

Contrasting Thermal and Photochemical Intramolecular Coupling in Alkynylphosphine Platinum(II) Complexes

Ana García, Julio Gómez, Elena Lalinde,* and M. Teresa Moreno

Departamento de Química, Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de La Rioja, 26006, Logroño, Spain

Received April 18, 2006

The thermal and photochemical transformations of a series of alkynylphosphine platinum(II) complexes are described. Compounds $[\text{Pt}](\text{PPh}_2\text{C}\equiv\text{CR})_2$ ($[\text{Pt}] = \text{cis-Pt}(\text{C}_6\text{F}_5)_2$, $\text{R} = \text{Ph}$, Tol) rearrange thermally to generate naphthalene-based diphenylphosphine complexes (**1a**, **1b**) containing the fragment $\{\text{C}_{10}\text{H}_5\text{-1-Ph-2,3-}\kappa\text{PP}'(\text{PPh}_2)_2\}$ or $\{7\text{-CH}_3\text{-C}_{10}\text{H}_4\text{-1-Tol-2,3-}\kappa\text{PP}'(\text{PPh}_2)_2\}$, formed by intramolecular coupling of two adjacent $\text{PPh}_2\text{C}\equiv\text{CR}$ ligands. By contrast, irradiation of these alkynylphosphine derivatives in toluene results in the formation of a mixture of **1a/1b** and the 1,2-diphosphino-alk-1-ene complexes $[\text{Pt}]\{\text{PPh}_2\text{C}(\text{Ph})=\text{C}(\text{R})\text{PPh}(\text{C}\equiv\text{CR})\}$ ($\text{R} = \text{Ph}$, **2a**; Tol , **2b**) in a final ratio of 60:40. However, irradiation of the mixed alkynylphosphine derivatives $[\text{Pt}](\text{PPh}_2\text{C}\equiv\text{CR})(\text{PPh}_2\text{C}\equiv\text{Ct-Bu})$ gives selectively $[\text{Pt}]\{\text{Ph}_2\text{PC}(\text{Ph})=\text{C}(\text{R})\text{PPh}(\text{C}\equiv\text{Ct-Bu})\}$ ($\text{R} = \text{Ph}$, **3a**; Tol , **3b**; $t\text{-Bu}$, **3c**) as result of a $\text{P-C}(\text{Ph})$ activation of a *tert*-butylalkynylphosphine, $\text{PPh}_2\text{C}\equiv\text{Ct-Bu}$. Under thermolysis, bis(*tert*-butyl)alkynyl derivatives produce no evidence of any cyclization product, but the mixed alkynylphosphine derivatives $[\text{Pt}](\text{PPh}_2\text{C}\equiv\text{CR})(\text{PPh}_2\text{C}\equiv\text{Ct-Bu})$ evolve giving small amounts of **1a/1b** and *trans*- $[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{C}\equiv\text{Ct-Bu})_2]$, **4**. Under photolytic conditions, the diynyl phosphine derivatives $[\text{Pt}](\text{PPh}_2\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CR})_2$ ($\text{R} = \text{Ph}$, $t\text{-Bu}$) rearrange directly to the naphthalene complexes $[\text{Pt}]\{7\text{-C}\equiv\text{CR-C}_{10}\text{H}_4\text{-1-(C}_6\text{H}_4\text{-pC}\equiv\text{CR)-2,3-}\kappa\text{PP}'(\text{PPh}_2)_2\}$ ($\text{R} = \text{Ph}$, **5a**; $t\text{-Bu}$, **5c**), resulting from the intramolecular coupling of the two inner alkynyl fragments, with no observable intermediates. Finally, site-selective activation takes place by photochemical or thermal treatment of $[\text{Pt}](\text{PPh}_2\text{C}\equiv\text{CPh})(\text{PPh}_2\text{H})$, **6**. Thus, while under photochemical conditions complex **6** yields selectively $[\text{Pt}]\{\text{Ph}_2\text{PC}(\text{Ph})=\text{C}(\text{Ph})\text{PPhH}\}$, **7**, by a ligand rearrangement coupling process involving activation of a $\text{P-C}(\text{Ph})$ bond, the regioisomer $[\text{Pt}]\{\text{Ph}_2\text{PC}(\text{H})=\text{C}(\text{Ph})\text{PPh}_2\}$, **8**, is generated by a thermal activation of the P-H bond.

Introduction

Coordination chemistry of alkynylphosphines has long been investigated. The η^2 -binding at the triple bond and coordination of metal ions at the P donor allow the straightforward formation of a variety of polynuclear species.^{1–14} Several strategies of reactivity of alkynylphosphines coordinated via phosphorus to

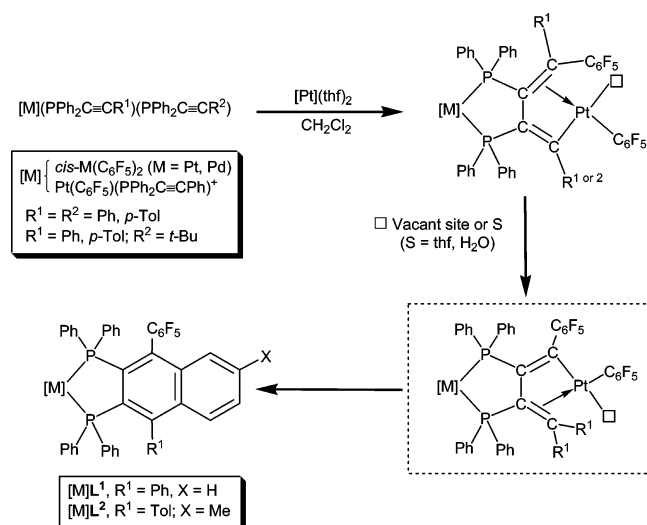
metal complexes have been designed. The cleavage of the phosphorus–carbon bond to generate bridging diphenylphosphido and alkynyl groups has been observed by pyrolyzing metal carbonyl clusters.^{15–21} The cyclization reactions are of particular interest for the work presented here. Several years ago, Carty et al. showed the thermal intramolecular coupling of the two alkynyl moieties located in close proximity in *cis*- $[\text{PtX}_2\text{-}(\text{PPh}_2\text{C}\equiv\text{CR})_2]$ to form substituted naphthalenes.^{22,23} One of the parameters that seems to play a role in this reaction is the separation between the acetylenic carbon atoms (commonly referred to as the $\text{C}_\alpha\text{-C}_\alpha$ distance). Recently, we have demonstrated^{4,6,9} the formation of novel coordinated naphthalene diphosphine ligands ($\{\text{C}_{10}\text{H}_4\text{-1-C}_6\text{F}_5\text{-4-Ph-2,3-}\kappa\text{PP}'(\text{PPh}_2)_2\}$ (**L**¹) and $\{7\text{-CH}_3\text{-C}_{10}\text{H}_3\text{-1-C}_6\text{F}_5\text{-4-Tol-2,3-}\kappa\text{PP}'(\text{PPh}_2)_2\}$ (**L**²)) facili-

* Corresponding author. E-mail: elena.lalinde@dq.unirioja.es.

- (1) Went, M. J. *Polyhedron* **1995**, *14*, 465, and references therein.
- (2) Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Welch, A. J. *J. Chem. Soc., Dalton Trans.* **1995**, 1333.
- (3) Ara, I.; Falvello, L. R.; Fernández, S.; Forniés, J.; Lalinde, E.; Martín, A.; Moreno, M. T. *Organometallics* **1997**, *16*, 5923.
- (4) Charmant, J. P. H.; Forniés, J.; Gómez, J.; Lalinde, E.; Moreno, M. T.; Orpen, A. G.; Solano, S. *Angew. Chem., Int. Ed.* **1999**, *38*, 3058.
- (5) Berenguer, J. R.; Bernechea, M.; Forniés, J.; Gómez, J.; Lalinde, E. *Organometallics* **2002**, *21*, 2314.
- (6) Ara, I.; Forniés, J.; García, A.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Chem. Eur. J.* **2002**, *8*, 3698.
- (7) Forniés, J.; García, A.; Gómez, J.; Lalinde, E.; Moreno, M. T. *Organometallics* **2002**, *21*, 3733.
- (8) Berenguer, J. R.; Bernechea, M.; Forniés, J.; García, A.; Lalinde, E. *Organometallics* **2004**, *23*, 4288.
- (9) Berenguer, J. R.; Bernechea, M.; Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2004**, *43*, 8185.
- (10) Forniés, J.; García, A.; Gil, B.; Lalinde, E.; Moreno, M. T. *Dalton Trans.* **2004**, 3954.
- (11) Louattani, E.; Suades, J. *J. Organomet. Chem.* **2000**, *604*, 234.
- (12) Baumgartner, T.; Huynh, K.; Schleidt, S.; Lough, A. J.; Manners, I. *Chem. Eur. J.* **2002**, *8*, 4622.
- (13) Bardají, M.; de la Cruz, M. T.; Jones, P. G.; Laguna, A.; Martínez, J.; Villacampa, M. D. *Inorg. Chim. Acta* **2005**, *358*, 1365.
- (14) Albinati, A.; Filippi, V.; Leoni, P.; Marchetti, L.; Pasquali, M.; Passarelli, V. *Chem. Commun.* **2005**, 2155.

- (15) Davies, J. E.; Mays, M. J.; Raithby, P. R.; Sarveswaran, K.; Solan, G. A. *J. Chem. Soc., Dalton Trans.* **2001**, 1269.
- (16) Davies, J. E.; Mays, M. J.; Raithby, P. R.; Sarveswaran, K.; Shields, G. P. *J. Organomet. Chem.* **1999**, *573*, 180.
- (17) Blenkiron, P.; Enright, G. D.; Low, P. J.; Corrigan, J. F.; Taylor, N. J.; Chi, Y.; Saillard, J. Y.; Carty, A. J. *Organometallics* **1998**, *17*, 2447.
- (18) Hogarth, G.; Redmond, S. P. *J. Organomet. Chem.* **1997**, *534*, 221.
- (19) Pereira, R. M. S.; Fujiwara, F. Y.; Vargas, M. D.; Braga, D.; Crepioni, F. *Organometallics* **1997**, *16*, 4833.
- (20) Benvenuti, M. H.; Vargas, M. D.; Braga, D.; Crepioni, F.; Mann, B. E.; Taylor, S. *Organometallics* **1993**, *12*, 2947.
- (21) Mays, M. J.; Sarveswaran, K.; Solan, G. A. *Inorg. Chim. Acta* **2003**, *354*, 21.
- (22) Johnson, D. K.; Rukachaisirikul, T.; Sun, Y.; Taylor, N. J.; Carty, A. J.; Carty, A. J. *Inorg. Chem.* **1993**, *32*, 5544.
- (23) Carty, A. J.; Taylor, N. J.; Johnson, D. K. *J. Am. Chem. Soc.* **1979**, *101*, 5422.

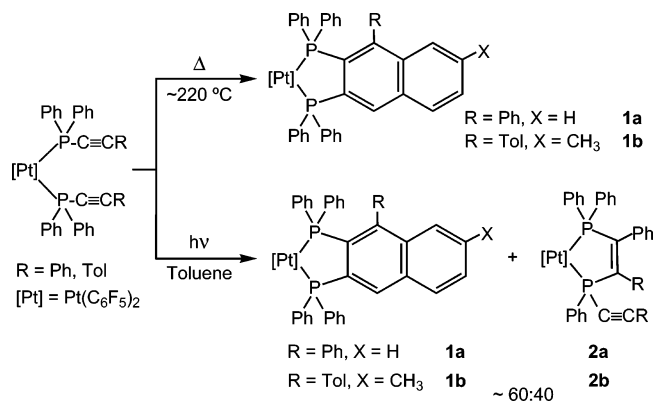
Scheme 1



tated by complexation of the “Pt(C₆F₅)₂” fragment to platinum and palladium precursors containing at least two alkynylphosphine ligands (see Scheme 1). The formation of the ligands takes place through initial μ -2,3-bis(diphenylphosphino)-1,3-butadien-1-yl binuclear complexes $\{\mu-C(R)(C_6F_5)=C(PPh_2)C(PPh_2)=C(R)\}$ formed by successive insertion of both $PPh_2C\equiv CR$ ligands into a Pt–C₆F₅ bond, which evolve through a formal 4–1 migration to analogous $\{\mu-C(C_6F_5)=C(PPh_2)C(PPh_2)=C(R)_2\}$ isomers and finally to 1-pentafluorophenyl-2,3-bis(diphenylphosphine)naphthalene derivatives.

In the context of this chemistry we note the Bergman-cyclization processes of bis(phosphino)enediynes upon complexation to metal ions. The thermal reactivity of such systems is elegantly modulated by the adequate choice of the metal ion geometry, indicating that both conformational and electronic effects play a prominent role in the final reactivity of the enediyne ligands.^{24–26} More recently, two examples of cycloaddition reactions of rigid diyne-based bis(diphenylphosphino) complexes to give strained macrocyclic ring systems have been also described.^{12,27} Apart from thermal effects or metal ion complexation, other cyclization strategies have been employed for the activation of alkynylphosphines. Examples of these are the insertion of the alkynyl functionality into a metal–carbon bond^{4,6,9,28–33} or reactions with nucleophilic or electrophilic substrates.^{34–39} To get a better insight into the parameters that

Scheme 2



control the cyclization process involving alkynylphosphine ligands, we have examined the behavior of several pentafluorophenyl mononuclear platinum complexes bearing different alkynylphosphines, $[Pt](PPh_2C\equiv CR)_2$ (R = Ph, Tol), $[Pt](PPh_2C\equiv CR)(PPh_2C\equiv Ct-Bu)$, $[Pt](PPh_2C\equiv CC_6H_4C\equiv CR)_2$ (R = Ph, *t*-Bu), and $[Pt](PPh_2C\equiv CPh)(PPh_2H)$, under thermal and photochemical conditions, which have been shown to promote cyclization reactions in all cases.

Results and Discussion

Carty and co-workers reported that pyrolysis of a solid sample of $[Pt](PPh_2C\equiv CPh)_2$ at 210 °C for 2.5 h afforded the bis(diphenylphosphine)naphthalene species $[Pt]\{C_{10}H_5-1-Ph-2,3-\kappa PP'(PPh_2)_2\}$, **1a**, by the intramolecular coupling reaction of two coordinated *cis*-alkynylphosphine ligands.²² The ligand has been suggested to be formed via a biradical intermediate or a concerted [2+2+2] cycloaddition to form a common intermediate followed by a 1,3-hydrogen shift.²² Likewise, we have found that thermal treatment (~220 °C, 1 h) of the analogous tolylalkynylphosphine complex $[Pt](PPh_2C\equiv CTol)_2$ gives the related derivative $[Pt]\{7-CH_3-C_{10}H_4-1-Tol-2,3-\kappa PP'(PPh_2)_2\}$, **1b**, as the only phosphorus-containing final species (Scheme 2). The formation of the chelating bis(diphenylphosphine)naphthalene ligands, characterized by X-ray in **1a**,²² is inferred by the presence of two relatively close and characteristic, deshielded ³¹P{¹H} NMR resonances (δ 46.53, 41.06, **1a**; 46.17, 40.24, **1b**) with a slightly smaller ¹J_{Pt–P} coupling constant for the high-energy signal (2267/2322 Hz, **1a**; 2242/2309 Hz, **1b**) and both values, as expected, smaller than in the corresponding starting materials (2400 Hz, R = Ph; 2407 Hz, R = Tol). The ¹⁹F NMR spectra confirm the existence of two different sets of C₆F₅ ligands, and in the proton spectrum of **1b**, two methyl resonances at 2.29 and 2.24 ppm are in agreement with the formation of the $\{7-CH_3-C_{10}H_4-1-Tol-2,3-\kappa PP'(PPh_2)_2\}$ ligand.

Under photolytic conditions, these *cis*-bis(alkynylphosphine)-platinum(II) complexes simultaneously afford not only the diphosphinenaphthalene derivatives **1** but also new diphosphine complexes **2**, resulting from an easy P–C(Ph) activation in one $PPh_2C\equiv CR$ ligand and its formal final 2,1-addition to the triple bond of the second $PPh_2C\equiv CR$ group (Scheme 2). Thus, photochemical reaction of *cis*- $[Pt](C_6F_5)_2(PPh_2C\equiv CR)_2$ (R = Ph, Tol) in toluene solutions for 1 h at room temperature using

(24) Coalter, N. L.; Concolino, T. E.; Streib, W. E.; Hughes, C. G.; Rheingold, A. L.; Zaleski, J. M. *J. Am. Chem. Soc.* **2000**, *122*, 3112.

(25) Basak, A.; Mandal, S.; Bag, S. S. *Chem. Rev.* **2003**, *103*, 4077.

(26) Schmitt, E. W.; Huffman, J. C.; Zaleski, J. M. *Chem. Commun.* **2001**, 167.

(27) Martin-Redondo, M.; Scoles, L.; Sterenberg, B. T.; Udachin, K. A.; Carty, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 5038.

(28) Dupuis, L.; Piro, N.; Meunier, P.; Igau, A.; Donnadieu, D.; Mayoral, J.-P. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 987.

(29) Rosa, P.; Le Floch, P.; Ricard, L.; Mathey, F. *J. Am. Chem. Soc.* **1997**, *119*, 9417.

(30) Miquel, Y.; Igau, A.; Donnadieu, B.; Mayoral, J. P.; Dupuis, L.; Piro, N.; Meunier, P. *Chem. Commun.* **1997**, 279.

(31) Bennett, M. A.; Cobley, C. J.; Rae, A. D.; Wenger, E.; Willis, A. C. *Organometallics* **2000**, *19*, 1522.

(32) Edwards, A. J.; Macgregor, S. A.; Rae, A. D.; Wenger, E.; Willis, A. C. *Organometallics* **2001**, *20*, 2864.

(33) El Harouch, Y.; Cadierno, V.; Igau, A.; Donnadieu, B.; Mayoral, J. P. *J. Organomet. Chem.* **2004**, *689*, 953.

(34) Bennett, M. A.; Castro, J.; Edwards, A. J.; Kopp, M. R.; Wenger, E.; Willis, A. C. *Organometallics* **2001**, *20*, 980.

(35) Bennett, M. A.; Kwan, L.; Rae, A. D.; Wenger, E.; Willis, A. C. *J. Chem. Soc., Dalton Trans.* **2002**, 226.

(36) Liu, X.; Mok, K. F.; Leung, P. H. *Organometallics* **2001**, *20*, 3918.

(37) Liu, X.; Ong, T. K. W.; Selvaratnam, S.; Vittal, J. J.; White, A. J. P.; Williams, D. J.; Leung, P. H. *J. Organomet. Chem.* **2002**, *643*, 4.

(38) Carty, A. J.; Jacobson, S.; Simpson, R. T.; Taylor, N. J. *J. Am. Chem. Soc.* **1975**, *97*, 7254.

(39) Jacobson, S. E.; Taylor, N. J.; Carty, A. J. *J. Chem. Soc., Chem. Commun.* **1974**, 668.

Table 1. Selected Bond Distances (Å) and Angles (deg) for *trans*-[Pt(C₆F₅)₂(PPh₂C≡C*t*-Bu)₂], **4**^a

Pt(1)–C(19)	2.063(3)	P(1)–C(1)	1.747(4)
Pt(1)–P(1)	2.2986(9)	C(1)–C(2)	1.199(4)
C(19)–Pt(1)–P(1)	90.06(9)	P(1)–C(1)–C(2)	175.2(3)
C(19a)–Pt(1)–P(1)	89.94(9)	C(1)–C(2)–C(3)	179.7(4)
P(1)–Pt(1)–P(1a)	180.00(3)	Pt(1)–P(1)–C(1)	114.54(11)

^a Symmetry transformations used to generate equivalent atoms are #1 –x+2, –y, –z.

Table 2. Selected Bond Distances (Å) and Angles (deg) for *cis*-[Pt(C₆F₅)₂{Ph₂PC(Ph)=C(Ph)PPh(C≡C*t*-Bu)}], **3a**

Pt(1)–C(39)	2.065(9)	Pt(1)–P(1)	2.2527(18)
Pt(1)–C(45)	2.083(7)	Pt(1)–P(2)	2.268(2)
P(1)–C(1)	1.830(8)	C(1)–C(2)	1.333(10)
P(2)–C(2)	1.847(7)	C(27)–C(28)	1.167(12)
C(39)–Pt(1)–C(45)	90.9(3)	C(39)–Pt(1)–P(1)	92.7(2)
P(1)–Pt(1)–P(2)	85.42(7)	C(45)–Pt(1)–P(2)	91.1(2)
C(1)–P(1)–Pt(1)	109.3(2)	C(2)–C(1)–P(1)	118.7(5)
C(2)–P(2)–Pt(1)	108.9(2)	C(1)–C(2)–P(2)	117.5(6)
C(21)–C(1)–P(1)	116.6(5)	C(28)–C(27)–P(1)	168.3(8)
C(3)–C(2)–P(2)	120.2(5)	C(27)–C(28)–C(29)	177.1(10)

Table 3. Selected Bond Distances (Å) and Angles (deg) for *cis*-[Pt(C₆F₅)₂{Ph₂PC(Ph)=C(Ph)PPhH}·CHCl₃, **7**·CHCl₃

Pt(1)–C(33)	2.092(6)	Pt(1)–P(1)	2.2419(14)
Pt(1)–C(39)	2.074(5)	Pt(1)–P(2)	2.2751(15)
P(1)–C(1)	1.826(6)	C(1)–C(2)	1.345(8)
P(2)–C(2)	1.840(6)	P(1)–H(1)	0.9800
C(33)–Pt(1)–C(39)	87.5(2)	C(33)–Pt(1)–P(1)	91.35(17)
P(1)–Pt(1)–P(2)	85.44(5)	C(39)–Pt(1)–P(2)	96.01(18)
C(1)–P(1)–Pt(1)	109.14(18)	C(2)–C(1)–P(1)	118.0(4)
C(2)–P(2)–Pt(1)	108.18(19)	C(1)–C(2)–P(2)	117.8(4)
C(3)–C(1)–P(1)	116.9(4)	C(9)–C(2)–P(2)	121.8(4)

Table 4. Selected Bond Distances (Å) and Angles (deg) for *cis*-[Pt(C₆F₅)₂{Ph₂PC(H)=C(Ph)PPh₂}], **8**

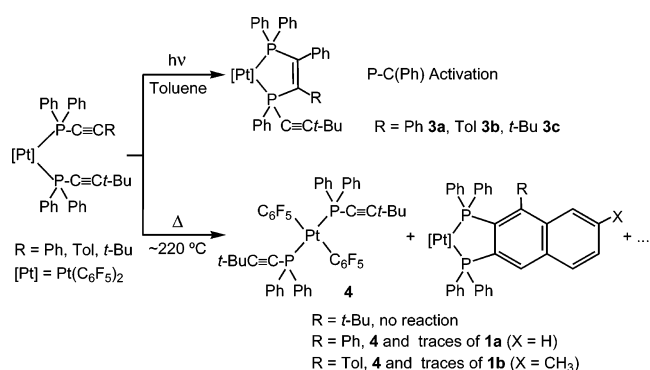
Pt(1)–C(33)	2.075(4)	Pt(1)–P(1)	2.2608(13)
Pt(1)–C(39)	2.094(5)	Pt(1)–P(2)	2.2756(12)
P(1)–C(1)	1.806(5)	C(1)–C(2)	1.324(6)
P(2)–C(2)	1.854(5)	C(1)–H(1)	0.9300
C(33)–Pt(1)–C(39)	88.98(18)	C(33)–Pt(1)–P(1)	91.43(13)
P(1)–Pt(1)–P(2)	85.66(4)	C(39)–Pt(1)–P(2)	93.94(14)
C(1)–P(1)–Pt(1)	107.21(17)	C(2)–C(1)–P(1)	121.0(4)
C(2)–P(2)–Pt(1)	107.74(15)	C(1)–C(2)–P(2)	116.3(4)
H(1)–C(1)–P(1)	119.5	C(1)–C(2)–C(3)	122.2(4)

Table 5. Control of the Formation of **1a** and **2a** by ³¹P{¹H} NMR

time (min)	<i>cis</i> -[Pt(C ₆ F ₅) ₂ (PPh ₂ C≡CPh) ₂]	1a	2a
5	70	20	10
25	43	37	20
45	15	55	30
60 ^a	6	61	33
75 ^a	≈3	58	39

^a Small signals at δ 54.9, 43.1, and 18.1 were also observed.

a 400 W Hg lamp results in the formation of a mixture of the naphthalene complexes **1a** and **1b** and new platinum complexes **2a** and **2b** (Scheme 2). Monitoring these reactions over a period of time (Table 5) indicated the parallel formation of both species **1a/2a**, **1b/2b** resulting in a final 60:40 ratio, even with longer reaction times. All attempts to separate both types of complexes have been unsuccessful. The formulation of **2a** and **2b** as 1,2-diarylalkene-1,2-diphosphine complexes is clearly supported by the photochemical reaction of the related mixed *tert*-butylalkynylphosphine species [Pt](PPh₂C≡CR)(PPh₂C≡C*t*-Bu) (R = Ph, Tol) in toluene. With these precursors the formation of 1-*t*-Bu-naphthalene complexes was not observed. The reactions were

Scheme 3

also monitored by NMR spectroscopy, and transformation to [Pt]{Ph₂PC(Ph)=C(R)PPh(C≡C*t*-Bu)} (R = Ph, **3a**; Tol, **3b**) (Scheme 3) was only quantitatively observed with the mixed aryl/*tert*-butylalkynylphosphine derivatives. As was expected, the related [Pt](PPh₂C≡C*t*-Bu)₂ gives, by photolysis, the corresponding complex [Pt]{Ph₂PC(Ph)=C(*t*-Bu)PPh(C≡C*t*-Bu)}, **3c**. The site-selective activation of P–C(phenyl) bonds with respect to the P–C≡CR bonds in the ligands PPh₂C≡CR (R = Ph, **2a**; Tol, **2b**; *t*-Bu, **3**) is in contrast with previous observations, according to which the bond cleavage in phosphines follows the order P–C(sp) > P–C(sp²) > P–C(sp³).^{40,41}

The X-ray molecular structure of **3a** (see below) indicates that the photochemical reaction produces regiospecifically 1,2-diphosphinoalk-1-ene complexes, involving a formal 2,1-addition of a P–C(Ph) bond in one phosphine through the C≡CR of the other phosphine. The ³¹P{¹H} NMR spectra of complexes **3a–c** show two broad, well-separated singlet resonances (δ 62.97–58.42/33.12–27.33) strongly deshielded with respect to the starting material, arising from two non-equivalent phosphorus atoms in the final five-membered chelate ring. The low-frequency resonances are tentatively assigned to the phosphorus atom of the PPhC≡C*t*-Bu group, whereas the highly deshielded signals are therefore attributed to the PPh₂ fragment of the diphenylphosphine alkene ligand. This assignment is in accord with the chemical shifts of phosphines such as PPh₃ (δ ≈ –6 ppm) and PPh₂C≡C*t*-Bu (δ –34.24).³¹ At low temperature (223 K), the ¹⁹F NMR spectra display two different sets of rigid C₆F₅ groups (AFMRX systems), confirming that the platinum coordination plane is not a symmetry plane. Upon heating to 293 K, the pattern in the *ortho*-fluorine region indicates that one of the C₆F₅ groups is still rigid on the NMR time scale. Their IR spectra exhibit two characteristic ν(C≡C) absorptions in the range 2167–2219 cm^{–1} due to the uncoordinated C≡C*t*-Bu fragments.

The ³¹P{¹H} NMR spectra of complexes **3** and **1** allow us to assign the corresponding signals for compounds **2** in the final mixtures **1/2** (60:40) obtained from photolysis of [Pt](PPh₂C≡CR)₂ (R = Ph, Tol) (see Experimental Section). As described for **3a–c**, complexes **2a** and **2b** show two separated signals (δ_P 58.92/28.38, **2a**; 58.50/28.48, **2b**) versus the close signals assigned to naphthalene complexes **1** (46.50/41.03, **1a**; 46.18/40.25, **1b**).

The thermolysis reactions of the *tert*-butylalkynylphosphine complexes [Pt](PPh₂C≡CR)(PPh₂C≡C*t*-Bu) (R = Ph, Tol, *t*-Bu) were also examined (Scheme 3). Surprisingly, no reaction was observed with the sterically bulky bis(*tert*-butylalky-

(40) Carty, A. J. *Pure Appl. Chem.* **1982**, *54*, 113, and references therein.

(41) Tschan, M. J. L.; Chérioux, F.; Karmazin-Brelot, L.; Süß-Fink, G. *Organometallics* **2005**, *24*, 1974.

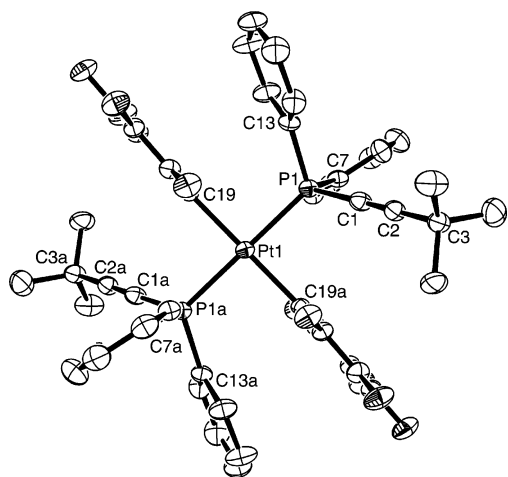
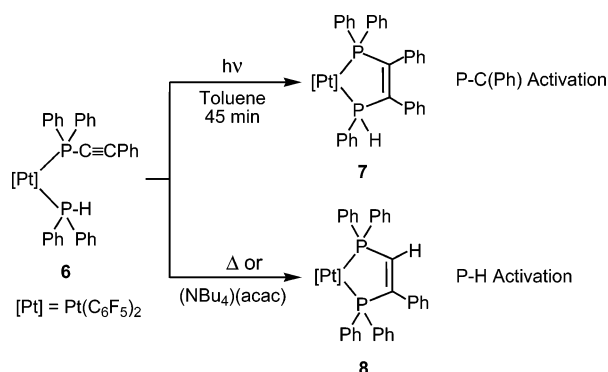


Figure 1. Molecular structure of *trans*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂], **4**. Ellipsoids are drawn at the 50% probability level.

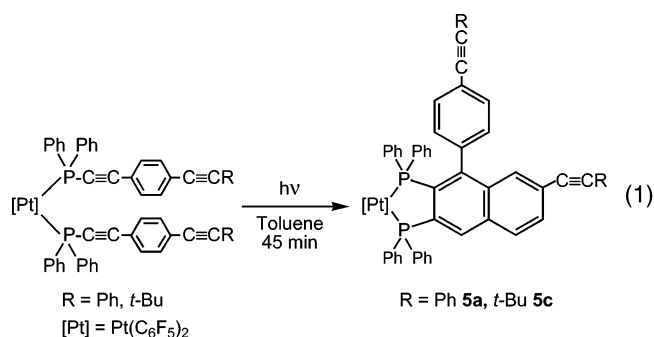
nylphosphine) complex. However, when the mixed aryl/*tert*-butylphosphine derivatives were heated at their melting point for 2 h, the ³¹P{¹H} NMR spectrum of the final brown oily residue obtained showed the formation of a mixture of complexes, which contain (see Experimental Section) small amounts of the corresponding precursors, the naphthalene species **1a** or **1b** and, surprisingly, the *trans*-derivative *trans*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂], **4**, common to both reactions. Crystallization of these mixtures at low temperature generates colorless crystals of **4**. Figure 1 shows the X-ray structure of complex **4**, which contains two *trans*-oriented C₆F₅ and two *tert*-butylethynylphosphine ligands. This complex can be alternatively prepared in high yield by simple displacement of the tetrahydrothiophene ligands (tht) in *trans*-[Pt(C₆F₅)₂(tht)₂] by PPh₂C≡Ct-Bu (see Experimental Section). We recently reported the isomeric *cis*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂] (δ_P -8.79; $^1J_{P-Pt}$ = 2426 Hz).⁴ The *trans* derivative **4** is characterized by a single resonance at δ -7.60 with a $^1J_{P-Pt}$ of 2854 Hz, in agreement with the higher *trans* influence of PPh₂C≡Ct-Bu relative to the C₆F₅ ligand. It should be noted that *trans*-configured mononuclear platinum complexes containing alkynylphosphines had not been previously reported, probably due to the fact that the precursors previously employed (K₂PtCl₄^{12,42–44} or [PtR₂(cod)]^{3,7}) usually generate final *cis*-derivatives. The structural parameters of the *trans* complex **4** are unexceptional (Table 1), with structural data comparable to those of the related palladium complexes, *trans*-[PdX₂(PPh₂C≡CPh)₂] (X = Br, I).¹² The two P–C≡C units exhibit a *transoid* arrangement with a torsion angle C_α–P–Pt–P–C_α of 180° and the C₆F₅ rings are coplanar, forming a dihedral angle with the platinum plane of 85.56°. The details of alkynyl fragments (P–C_α–C_β 175.2(3)°, C_α–C_β–C_γ 179.7(4)°, C_α≡C_β 1.199(4) Å) are typical of P-coordinated alkynylphosphine ligands.

As an extension of our investigation, we studied the thermal and photochemical reactions of the P-coordinated diynylphosphine Pt(II) mononuclear complexes [Pt](PPh₂C≡C–C₆H₄–C≡CR)₂ (R = Ph, *t*-Bu),¹⁰ to compare, in particular, the reactivity of inner and outer units. Unfortunately, no change was observed with these precursors after heating for 6 h at 250 °C. However, photolysis of toluene solutions of these complexes for 45 min clearly afforded the new naphthalene products

Scheme 4



[Pt]{7-C≡CR–C₁₀H₄–1-(C₆H₄–pC≡CR)–2,3-κPP'(PPh₂)₂} (R = Ph, **5a**; *t*-Bu, **5c**), resulting from the intramolecular coupling of the two inner alkynyl fragments (eq 1). The formation of these



species is inferred by the similarity of their spectroscopic data with those of the products **1a** and **1b**. The most characteristic feature appears in their ³¹P{¹H} NMR spectra, which exhibit two close doublets in the region of 40–46 ppm, the P–P coupling constants being ca. 9 Hz, with the corresponding platinum satellites ($^1J_{Pt-P}$ = 2310–2250 Hz). Their IR spectra showed, in each case, two ν (C≡C) absorptions (range 2219–2173 cm^{–1}) due to the uncoordinated alkyne fragments, and two different alkyne moieties are inferred from their ¹³C{¹H} NMR spectra. Thus, four singlet signals (δ 92.0, 90.1, 88.6, 88.4, **5a**; 101.6, 99.3, 78.5, 78.1, **5b**) corresponding to both alkyne C_β and both C_α carbon resonances are seen, contrasting with the typical AXX' pattern for the inner (P–C_α≡C_β) alkyne carbons of the precursors [Pt](PPh₂C≡C–C₆H₄–C≡CR)₂ (R = Ph, *t*-Bu) [81.9 (C_α, $^{1+3}J_{C-P}$ 101.3 Hz, $^2J_{Cα-Pt}$ 17 Hz); 107.3 (C_β, $^{2+4}J_{C-P}$ 15 Hz) R = Ph; 81.3 (C_α, $^{1+3}J_{C-P}$ 102 Hz, C_α); 107.5 (C_β, $^{2+4}J_{C-P}$ 15.1 Hz) R = *t*-Bu]. As expected, the ¹⁹F NMR spectra show two sets (AA'MXX' systems) of C₆F₅ signals in accordance with the presence of two nonequivalent C₆F₅ groups.

Despite several attempts to grow crystals for X-ray analysis of **5a** or **5c**, no crystals were obtained. In an attempt to isolate one of the free phosphines, complex **5c** in DMSO was treated with an excess of KCN for 24 h. The ³¹P{¹H} NMR spectrum of the residue, obtained after usual workup, exhibits an AB spin system (δ_A -6.14, δ_B -10.52, J_{AB} = 155 Hz) in good agreement with the formation of free ligand. However, all attempts to obtain crystals from the ligand were also unsuccessful.

Finally, we present the results of the thermal and photochemical reactions of a platinum(II) complex bearing one alkynylphosphine and a diphenylphosphine ligand, [Pt](PPh₂C≡CPh)(PPh₂H), **6** (Scheme 4). This kind of system may be of interest, taking into account the precedents on P–H activation by addition of a secondary phosphine to a coordinated alkynyl

(42) Simpson, R. T.; Carty, A. J. *J. Coord. Chem.* **1973**, 2, 207.

(43) Carty, A. J.; Johnson, D. K.; Jacobson, S. *J. Am. Chem. Soc.* **1979**, 101, 5612.

(44) Carty, A. J.; Efrati, A. *Can. J. Chem.* **1969**, 47, 2573.

phosphine. Along this line, several years ago Carty et al. showed that the addition of secondary phosphines to coordinated alkynylphosphines in metal complexes (Ni, Pd, Pt) yields stereospecifically unsymmetrical diphosphine (*cis*-1,2-diphosphinoalk-1-ene) complexes.^{22,43} We have recently reported the synthesis of the cationic related complex [Pt(bzq)(PPh₂C≡CPh)-(PPh₂H)]ClO₄ (bzq = benzoquinolate)⁴⁵ and its evolution, even at low temperature, to a mixture of isomers of 1,2-diphosphinoalk-1-ene complex [Pt(bzq)(PPh₂C(Ph)=C(H)PPh₂)]ClO₄, formally generated by addition of a P–H bond to the coordinated PPh₂C≡CPh ligand.

Complex [Pt](PPh₂C≡CPh)(PPh₂H), **6**, was synthesized by displacement of the tetrahydrothiophene labile ligand on [Pt](PPh₂C≡CPh)(tht)⁷ by diphenylphosphine and characterized by usual analytical and spectroscopic means. In particular, **6** shows two characteristic absorptions in its IR spectrum due to $\nu(\text{P}–\text{H})$ (2358 cm^{−1}) and to $\nu(\text{C}≡\text{C})$ (2177 cm^{−1}) vibrations, and its ³¹P{¹H} spectrum exhibits two broad doublets flanked by platinum satellites (δ −5.56, ¹J_{Pt–P} = 2223 Hz; −7.39 ¹J_{Pt–P} = 2338 Hz, J_{P–P} ≈ 10 Hz). The high-field signal (δ −5.56), which splits into a doublet due to the P–H coupling (378 Hz) under off conditions, is attributed to the phosphorus atom of the PPh₂H ligand, whereas the signal at −7.39 is assigned to the PPh₂C≡CPh ligand. The resonance corresponding to the C_α alkyne carbon is found as a doublet of doublets at lower frequency than the C_β atom (δ C_α 78.1 vs C_β 108.6) and shifted with respect to that of free PPh₂C≡CPh (δ C_α 86.5/C_β 109.4). The resulting shift difference ($\Delta(\delta\text{C}_\beta - \delta\text{C}_\alpha)$), which can be related to the triple bond polarization,^{5,8,11,46} is, in this case, 30.5, which is similar to those observed in other alkynylphosphine neutral platinum complexes.^{3,6,7,9}

The photochemical reaction of [Pt](PPh₂C≡CPh)(PPh₂H), **6**, in toluene for 45 min, yields the asymmetric diphosphine compound [Pt]{Ph₂PC(Ph)=C(Ph)PPhH}, **7**, in an intramolecular ligand coupling reaction that involves a very unusual and selective activation of a P–C(Ph) bond in the PPh₂H ligand with formal final 2,1-addition to the triple bond of the PPh₂C≡CPh group. Activation of the P–C(Ph) bond is a well-known process,^{41,47–50} but the observed site-selective activation in the presence of the P–H bond is noteworthy because the chemistry of secondary phosphines is usually dominated by the reactive P–H bond.^{51–56} However, the behavior of **6** upon thermolysis contrasts that of the photolysis. Thus, by heating the solid **6** at ~175 °C for 1 h the isomeric chelating diphosphine compound [Pt]{Ph₂PC(H)=C(Ph)PPh₂}, **8**, is cleanly obtained. The induced 2,1-addition of the P–H bond to the alkynylphosphine ligand is in accordance with the triple bond polarization of this group

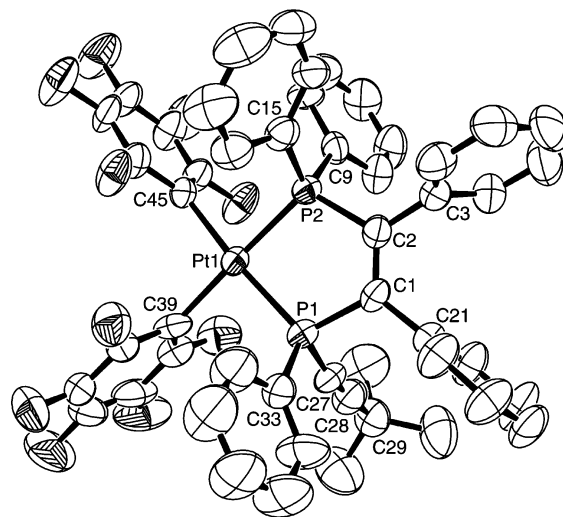


Figure 2. Molecular structure of *cis*-[Pt(C₆F₅)₂{Ph₂PC(Ph)=C(Ph)-PPh(C≡t-Bu)}], **3a**. Ellipsoids are drawn at the 50% probability level.

upon coordination to the platinum center (Pt–PPh₂C^{δ−}≡C^{δ+}Ph). This product **8** can also be alternatively generated in high yield by treatment of a dichloromethane solution of complex **6** with (NBu₄)(acac) (Scheme 4). The molecular structures of both derivatives (see below) unambiguously confirm that they are regioisomers, a fact previously confirmed by spectroscopic means. Thus, in their IR spectra both complexes (**7** and **8**) show an absence of $\nu(\text{C}≡\text{C})$ absorptions, but in complex **7** a weak absorption due to the $\nu(\text{P}–\text{H})$ at 2365 cm^{−1} can be observed. The proton spectrum of complex **7** shows the expected large doublet due to the P–H proton centered at δ 6.60 (¹J_{P–H} = 389 Hz) and flanked by platinum satellites (²J_{Pt–H} = 32.3 Hz), confirming that this proton is not removed from the phosphorus. However, complex **8** exhibits, in CD₃COCD₃, a broad doublet resonance at 7.92 ppm with platinum satellites (³J_{Pt–H} = 40 Hz), which is modified by selective ³¹P decoupling, being therefore assigned to the unique vinylic proton. Carty et al. assigned the doublet separation (10.4 Hz in **8**) of the vinyl proton resonance in related systems to $|^2J_{\text{P}–\text{H}} + ^3J_{\text{P}–\text{H}}|$.⁴³ Complex **7** exhibits two phosphorus resonances with platinum satellites at δ 61.05 and 28.06, respectively, in accordance with the formation of the five-membered phosphinoplatinacycle.^{22,43,45,57,58} In the proton-coupled ³¹P experiment, the high-field signal (δ 28.06) splits into a doublet resonance by P–H coupling (¹J_{P–H} = 389 Hz), being attributed to the phosphorus atom of the unit PPhH. In agreement with the formation of the chelating diphosphine {Ph₂PC(H)=C(Ph)-PPh₂}, complex **8** also displays two singlets at δ 61.07 and 38.98, but under off conditions, only the downfield signal (δ 61.07) splits into a doublet resonance by P–H coupling (³J_{P–H} ≈ 55 Hz), being assigned to phosphorus *trans* to the vinylic proton.

The X-ray structures of **3a**, **7**, and **8** (Figures 2–4 and Tables 2–4) confirm the formation of unsymmetrical diphosphine alkene ligands coordinated in a chelate-like fashion to the platinum centers. The observed C(1)–C(2) alkene bond lengths of 1.333(10) (**3a**), 1.345(8) (**7**), and 1.324(6) Å (**8**) are comparable to those observed in related complexes.^{45,58,59} The bond angles P(1)–C(1)–C(2) and C(1)–C(2)–P(2) are in the

(45) Díez, A.; Forniés, J.; García, A.; Lalinde, E.; Moreno, M. T. *Inorg. Chem.* **2005**, *44*, 2443.

(46) Louattani, E.; Lledós, A.; Suades, J.; Alvarez-Larena, A.; Piniella, J. F. *Organometallics* **1995**, *14*, 1053.

(47) Garrou, P. E. *Chem. Rev.* **1985**, *3*, 171.

(48) Shima, T.; Suzuki, H. *Organometallics* **2005**, *24*, 1703.

(49) Adams, R. D.; Captain, B.; Fu, W.; Smith, M. D. *J. Organomet. Chem.* **2002**, *651*, 124.

(50) Xia, C. G.; Yang, K.; Bott, S. G.; Richmond, M. G. *Organometallics* **1996**, *15*, 4480.

(51) Levason, W. In *The Chemistry of Organophosphorus Compounds*; Hartley, F. R., Ed.; Wiley: Chichester, England, 1990; Vol. 1, pp 567–641.

(52) Zhuravel, M. A.; Grewal, N. S.; Glueck, D. S.; Lam, K. C.; Rheingold, A. L. *Organometallics* **2000**, *19*, 2882.

(53) Kourkine, I. V.; Sargent, M. D.; Glueck, D. S. *Organometallics* **1998**, *17*, 125.

(54) Witch, D. K.; Kourkine, I. V.; Lew, B. M.; Nthenge, J. M.; Glueck, D. S. *J. Am. Chem. Soc.* **1997**, *119*, 5039.

(55) Leoni, P. *Organometallics* **1993**, *12*, 2432.

(56) Alonso, E.; Forniés, J.; Fortuño, C.; Martín, A.; Orpen, A. G. *Organometallics* **2001**, *20*, 850.

(57) Garrou, P. E. *Chem. Rev.* **1981**, *81*, 229.

(58) Falvello, L. R.; Forniés, J.; Gómez, J.; Lalinde, E.; Martín, A.; Moreno, M. T.; Sacristán, J. *Chem. Eur. J.* **1999**, *5*, 474.

(59) Taylor, N. J.; Jacobson, S.; Carty, A. J. *Inorg. Chem.* **1975**, *14*, 2648.

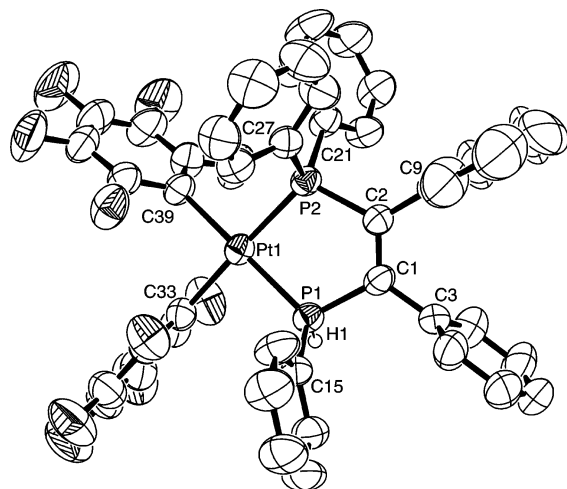


Figure 3. Molecular structure of *cis*-[Pt(C₆F₅)₂{Ph₂PC(Ph)=C(Ph)-PPhH}], **7**. Ellipsoids are drawn at the 50% probability level.

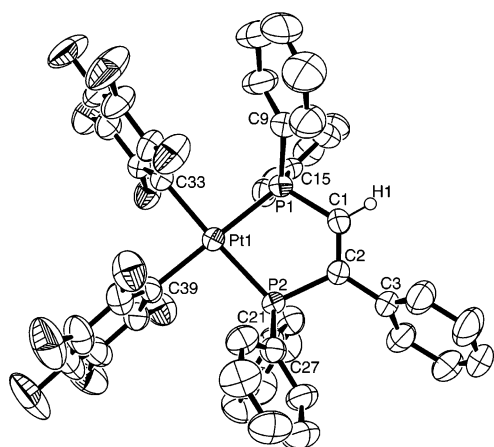


Figure 4. Molecular structure of *cis*-[Pt(C₆F₅)₂{Ph₂PC(Ph)=C(H)-PPh₂}], **8**. Ellipsoids are drawn at the 50% probability level.

116.3(4)–121.0(4)° range, close to the ideal value of 120° for sp² carbon atoms, the most marked difference between these angles being found in **8**. The planarity of the five-membered chelate rings is reflected in the angle sum of 539.82° (**3a**), 538.56° (**7**), and 537.91° (**8**) with acute PpTp angles (85.42- (7)°, **3a**; 85.44(5)°, **7**; 85.66(4)°, **8**). The hydrogen atoms in **7** and **8** were located in the Fourier map with P–H and C–H bond distances of 0.98 Å (**7**) and 0.93 Å (**8**), respectively.

Conclusions

In conclusion, we have examined the reactivity of alkynyl-diphenylphosphine platinum(II) complexes under thermal or photochemical conditions. [Pt](PPh₂C≡CR)₂ (R = Ph, Tol) were found to rearrange by thermolysis to naphthalene-based diphenylphosphine complexes [Pt]{C₁₀H₅-1-Ph-2,3-κPP'(PPh₂)₂}, **1a**, and [Pt]{7-CH₃-C₁₀H₄-1-Tol-2,3-κPP'(PPh₂)₂}, **1b**, presumably through a [2+2+2] cycloaddition with subsequent 1,3-H shift in a manner similar to that observed for dichloro Pt(II) derivatives containing monophosphine²² and diphosphinoacetylene¹² ligands. Similar naphthalene species [Pt]{7-C≡CR-C₁₀H₄-1-(C₆H₄-pC≡CR)-2,3-κPP'(PPh₂)₂} (R = Ph, **5a**; *t*-Bu, **5c**) were also generated starting from the diynyl systems [Pt](PPh₂C≡CC₆H₄C≡CR)₂, but only under photolytical reaction conditions (toluene, 45 min, eq 1). In contrast, the photolysis of the monoalkynyl complexes [Pt](PPh₂C≡CR)₂ (R = Ph, Tol) evolves with parallel formation of naphthalene species **1** and

the new chelating diphosphine complexes [Pt]{PPh₂C(Ph)=C(R)PPh(C≡CR)}, **2**, generated by an unexpected selective activation of a P–C(Ph) bond in one of the ligands with formal 2,1-addition to the C≡C triple bond of the second phosphine. Similar final 1,2-diphosphinoalk-1-ene complexes [Pt]{Ph₂PC(Ph)=C(R)PPh(C≡C*t*-Bu)}, **3**, were formed by photolysis of [Pt](PPh₂C≡CR)(PPh₂C≡C*t*-Bu) (R = Ph, Tol, *t*-Bu). Under thermal conditions, these later evolve (except for R = *t*-Bu) giving a mixture of species containing the *trans*-derivative *trans*-[Pt(C₆F₅)₂(PPh₂C≡C*t*-Bu)₂], **4**, along with trace amounts of **1** and the corresponding precursors. The mixed ligand complex [Pt](PPh₂C≡CPh)(PPh₂H), **6**, selectively gives under photolysis [Pt]{Ph₂PC(Ph)=C(Ph)PPhH}, **7**, by an activation of the P–C(Ph) bond, while the expected isomer [Pt]{Ph₂PC(H)=C(Ph)PPh₂}, **8**, is formed under thermolysis or alternatively in the presence of a base such as (NBU₄)(acac).

Experimental Section

General Considerations. All reactions and manipulations were carried out under an argon atmosphere using Schlenk techniques, and distilled solvents were purified by known procedures. IR spectra were obtained on a Perkin-Elmer FT-IR 1000 spectrometer using Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Bruker ARX 300 spectrometer; chemical shifts are reported in ppm relative to external standards (SiMe₄, CFCl₃, and 85% H₃PO₄), the temperature of the routine NMR being 293 K. Elemental analyses were carried out with Carlo Erba EA1110 CHNS/O or Perkin-Elmer 2400 CHNS/O microanalyzers. Mass spectra were recorded on a VG Autospec double-focusing mass spectrometer operating in the FAB mode, on a HP-5989B mass spectrometer using the ES techniques, and on a Microflex MALDI-TOF Bruker spectrometer for MALDI-TOF spectra operating in the linear and reflector modes using dithranol as matrix. The precursors *cis*-[Pt(C₆F₅)₂(tht)(PPh₂C≡CPh)],⁷ *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)₂] (R = *t*-Bu,⁴ Ph,⁴ Tol⁶), *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(PPh₂C≡C*t*-Bu)] (R = Ph, Tol),⁶ and *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡CR)₂] (R = *t*-Bu, Ph)¹⁰ were prepared according to literature methods. PPh₂H was used as received.

General Procedure for Irradiation. The platinum mononuclear complexes (~0.20 mmol) were dissolved in ~100 mL of deoxygenated toluene. The resulting colorless solutions were irradiated at room temperature under an argon atmosphere through Pyrex glass with a medium-pressure mercury lamp (400 W).

Synthesis of *cis*-[Pt(C₆F₅)₂{C₁₀H₅-1-Ph-2,3-κPP'(PPh₂)₂}], **1a.**²² A small quantity (~0.05 g, 0.045 mmol) of solid *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)₂] was heated at ~220 °C in an oil bath for 1 h, giving rise to a brown oil, the NMR data of which indicate the formation of **1a** in nearly quantitative yield. ¹H NMR (δ, CDCl₃): 8.43 (d, 1H, J_{H-H} = 9.5 Hz); 7.93 (d, 1H, J_{H-H} = 7.8 Hz); 7.63–6.78 (m, 27H); 6.35 (d, 1H, J_{H-H} = 7.3 Hz) (aromatics). ¹⁹F NMR (δ, CDCl₃): -116.6 (m, ³J_{Pt-O-F} ≈ 290 Hz, 2o-F); -117.3 (m, ³J_{Pt-O-F} ≈ 305 Hz, 2o-F); -162.8 (t, 1p-F); -162.9 (t, 1p-F); -164.5 (m, 2m-F); -164.9 (m, 2m-F). ³¹P{¹H} NMR (δ, CDCl₃): 46.53 (d, ¹J_{Pt-P} = 2267 Hz, ²J_{P-P} = 9.3 Hz); 41.06 (d, ¹J_{Pt-P} = 2322 Hz).

Synthesis of *cis*-[Pt(C₆F₅)₂{7-CH₃-C₁₀H₄-1-Tol-2,3-κPP'(PPh₂)₂}], **1b.** Solid *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)₂] (0.189 g, 0.168 mmol) was heated at ~220 °C for 1 h, obtaining a brown oil. The residue was treated with CH₂Cl₂ (10 mL) and charcoal and filtered through Celite. Evaporation to small volume and addition of *n*-hexane gave **1b** as a brown solid (0.088 g, 47% yield). Anal. Calcd for C₅₄F₁₀H₃₄P₂Pt (1129.88): C, 57.40; H, 3.03. Found: C, 57.32; H, 2.98. MS (MALDI-TOF (-): *m/z* 1128 [M - 2H]⁻ 47%. IR (cm⁻¹): ν(C≡C) 1605 (w); ν(C₆F₅)_{X-sens} 790 (m), 780 (m). ¹H NMR (δ, CDCl₃): 8.35 (d, 1H, J_{H-H} = 9.3 Hz); 7.82 (d, 1H, J_{H-H} = 8.3 Hz); 7.60–6.69 (m, 22H) (aromatics); 6.57 (d, J_{H-H} = 7.8 Hz); 6.22 (d, J_{H-H} = 7.8 Hz) (C₆H₄, Tol); 2.29 (s, 3H, CH₃); 2.24

(s, 3H, CH₃). ¹⁹F NMR (δ, CDCl₃): −116.4 (m, ³J_{Pt-o-F} ≈ 310 Hz, 2o-F); −117.3 (m, ³J_{Pt-o-F} ≈ 310 Hz, 2o-F); −162.9 (t, 1p-F); −163.1 (t, 1p-F); −164.5 (m, 2m-F); −164.9 (m, 2m-F). ³¹P{¹H} NMR (δ, CDCl₃): 46.17 (d br, ¹J_{Pt-P} = 2242 Hz, ²J_{P-P} ≈ 8 Hz); 40.24 (d br, ¹J_{Pt-P} = 2309 Hz).

Irradiation of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)₂]. Formation of *cis*-[Pt(C₆F₅)₂{C₁₀H₅-1-Ph-2,3-*k*PP'(PPh₂)₂}], **1a**, and *cis*-[Pt(C₆F₅)₂{PPh₂C(Ph)=C(Ph)PPh(C≡CPh)}], **2a**. Irradiation of a colorless solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)₂] (0.412 g, 0.374 mmol) in toluene was followed by ³¹P{¹H} NMR and ¹⁹F NMR spectroscopy in CDCl₃ at room temperature. The formation of a mixture of **1a** and **2a** was observed, the approximate proportion of which, in relation with time, is shown in Table 5. After 1 h and 15 min of irradiation the resulting light yellow solution was evaporated to small volume (~2 mL) and treated with diethyl ether (~10 mL), causing the precipitation of a pale yellow solid, which was a mixture of **1a** and **2a** (60:40) (0.322 g).

If the solution was irradiated for a longer time (~8 h), the resulting pale yellow solid was a mixture of **1a** and **2a** in a similar molar ratio (60:40).

Data for **2a** were obtained from this mixture (**1a** + **2a**, 60:40). IR (cm^{−1}): ν(C≡C) 2176 (s), **2a**. ¹H NMR (δ, CDCl₃): 8.38 (d, J_{H-H} = 9.4 Hz); 7.87 (d, J_{H-H} = 8.1 Hz); 7.60–6.72 (m); 6.62 (d, J_{H-H} = 6.9 Hz); 6.29 (d, J_{H-H} = 7.2 Hz) (aromatics, **1a** + **2a**). ¹⁹F NMR (δ, CDCl₃): −116.6 (m, ³J_{Pt-o-F} ≈ 290 Hz, o-F, **1a**); −117.3 (m, o-F, **1a** + **2a**); −117.7 (m, ³J_{Pt-o-F} ≈ 265 Hz, o-F, **2a**); −161.9 (t), −162.0 (t) (p-F, **2a**); −162.7 (t), −162.9 (t) (p-F, **1a**); −164.4 to −164.9 (m-F, **1a** + **2a**). ³¹P{¹H} NMR (δ, CDCl₃): 58.92 (s, ¹J_{Pt-P} = 2270 Hz); 28.38 (s, ¹J_{Pt-P} = 2358 Hz), **2a**; signals due to **1a** were also present at δ 46.50 and 41.03 (≈ 40:60 **2a**:**1a**).

Irradiation of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)₂]. Formation of *cis*-[Pt(C₆F₅)₂{7-CH₃-C₁₀H₇-1-Tol-2,3-*k*PP'(PPh₂)₂}], **1b**, and *cis*-[Pt(C₆F₅)₂{PPh₂C(Ph)=C(Tol)PPh(C≡CTol)}], **2b**. Following a procedure similar to that described for *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)₂], irradiation of a colorless solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)₂] in toluene (0.125 g, 0.111 mmol) for 45 min caused the formation of a yellow solid, which was identified as a mixture of **1b** and **2b** (60:40) (0.066 g).

Data from the mixture (**1b** + **2b**, 60:40): IR (cm^{−1}): ν(C≡C) 2173 (s), **2b**. ¹H NMR (δ, CDCl₃): 8.35 (d, J_{H-H} = 9.3 Hz, **1b**); 7.82 (d, J_{H-H} = 8.3 Hz, **1b**); 7.60–6.69 (m, **1b** + **2b**) (aromatics); 6.57 (d, J_{H-H} = 7.8 Hz, **1b** + **2b**, C₆H₄, Tol); 6.36 (d, J_{H-H} = 7.6 Hz, **2b**, C₆H₄, Tol); 6.22 (d, J_{H-H} = 7.8 Hz, **1b**, C₆H₄, Tol); 2.40, 2.18 (s, CH₃), **2b**; 2.29, 2.24 (s, CH₃), **1b**. ¹⁹F NMR (δ, CDCl₃): −116.4 (m, **1b**), −117.3 (m, **1b** + **2b**), −117.7 (m, **2b**) (o-F); −162.0 (t), −162.2 (t) (p-F, **2b**); −162.9 (t), −163.1 (t) (p-F, **1b**); −164.5 (m br, m-F, **1b** + **2b**). ³¹P{¹H} NMR (δ, CDCl₃): 58.50 (s br, ¹J_{Pt-P} = 2261 Hz); 28.48 (s br, ¹J_{Pt-P} = 2370 Hz), **2b**; signals due to **1b** at δ 46.18 and 40.25 (≈ 40:60 **2b**:**1b**) were also present.

Irradiation of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(PPh₂C≡Ct-Bu)]. Synthesis of *cis*-[Pt(C₆F₅)₂{Ph₂PC(Ph)=C(R)PPh(C≡Ct-Bu)}] (**R** = Ph, **3a**; Tol, **3b**; t-Bu, **3c**). Irradiation of a solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂C≡Ct-Bu)] (0.198 g, 0.183 mmol) in toluene (50 mL) for 30 min, evaporation to small volume, and addition of *n*-hexane (~8 mL) gave complex **3a** as a white solid (0.083 g, 42% yield).

Complexes **3b** and **3c** were prepared similarly as white (**3b**) or beige (**3c**, 2 h) solids starting from *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)(PPh₂C≡Ct-Bu)] (0.200 g, 0.182 mmol; 0.128 g, 64% yield) or *cis*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂] (0.225 g, 0.212 mmol; 0.131 g, 58% yield). In the synthesis of **3c** on several occasions small amounts of *trans*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂], **4**, were also detected in the final reaction mixture.

Data for **3a**. Anal. Calcd for C₅₀F₁₀H₃₄P₂Pt (1081.84): C, 55.51; H, 3.17. Found: C, 55.48; H, 3.01. MS (FAB+): *m/z* 1005 [M − Ph]⁺ 6%; 915 [M − C₆F₅]⁺ 75%; 748 [M − 2C₆F₅]⁺ 100%. MS (apci−): *m/z* 1081 [M][−] 28%. IR (cm^{−1}): ν(C≡C) 2210 (m), 2167

(s); ν(C=C) 1605 (w); ν(C₆F₅)_{X-sens} 789 (s), 780 (s). ¹H NMR (δ, CDCl₃): 7.54–7.32 (m, 15H); 6.92 (m, 4H); 6.76 (m, 2H); 6.53 (d, 2H, J_{H-H} = 6.8 Hz); 6.28 (d, 2H, J_{H-H} = 7.1 Hz) (Ph); 1.24 (s, 9H, C(CH₃)₃). ¹⁹F NMR (δ, CDCl₃): at 293 K, −116.7 (br, 1o-F); −117.8 (m, ³J_{Pt-o-F} ≈ 300 Hz, 2o-F); −118.3 (br, 1o-F); −162.2 (m, 2p-F); −164.7 (m, 3m-F); −165.2 (br, 1m-F); at 223 K, −116.9 (m, ³J_{Pt-o-F} ≈ 305 Hz, 1o-F); −118.1 (m, ³J_{Pt-o-F} ≈ 295 Hz, 1o-F); −118.7 (m, ³J_{Pt-o-F} ≈ 295 Hz, 2o-F); −161.48, −161.51 (2p-F); −163.9 (m, 2m-F); −164.2 (m, 1m-F); −164.7 (m, 1m-F). Between 243 and 253 K, the signal at −118.1 ppm and one of the o-F at −118.7 ppm coalesce to one slightly shifted and centered at ca. −118.1 ppm. ³¹P{¹H} NMR (δ, CDCl₃): 58.84 (s, ¹J_{Pt-P} = 2283 Hz); 27.33 (s, ¹J_{Pt-P} = 2371 Hz).

Data for **3b**. Anal. Calcd for C₅₁F₁₀H₃₆P₂Pt (1095.87): C, 55.90; H, 3.31. Found: C, 55.68; H, 3.00. MS (FAB+): *m/z* 929 [M − C₆F₅]⁺ 18%; 762 [M − 2C₆F₅]⁺ 32%. MS (apci−): *m/z* 1095 [M][−] 25%; 1018 [M − Ph][−] 100%. IR (cm^{−1}): ν(C≡C) 2219 (m), 2176 (s); ν(C=C) 1600 (w); ν(C₆F₅)_{X-sens} 790 (m), 781 (s). ¹H NMR (δ, CDCl₃): 7.60–7.34 (m, 15H); 6.92 (t, 1H, J_{H-H} = 7.3 Hz); 6.83 (d, 2H, J_{H-H} = 7.6 Hz); 6.69 (d, 2H, J_{H-H} = 8.2 Hz) (Ph); 6.48 (d, 2H, J_{H-H} = 7.7 Hz); 6.34 (d, 2H, J_{H-H} = 7.6 Hz) (Ph, Tol); 2.15 (s, 3H, CH₃); 1.30 (s, 9H, −C(CH₃)₃). ¹⁹F NMR (δ, CDCl₃): at 293 K, −116.8 (vbr), −117.8 (m, ³J_{Pt-o-F} ≈ 320 Hz) (4o-F); −162.4, −162.3 (overlapping of two triplets, 2p-F); −164.8 (m, 3m-F); −165.3 (br, 1m-F); at 223 K, −116.8 (m, ³J_{Pt-o-F} ≈ 310 Hz, 1o-F); −118.2 (m, ³J_{Pt-o-F} ≈ 310 Hz, 1o-F); −118.7 (m, overlapping of two o-F); −161.5, −161.6 (overlapping of two triplets, 2p-F); −164.0 (m, 2m-F); −164.3 (m, 1m-F); −164.8 (m, 1m-F). ³¹P{¹H} NMR (δ, CDCl₃): 58.42 (s, ¹J_{Pt-P} = 2260 Hz); 27.60 (s, ¹J_{Pt-P} = 2375 Hz).

Data for **3c**. Anal. Calcd for C₄₈F₁₀H₃₈P₂Pt (1061.85): C, 54.29; H, 3.61. Found: C, 53.94; H, 3.91. MS (FAB+): *m/z* 983 [M − Ph]⁺ 42%; 894 [M − C₆F₅]⁺ 36%; 727 [M − 2C₆F₅]⁺ 46%. IR (cm^{−1}): ν(C≡C) 2211 (m), 2169 (s); ν(C=C) 1603 (w); ν(C₆F₅)_{X-sens} 790 (sh), 779 (s). ¹H NMR (δ, CDCl₃): 7.44–6.92 (m, 18H); 6.61 (d, 1H, J_{H-H} = 7.4 Hz); 6.35 (d, 1H, J_{H-H} = 7.5 Hz); (aromatics); 1.39 (s, 9H, C(CH₃)₃); 1.02 (s, 9H, C(CH₃)₃). ¹⁹F NMR (δ, CDCl₃): −116.5 (m, br, o-F); −117.6 (vbr, 2o-F); −119.3 (m, ³J_{Pt-o-F} ≈ 275 Hz, 1o-F); −162.7 (t), −162.8 (t) (2p-F); −165.0 (m, 4m-F). ³¹P{¹H} NMR (δ, CDCl₃): 62.97 (s br, ¹J_{Pt-P} = 2241 Hz); 33.12 (s br, ¹J_{Pt-P} = 2222 Hz).

Thermal Reactions of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(PPh₂C≡Ct-Bu)]. (a) Solid *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂C≡Ct-Bu)] (0.05 g, 0.046 mmol) was heated at its melting point (220 °C) for 2 h, giving rise to a dark brown oil. After cooling to room temperature, the residue was treated with CDCl₃ (0.5 mL). Its ³¹P{¹H} NMR spectrum indicates the presence of a mixture of complexes including **1a** (δ 46.53, 41.06), *trans*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂] (**4**) (δ −7.60, ¹J_{Pt-P} = 2854 Hz), the precursor, and other nonidentified species.

(b) A similar experiment with solid *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)(PPh₂C≡Ct-Bu)] (0.05 g, 0.045 mmol) gave a brown oily liquid, whose ³¹P{¹H} NMR spectrum in CDCl₃ mainly shows the presence of **1b**, **4** (~0.37:1), and the precursor.

(c) *cis*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂] was unchanged when heated at 220 °C for 2 h, showing in the ³¹P{¹H} NMR spectrum only signals of the starting material.

Synthesis of *trans*-[Pt(C₆F₅)₂(PPh₂C≡Ct-Bu)₂], **4.** A solution of *trans*-[Pt(C₆F₅)₂(tht)₂] (0.122 g, 0.181 mmol) in CH₂Cl₂ was treated with PPh₂C≡Ct-Bu (0.096 g, 0.362 mmol), and the mixture was stirred for 10 min. The solvent was reduced to 2 mL, and addition of *n*-hexane (5 mL) afforded **4** as a white solid (0.136 g, 71% yield). Anal. Calcd for C₄₈F₁₀H₃₈P₂Pt (1061.86): C, 54.29; H, 3.61. Found: C, 54.22; H, 3.57. MS (FAB+): *m/z* 1061 [M]⁺ 5%; 984 [M − Ph]⁺ 9%; 894 [M − C₆F₅]⁺ 57%; 813 [M − C₆F₅ − C≡Ct-Bu]⁺ 100%; 727 [M − 2C₆F₅]⁺ 62%. IR (cm^{−1}): ν(C≡C) 2215 (m), 2171 (s); ν(C₆F₅)_{X-sens} 777 (vs). ¹H NMR (δ,

CDCl₃): 7.53 (m, 8H); 7.28 (m, 12H) (Ph); 1.23 (s, 18H, C(CH₃)₃). ¹⁹F NMR (δ, CDCl₃): -116.7 (m, ³J_{Pt-O-F} = 240 Hz, 4o-F); -163.3 (m, 2p-F); -164.6 (m, 4m-F). ³¹P{¹H} NMR (δ, CDCl₃): -7.60 (s, ¹J_{Pt-P} = 2854 Hz).

Irradiation of *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡CR)₂] (R = Ph, *t*-Bu). Synthesis of *cis*-[Pt(C₆F₅)₂{7-C≡CR-C₁₀H₄-1-(C₆H₄-pC≡C)-2,3-κPP'(PPh₂)₂}] (R = Ph, **5a; *t*-Bu, **5c**). Irradiation (45 min) of a solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡CPh)₂] (0.200 g, 0.154 mmol) in toluene, evaporation to small volume, and addition of *n*-hexane (~5 mL) produced **5a** as a light yellow solid (0.154 g, 77% yield).**

Complex **5c** (0.097 g, 54% yield) was prepared as a beige solid following a similar procedure, by irradiation of *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡C*t*-Bu)₂] (0.180 g, 0.143 mmol).

Data for **5a**. Anal. Calcd for C₆₈F₁₀H₃₈P₂Pt (1302.07): C, 62.73; H, 2.94. Found: C, 62.87; H, 3.04. MS (FAB+): *m/z* 1135 [M - C₆F₅]⁺ 56%; 967 [M - 2C₆F₅ - 1H]⁺ 88%. IR (cm⁻¹): ν(C≡C) 2213 (w), 2173 (w); ν(C₆F₅)_{X-sens} 790 (m), 780 (m). ¹H NMR (δ, CDCl₃): 8.40 (d, 2H, J_{H-H} = 9.2 Hz); 7.91 (d, 2H, J_{H-H} = 8.5 Hz); 7.70 (d, 2H, J_{H-H} = 8.5 Hz); 7.62–6.98 (m, 28H); 6.36 (d, 4H, J_{H-H} = 8.0 Hz) (Ph, aromatic). ¹³C{¹H} NMR (δ, CDCl₃): 146.6 (dm), 137.1 (dm) (C₆F₅); 133.5–127.7; 124.1–121.8 (aromatics); 92.0; 90.1; 88.6; 88.4 (C≡C). ¹⁹F NMR (δ, CDCl₃): -116.6 (m, ³J_{Pt-O-F} ≈ 335 Hz, 2o-F); -117.3 (m, ³J_{Pt-O-F} ≈ 310 Hz, 2o-F); -162.5 (t, 1p-F); -162.8 (t, 1p-F); -164.4 (m, 2m-F); -164.7 (m, 2m-F). ³¹P{¹H} NMR (δ, CDCl₃): 46.53 (d, ¹J_{Pt-P} = 2260 Hz, J_{P-P} = 9.2 Hz); 40.95 (d, ¹J_{Pt-P} = 2308 Hz, J_{P-P} = 9.2 Hz).

Data for **5c**. Anal. Calcd for C₆₄F₁₀H₄₆P₂Pt (1262.09): C, 60.91; H, 3.67. Found: C, 61.05; H, 4.05. MS (FAB+): *m/z* 1262 [M]⁺ 12%; 1095 [M - C₆F₅]⁺ 60%; 927 [M - 2C₆F₅ - 1H]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2219 (w), 2174 (w); ν(C₆F₅)_{X-sens} 790 (m), 781 (m). ¹H NMR (δ, CDCl₃): 8.32 (d, 2H, J_{H-H} = 9.1 Hz); 7.80 (d, 2H, J_{H-H} = 8.5 Hz); 7.60–6.92 (m); 6.81 (d, J_{H-H} = 7.9 Hz); 6.25 (d, J_{H-H} = 7.9 Hz) (aromatics); 1.32 (s, 9H, C(CH₃)₃); 1.24 (s, 9H, C(CH₃)₃). ¹³C{¹H} NMR (δ, CDCl₃): 145.5 (dm), 136.6 (dm) (C₆F₅); 133.5–127.6; 124.9; 122.9; (aromatics); 101.6; 99.3; 78.5; 78.1 (C≡C); 30.7 (s); 30.4 (s) (C(CH₃)₃); 27.74 (s); 27.70 (s) ((C(CH₃)₃)). ¹⁹F NMR (δ, CDCl₃): -116.5 (m, ³J_{Pt-O-F} ≈ 300 Hz, 2o-F); -117.3 (m, ³J_{Pt-O-F} ≈ 310 Hz, 2o-F); -162.7 (t, 1p-F); -162.9 (t, 1p-F); -164.4 (m, 2m-F); -164.8 (m, 2m-F). ³¹P{¹H} NMR (δ, CDCl₃): 46.36 (d, ¹J_{Pt-P} = 2250 Hz, J_{P-P} ≈ 9 Hz); 40.70 (d, ¹J_{Pt-P} = 2310 Hz, J_{P-P} ≈ 9 Hz).

{7-C≡C*t*-Bu-C₁₀H₄-1-(C₆H₄-pC≡C*t*-Bu)-2,3-(PPh₂)₂}. A solution of *cis*-[Pt(C₆F₅)₂{7-C≡C*t*-Bu-C₁₀H₄-1-(C₆H₄-pC≡C*t*-Bu)-2,3-κPP'(PPh₂)₂}] (**5c** (0.1 g, 0.079 mmol), in DMSO (15 mL) was treated with KCN (0.206 g, 3.16 mmol), and the mixture was stirred at room temperature for 24 h. Addition of *n*-hexane (30 mL) and successive portions of water (3 × 5 mL), separation, and evaporation of the organic phase gave a yellow residue. ¹H NMR (δ, CDCl₃): 7.63–6.88 (m, 26 H), 6.45 (d, 2H, J_{H-H} = 8 Hz) (aromatics); 1.32 (s, 9H, C(CH₃)₃); 1.24 (s, 9H, C(CH₃)₃). ³¹P{¹H} NMR (δ, CDCl₃): -8.33 (AB, ²J_{P-P} = 155 Hz, δ_A = -6.14, δ_B = -10.52).

Thermolysis of *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡CR)₂] (R = Ph, *t*-Bu). (a) *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡CPh)₂] (0.05 g, 0.038 mmol) and *cis*-[Pt(C₆F₅)₂(PPh₂C≡C-C₆H₄-C≡C*t*-Bu)₂] (0.05 g, 0.040 mmol) were unchanged when heated 6 h at 240–250 °C (³¹P{¹H} NMR identification).

Synthesis of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂H)], **6**. PPh₂H (85 μL, 0.465 mmol) was added to a colorless solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(tht)] (0.420 g, 0.465 mmol) in CH₂Cl₂ (20 mL) at -20 °C, and the mixture was stirred for 2 h. The colorless solution obtained was evaporated to small volume (~2 mL) and treated with EtOH absolute (10 mL) to give **6** as a white solid (0.400 g, 86% yield). Anal. Calcd for C₄₄F₁₀H₂₆P₂Pt (1001.71): C, 52.76; H, 2.62. Found: C, 52.92; H, 2.51. MS (ES-): *m/z* 1004 [M]⁻ 100%. IR (cm⁻¹): ν(P-H) 2358 (m); ν(C≡C) 2177 (s); ν(C₆F₅)_{X-sens}

796 (s), 786 (s). ¹H NMR (δ, CDCl₃): 7.62 (m, 4H); 7.34–7.16 (m, 19H); 6.99 (d, 2H, J_{H-H} = 7.5 Hz) (Ph); 5.98 (dd, 1H, ¹J_{P-H} = 372 Hz, ²J_{Pt-H} ≈ 14 Hz, ³J_{P-H} = 14.5 Hz, P-H). ¹³C{¹H} NMR (δ, CDCl₃): 145.4 (dt, ¹J_{C-F} = 230 Hz, ²J_{C-F} ≈ 20 Hz); 136.9 (dm, ¹J_{C-F} ≈ 240 Hz) (C₆F₅); 133.4 (d, ²J_{C-P} = 10.9 Hz, ³J_{C-Pt} ≈ 18.4 Hz, o-C, PPh₂); 132.3 (d, ²J_{C-P} = 12.9 Hz, ³J_{C-Pt} ≈ 16.9 Hz, o-C, PPh₂); 131.9 (d, ⁴J_{C-P} = 1.3 Hz, o-C, C≡CPh); 130.9 (d, ⁴J_{C-P} = 2.3 Hz, p-C, PPh₂); 130.7 (d, ⁴J_{C-P} = 2.1 Hz, p-C, PPh₂); 130.2 (s, p-C, C≡CPh); 129.1 (dd, ³J_{C-P} = 1.8 Hz, ¹J_{C-P} = 63.5 Hz, ²J_{C-Pt} = 23.8 Hz, i-C, PPh₂); 128.2 (overlapping of two d, J_{C-P} = 10 Hz, m-C, PPh₂); 128.1 (s, m-C, Ph); 126.0 (dd, ³J_{C-P} = 1.8 Hz, ¹J_{C-P} = 56 Hz, ²J_{C-Pt} = 15.4 Hz, i-C, PPh₂); 119.7 (d, ³J_{C-P} = 3.0 Hz, i-C, C≡CPh); 108.6 (d, ²J_{C-P} = 15.2 Hz, ³J_{C-Pt} ≈ 17.8 Hz, C_β, -PC≡CPh); 78.1 (dd, ¹J_{C-P} = 99.6 Hz, ³J_{C-P} = 4.7 Hz, C_α, -PC≡CPh). ¹⁹F NMR (δ, CDCl₃): -117.8 (m, ³J_{Pt-O-F} ≈ 330 Hz, 4o-F); -162.0 (t, 1p-F); -162.6 (t, 1p-F); -163.9 (m, 4m-F). ³¹P{¹H} NMR (δ, CDCl₃): -5.56 (s br, ¹J_{Pt-P} = 2223 Hz, PPh₂H); -7.39 (d br, ¹J_{Pt-P} = 2338 Hz, J_{P-P} ≈ 10 Hz, PPh₂C≡CPh). ³¹P NMR (δ, CDCl₃): -5.70 (d, ¹J_{Pt-P} = 2238 Hz, ¹J_{H-P} = 378 Hz, PPh₂H); -7.31 (s br, ¹J_{Pt-P} = 2322 Hz, PPh₂C≡CPh).

Irradiation of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂H)], **7**. A colorless solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂H)] (0.100 g, 0.100 mmol) was irradiated for 45 min in toluene. The colorless solution was evaporated to small volume (~2 mL) and treated with EtOH absolute (~10 mL), which caused the precipitation of a white solid, **7** (0.052 g, 52% yield). Anal. Calcd for C₄₄F₁₀H₂₆P₂Pt (1001.71): C, 52.76; H, 2.62. Found: C, 53.01; H, 2.69. MS (ES-): *m/z* 1001 [M]⁻ 100%. IR (cm⁻¹): ν(P-H) 2365 (w); ν(C≡C) 1605 (w); ν(C₆F₅)_{X-sens} 791 (br s). ¹H NMR (δ, CDCl₃): 7.61–6.80 (m, 23H), 6.37 (d, 2H, J_{H-H} = 7.6 Hz) (Ph); 6.60 (d, 1H, ¹J_{P-H} = 389 Hz, ²J_{Pt-H} = 32.3 Hz, P-H). ¹⁹F NMR (δ, CDCl₃): -118.0 (m, ³J_{Pt-O-F} ≈ 325 Hz, 4o-F); -161.4 (t, 1p-F); -162.0 (t, 1p-F); -163.9 (m, 2m-F); -164.6 (m, 2m-F). ³¹P{¹H} NMR (δ, CDCl₃): 61.05 (s, ¹J_{Pt-P} = 2247 Hz, PPh₂); 28.06 (s, ¹J_{Pt-P} = 2190 Hz, PPhH). ³¹P NMR (δ, CDCl₃): 61.03 (s, ¹J_{Pt-P} = 2245 Hz); 28.04 (d, ¹J_{Pt-P} ≈ 2190 Hz, ¹J_{P-H} = 389 Hz).

Synthesis of *cis*-[Pt(C₆F₅)₂{Ph₂PC(H)=C(Ph)PPh₂}], **8**. Complex **8** was obtained quantitatively (³¹P{¹H}) by heating *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂H)] (0.050 g, 0.05 mmol) at ~175 °C for 1 h. Alternatively, complex **8** was obtained by using (NBu₄)-(acac) prepared in situ: Tl(acac) (0.046 g, 0.150 mmol) was treated with a CH₂Cl₂ solution (15 mL) of (NBu₄)Br (0.048 g, 0.150 mmol) at room temperature for 3 h. The resulting TlBr was filtered off and the filtrate added to a colorless solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂H)] (0.100 g, 0.100 mmol) at 0 °C. The mixture was stirred for 1 h and then evaporated to small volume (~4 mL). Addition of *i*-PrOH (~10 mL) caused the precipitation of a white solid, **8** (0.088 g, 88% yield). Anal. Calcd for C₄₄F₁₀H₂₆P₂Pt (1001.71): C, 52.76; H, 2.62. Found: C, 52.35; H, 2.55. MS (es-): *m/z* 1001 [M]⁻ 100%. IR (cm⁻¹): ν(C≡C) 1601 (m); ν(C₆F₅)_{X-sens} 790 (m), 782 (w). ¹H NMR (δ, CDCl₃): 7.57–7.10 (m, 24H); 6.84 (d, J_{H-H} = 7.4 Hz, 2H). ¹H NMR (δ, CD₃COCD₃): 7.92 (d br, 1H, J_{H-P} = 10.4 Hz, ³J_{Pt-H} ≈ 40 Hz), 7.77–7.47 (m, 20H); 7.27 (d, 1pH, J_{H-H} = 7.5 Hz, C-Ph); 7.18 (t, 2mH, C-Ph); 7.02 (d, 2oH, J_{H-H} = 7.5 Hz, C-Ph). ¹⁹F NMR (δ, CDCl₃): -117.8 (m, ³J_{Pt-O-F} ≈ 325 Hz, 4o-F); -162.0 (t), -162.2 (t) (2p-F); -164.4 (m, 4m-F). ³¹P{¹H} NMR (δ, CDCl₃): 61.07 (s, ¹J_{Pt-P} = 2327 Hz, PPh₂C(Ph)=); 38.98 (s, ¹J_{Pt-P} = 2294 Hz, PPh₂C(H)=). ³¹P NMR (δ, CDCl₃): 61.07 (d, ¹J_{Pt-P} = 2327 Hz, ³J_{P-H} ≈ 55 Hz); 38.98 (s, ¹J_{Pt-P} = 2294 Hz).

Treatment of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(PPh₂H)] (0.050 g, 0.05 mmol) in toluene at 383 K for 5 h afforded unchanged starting material.

X-ray Crystallography. Table 6 reports details of the structural analyses for all complexes. Colorless crystals of complexes **3a**, **7**, and **8** were obtained at low temperature (-30 °C) by slow diffusion

Table 6. Crystal Data and Structure Refinement Details for **3a**, **4**, **7·CHCl₃**, and **8**

	3a	4	7·CHCl₃	8
empirical formula	C ₅₀ H ₃₄ F ₁₀ P ₂ Pt	C ₄₈ H ₃₈ F ₁₀ P ₂ Pt	C ₄₅ H ₂₇ Cl ₃ F ₁₀ P ₂ Pt	C ₄₄ H ₂₆ F ₁₀ P ₂ Pt
fw	1081.80	1061.81	1121.05	1001.68
temp (K)	293(2)	173(1)	293(2)	293(2)
wavelength (Å)	0.71073	0.71073	0.71073	0.71073
cryst syst	monoclinic	monoclinic	triclinic	monoclinic
space group	<i>Pc</i>	<i>P2₁/c</i>	<i>P1</i>	<i>P2₁/n</i>
<i>a</i> (Å); α (deg)	10.8190(3); 90	11.0706(2); 90	11.7815(2); 73.6040(10)	10.6341(2); 90
<i>b</i> (Å); β (deg)	10.4640(4); 101.693(2)	17.8513(3); 93.4910(10)	12.7708(3); 83.7160(10)	15.9946(3); 91.3550(10)
<i>c</i> (Å); γ (deg)	20.2720(6); 90	11.1888(2); 90	15.9553(4); 71.1300(10)	22.6780(4); 90
<i>V</i> (Å ³); <i>Z</i>	2247.37(13); 2	2207.08(7); 2	2178.79(8); 2	3856.18(12); 4
calcd density (Mg/m ³)	1.599	1.598	1.709	1.725
abs correction (mm ⁻¹)	3.269	3.327	3.553	3.802
<i>F</i> (000)	1064	1048	1092	1952
cryst size (mm ³)	0.20 × 0.15 × 0.10	0.40 × 0.30 × 0.10	0.20 × 0.15 × 0.10	0.15 × 0.10 × 0.10
2 θ range (deg)	2.74 to 25.36	3.40 to 27.88	2.98 to 27.90	3.19 to 27.87
index ranges	−11 ≤ <i>h</i> ≤ 13, −11 ≤ <i>k</i> ≤ 12, −24 ≤ <i>l</i> ≤ 23	−14 ≤ <i>h</i> ≤ 14, −21 ≤ <i>k</i> ≤ 23, −14 ≤ <i>l</i> ≤ 14	−15 ≤ <i>h</i> ≤ 15, −16 ≤ <i>k</i> ≤ 16, −20 ≤ <i>l</i> ≤ 20	−13 ≤ <i>h</i> ≤ 13, −21 ≤ <i>k</i> ≤ 21, −29 ≤ <i>l</i> ≤ 29
no. of reflns collected	14 546	35 418	19 790	29 758
no. of indep reflns	7327 [<i>R</i> (int) = 0.0370]	5264 [<i>R</i> (int) = 0.0676]	10 153 [<i>R</i> (int) = 0.0462]	9133 [<i>R</i> (int) = 0.0709]
no. of data/restraints/params	7327/2/571	5264/0/280	10 153/3/545	9133/0/514
goodness of fit on <i>F</i> ² ^a	1.077	1.036	1.026	1.050
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)] ^a	<i>R</i> 1 = 0.0349, <i>wR</i> 2 = 0.0788	<i>R</i> 1 = 0.0314, <i>wR</i> 2 = 0.0705	<i>R</i> 1 = 0.0485, <i>wR</i> 2 = 0.1144	<i>R</i> 1 = 0.0429, <i>wR</i> 2 = 0.0680
<i>R</i> indices (all data) ^a	<i>R</i> 1 = 0.0407, <i>wR</i> 2 = 0.0823	<i>R</i> 1 = 0.0554, <i>wR</i> 2 = 0.0779	<i>R</i> 1 = 0.0676, <i>wR</i> 2 = 0.1261	<i>R</i> 1 = 0.0838, <i>wR</i> 2 = 0.0788
largest diff peak and hole (e Å ⁻³)	0.862 and −1.241	2.156 and −0.969	1.409 and −1.231	0.558 and −1.087

^a *R*1 = $\Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; *wR*2 = $[\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$; goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{\text{obs}} - N_{\text{param}})\}^{1/2}$; *w* = $[\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; *P* = $[\max(F_o^2; 0) + 2F_c^2]/3$.

of ethanol into a dichloromethane (**3a**) solution or by slow diffusion of *n*-hexane into chloroform (**7**, **8**) solutions. Colorless crystals of **4** were obtained leaving a diethyl ether solution of this complex to evaporate at room temperature. For complex **7** one molecule of chloroform was found in the asymmetric unit (**7·CHCl₃**). X-ray intensity data were collected with a NONIUS κ -CCD area-detector diffractometer, using graphite-monochromated Mo K α radiation. Images were processed using the DENZO and SCALEPACK suite of programs.⁶⁰ The structures of **3a**, **4**, and **8** were solved by Patterson and Fourier methods using the DIRDIF92 program,⁶¹ and the absorption corrections were performed using SORTAV.⁶² The structure of **7·CHCl₃** was solved by Patterson using the SHELXS-97 program,⁶³ and the absorption correction was performed using MULTISCAN.⁶² All structures were refined by full-matrix least squares on *F*² with SHELXL-97.⁶⁴

(60) Otwinowski, Z.; Minor, W. In *Methods in Enzymology*; Carter, C. V., Jr., Sweet, R. M., Eds.; Academic Press: New York, 1997; Vol. 276A, p 307.

(61) Beursken, P. T.; Beursken, G.; Bosman, W. P.; de Gelder, R.; García-Granda, S.; Gould, R. O.; Smith, J. M. M.; Smykalla, C. *The DIRDIF92 program system*; Technical Report of the Crystallography Laboratory; University of Nijmegen: The Netherlands, 1992.

(62) Blessing, R. H. *Acta Crystallogr.* **1995**, A51, 33.

(63) Sheldrick, G. M. *SHELXS97: Program for the Solution of Crystal Structures*; University of Göttingen: Göttingen, Germany, 1997.

(64) Sheldrick, G. M. *SHELX-97, a program for the refinement of crystal structures*; University of Göttingen: Germany, 1997.

All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms were constrained to idealized geometries, fixing isotropic displacement parameters of 1.2 times the *U*_{iso} value of their attached carbon for the phenyl and methine hydrogens and 1.5 for the methyl groups. For complexes **4** and **7·CHCl₃**, there are peaks of electron density higher than 1 e/Å³ in the final map, but they are located very close to the platinum atoms and have no chemical meaning. Complexes **3a** and **7·CHCl₃** have a chiral center at the phosphorus P(1). The absolute structure parameter for **3a** is 0.007(2), which crystallizes in the space group *Pc*, and shows the enantiomorphic *R* form in the crystallographic study present in this paper (Figure 2). Complex **7·CHCl₃** crystallizes in the space group *P1*; in this case both enantiomers, *R* and *S*, are present in the unit cell (Figure 3 shows the enantiomer *S*). Finally, for complex **3a**, the low quality of the crystals does not allow the observation of reflections at high θ .

Acknowledgment. This work was supported by the Ministerio de Educación y Ciencia (Project CTQ2005-08606-C02-02 and a grant for A.G.).

Supporting Information Available: Crystallographic data in CIF format. This material is available free of charge via the Internet at <http://pubs.acs.org>.

OM060342Z