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C−H Activation in Phosphonium Salts Promoted by Platinum(II) Complexes

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The reaction of $PtCl_2(NCPh)_2$ with the bis-phosphonium salts $\{[R_2PhPCH_2]_2C(O)\}Cl_2$ (R_2 = Ph_2, PhEt, Et_2) (1:1 molar ratio) in refluxing 2-methoxyethanol affords the C,C-orthometalated complexes $[PtCl_2(\mathit{C}_6H_4\text{-}2\text{-}PR_2\mathit{C}(H)C(O)CH_2PPhR_2)]$ (R_2 = Ph_2 **1a**, PhEt **1b**, Et_2 **1c**). The reaction of $PtCl_2$ with the bis-phosphonium salt $\{[Ph_3PCH_2]_2C(O)\}Cl_2$ (1:1 molar ratio) gives $\{[Ph_3PCH_2]_2C(O)\}[PtCl_4]$, **2**, while treatment of $PtCl_2$ with the perchlorate salts $\{[R_2PhPCH_2]_2C(O)\}(ClO_4)_2$ (1:1 molar ratio) results in the formation of the cationic dinuclear orthometalated derivatives $[Pt(\mu\text{-}Cl)(\mathit{C}_6H_4\text{-}2\text{-}PR_2\mathit{C}(H)C(O)CH_2PPhR_2)]_2(ClO_4)_2$ (R_2 = Ph_2 **3a**, PhEt **3b**, Et_2 **3c**). The cycloplatination of the bis-phosphonium salts to give the C,C-orthometalated derivatives implies two C−H bond activation processes at two types of carbon atoms, one arylic and one alkylic. The reaction of $PtCl_2(NCPh)_2$ or $PtCl_2$ with the allyl-phosphonium salts $[PhR_2PCH_2CH{=}CH_2]Cl$ (R_2 = Ph_2, Me_2) or $[Ph_3PCH_2CH{=}CHMe]Cl$ (1:1 molar ratio) in refluxing 2-methoxyethanol gives the orthometalated vinyl-phosphonium derivatives $[PtCl_2(\mathit{C}_6H_4\text{-}2\text{-}PR_2\text{-}\eta^2\text{-}\mathit{E}\text{-}\mathit{C}(H){=}\mathit{C}(H)CH_3)]$ (R_2 = Ph_2 **4a**, Me_2 **4b**) or $[PtCl_2(\mathit{C}_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}\mathit{E}\text{-}\mathit{C}(H){=}\mathit{C}(H)CH_2CH_3)]$, **7**, respectively, while the reaction of $PtCl_2$ with $[Ph_3PCH_2\text{-}CH{=}CH_2]ClO_4$ (1:1 molar ratio) gives the η^2-olefin-bonded derivative $[Cl_3Pt(\eta^2\text{-}\mathit{C}H_2{=}\mathit{C}H{-}CH_2PPh_3)]$, **5**. The reaction of $[Ph_3PCH_2CH{=}CHPh]Cl$ with $PtCl_2$ (1:1 molar ratio, 2-methoxyethanol, reflux) gives an easily separable mixture of products: the η^2-olefin-bonded $[Cl_3Pt(\eta^2\text{-}\mathit{C}HPh{=}\mathit{C}H{-}CH_2PPh_3)]$, **8**, and the orthometalated $[PtCl_2(\mathit{C}_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}\mathit{E}\text{-}\mathit{C}(H){=}\mathit{C}(H)CH_2Ph)]$, **9**, while the reaction of $[Ph_3PCH_2CMe{=}CH_2]Cl$ with $PtCl_2$ (1:1 molar ratio) gives a mixture of the cycloplatinated $[PtCl_2(\mathit{C}_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}\mathit{C}(H){=}\mathit{C}Me_2)]$, **10**, and the isomerized vinyl-phosphonium salt $[Ph_3P{-}C(H){=}CMe_2]Cl$, **11**. The synthesis of complexes **4**, **7**, **9**, and **10** implies the activation of one C(aryl)−H bond (instead of the more active methylene group adjacent to the phosphonium unit $P{-}CH_2$) and the rearrangement of the allyl group into a vinyl group by 1,3-prototropic shift, this shift being produced in the absence of external base. The complexes **4a**·CH_2Cl_2 and **8** have been characterized by X-ray diffraction methods.

Introduction

The activation of C−H bonds induced by transition metals is, at present, one of the most active fields of research in organometallic chemistry, due to its implications in several fundamental steps in catalytic cycles, in the functionalization of simple substrates, and in other important chemical processes.[1] Pt^{II} complexes have been employed frequently to promote C−H bond activation,[2] and interest in this class of reaction is growing continuously (as evidenced by the number of contributions from this field appearing in the literature[3]), because of its practical importance.[4] We recently reported the intramolecular rearrangement of the C,C-chelating bis-ylide ligand $[\mathit{C}(H)PPh_3]_2CO$ to the C,C-orthometalated ligand $[(\mathit{C}_6H_4\text{-}2\text{-}PPh_2\mathit{C}(H)COCH_2PPh_3)]$,[5a] using Pd^{II} complexes, as well as the synthesis of Pt^{II} complexes with the orthometalated group $[(\mathit{C}_6H_4\text{-}2\text{-}PPh_2\mathit{C}(H)COCH_2PPh_3)]$ through cycloplatination of the phosphonium-ylide $[Ph_3P{=}C(H)C(O)CH_2PPh_3]ClO_4$.[5b] The orthometalation of ylide ligands is a known reaction, not only for the platinum group metals[6] but also in early transition metals such as Nb.[7]

As part of our ongoing work on systems derived from ylide groups,[8] we have explored the reactivity of some simple compounds of Pt^{II}, such as $PtCl_2$ itself or $PtCl_2(NCR)_2$ (R = Me, Ph), toward stabilized bis-phosphonium salts $[R_2PhPCH_2C(O)CH_2PPhR_2](X)_2$ (R = Et, Ph;

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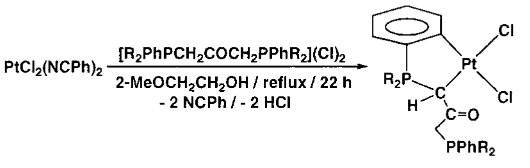
$X = Cl, ClO_4$)[9a−c] and also toward several allyl-phosphonium salts $[PhR_2PCH_2{-}C(R'){=}C(H)(R'')]X$ (R = Me, Ph; R′ = H, Me; R″ = H, Me, Ph; X = Cl, ClO_4).[9d,e] In the case of the bis-phosphonium salts, we have found that the reaction occurs through two C−H bond activations—the transformation of one phosphonium unit into an ylide group and an unexpectedly easy cycloplatination reaction—which result in the preparation of complexes containing the C,C-orthometalated ligand $[C_6H_4\text{-}2\text{-}PR_2C(H)COCH_2PPhR_2]$. However, in the case of the allyl-phosphonium salts, we have found two different behaviors: (i) simple η^2-coordination of the olefin moiety of the allyl group to the Pt^{II} center, or (ii) orthometalation through C(aryl)−H bond activation *and* isomerization of the allyl group into a vinyl group, resulting in complexes containing the cycloplatinated ligand $[C_6H_4\text{-}2\text{-}PR_2C(H){=}C(R')\text{-}CH_2R'']$, σ-bonded to the Pt^{II} center through one aryl carbon atom and π-bonded through the vinylic C=C double bond.

Results

1. Reactivity of Pt^{II} Complexes toward α-Stabilized Bis-phosphonium Salts. The treatment of $PtCl_2(NCPh)_2$ with $[R_2PhPCH_2C(O)CH_2PPhR_2](Cl)_2$ (R = Et and/or Ph) (1:1 molar ratio, 2-methoxyethanol, reflux, 22 h) results in the formation of the C,C-orthometalated derivatives $[PtCl_2(C_6H_4\text{-}2\text{-}PR_2C(H)COCH_2PPhR_2)]$ (R_2 = Ph_2 **1a**; PhEt **1b**; Et_2 **1c**), characterized by elemental analysis and mass spectroscopy (see eq 1 and Experimental Section). The IR spectra of **1a**−**c** show the carbonyl absorption in the range 1641−1647 cm^{-1}, in the same region as that reported for the Pd^{II} homologue $[PdCl_2(C_6H_4\text{-}2\text{-}PR_2C(H)COCH_2PPhR_2)]$ (1636 cm^{-1}).[5a] The ^1H NMR spectra of **1a** and **1c** show a single set of resonances, in accord with the presence of only one isomer. The methine proton [Pt]-C(H)P appears in the range 4.0−4.5 ppm as a doublet of doublets, through coupling with two P nuclei, and shows ^{195}Pt satellites. The value of the coupling constant $^2J_{Pt-H}$ is about 114−119 Hz, typical for C-bonded ylides.[6f] The presence of the CH_2PPhR_2 unit can also be inferred from the ^1H spectra, since these protons appear as the AB part of an ABX spin sytem (X = ^{31}P). The $^{31}P\{^1H\}$ NMR spectra of **1a** and **1c** show, as expected, two doublets corresponding to the two inequivalent P atoms. The presence of the orthometalated aryl group can be clearly seen from the $^{13}C\{^1H\}$ NMR spectrum of **1a**, since there appears a resonance at 145.96 ppm, typical for orthometalated carbon atoms[5a] and attributed to C_1.



(1)

R_2 = Ph_2 **1a**; PhEt **1b**; Et_2 **1c**

Each of the complexes **1a** and **1c** possesses only one chiral center (the ylidic carbon) and is presumably obtained as the racemic mixture of the two enantiomers (R_C and S_C). The situation found in complex **1b** is somewhat complicated since two chiral centers are present, the P atom in the orthometalated ring and the ylide carbon, leading to two possible diastereoisomers. In fact, two fractions have been obtained in the synthesis of **1b**, the first one insoluble in the alcoholic reaction medium and the second one soluble and precipitated with Et_2O. The spectroscopic characterization of the first fraction (see Experimental Section) shows that it consists of a single product (**1b**α), while the second fraction is a mixture of the two possible diastereoisomers (**1b**α/**1b**β) in 1:4 molar ratio, thus permitting their separate characterization. Each diastereoisomer will be the racemic mixture of the two enantiomers (R_PR_C/S_PS_C or R_PS_C/S_PR_C), since the reaction was performed in the absence of chiral sources, and we would not expect any enantioselective induction. To ascertain the relative configurations of the neighboring chiral P and C atoms of the orthometalated ring, we have measured the $^1H-{}^1H$ NOESY spectra of **1b**α and that of the mixture (**1b**α/**1b**β). For compound **1b**α, the NOESY spectrum does not show NOE interactions between the ylidic proton Pt−C(*H*) and the CH_2 protons of the ethyl group bonded to the P atom. However, in the case of the mixture (**1b**α/**1b**β) there is a clear NOE interaction between the resonance at 4.25 ppm, attributed to the ylidic proton of complex **1b**β, and the resonances at 3.30 and 3.08

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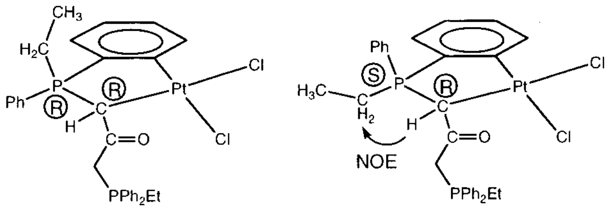


Complex 1bα
Figure 1a

Complex 1bβ
Figure 1b

Figure 1. Structures of complexes **1bα** and **1b**β.

ppm, attributed to a methylene group in the same complex. It is very likely that this NOE interaction is due to the relative proximity of the ylide proton and the ethyl group bonded to the P atom in the ring (see Figure 1), since the other ethyl group (resonances at 2.99 and 2.85) is found in a position more distant from the ylidic proton. A plausible arrangement, such as that depicted in Figure 1b, in which the ylidic proton and the ethyl group are in equatorial positions could explain the observed interactions, since any other arrangement would leave these groups farther apart. Moreover, it is sensible to assume that the bulky group $-C(O)CH_2PPh_2Et$ on the ylidic carbon would adopt an axial position in order to minimize steric repulsions with other groups present in the molecule. This has already been observed in the cyclopalladated complex $[Pd(C_6H_4\text{-}2\text{-}PPh_2{-}C(H){-}C(O){-}CH_2PPh_3)(PPh_3)(NCMe)]ClO_4$.[5a] This arrangement results in absolute configurations (S_PR_C/R_PS_C) for isomer **1b**β (Figure 1b) and hence (R_PR_C/S_PS_C) for isomer **1bα** (Figure 1a).

The synthesis of **1a**$-$**c** starting from the bis-phosphonium salts is noteworthy from several different points of view. Two C$-$H bond activations have occurred, one in the "activated" $-C(=O){-}C(sp^3)H_2$ group and the other one in the $C(aryl\text{-}sp^2){-}H$ moiety. Formally, two dehydrohalogenations have occurred but involving two different types of C$-$H bonds since, instead of a second C$-$H activation in the remaining "activated" methylene adjacent to the carbonyl group, reaction occurs at an arylic C$-$H bond. Probably the different size of the resulting metallacycles—four versus five links—could account for this behavior, obtaining the more thermodynamically stable five-membered ring. Moreover, in a recent communication,[5b] we have reported difficulties in obtaining Pt^{II} complexes with the bis-ylide C,C-coordinated $[L_nPt\{C(H)PPh_3\}_2CO]^{0,n+}$, analogous to those reported for Pd^{II}.[5a,8]

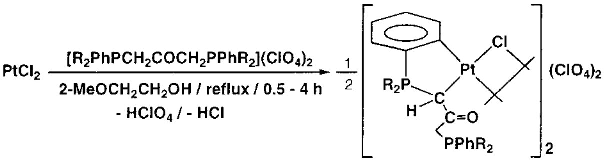
Moreover, as far as we know, there is only one precedent reported in the literature for this rare double C$-$H bond activation in phosphonium salts,[6d] and very few examples of any double C$-$H bond activation promoted by the same metal have been reported.[3b] Another interesting fact is that the orthometalation of the bis-phosphonium salts $[R_2PhPCH_2C(O)CH_2PPhR_2](Cl)_2$ occurs without the assistance of an external base, while the orthometalation of $[To_3PCH_2(py\text{-}2)]Cl$[6d] (To = *ortho*-tolyl, 2-Me-C_6H_4) occurs only in the presence of Proton Sponge [1,8-bis(dimethylamino)naphthalene] or Na_2CO_3. Moreover, it seemed to have been established that the species containing the C$-$H bond to be activated should be coordinated to the metal center prior to the activation step itself. In the present case, only the carbonyl oxygen is available to act as a ligating agent, displacing one NCPh ligand.

To shed light on all of these questions, we have performed a control experiment by refluxing the bis-phosphonium salt $\{[Ph_3PCH_2]_2CO\}Cl_2$ in 2-methoxyethanol for 22 h. At the end of the reaction and after evaporation of the solvent, a very small (but detectable) amount of the ylide-phosphonium salt $[Ph_3P{=}C(H){-}COCH_2PPh_3]Cl$, probably formed as a result of a spontaneous loss of HCl, was found in the NMR of the residue. Thus, it seems plausible that this ylide-phosphonium salt $[Ph_3P{=}C(H)COCH_2PPh_3]Cl$, formed during the reaction, could interact with the Pt^{II} center by displacement of one NCPh group and C-coordination. The subsequent orthometalation of the C-bonded ylide should not differ from those described for other thermal C$-$H bond activations of ylides promoted by metal complexes.[6] A similar mechanism (formation of the ylide, C-coordination, and C$-$H activation) was proposed for the orthometalation of $[To_3PCH_2(py\text{-}2)]Cl$,[6d] except that in that case the formation of the ylide was accomplished by an external base. Another interesting observation on the synthesis of **1a**$-$**c** is that the three complexes can be obtained in satisfactory yields, showing that the orthometalation proceeds regardless of the number of alkyl groups attached to the P atom (0, 1, or 2). These results contrast with those reported by us[5a] for the cyclopalladation of the bis-ylide complexes $\{Pd(\mu\text{-}Cl)[C(H)PPhR_2]_2CO\}_2(ClO_4)_2$, in which a decrease of the cone angle of the phosphine $PPhR_2$ promoted a dramatic decrease in the conversion to the metalated derivative. In this context, the differences between the Pd^{II} and Pt^{II} complexes are clear. In the case of Pd^{II} complexes, the C,C-coordinated bonding mode of the bis-ylide (obtained by deprotonation of the bis-phosphonium salt with acetate as external base) is stable, and this bonding mode is still unknown in Pt^{II} derivatives. Further heating of the Pd(bis-ylide) complexes results in the formation of the orthometalated derivatives (although not in all cases) by intramolecular rearrangement. In the case of Pt^{II} orthometalated complexes, the synthesis is accomplished in all cases in a single step without addition of external base. Thus, the method reported here expands the synthetic accessibility of orthometalated compounds.

The role of the ancillary ligands in the platinum starting material is significant. Thus, the reaction of $PtCl_2$ with $\{[Ph_3PCH_2]_2CO\}Cl_2$ (1:1 molar ratio, 2-methoxyethanol, reflux) results in the formation of the ionic derivative $[Ph_3PCH_2COCH_2PPh_3][PtCl_4]$, **2** (see eq 2). This complex was characterized on the basis of its elemental analysis, mass spectrum, and IR spectrum, but no NMR data could be obtained due to its insolubility in all common organic solvents. The IR spectrum of **2** has the carbonyl absorption at 1723 cm^{-1}, that is, at almost the same frequency found for $[Ph_3PCH_2COCH_2PPh_3](ClO_4)_2$ (1722 cm^{-1}).[9a,b] It also shows a strong absorption at 318 cm^{-1}, attributed to the Pt$-$Cl stretch, and which appears very close to the frequency reported for $K_2[PtCl_4]$ (321 cm^{-1}).[10]

$$PtCl_2 \xrightarrow[\text{2-MeOCH}_2\text{CH}_2\text{OH / reflux / 3 h}]{[Ph_3PCH_2COCH_2PPh_3](Cl)_2} [Ph_3PCH_2COCH_2PPh_3][PtCl_4] \quad (2)$$

Moreover, the role of the counterion in stabilizing the bis-phosphonium salts is relevant. Thus, the reaction of $PtCl_2$ (or $PtCl_2L_2$; L = NCPh or NCMe) with the perchlorates $\{[PhR_2PCH_2]_2CO\}(ClO_4)_2$ (1:1 molar ratio, 2-methoxyethanol, reflux) gives the dicationic complexes $[Pt(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PR_2C(H)COCH_2PPhR_2)]_2(ClO_4)_2$ (R_2 = Ph_2 **3a**; PhEt **3b**; Et_2 **3c**) (see eq 3), characterized by their elemental analyses and mass spectra (see Experimental Section). In this case, the reaction proceeds faster (0.5−4 h) than in the synthesis of complexes **1a**−**c** (22 h). The NMR spectra of complexes **3a** and **3c** show two sets of resonances, revealing the presence of two isomers. Due to the presence of two chiral centers in each dinuclear derivative, two diastereoisomers (each one as the mixture of two enantiomers) are expected, (*RR*/*SS*) and (*RS*/*SR*). The resemblance of the NMR spectra of **3a** to those obtained for the palladium analogue[5a] $[Pd(\mu\text{-}Cl)(C_6H_4\text{-}2\text{-}PPh_2C(H)COCH_2PPh_3)]_2(ClO_4)_2$ allows us to propose a similar stereochemistry for these compounds; that is, complexes **3a** and **3c** have been obtained as mixtures of the two diastereoisomers (*RR*/*SS*) and (*RS*/*SR*) and the dinuclear skeleton adopts an *anti* arrangement of the orthometalated fragments. The observed molar ratio of the diastereoisomers is 1.6:1 for **3a** (major/minor) and 1:1 for **3c**; we have not attempted the elucidation of the absolute configurations for each isomer.



(3)

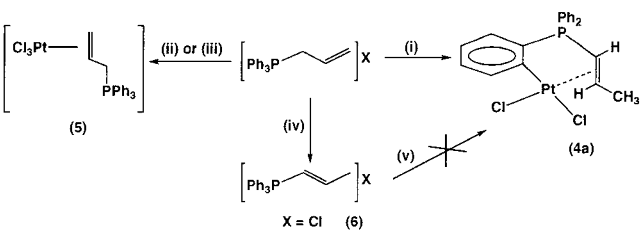
R_2 = Ph_2 **3a**; PhEt **3b**; Et_2 **3c**

With respect to complex **3b**, we have observed a behavior more or less similar to that described for **1b**, except that the number of expected diastereoisomers for **3b** is 8 (16 enantiomers), assuming an *anti* arrangement of the orthometalated rings. Two fractions were obtained, the first one precipitated in the alcoholic medium and the second one precipitated by addition of Et_2O (see Experimental Section). The first fraction corresponds to the mixture of two compounds (1.5:1 molar ratio), and the second one shows, in its $^{31}P\{^1H\}$NMR spectrum, eight different resonances corresponding to the P atom in the ring $C_6H_4\text{-}2\text{-}PPhEtC(H)Pt$. Due to the complexity of the mixture obtained, we have not attempted to assign absolute configurations to the isomers obtained.

In summary, we have found a very easy method for the synthesis of orthometalate-ylide complexes of Pt^{II} starting from bis-phosphonium salts, thus avoiding the preparation of the sometimes unstable ylides or bis-ylides.

2. Reactivity of Pt^{II} Complexes toward Semistabilized Allyl-phosphonium Salts. In the preceding examples the presence of a carbonyl group adjacent to a methylene group activated the latter, and we have observed more or less easy dehydrohalogenations through C−H bond activation, resulting in Pt^{II}-ylide complexes. The substitution of the carbonyl group by an olefin moiety (allyl-phosphonium salts), although it should produce a decrease in the acidity of the methylenic $P\text{-}CH_2$ protons, would not promote dramatic changes in reactivity, and coordinated allyl-ylides are expected to be obtained. The reactivity of allyl-ylides continues to attract some interest,[11] and some Pd^{II} complexes with allyl-ylides have been synthesized,[12] although no platinum complexes with allyl-ylides have been reported until now. Because of all this, we have explored the reactivity of Pt^{II} complexes toward allyl-phosphonium salts.

Scheme 1



(i): $PtCl_2$ or $PtCl_2(NCR)_2$ / X = Cl, -HCl / 2-methoxyethanol, reflux, 22 h
(ii): $PtCl_2$ / X = ClO_4 / 2-methoxyethanol, reflux, 22 h
(iii): $PtCl_2$ / X = Cl / Toluene, reflux, 22 h
(iv): X = Cl, Br / 2-methoxyethanol, reflux, 22 h
(v): $PtCl_2$ or $PtCl_2(NCR)_2$ / 2-methoxyethanol, reflux, 22 h

The reaction of $PtCl_2(NCPh)_2$ or $PtCl_2$ with $[Ph_3P-CH_2CH{=}CH_2]Cl$ (1:1 molar ratio) in refluxing 2-methoxyethanol (22 h) results in the formation of the orthometalated vinyl-phosphonium derivative *cis*-$[Cl_2Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}E\text{-}\eta^2\text{-}C(H){=}C(H)Me]$ (**4a**, see Experimental and Scheme 1). Compound **4a** crystallizes from CH_2Cl_2/Et_2O as a solvate in the form of colorless prisms and shows correct elemental analyses and mass spectrum. The IR spectrum shows clearly the *cis* disposition of the two chloride ligands by the appearance of two absorptions at 326 and 285 cm^{-1}.

The analysis of the ^1H NMR spectrum of **4a** provides important structural information. Thus, the presence of the orthometalated $Pt-C_6H_4$ group can be inferred from the observation of four different resonances, well spread in the frequency domain (8.11, 7.42, 7.24, and 7.17 ppm), one of them (H_6, 8.11 ppm) showing ^{195}Pt satellites ($^3J_{Pt-H6}$ = 42 Hz) and giving proof of the metalation of one aryl ring of the PPh_3 unit. Interestingly, we have not observed a similar dispersion of the arylic resonances, nor platinum satellites, in the closely related complexes **1a**−**c** or **3a**−**c**. Going to high field, it is clearly seen that the resonances attributed to the starting allyl group have disappeared and that new resonances attributed to the vinylic fragment *E*-PC(H)=C(H)Me have appeared. The olefinic protons appear as an AB spin system coupled with other nuclei; the MeC(*H*)= proton appears at 4.56 ppm as a doublet of doublets by coupling with the other olefinic proton and the P atom, and the =C(*H*)P proton appears at 4.66 ppm as a complex multiplet, due to the additional coupling with the P and CH_3 nuclei. The methyl group appears as a doublet at 1.84 ppm, flanked by ^{195}Pt satellites. The *E*-configuration of the alkenyl fragment can be inferred from the observation of the value of the coupling constant $^3J_{P-H}$ = 17.1 Hz for the resonance at 4.56 ppm, indicating a mutual *cis* arrangement,[13a] thus implying a *trans* disposition of the methyl group and the P atom.

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[10] Nakamoto, K. *Infrared Spectra of Inorganic and Coordination Compounds*, 2nd ed.; Wiley and Sons: New York, 1970; p 115.

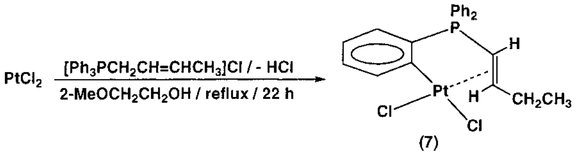
[11] (a) Wang, Q.; El Khoury, M.; Schlosser, M. *Chem. Eur. J.* **2000**, *6*, 420. (b) Breitsameter, F.; Polborn, K.; Schmidpeter, A. *Eur. J. Inorg. Chem.* **1998**, 1907.

[12] (a) Hirai, M.-F.; Miyasaka, M.; Itoh, K.; Ishii, Y. *J. Chem. Soc., Dalton Trans.* **1979**, 1200. (b) Hirai, M.-F.; Miyasaka, M.; Itoh, K.; Ishii, Y. *J. Organomet. Chem.* **1979**, *165*, 391. (c) Hirai, M.-F.; Miyasaka, M.; Itoh, K.; Ishii, Y. *J. Organomet. Chem.* **1978**, *160*, 25.

This *E*-configuration seems to be preferred in substituted vinyl-phosphonium salts.[13] The coordination of the olefinic C═C double bond to the platinum atom is evident from the presence of ^{195}Pt satellites in the methyl resonance and in that attributed to the C(*H*)Me proton. The $^{31}P\{^1H\}$ NMR spectrum of **4a** shows a resonance at 25.84 ppm, flanked by platinum satellites ($^3J_{Pt-P} = 48.6$ Hz), downfield relative to the corresponding resonance in the free allyl-phosphonium salt (21.20 ppm).

The presence of the orthometalated ligand and the coordination of the generated vinylic unit to the platinum center can also be inferred from the APT $^{13}C\{^1H\}$ NMR spectrum of **4a** (see Experimental Section). Six separate resonances (two with negative phase and four with positive phase) in the range 150−120 ppm can be attributed to the C_6H_4 fragment. Moreover, this spectrum shows resonances corresponding to two inequivalent Ph groups, since in this molecule the molecular plane is not a plane of symmetry. The C_β carbon atom [═*C*(H)Me] appears as a singlet at 81.53 ppm, with Pt satellites ($^1J_{Pt-C} = 223.2$ Hz), and the C_α carbon atom [═*C*(H)P] appears as a doublet at 57.91 ppm ($^1J_{P-C} = 77.8$ Hz), also showing Pt satellites ($^1J_{Pt-C} = 244.6$ Hz). These two resonances are shifted to high field by more than 52 ppm with respect to the corresponding resonances in the free vinyl phosphonium **6** (see below and Experimental Section), and similar upfield shifts have been reported in the coordination of ethylene, for instance in the Zeise's salt $K[Cl_3Pt(C_2H_4)]$.[14] Finally, the methyl group appears at 21.61 ppm as a doublet. Further characterization of complex **4a** is provided by its X-ray structure (see below).

The allyl-phosphonium salts $[PhMe_2PCH_2CH{=}CH_2]Br$ and $[Ph_3PCH_2CH{=}CHMe]Br$ behave similarly toward $PtCl_2$ in refluxing 2-methoxyethanol. Thus, the corresponding complexes *cis*-$[Cl_2Pt(C_6H_4\text{-}2\text{-}PMe_2\text{-}E\text{-}\eta^2\text{-}C(H){=}C(H)Me]$ (**4b**, very insoluble in most common organic solvents) and *cis*-$[Cl_2Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}E\text{-}\eta^2\text{-}C(H){=}C(H)Et]$ (**7**) can be isolated and characterized similarly to **4a** (see Scheme 1 and eq 4).



(7)

(4)

However, the presence of different counterions in the starting allyl-phosphonium salt gives different behaviors, as has already been observed in complexes **1a**−**c** and **3a**−**c**. Thus, in the reaction of $[Ph_3PCH_2CH{=}CH_2]ClO_4$ with $PtCl_2$ (1:1 molar ratio) in refluxing 2-methoxyethanol (22 h) extensive decomposition can be observed. After removal of the Pt^0, the complex $[PtCl_3(\eta^2\text{-}CH_2{=}CH{-}CH_2PPh_3)]$, **5**, can be obtained from the alcohol solution in low yield (see Scheme 1). Complex **5** gives the correct elemental analysis and mass spectra (the phosphonium cation and the trichloroplatinate anion are the only species detected in the positive and negative FAB spectrum, respectively). The IR spectrum of **5** shows absorptions corresponding to the Pt−Cl stretch, which are very similar to those observed in $K[PtCl_3(C_2H_4)]$, and does not show absorptions corresponding to the ClO_4^- group.

The ^1H NMR spectrum of **5** does not show signals in the aromatic region other than those attributed to the Ph groups and shows the resonances corresponding to the allyl moiety shifted to high field (range 4.77−4.00 ppm) with respect to the corresponding resonances in the free allyl-phosphonium (range 5.61−5.17 ppm), as expected for the η^2-coordination of the C═C double bond. Moreover, the relative intensity of the aromatic and allylic resonances is 15:5, showing that in this case no orthometalation has occurred. The $^{31}P\{^1H\}$ NMR spectrum of **5** shows a single signal at 18.34 ppm with platinum satellites ($J_{Pt-P} = 156.1$ Hz). In contrast to that observed in **4a**, this resonance appears shifted to high field with respect to the resonance of the free phosphonium (21.20 ppm). The η^2-coordination of the allyl group can also be inferred from the $^{13}C\{^1H\}$ NMR spectrum, since the C_β carbon appears at 68.95 ppm ($^1J_{Pt-C} = 217$ Hz) and the C_γ carbon at 67.52 ppm ($^1J_{Pt-C} = 193$ Hz). Both signals show platinum satellites and are shifted to high field with respect to the corresponding values in the free allyl-phosphonium ($C_\beta = 123.12$ ppm; $C_\gamma = 126.09$ ppm). In accord with the structure (see Scheme 1), signals corresponding to the presence of only one type of Ph group are observed, and the PCH_2 moiety remains unaltered, as can be deduced from the position of the resonance (27.35 ppm) and its shape (doublet, $^1J_{P-C} = 48$ Hz).

The solvent used in the reaction also exerts a considerable influence on the synthesis of complexes of type **4** or **5**. Thus, the reaction of $[Ph_3P{-}CH_2CH{=}CH_2]Cl$ with $PtCl_2$ (1:1 molar ratio) in refluxing toluene for only 1 h affords complex **5** in good yields (see Experimental Section and Scheme 1). When the reaction time in refluxing toluene is prolonged to 22 h, complex **5** is the only species detected in the reaction mixture. However, if complex **5** (isolated) is dissolved in 2-methoxyethanol and this solution is refluxed for 22 h, complex **4a** can be obtained, although in lower yields than in the procedure reported above.

The synthesis of the orthometalated vinyl-phosphonium complexes **4a** and **4b** starting from allyl-phosphonium salts implies, formally, a dehydrohalogenation by C−H activation, but this C−H activation is produced in one aryl ring of the PPh_3 (or $PPhMe_2$) unit, instead of the more "expected" position, namely, the C_α of the allyl group. Moreover, the allyl group $CH_2{-}CH{=}CH_2$ undergoes isomerization, giving the methyl-vinyl group $-CH{=}CH{-}CH_3$, probably through a 1,3-prototropic shift, and the vinylic moiety is η^2-coordinated to the Pt^{II} center. These facts constitute a clear difference with respect to the reactivity of Pd^{II} compounds toward allyl-phosphonium salts, since η^3-allyl-phosphonium derivatives of Pd^{II} have been reported[12] (through deprotona-

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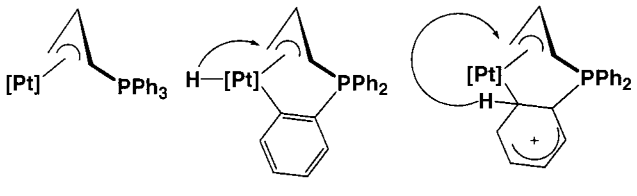
(13) (a) Huang, C.-C.; Duan, J.-P.; Wu, M.-Y.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1998**, *17*, 676. (b) Duan, J.-P.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1997**, *16*, 3934. (c) Rybin, L. V.; Petrovskaya, E. A.; Rubinskaya, M. I.; Kuz'mina, L. G.; Struchkov, Y. T.; Kaverin, V. V.; Koneva, N. Y. *J. Organomet. Chem.* **1985**, *288*, 119. (d) Scordia, H.; Kergoat, R.; Kubicki, M. M.; Guerchais, J. E.; L'Haridon, P. *Organometallics* **1983**, *2*, 1681. (e) Chin, C. S.; Lee, M.; Oh, M.; Won, G.; Kim, M.; Park, Y. J. *Organometallics* **2000**, *19*, 1572. (f) Arisawa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2000**, *122*, 2387. (g) Reynolds, K. A.; Dopico, P. G.; Brody, M. S.; Finn, M. G. *J. Org. Chem.* **1997**, *62*, 2564.

(14) Mann, B. E.; Taylor, B. F. *^{13}C NMR Data for Organometallic Compounds*; Academic Press: London, 1981; pp 192−197.

tion at C_α by external base), and they are stable. The isomerization of allyl-phosphonium derivatives into the vinylic species was known several years ago.[15] Thus, the first plausible hypothesis one can imagine is that the reaction occurs in two steps: The first is the generation of the vinyl-phosphonium from the allylic salt, which makes C−H activation at C_α more difficult; the second step is the orthometalation of the resulting vinyl-phosphonium salt, which should not differ from those described for other thermal C−H bond activations of ylides.[6]

However, some experimental facts militate against this proposal. First, the known allyl-vinyl isomerization always requires the presence of base,[15] since the reaction proceeds via ylide and the ylide is generated by deprotonation with base, even in catalytic amounts.[15a] To confirm that the allyl-vinyl isomerization really occurs under our reaction conditions, we have refluxed $[Ph_3P{-}CH_2CH{=}CH_2]X$ (X = Br, Cl) in 2-methoxyethanol for 22 h, in the absence of base. To our surprise, this yielded (after workup) a white solid whose spectroscopic parameters are identical to those reported in the literature for *E*-$[Ph_3PCH{=}CH{-}CH_3]X$,[15a,b] **6** (see Experimental Section and Scheme 1). The same behavior was observed when the allyl-phosphonium salt $[Ph_3P{-}CH_2C(Me){=}CH_2]Cl$ was refluxed in 2-methoxyethanol; that is, the vinyl-phosphonium salt $[Ph_3P{-}CH{=}CMe_2]Cl$ was obtained in good yield (see below, compounds **10** and **11**). However, when the allyl-phosphonium salts $[Ph_3P{-}CH_2CH{=}CH{-}R]Cl$ (R = Me, Ph, employed in the synthesis of the orthometalated complexes **7** and **9**; see below) were treated in the same fashion (2-methoxyethanol, reflux, 22 h), the starting salts were recovered in quantitative yield. Nevertheless, and although the isomerization occurs in some cases under our reaction conditions, another factor mitigates against the proposed mechanism. When the vinyl-phosphonium salts *E*-$[Ph_3PCH{=}CH{-}CH_3]X$, **6**, and $[Ph_3P{-}CH{=}CMe_2]Cl$, **11**, were refluxed in 2-methoxyethanol with $PtCl_2$ or $PtCl_2(NCR)_2$ (R = Me, Ph, 1:1 molar ratio), the orthometalation reaction did not take place, and the starting products were always recovered, even after longer refluxing periods (48 h or more).

These two facts—(i) the nonisomerization of the C_γ-substituted allyl-phosphonium salts $[Ph_3P{-}CH_2CH{=}CH{-}R]Cl$ (R = Me, Ph) and (ii) the lack of reactivity of the isomerized vinyl-phosphonium salts *E*-$[Ph_3PCH{=}CH{-}CH_3]Cl$, **6**, and $[Ph_3P{-}CH{=}CMe_2]Cl$, **11**, with Pt^{II} complexes—suggest that the mechanism operating in this reaction must be different from that proposed and also suggest that the isomerization step should occur *after*, and probably as a consequence of, the orthometalation.

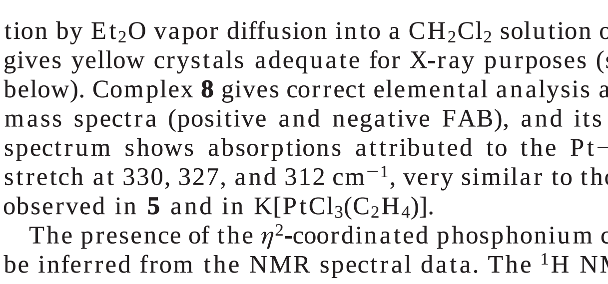


(A) (B) (C)

Figure 2. Proposed intermediates in the orthometalation of allyl-phosphonium salts.

Once the notion of direct orthometalation of the vinyl-phosphonium salts has been discarded, it seems clear that the reaction should begin by direct interaction of the allyl moiety with the Pt^{II} center. Two possibilities can be envisaged: a structure similar to complex **5** or, better, a platinum-ylide complex such as that represented in Figure 2, structure **A**, obtained by dehydrohalogenation of the phosphonium salt at C_α. Since it has been proved that under our reaction conditions the allyl−vinyl isomerization takes place, and that this isomerization proceeds via ylide formation, it seems reasonable to assume that, in the presence of the metal, the ylide generated could coordinate to the platinum center. We have represented this coordination as η^3-allyl-phosphonium by analogy with similar known palladium complexes.[12] Once the ylide is coordinated, the carbon−hydrogen activation step should occur, promoted by the metal through either an oxidative addition (intermediate **B**, Figure 2), an electrophilic substitution (intermediate **C**, Figure 2), or a multicentered pathway, since it has been reported[1a] that all of these mechanisms could operate in C−H activation processes promoted by platinum complexes. Finally, the hydrogen liberated by the C−H activation is captured by C_γ of the allyl unit, which thus becomes a vinylic moiety, giving the orthometalated-vinyl derivatives.

The reactivity of $PtCl_2$ with other allyl-phosphonium salts is similar to that described in the synthesis of **4a**, **4b**, **5**, and **7**. Thus, $PtCl_2$ reacts with $[Ph_3P{-}CH_2{-}CH{=}CH(Ph)]Cl$ in refluxing 2-methoxyethanol to give two different, and easily separable, products. The first product precipitates from the alcoholic medium as a greenish powder. Recrystallization from CH_2Cl_2/Et_2O gives a deep yellow solid characterized as $[PtCl_3(\eta^2\text{-}PhCH{=}CH{-}CH_2PPh_3)]$, **8** (see eq 5). Slow crystallization by Et_2O vapor diffusion into a CH_2Cl_2 solution of **8** gives yellow crystals adequate for X-ray purposes (see below). Complex **8** gives correct elemental analysis and mass spectra (positive and negative FAB), and its IR spectrum shows absorptions attributed to the Pt−Cl stretch at 330, 327, and 312 cm^{-1}, very similar to those observed in **5** and in $K[PtCl_3(C_2H_4)]$.



(5)

The presence of the η^2-coordinated phosphonium can be inferred from the NMR spectral data. The ^1H NMR spectrum shows, in addition to the expected aromatic signals, four different resonances corresponding to the

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(15) (a) Keough, P. T.; Grayson, M. *J. Org. Chem.* **1964**, *29*, 631. (b) Seyferth, D.; Fogel, J. *J. Organomet. Chem.* **1966**, *6*, 205. (c) Schweizer, E. E.; Shaffer, E. T.; Hughes, C. T.; Berninger, C. J. *J. Org. Chem.* **1966**, *31*, 2907. (d) Vedejs, E.; Bershas, J. P.; Fuchs, P. L. *J. Org. Chem.* **1973**, *38*, 3625. (e) Corey, E. J.; Erickson, B. W. *J. Org. Chem.* **1974**, *39*, 821. (f) Kim, S.; Kim, Y. C. *Tetrahedron Lett.* **1990**, *31*, 2901. (g) Shen, Y.; Wang, T. *Tetrahedron Lett.* **1990**, *31*, 543. (h) Shen, Y.; Wang, T. *Tetrahedron Lett.* **1990**, *31*, 3161. (i) Kim, S.; Kim, Y. C. *Synlett* **1990**, 115. (j) Hatanaka, M.; Himeda, Y.; Ueda, I. *J. Chem. Soc., Chem. Commun.* **1990**, 526. (k) Shen, Y.; Wang, T. *Tetrahedron Lett.* **1991**, *32*, 4353.

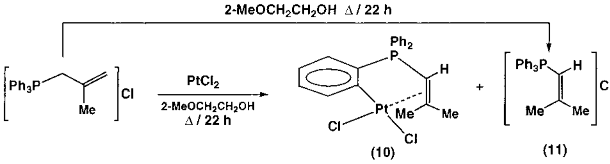
four inequivalent protons of the $-CH_2-CH=CH-$ unit. The two olefinic protons appear at 6.06 (with ^{195}Pt satellites) and 5.29 ppm, and the two diastereotopic PCH_2 protons appear at 4.43 and 4.10 ppm as the AB part of an ABMX spin system (M = ^{31}P; X = $^{1}HC_{\beta}$ olefinic), this fact reflecting clearly the η^2-coordination of the olefin. The $^{13}C\{^1H\}$ NMR spectrum also reflects the η^2-coordination of the olefin, since the resonances attributed to the olefinic carbons C_β and C_γ show ^{195}Pt satellites (signal at 87.83 ppm) and are shifted downfield (87.83 and 61.52 ppm) with respect to the corresponding resonances in the free phosphonium (140.05 and 113.74 ppm). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 18.37 ppm, with platinum satellites, and it is shifted upfield with respect to the free phosphonium (21.67 ppm), similar to what is observed for **5**.

The second product obtained in this reaction is soluble in the alcohol medium. After workup (see Experimental Section) a white crystalline solid was obtained, which was characterized as the orthometalated $[Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}E\text{-}C(H){=}C(H)CH_2Ph)Cl_2]$ **9** (see eq 5). Complex **9** gives the correct elemental analysis and mass spectrum. The IR spectrum shows two absorptions at 323 and 278 cm^{-1} corresponding to the Pt$-$Cl stretch, in keeping with the presence of the *cis*-Cl_2Pt moiety. The spectroscopic characterization of **9** (see Experimental Section) yields the same key features as those described for **4a**, **4b**, and **7**. The ^{1}H NMR spectrum shows the resonance attributed to the proton *ortho* to the cyclometalation position (H_6) at 8.18 ppm as a doublet of doublets of doublets with platinum satellites ($^3J_{Pt-H6} = 37.8$ Hz). The olefinic protons (HC_α and HC_β) appear at 4.68 and 4.56 ppm as a split AB spin system, due to the coupling with the P atom and with the diastereotopic methylene protons of the benzyl group ($C_\gamma H_2$-Ph). In turn, these methylenic protons appear at 3.76 and 3.67 ppm, also as a coupled AB spin system (coupled to HC_β). The $^{31}P\{^1H\}$ NMR spectrum shows a singlet resonance at 26.79 ppm with platinum satellites ($^3J_{Pt-P} = 35.6$ Hz). This resonance is shifted downfield with respect to its position in the starting allyl-phosphonium (21.67 ppm), similar to what was observed for **4a**, **4b**, and **7**. Finally, the $^{13}C\{^1H\}$ NMR spectrum of **9** shows the expected resonances in accord with the proposed structure.

It is worth noting that complexes **5** and **8** contain the allyl-phosphonium η^2-coordinated, obviously nonisomerized, but complexes **4a** and **9** contain the isomerized and orthometalated vinyl-phosphonium; that is, the coordination alone does not imply isomerization, but orthometalation always implies isomerization. All attempts simply to coordinate the vinyl-phosphonium salts (processes similar to those described for **5** and **8**) did not result in the expected η^2-coordination, and the starting vinyl salts were recovered.

From the observed reactivity in the synthesis of complexes **4a** (starting from $[Ph_3P-CH_2-CH=CH_2]^+$), **7** (starting from $[Ph_3P-CH_2-CH=CHMe]^+$), and **9** (starting from $[Ph_3P-CH_2-CH=CHPh]^+$), it seems that the introduction of different substituents at C_γ does not have any influence over the orthometalation reaction, since in all cases the cycloplatinated derivatives can be obtained. We have therefore also examined the influence of multiple substituent on the allyl group. When the carbon atom C_γ has two substituents, for instance $[Ph_3P-CH_2-CH=CMe_2]^+$, there is a complete lack of reactivity toward the platinum complexes $PtCl_2(NCR)_2$ (R = Me, Ph) or toward $PtCl_2$ under the same experimental conditions (2-methoxyethanol, reflux), and the phosphonium salt is recovered at the end of the reaction in almost quantitative yields. The same behavior was observed when cyclic allyl-phosphonium salts were employed, such as [(2-cyclohexenyl)triphenylphosphonium]bromide. However, if the substituent is located at the C_β carbon atom, new complexes can be obtained, although with some difficulties.

The reaction of $[Ph_3P-CH_2-C(Me)=CH_2]Cl$ with $PtCl_2$ (1:1 molar ratio) in refluxing 2-methoxyethanol (22 h) gives a white solid after workup. The spectroscopic parameters of this solid show that it is actually a mixture of the expected orthometalated derivative $[Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}C(H){=}CMe_2)Cl_2]$, **10**, and the corresponding vinyl-phosphonium salt $[Ph_3PC(H){=}CMe_2]Cl$, **11** (see Experimental Section and eq 6). Exhaustive washing of this solid with water in order to separate the soluble phosphonium salt results in the decomposition of the platinum derivative, and after workup, only **11** is obtained. Attempts to recrystallize this mixture always led to other mixtures with different molar ratios, but never to pure products. Finally, attempts to separate the mixture by column chromatography also led to mixtures or to the decomposition of the organometallic product **10**. Thus, although it is possible to obtain a complete spectroscopic characterization of both compounds (see Experimental Section), satisfactory elemental analytical data and mass spectra could only be obtained for the phosphonium salt **11**.



(6)

The spectroscopic characterization of **10** clearly shows the presence of the orthometalated vinyl-phosphonium group. The ^{1}H NMR shows the presence of resonances attributed to the cycloplatinated C_6H_4 ring, the HC_α proton (4.63 ppm, $^2J_{Pt-H} = 68.7$ Hz), and two different methyl groups (2.02 and 1.28 ppm), both with platinum satellites (36.0 and 51.6 Hz, respectively). The $^{31}P\{^1H\}$ NMR shows a resonance at 23.35 ppm with platinum satellites ($^3J_{Pt-P} = 45.1$ Hz), shifted downfield with respect to the starting allyl derivative (20.33 ppm) and also with respect to the corresponding free vinyl-phosphonium **11** (11.38 ppm). The $^{13}C\{^1H\}$ NMR spectrum shows the expected upfield shifts for the C_α and C_β carbons on going from **11** to **10** due to the η^2-coordination (C_α, 103.13 ppm in **11** to 58.56 ppm in **10**; C_β, 172.62 ppm in **11** to 101.36 ppm in **10**) and also shows the presence of the two methyl groups (33.08 and 28.35 ppm).

3. X-ray Crystal Structures. A drawing of the organometallic compound **4a** is shown in Figure 3, relevant crystallographic parameters are shown in Table 1, and selected bond distances and angles are collected in Table 2. The platinum atom is bonded to two mutually *cis* chlorine atoms, to the *ortho* carbon

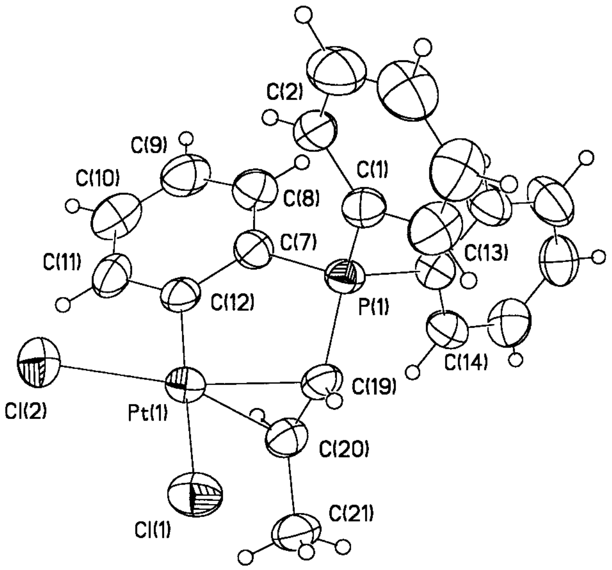


Figure 3. Thermal ellipsoid plot of [Pt(C_6H_4-2-PPh_2-*E*-η^2-*C*(H)=*C*(H)Me)Cl_2], **4a**. Non-hydrogen atoms are drawn at the 50% probability level.

Table 1. Crystal Data and Structure Refinement for 4a·CH_2Cl_2 and 8

	4a·CH_2Cl_2	**8**
formula	$C_{22}H_{21}Cl_4PPt$	$C_{27}H_{24}Cl_3PPt$
mol wt	653.29	680.87
data collecn *T*, K	300(2)	298(2)
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a, Å	12.5634(10)	10.1058(9)
b, Å	11.4472(9)	14.9236(13)
c, Å	16.6823(11)	17.1015(14)
β, deg	102.882(6)	90.517(2)
V, Å^3	2338.8(3)	2579.1(4)
Z	4	4
D_{calc} Mg m^{-3}	1.849	1.754
μ(Mo Kα), mm^{-1}	6.531	5.827
F(000)	1248	1320
cryst size, mm	0.29 × 0.19 × 0.10	0.32 × 0.22 × 0.13
θ range, deg	2.18−27.47	1.81−30.52
rflns collected	5585	21457
rflns unique (R_{int})	5347 (0.0415)	7864 (0.0318)
max./min. transmn factor	0.5612/0.2532	0.5180/0.2571
no. of data/restr/params	5347/6/260	7864/1/297
GOF[a]	1.053	0.841
R indices [$I > 2\sigma(I)$][b]	R1 = 0.0493 wR2 = 0.1161	R1 = 0.0244 wR2 = 0.0383
R indices (all data)	R1 = 0.0731 wR2 = 0.1293	R1 = 0.0475 wR2 = 0.0413
largest peak, hole, e·Å^{-3}	1.114, −0.843	0.873, −0.777

[a] GOF = $[\sum w(F_o^2 - F_c^2)^2/(n_{obs} - n_{param})]^{1/2}$. [b] R1 = $\sum||F_o| - |F_c||/\sum|F_o|$; wR2 = $[\sum w(F_o^2 - F_c^2)^2/\sum w(F_o^2)^2]^{1/2}$.

atom of one phenyl ring (supplying proof of the orthometalation), and to the vinylic C=C double bond. The Pt−Cl bond distances [Pt(1)−Cl(1) = 2.394(2) Å and Pt(1)−Cl(2) = 2.291(3) Å] are in the usual range of distances found for this type of bond.[16] These distances are clearly different from each other, with the longer Pt−Cl bond *trans* to the arylic carbon atom. Although it is known that olefin groups have a stronger *trans effect* than aryl groups,[17] it has also been reported that olefins have a weak *trans influence*,[18] and compound **4a** could be a good example. The Pt−C_{aryl} bond distance [Pt(1)−C(12) = 1.997(9) Å] is similar, within experimental error, to those found in other orthometalated ylide complexes.[6a,e] The bond distances Pt−C_{vinyl} are similar, within experimental error [Pt(1)−C(19) = 2.108(8) Å and Pt(1)−C(20) = 2.161(9) Å] and fall in the usual range of distances found in η^2-coordinated olefins.[16,19] The environment around the P atom is tetrahedral, and all P−C bond distances are similar within experimental error. The vinylic C=C bond distance [C(19)−C(20) = 1.395(12) Å] is longer than that expected for a C=C double bond with *trans* substituents [1.312(11) Å],[20] due to the coordination to the Pt atom, and the C−CH_3 bond distance [C(20)−C(21) = 1.516(12) Å] is typical for a C−C single bond.[20] The olefin is almost perpendicular to the coordination plane, as the dihedral angle between Pt1−C20−C19 and Pt1−C12−Cl2−Cl1 is 86.2(4)°. In addition, the olefin unit, including substituents, deviates from planarity, as can be seen from the torsion angle P1−C19−C20−C21, which is 155.6(7)°.

Table 2. Selected Bond Lengths [Å] and Angles [deg] for 4a·CH_2Cl_2.

Pt(1)−C(12)	1.997(9)	Pt(1)−C(19)	2.108(8)
Pt(1)−C(20)	2.161(9)	Pt(1)−Cl(2)	2.291(3)
Pt(1)−Cl(1)	2.394(2)	P(1)−C(19)	1.769(8)
P(1)−C(7)	1.772(9)	P(1)−C(1)	1.787(9)
P(1)−C(13)	1.797(9)	C(7)−C(8)	1.391(12)
C(7)−C(12)	1.413(12)	C(8)−C(9)	1.387(14)
C(9)−C(10)	1.373(15)	C(10)−C(11)	1.389(14)
C(11)−C(12)	1.404(12)	C(19)−C(20)	1.395(12)
C(20)−C(21)	1.516(12)		

C(12)−Pt(1)−C(19)	87.7(3)	C(12)−Pt(1)−C(20)	87.3(4)
C(19)−Pt(1)−C(20)	38.1(3)	C(12)−Pt(1)−Cl(2)	90.8(3)
C(19)−Pt(1)−Cl(2)	167.2(2)	C(20)−Pt(1)−Cl(2)	154.5(3)
C(12)−Pt(1)−Cl(1)	175.2(2)	C(19)−Pt(1)−Cl(1)	91.4(2)
C(20)−Pt(1)−Cl(1)	95.0(3)	Cl(2)−Pt(1)−Cl(1)	89.04(10)
C(19)−P(1)−C(7)	103.1(4)	C(19)−P(1)−C(1)	109.3(4)
C(7)−P(1)−C(1)	112.8(4)	C(19)−P(1)−C(13)	112.9(4)
C(7)−P(1)−C(13)	111.2(4)	C(1)−P(1)−C(13)	107.6(4)
C(20)−C(19)−P(1)	121.2(7)	C(20)−C(19)−Pt(1)	73.0(5)
P(1)−C(19)−Pt(1)	104.8(4)	C(19)−C(20)−C(21)	123.5(8)
C(19)−C(20)−Pt(1)	68.9(5)	C(21)−C(20)−Pt(1)	115.3(6)
C(7)−C(12)−Pt(1)	118.2(6)	C(11)−C(12)−Pt(1)	125.9(7)

A drawing of the organometallic compound **8** is shown in Figure 4, relevant crystallographic parameters are listed in Table 1, and selected bond distances and angles are collected in Table 3. The platinum atom is surrounded by three chlorine atoms and by the *trans*-cinnamyl-triphenylphosphonium cation, which is coordinated through the C=C double bond. A pair of *trans* chlorine atoms are disordered, with populations of 95%/5% for the disordered congeners. The two sets of positions correspond to different orientations of the olefin, which has free rotation with respect to the $PtCl_3$ unit. The dihedral angle between the planes Pt−Cl1−Cl2−Cl3 and Pt−C2−C3 is 74.70(12)°, and that between Pt−C2−C3 and Pt−Cl1′−Cl2−Cl3′ is 46.8(3)°. The Pt−Cl bond distances [Pt(1)−Cl(1) 2.3220(7), Pt(1)−Cl(2) =

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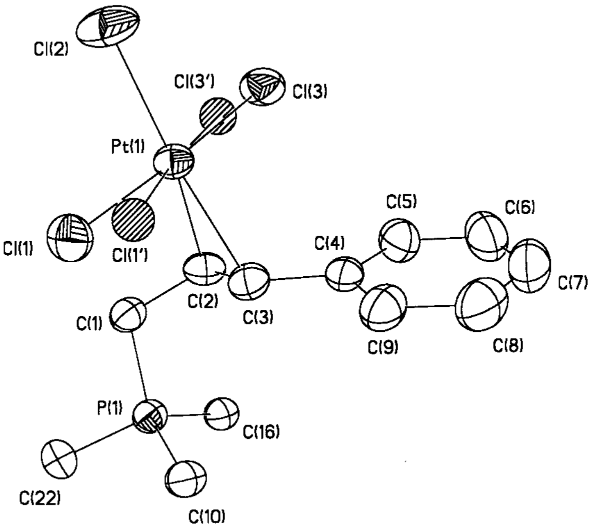

Figure 4. Thermal ellipsoid plot of $[PtCl_3(\eta^2\text{-Ph}CH{=}CH\text{-}CH_2PPh_3)]$, **8**. Ph groups of the PPh_3 fragment (except C_{ipso}) and H atoms are omitted for clarity. Atoms are drawn at the 50% probability level. Cl(1′) and Cl(3′) are the minor disordered components.

Table 3. Selected Bond Lengths [Å] and Angles [deg] for 8

Pt(1)−C(2)	2.138(3)	Pt(1)−C(3)	2.178(3)
Pt(1)−Cl(1′)	2.274(14)	Pt(1)−Cl(3′)	2.295(14)
Pt(1)−Cl(3)	2.2956(7)	Pt(1)−Cl(2)	2.3104(8)
Pt(1)−Cl(1)	2.3220(7)	P(1)−C(16)	1.791(3)
P(1)−C(22)	1.791(3)	P(1)−C(10)	1.795(3)
P(1)−C(1)	1.814(3)	C(1)−C(2)	1.504(4)
C(2)−C(3)	1.383(4)	C(3)−C(4)	1.477(4)
C(2)−Pt(1)−C(3)	37.37(10)	C(2)−Pt(1)−Cl(1′)	105.0(5)
C(3)−Pt(1)−Cl(1′)	79.0(5)	C(2)−Pt(1)−Cl(3′)	72.6(4)
C(3)−Pt(1)−Cl(3′)	97.2(4)	Cl(1′)−Pt(1)−Cl(3′)	175.6(6)
C(2)−Pt(1)−Cl(3)	87.48(8)	C(3)−Pt(1)−Cl(3)	97.19(7)
C(2)−Pt(1)−Cl(2)	160.48(8)	C(3)−Pt(1)−Cl(2)	162.08(8)
Cl(1′)−Pt(1)−Cl(2)	87.7(5)	Cl(3′)−Pt(1)−Cl(2)	95.5(4)
Cl(3)−Pt(1)−Cl(2)	88.38(3)	C(2)−Pt(1)−Cl(1)	95.52(8)
C(3)−Pt(1)−Cl(1)	85.81(7)	Cl(3)−Pt(1)−Cl(1)	176.84(3)
Cl(2)−Pt(1)−Cl(1)	88.47(3)	C(2)−C(1)−P(1)	112.75(18)
C(3)−C(2)−C(1)	124.7(2)	C(3)−C(2)−Pt(1)	72.86(15)
C(2)−C(3)−C(4)	129.3(3)	C(2)−C(3)−Pt(1)	69.77(15)
C(4)−C(3)−Pt(1)	116.53(18)		

2.3104(8), Pt(1)−Cl(3) = 2.2956(7) Å] are in the usual range of distances found for this type of bond,[16] and similarly for the $Pt-C_{vinyl}$ bond distances [Pt(1)−C(2) = 2.138(3) Å and Pt(1)−C(3) = 2.178(3) Å].[19] The environment around the P atom is tetrahedral; the $P-C_{aryl}$ bond distances are nearly identical [P(1)−C(16) = 1.791(3) Å, P(1)−C(22) = 1.791(3) Å, P(1)−C(10) = 1.795(3) Å], but the $P-C_{\alpha}$ bond is slightly longer [P(1)−C(1) = 1.814(3) Å]. The C2−C3 bond distance [1.383(4) Å] is similar to that found in **4a** and elongated for the same reasons; the C1−C2 bond distance [1.504(4) Å] is typical for a C−C single bond,[20] and the C3−C4 bond distance [1.477(4) Å] matches the value expected [1.470(15) Å] for a $C_{sp^2}-C_{aryl}$ bond.[20] Finally, the olefin unit again deviates from planarity, as seen from the dihedral angle C1−C2−C3−C4, which is 147.2(5)°.

4. Conclusion. We have found that simple Pt^{II} complexes such as $PtCl_2(NCR)_2$ (R = Me, Ph) or $PtCl_2$ itself are excellent precursors for the synthesis of orthometalated compounds derived from keto-stabilized bis-phosphonium salts or semistabilized allyl-phosphonium salts. In the case of keto-stabilized bis-phosphonium salts the reaction occurs with double C−H activation at two different sites, one methylene group and one phenyl ring, while in the case of semistabilized allyl-phosphonium salts the reaction formally involves C−H activation at a phenyl ring followed by an isomerization process. Moreover, we have found an easy synthesis of vinyl-phosphonium salts from the corresponding allyl-phosphonium salts by thermal isomerization. Further work on the reactivity of the coordinated vinyl group is now in progress.

Experimental Section

Safety Note: *Caution!* Perchlorate salts of metal complexes with organic ligands are potentially explosive. Only small amounts of these materials should be prepared, and they should be handled with great caution. See *J. Chem. Ed.* **1973**, *50*, A335−A337.

General Methods. Solvents were dried and distilled under nitrogen before use. Elemental analyses were carried out on a Perkin-Elmer 240-B microanalyzer. Infrared spectra (4000−200 cm^{-1}) were recorded on a Perkin-Elmer 883 infrared spectrophotometer from Nujol mulls between polyethylene sheets. ^1H (300.13 MHz), $^{13}C\{^1H\}$ (75.47 MHz), and $^{31}P\{^1H\}$ (121.49 MHz) NMR spectra were recorded in $CDCl_3$ or CD_2Cl_2 solutions at room temperature (unless otherwise stated) on a Bruker ARX-300 spectrometer; ^1H and $^{13}C\{^1H\}$ were referenced using the solvent signal as internal standard, and $^{31}P\{^1H\}$ was externally referenced to H_3PO_4 (85%). The two-dimensional $^1H-^1H$ NOESY experiments for complexes **1b** (**1b**α and the mixture **1b**α/**1b**β) were performed at a measuring frequency of 300.13 MHz. The data were acquired using a phase-sensitive method into a 512 × 1024 matrix and then transformed into 1024 × 1024 points using a sine window in each dimension. The mixing time was 400 ms. Mass spectra (positive and/or negative ion FAB) were recorded on a V. G. Autospec spectrometer from CH_2Cl_2 solutions. The bisphosphonium salts $[R_2PhPCH_2C(O)CH_2PPhR_2]X_2$ (R = Ph and/or Et; X = Cl, ClO_4)[9a−c] and the allyl-phosphonium salts $[PhR_2PCH_2-C(R'){=}C(H)(R'')]X$ (R = Me, Ph; R′ = H, Me; R″ = H, Me, Ph; X = Cl, ClO_4; not all possible combinations)[9d,e] were prepared according to published methods or with slight modifications.

[Pt(*C*₆H₄-2-PPh₂*C*(H)COCH₂PPh₃)Cl₂], 1a. To a suspension of $PtCl_2(NCPh)_2$ (0.200 g, 0.42 mmol) in 2-methoxyethanol (20 mL) was added $[Ph_3PCH_2COCH_2PPh_3]Cl_2$ (0.270 g, 0.42 mmol), and this mixture was stirred at the reflux temperature for 22 h. During this time some decomposition was evident, and a green solution was obtained. The cold solution was filtered over Celite, and the resulting pale yellow solution was treated with 200 mL of Et_2O. Further stirring gave **1a** as a white solid, which was filtered, washed with Et_2O (100 mL), and dried in vacuo. Obtained: 0.240 g (67% yield). Anal. Calcd for $C_{39}H_{32}Cl_2OP_2Pt{\cdot}C_3H_8O_2$: C, 54.79; H, 4.37. Found: C, 54.39; H, 4.28. IR (ν, cm^{-1}): 1647 (ν_{CO}), 293 (ν_{Pt-Cl}), 263 (ν_{Pt-Cl}). ^1H NMR (CD_2Cl_2): δ (ppm) 7.97−6.99 (m, 29H, Ph+C_6H_4), 6.43 (ddd, CH_2P, 1H, $^2J_{H-H} = 17.4$ Hz, $^2J_{P-H} = 10.5$ Hz, $^4J_{P-H} = 1.5$ Hz), 4.50 (dd, C(H)Pt, 1H, $^2J_{P-H} = 4.8$ Hz, $^4J_{P-H} = 2.1$ Hz, $^2J_{Pt-H} = 114$ Hz), 4.33 (dd, CH_2P, 1H, $^2J_{P-H} = 13.8$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 25.10 (d, PPh_2 in ring, $^4J_{P-P} = 8.1$ Hz), 20.91 (d, CH_2PPh_3). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) 186.44 (d, CO, $^2J_{P-C} = 6$ Hz), 145.96 (d, C_1, C_6H_4, $^2J_{P-C} = 22.64$ Hz), 137.21 (d, C_6H_4, $J_{P-C} = 14$ Hz), 135.04−128.92 (m, Ph+C_6H_4), 126.15 (d, C_6H_4, $J_{P-C} = 15$ Hz), 125.10 (d, C_6H_4, $J_{P-C} = 13$ Hz), 122.96 (d, C_6H_4, $J_{P-C} = 13$ Hz), 119.21 (d, $C_{ipso-Ph}$, $^1J_{P-C} = 88$ Hz), 37.56 (dd, CH_2P, $^1J_{P-C} = 56$ Hz, $^3J_{P-C} = 12$ Hz), 36.00 (dd, C(H)Pt, $^1J_{P-C} = 62$ Hz, $^3J_{P-C} = 7$ Hz).

[Pt(*C*₆H₄-2-PPhEt*C*(H)COCH₂PPh₂Et)Cl₂], 1b. $PtCl_2(NCPh)_2$ (0.200 g, 0.42 mmol) and $[EtPh_2PCH_2COCH_2PPh_2Et]Cl_2$ (0.230 g, 0.42 mmol) were refluxed for 22 h in 25 mL of

2-methoxyethanol. After cooling, a white solid precipitated. This solid was filtered, washed with Et_2O (20 mL), and dried in vacuo. Obtained: 0.108 g (34.3% yield). This solid was identified by NMR as one of the two possible diastereoisomers of **1b** (**1b**α, R_PR_C/S_PS_C, see text). The alcohol solution was treated with 150 mL of Et_2O, giving a second fraction of **1b**. Obtained: 0.119 g (37.5% yield). This second fraction was characterized spectroscopically as a mixture of the two diastereoisomers (**1b**α/**1b**β) in molar ratio (α/β = 1:4; configuration of **1b**β: S_PR_C/R_PS_C, see text). Total yield: 71.8%. Anal. Calcd for $C_{31}H_{32}Cl_2OP_2Pt$: C, 49.74; H, 4.31. Found: C, 49.62; H, 4.67. IR (ν, cm^{-1}): 1644 (ν_{CO}), 289 (ν_{Pt-Cl}), 250 (ν_{Pt-Cl}). MS (FAB +) [*m*/*z*, (%)]: 748 (2%) [M^+]. ^1H NMR (CD_2Cl_2): δ (ppm) for the α isomer, 8.18−7.57 (m, 16H, Ph+C_6H_4), 7.16−7.06 (m, 3H, C_6H_4), 6.15 (t, CH_2P, 1H, $^2J_{H-H} = {}^2J_{P-H} = 14$ Hz), 4.31 (d, C(H)Pt, 1H, $^2J_{P-H} = 1.8$ Hz, $^2J_{Pt-H} = 114$ Hz), 3.72 (t, CH_2P, 1H, $^2J_{H-H} = {}^2J_{P-H} = 14$ Hz), 3.54 (m, CH_2, 1H), 3.24 (m, CH_2, 1H), 2.64 (m, CH_2, 1H), 2.50 (m, CH_2, 1H), 1.32 (dt, CH_3, 3H, $^3J_{P-H} = 20.4$ Hz, $^3J_{H-H} = 7.5$ Hz), 1.04 (dt, CH_3, 3H, $^3J_{P-H} = 18.6$ Hz, $^3J_{H-H} = 6.9$ Hz); δ (ppm) for the β isomer, 8.10−7.53 (m, 16H, Ph+C_6H_4), 7.11−6.95 (m, 3H, C_6H_4), 5.79 (ddd, CH_2P, 1H, $^2J_{H-H} = 16.5$ Hz, $^2J_{P-H} = 10.5$ Hz, $^4J_{P-H} = 1.2$ Hz), 4.25 (dd, C(H)Pt, 1H, $^2J_{P-H} = 5.7$ Hz, $^4J_{P-H} = 1.8$ Hz, $^2J_{Pt-H} = 117$ Hz), 3.78 (dd, CH_2P, 1H, $^2J_{P-H} = 14.7$ Hz), 3.30 (m, CH_2, 1H), 3.08 (m, CH_2, 1H), 2.99 (m, CH_2, 1H), 2.85 (m, CH_2, 1H), 1.23 (dt, CH_3, 3H, $^3J_{P-H} = 20.4$ Hz, $^3J_{H-H} = 7.5$ Hz), 1.18 (dt, CH_3, 3H, $^3J_{P-H} = 19$ Hz, $^3J_{H-H} = 7.8$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm) for the α isomer, 32.91 (d, PPhEt in ring, $^4J_{P-P} = 7.2$ Hz), 26.67 (d, CH_2PPh_2Et); δ (ppm) for the β isomer, 31.32 (d, PPhEt in ring, $^4J_{P-P} = 6.6$ Hz), 26.37 (d, CH_2PPh_2Et).

[Pt(*C*$_6$H$_4$-2-PEt$_2$*C*(H)COCH$_2$PPhEt$_2$)Cl$_2$], 1c. Following the same experimental method as that described for **1a**, $PtCl_2(NCPh)_2$ (0.200 g, 0.42 mmol) reacted with $[Et_2PhPCH_2COCH_2PPhEt_2]Cl_2$ (0.190 g, 0.42 mmol) in 25 mL of 2-methoxyethanol for 22 h. Complex **1c** precipitated as an off-white solid. Obtained: 0.220 g (80% yield). Anal. Calcd for $C_{23}H_{32}Cl_2OP_2Pt$: C, 42.34; H, 4.94. Found: C, 42.17; H, 4.62. IR (ν, cm^{-1}): 1641 (ν_{CO}), 290 (ν_{Pt-Cl}), 257 (ν_{Pt-Cl}). MS (FAB +) [*m*/*z*, (%)]: 652 (45%) [M^+]. ^1H NMR (CD_2Cl_2): δ (ppm), 8.07−7.95 (m, Ph, 2H), 7.71−7.66 (m, Ph, 3H), 7.08−7.01 (m, C_6H_4, 4H), 5.54 (dd, CH_2P, 1H, $^2J_{H-H} = 15.9$ Hz, $^2J_{P-H} = 11.7$ Hz), 4.05 (dd, C(H)Pt, 1H, $^2J_{P-H} = 5.4$ Hz, $^4J_{P-H} = 1.2$ Hz, $^2J_{Pt-H} = 119$ Hz), 3.54 (t, CH_2P, 1H, $^2J_{H-H} = {}^2J_{P-H} = 15.9$ Hz), 3.00 (m, CH_2, 2H), 2.88 (m, CH_2, 2H), 2.56 (m, CH_2, 1H), 2.43 (m, CH_2, 1H), 2.21 (m, CH_2, 2H), 1.22 (m, CH_3, 12H). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 39.19 (d, PEt_2 in ring, $^4J_{P-P} = 5.22$ Hz), 32.87 (d, CH_2PPhEt_2).

[Ph$_3$PCH$_2$COCH$_2$PPh$_3$][PtCl$_4$], 2. To a suspension of $PtCl_2$ (0.200 g, 0.75 mmol) in 25 mL of 2-methoxyethanol was added $[Ph_3PCH_2COCH_2PPh_3]Cl_2$ (0.48 g, 0.75 mmol), and the resulting suspension was refluxed for 3 h. During this time the initial suspension gradually dissolved, and after dissolution, a pale-rose solid precipitated. The cool suspension was filtered, and the solid was washed with 2-methoxyethanol (10 mL), then with Et_2O (30 mL), and dried in vacuo. Obtained: 0.400 g (58.6% yield). Anal. Calcd for $C_{39}H_{34}Cl_4OP_2Pt$: C, 51.05; H, 3.72. Found: C, 50.63; H, 3.71. IR (ν, cm^{-1}): 1723 (ν_{CO}), 318 (ν_{Pt-Cl}). MS (FAB +) [*m*/*z*, (%)]: 579 (60%) [$(Ph_3PC(H)COCH_2PPh_3)^+$]. This compound was insoluble in the usual organic solvents (including DMSO-d_6), preventing the measurement of NMR spectra.

[Pt(*C*$_6$H$_4$-2-PPh$_2$*C*(H)COCH$_2$PPh$_3$)(μ-Cl)]$_2$(ClO$_4$)$_2$, 3a. (a) To a suspension of $PtCl_2$ (0.200 g, 0.75 mmol) in 20 mL of 2-methoxyethanol was added $[Ph_3PCH_2COCH_2PPh_3](ClO_4)_2$ (0.580 g, 0.75 mmol), and the resulting suspension was refluxed for 30 min. During this time the color of the suspension changed from brown to white. The resulting solid was filtered, washed with Et_2O (30 mL), dried in vacuo, and identified spectroscopically as **3a**, as a mixture of the two *anti* diastereoisomers (*RR*/*SS*) and (*RS*/*SR*). The molar ratio was (major/minor) = 1.6:1 (see text). Obtained: 0.540 g (80.3% yield). (b) To a suspension of $PtCl_2(NCMe)_2$ (0.200 g, 0.52 mmol) in 20 mL of 2-methoxyethanol was added $[Ph_3PCH_2COCH_2PPh_3](ClO_4)_2$ (0.410 g, 0.52 mmol), and this mixture was refluxed for 5 h. The initial suspension gradually dissolved, and some decomposition was evident. After reflux, the hot solution was filtered and the yellow filtrate was allowed to cool, resulting in the precipitation of **3a** as an off-white solid. Obtained: 0.350 g (75% yield). (c) In a way similar to that described in (b) $PtCl_2(NCPh)_2$ (0.200 g, 0.42 mmol) reacted with $[Ph_3PCH_2COCH_2PPh_3](ClO_4)_2$ (0.320 g, 0.42 mmol) in refluxing 2-methoxyethanol, giving **3a** as a white solid. Obtained: 0.260 g (55% yield). Anal. Calcd for $C_{78}H_{64}Cl_4O_{10}P_4Pt_2$: C, 51.55; H, 3.55. Found: C, 51.73; H, 3.98. IR (ν, cm^{-1}): 1652 (ν_{CO}), 283 (ν_{Pt-Cl}). MS (FAB +) [*m*/*z*, (%)]: 1717 (40%) [$(M_2 - ClO_4)^+$]. ^1H NMR (CD_2Cl_2): δ (ppm), 7.86−7.09 (m, Ph, both isomers), 5.26 (dd, CH_2P, major, $^2J_{H-H} = 19.2$ Hz, $^2J_{P-H} = 11.4$ Hz), 5.16 (dd, CH_2P, major, $^2J_{P-H} = 10.2$ Hz), 4.89 (dd, CH_2P, minor, $^2J_{H-H} = 17.7$ Hz, $^2J_{P-H} = 14.1$ Hz), 4.68 (dd, CH_2P, minor, $^2J_{P-H} = 14.10$ Hz), 4.69 (d, C(H)Pt, major, $^2J_{P-H} = 1.5$ Hz), 4.61 (t, C(H)Pt, minor, $^2J_{P-H} = {}^4J_{P-H} = 2.1$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 32.10 (d, PPh_2 in ring, minor, $^4J_{P-P} = 7.9$ Hz), 30.59 (d, PPh_2 in ring, major, $^4J_{P-P} = 7.9$ Hz), 22.96 (d, CH_2PPh_3, minor), 22.91 (d, CH_2PPh_3, major).

[Pt(*C*$_6$H$_4$-2-PPhEt*C*(H)COCH$_2$PPh$_2$Et)(μ-Cl)]$_2$(ClO$_4$)$_2$, 3b. Complex **3b** was synthesized following the same experimental method as that described for **3a**: $PtCl_2$ (0.250 g, 0.96 mmol) was reacted with $[EtPh_2PCH_2COCH_2PPh_2Et](ClO_4)_2$ (0.650 g, 0.96 mmol) in 2-methoxyethanol (40 mL) for 4 h, giving **3b** as a white solid. Obtained: 0.379 g (48.5 % yield). This fraction was identified spectroscopically as the mixture of two diastereoisomers, with molar ratio (major/minor) = 1.5:1. The alcohol solution was stirred with 150 mL of Et_2O, giving a second crop of **3b**. Obtained: 0.298 g (38.2% yield). This fraction shows eight resonances in its $^{31}P\{^1H\}$ NMR, around 36 ppm, with the same distribution as that observed in the first fraction (see text). (Total yield: 86.7%). Anal. Calcd for $C_{62}H_{64}Cl_4O_{10}P_4Pt_2$: C, 45.82; H, 3.96. Found: C, 45.62; H, 4.15. IR (ν, cm^{-1}): 1652 (ν_{CO}), 284 (ν_{Pt-Cl}). MS (FAB +) [*m*/*z*, (%)]: 1425 (40%) [$(M_2 - 2\,ClO_4 - H)^+$]. ^1H NMR (CD_2Cl_2) for the first fraction: δ (ppm), 7.77−7.13 (m, Ph+C_6H_4), 4.81 (dd, CH_2P, major, $^2J_{H-H} = 17.4$ Hz, $^2J_{P-H} = 14.4$ Hz), 4.80 (dd, CH_2P, minor, $^2J_{H-H} = 17.4$ Hz, $^2J_{P-H} = 14$ Hz), 4.70 (dd, CH_2P, major, $^2J_{P-H} = 14.4$ Hz), 4.49 (dd, CH_2P, minor, $^2J_{P-H} = 14.4$ Hz), 4.35 (t, C(H)Pt, major, $^2J_{P-H} = {}^4J_{P-H} = 1.8$ Hz), 4.22 (t, C(H)Pt, minor, $^2J_{P-H} = {}^4J_{P-H} = 2$ Hz, $^2J_{Pt-H} = 40$ Hz), 3.06−2.53 (m, CH_2), 1.31−1.03 (m, CH_3). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) for the first fraction: δ (ppm), 38.33 (d, PPhEt in ring, major, $^4J_{P-P} = 7.5$ Hz), 36.95 (d, PPhEt in ring, minor, $^4J_{P-P} = 7$ Hz), 26.31 (d, CH_2PPhEt_2, minor), 26.12 (d, CH_2PPhEt_2, major). $^{31}P\{^1H\}$ NMR (CD_2Cl_2) for the second fraction: δ (ppm), 38.47, 38.34, 37.65, 37.02, 36.86, 36.37, 35.83, 35.79 (d, PPhEt in ring), 26.32−25.20 (m, CH_2PPhEt_2).

[Pt(*C*$_6$H$_4$-2-PEt$_2$*C*(H)COCH$_2$PPhEt$_2$)(μ-Cl)]$_2$(ClO$_4$)$_2$, 3c. Complex **3c** was obtained similarly to **3a**: $PtCl_2$ (0.250 g, 0.96 mmol) was reacted with $[Et_2PhPCH_2COCH_2PPhEt_2](ClO_4)_2$ (0.552 g, 0.96 mmol) in refluxing 2-methoxyethanol (20 mL) for 4 h, giving **3c** as a white solid. Obtained: 0.613 g (91% yield). Complex **3c** was obtained as a mixture of the two diastereoisomers (*RR*/*SS*) and (*RS*/*SR*) in 1:1 molar ratio. Anal. Calcd for $C_{64}H_{64}Cl_4O_{10}P_4Pt_2$: C, 38.78; H, 4.65. Found: C, 38.92; H, 5.07. IR (ν, cm^{-1}): 1656 (ν_{CO}), 285, 249 (ν_{Pt-Cl}). MS (FAB +) [*m*/*z*, (%)]: 1333 (65%) [$(M_2-ClO_4)^+$]. ^1H NMR (CD_2Cl_2): δ (ppm), 8.05−7.09 (m, Ph+C_6H_4, both isomers), 4.69−4.53 (m, CH_2P), 4.31−4.14 (m, CH_2P), 4.07 (t, C(H)Pt, $^2J_{P-H} = {}^4J_{P-H} = 2.1$ Hz), 4.00 (t, C(H)Pt, $^2J_{P-H} = {}^4J_{P-H} = 1.8$ Hz), 2.82−2.13 (m, CH_2, both isomers), 1.45−1.06 (m, CH_3, both isomers). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 43.17 (d, PEt_2 in ring, $^4J_{P-P} = 6.7$ Hz), 42.99 (d, PEt_2 in ring, $^4J_{P-P} = 6.7$ Hz), 32.43 (d, CH_2PPhEt_2) 32.24 (d, CH_2PPhEt_2).

[Pt(*C*$_6$H$_4$-2-PPh$_2$-*E*-η^2-*C*(H)=*C*(H)Me)Cl$_2$], 4a. To a solution of $PtCl_2(NCPh)_2$ (0.200 g, 0.42 mmol) in 2-methoxyethanol (20 mL) was added $[Ph_3PCH_2CH{=}CH_2]Cl$ (0.143 g, 0.42 mmol), and this mixture was refluxed for 22 h. Some decomposition was evident after the reaction time, and the warm suspension was filtered over Celite. The resulting pale yellow solution was evaporated to ca. 5 mL, giving **4a** as a white solid, which was filtered, washed with Et_2O (20 mL), and dried in vacuo. Obtained: 0.148 g (61% yield). White crystals of **4a** were obtained by crystallization from CH_2Cl_2/Et_2O. These crystals contain dichloromethane of crystallization, as can be observed in the ^1H NMR and in the crystal structure of **4a**·CH_2Cl_2. Anal. Calcd for $C_{21}H_{19}Cl_2PPt\cdot 1.5CH_2Cl_2$: C, 38.84; H, 3.19. Found: C, 38.49; H, 2.82. IR (ν, cm^{-1}): 1587, 1571, 1548 ($\nu_{C=C}$), 326, 285 (ν_{Pt-Cl}). MS (FAB +) [m/z, (%)]: 533 (20%) [$(M - Cl)^+$], 496 (40%) [$(M - 2Cl - H)^+$]. ^1H NMR (CD_2Cl_2): δ (ppm), 8.11 (ddq, 1H, H_6, $^3J_{H6-H5} = 8.1$ Hz, $^4J_{H6-H4} = 3.3$ Hz, $^6J_{H6-Me} = 0.3$ Hz, $^3J_{Pt-H6} = 42$ Hz), 7.91−7.52 (m, 10H, Ph), 7.42 (tt, 1H, H_5, $^3J_{H5-H6} = {}^3J_{H5-H4} = 8.1$ Hz, $^4J_{H5-H3} \cong {}^5J_{P-H5} = 1.5$ Hz), 7.24 (tdd, 1H, H_4, $^3J_{H4-H3} = {}^3J_{H4-H5} = 8.1$ Hz, $^4J_{H4-H6} = 3.3$ Hz, $^4J_{P-H4} = 1.2$ Hz), 7.17 (ddd, 1H, H_3, $^3J_{P-H3} = 11.1$ Hz), 4.66 (m, 1H, $=C(H)P$), 4.56 (dd, 1H, $=C(H)Me$, $^3J_{H-H} = 12$ Hz, $^3J_{P-H} = 17.1$ Hz, $^2J_{Pt-H} = 59$ Hz), 1.84 (d, 3H, $=C(H)Me$, $^4J_{Me-Hcis} = 5.7$ Hz, $^3J_{Pt-Me} = 44$ Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 25.84 ($^3J_{Pt-P} = 48.6$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 146.56 (d, C_1, C_6H_4, $^2J_{P-C} = 16.4$ Hz), 137.29 (d, C_4, C_6H_4, $^3J_{P-C} = 14.1$ Hz), 135.36 (d, C_{para}, Ph, $^4J_{P-C} = 2.6$ Hz), 135.15 (d, C_{para}, Ph, $^4J_{P-C} = 2.6$ Hz), 133.41 (d, C_{meta}, Ph, $^3J_{P-C} = 10.2$ Hz), 133.38 (d, C_{meta}, Ph, $^3J_{P-C} = 10.5$ Hz), 133.17 (d, C_5, C_6H_4, $^4J_{P-C} = 2.9$ Hz), 132.64 (d, C_6, C_6H_4, $^3J_{P-C} = 15.1$ Hz), 130.71 (d, C_{ortho}, Ph, $^2J_{P-C} = 13$ Hz), 130.68 (d, C_{ortho}, Ph, $^2J_{P-C} = 12$ Hz), 126.80 (d, C_3, C_6H_4, $^2J_{P-C} = 13.5$ Hz), 125.14 (d, C_2, C_6H_4, $^1J_{P-C} = 106$ Hz), 121.60 (d, C_{ipso}, Ph, $^1J_{P-C} = 76$ Hz), 120.83 (d, C_{ipso}, Ph, $^1J_{P-C} = 93$ Hz), 81.53 (s, $=CHMe$, $^1J_{Pt-C} = 223.2$ Hz), 57.91 (d, $=C(H)P$, $^1J_{P-C} = 77.8$ Hz, $^1J_{Pt-C} = 244.6$ Hz), 21.61 (d, $=C(H)Me$, $^3J_{P-C} = 10.1$ Hz).

$[Pt(C_6H_4\text{-}2\text{-}PMe_2\text{-}E\text{-}\eta^2\text{-}C(H){=}C(H)Me)Cl_2]$, 4b. Complex **4b** was obtained following the same experimental method as that described for **4a**: $PtCl_2(NCPh)_2$ (0.200 g, 0.42 mmol) and $[PhMe_2PCH_2CH{=}CH_2]Br$ (0.110 g, 0.42 mmol) were refluxed in 2-methoxyethanol (20 mL) for 22 h, giving **4b** as a white solid, which was filtered, washed with Et_2O (20 mL), and dried in vacuo. Obtained: 0.174 g (92% yield). Anal. Calcd for $C_{11}H_{15}Cl_2PPt$: C, 29.74; H, 3.40. Found: C, 29.36; H, 3.22. IR (ν, cm^{-1}): 1573, 1550 ($\nu_{C=C}$), 289, 271 (ν_{Pt-Cl}). MS (FAB +) [m/z, (%)]: 407 (35%) [$(M - Cl)^+$], 371 (60%) [$(M - 2Cl - H)^+$]. ^1H NMR (DMSO-d_6): δ (ppm), 7.83 (m, 1H, C_6H_4), 7.54 (m, 1H, C_6H_4), 7.23 (m, 1H, C_6H_4), 4.56−4.09 (br m, 2H, $C(H){=}C(H)P$), 2.22 (d, 3H, PMe, $^2J_{P-H} = 14.4$ Hz), 2.20 (d, 3H, PMe, $^2J_{P-H} = 14.7$ Hz), 1.58 (d, 3H, $=C(H)Me$, $^4J_{Me-Hcis} = 5.4$ Hz, $^3J_{Pt-Me} = 28.2$ Hz). $^{31}P\{^1H\}$ NMR (DMSO-d_6): δ (ppm), 32.38 ($^3J_{Pt-P} = 48.7$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): This compound was insoluble for ^{13}C NMR measurements, even in DMSO-d_6.

$[PtCl_3(\eta^2\text{-}CH_2{=}CH{-}CH_2PPh_3)]$, 5. (a) To a suspension of $PtCl_2$ (0.200 g, 0.75 mmol) in 2-methoxyethanol (15 mL) was added $[Ph_3PCH_2CH{=}CH_2]ClO_4$ (0.303 g, 0.75 mmol), and this suspension was refluxed for 22 h. During this time, extensive decomposition and formation of a Pt^0 mirror was observed. The black mixture was filtered through Celite, and the resulting yellow solution was evaporated to dryness. The addition of Et_2O (30 mL) to the oily residue and subsequent stirring gave **5** as a yellow solid, which was filtered, washed with additional Et_2O (15 mL), and air-dried. Obtained: 0.159 g (35% yield). (b) To a suspension of $PtCl_2$ (0.200 g, 0.75 mmol) in toluene (15 mL) was added $[Ph_3PCH_2CH{=}CH_2]Cl$ (0.255 g, 0.75 mmol), and this suspension was refluxed for 1 h. During this time, the color of the suspension changed from brown to pale yellow. After cooling, **5** was obtained as a yellow solid, which was filtered, washed with toluene (10 mL) and Et_2O (25 mL), and air-dried. Obtained: 0.394 g (86.6% yield). Anal. Calcd for $C_{21}H_{20}Cl_3PPt$: C, 41.70; H, 3.33. Found: C, 42.16; H, 3.37. IR (ν, cm^{-1}): 1589 ($\nu_{C=C}$), 340 (sh), 332, 317 (ν_{Pt-Cl}). MS (FAB +) [m/z, (%)]: 303 (100%) [$(Ph_3PCH_2CHCH_2)^+$]. MS (FAB −) [m/z, (%)]: 301 (100%) [$(PtCl_3)^-$]. ^1H NMR (CD_2Cl_2): δ (ppm), 7.91−7.60 (m, 15H, Ph), 4.77 (m, 1H, $=CH$), 4.39−4.25 (m, 3H, CH_2P + $=CH_2$), 4.00 (m, 1H, $=CH_2$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 18.34 ($J_{Pt-P} = 156.1$ Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2): 136.12 (d, C_{para}, $^4J_{P-C} = 2.5$ Hz), 134.23 (d, C_{meta}, $^3J_{P-C} = 9.9$ Hz), 131.17 (d, C_{ortho}, $^2J_{P-C} = 12.7$ Hz), 117.47 (d, C_{ipso}, $^1J_{P-C} = 86.0$ Hz), 68.95 (s, $=CH$, $^1J_{Pt-C} = 217$ Hz), 67.52 (d, $=CH_2$, $^3J_{P-C} = 4.6$ Hz, $^1J_{Pt-C} = 193$ Hz), 27.35 (d, PCH_2, $^1J_{P-C} = 48$ Hz).

Isomerization of the Allyl-phosphonium salt $[Ph_3PCH_2CH{=}CH_2]Br$. Synthesis of the Vinyl-phosphonium E-$[Ph_3PCH{=}CHMe]Br$, 6. The allyl-phosphonium salt $[Ph_3PCH_2CH{=}CH_2]Br$ (0.223 g, 0.58 mmol) was refluxed in 2-methoxyethanol (10 mL) for 22 h. The resulting solution was evaporated to a small volume (ca. 2 mL) and Et_2O was added, giving **6** as a white solid, which was filtered and air-dried. Obtained: 0.193 g (87% yield). ^1H NMR ($CDCl_3$): δ (ppm), 7.79−7.54 (m, 15H, Ph), 7.50 (ddq, 1H, $PC(H){=}$, $^2J_{P-H} = 22.2$ Hz, $^3J_{H-H} = 16.5$ Hz, $^4J_{H-Me} = 1.5$ Hz), 6.55 (ddq, 1H, $=C(H)Me$, $^3J_{P-H} = 21.9$ Hz, $^3J_{H-H} = 16.5$ Hz, $^3J_{H-Me} = 6.6$ Hz), 2.25 (ddd, 3H, $=C(H)Me$, $^3J_{H-Me} = 6.6$ Hz, $^4J_{P-H} = 2.1$ Hz, $^4J_{H-Me} = 1.5$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 18.62 (s). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 159.77 (d, $=C(H)Me$), $^2J_{P-C} = 2.2$ Hz), 135.29 (d, C_{para}, PPh_3, $^4J_{P-C} = 2.5$ Hz), 133.87 (d, C_{meta}, PPh_3, $^3J_{P-C} = 10.5$ Hz), 130.53 (d, C_{ortho}, PPh_3, $^2J_{P-C} = 12.9$ Hz), 118.11 (d, C_{ipso}, PPh_3, $^1J_{P-C} = 90.8$ Hz), 110.25 (d, $PC(H)$, $^1J_{P-C} = 86.5$ Hz), 21.89 (d, $=C(H)Me$, $^3J_{P-C} = 19.4$ Hz).

Other Attempted Isomerizations of Allyl-phosphonium Salts. The allyl-phosphonium salt $[Ph_3PCH_2CH{=}CH_2]ClO_4$ was refluxed in 2-methoxyethanol (10 mL) for 22 h. The resulting solution was evaporated to a small volume (ca. 2 mL) and Et_2O was added, giving a white solid. The NMR spectra of this solid show the presence of the allyl and vinyl phosphoniums in a molar ratio (allyl:vinyl) = 1.88:1.

$[Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}E\text{-}\eta^2\text{-}C(H){=}C(H)Et)Cl_2]$, 7. Complex **7** was obtained following the same experimental method as that described for **4a**: $PtCl_2$ (0.250 g, 0.94 mmol) and $[Ph_3PCH_2CH{=}CHMe]Br$ (0.373 g, 0.94 mmol) were refluxed in 2-methoxyethanol (20 mL) for 22 h, giving **7** as a white solid, which was filtered, washed with Et_2O (20 mL), and dried in vacuo. Obtained: 0.121 g (22% yield). White crystals of **7** can be obtained by crystallization from CH_2Cl_2/Et_2O. These crystals contain dichloromethane of crystallization, as can be observed in the ^1H NMR. Anal. Calcd for $C_{22}H_{21}Cl_2PPt\cdot 2CH_2Cl_2$: C, 38.32; H, 3.35. Found: C, 38.66; H, 3.10. IR (ν, cm^{-1}): 1589, 1569, 1546 ($\nu_{C=C}$), 315, 278 (ν_{Pt-Cl}). MS (FAB +) [m/z, (%)]: 548 (40%) [$(M - Cl)^+$], 509 (75%) [$(M - 2Cl - H)^+$]. ^1H NMR ($CDCl_3$): δ (ppm), 8.18 (dd, 1H, H_6, $^3J_{H6-H5} = 7.5$ Hz, $^4J_{H6-H4} = 3.0$ Hz, $^3J_{Pt-H6} = 36$ Hz), 7.91−7.50 (m, 10H, Ph), 7.36 (tt, 1H, H_5, $^3J_{H5-H6} = {}^3J_{H5-H4} = 7.5$ Hz, $^4J_{H5-H3} \cong {}^5J_{P-H5} = 0.9$ Hz), 7.15 (m, 2H, H_3 + H_4), 4.61 (dd, 1H, $=C(H)P$, $^3J_{H-H} = 13.5$ Hz, $^2J_{P-H} = 17.1$ Hz), 4.53 (m, 1H, $=C(H)Et$), 2.47 (m, 1H, $=C(H)CH_2CH_3$), 1.95 (m, 1H, $=C(H)CH_2CH_3$), 1.21 (t, 3H, $=C(H)CH_2CH_3$, $^3J_{H-H} = 7.2$ Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 25.42 ($^3J_{Pt-P} = 45.8$ Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 146.11 (d, C_1, C_6H_4, $^2J_{P-C} = 16.4$ Hz), 137.18 (d, C_4, C_6H_4, $^3J_{P-C} = 14.1$ Hz), 134.95 (s, C_{para}, Ph), 134.65 (d, C_{para}, Ph, $^4J_{P-C} = 2.3$ Hz), 133.07 (d, C_{meta}, Ph, $^3J_{P-C} = 10.5$ Hz), 132.95 (s, C_5, C_6H_4), 132.80 (d, C_{meta}, Ph, $^3J_{P-C} = 10.4$ Hz), 132.00 (d, C_6, C_6H_4, $^3J_{P-C} = 15.2$ Hz), 130.30 (d, 2 C_{ortho}, Ph, $^2J_{P-C} = 11.8$ Hz), 126.41 (d, C_3, C_6H_4, $^2J_{P-C} = 13.4$ Hz), 124.70 (d, C_2, C_6H_4, $^1J_{P-C} = 106.3$ Hz), 121.35 (d, C_{ipso}, Ph, $^1J_{P-C} = 97.4$ Hz), 120.23 (d, C_{ipso}, Ph, $^1J_{P-C} = 114.8$ Hz), 86.87 (s, $=CHEt$, $^1J_{Pt-C} = 233.5$ Hz), 55.67 (d, $=C(H)P$, $^1J_{P-C} = 77.4$ Hz, $^1J_{Pt-C} = 235.2$ Hz), 28.58 (d, $=C(H)CH_2CH_3$, $^3J_{P-C} = 9.3$ Hz), 13.47 (s, $=C(H)CH_2CH_3$).

$[PtCl_3(\eta^2\text{-}PhCH{=}CH{-}CH_2PPh_3)]$, 8, and $[Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}E\text{-}C(H){=}C(H)CH_2Ph)Cl_2]$, 9. To a suspension of $PtCl_2$ (0.250 g, 0.94 mmol) in 2-methoxyethanol (20 mL) was added $[Ph_3PCH_2CH{=}CHPh]Cl$ (0.389 g, 0.94 mmol), and this mixture was refluxed for 22 h. The resulting suspension was cooled, and the green precipitate was filtered. This green solid was recrystallized from CH_2Cl_2/Et_2O, giving **8** as a deep yellow solid. Obtained: 0.200 g (31.2% yield based on Pt). The alcoholic mother liquor was evaporated to dryness, and the oily residue was washed with water (3 × 10 mL), to eliminate some remaining starting phosphonium salt. The residue was redissolved in 5 mL of CH_2Cl_2, dried with $MgSO_4$, evaporated to dryness, and treated with Et_2O (20 mL), giving **9** as a white solid. Obtained: 0.342 g (56.5% yield based on Pt). White crystals of **9**·$0.3CH_2Cl_2$, obtained by recrystallization of **9** from CH_2Cl_2/Et_2O, were used for analytical and spectroscopic measurements.

Compound 8. Anal. Calcd for $C_{27}H_{24}Cl_3PPt$: C, 47.63; H, 3.55. Found: C, 47.23; H, 3.59. IR (ν, cm^{-1}): 1588 ($\nu_{C=C}$), 330, 327, 312 (ν_{Pt-Cl}). MS (FAB +) [m/z, (%)]: 379 (100%) [$(Ph_3PCH_2CHCHPh)^+$]. (FAB −) [m/z, (%)]: 301 (100%) [$PtCl_3^-$]. ^1H NMR (CD_2Cl_2): δ (ppm), 7.87−7.63 (m, 15H, PPh_3), 7.38−7.29 (m, 3H, Ph), 7.23−7.18 (m, 2H, Ph), 6.06 (dd, 1H, =C(H), $^3J_{H-H}$ = 12.6 Hz, $^4J_{P-H}$ = 0.9 Hz, J_{Pt-H} = 69.9 Hz), 5.29 (m, 1H, =C(H)), 4.43 (ddd, 1H, PCH_2, $^2J_{H-H}$ = 15.6 Hz, $^2J_{P-H}$ = 12.3 Hz, $^3J_{H-H}$ = 4.8 Hz), 4.10 (ddd, 1H, PCH_2, $^2J_{H-H}$ = 15.6 Hz, $^2J_{P-H}$ = 12.3 Hz, $^3J_{H-H}$ = 9.0 Hz). $^{31}P\{^1H\}$ NMR (CD_2Cl_2): δ (ppm), 18.37 ($^3J_{Pt-P}$ = 177.2 Hz). $^{13}C\{^1H\}$ NMR (CD_2Cl_2) (the C_{ipso} of the olefinic Ph group was not observed): δ (ppm), 137.51 (s, C_{para}, PPh_3), 135.61 (d, C_{meta}, PPh_3, $^3J_{P-C}$ = 9.9 Hz), 132.56 (d, C_{ortho}, PPh_3, $^2J_{P-C}$ = 12.6 Hz), 130.77 (s, C_{meta}, Ph), 130.54 (s, C_{para}, Ph), 130.37 (s, C_{ortho}, Ph), 118.94 (d, C_{ipso}, PPh_3, $^1J_{P-C}$ = 85.6 Hz), 87.83 (d, =CH, $^2J_{P-C}$ = 5.2 Hz), 61.52 (d, =C(H), $^3J_{P-C}$ = 1.8 Hz, $^1J_{Pt-C}$ = 226.4 Hz), 28.41 (d, CH_2P, $^1J_{P-C}$ = 45.8 Hz).

Compound 9. Anal. Calcd for $C_{27}H_{23}Cl_2PPt \cdot 0.3CH_2Cl_2$: C, 48.94; H, 3.55. Found: C, 48.81; H, 3.74. IR (ν, cm^{-1}): 1588, 1571, 1547 ($\nu_{C=C}$), 323, 278 (ν_{Pt-Cl}). MS (FAB +) [m/z, (%)]: 573 (15%) [$(M - 2Cl-H)^+$]. ^1H NMR ($CDCl_3$): δ (ppm), 8.18 (ddd, 1H, H_6, $^3J_{H6-H5}$ = 7.8 Hz, $^4J_{H6-H4}$ = 3.3 Hz, $^4J_{P-H6}$ = 0.3 Hz, $^3J_{Pt-H6}$ = 37.8 Hz), 7.82−6.93 (m, 18H, $PPh_2 + C_6H_4$ + Ph), 4.68 (dd, 1H, =C(*H*)P, $^3J_{H-H}$ = 16.5 Hz, $^2J_{P-H}$ = 11.7 Hz, $^2J_{Pt-H}$ = 58.8 Hz), 4.56 (m, 1H, =C(*H*)CH_2Ph), 3.76 (dd, 1H, =C(H)CH_2Ph, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 9.6 Hz), 3.67 (dd, 1H, =C(H)CH_2Ph, $^2J_{H-H}$ = 13.8 Hz, $^3J_{H-H}$ = 4.5 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 26.79 ($^3J_{Pt-P}$ = 35.6 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (two quaternary C atoms of the C_6H_4 ring were not found, probably because of overlapping): δ (ppm), 145.78 (d, C_1, C_6H_4, $^2J_{P-C}$ = 16.3 Hz), 137.42 (s, C_{ipso}, Ph), 137.07 (d, C_6H_4, J_{P-C} = 14.0 Hz), 135.57 (s, C_{para}, PPh_2), 135.52 (s, C_{para}, PPh_2), 133.90 (d, C_{meta}, PPh_2, $^3J_{P-C}$ = 10.7 Hz), 132.66 (d, C_{meta}, PPh_2, $^3J_{P-C}$ = 10.4 Hz), 131.09 (d, C_6H_4, J_{P-C} = 15.1 Hz), 130.55 (d, C_{ortho}, PPh_2, $^2J_{P-C}$ = 12.6 Hz), 130.28 (d, C_{ortho}, PPh_2, $^2J_{P-C}$ = 12.7 Hz), 127.14 (s, C_{ortho}, Ph), 126.64 (s, C_{para}, Ph), 126.51 (s, C_{meta}, Ph), 124.33 (d, C_2, C_6H_4, $^1J_{P-C}$ = 106.3 Hz), 120.51 (d, C_{ipso}, PPh_2, $^1J_{P-C}$ = 76.4 Hz), 120.02 (d, C_{ipso}, PPh_2, $^1J_{P-C}$ = 92.7 Hz), 82.85 (s, =*C*HCH_2Ph, $^1J_{Pt-C}$ = 237.2 Hz), 55.25 (d, =*C*(H)P, $^1J_{P-C}$ = 77.1 Hz, $^1J_{Pt-C}$ = 255.6 Hz), 41.21 (d, =CH*C*H_2Ph, $^3J_{P-C}$ = 8.9 Hz).

[Pt(*C*$_6$H$_4$-2-PPh$_2$-η^2-*C*(H)=*C*Me$_2$)Cl$_2$], 10, and [Ph$_3$PC(H)=CMe$_2$]Cl, 11. Following the same experimental method as that described for **4a**, $PtCl_2$ (0.250 g, 0.939 mmol) and [$Ph_3PCH_2C(Me)=CH_2$]Cl (0.331 g, 0.939 mmol) were reacted in refluxing 2-methoxyethanol (15 mL) for 22 h to give 0.220 g of a mixture of the organometallic compound **10** and the vinylphosphonium salt **11** in 1:2.1 molar ratio (see text).

Compound 10. ^1H NMR ($CDCl_3$): δ (ppm), 8.12 (ddt, 1H, H_6, $^3J_{H6-H5}$ = 7.8 Hz, $^4J_{H6-H4}$ = 3.0 Hz, $^4J_{P-H6}$ = $^5J_{H6-H3}$ = 0.9 Hz, $^3J_{Pt-H6}$ = 46.8 Hz), 7.93−7.53 (m, 10H, PPh_2), 7.36−7.29 (m, 1H, C_6H_4), 7.21−7.17 (m, 2H, C_6H_4), 4.63 (d, 1H, =C(*H*)P, $^2J_{P-H}$ = 15.6 Hz, $^2J_{Pt-H}$ = 68.7 Hz), 2.02 (s, 3H, =CMe_2, $^3J_{Pt-H}$ = 36.0 Hz), 1.28 (s, 3H, =CMe_2, $^3J_{Pt-H}$ = 51.6 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 23.35 ($^3J_{Pt-P}$ = 45.1 Hz). $^{13}C\{^1H\}$ NMR ($CDCl_3$) (two carbon atoms of the C_6H_4 group were not found): δ (ppm), 147.60 (d, C_1, C_6H_4, $^2J_{P-C}$ = 18.3 Hz), 136.99 (d, C_6H_4, J_{P-C} = 14.6 Hz), 134.97 (s, C_{para}, PPh_2), 134.46 (d, C_{para}, PPh_2, $^4J_{P-C}$ = 2.6 Hz), 133.19 (d, C_{meta}, PPh_2, $^3J_{P-C}$ = 10.9 Hz), 132.80 (d, C_{meta}, PPh_2, $^3J_{P-C}$ = 10.3 Hz), 130.45 (d, C_{ortho}, PPh_2, $^2J_{P-C}$ = 13.4 Hz), 130.27 (d, C_{ortho}, PPh_2, $^2J_{P-C}$ = 13.7 Hz), 127.34 (d, C_2, C_6H_4, $^1J_{P-C}$ = 105.9 Hz), 126.09 (d, C_6H_4, J_{P-C} = 13.6 Hz), 121.95 (d, C_{ipso}, PPh_2, $^1J_{P-C}$ = 92.6 Hz), 120.37 (d, C_{ipso}, PPh_2, $^1J_{P-C}$ = 75.9 Hz), 101.36 (s, =*C*Me_2), 58.56 (d, =*C*(H)P, $^1J_{P-C}$ = 79.2 Hz), 33.08 (d, =C*Me*$_2$, $^3J_{P-C}$ = 10.7 Hz), 28.35 (d, =C*Me*$_2$, $^3J_{P-C}$ = 3.4 Hz).

Compound 11. Anal. Calcd for $C_{22}H_{22}ClP$: C, 74.89; H, 6.28. Found: C, 74.81; H, 6.47. IR (ν, cm^{-1}): 1621, 1587 ($\nu_{C=C}$). MS (FAB +) [m/z, (%)]: 317 (100%) [$M - Cl^+$]. ^1H NMR ($CDCl_3$): δ (ppm), 7.81−7.53 (m, 15H, PPh_3), 6.20 (d, 1H, =C(*H*)P, $^2J_{P-H}$ = 22.8 Hz), 2.36 (s, 3H, Me-*cis*-to-P), 1.72 (dd, 3H, Me-*trans*-to-P, $^4J_{P-H}$ = 2.4 Hz). $^{31}P\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 11.38. $^{13}C\{^1H\}$ NMR ($CDCl_3$): δ (ppm), 172.62 (s, =*C*Me_2), 135.15 (d, C_{para}, PPh_3, $^4J_{P-C}$ = 2.2 Hz), 133.42 (d, C_{meta}, PPh_3, $^3J_{P-C}$ = 10.6 Hz), 130.78 (d, C_{ortho}, PPh_3, $^2J_{P-C}$ = 12.8 Hz), 119.34 (d, C_{ipso}, PPh_3, $^1J_{P-C}$ = 89.8 Hz), 103.13 (d, =*C*(H)P, $^1J_{P-C}$ = 89.6 Hz), 30.26 (d, Me-*trans*-to-P, $^3J_{P-C}$ = 18.2 Hz), 24.95 (d, Me-*cis*-to-P, $^3J_{P-C}$ = 7.6 Hz).

Isomerization of [Ph$_3$PCH$_2$C(Me)=CH$_2$]Cl. Synthesis of [Ph$_3$PCH=CMe$_2$]Cl, 11. The allyl-phosphonium salt [$Ph_3PCH_2CMe=CH_2$]Cl (0.200 g, 0.567 mmol) was refluxed in 2-methoxyethanol (10 mL) for 22 h. The resulting solution was evaporated to a small volume (ca. 2 mL) and Et_2O was added, giving **11** as a white solid, which was filtered and air-dried. Obtained: 0.180 g (90% yield).

Crystal Structure Determination of 4a·CH$_2$Cl$_2$ and 8. Crystals of complexes **4a**·CH_2Cl_2 and **8** of adequate quality for X-ray measurements were obtained by slow vapor condensation of Et_2O over a CH_2Cl_2 solution of the corresponding crude complex (**4a** or **8**). Each crystal was mounted at the end of a quartz fiber and covered with epoxy.

Data Collection for 4a·CH$_2$Cl$_2$. Geometric and intensity data were measured using normal procedures on an automated Nonius CAD-4 four-circle diffractometer. After preliminary indexing and transformation of the cell to a conventional setting, axial photographs were taken of the *a*-, *b*- and *c*-axes to verify the Laue symmetry and cell dimensions. The scan parameters for intensity data collection were chosen on the basis of two-dimensional ($\omega-\theta$) plots of 25 reflections. Three monitor reflections were measured after every 3 h of beam time, and the orientation of the crystal was checked after every 400 intensity measurements. Absorption corrections[21] were based on azimuthal scans of 14 reflections which had Eulerian angles χ spread between 50° and −40° when in their bisecting positions. Accurate unit cell dimensions were determined from 25 centered reflections in the 2θ range $27.3° \leq 2\theta \leq 30.9°$, each centered at four distinct goniometer positions.

Data Collection for 8. A single crystal of dimensions 0.32 × 0.22 × 0.13 mm was mounted on a glass fiber in a random orientation. Data collection was performed at room temperature on a Bruker Smart CCD diffractometer using graphite-monocromated Mo Kα radiation (λ = 0.71073 Å) with a nominal crystal-to-detector distance of 4.0 cm. A hemisphere of data was collected based on three ω-scan runs (starting ω = −30°) at values ϕ = 0°, 90°, and 180° with the detector at 2θ = 30°. For each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 20 s per frame. The diffraction frames were integrated using the program SAINT,[22] and the integrated intensities were corrected for absorption with SADABS.[23]

Structure Solution and Refinement. The structures were solved and developed by Patterson and Fourier meth-

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(21) Absorption corrections and molecular graphics were done using the commercial package: *SHELXTL-PLUS*, Release 5.05/V; Siemens Analytical X-ray Instruments, Inc.: Madison, WI, 1996.

(22) *SAINT* Version 5.0; Bruker Analytical X-ray Systems, Madison, WI, 1996.

(23) Sheldrick, G. M. *SADABS*: Empirical absorption correction program; University of Gottingen, 1996.

ods.[24] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in idealized positions and treated as riding atoms, except for those of the methyl groups, which were first located in a local slant-Fourier calculation and then refined as riding atoms with the torsion angles about the C−C(methyl) bonds treated as variables. Each hydrogen atom was assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. For complex **8** the chlorine atoms Cl1 and Cl3 are disordered over two positions, with relative populations 95% and 5%. The major congener was refined with anisotropic displacement parameters and the minor one with isotropic displacement parameters. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[25] Crystallographic calculations were done on an AlphaStation (OPEN/VMS V6.2). Data reduction for **4a**·CH_2Cl_2 was done by the program XCAD4B.[26]

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Supporting Information Available: Tables giving complete data collection parameters, atomic coordinates, complete bond distances and angles, and thermal parameters for **4a**·CH_2Cl_2 and **8**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(24) Sheldrick, G. M. SHELXS-86. *Acta Crystallogr.* **1990**, *A46*, 467.

(25) Sheldrick, G. M. *SHELXL-97*: FORTRAN program for the refinement of crystal structures from diffraction data; Göttingen University, 1997.

(26) Harms, K. Private communication, 1995.