Organometallics **2003,** *22,* 4910−4921

C−P and C−H Bond Activations and C−C Coupling in Bis-Phosphonium Salts Induced by Platinum(II) Complexes

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Received July 26, 2003

The reaction of $[Ph_3PCH_2\text{-}(E)\text{-}C(Me){=}C(H)PPh_3]Cl_2$ (**1b**) with $PtCl_2(NCPh)_2$ (1:1 molar ratio) in refluxing 2-methoxyethanol gives the ortho-metalated complex $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2PPh_2\text{-}\kappa C,C,P)Cl]$ (**3**). The synthesis of complex **3** formally involves three C−H and one C−P bond activation and one C−C bond coupling. Complex **3** reacts with excess KBr or NaI to give, after halide metathesis, the complexes $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2PPh_2\text{-}\kappa C,C,P)X]$ (X = Br (**4**), I (**5**)). Complex **5** has been characterized by X-ray diffraction methods. The influences of several factors, such as the solvent, the platinum starting complex, and the bis-phosphonium salt, in the synthesis of **3** have been examined, and a plausible reaction mechanism for the synthesis of **3** is proposed. This mechanism is supported by the isolation of the Pt(IV) derivative $[Pt(C_6H_4\text{-}4\text{-}F)\{C_6H_3\text{-}5\text{-}F\text{-}2\text{-}P(p\text{-}FC_6H_4)_2\text{-}C{=}C(Me)CH_2P(p\text{-}FC_6H_4)_2\text{-}\kappa C,C,P\}Cl_2]$ (**6**), obtained by reaction of $[(p\text{-}FC_6H_4)_3PCH_2\text{-}(E)\text{-}C(Me){=}C(H)P(p\text{-}FC_6H_4)_3]Cl_2$ (**1f**) with $PtCl_2(NCPh)_2$ in refluxing 2-methoxyethanol. Complex **3** reacts with $AgClO_4$ and neutral monodentate (L) and bidentate (L−L) ligands, giving the cationic derivatives $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2PPh_2\text{-}\kappa C,C,P)(L)](ClO_4)$ (L = NCMe (**8**), PPh_3 (**9**), pyridine (**10**), $C{\equiv}N^tBu$ (**11**)) and $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2PPh_2\text{-}\kappa C,C,P)(L{-}L\text{-}\kappa P)](ClO_4)$ (L−L = $Ph_2PCH_2PPh_2$ (**12**)). Complex **3** reacts with excess X_2 (Cl_2, I_2) to give the expected Pt(IV) derivatives $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2PPh_2\text{-}\kappa C,C,P)(Cl)(X)_2]$ ($(X)_2$ = $(Cl)_2$ (**13**), $(I)_2$ (**14**)) through a typical oxidative addition process. Complex **14** has also been characterized by X-ray diffraction methods.

Introduction

The topic of C−H bond activation reactions promoted by Pt(II) complexes, as a key step in the functionalization of small molecules,[1] has undergone a continuous and impressive growth, due to its important implications. Representative examples are alkane[1,2] and arene[3] functionalization, the study of thermodynamic properties,[3i,4] the synthesis of complexes with interesting optical properties (e.g. luminiscence)[5] or structures,[6] and the preparation of chiral auxiliaries,[2d,3d,l,7] their involvement in C−C bond coupling reactions,[3b,m,n,8] or their critical role in catalytic cycles.[3c,m,4a]

We recently reported the cycloplatination of several types of bis-phosphonium salts.[9,10] The carbonyl bis-phosphonium salts $[R_2PhPCH_2C(O)CH_2PPhR_2](X)_2$ (R = Et, Ph; X = Cl, ClO_4) react with $PtCl_2(NCPh)_2$, giving ortho-metalated derivatives containing the C,C-chelating ligand $[C_6H_4\text{-}2\text{-}PR_2C(H)C(O)CH_2PR_2Ph]$[9,10] (see Figure 1A), while the allyl−phosphonium salts $[PhR_2PCH_2C(R'){=}C(H)R''](X)$ (R = Me, Ph; R′ = H, Me; R″ = H, Me, Ph; X = Cl, ClO_4) gave cycloplatinated

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10.1021/om0305465 CCC: $25.00
Publication on Web 10/23/2003

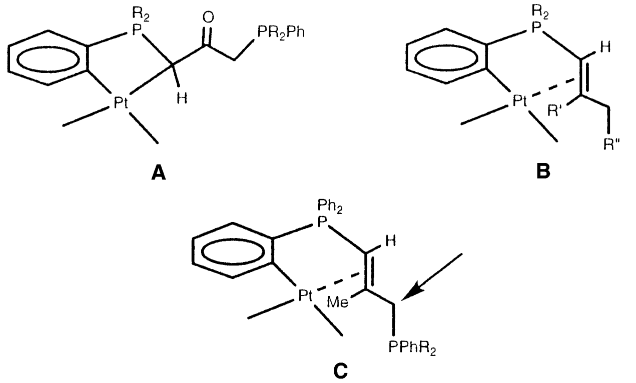


Figure 1.

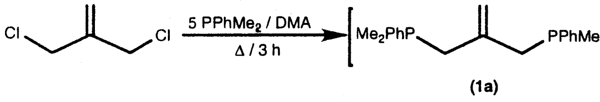
complexes (see Figure 1B) containing the σ,π-vinyl ligand C_6H_4-2-$PR_2C(H){=}C(R')CH_2R''$.[10]

When the reported reactivity is taken into account, it seems very likely that the presence of functional groups at the C_β or C_γ atoms of the allyl unit (R′ or R″) should give, after cycloplatination, complexes in which the functional groups still remain incorporated to the η^2-bonded vinylic skeleton. Due to our interest in the chemistry of ylides as ligands, we have chosen phosphonium units—precursor of ylides—as functional groups, since they could be new reactive points in the molecule. Aiming to obtain new metalated Pt(II) derivatives with an additional free phosphonium unit (Figure 1C), we have explored the synthesis of the bis-phosphonium salts $[H_2C{=}C(CH_2PPhR_2)_2](X)_2$ (R = Me, Ph; X = Cl, Br, ClO_4) and their reactivity toward Pt(II) complexes. In this paper we report the results obtained in this area.

Results and Discussion

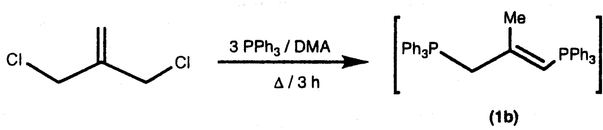
1. Synthesis of Bis-Phosphonium Salts. Linear and cyclic phosphonium salts of the type $[H_2C{=}C(CH_2\text{-}PPh_2R)_2](X)_2$ are known,[11] and they have been synthesized through quaternization of the two P atoms of $H_2C{=}C(CH_2PPh_2)_2$. We have recently reported[11e] the synthesis of a related cyclic derivative by reaction of $H_2C{=}C(CH_2Cl)_2$ with $Ph_2PCH_2PPh_2$ (dppm), a less complicated (and less expensive) method. We have thus attempted the synthesis of allyl bis-phosphonium salts through quaternization of a given phosphine by its reaction with the appropiate amount of 3-chloro-2-(chloromethyl)propene.

The reaction of $H_2C{=}C(CH_2Cl)_2$ with an excess of $PPhMe_2$ (1:5 molar ratio, refluxing *N*,*N*-dimethylacetamide (DMA)) gives the expected salt **1a** (see eq 1). The



(1)

NMR spectra of **1a** show a good agreement with the symmetrical proposed structure (see the Experimental Section). However, the reaction of $H_2C{=}C(CH_2Cl)_2$ with an excess of PPh_3 (1:3 molar ratio, refluxing DMA) gives a quite different result, since the allyl−vinyl bis-phosphonium salt $[Ph_3PCH_2\text{-}(E)\text{-}C(Me){=}C(H)PPh_3]Cl_2$ (**1b**) (see eq 2) is obtained. The $^{31}P\{^1H\}$ NMR spectrum



(2)

of **1b** shows two doublet signals, one at 22.98 ppm (PCH_2) and another at 11.06 ppm ($=CP$).[10] The ^1H NMR spectrum of **1b** shows a doublet of doublets at 8.05 ppm ($=CH$), a doublet at 5.87 ppm (CH_2P), and a triplet at 1.63 ppm (CH_3). The *E* configuration of **1b** is inferred from the $^{13}C\{^1H\}$ NMR spectrum, since the signal due to the CH_3 carbon appears at 24.67 ppm (dd, $^3J_{PC} = 7.0$ Hz, $^3J_{PC} = 0.9$ Hz) while the signal due to the CH_2 carbon appears at 35.02 ppm (dd, $^1J_{PC} = 46.5$ Hz, $^3J_{PC} = 19.6$ Hz). The value of $^3J_{PC}$ for the CH_2 carbon atom indicates clearly its trans arrangement with respect to the vinylic P atom. The comparison of these values with those reported for $[Ph_3PC(H){=}CMe_2]Cl$ is also in good agreement with the *E* configuration.[10,12]

Several methods have been reported for the synthesis of vinyl phosphonium salts, including processes catalyzed by Pd, Ti, or Rh complexes[12a,b,13] and electrochemical,[12c] stoichiometric (giving metalated species),[14] or

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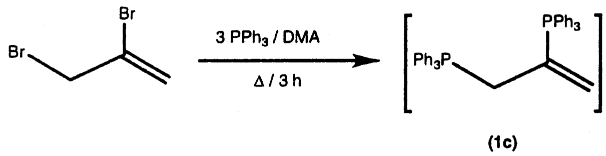
base-catalyzed processes.[10,15] Despite this, it is worth noting that the synthesis of **1b** can be performed in a single-step procedure, in the absence of catalysts or external base, giving a single isomer in quantitative yield.

Due to these facts, we have explored in more detail this easy synthesis of allyl–vinyl bis-phosphonium salts. The reaction of 2,3-dibromopropene with PPh_3 under the same experimental conditions as those described for **1b** gives $[Ph_3PCH_2C(PPh_3){=}CH_2]Br_2$ (**1c**) (see eq 3 and the Experimental Section), in accord with its analytic and spectroscopic data. The expected allyl–vinyl product is obtained in very good yield, as a result of the replacement of the two Br atoms by PPh_3 groups. We have not observed isomerization to the bis-vinyl species $[Ph_3PC(H){=}C(Me)PPh_3]Br_2$, even at prolonged reaction times (22 h reflux, DMA). Thus, the bromine atom can be replaced efficiently at the two positions (aliphatic and vinylic) without the need of a catalyst.[13a] When the starting dihalo derivative is 1,3-dichloropropene, its reaction with PPh_3 (under the same experimental conditions) gives $[Ph_3PCH_2$-(*E*)-$C(H){=}C(H)PPh_3]Cl_2$ (**1d**) (see eq 4 and the Experimental Section), although in low yield (34.7%). With the dibromo derivative as the starting material, the yield for the corresponding salt $[Ph_3PCH_2$-(*E*)-$C(H){=}C(H)PPh_3]Br_2$ (**1e**) (eq 4) improves notably (91%), due to the fact that the bromide anion is a better leaving group than the chloride. Compounds **1d** and **1e** show virtually identical NMR spectra, from which the *E* configuration can be inferred.[16] The presence of substituents on the phosphine aryl groups does not modify the type of bis-phosphonium salt obtained. The reaction of $H_2C{=}C(CH_2Cl)_2$ with $P(p\text{-}FC_6H_4)_3$ gives the expected $[(p\text{-}FC_6H_4)_3PCH_2$-(*E*)-$C(Me){=}C(H)P(p\text{-}FC_6H_4)_3]Cl_2$ (**1f**) (see eq 5 and the Experimental Section).



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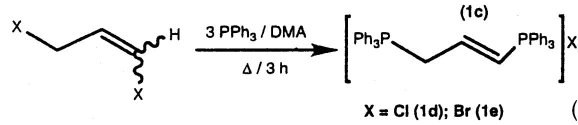

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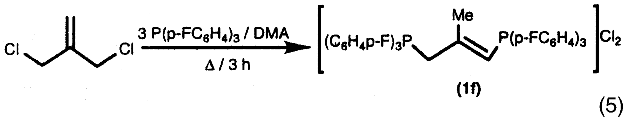


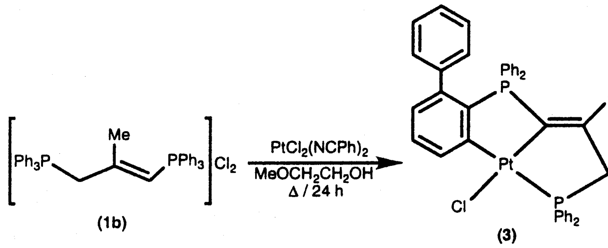
(5)

The salts **1a**–**f**, prepared without the need of a catalyst or other inductive processes, share a common characteristic, which is the presence of an allyl phosphonium unit possessing different substituents at different positions (Me, H, or PPh_3 at C_β; H or PPh_3 at C_γ; F at the para position of the Ph groups). Our purpose is now the study of the reactivity of these salts toward Pt(II) complexes, to obtain cycloplatinated derivatives with an additional phosphonium group.

2. Ortho-Metalation Reactions. The reaction of **1a** with $PtCl_2(NCPh)_2$ (1:1 molar ratio) in refluxing 2-methoxyethanol results in the formation of a solid identified as $[H_2C{=}C(CH_2PPhMe_2)_2][PtCl_4]$ (**2**) (see eq 6). The NMR data of **2** (see the Experimental Section) are quite similar to those described for **1a**. For instance, $\delta(P)$ in the $^{31}P\{^1H\}$ NMR spectrum for **1a** is 24.76 ppm and that of **2** is 26.61 ppm. Moreover, signals corresponding to the presence of the C_6H_5 groups in the ^1H NMR spectrum and the persistence of the olefinic and methylenic protons show that no ortho metalation has taken place. This reaction was not investigated further.

$$\mathbf{1a}\ \xrightarrow[\text{MeOCH}_2\text{CH}_2\text{OH},\ \Delta,\ 24\ \text{h}]{\text{PtCl}_2(\text{NCPh})_2}\ \underset{\mathbf{2}}{[H_2C{=}C(CH_2PPhMe_2)_2][PtCl_4]} \qquad (6)$$

The reaction of **1b** with $PtCl_2(NCPh)_2$ in refluxing 2-methoxyethanol gives a quite different result. After the reaction time (22 h), a pale yellow solid remained insoluble in the alcoholic media, which was identified as the cycloplatinated derivative $[Pt(C_6H_3$-3-Ph-2-$PPh_2C{=}C(Me)CH_2PPh_2$-$\kappa C,C,P)Cl]$ (**3**) (see eq 7). The synthesis of **3** formally involves three C–H bond activations (one at the vinylic position and two in two different phenyl rings), one P–C bond activation, and one C–C bond coupling. The chloride ligand in complex **3** can be easily replaced by bromide (**4**) or iodide anions (**5**) (see eq 8) by reaction of **3** with an excess of the corresponding halide salts. The crystallization of **5** from CH_2Cl_2/Et_2O affords crystals of adequate quality for X-ray purposes.



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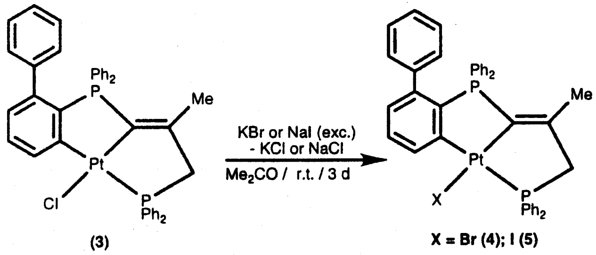

(8)

A drawing of the organometallic complex **5** is presented in Figure 2; some relevant parameters concerning the data acquisition and structure solution and refinement are given in Table 1, and selected bond distances and angles are collected in Table 2. The platinum atom is located in a distorted-square-planar environment, which is defined by the iodine atom I(1) and by the three donor atoms of the new ligand C_6H_3-3-Ph-2-PPh_2-*C*$=C(Me)CH_2$*P*Ph_2-$\kappa C,C,P$: the arylic car-

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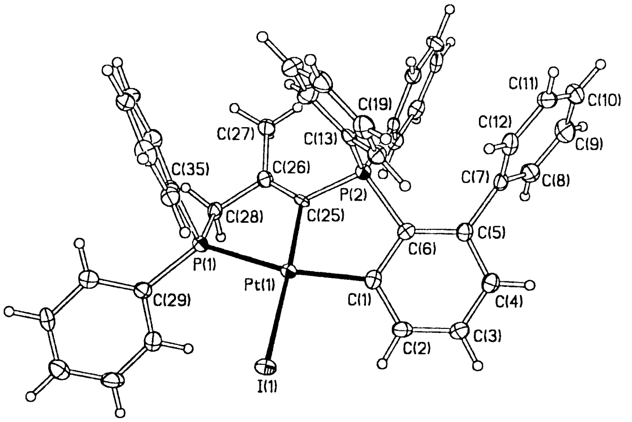

Figure 2.

Table 1. Crystal Data and Structure Refinement Details for 5 and 14·CHCl$_3$

	5	14·CHCl$_3$
empirical formula	$C_{40}H_{33}IP_2Pt$	$C_{41}H_{34}Cl_4I_2P_2Pt$
formula wt	897.59	1179.31
T (K)	100(2)	100(2)
λ, Å	0.71073	0.71073
cryst syst	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$
a, Å	9.8225(16)	9.9831(9)
b, Å	13.373(2)	12.2541(11)
c, Å	14.254(2)	17.9378(16)
α, deg	65.30(3)	72.174(1)
β, deg	76.17(3)	88.082(2)
γ, deg	72.61(3)	72.854(1)
V, Å^3	1609.2(4)	1992.3(3)
Z	2	2
ρ_{calcd}, Mg/m^3	1.852	1.966
μ, mm^{-1}	5.448	5.449
F(000)	868	1124
θ range for data collecn, deg	1.59−25.07	2.14−25.03
no. of rflns collected	15 791	10 852
no. of indep rflns	5681 (R_{int} = 0.0347)	6935 (R_{int} = 0.0232)
no. of data/restraints/params	5681/0/398	6935/0/452
goodness of fit on F^2 [a]	0.957	0.995
final R indices ($I > 2\sigma(I)$)[a]	R1 = 0.0263 wR2 = 0.0519	R1 = 0.0430 wR2 = 0.1268
R indices (all data)[a]	R1 = 0.0304 wR2 = 0.0528	0.0561 wR2 = 0.1325
largest diff peak, hole, e Å^{-3}	1.161, −0.741	2.414, −1.939

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

Table 2. Selected Bond Lengths (Å) and Angles (deg) for 5

Pt(1)−C(25)	2.010(4)	Pt(1)−C(1)	2.042(4)
Pt(1)−P(1)	2.2697(13)	Pt(1)−I(1)	2.6628(9)
P(1)−C(35)	1.805(4)	P(1)−C(29)	1.810(5)
P(1)−C(28)	1.832(4)	P(2)−C(25)	1.759(4)
P(2)−C(6)	1.793(4)	P(2)−C(13)	1.798(4)
P(2)−C(19)	1.805(4)	C(1)−C(2)	1.392(6)
C(1)−C(6)	1.420(6)	C(2)−C(3)	1.378(6)
C(3)−C(4)	1.375(6)	C(4)−C(5)	1.395(6)
C(5)−C(6)	1.401(6)	C(5)−C(7)	1.492(6)
C(7)−C(8)	1.389(6)	C(7)−C(12)	1.392(6)
C(8)−C(9)	1.355(6)	C(9)−C(10)	1.378(6)
C(10)−C(11)	1.368(6)	C(11)−C(12)	1.370(6)
C(25)−C(26)	1.348(6)	C(26)−C(27)	1.497(6)
C(26)−C(28)	1.509(6)		
C(25)−Pt(1)−C(1)	86.05(17)	C(25)−Pt(1)−P(1)	79.31(13)
C(1)−Pt(1)−P(1)	164.99(12)	C(25)−Pt(1)−I(1)	175.98(12)
C(1)−Pt(1)−I(1)	96.31(12)	P(1)−Pt(1)−I(1)	98.50(4)
C(35)−P(1)−C(29)	103.6(2)	C(35)−P(1)−C(28)	104.2(2)
C(29)−P(1)−C(28)	110.5(2)	C(35)−P(1)−Pt(1)	114.63(15)
C(29)−P(1)−Pt(1)	123.92(15)	C(28)−P(1)−Pt(1)	98.47(14)
C(25)−P(2)−C(6)	102.5(2)	C(25)−P(2)−C(13)	107.3(2)
C(6)−P(2)−C(13)	110.3(2)	C(25)−P(2)−C(19)	114.8(2)
C(6)−P(2)−C(19)	111.8(2)	C(13)−P(2)−C(19)	109.8(2)
C(26)−C(25)−P(2)	129.4(3)	C(26)−C(25)−Pt(1)	122.9(3)
P(2)−C(25)−Pt(1)	106.7(2)	C(25)−C(26)−C(27)	128.3(4)
C(25)−C(26)−C(28)	116.0(4)	C(27)−C(26)−C(28)	115.6(4)
C(26)−C(28)−P(1)	103.7(3)		

bon C(1), the vinylic carbon C(25), and the phosphorus P(1) of the terminal PPh$_2$ group. The Pt(1)−I(1) bond distance (2.6628(9) Å) falls in the range of bond distances usually reported for this type of bond.[17]

The most remarkable feature of this structure is the dramatic transformation undergone by the bis-phosphonium salt **1b** after reaction with the Pt(II) metallic center: (i) one of the PPh$_3$ groups has been cleaved into a PPh$_2$ fragment (Pt bonded) and a phenyl ring; (ii) one phenyl of the other PPh$_3$ group has been metalated, and moreover, it has been transformed into a σ-bonded biphenyl moiety due to C−C coupling with the phenyl fragment formed in (i); (iii) the vinylic C−H bond has also been activated, and a new Pt−C bond is formed. The description of the bonding of the C_6H_3-3-Ph-2-PPh$_2$-C=C(Me)CH$_2$$PPh_2$-$\kappa C,C,P$ ligand merits some comments. The Pt(1)−C(1) bond distance (2.042(4) Å) is longer than that found in the closely related complex [Pt(C$_6$H$_4$-2-PPh$_2$-(E)-η^2-C(H)=C(H)Me)Cl$_2$][10] (1.997(9) Å, C−*trans*-Cl) due to the higher trans influence of the P atom with respect to the Cl atom. On the other hand, the Pt(1)−C(1) and the Pt(1)−P(1) bond distances (2.2697(13) Å) are typical for the C$_{aryl}$−*trans*-P arrangement in Pt(II) complexes.[17a,e−i] The Pt−C(25) bond distance (2.010(4) Å) is similar, within experimental error, to that found in the vinyl derivative *trans*-[Pt(CH=CMe$_2$)(I)(PPh$_3$)$_2$] (2.032(7) Å).[17d] The P(2)−C(25) bond distance (1.759(4) Å) is shorter than the other P−C bond distances involving P(2), and this fact has been observed in other metalated vinyl phosphonium systems.[18] All bond distances within the rings C(1)−C(6) and C(7)−C(12) are typical for Ph groups, and the C(5)−C(7) bond distance (1.492(6) Å) shows clearly that it is a single σ(C−C) bond.[19] The bond distances C(26)−C(27) (1.497(6) Å) and C(26)−C(28) (1.509(6) Å) are also single C−C bonds, while the C(25)−C(26) bond distance (1.348(6) Å) indicates a double bond.[19] The dihedral angle between the best least-squares planes defined by the Ph rings C(1)−(C6) and C(7)−C(12) is 65.0(4)°.

The analytical data of complexes **3**−**5** are in good agreement with the proposed stoichiometries, and their mass spectra show in each case the molecular peak with the correct isotopic distribution. The ^{1}H NMR spectra

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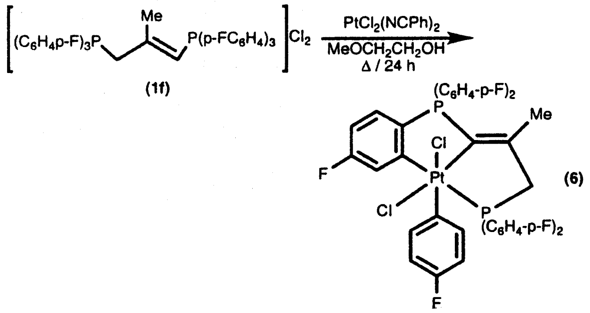
of **3**−**5** show the same pattern of signals, with logical differences arising from the presence of the ligands Cl^-, Br^-, and I^-. Key features of the ^1H NMR spectra are (i) the presence of a multiplet signal at the lowest field, attributed to the H(6) proton (ortho to the metalated position) showing ^{195}Pt satellites, (ii) the position of this peak varying as a function of the X ligand (8.77 ppm (**3**), 8.83 ppm (**4**), and 9.09 ppm (**5**)), suggesting a weak, but perceptible, contact between X and H(6), (iii) the similarity of the coupling constant $^3J_{Pt-H(6)}$ (ranging from 41.4 to 45.9 Hz) with that reported for related cycloplatinated derivatives (42 Hz),[10] and (iv) the observation of four signals (relative intensity 1:1:2:2) in the aromatic region, due to the H_4 proton and to the C_6H_5 group at the 3-position of the metalated ring. The $^{31}P\{^1H\}$ NMR spectra of **3**−**5** show also common features. They show two doublet signals ($^3J_{PP}$ about 25 Hz) with ^{195}Pt satellites each. The signals at lowest field appear almost at the same frequency (34.14 ppm (**3**), 34.16 ppm (**4**), and 34.29 ppm (**5**)), show values of the coupling constant $^2J_{PtP}$ at about 590 Hz, and are attributed to the P atom in the metalated ring. The value of $^2J_{PtP}$ is similar to those reported for structurally related systems.[20] The signals at highest field are assigned to the Pt-bonded PPh_2 group and show values of the coupling constant $^1J_{PtP}$ consistent with their structures, and their positions also change as the halide changes (25.48 ppm (**3**), 26.53 (**4**), and 27.61 ppm (**5**)). The ^{195}Pt NMR spectra of **3** and **5** show the expected doublets of doublets at −5774.3 ppm (**3**) and −6000.0 ppm (**5**). Both signals appear in the usual range of frequencies reported for other Pt(II) complexes,[17f−i,21] that of **5** being slightly shifted to high field with respect to that of **3**. The substitution of the Cl^- by the I^- ligand accounts for the shielding of the metal center.[22] Finally, the $^{13}C\{^1H\}$ NMR spectra of **3** and **5** show the expected peaks of the tridentate-C,C,P ligand. The signals due to the ortho-metalated carbon atom C(1) appear at very low field (about 174 ppm, dd) and show $^2J_{PC}$ coupling constants in keeping with the C−*trans*-P arrangment (126.0 Hz (**3**), 124.8 Hz (**5**)). Other resonances attributed to the C_6H_3 unit (except that of C(3)) are clearly seen. The peaks due to the vinylic carbon atoms appear at about 154 ppm (C_β) and 145 ppm (C_α), and those corresponding to the phenyl group at the 3-position of the metalated ring are observed at about 141 ppm (C(1′)) and in the range 129−126 ppm (C(2′)−C(4′)).

The presence of different substituents in the phosphonium salts induces notable changes in the reactivity. The reaction of **1c** with $PtCl_2(NCPh)_2$ gives a mixture of $PtCl_2(PPh_3)_2$, $PtClBr(PPh_3)_2$, and $PtBr_2(PPh_3)_2$, as a result of the complete cleavage of the Ph_3P-C bonds. The same result applies for the reaction of **1d** or **1e**, despite the similarity of their structures with that of **1b**. Given these results, these reactions were not further investigated. The presence of substituents in the aryl groups has also been considered. The reaction of **1f** with $PtCl_2(NCPh)_2$ affords the Pt(IV) complex $[Pt(C_6H_4\text{-}4\text{-}F)\{C_6H_3\text{-}5\text{-}F\text{-}2\text{-}P(p\text{-}FC_6H_4)_2\text{-}C{=}C(Me)CH_2P(p\text{-}FC_6H_4)_2\text{-}\kappa C,C,P\}Cl_2]$ (**6**) (see eq 9 and the Experimental Section).



(9)

The complete characterization of complex (**6**) shows relevant features.

The presence of two cis chloride ligands in **6** can be inferred from the observation in the IR spectrum of two absorptions at 285 and 270 cm^{-1}. The mass spectrum (positive FAB) shows the presence of two main peaks at 915 and 878 amu. The peak at 915 amu shows the correct isotopic distribution for the stoichiometry $C_{40}H_{28}ClF_6P_2Pt$ (loss of a Cl^- anion), this fact showing that only two protons have been lost from the original bisphosphonium salt and, hence, that only two C−H bond activations have been promoted in the synthesis of **6**. The NMR spectra of **6** are particularly informative.

The ^1H NMR spectrum of **6** shows clearly that an ortho-metalation reaction has taken place, due to the observation of a signal at low field (8.53 ppm) with ^{195}Pt satellites, attributed to the H(6) proton. The value of the coupling constant ($^3J_{PtH(6)} = 38.6$ Hz) is slightly lower than those found for **3**−**5** and is similar to that observed for the Pt(IV) derivatives **13** and **14** (see below). Moreover, resonances due to a Pt−C_6H_4-4-F group are clearly seen: the meta protons (H(3′)) appear at 5.99 ppm and the ortho protons (H(2′)) at 6.67 ppm, the latter also showing ^{195}Pt satellites ($^3J_{PtH(2')} = 52.8$ Hz). The magnitude of $^3J_{PtH(2')}$ is somewhat smaller than those found in related Pt(II) complexes with the C_6H_4-4-F ligand.[23] Moreover, signals due to the H(3) and H(4) protons are also observed, meaning that on the metalated ring only one C−H bond activation has been produced, and this fact is in keeping with the mass spectrum interpretation. The $^{31}P\{^1H\}$ NMR spectrum shows two peaks with ^{195}Pt satellites each. The signal attributed to the P atom on the metalated ring appears at 30.63 ppm ($^2J_{PtP} = 412.1$ Hz), while that assigned to the P atom bonded to Pt appears at 4.25 ppm ($^1J_{PtP} = 1510$ Hz). The comparison of these data with those obtained for **3**−**5** shows notable differences: while the

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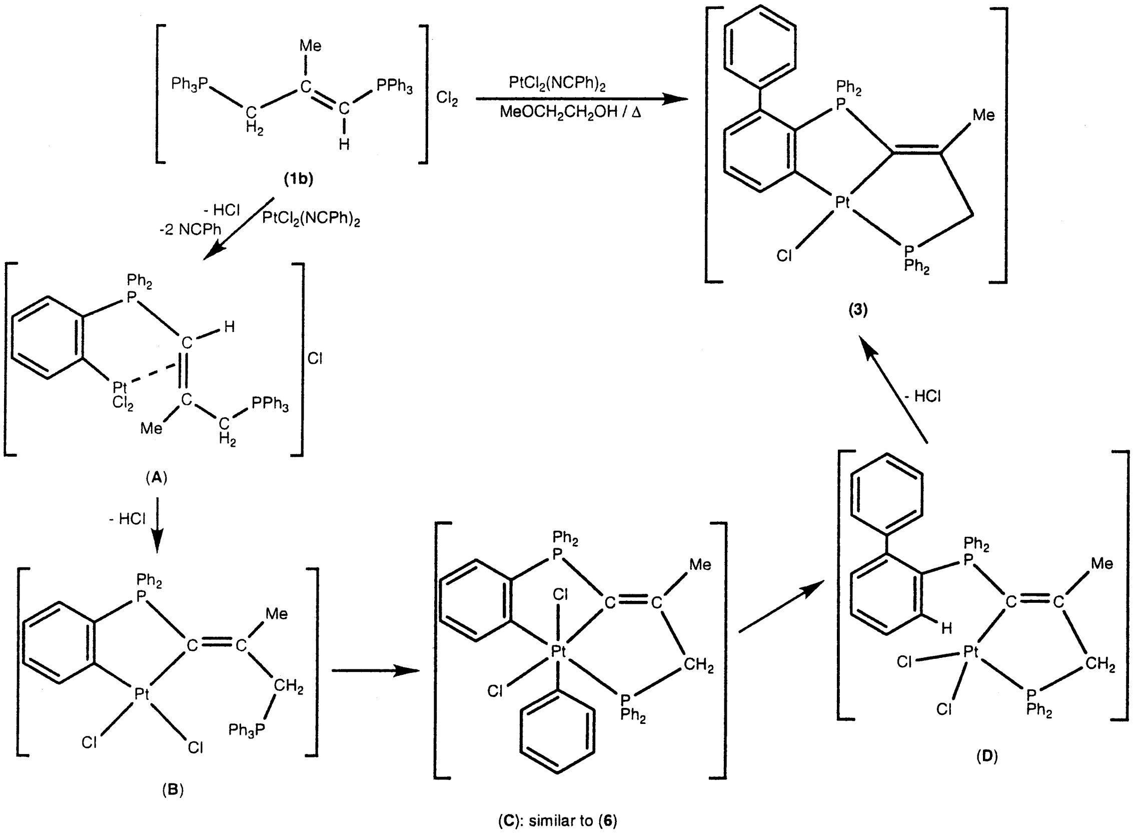
Scheme 1



chemical shift of the P atom on the metalated ring of **6** moves only about 4 ppm to high field with respect to the signals for **3**−**5**, the P atom bonded directly to the Pt atom has been shifted, also to high field, at least 21 ppm; in addition, there is a notable decrease in the values of both $^{n}J_{\mathrm{PtP}}$ coupling constants ($n = 1, 2$). Once again, the ^{31}P data of **6** are closer to those obtained from **13** and **14** than to those corresponding to **3**−**5**. Considering the oxidation reaction Pt(II) → Pt(IV), the decrease in the values of the coupling constants and the observation of the "oxidation shift" for the δ values (high-field shifts) are well-established phenomena in NMR spectroscopy.[17i,21a,c,22a,b,24] These facts and the close resemblance of the spectroscopic parameters of **6** with those obtained for the Pt(IV) derivatives **13** and **14** supports strongly the proposal shown in eq 9.

Additional evidence for the existence of the Pt−C_6H_4-4-F ligand in **6** comes from its ^{19}F NMR spectrum. In this spectrum, six different complex signals are seen, corresponding to the six chemically nonequivalent F atoms of the molecule. The attribution of all resonances has been performed through ^{1}H{^{19}F} NMR experiments. One of the signals appears at higher field (−122.38 ppm) than the others (ranging from −102 to −109 ppm), and this resonance correlates with both the H(2′) and H(3′) protons. Hence, this signal is assigned to the Pt−C_6H_4-4-*F* atom. The high-field shift undergone by this resonance, with respect to its position in the free bisphosphonium salt **1f**, is similar to that reported for the F_{para} atom on C_6F_5 groups after metalation.[25] On the other hand, the ^{195}Pt NMR spectrum of **6** provides unambiguous proof of the Pt(IV) nature of the metal center. The chemical shift of the Pt atom was obtained through inverse correlation ^{1}H−^{195}Pt experiments. The obtained value (δ −3352.0 ppm) is located at the lowest field among the ^{195}Pt NMR spectra described here (see the Experimental Section). A sensible explanation can be given, taking into account two main facts: the Pt(IV) nature of the metal center and the presence of a σ-bonded C_6H_4-4-F group.[22a,b] Finally, the ^{13}C{^{1}H} NMR spectrum of **6** is also in good agreement with the preceding data. Relevant key features are the observation of signals corresponding to the C(2′) (137.62 ppm) and C(3′) (113.04 ppm) carbon atoms, each showing ^{195}Pt satellites (22.3 and 58.7 Hz, respectively). These values are similar to those found in related Pt−phenyl derivatives.[26] The ortho-metalated C(1) atom appears at 169.72 ppm as a doublet of doublets but, as expected, with coupling constants $^{2}J_{\mathrm{PtransC}}$ (87.7 Hz) smaller than those reported for **3** and **5** (about 125 Hz); the C_β and C_α carbons appear at 157.01 and 122.22 ppm, respectively, the C_α signal being shifted to high field more than 20 ppm with respect to its position in **3** or **5**.

3. Proposed Mechanism for the Synthesis of 3. The isolation and characterization of **6** allows us to shed some light on a plausible reaction pathway through which **3** could be obtained from **1b**. This proposal is depicted in Scheme 1.

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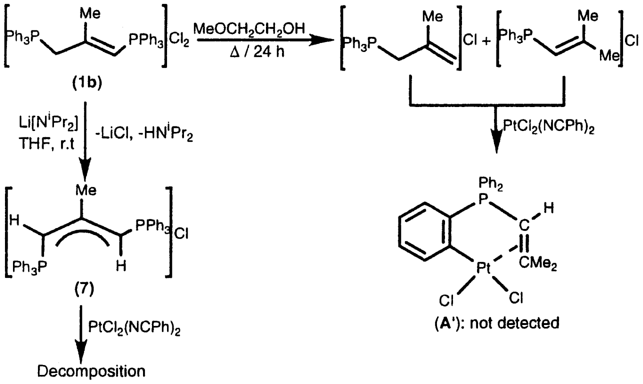
Scheme 2



Since the bis-phosphonium salt **1b** contains an allyl group, it seems possible that the first step of the reaction should be an ortho-metalation reaction similar to those described by us recently.[10] This metalation should give intermediate **A** in Scheme 1. With respect to this step, some points need to be considered. There are two phosphonium units in **1b**, one at an allylic position and the other at a vinylic position. The ortho metalation should proceed at the PPh_3 unit on an allylic position—followed by a 1,3-prototropic shift—since we have shown that the vinyl phosphonium salts do not metalate.[10] In our previous contribution we have proposed that the initial step of the metalation reaction should begin with the direct interaction of the allyl moiety with the Pt(II) center. To achieve this interaction, two possibilities could be envisaged: η^2 coordination of the C═C bond or a platinum−ylide complex. Aiming to determine which of the two possibilities are actually operating, we have synthesized the intermediate ylide phosphonium salt **7** (see Scheme 2) by deprotonation of **1b** with $Li(N^iPr_2)$. Compound **7** has been characterized through its analytic and spectroscopic data. Similar 1,3-bis(phosphonio)propenide cations have been reported previously,[11a,27] and they show spectroscopic behavior closely related to that observed for **7**. Hence, a similar structure is proposed, in accord with the NMR data. However, the reaction of **7** with $PtCl_2(NCPh)_2$ (1:1 molar ratio, refluxing 2-methoxyethanol) did not give the expected results, since extensive decomposition was observed, showing that **7** does not seem to be a plausible intermediate in the synthesis of **3**.

The observed reactivity of **7** toward $PtCl_2(NCPh)_2$ prompted us to determine if other species are generated from **1b** under the experimental conditions, which might be able to interact with the Pt(II) salt. However, the treatment of **1b** under the metalation conditions affords a mixture of the phosphonium salts $[Ph_3PCH_2C(Me){=}CH_2]Cl$ and $[Ph_3PC(H){=}CMe_2]Cl$ (Scheme 2), the latter being produced from the former by a 1,3-prototropic shift, showing that **1b** evolves through P−C bond cleavage and loss of one PPh_3 unit. Moreover, the reaction of these phosphonium salts with $PtCl_2(NCPh)_2$ should result in the formation of the previously reported ortho-metalated derivative $[Pt(C_6H_4\text{-}2\text{-}PPh_2\text{-}\eta^2\text{-}C(H){=}CMe_2)Cl_2]$ (**A′** in Scheme 2), which was not observed during the synthesis of **3**. Thus, the bis-phosphonium salt **1b** does not suffer this type of side reaction during the formation of **3**. Once we discard these two possiblities, it seems likely that the initial step in the obtainment of intermediate **A** should be the η^2 coordination of the olefinic fragment to the Pt(II) metal center in a way similar to that described and characterized by us recently for allyl phosphonium systems.[10]

Once derivative **A** has been formed, the next logical step should be the metalation of the olefinic fragment, with concomitant elimination of HCl, and formation of the intermediate **B** in Scheme 1. The metalation of olefin groups to give σ-bonded vinyl derivatives is a process known for Pt(II) complexes.[28] Moreover, this metalation can also be assisted by the presence of the nonbonded phosphonium group, since it has been shown that the presence of a phosphonium group can enhance the reactivity of adjacent electrophilic centers.[29] The next step, **B** → **C**, involves an unprecedented transformation for Pt(II) complexes. The pendant PPh_3 phosphonium group adds oxidatively to the Pt(II) metal center in **B** to give the phenylphosphino Pt(IV) derivative **C**, which is basically identical with the isolated complex **6**. While the P−C bond activation process in phosphine groups promoted by transition metals is a known process,[30] the related P−C bond activation where the PPh_nR_{3-n} unity belongs to a phosphonium or an ylide functionality is rare.[31] In fact, this type of P−C bond activation on ylide or phosphonium salts have been described to proceed usually with metals in low oxidation states and results in interesting reactions: synthesis of catalysts for the polymerization of ethylene,[31a,b] studies and applications of aryl−aryl exchange processes,[31d−m] and synthesis of iminophosphoranes.[31n,o] In our case, a phosphonium $-CH_2PPh_3$ group is transformed into a $-CH_2PPh_2-Pt-Ph$ unit; up to now, the activation of a phosphonium group to give a phenylphosphino derivative has been

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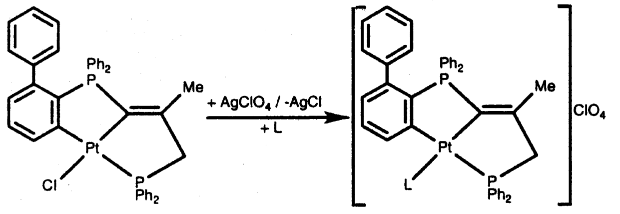
reported to occur, stoichiometrically or catalytically, only induced by Pd(0) complexes,[31e−i] but in any case assisted by Pt(II) complexes. The only reported process in which Pt(II) salts are involved[31n,o] occurs with migration of the entire PPh_3 group and P−N coupling to give iminophosphoranes or related species.

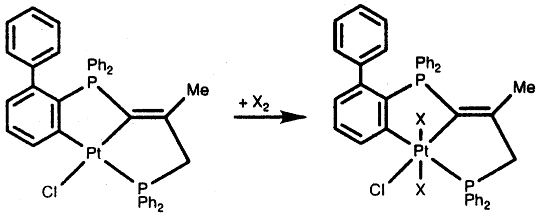
Since intermediate **C** has been isolated and characterized (as the related complex **6**), the question remains as to whether the reaction progresses further (C−C coupling in the case of **3**) or is stopped at this point (in complex **6**). The C−C coupling reaction mediated by Pt(IV) complexes is a well-known process and, from mechanistic and kinetic studies, it seems clearly established that, prior to the C−C coupling step, the dissociation of a ligand to give a 16-electron species is a mandatory prerequisite.[24a,32] Considering the intermediate **C** in Scheme 1 and complex **6**, the main difference between them is the presence of a F atom at a para position. The strong electron-withdrawing nature of the F atom[32d,e] results in the electron density around the metal being less in **6** than in **C**, which should then force a lesser degree of dissociation in **6** than in **C**. This reasoning could allow us to explain the observed C−C coupling in **C** (one of the ligands dissociates easily) and the isolation of the 18-electron complex **6** (presence of two ligands with strong electron-withdrawing substituents). Finally, the next step from **C** is the C−C coupling to give **D**, which contains a phosphonium group with a biphenyl unit as substituent. The rotation of the biphenyl unit around the P−C bond and subsequent C−H bond activation at the ortho position with elimination of HCl gives complex **3** in a typical ortho-metalation reaction.

4. Ligand-Substitution Reactions. Further reactivity of complex **3** has been examined. The treatment of **3** with $AgClO_4$ and neutral ligands L (1:1:1 molar ratio) results in the formation of the corresponding cationic derivatives $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2\text{-}PPh_2\text{-}\kappa C,C,P)(L)]ClO_4$ (L = NCMe (**8**), PPh_3 (**9**), pyridine (**10**), $C{\equiv}N^tBu$ (**11**), $Ph_2PCH_2PPh_2\text{-}\kappa P$ (**12**)) (see the Experimental Section and eq 10). The analytical data are in good agreement with the proposed stoichiometries. The presence of the coordinated L ligands can be inferred from the IR and NMR data of **8**−**12**. In the case of **8**, the NCMe ligand gives absorptions at 2323 cm^{-1} in the IR spectrum and a signal in the ^1H NMR spectrum at 2.50 ppm assigned to the NC*Me* group. For complex **9** the presence of coordinated PPh_3 is clearly seen in the $^{31}P\{^1H\}$ NMR, in which an ABX spin system (each signal showing ^{195}Pt satellites) is observed. Moreover, the ^{195}Pt NMR spectrum shows the presence of a signal at −4316 ppm (ddd), shifted to low field with respect to those obtained in **3** and **5**, this unshielding in keeping with the cationic nature of **9**. Complex **10** shows the expected signals for the N-bonded pyridine ligand, and in addition, the proton H(6) appears strongly shifted to high field, due to the anisotropic shielding of the adjacent pyridine ring.[33] The $^{31}P\{^1H\}$, ^{195}Pt, and $^{13}C\{^1H\}$ NMR spectra are consistent with the structure depicted in eq 10. The comparison of the ^{195}Pt NMR spectra of **9** (δ −4316 ppm, PPh_3) and **10** (δ −3741 ppm, py) follows the expected trends.[22] Thus, the Pt chemical shift moves to high field from **10** to **9**, indicating a more shielded Pt atom, as expected when the increase of the covalency of the donor atom from an N-donor to a P-donor is taken into account. Complex **11** shows the presence of a $^tBuN{\equiv}C$ ligand C-bonded to the Pt atom. The reaction was performed in the presence of an excess of ligand (1:2 molar ratio) in order to check if insertion of the isocyanide into the Pt−C bond occurs,[34] but no inserted products were detected. The simple C-coordination of the isocyanide ligand is inferred from the observation of a strong absorption in the IR spectrum at 2182 cm^{-1}.[34] Finally, the coordination of the $Ph_2PCH_2PPh_2$ (dppm) ligand in complex **12** is produced through only one of the P atoms, as is reflected in its $^{31}P\{^1H\}$ NMR spectrum. There, the appearance of only one signal at high field (−23.74 ppm) shows that one of the P atoms of the dppm ligand remains uncoordinated. In complexes **9** and **12**, the differences between the $^1J_{Pt-P}$ coupling constants (e.g. in **9** 1923 Hz for the Pt−*P*Ph$_2$ atom (trans to the aryl group) and 2513 Hz for the Pt−*P*Ph$_3$ atom (trans to the vinyl ligand)) can be explained by taking into account the higher trans influence of the aryl group compared with the vinyl moiety.



L = NCMe (**8**), PPh_3 (**9**), py (**10**), CN^tBu (**11**), dppm-P (**12**) (10)

5. Oxidative Addition Reactions. Complex **3** also undergoes oxidative additions of halogens X_2. The treatment of a CH_2Cl_2 solution of **3** with halogens X_2 (X = Cl, I) gives the Pt(IV) derivatives $[Pt(C_6H_3\text{-}3\text{-}Ph\text{-}2\text{-}PPh_2\text{-}C{=}C(Me)CH_2PPh_2\text{-}\kappa C,C,P)Cl(X)_2]$ (X = Cl (**13**), I (**14**)) (see eq 11), in accord with their elemental analyses and NMR data.



X = Cl (**13**), I (**14**) (11)

The ^1H NMR spectra of **13** and **14** are quite similar to those described for **3**−**5** and reflect the expected differences arising from the presence of a Pt(IV) metal center. The signal assigned to proton H(6) appears in

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both cases (8.84 ppm (**13**), 8.71 ppm (**14**)) at a frequency similar to that observed in **3** (8.77 ppm) and with the same hyperfine structure, but shows smaller values of the coupling constant $^3J_{PtH(6)}$ (37.5 Hz (**13**); 33.3 Hz (**14**)) than those of **3** (41.4 Hz). The upfield changes in the chemical shifts of the nuclei directly bonded to the Pt center and the decrease in the values of the coupling constants are typical features for the changes from Pt(II) to Pt(IV) derivatives and are called "oxidation shift".[17i,21a,c,22a,b,24] The CH_2 protons appear in both complexes as equivalent, showing that there is a symmetry plane containing the C,C,P-metalated ligand. The $^{31}P\{^1H\}$ NMR spectrum shows the presence of two doublet signals with ^{195}Pt satellites. While the signals attributed to the metalated P atom vary only slightly their position with respect to that in **3**, those assigned to the $Pt-PPh_2$ unit are shifted to high field up to 39 ppm (2.76 ppm (**13**); −13.46 ppm (**14**); 25.48 ppm (**3**)), in good agreement with the oxidation shift, and a substantial decrease of the values of the coupling constants $^nJ_{PtP}$ is observed. The ^{195}Pt NMR spectrum of **14** shows a doublet of doublets at −3978.5 ppm.

Concerning the stereochemistry of **13** and **14**, we have depicted in eq 11 the mer arrangement of the chloride ligands in **13** and the trans disposition of the iodide ligands in **14**. Assuming that the metalated ligand preserves the structural arrangment shown in **5** (and this is logical on the basis of the NMR data), this structure is the only possibility for **13**, while for **14** two isomers are possible (cis and trans). The NMR data of **14** show the presence of only one isomer, in which the equivalence of the CH_2 protons due to the presence of a symmetry plane means that the two iodide ligands are mutually trans. This trans addition of the halogen is in good agreement with the accepted mechanism for oxidative additions of X_2 to Pt(II) derivatives,[35,36a,b] although it should be noted that cis additions have also been reported.[36c,d] To confirm the trans geometry, the structure of **14** has been determined through X-ray diffraction methods.

A drawing of the organometallic complex is shown in Figure 3, some relevant parameters concerning the data acquisition and structure solution and refinement are given in Table 1, and selected bond distances and angles are collected in Table 3. The platinum atom is located in a distorted-octahedral environment, which is defined by the three donor atoms of the ligand [C_6H_3-3-Ph-2-PPh_2-*C*=C(Me)-CH_2-*P*Ph_2-*κC,C,P*] (C(1), C(13), and P(1)), the chlorine atom Cl(1), and the two iodine atoms I(1) and I(2). As expected, the metalated ligand displays the same structural arrangement as that observed in **5** and occupies three positions of the equatorial plane. The chlorine ligand is at the remaining equatorial position, and the two iodine atoms are in axial trans positions. A comparison of the structural parameters in **14** with respect to those in **5** shows similar values, within experimental error, for the Pt−C bond distances and a slightly longer Pt−P bond distance in **14** (2.364(2) Å) than in (**5**) (2.2697(13) Å). The Pt−I bond distances (2.6291(8) and 2.6584(9) Å) fall in the usual range found in the literature for this type of bond.[37] The environment around the Pt(1) atom can be considered as distorted octahedral, as can be seen from the angles C(1)−Pt(1)−P(1) (171.1(3)°), C(13)−Pt(1)−P(1) (83.6(3)°), and C(1)−

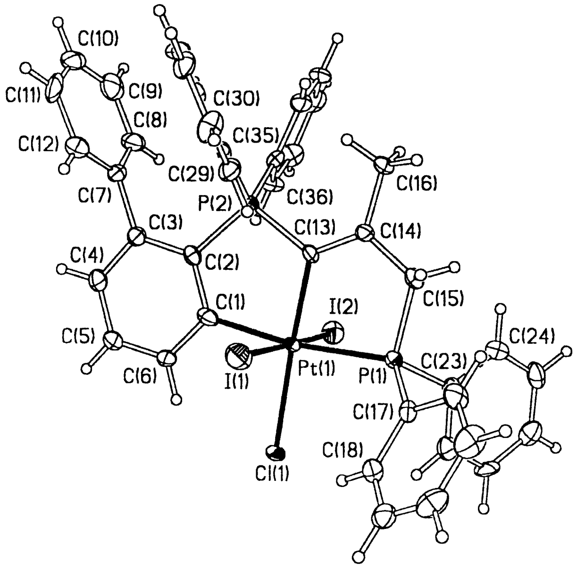

Figure 3.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 14·$CHCl_3$

Pt(1)−C(13)	2.026(9)	Pt(1)−C(1)	2.073(10)
Pt(1)−P(1)	2.364(2)	Pt(1)−Cl(1)	2.444(2)
Pt(1)−I(2)	2.6291(8)	Pt(1)−I(1)	2.6584(9)
C(1)−C(6)	1.388(13)	C(1)−C(2)	1.407(13)
C(2)−C(3)	1.418(13)	C(2)−P(2)	1.802(9)
C(3)−C(4)	1.389(13)	C(3)−C(7)	1.505(13)
C(4)−C(5)	1.399(14)	C(5)−C(6)	1.370(14)
C(7)−C(12)	1.378(15)	C(7)−C(8)	1.388(15)
C(8)−C(9)	1.387(16)	C(9)−C(10)	1.380(18)
C(10)−C(11)	1.370(19)	C(11)−C(12)	1.422(16)
C(13)−C(14)	1.343(13)	C(13)−P(2)	1.801(9)
C(14)−C(15)	1.501(13)	C(14)−C(16)	1.511(12)
C(15)−P(1)	1.835(9)	P(1)−C(17)	1.819(9)
P(1)−C(23)	1.819(10)	P(2)−C(35)	1.809(10)
P(2)−C(29)	1.817(9)		

C(13)−Pt(1)−C(1)	87.5(4)	C(13)−Pt(1)−P(1)	83.6(3)
C(1)−Pt(1)−P(1)	171.1(3)	C(13)−Pt(1)−Cl(1)	177.4(3)
C(1)−Pt(1)−Cl(1)	95.0(3)	P(1)−Pt(1)−Cl(1)	93.96(8)
C(13)−Pt(1)−I(2)	90.5(3)	C(1)−Pt(1)−I(2)	88.7(3)
P(1)−Pt(1)−I(2)	91.98(6)	Cl(1)−Pt(1)−I(2)	88.87(6)
C(13)−Pt(1)−I(1)	90.1(3)	C(1)−Pt(1)−I(1)	87.7(3)
P(1)−Pt(1)−I(1)	91.66(6)	Cl(1)−Pt(1)−I(1)	90.70(6)
I(2)−Pt(1)−I(1)	176.36(3)	C(14)−C(13)−P(2)	22.8(7)
C(14)−C(13)−Pt(1)	122.8(7)	P(2)−C(13)−Pt(1)	114.4(4)
C(13)−C(14)−C(15)	120.7(8)	C(13)−C(14)−C(16)	125.9(9)
C(15)−C(14)−C(16)	113.4(8)	C(14)−C(15)−P(1)	112.1(6)
C(17)−P(1)−C(23)	102.2(4)	C(17)−P(1)−C(15)	106.6(4)
C(23)−P(1)−C(15)	108.9(4)	C(17)−P(1)−Pt(1)	119.2(3)
C(23)−P(1)−Pt(1)	119.0(3)	C(15)−P(1)−Pt(1)	100.1(3)
C(13)−P(2)−C(2)	102.7(4)	C(13)−P(2)−C(35)	111.3(4)
C(2)−P(2)−C(35)	110.8(4)	C(13)−P(2)−C(29)	110.3(4)
C(2)−P(2)−C(29)	113.1(4)	C(35)−P(2)−C(29)	108.5(4)

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Pt(1)−Cl(1) (95.0(3)°). The bond angle I(1)−Pt(1)−I(2) is 176.36(3)°, indicating an almost linear arrangement of the two trans iodine atoms.

Conclusions

Several allyl−vinyl bis-phosphonium salts have been obtained through direct reaction of the corresponding halo derivatives with PPh$_3$ or P(C$_6$H$_4$-*p*-F)$_3$ without the need of added catalyst. The complex PtCl$_2$(NCPh)$_2$ is an excellent precursor for the synthesis of ortho-platinated derivatives derived from these bis-phosphonium salts. The metalation of the bis-phosphonium salt **1b** gives the complex [Pt(*C*$_6$H$_3$-3-Ph-2-PPh$_2$-*C*=C(Me)-CH$_2$*P*Ph$_2$-κ*C*,*C*,*P*)Cl] (**3**) through three C−H bond activations, one P−C bond activation, and one C−C bond coupling. The isolation of the Pt(IV) complex [Pt(C$_6$H$_4$-4-F){C$_6$H$_3$-5-F-2-P(*p*-FC$_6$H$_4$)$_2$C=C(Me)CH$_2$P(*p*-FC$_6$H$_4$)$_2$-κ*C*,*C*,*P*}Cl$_2$] (**6**) allows us to propose a plausible reaction mechanism which involves, for the first time, a P−C bond activation in a phosphonium salt promoted by a Pt(II) complex. Further work on the reactivity of phosphonium salts toward Pt(II) complexes is now in progress.

Experimental Section

General Methods. Details for general procedures are given in the Supporting Information. The compound PtCl$_2$(NCPh)$_2$ was prepared according to published methods.[38]

Synthesis. The complete synthetic methods and full analytic and spectroscopic data are collected as Supporting Information. Only representative synthetic procedures and selected spectroscopic NMR data (δ, ppm; *J*, Hz) are described below.

[Me$_2$PhPCH$_2$C(=CH$_2$)CH$_2$PPhMe$_2$]Cl$_2$ (1a). To a solution of 3-chloro-2-(chloromethyl)propene (1.85 mL, 16.0 mmol) in 20 mL of deoxygenated *N*,*N*-dimethylacetamide under Ar atmosphere was added PPhMe$_2$ (11.38 mL, 80 mmol). The resulting solution was refluxed for 3 h. After the mixture was cooled, the white solid that precipitated was filtered, washed with Et$_2$O (75 mL), dried in vacuo, and identified as **1a**. Yield: 4.423 g (68.9%). ^{1}H NMR (CDCl$_3$, room temperature): 8.02−7.96 (m, 4H, H$_{ortho}$, Ph), 7.53−7.40 (m, 6H, H$_{meta}$ + H$_{para}$, Ph), 5.13 (t, 2H, =CH$_2$, $^4J_{PH}$ = 6.0), 4.07 (d, 4H, PCH$_2$, $^2J_{PH}$ = 18.6), 2.38 (d, 12H, PMe, $^2J_{PH}$ = 13.5). ^{31}P{^{1}H} NMR (CDCl$_3$, room temperature): 24.76.

[Ph$_3$PCH$_2$-(*E*)-C(Me)=C(H)PPh$_3$]Cl$_2$ (1b). Quantitative yield. ^{1}H NMR (CDCl$_3$, room temperature): 8.05 (dd, 1H, =CH, $^2J_{PH}$ = 19.2, $^4J_{PH}$ = 3.6), 7.97−7.89 (m, 6H, PPh$_3$), 7.65−7.39 (m, 24H, PPh$_3$), 5.87 (d, 2H, CH$_2$, $^2J_{PH}$ = 16.5), 1.63 (t, 3H, CH$_3$, $^4J_{PH}$ = 2.4). ^{31}P{^{1}H} NMR (CDCl$_3$, room temperature): 22.98 (d, CH$_2$P, $^4J_{PP}$ = 5.5), 11.06 (d, =CHP).

[Ph$_3$PCH$_2$C(=CH$_2$)PPh$_3$]Br$_2$ (1c). Yield: 98%. ^{1}H NMR (CDCl$_3$, room temperature): 7.76−7.61 (m, 30H, PPh$_3$), 6.76 (d, 1H, =CH trans P, $^3J_{PH}$ = 45.9), 6.37 (dt, 1H, =CH cis P, $^3J_{PH}$ = 22.2, $^4J_{HH}$ = 2.7), 5.32 (dd, 2H, CH$_2$, $^2J_{PH}$ = 14.7, $^3J_{PH}$ = 11.1). ^{31}P{^{1}H} NMR (CDCl$_3$, room temperature): 27.48 (d, PCH$_2$, $^3J_{PP}$ = 18.7), 23.29 (d, =CHP).

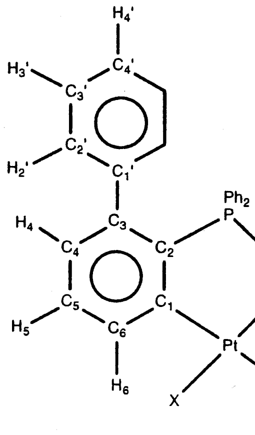
[Ph$_3$PCH$_2$-(*E*)-C(H)=C(H)PPh$_3$]Cl$_2$ (1d). Yield: 34.7%. ^{1}H NMR (CDCl$_3$, room temperature): 9.11 (pseudo t, 1H, =CHP, $^3J_{HH} \approx {}^2J_{PH}$ = 16.8), 7.86−7.40 (m, 30H, PPh$_3$), 6.38 (t, broad, not resolved, 1H, =CH), 5.72 (d, broad, 2H, PCH$_2$, $^2J_{PH}$ = 11.1). ^{31}P{^{1}H} NMR (CDCl$_3$, room temperature): 22.56 (s, PCH$_2$), 18.29 (s, =CHP).

[Ph$_3$PCH$_2$-(*E*)-C(H)=C(H)PPh$_3$]Br$_2$ (1e). Yield: 90.7%. ^{1}H NMR (CDCl$_3$, room temperature): 8.91 (ddd, 1H, =CHP, $^2J_{PH}$ = 20.7, $^3J_{HH}$ = 16.0, $^4J_{PH}$ = 3.0), 7.83−7.39 (m, 30H, PPh$_3$), 6.42 (ttd, 1H, =CH, $^3J_{HH} \approx {}^3J_{PH}$ = 16, $^3J_{HCH2}$ = 7.2, $^3J_{P'H}$ = 2.7), 5.67 (dd, 2H, PCH$_2$, $^2J_{PH}$ = 16.2, $^3J_{HH}$ = 7.2). ^{31}P{^{1}H} NMR (CDCl$_3$, room temperature): 22.43 (d, PCH$_2$, $^4J_{PP}$ = 6.1), 18.50 (d, =CHP).

[(*p*-FC$_6$H$_4$)$_3$PCH$_2$-(*E*)-C(Me)=C(H)P(*p*-FC$_6$H$_4$)$_3$]Cl$_2$ (1f). Yield: 60.9%. ^{1}H NMR (DMSO-*d*$_6$, room temperature): 8.17−8.08 (m, 6H, *p*-F-C$_6$H$_4$), 7.76−7.60 (m, 19H, *p*-F-C$_6$H$_4$ + =CHP), 5.63 (d, 2H, PCH$_2$, $^2J_{PH}$ = 17.4), 1.52 (s, 3H, Me). ^{31}P-{^{1}H} NMR (DMSO-*d*$_6$, room temperature): 23.29 (d, PCH$_2$, $^4J_{PP}$ = 5.5), 10.67 (d, =CHP).

[H$_2$C=C(CH$_2$PPhMe$_2$)$_2$][PtCl$_4$] (2). To a solution of the bis-phosphonium salt **1a** (0.425 g, 1.06 mmol) in 2-methoxyethanol (15 mL) was added PtCl$_2$(NCPh)$_2$ (0.500 g, 1.06 mmol). This suspension was refluxed for 24 h. During this time, the initial yellow suspension dissolved and changed its color from yellow to pale brown and finally a solid precipitated. After the mixture was cooled, the pale brown solid was filtered, washed with additional 2-methoxyethanol (5 mL) and Et$_2$O (25 mL), air-dried, and identified spectroscopically as **2**. Yield: 0.544 g (77%). ^{1}H NMR (DMSO-*d*$_6$, room temperature): 8.08−8.01 (m, 4H, H$_{ortho}$, Ph), 7.83−7.78 (m, 2H, H$_{para}$, Ph), 7.73−7.67 (m, 4H, H$_{meta}$, Ph), 5.13 (t, 2H, =CH$_2$, $^4J_{PH}$ = 6.0), 3.59 (d, 4H, CH$_2$P, $^2J_{PH}$ = 17.7), 2.34 (d, 12H, PMe, $^2J_{PH}$ = 14.1). ^{31}P{^{1}H} NMR (DMSO-*d*$_6$, room temperature): 26.61.

[Pt(C$_6$H$_3$-3-Ph-2-PPh$_2$-C=C(Me)CH$_2$PPh$_2$-κ*C*,*C*,*P*)Cl] (3). The bis-phosphonium salt **1b** (0.585 g, 0.90 mmol) and PtCl$_2$(NCPh)$_2$ (0.425 g, 0.90 mmol) were refluxed in 2-methoxyethanol (10 mL) under Ar for 24 h. The resulting cold suspension was filtered, and the obtained pale yellow solid was washed with additional 2-methoxyethanol (2 × 2 mL) and Et$_2$O (10 mL), air-dried, and identified as **3**. Yield: 0.324 g (44.6%). Atom numbering for complexes **3**−**5** is as follows:



^{1}H NMR (CDCl$_3$, room temperature): 8.77 (ddt, 1H, H$_6$, $^3J_{H6H5}$ = 7.8, $^4J_{H6P(Pt)}$ = 5.1, $^4J_{H6\ H4} \approx {}^4J_{H6P}$ = 1.2, $^3J_{H6Pt}$ = 41.4), 7.77−7.68 (m, 4H, H$_o$, PPh$_2$), 7.51−7.38 (m, 9H, PPh$_2$ + H$_5$), 7.33−7.22 (m, 8H, PPh$_2$), 7.03 (tt, 1H, H$_{4'}$, $^3J_{H4'H3'}$ = 7.5, $^4J_{H4'H2'}$ = 1.2), 6.85−6.77 (m, 3H, H$_4$ + H$_{3'}$), 6.41 (dd, 2H, H$_{2'}$, $^3J_{H3'H2'}$ = 7.8), 2.99 (dq, 2H, CH$_2$, $^2J_{PH}$ = 9.3, $^4J_{H-Me}$ = 0.9, $^3J_{H-Pt}$ = 17.7), 1.31 (dm, 3H, Me, $^4J_{PH}$ = 2.4). ^{31}P{^{1}H} NMR (CD$_2$Cl$_2$, room temperature): 34.14 (d, Ph$_2$P−C−Pt, $^3J_{PP}$ = 25.0, $^2J_{PtP}$ = 601), 25.48 (d, Ph$_2$P−Pt, $^1J_{PtP}$ = 2064.5).

[Pt(C$_6$H$_3$-3-Ph-2-PPh$_2$-C=C(Me)CH$_2$PPh$_2$-κ*C*,*C*,*P*)Br] (4). Complex **3** (0.100 g, 0.124 mmol) was suspended in 20 mL of a mixture of acetone and MeOH (1/1), and KBr (0.118 g, 1.00 mmol) was added. The resulting mixture was stirred at 25 °C for 3 days and then evaporated to dryness. The gray residue was extracted with CH$_2$Cl$_2$ (2 × 30 mL), and the extracts were filtered. The solid was discarded, and the clear yellow solution was evaporated to dryness. By Et$_2$O addition (20 mL) and vigorous stirring, a yellow solid (**4**) was obtained, which was filtered, washed with Et$_2$O (10 mL), and air-dried. Yield: 0.082 g (78%). ^{1}H NMR (CDCl$_3$, room temperature): 8.83 (ddt, 1H, H$_6$, $^3J_{H6H5}$ = 7.8, $^4J_{H6P(Pt)}$ = 6.3, $^4J_{H6H4} \approx {}^4J_{H6P}$ = 1.5, $^3J_{H6Pt}$ =

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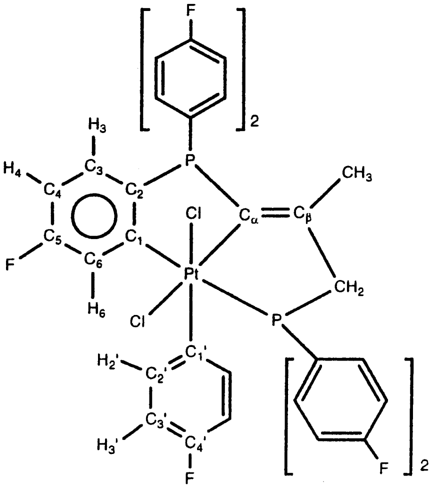
(38) Anderson, G. K.; Lin, M. *Inorg. Synth.* **1990**, *28*, 60.

43.8), 7.77−7.67 (m, 4H, H_o, PPh_2), 7.57−7.29 (m, 17H, PPh_2 + H_5), 7.07 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'}$ = 7.5, $^4J_{H4'H2'}$ = 1.2), 6.89−6.81 (m, 3H, H_4 + $H_{3'}$), 6.46 (dd, 2H, $H_{2'}$, $^3J_{H3'H2'}$ = 7.8), 3.05 (dq, 2H, CH_2, $^2J_{PH}$ = 8.4, $^4J_{H-Me}$ = 0.9), 1.31 (dm, 3H, Me, $^4J_{PH}$ = 2.7). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 34.16 (d, $Ph_2P-C-Pt$, $^3J_{PP}$ = 24.6, $^2J_{PtP}$ = 599), 26.53 (d, Ph_2P-Pt, $^1J_{PtP}$ = 2035.6).

[Pt(C_6H_3-3-Ph-2-PPh_2-C=C(Me)CH_2PPh_2-*κC,C,P*)I] (5). Yield: 81%. ^1H NMR (CD_2Cl_2, room temperature): 9.09 (ddt, 1H, H_6, $^3J_{H6H5}$ = 7.8, $^4J_{H6P(Pt)}$ = 6.3, $^4J_{H6H4} \approx {}^4J_{H6P}$ = 1.5, $^3J_{H6Pt}$ = 45.9), 7.68−7.61 (m, 4H, H_o, PPh_2), 7.56−7.28 (m, 17H, PPh_2 + H_5), 7.06 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'}$ = 7.5, $^4J_{H4'H2'}$ = 1.2), 6.85 (m, 1H, H_4), 6.83 (t, 2H, $H_{3'}$, $^3J_{H4'H3'} \approx {}^3J_{H3'H2'}$ = 7.5), 6.48 (dd, 2H, $H_{2'}$), 3.12 (dq, 2H, CH_2, $^2J_{PH}$ = 9.3, $^4J_{H-Me}$ = 0.6), 1.27 (dm, 3H, Me, $^4J_{PH}$ = 2.4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 34.29 (d, $Ph_2P-C-Pt$, $^3J_{PP}$ = 23.4, $^2J_{PtP}$ = 580.5), 27.61 (d, Ph_2P-Pt, $^1J_{PtP}$ = 1981.4).

[Pt(C_6H_4-4-F){C_6H_3-5-F-2-P(*p*-FC_6H_4)$_2$-C=C(Me)CH_2P(*p*-FC_6H_4)$_2$-*κC,C,P*}Cl_2] (6). The bis-phosphonium salt **1f** (0.533 g, 0.704 mmol) and $PtCl_2(NCPh)_2$ (0.332 g, 0.704 mmol) were refluxed in 2-methoxyethanol (15 mL) for 24 h. After the reaction time, some decomposition was evident. The cool suspension was then evaporated to dryness, leaving a yellow greenish oil. This oily residue was extracted with CH_2Cl_2 (3 × 10 mL), dried with $MgSO_4$, evaporated to drynesss, and treated with Et_2O (15 mL), giving a pale yellow solid, which was identified spectroscopically as a mixture of **6** and the starting bis-phosphonium salt **1f**. Recrystallization from 2-methoxyethanol affords **6** in analytically pure form as a white solid. Yield: 0.174 g (26.0%). Atom numbering for compound **6** is as follows:



^1H NMR (CD_2Cl_2, room temperature): 8.53 (td, 1H, H_6, $^3J_{H6F} \approx {}^4J_{H6P(Pt)}$ = 10.0, $^4J_{H6H4}$ = 1.0, $^3J_{PtH6}$ = 38.6), 8.13 (ddd, 2H, H_o, $Pt-PC_6H_4F$, $^3J_{HP}$ = 10.2, $^3J_{H6Hm}$ = 8.7, $^4J_{HF}$ = 5.4), 7.97 (ddd, 2H, H_o, PC_6H_4F, $^3J_{HP}$ = 12.0, $^3J_{HoHm}$ = 9.0, $^4J_{HF}$ = 5.4), 7.47 (ddd, 2H, H_o, $Pt-PC_6H_4F$, $^3J_{HP}$ = 10.2, $^3J_{HoHm}$ = 8.7, $^4J_{HF}$ = 5.4), 7.31 (td, 2H, H_m, PC_6H_4F, $^3J_{HmHo} = {}^3J_{HmF}$ = 9.0, $^4J_{HmP}$ = 2.1), 7.10 (td, 2H, H_m, $Pt-PC_6H_4F$, $^3J_{HmHo} = {}^3J_{HmF}$ = 8.7, $^4J_{HmP}$ = 2.1), 7.02−6.97 (m, 4H, $2H_o$ (PC_6H_4F) + $2H_m$ (PC_6H_4F)), 6.89−6.80 (m, 4H, $2H_m$ ($Pt-PC_6H_4F$) + H_3 + H_4), 6.67 (dd, 2H, $H_{2'}$, $^3J_{H2'H3'}$ = 9.0, $^4J_{H2'F}$ = 6.0, $^3J_{PtH2'}$ = 52.8), 5.99 (t, 2H, $H_{3'}$, $^3J_{H2'H3'} = {}^3J_{H3'F}$ = 9.0), 3.95 (dd, 2H, CH_2, $^2J_{PH}$ = 10.5, $^4J_{PH}$ = 1.5), 2.13 (d, 3H, CH_3, $^4J_{PH}$ = 2.4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 30.63 (d, $P_{ring}-C-Pt$, $^3J_{PP}$ = 21.4, $^2J_{PtP}$ = 412), 4.25 (dd, Pt−P, $^5J_{PF}$ = 8.3, $^1J_{PtP}$ = 1510).

[$Ph_3PC(H)C(Me)C(H)PPh_3$]Cl (7). The bis-phosphonium salt **1b** (1.000 g, 1.54 mmol) was suspended in dry THF (30 mL) under Ar, and $Li(NiPr_2)$ (0.77 mL of a 2.0 M solution, 1.54 mmol) was added dropwise at room temperature. A deep red solution was obtained, which was stirred overnight. The resulting solution was evaporated to dryness, the residue was extracted with CH_2Cl_2 (2 × 20 mL), and the extracts were filtered over a Celite pad. The obtained solution was washed with H_2O (10 mL), dried with $MgSO_4$, and evaporated to dryness, giving a yellow residue. This residue was triturated with Et_2O (50 mL), and the resulting yellow solid (**7**) was filtered, washed with additional Et_2O (50 mL), and dried in vacuo. Yield: 0.822 g (87%). ^1H NMR ($CDCl_3$, room temperature): 7.63−7.16 (m, 30H, PPh_3), 3.62 (dd, 1H, CH, $^2J_{PH}$ = 23.0, $^4J_{PH}$ = 7.5), 2.99 (d, 1H, CH, $^2J_{PH}$ = 16.4), 1.74 (s, 3H, CH_3). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature): 11.62 (s), 11.42 (s).

[Pt(C_6H_3-3-Ph-2-PPh_2-C=C(Me)CH_2PPh_2-*κC,C,P*)(NCMe)]ClO_4 (8). To a suspension of **3** (0.100 g, 0.124 mmol) in 15 mL of NCMe was added $AgClO_4$ (0.026 g, 0.124 mmol). The resulting suspension was stirred at room temperature for 2 h with exclusion of light and then filtered over a Celite pad. The clear pale yellow solution was evaporated to small volume (2 mL). By Et_2O addition (20 mL) and continuous stirring **8** was obtained as a light yellow solid, which was filtered and air-dried. Yield: 0.075 g (66.3%). ^1H NMR ($CDCl_3$, room temperature): 7.91 (ddt, 1H, H_6, $^3J_{H6H5}$ = 7.5, $^4J_{H6P(Pt)}$ = 6.3, $^4J_{H6H4} = {}^4J_{H6P}$ = 1.2, $^3J_{H6Pt}$ = 43.5), 7.59−7.34 (m, 21H, PPh_2 + H_5), 7.06 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'}$ = 7.2, $^4J_{H4'H2'}$ = 1.2), 6.96 (ddd, 1H, H_4, $^3J_{H4H5}$ = 7.2, $^4J_{H4P}$ = 6.3, $^4J_{H4H6}$ = 1.2), 6.82 (t, 2H, $H_{3'}$, $^3J_{H3'H2'} = {}^3J_{H3'H4'}$ = 7.2), 6.42 (dd, 2H, $H_{2'}$), 3.23 (d, 2H, CH_2, $^2J_{PH}$ = 9.0), 2.50 (d, 3H, NCMe, $^5J_{PH}$ = 0.9), 1.46 (d, 3H, CH_3, $^4J_{PH}$ = 2.4). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature): 37.93 (d, PPh_2, $^3J_{PP}$ = 24.4, $^2J_{PtP}$ = 583), 31.80 (d, $Pt-PPh_2$, $^1J_{PtP}$ = 2002).

[Pt(C_6H_3-3-Ph-2-PPh_2-C=C(Me)CH_2PPh_2-*κC,C,P*)(PPh_3)]ClO_4 (9). Yield: 79.5%. ^1H NMR ($CDCl_3$, room temperature): 7.64−7.58 (m, 2H, Ph), 7.43−7.16 (m, 27H, Ph (25H) + C_6H_3 (2H)), 7.08−6.92 (m, 8H, Ph), 6.87−6.82 (m, 2H, $H_{4'}$ + C_6H_3 (1H)), 6.78 (t, 2H, $H_{3'}$, $^3J_{H3'H4'} = {}^3J_{H3'H2'}$ = 7.5), 6.64 (dd, 2H, $H_{2'}$, $^4J_{H2'H4'}$ = 1.2), 3.45 (d, 2H, CH_2, $^2J_{PH}$ = 9.0), 1.36 (d, 3H, CH_3, $^4J_{PH}$ = 2.1). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 35.64 (dd, A part of an ABX spin system, PPh_2, $^3J_{PAPB}$ = 20.4, $^3J_{PAPPh3}$ = 7.4, $^2J_{PtPA}$ = 472), 35.04 (dd, B part of an ABX spin system, $Pt-PPh_2$, $^3J_{PAPB}$ = 20.4, $^2J_{PBPPh3}$ = 16.0, $^1J_{PtPB}$ = 1923), 25.67 (dd, X part of an ABX spin system, $Pt-PPh_3$, $^1J_{PtP}$ = 2513).

[Pt(C_6H_3-3-Ph-2-PPh_2-C=C(Me)CH_2PPh_2-*κC,C,P*)(py)]ClO_4 (10). Yield: 78.4%. ^1H NMR ($CDCl_3$, room temperature): 8.50 (dd, 2H, H_o, py, $^3J_{HoHm}$ = 6.6, $^4J_{HoHp}$ = 1.5, $^3J_{PtHo}$ = 25.2), 7.91 (tt, 1H, H_p, py, $^3J_{HpHm}$ = 7.8, $^4J_{HpHo}$ = 1.5), 7.63−7.59 (m, 2H, Ph), 7.47−7.35 (m, 12H, Ph + $2H_m$ (py)), 7.28−7.15 (m, 9H, Ph + H_5), 7.05 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'}$ = 7.8, $^4J_{H4'H2'}$ = 1.2), 6.91 (td, 1H, H_4, $^3J_{H4H5} = {}^4J_{H4P}$ = 6.7, $^4J_{H4H6}$ = 1.2), 6.82 (t, 2H, $H_{3'}$, $^3J_{H3'H4'} = {}^3J_{H3'H2'}$ = 7.8), 6.60 (ddt, 1H, H_6, $^3J_{H6H5}$ = 7.2, $^4J_{H6P(Pt)}$ = 6.0, $^4J_{H6H4} = {}^4J_{H6P}$ = 1.2, $^3J_{PtH6}$ = 44.1), 6.47 (dd, 2H, $H_{2'}$), 3.33 (d, 2H, CH_2, $^2J_{PH}$ = 9.0), 1.47 (d, 3H, CH_3, $^4J_{PH}$ = 2.4). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 35.87 (d, PPh_2, $^3J_{PP}$ = 24.7, $^2J_{PtP}$ = 546), 33.28 (d, $Pt-PPh_2$, $^1J_{PtP}$ = 2033).

[Pt(C_6H_3-3-Ph-2-PPh_2-C=C(Me)CH_2PPh_2-*κC,C,P*)(C≡N^tBu)]ClO_4 (11). Yield: 80.7%. ^1H NMR ($CDCl_3$, room temperature): 8.05 (dddd, 1H, H_6, $^3J_{H6H5}$ = 8.7, $^4J_{H6P(Pt)}$ = 6.3, $^4J_{H6H4}$ = 1.8, $^4J_{H6P}$ = 1.5, $^3J_{PtH6}$ = 55.2), 7.59−7.28 (m, 21H, Ph + H_5), 7.07 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'}$ = 7.8, $^4J_{H4'H2'}$ = 1.2), 7.00 (ddd, 1H, H_4, $^3J_{H4H5}$ = 7.2, $^4J_{H4P}$ = 5.7, $^4J_{H4H6}$ = 1.8), 6.81 (t, 2H, $H_{3'}$, $^3J_{H3'H4'} = {}^3J_{H3'H2'}$ = 7.8), 6.41 (dd, 2H, $H_{2'}$), 3.61 (d, 2H, CH_2, $^2J_{PH}$ = 9.3), 1.57 (d, 3H, CH_3, $^4J_{PH}$ = 2.4), 1.46 (s, 9H, ^tBu). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature): 39.22 (d, PPh_2, $^3J_{PP}$ = 23.4, $^2J_{PtP}$ = 465), 31.83 (d, $Pt-PPh_2$, $^1J_{PtP}$ = 1824).

[Pt(C_6H_3-3-Ph-2-PPh_2-C=C(Me)CH_2PPh_2-*κC,C,P*)(dppm-*κP*)]ClO_4 (12). Yield: 87%. ^1H NMR ($CDCl_3$, room temperature): 7.68−7.00 (m, 44H, PPh_2 + C_6H_3 + $H_{4'}$), 6.77 (t, 2H, $H_{3'}$, $^3J_{H3'H4'} = {}^3J_{H3'H2'}$ = 7.2), 6.53 (d, 2H, $H_{2'}$), 3.46 (m, 2H, CH_2, dppm), 3.11 (dd, 2H, $Pt-PCH_2$, $^2J_{PH}$ = 9.9, $^4J_{PH}$ = 3.00), 1.38

(d, 3H, CH_3, $^4J_{PH} = 2.4$). $^{31}P\{^1H\}$ NMR ($CDCl_3$, room temperature): 36.84 (dd, PPh_2, $^3J_{PP} = 19.0$, $^3J_{PP(dppm)} = 7.2$, $^2J_{PtP} = 467$), 35.51 (t, Pt−PPh_2, $^3J_{PP} = {}^2J_{P(cis)P(dppm)} = 19.0$, $^1J_{PtP} = 1913$), 15.84 (ddd, Pt−PPh_2, dppm, $^2J_{PP} = 94$, $^1J_{PtP} = 2526$), −23.74 (d, free PPh_2, dppm, $^2J_{PP} = 94$).

***mer*-[Pt(C_6H_3-3-Ph-2-PPh_2-C═C(Me)CH_2PPh_2-κ*C,C,P*)-(Cl)$_3$] (13).** A suspension of complex **3** (0.100 g, 0.124 mmol) in 20 mL of CH_2Cl_2 was treated with a solution of Cl_2 in CCl_4 (15% excess, 0.143 mmol) at room temperature. The initial pale yellow suspension gradually dissolved, and a deep yellow solution was obtained. After 1 h of stirring, a very small amount of solid remained in suspension. The solid was filtered and discarded, and the clear solution was evaporated to dryness. By addition of Et_2O (20 mL) and continuous stirring, **13** was obtained as a deep yellow solid, which was filtered and air-dried. Yield: 0.0745 g (68.5%). ^1H NMR (CD_2Cl_2, room temperature): 8.84 (dddd, 1H, H_6, $^3J_{H6H5} = 10.5$, $^4J_{H6P(Pt)} = 8.1$, $^4J_{H6H4} = 2.4$, $^4J_{H6P} = 1.2$, $^3J_{PtH6} = 37.5$), 8.14−8.07 (m, 2H, PPh_2), 7.97−7.79 (m, 5H, $PPh_2 + H_5$), 7.69−7.36 (m, 14H, PPh_2), 7.16 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'} = 7.8$, $^4J_{H4'H2'} = 1.2$), 6.93 (ddd, 1H, H_4, $^3J_{H4H5} = 6.0$, $^4J_{H4P} = 5.2$, $^4J_{H4H6} = 2.4$), 6.87 (t, 2H, $H_{3'}$, $^3J_{H3'H4'} = {}^3J_{H3'H2'} = 7.8$), 6.42 (dd, 2H, $H_{2'}$), 3.77 (dd, 2H, CH_2, $^2J_{PH} = 11.1$, $^4J_{PH} = 2.4$), 1.89 (d, 3H, CH_3, $^4J_{PH} = 1.8$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 32.48 (d, PPh_2, $^3J_{PP} = 25.5$, $^2J_{PtP} = 296$), 2.76 (d, Pt−PPh_2, $^1J_{PtP} = 1371$).

***trans*-[Pt(C_6H_3-3-Ph-2-PPh_2-C═C(Me)CH_2PPh_2-κ*C,C,P*)(Cl)(I)$_2$] (14).** Yield: 77.9%. ^1H NMR (CD_2Cl_2, room temperature): 8.71 (dddd, 1H, H_6, $^3J_{H6H5} = 9.3$, $^4J_{H6P(Pt)} = 8.1$, $^4J_{H6H4} = 2.4$, $^4J_{H6P} = 1.2$, $^3J_{PtH6} = 33.3$), 7.86−7.79 (m, 4H, PPh_2), 7.67−7.55 (m, 7H, $PPh_2 + H_5$), 7.46−7.33 (m, 10H, PPh_2), 7.06 (tt, 1H, $H_{4'}$, $^3J_{H4'H3'} = 7.5$, $^4J_{H4'H2'} = 1.2$), 6.79 (t, 2H, $H_{3'}$, $^3J_{H3'H4'} = {}^3J_{H3'H2'} = 7.5$), 6.76 (m, 1H, H_4, overlapped with $H_{3'}$), 6.51 (dd, 2H, $H_{2'}$), 3.93 (dd, 2H, CH_2, $^2J_{PH} = 10.8$, $^4J_{PH} = 1.8$), 2.13 (d, 3H, CH_3, $^4J_{PH} = 2.1$). $^{31}P\{^1H\}$ NMR (CD_2Cl_2, room temperature): 34.41 (d, PPh_2, $^3J_{PP} = 23.3$, $^2J_{PtP} = 338$), −13.46 (d, Pt−PPh_2, $^1J_{PtP} = 1427$).

Crystal Structure Determination of Complexes 5 and 14. Crystals of **5** and of **14**·$CHCl_3$ of adequate quality for X-ray measurements were grown by slow vapor diffusion of Et_2O into a CH_2Cl_2 (**5**) or $CHCl_3$ (**14**) solution of the corresponding crude complex. A single crystal of dimensions 0.29 × 0.26 × 0.07 mm (**5**) or 0.12 × 0.11 × 0.087 mm (**14**) was mounted at the end of a quartz fiber in a random orientation and covered with epoxy.

Data Collection. Data collection was performed in both cases at 100 K on a Bruker Smart CCD diffractometer using graphite-monochromated Mo Kα radiation ($\lambda = 0.710\,73$ Å). For complex **5** a full sphere of data was collected on the basis of four ω-scan runs (starting ω −30°) at values $\phi = 0$, 90, 180, and 270° with the detector at $2\theta = 30°$. For each of these runs, 606 frames were collected at 0.3° intervals and 5 s per frame. For the complex **14**·$CHCl_3$ a hemisphere of data was collected on the basis of three ω-scan runs (starting ω −30°) at values $\phi = 0$, 90, and 180° with the detector at $2\theta = 30°$. For each of these runs, frames (606, 435, and 230, respectively) were collected at 0.3° intervals and 10 s per frame. In both cases, the diffraction frames were integrated using the program SAINT[39] and the integrated intensities were corrected for absorption with SADABS.[40]

Structure Solution and Refinement. The two structures were solved and developed by Patterson and Fourier methods.[41] All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed at idealized positions and treated as riding atoms. Each hydrogen atom was assigend an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o^2, and all reflections were used in the least-squares calculations.[42]

Acknowledgment. Funding by the Dirección General de Investigación Científica y Técnica (DGICYT) (Spain, Projects BQU2002-0510 and BQU2002-00554) is gratefully acknowledged. T.S. thanks the MECD (Spain) for a postdoctoral fellowship.

Supporting Information Available: Text giving general procedures, full experimental details, synthetic methods, and analytic and spectroscopic data for all compounds prepared in this paper and tables giving complete data collection parameters, atomic coordinates, all bond distances and angles, and thermal parameters for **5** and **14**·$CHCl_3$. This material is available free of charge via the Internet at http://pubs.acs.org.

OM0305465

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

(40) Sheldrick, G. M. SADABS: Empirical Absorption Correction Program; Universität Göttingen, Göttingen, Germany, 1996.

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(42) Sheldrick, G. M. SHELXL-97: FORTRAN Program for the Refinement of Crystal structures from Diffraction Data; Universität Göttingen, Göttingen, Germany, 1997. Molecular graphics were done using the commercial package SHELXTL-PLUS: SHELXTL-PLUS, Release 5.05/V; Siemens Analytical X-ray Instruments, Inc., Madison, WI, 1996.