 2.81 (s, 3H), CH_3N(1); 2.62 (m, 1H) and 2.89 (m, 1H), $-CH_2N$(1); 2.90 (s, 3H, $^3J_{Pt-H}$ = 41 Hz) and 3.02 (s, 3H, $^3J_{Pt-H}$ = 38 Hz), CH_3N(2); 2.99 (m, 2H), $-CH_2N$(2); 3.03 (s, 3H, $^3J_{Pt-H}$ = 41 Hz) and 3.18 (s, 3H, $^3J_{Pt-H}$ = 34 Hz), CH_3N-(3); 2.89 (m, 2H), $-CH_2N$(3); 3.12 (s, 3H, $^3J_{Pt-H}$ = 34 Hz) and 3.82 (s, 3H, $^3J_{Pt-H}$ = 32 Hz), CH_3N(4); 2.68 (m, 1H) and 3.26 (m, 1H), $-CH_2N$(4); 1.84 (dd, 1H, $^2J_{H-H}$ = 1.5 Hz, $^3J_{H-H}$ = 11 Hz, $^2J_{Pt-H}$ = 75 Hz) and 3.12 (dd, 1H, $^3J_{H-H}$ = 5 Hz), C(9)H; 3.12 (d, 1H, $^3J_{H-H}$ = 11 Hz), C(7)H; 4.75 (m, 1H, $^2J_{Pt-H}$ = 70 Hz), C(8)H. ^{13}C NMR: δ(^{13}C) 48.5 and 50.2, CH_3N(1); 61.1, $-CH_2N$(1); 52.0 and 53.6, CH_3N(2); 66.7, $-CH_2N$(2); 51.2 and 55.0, CH_3N(3); 63.4, $-CH_2N$(3); 52.8 and 55.5, CH_3N(4); 62.5, $-CH_2N$(4); 37.0 ($^1J_{Pt-C}$ = 300 Hz), C(9); 53.7 ($^1J_{Pt-C}$ = 1060 Hz), C(7); 111.1 ($^1J_{Pt-C}$ = 90 Hz), C(8). ^{195}Pt NMR: δ(^{195}Pt) −4557.3, Pt(2); −3231.1, Pt(1).

The same reaction was also monitored via NMR. **1a** (3−4 mg) was placed in an NMR tube and suspended in $CDCl_3$ (0.8 mL); NEt_3 (dissolved in the same solvent) was then added in the quantity required for a base/complex ratio of ca. 0.5. Apart from the set of signals reported above for **5a**, which are most intense at the end of the reaction, another set of signals, which reaches the maximum intensity after a few hours and then decreases to zero, was observed. The latter set had the following signals. ^{1}H NMR: δ(^{1}H) 2.85 (s, 6H) and 2.88 (s, 6H), CH_3N; 2.78 (m, 2H) and 3.00 (m, 2H), $-CH_2N$; 3.56 (d, 4H, $^3J_{H-H}$ = 10 Hz, $^2J_{Pt-H}$ = 85 Hz), C*H*$_2$CHC*H*$_2$; 6.45 (m, 1H), CH$_2$C*H*CH$_2$. This set of signals has been assigned to compound **4a**.

Using a substoichiometric amount of NEt_3 at the end of the reaction, in addition to the final product **5a** and to unreacted **1a**, also another species, [Pt(η^3-CH$_2$CHCH$_2$)(tmeda)]$^+$ (**3a**; see Results and Discussion) was detected in solution. Its signals were as follows. ^{1}H NMR: δ(^{1}H) 3.01 (s, 6H, $^3J_{Pt-H}$ = 37 Hz) and 3.26 (s, 6H, $^3J_{Pt-H}$ = 35 Hz), CH_3N; 3.07 (m, 2H) and 3.19 (m, 2H), $-CH_2N$; 2.42 (d, 2H, $^3J_{H-H}$ = 11.5 Hz, $^2J_{Pt-H}$ = 76 Hz) and 3.59 (d, 2H, $^3J_{H-H}$ = 8 Hz, $^2J_{Pt-H}$ = 24 Hz), C*H*$_2$-CHC*H*$_2$; 4.72 (m, 1H), CH$_2$C*H*CH$_2$. ^{13}C NMR: δ(^{13}C) 54.3, 54.7 *C*H$_3$N; 63.1, $-CH_2N$; 44.3, *C*H$_2$CHCH$_2$; 105.9, CH$_2$CHCH$_2$. For

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the methyl signals of the tmeda ligand the more shielded proton signal is associated with the less shielded carbon signal.

[PtCl(η^2-1-butene)(tmeda)](ClO$_4$) (1b). The reaction was carried out as in the case of **1a**; the final product was the monomeric complex [Pt{η^3-CH$_2$CHCH(CH$_3$)}(tmeda)](ClO$_4$) (**3b**). A 201 mg portion of **1b** (0.4 mmol) afforded 156 mg of the product; the yield, referenced to platinum, was 84%. Anal. Calcd for $C_{10}H_{23}N_2ClO_4Pt$: C, 25.78; H, 4.98; N, 6.01. Found: C, 25.43; H, 4.99; N, 6.02. NMR data in $CDCl_3$ of the initially formed syn isomer are as follows. ^{1}H NMR: $\delta(^1H)$ 2.84 (s, 3H), 3.05 (s, 3H), 3.19 (s, 3H), and 3.20 (s, 3H), CH$_3$N; 1.29 (s, 3H, $^3J_{H-H}$ = 6 Hz, $^3J_{Pt-H}$ = 28 Hz), CH$_2$CHCH(C*H*$_3$); 2.37 (dd, 1H, $^2J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 11.5 Hz, $^2J_{Pt-H}$ = 76 Hz) and 3.44 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^2J_{Pt-H}$ = 22 Hz), C*H*$_2$CHCH(CH$_3$); 2.91 (m, 1H), CH$_2$CHC*H*(CH$_3$); 4.46 (m, 1H, $^2J_{Pt-H}$ = 79 Hz), CH$_2$C*H*CH(CH$_3$). ^{13}C NMR: $\delta(^{13}C)$ 51−57, *C*H$_3$N; 62.8, −*C*H$_2$N; 17.5, CH$_2$CHCH(*C*H$_3$); 42.8 ($^1J_{Pt-C}$ = 252 Hz), *C*H$_2$CHCHMe; 55.9 ($^1J_{Pt-C}$ = 215 Hz), CH$_2$CH*C*H(CH$_3$); 106.5 ($^1J_{Pt-C}$ = 74 Hz), CH$_2$*C*HCH(CH$_3$). NMR signals of the anti isomer (only allyl group resonances are given) are as follows. ^{1}H NMR: $\delta(^1H)$ 1.03 (s, 3H, $^3J_{H-H}$ = 6 Hz, $^3J_{Pt-H}$ = 28 Hz), CH$_2$CHCH(C*H*$_3$); 2.48 (dd, 1H, $^2J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 11.5 Hz, $^2J_{Pt-H}$ = 76 Hz) and 3.51 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^2J_{Pt-H}$ = 22 Hz), C*H*$_2$CHCH(CH$_3$); 4.18 (m, 1H), CH$_2$CHC*H*(CH$_3$); 4.74 (m, 1H, $^2J_{Pt-H}$ = 79 Hz), CH$_2$C*H*CH(CH$_3$).

The reaction, performed with a substoichiometric amount of NEt$_3$ and monitored by NMR, showed a transient species which was identified as the η^1-allyl complex [PtCl{η^1-CH$_2$CH=CH(CH$_3$)}(tmeda)] (**2b**). ^{1}H NMR data in $CDCl_3$: $\delta(^1H)$ 1.45 (d, 3H, $^3J_{H-H}$ = 6 Hz), CH$_2$CH=CHC*H*$_3$; 2.37 (m, 2H), C*H*$_2$CH=CHCH$_3$; 5.36 (m, 1H, $^3J_{H-H}$ = 15 Hz), CH$_2$CH=C*H*CH$_3$; 5.62 (m, 1H), CH$_2$C*H*=CHCH$_3$.

[PtCl(η^2-1-hexene)(tmeda)](ClO$_4$) (1c). The reaction was carried out as in the previous case, the only difference being the much higher solubility of **1c** in the solvent used. The final product was the monomeric complex [Pt{η^3-CH$_2$CHCH(CH$_2$CH$_2$CH$_3$)}(tmeda)](ClO$_4$)] (**3c**). A 212 mg portion of **1b** (0.4 mmol) afforded 168 mg of the product; the yield, referenced to platinum, was 85%. Anal. Calcd for $C_{12}H_{27}N_2ClO_4Pt$: C, 29.18; H, 5.51; N, 5.67. Found: C, 29.13; H, 5.71; N, 5.80. NMR data in $CDCl_3$ for the initially formed syn isomer are as follows. ^{1}H NMR: $\delta(^1H)$ 2.83 (s, 3H, $^3J_{Pt-H}$ = 38 Hz), 2.98 (s, 3H), 3.18 (s, 3H, $^3J_{Pt-H}$ = 34 Hz), and 3.20 (s, 3H, $^3J_{Pt-H}$ = 35 Hz), CH$_3$N; 3.20 (m, 2H) and 3.00 (m, 2H), −CH$_2$N; 0.96 (t, 3H, $^3J_{H-H}$ = 7 Hz), CH$_2$CHCH(CH$_2$CH$_2$C*H*$_3$); 1.46 (m, 1H) and 1.70 (m, 1H), CH$_2$CHCH(C*H*$_2$CH$_2$CH$_3$); 1.54 (m, 1H) and 1.64 (m, 1H), CH$_2$CHCH(CH$_2$C*H*$_2$CH$_3$); 2.38 (dd, 1H, $^2J_{H-H}$ = 2.0 Hz, $^3J_{H-H}$ = 11.5 Hz, $^2J_{Pt-H}$ = 76 Hz) and 3.46 (dd, 1H, $^3J_{H-H}$ = 7 Hz, $^2J_{Pt-H}$ = 22 Hz), C*H*$_2$CHCH(CH$_2$CH$_2$CH$_3$); 2.91 (m, 1H), CH$_2$CHC*H*(CH$_2$CH$_2$CH$_3$); 4.56 (m, 1H, $^2J_{Pt-H}$ = 79 Hz), CH$_2$C*H*CH(CH$_2$CH$_2$CH$_3$). ^{13}C NMR: $\delta(^{13}C)$ 51.1, 52.7, 53.2, and 54.1, *C*H$_3$N; 62.0 and 63.3, −*C*H$_2$N; 13.7, CH$_2$CHCH(CH$_2$CH$_2$*C*H$_3$); 23.9, CH$_2$CHCH(CH$_2$*C*H$_2$CH$_3$); 34.2, CH$_2$CHCH(*C*H$_2$CH$_2$CH$_3$); 43.1, $^1J_{Pt-C}$ = 249 Hz, *C*H$_2$CHCH(CH$_2$CH$_2$CH$_3$); 61.1 ($^1J_{Pt-C}$ = 210 Hz), CH$_2$CH*C*H(CH$_2$CH$_2$CH$_3$); 105.7 ($^1J_{Pt-C}$ = 74 Hz), CH$_2$*C*HCH(CH$_2$CH$_2$CH$_3$).

Using a substoichiometric amount of NEt$_3$ and monitoring the reaction by NMR, a transient species, identified as the η^1-allyl complex [PtCl(η^1-CH$_2$CH=CHCH$_2$CH$_2$CH$_3$)(tmeda)] (**2c**), was detected.. ^{1}H NMR signals in $CDCl_3$ are as follows: $\delta(^1H)$ 0.90 (t, 3H, $^3J_{H-H}$ = 7 Hz), CH$_2$CH=CHCH$_2$CH$_2$C*H*$_3$; 1.31 (m, 2H), CH$_2$CH=CHCH$_2$C*H*$_2$CH$_3$; 1.80 (m, 2H), CH$_2$CH=CHC*H*$_2$CH$_2$CH$_3$; 2.40 (m, 2H), C*H*$_2$CH=CHCH$_2$CH$_2$CH$_3$; 5.34 (m, 1H, $^3J_{H-H}$ = 15 Hz), CH$_2$CH=C*H*CH$_2$CH$_2$CH$_3$; 5.59 (m, 1H), CH$_2$C*H*=CHCH$_2$CH$_2$CH$_3$.

[Pt(NO$_2$)(η^2-(*E*)-2-butene)(tmeda)](ClO$_4$) (1d) and [Pt(NO$_2$)(η^2-(*Z*)-2-butene)(tmeda)](ClO$_4$) (1e). The deprotonation reaction was carried out as previously described for the propene complex **1a** and led to the same products, starting from either **1d** or **1e**. In this system, however, the addition of triethylamine did not cause the complete disappearance of the solid phase. After several hours of mixing, the reaction mixture was filtered and the solution was treated as in the case of **1a** to afford a mixture of **3d**,**e** (coincident with **3b**) and **5d**,**e**. The yield, referenced to platinum, did not exceed 50%. The solid residue proved to be [Pt(NO$_2$)$_2$(tmeda)] (IR spectrum coincident with that of an authentic sample of [Pt(NO$_2$)$_2$(tmeda)]) originating from the reaction of the parent cationic species with NO_2^- released during the reaction course. The NMR spectrum of isolated **5d**,**e** is complicated by the presence of several isomers; therefore listed data are limited to unambiguously assigned resonances. NMR data for the major isomer are as follows. ^{1}H NMR: $\delta(^1H)$ 2.73 (s, 3H), 2.85 (s, 3H), 3.24 (s, 3H), and 3.63 (s, 3H), CH$_3$N; 1.06 (d, 3H, $^3J_{H-H}$ = 6 Hz), −CHCH-CH(C*H*$_3$); 2.34 (m, 1H), −CHCHC*H*(CH$_3$); 2.88 (m, 1H), −C*H*CHCH(CH$_3$); 4.44 (m, 1H, $^3J_{H-H}$ = 10 and 12 Hz, $^2J_{Pt-H}$ = 79 Hz), −CHC*H*CH(CH$_3$). ^{195}Pt NMR: $\delta(^{195}Pt)$ −4650, Pt(2); −3110, Pt(1). NMR data for the minor isomer are as follows. ^{1}H NMR: $\delta(^1H)$ 2.92 (s, 3H), 3.12 (s, 3H), 3.27 (s, 3H), and 3.58 (s, 3H), CH$_3$N; 0.85 (d, 3H, $^3J_{H-H}$ = 6 Hz), −CHCH-CH(C*H*$_3$); 3.00 (m, 1H), −C*H*CHCH(CH$_3$); 3.67 (m, 1H), −CHCHC*H*(CH$_3$); 4.67 (m, 1H, $^3J_{H-H}$ = 7 and 12 Hz), CH$_2$C*H*CH(CH$_3$). ^{195}Pt NMR: $\delta(^{195}Pt)$ −4550, Pt(2); −3110, Pt(1). NMR data for the third form are as follows. ^{1}H NMR: $\delta(^1H)$ 2.72 (s, 3H), 2.89 (s, 3H), 2.98 (s, 3H), and 3.67 (s, 3H), CH$_3$N. ^{195}Pt NMR: $\delta(^{195}Pt)$ −4400, Pt(2); −3050, Pt(1).

Using a substoichiometric amount of NEt$_3$ and monitoring the reaction by NMR, a transient species, identified as the η^1-allyl complex [PtCl{η^1-C*H(CH$_3$)CH=CH$_2$}(tmeda)}] (**2d**,**e**), was detected also in this case. NMR data in $CDCl_3$ of **2d**,**e** are as follows. ^{1}H NMR: $\delta(^1H)$ 1.00 (d, 3H, $^3J_{H-H}$ = 7 Hz), −CH(C*H*$_3$)CH=CH$_2$; 2.13 (m, 1H), −C*H*(CH$_3$)CH=CH$_2$; 4.76 (dd, 1H, $^2J_{H-H}$ = 2 Hz, $^3J_{H-H}$ = 11 Hz) and 4.88 (dd, 1H, $^3J_{H-H}$ = 17 Hz), −CH(CH$_3$)CH=C*H*$_2$; 6.14 (m, 1H), −CH(CH$_3$)-C*H*=CH$_2$.

NMR Spectroscopy. ^{1}H, ^{13}C, and ^{195}Pt NMR spectra were recorded on DRX500 Avance and DPX300 Avance Bruker instruments equipped with probes for inverse detection and with *z* gradient for gradient-accelerated spectroscopy. ^{1}H and ^{13}C spectra were referenced to TMS; the residual proton signal of the solvent was used as an internal standard. ^{195}Pt NMR spectra were referenced to H_2PtCl_6 used as an external standard.

Standard Bruker automation programs and pulse sequences were used for 2D NMR experiments: ^{1}H 2D *J*-resolved spectroscopy (JRES), ^{1}H 2D gradient-accelerated correlation spectroscopy (COSYGS), ^{1}H/^{13}C inversely detected gradient-sensitivity enhanced heterocorrelated 2D NMR for normal (INVIEAGSSI) and long-range (INV4GPLRND) coupling, and ^{1}H/^{195}Pt inversely detected gradient-sensitivity enhanced heterocorrelated 2D NMR (INVIETGPSI).

X-ray Crystallography. Crystal data for $C_{15}H_{36}Cl_2N_4O_4Pt_2$ (**5a**): M_r = 797.6, monoclinic, space group $P2_1/c$ (No. 14), a = 13.030(5) Å, b = 13.885(6) Å, c = 13.567(6) Å, β = 101.09(3)°, U = 2409(2) Å^3, $F(000)$ = 1504, μ(Mo Kα) = 118.5 cm^{-1}, Z = 4, D_c = 2.199 g cm^{-3}. Data were collected using a cuboid crystal of dimension 0.2 mm on a Siemens-Nicolet *R*3m/*V* four-circle diffractometer, using graphite-crystal-monochromated Mo Kα radiation (λ = 0.71073 Å). A total of 4206 reflections ($2\theta_{max}$ = 50.2°) were collected, of which 4022 were unique (R_{int} = 0.040 based on F^2). An empirical absorption correction was applied using ψ-scans (minimum and maximum transmission factors 0.712 and 0.874, respectively).

The structure was solved by Patterson methods and refined on F^2 using the SHELXTL[34] suite of programs. All non-hydrogen atoms were refined with anisotropic displacement coefficients, apart from the oxygen atoms of the ClO_4^- group. Hydrogen atoms were treated as idealized contributions. The

(34) Sheldrick, G. M.; SHELXTL-NT V.5.1; Bruker AXS Inc., Madison WI, 1997.

Table 1. Relevant Bond Lengths (Å) and Angles (deg) for [{PtX(tmeda)}{Pt(tmeda)}(μ,η^1:η^3-CHCHCHR)]$^+$ (5a)

Pt(1)-Cl(1)	2.308(4)	Pt(2)−N(3)	2.14(1)
Pt(1)−N(1)	2.17(1)	Pt(2)−N(4)	2.14(1)
Pt(1)−N(2)	2.09(1)	Pt(2)−C(7)	2.24(1)
Pt(1)−C(7)	2.00(1)	Pt(2)−C(8)	2.15(2)
		Pt(2)−C(9)	2.07(2)
Cl(1)−Pt(1)−N(1)	91.3(4)	N(3)−Pt(2)−N(4)	83.0(4)
Cl(1)−Pt(1)−N(2)	174.4(4)	N(3)−Pt(2)−C(7)	167.1(5)
Cl(1)−Pt(1)−C(7)	92.3(4)	N(3)−Pt(2)−C(8)	138.8(5)
N(1)−Pt(1)−N(2)	84.5(5)	N(3)−Pt(2)−C(9)	101.4(6)
N(1)−Pt(1)−C(7)	176.2(5)	N(4)−Pt(2)−C(7)	104.9(5)
N(2)−Pt(1)−C(7)	91.9(5)	N(4)−Pt(2)−C(8)	136.2(5)
C(7)−C(8)−C(9)	119(2)	N(4)−Pt(2)−C(9)	174.5(6)
		Pt(1)−C(7)−Pt(2)	124.8(6)

final R values were R1 = 0.053, wR2 = 0.142, and GOF (goodness of fit) = 1.022 for the 3818 observed ($I \geq 2\sigma(I)$) reflections. Most likely the unresolved disorder at ClO_4^- is responsible for the somewhat high R values. Selected bond distances and angles are listed in Table 1.

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Supporting Information Available: Figures giving the long range [^{1}H/^{13}C] HETCOR spectrum ($CDCl_3$) of **5a** (Figure S1), the [^{1}H/^{13}C] HETCOR spectrum ($CDCl_3$) of compound **5a** (Figure S2), the ^{1}H NMR COSY spectrum ($CDCl_3$) showing cross-peaks related to couplings of $C_{central}H$ with $C_{terminal}H$'s of the allyl group for the compounds obtained in the deprotonation reaction of **1e** with NEt_3 (Figure S3), and [^{1}H/^{195}Pt] HETCOR spectra for the compounds formed in the deprotonation reaction of **1e** with NEt_3 (Figure S4). This material is available free of charge via the Internet at http://pubs.acs.org.

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