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

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Received April 18, 2006

The thermal and photochemical transformations of a series of alkynylphosphine platinum(II) complexes are described. Compounds [Pt]($PPh_2C{\equiv}CR)_2$ ([Pt] = *cis*-Pt($C_6F_5)_2$, R = Ph, Tol) rearrange thermally to generate naphthalene-based diphenylphosphine complexes (**1a**, **1b**) containing the fragment {$C_{10}H_5$-1-Ph-2,3-$\kappa PP'(PPh_2)_2$} or {7-CH_3-$C_{10}H_4$-1-Tol-2,3-$\kappa PP'(PPh_2)_2$}, formed by intramolecular coupling of two adjacent $PPh_2C{\equiv}CR$ 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 [Pt]{PPh_2C-(Ph)=C(R)PPh(C≡CR)} (R = Ph, **2a**; Tol, **2b**) in a final ratio of 60:40. However, irradiation of the mixed alkynylphosphine derivatives [Pt]($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}C$*t*-Bu) gives selectively [Pt]{Ph_2PC(Ph)=C(R)PPh(C≡C*t*-Bu)} (R = Ph, **3a**; Tol, **3b**; *t*-Bu, **3c**) as result of a P−C(Ph) activation of a *tert*-butylalkynylphosphine, $PPh_2C{\equiv}C$*t*-Bu. Under thermolysis, bis(*tert*-butyl)alkynyl derivatives produce no evidence of any cyclization product, but the mixed alkynylphosphine derivatives [Pt]($PPh_2C{\equiv}CR$)-($PPh_2C{\equiv}C$*t*-Bu) evolve giving small amounts of **1a**/**1b** and *trans*-[Pt($C_6F_5)_2$($PPh_2C{\equiv}C$*t*-Bu)$_2$], **4**. Under photolytic conditions, the diynyl phosphine derivatives [Pt]($PPh_2C{\equiv}CC_6H_4C{\equiv}CR)_2$ (R = Ph, *t*-Bu) rearrange directly to the naphthalene complexes [Pt]{7-C≡CR-$C_{10}H_4$-1-(C_6H_4-*p*C≡CR)-2,3-$\kappa PP'(PPh_2)_2$} (R = Ph, **5a**; *t*-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 [Pt]($PPh_2C{\equiv}CPh$)(PPh_2H), **6**. Thus, while under photochemical conditions complex **6** yields selectively [Pt]{Ph_2PC(Ph)=C(Ph)PPhH}, **7**, by a ligand rearrangement coupling process involving activation of a P−C(Ph) bond, the regioisomer [Pt]{Ph_2PC(H)=C(Ph)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 pyrolizing 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*-[PtX_2-($PPh_2C{\equiv}CR)_2$] 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 $C_\alpha-C_\alpha$ distance). Recently, we have demonstrated[4,6,9] the formation of novel coordinated naphthalene diphosphine ligands ({$C_{10}H_4$-1-C_6F_5-4-Ph-2,3-$\kappa PP'(PPh_2)_2$} (**L**^{1}) and {7-CH_3-$C_{10}H_3$-1-C_6F_5-4-Tol-2,3-$\kappa PP'(PPh_2)_2$} (**L**^{2})) facili-

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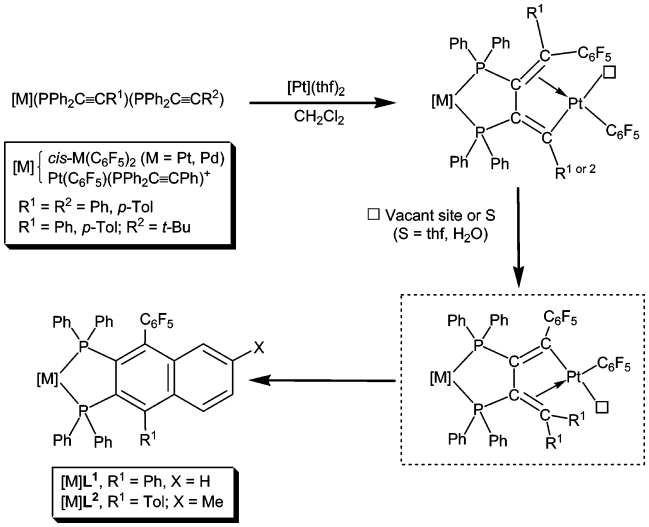
10.1021/om060342z CCC: $33.50
Publication on Web 07/01/2006

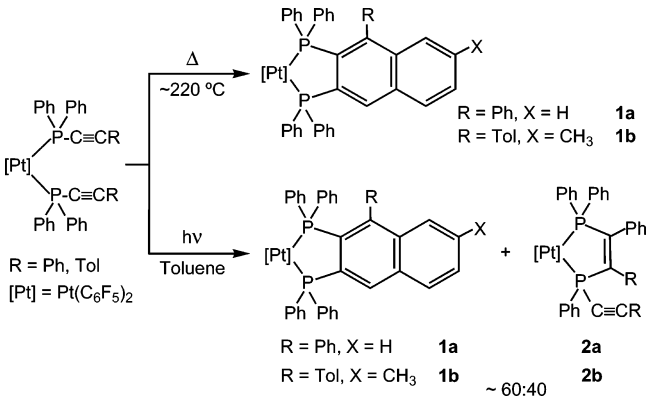
Scheme 1



tated by complexation of the "$Pt(C_6F_5)_2$" 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−C_6F_5 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 control the cyclization process involving alkynylphosphine ligands, we have examined the behavior of several pentafluophenyl mononuclear platinum complexes bearing different alkynylphosphines, $[Pt](PPh_2C{\equiv}CR)_2$ (R = Ph, Tol), $[Pt](PPh_2C{\equiv}CR)(PPh_2C{\equiv}Ct\text{-Bu})$, $[Pt](PPh_2C{\equiv}CC_6H_4C{\equiv}CR)_2$ (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.

Scheme 2



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 $[Pt]\{7\text{-}CH_3\text{-}C_{10}H_4$-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 $^{31}P\{^1H\}$ 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 ^{19}F NMR spectra confirm the existence of two different sets of C_6F_5 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 $\{7\text{-}CH_3\text{-}C_{10}H_4$-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

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Table 1. Selected Bond Distances (Å) and Angles (deg) for *trans*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$C≡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(C$_6$F$_5$)$_2${Ph$_2$PC(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(C$_6$F$_5$)$_2${Ph$_2$PC(Ph)═C(Ph)PPhH}]·CHCl$_3$, 7·CHCl$_3$

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(C$_6$F$_5$)$_2${Ph$_2$PC(H)═C(Ph)PPh$_2$}], 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)

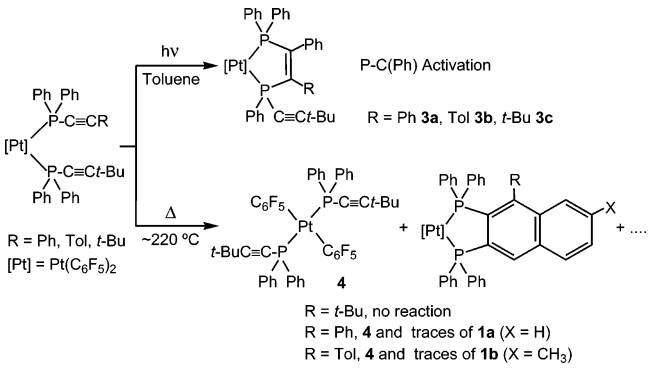
Table 5. Control of the Formation of 1a and 2a by ^{31}P{^{1}H} NMR

time (min)	*cis*-[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](PPh$_2$C≡CR)(PPh$_2$C≡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]{Ph$_2$PC(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](PPh$_2$C≡C*t*-Bu)$_2$ gives, by photolysis, the corresponding complex [Pt]{Ph$_2$PC(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 PPh$_2$C≡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(sp^2) > P−C(sp^3).[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 ^{31}P{^{1}H} 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 nonequivalent 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 PPh$_2$ fragment of the diphenylphosphine alkene ligand. This assignment is in accord with the chemical shifts of phosphines such as PPh$_3$ ($\delta \approx -6$ ppm) and PPh$_2$C≡C*t*-Bu (δ −34.24).[31] At low temperature (223 K), the ^{19}F NMR spectra display two different sets of rigid C$_6$F$_5$ 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 C$_6$F$_5$ 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 ^{31}P{^{1}H} 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](PPh$_2$C≡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](PPh$_2$C≡CR)(PPh$_2$C≡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-

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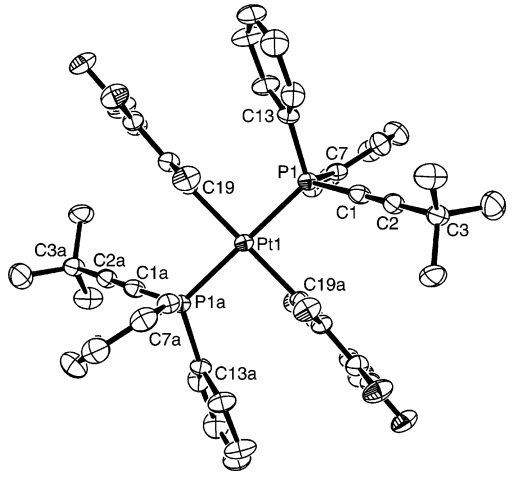
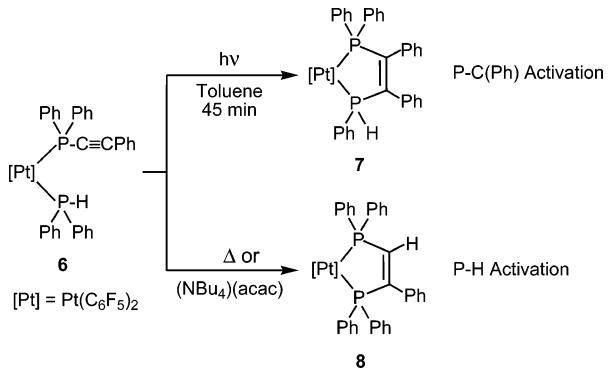


Figure 1. Molecular structure of *trans*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-Bu)$_2$], **4**. Ellipsoids are drawn at the 50% probability level.

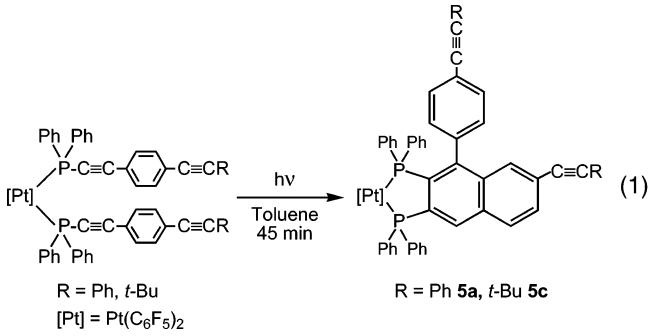
nylphosphine) complex. However, when the mixed aryl/*tert*-butylphosphine derivatives were heated at their melting point for 2 h, the $^{31}P\{^1H\}$ NMR spectrum of the final brown oily residue obtained showed the formation of a mixture of complexes, which contain (see Experimental Section) small amounts of the corresponding precursors, the naphthalene species **1a** or **1b** and, surprisingly, the *trans*-derivative *trans*-[Pt(C_6F_5)$_2$-($PPh_2C{\equiv}Ct$-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 C_6F_5 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(C_6F_5)$_2$(tht)$_2$] by $PPh_2C{\equiv}Ct$-Bu (see Experimental Section). We recently reported the isomeric *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-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 $PPh_2C{\equiv}Ct$-Bu relative to the C_6F_5 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 (K_2PtCl_4[12,42−44] or [PtR_2(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*-[PdX_2($PPh_2C{\equiv}CPh$)$_2$] (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 C_6F_5 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−Cγ 179.7(4)°, $C_\alpha{\equiv}C_\beta$ 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]($PPh_2C{\equiv}C$-C_6H_4-$C{\equiv}CR)_2$ (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 cleanly afforded the new naphthalene products

Scheme 4



[Pt]{7-C≡CR-$C_{10}H_4$-1-(C_6H_4-*p*C≡CR)-2,3-$\kappa PP'$(PPh_2)$_2$} (R = Ph, **5a**; *t*-Bu, **5c**), resulting from the intramolecular coupling of the two inner alkynyl fragments (eq 1). The formation of these



(1)

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 $^{31}P\{^1H\}$ 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 $^{13}C\{^1H\}$ 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−$C_\alpha{\equiv}C_\beta$−) alkyne carbons of the precursors [Pt]($PPh_2C{\equiv}C-C_6H_4-C{\equiv}CR)_2$ (R = Ph, *t*-Bu) [81.9 (C_α, $^{1+3}J_{C-P}$ 101.3 Hz, $^2J_{C\alpha\text{-}Pt}$ 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 ^{19}F NMR spectra show two sets (AA′MXX′ systems) of C_6F_5 signals in accordance with the presence of two nonequivalent C_6F_5 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 $^{31}P\{^1H\}$ 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]($PPh_2C{\equiv}$CPh)(PPh_2H), **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

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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 $[Pt(bzq)(PPh_2C{\equiv}CPh)(PPh_2H)]ClO_4$ (bzq = benzoquinolate)[45] and its evolution, even at low temperature, to a mixture of isomers of 1,2-diphosphinoalk-1-ene complex $[Pt(bzq)(PPh_2C(Ph){=}C(H)PPh_2)]ClO_4$, formally generated by addition of a P−H bond to the coordinated $PPh_2C{\equiv}CPh$ ligand.

Complex $[Pt](PPh_2C{\equiv}CPh)(PPh_2H)$, **6**, was synthesized by displacement of the tetrahydrothiophene labile ligand on $[Pt](PPh_2C{\equiv}CPh)(tht)$[7] by diphenylphosphine and characterized by usual analytical and spectroscopic means. In particular, **6** shows two characteristic absorptions in its IR spectrum due to ν(P−H) (2358 cm^{-1}) and to ν(C≡C) (2177 cm^{-1}) vibrations, and its $^{31}P\{^1H\}$ spectrum exhibits two broad doublets flanked by platinum satellites (δ −5.56, $^1J_{Pt-P}$ = 2223 Hz; −7.39 $^1J_{Pt-P}$ = 2338 Hz, $J_{P-P} \approx 10$ 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 PPh_2H ligand, whereas the signal at −7.39 is assigned to the $PPh_2C{\equiv}CPh$ 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 $PPh_2C{\equiv}CPh$ (δ C_α 86.5/C_β 109.4). The resulting shift difference ($\Delta(\delta C_\beta - \delta C_\alpha)$), 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 $[Pt](PPh_2C{\equiv}CPh)(PPh_2H)$, **6**, in toluene for 45 min, yields the asymmetric diphosphine compound $[Pt]\{Ph_2PC(Ph){=}C(Ph)PPhH\}$, **7**, in an intramolecular ligand coupling reaction that involves a very unusual and selective activation of a P−C(Ph) bond in the PPh_2H ligand with formal final 2,1-addition to the triple bond of the $PPh_2C{\equiv}CPh$ 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 $[Pt]\{Ph_2PC(H){=}C(Ph)PPh_2\}$, **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 upon coordination to the platinum center ($Pt-PPh_2C^{\delta-}{\equiv}C^{\delta+}Ph$). This product **8** can also be alternatively generated in high yield by treatment of a dichloromethane solution of complex **6** with $(NBu_4)(acac)$ (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 ν(C≡C) absorptions, but in complex **7** a weak absorption due to the ν(P−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 CD_3COCD_3, a broad doublet resonance at 7.92 ppm with platinum satellites ($^3J_{Pt-H}$ = 40 Hz), which is modified by selective ^{31}P 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 $|^2J_{P-H} + {}^3J_{P-H}|$.[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 ^{31}P 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 *P*PhH. In agreement with the formation of the chelating diphosphine $\{Ph_2PC(H){=}C(Ph)PPh_2\}$, complex **8** also display 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 ($^3J_{P-H} \approx 55$ 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

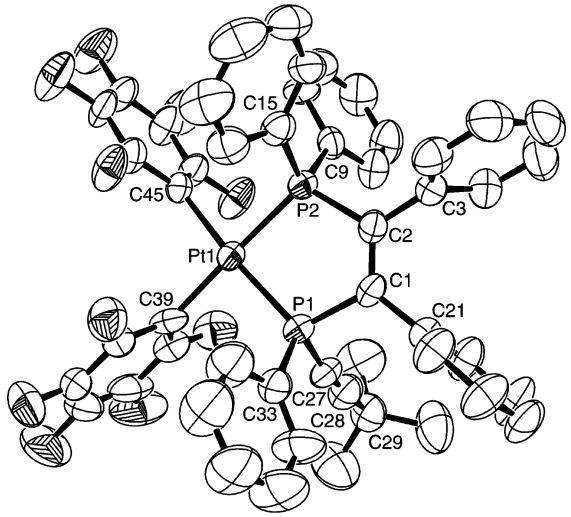

Figure 2. Molecular structure of *cis*-$[Pt(C_6F_5)_2\{Ph_2PC(Ph){=}C(Ph)PPh(C{\equiv}C\textit{t}\text{-}Bu)\}]$, **3a**. Ellipsoids are drawn at the 50% probability level.

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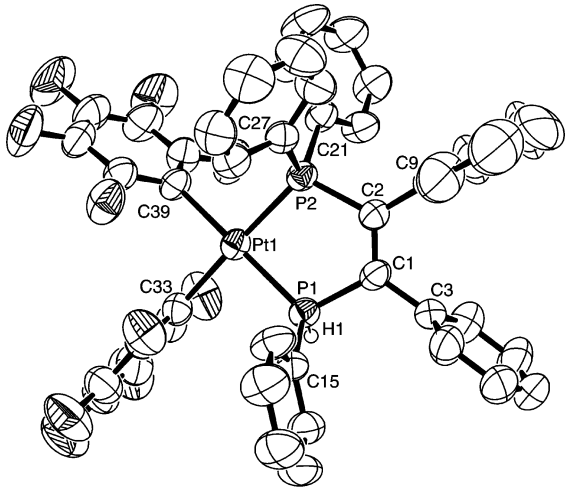

Figure 3. Molecular structure of *cis*-[Pt(C_6F_5)$_2${$Ph_2PC(Ph)$═$C(Ph)$-PPhH}], **7**. Ellipsoids are drawn at the 50% probability level.

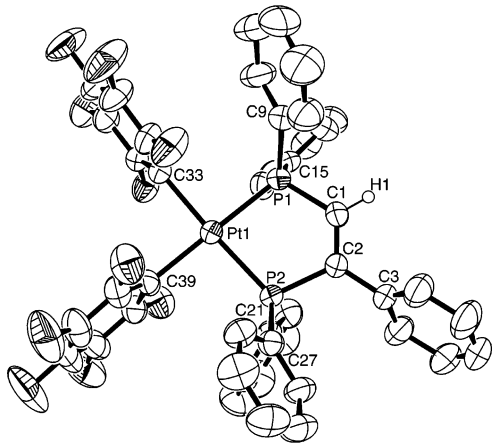

Figure 4. Molecular structure of *cis*-[Pt(C_6F_5)$_2${$Ph_2PC(Ph)$═$C(H)$-PPh_2}], **8**. Ellipsoids are drawn at the 50% probability level.

116.3(4)−121.0(4)° range, close to the ideal value of 120° for sp^2 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 alkynyldiphenylphosphine platinum(II) complexes under thermal or photochemical conditions. [Pt](PPh_2C≡$CR)_2$ (R = Ph, Tol) were found to rearrange by thermolysis to naphthalene-based diphenylphosphine complexes [Pt]{$C_{10}H_5$-1-Ph-2,3-$\kappa PP'$($PPh_2)_2$}, **1a**, and [Pt]{7-CH_3-$C_{10}H_4$-1-Tol-2,3-$\kappa PP'$($PPh_2)_2$}, **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 monophosphine[22] and diphosphinoacetylene[12] ligands. Similar naphthalene species [Pt]{7-C≡CR-$C_{10}H_4$-1-(C_6H_4-*p*C≡CR)-2,3-$\kappa PP'$($PPh_2)_2$} (R = Ph, **5a**; *t*-Bu, **5c**) were also generated starting from the diynyl systems [Pt](PPh_2C≡CC_6H_4C≡$CR)_2$, but only under photolytical reaction conditions (toluene, 45 min, eq 1). In contrast, the photolysis of the monoalkynyl complexes [Pt](PPh_2C≡$CR)_2$ (R = Ph, Tol) evolves with parallel formation of naphthalene species **1** and the new chelating diphosphine complexes [Pt]{$PPh_2C(Ph)$═$C(R)PPh(C$≡$CR)$}, **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]{Ph_2PC-(Ph)═C(R)PPh(C≡C*t*-Bu)}, **3**, were formed by photolysis of [Pt](PPh_2C≡CR)(PPh_2C≡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($C_6F_5)_2$(PPh_2C≡C*t*-$Bu)_2$], **4**, along with trace amounts of **1** and the corresponding precursors. The mixed ligand complex [Pt](PPh_2C≡CPh)(PPh_2H), **6**, selectively gives under photolysis [Pt]{$Ph_2PC(Ph)$═$C(Ph)PPhH$}, **7,** by an activation of the P−C(Ph) bond, while the expected isomer [Pt]{$Ph_2PC(H)$═$C(Ph)PPh_2$}, **8**, is formed under thermolysis or alternatively in the presence of a base such as (NBu_4)(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 ($SiMe_4$, $CFCl_3$, and 85% H_3PO_4), 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($C_6F_5)_2$(tht)(PPh_2C≡CPh)],[7] *cis*-[Pt($C_6F_5)_2$(PPh_2C≡$CR)_2$] (R = *t*-Bu,[4] Ph,[4] Tol[6]), *cis*-[Pt($C_6F_5)_2$(PPh_2C≡CR)(PPh_2C≡C*t*-Bu)] (R = Ph, Tol),[6] and *cis*-[Pt($C_6F_5)_2$(PPh_2C≡C-C_6H_4-C≡$CR)_2$] (R = *t*-Bu, Ph)[10] were prepared according to literature methods. PPh_2H 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($C_6F_5)_2${$C_{10}H_5$-1-Ph-2,3-$\kappa PP'$($PPh_2)_2$}], 1a.[22] A small quantity (∼0.05 g, 0.045 mmol) of solid *cis*-[Pt($C_6F_5)_2$-(PPh_2C≡$CPh)_2$] 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. ^{1}H NMR (δ, $CDCl_3$): 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). ^{19}F NMR (δ, $CDCl_3$): −116.6 (m, $^3J_{Pt-o-F}$ ≈ 290 Hz, 2*o*-F); −117.3 (m, $^3J_{Pt-o-F}$ ≈ 305 Hz, 2*o*-F); −162.8 (t, 1*p*-F); −162.9 (t, 1*p*-F); −164.5 (m, 2*m*-F); −164.9 (m, 2*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 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($C_6F_5)_2${7-CH_3-$C_{10}H_4$-1-Tol-2,3-$\kappa PP'$-($PPh_2)_2$}], 1b. Solid *cis*-[Pt($C_6F_5)_2$(PPh_2C≡$CTol)_2$] (0.189 g, 0.168 mmol) was heated at ∼220 °C for 1 h, obtaining a brown oil. The residue was treated with CH_2Cl_2 (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 $C_{54}F_{10}H_{34}P_2Pt$ (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($C_6F_5)_{X-sens}$ 790 (m), 780 (m). ^{1}H NMR (δ, $CDCl_3$): 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) (C_6H_4, Tol); 2.29 (s, 3H, CH_3); 2.24

(s, 3H, CH_3). ^{19}F NMR (δ, $CDCl_3$): −116.4 (m, $^3J_{Pt-o-F} \approx 310$ Hz, 2*o*-F); −117.3 (m, $^3J_{Pt-o-F} \approx 310$ Hz, 2*o*-F); −162.9 (t, 1*p*-F); −163.1 (t, 1*p*-F); −164.5 (m, 2*m*-F); −164.9 (m, 2*m*-F). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 46.17 (d br, $^1J_{Pt-P} = 2242$ Hz, $^2J_{P-P} \approx 8$ Hz); 40.24 (d br, $^1J_{Pt-P} = 2309$ Hz).

Irradiation of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CPh$)$_2$]. Formation of *cis*-[Pt(C_6F_5)$_2${$C_{10}H_5$-1-Ph-2,3-$\kappa PP'$(PPh_2)$_2$}], 1a, and *cis*-[Pt(C_6F_5)$_2$-{$PPh_2C(Ph){=}C(Ph)PPh(C{\equiv}CPh)$}], 2a. Irradiation of a colorless solution of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CPh$)$_2$] (0.412 g, 0.374 mmol) in toluene was followed by $^{31}P\{^1H\}$ NMR and ^{19}F NMR spectroscopy in $CDCl_3$ 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**. ^{1}H NMR (δ, $CDCl_3$): 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**). ^{19}F NMR (δ, $CDCl_3$): −116.6 (m, $^3J_{Pt-o-F} \approx 290$ Hz, *o*-F, **1a**); −117.3 (m, *o*-F, **1a** + **2a**); −117.7 (m, $^3J_{Pt-o-F} \approx 265$ 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**). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 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(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)$_2$]. Formation of *cis*-[Pt(C_6F_5)$_2${7-CH_3-$C_{10}H_4$-1-Tol-2,3-$\kappa PP'$(PPh_2)$_2$}], 1b, and *cis*-[Pt(C_6F_5)$_2${$PPh_2C(Ph){=}C(Tol)PPh(C{\equiv}CTol)$}], 2b. Following a procedure similar to that described for *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CPh$)$_2$], irradiation of a colorless solution of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)$_2$] 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**. ^{1}H NMR (δ, $CDCl_3$): 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**, C_6H_4, Tol); 6.36 (d, $J_{H-H} = 7.6$ Hz, **2b**, C_6H_4, Tol); 6.22 (d, $J_{H-H} = 7.8$ Hz, **1b**, C_6H_4, Tol); 2.40, 2.18 (s, CH_3), **2b**; 2.29, 2.24 (s, CH_3), **1b**. ^{19}F NMR (δ, $CDCl_3$): −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**). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 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(C_6F_5)$_2$($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}Ct$-Bu)]. Synthesis of *cis*-[Pt(C_6F_5)$_2${$Ph_2PC(Ph){=}C(R)PPh(C{\equiv}Ct$-Bu)}] (R = Ph, 3a; Tol, 3b; *t*-Bu, 3c). Irradiation of a solution of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CPh$)($PPh_2C{\equiv}Ct$-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(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)-($PPh_2C{\equiv}Ct$-Bu)] (0.200 g, 0.182 mmol; 0.128 g, 64% yield) or *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-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(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-Bu)$_2$], **4**, were also detected in the final reaction mixture.

Data for **3a**. Anal. Calcd for $C_{50}F_{10}H_{34}P_2Pt$ (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 − C_6F_5]$^+$ 75%; 748 [M − 2C_6F_5]$^+$ 100%. MS (apci−): *m*/*z* 1081 [M]$^-$ 28%. IR (cm^{-1}): ν(C≡C) 2210 (m), 2167 (s); ν(C═C) 1605 (w); ν(C_6F_5)$_{X-sens}$ 789 (s), 780 (s). ^{1}H NMR (δ, $CDCl_3$): 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(CH_3)$_3$). ^{19}F NMR (δ, $CDCl_3$): at 293 K, −116.7 (br, 1*o*-F); −117.8 (m, $^3J_{Pt-o-F} \approx 300$ Hz, 2*o*-F); −118.3 (br, 1*o*-F); −162.2 (m, 2*p*-F); −164.7 (m, 3*m*-F); −165.2 (br, 1*m*-F); at 223 K, −116.9 (m, $^3J_{Pt-o-F} \approx 305$ Hz, 1*o*-F); −118.1 (m, $^3J_{Pt-o-F} \approx 295$ Hz, 1*o*-F); −118.7 (m, $^3J_{Pt-o-F} \approx 295$ Hz, 2*o*-F); −161.48, −161.51 (2*p*-F); −163.9 (m, 2*m*-F); −164.2 (m, 1*m*-F); −164.7 (m, 1*m*-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. $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 58.84 (s, $^1J_{Pt-P} = 2283$ Hz); 27.33 (s, $^1J_{Pt-P} = 2371$ Hz).

Data for **3b**. Anal. Calcd for $C_{51}F_{10}H_{36}P_2Pt$ (1095.87): C, 55.90; H, 3.31. Found: C, 55.68; H, 3.00. MS (FAB+): *m*/*z* 929 [M − C_6F_5]$^+$ 18%; 762 [M − 2C_6F_5]$^+$ 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(C_6F_5)$_{X-sens}$ 790 (m), 781 (s). ^{1}H NMR (δ, $CDCl_3$): 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, CH_3); 1.30 (s, 9H, −C(CH_3)$_3$). ^{19}F NMR (δ, $CDCl_3$): at 293 K, −116.8 (vbr), −117.8 (m, $^3J_{Pt-o-F} \approx 320$ Hz) (4*o*-F); −162.4, −162.3 (overlapping of two triplets, 2*p*-F); −164.8 (m, 3*m*-F); −165.3 (br, 1*m*-F); at 223 K, −116.8 (m, $^3J_{Pt-o-F} \approx 310$ Hz, 1*o*-F); −118.2 (m, $^3J_{Pt-o-F} \approx 310$ Hz, 1*o*-F); −118.7 (m, overlapping of two *o*-F); −161.5, −161.6 (overlapping of two triplets, 2*p*-F); −164.0 (m, 2*m*-F); −164.3 (m, 1*m*-F); −164.8 (m, 1*m*-F). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 58.42 (s, $^1J_{Pt-P} = 2260$ Hz); 27.60 (s, $^1J_{Pt-P} = 2375$ Hz).

Data for **3c**. Anal. Calcd for $C_{48}F_{10}H_{38}P_2Pt$ (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 − C_6F_5]$^+$ 36%; 727 [M − 2C_6F_5]$^+$ 46%. IR (cm^{-1}): ν(C≡C) 2211 (m), 2169 (s); ν(C═C) 1603 (w); ν(C_6F_5)$_{X-sens}$ 790 (sh), 779 (s). ^{1}H NMR (δ, $CDCl_3$): 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(CH_3)$_3$); 1.02 (s, 9H, C(CH_3)$_3$). ^{19}F NMR (δ, $CDCl_3$): −116.5 (m, br, *o*-F); −117.6 (vbr, 2*o*-F); −119.3 (m, $^3J_{Pt-o-F} \approx 275$ Hz, 1*o*-F); −162.7 (t), −162.8 (t) (2*p*-F); −165.0 (m, 4*m*-F). $^{31}P\{^1H\}$ NMR (δ, $CDCl_3$): 62.97 (s br, $^1J_{Pt-P} = 2241$ Hz); 33.12 (s br, $^1J_{Pt-P} = 2222$ Hz).

Thermal Reactions of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}Ct$-Bu)]. (a) Solid *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CPh$)($PPh_2C{\equiv}Ct$-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 $CDCl_3$ (0.5 mL). Its $^{31}P\{^1H\}$ NMR spectrum indicates the presence of a mixture of complexes including **1a** (δ 46.53, 41.06), *trans*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-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(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)-($PPh_2C{\equiv}Ct$-Bu)] (0.05 g, 0.045 mmol) gave a brown oily liquid, whose $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ mainly shows the presence of **1b**, **4** (∼0.37:1), and the precursor.

(c) *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-Bu)$_2$] was unchanged when heated at 220 °C for 2 h, showing in the $^{31}P\{^1H\}$ NMR spectrum only signals of the starting material.

Synthesis of *trans*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$-Bu)$_2$], 4. A solution of *trans*-[Pt(C_6F_5)$_2$(tht)$_2$] (0.122 g, 0.181 mmol) in CH_2Cl_2 was treated with $PPh_2C{\equiv}Ct$-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 $C_{48}F_{10}H_{38}P_2Pt$ (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 − C_6F_5]$^+$ 57%; 813 [M − C_6F_5 − C≡C*t*-Bu]$^+$ 100%; 727 [M − 2C_6F_5]$^+$ 62%. IR (cm^{-1}): ν(C≡C) 2215 (m), 2171 (s); ν(C_6F_5)$_{X-sens}$ 777 (vs). ^{1}H NMR (δ,

$CDCl_3$): 7.53 (m, 8H); 7.28 (m, 12H) (Ph); 1.23 (s, 18H, C(CH_3)$_3$). ^{19}F NMR (δ, $CDCl_3$): −116.7 (m, $^3J_{Pt-o-F}$ = 240 Hz, 4*o*-F); −163.3 (m, 2*p*-F); −164.6 (m, 4*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −7.60 (s, $^1J_{Pt-P}$ = 2854 Hz).

Irradiation of *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡C-C_6H_4-C≡CR)$_2$] (R = Ph, *t*-Bu). Synthesis of *cis*-[Pt(C_6F_5)$_2${7-C≡CR-$C_{10}H_4$-1-(C_6H_4-*p*C≡CR)-2,3-κ*PP′*(PPh$_2$)$_2$}] (R = Ph, 5a; *t*-Bu, 5c). Irradiation (45 min) of a solution of *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡C-C_6H_4-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(C_6F_5)$_2$-(PPh$_2$C≡C-C_6H_4-C≡C*t*-Bu)$_2$] (0.180 g, 0.143 mmol).

Data for **5a**. Anal. Calcd for $C_{68}F_{10}H_{38}P_2Pt$ (1302.07): C, 62.73; H, 2.94. Found: C, 62.87; H, 3.04. MS (FAB+): *m*/*z* 1135 [M − C_6F_5]$^+$ 56%; 967 [M − 2C_6F_5 − 1H]$^+$ 88%. IR (cm^{-1}): ν(C≡C) 2213 (w), 2173 (w); ν(C_6F_5)$_{X-sens}$ 790 (m), 780 (m). ^{1}H NMR (δ, $CDCl_3$): 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). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 146.6 (dm), 137.1 (dm) (C_6F_5); 133.5−127.7; 124.1−121.8 (aromatics); 92.0; 90.1; 88.6; 88.4 (C≡C). ^{19}F NMR (δ, $CDCl_3$): −116.6 (m, $^3J_{Pt-o-F}$ ≈ 335 Hz, 2*o*-F); −117.3 (m, $^3J_{Pt-o-F}$ ≈ 310 Hz, 2*o*-F); −162.5 (t, 1*p*-F); −162.8 (t, 1*p*-F); −164.4 (m, 2*m*-F); −164.7 (m, 2*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 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 $C_{64}F_{10}H_{46}P_2Pt$ (1262.09): C, 60.91; H, 3.67. Found: C, 61.05; H, 4.05. MS (FAB+): *m*/*z* 1262 [M]$^+$ 12%; 1095 [M − C_6F_5]$^+$ 60%; 927 [M − 2C_6F_5 −1H]$^+$ 100%. IR (cm^{-1}): ν(C≡C) 2219 (w), 2174 (w); ν(C_6F_5)$_{X-sens}$ 790 (m), 781 (m). ^{1}H NMR (δ, $CDCl_3$): 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(CH_3)$_3$); 1.24 (s, 9H, C(CH_3)$_3$). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 145.5 (dm), 136.6 (dm) (C_6F_5); 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(*C*H$_3$)$_3$); 27.74 (s); 27.70 (s) ((*C*(CH$_3$)$_3$). ^{19}F NMR (δ, $CDCl_3$): −116.5 (m, $^3J_{Pt-o-F}$ ≈ 300 Hz, 2*o*-F); −117.3 (m, $^3J_{Pt-o-F}$ ≈ 310 Hz, 2*o*-F); −162.7 (t, 1*p*-F); −162.9 (t, 1*p*-F); −164.4 (m, 2*m*-F); −164.8 (m, 2*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 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-$C_{10}H_4$-1-(C_6H_4-*p*C≡C*t*-Bu)-2,3-(PPh$_2$)$_2$}. A solution of *cis*-[Pt(C_6F_5)$_2${7-C≡C*t*-Bu-$C_{10}H_4$-1-(C_6H_4-*p*C≡C*t*-Bu)-2,3-κ*PP′*(PPh$_2$)$_2$}], **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. ^{1}H NMR (δ, $CDCl_3$): 7.63−6.88 (m, 26 H), 6.45 (d, 2H, J_{H-H} = 8 Hz) (aromatics); 1.32 (s, 9H, C(CH_3)$_3$); 1.24 (s, 9H, C(CH_3)$_3$). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −8.33 (AB, $^2J_{P-P}$ =155 Hz, δ_A = −6.14, δ_B = −10.52).

Thermolysis of *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡C-C_6H_4-C≡CR)$_2$] (R = Ph, *t*-Bu). (a) *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡C-C_6H_4-C≡CPh)$_2$] (0.05 g, 0.038 mmol) and *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡C-C_6H_4-C≡C*t*-Bu)$_2$] (0.05 g, 0.040 mmol) were unchanged when heated 6 h at 240−250 °C (^{31}P{^{1}H} NMR identification).

Synthesis of *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡CPh)(PPh$_2$H)], 6. PPh$_2$H (85 μL, 0.465 mmol) was added to a colorless solution of *cis*-[Pt-(C_6F_5)$_2$(PPh$_2$C≡CPh)(tht)] (0.420 g, 0.465 mmol) in CH_2Cl_2 (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 $C_{44}F_{10}H_{26}P_2Pt$ (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(C_6F_5)$_{X-sens}$ 796 (s), 786 (s). ^{1}H NMR (δ, $CDCl_3$): 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*). ^{13}C{^{1}H} NMR (δ, $CDCl_3$): 145.4 (dt, $^1J_{C-F}$ = 230 Hz, $^2J_{C-F}$ ≈ 20 Hz); 136.9 (dm, $^1J_{C-F}$ ≈ 240 Hz) (C_6F_5); 133.4 (d, $^2J_{C-P}$ = 10.9 Hz, $^3J_{C-Pt}$ ≈ 18.4 Hz, *o*-C, PPh$_2$); 132.3 (d, $^2J_{C-P}$ = 12.9 Hz, $^3J_{C-Pt}$ ≈ 16.9 Hz, *o*-C, PPh$_2$); 131.9 (d, $^4J_{C-P}$ = 1.3 Hz, *o*-C, C≡CPh); 130.9 (d, $^4J_{C-P}$ = 2.3 Hz, *p*-C, PPh$_2$); 130.7 (d, $^4J_{C-P}$ = 2.1 Hz, *p*-C, PPh$_2$); 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, PPh$_2$); 128.2 (overlapping of two d, J_{C-P} = 10 Hz, *m*-C, PPh$_2$); 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, PPh$_2$); 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≡*C*Ph); 78.1 (dd, $^1J_{C-P}$ = 99.6 Hz, $^3J_{C-P}$ = 4.7 Hz, C_α, −P*C*≡CPh). ^{19}F NMR (δ, $CDCl_3$): −117.8 (m, $^3J_{Pt-o-F}$ ≈ 330 Hz, 4*o*-F); −162.0 (t, 1*p*-F); −162.6 (t, 1*p*-F); −163.9 (m, 4*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): −5.56 (s br, $^1J_{Pt-P}$ = 2223 Hz, *P*Ph$_2$H); −7.39 (d br, $^1J_{Pt-P}$ = 2338 Hz, J_{P-P} ≈ 10 Hz, *P*Ph$_2$C≡CPh). ^{31}P NMR (δ, $CDCl_3$): −5.70 (d, $^1J_{Pt-P}$ = 2238 Hz, $^1J_{H-P}$ = 378 Hz, *P*Ph$_2$H); −7.31 (s br, $^1J_{Pt-P}$ = 2322 Hz, *P*Ph$_2$C≡CPh).

Irradiation of *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡CPh)(PPh$_2$H)]. Synthesis of *cis*-[Pt(C_6F_5)$_2${Ph$_2$PC(Ph)═C(Ph)PPhH}], 7. A colorless solution of *cis*-[Pt(C_6F_5)$_2$(PPh$_2$C≡CPh)(PPh$_2$H)] (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 $C_{44}F_{10}H_{26}P_2Pt$ (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(C_6F_5)$_{X-sens}$ 791 (br s). ^{1}H NMR (δ, $CDCl_3$): 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*). ^{19}F NMR (δ, $CDCl_3$): −118.0 (m, $^3J_{Pt-o-F}$ ≈ 325 Hz, 4*o*-F); −161.4 (t, 1*p*-F); −162.0 (t, 1*p*-F); −163.9 (m, 2*m*-F); −164.6 (m, 2*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 61.05 (s, $^1J_{Pt-P}$ = 2247 Hz, *P*Ph$_2$); 28.06 (s, $^1J_{Pt-P}$ = 2190 Hz, *P*PhH). ^{31}P NMR (δ, $CDCl_3$): 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(C_6F_5)$_2${Ph$_2$PC(H)═C(Ph)PPh$_2$}], 8. Complex **8** was obtained quantitatively (^{31}P{^{1}H}) by heating *cis*-[Pt-(C_6F_5)$_2$(PPh$_2$C≡CPh)(PPh$_2$H)] (0.050 g, 0.05 mmol) at ∼175 °C for 1 h. Alternatively, complex **8** was obtained by using (NBu_4)-(acac) prepared in situ: Tl(acac) (0.046 g, 0.150 mmol) was treated with a CH_2Cl_2 solution (15 mL) of (NBu_4)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(C_6F_5)$_2$-(PPh$_2$C≡CPh)(PPh$_2$H)] (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 $C_{44}F_{10}H_{26}P_2Pt$ (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(C_6F_5)$_{X-sens}$ 790 (m), 782 (w). ^{1}H NMR (δ, $CDCl_3$): 7.57−7.10 (m, 24H); 6.84 (d, J_{H-H} = 7.4 Hz, 2H). ^{1}H NMR (δ, CD_3COCD_3): 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, 1*p*H, J_{H-H} = 7.5 Hz, C−Ph); 7.18 (t, 2*m*H, C−Ph); 7.02 (d, 2*o*H, J_{H-H} = 7.5 Hz, C−Ph). ^{19}F NMR (δ, $CDCl_3$): −117.8 (m, $^3J_{Pt-o-F}$ ≈ 325 Hz, 4*o*-F); −162.0 (t), −162.2 (t) (2*p*-F); −164.4 (m, 4*m*-F). ^{31}P{^{1}H} NMR (δ, $CDCl_3$): 61.07 (s, $^1J_{Pt-P}$ = 2327 Hz, *P*Ph$_2$C(Ph)═); 38.98 (s, $^1J_{Pt-P}$ = 2294 Hz, *P*PhC(H)═). ^{31}P NMR (δ, $CDCl_3$): 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(C_6F_5)$_2$(PPh$_2$C≡CPh)(PPh$_2$H)] (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·$CHCl_3$, and 8

	3a	**4**	**7**·$CHCl_3$	**8**
empirical formula	$C_{50}H_{34}F_{10}P_2Pt$	$C_{48}H_{38}F_{10}P_2Pt$	$C_{45}H_{27}Cl_3F_{10}P_2Pt$	$C_{44}H_{26}F_{10}P_2Pt$
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	*Pc*	$P2_1/c$	$P\bar{1}$	$P2_1/n$
a (Å); α (deg)	10.8190(3); 90	11.0706(2); 90	11.7815(2); 73.6040(10)	10.6341(2); 90
b (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)
c (Å); *γ* (deg)	20.2720(6); 90	11.1888(2); 90	15.9553(4); 71.1300(10)	22.6780(4); 90
V (Å^3); *Z*	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
F(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	$-11 \le h \le 13$, $-11 \le k \le 12$, $-24 \le l \le 23$	$-14 \le h \le 14$, $-21 \le k \le 23$, $-14 \le l \le 14$	$-15 \le h \le 15$, $-16 \le k \le 16$, $-20 \le l \le 20$	$-13 \le h \le 13$, $-21 \le k \le 21$, $-29 \le l \le 29$
no. of reflens collected	14 546	35 418	19 790	29 758
no. of indep reflns	7327 [*R*(int) = 0.0370]	5264 [*R*(int) = 0.0676]	10 153 [*R*(int) = 0.0462]	9133 [*R*(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 F^2 [a]	1.077	1.036	1.026	1.050
final *R* indices [$I > 2\sigma(I)$][a]	R1 = 0.0349, wR2 = 0.0788	R1 = 0.0314, wR2 = 0.0705	R1 = 0.0485, wR2 = 0.1144	R1 = 0.0429, wR2 = 0.0680
R indices (all data)[a]	R1 = 0.0407, wR2 = 0.0823	R1 = 0.0554, wR2 = 0.0779	R1 = 0.0676, wR2 = 0.1261	R1 = 0.0838, wR2 = 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] $R1 = \sum(|F_o| - |F_c|)/\sum|F_o|$; $wR2 = [\sum w(F_o^2 - F_c^2)^2/\sum wF_o^2]^{1/2}$; goodness of fit = $\{\sum[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

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**·$CHCl_3$). X-ray intensity data were collected with a NONIUS *κ*-CCD area-detector diffractometer, using graphite-monochromated Mo Kα 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**·$CHCl_3$ 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]

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**·$CHCl_3$, there are peaks of electron density higher than 1 e/Å^3 in the final map, but they are located very close to the platinum atoms and have no chemical meaning. Complexes **3a** and **7**·$CHCl_3$ 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**·$CHCl_3$ crystallizes in the space group $P\bar{1}$; 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

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