Rearrangement or C−H Activation Processes Promoted by Reaction with the Solvate [*cis*-Pt(C_6F_5)$_2$(thf)$_2$]

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A new series of functionalized (μ-hydride)(μ-acetylide) isomeric derivatives [*trans*-(PPh$_3$)(C_6F_5)Pt(μ-H)(μ-1κC^α:η^2-C≡CR)Pt(C_6F_5)(PPh$_3$)] (**3**) and [*cis,cis*-(PPh$_3$)$_2$Pt(μ-H)(μ-1κC^α:η^2-C≡CR)Pt(C_6F_5)$_2$] (**4**) (R = (4-CH$_3$)C$_6$H$_4$, **a**; (4-CN)C$_6$H$_4$, **b**; CMe=CH$_2$, **c**; C(OH)Me$_2$, **d**; C(OH)EtMe, **e**; C(OH)Ph$_2$, **f**) have been prepared by reaction in mild conditions of the disolvated [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] with the corresponding Pt(II) [*trans*-PtH(C≡CR)(PPh$_3$)$_2$] (**1**) or Pt(0) [Pt(η^2-HC≡CR)(PPh$_3$)$_2$] (**2**) isomers. The course of these reactions seems to be rather general, but in the case of the diphenylhydroxy precursors is strongly influenced by an easy *gem* (**4f**) to *trans* (**3f**) isomerization and the presence of water, which leads to the formation of the unexpected (μ-hydroxy)(μ-vinyl) complex [*cis,cis*-(PPh$_3$)$_2$Pt{μ-1κC^α:η^2-CH=CHC(OH)Ph$_2$}(μ-OH)Pt(C_6F_5)$_2$] (**5f**). Control of the latter reaction has allowed us to detect the mixed-valence intermediate [*cis,cis*-(PPh$_3$)$_2$Pt{μ-η^2:η^2-HC≡C(OH)Ph$_2$}Pt(C_6F_5)$_2$(thf)] (**6f**). Starting from [Pt(η^2-HC≡C$_5$H$_4$N-4)(PPh$_3$)$_2$] (**2g**) and [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] only the trinuclear mixed-valence adduct [{(PPh$_3$)$_2$Pt(μ-η^2:2κN-HC≡C$_5$H$_4$N-4)}$_2${*cis*-Pt(C_6F_5)$_2$}] (**7g**) is obtained.

Introduction

The use of transition metal complexes to activate carbon−hydrogen bonds has become one of the most pursued goals of organometallic chemistry.[1−5] Nowadays, the activation of C−H bonds in alkynes is one of the most active fields of research in this area, mainly due to their implications in the alkyne/vinylidene tautomerization, as well as in some catalytic processes.[6−21] In this context, we have recently reported that [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] reacts with the alkyne platinum(0) derivative [Pt(η^2-HC≡CPh)(PPh$_3$)$_2$] to yield, through an unexpectedly easy C−H activation, the (μ-hydride)(μ-alkynyl) diplatinum complex [*cis,cis*-(PPh$_3$)$_2$Pt(μ-H)(μ-1κC^α:η^2-C≡CPh)Pt(C_6F_5)$_2$],[22] while the reaction of the same solvate substrate [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] with the hydride−alkynyl platinum(II) complex [*trans*-PtH(C≡CPh)(PPh$_3$)$_2$] leads, also under very mild reaction conditions, to the (μ-hydride)(μ-alkynyl) diplatinum isomer [*trans*-(PPh$_3$)(C_6F_5)Pt(μ-H)(μ-1κC^α:η^2-C≡CPh)Pt(C_6F_5)(PPh$_3$)].[22,23] Although many different structural types of dimeric hydride-bridged platinum complexes have been reported,[23−27] these two acetylide-bridged diplatinum isomers belong to a rare class of these compounds, which contains mixed bridging systems consisting of a hydride and a hydrocarbon ligand. In fact, as far as we are aware, the only other reported examples are the analogous cationic (μ-alkylidene)(μ-hydride) complexes [Pt$_2$(L−L)$_2$(μ-CHCH$_2$Ar)(μ-H)]$^+$ [28−31] and the cationic (μ-hydride)(μ-carbonyl) or (μ-hydride)(μ-isocyanide) derivatives [Pt$_2$(L−L)$_2$(μ-CX)(μ-H)]$^+$ (X = O[32,33] or NR[33]), which are

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formally diplatinum(I) species. Our research group has also reported the (μ-H)(μ-C_6F_5) platinum(II) derivative [*trans*-{Pt(C_6F_5)(PPh_3)}$_2$(μ-H)(μ-C_6F_5)], generated through an initial adduct stabilized by a mixed (μ-H)(μ-κP:η^2-PPh_3) bridging system, by reaction of [*trans*-PtH(C_6F_5)(PPh_3)$_2$] with [*cis*-Pt(C_6F_5)$_2$(thf)$_2$].[23]

Nevertheless, the course of the formation of the (μ-hydride)(μ-alkynyl) diplatinum(II) isomers can be influenced by the nature of the substituent at the alkynyl or alkyne ligands in the mononuclear substrates. Thus, we have observed that the reaction of [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] with the pyridylacetylide complex [*trans*-PtH(C≡C_5H_4N-2)(PPh_3)$_2$] affords the initial adduct [*trans*,*cis*-(PPh_3)$_2$HPt(μ-1κC^{α}:$\eta^2{}_{\alpha,\beta}$:2κN-C≡C_5H_4N-2)Pt(C_6F_5)$_2$], which finally rearranges to form a tetranuclear platinum cluster containing both an edge-bridging alkynyl group and a face-capping vinyl ligand.[34]

These results prompted us to investigate the influence of the functionalized substituents (R) at the alkynyl or alkyne ligand, and we present here a systematic study of the reactivity of several alkyne Pt(0) [Pt(η^2-HC≡CR)(PPh_3)$_2$] and alkynyl Pt(II) [*trans*-PtH(C≡CR)(PPh_3)$_2$] isomers (R = (4-CH_3)C_6H_4, (4-CN)C_6H_4, CMe_2═CH_2, C(OH)Me_2, C(OH)EtMe, C(OH)Ph_2, C_5H_4N-4) toward the disolvated substrate [*cis*-Pt(C_6F_5)$_2$(thf)$_2$]. This work has allowed us to obtain a good number of new functionalized (μ-hydride)(μ-alkynyl) diplatinum complexes. In addition, we also report the isolation of an unexpected (μ-hydroxy)(μ-vinyl) diplatinum derivative in the reaction with the α-diphenylpropinol Pt(0) complex.

Results and Discussion

With the aim of completing a series of alkynyl Pt(II) and alkyne Pt(0) mononuclear isomers containing vinyl, propargyl, or functionalized aryl groups as radicals in the alkynylic rest (≡C−R), we have synthesized, following previously reported synthetic strategies,[35] the precursors [*trans*-PtH(C≡CR)(PPh_3)$_2$] (**1**) and [Pt(η^2-HC≡CR)(PPh_3)$_2$] (**2**) (R = (4-CH_3)C_6H_4, **a**; (4-CN)C_6H_4, **b**; CMe═CH_2, **c**; C(OH)Me_2, **d**; C(OH)EtMe, **e**; C(OH)Ph_2, **f**; C_5H_4N-4, **g**), from which **1a**, **1b**, and **2b** are new complexes. We have not been able to obtain the pyridyl−acetylide complex [*trans*-PtH(C≡CC_5H_4N-4)(PPh_3)$_2$] from the corresponding [*trans*-PtHCl(PPh_3)$_2$]/HC≡CPy/NEt_3 system, but the new Pt(0) isomer [Pt(η^2-HC≡CC_5H_4N-4)(PPh_3)$_2$] (**2g**) can be easily obtained by reaction of [Pt(C_2H_4)(PPh_3)$_2$] with HC≡CPy (see Supporting Information). The complete characterization of these new compounds, as well as the spectroscopic data of the alkyne derivatives **2a**, **2d**, and **2e**, are collected in the Supporting Information. For complex **1b** (R = (4-CN)C_6H_4), an X-ray diffraction structural analysis has been also carried out (Figure 1 and Table 1), with the aim of observing a possible intermolecular interaction between the cyanide group of the acetylide and the hydride ligand. Unfortunately, although the hydride (H(1)) has been located from difference maps, the distance H(1)···N(1)C−C_6H_4 (4.255 Å) is too long to suggest the existence of any kind of interaction. The rest of the structural features of the structure of complex **1b** are similar to those described for other mononuclear hydride−alkynyl platinum(II) complexes.[36,37]

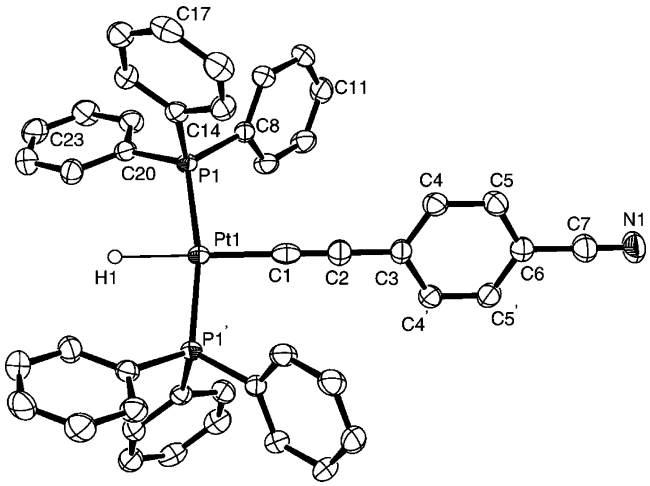


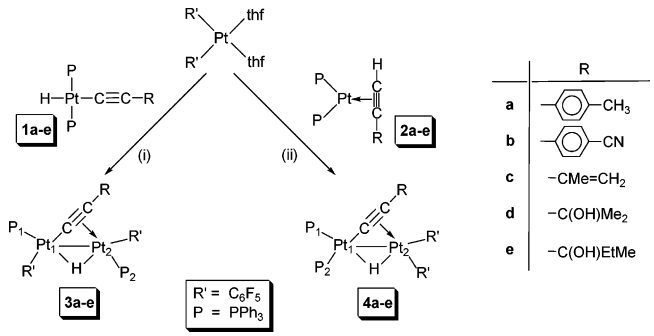
Figure 1. ORTEP view of [*trans*-PtH{C≡C(4-CN)C_6H_4}(PPh_3)$_2$] (**1b**). Ellipsoids are drawn at the 50% probability level. Aromatic hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [*trans*-PtH{C≡C(4-CN)C_6H_4}(PPh_3)$_2$] (1b)[a]

Pt(1)−C(1)	2.018(5)	Pt(1)−P(1)	2.2732(8)	Pt(1)−H(1)	1.68(9)
C(1)−C(2)	1.224(7)	C(2)−C(3)	1.425(6)		
C(1)−Pt(1)−P(1)	95.60(2)	P(1)−Pt(1)−P(1)'	168.81(4)		
C(1)−Pt(1)−H(1)	180.000(12)	Pt(1)−C(1)−C(2)	180.0		
C(1)−C(2)−C(3)	180.000(1)				

[a] Symmetry transformations used to generate equivalent atoms (′): $-x+1, y, -z+1/2$.

Scheme 1



Reaction of [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] with [*trans*-PtH(C≡CR)(PPh_3)$_2$] (1a−e) and [Pt(η^2-HC≡CR)(PPh_3)$_2$] (2a−e). As is shown in Scheme 1 (i), the reaction of [*trans*-PtH(C≡CR)(PPh_3)$_2$] (**1a**−**e**) with [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] (after 30 min) causes a complex ligand rearrangement, yielding the dinuclear (μ-hydride)(μ-acetylide) complexes [*trans*-(PPh_3)(C_6F_5)Pt(μ-H)(μ-1κC^{α}:η^2-C≡CR)Pt(C_6F_5)(PPh_3)] (**3a**−**e**, "*trans*"-type) in high yield (50−80%). On the other hand, treatment of the alkyne substrates [Pt(η^2-HC≡CR)(PPh_3)$_2$] (**2a**−**e**) with an equimolecular amount of [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] (Scheme 1, ii) results in C−H activation to generate the "*gem*"-type (μ-hydride)(μ-acetylide) isomers [*cis*,*cis*-(PPh_3)$_2$Pt(μ-H)(μ-1κC^{α}:η^2-C≡CR)-Pt(C_6F_5)$_2$] (**4a**−**e**) in moderate to good yields (50−66%, except for **4c**, 12%). It must be noted that, in spite of the presence of oxygen or nitrogen atoms or vinylic groups on the functionalized radicals of the alkynylic rest (≡C−R), the course of the reaction is the same as that previously described for the phenylacetylide- or phenylalkyne-related precursors.[22,23] In particular, it is remarkable that in all the cases the activation reaction of the

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alkyne C−H bond occurs at room temperature within seconds, except for the 1-cyano-4-ethynylbenzene complex **4b**, the formation of which takes about 24 h to complete. Probably, in this case, the presence of the nitrogen atom of the cyano−phenyl group influences the course of the reaction. Nevertheless, the study of the evolution of the reaction mixture by multinuclear NMR spectroscopy at room temperature shows only signals due to the corresponding precursors and the final diplatinum complex **4b** during the course of the reaction. At the end, when the alkyne precursor **2b** has been consumed (within 24 h), the NMR spectra additionally show signals due to $OPPh_3$ and other unidentified decomposition products. It should be noted that the "*gem*"-type complexes **4**, which are stable in solution at room temperature, isomerize to the "*trans*"-type derivatives **3** by prolonged heating in acetone or toluene (ca. 20 or 2 h, respectively), although with considerable decomposition. This fact seems to suggest that the "*trans*"-type complexes are probably the most stable thermodynamic species, but their formation starting from [*trans*-PtH(C≡CR)(PPh_3)$_2$] does not occurs through the "gem"-type derivatives (**4**) as intermediates. Moreover, complexes **4a**−**e** are more insoluble than complexes **3a**−**e**, which precludes the recording of their $^{13}C\{^1H\}$ NMR spectra.

Complexes **3a**−**e** and **4a**−**e** have been characterized by the usual analytical and spectroscopic means (see Experimental Section and Supporting Information). In addition, the structures of complexes **3a**, **3b**, **4a**, **4c**, and **4e** have been confirmed by single-crystal X-ray diffraction. All the complexes present structural features in the solid state similar to those observed for the phenylethynyl-related complexes.[22,23] Figure 2 shows the structures of a "*trans*"- (**3b**) and a "*gem*"-type (**4a**) complex as representative examples, which have been chosen because the hydride ligands have been located directly from the final difference Fourier map (selected bond distances and angles are shown in Table 2 and details for **3a**, **4c**, and **4e** derivatives can be found in Figure S1 and Tables S1 and S2 in the Supporting Information). In both complexes **3b** and **4a**, the hydride ligand is bonded in an essentially symmetrical way to both platinum centers, the Pt−H distances (Pt(1)−H(1) 1.83(6) Å **3b**, 1.63(8) Å **4a**; Pt(2)−H(1) 1.72(6) Å **3b**, 1.61(8) Å **4a**), as well as the Pt−Pt−H angles (Pt(1)−Pt(2)−H(1) 38.2(18)° **3b**, 29(3)° **4a**; Pt(2)−Pt(1)−H(1) 35.6(18)° **3b**, 28(3)° **4a**), being identical within experimental error, although some difference could be expected due to the different *trans* influence of the C_6F_5 and PPh_3 ligands. The hydride is coordinated essentially *trans* to the *ipso*-carbon atom, C(1), of one C_6F_5 group (C(1)−Pt(2)−H(1) 160.1(18)° **3b**, 167(3)° **4a**) and to the phosphorus atom P(1) (P(1)−Pt(1)−H(1) 168.1(18)° **3b**, 169(3)° **4a**).

Although the distribution of the PPh_3 and C_6F_5 ligands is different in both types of complexes, all derivatives (**3a**, **3b**, **4a**, **4c**, and **4e**) show a roughly planar central core formed by the platinum and phosphorus atoms, the acetylenic carbons, and the *ipso*-C atoms of the C_6F_5 rings (for complexes **3b** and **4a**, the hydride ligand also lies in this plane), with the alkynyl ligand σ-bonded to Pt(1) (Pt(1)−C(13) 1.935(15)−2.024(10) Å) and unsymmetrically π-bonded to Pt(2) (Pt(2)−C(13) 2.186(5)−2.249(7) Å, Pt(2)−C(14) 2.286(5)−2.325(6) Å). The presence of the bridging hydride ligand causes a remarkable dissimilarity in the angles around the Pt centers. The angles P(1)−Pt(1)−Pt(2) (141.57(4)−157.92(6)°) and C(1)−Pt(2)−Pt(1) (160.96(14)−167.2(4)°) are substantially larger than the corresponding angles P(2)−Pt−Pt (108.71(3)−112.88(5)°) and C(7)−Pt−Pt (110.3(2)−112.49(13)°), thus reflecting a considerable bending of both P(2)Ph_3 and C_6F_5 (with C(7)) ligands toward the less sterically demanding bridging hydride ligand. The Pt−Pt distances (2.8293(5)−2.8459(3) Å) compare to those found in the phenylethynyl-related complexes[22,23] and in other 30e$^-$ diplatinum hydride species containing mixed (μ-H)(μ-X) bridging systems[38,39] and are in accordance with theoretical calculations that suggest the existence of a through-ring platinum−platinum bonding interaction.[40]

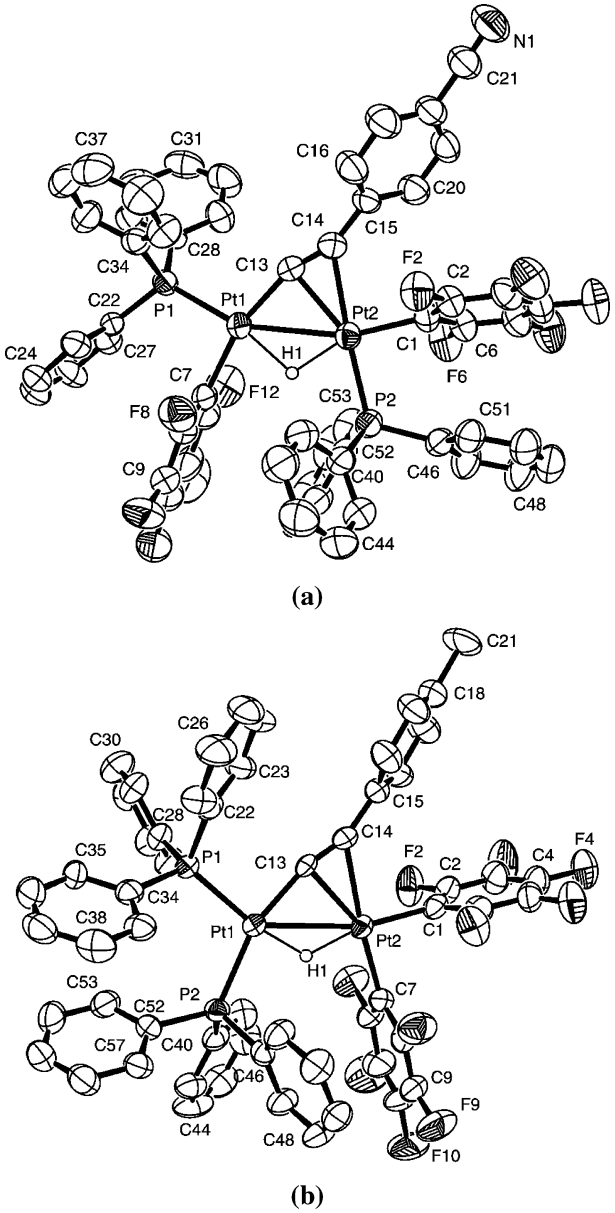

Figure 2. Molecular structures of (a) [*trans*-(PPh_3)(C_6F_5)Pt(μ-H){μ-1κC^α:η^2-C≡C(4-CN)C_6H_4}Pt(C_6F_5)(PPh_3)] (**3b**) and (b) [*cis,cis*-(PPh_3)$_2$Pt(μ-H){μ-1κC^α:η^2-C≡C(4-CH_3)C_6H_4}Pt(C_6F_5)$_2$] (**4a**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Although the hydride ligand has not been located in the structures of complexes **3a**, **4c**, and **4e**, the proton NMR spectra of all complexes show the expected hydride resonance as a doublet of doublets (between −7.11 (**4b**) and −7.68 (**3d**) ppm) with two different sets of ^{195}Pt satellites, in accordance with its bridging nature, as can be seen in Figure 3, as an illustrative example. In both types of complexes (**3** and **4**) the highest

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Table 2. Selected Bond Lengths (Å) and Angles (deg) for [*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-H){μ-1κC^{α}:η^2-C≡C(4-CN)C$_6$H$_4$}-Pt(C$_6$F$_5$)(PPh$_3$)] (3b) and [*cis,cis*-(PPh$_3$)$_2$Pt(μ-H)-{μ-1κC^{α}:η^2-C≡C(4-CH$_3$)C$_6$H$_4$}Pt(C$_6$F$_5$)$_2$]·CH$_2$Cl$_2$·H$_2$O (4a·CH$_2$Cl$_2$·H$_2$O)

	3b	**4a**·CH$_2$Cl$_2$·H$_2$O	
Pt(1)−C(13)	1.984(5)	1.989(6)	
Pt(1)−P(1)	2.2622(12)	2.2923(15)	
Pt(2)−P(2)	2.2521(13)	2.3181(17)	Pt(1)−P(2)
Pt(1)−Pt(2)	2.8409(3)	2.8459(3)	
Pt(1)−H(1)	1.83(6)	1.63(8)	
Pt(2)−C(1)	2.039(5)	2.034(7)	
Pt(1)−C(7)	2.053(5)	2.043(7)	Pt(2)−C(7)
Pt(2)−C(13)	2.230(5)	2.186(5)	
Pt(2)−C(14)	2.286(5)	2.325(6)	
Pt(2)−H(1)	1.72(6)	1.61(8)	
C(13)−C(14)	1.216(7)	1.213(9)	
P(1)−Pt(1)−C(7)	91.21(13)	106.50(6)	P(1)−Pt(1)−P(2)
C(13)−Pt(1)−Pt(2)	51.40(14)	50.00(15)	
P(1)−Pt(1)−Pt(2)	156.24(3)	141.57(4)	
C(7)−Pt(1)−Pt(2)	112.49(13)	111.93(4)	P(2)−Pt(1)−Pt(2)
P(1)−Pt(1)−H(1)	168.1(18)	169(3)	
C(7)−Pt(1)−H(1)	77.0(8)	84(3)	P(2)−Pt(1)−H(1)
C(1)−Pt(2)−P(2)	89.78(14)	85.6(3)	C(1)−Pt(2)−C(7)
C(1)−Pt(2)−C(13)	117.46(19)	119.8(2)	
C(1)−Pt(2)−C(14)	86.41(19)	88.8(2)	
C(1)−Pt(2)−Pt(1)	160.96(14)	163.80(18)	
P(2)−Pt(2)−Pt(1)	108.71(3)	110.50(18)	C(7)−Pt(2)−Pt(1)
C(1)−Pt(2)−H(1)	160.1(18)	167(3)	
P(2)−Pt(2)−H(1)	70.5(18)	82(3)	C(7)−Pt(2)−H(1)
Pt(1)−C(13)−C(14)	161.5(5)	166.5(5)	
C(13)−C(14)−C(15)	157.2(5)	158.6(6)	

coupling constant observed, $^2J_{H-P1}$ (96.5−69.8 Hz), is assigned to the phosphorus atom P1, which is seen practically *trans* to the hydride ligand in the solid state. Thus, the other constant, $^2J_{H-P2}$ (16.8−11.8 Hz), is attributed to the phosphorus atom P2, located in a practically *cis* arrangement to the hydride bridging ligand. For the "*trans*"-type derivatives, in which the hydride atom bonds two "Pt(C$_6$F$_5$)(PPh$_3$)" organometallic units, two rather similar coupling $^1J_{H-Pt}$ are observed ($^1J_{H-Pt1}$ 564−550 Hz, $^1J_{H-Pt2}$ 515−510 Hz), which have been assigned on the basis of the different *trans* influence of the C$_6$F$_5$ and PPh$_3$ ligands (C$_6$F$_5$ > PPh$_3$). The remarkable asymmetry of the "*gem*" isomers (**4**) is clearly reflected in the greater difference of the $^1J_{H-Pt}$ coupling constants ($^1J_{H-Pt1}$ 638−555 Hz, $^1J_{H-Pt2}$ 465−448 Hz).

Nevertheless, the most significant spectroscopic difference between both types of isomers is found in the ^{31}P NMR spectra (Figure 4). Both of them show the signals that are due to the presence of two nonequivalent PPh$_3$ ligands. However, while the "*gem*"-type complexes display two sharp doublet resonances ($^2J_{P-P} \approx 22$ Hz) with the corresponding platinum satellites, the "*trans*"-type derivatives show only two singlets with the corresponding platinum satellites, and because of this, the three-bond phosphorus−phosphorus coupling, $^3J_{P-P}$, is not resolved. In the "*trans*"-type complexes **3** (Figure 4a), the most deshielded singlet resonance (δ 27.4−29.2), which exhibits larger short-range ($^1J_{Pt1-P1}$ = 3853−3826 Hz) and long-range ($^2J_{Pt2-P1} \approx$ 100 Hz) coupling constants, is assigned to the nucleus P1, in accordance with the observed open angle P(1)−Pt(1)−Pt(2) (141.57(4)−157.92(6)°). The low-frequency signal centered at ca. 10 ppm, which exhibits only one set of platinum satellites ($^1J_{Pt2-P2}$ = 3593−3401 Hz) except for **3a** (R = (4-CH$_3$)C$_6$H$_4$, $^2J_{Pt1-P2}$ = 30 Hz), is, therefore, assigned to the phosphorus atom (P2) of the phosphine *cis* to the hydride ligand. The assignation has been unambiguously confirmed by recording the spectrum of complex **3a** while decoupling only the phosphine protons (Figure 4b). In this case, only the downfield signal (δP1 29.0) splits into a doublet by the large expected coupling to the *trans* bridging hydride ($^2J_{P1-H}$ = 75 Hz). For the "*gem*"-type complexes **4** (Figure 4c) the signals, which exhibit two sets of platinum satellites, have tentatively been assigned in accordance with the solid-state structures. Thus, the doublet with the bigger coupling constants (δ 13.2−11.0, $^1J_{P1-Pt1} \approx$ 3300 Hz, $^2J_{P1-Pt2}$ = 61.4−51.3 Hz) is assigned to the phosphorus atom P1, with the bigger angle P(1)−Pt(1)−Pt(2) (∼145°), while the other signal (δ 13.1−11.0, $^1J_{P2-Pt1}$ = 2810−2696 Hz, $^2J_{P2-Pt2}$ = 58.6−47.0 Hz) has been attributed to P(2) (P(2)−Pt(1)−Pt(2) ≈ 112°).

Reaction of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] with [*trans*-PtH{C≡C-(OH)Ph$_2$}(PPh$_3$)$_2$] (1f) and [Pt{η^2-HC≡C(OH)Ph$_2$}(PPh$_3$)$_2$] (2f). The disolvate [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] reacts with the mononuclear complexes derived from 1,1-diphenyl-2-propyn-1-ol [*trans*-PtH{C≡C(OH)Ph$_2$}(PPh$_3$)$_2$] (**1f**) and [Pt{η^2-HC≡C(OH)-Ph$_2$}(PPh$_3$)$_2$] (**2f**) in a different way (Scheme 2). As has been shown,[36] the hydride−acetylide complex **1f** has still not been prepared as a pure complex; it is always accompanied by variable amounts of the Pt(0) isomer **2f**. Thus, a mixture containing the Pt(II) alkynyl **1f** and the Pt(0) alkyne **2f** substrates (80/20 molar ratio, respectively) was reacted with an equimolecular amount of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] at room temperature (Scheme 2, i), and the reaction was studied by ^{31}P{^{1}H} NMR. As expected, the orange solution obtained after 2 min consisted of a mixture of the dinuclear (μ-hydride)(μ-acetylide) isomers [*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-H){μ-1κC^{α}:η^2-C≡CC(OH)Ph$_2$}Pt(C$_6$F$_5$)-(PPh$_3$)] (**3f**, "*trans*"-type) and [*cis,cis*-(PPh$_3$)$_2$Pt(μ-H){μ-1κC^{α}:η^2-C≡CC(OH)Ph$_2$}Pt(C$_6$F$_5$)$_2$] (**4f**, "*gem*"-type), from which pure complex **3f** can be isolated as a white complex with moderate yield (42%). However, it must be noted that the molar ratio observed in the reaction mixture (**3f**:**4f**, 85:15 vs **1f**:**2f**, 80:20) indicates that the "*gem*"-type isomer **4f** probably isomerizes to some extent to the "*trans*"-type **3f**. As has been mentioned, this kind of process has been observed in complexes **4a**−**e** but only at high temperature and with a considerable decomposition. The confirmation of this mild isomerization process was obtained in the study by ^{31}P{^{1}H} NMR of the reaction at room temperature between the corresponding equimolecular amounts of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] and [Pt{η^2-HC≡C(OH)Ph$_2$}(PPh$_3$)$_2$] (**2f**) (Scheme 2, ii). Surprisingly, after 2 min of reaction, the solution was observed to contain the "*trans*"-type isomer **3f** as the main product (molar ratio **3f**:**4f** 65:35), together with traces of the (μ-hydroxy)(μ-vinyl) complex [*cis,cis*-(PPh$_3$)$_2$Pt{μ-1κC^{α}:η^2-CH=CHC(OH)Ph$_2$}(μ-OH)Pt(C$_6$F$_5$)$_2$] (**5f**) (δP 22.8 (d), 8.1 (d)). Nevertheless, the low solubility of **4f** allows its precipitation from this solution mixture as a beige solid, although in low yield (19%). For complexes **3f** and **4f** no adequate crystals for X-ray diffraction studies have been obtained, but both of the complexes have been fully characterized by the usual analytical and spectroscopic means, with all the spectroscopic data being similar to those previously described for complexes **3a**−**e** and **4a**−**e** (see Experimental Section and Supporting Information).

Finally, the (μ-hydroxy)(μ-vinyl) complex **5f** can be obtained in good yield (77%) as a yellow solid by addition of two drops of deoxygenated water to an anhydrous solution of [Pt{η^2-HC≡C(OH)Ph$_2$}(PPh$_3$)$_2$] (**2f**) in CH$_2$Cl$_2$, followed by the immediate addition of a stoichiometric amount of [*cis*-Pt(C$_6$F$_5$)$_2$-(thf)$_2$] (Scheme 2, iii). Under these conditions, the reaction mixture is shown to contain (^{31}P{^{1}H} NMR) a mixture of the (μ-hydroxy)(μ-vinyl) complex **5f** and the "*trans*"-type (μ-hydride)(μ-acetylide) derivative **3f** (molar ratio 80:20, respectively), together with traces of the "*gem*"-type (μ-hydride)-(μ-acetylide) isomer **4f**.

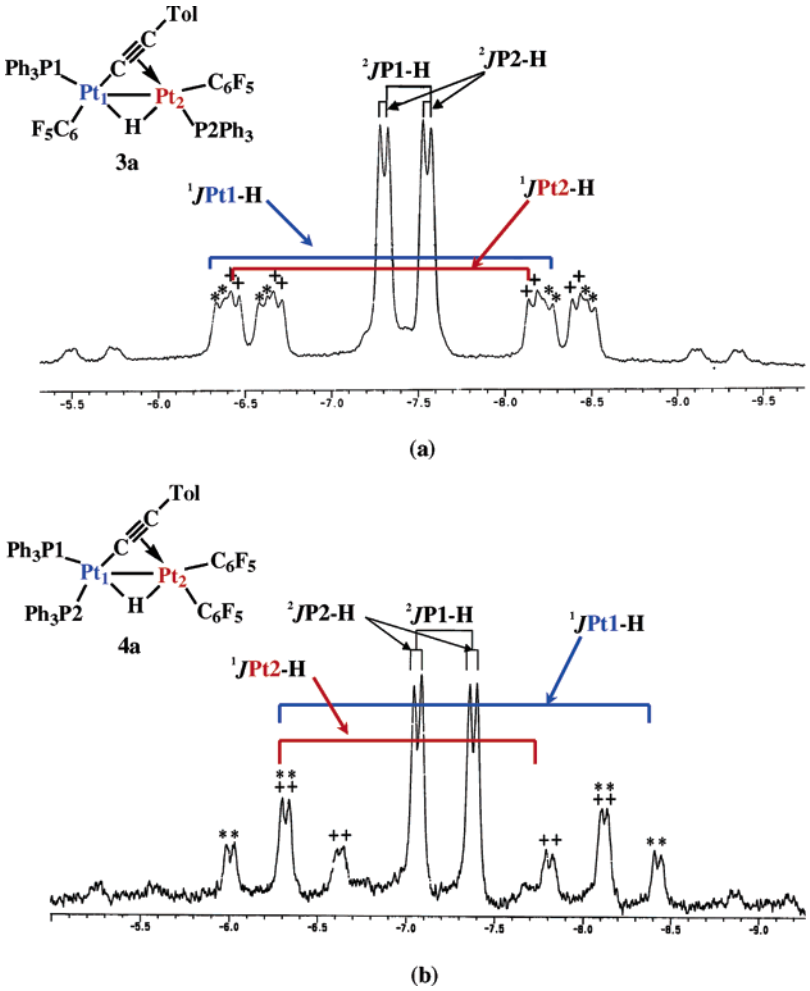

Figure 3. High-field region of the ^{1}H NMR spectra of **3a** (a) and **4a** (b).

In view of these results, we have tried to obtain some other counterpart dinuclear hydroxy−vinyl derivatives, starting from two representative Pt(0) mononuclear complexes, [Pt(η^2-HC≡CR)(PPh$_3$)$_2$] **2a** (R = (4-CH$_3$)C$_6$H$_4$) and **2d** (R = C(OH)Me$_2$), although in spite of the presence of water in both reactions only the "*gem*"-type complexes [*cis*,*cis*-(PPh$_3$)$_2$Pt-(μ-H)(μ-1κC^{α}:η^2-C≡CR)Pt(C$_6$F$_5$)$_2$] (R = (4-CH$_3$)C$_6$H$_4$, **4a**; C(OH)Me$_2$, **4d**) have been detected and isolated.

Complex **5f** has been characterized by an X-ray diffraction structural analysis (Figure 5, Table 3), confirming the presence of a mixed (μ-hydroxy)(μ-vinyl) bridging system. As far as we know, this structural feature has no precedent in the literature, the most similar examples being a (μ-hydroxy)(μ-alkyne) bridging system in a pentanuclear ruthenium cluster[41] and a (μ-hydroxy)(μ-allenylidene) trinuclear osmium cluster.[42] Notwithstanding, a good number of vinyl groups acting as bridging ligands between two transition metals have been reported,[43−51] although the examples containing platinum are really scarce,[52−58] in particular, those referring to homopolynuclear derivatives.[15,34,59] It should be noted that recently a (μ-hydride)-(μ-vinyl) dinuclear intermediate species has been proposed in the formation of the (μ-alkylidene) complex [Pt$_2$(dppm)$_2$(μ-H)-(μ-CHCH$_2$Ph)](BF$_4$).[28]

In **5f** both platinum centers present a practically square-planar environment, the dihedral angle between the two platinum coordination planes being 56.80(9)°. The loss of the planarity of **5f**, which contrasts to the planar cores shown by the (μ-hydride)(μ-acetylide) complexes **3** and **4**, is reflected in the dihedral angle between the vectors defined by Pt(1)−Pt(2) and

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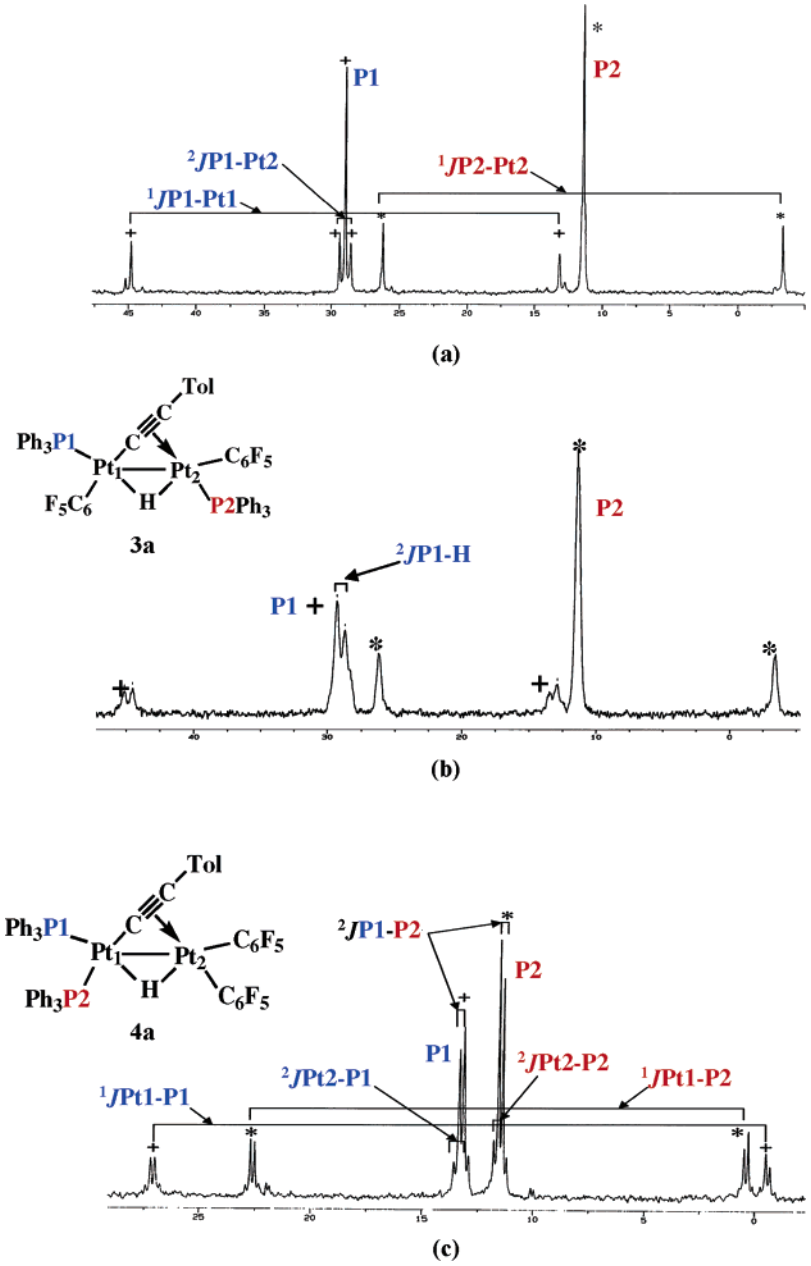

Figure 4. $^{31}P\{^1H\}$ NMR spectra of **3a** (a), **3a** with selective decoupling of the aromatic protons only (b), and **4a** (c).

C(13)−C(14) (57.11(24)°). The hydroxyl ligand connects both platinum atoms symmetrically (Pt(1)−O(1) 2.115(2) Å, Pt(2)−O(1) 2.107(3) Å), while the vinyl groups are σ-bonded to the atom Pt(1) (Pt(1)−C(13) 2.041(3) Å) and π-bonded in a slightly asymmetrical way to Pt(2) (Pt(2)−C(13), C(14) 2.216-(3), 2.257(3) Å). These features, as well as the C(13)═C(14) distance (1.373(5) Å), are similar to those observed for other μ-vinyl platinum derivatives.[15,34,52] In accordance with the formation of a 32-electron complex, the distance Pt···Pt of 3.06274(17) Å is larger than that observed for **3** and **4** (∼2.83 Å), indicating the absence of a Pt−Pt bond in this complex (in addition, no $^2J_{Pt-P}$ coupling constants are observed in the $^{31}P\{^1H\}$ NMR spectrum). Nevertheless, this distance is shorter than the sum of van der Waals radii (3.50 Å),[60] and the presence of any weak interaction between the metal centers cannot be excluded.[61−64] Finally, it should be noted that both Pt−P distances are quite different (Pt(1)−P(1), P(2) 2.2125(8), 2.3457-(9) Å), in agreement with the greater *trans* influence of the σ-vinyl group in relation to the hydroxy ligand. This structural feature has also been used in the assignation of the two doublets observed in the $^{31}P\{^1H\}$ NMR spectrum of **5f** (δP1 8.1, $^1J_{Pt1-P1}$ = 4272 Hz; δP2 22.8, $^1J_{Pt1-P2}$ = 1619 Hz; $^2J_{P-P}$ = 14.5 Hz). Its ^{19}F NMR spectrum confirms the presence of two nonequivalent pentafluorophenyl rings with different energetic barriers for rotation around the corresponding Pt−C(*ipso*) bonds, as is observed by the different pattern of the *ortho*-fluorine resonances of both rings (see Experimental Section).

The ^{195}Pt NMR spectrum has also been recorded. It shows only the signal assigned to Pt1 as a doublet of doublets at −4240

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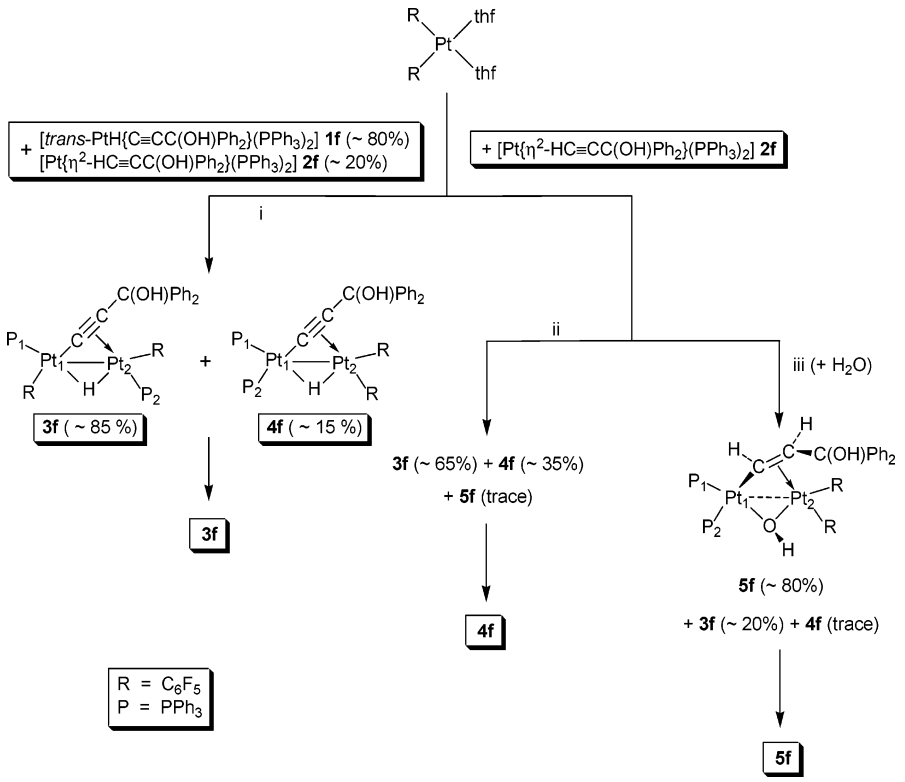
Scheme 2



ppm ($^1J_{Pt1-P1} \approx 4300$ Hz, $^1J_{Pt1-P2} \approx 1900$ Hz). We have not been able to observe the signal corresponding to Pt2, probably due to its coupling with the four *ortho*-F of the C_6F_5 groups. Particularly significant is the ^{1}H NMR spectrum of complex **5f**, which shows the signals due to the vinylic protons at δ 6.46 (H_α, dd, $^3J_{P-H} = 14.0$ Hz, $J_{H-H} = 7.4$ Hz, $-CH_\alpha{=}CH_\beta C(OH)Ph_2$) and 5.85 ($H_\beta$, m) (see Figure S2a in the Supporting Information). H_β is also coupled to the platinum nucleus Pt2, showing the corresponding platinum satellites ($^2J_{H\beta-Pt2} \approx 60$ Hz). This assignation has been confirmed by selective decoupling of Pt1 in the proton NMR spectrum, which shows no modification in the signal at 5.85 ppm, and also previous assignments in vinyl bridging ligands.[15,34,45,50,52,55,56,65,66] The C_α and C_β vinylic signals appear at 117.6 and 105.0 ppm, as has been confirmed by a C,H correlation experiment (see Figure S2b).

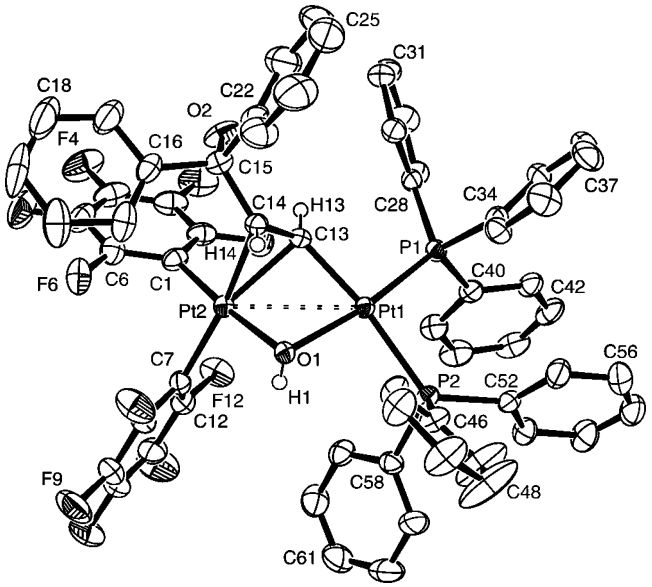


Figure 5. ORTEP view of [*cis,cis*-$(PPh_3)_2$Pt{μ-1κC^α:η^2-CH=CHC(OH)Ph_2}(μ-OH)Pt(C_6F_5)$_2$] (**5f**). Ellipsoids are drawn at the 50% probability level. Aromatic hydrogen atoms have been omitted for clarity.

With the aim of establishing the mechanism concerned with the formation of **5f**, we have carried out a series of experiments. First, it was confirmed by ^{1}H and ^{31}P{^{1}H} NMR spectroscopy in $CDCl_3$ that the alkyne precursor [Pt{η^2-HC≡C(OH)Ph_2}-(PPh_3)$_2$] (**2f**) does not react with H_2O (2 drops for 2 weeks). It was observed that water attacks only when [*cis*-Pt(C_6F_5)$_2$(THF)$_2$] is present in the reaction mixture and has started to react with the alkyne Pt(0) precursor. The reaction between [Pt{η^2-HC≡C(OH)Ph_2}(PPh_3)$_2$] (**2f**) and [*cis*-Pt(C_6F_5)$_2$(THF)$_2$] was also monitored (^{1}H, ^{19}F, and ^{31}P{^{1}H} NMR), starting from 223 K. (This reaction was not carried out in anhydrous conditions, but without addition of H_2O. See Experimental Section and Figure S3 in the Supporting Information for details.) On raising the temperature, the resonances due to the starting materials decreased in their relative intensity, while signals corresponding to a unique, new compound, which has been identified spectroscopically as the mixed-valence intermediate [*cis,cis*-$(PPh_3)_2$-Pt{μ-η^2:η^2-HC≡C(OH)Ph_2}Pt(C_6F_5)$_2$(thf)] (**6f**), appeared and grew in intensity until 263 K. Above this temperature, the signals due to **6f** started to decrease in intensity, while the resonances assigned to the (μ-hydroxy)(μ-vinyl) complex [*cis,cis*-$(PPh_3)_2$Pt{μ-1κC^α:η^2-CH=CHC(OH)Ph_2}(μ-OH)Pt(C_6F_5)$_2$] (**5f**) appeared. The signals corresponding to the (μ-hydride)-(μ-acetylide) isomers [*trans*-$(PPh_3)(C_6F_5)$Pt(μ-H){μ-1κC^α:η^2-C≡CC(OH)Ph_2}Pt(C_6F_5)(PPh_3)] (**3f**) and [*cis,cis*-$(PPh_3)_2$Pt-

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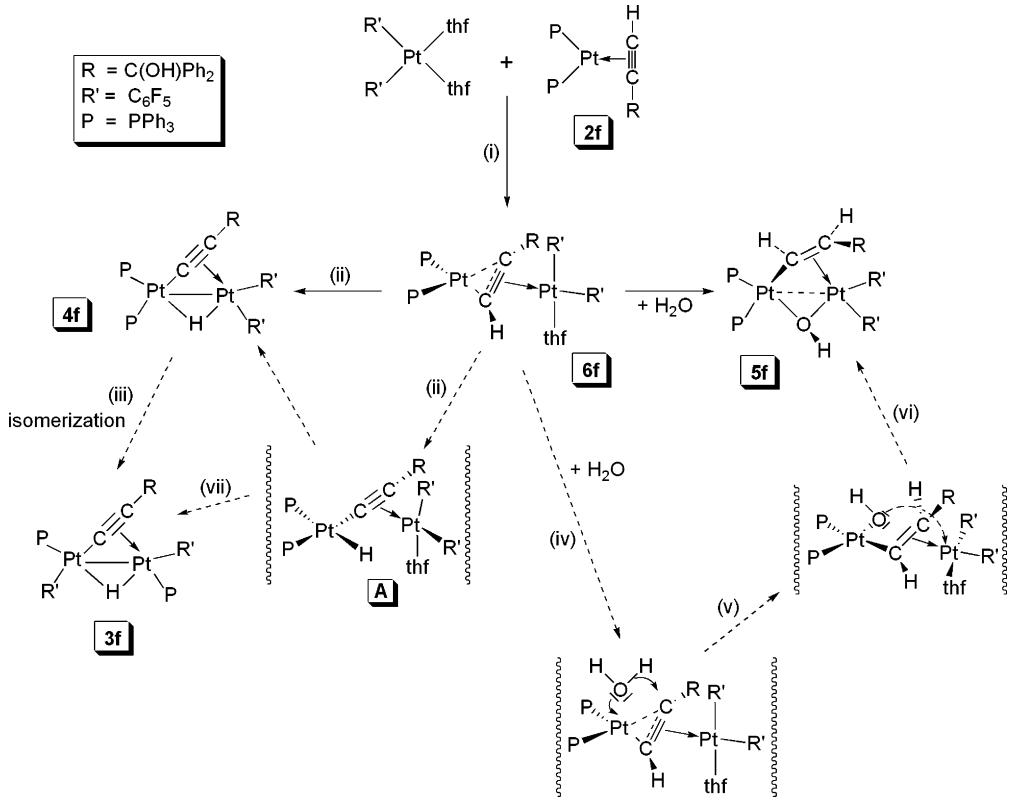
Table 3. Selected Bond Lengths (Å) and Angles (deg) for [*cis,cis*-$(PPh_3)_2Pt(\mu\text{-}OH)\{\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2\text{-}CH{=}CHC(OH)Ph_2\}Pt(C_6F_5)_2$] (5f)

Pt(1)−C(13)	2.041(3)	Pt(1)−P(1)	2.2125(8)	Pt(1)−P(2)	2.3457(9)
Pt(1)−O(1)	2.115(2)	Pt(2)−O(1)	2.107(3)	Pt(2)−C(1)	1.998(4)
Pt(2)−C(7)	2.021(3)	Pt(2)−C(13)	2.216(3)	Pt(2)−C(14)	2.257(3)
C(13)−C(14)	1.373(5)	C(14)−C(15)	1.523(5)	O(1)−H(1)	0.63(4)
Pt(1)−Pt(2)	3.06274(17)	C(13)−H(13)	0.92(3)	C(14)−H(14)	0.92(4)

C(13)−Pt(1)−P(1)	91.53(10)	P(1)−Pt(1)−P(2)	97.13(3)
C(13)−Pt(1)−O(1)	80.01(12)	O(1)−Pt(1)−P(2)	91.32(8)
P(1)−Pt(1)−Pt(2)	129.08(2)	P(2)−Pt(1)−Pt(2)	126.26(2)
C(1)−Pt(2)−C(7)	88.35(14)	C(7)−Pt(2)−O(1)	95.77(13)
O(1)−Pt(2)−C(13,14)	76.83	C(1)−Pt(2)−Pt(1)	131.68(11)
C(1)−Pt(2)−C(13,14)	99.01	C(7)−Pt(2)−Pt(1)	120.89(10)
Pt(1)−C(13)−C(14)	120.8(3)	C(13)−C(14)−C(15)	124.2(3)

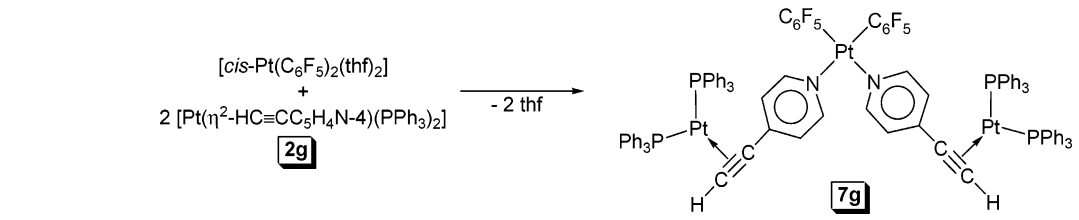
Scheme 3



(μ-H)$\{\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2\text{-}C{\equiv}CC(OH)Ph_2\}Pt(C_6F_5)_2$] (**4f**) were observed for the first time at 283 K, showing that, although the C−H activation process that is involved in their formation occurs in smooth conditions, it does not work at low temperature. Finally, at 293 K, the reaction mixture consists of a small amount (less than 10%) of **4f**, together with an approximately equimolecular mixture of **3f** and **5f**, revealing that the formation of **5f** is very sensitive to the presence of small amounts of water, since when the reaction is performed in anhydrous conditions (as previously described), only traces of **5f** can be detected.

The intermediate mixed-valence species **6f** has been detected by ^{1}H, ^{19}F, and ^{31}P$\{^1$H$\}$ NMR spectroscopy, and its spectroscopic data are given at 263 K (see Experimental Section). Thus, the ^{19}F NMR spectrum shows the signals corresponding to the presence of two nonequivalent C_6F_5 groups, while two doublet resonances with platinum satellites are observed in the phosphorus NMR spectrum (see Figure S3a), their corresponding coupling constants being similar to those observed for the Pt(0) precursor [Pt$\{\eta^2$-HC≡C(OH)Ph$_2\}$(PPh$_3)_2$] (**2f**) (δP 32.2, $^1J_{Pt-P} = 3665$ Hz; δP 27.9, $^1J_{Pt-P} = 3571.8$ Hz; $^2J_{P-P} = 14$ Hz **6f** vs δP 26.9, $^1J_{Pt-P} = 3553$ Hz; δP 24.9, $^1J_{Pt-P} = 3503$ Hz; $^2J_{P-P} = 27.5$ Hz **2f**). In the ^{1}H NMR spectrum, the most significant feature is the appearance of a doublet of doublets resonance, also with platinum satellites (δH 5.97, $^2J_{H-Pt} \approx 47$ Hz, $^3J_{H-Ptrans} \approx 24$ Hz, $^3J_{H-Pcis} \approx 7$ Hz, see Figure S3b), that is very similar to that observed for the acetylenic proton (≡C−H) in the precursor **2f** (δH 6.46, $^2J_{H-Pt} = 57.2$ Hz, $^3J_{H-Ptrans} = 22.7$ Hz, $^3J_{H-Pcis} = 9.6$ Hz). Bearing in mind the intermediate species **6f**, the mechanism illustrated in Scheme 3 could be tentatively proposed. It seems clear that in the absence of water, the coordination of the electron-acceptor synthon "*cis*-Pt$(C_6F_5)_2$(thf)" (Scheme 3, i) favors the activation of the acetylenic C−H bond and its subsequent oxidative addition on the Pt(0) center to give the "*gem*"-type derivative [*cis,cis*-$(PPh_3)_2Pt(\mu$-H$)\{\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2$-C≡CC(OH)Ph$_2\}Pt(C_6F_5)_2$] (**4f**) (Scheme 3, ii) and the "*trans*"-type isomer [*trans*-(PPh$_3$)(C_6F_5)Pt(μ-H)$\{\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2$-C≡CC(OH)Ph$_2\}Pt(C_6F_5)$(PPh$_3$)] (**3f**). Nevertheless, the coordination of the synthon "*cis*-Pt$(C_6F_5)_2$(thf)" should also decrease the electron density over the fragment "*cis*-Pt$(PPh_3)_2$", which could allow the nucleophillic attack of the water on the Pt(0) center (Scheme 3, iv), leading to the formation of the (μ-hydroxy)(μ-vinyl) complex [*cis,cis*-$(PPh_3)_2Pt\{\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2$-CH=CHC(OH)Ph$_2\}(\mu$-OH)Pt$(C_6F_5)_2$] (**5f**) (Scheme 3, steps v and vi). Notwithstanding, it must be noted that the substituent of the alkyne ligand (R = C(OH)Ph$_2$) must also play a certain role in the process, since we have not been able to obtain other related

Scheme 4



(μ-hydroxy)(μ-vinyl) species starting from **2a** and **2d**, as previously mentioned. In fact, it should be also noted that the formation of **3f** under these mild conditions in this system is rather surprising, and it is unclear at this moment whether **3f** comes from isomerization of the final **4f** (Scheme 3, iii) or, more likely, by isomerization of a previous 32e$^-$ intermediate species such as **A** (Scheme 3, vii).

Reaction of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] with [Pt(η^2-HC≡CC$_5$H$_4$N-4)(PPh$_3$)$_2$] (2g). As commented on in the Introduction, some time ago we reported that the treatment of the pyridylacetylide complex [*trans*-PtH(C≡CC$_5$H$_4$N-2)(PPh$_3$)$_2$] with [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] affords the initial adduct [*trans*,*cis*-(PPh$_3$)$_2$HPt(μ-1κC^α:$\eta^2_{\alpha,\beta}$:2κN-C≡CC$_5$H$_4$N-2)Pt(C$_6$F$_5$)$_2$], which finally rearranges to form an unexpected tetranuclear platinum cluster containing a vinyl group capping three platinum atoms.[34] This reaction, which reveals the influence of the donor nitrogen atom at the pyridyl−acetylide ligand in the course of this type of reactions, has encouraged us to explore the reactivity of the Pt(II) isomer [*trans*-PtH(C≡CC$_5$H$_4$N-4)(PPh$_3$)$_2$], with the nitrogen atom in the *para* position. Unfortunately, we have not succeeded in obtaining this complex, although the new Pt(0) isomer [Pt(η^2-HC≡CC$_5$H$_4$N-4)(PPh$_3$)$_2$] (**2g**) is easily synthesized.

A completely different reaction route has been found in the reaction of [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] with [Pt(η^2-HC≡CC$_5$H$_4$N-4)(PPh$_3$)$_2$], **2g**. Thus, the equimolecular reaction leads only to complex mixtures, from which we have not been able to isolate a pure complex. Nevertheless, when the reaction is carried out using 2 equiv of the Pt(0) substrate **2g** (Scheme 4), a stable yellow solid, identified as the trinuclear mixed-valence adduct [{(PPh$_3$)$_2$Pt(μ-η^2:2κN-HC≡CC$_5$H$_4$N-4)}$_2${*cis*-Pt(C$_6$F$_5$)$_2$}] (**7g**), is obtained in good yield (76%). This complex is also stable in solution for a long time if it is stored cold.

7g has been fully characterized by the usual analytical and spectroscopic means, and all the spectroscopic data are in agreement with the proposed structure (see Experimental Section). In accordance with the presence of the Pt(0) fragments "*cis*-Pt(PPh$_3$)$_2$" bonded in a η^2-fashion to the triple bond of the alkynes, the IR spectrum shows a medium-intensity absorption at 1685 cm^{-1} and in the proton NMR spectrum the signal due to the acetylenic proton is observed as a doublet of doublets at 7.51 ppm ($^3J_{Ptrans-H}$ = 21.1 Hz, $^3J_{Pcis-H}$ = 12.0 Hz). The ^{31}P{^{1}H} and ^{13}C{^{1}H} spectra display resonances corresponding to the presence of two types of nonequivalent PPh$_3$ ligands, these signals being very similar to those observed for the mononuclear Pt(0) precursor **2f** (e.g., δP 27.3, $^1J_{Pt-P}$ = 3477.8 Hz; δP 25.8, $^1J_{Pt-P}$ = 3587.8 Hz; $^2J_{P-P}$ = 26.8 Hz **7g** vs δP 28.8, $^1J_{Pt-P}$ = 3499.6 Hz; δP 26.0, $^1J_{Pt-P}$ = 3527.5 Hz; $^2J_{P-P}$ = 29.8 Hz **2f**). Finally, the symmetry of the molecule is well established by the presence of only three signals (δF −120.48, $^3J_{Pt-F} \approx$ 470, 4*ortho*-F; δF −163.66, 2*para*-F; δF −165.52, 4*meta*-F) in the ^{19}F NMR spectrum, which indicates that both of the C$_6$F$_5$ rings are chemically equivalent.

Conclusions

In this paper we explore the influence of the nature of the radicals in the alkynylic rest (≡C−R) in two easy entries to polymetallic mixed-bridged (μ-hydride)(μ-acetylide) complexes. Thus, a good number of new functionalized isomeric derivatives [*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(μ-H)(μ-1κC^α:η^2-C≡CR)Pt(C$_6$F$_5$)-(PPh$_3$)] (**3**, "*trans*"-type) and [*cis*,*cis*-(PPh$_3$)$_2$Pt(μ-H)(μ-1κC$^\alpha$:η^2-C≡Cr)Pt(C$_6$F$_5$)$_2$] (**4**, "*gem*"-type) (R = (4-CH$_3$)-C$_6$H$_4$, **a**; (4-CN)C$_6$H$_4$, **b**; CMe=CH$_2$, **c**; C(OH)Me$_2$, **d**; C(OH)EtMe, **e**; C(OH)Ph$_2$, **f**) have been prepared by reaction of the disolvated [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] with the corresponding Pt(II) [*trans*-PtH-(C≡CR)(PPh$_3$)$_2$] (**1**) or Pt(0) [Pt(η^2-HC≡CR)(PPh$_3$)$_2$] (**2**) isomers. The most thermodynamically stable of the two dinuclear isomers seem to be the "*trans*"-type derivatives **3**, since continuous heating of solutions of the "*gem*"-type complexes **4** leads to their isomerization to **3**, although with abundant decomposition. In spite of being such different processes, the first involves a deep reorganization of the ligands around the metal centers, while the second occurs through a C−H activation of the acetylenic proton, the formation of both of the (μ-hydride)(μ-acetylide) compounds occurs in mild conditions, and they seem to be rather general. Notwithstanding, the course of the reaction with the alkyne Pt(0) precursors can be influenced by the nature of the same radicals at the alkynylic rest (≡C−R). Thus, the use of [Pt{η^2-HC≡C(OH)Ph$_2$}(PPh$_3$)$_2$] (**2f**) in the presence of water leads to the formation of the unexpected (μ-hydroxy)(μ-vinyl) complex [*cis*,*cis*-(PPh$_3$)$_2$Pt{μ-1κC^α:η^2-CH=CHC(OH)Ph$_2$}(μ-OH)Pt(C$_6$F$_5$)$_2$] (**5f**), while the reaction with [Pt(η^2-HC≡C$_5$H$_4$N-4)(PPh$_3$)$_2$] (**2g**) produces the stable trinuclear mixed-valence adduct [{(PPh$_3$)$_2$Pt(μ-η^2:2κN-HC≡CC$_5$H$_4$N-4)}$_2${*cis*-Pt(C$_6$F$_5$)$_2$}] (**7g**).

Experimental Section

All reactions were carried out under an atmosphere of dry argon, using standard Schlenk techniques. Solvents were dried by standard procedures and distilled under dry Ar before use. 1-Cyano-4-ethynylbenzene[67] was prepared by literature methods, while the rest of the alkynes and NEt$_2$H were used as received. NMR spectra were recorded at 293 K on a Bruker ARX 300 or ARX 400 spectrometer. Chemical shifts are reported in ppm relative to external standards (SiMe$_4$, CFCl$_3$, 85% H$_3$PO$_4$, or Na$_2$PtCl$_6$ in D$_2$O for ^{195}Pt), and all coupling constants are given in Hz. The NMR spectral assignments of the alkynyl ligands containing substituted aryl and pyridyl groups follow the numbering scheme shown in Figure 6. IR spectra were obtained on Perkin-Elmer 883 or Perkin-Elmer FT-IR Spectrum 1000 spectrometers, using Nujol mulls between polyethylene sheets. Elemental analyses were carried out with a Perkin-Elmer 2400 CHNS/O or Carlo Erba EA1110 CHNS-O microanalyzer. Mass spectra were recorded on a HP-5989B (ES) or a VG Autospec double-focusing (FAB) mass spectrometer. [*trans*-PtHCl(PPh$_3$)$_2$],[68] [*trans*-PtH(C≡CR)(PPh$_3$)$_2$] (R = CMe=CH$_2$, **1c**; C(OH)Me$_2$, **1d**; C(OH)EtMe, **1e**),[35] [η^2-Pt-(HC≡CCMe$_2$=CH$_2$)(PPh$_3$)$_2$] (**2c**),[69] [Pt{η^2-HC≡CC(OH)Ph$_2$}-

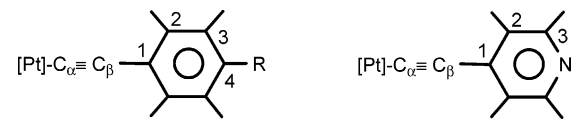


Figure 6.

$(PPh_3)_2$] (**2f**) and its mixture with [*trans*-PtH{C≡CC(OH)Ph_2}-$(PPh_3)_2$] (**1f**),[36] and [*cis*-Pt$(C_6F_5)_2$(thf)$_2$][70] were prepared by published methods. The syntheses of the rest of the complexes **1** and **2**, as well as the derivatives **3b**−**e** and **4b**−**e**, are included in the Supporting Information.

Synthesis of [*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡C(4-CH$_3$)C$_6$H$_4$}Pt(C$_6$F$_5$)(PPh$_3$)] (3a). [*cis*-Pt$(C_6F_5)_2$(thf)$_2$] (0.15 g, 0.22 mmol) was added to a CH_2Cl_2 solution (20 mL) of [*trans*-PtH-{C≡C(4-CH_3)C_6H_4}$(PPh_3)_2$]·$CHCl_3$ (**1a**) (0.20 g, 0.21 mmol), and the mixture was stirred at room temperature for 30 min. The resulting pale orange solution was evaporated to dryness, and the residue was treated with hexane, yielding **3a** as a white solid. Yield: 0.25 g (87%). Anal. Calcd for $C_{57}F_{10}H_{38}P_2Pt_2$: C, 50.15; H, 2.81. Found: C, 49.72; H, 3.04. MS ES(+): *m*/*z* 1474 [M + Ag + H]$^+$ 100% (sample ionizated with Ag$^+$). IR (cm^{-1}): *ν*(C≡C) 2018 (w); *ν*$(C_6F_5)_{x-sensitive}$ 820 (m), 794 (m). ^{1}H NMR ($CDCl_3$, *δ*): 7.61 (m, 6H), 7.33 (m, 24H) (Ph, PPh_3); 6.93, 6.82 (AB, J_{H-H} = 7.4, 4H, C_6H_4, Tol); 2.20 (s, 3H, CH_3, Tol); −7.42 (dd, $^2J_{P1-H}$ = 74.6, $^2J_{P2-H}$ = 13.9, $^1J_{Pt1-H}$ = 564.0, $^1J_{Pt2-H}$ = 510.0, Pt−*μ*H−Pt). ^{13}C NMR ($CDCl_3$, *δ*): 148−134.5 (C_6F_5); 138.6 (s, C^4); 134.3 (d, $^2J_{C-P}$ = 12.0, *ortho*-C, Ph, PPh_3); 133.8 (d, $^2J_{C-P}$ = 11.1, *ortho*-C, Ph, PPh_3); 131.0 (d, $^4J_{C-P}$ = 2.6, *para*-C, Ph, PPh_3); 130.8 (d, $^4J_{C-P}$ = 2.5, *para*-C, Ph, PPh_3); 131.4, 131.2, 130.4, 130.2, 129.3 (C^2, C^3, 2*ipso*-C of Ph); 128.1 (d, $^3J_{C-P}$ = 7.3, *meta*-C, Ph, PPh_3); 128.0 (d, $^3J_{C-P}$ = 7.3, *meta*-C, Ph, PPh_3); 121.7 (d, $^4J_{C-P}$ = 3.5, $^3J_{Pt-C}$ = 21.4, C^1); 110.4 (d, $^2J_{C-P}$ = 20.8, C$_α$); 21.3 (s, CH_3). ^{19}F NMR ($CDCl_3$, *δ*): −116.33 (dd, $^3J_{Pt-F}$ = 288.0, 2*ortho*-F); −118.62 (d, $^3J_{Pt-F}$ = 346.1, 2*ortho*-F); −163.87 (tt, 1*para*-F); −164.39 (m, 2*meta*-F); −164.68 (t, 1*para*-F); −165.30 (m, 2*meta*-F). ^{31}P NMR ($CDCl_3$, *δ*): 29.0 (s, $^1J_{Pt1-P1}$ = 3845.7, $^2J_{Pt2-P1}$ = 97.4, P1 *trans* to hydride); 11.5 (s, $^1J_{Pt2-P2}$ = 3593.0, $^2J_{Pt1-P2}$ ≈ 30, P2 *trans* to C≡C).

Synthesis of [*trans*-(PPh$_3$)(C$_6$F$_5$)Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)Ph$_2$}Pt(C$_6$F$_5$)(PPh$_3$)] (3f). To a solution of 0.14 g (0.15 mmol) of a mixture of [*trans*-PtH{C≡CC(OH)Ph_2}$(PPh_3)_2$] (**1f**) and [Pt-{*η*^{2}-HC≡C(OH)Ph_2}$(PPh_3)_2$] (**2f**) (molar ratio ∼80:20, respectively) in CH_2Cl_2 (∼15 mL) was added 0.10 g (0.15 mmol) of [*cis*-Pt-$(C_6F_5)_2$(thf)$_2$], and the reaction was studied by ^{31}P{^{1}H} NMR. After 2 min the orange solution obtained consisted of a mixture of complex **3f** and its isomer [*cis*,*cis*-$(PPh_3)_2$Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)Ph_2}Pt$(C_6F_5)_2$] (**4f**), in a molar ratio ∼85:15, respectively. The solution was evaporated to dryness and the solid residue treated with MeOH to give an orange solid. Its recrystallization from $CHCl_3$/hexane afforded pure **3f** as a white solid. Yield: 0.09 g (42%). Anal. Calcd for $C_{63}F_{10}H_{42}OP_2Pt_2$: C, 51.93; H, 2.91. Found: C, 51.50; H, 2.36. MS ES(+): *m*/*z* 1313 [M − (C_6F_5) + Na + H]$^+$ 1%; 1052 [M − (C_6F_5) − (PPh_3) + Na + 2H]$^+$ 28%; 831 [Pt(CCCPh$_2$OH)$(C_6F_5)(PPh_3)$]$^+$ 5%; 791 [M − (C_6F_5) − 2(PPh_3) + Na + 3H]$^+$ 100%; 628 [Pt$(C_6F_5)(PPh_3)$ + 4H]$^+$ 37%; (sample ionized with Na$^+$). IR (cm^{-1}): *ν*(OH) 3598 (m); *ν*(C≡C) 2019 (w); *ν*$(C_6F_5)_{x-sensitive}$ 794 (m). ^{1}H NMR ($CDCl_3$, *δ*): 7.43, 7.34, 7.12, 6.91, 6.86 (m, 40H, Ph, PPh_3, and C(OH)Ph_2); 2.71 (s, 1H, OH); −7.57 (dd, $^2J_{P1-H}$ = 72.4, $^2J_{P2-H}$ = 13.6, $^1J_{Pt1-H}$ ≈ 550, $^1J_{Pt2-H}$ ≈ 505, Pt−*μ*H−Pt). ^{13}C NMR ($CDCl_3$, *δ*): 150−135 (C_6F_5); 145.5 (tentatively attributed to *ipso*-C, Ph, C(OH)Ph_2); 134.3 (d, $^2J_{C-P}$ = 12.2, *ortho*-C, Ph, PPh_3); 133.8 (d, $^2J_{C-P}$ = 11.5, *ortho*-C, Ph, PPh_3); 131.1 (s), 130.9 (s) (*para*-C, Ph, PPh_3; the signals due to *ipso*-C of both PPh_3 overlap with the *para*-C); 128.1, 128.0 (s, *meta*-C, Ph, PPh_3); 127.5 (s, *ortho*-C, Ph, C(OH)Ph_2); 126.8 (s, *para*-C, Ph, C(OH)Ph_2); 124.9 (s, *meta*-C, Ph, C(OH)Ph_2); *C*(OH)-Ph_2, $C_α$ and $C_β$ are not seen in the spectrum. ^{19}F NMR ($CDCl_3$, *δ*): −115.00 (d, $^3J_{Pt-F}$ = 362.6, 2*ortho*-F); −115.98 (dd, $^3J_{Pt-F}$ = 286.5, 2*ortho*-F); −162.60 (m, 1*para*-F); −163.45 (m, 2*meta*-F); −164.41 (t, 1*para*-F); −165.01 (m, 2*meta*-F). ^{31}P NMR ($CDCl_3$, *δ*): 29.4 (s, $^1J_{Pt1-P1}$ = 3811.2, $^2J_{Pt2-P1}$ = 99.6, P1 *trans* to hydride); 10.1 (s, $^1J_{Pt2-P2}$ = 3441.8, P2 *trans* to C≡C).

Synthesis of [*cis*,*cis*-(PPh$_3$)$_2$Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡C(4-CH$_3$)-C$_6$H$_4$}Pt(C$_6$F$_5$)$_2$] (4a). [*cis*-Pt$(C_6F_5)_2$(thf)$_2$] (0.10 g, (0.15 mmol) was added to a CH_2Cl_2 solution (10 mL) of [Pt{*η*^{2}-HC≡C(4-CH_3)-C_6H_4}$(PPh_3)_2$] (**2a**) (0.13 g, 0.16 mmol), and the mixture was stirred at room temperature for 5 min. The resulting orange solution was evaporated to dryness, and the residue was treated with cold EtOH, yielding **4a** as a beige solid. Yield: 0.10 g (65%). Anal. Calcd for $C_{57}F_{10}H_{38}P_2Pt_2$: C, 50.15; H, 2.81. Found: C, 50.47; H, 2.50. MS ES(−): *m*/*z* 736 [Pt(CCTol)$(C_6F_5)(PPh_3)$ − 3]$^-$ 20%; 563 [Pt$(PPh_2)_2$ − 2]$^-$ 100%; 530 [Pt$(C_6F_5)_2$ + 1] 15%. IR (cm^{-1}): *ν*(C≡C) 2019 (w); *ν*$(C_6F_5)_{x-sensitive}$ 803 (m), 794 (m). ^{1}H NMR ($CDCl_3$, *δ*): 7.39, 7.27, 7.15 (m, 30H, Ph, PPh_3); 6.73 (d, J_{H-H} = 7.3, 2H), 6.55 (d, J_{H-H} = 7.3, 2H) (C_6H_4, Tol); 2.19 (s, 3H, CH_3, Tol); −7.21 (dd, $^2J_{P1-H}$ = 96.5, $^2J_{P2-H}$ = 13, $^1J_{Pt1-H}$ = 638, $^1J_{Pt2-H}$ = 448, Pt−*μ*H−Pt). ^{19}F NMR ($CDCl_3$, *δ*): −116.86 (dm, $^3J_{Pt-F}$ = 406.2, 2*ortho*-F); −118.78 (d, $^3J_{Pt-F}$ = 458.4, 2*ortho*-F); −164.48 (t, 1*para*-F); −164.52 (t, 1*para*-F); −165.32 (m, 2*meta*-F); −165.65 (m, 2*meta*-F). ^{31}P NMR ($CDCl_3$, *δ*): 13.2 (d, $^1J_{Pt1-P1}$ = 3364.9, $^2J_{Pt2-P1}$ = 55.8, $^2J_{P-P}$ = 22.4, P1 *trans* to hydride); 11.5 (d, $^1J_{Pt1-P2}$ = 2701.0, $^2J_{Pt2-P2}$ = 48.5, $^2J_{P-P}$ = 22.4, P2 *trans* to *σ*-C≡C). The complex is not soluble enough for ^{13}C NMR.

Synthesis of [*cis*,*cis*-(PPh$_3$)$_2$Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)-Ph$_2$}Pt(C$_6$F$_5$)$_2$] (4f). [*cis*-Pt$(C_6F_5)_2$(thf)$_2$] (0.14 g, 0.21 mmol) was added to a solution of 0.20 g (0.21 mmol) of [Pt{*η*^{2}-HC≡C(OH)-Ph_2}$(PPh_3)_2$] (**2f**) in CH_2Cl_2 (∼20 mL), and the reaction was studied by ^{31}P{^{1}H} NMR. After 2 min, the orange solution obtained consisted of a mixture of the isomers [*trans*-$(PPh_3)(C_6F_5)$Pt(*μ*-H)-{*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)Ph_2}Pt$(C_6F_5)(PPh_3)$] (**3f**) and [*cis*,*cis*-$(PPh_3)_2$Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)Ph_2}Pt$(C_6F_5)_2$] (**4f**) (molar ratio ∼65:35, respectively) and traces of the (*μ*-hydroxy)(*μ*-vinyl) complex [*cis*,*cis*-$(PPh_3)_2$Pt{*μ*-1*κC*^{α}:*η*^{2}-CH═CHC(OH)Ph_2}(*μ*-OH)-Pt$(C_6F_5)_2$] (**5f**). The solution was evaporated to small volume (∼4 mL), and 5 mL of EtOH was added. On cooling the mixture, **4f** was obtained as a beige solid. Yield: 0.06 g (19%). Anal. Calcd for $C_{63}F_{10}H_{42}OP_2Pt_2$: C, 51.93; H, 2.91. Found: C, 51.41; H, 3.60. MS ES(+): *m*/*z* 1052 [M − (C_6F_5) − (PPh_3) + Na + 2H]$^+$ 16%; 833 [Pt(CCCPh$_2$OH)$(C_6F_5)(PPh_3)$ + 2H]$^+$ 14%; 791 [M − (C_6F_5) − 2(PPh_3) + Na + 3H]$^+$ 100%; 721 [Pt$(PPh_3)_2$ + 2H]$^+$ 20%; 628 [Pt$(C_6F_5)(PPh_3)$ + 4H]$^+$ 18% (sample ionized with Na$^+$). IR (cm^{-1}): *ν*(OH) 3592 (w); *ν*(C≡C) 1987 (w); *ν*$(C_6F_5)_{x-sensitive}$ 802 (s), 793 (s). ^{1}H NMR ($CDCl_3$, *δ*): 7.26, 7.14, 6.87, 6.80 (m, 40H, Ph, PPh_3, and C(OH)Ph_2); 3.13 (s, 1H, OH); −7.74 (dd, $^2J_{P1-H}$ = 91.1, $^2J_{P2-H}$ = 11.7, $^1J_{Pt1-H}$ ≈ 640, $^1J_{Pt2-H}$ ≈ 460, Pt-*μ*H−Pt). ^{19}F NMR ($CDCl_3$, *δ*): −115.55 (m, $^3J_{Pt-F}$ ≈ 486, 2*ortho*-F); −118.57 (dm $^3J_{Pt-F}$ ≈ 414, 2*ortho*-F); −163.34 (t, 1*para*-F); −163.59 (t, 1*para*-F); −164.28 (m, 2*meta*-F); −164.84 (m, 2*meta*-F). ^{31}P NMR ($CDCl_3$, *δ*): 15.3 (d, $^1J_{Pt1-P2}$ = 2849.0, $^2J_{Pt2-P2}$ ≈ 60, $^2J_{P1-P2}$ = 22.4, P2 *trans* to C≡C); 14.1 (d, $^1J_{Pt1-P1}$ ≈ 3250, $^2J_{P1-P2}$ = 22.4, P1 *trans* to hydride). The complex is not soluble enough for ^{13}C NMR.

Synthesis of [*cis*,*cis*-(PPh$_3$)$_2$Pt{*μ*-1*κC*^{α}:*η*^{2}-CH═CHC(OH)-Ph$_2$}(*μ*-OH)Pt(C$_6$F$_5$)$_2$] (5f). Two drops of deoxygenated water were added to a solution of 0.05 g (0.05 mmol) of [Pt{*η*^{2}-HC≡C(OH)-Ph_2}$(PPh_3)_2$] (**2f**) in CH_2Cl_2 (∼15 mL), and then 0.04 g (0.05 mmol) of [*cis*-Pt$(C_6F_5)_2$(thf)$_2$] was also added to the mixture, which was studied by ^{31}P{^{1}H} NMR. After 2 min the orange solution obtained consists of a mixture of the (*μ*-hydride)(*μ*-alkynyl) complex [*trans*-$(PPh_3)(C_6F_5)$Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)Ph_2}Pt$(C_6F_5)(PPh_3)$] (**3f**) and the (*μ*-hydroxy)(*μ*-vinyl) complex [*cis*,*cis*-$(PPh_3)_2$Pt{*μ*-1*κC*^{α}:*η*^{2}-CH═CHC(OH)Ph_2}(*μ*-OH)Pt$(C_6F_5)_2$] (**5f**) (molar ratio ∼20:80, respectively) and traces of [*cis*,*cis*-$(PPh_3)_2$Pt(*μ*-H){*μ*-1*κC*^{α}:*η*^{2}-C≡CC(OH)Ph_2}Pt$(C_6F_5)_2$] (**4f**). The solution was evaporated to small volume (∼1 mL), and 5 mL of cold hexane was added, causing

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the precipitation of **5f** as a yellow solid. Yield: 0.06 g (77%). Anal. Calcd for $C_{63}F_{10}H_{44}O_2P_2Pt_2$: C, 51.30; H, 3.01. Found: C, 51.09; H, 2.99. MS ES(+): *m*/*z* 1052 [M − (C_6F_5) − (PPh_3) − (H_2O) + Na + 2H]$^+$ 13%; 910 [Pt(CCCPh$_2$)(PPh_3)$_2$]$^+$ 7%; 791 [M − (C_6F_5) − 2(PPh_3) − (H_2O) + Na + 3H]$^+$ 100% (sample ionized with Na$^+$). IR (cm^{-1}): ν(OH) 3580 (m), 3562 (m); ν(C═C) 1603 (w); ν(C_6F_5)$_{x-sensitive}$ 806 (m), 794 (m). ^{1}H NMR ($CDCl_3$, δ): 7.67, 7.46, 7.28, 7.15, 7.00, 6.89 (m, 40H, Ph, PPh_3, and C(OH)Ph$_2$); 6.46 (dd, $^3J_{H-P}$ = 14.0, $^3J_{H-H}$ = 7.4, 1H, μ-C$_\alpha$*H*═C$_\beta$H); 5.85 (m, J_{H-Pt} ≈ 60, $^3J_{H-H}$ = 7.4, 1H, μ-C$_\alpha$H═C$_\beta$*H*); 1.34 (s, 1H, OH); −0.33 (s, 1H, OH). ^{13}C NMR ($CDCl_3$, δ): 140−135 (*C*$_6$F$_5$); 146.2, 146.1 (s, *ipso*-C, Ph, C(OH)Ph$_2$); 134.4 (d, $^2J_{C-P}$ = 11.2, *ortho*-C, Ph, PPh_3); 134.2 (d, $^2J_{C-P}$ = 11.7, *ortho*-C, Ph, PPh_3); 131.2 (s), 131.0 (s), (*para*-C, Ph, PPh_3); 129.2(d, $^1J_{P-C}$ ≈ 60, *ipso*-C, Ph, PPh_3; this signal, with the appearance of an overlapped doublet of doublets, overlaps with the next signal); 128.8 (d, $^3J_{P-C}$ = 10.2, *meta*-C, Ph, PPh_3); 128.5 (d, $^3J_{P-C}$ = 11.6, *meta*-C, Ph, PPh_3; This signal probably overlaps with a signal due to *para*-C of C(OH)Ph$_2$); 128.2, 127.6, 127.0, 126.1 (*para*-C); 126.0 (s, Ph, C(OH)Ph$_2$); 117.6 (C$_\alpha$, C═C); 105.0 (C$_\beta$, C═C); 77.9 (d, $^4J_{P-C}$ = 6.7, C(OH)Ph$_2$). ^{19}F NMR ($CDCl_3$, δ): −114.94 (d, $^3J_{Pt-F}$ ≈ 400, 1*ortho*-F); −118.76 (d, $^3J_{Pt-F}$ ≈ 400, 1*ortho*-F); −119.26 (d, $^3J_{Pt-F}$ ≈ 420, 2*ortho*-F); −162.04 (t, 1*para*-F); −162.74 (t, 1*para*-F); −164.53 (m, 2*meta*-F); −164.85 (m, 1*meta*-F); −165.34 (m, 1*meta*-F). ^{31}P NMR ($CDCl_3$, δ): 22.8 (d, $^1J_{Pt-P2}$ = 1619.0, $^2J_{P1-P2}$ = 14.5, P2 *trans* to CH═CH); 8.1 (d, $^1J_{Pt-P1}$ = 4272.0, $^2J_{P1-P2}$ = 14.5, P1 *trans* to hydroxy). ^{195}Pt NMR ($CDCl_3$, δ): −4240 (dd, $^1J_{Pt1-P1}$ ≈ 4300, $^1J_{Pt1-P2}$ ≈ 1900, Pt1); the signal due to Pt2 is not observed probably because of the coupling with the *ortho*-F of the C_6F_5 groups.

Study of the Reaction between [Pt{η^2-HC≡CC(OH)Ph$_2$}(PPh$_3$)$_2$] (2f) and [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] at NMR Scale. This reaction was not done in anhydrous conditions. [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] (0.013 g, 0.02 mmol) was added, at 223 K, to a solution of [Pt{η^2-HC≡C(OH)Ph$_2$}(PPh_3)$_2$] (**2f**) (0.019 g, 0.02 mmol) in 1 mL of $CDCl_3$, and the mixture was studied by multinuclear NMR spectroscopy (^{1}H, ^{19}F, and ^{31}P{^{1}H}). On raising the temperature, the resonances due to the starting materials decreased in their relative intensity, while signals corresponding to a unique, new compound, which has been identified as the mixed-valence intermediate [*cis*,*cis*-(PPh_3)$_2$Pt{μ-η^2:η^2-HC≡C(OH)Ph$_2$}Pt(C_6F_5)$_2$(thf)] (**6f**), appeared, and they grew in intensity until 263 K. Above this temperature, the signals due to **6f** started to decrease in intensity, while the resonances assigned to the (μ-hydroxy)(μ-vinyl) complex [*cis*,*cis*-(PPh_3)$_2$Pt{μ-1κC^α:η^2-CH═CHC(OH)Ph$_2$}(μ-OH)Pt(C_6F_5)$_2$] (**5f**) appeared. The signals corresponding to the (μ-hydride)(μ-acetylide) isomers [*trans*-(PPh_3)(C_6F_5)Pt(μ-H){μ-1κC^α:η^2-C≡CC(OH)Ph$_2$}Pt(C_6F_5)(PPh_3)] (**3f**) and [*cis*,*cis*-(PPh_3)$_2$Pt(μ-H){μ-1κC^α:η^2-C≡CC(OH)Ph$_2$}Pt(C_6F_5)$_2$] (**4f**) were observed for the first time at 283 K. At 293 K, the reaction mixture consists of an approximately equimolecular mixture of **3f** and **5f**, together with a small amount (less than 10%) of **4f**. At this temperature there are also still signals due to the alkyne Pt(0) precursor **2f**. Spectroscopic data for **6f** at 263 K: ^{1}H NMR ($CDCl_3$, δ): 5.97 (dd, $^2J_{H-Pt}$ ≈ 47, $^3J_{H-Ptrans}$ ≈ 24, $^3J_{H-Pcis}$ ≈ 7, ≡CH). ^{19}F NMR ($CDCl_3$, δ): −117.4 (d, $^3J_{Pt-F}$ ≈ 360, 2*ortho*-F); −119.6 (d, $^3J_{Pt-F}$ ≈ 400, 2*ortho*-F); −161.4 (t, 1*para*-F); −161.9 (t, 1*para*-F); −163.3 (m, 2*meta*-F); −164.2 (m, 2*meta*-F). ^{31}P NMR ($CDCl_3$, δ): 32.2 (d, $^1J_{Pt-P}$ = 3665, $^2J_{P-P}$ = 14); 27.9 (d, $^1J_{Pt-P}$ = 3571.8, $^2J_{P-P}$ = 14).

Study of the Reaction between [Pt{η^2-HC≡CC(OH)Ph$_2$}(PPh$_3$)$_2$] (2f) and [*cis*-Pt(C$_6$F$_5$)$_2$(thf)$_2$] with Addition of Water at NMR Scale. [*cis*-Pt(C_6F_5)$_2$(thf)$_2$] (0.013 g, 0.02 mmol) was added at 223 K to a solution of [Pt{η^2-HC≡C(OH)Ph$_2$}(PPh_3)$_2$] (**2f**) (0.019 g, 0.02 mmol) and two drops of water in 1 mL of $CDCl_3$, and the mixture was studied by multinuclear NMR spectroscopy (^{1}H, ^{19}F, and ^{31}P{^{1}H}). On raising the temperature, the resonances due to the starting materials decreased their relative intensity, while the signals corresponding to the mixed-valence intermediate [*cis*,*cis*-(PPh_3)$_2$Pt{μ-η^2:η^2-HC≡C(OH)Ph$_2$}Pt(C_6F_5)$_2$-(thf)] (**6f**) appeared and grew in intensity until 263 K (showing in the ^{31}P{^{1}H} NMR spectrum the same relative intensity as that observed in the study mentioned before without addition of water). Above this temperature the signals due to **6f** started to decrease in intensity, while the resonances assigned to the (μ-hydroxy)(μ-vinyl) complex **5f** started to appear, which are the main signals observed at 293 K. At this temperature the spectra also show the signals assigned to **3f** (**3f**:**5f**, 20:80 approximately) and **4f** (trace).

Synthesis of [{(PPh$_3$)$_2$Pt(μ-η^2:2κN-HC≡CC$_5$H$_4$N-4)}$_2${*cis*-Pt(C$_6$F$_5$)$_2$}] (7g). A suspension of 0.11 g (0.13 mmol) of [Pt(η^2-HC≡CC_5H_4N-4)(PPh_3)$_2$] in 10 mL of CH_2Cl_2 was treated with 0.05 g (0.07 mmol) of [*cis*-Pt(C_6F_5)$_2$(thf)$_2$], and the mixture was stirred at room temperature for 5 min. The resulting yellow solution was evaporated to dryness, and the residue was treated with hexane to yield **4e** as a yellow solid. Yield: 0.11 g (76%). Anal. Calcd for $C_{98}F_{10}H_{70}N_2P_4Pt_3$: C, 54.12; H, 3.24; N, 1.29. The best analyses found (C, 52.93; H, 2.74; N, 1.36) fit well with $C_{98}F_{10}H_{70}N_2P_4Pt_3$·$CH_2Cl_2$: C, 52.62; H, 3.21; N, 1.24. MS ES(+): *m*/*z* 673 [Pt(C_6F_5)(HC≡C_5H_4N)$_3$ + 2H]$^+$ 35%; 625 [Pt(C_6F_5)(PPh_3) + H]$^+$ 100%; 568 [Pt(C_6F_5)(HC≡C_5H_4N)$_2$]$^+$ 40%. IR (cm^{-1}): ν(C≡C) 1688 (m); ν(C_6F_5)$_{x-sensitive}$ 808 (m), 798 (m). ^{1}H NMR ($CDCl_3$, δ): 7.86 (d, $^3J_{H-H}$ = 5.7, 4H^3, C_5H_4N); 7.51 (dd, $^3J_{Ptrans-H}$ = 21.1, $^3J_{Pcis-H}$ = 12.0, 2H, ≡C*H*; this signal partially overlaps with the next one; platinum satellites are observed, but $^2J_{Pt-H}$ cannot be unambiguously calculated); 7.24, 7.13, 7.00 (m, 60H, PPh_3); 6.57 (d, $^3J_{H-H}$ = 5.7, 4H^2, C_5H_4N). ^{13}C NMR ($CDCl_3$, δ): 151−137 (m br, C_6F_5); 150.0 (s, C^3, C_5H_4N); 143.5 ("t", $^3J_{Ptrans-C}$ ≈ $^3J_{Pcis-C}$ ≈ 9, C^1, C_5H_4N); ∼136 (overlapping of two doublets of doublets due to the *ipso*-C of PPh_3); 133.9 (d, $^2J_{C-P}$ = 13.1, $^3J_{C-Pt}$ = 20.2, overlapping of two practically isochronous doublets, with similar *J*, due to the *ortho*-C of PPh_3); 129.61 (d, $^4J_{P-C}$ ≈ 2.5, *para*-C, PPh_3); 129.57 (d, $^4J_{P-C}$ ≈ 2.4, *para*-C, PPh_3); 128 (d"t", $^3J_{C-P}$ ≈ 10,$^5J_{C-P}$ ≈ 1.4, overlapping of two practically isochronous doublets, with similar *J*, due to the *meta*-C of PPh_3); 125.4 ("t", $^4J_{P-C}$ ≈ 4, $^3J_{Pt-C}$ ≈ 30, C^2, C_5H_4N). The signals due to C$_\alpha$ and C$_\beta$ are not observed. ^{19}F NMR ($CDCl_3$, δ): −120.48 (d, $^3J_{Pt-F}$ ≈ 470, 4*ortho*-F); −163.66 (t, 2*para*-F); −165.52 (m, 4*meta*-F). ^{31}P NMR ($CDCl_3$, δ): 27.3 (d, $^1J_{Pt-P}$ = 3477.8, $^2J_{P-P}$ = 26.8); 25.8 (d, $^1J_{Pt-P}$ = 3587.8, $^2J_{P-P}$ = 26.8).

X-ray Crystallography. Table 4 reports details of the structural analyses for all complexes studied. Pale yellow (**1b**), colorless (**3a**, **4c**, **5f**), yellow (**3b**, **4a**), or orange (**4e**) crystals were obtained by slow diffusion of *n*-hexane into chloroform (**3a**, **4e**, and **5f**, room temperature), dichloromethane (**3b**, **4a**, and **4c**, room temperature), or acetone (**1b**, −30 °C) solutions of each compound. For complex **4a** one molecule of CH_2Cl_2 and one of water, for complex **4c** one and a half molecules of CH_2Cl_2, and for complex **4e** one molecule of $CHCl_3$ were found in the asymmetric unit. X-ray intensity data were collected with a NONIUS κCCD area-detector diffractometer, using graphite-monochromated Mo Kα radiation. Images were processed using the DENZO and SCALEPACK suites of programs,[71] carrying out the absorption correction at this point for complexes **1b**, **3a**, and **3b**. For the rest of the complexes, the absorption correction was performed using SORTAV.[72] The structures of **4e**·$CHCl_3$ and **5f** were solved by Patterson or direct methods, respectively, using the SHELXL-97 program,[73] while the rest of the structures were solved by Patterson and Fourier methods using the DIRDIF92 program.[74] All structures were refined by full-

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Table 4. Crystallographic Data for 1b, 3a, 3b, 4a, 4c, 4e, and 5f

	1b	**3a**	**3b**
empirical formula	$C_{42}H_{35}NP_2Pt$	$C_{57}H_{37}F_{10}P_2Pt_2$	$C_{57}H_{35}F_{10}NP_2Pt_2$
fw	846.77	1363.99	1375.98
temperature (K)	123(1)	293(2)	293(2)
cryst syst	monoclinic	monoclinic	monoclinic
space group	*C*2/*c*	$P2_1/c$	$P2_1/c$
a (Å)	15.5902(3)	23.6302(2)	23.2380(1)
b (Å)	16.2396(4)	14.7458(3)	14.8000(2)
c (Å)	15.3325(4)	28.5730(5)	28.1530(2)
α (deg)	90	90	90
β (deg)	113.620(1)	150.658(1)	149.6591(6)
γ (deg)	90	90	90
volume (Å^3)	3556.65(14)	4878.72(14)	4891.02(8)
Z	4	4	4
D_{calcd} (Mg/m^3)	1.581	1.857	1.869
abs coeff (mm^{-1})	4.0696	5.872	5.858
F(000)	1680	2620	2640
cryst size (mm)	0.70 × 0.40 × 0.40	0.50 × 0.05 × 0.05	0.60 × 0.10 × 0.075
θ range for data collection (deg)	2.95 to 27.90	5.13 to 25.68	4.12 to 27.10
no. of data/restrains/params	4197/0/223	9174/0/641	10 743/0/653
goodness-of-fit on F^2	1.018	0.999	1.003
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0273$, $wR_2 = 0.0671$	$R_1 = 0.0504$, $wR_2 = 0.0771$	$R_1 = 0.0344$, $wR_2 = 0.0620$
R indices (all data)	$R_1 = 0.0305$, $wR_2 = 0.0698$	$R_1 = 0.1186$, $wR_2 = 0.0938$	$R_1 = 0.0634$, $wR_2 = 0.0702$
largest diff peak and hole (e·A^{-3})	1.440 and −1.497	0.805 and −0.687	1.089 and −0.705

	4a·CH_2Cl_2·H_2O	**4c**·1.5CH_2Cl_2	**4e**·$CHCl_3$	**5f**
empirical formula	$C_{58}H_{40}Cl_2F_{10}OP_2Pt_2$	$C_{54.5}H_{38}Cl_3F_{10}P_2Pt_2$	$C_{55}H_{40}Cl_3F_{10}OP_2Pt_2$	$C_{63}H_{44}F_{10}O_2P_2Pt_2$
fw	1465.92	1441.32	1465.34	1475.10
temperature (K)	293(2)	173(1)	293(2) K	173(1)
cryst syst	triclinic	orthorhombic	triclinic	monoclinic
space group	$P\bar{1}$	*Pcab*	$P\bar{1}$	*P*2/*c*
a (Å)	12.4140(3)	17.3760(2)	13.7330(5)	22.44670(1)
b (Å)	13.7921(3)	24.1390(2)	14.6640(5)	10.9348(1)
c (Å)	17.2697(5)	25.1940(2)	16.6710(7)	24.7410(2)
α (deg)	79.742(1)	90	64.420(2)	90
β (deg)	74.228(1)	90	88.728(2)	116.5999(4)
γ (deg)	73.240(1)	90	64.725(2)	90
volume (Å^3)	2708.64(12)	10567.35(17)	2683.61(17)	5429.92(7)
Z	2	8	2	4
D_{calcd} (Mg/m^3)	1.797	1.812	1.813	1.804
abs coeff (mm^{-1})	5.391	5.573	5.490	5.286
F(000)	1412	5536	1410	2856
cryst size (mm)	0.15 × 0.10 × 0.05	0.15 × 0.10 × 0.075	0.25 × 0.25 × 0.10	0.35 × 0.27 × 0.25
θ range for data collection (deg)	4.11 to 27.87	4.08 to 25.68	4.10 to 24.43	2.12 to 28.72
no. of data/restrains/params	12 838/0/682	9996/8/639	8292/0/661	14 048/0/724
goodness-of-fit on F^2	1.041	1.007	1.026	1.028
final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0480$, $wR_2 = 0.0995$	$R_1 = 0.0456$, $wR_2 = 0.1163$	$R_1 = 0.0683$, $wR_2 = 0.1621$	$R_1 = 0.0302$, $wR_2 = 0.0610$
R indices (all data)	$R_1 = 0.0845$, $wR_2 = 0.1089$	$R_1 = 0.0714$, $wR_2 = 0.1286$	$R_1 = 0.1106$, $wR_2 = 0.1901$	$R_1 = 0.0479$, $wR_2 = 0.0659$
largest diff peak and hole (e·A^{-3})	1.075 and −1.121	2.614 and −1.724	1.761 and −2.214	0.850 and −1.094

matrix least-squares on F^2 with SHELXL-97,[73] and all non-hydrogen atoms were assigned anisotropic displacement parameters. The hydride ligand H(1) in **1b**, **3b**, and **4a**·CH_2Cl_2·H_2O, as well as the hydroxyl H(1) and the vinyl H(13,14) protons in **5f**, have been located from difference maps and assigned isotropic parameters. The rest of the hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters of 1.2 times the U_{iso} value of their attached carbon for the aromatic and CH_2 hydrogens and 1.5 times U_{iso} for the methyl groups. For complex **4c**·1.5CH_2Cl_2, the methyl and methylenic groups of the vinylic fragment present positional disorder, which could be refined over two positions with partial occupancy factors of 0.50. In this structure, the CH_2Cl_2 was also disordered and modeled adequately. Complex **4e** possesses a chiral center at the C_γ atom of the acetylide ligand with both of the enantiomers, *R* and *S*, present in the unit cell (Figure S1c in the Supporting Information shows the enantiomer *S*). Finally, for complexes **1b**, **3b**, **4a**·CH_2Cl_2·H_2O, **4c**·1.5CH_2Cl_2, and **4e**·$CHCl_3$ some residual peaks larger than 1 e Å^{-3} were observed in the vicinity of the heavy atoms or the disorder solvents, but with no chemical significance.

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Supporting Information Available: Selected bond lengths and angles for complexes **3a**, **4c**, and **4e** and the view of their molecular structures. ^{1}H and ^{31}P{^{1}H} NMR spectra of complexes **3a** and **4a**. ^{1}H NMR and heteronuclear C,H correlation spectra of **5f**. Study of the reaction of [Pt{η^2-HC≡C(OH)Ph_2}(PPh_3)$_2$] with [*cis*-Pt(C_6F_5)$_2$-(THF)$_2$] without addition of water by NMR at different temperatures. Further crystallographic data of **1b**, **3a**, **3b**, **4a**·CH_2Cl_2·H_2O, **4c**·1.5CH_2Cl_2, **4e**·$CHCl_3$, and **5f** are given in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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