

Synthesis, Photophysical Properties, and Theoretical Studies of Hydride–Alkynyl Platinum(II) Complexes. Molecular Structures of [*trans*-PtH(C≡CC₅H₄N-2)(PPh₃)₂] and [Pt(η²-HC≡CCPh₂OH)(PPh₃)₂]

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A series of mononuclear, [*trans*-PtH(C≡CR)(PPh₃)₂] (R = C₅H₄N-2 (**1**), (6-C≡CH)C₅H₃N-2 (**2**), C₆H₄NH₂-4 (**3**), (4-C≡CH)C₆H₄ (**4**), (CH₂)₅C≡CH (**5**)), and binuclear, [*trans,trans*-(PPh₃)₂-HPt{μ-σ:σ-(C≡C)₂R}PtH(PPh₃)₂] (R = C₅H₃N-2 (**7**), C₆H₄-1,4 (**8**)), hydride–alkynyl platinum complexes has been prepared in good to moderate yields from the reactions of [*trans*-PtHCl(PPh₃)₂] with an excess of the corresponding alkyne in the presence of an excess of NEt₂H and from the reactions of [*trans*-PtHCl(PPh₃)₂] with 1 equiv of **2** or **4** in the presence of diethylamine. An analogous reaction with HC≡CCPh₂OH leads to a mixture of [*trans*-PtH(C≡CCPh₂OH)(PPh₃)₂] (**6a**) and [Pt(η²-HC≡CCPh₂OH)(PPh₃)₂] (**6b**). The binuclear diyne complex [{(PPh₃)₂Pt}₂{μ-η²:η²-(C≡CH)₂C₆H₄-1,4}] (**9**), prepared in high yield from [Pt(η²-C₂H₄)(PPh₃)₂] and HC≡CC₆H₄-1,4-C≡CH (0.5 equiv), is also formed in the reaction leading to **8**. Complexes **5**, **7**, and **8** have been used as precursors to form the mixed-valence Pt(II)–Pt(0) complexes **10**–**12**. The spectroscopic characterization of the complexes and X-ray crystal structure determination of **1** and **6b** are included. Their absorption and some selected emission spectra, examined on the basis of theoretical studies (EHMO), are also reported.

Introduction

Alkynyl complexes have been actively investigated from a variety of viewpoints (structure, catalytic activity, development of functional materials, etc.),¹ and in recent years, there has been a growing interest in the design of oligomeric and polymeric (including branched systems) transition-metal complexes containing σ-bonded acetylide units because of their significantly altered physical properties compared to organic oligomers and polymers.² In this area, particular attention has been paid to hydride–alkynyl and also to hydride–acetylene complexes, since they are important reagents or intermediates in many stoichiometric and catalytic processes.³

In the course of our studies designed to explore the chemistry of alkynyl platinum complexes, we have observed that the complex [*trans*-PtH(C≡CPh)(PPh₃)₂]⁴

behaves differently toward platinum species containing labile sites. Thus, it has been reported that this monohydride reacts with [*cis*-Pt(C₆F₅)₂(thf)₂], yielding [*trans*-(PPh₃)(C₆F₅)Pt(μ-H)(μ-C≡CPh)Pt(C₆F₅)(PPh₃)],⁵ while the analogous reaction with [*cis*-Pt(C₆F₅)₂(CO)(thf)] affords the μ-phenylethenylidene bridging complex [*cis,cis*-(CO)(C₆F₅)₂Pt(μ-C=CHPh)Pt(PPh₃)₂].⁶ In an attempt to understand these reactions,⁷ we focused our interest on new hydride–alkynyl platinum substrates.

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Although σ -bonded alkynyl and η^2 -bonded alkyne complexes of platinum have been thoroughly investigated,^{1a,b,g,2l,8,9} the number of reports about mixed hydride–alkynyl derivatives is very small^{4,5,10,11} and, as far as we know, only two structures of mononuclear complexes have been reported.^{4,10a}

We report here the synthesis and characterization of several new mononuclear (**1–5**, **6a**) and binuclear (**7**, **8**) hydride–alkynyl platinum complexes, together with the monoynone [Pt(η^2 -HC≡CCPh₂OH)(PPh₃)₂] (**6b**) and diyne [{"(PPh₃)₂Pt}₂{ μ - η^2 : η^2 -(C≡CH)₂C₆H₄-1,4}] (**9**) derivatives, formed during the synthesis of **6a** and **8**, respectively. The mixed-valence (Pt(II),Pt(0)) complexes [{"*trans*-(PPh₃)₂HPtC≡CRC≡CH}Pt(PPh₃)₂] (R = C₅H₁₀ (**10**), C₅H₃N-2,6 (**11**), C₆H₄-1,4 (**12**)) and structural studies for **1** and **6b** are also reported. Finally, their photophysical properties, examined on the basis of some EHMO calculations, are also included.

Results and Discussion

(i) Synthesis and Characterization. A few hydride–alkynyl mononuclear platinum complexes have been prepared by different methods, such as addition of the alkyne in the presence of base,^{4,10a} chloride/hydride exchange using NaBH₄^{10g,h} or NaC≡CPh,^{10f} or oxidative addition to a platinum(0) precursor.^{10b,c} The purpose of this study was to synthesize several hydride–alkynyl complexes starting from [*trans*-PtHCl(PPh₃)₂] and suitable acetylene and diacetylene ligands (Schemes 1 and 2).

The synthesis of [*trans*-PtH(C≡CR)(PPh₃)₂] (R = C₅H₄N-2 (**1**), (6-C≡CH)C₅H₃N-2 (**2**), C₆H₄NH₂-4 (**3**), (4-C≡CH)C₆H₄ (**4**), (CH₂)₅C≡CH (**5**)) was based on a slight modification of the method reported by Russo et al.,^{4,10a} by reacting [*trans*-PtHCl(PPh₃)₂] with an excess of the corresponding acetylene in refluxing chloroform and in the presence of NEt₂H (path i, Scheme 1), to give the final complexes in high yield (72–94%). The diethylamine facilitates the proton elimination of the acetylene as NEt₂H⁺Cl⁻, avoiding insertion reactions in the Pt–H bond¹² or the facile formation of chloroacetylides by formal elimination of hydrogen,¹³ which had been previously observed with HC≡CPh and α -hydroxyacetylenes. The resulting pale orange solid obtained in the reaction between [*trans*-PtHCl(PPh₃)₂] and *p*-diethynylbenzene (HC≡CC₆H₄C≡CH), even in the presence of an excess (3.2 equiv) of this latter, was identified (³¹P and ¹H NMR) as a mixture of the mononuclear **4** and the dinuclear [*trans,trans*-(PPh₃)₂HPt{ μ - σ : σ -(C≡C)₂-C₆H₄-1,4}PtH(PPh₃)₂] (**8**) complexes (**4**:**8** molar ratio 4:1). Recrystallization of this solid from acetone/methanol gave complex **4** as an orange powder (65% yield). In a similar manner, the diplatinum complex **8** and the analogous binuclear derivative [*trans,trans*-(PPh₃)₂HPt{ μ - σ : σ -(C≡C)₂C₅H₃N-2,6}PtH(PPh₃)₂] (**7**) were prepared in high yield (~70%) by refluxing [*trans*-PtHCl(PPh₃)₂] for 1 h with 1 equiv of the precursor **4** or **2**, respectively, in CHCl₃ in the presence of NEt₂H (path ii, Scheme 1). The synthetic approach based on the direct condensation between the diterminal alkynes with [*trans*-PtHCl(PPh₃)₂] gave worse results (path i, Scheme 2). Thus, when 2,6-diethynylpyridine was treated with 1 equiv of [*trans*-PtHCl(PPh₃)₂] under similar conditions, the diplatinum complex **7** was formed along with the mononuclear derivative **2** (**7**:**2** ratio ~1.4:1), as confirmed by NMR spectroscopy after crystallization. Subsequent recrystallization from CH₂Cl₂/MeOH gave **7** in very low yield (20%). The analogous reaction of *p*-diethynylbenzene with 2 equiv of [*trans*-PtHCl(PPh₃)₂] generated a mixture of **4** and **8** with the novel binuclear diyne platinum(0) complex [{"(PPh₃)₂Pt}₂{ μ - η^2 : η^2 -(C≡CH)₂C₆H₄-1,4}] (**9**), in which both alkyne linkages of the *p*-diethynylbenzene are η^2 -bonded to two reduced "Pt⁰-(PPh₃)₂" fragments. The yield of the three complexes depends on the reaction times, the final solid obtained after 75 min of reflux being a mixture of **4**, **8**, and **9** in a 1.4:1:1.6 molar ratio. Recrystallization of this mixture from CH₂Cl₂/acetone yields complex **8** in 18% yield.

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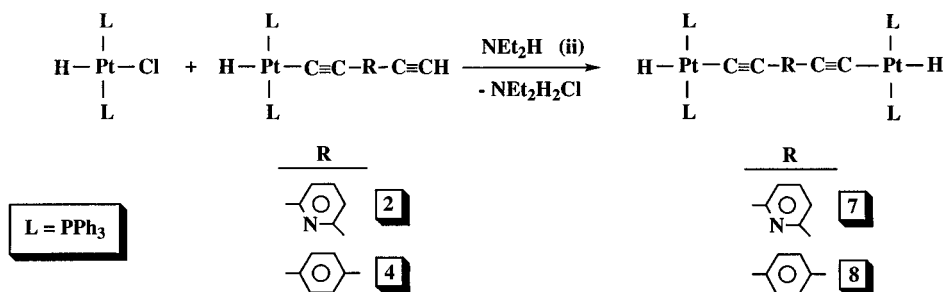
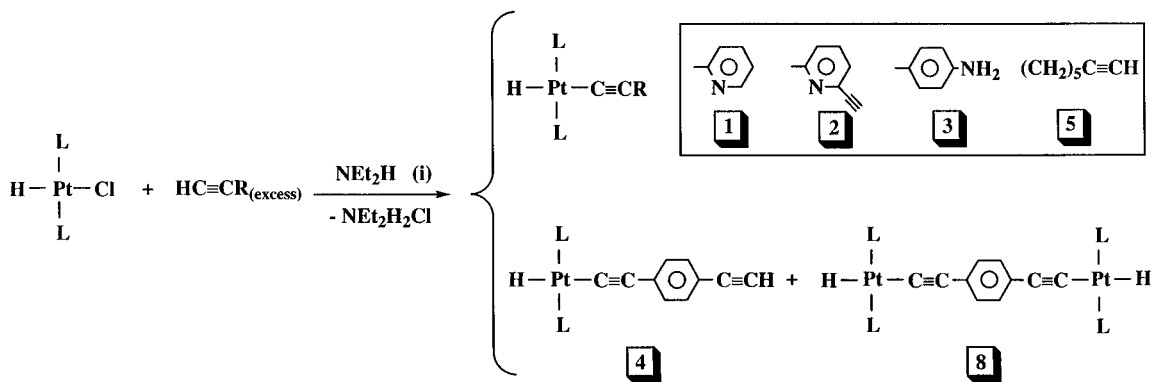
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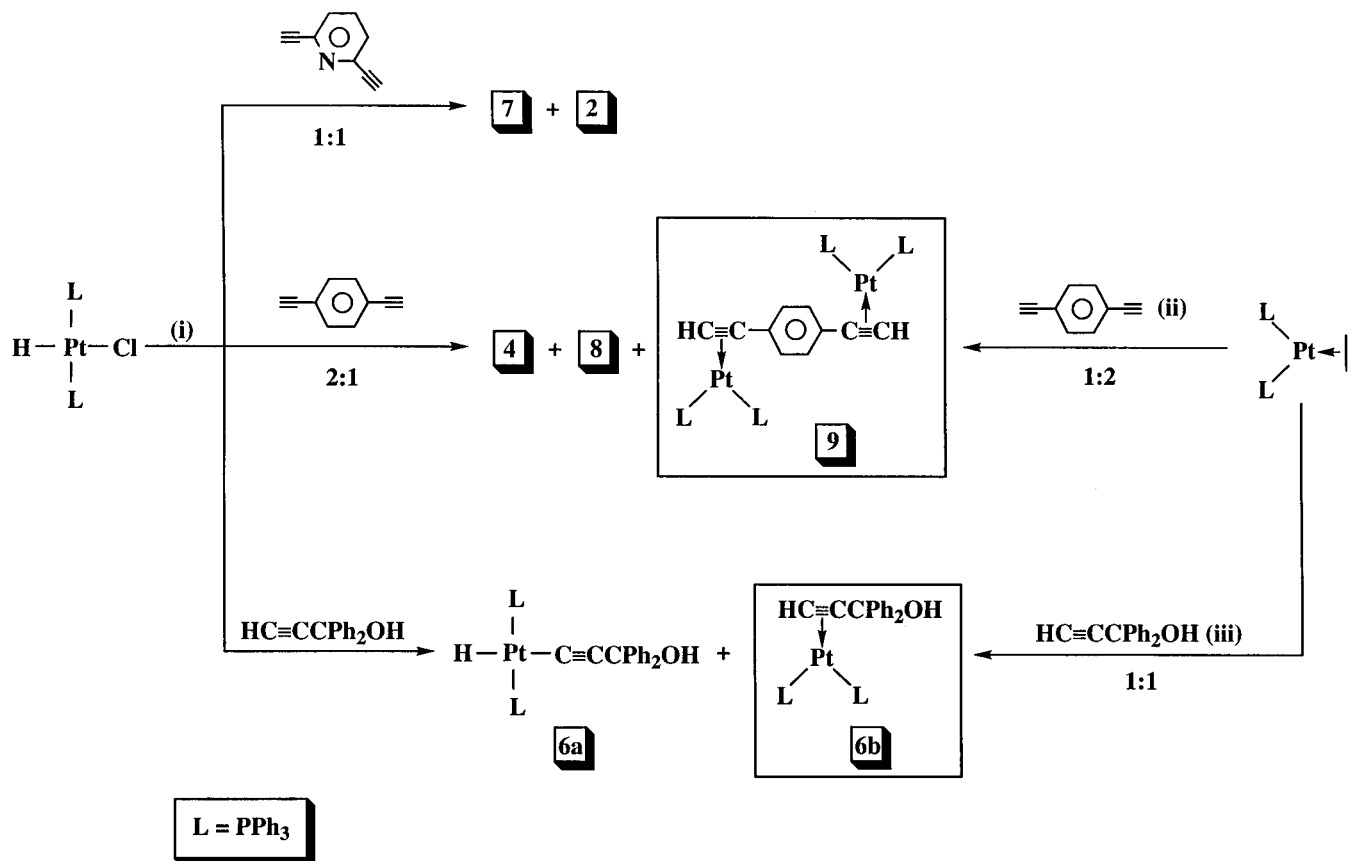
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Scheme 1



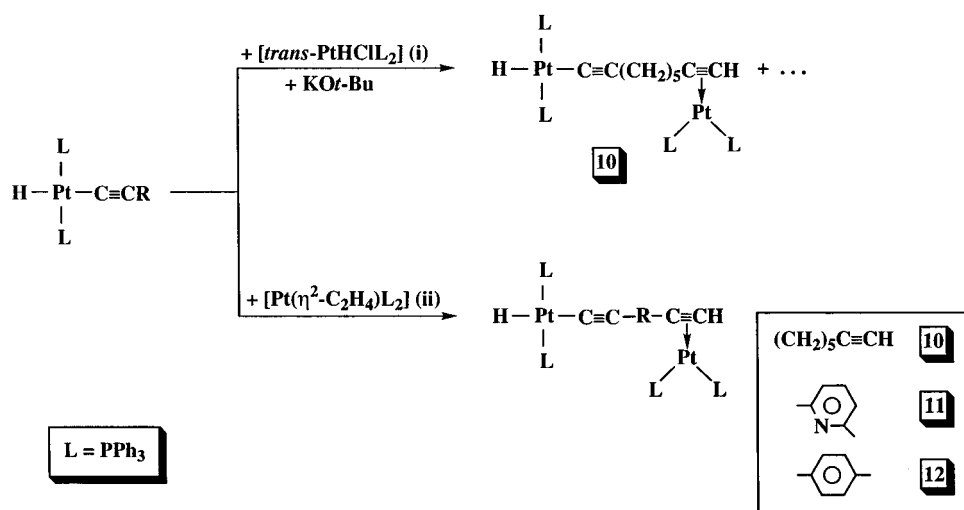
Scheme 2



However, as expected, the binuclear diene complex **9** was prepared in very high yield (83%) by treatment of [Pt(η^2 -C₂H₄)(PPh₃)₂], suspended in acetone at room temperature, with *p*-diethynylbenzene (molar ratio 1:2) (ii, Scheme 2). Although the mechanism of the reductive

process in the above reaction is not clear, similar intramolecular elimination of HCl on [trans-PtHCl(PPh₃)₂], yielding η^2 -bonded alkyne complexes [Pt(η^2 -HC≡CR)(PPh₃)₂], had been previously observed in analogous reactions in the presence of hydrazine.^{12,14}

Scheme 3



As had been previously noted,⁴ the nature of the substituent R of the alkyne molecule influences strongly the course of these reactions. Thus, we have been unable to prepare the mononuclear complex [*trans*-PtH(C≡CCPh₂OH)(PPh₃)₂] (**6a**) in a pure form starting from [*trans*-PtHCl(PPh₃)₂] and the α -hydroxyalkyne 1,1-diphenyl-2-propyn-1-ol (HC≡CCPh₂OH). For different reaction times and concentrations of the reactants, the reaction always yielded a mixture of **6a** (major component) and the η^2 -bonded alkyne complex [Pt(η^2 -HC≡CCPh₂OH)(PPh₃)₂] (**6b**) (minor component), which we were not able to separate (path i, Scheme 2) in a complete form. Complex **6b** (described previously)^{10d} was prepared alternatively in 60% yield by treatment of [Pt(η^2 -C₂H₄)(PPh₃)₂] with an equimolecular amount of the propynol (HC≡CCPh₂OH) in acetone (path iii, Scheme 2).

However, we have not succeeded in obtaining the dihydride diplatinum compound [*trans,trans*-(PPh₃)₂-HPt{C≡C(CH₂)₅C≡C}PtH(PPh₃)₂] under reaction conditions similar to those used for **7** and **8**, despite many attempts. The free C≡CH fragment on **5** seems to be reluctant to further deprotonation, even in the presence of stronger deprotonating agents such as *n*-BuLi and KO*t*-Bu. Thus, in the reaction with *n*-BuLi, only the starting materials **5** and [*trans*-PtHCl(PPh₃)₂] were detected by NMR spectroscopy. However, the reaction between **5** and [*trans*-PtHCl(PPh₃)₂] in the presence of an excess of KO-*t*-Bu, in tetrahydrofuran, afforded a mixture of products with the unexpected mixed-valence Pt(II),Pt(0) complex [{*trans*-(PPh₃)₂HPtC≡C(CH₂)₅C≡CH}Pt(PPh₃)₂] (**10**) as the main component (path i, Scheme 3). Although this complex can be isolated from the mixture in a very low yield (~15%), its preparation, as expected, is more straightforward starting from the platinum(0) precursor [Pt(η^2 -C₂H₄)(PPh₃)₂]. Thus (path ii, Scheme 3), treatment of an acetone solution of complex **5** with [Pt(η^2 -C₂H₄)(PPh₃)₂] (molar ratio 1:1) at room temperature cleanly gave complex **10** as a beige solid in a 87% yield. The synthesis of this complex prompted us to explore the preparation of related binuclear Pt(II),Pt(0) with C≡CRC≡CH (R = C₅H₃N-2

and C₆H₄-1,4) as connecting bridging ligands. As expected, following a procedure similar to that used for **10**, the reaction of the ethylene Pt(0) derivative [Pt(η^2 -C₂H₄)(PPh₃)₂] with the mononuclear Pt(II) starting materials [*trans*-PtH(C≡CR)(PPh₃)₂] (R = (6-C≡CH)-C₅H₃N-2 (**2**), (4-C≡CH)C₆H₄ (**4**)) (path ii, Scheme 3) gave the desired mixed-valence complexes [{*trans*-(PPh₃)₂-HPtC≡CRC≡CH}Pt(PPh₃)₂] (R = C₅H₃N-2,6 (**11**), C₆H₄-1,4 (**12**)). Compounds **10–12** are rather stable, and no isomerization toward the corresponding dihydride-dialkynyl compounds (**7** and **8**) has been detected. In fact, on standing in solution, complexes **10–12** only evolve with loss of the Pt⁰(PPh₃)₂ fragment, regenerating the corresponding mononuclear hydride-alkynyl derivatives **5**, **2**, and **4**, respectively. Isomerization from an acetylene to an alkynide complex has been shown to be an important step in polymerization reactions. Although most of these processes proceed thermally, some experimental studies on photoassisted C–C bond cleavage of [Pt(PPh₃)₂(RC≡CR)] to give [Pt(R)(C≡CR)(PPh₃)₂] (R = CN, COOMe) have also been reported.¹⁵ Nevertheless, photolysis of solutions of the alkyne complexes **6b** and **9** and the mixed-valence compound **12**, in different solvents (CDCl₃, CD₃COCD₃, and C₆D₆) and under different conditions (125 or 400 W, Hg lamps), only yielded complex mixtures in which the expected hydride-alkynyl complexes **6a** and **8** were not detected.

The analytical and spectroscopic (IR and ¹H, ³¹P{¹H}, and ¹³C{¹H} NMR) data are in agreement with the formulation proposed for the new complexes (see Experimental Section for details). In addition, the molecular structures of complexes **1** and **6b** have been determined by X-ray crystallography.

The most remarkable feature of the IR spectra of all hydride derivatives is the presence of two absorptions in the 2031–2121 cm⁻¹ region which, on the basis of previous assignments,^{1,4,7,10a} can be attributed to $\nu(\text{C}\equiv\text{C})$ (high-wavenumber band 2099–2121 cm⁻¹) and $\nu(\text{Pt}-\text{H})$ (2031–2073 cm⁻¹) stretching vibrations, respectively. Despite the presence of two C≡C entities in the mono-

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nuclear complexes **2**, **4**, and **5**, only one $\nu(\text{C}\equiv\text{C})$ absorption is observed ($\sim 2100\text{ cm}^{-1}$, **2** and **4**; 2121 cm^{-1} , **5**). However, the terminal acetylenic protons are clearly seen in their proton NMR spectra, appearing as a singlet at ca. 3 ppm, except for complex **5**, for which a broad signal at 1.89 ppm is assigned on the basis of $^1\text{H}-^1\text{H}$ COSY and $^1\text{H}-^{13}\text{C}$ correlation NMR spectra, to the $\text{C}\equiv\text{CH}$ proton. All complexes display the hydride resonance ($\delta -6.54$ to -6.11) as a triplet ($^2J_{\text{P}-\text{H}} = 14.3-15.5\text{ Hz}$), confirming the trans arrangement of the phosphine ligands. Both the chemical shifts and the platinum coupling constants ($^1J_{\text{Pt}-\text{H}} = 640-656\text{ Hz}$) compare well to those already reported for similar complexes^{4,7,10a,e} and are in the expected range observed for Pt(II) hydrides having a C atom (alkynyl, alkyl, carbene) trans to the hydride ligand.¹⁶ The presence of a singlet in their $^{31}\text{P}\{^1\text{H}\}$ NMR spectra ($\delta 26.33-29.34$) and especially the magnitude of $^1J_{\text{Pt}-\text{P}}$ ($2907-2948\text{ Hz}$) also confirms the trans configuration of the ligands about platinum centers.¹⁷ The alkynyl carbon resonances, in the $^{13}\text{C}\{^1\text{H}\}$ NMR spectra, fall in the range $107.17-124.84\text{ ppm}$. These signals could not be located for all of the complexes (see Experimental Section), while the characteristic carbon signals for terminal $\text{C}_\beta=\text{C}_\alpha\text{H}$ acetylenic units in monomers **2**, **4**, and **5** were found at lower frequencies ($\delta 67.86-79.1$, C_α ; $\delta 83.47-85.01$, C_β).

Concerning the IR spectra of the alkyne derivatives, both complexes **6b** and **9** display one absorption due to the $\nu(\text{C}\equiv\text{C})$ stretching vibration (1692 and 1688 cm^{-1} , respectively) in the region of coordinated triple bonds.^{8,9i-r,10d,18,19} Although for complex **9** the terminal $\equiv\text{CH}$ proton resonance is obscured by the phenyl protons of PPh_3 ligands, complex **6b** exhibits a characteristically low-field signal¹⁹ for the alkyne hydrogen at $\delta 6.46$ ($^2J_{\text{Pt}-\text{C}} = 57.7\text{ Hz}$) as a doublet of doublets, due to the different couplings $^3J_{\text{P}^{\text{trans}}-\text{H}} = 22.7$ and $^3J_{\text{P}^{\text{cis}}-\text{H}} = 9.6\text{ Hz}$. The proton resonance of the C_6H_4 ring in **9** appears as a singlet at low frequency ($\delta 6.59$), probably due to the shielding effect of PPh_3 .^{9i,p} Both compounds display a sharp ABX spin system ($\text{X} = ^{195}\text{Pt}$) in the ^{31}P NMR spectra consistent with in-plane coordination of the alkyne unit and slow (relative to the NMR time scale) rotation about the platinum-alkyne bond, and in the ^{13}C NMR spectra, the downfield complexation shifts expected^{18,19} of the acetylenic $\text{HC}\equiv\text{C}$ carbon resonances are observed (see Experimental Section for details). Finally, in agreement with the formulation given in Scheme 3, the mixed-valence complexes **10-12** exhibit in their IR and ^1H , $^{31}\text{P}\{^1\text{H}\}$, and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra the expected spectroscopic data due to both the Pt(0) and Pt(II) fragments (see Experimental

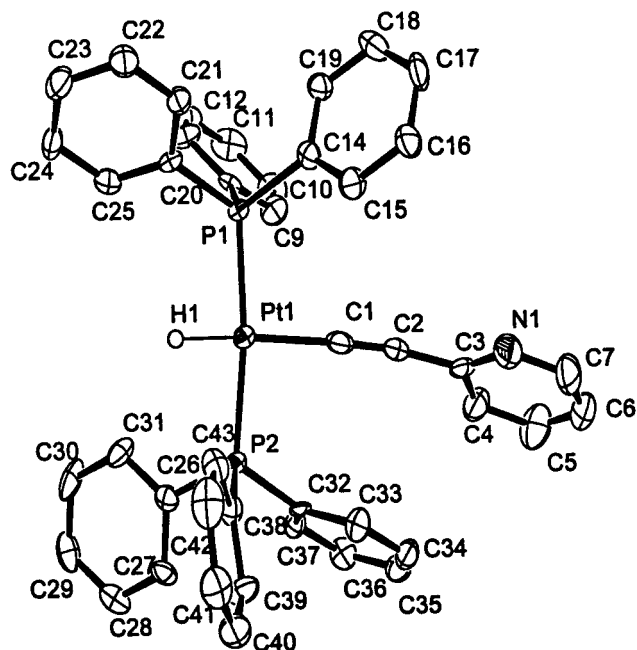


Figure 1. View of the molecular structure of complex **1** (50% probability thermal ellipsoids), showing the atom-numbering scheme. Hydrogen atoms, except H(1), have been omitted for clarity.

Table 1. Bond Lengths (Å) and Angles (deg) for Complexes 1 and 6b

[<i>trans</i> -PtH(C≡CC ₅ H ₄ N-2)(PPh ₃) ₂] (1)			
Pt(1)–C(1)	2.028(6)	Pt(1)–P(1)	2.2718(16)
Pt(1)–P(2)	2.2977(16)	Pt(1)–H(1)	1.45(7)
C(1)–C(2)	1.202(8)	C(2)–C(3)	1.446(8)
C(1)–Pt(1)–P(1)	94.54(18)	C(1)–Pt(1)–P(2)	91.81(18)
P(1)–Pt(1)–H(1)	90(3)	P(2)–Pt(1)–H(1)	84(3)
P(1)–Pt(1)–P(2)	172.94(5)	C(1)–Pt(1)–H(1)	172(3)
C(2)–C(1)–Pt(1)	175.6(7)	C(1)–C(2)–C(3)	172.3(7)
[Pt(η^2 -HC≡CCPh ₂ OH)(PPh ₃) ₂] (6b)			
Pt(1)–C(37)	2.045(5)	Pt(1)–C(38)	2.075(5)
Pt(1)–P(1)	2.2836(12)	Pt(1)–P(2)	2.2787(13)
C(37)–C(38)	1.269(7)	C(38)–C(39)	1.486(6)
C(37)–Pt(1)–C(38)	35.9(2)	C(37)–Pt(1)–P(1)	101.7(2)
C(38)–Pt(1)–P(2)	112.5(2)	P(1)–Pt(1)–P(2)	109.88(4)
C(37)–C(38)–C(39)	146.2(5)		

Section). Again, the most remarkable feature of these spectra is the absence of the terminal $\equiv\text{CH}$ proton resonances in the ^1H NMR spectra of **11** and **12**, which are obscured, as in **9**, by the phenyl protons of PPh_3 ligands.

(ii) Structural Studies. The crystal structure of [*trans*-PtH(C≡CC₅H₄N-2)(PPh₃)₂] (**1**) contains discrete molecules separated by normal distances. No significant intermolecular contact between the pyridyl N and the hydride ligand (6.042 Å) is found. The molecular structure is illustrated in Figure 1, and selected bond parameters are collected in Table 1. In agreement with our expectations based on NMR data, the molecule has trans phosphine ligands. The acetylide group and the hydrogen atom complete a distorted-square-planar geometry around the Pt center, with deviations from the best least-squares plane ranging from 0.01 to 0.101 Å. Despite the small steric demand of the hydride ligand, the P(1)–Pt–P(2) axis is almost linear (172.94(5)°), suggesting that the steric repulsion of the alkynyl

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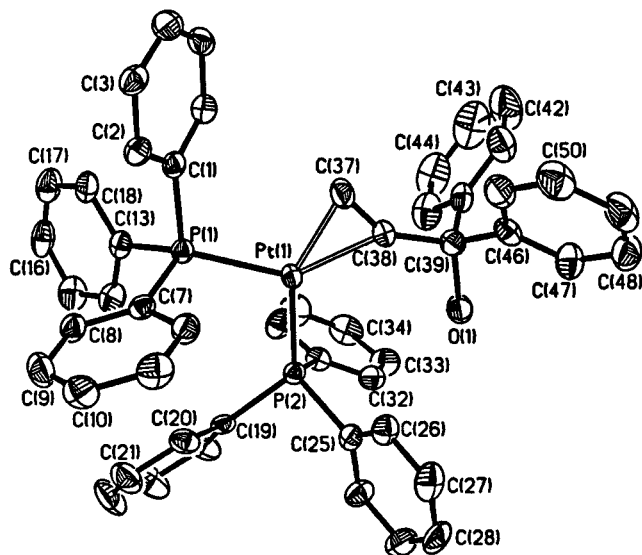


Figure 2. View of the molecular structure of complex **6b** (50% probability thermal ellipsoids), showing the atom-numbering scheme. Hydrogen atoms have been omitted for clarity.

moiety (C(1)–Pt–P(1,2) angles 94.54(18), 91.81(18)° is probably relaxed, twisting the pyridyl substituent from the platinum square plane (dihedral angle 116.12°). The bond lengths Pt–P (2.2977(16), 2.2718(16) Å) and Pt– σ -C (2.028(6) Å) and geometrical details of the alkynyl fragment (C≡C = 1.202(8) Å, Pt–C(1)–C(2) = 175.6(7)°, C(1)–C(2)–C(3) = 172.3(7)°) are in agreement with the values expected for both types of ligands.

The hydride ligand is localized at a Pt–H distance (1.45(7) Å) within comparable experimental error of those reported for [*trans*-PtH(C≡CEtMeOH)(PPh₃)₂]¹⁴ (1.98 Å) and other hydride platinum(II) complexes

such as [*trans*-PtH(COCH₂CH₂O)(PPh₃)₂] (1.72(8) Å), [*trans*-PtH(CF₃)(PPh₃)₂] (1.72(9) Å),²⁰ [PtH(SB₉H₁₀)(PEt₃)₂] (1.66 Å),²¹ [*cis*-PtH(SiPh₃)(PEt₃)₂] (1.75 Å),²²

and [PtH(CH₂CN)[C(NCH₂CH₂CH₂)NH(C₆H₄-*p*-MeO)](PPh₃) (1.61(4) Å).^{16d}

The structure of the η^2 -alkyne complex **6b** has also been unambiguously established by X-ray crystallography. The results are shown in Figure 2 and Table 1. Despite the presence of an OH group, the complex crystallizes as discrete molecules. No intermolecular hydrogen bonding pattern has been observed, with the shortest O...O separation being approximately 9 Å. The geometry at platinum is close to planar, the dihedral angle between Pt(1)–P(1)–P(2) and Pt(1)–C(37)–C(38) being 0.56(27)°. This angle is the usual one for η^2 -acetylene Pt(0) complexes^{8a–c,9i–p} and can be compared with those reported for [Pt(1-ethynylcyclohexanol)(PPh₃)₂] (6.7(8) and 7.2(7)°).²³ Although the coordinated alkyne is unsymmetrical, the coordination geometry at the Pt center is essentially symmetrical, with both Pt–

Table 2. UV/Vis Spectral Data in Benzene at Room Temperature (Concentration $\sim 5 \times 10^{-5}$ M)^a

compd	λ_{\max} /nm ($\epsilon/10^3$ dm ³ mol ⁻¹ cm ⁻¹)
1	279 (21), 302 (16), 329 (9.7)
2	280 (22), 296 (15) (sh), 332 (13)
3	282 (29), 353 (8.9)
4	286 (24), 308 (23), 342 (19), 374 (7.4) (sh)
5	281 (25), 327 (3.3) (sh)
6a + 6b (5:1)	278 (11), 312 (2.0) (sh)
6b	278 (11)
7	281 (42), 344 (19), 399 (5.7)
8	286 (43), 309 (29) (sh), 351 (23), 373 (35)
9	279 (36), 373 (20)
10	279 (24), 323 (4.9) (sh)
11	280 (31), 338 (14)
12	280 (32), 307 (27), 343 (21), 375 (12)
[<i>trans</i> -PtHCl(PPh ₃) ₂]	279 (13)
HC≡CC ₅ H ₄ N-2	282 (11)
(HC≡C) ₂ C ₅ H ₃ N-2,6	283 (41)
HC≡CC ₆ H ₄ NH ₂ -4	279 (26), 335 (1.5)
(HC≡C) ₂ C ₆ H ₄ -1,4	278 (16), 293 (4.8) (sh)
HC≡C(CH ₂) ₅ C≡CH	278 (3.2), 287 (2.2) (sh)
HC≡CCPh ₂ OH	283 (7.7)

^a For complexes **4** and **8**, the absorption spectra were also taken in acetone, the solvent dependence being minimal: **4**, 327 (11) (sh), 339 (14), 371 (4.1) (sh); **8**, 325 (12), 346 (15), 369 (22).

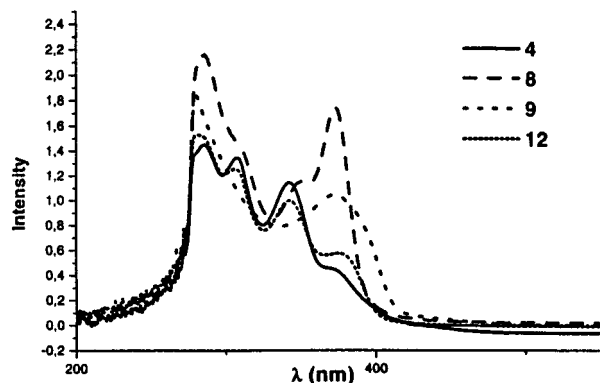


Figure 3. Absorption spectra of complexes **4**, **8**, **9**, and **12** in benzene at room temperature ([**4**] = 5.9×10^{-5} M; [**8**] = 5.0×10^{-5} M; [**9**] = 5.2×10^{-5} M; [**12**] = 4.7×10^{-5} M).

C(sp) distances (2.045(5), 2.075(5) Å) being identical within experimental error. However, the P(2)–Pt(1)–C(38) angle is larger (112.5(2)°) than that of P(1)–Pt(1)–C(37) (101.7(2)°). Similar differences have been observed in [Pt(1-ethynylcyclohexanol)(PPh₃)₂].²³ The length of the C≡C triple bond (1.269(7) Å) and the bending of the alkyne fragment C(37)–C(38)–C(39) (146.2(5)°) lie well within the range previously observed for this type of compounds.

(iii) Absorption–Emission Spectra and Selected EHMO Calculations. The data of the electronic absorption spectra of the new complexes (as well as for the ligands), which were taken at room temperature in benzene solutions, are summarized in Table 2. As representative examples, the absorption spectra of **4**, **8**, **9**, and **12** are shown in Figure 3. The ligands show a strong absorption in the UV region (278–283 nm), which can be ascribed to a $\pi \rightarrow \pi^*$ transition. Comparison of the absorption spectra of the hydride–alkynyl complexes with those of the alkyne entities and the platinum precursor [*trans*-PtHCl(PPh₃)₂] (λ_{\max} 279 nm with a tail extending to ~ 330 – 340 nm) reveals the appearance of new low-energy absorption bands being more pronounced in the aryl derivatives. For the

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Table 3. Emission and Excitation Spectral Data in Benzene at 77 K (Concentration $\sim 5 \times 10^{-3}$ M)

compd	$\pi_{\max}^{\text{em}}/\text{nm}$	$\pi_{\max}^{\text{exc}}/\text{nm}$
[<i>trans</i> -PtH{C≡C(4-C≡CH)C ₆ H ₄ }(PPh ₃) ₂] (4)	514, 544, 581	~305, 383
[<i>trans,trans</i> -(PPh ₃) ₂ HPt{ μ - σ - σ -(C≡C) ₂ C ₆ H ₄ -1,4}PtH(PPh ₃) ₂] (8)	508, 543, 590	302, 366, 387
[{(PPh ₃) ₂ Pt] ₂ { μ - η^2 : η^2 -(C≡CH) ₂ C ₆ H ₄ -1,4}] (9)	571, 598, 630, 663	330, 397
[<i>trans</i> -(PPh ₃) ₂ H–Pt–C≡C(C ₆ H ₄ -1,4)C≡CH]Pt(PPh ₃) ₂] (12)	544, 596	391
[<i>trans</i> -PtH{C≡C(6-C≡CH)C ₅ H ₃ N-2}(PPh ₃) ₂] (2)	513	358, 391, 432
[<i>trans,trans</i> -(PPh ₃) ₂ HPt{ μ - σ - σ -(C≡C) ₂ C ₅ H ₃ N-2,6}PtH(PPh ₃) ₂] (7)	544	367, 393, 455
[<i>trans</i> -(PPh ₃) ₂ H–Pt–C≡C–(C ₅ H ₃ N-2,6)–C≡CH]Pt(PPh ₃) ₂] (11)	518, 542	371
(HC≡C) ₂ C ₆ H ₄ -1,4	404, 423, 466, 492	271, 337, 355, 369
(HC≡C) ₂ C ₅ H ₃ N-2,6	523	271

complexes [*trans*-PtH{C≡C(CH₂)₅C≡CH}(PPh₃)₂] (**5**) and [*trans*-PtH(C≡CCPh₂OH)(PPh₃)₂] (**6a**) (5:1 mixture of **6a,b**) the absorption maxima (λ_{\max}) occurs only as a shoulder at 327 and 312 nm, respectively. The lowest absorption band shifts to lower energies in the remaining mononuclear complexes, following the order **1** (329 nm) < **2**, (332 nm) < **3** (353 nm) < **4** (374 nm). On the basis of previous assignments and theoretical and photoelectron studies²⁴ on neutral bis(alkynyl)platinum complexes, the moderately intense low-energy band is tentatively assigned as ¹MLCT $\pi \rightarrow \pi^*$,^{21,p,9e,g,24a,d,25} the HOMO is of Pt–C π -antibonding character, resulting from a metal d and acetylide π -fragment interaction, and the LUMO mainly has a ligand π^* -orbital character. The tendency observed can be rationalized on the basis of previous theoretical results, which show that aryl substituents allow further electronic mixing with either π or π^* levels, producing a large decrease in the energy of the acetylenic π^* orbitals and a somewhat smaller increase in the energy of metal–acetylene bonding, reducing the HOMO–LUMO gap.^{24c,e}

It is worthy of note that the introduction of a second platinum fragment in the 2,6-bis(ethynyl)pyridine ligand clearly shifts this absorption toward longer wavelengths (λ_{\max} 399 nm for **7** vs 332 nm for **2**), reflecting a higher degree of conjugation, which probably reduces the energy gap between the highest occupied and lowest unoccupied molecular orbitals (HOMO and LUMO). For the mononuclear derivative **4**, the absorptions at 342 nm ($\epsilon = 19 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) and 374 nm ($\epsilon = 7.4 \times 10^3 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) are tentatively assigned to spin-allowed and spin-forbidden (¹MLCT and ³MLCT $\pi \rightarrow \pi^*$) transitions, respectively. This assignment is in agreement with a red shift on going from **4** to **8** (342 vs 373 nm) and is in line with the value of λ_{\max} absorption recently reported for [*trans*-PtPh(C≡C-*p*-C₆H₄C≡CH)-(PEt₃)₂] (327 nm, $\log \epsilon$ 4.58).²⁶ The presence of a hydride ligand trans to the alkynyl, instead of the Ph group, should increase the electron density on the platinum center, raising the energy of the HOMO and, thereby,

decreasing the HOMO–LUMO gap, explaining the red shift observed in **4**.

The introduction of the platinum(0) fragment Pt(PPh₃)₂ on the terminal acetylenic fragment in the mononuclear complexes **2**, **4**, and **5** causes only minor modifications in their spectra, suggesting very little electronic communication between the platinum centers. For the resulting complexes **10–12**, the observed low-energy absorptions (λ , nm (ϵ , $\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$): **2** 323 (4.9×10^3), **10** 338 (14×10^3), **11** 375 (12×10^3), **12**) are ascribed to Pt(0)-to-alkyne entity charge transfer on basis of EHMO analyses (see below).

In the last few years, the search for novel luminescent materials has attracted considerable attention.²⁷ In this area in particular, since the first observation of luminescence on a platinum compound containing alkynyl ligands,²⁸ a series of platinum alkynyl complexes have been described to exhibit a rich and remarkable photoluminescence.^{24d,25c,27a,29–32} The luminescence properties of mononuclear (**2**, **4**) and binuclear (**7–9**, **11**, **12**) compounds have been examined. They are strongly emissive in frozen (77 K) benzene solutions, whereas the corresponding free diynes emit weakly (Table 3 and Figure 4 for **4**, **8**, **9**, and **12**). Vibronically structured emission bands are detected for **4**, **8**, **9**, and **12** at λ_{\max} 508–571 nm, which are slightly red-shifted relative to the free diyne HC≡CC₆H₄-1,4-C≡CH. As can be observed in Figure 4, the influence of the second Pt(II) center in going from **4** to **8** has little effect on the emission maximum. However, a clear red shift is observed on going from the Pt(II)–Pt(II) compound **8**

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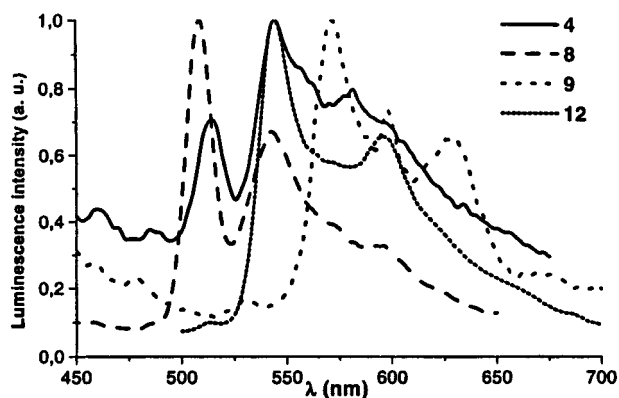


Figure 4. Emission spectra of complexes **4**, **8**, **9**, and **12** in benzene at 77 K ($\lambda_{\text{ex}} = 383$ nm for **4**, 387 nm for **8**, 397 nm for **9**, and 391 nm for **12**; concentration $\sim 5 \times 10^{-3}$ M).

(λ_{max} 508 nm) to the diyne isomer Pt(0)–Pt(0) **9** (571 nm). For **9**, the vibrational spacings of ~ 790 and 1640 cm^{-1} observed correlate well with phenyl-ring skeletal and alkyne $\text{C}\equiv\text{C}$ ($\nu(\text{C}\equiv\text{C})$ for **9** 1688 cm^{-1}) stretching vibrations. Vibrational peaks for **4** (at 1073 , 1171 cm^{-1}) and **8** (at 1269 , 1467 cm^{-1}) may be due to C–H bends and ring C–C stretches, indicating distortion of the central phenylene ring in the excited state. The third isomer, the alkynyl–alkyne mixed-valence, Pt(II)–Pt(0) derivative **12**, exhibits an structured band with a λ_{max} value (544 nm) between those found for **8** and **9**. In this case, the vibrational progression of 1604 cm^{-1} observed compares favorably with the ground-state $\nu(\text{C}\equiv\text{C})$ of the complexed η^2 -alkyne Pt(0) fragment, suggesting that the emission of this complex has to be associated with this entity. An extended Hückel calculation on [$\{trans\text{-}(\text{PH}_3)_2\text{HPt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{CH})\}\text{Pt}^0(\text{PH}_3)_2$] (**D**) as a model complex also predicts that the HOMO is mainly located on the Pt(0) fragment (see below). The emission of complexes formed from 2,6-diethynylpyridine (λ_{max} , nm: **513**, **2**, Pt(II); **544**, **7**, Pt(II)–Pt(II); **518**, **542**, **11**, Pt(II)–Pt(0)) shows broad features (with a poorly resolved vibronic structure for **11**) similar to that observed for the free diyne (see Table 3). The most remarkable difference is found in their excitation spectra; free diyne shows one excitation maximum at 271 nm, whereas **2** and **7** exhibit three distinctive features (358 , 391 , 432 cm^{-1} , **2**; 367 , 393 , 455 cm^{-1} , **7**), a phenomenon which had been previously observed in bis(alkynyl) platinum complexes, for which the emissions have been associated with MLCT excited states.^{24d,25c} The excitation spectrum of complex **11** is different from those observed for **2** and **7**, showing only an excitation maximum in the low-energy region at 371 nm. Therefore, the emission for this complex, as the emission for **12**, is thought to be largely localized on the low-valence fragment.

To clarify the nature of these transitions, simple extended Hückel calculations³³ were performed on [$trans\text{-PtH}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{CH})(\text{PH}_3)_2$] (**A**) and [$trans\text{-}trans\text{-}(\text{PH}_3)_2\text{HPt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{C})\text{PtH}(\text{PH}_3)_2$] (**B**) as model complexes for hydride alkynyl compounds **4** and **8** and on [$\{\text{Pt}^0(\text{PH}_3)_2\}_2(\text{HC}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{CH})$] (**C**) and [$\{trans\text{-}(\text{PH}_3)_2\text{HPt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{CH})\}\text{Pt}^0(\text{PH}_3)_2$] (**D**) as models for **9** and **12**.

For complexes **A** and **B**, the calculations were performed in C_{2v} and D_{2h} symmetries, respectively. The coordinate system chosen is shown in Figure 5. The results of these studies for both complexes, which provide a qualitative description of the frontier orbitals, are collected in Table 4 and an schematic view of the HOMO and LUMO for the diplatinum complex **B** is given in Figure 5. In agreement with previous theoretical and photoelectronic studies,²⁴ the interaction between the Pt centers and the alkynyl ligand is of filled–filled type with Pt– π^* back-bonding being of minimal importance. In both, the HOMO arises from a π interaction between platinum orbitals (symmetry $2b_2$ (**A**) and $4b_{2g}$ (**B**) for PtH(PH_3)₂ fragments) with the π system of the acetylenic fragment ($4b_2$ for **A** and $2b_{2g}$ for **B**) having, as shown in Figure 5, a Pt–C $_{\alpha}$ antibonding and C \equiv C bonding nature ($6b_2$, **A**; $6b_{2g}$, **B**). The LUMO in both compounds is mainly located in the alkynyl system and is rather similar to that obtained for HC \equiv CC $_6$ H $_4$ -1,4-C \equiv CH.^{24c} The participation of the Pt atoms (a mixed p_z – d_{xz} orbital) is very small (3%, **A**; 6%, **B**). Thus, on the basis of these results, it seems appropriate to assign a considerable character of MLCT to the transitions measured in the absorption and emission spectra of the hydride alkynyl complexes.

The results of the EHMO calculations on the electronic structures of the model complexes [$\{\text{Pt}^0(\text{PH}_3)_2\}_2\text{-}(\text{HC}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{CH})$] (**C**) and [$\{trans\text{-}(\text{PH}_3)_2\text{HPt}(\text{C}\equiv\text{CC}_6\text{H}_4\text{-1,4-C}\equiv\text{CH})\}\text{Pt}^0(\text{PH}_3)_2$] (**D**) (Table 4 and Figure 6 for **D**) confirm that, not only in **C** but also in the mixed-valence **D**, the HOMO has a significant participation of the platinum(0) atoms. Thus, in both **C** and **D** complexes, the lowest unoccupied molecular orbital (LUMO) is, as in compounds **A** and **B**, mainly located in the hydrocarbon fragment (in this case the diyne fragment). It is also labeled as π^* and shows a considerable delocalization through the phenylene bridge. However, their HOMO possesses approximately half-and-half metal–carbon character. As can be observed in Figure 6, which shows a schematic representation of the contribution to the HOMO in **D**, in this case the participation of the metals is located on Pt(0) and has a notable d character. The remaining participation is delocalized along the whole carbon skeleton with a very small contribution of the Pt(II) center. The HOMO has σ^* antibonding nature relative to the Pt(0) atom because it arises from a filled–filled type interaction between fragment **A** and a mixed (d_{xz} – d_{z^2} – p_x – p_z) platinum orbital. In **C**, the HOMO is symmetrical with the participation of both Pt centers (25% each) and of all diyne fragments. In both, since the Pt(0) d character is remarkable in the HOMO, and the LUMO is mainly localized in the π^* system, the corresponding electronic transitions are also essentially metal-to-ligand charge transfer (MLCT). Similar assignments had been previously reported for more simple [$\text{Pt}(\text{RC}\equiv\text{CR})(\text{PPh}_3)_2$] complexes.³⁴

(iv) Conclusions. In summary, several mononuclear (**1–6**) and binuclear (**7**, **8**) hydride–alkynyl platinum(II) complexes have been reported, together with some Pt(0)–diyne (**9**) and mixed Pt(II)–Pt(0) hydride–alkynyl–alkyne (**10–12**) binuclear derivatives. Their ab-

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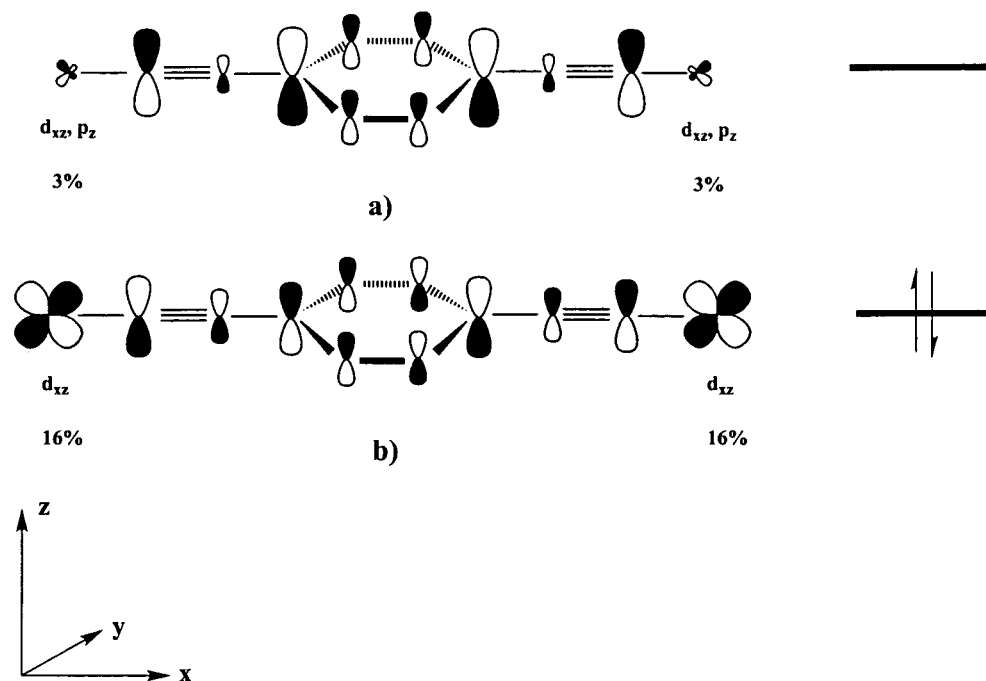


Figure 5. Representation of the most important contributions to the LUMO (a) and HOMO (b) in $[trans,trans-(PH_3)_2HPt(C\equiv CC_6H_4-1,4-C\equiv C)PtH(PH_3)_2]$ (B).

Table 4. Summary of Computational Results for $[trans-PtH(C\equiv C-C_6H_4-1,4-C\equiv CH)(PH_3)_2]$ (A), $[trans,trans-(PH_3)_2HPt(C\equiv CC_6H_4-1,4-C\equiv C)PtH(PH_3)_2]$ (B), $[\{Pt^0(PH_3)_2\}_2(HC\equiv CC_6H_4-1,4-C\equiv CH)]$ (C), and $[\{trans-(PH_3)_2HPt(C\equiv CC_6H_4-1,4-C\equiv CH)\}Pt^0(PH_3)_2]$ (D)

compd	HOMO [E/eV]	LUMO [E/eV]
A	$\pi(C\equiv CC_6H_4-1,4-C\equiv C) - \pi^*(Pt)$ (29% d_{xz}) [-12.04]	$\pi^*(C\equiv CC_6H_4-1,4-C\equiv C)$ [-9.14]
B	$\pi^*(Pt)$ (16%) - $\pi(C\equiv CC_6H_4-1,4-C\equiv C) - \pi^*(Pt)$ (16% d_{xz}) [-11.92]	$\pi^*(C\equiv C-C_6H_4-1,4-C\equiv C)$ [-9.12]
C	$\sigma^*(Pt^0)$ (25%) - $\pi(C\equiv CC_6H_4-1,4-C\equiv C) - \sigma^*(Pt^0)$ (25%) [-11.56]	π^*Pt^0 (5%) - $\pi^*(C\equiv CC_6H_4-1,4-C\equiv C) - \pi^*(Pt^0)$ (5%) [-8.50]
D	$\pi^*(Pt)$ (3%) - $\pi(C\equiv C-C_6H_4-1,4-C\equiv C) - \sigma^*Pt^0$ (60%) [-11.65]	$\pi^*(Pt)$ (4%) - $\pi^*(C\equiv CC_6H_4-1,4-C\equiv C) - \pi^*(Pt^0)$ (4%) [-8.86]

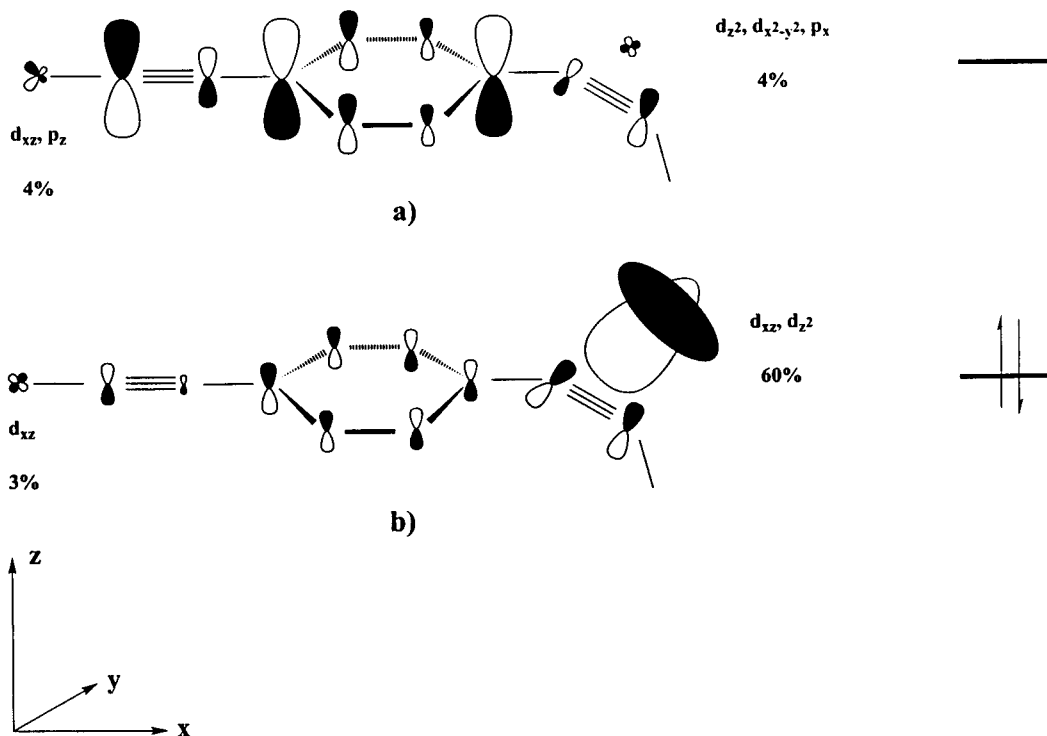
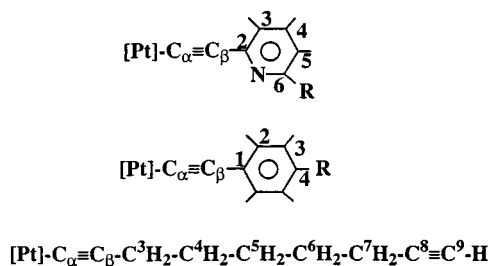


Figure 6. Schematic representation of the calculated LUMO (a) and HOMO (b) in $[\{trans-(PH_3)_2HPt(C\equiv CC_6H_4-1,4-C\equiv CH)\}Pt^0(PH_3)_2]$ (D).

sorption and some emission spectra have been examined and analyzed on the basis of EHMO calculations on

$[trans-PtH(C\equiv CC_6H_4-1,4-C\equiv CH)(PH_3)_2]$ (A) and the isomeric compounds $[trans,trans-(PH_3)_2HPt(C\equiv CC_6H_4-$

**Figure 7.**

1,4-C≡C)PtH(PPh₃)₂] (**B**), [(Pt⁰(PPh₃)₂)₂(HC≡CC₆H₄-1,4-C≡CH)] (**C**), and [(*trans*-(PPh₃)₂H)Pt(C≡CC₆H₄-1,4-C≡CH)]Pt⁰(PPh₃)₂] (**D**) as model complexes.

The results suggest that (i) the LUMO is always centered on the π* skeleton carbon, (ii) the HOMO in the hydride-alkynyl Pt(II) compounds **A** and **B** is a π orbital with a notable Pt d orbital and a Pt-C antibonding character, and (iii) the HOMO in **C** and **D** consists of the valence d orbitals of Pt(0).

It is worth to note that compounds **10–12** which are the first reported hydride-alkynyl-alkyne Pt(II)-Pt(0) mixed-valence derivatives, are rather stable and no isomerization toward the corresponding dihydride-dialkynyl compounds (**7** and **8**) has been detected.

Experimental Section

¹H, ¹³C, and ³¹P NMR spectra were recorded at 20 °C on a Bruker ARX-300 spectrometer. Chemical shifts are reported in ppm relative to external standards (SiMe₄ and 88% H₃PO₄), and coupling constants are given in Hz. The NMR spectral assignments follow the numbering scheme shown in Figure 7. Infrared spectra were recorded with Perkin-Elmer 883 or Spectrum 1000 spectrometers as Nujol mulls between polyethylene sheets (**1–3**, **6a**, **b**, **9**) or as pellets in KBr (**4**, **5**, **7**, **8**, **10–12**). C, H, and N analyses were carried out with a Perkin-Elmer 240 microanalyzer or a Perkin-Elmer 2400 CHNS/O analyzer. Mass spectra were obtained in a VG Autospec double-focusing mass spectrometer operating in the FAB⁺ mode, except for complexes **9–11** (HP-5989B mass spectrometer using the ES(+) technique). The synthesis and spectroscopic and analytical data of **1** have been previously reported by us.⁷ The syntheses of complexes **6b** and **9–12** were carried out under a nitrogen atmosphere with the acetone treated with KMnO₄ and distilled prior to use. The EH-MO calculations were performed using the program CACAO, version 4.0, developed by Meally and Proserpio³³ and standard atomic parameters.

The complex [*trans*-PtHCl(PPh₃)₂]³⁵ and the alkynes 2-ethynylpyridine,³⁶ 2,6-bis(ethynyl)pyridine,³⁷ 1,4-bis(ethynyl)benzene,³⁷ and (4-ethynyl)phenylamine³⁷ were prepared by literature methods. Nonadiyne, 1,1-diphenyl-2-propynol, and NEt₂H were used as received.

Synthesis of [*trans*-PtH(C≡CC₅H₄N-2)(PPh₃)₂] (1**).** A solution of [*trans*-PtHCl(PPh₃)₂] (0.40 g, 0.53 mmol) in CHCl₃ (10 mL) was treated with 0.30 mL of 2-ethynylpyridine (3.05 mmol) and 0.5 mL of NEt₂H. After the mixture was refluxed for 30 min, it was concentrated to small volume. By addition of methanol (20 mL) and cooling for ~12 h, complex **1** precipitated as a white microcrystalline solid. Yield: 74%.

Data for **1** are as follows. Anal. Calcd for C₄₃H₃₅NP₂Pt: C, 62.77; H, 4.28; N, 1.70. Found: C, 62.28; H, 3.87; N, 1.73. MS: *m/z* 823 [M + H]⁺ 35%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν-

(C≡C) 2109 (s); ν(Pt-H) 2044 (m). ¹H NMR (CDCl₃, δ; *J* in Hz): 8.28 (d, *J*_{H-H} = 4.2, H⁶); 7.71 (m, *o*-H, Ph, PPh₃); 7.35 (m, *m*-H and *p*-H, Ph, PPh₃); 7.23 (t, *J*_{H-H} = 7.6, H⁴); 6.82 (m, H⁵); 6.42 (d, *J*_{H-H} = 7.8, H³); -6.30 (t, ²*J*_{P-H} = 15.5; ¹*J*_{Pt-H} = 645, Pt-H) (based on ¹H-¹H COSY NMR spectrum). ¹³C NMR (CDCl₃, δ; *J* in Hz): 148.52 (s, C⁶); 147.25 (s, ³*J*_{Pt-C} = 23, C²); 134.60 (s, *o*-C, Ph, PPh₃); 133.13 (t, ¹*J*_{P-C} + ³*J*_{P-C} = 54, *i*-C, Ph, PPh₃); 130.14 (s, *p*-C, Ph, PPh₃); 127.99 (s, *m*-C, Ph, PPh₃ and probably C⁴ or C⁵); 126.04 (s, ⁴*J*_{Pt-C} = 6.4, C³); 118.95 (s, C⁴ or C⁵); 115.01 (s, ²*J*_{Pt-Cβ} = 236, C_β); C_α is not observed. ³¹P NMR (CDCl₃, δ; *J* in Hz): 26.50 (s, ¹*J*_{Pt-P} = 2917).

Synthesis of [*trans*-PtH{C≡C(6-C≡CH)C₅H₃N-2}(PPh₃)₂] (2**).** Complex **2** was prepared as a beige solid following a procedure identical with that described for **1**: 0.40 g (0.53 mmol) of [*trans*-PtHCl(PPh₃)₂], 0.14 g (1.10 mmol) of 2,6-bis(ethynyl)pyridine, and 1 mL of NEt₂H were used with a refluxing time of 2.5 h. Yield: 94%.

Data for **2** are as follows. Anal. Calcd for C₄₅H₃₅NP₂Pt: C, 63.82; H, 4.16; N, 1.65. Found: C, 63.69; H, 3.87; N, 1.68. MS: *m/z* 847 [M + H]⁺ 20%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν-(C≡C) 2100 (s); ν(Pt-H) ~2040 (sh). ¹H NMR (CDCl₃, δ; *J* in Hz): 7.69 (m, *o*-H, Ph, PPh₃); 7.35 (m, *m*-H and *p*-H, Ph, PPh₃); 7.19 (t, *J*_{H-H} = 7.7, H⁴); 7.04 (d, *J*_{H-H} = 7.5, H⁵); 6.40 (d, *J*_{H-H} = 7.8, H³); 2.98 (s, C≡CH); -6.27 (t, ²*J*_{P-H} = 14.3; ¹*J*_{Pt-H} = 646, Pt-H). ¹³C NMR (CDCl₃, δ; *J* in Hz): 147.47 (s, ³*J*_{Pt-C} = 24, C²); 140.98 (s, C⁶); 134.74 (s, C⁴); 134.60 (s br, *o*-C, Ph, PPh₃); 133.09 (m, *i*-C, Ph, PPh₃); 130.15 (s, *p*-C, Ph, PPh₃); 128.00 (s, *m*-C, Ph, PPh₃); 125.90 (s, ⁴*J*_{Pt-C} = 7.1, C³); 122.90 (s, C⁵); 114.34 (s, ²*J*_{Pt-Cβ} = 236, C_β); C_α is not observed; 83.47 (s, C_β, C_β≡C_αH); 75.39 (s, C_α, C_β≡C_αH). ³¹P NMR (CDCl₃, δ; *J* in Hz): 26.52 (s, ¹*J*_{Pt-P} = 2914).

Synthesis of [*trans*-PtH{C≡CC₆H₄NH₂-4}(PPh₃)₂]^{3/4}·CHCl₃ (3**·^{3/4}CHCl₃).** The complex **3**·^{3/4}CHCl₃ was prepared as a yellow solid as described for complex **1**, but starting from 0.48 g (0.63 mmol) of [*trans*-PtHCl(PPh₃)₂], 0.20 g (1.71 mmol) of (4-ethynyl)phenylamine, and 1 mL of NEt₂H. The mixture was refluxed for 10 min. Yield: 79%.

Data for **3**·^{3/4}CHCl₃ are as follows. Anal. Calcd for C₄₄H₃₇NP₂Pt·^{3/4}CHCl₃: C, 58.02; H, 4.11; N, 1.51. Found: C, 57.82; H, 4.02; N, 1.65. MS: *m/z* 836 [M]⁺ 8%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2114 (s); ν(Pt-H) 2073 (m). ¹H NMR (CDCl₃, δ; *J* in Hz): 7.71 (m, *o*-H, Ph, PPh₃); 7.36 (m, *m*-H and *p*-H, Ph, PPh₃); 6.36 (AB, *J*_{H-H} = 8.35, *v*_A = 6.42, *v*_B = 6.30); 3.44 (s br, NH₂); -6.27 (t, ²*J*_{P-H} = 15.3, ¹*J*_{Pt-H} = 644, Pt-H). ¹³C NMR (CDCl₃, δ; *J* in Hz): 143.18 (s, C⁴); 134.67 (t, ²*J*_{P-C} = 6.6, *o*-C, Ph, PPh₃); 133.40 (t, ¹*J*_{P-C} + ³*J*_{P-C} = 56, *i*-C, Ph, PPh₃); 132.21 (s, ⁴*J*_{Pt-C} ≈ 10, C²); 130.03 (s, *p*-C, Ph, PPh₃); 127.95 (t, ³*J*_{P-C} = 5.2, *m*-C, Ph, PPh₃); 119.50 (s, C¹); 114.28 (s, C³); C_α and C_β are not observed. ³¹P NMR (CDCl₃, δ; *J* in Hz): 27.34 (s, ¹*J*_{Pt-P} = 2931). The presence of CHCl₃ has been confirmed by ¹H NMR in acetone-*d*₆ (δ 8.02) and C₆D₆ (δ 6.15).

Synthesis of [*trans*-PtH{C≡C(4-C≡CH)C₆H₄}(PPh₃)₂] (4**).** A solution of [*trans*-PtHCl(PPh₃)₂] (0.40 g, 0.53 mmol) in CHCl₃ (10 mL) was treated with 0.13 g of 1,4-bis(ethynyl)benzene (1.71 mmol) and 1 mL of NEt₂H, and the mixture was refluxed for 15 min. Evaporation to dryness of the mixture and addition of cold methanol (~5 mL) afforded the precipitation of a pale orange solid (0.414 g), which was identified (¹H and ³¹P{¹H} NMR) as a mixture of complexes **4** and **8** in a 4:1 molar proportion. Recrystallization of the solid in acetone/MeOH yielded complex **4** as an orange solid. Yield: 65%.

Data for **4** are as follows. Anal. Calcd for C₄₆H₃₆P₂Pt: C, 65.32; H, 4.29. Found: C, 65.22; H, 4.59. MS: *m/z* 845 [M]⁺ 8%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2099 (s); ν(Pt-H) 2031 (m). ¹H NMR (CDCl₃, δ; *J* in Hz): 7.72 (m, *o*-H, Ph, PPh₃); 7.38 (m, *m*-H and *p*-H, Ph, PPh₃); 7.13 (d, *J*_{H-H} = 8.1); 6.50 (d, *J*_{H-H} = 8.1); 3.04 (s, C≡CH); -6.11 (t, ²*J*_{P-H} = 14.9; ¹*J*_{Pt-H} = 651, Pt-H). ¹³C NMR (CDCl₃, δ; *J* in Hz): 134.57 (s br, *o*-C, Ph, PPh₃); 133.06 (t, ¹*J*_{P-C} + ³*J*_{P-C} = 55, *i*-C, Ph, PPh₃); 131.02 (s, C³); 130.89 (s, ³*J*_{Pt-C} = 8.5, C²); 130.16 (s, *p*-C, Ph, PPh₃); 129.59 (s, ²*J*_{Pt-C} = 23, C¹); 128.00 (s br, *m*-C, Ph, PPh₃);

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117.64 (s, C $^{\alpha}$); 113.80 (s, $^2J_{\text{Pt}-\text{C}\beta}$ = 236, C $_{\beta}$); C $_{\alpha}$ is not observed; 84.41 (s, C $_{\beta}$, C $_{\beta}$ =C $_{\alpha}$ H); 79.91 (s, C $_{\alpha}$, C $_{\beta}$ =C $_{\alpha}$ H). ^{31}P NMR (CDCl $_3$, δ ; J in Hz): 27.60 (s, $^1J_{\text{Pt}-\text{P}}$ = 2914).

Synthesis of [*trans*-PtH{C≡C(CH $_2$) $_5$ C≡CH}(PPh $_3$) $_2$] (5). Complex **5** was prepared as a white solid following a procedure identical with that described for **1**: 0.50 g (0.66 mmol) of [*trans*-PtHCl(PPh $_3$) $_2$], 1 mL (6.65 mmol) of nonadiyne, and 1 mL of NEt $_2$ H were used with a refluxing time of 2 h. Yield: 72%.

Data for **5** are as follows. Anal. Calcd for C $_{45}$ H $_{42}$ Pt $_2$: C, 64.35; H, 5.00. Found: C, 64.23; H, 4.81. MS: m/z 839 [M] $^+$ 5%; 719 [Pt(PPh $_3$) $_2$] $^+$ 100%. IR (cm $^{-1}$): $\nu(\text{C}\equiv\text{C})$ 2121 (m); $\nu(\text{Pt}-\text{H})$ 2034 (m). ^1H NMR (CDCl $_3$, δ ; J in Hz): 7.70 (m, *o*-H, Ph, PPh $_3$); 7.36 (m, *m*-H and *p*-H, Ph, PPh $_3$); 2.01 (dt, $J_{\text{H}-\text{H}}$ = 13.42, $J_{\text{H}-\text{H}}$ = 1.47, H 7); 1.89 (br, C≡CH); 1.83 (t, $J_{\text{H}-\text{H}}$ = 12.08, H 3); 1.34 (t, $J_{\text{H}-\text{H}}$ = 14.04, H 6); 1.08 (m, H 4 , H 5); -6.54 (t, $^2J_{\text{P}-\text{H}}$ = 15.5; $^1J_{\text{Pt}-\text{H}}$ = 640, Pt-H). ^{13}C NMR (CDCl $_3$, δ ; J in Hz): 134.70 (s br, *o*-C, Ph, PPh $_3$); 133.57 (t, $^1J_{\text{P}-\text{C}}$ + $^3J_{\text{P}-\text{C}}$ = 56.2, *i*-C, Ph, PPh $_3$); 129.96 (s, *p*-C, Ph, PPh $_3$); 127.81 (s br, *m*-C, Ph, PPh $_3$); 113.96 (s, $^2J_{\text{Pt}-\text{C}\beta}$ = 236, C $_{\beta}$); 107.17 (m, C $_{\alpha}$); 85.01 (s, C $_{\beta}$, C $_{\beta}$ =C $_{\alpha}$ H); 67.86 (s, C $_{\alpha}$, C $_{\beta}$ =C $_{\alpha}$ H); 29.47 (s, $^4J_{\text{Pt}-\text{C}}$ ~ 9, C 4); 28.32 (s, C 5 or C 6); 28.20 (s, C 5 or C 6); 21.46 (s, $^3J_{\text{Pt}-\text{C}}$ = 19, C 3); 18.30 (s, C 7). ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra were assigned on the basis on $^1\text{H}-^1\text{H}$ COSY and $^1\text{H}-^{13}\text{C}$ correlation NMR spectra. ^{31}P NMR (CDCl $_3$, δ ; J in Hz): 26.91 (s, $^1J_{\text{Pt}-\text{P}}$ = 2948).

Reaction of [*trans*-PtHCl(PPh $_3$) $_2$] with HC≡CCPh $_2$ OH. 1,1-Diphenyl-2-propynol (0.4 g, 1.92 mmol) and 0.5 mL of NEt $_2$ H were added to a solution of 0.4 g (0.53 mmol) of [*trans*-PtHCl(PPh $_3$) $_2$] in 20 mL of CHCl $_3$. The mixture was refluxed for 3.5 h, evaporated to dryness, and treated with 15 mL of MeOH, causing the precipitation of a white solid which was identified (^1H and ^{31}P NMR) as a mixture of the isomers [*trans*-PtH(C≡CCPh $_2$ OH)(PPh $_3$) $_2$] (**6a**) and [Pt(η^2 -HC≡CCPh $_2$ OH)(PPh $_3$) $_2$] (**6b**) in a 2:1 molar proportion. Yield: 35% (based on Pt). (Anal. Calcd for C $_{51}$ H $_{42}$ OP $_2$ Pt: C, 66.01; H, 4.56. Found: C, 65.57; H, 4.89. MS: m/z [M $^+$] 927 5%). Further attempts to separate completely both complexes by standard recrystallization methods were unsuccessful.

Complex **6b** can also be obtained pure as a pale yellow microcrystalline solid by literature methods^{10d} or reacting the equimolar amount of [Pt(η^2 -C $_2$ H $_4$)(PPh $_3$) $_2$] (0.2 g, 0.27 mmol) and 1,1-diphenyl-2-propynol (0.056 g, 0.27 mmol) in 10 mL of acetone. Evaporation of the reaction mixture to ca. 5 mL causes the precipitation of **6b** in 60% yield.

Complex **6a** was spectroscopically characterized from the mixture of **6a,b**. IR (cm $^{-1}$): $\nu(\text{C}\equiv\text{C})$ 2106 (m); $\nu(\text{Pt}-\text{H})$ 2047 (m). ^1H NMR (CDCl $_3$, δ ; J in Hz): 7.65 (m, *o*-H, Ph, PPh $_3$); 7.30 (m, *m*-H and *p*-H, Ph, PPh $_3$); 7.10, 7.05 (m, Ph, CPh $_2$ -OH); 1.37 (s, OH); -6.35 (t, $^2J_{\text{P}-\text{H}}$ = 14.6; $^1J_{\text{Pt}-\text{H}}$ = 666, Pt-H). ^{13}C NMR (CDCl $_3$, δ ; J in Hz): 147.45 (s, *i*-C, Ph, CPh $_2$ OH); 134.63 (s br, *o*-C, Ph, PPh $_3$); 133.06 (t, $^1J_{\text{P}-\text{C}}$ + $^3J_{\text{P}-\text{C}}$ = 56, *i*-C, Ph, PPh $_3$); 130.20 (s, *p*-C, Ph, PPh $_3$); 128.07 (s br, *m*-C, Ph, PPh $_3$); 127.30 (s, Ph, CPh $_2$ OH); 126.21 (s, Ph, CPh $_2$ OH); 125.93 (s, *p*-C, Ph, CPh $_2$ OH); 115.47 (s, $^2J_{\text{Pt}-\text{C}\beta}$ = 231.4, C $_{\beta}$); C $_{\alpha}$ is not observed; 75.23 (s, $^3J_{\text{Pt}-\text{C}}$ ~ 20, CPh $_2$ OH). ^{31}P NMR (CDCl $_3$, δ ; J in Hz): 29.37 (s, $^1J_{\text{Pt}-\text{P}}$ = 2907).

Data for complex **6b** are as follows. Anal. Calcd for C $_{51}$ H $_{42}$ OP $_2$ Pt: C, 66.01; H, 4.56. Found: C, 66.03; H, 4.51. IR (cm $^{-1}$): $\nu(\text{C}\equiv\text{C})$ 1692 (s). ^1H NMR (CDCl $_3$, δ ; J in Hz): 7.44, 7.18, 6.98 (m, Ph, PPh $_3$ and CPh $_2$ OH); 6.46 (dd, $^2J_{\text{Pt}-\text{H}}$ = 57.7, $^3J_{\text{Pt}-\text{H}}$ = 22.7, $^3J_{\text{Pcis}-\text{H}}$ = 9.6, C≡CH); 2.11 (s, OH). ^{13}C NMR (CDCl $_3$, δ ; J in Hz): 147.98 (d, $^4J_{\text{P}-\text{C}}$ = 1.2, $^3J_{\text{Pt}-\text{C}}$ = 13.2, *i*-C, Ph, CPh $_2$ -OH); 137.08 (dd, $^1J_{\text{P}-\text{C}}$ = 41.4, $^3J_{\text{P}-\text{C}}$ = 3.2, $^2J_{\text{Pt}-\text{C}}$ = 25, *i*-C, Ph, PPh $_3$); 136.17 (dd, $^1J_{\text{P}-\text{C}}$ = 42.6, $^3J_{\text{P}-\text{C}}$ = 2.5, $^2J_{\text{Pt}-\text{C}}$ = 29.3, *i*-C, Ph, PPh $_3$); 134.01 (d, $^2J_{\text{P}-\text{C}}$ = 13.4, $^3J_{\text{Pt}-\text{C}}$ = 20.8, *o*-C, Ph, PPh $_3$); 133.86 (d, $^2J_{\text{P}-\text{C}}$ = 12.9, $^3J_{\text{Pt}-\text{C}}$ = 19.8, *o*-C, Ph, PPh $_3$); 129.3 (d, $^4J_{\text{P}-\text{C}}$ = 1.4, *p*-C, Ph, PPh $_3$); 129.0 (d, $^4J_{\text{P}-\text{C}}$ = 1.8, *p*-C, Ph, PPh $_3$); 127.77 (d, $^3J_{\text{P}-\text{C}}$ = 9.7, *m*-C, Ph, PPh $_3$); 127.59 (d, $^3J_{\text{P}-\text{C}}$ = 9.9, *m*-C, Ph, PPh $_3$); 127.47 (s, Ph, CPh $_2$ OH); 126.57 (s, Ph, CPh $_2$ OH); 126.12 (s, *p*-C, Ph, CPh $_2$ OH); 113.20 (dd, $^2J_{\text{C}-\text{Ptrans}}$ = 62.5, $^2J_{\text{P}-\text{Ccis}}$ = 5.5, C $_{\alpha}$ or C $_{\beta}$); 77.98 (dd, $^3J_{\text{C}-\text{Ptrans}}$ =

7.6, $^3J_{\text{P}-\text{Ccis}}$ = 5.8, CPh $_2$ OH). ^{31}P NMR (CDCl $_3$, δ ; J in Hz): 26.88 (d, $^1J_{\text{Pt}-\text{P}}$ = 3552, $^2J_{\text{P}-\text{P}}$ = 27.5); 24.92 (d, $^1J_{\text{Pt}-\text{P}}$ = 3503, $^2J_{\text{P}-\text{P}}$ = 27.5). Acetylenic C resonances for HC≡CCPh $_2$ OH (CDCl $_3$, δ ; J in Hz): 75.58, 75.51.

Synthesis of [*trans,trans*-(PPh $_3$) $_2$ HPT{ μ - σ - σ -(C≡C) $_2$ C $_5$ -H $_3$ N-2,6}PtH(PPh $_3$) $_2$] (7). An equimolar mixture of [*trans*-PtHCl(PPh $_3$) $_2$] (0.33 g, 0.44 mmol) and complex **2** (0.37 g, 0.44 mmol) was refluxed with 2 mL of NEt $_2$ H, in 20 mL of CHCl $_3$, for 1 h. By concentration to small volume (ca. 5 mL) and addition of 20 mL of MeOH, complex **7** precipitates as an orange solid. Yield: 72%.

Complex **7** was alternatively obtained by refluxing [*trans*-PtHCl(PPh $_3$) $_2$] (0.4 g, 0.53 mmol) and 2,6-bis(ethynyl)pyridine (0.07 g, 0.55 mmol) with 0.5 mL of NEt $_2$ H, in 20 mL of CHCl $_3$, for 90 min. Concentration to small volume (ca. 5 mL) and addition of 20 mL of MeOH yielded 0.147 g of a beige solid, which was identified (^{31}P NMR) as a mixture of **2** and **7** (molar ratio 1:1.4, respectively). Recrystallization of the mixture in CHCl $_3$ /MeOH gave 0.085 g of complex **7**. Yield: 20.5% (based on Pt).

Data for **7** (by using the sample obtained by the first synthetic method). Anal. Calcd for C $_{81}$ H $_{65}$ NP $_4$ Pt $_2$: C, 62.11; H, 4.18; N, 0.89. Found: C, 62.06; H, 3.66; N, 1.33. MS: m/z 1566 [M + H] $^+$ 11%; 377 [PtPPh $_2$ - 1] $^+$ 100%. IR (cm $^{-1}$): $\nu(\text{C}\equiv\text{C})$ 2099 (s); $\nu(\text{Pt}-\text{H})$ ~2041 (sh). ^1H NMR (CDCl $_3$, δ ; J in Hz): 7.72 (m, *o*-H, Ph, PPh $_3$); 7.31 (m, *m*-H and *p*-H, Ph, PPh $_3$); 6.85 (t, $J_{\text{H}-\text{H}}$ = 7, H 4); 6.08 (d, $J_{\text{H}-\text{H}}$ = 7, H 3); -6.30 (t, $^2J_{\text{P}-\text{H}}$ = 15.3; $^1J_{\text{Pt}-\text{H}}$ = 646, Pt-H). ^{13}C NMR (CDCl $_3$, δ ; J in Hz): 146.10 (s, $^3J_{\text{Pt}-\text{C}}$ = 22.4, C 2); 133.43 (s, C 4); 134.62 (t, $^2J_{\text{P}-\text{C}}$ = 6.2, *o*-C, Ph, PPh $_3$); 133.23 (t, $^1J_{\text{P}-\text{C}}$ + $^3J_{\text{P}-\text{C}}$ = 56.4, *i*-C, Ph, PPh $_3$); 130.03 (s, *p*-C, Ph, PPh $_3$); 127.98 (s br, *m*-C, Ph, PPh $_3$); 124.84 (t, $^2J_{\text{P}-\text{C}\alpha}$ = 10.6, C $_{\alpha}$); 122.03 (s, C 3); 115.90 (s, $^2J_{\text{Pt}-\text{C}\beta}$ = 235, C $_{\beta}$). ^{31}P NMR (CDCl $_3$, δ ; J in Hz): 26.33 (s, $^1J_{\text{Pt}-\text{P}}$ = 2919).

Synthesis of [*trans,trans*-(PPh $_3$) $_2$ HPT{ μ - σ - σ -(C≡C) $_2$ C $_6$ H $_4$ -1,4}PtH(PPh $_3$) $_2$] (8). Complex **8** was prepared as a pale yellow solid following a procedure identical with that described for **7**: 0.21 g (0.28 mmol) of [*trans*-PtHCl(PPh $_3$) $_2$], 0.24 g (0.28 mmol) of **4**, and 1 mL of NEt $_2$ H were used with a refluxing time of 3.5 h. Yield: 71%.

Complex **8** was alternatively obtained by refluxing [*trans*-PtHCl(PPh $_3$) $_2$] (0.4 g, 0.53 mmol) and 1,4-bis(ethynyl)benzene (0.033 g, 0.26 mmol) with 0.5 mL of NEt $_2$ H, in 20 mL of CHCl $_3$, for 75 min. Concentration to small volume (ca. 5 mL) and addition of 20 mL of MeOH yielded 0.212 g of a beige solid, which was identified (^{31}P NMR) as a mixture of **4**, **8**, and [{- (PPh $_3$) $_2$ Pt] $_2$ { μ - η^2 - η^2 -(C≡CH) $_2$ C $_6$ H $_4$ -1,4}] (**9**) (molar ratio ~1.4:1:1.6, respectively). Recrystallization of the mixture in CH $_2$ Cl $_2$ /acetone rendered 0.075 g of complex **8**. Yield: 18% (based on Pt).

Data for **8** are as follows (by using the sample obtained by the first synthetic method). Anal. Calcd for C $_{82}$ H $_{66}$ P $_4$ Pt $_2$: C, 62.91; H, 4.25. Found: C, 62.34; H, 3.98. MS: m/z 1565 [M + H] $^+$ 2%; 719 [Pt(PPh $_3$) $_2$] $^+$ 100%. IR (cm $^{-1}$): $\nu(\text{C}\equiv\text{C})$ 2102 (s); $\nu(\text{Pt}-\text{H})$ 2038 (m). ^1H NMR (CDCl $_3$, δ ; J in Hz): 7.69 (m, *o*-H, Ph, PPh $_3$); 7.34 (m, *m*-H and *p*-H, Ph, PPh $_3$); 6.21 (s, H 2); -6.26 (t, $^2J_{\text{P}-\text{H}}$ = 15.4; $^1J_{\text{Pt}-\text{H}}$ = 646, Pt-H). ^{13}C NMR (CDCl $_3$, δ ; J in Hz): 134.65 (t, $^2J_{\text{P}-\text{C}}$ = 6.6, *o*-C, Ph, PPh $_3$); 133.32 (t, $^1J_{\text{P}-\text{C}}$ + $^3J_{\text{P}-\text{C}}$ = 56, *i*-C, Ph, PPh $_3$); 130.05 (s, *p*-C, Ph, PPh $_3$ and probably C 2); 127.97 (t, $^3J_{\text{P}-\text{C}}$ = 5.2, *m*-C, Ph, PPh $_3$); 124.92 (s, $^3J_{\text{Pt}-\text{C}}$ = 22, C 1); 123.13 (t, $^2J_{\text{P}-\text{C}\alpha}$ = 11.9, C $_{\alpha}$); 115.29 (s, $^2J_{\text{Pt}-\text{C}\beta}$ = 235.5, C $_{\beta}$). ^{31}P NMR (CDCl $_3$, δ ; J in Hz): 27.23 (s, $^1J_{\text{Pt}-\text{P}}$ = 2929).

Synthesis of [{(PPh $_3$) $_2$ Pt] $_2$ { μ - η^2 - η^2 -(C≡CH) $_2$ C $_6$ H $_4$ -1,4}] (9). Complex **9** was prepared, as described for **6b**, by treating a suspension of 0.3 g (0.4 mmol) of [Pt(η^2 -C $_2$ H $_4$)(PPh $_3$) $_2$] in 10 mL of acetone with 0.025 g (0.2 mmol) of 1,4-bis(ethynyl)benzene. The mixture was stirred for 10 min, giving a suspension, which was evaporated to ca. 5 mL and filtered to yield complex **9** as a pale orange solid. Yield: 83%.

Data for **9** are as follows. Anal. Calcd for C $_{82}$ H $_{66}$ P $_4$ Pt $_2$: C, 62.91; H, 4.25. Found: C, 62.94; H, 4.29. MS (ES $^+$): m/z 1566

[M + 2H]⁺ 1%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν(C≡C) 1688 (m). ¹H NMR (CDCl₃, δ; J in Hz): 7.29, 7.18, 7.12, 7.00 (m, PPh₃ and C≡CH); 6.59 (s, C₆H₄). ¹³C NMR (CDCl₃, δ; J in Hz): 136.79 (dd, ¹J_{P-C} = 41.2, ³J_{P-C} = 3.0, ²J_{Pt-C} = 25.3, *i*-C, Ph, PPh₃); 136.40 (dd, ¹J_{P-C} = 41.9, ³J_{P-C} = 2.5, ²J_{Pt-C} = 28.9, *i*-C, Ph, PPh₃); 134.02 (d, ²J_{P-C} = 13.7, ³J_{Pt-C} = 20.45, *o*-C, Ph, PPh₃); 133.78 (d, ²J_{P-C} = 13.1, ³J_{Pt-C} = 19.2, *o*-C, Ph, PPh₃); 130.83 (m br, C₆H₄); 128.9 (s br, *p*-C, Ph, PPh₃); 127.58 (d, ³J_{P-C} = 9.4, *m*-C, Ph, PPh₃); 127.51 (d, ³J_{P-C} = 9.7, *m*-C, Ph, PPh₃); 114.85 (overlapping of two dd, ²J_{C-Ptrans} ≈ 63, ²J_{C-Pcis} ≈ 6.5, ¹J_{Pt-C} ≈ 260, C_α and C_β). ³¹P NMR (CDCl₃, δ; J in Hz): 30.76 (d, ¹J_{Pt-P} = 3535.5, ²J_{P-P} = 33.9); 26.22 (d, ¹J_{Pt-P} = 3427, ²J_{P-P} = 33.9). Acetylenic C resonances for 1,4-bis(ethynyl)benzene (CDCl₃, δ; J in Hz): 79.07, 82.98.

Synthesis of [(*trans*-PPh₃)₂H-Pt-C≡C-C≡CH]Pt(PPh₃)₂ (R = (CH₂)₅ (10), C₅H₃N-2,6 (11), C₆H₄-1,4 (12)). Solutions of [*trans*-PtH(C≡CR)(PPh₃)₂] (R = (CH₂)₅C≡CH (5), 0.137 g (0.16 mmol); R = (6-C≡CH)C₅H₃N-2 (2), 0.052 g (0.06 mmol); R = (4-C≡CH)C₆H₄ (4), 0.1 g (0.12 mmol)) in 10 mL of acetone were treated with [Pt(η²-C₂H₄)(PPh₃)₂] (0.122 g (0.16 mmol) for 5; 0.046 g (0.06 mmol) for 2; 0.088 g (0.12 mmol) for 4), and the mixtures were stirred for 10 min. After this time, the resulting solutions were evaporated to dryness and the residues treated with cold EtOH (~5 mL), yielding complexes 10 (87%) and 11 (73%) as beige solids. For 12, evaporation of the acetone solution to ca. 5 mL caused the precipitation of this complex as a yellow solid (65%).

Data for complex 10 are as follows. Anal. Calcd for C₈₁H₇₂Pt₄: Pt₂: C, 62.38; H, 4.65. Found: C, 62.55; H, 4.32. MS (ES+, ionized with Ag⁺): *m/z* 1666 [M + Ag]⁺ 12%, 718 [Pt(PPh₃)₂ - H]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2124 (m), 1718 (m); ν(Pt-H) 2037 (m). ¹H NMR (CDCl₃, δ; J in Hz): 7.68, 7.31, 7.10 (m, PPh₃); 6.40 (dd, ³J_{Ptrans-H} = 20.7, ³J_{Pcis-H} = 11.2); 2.24 (m, H⁷); 1.75 (m, H³); 1.29, 1.21 (m, H⁵, H⁶); 0.95 (m, H⁴); -6.53 (t, ²J_{P-H} = 15.4; ¹J_{Pt-H} = 639.5, Pt-H); (based on ¹H-¹H COSY spectrum). ¹³C NMR (CDCl₃, δ; J in Hz): at -50 °C, 136.32 (dt, overlapping of two dd, ¹J_{P-C} ≈ 41, ³J_{P-C} ≈ 3, ²J_{Pt-C} ≈ 30, *i*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 134.38 (t, ²J_{P-C} = 6.6, *o*-C, Ph, PtH(PPh₃)₂); 133.49 (d, ²J_{P-C} = 13.05, *o*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 133.43 (d, ²J_{P-C} = 13.7, *o*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 132.74 (t, ¹J_{P-C} + ³J_{P-C} = 58.6, *i*-C, Ph, PtH(PPh₃)₂); 129.93 (s, *p*-C, Ph, PtH(PPh₃)₂); 128.83 (s, *p*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 128.77 (s, *p*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 127.56 (m, *m*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂ and PtH(PPh₃)₂); 114.46 (s, ²J_{Pt-Cβ} = 235.4, C_β); 106.5 (t, ²J_{P-Cα} = 11.4, C_α); 104.55 (dm, probably overlapping of two dd, ²J_{C-Ptrans} ≈ 67, C_α = C_βH, C⁸ and C⁹); 31.50 (d, ³J_{C-Ptrans} = 5.8, ³J_{C-Pcis} = 1.0, ²J_{Pt-C} = 42.8, C⁷); 29.58 (s br), 28.99 (s br), 27.72 (m), 21.44 (s br) (CH₂). ³¹P NMR (CDCl₃, δ; J in Hz): 31.33 (d, ¹J_{Pt-P} = 3599, ²J_{P-P} = 31.3); 28.44 (d, ¹J_{Pt-P} = 3425, ²J_{P-P} = 31.3); 26.79 (s, ¹J_{Pt-P} = 2965).

Data for complex 11 are as follows. Anal. Calcd for C₈₁H₆₅NPt₂: C, 62.24; H, 4.23; N 0.91. Found: C, 62.47; H, 4.28, N, 0.95. MS (ES+, in the range 1500–1600): *m/z* 1566 [M + 1]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2102 (m), 1685 (s); ν(Pt-H) 2040 (sh). ¹H NMR (CDCl₃, δ; J in Hz): 7.67, 7.26, 7.15, 7.08, 6.97 (m, PPh₃ and C≡CH); 6.50 (t, J_{H-H} = 7.8, H⁴); 6.03 (d, J_{H-H} = 8.5), 6.00 (d, J_{H-H} = 8.3) (H³, H⁵); -6.36 (t, ²J_{P-H} = 15.2; ¹J_{Pt-H} = 644.1, Pt-H). ¹³C NMR (CDCl₃, δ; J in Hz): at -50 °C, 149.54 (m, C⁶); 145.79 (s, C²); 135.55 (dm, overlapping of two dd, *i*-C, ¹J_{P-C} ≈ 43, ²J_{Pt-C} ≈ 25, *i*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 134.32 (t, ²J_{P-C} = 6.6, *o*-C, Ph, PtH(PPh₃)₂); 133.59 (m, overlapping of two d, *o*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 132.38 (t, ¹J_{P-C} + ³J_{P-C} = 57, *i*-C, Ph, PtH(PPh₃)₂); 130.10 (s, *p*-C, Ph, PtH(PPh₃)₂); 128.88 (s br, overlapping of two s, *p*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 127.89 (t, ³J_{P-C} = 5.1, *m*-C, Ph, PtH(PPh₃)₂); 127.46 (d, ³J_{P-C} = 9.3, *m*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 127.39 (d, ³J_{P-C} = 9.7, *m*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 122.66 (dm, probably overlapping of two dd, ²J_{C-Ptrans} ≈ 85, C_α = C_βH); 114.72 (s, C_β); carbon atoms C³, C⁴ and C⁵ of the pyridyl group cannot be assigned. ³¹P NMR (CDCl₃, δ; J in Hz): 30.17 (d,

Table 5. Crystal Data and Structure Refinement Parameters for 1 and 6b

	1	6b
empirical formula	C ₄₃ H ₃₅ NP ₂ Pt	C ₅₁ H ₄₂ OP ₂ Pt
fw	822.75	927.88
temp (K)	173(2)	200(2)
wavelength (Å)	0.710 73	0.710 73
cryst syst	monoclinic	monoclinic
space group	<i>P</i> 2 ₁ / <i>n</i>	<i>P</i> 2 ₁ / <i>n</i>
unit cell dimens		
<i>a</i> (Å)	9.769(1)	9.255(1)
<i>b</i> (Å)	19.182(1)	18.010(2)
<i>c</i> (Å)	18.487(1)	24.330(3)
α (deg)	90	90
β (deg)	98.45(1)	94.60(1)
γ (deg)	90	90
<i>V</i> (Å ³)	3426.6(4)	4042.3(8)
<i>Z</i>	4	4
calcd density (Mg/m ³)	1.595	1.525
abs coeff (mm ⁻¹)	4.221	3.589
<i>F</i> (000)	1632	1856
cryst size	0.50 × 0.15 × 0.10	0.74 × 0.50 × 0.26
θ range for data	1.54–30.47	2.02–25.00
collec (deg)		
index ranges	0 ≤ <i>h</i> ≤ 13 0 ≤ <i>k</i> ≤ 27 -26 ≤ <i>l</i> ≤ 26	-11 ≤ <i>h</i> ≤ 0 -21 ≤ <i>k</i> ≤ 1 -28 ≤ <i>l</i> ≤ 28
no. of rflns collected	10 098	7816
no. of indep rflns	10 098 (<i>R</i> (int) = 0.05)	7038 (<i>R</i> (int) = 0.0204)
refinement method	full-matrix least-squares on <i>F</i> ²	
no. of data/restraints/params	10 098/0/428	6568/0/496
goodness of fit on <i>F</i> ² ^a	1.019	1.061
final <i>R</i> indices	<i>R</i> 1 = 0.0564, w <i>R</i> 2 = 0.0911	<i>R</i> 1 = 0.0323, w <i>R</i> 2 = 0.0560
<i>R</i> indices (all data)	<i>R</i> 1 = 0.1341, w <i>R</i> 2 = 0.1113	<i>R</i> 1 = 0.0572, w <i>R</i> 2 = 0.0627
largest diff peak and hole (e/Å ³)	1.166 and -1.523	1.114 and -0.555

^a Goodness of fit = [Σw(*F*_o² - *F*_c²)²/(*n*_{observns} - *n*_{params})]^{1/2}; *w* = [σ²(*F*_o) + (*g*₁*P*)² + (*g*₂*P*)²]⁻¹; *P* = [max(*F*_o²; 0) + 2*F*_c²]/3. ^b *R*1 = Σ(|*F*_o - *F*_c||Σ|*F*_o); w*R*2 = [Σw(*F*_o² - *F*_c²)²]/Σw(*F*_c²)^{1/2}.

¹J_{Pt-P} = 3535, ²J_{P-P} = 34.1); 26.46 (d, ¹J_{Pt-P} = 3527, ²J_{P-P} = 34.1); 26.30 (s, ¹J_{Pt-P} = 2918).

Data for complex 12 are as follows. Anal. Calcd for C₈₂H₆₆Pt₄: Pt₂: C, 62.91; H, 4.25. Found: C, 62.48; H, 4.10. MS: *m/z* 1565 [M + H]⁺ 3%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2103 (s), 1678 (m); ν(Pt-H) 2050 (s). ¹H NMR (CDCl₃, δ; J in Hz): 7.67, 7.32, 7.11 (m, PPh₃ and C≡CH); 6.69 (d, J_{H-H} = 6.5); 6.12 (d, J_{H-H} = 6.5); -6.24 (t, ²J_{P-H} = 15.4; ¹J_{Pt-H} = 645, Pt-H). ¹³C NMR (CDCl₃, δ; J in Hz): 136.94 (dd, ¹J_{P-C} = 41.2, ³J_{P-C} = 3.2, *i*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 136.43 (dd, ¹J_{P-C} = 41.6, ³J_{P-C} = 2.6, *i*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 134.61 (t, ²J_{P-C} = 6.3, *o*-C, Ph, PtH(PPh₃)₂); 134.11 (d, ²J_{P-C} = 13.5, *o*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 133.83 (d, ²J_{P-C} = 13.15, *o*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 133.2 (t, ¹J_{P-C} + ³J_{P-C} = 55.1, *i*-C, Ph, PtH(PPh₃)₂); 130.05 (s, *p*-C, Ph, PtH(PPh₃)₂); 128.92 (overlapping of two singlets, *p*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 127.95 (t, ³J_{P-C} = 4.8, *m*-C, Ph, PtH(PPh₃)₂); 127.64 (d, ³J_{P-C} = 7.9, *m*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 127.53 (d, ³J_{P-C} = 9.5, *m*-C, Ph, (η²-C≡CH)Pt(PPh₃)₂); 115.18 (s, C_β); 113.92 (dm, probably overlapping of two dd, ²J_{C-Ptrans} ≈ 64, C_α = C_βH); due to the low solubility of the complex carbon atoms of the C₆H₄ group cannot be unequivocally assigned (130.67 (m), 130.45 (m), 126.40 (s)). ³¹P NMR (CDCl₃, δ; J in Hz): 30.94 (d, ¹J_{Pt-P} = 3543, ²J_{P-P} = 34.2); 27.15 (s, ¹J_{Pt-P} = 2927); 26.20 (d, ¹J_{Pt-P} = 3425, ²J_{P-P} = 34.2).

X-ray Crystallographic Analysis of 1. Table 5 reports details of the structure analyses for 1 and 6b.

A colorless rod-shaped crystal of 1, obtained by slow diffusion of hexane into a tetrahydrofuran solution of this complex at -30 °C, was fixed with high-vacuum grease on top of a glass

fiber. The diffraction measurements were made at 173 K with a NONIUS κ CCD instrument, using graphite-monochromated Mo K α radiation. No crystal decay was observed over the data collection period. The structure was solved by direct methods and refined using full-matrix least-squares refinement on F^2 with the SHELXL-97 program.³⁸ All non-hydrogen atoms and H(1) were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. All hydrogen atoms were constrained to idealized geometries and assigned isotropic displacement parameters 1.2 times the U_{iso} value of their carbon attached for the aromatic hydrogens. Final difference electron density maps showed no features outside the range 1.166 to -1.523 e/Å³.

X-ray Crystallographic Analysis of 6b. A pale yellow trigonal-prism-shaped crystal of **6b**, obtained by slow diffusion of hexane into a CHCl₃ solution of the crude mixture of **6a,b** at -30 °C, was fixed with epoxy on top of a glass fiber and transferred to the cold stream of the low-temperature device of a Siemens P4 automated four-circle diffractometer. Cell constants were calculated from 50 well centered reflections with 2θ angles ranging from 24 to 26° . Data were collected at 200 K by the ω method. Three check reflections measured at regular intervals showed no loss of intensity at the end of data

(38) Sheldrick, G. M. SHELXL-97: Program for Crystal Structure Determination from Diffraction Data; University of Göttingen, Göttingen, Germany, 1997.

collection. An empirical absorption correction based on ψ scans was applied (12 reflections, maximum and minimum transmission factors 0.878, 0.588). The structure was solved by the Patterson method, which revealed the position of the platinum atom. All non-hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters equal to 1.2 times the U_{iso} value of their respective parent carbon atoms. There is a peak of electron density higher than 1 e/Å³ (1.11 e/Å³) in the final map, but it is located very close to the platinum atom and has no chemical meaning.

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Supporting Information Available: Tables of all atomic positional and equivalent isotropic displacement parameters, anisotropic displacement parameters, all bond distances and bond angles, and hydrogen coordinates and isotropic displacement parameters for the crystal structures of complexes **1** and **6b**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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