

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

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The reaction of $[\text{Ph}_3\text{PCH}_2\text{-(E)-C(Me)=C(H)PPh}_3]\text{Cl}_2$ (**1b**) with $\text{PtCl}_2(\text{NPh})_2$ (1:1 molar ratio) in refluxing 2-methoxyethanol gives the ortho-metallated complex $[\text{Pt}(\text{C}_6\text{H}_3\text{-3-Ph-2-PPh}_2\text{-C=C(Me)CH}_2\text{PPh}_2\text{-}\kappa\text{C,C,P})\text{Cl}]$ (**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 $[\text{Pt}(\text{C}_6\text{H}_3\text{-3-Ph-2-PPh}_2\text{-C=C(Me)CH}_2\text{PPh}_2\text{-}\kappa\text{C,C,P})\text{X}]$ (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 $[\text{Pt}(\text{C}_6\text{H}_4\text{-4-F})\{\text{C}_6\text{H}_3\text{-5-F-2-P(p-FC}_6\text{H}_4)_2\text{-C=C(Me)CH}_2\text{P(p-FC}_6\text{H}_4)_2\text{-}\kappa\text{C,C,P}}\}\text{Cl}_2]$ (**6**), obtained by reaction of $[(\text{p-FC}_6\text{H}_4)_3\text{PCH}_2\text{-(E)-C(Me)=C(H)P(p-FC}_6\text{H}_4)_3]\text{Cl}_2$ (**1f**) with $\text{PtCl}_2(\text{NPh})_2$ in refluxing 2-methoxyethanol. Complex **3** reacts with AgClO_4 and neutral monodentate (L) and bidentate (L–L) ligands, giving the cationic derivatives $[\text{Pt}(\text{C}_6\text{H}_3\text{-3-Ph-2-PPh}_2\text{-C=C(Me)CH}_2\text{PPh}_2\text{-}\kappa\text{C,C,P})(\text{L})](\text{ClO}_4)$ (L = NMe (**8**), PPh_3 (**9**), pyridine (**10**), $\text{C}\equiv\text{N}^t\text{Bu}$ (**11**)) and $[\text{Pt}(\text{C}_6\text{H}_3\text{-3-Ph-2-PPh}_2\text{-C=C(Me)CH}_2\text{PPh}_2\text{-}\kappa\text{C,C,P})(\text{L-L-}\kappa\text{P})](\text{ClO}_4)$ (L–L = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (**12**)). Complex **3** reacts with excess X_2 (Cl_2 , I_2) to give the expected Pt(IV) derivatives $[\text{Pt}(\text{C}_6\text{H}_3\text{-3-Ph-2-PPh}_2\text{-C=C(Me)CH}_2\text{PPh}_2\text{-}\kappa\text{C,C,P})(\text{Cl})(\text{X})_2]$ ($(\text{X})_2 = (\text{Cl})_2$ (**13**), $(\text{I})_2$ (**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 arene³ functionalization, the study of thermodynamic properties,^{3i,4} the synthesis of complexes with interesting optical properties (e.g. luminescence)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 $[\text{R}_2\text{PhPCH}_2\text{C(O)CH}_2\text{PPhR}_2](\text{X})_2$

(R = Et, Ph; X = Cl, ClO_4) react with $\text{PtCl}_2(\text{NPh})_2$, giving ortho-metallated derivatives containing the C,C-chelating ligand $[\text{C}_6\text{H}_4\text{-2-PR}_2\text{C(H)C(O)CH}_2\text{PR}_2\text{Ph}]$ ^{9,10} (see Figure 1A), while the allyl–phosphonium salts $[\text{PhR}_2\text{PCH}_2\text{C(R')=C(H)R''}](\text{X})$ (R = Me, Ph; R' = H, Me; R'' = H, Me, Ph; X = Cl, ClO_4) gave cycloplatinated

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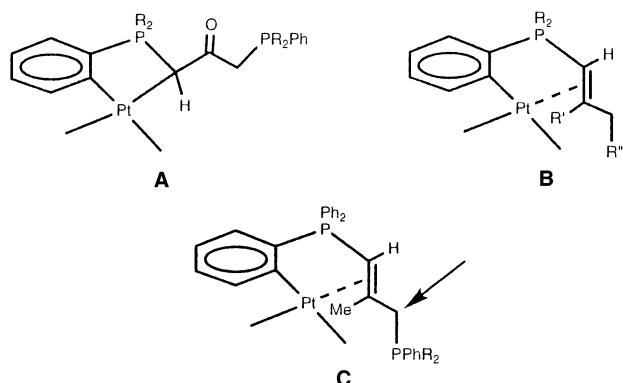
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(1) (a) Crabtree, R. H. *J. Chem. Soc., Dalton Trans.* **2001**, 2437. (b) Jia, C.; Kitamura, T.; Fujiwara, Y. *Acc. Chem. Res.* **2001**, *34*, 633.

(2) (a) Baratta, W.; Stoccoro, S.; Doppin, A.; Herdtweck, E.; Zucca, A.; Rigo, P. *Angew. Chem., Int. Ed.* **2003**, *42*, 105. (b) Zucca, A.; Stoccoro, S.; Cinellu, M. A.; Minghetti, G.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 3336. (c) Vedernikov, A. N.; Caulton, K. G. *Angew. Chem., Int. Ed.* **2002**, *41*, 4102. (d) Ryabov, A. D.; Panyashkina, I. M.; Polyakov, V. A.; Fischer, A. *Organometallics* **2002**, *21*, 1633. (e) Wong-Foy, A. G.; Henling, L. M.; Day, M.; Labinger, J. A.; Bercaw, J. E. *J. Mol. Catal. A* **2002**, *189*, 3.

(3) (a) Zucca, A.; Doppin, A.; Cinellu, M. A.; Stoccoro, S.; Minghetti, G.; Manassero, M. *Organometallics* **2002**, *21*, 783. (b) Konze, W. V.; Scott, B. L.; Kubas, G. J. *J. Am. Chem. Soc.* **2002**, *124*, 12550. (c) Fossey, J. S.; Richards, C. J. *Organometallics* **2002**, *21*, 5259. (d) Minghetti, G.; Doppin, A.; Stoccoro, S.; Zucca, A.; Cinellu, M. A.; Manassero, M.; Sansoni, M. *Eur. J. Inorg. Chem.* **2002**, 431. (e) Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *J. Am. Chem. Soc.* **2002**, *124*, 1378. (f) Ryabov, A. D.; Otto, S.; Samuleev, P. V.; Polyakov, V. A.; Alexandrova, L.; Kazankov, G. M.; Shova, S.; Revenco, M.; Lipkowski, J.; Johansson, M. H. *Inorg. Chem.* **2002**, *41*, 4286. (g) Harkins, S. B.; Peters, J. C. *Organometallics* **2002**, *21*, 1753. (h) Slater, J. W.; Lydon, D. P.; Alcock, N. W.; Rourke, J. P. *Organometallics* **2001**, *20*, 4418. (i) Reinartz, S.; White, P. S.; Brookhart, M.; Templeton, J. L. *J. Am. Chem. Soc.* **2001**, *123*, 12724. (j) Thomas, J. C.; Peters, J. C. *J. Am. Chem. Soc.* **2001**, *123*, 5100. (k) Doppin, A.; Minghetti, G.; Cinellu, M. A.; Stoccoro, S.; Zucca, A.; Manassero, M. *Organometallics* **2001**, *20*, 1148. (l) Riera, X.; López, C.; Caubet, A.; Moreno, V.; Solans, X.; Font-Bardia, M. *Eur. J. Inorg. Chem.* **2001**, 2135. (m) Albrecht, M.; van Koten, G. *Angew. Chem., Int. Ed.* **2001**, *40*, 3750. (n) Albrecht, M.; Spek, A. L.; van Koten, G. *J. Am. Chem. Soc.* **2001**, *123*, 7233. (o) Meijer, M. D.; Kleij, A. W.; Lutz, M.; Spek, A. L.; van Koten, G. *J. Organomet. Chem.* **2001**, *640*, 166.

(4) (a) Kua, J.; Xu, X.; Periana, R. A.; Goddard, W. A., III. *Organometallics* **2002**, *21*, 511. (b) Procelewska, J.; Zahl, A.; van Eldik, R.; Zhong, H. A.; Labinger, J. A.; Bercaw, J. E. *Inorg. Chem.* **2002**, *41*, 2808.

**Figure 1.**

complexes (see Figure 1B) containing the σ,π -vinyl ligand $\text{C}_6\text{H}_4\text{-2-PR}_2\text{C(H)=C(R')CH}_2\text{R''}$.¹⁰

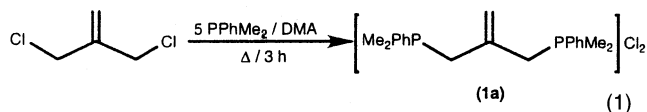
When the reported reactivity is taken into account, it seems very likely that the presence of functional groups at the C_β or C_γ atoms of the allyl unit (R' or R'') should give, after cycloplatination, complexes in which the functional groups still remain incorporated to the η^2 -bonded vinylic skeleton. 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 $[\text{H}_2\text{C=C(CH}_2\text{PPhR}_2)_2](\text{X})_2$ ($\text{R} = \text{Me, Ph; X} = \text{Cl, Br, ClO}_4$) and their reactivity toward Pt(II) complexes. In this paper we report the results obtained in this area.

Results and Discussion

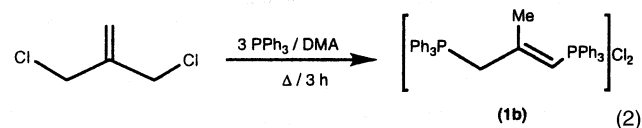
1. Synthesis of Bis-Phosphonium Salts. Linear and cyclic phosphonium salts of the type $[\text{H}_2\text{C=C(CH}_2\text{PPh}_2\text{R)}_2](\text{X})_2$ are known,¹¹ and they have been synthesized through quaternization of the two P atoms of $\text{H}_2\text{C=C(CH}_2\text{PPh}_2)_2$. We have recently reported^{11e} the synthesis of a related cyclic derivative by reaction of $\text{H}_2\text{C=C(CH}_2\text{Cl)}_2$ with $\text{Ph}_2\text{PCH}_2\text{PPh}_2$ (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 appropriate amount of 3-chloro-2-(chloromethyl)propene.

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



NMR spectra of **1a** show a good agreement with the symmetrical proposed structure (see the Experimental Section). However, the reaction of $\text{H}_2\text{C=C(CH}_2\text{Cl)}_2$ with an excess of PPh_3 (1:3 molar ratio, refluxing DMA) gives a quite different result, since the allyl–vinyl bis-phosphonium salt $[\text{Ph}_3\text{PCH}_2\text{-(E)-C(Me)=C(H)PPh}_3]\text{Cl}_2$ (**1b**) (see eq 2) is obtained. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum



of **1b** shows two doublet signals, one at 22.98 ppm (PCH_2) and another at 11.06 ppm ($=\text{CP}$).¹⁰ The ^1H NMR spectrum of **1b** shows a doublet of doublets at 8.05 ppm ($=\text{CH}$), 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 $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum, since the signal due to the CH_3 carbon appears at 24.67 ppm (dd, $^3J_{\text{PC}} = 7.0$ Hz, $^3J_{\text{PC}} = 0.9$ Hz) while the signal due to the CH_2 carbon appears at 35.02 ppm (dd, $^1J_{\text{PC}} = 46.5$ Hz, $^3J_{\text{PC}} = 19.6$ Hz). The value of $^3J_{\text{PC}}$ 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 $[\text{Ph}_3\text{PC(H)=CMe}_2]\text{Cl}$ 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

(5) (a) Yam, V. W.-W.; Tang, R. P.-L.; Wong, K. M.-C.; Lu, X.-X.; Cheung, K.-K.; Zhu, N. *Chem. Eur. J.* **2002**, *8*, 4066. (b) Lu, W.; Zhu, N.; Che, C.-M. *Chem. Commun.* **2002**, *900*. (c) Brooks, J.; Babayan, Y.; Lamansky, S.; Djurovich, P. I.; Tsyba, I.; Bau, R.; Thompson, M. E. *Inorg. Chem.* **2002**, *41*, 3055. (d) Yersin, H.; Donges, D.; Humbs, W.; Strasser, J.; Sitters, R.; Glasbeek, M. *Inorg. Chem.* **2002**, *41*, 4915. (e) Song, D.; Wu, Q.; Hook, A.; Kozin, I.; Wang, S. *Organometallics* **2001**, *20*, 4683.

(6) Yamaguchi, T.; Yamazaki, F.; Ito, T. *J. Am. Chem. Soc.* **2001**, *123*, 743.

(7) Yeo, W.-C.; Vittal, J. J.; White, A. J. P.; Williams, D. J.; Leung, P.-H. *Organometallics* **2001**, *20*, 2167.

(8) Albéniz, A. C.; Calle, V.; Espinet, P.; Gómez, S. *Chem. Commun.* **2002**, 610.

(9) Larraz, C.; Navarro, R.; Urriolabeitia, E. P. *New J. Chem.* **2000**, *24*, 623.

(10) Falvello, L. R.; Fernández, S.; Larraz, C.; Llusar, R.; Navarro, R.; Urriolabeitia, E. P. *Organometallics* **2001**, *20*, 1424 and references therein.

(11) (a) Schmidbaur, H.; Paschalidis, C.; Steigelmann, O.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1989**, *28*, 1700. (b) Schmidbaur, H.; Paschalidis, C.; Steigelmann, O.; Müller, G. *Chem. Ber.* **1989**, *122*, 1851. (c) Schmidbaur, H.; Paschalidis, C.; Steigelmann, O.; Müller, G. *Angew. Chem., Int. Ed. Engl.* **1990**, *29*, 516. (d) Schmidbaur, H.; Gamper, S. F. *Organometallics* **1992**, *11*, 986. (e) Falvello, L. R.; Margalejo, M. M.; Navarro, R.; Urriolabeitia, E. P. *Inorg. Chim. Acta* **2003**, *347*, 75.

(12) (a) Kowalski, M. H.; Hinkle, R. J.; Stang, P. J. *J. Org. Chem.* **1989**, *54*, 2783. (b) Hinkle, R. J.; Stang, P. J.; Kowalski, M. H. *J. Org. Chem.* **1990**, *55*, 5033 and references therein. (c) Ohmori, H.; Takamami, T.; Masui, M. *Tetrahedron Lett.* **1985**, *26*, 2199.

(13) (a) Pd: Huang, C.-C.; Duan, J.-P.; Wu, M.-Y.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1998**, *17*, 676. (b) Pd: Duan, J.-P.; Liao, F.-L.; Wang, S.-L.; Cheng, C.-H. *Organometallics* **1997**, *16*, 3934. (c) Pd or Rh: Ariwasa, M.; Yamaguchi, M. *J. Am. Chem. Soc.* **2000**, *122*, 2387. (d) Ti: Reynolds, K. A.; Dopico, P. G.; Brody, M. S.; Finn, M. G. *J. Org. Chem.* **1997**, *62*, 2564.

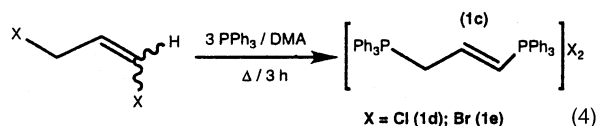
(14) (a) Pt: Yam, V. W.-W.; Yu, K.-L.; Chu, B. W.-K.; Cheung, K.-K. *Organometallics* **2001**, *20*, 3632. (b) Ru: Cadierno, V.; Gamasa, M. P.; Gimeno, J.; González-Bernardo, C.; Pérez-Carreño, E.; García-Granda, S. *Organometallics* **2001**, *20*, 5177. (c) Ir: Chin, C. S.; Lee, M.; Oh, M.; Won, G.; Kim, M.; Park, Y. J. *Organometallics* **2000**, *19*, 1572. (d) Pd: Allen, A.; Lin, W. *Organometallics* **1999**, *18*, 2922. For related synthesis (metal-mediated P–C bond coupling) see: (e) Netz, A.; Polborn, K.; Müller, T. J. J. *Organometallics* **2001**, *20*, 376. (f) Bruce, M. I.; Skelton, B. W.; White, A. H.; Zaitseva, N. N. *J. Chem. Soc., Dalton Trans.* **2001**, 355. (g) Casey, C. P.; Kraft, S.; Powell, D. R.; Kavana, M. J. *Organomet. Chem.* **2001**, *617–618*, 723. (h) Hansen, H. D.; Nelson, J. H. *Organometallics* **2000**, *19*, 4740. (i) Esteruelas, M. A.; Lahoz, F. J.; Martín, M.; Oñate, E.; Oro, L. A. *Organometallics* **1997**, *16*, 4572.

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.

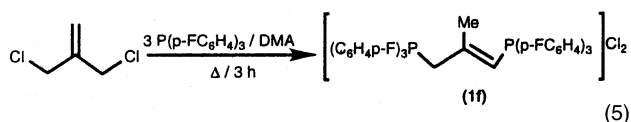
Due to these facts, we have explored in more detail this easy synthesis of allyl–vinyl bis-phosphonium salts. The reaction of 2,3-dibromopropene with PPh₃ under the same experimental conditions as those described for **1b** gives [Ph₃PCH₂C(PPh₃)=CH₂]Br₂ (**1c**) (see eq 3 and the



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 PPh₃ groups. We have not observed isomerization to the bis-vinyl species [Ph₃PC(H)=C(Me)PPh₃]Br₂, 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 PPh₃ (under the same experimental conditions) gives [Ph₃PCH₂-(*E*)-C(H)=C(H)PPh₃]Cl₂ (**1d**) (see eq 4 and the Experimental Section), although in



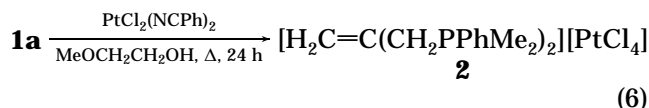
low yield (34.7%). With the dibromo derivative as the starting material, the yield for the corresponding salt [Ph₃PCH₂-(*E*)-C(H)=C(H)PPh₃]Br₂ (**1e**) (eq 4) improves notably (91%), due to the fact that the bromide anion is a better leaving group than the chloride. Compounds **1d** and **1e** show virtually 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 H₂C=C(CH₂Cl)₂ with P(*p*-FC₆H₄)₃ gives the expected [(*p*-FC₆H₄)₃PCH₂-(*E*)-C(Me)=C(H)P(*p*-FC₆H₄)₃]Cl₂ (**1f**) (see eq 5 and the Experimental Section).



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 dif-

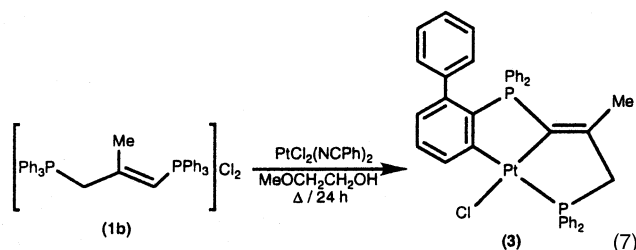
ferent positions (Me, H, or PPh₃ at C_β; H or PPh₃ at C_γ; F at the para position of the Ph groups). Our purpose is now the study of the reactivity of these salts toward Pt(II) complexes, to obtain cycloplatinated derivatives with an additional phosphonium group.

2. Ortho-Metalation Reactions. The reaction of **1a** with PtCl₂(NPh)₂ (1:1 molar ratio) in refluxing 2-methoxyethanol results in the formation of a solid identified as [H₂C=C(CH₂PPhMe₂)₂][PtCl₄] (**2**) (see eq 6). The

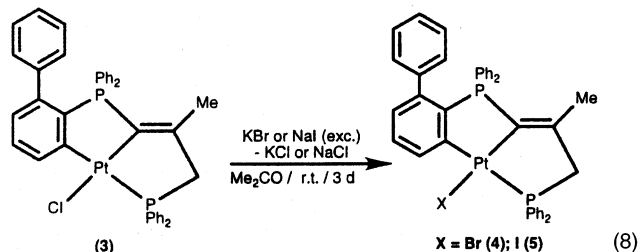


NMR data of **2** (see the Experimental Section) are quite similar to those described for **1a**. For instance, δ(P) in the ³¹P{¹H} NMR spectrum for **1a** is 24.76 ppm and that of **2** is 26.61 ppm. Moreover, signals corresponding to the presence of the C₆H₅ groups in the ¹H NMR spectrum and the persistence of the olefinic and methylenic protons show that no ortho metalation has taken place. This reaction was not investigated further.

The reaction of **1b** with PtCl₂(NPh)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(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,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 CH₂Cl₂/Et₂O affords crystals of adequate quality for X-ray purposes.

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 C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P: the allylic car-

(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. For more references, see ref 10 in this work.

(16) Pretsch, E.; Bühlmann, P.; Affolter, C.; Herrera, A.; Martínez, R. *Structure Determination of Organic Compounds*; Springer-Verlag Ibérica: Barcelona, Spain, 2001.

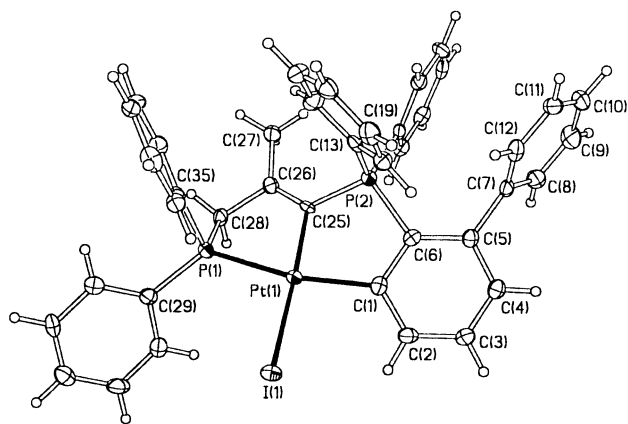


Figure 2.

Table 1. Crystal Data and Structure Refinement Details for 5 and 14·CHCl₃

	5	14·CHCl ₃
empirical formula	C ₄₀ H ₃₃ IP ₂ Pt	C ₄₁ H ₃₄ Cl ₄ I ₂ P ₂ Pt
formula wt	897.59	1179.31
T (K)	100(2)	100(2)
λ, Å	0.71073	0.71073
cryst syst	triclinic	triclinic
space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
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
<i>F</i> (000)	868	1124
θ range for data collec, deg	1.59–25.07	2.14–25.03
no. of rflns collected	15 791	10 852
no. of indep rflns	5681 (<i>R</i> _{int} = 0.0347)	6935 (<i>R</i> _{int} = 0.0232)
no. of data/restraints/params	5681/0/398	6935/0/452
goodness of fit on <i>F</i> ² ^a	0.957	0.995
final <i>R</i> indices [<i>I</i> > 2σ(<i>I</i>)] ^a	<i>R</i> 1 = 0.0263 <i>wR</i> 2 = 0.0519	<i>R</i> 1 = 0.0430 <i>wR</i> 2 = 0.1268
<i>R</i> indices (all data) ^a	<i>R</i> 1 = 0.0304 <i>wR</i> 2 = 0.0528	0.0561 <i>wR</i> 2 = 0.1325
largest diff peak, hole, e Å ⁻³	1.161, -0.741	2.414, -1.939

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

bon C(1), the vinylic carbon C(25), and the phosphorus P(1) of the terminal PPh₂ 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 PPh₃ groups has been cleaved into a PPh₂ fragment (Pt bonded) and a phenyl ring; (ii) one phenyl of the other PPh₃ group has been metalated, and

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)		

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 C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,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(C₆H₄-2-PPh₂-(*E*)-η²-C(H)=C(H)Me)Cl₂]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=CMe₂)(I)(PPh₃)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 ¹H NMR spectra

(17) (a) Orpen, A. G.; Brammer, L.; Allen, F. H.; Kennard, O.; Watson, D. G.; Taylor, R. *J. Chem. Soc., Dalton Trans.* **1989**, S1. (b) Giordano, T. J.; Rasmussen, P. G. *Inorg. Chem.* **1975**, *14*, 1628. (c) Hoover, J. F.; Stryker, J. M. *Organometallics* **1988**, *7*, 2082. (d) Stang, P. J.; Zhong, Z.; Kowalski, M. H. *Organometallics* **1990**, *9*, 833. (e) Romeo, R.; Sclaro, L. M.; Plutino, M. R.; Romeo, A.; Nicolo, F.; Del Zotto, A. *Eur. J. Inorg. Chem.* **2002**, 629. (f) Gaw, K. G.; Slawin, A. M. Z.; Smith, M. B. *Organometallics* **1999**, *18*, 3255. (g) Blacker, A. J.; Clarke, M. L.; Loft, M. S.; Mahon, M. F.; Williams, J. M. J. *Organometallics* **1999**, *18*, 2867. (h) Crespo, M.; Solans, X.; Font-Bardía, M. *Organometallics* **1995**, *14*, 355. (i) Crespo, M.; Font-Bardía, M.; Solans, X. *Polyhedron* **2002**, *21*, 105.

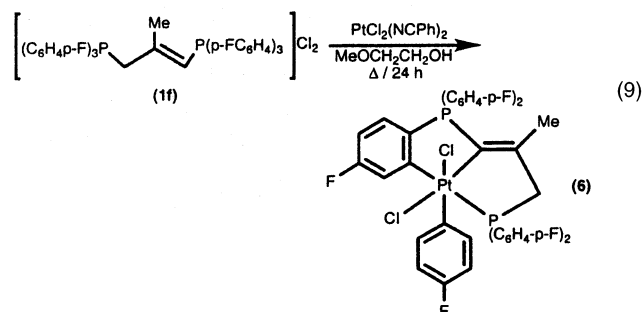
(18) (a) Bennett, M. A.; Kwan, L.; Rae, A. D.; Wenger, E.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **2002**, 226. (b) Bertani, R.; Casarin, M.; Ganis, P.; Maccato, C.; Pandolfo, L.; Vanzo, A.; Vittadini, A.; Zanotto, L. *Organometallics* **2000**, *19*, 1373.

(19) Allen, F. H.; Kennard, O.; Watson, D. G.; Brammer, L.; Orpen, A. G.; Taylor, R. *J. Chem. Soc., Perkin Trans. 2* **1987**, 685.

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 $^3J_{\text{Pt-H(6)}}$ (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 H₄ proton and to the C_6H_5 group at the 3-position of the metalated ring. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **3**–**5** show also common features. They show two doublet signals ($^3J_{\text{PP}}$ 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 $^2J_{\text{PtP}}$ at about 590 Hz, and are attributed to the P atom in the metalated ring. The value of $^2J_{\text{PtP}}$ 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 $^1J_{\text{PtP}}$ consistent with their structures, and their positions also change as the halide changes (25.48 ppm (**3**), 26.53 ppm (**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 $^{13}\text{C}\{^1\text{H}\}$ 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 $^2J_{\text{PC}}$ coupling constants in keeping with the C–*trans*-P arrangement (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 ($\text{C}(1')$) and in the range 129–126 ppm ($\text{C}(2')$ – $\text{C}(4')$).

The presence of different substituents in the phosphonium salts induces notable changes in the reactivity. The reaction of **1c** with $\text{PtCl}_2(\text{NPh})_2$ gives a mixture

of $\text{PtCl}_2(\text{PPh}_3)_2$, $\text{PtClBr}(\text{PPh}_3)_2$, and $\text{PtBr}_2(\text{PPh}_3)_2$, as a result of the complete cleavage of the $\text{Ph}_3\text{P}–\text{C}$ 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 $\text{PtCl}_2(\text{NPh})_2$ affords the Pt(IV) complex $[\text{Pt}(\text{C}_6\text{H}_4-4-\text{F})\{\text{C}_6\text{H}_3-5-\text{F}-2-\text{P}(p\text{-FC}_6\text{H}_4)_2-\text{C}=\text{C}(\text{Me})\text{CH}_2\text{P}(p\text{-FC}_6\text{H}_4)_2-\kappa\text{C},\text{C},\text{P}\}\text{Cl}_2]$ (**6**) (see eq 9 and the Experimental Section).



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 $\text{C}_{40}\text{H}_{28}\text{ClF}_6\text{P}_2\text{Pt}$ (loss of a Cl^- anion), this fact showing that only two protons have been lost from the original bis-phosphonium 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 ($^3J_{\text{PtH(6)}} = 38.6$ 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 $\text{Pt}–\text{C}_6\text{H}_4-4-\text{F}$ 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 ($^3J_{\text{PtH(2')}} = 52.8$ Hz). The magnitude of $^3J_{\text{PtH(2')}}$ is somewhat smaller than those found in related Pt(II) complexes with the $\text{C}_6\text{H}_4-4-\text{F}$ 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 $^{31}\text{P}\{^1\text{H}\}$ 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 ($^2J_{\text{PtP}} = 412.1$ Hz), while that assigned to the P atom bonded to Pt appears at 4.25 ppm ($^1J_{\text{PtP}} = 1510$ Hz). The comparison of these data with those obtained for **3**–**5** shows notable differences: while the

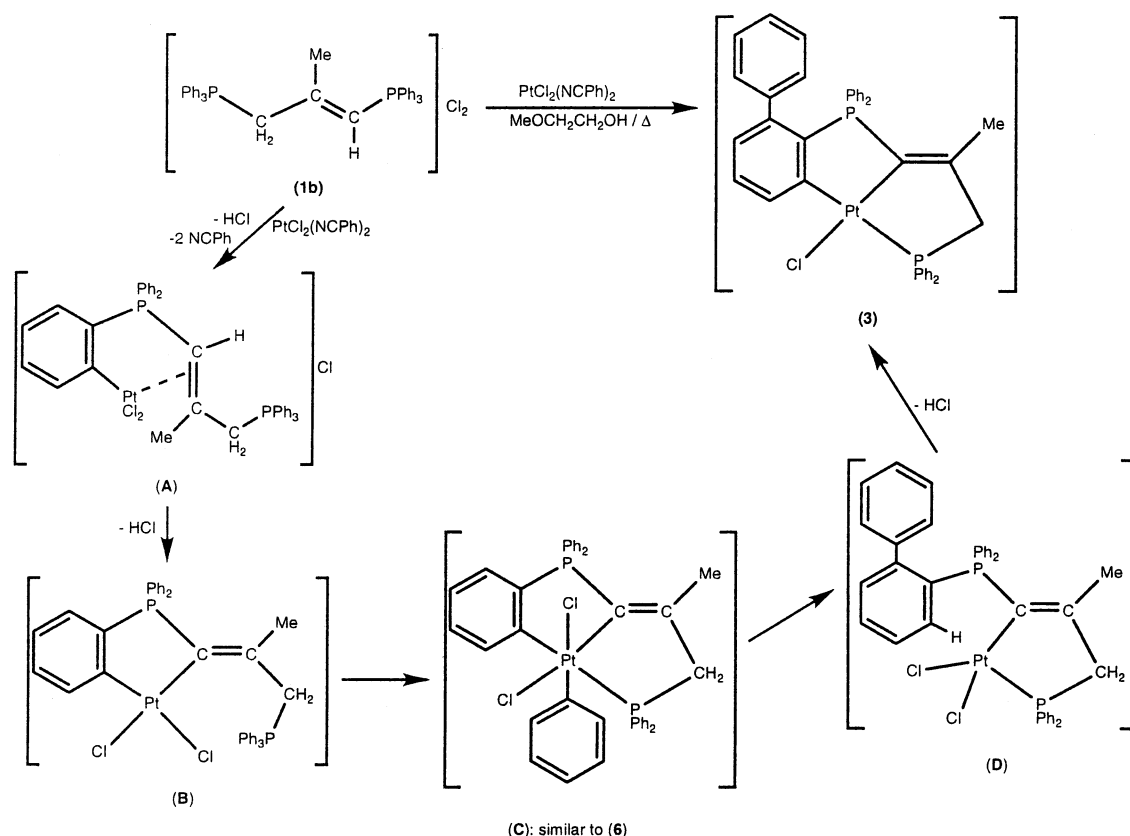
(20) (a) Jun, H.; Young, V. G., Jr.; Angelici, R. J. *J. Am. Chem. Soc.* **1991**, *113*, 9379. (b) Jun, H.; Angelici, R. J. *Organometallics* **1993**, *12*, 4265. (c) Jun, H.; Young, V. G., Jr.; Angelici, R. J. *Organometallics* **1994**, *13*, 2444. (d) Jun, H.; Angelici, R. J. *Organometallics* **1994**, *13*, 2454.

(21) (a) Forníes, J.; Menjón, B.; Sanz-Carrillo, R. M.; Tomás, M.; Connelly, N. G.; Crossley, J. G.; Orpen, A. G. *J. Am. Chem. Soc.* **1995**, *117*, 4295. (b) Crespo, M.; Sales, J.; Solans, X.; Font Altaba, M. *J. Chem. Soc., Dalton Trans.* **1988**, 1617. (c) Ling, S. S. M.; Payne, N. C.; Puddephatt, R. J. *Organometallics* **1985**, *4*, 1546.

(22) (a) Pregosin, P. S. *Coord. Chem. Rev.* **1982**, *44*, 247. (b) Pregosin, P. S. *Transition Metal Nuclear Magnetic Resonance*; Elsevier: Amsterdam, 1991; pp 217–263. Recent examples: (c) Anderson, C.; Crespo, M.; Font-Bardía, M.; Klein, A.; Solans, X. *J. Organomet. Chem.* **2000**, *601*, 22. (d) Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *J. Organomet. Chem.* **2000**, *604*, 290. (e) Ananikov, V. P.; Mitchenko, S. A.; Beletskaya, I. P. *J. Organomet. Chem.* **2001**, *636*, 175. (f) Crespo, M.; Font-Bardía, M.; Pérez, S.; Solans, X. *J. Organomet. Chem.* **2002**, *642*, 171.

(23) Osakada, K.; Sakata, R.; Yamamoto, T. *Organometallics* **1997**, *16*, 5354.

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 nJ_{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 $\text{Pt(II)} \rightarrow \text{Pt(IV)}$, 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–C₆H₄–4-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 $^1\text{H}\{^{19}\text{F}\}$ 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–C₆H₄–4-F atom. The high-field shift undergone by this reso-

nance, with respect to its position in the free bis-phosphonium salt **1f**, is similar to that reported for the F_{para} atom on C₆F₅ 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 ^1H – ^{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 C₆H₄–4-F group.^{22a,b} Finally, the $^{13}\text{C}\{^1\text{H}\}$ 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 $^2J_{\text{PttransC}}$ (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**.

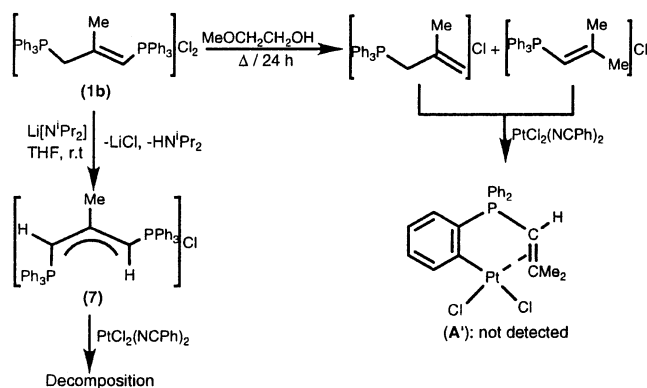
3. Proposed Mechanism for the Synthesis of 3. The isolation and characterization of **6** allows us to shed some light on a plausible reaction pathway through which **3** could be obtained from **1b**. This proposal is depicted in Scheme 1.

(24) (a) Edelbach, B. L.; Lachicotte, R. J.; Jones, W. D. *J. Am. Chem. Soc.* **1998**, *120*, 2843. (b) Alcock, N. W.; Bryars, K. H.; Pringle, P. G. *J. Chem. Soc., Dalton Trans.* **1990**, 1433. (c) Hoover, J. F.; Stryker, J. M. *Organometallics* **1989**, *8*, 2973. (d) Hoover, J. F.; Stryker, J. M. *J. Am. Chem. Soc.* **1989**, *111*, 6466. (e) Hassan, F. S. M.; Higgins, S. J.; Jacobsen, G. B.; Shaw, B. L.; Thornton-Pett, M. *J. Chem. Soc., Dalton Trans.* **1988**, 3011.

(25) Usón, R.; Fornies, J. *Adv. Organomet. Chem.* **1988**, *28*, 219.

(26) Clark, H. C.; Ward, J. E. H. *J. Am. Chem. Soc.* **1974**, *96*, 1741.

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 PPh₃ 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(NiPr₂). 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 PtCl₂(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 PtCl₂(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 [Ph₃PCH₂C(Me)=CH₂]Cl and [Ph₃PC(H)=CMe₂]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 PPh₃ unit. Moreover, the reaction of these phosphonium salts with PtCl₂(NCPh)₂ should result in the formation of the previously reported ortho-metalated derivative [Pt(C₆H₄-2-PPh₂- η^2 -C(H)=CMe₂)Cl₂] (**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 possibilities, 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 PPh₃ 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 –CH₂PPh₃ group is transformed into a –CH₂PPh₂–Pt–Ph unit; up to now, the activation of a phosphonium group to give a phenylphosphino derivative has been

(28) (a) Bennett, M. A.; Clark, P. W.; Robertson, G. B.; Whimp, P. O. *J. Organomet. Chem.* **1973**, *63*, C15. (b) Robertson, G. B.; Whimp, P. O. *Inorg. Chem.* **1974**, *13*, 2082. (c) Bennett, M. A.; Johnson, R. N.; Robertson, G. B.; Tomkins, I. B.; Whimp, P. O. *J. Am. Chem. Soc.* **1976**, *98*, 3514. (d) Cooper, M. K.; Guernsey, P. J.; Goodwin, H. J.; McPartlin, M. *J. Chem. Soc., Chem. Commun.* **1978**, 861.

(29) Zhang, Y.; Aguirre, S. L.; Klumpp, D. A. *Tetrahedron Lett.* **2002**, *43*, 6837.

(30) (a) Garrou, P. E. *Chem. Rev.* **1985**, *85*, 171. Some selected references: (b) Soleilhavoup, M.; Vial, L.; Commenges, G.; Lepetit, C.; Chauvin, R. *Eur. J. Inorg. Chem.* **2003**, 207. (c) Fryzuk, M. D.; Kozak, C. M.; Mehrkhodavandi, P.; Morello, L.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 516. (d) Cabeza, J. A.; Martínez-García, M. A.; Riera, V.; Ardura, D.; García-Granda, S. *Eur. J. Inorg. Chem.* **2000**, 499. (e) Bandini, A. L.; Banditelli, G.; Minghetti, G. *J. Organomet. Chem.* **2000**, *595*, 224. (f) Viñas, C.; Núñez, R.; Teixidor, F.; Sillanpää, R.; Kivekäs, R. *Organometallics* **1999**, *18*, 4712. (g) Bender, R.; Bouaoud, S.-E.; Braunstein, P.; Dusaouy, Y.; Merabet, N.; Raya, J.; Rouag, D. *J. Chem. Soc., Dalton Trans.* **1999**, 735. (h) Crochet, P.; Demerseman, B.; Rocaboy, C.; Schleyer, D. *Organometallics* **1996**, *15*, 3048.

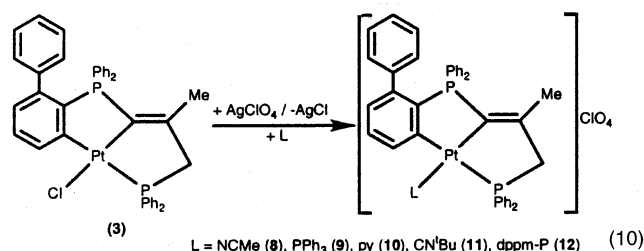
(31) (a) Keim, W.; Kowaldt, F. H.; Goddard, R.; Krüger, C. *Angew. Chem., Int. Ed. Engl.* **1978**, *17*, 466. (b) Ostojka Starzewski, A.; Witte, J. *Angew. Chem., Int. Ed. Engl.* **1985**, *24*, 599. (c) Heyn, R. H.; Görbitz, C. H. *Organometallics* **2002**, *21*, 2781. (d) Kwong, F. Y.; Lai, C. W.; Chan, K. S. *J. Am. Chem. Soc.* **2001**, *123*, 8864. (e) Kwong, F. Y.; Chan, K. S. *Organometallics* **2001**, *20*, 2570. (f) de la Torre, G.; Gouloumis, A.; Vázquez, P.; Torres, T. *Angew. Chem., Int. Ed.* **2001**, *40*, 2895. (g) Lai, C. W.; Kwong, F. Y.; Wang, Y.; Chan, K. S. *Tetrahedron Lett.* **2001**, *42*, 4883. (h) Kwong, F. Y.; Chan, K. S. *Chem. Commun.* **2000**, 1069. (i) Kwong, F. Y.; Chan, K. S. *Organometallics* **2000**, *19*, 2058. (j) Grushin, V. V. *Organometallics* **2000**, *19*, 1888. (k) Reetz, M. T.; Lohmer, G.; Schwickardi, R. *Angew. Chem., Int. Ed.* **1998**, *37*, 481. (l) Goodson, F. E.; Wallow, T. I.; Novak, B. M. *J. Am. Chem. Soc.* **1997**, *119*, 12441. (m) Kong, K. C.; Cheng, C. H. *J. Am. Chem. Soc.* **1991**, *113*, 6313. (n) Vicente, J.; Chicote, M. T.; Beswick, M. A.; Ramírez de Arellano, M. C. *Inorg. Chem.* **1996**, *35*, 6592. (o) Vicente, J.; Chicote, M. T.; Fernández-Baeza, J.; Lahoz, F. J.; López, J. A. *Inorg. Chem.* **1991**, *30*, 3617.

(27) Bestmann, H. J.; Kisielowski, L. *Tetrahedron: Lett.* **1990**, *31*, 3301.

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 PPh₃ 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.

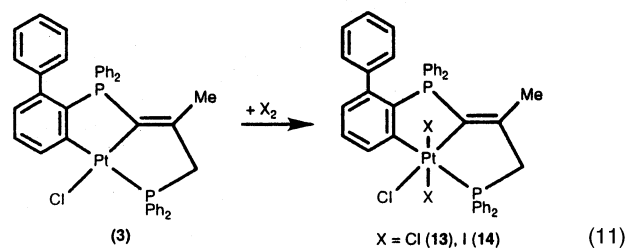
4. Ligand-Substitution Reactions. Further reactivity of complex **3** has been examined. The treatment of **3** with AgClO₄ and neutral ligands L (1:1:1 molar ratio) results in the formation of the corresponding cationic derivatives [Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂-PPh₂-κC,C,P(L))ClO₄ (L = NCMe (**8**), PPh₃ (**9**), pyridine (**10**), C≡N⁺Bu (**11**), Ph₂PCH₂PPh₂-κP (**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 NCMe group. For complex **9** the presence of coordinated PPh₃ is clearly

seen in the ³¹P{¹H} NMR, in which an ABX spin system (each signal showing ¹⁹⁵Pt satellites) is observed. Moreover, the ¹⁹⁵Pt 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 ³¹P{¹H}, ¹⁹⁵Pt, and ¹³C{¹H} NMR spectra are consistent with the structure depicted in eq 10. The comparison of the ¹⁹⁵Pt NMR spectra of **9** (δ -4316 ppm, PPh₃) 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 'BuN≡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 Ph₂PCH₂PPh₂ (dppm) ligand in complex **12** is produced through only one of the P atoms, as is reflected in its ³¹P{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–PPh₂ atom (trans to the aryl group) and 2513 Hz for the Pt–PPh₃ 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.

5. Oxidative Addition Reactions. Complex **3** also undergoes oxidative additions of halogens X₂. The treatment of a CH₂Cl₂ solution of **3** with halogens X₂ (X = Cl, I) gives the Pt(IV) derivatives [Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂-PPh₂-κC,C,P)Cl(X)₂] (X = Cl (**13**), I (**14**)) (see eq 11), in accord with their elemental analyses and NMR data.



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

(32) (a) Puddephatt, R. J. *Angew. Chem., Int. Ed.* **2002**, *41*, 261 and references therein. (b) Goldberg, K. I.; Yan, J.; Winter, E. L. *J. Am. Chem. Soc.* **1994**, *116*, 1573. (c) Font-Bardia, M.; Gallego, C.; Martínez, M.; Solans, X. *Organometallics* **2002**, *21*, 3305. (d) Bernhardt, P. V.; Gallego, C.; Martínez, M.; Parella, T. *Inorg. Chem.* **2002**, *41*, 1747. (e) Bernhardt, P. V.; Gallego, C.; Martínez, M. *Organometallics* **2000**, *19*, 4862.

(33) Deeming, A. J.; Rothwell, I. P.; Hursthouse, M. B.; New, L. J. *Chem. Soc., Dalton Trans.* **1978**, 1490.

(34) Cross, R. J. In *Comprehensive Organometallic Chemistry II*; Abel, E. W.; Stone, F. G. A.; Wilkinson, G., Editors-in-Chief; Puddephatt, R. J., Volume Ed.; Pergamon Press: Oxford, U.K., 1995; Vol. 9, pp 411–430.

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 $^3J_{\text{PtH(6)}}$ (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 CH₂ protons appear in both complexes as equivalent, showing that there is a symmetry plane containing the C,C,P-metallated ligand. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectrum shows the presence of two doublet signals with ^{195}Pt satellites. While the signals attributed to the metallated P atom vary only slightly their position with respect to that in **3**, those assigned to the Pt–PPh₂ 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 $^nJ_{\text{PtP}}$ 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 metallated ligand preserves the structural arrangement 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 CH₂ 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 X₂ 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 [C₆H₃-3-Ph-2-PPh₂-C≡C(Me)-CH₂-PPh₂-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 metallated 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)

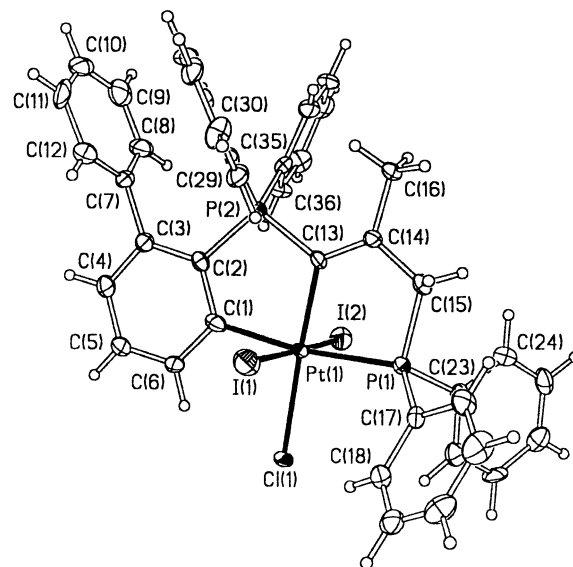


Figure 3.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for 14-CHCl₃

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)

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)–

(35) Skinner, C. E.; Jones, M. M. *J. Am. Chem. Soc.* **1969**, *91*, 4405.

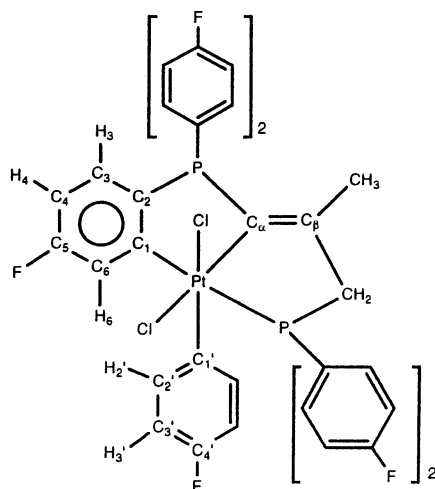
(36) (a) Ruiz, J.; López, J. F. J.; Rodríguez, V.; Pérez, J.; Ramírez de Arellano, M. C.; López, G. *J. Chem. Soc., Dalton Trans.* **2001**, 2683. (b) Vicente, J.; Chicote, M. T.; Martín, J.; Jones, P. G.; Fittschen, C. *J. Chem. Soc., Dalton Trans.* **1987**, 881. (c) Fornies, J.; Fortuño, C.; Gómez, M. A.; Menjón, B.; Herdtweck, E. *Organometallics* **1993**, *12*, 4368. (d) Fornies, J.; Martín, A.; Navarro, R.; Sicilia, V.; Villarroja, P. *Organometallics* **1996**, *15*, 1826.

(37) (a) Lai, S.-W.; Chan, M. C.-W.; Cheung, K.-K.; Che, C.-M. *Organometallics* **1999**, *18*, 3327. (b) van Beek, J. A. M.; van Koten, G.; Wehman-Ooyevaar, I. C. M.; Smeets, W. J. J.; van der Sluis, P.; Spek, A. L. *J. Chem. Soc., Dalton Trans.* **1991**, 883. (c) Canty, A. J.; Honeyman, T.; Skelton, B. W.; White, A. H. *J. Organomet. Chem.* **1990**, *396*, 105. (d) Clark, H. C.; Ferguson, G.; Jain, V. K.; Parvez, M. *Organometallics* **1983**, *2*, 806. (e) Cheetham, A. K.; Puddephatt, R. J.; Zalkin, A.; Templeton, D. H.; Templeton, L. K. *Inorg. Chem.* **1976**, *15*, 2997.

43.8), 7.77–7.67 (m, 4H, H_o, PPh₂), 7.57–7.29 (m, 17H, PPh₂ + H₅), 7.07 (tt, 1H, H_{4'}, ³J_{H4'H3'} = 7.5, ⁴J_{H4'H2'} = 1.2), 6.89–6.81 (m, 3H, H₄ + H_{3'}), 6.46 (dd, 2H, H_{2'}, ³J_{H3'H2'} = 7.8), 3.05 (dq, 2H, CH₂, ²J_{PH} = 8.4, ⁴J_{H-Me} = 0.9), 1.31 (dm, 3H, Me, ⁴J_{PH} = 2.7). ³¹P{¹H} NMR (CD₂Cl₂, room temperature): 34.16 (d, Ph₂P–C–Pt, ³J_{PP} = 24.6, ²J_{PtP} = 599), 26.53 (d, Ph₂P–Pt, ¹J_{PtP} = 2035.6).

[Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)] (5). Yield: 81%. ¹H NMR (CD₂Cl₂, room temperature): 9.09 (ddt, 1H, H₆, ³J_{H6H5} = 7.8, ⁴J_{H6P(Pt)} = 6.3, ⁴J_{H6H4} ≈ ⁴J_{H6P} = 1.5, ³J_{H6Pt} = 45.9), 7.68–7.61 (m, 4H, H_o, PPh₂), 7.56–7.28 (m, 17H, PPh₂ + H₅), 7.06 (tt, 1H, H_{4'}, ³J_{H4'H3'} = 7.5, ⁴J_{H4'H2'} = 1.2), 6.85 (m, 1H, H₄), 6.83 (t, 2H, H_{3'}, ³J_{H4'H3'} ≈ ³J_{H3'H2'} = 7.5), 6.48 (dd, 2H, H_{2'}), 3.12 (dq, 2H, CH₂, ²J_{PH} = 9.3, ⁴J_{H-Me} = 0.6), 1.27 (dm, 3H, Me, ⁴J_{PH} = 2.4). ³¹P{¹H} NMR (CD₂Cl₂, room temperature): 34.29 (d, Ph₂P–C–Pt, ³J_{PP} = 23.4, ²J_{PtP} = 580.5), 27.61 (d, Ph₂P–Pt, ¹J_{PtP} = 1981.4).

[Pt(C₆H₄-4-F){C₆H₃-5-F-2-P(p-FC₆H₄)₂-C=C(Me)CH₂P(p-FC₆H₄)₂-κC,C,P]Cl₂] (6). The bis-phosphonium salt **1f** (0.533 g, 0.704 mmol) and PtCl₂(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 CH₂Cl₂ (3 × 10 mL), dried with MgSO₄, evaporated to dryness, and treated with Et₂O (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 (CD₂Cl₂, room temperature): 8.53 (td, 1H, H₆, ³J_{H6F} ≈ ⁴J_{H6P(Pt)} = 10.0, ⁴J_{H6H4} = 1.0, ³J_{PtH6} = 38.6), 8.13 (ddd, 2H, H_o, Pt–PC₆H₄F, ³J_{HP} = 10.2, ³J_{H6Hm} = 8.7, ⁴J_{HF} = 5.4), 7.97 (ddd, 2H, H_o, PC₆H₄F, ³J_{HP} = 12.0, ³J_{HoHm} = 9.0, ⁴J_{HF} = 5.4), 7.47 (ddd, 2H, H_o, Pt–PC₆H₄F, ³J_{HP} = 10.2, ³J_{HoHm} = 8.7, ⁴J_{HF} = 5.4), 7.31 (td, 2H, H_m, PC₆H₄F, ³J_{HmHo} = ³J_{HmF} = 9.0, ⁴J_{HmP} = 2.1), 7.10 (td, 2H, H_m, Pt–PC₆H₄F, ³J_{HmHo} = ³J_{HmF} = 8.7, ⁴J_{HmP} = 2.1), 7.02–6.97 (m, 4H, 2H_o (PC₆H₄F) + 2H_m (PC₆H₄F)), 6.89–6.80 (m, 4H, 2H_m (Pt–PC₆H₄F) + H₃ + H₄), 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, CH₂, ²J_{PH} = 10.5, ⁴J_{PH} = 1.5), 2.13 (d, 3H, CH₃, ⁴J_{PH} = 2.4). ³¹P{¹H} NMR (CD₂Cl₂, 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).

[Ph₃PC(H)C(Me)C(H)PPh₃]Cl (7). The bis-phosphonium salt **1b** (1.000 g, 1.54 mmol) was suspended in dry THF (30 mL) under Ar, and Li(NiPr₂) (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 CH₂Cl₂ (2 × 20 mL), and the extracts were filtered over a Celite pad. The obtained solution was washed with H₂O (10 mL), dried with MgSO₄, and evaporated to dryness, giving a yellow residue. This residue was triturated with Et₂O (50 mL), and the resulting yellow solid (**7**) was filtered, washed with additional Et₂O (50 mL), and dried in vacuo. Yield: 0.822 g (87%). ¹H NMR (CDCl₃, room temperature): 7.63–7.16 (m, 30H, PPh₃), 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, CH₃). ³¹P{¹H} NMR (CDCl₃, room temperature): 11.62 (s), 11.42 (s).

[Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)(NCMe)]ClO₄ (8). To a suspension of **3** (0.100 g, 0.124 mmol) in 15 mL of NCMe was added AgClO₄ (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 Et₂O 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 (CDCl₃, room temperature): 7.91 (ddt, 1H, H₆, 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, PPh₂ + H₅), 7.06 (tt, 1H, H_{4'}, ³J_{H4'H3'} = 7.2, ⁴J_{H4'H2'} = 1.2), 6.96 (ddd, 1H, H₄, 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, CH₂, ²J_{PH} = 9.0), 2.50 (d, 3H, NCMe, ⁵J_{PH} = 0.9), 1.46 (d, 3H, CH₃, ⁴J_{PH} = 2.4). ³¹P{¹H} NMR (CDCl₃, room temperature): 37.93 (d, PPh₂, ³J_{PP} = 24.4, ²J_{PtP} = 583), 31.80 (d, Pt–PPh₂, ¹J_{PtP} = 2002).

[Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)(PPh₃)]ClO₄ (9). Yield: 79.5%. ¹H NMR (CDCl₃, room temperature): 7.64–7.58 (m, 2H, Ph), 7.43–7.16 (m, 27H, Ph (25H) + C₆H₃ (2H)), 7.08–6.92 (m, 8H, Ph), 6.87–6.82 (m, 2H, H_{4'} + C₆H₃ (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, CH₂, ²J_{PH} = 9.0), 1.36 (d, 3H, CH₃, ⁴J_{PH} = 2.1). ³¹P{¹H} NMR (CD₂Cl₂, room temperature): 35.64 (dd, A part of an ABX spin system, PPh₂, ³J_{PAPB} = 20.4, ³J_{PAPPB3} = 7.4, ²J_{PtPA} = 472), 35.04 (dd, B part of an ABX spin system, Pt–PPh₂, ³J_{PAPB} = 20.4, ²J_{PBPB3} = 16.0, ¹J_{PtPB} = 1923), 25.67 (dd, X part of an ABX spin system, Pt–PPh₃, ¹J_{PtP} = 2513).

[Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)(py)]ClO₄ (10). Yield: 78.4%. ¹H NMR (CDCl₃, 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 + H₅), 7.05 (tt, 1H, H_{4'}, ³J_{H4'H3'} = 7.8, ⁴J_{H4'H2'} = 1.2), 6.91 (td, 1H, H₄, 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, H₆, 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, CH₂, ²J_{PH} = 9.0), 1.47 (d, 3H, CH₃, ⁴J_{PH} = 2.4). ³¹P{¹H} NMR (CD₂Cl₂, room temperature): 35.87 (d, PPh₂, ³J_{PP} = 24.7, ²J_{PtP} = 546), 33.28 (d, Pt–PPh₂, ¹J_{PtP} = 2033).

[Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)(C≡N'Bu)]ClO₄ (11). Yield: 80.7%. ¹H NMR (CDCl₃, room temperature): 8.05 (dddd, 1H, H₆, 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 + H₅), 7.07 (tt, 1H, H_{4'}, ³J_{H4'H3'} = 7.8, ⁴J_{H4'H2'} = 1.2), 7.00 (ddd, 1H, H₄, 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, CH₂, ²J_{PH} = 9.3), 1.57 (d, 3H, CH₃, ⁴J_{PH} = 2.4), 1.46 (s, 9H, 'Bu). ³¹P{¹H} NMR (CDCl₃, room temperature): 39.22 (d, PPh₂, ³J_{PP} = 23.4, ²J_{PtP} = 465), 31.83 (d, Pt–PPh₂, ¹J_{PtP} = 1824).

[Pt(C₆H₃-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)(dppm-κP)]ClO₄ (12). Yield: 87%. ¹H NMR (CDCl₃, room temperature): 7.68–7.00 (m, 44H, PPh₂ + C₆H₃ + H₄), 6.77 (t, 2H, H_{3'}, ³J_{H3'H4'} = ³J_{H3'H2'} = 7.2), 6.53 (d, 2H, H_{2'}), 3.46 (m, 2H, CH₂, dppm), 3.11 (dd, 2H, Pt–PCH₂, ²J_{PH} = 9.9, ⁴J_{PH} = 3.00), 1.38

(d, 3H, CH₃, ⁴J_{PH} = 2.4). ³¹P{¹H} NMR (CDCl₃, room temperature): 36.84 (dd, PPh₂, ³J_{PP} = 19.0, ³J_{PP(dppm)} = 7.2, ²J_{PtP} = 467), 35.51 (t, Pt–PPh₂, ³J_{PP} = ²J_{P(cis)P(dppm)} = 19.0, ¹J_{PtP} = 1913), 15.84 (ddd, Pt–PPh₂, dppm, ²J_{PP} = 94, ¹J_{PtP} = 2526), –23.74 (d, free PPh₂, dppm, ²J_{PP} = 94).

mer-[Pt(C₆H₅-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)-(Cl)₃] (13). A suspension of complex **3** (0.100 g, 0.124 mmol) in 20 mL of CH₂Cl₂ was treated with a solution of Cl₂ in CCl₄ (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 Et₂O (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 (CD₂Cl₂, room temperature): 8.84 (dddd, 1H, H₆, 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, PPh₂), 7.97–7.79 (m, 5H, PPh₂ + H₅), 7.69–7.36 (m, 14H, PPh₂), 7.16 (tt, 1H, H₄, ³J_{H4'H3'} = 7.8, ⁴J_{H4'H2'} = 1.2), 6.93 (ddd, 1H, H₄, ³J_{H4H5} = 6.0, ⁴J_{H4P} = 5.2, ⁴J_{H4H6} = 2.4), 6.87 (t, 2H, H₃, ³J_{H3'H4'} = ³J_{H3'H2'} = 7.8), 6.42 (dd, 2H, H₂), 3.77 (dd, 2H, CH₂, ²J_{PH} = 11.1, ⁴J_{PH} = 2.4), 1.89 (d, 3H, CH₃, ⁴J_{PH} = 1.8). ³¹P{¹H} NMR (CD₂Cl₂, room temperature): 32.48 (d, PPh₂, ³J_{PP} = 25.5, ²J_{PtP} = 296), 2.76 (d, Pt–PPh₂, ¹J_{PtP} = 1371).

trans-[Pt(C₆H₅-3-Ph-2-PPh₂-C=C(Me)CH₂PPh₂-κC,C,P)(Cl)(I)₂] (14). Yield: 77.9%. ¹H NMR (CD₂Cl₂, room temperature): 8.71 (dddd, 1H, H₆, 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, PPh₂), 7.67–7.55 (m, 7H, PPh₂ + H₅), 7.46–7.33 (m, 10H, PPh₂), 7.06 (tt, 1H, H₄, ³J_{H4'H3'} = 7.5, ⁴J_{H4'H2'} = 1.2), 6.79 (t, 2H, H₃, ³J_{H3'H4'} = ³J_{H3'H2'} = 7.5), 6.76 (m, 1H, H₄, overlapped with H₃), 6.51 (dd, 2H, H₂), 3.93 (dd, 2H, CH₂, ²J_{PH} = 10.8, ⁴J_{PH} = 1.8), 2.13 (d, 3H, CH₃, ⁴J_{PH} = 2.1). ³¹P{¹H} NMR (CD₂Cl₂, room temperature): 34.41 (d, PPh₂, ³J_{PP} = 23.3, ²J_{PtP} = 338), –13.46 (d, Pt–PPh₂, ¹J_{PtP} = 1427).

Crystal Structure Determination of Complexes 5 and 14. Crystals of **5** and of **14**·CHCl₃ of adequate quality for X-ray measurements were grown by slow vapor diffusion of Et₂O into a CH₂Cl₂ (**5**) or CHCl₃ (**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 (λ = 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 φ = 0, 90, 180, and 270° with the detector at 2θ = 30°. For each of these runs, 606 frames were collected at 0.3° intervals and 5 s per frame. For the complex **14**·CHCl₃ a hemisphere of data was collected on the basis of 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 10 s per frame. In both cases, the diffraction frames were integrated using the program SAINT³⁹ 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 assigned an isotropic displacement parameter equal to 1.2 times the equivalent isotropic displacement parameter of its parent atom. The structures were refined to F_o², and all reflections were used in the least-squares calculations.⁴²

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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**·CHCl₃. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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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.

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

(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.