Formation of Diphenylphosphanylbutadienyl Complexes by Insertion of Two P-Coordinated Alkynylphosphanes into a Pt−C_6F_5 Bond: Detection of Intermediate and Reaction Products

Irene Ara,[b] Juan Forniés,*[b] Ana García,[a] Julio Gómez,[a] Elena Lalinde,*[a] and M. Teresa Moreno[a]

Abstract: The reactions between *cis*-[M(C_6F_5)$_2$($PPh_2C{\equiv}CR$)$_2$] (M = Pt, Pd; R = Ph, *t*Bu, Tol **2**, **3**) or *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}CtBu$)] (R = Ph **4**, Tol **5**) and *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1** have been investigated. Whereas [M]($PPh_2C{\equiv}CtBu$)$_2$ ([M] = *cis*-M(C_6F_5)$_2$) is inert towards **1**, the analogous reactions starting from [M]($PPh_2C{\equiv}CR$)$_2$ or [Pt]($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}CtBu$) (R = Ph, Tol) afford unusual binuclear species [Pt(C_6F_5)(S)μ-{C(R′)=C(PPh_2)C(PPh_2)=C(R)(C_6F_5)}M(C_6F_5)$_2$] (R = R′ = Ph, Tol, M = Pt **6a**,**c**, M = Pd **7a**,**c**; M = Pt, R′ = *t*Bu, R = Ph **8**, Tol **9**) containing a bis(diphenylphosphanyl)butadienyl bridging ligand formed by an unprecedented sequential insertion reaction of two P-coordinated $PPh_2C{\equiv}CR$ ligands into a Pt−C_6F_5 bond. Although in solution the presence of coordinated solvent S (S = (thf)$_x$(H_2O)$_y$) in **6**, **7** is suggested by NMR spectroscopy, X-ray diffraction analyses of different crystals of the mixed complex [Pt(C_6F_5)μ-{C(*t*Bu)=C(PPh_2)-C(PPh_2)=C(Tol)(C_6F_5)}Pt(C_6F_5)$_2$] **9** unequivocally establish that in the solid state the steric crowding of the new diphenylbutadienyl ligand formed stabilizes an unusual coordinatively unsaturated T-shaped 3-coordinated platinum(II) center. Structure determinations of the mononuclear precursors *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)$_2$] (R = Ph, *t*Bu, Tol) have been carried out to evaluate the factors affecting the insertion processes. The reactions of the platinum complexes **6** towards neutral ligands (L = CO, py, PPh_2H, CN*t*Bu) in a 1:1 molar ratio afford related diplatinum derivatives **10**–**13**, whereas treatment with CN*t*Bu (1:2 molar ratio) or 2,2′-bipy (1:1 molar ratio) results in the opening of the chelating ring to give *cis*,*cis*-[Pt(C_6F_5)(L)$_2$$\mu$-{1-$\kappa C^1$:2-$\kappa PP'$-C(R)=C($PPh_2$)C($PPh_2$)=C(R)($C_6F_5$)}-Pt($C_6F_5$)$_2$] (**14**, **15**). The unsaturated or solvento complexes are unstable in solution evolving firstly, through an unexpected formal 4-1 R (Ph, Tol) migration, to the intermediate diphosphanylbutadienyl isomer derivatives [Pt(C_6F_5)(S)μ-{C(C_6F_5)=C(PPh_2)C(PPh_2)=C(R)$_2$}M-(C_6F_5)$_2$] (**16**, **18**) (X-ray, R = Ph, M = Pt) and, finally, to 1-pentafluorophenyl-2,3-bis(diphenylphosphanyl)naphthalene mononuclear complexes (**17**, **19**) by annulation of a phenyl or tolyl group.

Keywords: alkynes · butadienyl complexes · insertion · phosphanes · platinum

Introduction

Carbon–carbon bond forming and C−C bond activation reactions caused by transition metals have received great attention as a result of their inherent importance in the design of efficient and selective processes.[1] The facile migratory insertion of C≡C and C=C units into M−H and M−C bonds represents a crucial step involved in various synthetic organic reactions as well as polymer synthesis catalyzed by transition metals.[1, 2] In this context, complexes of Group 10 metals have been frequently employed[3] as exemplified by reactions of alkynes with nickelacycles and palladacycles giving entries to unusual and interesting free or coordinated poly- or heterocyclic compounds.[4] The insertion of alkynes across the Pt−H bond of mononuclear Pt complexes has been examined in detail by Clark and co-workers[5] and several mechanistic studies of the multiple insertion of alkynes into Ni−C and Pd−C have also been reported.[4e, 6] It is unlikely for metal−R_F bonds to undergo insertion reactions,[7] particularly when they are metal–fluoroaryl bonds, which are quite robust.[7a, b, 8] There have been only a few reports on the formal insertion of isonitriles into titanium[9] and palladium[10] M−C_6F_5 bonds

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Supporting information for this article is available on the WWW under http://www.chemeurj.org/ or from the author. The data include tables of crystal data and structure refinement for **2a**, **2b**, **2c**, **9**, **14c**, and **16a** and the ^{19}F-^{19}F COSY spectrum of complex **6a**.

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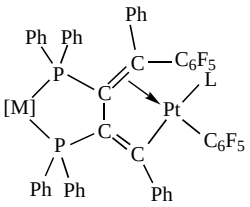
to give pentafluorobenzimidoyl derivatives, and more recently Espinet and co-workers have shown that the addition of Pd–C_6F_5 to coordinated olefins is also a relatively easy process.[11] Surprisingly, as far as we are aware, apart from the results reported in our preliminary communication,[12] the insertion of an acetylenic fragment into a M–C_6F_5 ligand has never been described. In that report,[12] we communicated an unprecendent insertion of two P-coordinated $PPh_2C{\equiv}CPh$ ligands into a Pt–C_6F_5 bond that yielded unexpected diphenylphosphanylbutadienyl homo- and heterobinuclear complexes. X-ray diffraction studies ([M] = $Pt(C_6F_5)_2$, L = PPh_2H) confirmed the presence of an unusual 2,3-bis(diphenylphosphanyl)-1,3-butadien-1-yl acting as a bischelating μ-1(3,4-η,κC^1):2$\kappa^2 P,P'$ bridging ligand. We now report: i) the extension of this reaction to other P-coordinated $PPh_2C{\equiv}CR$ ligands and detailed spectroscopic characterization data for all complexes including novel X-ray diffraction studies (**9**, **14c**); ii) the observation that the solvento derivatives (L = THF, H_2O) are unstable in solution leading, through an unexpected formal 4-1 (R = Ph, Tol) migration, to analogous μ-$C(C_6F_5){=}C(PPh_2)$–$C(PPh_2){=}C(R)_2$ phosphanylbutadienyl isomer derivatives (**16**, **18**) (X-ray **16a**) and, finally, to 1-pentafluorophenyl-2,3-bis(diphenylphosphanyl)naphthalene mononuclear complexes by annulation of a phenyl (**17a**, **19a**) or tolyl group (**17c**, **19c**). Furthermore, in order to gain an insight into the factors affecting the initial insertion and coupling processes, the molecular structures of several *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CR)_2]$ (R = Ph, *t*Bu, Tol) have been studied by X-ray diffraction and are also presented.



L = solvent or ligand,
[M] = $Pt(C_6F_5)_2$, $Pd(C_6F_5)_2$

Abstract in Spanish: *Se ha investigado la reactividad de los complejos* cis-*[M(C$_6$F$_5$)$_2$(PPh$_2$C≡CR)$_2$] (M = Pt, Pd; R = Ph, t*Bu, Tol **2**, **3**) *y* cis-*[Pt(C$_6$F$_5$)$_2$(PPh$_2$C≡CR)(PPh$_2$C≡CtBu)] (R = Ph **4**, Tol **5**) frente a* cis-*[Pt(C$_6$F$_5$)$_2$(thf)$_2$] **1**. En contraste con la ausencia de reactividad de [M](PPh$_2$C≡CtBu)$_2$ ([M] =* cis-*M(C$_6$F$_5$)$_2$) frente a **1**, las reacciones análogas utilizando como precursores [M](PPh$_2$C≡CR)$_2$ y [Pt](PPh$_2$C≡CR)-(PPh$_2$C≡CtBu) (R = Ph, Tol) dan lugar a especies binucleares poco usuales [Pt(C$_6$F$_5$)(S)*μ*-{C(R′)=C(PPh$_2$)C(PPh$_2$)=C(R)-(C$_6$F$_5$)}M(C$_6$F$_5$)$_2$] (R = R′ = Ph, Tol, M = Pt **6a**,**c**, M = Pd **7a**,**c**; M = Pt, R′ = tBu, R = Ph **8**, Tol **9**) que contienen un ligando puente del tipo bis(difenilfosfina)butadienilo, formado mediante inserción sucesiva de los dos ligandos P-coordinados PPh$_2$C≡CR en uno de los enlaces Pt–C$_6$F$_5$. Aunque mediante espectroscopía de RMN se sugiere la presencia en disolución de disolvente coordinado S (S = (thf)$_x$(H$_2$O)$_y$) en los complejos **6** y **7**, el análisis por difracción de Rayos X de diferentes cristales del complejo mixto [Pt(C$_6$F$_5$)*μ*-{C(tBu)=C(PPh$_2$)C-(PPh$_2$)=C(Tol)(C$_6$F$_5$)}Pt(C$_6$F$_5$)$_2$] **9** establece de forma inequívoca que en estado sólido el nuevo ligando difenilfosfinabutadienilo formado estabiliza un centro coordinativamente insaturado de Pt^{II} tricoordinado en forma de T. Con objeto de evaluar los factores que afectan a los procesos de inserción se ha llevado a cabo la determinación estructural de los precursores mononucleares* cis-*[Pt(C$_6$F$_5$)$_2$(PPh$_2$C≡CR)$_2$] (R = Ph, tBu, Tol). El tratamiento de los complejos de diplatino **6** frente a ligandos neutros (L = CO, py, PPh$_2$H, CNtBu) en relación molar 1:1 permite preparar los derivados análogos **10**–**13**, mientras que las reacciones con exceso de CNtBu (relación molar 1:2) o con 2,2′-bipy (1:1) provocan la apertura del anillo quelato generando los complejos* cis,cis-*[Pt(C$_6$F$_5$)(L)$_2$*μ*-{1-κC^1:2-κPP′-C(R)=C(PPh$_2$)C(PPh$_2$)=C(R)-(C$_6$F$_5$)}Pt(C$_6$F$_5$)$_2$] (**14**, **15**). Los complejos **6** y **7**, con moléculas de disolvente como ligando, son inestables en disolución evolucionando inicialmente, a través de una inesperada migración formal 4-1 R (Ph, Tol), a los derivados difosfinabutadienilo isómeros intermedios [Pt(C$_6$F$_5$)(S)-*μ*-{C(C$_6$F$_5$)=C(PPh$_2$)C(PPh$_2$)=C(R)$_2$}M(C$_6$F$_5$)$_2$] (**16**, **18**) (rayos-X, R = Ph, M = Pt) y, finalmente, a los complejos mononucleares 1-pentafluorofenil-2,3-bis(difenilfosfina)naftaleno (**17**, **19**) por anulación de un grupo fenilo o tolilo respectivamente.*

Results and Discussion

Alkynylphosphanes $PPh_2C{\equiv}CR$ are versatile molecules not only as polyfunctional ligands[13] but also because they participate in a number of coupling and insertion reactions.[14] Detailed studies of alkynylphosphanes with transition metal–carbonyl clusters have also shown that these ligands are excellent sources of metal-coordinated phosphide and ynyl fragments, which may also take part in further coupling or insertion processes.[15] Carty and co-workers have demonstrated in a highly elegant way that the reactivity of the alkynyl function of $PPh_2C{\equiv}CR$ molecules can be modulated by simple P-coordination to a palladium or platinum center in *cis*-$[PtX_2(PPh_2C{\equiv}CR)_2]$ complexes.[16] The thermal coupling of the pendant alkynyl groups of *cis*-$[PtX(Y)(PPh_2C{\equiv}CPh)_2]$ (X = Y = Cl, I, CF_3, C_6F_5; X(Y) = *o*-$C_6H_4O_2$, Me, Cl)[17] yielding the corresponding complexes containing the unsymmetrical diphosphane 1-phenyl-2,3-bis(diphenylphosphanyl)-naphthalene (Scheme 1, A, i) was of particular relevance to the work described here. X-ray diffraction studies revealed that in these *cis*-bis(alkynylphosphane) derivatives, the sterically less demanding alkynyl groups are forced into a configuration, which facilitates alkyne–alkyne interaction.[17] Along the same lines several recent reports have shown that the Bergman cyclization of 1,2-bis(diphenylphosphanylethynylbenzene) can be accelerated or inhibited by metal complexation because chelation of the ligand modulates the critical distance of the alkynyl termini (Scheme 1, B, ii).[18]

The aim of this work was to investigate the possibility of inducing alkyne coupling of two P-coordinated $PPh_2C{\equiv}CR$ ligands by simultaneous η^2-coordination to a second metal center (Scheme 1, iii). Thus, considering that *cis*-$[Pt(C_6F_5)_2(thf)_2]$ **1** is able to interact easily with systems such as PhC≡CPh[19] or alkynylmetal complexes,[2a, 13b, 20, 21] we decided to examine the reactivity of **1** towards compounds *cis*-$[M(C_6F_5)_2(PPh_2C{\equiv}CR)_2]$ (M = Pt, Pd; R = Ph, *t*Bu, Tol) or

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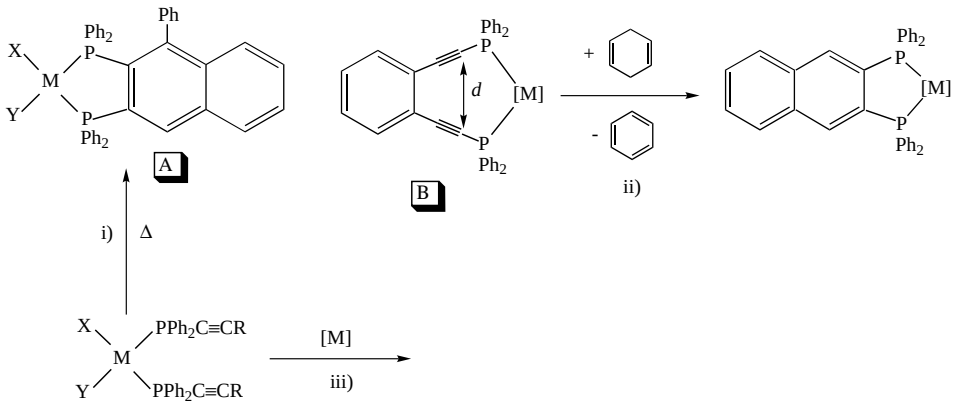
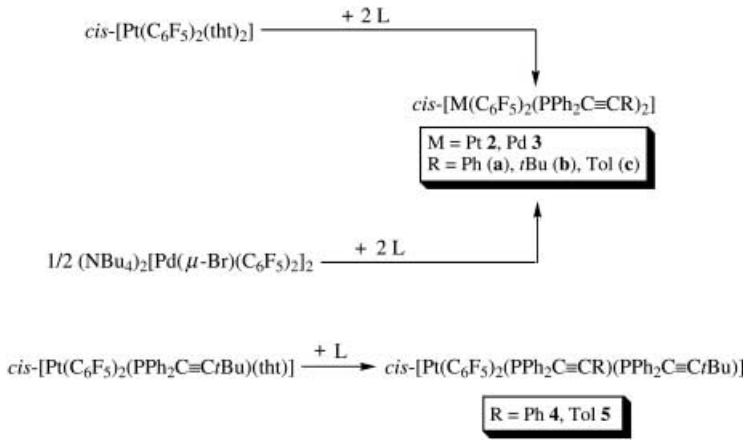


Scheme 1. The coupling of pendant alkynyl groups of *cis*-[MX(Y)($PPh_2C{\equiv}CPh)_2$] (M = Pt; X = Y = Cl, I, CF_3, C_6F_5; X(Y) = *o*-$C_6H_4O_2$, Me, Cl) to yield the corresponding complexes containing the unsymmetrical diphosphane 1-phenyl-2,3-bis(diphenylphosphanyl)naphthalene (A, i); Bergman cyclization of 1,2-bis(diphenylphosphanylethynylbenzene) by metal complexation (B, ii).

cis-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(PPh_2C{\equiv}CR')$] (R = Ph, Tol; R′ = *t*Bu) as a means of obtaining bis-[μ-κP:η^2-($PPh_2C{\equiv}CR$)] bridged complexes. We found that the initial η^2-alkyne adducts, spectroscopically detected at low temperature, evolve through an unexpectedly easy sequential double insertion of both $PPh_2C{\equiv}CR$ into a Pt–C_6F_5 bond, which yields unusual μ-2,3-bis(diphenylphosphanyl)-1,3-butadien-1-yl complexes.

Synthesis of the precursor mononuclear complexes: Mononuclear bis(diphenylphosphane)alkyne complexes *cis*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CR)_2$] (R = Ph **2a**, *t*Bu **2b**, Tol **2c**) and mixed *cis*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(PPh_2C{\equiv}C$*t*Bu)] (R = Ph **4**, Tol **5**) are synthesized in a straightforward manner by displacing the tetrahydrothiophene ligands (THT) from *cis*-[$Pt(C_6F_5)_2(tht)_2$] or *cis*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}C$*t*Bu)(tht)], respectively, with the appropriate diphenylalkynylphosphane ligand. The analogous palladium complexes *cis*-[$Pd(C_6F_5)_2(PPh_2C{\equiv}CR)_2$] **3a–c** were prepared from $(NBu_4)_2[Pd(\mu\text{-}Br)(C_6F_5)_2]_2$ by cleavage of the bridges and displacement of the halide ligands with $PPh_2C{\equiv}CR$ (Scheme 2). All compounds are air-stable white solids with spectroscopic properties characteristic of a *cis* geometry and a P-coordination mode for the $PPh_2C{\equiv}CR$ ligands. Their IR spectra showed typical ν(C≡C) strong absorptions (one for **2a**,**c**, and **3a**,**c** derivatives and two for **2b**, **3b**, **4**, and **5** derivatives) in the 2170–2214 cm^{-1} region due to the P-coordinated alkynylphosphane ligands[13b] and the expected two bands (798–774 cm^{-1}) assigned to the X-sensitive mode of the C_6F_5 groups,[22] which are characteristic of the *cis*-$M(C_6F_5)_2$ moiety. A singlet phosphorus resonance (δ range −8.79 to +0.23) and especially the magnitude of $^1J(^{195}Pt,^{31}P)$ (2400–2426 Hz) in complexes **2** and **3** are consistent with a *cis* configuration of the ligands about the platinum center. The mixed derivatives **4** and **5** showed, as expected, two singlets in their $^{31}P\{^1H\}$ NMR spectra and two sets of C_6F_5 or C≡CR signals in their ^{19}F and ^1H NMR spectra in agreement with the presence of two different alkynylphosphane ligands. Finally, in accordance with a *cis* geometry for complexes **2** and **3**, the acetylene carbon resonances appear [C_α/C_β δ = 69.6–81.6/106.0–119.0] as the typical A part of a second-order AXX′ system (see Experimental Section for details) with *N* values $^1J(C,P)+{}^3J(C,P)$ (89.8–106.9 Hz) and $^2J(C,P)+{}^4J(C,P)$ (11.8–16 Hz), respectively, typical of this type of compound.[13b] However, in the mixed complexes **4** and **5**, the C_β resonances appear as doublets (δ = 118.2 **4**, 118.1 **5** *t*Bu; 107.4 **4**, 107.9 **5** R) and the C_α signals as doublets of doublets (δ 69.5 **4**, 69.6 **5** *t*Bu; 80.1 **4** 79.3 **5** R), respectively.

Single-crystal X-ray analyses of **2a–c** were performed in order to determine the relative orientation of the two acetylenic moieties in the complexes. Perspective views of the three complexes are shown in Figure 1, and selected bond lengths and angles are listed in Table 1. All complexes have square-planar geometry at the metal center with Pt–C(C_6F_5) and Pt–P distances within the normal ranges found for related complexes.[23] It has been previously noted[17b, 18a, b] that the coupling of two proximate acetylenic fragments can only be activated by heating or induced by the presence of metal centers if the separation between the α-carbon atoms is < 3.4 Å (twice the van der Waals radius of carbon). The close proximity of the α-carbon atoms of the phenyl or tolyl alkynyl groups is shown by the C(7)–C(7a) [3.20(2) Å **2a**] and C(13)–C(34) distances [3.34(2) Å **2c**], which are considerably less (**2a**) or slightly (**2c**) less than 3.4 Å (the distance between C≡C middle points: 3.423 Å **2a**, 3.538 Å **2c**). It should be noted that for complex **2a**, the small separation between the alkyne termini [3.20(2) Å] is in keeping with



Scheme 2. Synthesis of mononuclear complexes **2–5** (L = $PPh_2C{\equiv}CR$).

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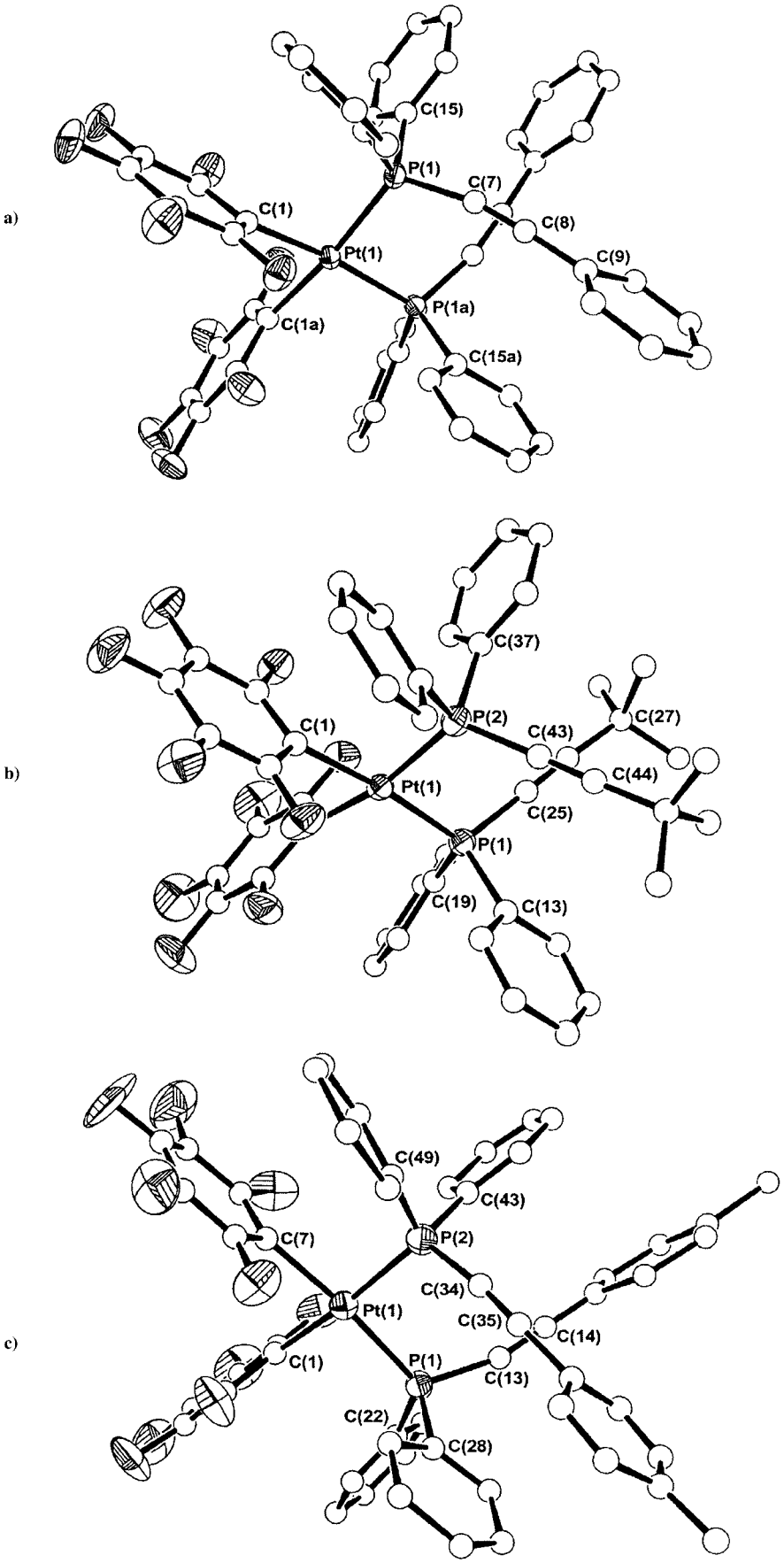


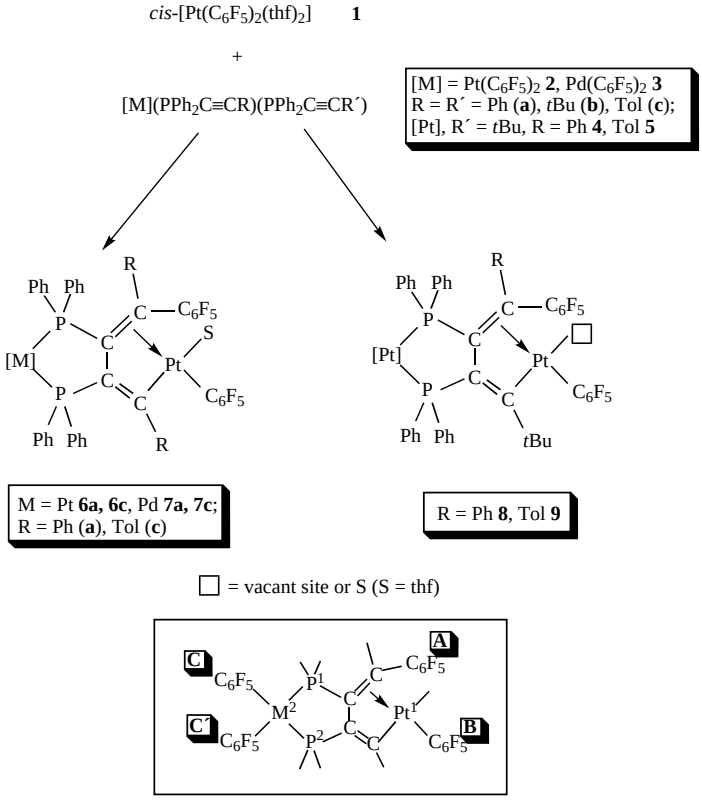
Figure 1. Perspective view of molecular structures of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CPh)_2]$. $0.5\,CCl_4$ (**2a**) (a, top); *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CtBu)_2]$. CH_2Cl_2 (**2b**) (b, middle); *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CTol)_2]$ (**2c**) (c, bottom).

the reported formation of the unsymmetrical diphosphane complex *cis*-$[Pt(C_6F_5)_2\{o\text{-}C_{16}H_{10}(PPh_2)_2\}]$ on heating.[17] In comparison, the corresponding distance in *cis*-$[PtCl_2(PPh_2C{\equiv}CPh)_2]$,[17] which also undergoes intramolecular coupling of the phosphanylacetylene ligands under relatively mild conditions, is 3.110(10) Å. The distance found for complex **2c** [3.34(2) Å] is longer than that found in *cis*-$[PtClMe(PPh_2C{\equiv}CPh)_2]$,[17b] [3.213(14) Å], which requires forcing conditions (melting of the solid sample) to achieve coupling. In contrast, the $PPh_2C{\equiv}CtBu$ ligands in complex **2b** have undergone a slight rotation away from one another, and thus they increase the separation between C(25) and C(43) atoms of the alkyne termini to 3.61(1) Å. In this case, the higher steric demand of the *t*Bu groups forces the separation between the C≡C middle point to a distance of 3.963 Å. Consequently, the torsional angles $C_\alpha{-}P(1){-}P(2){-}C_\alpha'$ [65.3(6)° **2a**, 68.9(6)° **2c**, 70.7(4)° **2b**] and the P–Pt–P′ angles [92.87(13)° **2a**, 93.32(7)° **2c**, 95.04(9)° **2b**] in the three complexes show an increase in the order *t*Bu > Tol > Ph, which is parallel to the increase of the distance between the C_α atoms. As expected, the distortion from the linearity of the alkynyl groups, which helps to keep the C_α atoms of both ligands in proximity, follows the order Ph > Tol(average) > *t*Bu(average) [P(1)–C(7)–C(8) 167.7(8)° **2a**; P(1)–C(13)–C(14) 165(3)°, P(2)–C(34)–C(35) 173(2)° **2c**; P(2)–C(43)–C(44) 175.9(8)° and P(1)–C(25)–C(26) 179.2(8)° **2b**].

Reactions of *cis*-$[M(C_6F_5)_2(PPh_2C{\equiv}CR)_2]$ and *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(PPh_2C{\equiv}CtBu)]$ with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ 1: As shown in Scheme 3, the (diphenylphosphanyl)alkyne *cis*-$[M(C_6F_5)_2(PPh_2C{\equiv}CR)(PPh_2C{\equiv}CR')]$ complexes (**2a**,**c**, **3a**,**c**) readily react with an equimolar amount of **1** in CH_2Cl_2 at temperatures between 0

Table 1. Selected bond lengths [Å] and angles [°] for *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)$_2$] (R = Ph **2a**·0.5 CCl_4, *t*Bu **2b**·CH_2Cl_2, and Tol **2c**).

	bond lengths			angles			torsion angle
	Pt–P	C≡C	C_α–C_α	P–C≡C	C≡C–C	P–Pt–P′	C_α–P–P′–C′$_\alpha$
2a·0.5 CCl_4	2.310(3)	1.200(11)	3.20(2)	167.7(8)	177.0(10)	92.87(13)	65.3(6)
2b·CH_2Cl_2	2.298(2)	1.176(10)	3.61(1)	179.2(8)	176.6(9)	95.04(9)	70.7(4)
	2.294(3)	1.182(10)		175.9(8)	178.4(9)		
2c	2.285(6)	1.18(4)	3.34(2)	165(3)	179(4)	93.32(7)	68.9(6)
	2.315(7)	1.20(3)		173(2)	176(3)		



Scheme 3. Synthesis of butadienyl bridging complexes. The notation used for inequivalent groups and metals is shown in the inset.

and +10 °C to give orange solutions, from which the double inserted products [Pt(C_6F_5)(S)μ-{C(R′)=C(PPh_2)-C(PPh_2)=C(R)(C_6F_5)}M(C_6F_5)$_2$] (R = R′ = Ph, Tol, M = Pt **6a**, **6c**, Pd **7a**, **7c**) are isolated in good (platinum) or moderate (palladium) yields as deep yellow solids. The *tert*-butyl derivatives (**2b**, **3b**) did not react with **1**, even under reflux conditions (CH_2Cl_2, 5 h for **2b** or 1 h for **3b**), perhaps for steric reasons. The lower η^2-bonding capability of $PPh_2C{\equiv}CtBu$ than $PPh_2C{\equiv}CPh$ groups in complexes *cis*-[M($C{=}CR')_2$($PPh_2C{\equiv}CR$)$_2$] (R = Ph or *t*Bu) has been previously observed.[13b] In contrast to this, the mixed mononuclear complexes *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}CtBu$)] (R = Ph **4**, Tol **5**) react cleanly with **1** to selectively form the corresponding double inserted complexes **8** (R = Ph) and **9** (R = Tol) as yellow solids and in high yields. It should be noted that at 25 °C in donor solvents (acetone or THF) neither the complexes **2a** or **2c**, nor the mixed derivatives **4** and **5** reacted with **1**. It is also noteworthy that all reactions are clean, no regioisomers are obtained, and the overall process is highly *regiospecific*, with the first insertion taking place selectively on the aryl acetylenic fragment for the mixed derivatives **4** and **5**, and *stereoselective* (*cis*,*cis* insertion).

The IR and ^{19}F NMR spectra of **6**–**9** confirm the presence of the C–C_6F_5 unit and the existence of four different types of C_6F_5 groups arising from an asymmetric structure (See Scheme 3 for notation). Thus, the IR spectra have absorptions characteristic of the C_6F_5 bonded to carbon[10a, b] (split bands at ≈1500 and 990 cm^{-1} are seen) and three absorptions corresponding to the νC_6F_5(X-sensitive) (range 820–777 cm^{-1}) concordant with an asymmetric structure. In all complexes the organic C–C_6F_5 group (ring **A**) is easily assigned, because the *ortho*- and *para*-fluorine resonances are up- and downfield shifted, respectively, and the separation between these signals is reduced to approximately $\delta = 30$. This ring (**A**) exhibits a typical pattern of five signals of equal intensity, and this indicates that, if any, very slow bond rotation takes place around the C–C_6F_5 bond on the NMR timescale (see below). In the palladium complexes (**7**), the C_6F_5 (**B**) group (assigned on the basis of the presence of platinum satellites) has the typical set of three resonances (2:1:2, AA′MXX′ spin system) of a freely rotating group, while the C_6F_5 ligands coordinated to the palladium center (type **C**,**C′**) produce the two expected different sets of resonances [AFMRX systems: 3*o*-F (1:2:1), 2*p*-F, 4*m*-F (1:1:1:1)] corresponding to rigid rings. In the platinum derivatives, the pattern for the C_6F_5 ring **B** also corresponds to a rigid ring as revealed by a ^{19}F-^{19}F COSY spectrum registered for complex **6a** at room temperature (See Figure 1S, Supporting information), which also confirms that the C_6F_5 ring **B** is indeed close to the organic ring (**A**) and that both *o*-fluorine signals of the C–C_6F_5 group (type **A**) are related to each other probably through slow rotation of this ring.[24] Examination of the ^{19}F NMR spectra of complexes **6** at different temperatures indicates the presence at low temperature (−50 °C) of at least three conformers in a ratio of 1:2:1; these are probably generated by different conformational modifications of the bis(diphenyl)butadienyl bridging ligand. Thus, as is clearly observed in the signals due to the organic fragment C–C_6F_5 group (**A**) (Figure 2), as the temperature is lowered both the *o*-fluorine and *p*-fluorine resonances broaden and split. In the low regime limit (−50 °C), one of the *o*-F_A is split into three signals [−127.0 (pst), −127.7 (m), −128.5 (m)] of relative intensities 2:1:1, and the other *o*-F_A into two [−129.5 (dm), −129.9 (dm)] of 2:2 intensities. The only *para*-F (C–C_6F_5 **A**) signal observed at room temperature is also split at −50 °C into three signals (2:1:1), which confirm the presence of three magnetically nonequivalent C_6F_5 organic rings.

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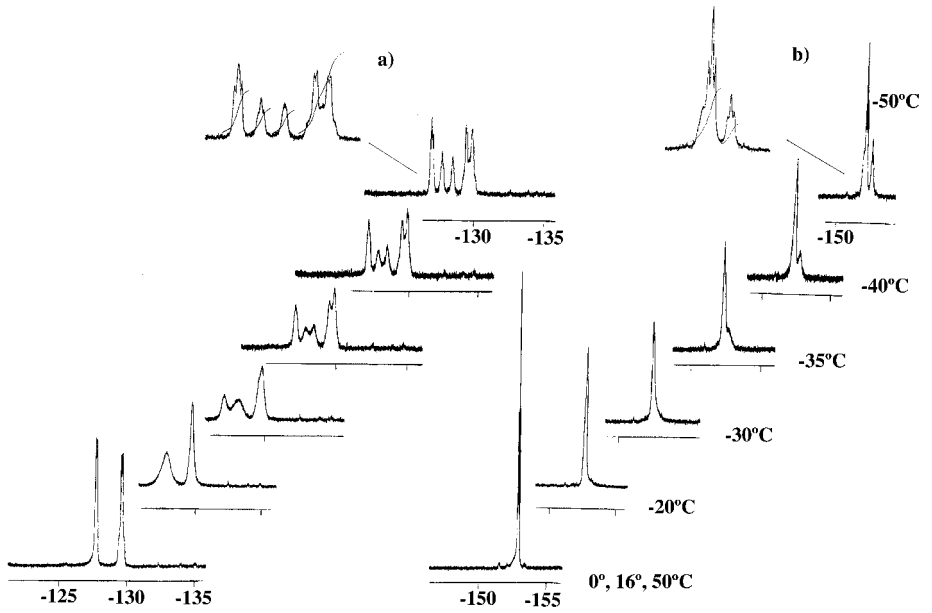

Figure 2. ^{19}F NMR spectra at different temperatures of complex **6c** in $CDCl_3$ (*ortho*-fluorine region (a), and *para*-fluorine region (b) of the C–C_6F_5 ring **A**).

All complexes (**6**–**9**) revealed two different phosphorus resonances, which are strongly deshielded (range $\delta = 24.81$–$40.0/34.2$–42.45), as expected for a rigid five-membered ring.[25] One of the signals (the upfield signal in complexes **6** and **7** or the downfield one in complexes **8** and **9**) appears as a broad doublet (**6**) or singlet (**7**–**9**) flanked by platinum satellites due to long-range (^3J(Pt,P) 270–379 Hz **6**–**9**) and short-range (^1J(Pt,P) 2284–2308 Hz **6**, **8**, **9**) coupling to ^{195}Pt, which is therefore, assigned to phosphorus P[2] (mutually *trans* to the platinum center Pt[1], see Scheme 3 for notation). The other resonance also appears as a broad doublet or singlet with the expected platinum satellites in complexes **6**, **8**, and **9** (range $\delta = 34.2$–42.45). The broadness of these signals is probably due to long-range unresolved coupling to the *o*-fluorine atoms of the C_6F_5 groups, which are located mutually *trans* to both phosphorus atoms. The low-temperature ($-50\,^\circ C$) $^{13}C\{^1H\}$ NMR spectra of the most soluble and stable complex **6c** have two doublets of multiplets at $\delta = 97.5$ and 71.5 (J(C,P) = 114.2 and 48.11 Hz, respectively) characteristic of sp^2 carbon atoms bound to phosphorus. The presence of solvent S in the final complexes (see Scheme 3) is inferred from their ^1H NMR spectra. Complexes **6** and **7** have signals due to coordinated THF [≈ 3.4 (s, OCH_2), ≈ 1.5 (s; CH_2)] and H_2O [≈ 1.8 (s)], which disappear or shift after the addition of D_2O or/and free THF. Careful examination of proton spectra of freshly precipitated samples of complexes **8** and **9** reveals only small amounts of THF (0.4 and 0.35 moles by mole of **8** and **9**, respectively vs. ≈ 0.6 mole observed in **6** and **7**). Even crystals of **9** obtained by slow diffusion of *n*-hexane in a solution in CH_2Cl_2 had traces of THF (0.05 mole by mole of product).

Complexes **6a** and **6c** crystallize easily in different solvent systems, but none of the crystals obtained were suitable for X-ray crystallography. An X-ray crystallographic investigation of **7a** was attempted, and, although the study confirmed the connectivity shown in Scheme 3, a high degree of disorder associated with the solvent coordination site at Pt (partial occupancy for THF and H_2O) prevented satisfactory refinement. Crystals of the mixed derivative **9** suitable for an X-ray diffraction study were obtained by diffusion at low temperature ($-30\,^\circ C$ *n*-hexane/CH_2Cl_2). The molecular structure is depicted in Figure 3, and important bond lengths and angles are indicated in Table 2. The structure confirms that the two acetylenic fragments of **5** have condensed with one of the C_6F_5 groups of **1** to form the new 2,3-bis(diphenylphosphanyl)butadienyl ligand that bridges the two platinum centers. A few similar $\eta^3(\kappa C^1{:}\eta^2 C^{3,4})$ butadienyl backbones have been previously described as having been

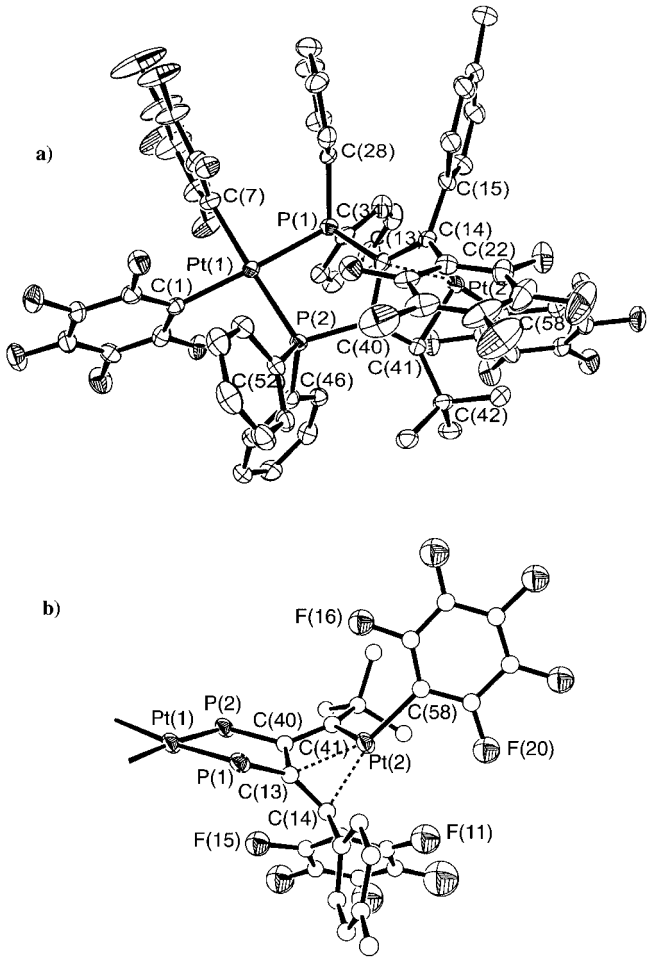

Figure 3. View of the molecular structure of complex **9**, showing the atom-numbering scheme (a, top); schematic view of the butadienyldiphosphane bridging ligand around the unsaturated platinum Pt(2) (b, bottom).

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Table 2. Selected bond lengths [Å] and angles [°] for [Pt(C_6F_5)μ-{C(*t*Bu)=C(PPh_2)C(PPh_2)=C(Tol)(C_6F_5)}Pt(C_6F_5)$_2$] (**9**).

Pt(1)–C(1)	2.089(5)	P(2)–C(40)	1.852(5)
Pt(1)–C(7)	2.079(5)	P(1)–C(13)	1.854(5)
Pt(1)–P(2)	2.2932(13)	C(13)–C(14)	1.453(7)
Pt(1)–P(1)	2.2718(13)	C(13)–C(40)	1.514(7)
Pt(2)–C(41)	1.986(5)	C(14)–C(15)	1.499(6)
Pt(2)–C(58)	2.041(5)	C(14)–C(22)	1.518(7)
Pt(2)–C(13)	2.153(4)	C(40)–C(41)	1.364(6)
Pt(2)–C(14)	2.170(4)	C(41)–C(42)	1.522(7)
Pt(2)–C(40)	2.576(5)		
C(7)–Pt(1)–C(1)	85.7(2)	C(40)–C(13)–P(1)	112.8(3)
C(7)–Pt(1)–P(1)	89.50(14)	C(15)–C(14)–C(22)	114.4(4)
C(1)–Pt(1)–P(2)	96.12(14)	C(13)–C(14)–Pt(2)	69.7(2)
P(1)–Pt(1)–P(2)	89.38(5)	C(13)–C(14)–C(22)	120.2(4)
C(41)–Pt(2)–C(58)	105.71(19)	C(13)–C(14)–C(15)	122.7(4)
C(58)–Pt(2)–C(14)	162.00(19)	C(41)–C(40)–C(13)	105.3(4)
C(58)–Pt(2)–C(13)	158.32(19)	C(41)–C(40)–P(2)	135.3(4)
C(40)–P(2)–Pt(1)	105.56(16)	C(13)–C(40)–P(2)	117.2(3)
C(13)–P(1)–Pt(1)	106.11(16)	C(40)–C(41)–C(42)	137.1(4)
C(14)–C(13)–C(40)	117.8(4)	C(40)–C(41)–Pt(2)	98.9(3)
C(14)–C(13)–P(1)	128.3(4)	C(42)–C(41)–Pt(2)	123.4(3)

formed by sequential insertion of two alkynes into Ru–X (X = H, Me),[26a] Pd–X (X = Cl, Ph),[26b, c] or into cyclometallated Pd^{II} or Ni^{II} complexes.[4] An unexpected structural feature of this complex is the fact that the new unsymmetrical butadienyldiphosphane generated ligand stabilizes an unusual coordinatively unsaturated T-shaped 3-coordinated platinum(II) center.[27] As can be observed, the novel ligand displays a κ^2PP':3,4-η-κC^1 bonding mode and acts as a vinyl–olefin (σ-η^2) ligand to the Pt(2)(C_6F_5) unit. In contrast to Pt(1), which exhibits a normal square-planar geometry, the Pt(2) center displays a slightly distorted T-shaped coordination environment formed by the C_{ipso} of the C_6F_5 group and the η^3-butadienyl backbone, which is σ-bonded through C(41) and η^2-bonded through the C(13)–C(14) double bond (see Figure 3b). Three-coordinated 14-electron species (d^8 ML_3, M = Pd, Pt) have been known to offer a low-energy reaction pathway for many fundamental organometallic reactions[28] including insertion processes into Pt–X bonds,[29] symmetrization,[30] atropisomerization,[31] and substitution processes,[32] thermal decomposition of mono- and dialkyl compounds,[33] or protonolysis.[34] Oxidative addition and reductive elimination of C–H bonds by d^8 ML_4 species also require an unsaturated 3-coordinated complex.[33f, 35] Strong support of the existence of these intermediate species comes mostly from kinetic studies, and their configurational stability has been supported by MO calculations.[29a, 36] Ground-state stabilization of some of these 14-electron species by a β-agostic interaction has been also reported,[37] but, to the best of our knowledge so far not a single example has been characterized by X-ray crystallography. In this context, the unusual stabilization of the Pt(C_6F_5) unit by the σ,η^2-butadienyl backbone provides very good additional support so that such species could be stable under adequate electronic and steric conditions.

In agreement with a T-shaped geometry around Pt(2), the angles C(58)–Pt(2)–C(14,13) [162.00(19)°, 158.32(19)°] and, particularly, the angle formed by C(58)–Pt(2) and the midpoint of C(13)–C(14) (176.58°) are almost linear. The *ortho*-F-platinum separations to both C_6F_5 rings [Pt(2)–F(16,20) 3.209(3), 3.207(3) Å; Pt(2)–F(11,15) 3.274(3), 4.560(3) Å] are out of the sum of the van der Waals radii (3.19 Å) excluding any bonding interaction. The vacant coordination site mutually *trans* to the vinyl carbon C(41) is also reflected in the Pt(2)–C(41) bond length [1.986(5) Å], which is notably shorter than the corresponding one in **12a** [2.022(9) Å][12] and also in **14c** [2.064(3) Å] (see below). This value [1.986(5) Å] is also short compared with those observed in other Pt–C(vinyl) bonds[38] (*trans*-[PtP(Cy)$_3$(H)C=(CHOH)-C(O)NHR] 2.11(2) Å,[38a] *cis*-[Pt(CH=CHSiPh_3)SiPh_3-($PPhMe_2$)$_2$] 2.043(6) Å,[29b] or *trans*-(*E*)-[PtBr(C(Ph)=C(Ph)-SiMe_3)(PEt_3)$_2$] 2.053(9) Å[38b]). Although the η^2-olefin interaction seems also to be stronger than that observed for the related complex **12a** [Pt(2)–C(13),C(14) 2.153(4), 2.170(4) Å in **9** vs. Pt(1)–C(13),C(14) 2.396(9), 2.322(9) Å in **12a**[12]], the bond lengths fall within the usual range found in η^2-coordinated olefins.[39] In contrast to the usual perpendicular orientation of the olefins to the platinum coordination plane, the dihedral angle between Pt(2)–C(13)–C(14) and Pt(2)–C(41)–C(58) is only 69.73° probably imposed by the steric constraints of the butadienyl backbone. The interatomic distances [C(40)–C(41) 1.364(6), C(13)–C(40) 1.514(7), C(13)–C(14) 1.453(7) Å] and angles about the butadienyl chain [torsional angle C(41)–C(40)–C(13)–C(14) 57.2(5)°] are within the expected range.[4] It is worth noting that the C_6F_5 group is located *gem* to the tolyl group, and this indicates that the reaction is *regioselective* with the first insertion taking place with the $PPh_2C{\equiv}CTol$ ligand. The lack of reactivity of the sterically bulky alkynyldiphenylphosphanes $PPh_2C{\equiv}CR$ (R = *t*Bu, $SiMe_3$) in double insertion reaction processes in Ni–C bonds of benzyne complexes [Ni{(1,2-η)-4,5-$X_2C_6H_2$}(PEt_3)$_2$] (X = H, F) has been previously observed.[14b] In the case of the mixed complexes **4** and **5**, the regioselectivity observed is probably governed by either electronic or steric demands of the alkyne termini. It could be related to an initial favored *cis* attack of the nucleophilic C_6F_5 group on the less-hindered and more polarized ($M{-}PC_\alpha^{\delta-}{\equiv}C_\beta^{\delta+}R$)[40] β-carbon of the alkyne. Another feature of the butadienyldiphosphane ligand, which merits comment, is the fact that in the final complex the PPh_2 groups are mutually *cis* not only in the vinyl unit but also in the η^2-alkene fragment, and this indicates that an overall *cis*,*cis* di-insertion process has taken place. As was commented above, there have been several studies on the insertion of alkynes into cyclometallated Ni^{II} or Pd^{II} complexes. For these systems, a *trans* arrangement about the η^2-alkene bond is usually displayed in the final butadienyl backbones [Pd-*cis*-CR=CR-*trans*-CR=CR(Ar)], which requires isomerization of the first inserted alkyne.[4d] However, *cis*,*cis* di-inserted products, in particular those leading to η^1-butadienyl systems,[3b] have also been observed.[4l, 26b, c] In complexes **6**–**9**, the final stereoselectivity could be attributed to the simultaneous coordination of both phosphorus atoms to the M(C_6F_5)$_2$ fragment, which prevents the usual *cis*,*trans* isomerization.[4e]

NMR spectroscopy follow-up of the reactions of **2a**,**c** and **3a**,**c** with **1** (see Experimental Section) leads us to suggest a stepwise pathway as the most plausible mechanism for the insertion of both *P*–$PPh_2C{\equiv}CR$ ligands into the Pt^{II}–C_6F_5

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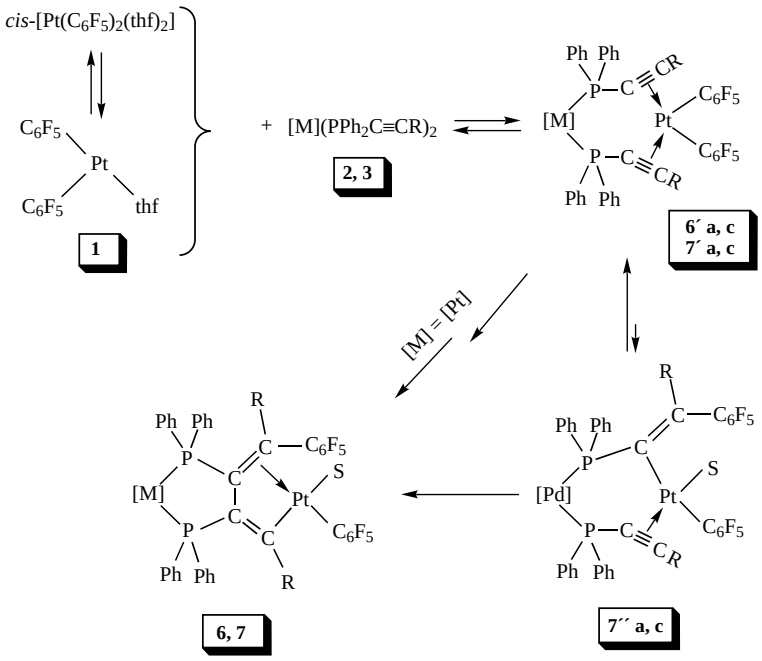
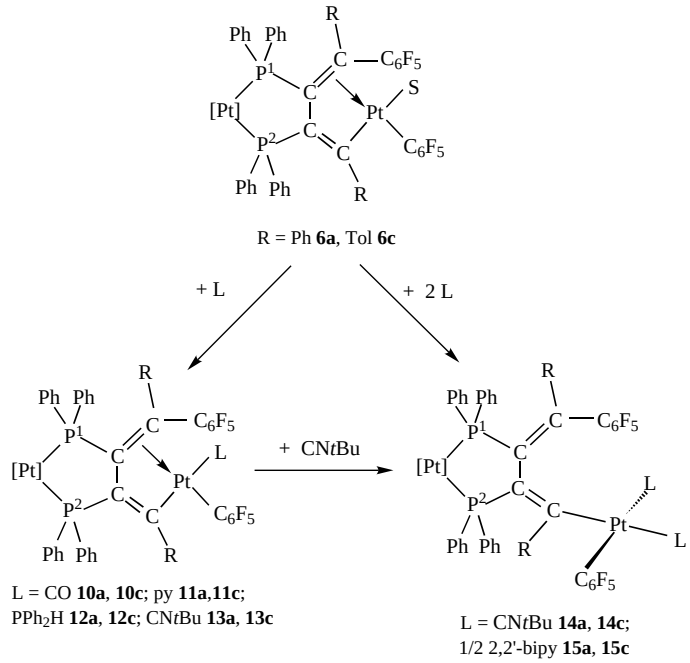
bond, which is outlined in Scheme 4. It should be noted that when the reactions are monitored at room temperature no intermediates are detected. However, monitoring the reactions at low temperature (−50 °C) indicates, in all cases, the formation of the expected η^2-bis(alkyne) adducts, which are in equilibrium with the starting complexes. It was clearly observed that the alkynyl substituent affects the equilibrium between the starting complex and the bis(η^2-alkyne) adduct, and the equilibrium was displaced to the latter to a much smaller degree for the tolyl derivatives **2c** and **3c**. Although the initial adducts $[(C_6F_5)_2M\{\mu\text{-}\kappa PP\text{:}\eta^2(PPh_2C{\equiv}CR)_2\}Pt(C_6F_5)_2]$ **6′**, **7′** were not isolated, they can be unambiguously characterized in solution by spectroscopic means. In particular, the presence of one downfield phosphorus resonance [δ(P) 2.15, ^1J(Pt,P) = 2341 Hz, **6′a** (Pt, Ph); 2.66, ^1J(Pt,P) = 2380 Hz **6′c** (Pt, Tol); 9.27 **7′a** (R = Ph); 9.55 **7′c** (R = Tol)], reflecting the deshielding effect of phosphorus atoms due to the bridging mode of $PPh_2C{\equiv}CR$ ligands[13b] and only one set of C_6F_5 signals (see Experimental Section for details) agrees with the formulation of **6′** and **7′** shown in Scheme 4. In the formation of the final diplatinum complexes **6a** and **6c** by raising the temperature (to −10 °C for **6a** or 20 °C for **6c**), no other intermediate species was detected by NMR spectroscopy, but we noted that the formation of the final di-inserted phenyl derivative **6a** is clearly enhanced and occurs at lower temperatures (≈ −20 °C for **6a** vs. ≈0 °C for **6c**). In both cases, the formation of **6** was only accompanied by the gradual and simultaneous disappearance of **6′** and **2**. Under these conditions, the subsequent insertion processes are believed to occur quickly and easily. The formal insertion produces an unsaturated 14-electron platinum fragment, which occasionally forms a more stable 16-electron fragment by a coordination of a donor molecule (THF, H_2O). The most definitive evidence for the proposed stepwise pathway came from the detection of the formation and disappearance of a new intermediate, in low proportion, in the Pd–Pt systems (**3**/**1**). At very low temperature (≈ −50 °C) in the **3a**/**1** system or higher (≈ −20 °C) in the **3c**/**1** system, the presence of two additional and somewhat broad phosphorus resonances [δ(P) 11.16, −3.29 **7″a**; 10.89, −3.29 **7″c**] and, particularly, the ^{19}F resonances for one C_6F_5 group at chemical shifts typical of a C–C_6F_5 unit[41] would suggest an asymmetric monoinserted alkyne–vinyl species in the course of the reaction. Raising the temperature results in the formation of **7**, which is observed again at lower temperatures in the phenyl derivative (**7a** ≈ −10 °C vs. **7c** ≈5 °C). The formation of **7a** occurred at −10 °C, and at this temperature the precursor **3a** and the intermediate species **7′a** and **7″a** gradually disappear (with a nearly constant ratio), and the signals due to **7a** grow concomitantly. At low temperature, the formation of **7a** is slow and requires about 12 h to complete it. In the tolyl system (**3c**/**1**) by raising the temperature from 5 to 20 °C, the amount of final complex **7c** gradually grows, whilst **3a** and **7′c** and also **7″c** decrease and disappear at this temperature. The fact that the first insertion process can not be observed in the platinum derivatives and that the η^2-bis(alkyne) adducts **6′** and **7′** and precursors remain at intermediate temperatures with the final di-inserted products suggest that the alkyne insertion steps are slow in relation to the formation of the initial η^2-bis(alkyne) products. In any case, it is remarkable that the insertion into the robust Pt–C_6F_5 takes place under relatively very mild conditions. In this context, the observed lack of reactivity of the bulky *tert*-butylethynyl derivatives **2b** could be attributed to their inability to form the initial bis(η^2-alkyne) adducts. In fact, as we noted above, the lower η^2-bonding capability of $PPh_2C{\equiv}CtBu$ with respect to that of the $PPh_2C{\equiv}CPh$ ligands has been previously noted[13a, b] and could be attributed mainly to steric reasons. Along the same lines, no evidence of formation of **6**–**9** is found in donor solvents such as acetone. This fact also shows the importance of having access to a very electrophilic 14-electron "$[Pt(C_6F_5)_2(thf)]$" type intermediate species, which is easier to generate in CH_2Cl_2 than in acetone and which should be captured by the precursors **2**–**5** to form the initial 1:1 bis(η^2-alkyne) adduct. This "*cis*-like", unsaturated solvento species is analogous to those previously proposed by R. Romeo, et al.[32b] "*cis*-$PtMe_2(Me_2SO)$" for the catalyzed *cis*–*trans* isomerization of *cis*-$[Pt(PEt_3)_2$-(neopentyl)Cl] by small amounts of *cis*-$[PtMe_2(Me_2SO)_2]$, or by Scott and Puddephatt "*cis*-$PtMe_2(SMe_2)$" for the chloro exchange reaction between *cis*-$[PtMe_2(SMe_2)_2]$ and *trans*-$[PtCl_2(SMe_2)_2]$ to yield *trans*-$[PtClMe(SMe_2)_2]$.[30]



Scheme 4. Mechanism of the reaction of complexes **2** and **3** with **1**.

Synthesis of $[Pt(C_6F_5)(L)\mu\text{-}\{C(R)=C(PPh_2)C(PPh_2)=C(R)\text{-}(C_6F_5)\}Pt(C_6F_5)_2]$ (10–15): In order to know the stability of the new bis(diphenylphosphanyl)-1,3-butadien-1-yl bridging ligand we considered it would be of interest to examine the reactivity of diplatinum complexes **6** toward different neutral ligands. The results of these reactions are summarized in Scheme 5. Bubbling CO through solutions of **6** in CH_2Cl_2 for



Scheme 5. Reactivity of **6** toward donor ligands.

5 min resulted in a clean and quantitative formation of related **10a** and **10c** complexes, which are isolated as yellow microcrystalline solids (72% **10a**, 80% **10c**). Related binuclear derivatives $[Pt(C_6F_5)(L)\mu\text{-}\{C(R)=C(PPh_2)C(PPh_2)=C(R)\text{-}(C_6F_5)\}Pt(C_6F_5)_2]$ (L = py **11**, PPh_2H **12**, CN*t*Bu **13**) are obtained in a similar way as air-stable yellow (**13**) or orange (**11**, **12**) microcrystalline solids by treatment of **6** with stoichiometric amounts of the corresponding ligand. It should be noted that the reactions with CN*t*Bu were carried out using a diluted solution ($\approx$0.044 N) of CN*t*Bu in diethyl ether in order to minimize the formation of the corresponding 1:2 adducts **14**, which are formed by displacement of the olefinic function. As expected, treatment of **6** with excess of CN*t*Bu (1:2 molar ratio) gives **14** as lemon yellow solids. The olefinic function is also displaced by a bidentate N–N ligand such as 2,2′-bipy to generate the corresponding stable $\mu\text{-}\kappa^2PP':\eta^1$-2,3-bis(diphenylphosphanyl)butadienyl diplatinum complexes **15**. η^1-Butadienyl backbones are rare but have been obtained previously by the insertion of two alkynes into M–X bonds[3b] or by selective addition of M–H bonds to the carbon–carbon triple bond of enynes.[42]

All complexes have been characterized by elemental analysis, mass spectrometry, IR and NMR (^{1}H, ^{19}F, ^{31}P{^{1}H}) spectroscopy and, in the case of **12a** and **14**, their structures have been confirmed by X-ray analyses. The ^{31}P{^{1}H} NMR spectra exhibit, both at room and low (–50 °C) temperature, two deshielded and well-separated signals attributed to the phosphorus atoms of the butadienyl ligand and, in the case of **12**, an additional low-frequency resonance (δ = 12.50 (dd) **12a**, **12c**) due to PPh_2H ligands. The most deshielded resonance (P^1 δ = 29.07, –38.11), flanked only by a set of platinum satellites, is attributed to phosphorus P^1 bonded to the olefin fragment and the other signal (P^2 δ = 22.57–28.55), which is flanked by two sets of platinum satellites [$^1J(Pt^2,P^2)$ and $^3J(Pt^1,P^2)$], to P^2 (bonded to the vinyl fragment). The ^{1}H NMR spectra confirm the asymmetry of the butadienyl backbone (two different methyl resonances for tolyl derivatives) and the presence of the incoming ligand. Thus, the *tert*-butylisocyanide derivatives exhibit one (**13**) or two (**14**) singlets confirming the coordination of one or two non-equivalent isocyanide ligands, respectively, and the terminal P–H proton in complexes **12** gives rise to a broad doublet (^1J(P,H) = 373 Hz) of doublets ($^{4,5}J$(P,H) = 5.1 Hz **12a**, 4.8 Hz **12c**). Although ^{19}F NMR spectroscopy revealed the presence of four different rigid C_6F_5 rings in all complexes, the different connectivity of the butadienyl backbone in the η^1-bonded derivatives **14** and **15** is particularly reflected in the *ortho*-fluorine resonances of rings **A** (C–C_6F_5) and **B** (*cis* to the vinyl fragment). One of the *o*-F_B is strongly shifted downfield and exhibits, as confirmed by a ^{19}F-^{19}F COSY spectrum of **14c** at low temperature (–50 °C, Figure 4a), a strong scalar coupling with the highest deshielded *o*-F_A resonance suggesting, in agreement with the solid-state structure of **14c**, that these rings are very close in the space. For complexes **14**, these two signals appear clearly at low temperature as *dd* due to a F–F coupling between different rings of approximately 50 Hz (54 Hz **14a**; 53 Hz **14c**) and a typical ^3J(*o*-F,*m*-F) of 20–28 Hz. Scalar couplings through the space between *ortho*-fluorine atoms of two mutually *cis* perfluoro rings have been previously noted,[24] and, along the same lines, a strong interaction between two *o*-F of both mutually *cis* rings **C** is also observed in complex **14c**. In complexes **14** (see Figure 4b), the *ortho*-fluorine resonances (and also the two *m*-F) broaden as the temperature is raised and finally collapse into a broad singlet (δ = –110) at the highest accessible temperature (ca. +50 °C) with a value of $\Delta G^{\neq}$ ($\Delta G^{\neq}_{323}$ = 56.2 kJ mol^{-1} **14c**) for the rotation of this ring, which is comparable to those observed in other pentafluorophenyl platinum complexes.[13b, 43]

The molecular structure of complexes **12a** and **14** have been confirmed by X-ray crystallography. Structural details for **12a** were given in the preliminary communication.[12] The structures of **14a** and **14c** are essentially identical, and therefore the geometrical details of **14c** only are included and commented on (Figure 5 and Table 3). As can be observed, the new ligand now acts as a five-electron $\mu\text{-}1\kappa PP':2\kappa C^1$ vinyl diphosphane bridging ligand [Pt(1)–P(1,2) 2.2844(7), 2.2743(7) Å; Pt(2)–C(53) 2.064(3) Å]. The absence of chelation reduces the strain on the butadienyl backbone, which is particularly reflected by the internal angles at C_α and C_β [C(52)–C(53)–Pt(2) 129.9(2)°, C(53)–C(52)–C(37) 125.3(3)° in **14c** vs. C(40)–C(41)–Pt(2) 98.9(3)°, C(41)–C(40)–C(13) 105.3(4)° in **9** and C(39)–C(40)–Pt(1) 101.0(7)°, C(40)–C(39)–C(13) 111.1(9)° in **12a**]. The C(38)–C(37) [1.362(4) Å] and C(52)–C(53) [1.363(4) Å] bond

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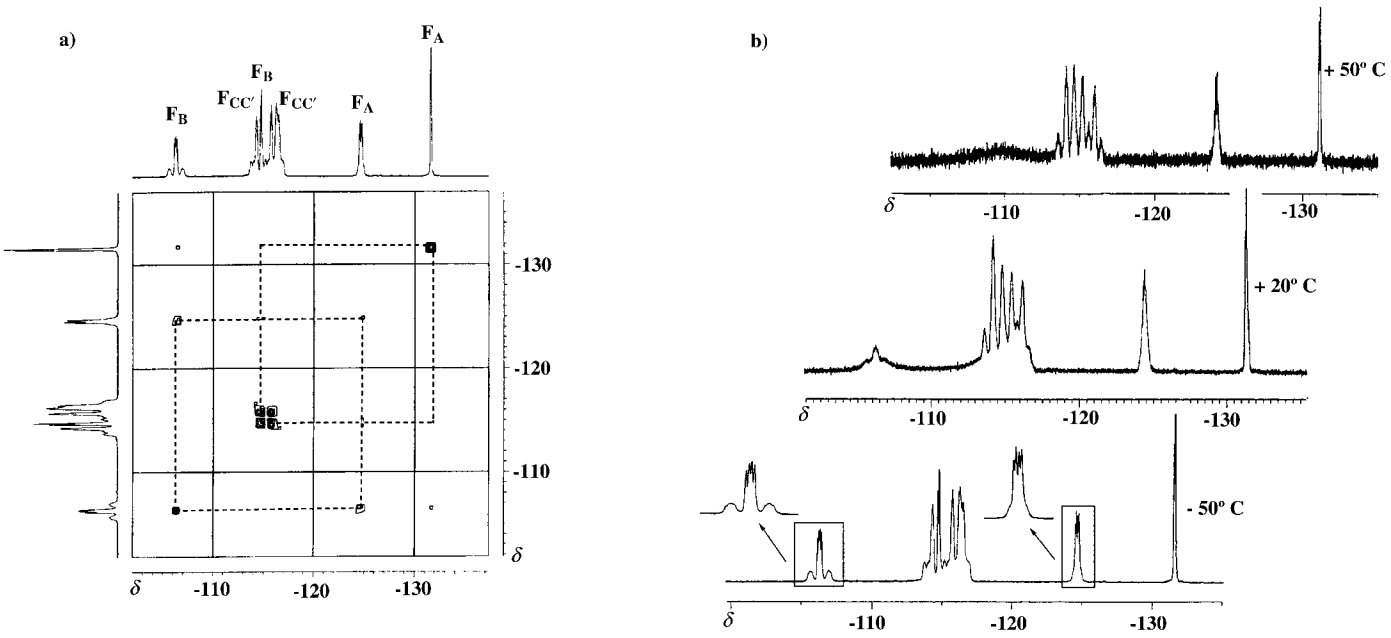


Figure 4. $^{19}F-^{19}F$ COSY spectrum of complex **14c** in $CDCl_3$ at $-50\,^{\circ}C$ (a); ^{19}F NMR spectra of complex **14c** in $CDCl_3$ at different temperatures (*o*-fluorine region) (b).

lengths are identical and in the range of double $Csp^2{=}Csp^2$ bonds, while the C(37)–C(52) length [1.511(4) Å] is typical of single $Csp^2{-}Csp^2$ bonds.[44] The dihedral angle between the unsaturated fragment C(53)–C(52)–C(37) and C(38) [torsion angle (46.4(4)°)] and the Pt(2) coordination plane is 59.33°. Finally, the two CN*t*Bu ligands remain linear [169.1(3)–175.0(3)°] and are in a *cis* position, and this confirms that the displacement of the η^2-olefin bond in the 1:1 adducts **13** has taken place with stereoretention.

Reaction in solution of $[Pt(C_6F_5)(S)\mu$-$\{C(R){=}C(PPh_2)$-$C(PPh_2){=}C(R)(C_6F_5)\}M(C_6F_5)_2]$ (M = Pt 6, M = Pd 7): Complexes **6** and **7** are stable in the solid state, for at least several weeks if stored in a freezer, but they are unstable in solution,

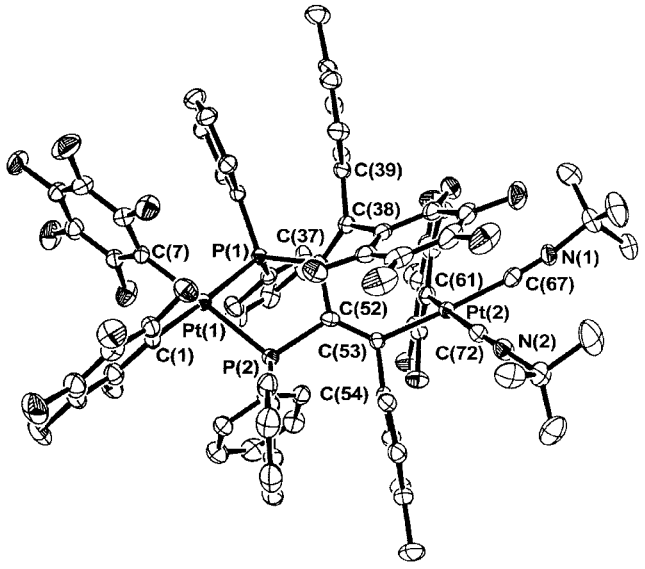


Figure 5. Molecular structure of **14c**.

Table 3. Selected bond lengths [Å] and angles [°] for *cis*,*cis*-$[Pt(C_6F_5)(CN\mathit{t}Bu)_2\mu$-$\{\kappa C^1{:}\kappa PP'$–C(Tol)=C($PPh_2$)C($PPh_2$)=C(Tol)-$(C_6F_5)\}Pt(C_6F_5)_2]$ (**14c**).

Pt(1)–C(1)	2.074(3)	P(2)–C(25)	1.826(3)
Pt(1)–C(7)	2.082(3)	P(2)–C(52)	1.865(3)
Pt(1)–P(2)	2.2743(7)	N(1)–C(67)	1.141(4)
Pt(1)–P(1)	2.2844(7)	N(1)–C(68)	1.464(4)
Pt(2)–C(72)	1.986(3)	N(2)–C(72)	1.133(4)
Pt(2)–C(67)	1.988(3)	N(2)–C(73)	1.469(4)
Pt(2)–C(61)	2.063(3)	C(38)–C(37)	1.362(4)
Pt(2)–C(53)	2.064(3)	C(38)–C(39)	1.482(4)
P(1)–C(13)	1.816(3)	C(38)–C(46)	1.506(4)
P(1)–C(19)	1.820(3)	C(37)–C(52)	1.511(4)
P(1)–C(37)	1.863(3)	C(52)–C(53)	1.363(4)
P(2)–C(31)	1.822(3)	C(53)–C(54)	1.508(4)
C(1)–Pt(1)–C(7)	84.58(11)	C(37)–C(38)–C(46)	121.7(3)
C(1)–Pt(1)–P(2)	98.01(8)	C(39)–C(38)–C(46)	110.9(2)
C(7)–Pt(1)–P(1)	95.41(8)	C(38)–C(37)–C(52)	123.2(3)
P(2)–Pt(1)–P(1)	82.76(3)	C(38)–C(37)–P(1)	124.8(2)
C(72)–Pt(2)–C(67)	86.84(12)	C(52)–C(37)–P(1)	110.7(2)
C(67)–Pt(2)–C(61)	87.25(12)	C(53)–C(52)–C(37)	125.3(3)
C(72)–Pt(2)–C(53)	91.18(11)	C(53)–C(52)–P(2)	122.2(2)
C(61)–Pt(2)–C(53)	95.32(11)	C(37)–C(52)–P(2)	112.33(19)
C(37)–P(1)–Pt(1)	102.24(9)	C(52)–C(53)–C(54)	119.8(2)
C(52)–P(2)–Pt(1)	108.09(9)	C(52)–C(53)–Pt(2)	129.9(2)
C(67)–N(1)–C(68)	173.0(3)	C(54)–C(53)–Pt(2)	109.86(17)
C(72)–N(2)–C(73)	175.0(3)	N(1)–C(67)–Pt(2)	172.0(3)
C(37)–C(38)–C(39)	127.1(3)	N(2)–C(72)–Pt(2)	169.1(3)

and these give rise to black solutions over a period of approximately four hours (M = Pt) or two hours (M = Pd) at room temperature. The resulting products were similar in all cases; here we only describe the studies carried out with complex **6a**, and the rest are detailed in the Experimental Section. Analyses of the black solutions obtained for **6a** showed the presence of two novel complexes **16a** and **17a** together with unchanged **6a** (Scheme 6); the relative amounts depended on the solvent and the time employed. For example, after 48 h in diethyl ether, a mixture of **6a**/**16a**/**17a** in a molar

ratio 0.72:0.7:1 was obtained, while in THF, only complex **17a** was observed. Although the mechanism by which both complexes are formed is unknown, we believe that the prolonged presence of light induces either the fast transformation of **16a** into **17a** or its decomposition. Thus, we have observed that while the absence of light increases the proportion of isomer **16a** in the final mixtures, in THF and under prolonged photolysis (45 min), the mononuclear derivative **17a** is the only final characterizable species, and only traces of **16a** were detected at the beginning of the irradiation.

A mixture of orange and white crystals of **16a** and **17a**, respectively, was obtained by slow diffusion of *n*-hexane at room temperature into a solution of **6a** in diethyl ether in the presence of light. These crystals were separated by hand and were suitable for spectroscopic characterization and for X-ray diffraction. Spectroscopic data for **16a** are quite similar to those of **6a**, and these suggest that both complexes are isomers. Thus, two different ^{31}P resonances are seen with an identical pattern [24.00 (br) $^1J(Pt,P) = 2278$ Hz, $^3J(Pt,P) \approx 320$ Hz; 36.33 (br) $^1J(Pt,P)$ 2159 Hz **16a** vs. 24.81 (d) $^1J(Pt,P) = 2284$ Hz, $^3J(Pt,P) = 276$ Hz; 36.03 (d) $^1J(Pt,P) = 2251$ Hz, $J(P,P) \approx 7$ Hz in **6a**], and ^{19}F spectroscopy clearly confirms not only the presence of a C–C_6F_5 but also the existence again of four different types of C_6F_5 moieties. The most remarkable difference is the unusual upfield shift found for the two *ortho*-fluorine resonances of the C–C_6F_5 unit [−132.4 (d), −135.35 (d) in **16a** vs. −128.0, −129.5 (d) **6a**], and this suggests a change in their electronic environment. The spectroscopic data for **17a** are clearly different and they point to a product of a different nature. In particular, **17a** exhibits two strongly deshielded phosphorus resonances ($\delta =$ 46.57, 43.83) with platinum coupling constants comparable with those of **6a** and **16a**. Its ^{19}F NMR spectrum clearly establishes the existence of only three different sets of resonances (each with an intensity ratio 2*o*-F:1*p*-F:2*m*-F) revealing the presence of only three types of C_6F_5 groups with one of them arising from a C–C_6F_5 organic entity [$\delta =$ −133.75 (2*o*-F), −151.98 (t, *p*-F), −160.9 (m; 2*m*-F)]. The geometry of both compounds has been elucidated by crystal structure analyses (Figure 6), but selected interatomic distances and angles are only given for **16a** (Table 4). For

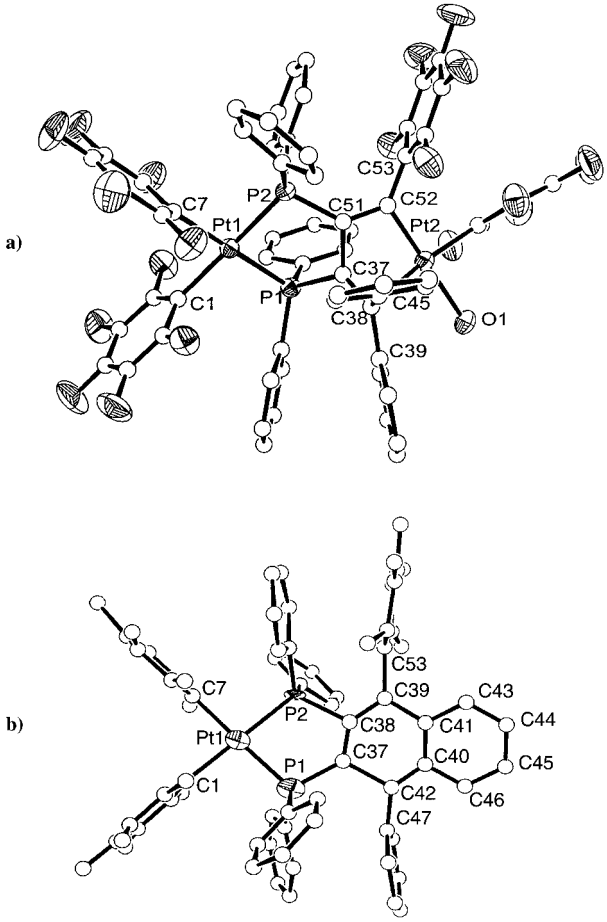
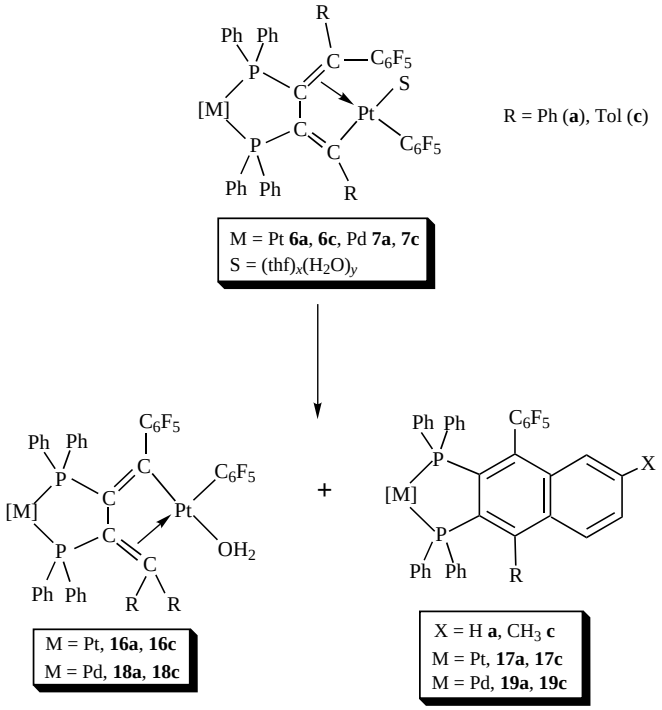


Figure 6. A view of the molecular structure of **16a** (a, top); schematic view of the preliminary X-ray diffraction study of **17a** showing the connectivity of the atoms (b, bottom).

Table 4. Selected bond lengths [Å] and angles [°] for [$Pt(C_6F_5)(H_2O)$-μ-{$C(C_6F_5)$=$C(PPh_2)C(PPh_2)$=$C(Ph)_2$}$Pt(C_6F_5)_2$] (**16a**).

Pt(1)–C(7)	2.061(5)	Pt(2)–C(37)	2.371(4)
Pt(1)–C(1)	2.079(4)	P(1)–C(37)	1.860(4)
Pt(1)–P(2)	2.2786(11)	P(2)–C(31)	1.819(5)
Pt(1)–P(1)	2.2966(12)	P(2)–C(51)	1.824(5)
Pt(2)–C(52)	1.955(4)	C(37)–C(38)	1.410(6)
Pt(2)–C(59)	2.025(4)	C(37)–C(51)	1.509(5)
Pt(2)–O(1)	2.186(3)	C(51)–C(52)	1.338(6)
Pt(2)–C(38)	2.304(4)	C(52)–C(53)	1.485(6)
P(2)–Pt(1)–P(1)	87.03(4)	C(52)–C(51)–C(37)	108.0(4)
C(37)–P(1)–Pt(1)	101.73(14)	C(52)–C(51)–P(2)	132.5(3)
C(51)–P(2)–Pt(1)	104.28(13)	C(37)–C(51)–P(2)	118.6(3)
C(38)–C(37)–C(51)	119.2(4)	C(51)–C(52)–C(53)	128.4(4)
C(38)–C(37)–P(1)	129.5(3)	C(51)–C(52)–Pt(2)	105.5(3)
C(51)–C(37)–P(1)	108.5(3)	C(53)–C(52)–Pt(2)	126.1(3)
C(37)–C(38)–Pt(2)	75.0(2)		



Scheme 6. Reaction in solution of complexes **6** and **7**.

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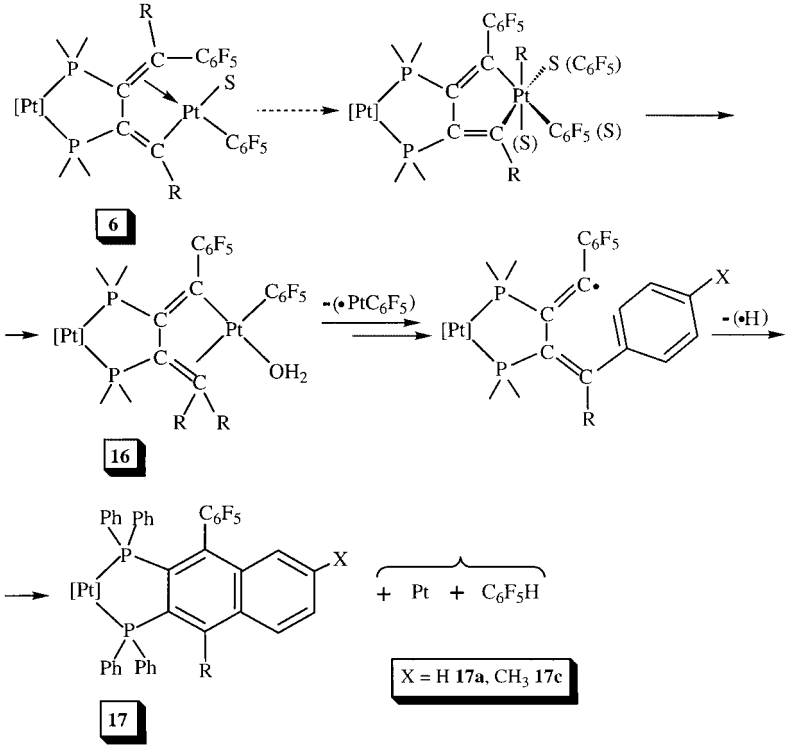
complex **17a**, the poor quality of the data prevents any detailed discussion. It is immediately apparent from the X-ray diffraction of **16a** that this complex is essentially an isomer of **6a** with a water molecule occupying one of the vacant coordination sites. The structure of **16a** could be produced from that of **6a** by a formal 4-1 phenyl migration from the olefinic carbon-4 to the vinyl carbon-1 with a concomitant change of the C_6F_5 ring **B**, again, mutually *cis* to the new vinyl function, and a coordination site, which is occupied by a molecule of H_2O [Pt(2)–O(1) 2.186(3) Å]. As can be observed, in the final dienyl chain the organic C_6F_5 group is bonded to the resulting vinylic carbon [C(52)–C(53) 1.485(6) Å], while both phenyl groups are mutually *gem* and connected to the new olefinic carbon C(38). The novel 2,3-bis(diphenylphosphanyl)-1,3-butadien-1-yl ligand is again bonded as a classic diphosphane to the $Pt(1)(C_6F_5)_2$ unit and as a 3,4-η-$\kappa C^1(\sigma,\pi)$ fragment to Pt(2) by C(52) [Pt(2)–C(52) 1.955(4) Å], C(37) [Pt(2)–C(37) 2.371(4) Å], and C(38) [Pt(2)–C(38) 2.304(4) Å]. The Pt–C(vinyl) bond length [Pt(2)–C(52) 1.955(4) Å] is short and it demonstrates the low *trans* influence of the oxygen donor ligand. The interatomic distances and angles for the butadienyl backbone [torsional angle C(38)–C(37)–C(51)–C(52) 62.5(5)°] are within the expected values compared with those observed for **9**, **12a**[12] and related systems.[4] As commented previously, because of the poor quality of the crystals of complex **17a**, the structure analysis is not of high accuracy. Nevertheless, the connectivity, shown in Scheme 6, was unequivocally established (Figure 6b), and it confirms the presence of the new unsymmetrical diphosphane ligand 1-pentafluorophenyl-2,3-bis(diphenylphosphanyl)-4-phenylnaphthalene, which acts as a chelating ligand to the $Pt(C_6F_5)_2$ organometallic fragment. Few examples of naphthalene-based bis(tertiary phosphanes) are known. The closest analogue systems are 1-phenylnaphthalene-2,3-bis(diphenylphosphane), which is obtained by thermal coupling of the pendant alkynyl groups of *cis*-$[PtClX(PPh_2C{\equiv}CPh)_2]$ (X = Cl, Me)[17] and 1,4-disubstituted-2,3-naphthalene(diphenylphosphane) derivatives generated by double insertion of the $PPh_2C{\equiv}CR$ ligands in the Ni^0–benzyne bond of the complexes $[Ni\{(1,2\text{-}\eta)\text{-}4,5\text{-}X_2C_6H_2\}(PEt_3)_2]$ (X = H, F).[14b]

Although the formation of these rearrangement products is beyond the initial scope of the present work we also explore the solution behavior of the remaining complexes **6c**, **7a**, and **7c**. We were unable to obtain the related **16c**, **17c**, and **18**–**19** (see Scheme 6) complexes as pure products, but NMR data of the final mixtures indicate that their formation follows an analogous pattern (see Experimental Section for details) to that for **6a** with a clear higher tendency of the mixtures toward the final naphthalene-based mononuclear derivatives. Although we have no evidence as to whether compounds **17** are formed from **16** or directly from **6** we believe that these mononuclear complexes are probably generated from **16** by intramolecular coupling of a phenyl (**16a**) or tolyl (**16c**) group (probably through a radical pathway) with concomitant loss of the remaining platinum organometallic unit as metallic platinum (and probably C_6F_5H). A plausible sequence of reactions leading to **16** and **17** is outlined in Scheme 7. In any case, starting from **6c**, only one regioisomer, that we believe to be **17c**, is generated. However, from the NMR data it cannot be unambiguously determined whether the methyl group (X) is in position 7 (and therefore coming from **16c**) or in position 6 (coming from **6c**). The formation of **16** starting from **6** may be rationalized as a formal 4-1 phenyl shift. Phenyl migrations in unsaturated systems are rare although there are precedents.[45] In our complexes, this shift could be envisaged as an initial olefinic C–C(Ph) bond activation promoted by the very electrophilic platinum center; this reaction leads to intermediate Pt^{IV} species, followed by a subsequent C–C reductive elimination to form the final observed butadienyl isomers **16** (see Scheme 7). Oxidative additions of C–C bonds have been achieved in the presence of highly reactive species, and those that lead to the formation of strong M–aryl bonds are particularly favorable.[46]

Conclusion

The present study provides novel reactivity patterns for P-coordinated alkynyl phosphanes. Unusual binuclear Pt_2 (**6**, **8**, **9**) or Pd–Pt (**7**) complexes stabilized by 2,3-bis(diphenylphosphanyl)-3,4-butadien-1-yl bridging ligands have been



Scheme 7. Proposed mechanism for the reaction of **6**.

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prepared by reaction of *cis*-[M(C_6F_5)$_2$($PPh_2C{\equiv}CR$)-($PPh_2C{\equiv}CR'$)] (R = R′ = Ph, Tol or R = Ph, Tol, R′ = *t*Bu) with *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1** in CH_2Cl_2 under relatively mild conditions. A likely reaction sequence (Scheme 4) for the unprecedented sequential insertion of both P-coordinated alkynyl phosphanes into the Pt–C_6F_5 bond of the "*cis*-Pt(C_6F_5)$_2$" synthon suggests the initial formation of the expected bis(η^2-alkyne) adducts, which were observed by NMR studies at low temperature. The formation of these 1:1 adducts probably requires the existence of a highly reactive, three-coordinated, 14 electron "*cis*-Pt(C_6F_5)$_2$(thf)" species, which is consistent with the lack of reactivity between [M]($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}Ct$Bu) (R = R′ **2**, **3**; R ≠ R′ **4**, **5**) and *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1** in donor solvents such as acetone or THF. The subsequent insertion steps (first insertion in the Pt–Pt **2**/**1** system or second insertion in the Pd–Pt **3**/**1** system) are believed to be rate-determining [or slower in relation to the formation of the bis(η^2-alkyne) adducts] and give rise to a formal 14-electron Pt(σ-, π-butadienyl)(C_6F_5) fragment occasionally stabilized by a donor molecule (THF, H_2O). The overall process is *regio*- and *stereoselective* leading in the case of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}Ct$Bu)] to a very crowded butadienyl {PPh_2}$_2$C(*t*Bu)–C=C(C_6F_5)(R) backbone, which stabilizes a very unusual T-shaped unsaturated three-coordinated platinum center as confirmed by X-ray diffraction (**9**). Complexes **6** exhibit a rich coordination chemistry, and are stable enough to react with donor ligands to form similar diplatinum complexes [Pt(C_6F_5)(L)μ-{C(R)=C(PPh_2)-C(PPh_2)=C(R)(C_6F_5)}Pt(C_6F_5)$_2$] (L = CO, py, PPh_2H, CN*t*Bu **10**–**13**) or related η^1-vinyldiphosphane derivatives *cis,cis*-[Pt(C_6F_5)(L)$_2$μ-{1-κ*C*^{1}:2-κ*PP*′–C(R)=C(PPh_2)C(PPh_2)=C(R)-(C_6F_5)}Pt(C_6F_5)$_2$] [L = CN*t*Bu **14**, 1/2 (2,2′-bipy) **15**]; these latter are formed by displacement of the η^2-olefin function. However, complexes **6** and **7** are unstable in solution and evolve through a formal 4-1 phenyl shift to related orange σ,π-butadienyl species [Pt(C_6F_5)(S)μ-{C(C_6F_5)=C(PPh_2)-C(PPh_2)=C(R)$_2$}M(C_6F_5)$_2$] (**16**, **18**) and white naphthalene-based diphenylphosphane mononuclear compounds **17** and **19**. We are currently investigating further synthetic applications of these P-coordinated alkynylphosphanes.

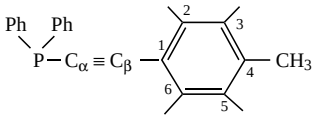
Experimental Section

General: All reactions and manipulations were carried out under a nitrogen atmosphere by using Schlenk techniques and distilled solvents purified by known procedures. The spectroscopic instrumentation employed has been previously reported.[20a] $PPh_2C{\equiv}CR$ (R = Ph,[47] *t*Bu,[47] Tol[48]), *cis*-[Pt(C_6F_5)$_2$(tht)$_2$],[49] (NBu_4)$_2$[Pd(μ-Br)(C_6F_5)$_2$]$_2$,[49] and *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1**[50] were prepared according to literature methods. The synthesis of complexes **2a**, **2b**, **3a**, **3b**, **6a**, and **7a** as well as **10a**–**12a**, **13a**, and **14a** was reported as supporting information,[12] and is therefore not included in this work. Complex *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$Bu)(tht)] used as precursor for the synthesis of compounds **4** and **5** has been prepared as in the following section.

Synthesis of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$Bu)(tht)]: A solution of $PPh_2C{\equiv}Ct$Bu (0.098 g, 0.367 mmol) in CH_2Cl_2 (20 mL) was treated with *cis*-[Pt(C_6F_5)$_2$(tht)$_2$] (0.259 g, 0.367 mmol), and the mixture was stirred for 1 hour. Evaporation to a small volume and addition of *n*-hexane (≈5 mL) afforded *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$Bu)(tht)] as a white solid (0.208 g, 64% yield).

^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.64 (dd, *o*-H; Ph), 7.35 (m, 6H; Ph), 2.83 (st, ^3J(Pt,H) ≈ 35 Hz, 4H; α-CH_2, tht), 1.69 (st, 4H; β-CH_2, tht), 1.33 (s, *t*Bu); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): δ = –118.3, –118.2 (m, ^3J(Pt,*o*-F) ≈ 400, 370 Hz; 4*o*-F), –160.5 (t; 1*p*-F), –162.8 (m; 2*m*-F), –163.3 (dt; 1*p*-F), –164.7 (m; 2*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = –7.22 (s, ^1J(Pt,P) = 2485 Hz); IR: $\tilde{\nu}$ = 2203 (m), 2163 (s) (C≡C), 801 (vs), 787 cm^{-1} (s)(C_6F_5)$_{X\text{-sens}}$; MS (ES$^+$): *m*/*z* (%): 895 (10) [Pt(PPh_2C_2tBu)$_2$(C_6F_5)$^+$+H], 727 (16) [Pt(PPh_2C_2tBu)$_2^+$], 549 (100) [Pt(PPh_2C_2tBu)(tht)$^+$], 461 (50) [Pt(PPh_2C_2tBu)$^+$]; elemental analysis calcd (%) for $C_{34}H_{27}F_{10}PPtS$ (883.7): C 46.21, H 3.08, S 3.63; found: C 46.20, H 3.37, S 3.61.

The following notation was employed for the carbon assignment in the tolyl derivatives.



Synthesis of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)$_2$] 2c: $PPh_2C{\equiv}CTol$ (0.281 g, 0.935 mmol) was added to a colorless solution of *cis*-[Pt(C_6F_5)$_2$(tht)$_2$] (0.300 g, 0.425 mmol) (2.2:1 molar ratio) in CH_2Cl_2 (15 mL), and the mixture stirred for one hour at room temperature. The solvent was removed under vacuum, and the residue treated with EtOH (≈5 mL), and this afforded **2c** as a white solid (0.427 g, 89% yield).

^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.66 (m, 8H; Ph), 7.24 (m, 12H; Ph), 6.85 (AB, *J*(H,H) = 7.7 Hz, δ$_A$ = 6.95, δ$_B$ = 6.75, 8H; C_6H_4), 2.31 (s, 6H; C_6H_4–CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): δ = –117.8 (m, ^3J(Pt,*o*-F) ≈ 327 Hz; *o*-F), –162.84 (t; *p*-F), –164.0 (m; *m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = –6.18 (s, ^1J(Pt,P) = 2407 Hz); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 145.0 (dd, ^1J(C,F) = 232, ^2J(C,F) ≈ 36 Hz; C_6F_5), 140.2 (s; C^4, Tol), 136.8 (br d, ^1J(C,F) ≈ 233 Hz; C_6F_5), 132.7 (*AXX*′, ^2J(C,P) + ^4J(C,P) = 12.1 Hz; *o*-C, PPh_2), 131.6 (s; *p*-C, PPh_2), 130.4 (s; *C*H, Tol), 130.1 (*AXX*′, four lines are observed, ^1J(C,P) + ^3J(C,P) = 66 Hz; *i*-C, PPh_2), 128.5 (s; *C*H, Tol), 127.9 (*AXX*′, ^3J(C,P) + ^5J(C,P) = 11.5 Hz; *m*-C, PPh_2), 117.0 (br s; C^1, Tol), 108.3 (*AXX*′, ^2J(C,P) + ^4J(C,P) = 16.0 Hz; ≡C$_β$Tol), 79.1 (d, *AXX*′, ^1J(C,P) + ^3J(C,P) = 105.6 Hz, ^2J(Pt,C$_α$) = 19 Hz; –PC$_α$≡), 21.35 (s; $C_6H_4CH_3$), 21.32 (s; $C_6H_4CH_3$) (These signals are tentatively attributed to the presence of two different rotamers in solution); IR: $\tilde{\nu}$ = 2181 (vs, C≡C), 796 (m), 780 cm^{-1} (m)(C_6F_5)$_{X\text{-sens}}$; MS (FAB$^+$): *m*/*z* (%): 1130 (12) [*M*$^+$+H]; elemental analysis calcd (%) for $C_{54}F_{10}H_{34}P_2Pt$ (1129.9): C 57.40, H 3.03; found: C 57.75, H 3.18.

Synthesis of *cis*-[Pd(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)$_2$] (3c): $PPh_2C{\equiv}CTol$ (0.354 g, 1.180 mmol) was added to a pale yellow solution of (NBu_4)$_2$[Pd(μ-Br)(C_6F_5)$_2$]$_2$ (0.450 g, 0.295 mmol) in CH_2Cl_2 (20 mL), and this immediately gave a colorless solution. Once the mixture had been stirred for one hour, the resulting solution was evaporated to dryness, and the residue was treated with cold EtOH (≈8 mL) to give **3c** as a white solid (0.467 g, 76% yield).

^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.62 (m, 8H; Ph), 7.24 (m, 12H; Ph), 6.87 (AB, *J*(H,H) = 6.4 Hz, δ$_A$ = 6.96, δ$_B$ = 6.78, 8H; C_6H_4), 2.32 (s, 6H; C_6H_4–CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): δ = –115.5 (dm; *o*-F), –162.0 (t; *p*-F), –163.1 (m; *m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = 0.07 (s); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 144.7 (dd, ^1J(C,F) = 232 Hz, ^2J(C,F) = 21 Hz; C_6F_5), 140.2 (s; C^4, Tol), 137.2 (br dt, ^1J(C,F) = 253 Hz; C_6F_5), 135.7 (br d, ^1J(C,F) ≈ 264 Hz; C_6F_5), 132.5 (*AXX*′, ^2J(C,P) + ^4J(C,P) = 13.0 Hz; *o*-C, PPh_2), 131.5 (s; *p*-C, PPh_2), 130.5 (*AXX*′, four lines are observed, ^1J(C,P) + ^3J(C,P) = 55.1 Hz; *i*-C, PPh_2), 130.3 (s, *C*H; Tol), 128.5 (s; *C*H, Tol), 128.0 (*AXX*′, ^3J(C,P) + ^5J(C,P) = 11.2 Hz; *m*-C, PPh_2), 117.2 (br s, C^1, Tol), 109.2 (*AXX*′, ^2J(C,P) + ^4J(C,P) = 14.2 Hz; ≡C$_β$Tol), 79.4 (dd, *AXX*′, ^1J(C,P) + ^3J(C,P) = 91.6 Hz; –PC$_α$≡), 21.35 (s; C_6H_4–CH_3), 21.32 (s; C_6H_4–CH_3); IR: $\tilde{\nu}$ = 2178 (vs; C≡C), 777 cm^{-1} (m)(C_6F_5)$_{X\text{-sens}}$; MS (ES$^+$ ionized with Ag$^+$): *m*/*z* (%): 1149 (100) [*M*$^+$+Ag], 876 (32) [*M*$^+$ – C_6F_5]; elemental analysis calcd (%) for $C_{54}F_{10}H_{34}P_2Pd$ (1041.2): C 62.29, H 3.29; found: C 62.05, H 3.03.

Synthesis of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)($PPh_2C{\equiv}Ct$Bu)] (R = Ph 4, Tol 5): A solution of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}Ct$Bu)(tht)] (0.200 g, 0.226 mmol) in CH_2Cl_2 (25 mL) was treated with $PPh_2C{\equiv}CPh$ (0.065 g, 0.226 mmol), and the mixture was stirred for one hour at room temperature. Evaporation to a

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small volume (≈2 mL) and addition of EtOH (≈8 mL) resulted in the precipitation of **4** as a white solid (0.160 g, 65% yield).

Complex **5** was prepared as a white solid following a similar procedure. *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CtBu$)(tht)] (0.280 g, 0.317 mmol), $PPh_2C{\equiv}CTol$ (0.095 g, 0.317 mmol), (0.242 g, 70% yield).

Data for **4**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.62$ (m, 7H; Ph), 7.36 (m, 16H; Ph), 6.87 (m, 2H; Ph), 0.82 (s, 9H; $-C(CH_3)_3$); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -117.9$ (m, ^3J(Pt,*o*-F) ≈ 325 Hz; 4*o*-F), −162.8 (t; 1*p*-F), −163.0 (t; 1*p*-F), −164.0 (m; 4*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = -6.80$ (br s, ^1J(Pt,P^1) = 2402 Hz), −8.11 (br s, ^1J(Pt,P^2) = 2386 Hz); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 145.2 (br dm, ^1J(C,F) ≈ 240 Hz; C_6F_5), 136.7 (br d, ^1J(C,F) ≈ 257 Hz; C_6F_5), 132.9 (d, ^2J(C,P) = 12.5 Hz, *o*-C; Ph, PPh_2), 132.5 (d, ^2J(C,P) = 12.4 Hz, *o*-C; Ph, PPh_2), 131.6 (s; *o*-C, Ph), 130.6 (s; *p*-C, PPh_2), 130.2 (s; *p*-C, PPh_2), 129.7 (s; *p*-C, Ph), 127.9–127.6 (m; *m*-C, Ph, PPh_2), 120.0 (d, J(C,P) ≈ 2 Hz; *i*-C, ≡–Ph), 118.2 (d, ^2J(C,P) = 12.6 Hz; $\equiv C_\beta tBu$), 107.4 (d, ^2J(C,P) = 14 Hz; $\equiv C_\beta$Ph), 80.1 (dd, ^1J(C,P) = 97.1 Hz, ^3J(C,P) = 5.9 Hz; C_α, $-PC_\alpha{\equiv}C_\beta$Ph), 69.5 (dd, ^1J(C,P) = 103.5, ^3J(C,P) = 5.4 Hz; C_α, $-PC_\alpha{\equiv}C_\beta tBu$), 29.3 (s; $C(CH_3)_3$), 28.0 (s; CMe_3); IR: $\tilde{\nu}$ = 2207 (m), 2180 (s) (C≡C), 796 (m), 778 cm^{-1} (m)(C_6F_5)$_{X\text{-sens}}$; MS (apci$^-$): *m*/*z* (%): 1081 (78) [M^-]; elemental analysis calcd (%) for $C_{50}F_{10}H_{34}P_2Pt$ (1081.8): C 55.51, H 3.17; found: C 55.77, H 2.89.

Data for **5**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.68$ (m, 8H; Ph), 7.64 (m, 12H; Ph), 6.86 (AB, J(H,H) = 8.0 Hz, $\delta_A = 6.98$, $\delta_B = 6.75$, 4H; C_6H_4), 2.32 (s, 3H; C_6H_4–CH_3), 0.81 (s, 9H; $-C(CH_3)_3$); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -117.9$ (m, ^3J(Pt,*o*-F) ≈ 320 Hz; 4*o*-F), −162.9 (t; 1*p*-F), −163.0 (t; 1*p*-F), −164.1 (m; 4*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = -7.01$ (s, ^1J(Pt,P^1) = 2426 Hz), −8.11 (s, ^1J(Pt,P^2) = 2423 Hz); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, 20 °C): δ = 145.2 (dd, ^1J(C,F) ≈ 232 Hz, ^3J(C,F) ≈ 24 Hz; C_6F_5), 140.2 (s; C^4, Tol), 136.6 (br d, ^1J(C,F) ≈ 253 Hz; C_6F_5), 132.9 (d, ^2J(C,P) = 12.5 Hz; *o*-C, PPh_2), 132.5 (d, ^2J(C,P) = 12.5 Hz; *o*-C, PPh_2), 131.6 (d, ^4J(C,P) = 1.4 Hz; C^{2,6}, Tol), 130.8 (dd, ^1J(C,P) = 63.8, ^3J(C,P) = 1.7 Hz; *i*-C, PPh_2), (for the other *i*-C(PPh_2) signal one of doublets is seen, the other is masked by the signal at 130.1), 130.4 (d, ^4J(C,P) = 2.4 Hz, *p*-C, PPh_2), 130.1 (d, ^4J(C,P) = 2.3 Hz; *p*-C, PPh_2), 128.5 (s; C^{3,5}, Tol), 127.81 (d, ^3J(C,P) = 5.8 Hz; *m*-C, PPh_2), 127.6 (d, ^3J(C,P) = 5.7 Hz; *m*-C, PPh_2), 118.1 (d, ^2J(C,P) = 12.7 Hz; $\equiv C_\beta tBu$), 117.1 (d, ^3J(C,P) = 3 Hz; C^1, Tol), 107.9 (d, ^2J(C,P) = 14.9 Hz; $\equiv C_\beta$Tol), 79.3 (dd, ^1J(C,P) = 99, ^3J(C,P) = 5.9 Hz; C_α, $-PC_\alpha{\equiv}C_\beta$Tol), 69.6 (dd, ^1J(C,P) = 101.3, ^3J(C,P) = 6.2 Hz; C_α, $-PC_\alpha{\equiv}C_\beta tBu$), 29.3 (d, ^4J(C,P) = 0.98 Hz; $C(CH_3)_3$), 27.9 (d, ^3J(C,P) = 1.8 Hz; CMe_3), 21.2 (s; $C_6H_4CH_3$); IR: $\tilde{\nu}$ = 2214 (m), 2176 (s) (C≡C), 798 (m), 780 cm^{-1} (m)(C_6F_5)$_{X\text{-sens}}$; MS (FAB$^+$): *m*/*z* (%): 1095 (7) [M^+]; elemental analysis calcd (%) for $C_{51}F_{10}H_{36}P_2Pt$ (1095.9): C 55.90, H 3.31; found: C 55.91, H 3.67.

Synthesis of [Pt(C_6F_5)(S)μ-{C(Tol)=C(PPh_2)C(PPh_2)=C(Tol)(C_6F_5)}-M(C_6F_5)$_2$] (M = Pt 6c, Pd 7c): *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1** (0.089 g, 0.133 mmol) was added to a stirred solution of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)$_2$] **2c** (0.150 g, 0.133 mmol) in CH_2Cl_2 (15 mL) at 0 °C, immediately forming an orange solution. After stirring the mixture at 0–10 °C for 45 min, the resulting solution was evaporated to a small volume (≈2 mL). The addition of *n*-hexane (10 mL) gave **6c** as a deep yellow solid (0.176 g, 80% yield).

Complex **7c** was prepared similarly as a brown-yellow solid starting from *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] (0.068 g, 0.100 mmol) and *cis*-[Pd(C_6F_5)$_2$($PPh_2C{\equiv}CTol$)$_2$] **3c** (0.104 g, 0.100 mmol) (0.68 g, 43% yield).

Data for **6c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.25$ (m, 2H), 7.80 (s, 4H), 7.30–6.27 (m, 18H), 6.28 (d, J = 7.5 Hz, 2H), 5.38 (d, J = 7.3 Hz, 2H; aromatics), 1.99 (s, 3H; $C_6H_4CH_3$), 1.91 (s, 3H; $C_6H_4CH_3$), 1.89 (s; H_2O), signals due to 0.6 mole of THF are observed: 3.4 (s; OCH_2), 1.52 (s; CH_2); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.1$ (br s, ^3J(Pt,*o*-F) ≈ 330 Hz, 1F), −116.1 (br s, ^3J(Pt,*o*-F) ≈ 300 Hz, 1F), −116.9 (br s, ^3J(Pt,*o*-F) ≈ 330 Hz, 1F), −118.3 (br s, ^3J(Pt,*o*-F) = 290 Hz, 1F, ^3J(Pt,*o*-F) ≈ 440 Hz, 2F) (*o*-$F_{B,C,C'}$) − 127.8 (br s; 1*o*-F_A), − 129.6 (d, ^4J(Pt,*o*-F_A) ≈ 95 Hz; 1*o*-F_A), −152.8 (t; 1*p*-F_A), −158.0 (m; 1*m*-F_A), −158.6 (t; 1*p*-F), −161.0 (m; 1*m*-F_A), −162.2 (t; *p*-F), −162.5 (m; 2*m*-F), −163.3 (t; *p*-F), −164.2 (m; 2*m*-F), −164.8 (m; 1*m*-F), −165.1 (m; 1*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 36.0$ (br s, ^1J(Pt^2,P^1) = 2252 Hz), 25.0 (br s, ^1J(Pt^2,P^2) = 2285, ^3J(Pt^1,P^2) = 305, ^2J(P^1,P^2) less than 5 Hz); ^{13}C{^{1}H} NMR (75.5 MHz, $CDCl_3$, −50 °C): δ = 160.3–117.5 (C_6F_5, Ph), 97.5 (dm, J(C,P) = 114.2 Hz; =C–P), 71.5 (dm, J(C,P) = 48.1 Hz; =C–P), 22.7 ($C_6H_4CH_3$), 21.1 ($C_6H_4CH_3$); IR: $\tilde{\nu}$ = 3602 (w; OH), 1520 (s), 1504 (vs), 1064 (vs), 992 (s), 981 (m), 959 (vs), 820 (m), 792 (m), 779 cm^{-1} (m) (C_6F_5); MS (FAB$^+$): *m*/*z* (%): 1491 (26) [$Pt_2(C_6F_5)_2${$(PPh_2C_2Tol)_2(C_6F_5)$}$^+$], 1324 (21) [$Pt_2(C_6F_5)$-{$(PPh_2C_2Tol)_2(C_6F_5)$}$^+$], 1156 (48) [Pt_2{$(PPh_2C_2Tol)_2(C_6F_5)$}$^+$ − H], 1079 (24) [$Pt_2(C_6F_5)(PPh_2C_2Tol)(PPhC_2Tol)^+$ − H], 1003 (26) [$Pt_2(C_6F_5)$-$(PPhC_2Tol)_2^+$], 962 (46) [Pt{$(PPh_2C_2Tol)_2(C_6F_5)$}$^+$]; elemental analysis calcd (%) for $C_{68.4}F_{20}H_{39.6}OP_2Pt_2$ (1709.6) with S = 0.4 H_2O + 0.6 THF: C 48.06, H 2.33; elemental analysis calcd (%) for $C_{66}F_{20}H_{34}P_2Pt_2$ (1659.1): C 47.78, H 2.06; found: C 48.06, H 1.90.

Data for **7c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.26$ (m, 2H), 7.82 (s, 4H), 7.30–6.40 (m, 18H), 6.29 (d, J = 7.7 Hz, 2H), 5.42 (d, J = 7.7 Hz, 2H; aromatics), 1.99 (s, 3H; $C_6H_4CH_3$), 1.96 (s, 3H; $C_6H_4CH_3$), 1.78 (s; H_2O), signals due to 0.6 mole of THF are observed: 3.45 (s; OCH_2), 1.56 (s; CH_2); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -111.6$ (m; 1*o*-$F_{CC'}$), −114.1 (m; 2*o*-$F_{CC'}$), −116.1 (m; 1*o*-$F_{CC'}$), −118.3 (m, ^3J(Pt,*o*-F) ≈ 465 Hz; 2*o*-F_B,), −128.2 (m; 1*o*-F_A), −129.8 (m; 1*o*-F_A), −152.6 (t; 1*p*-F_A), −157.5 (m; 1*m*-F_A), −158.4 (t; 1*p*-F), −160.7 (m; 1*m*-F_A), −161.4 (t; *p*-F), −162.4 (m; 1*p*-F + 2*m*-F), −163.2 (m; 1*m*-F), −163.7 (m; 1*m*-F), −164.1 (m; 1*m*-F), −164.5 (m; 1*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 42.45$ (br; P^1), 32.39 (br, ^3J(Pt^1,P^2) = 290 Hz; P^2); IR: $\tilde{\nu}$ = 3604 (w, OH), 1519 (s), 1504 (s), 1063 (s), 994 (m), 981 (m), 957 (s), 816 (m), 801 (m), 778 cm^{-1} (s) (C_6F_5); MS (ES$^+$): *m*/*z* (%): 1403 (100) [M^+ − C_6F_5], M = PtPd(C_6F_5)$_4$(PPh_2C_2Tol)$_2$; elemental analysis calcd (%) for $C_{68.4}F_{20}H_{39.6}OP_2PdPt$ (1620.9) with S = 0.6 THF + 0.4 H_2O: C 50.69, H 2.46; elemental analysis calcd (%) for $C_{66}F_{20}H_{34}P_2PdPt$ (1570.4): C 50.48, H 2.18; found: C 49.96, H 2.65.

Control of the formation of 6 and 7 by NMR spectroscopy: The control of the formation of **6a** and **7a** has already been reported.[12] Monitoring the reactions by multinuclear NMR spectroscopy in $CDCl_3$ at room temperature revealed that the formation of the insertion products **6c** or **7c** (together with decomposition in the latter case) takes place almost instantaneously (within 5 min). However monitoring the reaction between **2c** and *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1** in $CDCl_3$ at −50 °C by ^{31}P{^{1}H}, ^{19}F, and ^{1}H NMR spectroscopy (Table 5) revealed that this reaction takes place through the formation of the η^2-bis(alkyne) adduct, [$Pt(C_6F_5)_2\mu$-{κP:η^2($PPh_2C{\equiv}CTol)_2$}Pt(C_6F_5)$_2$] **6′c**. At −50 °C, the proportion of **6′c** is very small and remains at the initial molar ratio observed, which was essentially constant between −50 to −30 °C. Upon further warming, the proportion of **6′c** increased slightly. At 0 °C, the final double inserted derivative **6c** started to appear and it increased its proportion with the temperature (Table 5).

Table 5. Control of the formation of **6**.

T [°C]	**2c**	**6′c**	**6c**
−50 to −30	1	0.1	–
−20	1	0.25	–
−10	1	0.7	–
0	1	1	0.3
5	≈0.9	1	0.9
10	≈0.30	0.25	1
20	≈0.1	–	1
20 °C/30 min	traces	–	1
20 °C/1 h	–	–	1

Data for **6′c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 0 °C): $\delta = 2.32$ (s; Tol) the rest of the signals overlapped with those of **6c** and **2c**; ^{19}F NMR (282.4 MHz, $CDCl_3$, 0 °C): $\delta = -117.9$ *o*-F (overlapping with the signal of **2c**), −159.0 (t; *p*-F), −161.3 (t; *p*-F), −163.3 (m; *m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 0 °C): $\delta = +2.66$ (s, ^1J(Pt,P) = 2380 Hz).

The Pd–Pt reaction system (**3c**/*cis*-[Pt(C_6F_5)$_2$(thf)$_2$] **1**) showed similar behavior to that described for the Pt–Pt reaction system (**2c**/**1**) between −50 to −30 °C, and it revealed the presence of the reactants and the η^2-bis(alkyne) adduct **7′c** (Table 6). However, at −20 °C a new intermediary named **7″c** was also formed, which we proposed was the monoinserted alkyne–vinyl product analogous to that described for $PPh_2C{\equiv}CPh$.[12] This intermediate exhibited two different P resonances at 0 °C: $\delta = 10.89$ (br), −3.28 (br), although the signals in the ^{19}F and ^{1}H NMR spectrum could not be assigned. It appeared in very low proportion and remained essentially constant at increasing temperature (based on the ^{31}P{^{1}H} NMR spectra,

Table 6. Control of the formation of **7**.

T [°C]	**3c**	**7′c**	**7″c**	**7c**
−50 to −30	1	0.06–0.07	–	–
−20	1	0.09	0.06	–
−10	1	0.3	0.06	–
0	0.98	1	0.13	–
5	0.6	1	0.15	0.3
15	0.3	0.3	–	1
20 °C/1 h	–	–	–	1

Table 6). Besides the increasing proportion of **7′c** with temperature, the double inserted product started to form at 5 °C. The amount of **7c** gradually grew in the reaction mixture with a concomitant decrease of **3c** and **7′c**, and at 15 °C, **7″c** was not observed. Within 1 h at 20 °C, the formation of **7c** was completed, although small amounts of unidentified decomposition species (detected by ^{19}F NMR spectroscopy up 10 °C) were also present probably due to the low stability of **7c** in solution.

Data for **7′c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 0 °C): $\delta = 2.32$ (s; Tol). The rest of the signals overlap with the signals of **3c**; ^{19}F NMR (282.4 MHz, $CDCl_3$, 0 °C): $\delta = -115.3$, *o*-F (overlapping with the signal of **3c**), −158.9 (t; *p*-F), −160.5 (t; *p*-F), −162.4 (m; *m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 0 °C): $\delta = 9.55$ (s).

Synthesis of [Pt(C$_6$F$_5$)(S)μ-{C(*t*Bu)=C(PPh$_2$)C(PPh$_2$)=C(R)(C$_6$F$_5$)}-Pt(C$_6$F$_5$)$_2$] (R = Ph 8, Tol 9): *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] (0.087 g, 0.129 mmol) was added to a solution of *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$C≡CPh)(PPh$_2$C≡C*t*Bu)] **4** (0.140 g, 0.129 mmol) in CH_2Cl_2 (20 mL) at room temperature to give a deep yellow solution. The mixture was stirred for one hour, evaporated to a small volume (≈3 mL), and treated with *n*-hexane (≈8 mL), which caused the precipitation of a deep yellow solid **8** (0.180 g, 86% yield).

Complex **9** was prepared, as described for **8**, by treating *cis*-[Pt(C$_6$F$_5$)$_2$(PPh$_2$C≡CTol)(PPh$_2$C≡C*t*Bu)] **5** (0.150 g, 0.137 mmol) with *cis*-[Pt(C$_6$F$_5$)$_2$(thf)$_2$] (0.092 g, 0.137 mmol). A deep yellow solid was formed (0.161 g, 72% yield).

Data for **8**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.56$ (m, 2H), 7.79–6.78 (m, 21H), 6.46 (d, J(H,H) = 7.5 Hz, 2H; aromatics), 0.50 (s, 9H; C(CH_3)$_3$), signals due to 0.4 mole of THF were observed: 3.72 (brs; OCH_2), 1.83 (brs; CH_2); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -112.8$ (brs, ^3J(Pt,*o*-F) ≈ 497 Hz, 2F), −115.5 (brs, ^3J(Pt,*o*-F) ≈ 333 Hz, 1F), −115.8 (brs, ^3J(Pt,*o*-F) ≈ 243 Hz, 1F), −117.3 (brm, ^3J(Pt,*o*-F) ≈ 310 Hz, 1F), −117.6 (brm, ^3J(Pt,*o*-F) ≈ 220 Hz, 1F) (*o*-F$_{B,C,C'}$), −128.6 (dm, ^4J(F,Pt) = 79 Hz, J(F,F) = 25 Hz; 1*o*-F$_A$), −129.8 (dm, ^4J(F,Pt) ≈ 96, J(F,F) = 24 Hz; 1*o*-F$_A$), −150.9 (t; 1*p*-F$_A$), −154.0 (t; 1*p*-F), −159.5 (m; 2*m*-F), −161.2 (m; 2*m*-F), −161.8 (t; 1*p*-F), −162.6 (t; 1*p*-F), −164.0 (m; 2*m*-F), −164.5 (m; 2*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 39.7$ (brs, ^1J(Pt^2,P^2) = 2303, ^3J(Pt^1,P^2) = 361 Hz), 34.4 (brs, ^1J(Pt^2,P^1) = 2283 Hz); IR: $\tilde{\nu}$ = 1523 (s), 1504 (vs), 1063 (s), 989 (m), 976(m), 959 (s), 788 (m), 778 cm^{-1} (m) (C$_6$F$_5$); MS (ES$^-$): *m*/*z* (%): 1610 (7) [M^-]; elemental analysis calcd (%) for C$_{62.8}$F$_{20}$H$_{37.2}$O$_{0.4}$P$_2$Pt$_2$ (1630.3) with S = 0.4 THF: C 46.27, H 2.30; elemental analysis calcd (%) for C$_{62}$F$_{20}$H$_{34}$P$_2$Pt$_2$ (1611.0): C 46.22, H 2.13; found: C 46.64, H 1.89.

Data for **9**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.63$ (m, 2H), 7.70 (m, 3H), 7.54 (m, 3H), 7.34 (m, 3H), 7.19 (s, 4H), 6.95 (s, 3H), 6.76 (m, 2H), 6.65 (d, J = 6.98 Hz, 2H), 6.37 (d, J = 7.66 Hz, 2H; aromatics), 2.01 (s, 3H; C$_6$H$_4$CH_3), 0.50 (s, 9H; C(CH_3)$_3$), signals due to 0.35 mole of THF were observed: 3.71 (brs, OCH_2), 1.83 (brs, CH_2); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -112.8$ (brs, ^3J(Pt,*o*-F) = 440 Hz, 2F), −115.4 (brs, ^3J(Pt,*o*-F) ≈ 300 Hz, 1F), −115.7 (m, ^3J(Pt,*o*-F) ≈ 235 Hz, 1F), −117.4 (m, ^3J(Pt,*o*-F) ≈ 300 Hz, 1F), −117.5 (m, ^3J(Pt,*o*-F) ≈ 270 Hz, 1F) (*o*-F$_{B,C,C'}$), −128.8 (dm, ^4J(F,Pt) = 85 Hz; *o*-F$_A$), −129.7 (brm; 1*o*-F$_A$), −151.0 (t; 1*p*-F$_A$), −154.2 (t; 1*p*-F), −159.6 (m; 2*m*-F), −161.3 (m; 2*m*-F), −161.9 (t; 1*p*-F), −162.7 (t; 1*p*-F), −164.0 (m; 2*m*-F), −164.6 (m; 2*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 40.0$ (brs, ^1J(Pt^2,P^2) = 2308, ^3J(Pt^1,P^2) = 379 Hz), 34.2 (brs, ^1J(Pt^2,P^1) = 2263 Hz); IR: $\tilde{\nu}$ = 3602 (w; OH), 1520 (s), 1503 (vs), 1064 (s), 994 (m), 976 (m), 957 (s), 803 (w), 793 (m), 780 cm^{-1} (m) (C$_6$F$_5$); MS (ES$^+$): *m*/*z* (%): 1457 (32) [$M^+ - C_6F_5$], 1290 (17) [$M^+ - 2C_6F_5$], 1122 (41) [$M^+ - 3C_6F_5 - H$]; elemental analysis calcd (%) for C$_{63.7}$F$_{20}$H$_{38.8}$O$_{0.35}$P$_2$Pt$_2$ (1641.9) with S = 0.35 THF: C 46.60, H 2.38; elemental analysis calcd (%) for C$_{63}$F$_{20}$H$_{36}$P$_2$Pt$_2$ (1625.1): C 46.56, H 2.23; found: C 46.98, H 1.89.

Synthesis of [Pt(C$_6$F$_5$)(L)μ-{C(Tol)=C(PPh$_2$)C(PPh$_2$)=C(Tol)(C$_6$F$_5$)}-Pt(C$_6$F$_5$)$_2$] (L = CO 10c, py 11c, PPh$_2$H 12c): Bubbling CO for 5 min or addition of the corresponding ligand (0.090 mmol: 7.3 μL of pyridine, 15.6 μL of PPh$_2$H) to solutions which contained **6c** (0.15 g, 0.090 mmol) in CH_2Cl_2 (15 mL) at room temperature, immediately produced in each case dark orange solutions. After 5 min (CO) or 30 min (the rest) of stirring, the solutions were evaporated to a small volume (≈2 mL). Addition of *n*-hexane (5 mL) and standing at −30 °C gave microcrystalline yellow (**10c**) or orange solids (**11c**, **12c**) (0.121 g, 80% yield **10c**; 0.127 g, 80% **11c**; 0.151 g, 90% **12c**).

Data for **10c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.96$ (m, 2H), 7.79 (m, 3H), 7.33–6.53 (m, 17H), 6.46 (d, J(H,H) = 8.0 Hz, 2H), 6.29 (d, J(H,H) = 7.8 Hz, 2H), 5.16 (d, J(H,H) = 7.8 Hz, 2H) (aromatics), 2.08 (s, 3H; C$_6$H$_4$CH_3), 2.03 (s, 3H; C$_6$H$_4$CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.3$ (brs, ^3J(Pt,*o*-F) = 322 Hz), −116.0 (brs, ^3J(Pt,*o*-F) ≈ 335 Hz), −117.0 (brs, ^3J(Pt,*o*-F) ≈ 320 Hz), −117.8 (dm, ^3J(Pt,*o*-F) = can not be calculated), −118.5 (brs, ^3J(Pt,*o*-F) ≈ 209 Hz), −119.5 (m, ^3J(Pt,*o*-F) ≈ 437 Hz) (6*o*-F$_{BCC'}$), −125.6 (st; *o*-F$_A$), −128.8 (dm, ^4J(F,Pt) ≈ 85, J(F,F) = 26 Hz; *o*-F$_A$), −151.1 (t; 1*p*-F$_A$), −157.7 (t; 1*p*-F), −158.4 (m; 1*m*-F$_A$), −159.0 (m; *m*-F$_A$), −161.1 (m; 1*m*-F), −161.8 (t; 1*p*-F), −162.4 (m; 1*m*-F), −162.8 (t; 1*p*-F), −164.0 (m; 2*m*-F), −164.5 (m; 1*m*-F), −164.9 (m; 1*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 34.51$ (brs, ^1J(Pt^2,P^1) = 2206 Hz), 26.82 (brs, ^1J(Pt^2,P^2) = 2261, ^3J(Pt^1,P^2) = 196 Hz); IR: $\tilde{\nu}$ = 2105 (vs), 2058 (w) (CO), 1520 (s), 1502 (s), 1065 (s), 995 (s), 958 (s), 805 (s), 792 (s), 781 cm^{-1} (s) (C$_6$F$_5$); MS (ES$^-$): *m*/*z* (%): 1659 (20) [M^- − CO]; elemental analysis calcd (%) for C$_{67}$F$_{20}$H$_{34}$OP$_2$Pt$_2$ (1687.1): C 47.70, H 2.03; found: C 47.77, H 2.05.

Data for **11c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.27$ (m, 2H), 8.70 (brs, 2H), 7.88 (s, 4H), 7.51–6.60 (m), 6.20 (brs) (21H), 6.29 (d, J(H,H) = 7.7 Hz, 2H), 5.41 (d, J(H,H) = 7.6 Hz, 2H) (aromatics), 1.97 (s, 3H; C$_6$H$_4$CH_3), 1.78 (s, 3H; C$_6$H$_4$CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.0$ (brs, ^3J(Pt,*o*-F) = 328 Hz), −116.2 (brs, ^3J(Pt,*o*-F) = 288 Hz), −116.9 (brs, ^3J(Pt,*o*-F) = 384 Hz), −118.5 (brs, ^3J(Pt,*o*-F) = 237 Hz), −118.8 (d, ^3J(Pt,*o*-F) = 480 Hz), −121.3 (m, ^3J(Pt,*o*-F) = 445 Hz; 6*o*-F$_{BCC'}$), −128.9 (m; 2*o*-F$_A$), −153.1 (t; 1*p*-F$_A$), −157.0 (m; 1*m*-F$_A$), −160.5 (t; 1*p*-F), −161.3 (m; *m*-F$_A$), −162.3 (t; 1*p*-F), −162.9 (1*m*-F), −163.4 (t; *p*-F, *m*-F), −164.08 (m; 1*m*-F), −164.4 (m; 1*m*-F), −164.8 (m; 1*m*-F), −165.1 (m; 1*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 36.5$ (brs, ^1J(Pt^2,P^1) = 2248 Hz), 22.7 (brs, ^1J(Pt^2,P^2) = 2282, ^3J(Pt^1,P^2) = 293 Hz); IR: $\tilde{\nu}$ = 1520 (s), 1500 (vs), 1063 (vs), 993 (s), 959 (vs), 800 (s), 789 (s), 778 cm^{-1} (sh) (C$_6$F$_5$); MS (FAB$^+$): *m*/*z* (%): 1492 (9) [Pt$_2$(C$_6$F$_5$)$_2${(PPh$_2$C$_2$Tol)$_2$-(C$_6$F$_5$)}$^+$+H], 1157 (75) [Pt$_2${(PPh$_2$C$_2$Tol)$_2$(C$_6$F$_5$)}$^+$]; elemental analysis calcd (%) for C$_{71}$F$_{20}$H$_{39}$NP$_2$Pt$_2$ (1738.2): C 49.06, H 2.26, N 0.81; found: C 49.02, H 2.68, N 1.17.

Data for **12c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.14$ (m, 2H), 7.83–6.43 (m, 32H), 6.16 (d, J(H,H) = 7.8 Hz, 2H), 5.19 (d, J(H,H) = 7.8 Hz, 2H) (aromatics), 4.29 (dd, ^1J(P,H) = 373, $^{4,5}J$(P,H) = 4.8 Hz, 1H; PPh$_2$*H*), 1.97 (s, 3H; C$_6$H$_4$CH_3), 1.94 (s, 3H; C$_6$H$_4$CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.2$ (m, ^3J(Pt,*o*-F) = 350 Hz; 1*o*-F), −116.0 (m, ^3J(Pt,*o*-F) = 275 Hz; 1*o*-F), −116.6 (m, ^3J(Pt,*o*-F) ≈ 370 Hz; 1*o*-F), −118.07 (dm, ^3J(Pt,*o*-F) = 450 Hz; 2*o*-F), −118.4 (m, ^3J(Pt,*o*-F) ≈ 60 Hz; 1*o*-F) (*o*-F$_{BCC'}$), −125.4 (m; 1*o*-F$_A$), −128.2 (m, ^4J(F,Pt) = 90 Hz; 1*o*-F$_A$), −152.5 (t; 1*p*-F$_A$), −157.6 (m; 1*m*-F$_A$), −160.7 (m; 1*m*-F$_A$), −162.2 (2t overlapped; 2*p*-F), −163.20 (m; *m*-F), −163.37 (t; 1*p*-F), −164.1-(-165.2) (m; 5*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 36.7$ (brs, ^1J(Pt^2,P^1) = 2204 Hz), 25.9 (brs, ^1J(Pt^2,P^2) = 2239, ^3J(Pt,P^2) ≈ 180 Hz), 12.5 (m, ^1J(Pt^1,P^3) = 1775 Hz); IR: $\tilde{\nu}$ = 1520 (s), 1504 (vs), 1064 (s), 994 (s), 958 (vs), 803 (s), 792 (m), 785 cm^{-1} (w) (C$_6$F$_5$); MS (FAB$^+$): *m*/*z* (%): 1845 (4) [M^+], 1677 (14) [$M^+ - C_6F_5 - H$], 1492 (15) [$M^+ - C_6F_5 - PPh_2H$], 1342 (15) [Pt$_2${(PPh$_2$C$_2$Tol)$_2$(C$_6$F$_5$)}(PPh$_2$H)$^+$ − H]; elemental analysis calcd (%) for C$_{78}$F$_{20}$H$_{45}$P$_3$Pt$_2$ (1845.3): C 50.77, H 2.46; found: C 51.01, H 3.13.

Synthesis of [Pt(C$_6$F$_5$)(CN*t*Bu)μ-{C(Tol)=C(PPh$_2$)C(PPh$_2$)=C(Tol)-(C$_6$F$_5$)}Pt(C$_6$F$_5$)$_2$] (13c) and *cis*,*cis*-[Pt(C$_6$F$_5$)(CN*t*Bu)$_2$$\mu$-{1-$\kappa$*C*^{1}:2-$\kappa$*PP'*-C(Tol)=C(PPh$_2$)C(PPh$_2$)=C(Tol)(C$_6F_5$)}Pt(C$_6F_5$)$_2$] (14c): A solution of CN*t*Bu (0.044 N, 2 mL, 0.0885 mmol) in diethyl ether was added to a stirred solution of **6c** (0.155 g, 0.093 mmol) in CH_2Cl_2 (15 mL) at room temperature (0.95:1 molar ratio), and the mixture was stirred for 30 min. The resulting pale-orange solution was evaporated to a small volume (≈2 mL) and treated with *n*-hexane (5 mL) to give a yellow solid (0.137 g,

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89% yield) identified by NMR spectroscopy as $[Pt(C_6F_5)(CNtBu)\mu\text{-}\{C(Tol)=C(PPh_2)C(PPh_2)=C(Tol)(C_6F_5)\}Pt(C_6F_5)_2]$ **13c**.

The compound **14c** was obtained as a pure lemon-yellow solid, in a similar way, by addition of CN*t*Bu (20.5 μL, 0.180 mmol) to a solution of **6c** (0.150 g, 0.090 mmol) in a 2:1 molar ratio (0.120 g, 70% yield).

Data for **13c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.07$ (m, 2H), 7.73 (m), 7.29–6.33 (m, 22H), 6.25 (d, J(H,H) = 7.78 Hz, 2H), 5.17 (d, J(H,H) = 7.77 Hz, 2H) (aromatics), 2.02 (s, 3H; $C_6H_4CH_3$), 2.00 (s, 3H; $C_6H_4CH_3$), 1.07 (s, 9H; CN*t*Bu); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.5$ (brs, ^3J(Pt,*o*-F) ≈ 325 Hz), −115.8 (brs, ^3J(Pt,*o*-F) ≈ 260 Hz), −116.8 (brs, ^3J(Pt,*o*-F) ≈ 300 Hz), −117.8 (dm), −118.1 (brs), −119.7 (m, ^3J(Pt,*o*-F) ≈ 430 Hz) (6*o*-$F_{BCC'}$), −125.8 (m, ^4J(Pt,*o*-F) ≈ 100 Hz; 1*o*-F_A), −129.1 (m, ^4J(Pt,*o*-F) ≈ 110 Hz; 1*o*-F_A), −153.1 (t; 1*p*-F_A), −159.4 (m; 1*m*-F_A), −160.1 (t; 1*p*-F), −160.8 (m; 1*m*-F_A), −162.3 (t; 1*p*-F), −162.8 (m; 1*m*-F), −163.4 (t; 1*p*-F), −164.1 (m; 3*m*-F), −164.8 (m; 1*m*-F), −165.2 (m; 1*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 32.62$ (s, $^1J(Pt^2,P^1) = 2235$ Hz), 26.21 (s, $^1J(Pt^2,P^2) = 2254$, $^3J(Pt^1,P^2) = 181$ Hz); IR: $\tilde{\nu} = 2208$ (s; C≡N), 1519 (s), 1505 (s), 1066 (vs), 990 (s), 956 (s), 803 (s), 793 (s), 780 cm^{-1} (s) (C_6F_5); MS (FAB$^+$): *m*/*z* (%): 1658 (5) [M^+ − CN*t*Bu], 1491 (15) [M^+ − C_6F_5 − CN*t*Bu], 1407 (21) [$M^+ - 2C_6F_5$], 1323 (15) [$M^+ - 2C_6F_5$ − CN*t*Bu − H]; elemental analysis calcd (%) for $C_{71}F_{20}H_{43}NP_2Pt_2$ (1742.23): C 48.95, H 2.49, N 0.80; found: C 49.49, H 2.49, N 0.80.

Data for **14c**: ^{1}H NMR (300.1 MHz, CD_3COCD_3, −50 °C): $\delta = 8.17$ (m, 2H), 8.01 (m, 2H), 7.59–6.96 (m, 20H), 6.65 (m, 3H), 6.13 (d, J = 7.02 Hz, 1H) (aromatics), 2.14 (s, 3H; $C_6H_4CH_3$), 2.09 (s, 3H; $C_6H_4CH_3$), 1.32 (s, 9H; CN*t*Bu), 1.07 (s, 9H; CN*t*Bu); ^{19}F NMR (282.4 MHz, CD_3COCD_3, −50 °C): $\delta = -106.3$ (dd, ^3J(Pt,*o*-F) ≈ 363, J(F,F) = 53, 28 Hz; 1*o*-F_B), −114.3 (m, ^3J(Pt,*o*-F) ≈ 305 Hz), −114.7 (dm; 1*o*-F_B), −115.7 (m), −116.25 (m), −116.5 (m, ^3J(Pt,*o*-F) ≈ 230 Hz), (*o*-$F_{CC'}$) (assignment based on a COSY F–F experiment at −50 °C), −124.6 (dd, J(F,F) = 53, 22 Hz; 1*o*-F_A), −131.5 (d; 1*o*-F_A), −155.4 (t; 1*p*-F_A), −157.0 (t; 1*p*-F), −162.4 (m; 1*m*-F_A), −164.4 (m; 3*m*-F + 2*p*-F), −164.9 (m; 1*m*-F_A), −165.6 (m; 3*m*-F); (at +50 °C): $\delta = -110.0$ (coalescence signal, *o*-F), −114.1 (brs, ^3J(Pt,*o*-F) = 310 Hz), −114.6 (brs), −115.2 (brs, ^3J(Pt,*o*-F) ≈ 286 Hz), −116.0 (brs, ^3J(Pt,*o*-F) ≈ 205 Hz) (*o*-$F_{BCC'}$), −124.0 (d; 1*o*-F_A), −131.1 (d; 1*o*-F_A), −156.0 (t; 1*p*-F_A), −158.5 (t; 1*p*-F), −164.0 (brs, 2*m*-F), −164.7 (m; 1*m*-F), −165.4 (m; 2*p*-F + 3*m*-F), −166.5 (brs, 2*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, CD_3COCD_3, −50 °C): $\delta = 29.07$ (s, $^1J(Pt^2,P^1) = 2308$ Hz), 24.37 (brs, $^1J(Pt^2,P^2) = 2234$, $^3J(Pt^2,P^2) = 219$ Hz); IR: $\tilde{\nu} = 2220$ (vs), 2194 (vs) (CN), 1518 (s), 1504 (vs), 1062 (vs), 998 (s), 974 (s), 958 (vs), 789 (s), 777 cm^{-1} (m) (C_6F_5); MS (FAB$^+$): *m*/*z* (%): 1849 (8) [M^++Na+H], 1659 (10) $[Pt_2(C_6F_5)_3\{(PPh_2C_2Tol)_2(C_6F_5)\}^+ + H]$, 1491 (7) $[Pt_2(C_6F_5)_2\{(PPh_2C_2Tol)_2(C_6F_5)\}^+]$, 611 (61) $[Pt(C_6F_5)_2(CNtBu)^+ - H]$, 555 (34) $[Pt_2(CNtBu)_2^+ - H]$, 361 (24) $[Pt(CNtBu)_2^+]$; elemental analysis calcd (%) for $C_{76}F_{20}H_{52}N_2P_2Pt_2$ (1825.4): C 50.01, H 2.87, N 1.53; found: C 49.75, H 3.25, N 1.75.

Synthesis of $[Pt(C_6F_5)(2,2'\text{-bipy})\mu\text{-}\{C(R)=C(PPh_2)C(PPh_2)=C(R)(C_6F_5)\}Pt(C_6F_5)_2]$ (R = Ph 15a, Tol 15c): Complexes **15a** and **15c** were prepared as orange solids following an analogous procedure to that described for **11** and **12**. **15a**: **6a** (0.140 g, 0.086 mmol), 2,2′-bipy (0.013 g, 0.086 mmol) (0.130 g, 85% yield). **15c**: **6c** (0.130 g, 0.0785 mmol), 2,2′-bipy (0.012 g, 0.0785 mmol) (0.131 g, 92% yield).

Data for **15a**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.24–6.04$ (aromatics); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -107.6$ (dm, ^3J(Pt,*o*-F) ≈ 455 Hz; 1*o*-F_B), −115.8 (brs, ^3J(Pt,*o*-F) ≈ 340 Hz; 1*o*-F), −116.6 (brs; 1*o*-F), −117.0 (brs; 2*o*-F), −117.5 (brs, ^3J(Pt,*o*-F) ≈ 226 Hz; 1*o*-F) (*o*-$F_{BCC'}$), −125.4 (dm; 1*o*-F_A), −133.7 (d, J(F,F) = 22.9 Hz; 1*o*-F_A), −155.4 (t, 1*p*-F_A), −157.7 (m; 1*m*-F), −162.4 (m; 2*m*-F + 1*p*-F), −162.9 (m; 1*m*-F), −164.2 (t; 1*p*-F), −164.3 (t; 1*p*-F), −164.8 (m; 1*m*-F), −165.5 (m; 3*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 37.97$ (brs, $^1J(Pt^2,P^1) = 2260$ Hz), 28.55 (brs, $^1J(Pt^2,P^2) = 2214$, $^3J(Pt^2,P^2) \approx 230$ Hz); IR: $\tilde{\nu} = 1503$ (vs), 1064 (s), 996 (s), 958 (vs), 800 (m), 787 (m), 776 cm^{-1} (s) (C_6F_5); MS (FAB$^+$): *m*/*z* (%): 1620 (20) [$M^+ - C_6F_5$], 1452 (10) [$M^+ - 2C_6F_5$], 519 (40) $[Pt(C_6F_5)(bipy)^+ + H]$, 351 (100) $[Pt(bipy)^+]$; elemental analysis calcd (%) for $C_{74}F_{20}H_{38}N_2P_2Pt_2$ (1787.2): C 49.73, H 2.14, N 1.57; found: C 49.78, H 2.47, N 1.56.

Data for **15c**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 8.21–6.35$ (aromatics), 1.99 (brs, 6H; $C_6H_4CH_3$); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -107.5$ (m, ^3J(Pt,*o*-F) = 411 Hz; 1*o*-F_B), −115.7 (brs, ^3J(Pt,*o*-F) ≈ 317 Hz; 1*o*-F), −116.8 (brs; 3*o*-F), −117.3 (brs, ^3J(Pt,*o*-F) ≈ 285 Hz; 1*o*-F) (*o*-$F_{BCC'}$), −125.4 (m; 1*o*-F_A), −133.7 (brs; 1*o*-F_A), −155.6 (t; 1*p*-F_A), −158.1 (m; 1*m*-F), −162.7 (m; 3F), −163.1 (t; 1*p*-F), −164.4 (m; 2*p*-F), −164.5 (m; 1*m*-F), −165.3 (m; 3*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 38.11$ (s, $^1J(Pt^2,P^1) = 2267$ Hz), 28.24 (brs, $^1J(Pt^2,P^2) = 2232$ Hz, $^3J(Pt^2,P^2) \approx 213$ Hz); IR: $\tilde{\nu} = 1500$ (sh), 1496 (vs), 1064 (vs), 996 (s), 958 (vs), 800 (m), 787 (m), 776 cm^{-1} (w) (C_6F_5); MS (FAB$^+$): *m*/*z* (%): 1815 (50) [M^+], 1648 (34) [$M^+ - C_6F_5$], 1481 (22) [$M^+ - 2C_6F_5$], 1296 (16) [$M^+ - Pt(C_6F_5)$(bipy)], 1130 (90) [$M^+ - Pt(C_6F_5)_2$(bipy)], 519 (40) $[Pt(C_6F_5)(bipy)^+ + H]$; elemental analysis calcd (%) for $C_{76}F_{20}H_{42}N_2P_2Pt_2$ (1815.3): C 50.29, H 2.33, N 1.54; found: C 49.96, H 2.69, N 1.02.

Reaction of $[Pt(C_6F_5)(S)\mu\text{-}\{C(Ph)=C(PPh_2)C(PPh_2)=C(Ph)(C_6F_5)\}Pt(C_6F_5)_2]$ 6a: preparation of $[Pt(C_6F_5)(H_2O)\mu\text{-}\{C(C_6F_5)=C(PPh_2)C(PPh_2)=C(Ph)_2\}Pt(C_6F_5)_2]$ 16a and *cis*-$[(C_6F_5)_2Pt\{C_{10}H_4\text{-}1\text{-}C_6F_5\text{-}4\text{-}Ph\text{-}2,3\text{-}\kappa PP'(PPh_2)_2\}]$ 17a: The following experiments were carried out.

1) Compound **6a** (0.08 g, 0.048 mmol) was dissolved in diethyl ether (5 mL) in presence of air, and the yellow solution was exposed to ambient light without stirring for 48 h. The resulting black mixture was evaporated to dryness and analyzed by NMR spectroscopy, which indicated the presence of three products: compound **6a** and two novel complexes **16a** and **17a** in an approximate molar ratio of 0.72:0.7:1 (**6a**:**16a**:**17a**).
2) Under identical conditions but using THF as the solvent, mainly complex **17a** was observed in the final mixture.
3) Slow diffusion of *n*-hexane into a solution of complex **6a** in diethyl ether in ambient light generated a mixture of orange (**16a**) and white crystals (**17a**) in a 2:1 approximate proportion, suitable for spectroscopic characterization and for X-ray diffraction.
4) Compounds **16a** and **17a** could also be separated from the final residue obtained from **6a** (0.1 g, 0.060 mmol) in THF after 24 h of exposure to ambient light. After treatment of the residue with a mixture of diethyl ether/*n*-hexane (1:5, 10 mL), **17a** separated out as a white solid (0.030 g, 40% yield), and slow evaporation of the filtrate afforded orange crystals (0.015 g, 19% yield) of **16a**.
5) A solution of compound **6a** in THF for only 24 h, but in the absence of light, gave a mixture of **6a**, **16a**, and **17a** in an approximate molar ratio of 0.9:1:0.8.
6) Irradiation of a solution of **6a** in THF (0.125 g, 0.075 mmol) through a Pyrex glass at room temperature under an argon atmosphere with a medium-pressure mercury lamp (125 W) gave the molar proportions collected in Table 7.

Table 7. Results of the irradiation of **6a**.

time [min]	**6a**	**16a**	**17a**
15	1	traces	0.2
25	1	–	0.5
45	0.38	–	1
60	–	–	1

Data for **16a** (from crystals separated by hand): ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 9.42$ (brm), 7.81 (m), 7.57–6.64 (m, 30H) (aromatics), 1.65 (s; H_2O); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -115.2$ (brs, ^3J(Pt,*o*-F) = 340 Hz; 1*o*-F), −117.7 (m; 3*o*-F), −118.4 (d, ^3J(Pt,*o*-F) = 469 Hz; 2*o*-F), −132.4 (d; 1*o*-F_A), −135.35 (d; 1*o*-F_A), −155.2 (t; 1*p*-F_A), −157.4 (t; 1*p*-F), −161.8 (m; 2*m*-F_A), −162.2 (*p*-F), −162.66 (m; 1*m*-F), −162.8 (t; 1*p*-F), −163.33 (m; 1*m*-F), −163.8 (m; 1*m*-F), −164.0 (m; 1*m*-F), −164.43 (m; 2*m*-F); ^{31}P{^{1}H} NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 36.33$ (brs, ^1J(Pt,P) = 2159 Hz), 25.00 (brs, ^1J(Pt,P) = 2278, ^3J(Pt,P) ≈ 320 Hz); MS (FAB$^+$): *m*/*z* (%): 1648 (4) [M^+], 1464 (25) $[Pt_2(C_6F_5)_3(PPh_2C_2Ph)_2^+ + H]$, 1297 (25) $[Pt_2(C_6F_5)_2(PPh_2C_2Ph)_2^+ + H]$, 1102 (44) $[Pt(C_6F_5)_2(PPh_2C_2Ph)_2^+ + H]$, 934 (62) $[Pt(C_6F_5)(PPh_2C_2Ph)_2^+]$, 379 (80) $[Pt(PPh_2)^+ - H]$.

Data for **17a**: ^{1}H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.45–7.12$ (m), 6.87 (m) (27H), 6.39 (d, J = 7.7 Hz, 2H); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -116.5$ (dm, ^3J(Pt,*o*-F) = 275 Hz; 2*o*-F), −117.3 (dm, ^3J(Pt,*o*-F) = 277 Hz; 2*o*-F), −133.75 (d; 2*o*-F, C−C_6F_5), −151.98 (t; 1*p*-F, C−C_6F_5), −160.9 (m; 2*m*-F, C−C_6F_5), −162.51 (t; 1*p*-F), −162.58 (t; 1*p*-F), −164.7

(m; 4*m*-F); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 46.57$ (d, $^1J(Pt,P) = 2290$ Hz), 43.83 (d, $^1J(Pt,P) = 2249$ Hz, $^2J(P,P)$ less than 5 Hz); MS (apci+): *m/z* (%): 1100 (100) $[M^+ - C_6F_5]$, 933 (30) $[M^+ - 2C_6F_5]$; elemental analysis calcd (%) for $C_{58}F_{15}H_{29}P_2Pt$ (1267.9): C 54.94, H 2.31; found: C 55.31, H 2.85.

Reaction of $[Pt(C_6F_5)(S)\mu$-{C(Ph)=C(PPh$_2$)C(PPh$_2$)=C(Ph)(C$_6$F$_5$)}-Pd(C$_6$F$_5$)$_2$] (7a): characterization of $[(C_6F_5)_2Pd\{C_{10}H_4$-1-C$_6$F$_5$-4-Ph-2,3-$\kappa PP'$(PPh$_2$)$_2$}] (19a): The reaction of **7a** (0.05 mmol) in diethyl ether (20 mL) at room temperature and ambient light over three days produced a black solution, NMR spectra (^{31}P and ^{19}F) of which showed the presence of complex **19a** together with a small amount of **18a** (analogous to the species **17a** with M = Pd). However, monitoring by NMR spectroscopy of a sample after 24 h indicated the presence of **7a**, **18a**, and **19a** in an approximate molar ratio of 0.13:0.18:1.

Data for **19a**: ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.56 - 6.64$ (m, 27H), 6.39 (d, $J = 7.4$ Hz, 2H); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.2$ (m; 2*o*-F), −115.1 (m; 2*o*-F), −133.95 (d; 2*o*-F; C−C_6F_5), −151.96 (t; 1*p*-F, C−C_6F_5), −160.82 (m; 2*m*-F, C−C_6F_5), −161.81 (t; 1*p*-F), −161.88 (t; 1*p*-F), −164.1 (m; 4*m*-F); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 52.74$ (brs), 50.65 (brs); MS (FAB^+): *m/z* (%): 1011 (32) $[M^+ - C_6F_5]$, 844 (60) $[M^+ - 2C_6F_5]$, 767 (66) $[M^+ - 2C_6F_5 - Ph]$.

Reaction of $[Pt(C_6F_5)(S)\mu$-{C(Tol)=C(PPh$_2$)C(PPh$_2$)=C(Tol)(C$_6$F$_5$)}-Pt(C$_6$F$_5$)$_2$] (6c): characterization of $[(C_6F_5)_2Pt\{7$-CH$_3$−C$_{10}$H$_3$-1-C$_6$F$_5$-4-Tol-2,3-$\kappa PP'$(PPh$_2$)$_2$}] (17c): The following experiments were carried out with complex **6c**. A solution of **6c** (0.121 g, 0.071 mmol) in diethyl ether (25 mL) at room temperature was exposed to ambient room light for 7 h. Analysis of the final dark solution indicated the presence of **6c** and **17c** (1:0.87 molar ratio) together with a small amount of **16c**. After 24 h, only **17c** and trace amounts of **16c** were detected. Irradiation of a solution of **6c** (0.15 g, 0.088 mmol) in THF through Pyrex glass at room temperature under an argon atmosphere with a medium-pressure mercury lamp (125 W) also produced **17c** (Table 8). However, in this case, other unidentified species were also observed by ^{31}P NMR spectroscopy.

Table 8. Results of the irradiation of **6c**.

time [min]	**6c**	**17c**
5	1	0.12
15	1	0.54
25	0.86	–
35	0.25	1
45	–	1

Data for **17c** obtained from a mixture in diethyl ether after 24 h: ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.90 - 6.57$ (25H), 6.24 (d, $J = 7.7$ Hz, 2H) (aromatics), 2.31 (s; CH_3), 2.29 (s; CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -116.3$ (m; *o*-F), −117.2 (m; *o*-F), −134.0 (dm; 2*o*-F; C−C_6F_5), −152.3 (t; 1*p*-F, C−C_6F_5), −161.0 (m; 2*m*-F; C−C_6F_5), −162.7 (2t; 2*p*-F), −164.5 (m; 4*m*-F); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 45.56$ (d, $^1J(Pt^1,P^1) = 2279$ Hz), 43.52 (brs, $^1J(Pt^2,P^2) = 2213$ Hz); MS (FAB^+): *m/z* (%): 1491 (10) $[M^+ + Pt]$, 1128 (33) $[M^+ - C_6F_5]$, 962 (88) $[M^+ - 2C_6F_5]$, 795 (55) $[M^+ - 3C_6F_5]$, 377 (100) $[PPh_3C_2Tol^+]$.

Reaction of $[Pt(C_6F_5)(S)\mu$-{C(Tol)=C(PPh$_2$)C(PPh$_2$)=C(Tol)(C$_6$F$_5$)}-Pd(C$_6$F$_5$)$_2$] (7c): characterization of $[(C_6F_5)_2Pd\{7$-CH$_3$-C$_{10}$H$_3$-1-C$_6$F$_5$-4-Tol-2,3-$\kappa PP'$(PPh$_2$)$_2$}] (19c): The results of the reaction of yellow solutions of **7c** (0.120 g, 0.075 mmol) in diethyl ether or THF (40 mL) in the presence of light are collected in Table 9.

Data for **19c**: ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.45 - 6.80$ (23H), 6.66 (d, $J = 7.8$ Hz, 2H), 6.24 (d, $J = 7.9$ Hz, 2H) (aromatics), 2.30 (s; 2CH_3); ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -114.1$ (dm; 2*o*-F), −115.0 (dm; 2*o*-F), −134.15 (dm, 2*o*-F; C−C_6F_5), −152.3 (t; 1*p*-F; C−C_6F_5), −161.0 (m; 2*m*-F; C−C_6F_5), −161.9 (t; 1*p*-F), −162.0 (t; 1*p*-F), −164.2 (m; 4*m*-F); $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 51.7$ (m), 50.58 (m); MS (FAB^+): *m/z* (%): 1039 (55) $[M^+ - C_6F_5]$, 872 (100) $[M^+ - 2C_6F_5]$, 795 (70) $[M^+ - 2C_6F_5 - Ph]$, 377 (100) $[PPh_3C_2Tol^+]$.

For $[Pt(C_6F_5)(H_2O)\mu$-{C(C$_6$F$_5$)=C(PPh$_2$)C(PPh$_2$)=C(Tol)$_2$}Pd(C$_6$F$_5$)$_2$], **18c**, only the position of the *o*-*F* (C−C_6F_5): −132.5 (dm), −135.0 (dm) (data extracted from the ^{19}F NMR spectrum of a solution in THF) could be assigned.

Table 9. Results of the reaction of **7c**.

time [h]	**7c**	**18c**	**19c**
diethyl ether			
5	1	–	0.3
24	0.65	–	1
48	–	–	1
THF[a]			
5	1	–	–
24	1	–	0.26
48	1	0.48	0.55
144	0.62	0.66	1
200	traces	0.2	1

[a] Other unidentified products are also detected.

Crystallography: Data for **12a** and **14a** have been previously given.[12] Crystals of complexes **2a**, **2b**, **2c**, **9**, **14c**, and **16a** were obtained at low temperature (243 K) or room temperature (**16a**) by slow diffusion of *n*-hexane into a solution of the respective compound in $CHCl_3/CCl_4$ (**2a**), dichloromethane (**2b**, **9**), tetrahydrofuran (**2c**), acetone (**9**), or diethyl ether (**16a**). Tables 1S and 2S, available as Supporting information, contain details of the structural analyses for all complexes. Data for **2c**, **9**, **14c**, and **16a** were collected with a NONIUS kCCD area-detector diffractometer and for **2a** and **2b** with a four-circle Siemens P4 diffractometer by using graphite-monochromated $Mo_{K\alpha}$ radiation. An empirical absorption correction based on psi-scan was carried out for **2a** and **2b** and a scalepack for **2c**, **9**, **14c**, and **16a**. The structures were solved (SHELXL-93[51] **2a**, **2b**; SHELXL-97[52] **2c**, **9**, **14c**, **16a**) by the Patterson method and refined by a full-matrix least-squares method against F^2. All hydrogen atoms were constrained to idealized geometries, and isotropic displacement parameters of 1.2 (**2a**, **2b**) and 1.2, for the phenyl, and 1.5, for the methyl groups (**2c**, **9**, **14c**, **16a**), times the U_{iso} value of their attached carbon were fixed. Lattice solvent was found in **2a** (0.5 CCl_4), **2b** (1 CH_2Cl_2), **9** (0.5 CH_2Cl_2, disordered and two half molecules of water), **14c** (1 CH_3COCH_3 in two different positions), and **16a** (2/3 diethyl ether). For **2a**, **2c**, and **9** a residual peak (>1 e Å^{-3}) was observed close to the Pt atoms with no chemical meaning.

CCDC-172959 – 172964 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html (or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk).

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