

Synthesis of Pt(II)–Pt(II) and Pt/Pd(II)–Pt(0) Monoalkynylphosphine Bridging Complexes

Juan Forniés,^{*,†} Ana García,[‡] Julio Gómez,[‡] Elena Lalinde,^{*,‡} and M. Teresa Moreno[‡]

Departamento de Química Inorgánica, Instituto de Ciencia de Materiales de Aragón, Universidad de Zaragoza-Consejo Superior de Investigaciones Científicas, 50009 Zaragoza, Spain, and Departamento de Química-Grupo de Síntesis Química de La Rioja, UA-CSIC, Universidad de La Rioja, 26006, Logroño, Spain

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The monoalkynylphosphine complexes *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(tht)] (R = Ph **1a**, Tol **1b**, *t*Bu **1c**, tht = tetrahydrothiophene) have been prepared by bridge splitting [{Pt(C₆F₅)₂(μ-tht)}₂] or by displacement of only one tht ligand from *cis*-[Pt(C₆F₅)₂(tht)₂] with PPh₂C≡CR. Complexes **1** react with *cis*-[Pt(C₆F₅)₂(thf)₂] to give binuclear derivatives [(C₆F₅)₂Pt(μ-tht)-(μ-1κP:2η²-PPh₂C≡CR)Pt(C₆F₅)₂] (R = Ph **2a**, Tol **2b**, *t*Bu **2c**), containing a mixed tht/PPh₂C≡CR bridging system. In contrast, treatment of **1** with [Pt(η²-C₂H₄)(PPh₃)₂] affords mixed-valence Pt(II)–Pt(0) complexes [{(C₆F₅)₂(tht)Pt(μ-1κP:2η²-PPh₂C≡CR)}Pt(PPh₃)₂] (R = Ph **3a**, Tol **3b**) stabilized by only one κP:η² bridging alkynyl phosphine. The molecular structures of **2a** and **3a** have been confirmed by single-crystal X-ray diffraction. Similarly, reactions of *cis*-bis(diphenylphosphino)alkyne complexes *cis*-[M(C₆F₅)₂(PPh₂C≡CR)₂] and *cis*-[Pt(C≡CR')₂(PPh₂C≡CR)₂] (M = Pt, Pd; R = Ph, Tol; R' = Ph, *t*Bu) with 1 or 2 equiv of [Pt(η²-C₂H₄)(PPh₃)₂] yield the corresponding mixed-valence binuclear complexes *cis*-[{(C₆F₅)₂M(PPh₂C≡CR)(μ-1κP:2η²-PPh₂C≡CR)}Pt(PPh₃)₂] (M = Pt, R = Ph **4a**, Tol **4b**; M = Pd, R = Ph **5a**, Tol **5b**) and *cis*-[{(C≡CR')₂Pt(PPh₂C≡CR)(μ-1κP:2η²-PPh₂C≡CR)}Pt(PPh₃)₂] (R' = Ph, R = Ph **6a**, Tol **6b**; R' = *t*Bu, R = Ph **7a**, Tol **7b**), bearing only one PPh₂C≡CR η²-coordinated to a Pt(0)(PPh₃)₂ fragment.

Introduction

Alkynylidiphenylphosphines PPh₂C≡CR have been extensively used in transition metal chemistry, as they are able to act as simple P-donor phosphines,¹ as disubstituted acetylenes,² or to utilize the phosphorus pair and the alkyne function simultaneously.³ Furthermore, in some cases, these ligands undergo cleavage of the P–C(alkyne) bond to generate separate phos-

phido (PPh₂) and alkynide (C≡CR) fragments,⁴ alkyne coupling processes, and M–H or M–C insertion reactions.^{1f,2c,5} Although all these coordination possibilities have been described, it seems clear that P-coordination is favored, especially with metal fragments in their usual oxidation states. Alkyne coordination usually requires a low-valent metal site, and this type of coordination is favored only in a few cases.² It should be noted that even with low-valent metal fragments the P-coordination competes effectively. Thus, previous attempts to generate η²-alkyne complexes of zerovalent

* Corresponding authors. E-mail: elena.lalinde@dq.unirioja.es; forniésj@posta.unizar.es.

† Universidad de Zaragoza-CSIC.

‡ Universidad de La Rioja, UA-CSIC.

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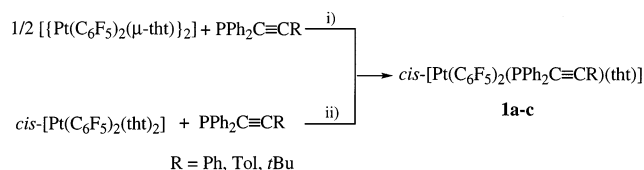
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palladium or platinum produced only P-coordinated species $M(PPh_2C\equiv CMe)_4$ ($M = Pt, Pd$),^{1h} although Carty and co-workers have reported the synthesis of binuclear derivatives $[M(\mu-\kappa P:\eta^2-PPh_2C\equiv CF_3)L\}_2]$ ($M = Pt, Pd$; $L = PPh_2C\equiv CF_3, PPh_3$)^{3c} containing two alkynylphosphine bridging ligands. Recently Bennett et al. have shown that the reactions between the Ni(0) or Pt(0) complexes $[M(\eta^2-C_2H_4)(dcpe)]$ ($dcpe$: 1,2-bis(dicyclohexylphosphino)ethane) and $PPh_2C\equiv CMe$ ^{2c,d} results in the formation of the monomeric η^2 -alkynylphosphine $[M(\eta^2-PPh_2C\equiv CMe)(dcpe)]$ complexes, although they are formed through initial P-coordinated species, detected at low temperature. Recently we have prepared complexes containing $\kappa P:\eta^2$ bridging ligands starting from Pt(II) precursors of the type $cis-[MX_2(PPh_2C\equiv CR)_2]$ ($M = Pt, Pd$; $X = Cl, C\equiv CR'$) and examining their reactivity toward the solvent species $cis-[M(C_6F_5)_2(thf)_2]$ ($M = Pt, Pd$; thf = tetrahydrofuran) in 1:1 molar ratio. This reactivity is versatile and dependent on the X and the R groups. Thus, while the reactions with $cis-[MCl_2(PPh_2C\equiv CR)_2]$ led to $(\mu-Cl)_2$ (when $R = tBu$) or mixed $\mu-Cl/\mu-PPh_2C\equiv CR$ (when $R = Ph$) binuclear complexes,⁶ only homo- and heterobimetallic double alkynyl bridged $(\mu-C\equiv CR)_2$ complexes were formed by using $cis-[Pt(C\equiv CR')_2(PPh_2C\equiv CR)_2]$ as precursors.⁷ Several unusual symmetrical $[Pt(\mu_3-\eta^2-C\equiv CPh)_2]\{M(C_6F_5)_2\}_2$ and $[Pt(\mu-\kappa P:\eta^2-PPh_2C\equiv CPh)_2(\mu-\eta^2-C\equiv CtBu)_2]\{Pt(C_6F_5)_2\}_2$ trimetallic species were also prepared when these cis -bis(alkynyl)bis(alkynylidiphenylphosphine) precursors react with $cis-[M(C_6F_5)_2(thf)_2]$ in 1:2 molar ratio, confirming again the low η^2 -bonding capability of the $PPh_2C\equiv CtBu$ groups.⁷ More recently we have observed that by forcing the η^2 -complexation of both P-coordinated $PPh_2C\equiv CR$ ($R = Ph, Tol$) molecules on $cis-[M(C_6F_5)_2(PPh_2C\equiv CR)_2]$, the initial bis(η^2 -alkyne) adducts $[(C_6F_5)_2M\{\mu-\kappa PP:\eta^2-(PPh_2C\equiv CR)_2\}-Pt(C_6F_5)_2]$ formed at low temperature evolve, through an unexpectedly easy sequential insertion of both $PPh_2C\equiv CR$ molecules into a $Pt-C_6F_5$ bond, yielding unusual μ -2,3-bis(diphenylphosphino)-1,3-butadien-1-yl binuclear complexes.⁸

Continuing with our interest in η^2 -coordinated alkynylphosphines, in this work, we describe the synthesis

Scheme 1



and characterization of novel P-coordinated monoalkynylphosphine complexes $cis-[Pt(C_6F_5)_2(PPh_2C\equiv CR)(tht)]$ ($R = Ph, Tol, tBu$) and examine their reactivity toward $cis-[Pt(C_6F_5)_2(thf)_2]$ and $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$. The preparation of unprecedented double hetero μ -tht/ μ - $PPh_2C\equiv CR$ and mono μ - $\kappa P:\eta^2$ - $PPh_2C\equiv CR$ bridged Pt(II)–Pt(II/0) binuclear complexes is reported. Similar mixed-valence M(II)–Pt(0) complexes bearing only a $PPh_2C\equiv CR$ η^2 -coordinated to the Pt(0)(PPh_3)₂ fragment are also generated by the reaction of cis -bis(alkynylphosphine) derivatives $cis-[MX_2(PPh_2C\equiv CR)_2]$ [$M = Pt, Pd$; $X = C_6F_5, C\equiv CR'$ ($R' = Ph, tBu$; $R = Ph, Tol$)] with $[Pt(\eta^2-C_2H_4)(PPh_3)_2]$.

Results and Discussion

To discover the behavior of complexes with only one P-coordinated alkynylphosphine on a platinum fragment, we have prepared the mononuclear complexes $cis-[Pt(C_6F_5)_2(PPh_2C\equiv CR)(tht)]$ **1** [$R = Ph$ (**a**), Tol (**b**), tBu (**b**)]. These complexes are isolated as white, air-stable solids by bridge splitting the tetrahydrothiophene-bridged binuclear complex $[Pt(C_6F_5)_2(\mu-tht)]_2$ with the appropriate alkynylphosphine (Scheme 1, i). Treatment of the mononuclear $cis-[Pt(C_6F_5)_2(tht)_2]$ with a molar equiv of $PPh_2C\equiv CR$ also results in the displacement of only one tht ligand, providing an alternative method for the synthesis of complexes **1** (Scheme 1, ii).

Analytical and spectroscopic data for these mixed-ligand complexes **1** are given in the Experimental Section. In the IR spectra the most remarkable absorptions are (a) the $\nu(C\equiv C)$ band (2163 – 2179 cm^{-1}) due to P-coordinated $PPh_2C\equiv CR$ ligands and (b) a double absorption corresponding to the X-sensitive modes of the C_6F_5 groups (786 – 812 cm^{-1}), which indicate a cis -structure,⁹ which is unequivocally confirmed by ^{19}F NMR spectroscopy. The presence of tht and $PPh_2C\equiv CR$ ligands is, as expected, established by $^{13}C\{^1H\}$, 1H (tht, $S-\alpha-CH_2$ 36.8 – $36.9/2.83$ – 2.89 ; $\beta-CH_2$ 29.4 – $29.6/1.69$ – 1.71), and $^{31}P\{^1H\}$ (δ_P -5.71 to -7.22 ; $^1J_{Pt-P}$ 2470 – 2482 Hz) NMR spectroscopy. The uncoordinated alkyne carbons are found as doublets in the expected chemical shift ranges with the C_α carbon resonances clearly upfield shifted with regard to those of free $PPh_2C\equiv CR$ ligands (Δ -7.9 **1a**, -6.82 **1b**, -6.9 **1c**). In accordance with previous observations, the C_β signals are less affected (Δ -1.3 **1a**, $+0.74$ **1b**, 0 **1c**) by simple P-coordination of the ligands, and consequently the chemical shift differences $\delta C_\beta - \delta C_\alpha$, which have been previously related to the triple-bond polarization,^{1d,4a,10,11} increase with respect to those of free alkynyl phosphines.

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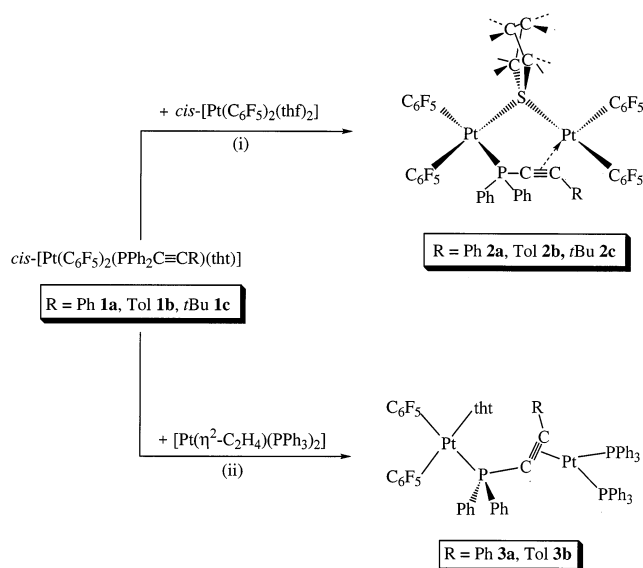
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Scheme 2



The reactivity of complexes **1** toward the Pt(II) and Pt(0) substrates, *cis*-[Pt(C₆F₅)₂(thf)₂] and [Pt(η²-C₂H₄)(PPh₃)₂], respectively, has been examined and the results of these reactions are summarized in Scheme 2. Treatment of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(tht)] (R = Ph **1a**, Tol **1b**, *t*Bu **1c**) with 1 equiv of *cis*-[Pt(C₆F₅)₂(thf)₂] at room temperature in CH₂Cl₂ immediately gives the binuclear heterobridged [(C₆F₅)₂Pt(μ-tht)(μ-1κP:2η²-PPh₂C≡CR)Pt(C₆F₅)₂] (R = Ph **2a**, Tol **2b**, *t*Bu **2c**) complexes in good (**2a**, **2b**) or moderate (**2c**) yields (Scheme 2, i). Complexes **2**, which are isolated as white solids, are stable in the solid state but not in solution. The dimetallic formulation with the mixed heterobridged (μ-tht)(μ-PPh₂C≡CR) system is consistent with their analytical and spectroscopic data and has been confirmed by an X-ray diffraction study on complex **2a**. Evidence for the coordination of the C≡C bond comes from the infrared spectra, which show two absorptions (1982–2059 cm⁻¹) [one of them weak (**2a**, **2b**) or one broad band (**2c**) due to ν(C≡C) and in the range of Pt(II)-coordinated carbon–carbon triple bonds.^{6,7,11} The bridging nature of the tht ligand as well as the asymmetric formulation of the dimers can be inferred from the ¹H NMR spectra, which show, at room temperature, two different signals for both the α-CH₂ (δ 3.82–3.18) and β-CH₂ [δ 2.17–1.55, only one broad (4H) signal for **2c**] proton resonances. It is remarkable that the α-proton resonances, in particular, are deshielded by about 1 ppm compared with those observed in the corresponding starting materials **1**. The ¹⁹F NMR spectra at room temperature confirm the presence of four rigid nonequivalent C₆F₅ groups (four *para*-fluorine triplets and AA'MXX' spin systems), and the ³¹P{¹H} NMR spectra show a singlet resonance (δ 24.25–22.09) with platinum satellites (*J*_{Pt–P} 2359–2332 Hz) which is notably shifted to higher frequencies (Δ 29.95 **2a**, 30.12 **2b**, 29.31 **2c**) with respect to those of **1**. This downfield shift has been previously observed in other complexes containing μ-η²-PPh₂C≡CR ligands, it being attributed to the loss of the electron ring current associated with the π-C≡C bonds upon complexation.^{3,6,7,10,11}

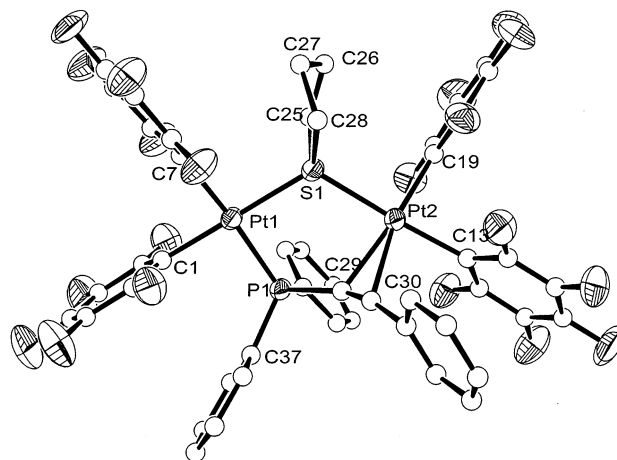


Figure 1. Molecular structure of [(C₆F₅)₂Pt(μ-tht)(μ-1κP:2η²-PPh₂C≡CPh)Pt(C₆F₅)₂], **2a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) [(C₆F₅)₂Pt(μ-tht)(μ-1κP:2η²-PPh₂C≡CPh)Pt(C₆F₅)₂] (**2a**·0.5C₆H₁₄)

Pt(1)–C(1)	2.041(5)	Pt(2)–C(30)	2.342(5)
Pt(1)–C(7)	2.078(4)	Pt(2)–S(1)	2.3813(11)
Pt(1)–P(1)	2.2706(11)	P(1)–C(29)	1.784(5)
Pt(1)–S(1)	2.3447(11)	S(1)–C(28)	1.842(5)
Pt(2)–C(19)	2.027(5)	S(1)–C(25)	1.848(5)
Pt(2)–C(13)	2.046(4)	C(29)–C(30)	1.203(7)
Pt(2)–C(29)	2.205(4)		
C(1)–Pt(1)–C(7)	86.32(18)	C(19)–Pt(2)–S(1)	90.82(13)
C(1)–Pt(1)–P(1)	90.34(13)	C(29)–Pt(2)–S(1)	84.37(12)
C(7)–Pt(1)–S(1)	95.06(13)	Pt(1)–S(1)–Pt(2)	117.54(5)
P(1)–Pt(1)–S(1)	88.38(4)	C(30)–C(29)–P(1)	156.2(4)
C(19)–Pt(2)–C(13)	86.64(18)	C(29)–C(30)–C(31)	167.9(5)
C(13)–Pt(2)–C(29)	98.52(17)	P(1)–C(29)–Pt(2)	117.7(2)
C(13)–Pt(2)–C(30)	81.18(18)		

The single-crystal X-ray structure of **2a** confirms that a diphenyl(phenylethynyl)phosphine group and a tht ligand bridge two identical "*cis*-Pt(C₆F₅)₂" platinum fragments. The molecular geometry is presented in Figure 1, and selected bond distances and angles are listed in Table 1. The alkynylphosphine ligand acts as a four-electron donor with the phosphorus atom bonded to Pt(1) and the alkyne function to Pt(2). It should be noted that heterobridged systems of the type (μ-κP:η²-PPh₂C≡CR)(μ-X) are very scarce. As far as we know, the only examples characterized by X-ray diffraction are the recently described dinuclear derivatives [(C₆F₅)₂Pt(μ-Cl)(μ-1κP:2η²-PPh₂C≡CPh)PtCl(PPh₂C≡CPh)],⁶ obtained by the reaction of *cis*-[PtCl₂(PPh₂C≡CPh)₂] with *cis*-[Pt(C₆F₅)₂(thf)₂], the trinuclear complex [{*cis*-Pt(μ-κP:η²-PPh₂C≡CPh)₂(μ-η¹:η²-PPh₂C≡C*t*Bu)₂}-{Pt(C₆F₅)₂}₂],⁷ in which two terminal "*cis*-Pt(C₆F₅)₂" moieties are linked to a central platinum atom through both alkynyl units (μ-η²) and both alkynylphosphine ligands (μ-κP:η²), and the d⁶–d⁸ species [(PPh₂C≡CPh)-Cp*Ru(μ-Cl)(μ-κP:η²-PPh₂C≡CPh)Pt(C₆F₅)₂].¹¹ In addition, several X-ray-characterized examples of platinum complexes with tht bridging ligands are known, in particular (NBu₄)₂[*trans*-PtCl₂{(μ-tht)Pt(C₆F₅)₃}₂]¹² (tht monobridge), (NBu₄)[Pt₂Ag(μ-tht)₂(C₆F₅)₆]¹³ (tht mono-

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bridge between a silver center and a platinum center), $[(C_6F_5)_2Pt(\mu\text{-tht})(\mu\text{-dppm})Pt(C_6F_5)_2]^{14}$ (mixed $\mu\text{-tht}/\mu\text{-dppm}$ bridge), and $[trans\text{-}PtCl_2\{\mu\text{-tht}(C_6F_5)_3PtAg(\eta^2\text{-}C_6H_5Me)_2\}]^{15}$.

Both platinum centers are located in distorted square-planar environments, with a *cis* arrangement of the C_6F_5 groups, the Pt–C(C_6F_5) distances being perceptibly different [range 2.027(5)–2.078(4) Å] (although within the range found in other pentafluorophenyl derivatives), reflecting the presence of different *trans* ligands. The $\mu\text{-tht}$ ligand is located asymmetrically [Pt(1)–S 2.3447(11), Pt(2)–S 2.3813(11) Å] between the two nonbonded platinum centers [Pt⋯Pt 4.042 Å], the angle at sulfur [117.54(5)°] being comparable to those found in related complexes.^{12,14,15} The plane SC(25)C(28) is almost orthogonal (95.68°) to the plane defined by two platinum atoms and the sulfur. The C–C alkyne distance [1.203(7) Å] and the angles at the acetylenic carbons of the $PPh_2C\equiv CPh$ ligand [C(30)–C(29)–P(1) 156.2(4)° and C(29)–C(30)–C(31) 167.9(5)°] follow the usual pattern observed for η^2 -coordinated phosphino-alkynes, the Pt(2)– π (alkyne) bond distances [Pt(2)–C(29) 2.205(4), Pt(2)–C(30) 2.342(5) Å] being comparable to those found in related platinum(II) derivatives.^{6,7} As expected for a η^2 -interaction to a d^8 metal center, the C(29)–C(30) acetylenic fragment is oriented by 40.2° to the local Pt(2) coordination plane. The resulting central core is not planar, the dihedral angle formed by the best square-planar metal coordination planes around Pt(1) and Pt(2) being 34.6°.

As is shown in Scheme 2, the uncoordinated alkyne function in **1** could also react with Pt(0) substrates to produce mixed-valence Pt(II)–Pt(0) bridging alkynylphosphine complexes. Thus, complexes *cis*-[Pt(C_6F_5)₂($PPh_2C\equiv CR$)(tht)] **1a** and **1b** react in acetone with [Pt($\eta^2\text{-}C_2H_4$)(PPh_3)₂] to give, in moderate yields, the novel $\{[(C_6F_5)_2\text{-}(\text{tht})Pt(\mu\text{-}1\kappa P:2\eta^2\text{-}PPh_2C\equiv CR)]Pt(PPh_3)_2\}$ (R = Ph **3a**, Tol **3b**) complexes (Scheme 2, ii), stabilized by only one $\kappa P:\eta^2\text{-}PPh_2C\equiv CR$ bridging ligand. Under similar reaction conditions, the *tert*-butylalkynylphosphine complex **1c** does not react with the Pt(0) substrate, and under more drastic conditions, decomposition takes place and most of the Pt(II) starting material is recovered. These results are in agreement with previous observations^{5b,6,7} which indicate the very low η^2 -bonding capability of the P-bonded $PPh_2C\equiv CtBu$ ligands toward unsaturated metal fragments. In this context, the driving force for the formation of the binuclear derivative **2c** could be attributed to the simultaneous presence of the tetrahydrothiophene bridging ligand. It is worth noting that binuclear Pt(I)–Pt(I) derivatives without supporting bridging ligands have been previously obtained by redox condensation reactions between *cis*-[Pt(C_6X_5)₂L₂] (X = F, Cl; L = CO, CNR) and [Pt($\eta^2\text{-}C_2H_4$)(PPh_3)₂].¹⁶ In this context, although the formation of the mixed Pt(II)–Pt(0) complexes **3** can be easily envisioned due to the presence of an uncoordinated alkyne fragment on the precursor derivatives **1**, its

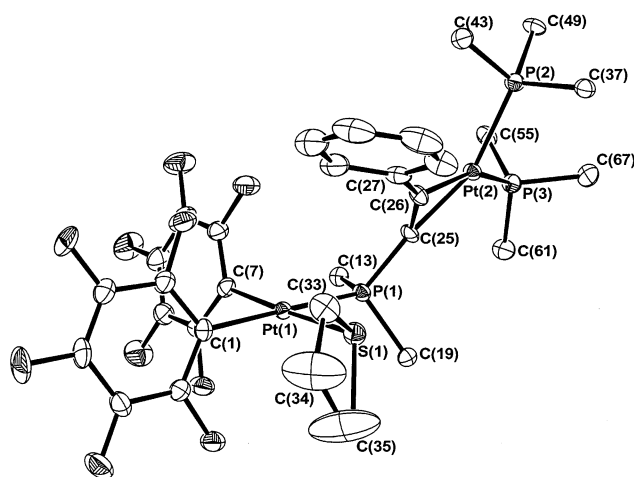


Figure 2. View of the molecular structure of $\{[(C_6F_5)_2\text{-}(\text{tht})Pt(\mu\text{-}1\kappa P:2\eta^2\text{-}PPh_2C\equiv CPh)]Pt(PPh_3)_2\}$, **3a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity, and the phenyl groups bound to the phosphorus atoms are represented by their *ipso*-carbons only.

formation is remarkable, as binuclear Pt(I)–Pt(I) derivatives or more simple Pt(II)–Pt(II) phosphido/alkynide species could have been also obtained by simple P–C(alkyne) bond cleavage.⁴

Complexes **3a** and **3b** are moderately stable in the solid state but decompose slowly in solution with the loss of the Pt(0) fragment and regeneration of the corresponding mononuclear derivatives **1**. The presence of η^2 -complexed fragments in these complexes is inferred from their IR spectra. They display one $\nu(C\equiv C)$ absorption (1715 cm^{-1} **3a**, 1714 cm^{-1} **3b**) in the typical region of coordinated triple bonds. The remarkable shifts in relation to the monomers **1** ($\Delta C\equiv C$ 464 **3a**; 457 cm^{-1} **3b**) are consistent with a simple η^2 -coordination to the Pt(0) center,^{2d,3c,17} the precursor platinum(II) center retaining coordination through the phosphorus atom. The proton resonances of the terminal tht ligand give rise to two broad signals at very low frequency (δ 1.99, 1.14 **3a**; 1.98, 1.16 **3b**) in relation to the starting materials. This high-field shift could be tentatively attributed to the shielding effect of the aromatic group on the $C\equiv CR$ fragment. As is observed in Figure 2, which shows the crystal structure of **3a**, the η^2 -coordination to Pt(0) causes a considerable distortion on the acetylenic fragment, placing the aromatic ring close to the tht protons [the closest protons: H(33a); H(33b)⋯ring–C(27)–C(32) 2.837; 2.968 Å]. The ^{31}P NMR spectra at room temperature (see Table 2) of complexes **3a** and **3b** show poorly resolved ABM spin systems with the corresponding platinum satellites. The two most deshielded signals (at ca. δ 24) are attributed to the inequivalent phosphorus atoms of PPh_3 ligands bonded to Pt(0), since they show the larger $^1J_{Pt-P}$ couplings and in the typical range of Pt(0)–alkyne complexes.^{2d,17} The low-frequency resonance ($\delta \approx -16$)

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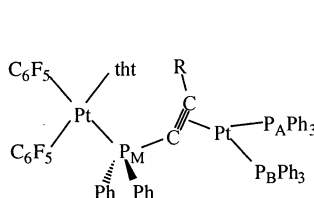
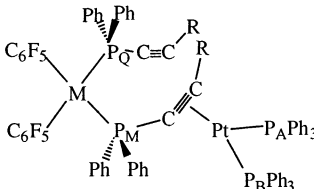
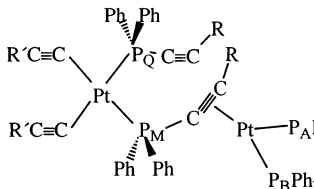
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Table 2. $^{31}\text{P}\{^1\text{H}\}$ NMR Data at 20 °C for Complexes 3–7 (δ in ppm, J in Hz, $^1J_{\text{Pt-P}}$ in brackets)

 R = Ph 3a, Tol 3b	 M = Pt; R = Ph 4a, Tol 4b M = Pd; R = Ph 5a, Tol 5b	 R' = Ph; R = Ph 6a, Tol 6b R' = <i>t</i>Bu; R = Ph 7a, Tol 7b						
compound	δ P _A	δ P _B	δ P _M	δ P _Q	$^2J_{\text{PA-PB}}$	$^3J_{\text{PA-PM}}$	$^3J_{\text{PB-PM}}$	$^2J_{\text{PM-PQ}}$
3a^a	24.84 (s, br) [3493]	24.38 (s, br) [3643]	−16.00 (s, br) [2386]					
3b^a		24.85 (s, br) [3480]	−15.70 (s, br) [2391]					
4a^a	25.64 [3492]	24.26 [3674]	−8.54 [2428]	−14.28 [2315]	27.9	20.3	17.7	
4b^b	25.72 [3474]	24.74 [3685]	−8.93 [2462]	−15.30 [2337]	27.9	29.7	27.6	
5a^b	25.79 [3488]	24.09 [3685]	−3.94	−7.75	27.2	27.5	23.1	
5b^b	25.81 [3470]	24.34 [3687]	−4.19	−7.97	27.6	27.6	19.7	
6a^b		24.90 [3535]	1.94 [2381]	−10.3 [2325]	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>
6b^a		25.00 [3645]	0.04 <i>c</i>	−10.36 [2338]				18.8
7a^a	24.33 [3770]	25.30 [3460]	5.11 [2418]	−10.56 [2292]	26.8	45.7	28.4	18.6
7b^b		25.40 [≈3443]	4.88 [2426]	−10.73 [2284]	<i>c</i>	<i>c</i>	<i>c</i>	<i>c</i>

^a In CDCl₃. ^b In CD₃COCD₃. ^c It cannot be calculated.**Table 3.** Selected Bond Lengths (Å) and Angles (deg) for $\{[(\text{C}_6\text{F}_5)_2(\text{tht})\text{Pt}(\mu\text{-}1\kappa\text{P:}2\eta^2\text{-PPh}_2\text{C}\equiv\text{CPh})]\text{Pt}(\text{PPh}_3)_2\}$ (**3a**·CH₂Cl₂)

Pt(1)–C(1)	2.076(3)	Pt(2)–C(26)	2.049(3)
Pt(1)–C(7)	2.032(3)	Pt(2)–C(25)	2.083(3)
Pt(1)–P(1)	2.3010(8)	Pt(2)–P(2)	2.2889(9)
Pt(1)–S(1)	2.3461(9)	Pt(2)–P(3)	2.3048(9)
S(1)–C(33)	1.829(4)	C(25)–C(26)	1.302(5)
S(1)–C(36)	1.835(4)	P(1)–C(25)	1.770(3)
C(7)–Pt(1)–C(1)	85.47(13)	C(25)–P(1)–Pt(1)	116.26(12)
C(7)–Pt(1)–P(1)	91.02(9)	C(26)–Pt(2)–P(2)	102.56(10)
C(1)–Pt(1)–S(1)	95.47(10)	P(2)–Pt(2)–P(3)	102.37(3)
P(1)–Pt(1)–S(1)	88.15(3)	C(26)–C(25)–P(1)	137.0(3)
C(25)–C(26)–C(27)	144.6(3)	C(25)–Pt(2)–P(3)	118.42(10)

is assigned to the alkynylphosphine bridging ligand (P_M). It is noteworthy that, in contrast to that observed for the alkynylphosphine-bridged Pt(II)–Pt(II) complexes **2**, the phosphorus resonance of the PPh₂ group in these mixed-valence Pt(II)–Pt(0) derivatives **3** is significantly more shielded than in the mononuclear precursors **1a** and **1b**, but as expected, these phosphorus atoms are still deshielded in relation to the free ligands (PPh₂C≡CPh δ −33.53; PPh₂C≡CTol −32.42).

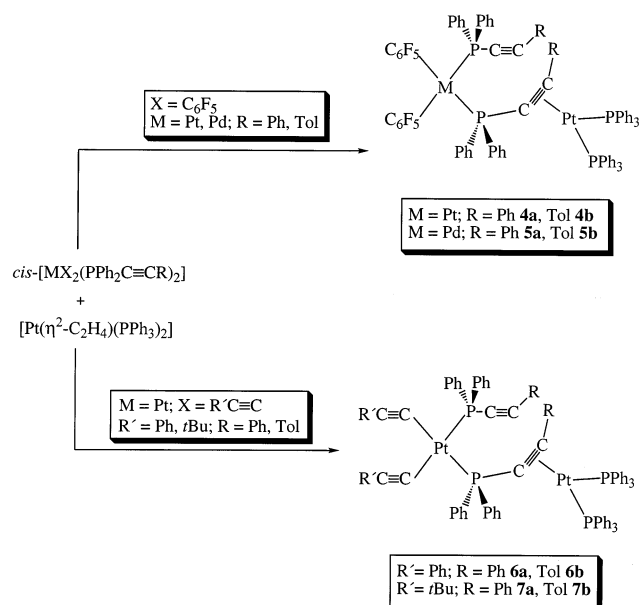
Crystals of the derivative **3a** suitable for single-crystal X-ray diffraction were obtained by slow diffusion (−30 °C) of *n*-hexane into a CH₂Cl₂ solution of the complex. The molecular structure is depicted in Figure 2, and selected bond lengths and angles are indicated in Table 3. The structure confirms the η^2 -alkyne coordination of the P-coordinated PPh₂C≡CPh ligand to the Pt(PPh₃)₂ fragment. The Pt(2) center displays a close to planar trigonal coordination, typical of metal (d¹⁰)–alkyne complexes,^{2d,17a,18} the dihedral angle between planes P(2)–Pt(2)–P(3) and C(25)–Pt(2)–C(26) being

only 5.07°. The torsion angle P(1)–C(25)–C(26)–C(27) is 0.7°. The Pt–C(sp) acetylenic distances [Pt(2)–C(25) 2.083(3); Pt(2)–C(26) 2.049(3) Å] are shorter than those observed in **2a**. The C(25)–Pt(2)–P(3) angle [118.42(10)°] is slightly larger than that of C(26)–Pt(2)–P(2) [102.56(10)°], probably due to greater steric hindrance of the PPh₂ end. As expected, the C≡C bond [1.302(5) Å] is perceptibly longer than that in the Pt(II)–Pt(II) derivative **2a** [1.203(7) Å], and the bend back angles at C_α and C_β are more acute [137.0(3)°/144.6(3)° in **3a** vs 156.2(4)°/167.9(5)° in **2a**]. Both facts are consistent with back-bonding from Pt(2) into the π^* C≡C orbital, affording some metallacyclopropene character to the bonding. However, the P(1)–C(acetylenic) distances are almost identical in both complexes [P(1)–C(25) 1.770(3) Å in **3a** versus P(1)–C(29) 1.784(5) Å in **2a**]. The Pt(1) atom retains its square-planar geometry and is bonded to the C_{ipso} carbon atoms of the two mutually *cis* C₆F₅ groups, to the phosphorus atom of the bridging PPh₂C≡CPh ligand, and to the sulfur atom of the terminal tht ligand. The Pt(1)–P(1) bridging bond distance [2.3010(8) Å] is slightly longer than the corresponding one in **2a** [2.2706(11) Å]. However, the terminal Pt(1)–S(1) distance [2.3461(9) Å] is similar within experimental error to the Pt–S bridging distance in **2a** [2.3447(11) Å].

As we commented in the Introduction, we have recently reported the reactivity of *cis*-[MX₂(PPh₂C≡CR)₂] (X = C₆F₅, M = Pt, Pd; X = C≡CR', M = Pt) toward the solvent tetrahydrothiophene Pt(II) complex

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Scheme 3



cis-[Pt(C₆F₅)₂(thf)₂]. The reactions of *cis*-[M(C≡CR')₂(PPh₂C≡CR)₂] with 1 equiv of the solvento complex lead to binuclear derivatives stabilized by alkynyl bridging ligands [(PPh₂C≡CR)₂Pt(μ-C≡CR')₂][Pt(C₆F₅)₂],⁷ indicating that alkynyl groups possess a higher η²-bonding capability to Pt(II) than alkynylphosphine ligands. In addition, we have shown that unusual μ-2,3-bis(diphenylphosphino)-1,3-butadien-1-yl binuclear compounds, which are the first examples of insertion of an acetylenic fragment into the robust Pt–C₆F₅ bond, are the only final species when the solvento complex *cis*-[Pt(C₆F₅)₂(thf)₂] reacts with *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)₂] (R = Ph, Tol).⁸ In this context and for comparative purposes, we decided to examine the reactivity of these *cis*-bis-(diphenylphosphino)alkyne mononuclear derivatives, *cis*-[M(C₆F₅)₂(PPh₂C≡CR)₂] (M = Pt, Pd; R = Ph, Tol) and *cis*-[Pt(C≡CR')₂(PPh₂C≡CR)₂] (R = Ph, Tol; R' = Ph, *t*Bu), toward [Pt(η²-C₂H₄)(PPh₃)₂]. Following a procedure similar to that used for complexes **3**, the reactions of the ethylene Pt(0) derivative [Pt(η²-C₂H₄)(PPh₃)₂] with the mononuclear Pt(II) or Pd(II) starting materials (Scheme 3) in acetone also resulted in the formation of white solids, which were identified as the mixed-valence complexes *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(μ-1κP:2η²-PPh₂C≡CR)]Pt(PPh₃)₂ (M = Pt, R = Ph **4a**, Tol **4b**; M = Pd, R = Ph **5a**, Tol **5b**) and *cis*-[Pt(C≡CR')₂(PPh₂C≡CR)(μ-1κP:2η²-PPh₂C≡CR)]Pt(PPh₃)₂ (R' = Ph, R = Ph **6a**, Tol **6b**; R' = *t*Bu, R = Ph **7a**, Tol **7b**), respectively, with a Pt(PPh₃)₂ fragment attached to the acetylenic bond of one alkynylphosphine group. The formation of binuclear derivatives **6** and **7** clearly indicates that Pt(0) has a much stronger preference for the π-donor acetylenic density of P-bonded alkynylphosphines than for that of the alkynyl ligands. This is in contrast to the behavior of Pt(II) or Pd(II) complexes since unsaturated metal fragments such as *cis*-[M(C₆F₅)₂(thf)₂] form exclusively double alkynide bridged systems. This difference can be explained in terms of a stronger π-acceptor ability of the –PC≡CR unit, which favors coordination to the relatively electron rich Pt(0). Recent theoretical calculations have shown that P-complexation of these ligands reduces the π**C*≡*C* occupancy.^{1d} This fact,

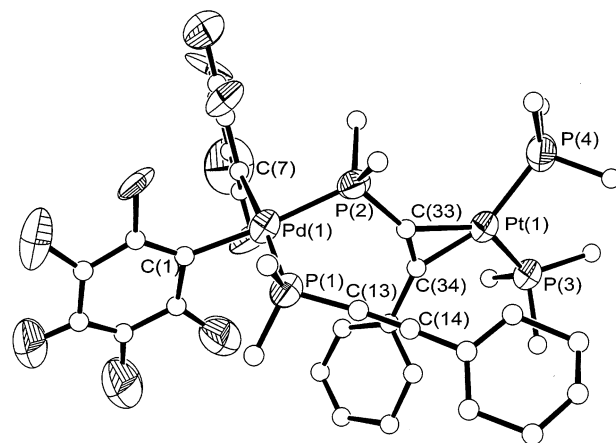


Figure 3. Schematic view of the preliminary X-ray diffraction study of **5a** showing the connectivity of the atoms. For the sake of clarity, the phenyl groups bound to the phosphorus atoms are represented by their *ipso*-carbons only.

which is related to the higher ν(*C*≡*C*) frequencies observed in P-bonded alkynylphosphines with respect to free ligands, could probably increase the π-acceptor nature of the acetylenic entity. In addition, the decrease of electron density at the phosphorus atom caused by complexation and reflected in part by low-field shifts (Δδ for [Pt(C≡CR')₂(PPh₂C≡CR)₂] 26.03–27.4) will also increase the electronegativity of P and raise the preference of the acetylenic M–PC≡CR entity toward relatively low valent metal fragments.

It should be noted that complexes **4–7** are moderately stable in the solid state, but on standing in solution, decompose with the loss of the Pt(PPh₃)₂ fragment, regenerating the corresponding mononuclear complexes. Compounds **4** and **5** are in fact always accompanied by trace amounts of starting Pt(II) materials, and these impurities could not be eliminated since attempts to recrystallize the solids caused the breakdown of the η²-alkyne interaction. Similar reactions were attempted between *cis*-[Pt(C₆F₅)₂(PPh₂C≡C*t*Bu)₂] or *cis*-[Pt(C≡CR')₂(PPh₂C≡C*t*Bu)₂] (R' = Ph, Tol) and [Pt(η²-C₂H₄)(PPh₃)₂], but in all cases, the Pt(II) precursors remained unreacted in solution, even after longer reaction times, confirming again the lower η²-bonding capability of PPh₂C≡C*t*Bu ligands. We also noted that attempts to involve both PPh₂C≡CR groups in η²-coordination failed. Thus, treatment of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)₂] or *cis*-[Pt(C≡CR')₂(PPh₂C≡CPh)₂] with 2 molar equiv of [Pt(η²-C₂H₄)(PPh₃)₂] yielded only the corresponding binuclear complexes **4b**, **6a**, and **7a**, indicating that the second alkynylphosphine ligand is not a good potential site for further coordination.

Compounds **4–7** have been characterized by usual analytical and spectroscopic [IR and ¹H, ¹⁹F, ³¹P{¹H}, and ¹³C{¹H} NMR (**4b**, **7a**)] means (see Experimental Section and Table 2 for details). In addition, the formulations proposed were backed by an X-ray diffraction study of complex **5a** (Figure 3). Although the poor quality of all crystals obtained prevented their satisfactory refinement, the connectivity, shown in Scheme 3, was unequivocally established, confirming the presence of a palladium(II) organometallic fragment “*cis*-Pd-(C₆F₅)₂(PPh₂C≡CPh)₂”, which acts as a monoacetylenic

ligand toward the low-valent metal in the Pt(PPh₃)₂ unit.

The IR spectra of **4**–**7** confirm the presence of bridging and terminal alkynylphosphine ligands. Thus, they exhibit two (**4**, **5**, **7**) or three (**6**) $\nu(\text{C}\equiv\text{C})$ absorptions; the low-frequency band (1691–1756 cm⁻¹), which appears with a shoulder (except in **4**) at a position similar to those observed in **3**, is assigned to the alkynylphosphine bridging group and the remaining high-frequency absorptions to the terminal P-coordinated PPh₂C≡CR (2173–2177 cm⁻¹) or alkynide (2121 **6a**, 2123 cm⁻¹ **6b**) ligands. The most relevant feature of the room-temperature ¹H NMR spectra is the presence of two different methyl signals in the tolyl derivatives (**4b**, **5b**, **6b**, **7b**) as well as two singlets attributed to the *t*Bu groups in the *tert*-butylalkynide complexes **7**. Complexes **4** and **5**, containing C₆F₅ groups, display at –50 °C a ¹⁹F NMR pattern characteristic of a rigid molecule (two different sets of resonances due to rigid C₆F₅ rings with non-equivalent halves). On raising the temperature, the two *o*-fluorine (and *meta*) resonances broaden and collapse near room temperature, to only one due to a fast rotation of C₆F₅ groups around their Pt–C bonds. The ³¹P{¹H} NMR data (20 °C) for these complexes (**4**–**7**) are shown in Table 2. All complexes display an ABMQ splitting pattern with the corresponding ¹⁹⁵Pt satellites, and from the analysis of the ABM part of the spectrum, δP_A , δP_B , δP_M , $^2J_{\text{P}_\text{A}-\text{P}_\text{B}}$, $^3J_{\text{P}_\text{A}-\text{P}_\text{M}}$, and $^3J_{\text{P}_\text{B}-\text{P}_\text{M}}$ are directly obtained. The analyses of the spectra obtained are consistent with the simulations carried out for all complexes using the g-NMR program (v3.6 for Macintosh). As an illustration both the real and simulated spectra of complex **7a** are presented in Figure 4. The two low-field resonances (δP 25.81–24.09, AB part) are due to the inequivalent phosphorus atoms bonded to Pt(0), and as noted in Table 2, the more deshielded resonance is, in each case (except in **7a**), attributed to P_A *trans* to the PPh₂ end on the basis of the larger $^3J_{\text{P}_\text{M}-\text{P}}$ coupling. The next higher-field signal (δ 5.11 to –8.93) appears as a complex multiplet due to extra coupling to P_Q and is attributed to the phosphorus atom (P_M) of the alkynylphosphine bridging ligand. Finally, the strongly shielded signal (δ –7.75 to –15.30), which occurs as a doublet ($^2J_{\text{P}_\text{M}-\text{P}_\text{Q}}$ 18.8, 18.6 Hz, in complexes **6b** and **7a**) is clearly assigned to the phosphorus of terminal P-coordinated alkynylphosphine (P_Q). In complexes **4** and **5**, the presence of C₆F₅ *trans* to P_M and P_Q gives rise to somewhat broad signals due to further unresolved coupling to *o*-fluorine nuclei. In keeping with what is observed in complexes **3**, the one-bond Pt(0)–P_{A,B} coupling constants (3443–3770 Hz) are again notably larger than the corresponding Pt(II)–P_{M,Q} (2284–2462 Hz). Due to solubility and/or stability problems, only the ¹³C NMR spectra of **4b** and **7b** at low temperature could be recorded. For complex **4b**, the acetylenic carbon signals corresponding to the terminal P-coordinated PPh₂C≡CTol ligands resonate close to those seen in the precursor (δ 78.5, $^1J_{\text{P}-\text{C}}$ 99.2 Hz, C_α: 106.2 br C_β vs 79.1 C_α and 108.3 C_β in [Pt(C₆F₅)₂(PPh₂C≡CTol)₂]), and a signal observed at δ 153.1 (d, $J_{\text{P}-\text{C}}$ = 57 Hz) is tentatively attributed to the α -C or β -C atom of the η^2 -coordinated alkynylphosphine group. In **7a**, four alkyne carbon signals (two alkynyl and two due to terminal PPh₂C≡CPh) occur at positions similar

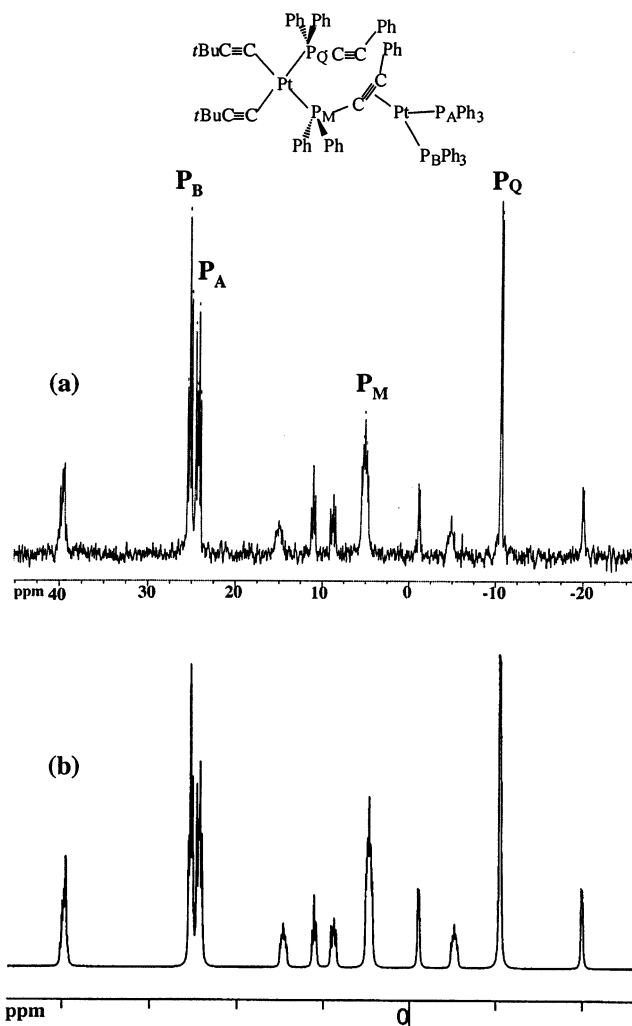


Figure 4. Real (a) and simulated (b) ³¹P{¹H} NMR spectra of **7a**.

to those observed in the starting material (see Experimental Section for details), but the alkynyl carbons of the alkynyl bridging $\kappa\text{P}:\eta^2$ -coordinated phosphine are not seen. The assignments of C_α and C_β are based on the observation of the phosphorus–carbon coupling.

Conclusions

In summary we report the preparation of some potentially useful platinum(II) complexes bearing a diphenylalkynylphosphine molecule and a tht ligand in mutually *cis* position, *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)(tht)] **1**, and investigate their reactivity toward *cis*-[Pt(C₆F₅)₂(thf)₂] and [Pt(η^2 -C₂H₄)(PPh₃)₂]. We have shown that while complexes **1** react with the solvent derivatives *cis*-[Pt(C₆F₅)₂(thf)₂] to give the first reported examples of hetero (μ -tht)/(μ - $\kappa\text{P}:\eta^2$ -PPh₂C≡CR) bridged diplatinum(II) complexes, the reaction with the ethylene platinum(0) complex results in the formation of the single μ - $\kappa\text{P}:\eta^2$ -PPh₂C≡CR bridged mixed-valence Pt(II)–Pt(0) complexes accessible through η^2 -alkyne complexation of the Pt(PPh₃)₂ unit. By comparison, the reactivity of [Pt(η^2 -C₂H₄)(PPh₃)₂] toward several *cis*-bis(alkynylphosphine) *cis*-[MX₂(PPh₂C≡CR)₂] (X = C₆F₅, M = Pt, Pd; X = C≡CR', M = Pt) has also been examined, showing that the behavior of these substrates bearing two alkynylphosphine ligands resembles that observed

for **1**. These complexes have been shown to bind only one $\text{Pt}(\text{PPh}_3)_2$ unit, leading to related $\text{M}(\text{II})\text{--Pt}(\text{0})$ homo (**4**, **6**, **7**) and hetero ($\text{Pd}\text{--Pt}$ **5**) binuclear complexes stabilized by a $\kappa\text{P}:\eta^2\text{-PPh}_2\text{C}\equiv\text{CR}$ bridging ligand. The formation of bimetallic complexes **6** and **7** is remarkable for several reasons. First bi- or polynuclear complexes containing terminal alkynyl ligands are rather rare,¹⁹ in part due to the strong preference of these groups to act as bridging ligands. Second, complexation of the low-valent fragment through the P-bonded $\text{PPh}_2\text{C}\equiv\text{CR}$ ligand indicates that the acetylenic unit on these molecules exhibits a stronger η^2 -bonding capability toward $\text{Pt}(\text{0})$ than the alkynyl groups do. This result is in clear contrast to those previously observed in related platinum(II) systems in which the alkynyl ligands have been always found to be the preferred bridging groups. The lack of reactivity of P-bonded *tert*-butylalkynylphosphine complexes toward $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ confirms previous observations that indicate the absence or very low η^2 -bonding capability of these bulky molecules. The successful synthesis of complex $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-tbt})(\mu\text{-1}\kappa\text{P}:\text{2}\eta^2\text{-PPh}_2\text{C}\equiv\text{CtBu})\text{Pt}(\text{C}_6\text{F}_5)_2]$, **2c**, is likely to be due to the simultaneous presence of the tetrahydrothiophene bridging ligand.

Experimental Section

General Considerations. All reactions and manipulations were carried out under nitrogen atmosphere using Schlenk techniques and distilled solvents purified by known procedures. IR spectra were recorded on a Perkin-Elmer FT-IR 1000 spectrometer as Nujol mulls between polyethylene sheets. NMR spectra were recorded on a Bruker ARX 300 spectrometer; chemical shifts are reported in ppm relative to external standards (SiMe_4 , CFCl_3 , and 85% H_3PO_4) and coupling constants in Hz. The low stability or solubility of **2**, **3b**, **4a**, **5**, **6**, and **7b** precluded their characterization by ^{13}C NMR spectroscopy. Elemental analyses were carried out with a Carlo Erba EA 1110 CHNS/O microanalyzer; the electrospray mass spectra on a HP5989B with interphase API-ES HP 59987A (in the negative ion mode with methanol as the mobile phase); and the mass spectra (FAB+) on a VG Autospec spectrometer. $\text{PPh}_2\text{C}\equiv\text{CR}$ ($\text{R} = \text{Ph}$,²⁰ ToI ,^{1k} tBu^{20}), $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tbt})_2]$,²¹ $[\text{Pt}(\mu\text{-tbt})(\text{C}_6\text{F}_5)_2]_2$,²² $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{thf})_2]$,²³ $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CR})_2\text{COD}]$ ($\text{R} = \text{Ph}$,²⁴ tBu^{25}), $\text{cis-}[\text{M}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{C}\equiv\text{CR})_2]$ ($\text{M} = \text{Pt}$, Pd ; $\text{R} = \text{Ph}$,^{8a} ToI^{8b}), and $[\text{Pt}(\eta^2\text{-C}_2\text{H}_4)(\text{PPh}_3)_2]$ ²⁶ were prepared according to literature methods. The synthesis of $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CR})_2\text{-}$

$(\text{PPh}_2\text{C}\equiv\text{CTol})_2]$ ($\text{R} = \text{Ph}$, tBu) was similar to that described for $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PPh}_2\text{C}\equiv\text{CPh})_2]$.⁷

Synthesis of $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CR})_2(\text{PPh}_2\text{C}\equiv\text{CTol})_2]$ ($\text{R} = \text{Ph}$, tBu). A solution of $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{COD})]$ (0.590 g, 1.167 mmol) in CH_2Cl_2 (20 mL) was treated at room temperature with $\text{PPh}_2\text{C}\equiv\text{CTol}$ (0.701 g, 2.334 mmol), and the resulting solution was stirred for 1 h. The solvent was then removed in a vacuum, and the addition of cold *n*-hexane (5 mL) caused its precipitation as a beige solid, $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{C}\equiv\text{CTol})_2]$ (0.606 g, 52% yield).

$\text{cis-}[\text{Pt}(\text{C}\equiv\text{CtBu})_2(\text{PPh}_2\text{C}\equiv\text{CTol})_2]$ was prepared similarly using $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CtBu})_2(\text{COD})]$ (0.500 g, 1.07 mmol) and $\text{PPh}_2\text{C}\equiv\text{CTol}$ (0.645 g, 2.148 mmol) (0.472 g, 46% yield).

Data for $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CPh})_2(\text{PPh}_2\text{C}\equiv\text{CTol})_2]$. Anal. Calcd for $\text{C}_{58}\text{H}_{44}\text{P}_2\text{Pt}$: C, 69.80; H, 4.44. Found: C, 69.51; H, 4.49. MS (ES^+ ionized with Ag^+): m/z 1196 $[\text{M} + \text{Ag} + \text{ToI}]^+$ 35%; 1106 $[\text{M} + \text{Ag} + \text{H}]^+$ 10%; 896 $[\text{Pt}(\text{C}_2\text{Ph})(\text{PPh}_2\text{C}_2\text{ToI})_2]^+$ 100%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2172 (vs), 2123 (s). ^1H NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 7.87 (s, br, 8H); 7.28 (m, 14H); 6.95 (m, 16H) CH, Ph, ToI; 2.33 (s, CH_3). ^{13}C NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 139.9 (s, C^4 , ToI); 133.4 ("t", $J_{\text{C-P}} = 6.3$, o-C, PPh_2); 131.7 (s, p-C, PPh_2); 131.3 (s, Ph); 130.1 (s, Ph); 128.5 (s, CH, ToI); 127.9 ("t", $J_{\text{C-P}} = 5.8$, m-C, PPh_2); 126.8 (s, CH, ToI); 124.8 (s, Ph); 117.6 (s, C^1 , ToI); 109.2 (AXX' five line pattern, $^3J_{\text{C-Ptrans}} + ^3J_{\text{C-Pcis}} = 36.4$, Pt satellites not observed, $\equiv\text{C}_\beta\text{Ph}$); 108.3 (AXX', $^2J_{\text{C-P}} + ^4J_{\text{C-P}} = 15.4$, $\equiv\text{C}_\beta\text{ToI}$); 101.7 (AXX', dd, $^2J_{\text{C-Ptrans}} + ^2J_{\text{C-Pcis}} = 178.1$, Pt- $\text{C}_\alpha\equiv$); 80.1 (AXX', d, $^1J_{\text{C-P}} + ^3J_{\text{C-P}} = 103.9$, $-\text{PC}_\alpha\equiv$); 21.4 (s, CH_3). ^{31}P NMR (CDCl_3 , 20 $^\circ\text{C}$): δ -6.39 (s, $^1J_{\text{Pt-P}} = 2347$).

Data for $\text{cis-}[\text{Pt}(\text{C}\equiv\text{CtBu})_2(\text{PPh}_2\text{C}\equiv\text{CTol})_2]$. Anal. Calcd for $\text{C}_{54}\text{H}_{52}\text{P}_2\text{Pt}$: C, 67.70; H, 5.47. Found: C, 67.46; H, 5.42. MS (ES^+ ionized with Ag^+): m/z 1065 $[\text{M} + \text{Ag}]^+$ 100%. IR (cm^{-1}): $\nu(\text{C}\equiv\text{C})$ 2173 (vs). ^1H NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 7.86 (m, 8H); 7.27 (m, 12H) Ph; 6.93 (AB, $J_{\text{H-H}} = 7.8$, δ_A 6.96, δ_B 6.90, C_6H_4); 2.32 (s, CH_3); 0.92 (s, tBu). ^{13}C NMR (CDCl_3 , 20 $^\circ\text{C}$): δ 139.6 (s, C^4 , ToI); 133.5 ("t", $J_{\text{C-P}} = 6.3$, o-C, PPh_2); 131.7 (s, p-C, PPh_2); 131.6 (AXX' four lines, $^1J_{\text{C-P}} + ^3J_{\text{C-P}} = 54.8$, i-C, PPh_2); 129.8 (s, CH, ToI); 128.5 (s, CH, ToI); 127.6 ("t", $J_{\text{C-P}} = 5.8$, m-C, PPh_2); 117.9 (s, C^1 , ToI); 116.9 (AXX' five line pattern, $^3J_{\text{C-Ptrans}} + ^3J_{\text{C-Pcis}} = 35.9$, $\equiv\text{C}_\beta\text{tBu}$); 107.6 (AXX', $^2J_{\text{C-P}} + ^4J_{\text{C-P}} = 14.8$, $\equiv\text{C}_\beta\text{ToI}$); 84.8 (AXX', dd, $^2J_{\text{C-Ptrans}} + ^2J_{\text{C-Pcis}} = 180.1$, Pt- $\text{C}_\alpha\equiv$); 80.9 (AXX', d, $^1J_{\text{C-P}} + ^3J_{\text{C-P}} = 100.0$, P- $\text{C}_\alpha\equiv$); 31.5, 31.4 (s, $-\text{C}(\text{CH}_3)_3$); 28.6 (s, $^3J_{\text{Pt-C}} = 21.5$, $-\text{CMe}_3$); 21.4, 21.3 (s, CH_3). ^{31}P NMR (CDCl_3 , 20 $^\circ\text{C}$): δ -6.19 (s, $^1J_{\text{Pt-P}} = 2319$).

Synthesis of $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{C}\equiv\text{CR})(\text{tbt})]$ ($\text{R} = \text{Ph}$ **1a, ToI **1b**, tBu^{8b} **1c**).** Method a. A solution of $\text{PPh}_2\text{C}\equiv\text{CPh}$ (0.101 g, 0.354 mmol) in CH_2Cl_2 (20 mL) was treated with $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tbt})_2]$ (0.250 g, 0.354 mmol), and the mixture was stirred for 1 h. Evaporation to a small volume and addition of *n*-hexane (≈ 5 mL) afforded **1a** as a white solid (0.280 g, 87% yield).

Method b. To a white suspension of $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-tbt})_2]$ (0.185 g, 0.150 mmol) in CH_2Cl_2 (10 mL) was added $\text{PPh}_2\text{C}\equiv\text{CPh}$ (0.086 g, 0.300 mmol). The suspension immediately dissolved, and the resulting colorless solution (~ 1 mL) was stirred for 1 h. Evaporation to a small volume and addition of cold EtOH (5–6 mL) caused the precipitation of **1a** as a white solid (0.240 g, 88% yield).

Using a similar procedure complex **1b** was prepared with the appropriate starting materials: $\text{PPh}_2\text{C}\equiv\text{CTol}$ (0.106 g, 0.354 mmol) and $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{tbt})_2]$ (0.250 g, 0.354 mmol) (5 h of stirring) (0.253 g, 78% yield) or $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-tbt})_2]$ (0.182 g, 0.147 mmol) and $\text{PPh}_2\text{C}\equiv\text{CTol}$ (0.088 g, 0.295 mmol) (0.230 g, 85% yield).

The synthesis of $\text{cis-}[\text{Pt}(\text{C}_6\text{F}_5)_2(\text{PPh}_2\text{C}\equiv\text{CtBu})(\text{tbt})]$, **1c**, using method a has been previously described.^{8b} **1c** can be also obtained following method b: $[\text{Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-tbt})_2]$ (0.178 g, 0.144 mmol) and $\text{PPh}_2\text{C}\equiv\text{CtBu}$ (0.077 g, 0.288 mmol) (0.173 g, 68% yield).

Data for **1a.** Anal. Calcd for $\text{C}_{36}\text{H}_{23}\text{F}_{10}\text{PPtS}$: C, 47.85; H, 2.56; S 3.55. Found: C 47.68; H 2.43; S 3.65. MS (ES^+): m/z

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926 [M + Na]⁺ 100%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 2179 (vs); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 803 (vs), 786 (s). ¹H NMR (CDCl₃, 20 °C): δ 7.73–7.41 (m, 15H, Ph); 2.89 (s, 4H, α -CH₂, tht), 1.71 (s, 4H, β -CH₂, tht). ¹³C NMR (CDCl₃, 20 °C): δ 146.7–136.6 (C₆F₅); 132.4 (d, ¹J_{C–P} = 12.9, *o*-C, PPh₂); 132.0 (s, *o*-C, Ph); 130.9 (d, ⁴J_{C–P} ≈ 1, *p*-C, PPh₂); 130.3 (s, *p*-C, Ph); 129.1 (d, ¹J_{C–P} = 62, *i*-C, PPh₂); 128.4 (s, *m*-C, Ph); 128.3 (d, ¹J_{C–P} = 11.5, *m*-C, PPh₂); 120.2 (d, ³J_{C–P} ≈ 2.5, *i*-C, Ph); 108.1 (d, ²J_{C–P} = 14.5, $\equiv\text{C}_\beta\text{Ph}$); 78.6 (d, ¹J_{C–P} = 98, $-\text{PC}_\alpha\equiv$); 36.9 (s, br, α -CH₂, tht); 29.6 (s, br, β -CH₂–, tht). ¹⁹F NMR (CDCl₃, 20 °C): δ –118.2 (m, ³J_{Pt–O–F} ≈ 410, 290, 4o-F); –160.4 (t, 1p-F); –162.7 (m, 2m-F); –163.1 (t, 1p-F); –164.5 (m, 2m-F). ³¹P NMR (CDCl₃, 20 °C): δ –5.71 (s, ¹J_{Pt–P} = 2470).

Data for 1b. Anal. Calcd for C₃₇H₂₅F₁₀PPtS: C, 48.43; H, 2.75; S, 3.49. Found: C, 48.75; H, 2.25; S, 3.73. MS (FAB+): *m/z* 917 [M]⁺ 7%; 583 [Pt(PPh₂C₂Tol)(tht)]⁺ 80%; 495 [Pt(PPh₂C₂Tol)]⁺ 85%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 2171 (vs); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 812 (s), 800 (s). ¹H NMR (CDCl₃, 20 °C): δ 7.73 (dd, *o*-H, Ph), 7.42 (m, 8H) (CH, Ph, Tol); 7.20 (d, ¹J_{H–H} ≈ 7.6, 2H, C₆H₄); 2.89 (s, 4H, α -CH₂, tht); 2.40 (s, 3H, CH₃); 1.70 (s, 4H, β -CH₂, tht). ¹³C NMR (CDCl₃, 20 °C): δ 147.9–135.0 (C₆F₅); 140.9 (s, C⁴, Tol); 132.4 (d, ¹J_{C–P} = 12.8, *o*-C, PPh₂); 131.9 (s, CH, Tol); 130.8 (d, ⁴J_{C–P} ≈ 1, *p*-C, PPh₂); 129.2 (s, CH, Tol); 129.25 (d, ¹J_{C–P} = 62.0, *i*-C, PPh₂); 128.2 (d, ¹J_{C–P} = 11.5, *m*-C, PPh₂); 117.1 (d, ³J_{C–P} ≈ 2.5, C¹, Tol); 108.6 (d, ²J_{C–P} = 15.0, $\equiv\text{C}_\beta\text{Tol}$); C_α should appear as a doublet, but one of the peaks overlaps with the CDCl₃ signal (≈77.83, ¹J_{C–P} ≈ 100); 36.9 (s, α -CH₂, tht), 29.5 (s, β -CH₂, tht); 21.4 (s, CH₃, Tol). ¹⁹F NMR (CDCl₃, 20 °C): δ –118.2 (m, ³J_{Pt–O–F} ≈ 390, 330, 4o-F); –160.4 (t, 1p-F); –162.8 (m, 2m-F); –163.2 (t, 1p-F); –164.5 (m, 2m-F). ³¹P NMR (CDCl₃, 20 °C): δ –5.87 (s, ¹J_{Pt–P} = 2472).

Data for 1c. Analytical, IR, ¹H, ³¹P, and ¹⁹F NMR data for this complex have been reported.^{8b} ¹³C NMR (CDCl₃, 20 °C): δ 147.9–135.0 (C₆F₅); 132.2 (d, ¹J_{C–P} = 12.8, *o*-C, PPh₂); 130.6 (d, ⁴J_{C–P} = 2.4, *p*-C, PPh₂); 129.8 (d, ¹J_{C–P} = 62, ²J_{Pt–C} = 24, *i*-C, PPh₂); 128.1 (d, ¹J_{C–P} = 11.5, *m*-C, PPh₂); 119.5 (d, ²J_{C–P} = 13.2, $\equiv\text{C}_\beta\text{tBu}$); 68.3 (d, ¹J_{Cα–P} = 102, $\text{P}-\text{C}_\alpha\equiv$); 36.8 (d, ³J_{C–P} = 3, α -CH₂, tht); 29.9 (d, ⁴J_{C–P} = 1.2, $-\text{C}(\text{CH}_3)_3$); 29.4 (s, β -CH₂, tht); 28.6 (d, ³J_{C–P} = 1.8, $-\text{CMe}_3$).

Synthesis of [(C₆F₅)₂Pt(μ-tht)(μ-1κP:2η²-PPh₂C≡CR)Pt(C₆F₅)₂] (R = Ph 2a, Tol 2b, tBu 2c). A general procedure for 2a is given: a solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(tht)], 1a (0.150 g, 0.166 mmol), in CH₂Cl₂ (20 mL) was treated with *cis*-[Pt(C₆F₅)₂(thf)₂] (0.112 g, 0.166 mmol), and the colorless solution was stirred for 1 h. By concentration to a small volume (≈3 mL) and addition of 5 mL of *n*-hexane, complex 2a precipitates as a white solid (0.199 g, 84% yield).

Complexes 2b and 2c were prepared as white solids following a procedure identical to that described for 2a: 0.150 g (0.163 mmol) of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)(tht)], 1b, and 0.110 g (0.163 mmol) of *cis*-[Pt(C₆F₅)₂(thf)₂] (0.200 g, 85% yield); 0.141 g (0.160 mmol) of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CtBu)(tht)], 1c, and 0.108 g (0.160 mmol) of *cis*-[Pt(C₆F₅)₂(thf)₂] (0.116 g, 52% yield).

Data for 2a. Anal. Calcd for C₄₈F₂₀H₂₃PPt₂S: C, 40.24; H, 1.62; S, 2.24. Found: C, 40.14; H, 1.25; S, 2.40. MS (FAB+): *m/z* 1432 [M]⁺ 1%; 1343 [M – tht]⁺ 1%; 1097 [M – 2C₆F₅]⁺ 1%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 2051 (w), 2006 (m); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 805 (s, br). ¹H NMR (CDCl₃, 20 °C): δ 7.66 (m, 8H), 7.47 (s, br, 7H) Ph; 3.82 (2H), 3.64 (2H) (s, br, α -CH₂, tht); 1.67 (2H), 1.55 (2H) (s, br, β -CH₂, tht). ¹⁹F NMR (CDCl₃, 20 °C): δ –117.6 (m, ³J_{Pt–O–F} ≈ 370, 2o-F); –118.3 (m, 2o-F); –118.6 (m, 2o-F); –119.2 (m, br, ³J_{Pt–O–F} ≈ 340, 2o-F); –156.5 (t, *p*-F); –157.5 (t, *p*-F); –158.9 (t, *p*-F); –160.8 (m, 4m-F + *p*-F); –163.2 (m, 4m-F). ³¹P NMR (CDCl₃, 20 °C): δ 24.25 (s, ¹J_{Pt–P} = 2349).

Data for 2b. Anal. Calcd for C₄₉F₂₀H₂₅PPt₂S: C, 40.68; H, 1.74; S, 2.22. Found: C, 40.80; H, 1.47; S, 2.45. MS (FAB+): *m/z* 1358 [M – tht]⁺ 1%; 1111 [M – 2C₆F₅ – 1H]⁺ 2%; 829 [Pt(C₆F₅)₂(PPh₂C₂Tol)]⁺ 5%; 662 [Pt(C₆F₅)(PPh₂C₂Tol)]⁺ 6%; 583 [Pt(PPh₂C₂Tol)(tht)]⁺ 10%; 495 [Pt(PPh₂C₂Tol)]⁺ 8%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 2059 (w), 2017 (m); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 815 (m), 804

(s). ¹H NMR (CDCl₃, 20 °C): δ 7.66, 7.59, 7.45 (12H); 7.25 (2H) (CH, Ph, Tol); 3.81 (2H), 3.64 (2H) (s, br, α -CH₂, tht); 2.42 (s, CH₃); 2.17 (2H), 1.66 (2H) (s, br, β -CH₂, tht). ¹⁹F NMR (CDCl₃, 20 °C): δ –117.6 (m, ³J_{Pt–O–F} = 365, 2o-F); –118.3 (m, 2o-F); –118.6 (m, 2o-F); –119.1 (m, br, ³J_{Pt–O–F} = 335, 2o-F); –156.7 (t, *p*-F); –157.6 (t, *p*-F); –159.1 (t, *p*-F); –160.9 (m, 4m-F + 1p-F); –163.3 (m, 4m-F). ³¹P NMR (CDCl₃, 20 °C): δ 24.25 (s, ¹J_{Pt–P} = 2359).

Data for 2c. Anal. Calcd for C₄₆F₂₀H₂₇PPt₂S: C, 39.10; H, 1.93; S, 2.27. Found: C, 38.75; H, 1.72; S, 2.36. MS (FAB+): *m/z* 1078 [M – 2C₆F₅]⁺ 12%; 894 [Pt(PPh₂C₂tBu)₂(C₆F₅)]⁺ 55%; 727 [Pt(PPh₂C₂tBu)₂]⁺ 87%; 549 [Pt(PPh₂C₂tBu)(tht)]⁺ 60%; 461 [Pt(PPh₂C₂tBu)]⁺ 75%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 1982 (m, br); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 806 (s, br), 791 (m), 774 (sh). ¹H NMR (CDCl₃): δ at 20 °C, 8.05–7.33 (vbr, Ph); 3.77, 3.18 (vbr, α -CH₂, tht); 1.92 (vbr, β -CH₂, tht); 1.38 (s, 9H, tBu); at –50 °C, 8.04 (s, br, 2H); 7.72–7.30 (m, 8H) Ph; 3.97 (2H), 3.71 (1H), 3.25 (1H) (s, br, α -CH₂, tht); 2.08 (s, br, 2H, β -CH₂, tht), the other signal corresponding to β -CH₂ protons could be overlapped with the signal of tBu group at δ 1.36. ¹⁹F NMR (CDCl₃): δ at 20 °C, –117.7 (s, br, 2o-F); –118.2 (s, br, 4o-F); –118.5 (s, br, 2o-F); –156.6 (t, *p*-F); –157.5 (t, *p*-F); –157.9 (t, *p*-F); –161.0 [overlapping of dt (1p-F and a broad signal due to 3m-F)]; –161.5 (m, br, 1m-F); –162.6 (m, 2m-F); –163.2 (m, br, 1m-F); –163.5 (m, br, 1m-F); at –50 °C, –116.5 (m, ³J_{Pt–O–F} ≈ 360, 1o-F); –117.8 (m, ³J_{Pt–O–F} ≈ 360, 1o-F); –118.2 (m, 1o-F); –118.5 (m, 2o-F); –119.3 (m, 2o-F); –120.3 (m, ³J_{Pt–O–F} ≈ 310, 1o-F); –156.2 (t, 1p-F); –156.9 (t, 1p-F); –157.4 (t, 1p-F); –160.2 (m, 3m-F); –160.5 (t, 1p-F); –160.9 (m, 1m-F); –161.8 (m, 1m-F); –162.2 (m, 1m-F); –162.8 (m, 1m-F); –163.1 (m, 1m-F). ³¹P NMR (CDCl₃, 20 °C): δ 22.09 (s, ¹J_{Pt–P} = 2332).

Synthesis of [(C₆F₅)₂(tht)Pt(μ-1κP:2η²-PPh₂C≡CR)Pt(PPh₃)₂] (R = Ph 3a, Tol 3b). To a solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CPh)(tht)] (0.141 g, 0.156 mmol) in acetone (30 mL) was added 0.117 g (0.156 mmol) of [Pt(η²-C₂H₄)(PPh₃)₂], and the mixture was stirred at room temperature for 2 h. The resulting colorless solution was filtered through Celite under N₂ and concentrated to a small volume (3 mL). By addition of *n*-hexane (≈10 mL) to the filtrate, complex 3a precipitates as a white solid (0.140 g, 55% yield).

Complex 3b was obtained by reacting an equimolecular amount to *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)(tht)] (0.146 g, 0.159 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (0.119 g, 0.159 mmol) in 30 mL of acetone (2 h). Filtration and evaporation of the reaction mixture to ca. 3 mL causes the precipitation of 3b as a white solid in 53% yield (0.139 g).

Data for 3a. Anal. Calcd for C₇₂F₁₀H₅₃P₃Pt₂S: C, 53.27; H, 3.29; S, 1.97. Found: C, 53.42; H, 3.56; S, 1.50. MS (FAB+): *m/z* 1359 [M – PPh₃ – 1H]⁺ 11%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 1715 (s); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 801 (m), 782 (m). ¹H NMR (CDCl₃, 20 °C): δ 7.55 (m), 7.47–6.75 (45H) Ph; 1.99 (br, 4H, α -CH₂, tht); 1.14 (br, 4H, β -CH₂, tht). ¹³C NMR (CDCl₃, –50 °C): δ 148–137 (C₆F₅); 135.3–126.3 (Ph), 31.4 (α -CH₂, tht); 29.5 (β -CH₂, tht). Signals due to C_α and C_β are not observed. ¹⁹F NMR (CDCl₃, 20 °C): δ –117.4 (m, ³J_{Pt–O–F} = 280, 2o-F); –118.0 (m, ³J_{Pt–O–F} = 430, 2o-F); –161.8 (t, 1p-F); –163.5 (m, 2m-F); –165.3 (m, 1p-F + 2m-F).

Data for 3b. Anal. Calcd for C₇₃F₁₀H₅₅P₃Pt₂S: C, 53.55; H, 3.38; S, 1.96. Found: C, 53.78; H, 3.56; S, 1.27. MS (FAB+): *m/z* 1380 [M – tht – C₆F₅ – 1H]⁺ 4.2%; 757 [Pt(PPh₃)(PPh₂C₂Tol)]⁺ 10%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): $\nu(\text{C}\equiv\text{C})$ 1714 (s, br); $\nu(\text{C}_6\text{F}_5)_{\text{X-sens}}$ 800 (m), 793 (m). ¹H NMR (CDCl₃, 20 °C): δ 7.53 (m, 6H); 7.23–6.65 (m, 38H) (CH, Ph, Tol); 2.12 (s, CH₃); 1.98 (br, 4H, α -CH₂, tht); 1.16 (br, 4H, β -CH₂, tht). ¹⁹F NMR (CDCl₃, 20 °C): δ –117.4 (m, ³J_{Pt–O–F} = 329, 2o-F); –118.0 (m, ³J_{Pt–O–F} = 425, 2o-F); –161.9 (t, 1p-F); –163.6 (m, 2m-F); –165.3 (m, 1p-F + 2m-F).

Synthesis of *cis*-[(C₆F₅)₂M(PPh₂C≡CR)(μ-1κP:2η²-PPh₂C≡CR)Pt(PPh₃)₂] (M = Pt, R = Ph 4a, Tol 4b; M = Pd, R = Ph 5a, Tol 5b). Synthesis of 4a. A solution of *cis*-

[Pt(C₆F₅)₂(PPh₂C≡CPh)₂] (0.166 g, 0.151 mmol) in 10 mL of acetone was treated with [Pt(η²-C₂H₄)(PPh₃)₂] (0.136 g, 0.181 mmol) (molar ratio 1:1.2) at room temperature, and after 15 min of stirring, a white solid started to precipitate. The suspension was stirred for 1 h, and then the solid was filtered and washed with acetone (0.173 g, 61% yield). **4a** crystallizes with one molecule of CH₃COCH₃.

Synthesis of 4b. A solution of *cis*-[Pt(C₆F₅)₂(PPh₂C≡CTol)₂] (0.188 g, 0.167 mmol) in 30 mL of acetone was treated with [Pt(η²-C₂H₄)(PPh₃)₂] (0.149 g, 0.200 mmol) (molar ratio 1:1.2), and the mixture was stirred for 2 h. The resulting turbid, pale yellow solution was filtered through Celite and the filtrate evaporated to dryness. The residue was treated with cold diethyl ether (≈5 mL), yielding complex **4b** (0.188 g, 61% yield) as a white solid. When the reaction was carried out in a molar ratio 1:2, only product **4b** was obtained (82% yield).

Synthesis of 5a and 5b. Complexes **5a** and **5b** were prepared as white solids following a procedure identical to that described for **4b**, using the corresponding starting materials. **5a**: *cis*-[Pd(C₆F₅)₂(PPh₂C≡CPh)₂] (0.167 g, 0.165 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (0.148 g, 0.198 mmol) (0.188 g, 66% yield). **5b**: *cis*-[Pd(C₆F₅)₂(PPh₂C≡CTol)₂] (0.175 g, 0.168 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (0.151 g, 0.200 mmol) (0.198 g, 67% yield). The NMR spectra of **4** and **5** always show trace amounts of the corresponding *cis*-bis(alkynylphosphine) precursors. However, attempts to recrystallize these products caused the loss of the Pt(PPh₃)₂ fragment, yielding solids that contained higher amounts of the corresponding mononuclear starting derivatives.

Data for 4a·CH₃COCH₃. Anal. Calcd for C₈₈F₁₀H₆₀P₄Pt₂·C₃H₆O: C, 58.15; H, 3.54. Found: C, 58.19; H, 3.24. MS (FAB+): *m/z* peak molecular not observed; 718 [Pt(PPh₃)₂ - 1H]⁺ 53%. IR (cm⁻¹): ν(C≡C) 2177 (s), 1756 (vs); ν(C₆F₅)_{X-sens} 792 (m), 778 (m); a medium band at 1716 cm⁻¹ probably due to CH₃COCH₃ is also observed. ¹H NMR (CDCl₃, 20 °C): δ 7.58–6.57 (m, 60H, Ph). ¹⁹F NMR (CDCl₃): δ at -50 °C, -113.4 (s, br, 1o-F); -113.8 (s, br, ³J_{Pt-o-F} ≈ 360, 1o-F); -116.5 (s, br, ³J_{Pt-o-F} = 302, 1o-F); -119.5 (s, br, 1o-F); -162.4 (t, 1p-F); -163.2 (m, 1m-F); -163.8 (m, 1p-F, 1m-F); -164.3 (m, 1m-F); -164.8 (m, 1m-F); at 20 °C, -115.4 (vbr, o-F); -163.3 (t, 1p-F); -164.3 (t, 1p-F); -164.6 (m, br, 4m-F).

Data for 4b. Anal. Calcd for C₉₀F₁₀H₆₄P₄Pt₂: C, 58.45; H, 3.49. Found: C, 58.56; H, 3.58. MS (ES+ ionized with Ag⁺): *m/z* 1957 [M + Ag]⁺ 100%; 1694 [M + Ag - PPh₃]⁺ 18%; 1656 [M + Ag - PPh₂C₂Tol]⁺ 36%. IR (cm⁻¹): ν(C≡C) 2177 (s), 1691 (m); ν(C₆F₅)_{X-sens} 791 (m), 778 (m). ¹H NMR (CD₃COCD₃, 20 °C): δ 7.61–6.72 (58H, Ph); 2.50, 2.20 (s, CH₃). ¹³C NMR (CD₃-COCD₃, -50 °C): δ 153.1 (d, J_{P-C} = 57 Hz, C_α or C_β, η²-C≡CTol); 146.4–137.4 (C₆F₅); 140.4 (s, C⁴, Tol); 135.6–126.5 (aromatics); 117.73, 117.70 (s, C¹, Tol); 106.2 (br, C_β, ≡C_βTol); 78.5 (J_{C-P} = 99.2, C_α, -PC_α≡); 20.7, 20.5 (s, CH₃). ¹⁹F NMR (CD₃COCD₃): δ at -50 °C, -112.4 (s, br, ³J_{Pt-o-F} ≈ 285, 2o-F); -115.0 (s, br, ³J_{Pt-o-F} ≈ 310, 1o-F); -117.5 (br, 1o-F); -162.8 (t, 1p-F); -163.3 (br, 1m-F); -163.8 (br, 1m-F); -164.2 (t, 1p-F); -164.7 (m, br, 2m-F); at 20 °C, -113.5, -114.8 (vbr, o-F); -163.9 (t, 1p-F); -164.9 (m, 1p-F, m-F).

Data for 5a. Anal. Calcd for C₈₈F₁₀H₆₀P₄PdPt: C, 61.00; H, 3.49. Found: C, 61.11; H, 3.59. MS (FAB+): *m/z* 1446 [M - PPh₂C₂Ph]⁺ 13%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2174 (s), 1753 (s), 1716 (sh); ν(C₆F₅)_{X-sens} 778 (m). ¹H NMR (CD₃COCD₃, 20 °C): 7.70–6.76 (60H, Ph). ¹⁹F NMR (CD₃-COCD₃): δ at -50 °C, -109.4 (m, 2o-F); -112.4 (s, 1o-F); -115.3 (s, br, 1o-F); -162.0 (t, 1p-F); -162.3 (m, 1m-F); -163.3 (m, 1m-F); -163.4 (t, 1p-F); -164.0 (m, 2m-F); at 20 °C, -110.9 (vbr); -112.4 (vbr) o-F; -163.0 (t, 1p-F); -163.4 (vbr, m-F); -164.0 (m, 1p-F); -164.3 (vbr, m-F).

Data for 5b. Anal. Calcd for C₉₀F₁₀H₆₄P₄PdPt: C, 61.39; H, 3.66. Found: C, 61.85; H, 3.92. MS (ES+ ionized with Ag⁺): 1869 [M + Ag]⁺ 3%; 1593 [M - C₆F₅]⁺ 38%; 1292 [M - C₆F₅ - PPh₂C₂Tol]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2176 (s), 1746 (sh), 1712 (m); ν(C₆F₅)_{X-sens} 776 (m, br). ¹H NMR (CD₃-

COCD₃): δ 7.57–6.74 (58H, Ph); 2.51, 2.22 (s, CH₃). ¹⁹F NMR (CD₃COCD₃): δ at -50 °C, -109.7 (m, 2o-F); -112.1 (s, br, 1o-F); -114.8 (s, br, 1o-F); -162.0 (t, 1p-F); -162.45 (br, 1m-F); -163.15 (br, 1m-F); -163.35 (t, 1p-F); -164.0 (m, 2m-F); at 20 °C, -110.8 (s, br, 2o-F); -112.2 (vbr, 2o-F); -163.0 (t, 1p-F); -163.9 (br, 2m-F); -164.0 (t, 1p-F); -164.4 (m, 2m-F).

Synthesis of *cis*-[(C≡CR')₂Pt(PPh₂C≡CR)(μ-1κP:2η²-PPh₂C≡CR)]Pt(PPh₃)₂ (R' = Ph, R = Ph **6a, Tol **6b**; R' = *t*Bu, R = Ph **7a**, Tol **7b**).** A solution of *cis*-[Pt(C≡CPh)₂(PPh₂C≡CPh)₂] (0.159 g, 0.164 mmol) in acetone (20 mL) was treated with [Pt(η²-C₂H₄)(PPh₃)₂] (0.147 g, 0.197 mmol) (molar ratio 1:1.2), and the reaction mixture was stirred at room temperature for 2 h. The resulting light brown solution was filtered through Celite and evaporated to dryness. The residue was treated with a cold mixture of diethyl ether/hexane (1:2), yielding complex **6a** as a pale yellow solid (0.194 g, 70% yield).

Complexes **6b** and **7b** (light brown) were prepared similarly to **6a**, starting from *cis*-[Pt(C≡CPh)₂(PPh₂C≡CTol)₂] (0.159 g, 0.160 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (0.143 g, 0.192 mmol) (0.205 g, 75% yield), or *cis*-[Pt(C≡C*t*Bu)₂(PPh₂C≡CTol)₂] (0.168 g, 0.175 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (0.158 g, 0.211 mmol) (0.194 g, 67%).

Complex **7a** was prepared as a pale yellow solid following a similar procedure, using *cis*-[Pt(C≡C*t*Bu)₂(PPh₂C≡CPh)₂] (0.162 g, 0.174 mmol) and [Pt(η²-C₂H₄)(PPh₃)₂] (0.155 g, 0.208 mmol), by evaporation to a small volume (≈2 mL) of the acetone solution (0.198 g, 69% yield).

Data for 6a. Anal. Calcd for C₉₂H₇₀P₄Pt₂: C, 65.16; H, 4.12. Found: C, 64.76; H, 4.50. MS (FAB+): *m/z* 1689 [M]⁺ 3%; 1427 [M - PPh₃]⁺ 28%; 1325 [M - PPh₃ - C₂Ph]⁺ 20%; 1224 [M - PPh₃ - 2(C₂Ph)]⁺ 57%; 1123 [M - PPh₃ - 3(C₂Ph)]⁺ 17%; 719 [Pt(PPh₃)₂]⁺ 80%. IR (cm⁻¹): ν(C≡C) 2174 (m), 2121 (m), 1743 (sh), 1705 (m, br). ¹H NMR (CD₃COCD₃): δ 7.10 (m, 70H, Ph).

Data for 6b. Anal. Calcd for C₉₄H₇₄P₄Pt₂: C, 65.73; H, 4.34. Found: C, 66.08; H, 4.65. MS (FAB+): (%) 1215 [M - 2(C₂Ph) - PPh₂C₂Tol + 1H]⁺ 24%; 719 [Pt(PPh₃)₂]⁺ 67%. IR (cm⁻¹): ν(C≡C) 2173 (m), 2123 (m), 1760 (sh), 1715 (m). ¹H NMR (CDCl₃, 20 °C): δ 7.87–6.28 (68 H, Ph); 2.29, 2.07 (s, CH₃).

Data for 7a. Anal. Calcd for C₈₈H₇₈P₄Pt₂: C, 64.07; H, 4.77. Found: C, 63.98; H, 4.64. MS (FAB+): *m/z* 1647 [M - 2H]⁺ 2%; 1386 [M - PPh₃]⁺ 3%; 1306 [M - PPh₃ - C₂*t*Bu + 1H]⁺ 3.5%; 1224 [M - PPh₃ - 2(C₂*t*Bu)]⁺ 10%; 1123 [M - PPh₃ - 2(C₂*t*Bu) - C₂Ph]⁺ 10%; 1022 [M - PPh₃ - 2(C₂*t*Bu) - 2(C₂-Ph)]⁺ 10%; 719 [Pt(PPh₃)₂]⁺ 75%. IR (cm⁻¹): ν(C≡C) 2175 (m), 1748 (sh), 1705 (m, br). ¹H NMR (CDCl₃, 20 °C): δ 7.96, 7.49–6.34, 6.13 (br, 60 H, Ph); 1.16, 1.10 (s, 9H, *t*Bu). ¹³C NMR (CD₃-COCD₃): δ at -50 °C, 136.3–126.1, 123.6 (s), 120.98 (s) (phenyl resonances); 115.0 (dd, ²J_{C-*Ptrans*}/²J_{C-*Pcis*} ≈ 240/33, Pt-C_α); 106.6 (d, ²J_{C-P} = 11.9, ≡C_βPh); 87.0 (pst, J_{C-P} ≈ 18.4, ≡C_β*t*Bu); 81.0 (dm, ¹J_{C-P} ≈ 85, -PC_α≡); 32.2, 31.5 (s, -C(CH₃)₃); 29.0, 28.8 (s, -CMe₃).

Data for 7b. Anal. Calcd for C₉₀H₈₂P₄Pt₂: C, 64.43; H, 4.93. Found: C, 64.40; H, 4.57. MS (FAB+): *m/z* 1678 [M + 1H]⁺ 5%; 1416 [M - PPh₃ + 2H]⁺ 11%; 1335 [M - PPh₃ - C₂*t*Bu + 2H]⁺ 12%; 1254 [M - PPh₃ - 2C₂*t*Bu + 2H]⁺ 26%; 1138 [M - PPh₃ - 2C₂*t*Bu - C₂Tol + 1H]⁺ 19%; 719 [Pt(PPh₃)₂]⁺ 100%. IR (cm⁻¹): ν(C≡C) 2174 (m), 1751 (sh), 1713 (m, br). ¹H NMR (CD₃COCD₃, 20 °C): δ 7.90–6.30 (m, 58H, Ph); 2.30, 2.26 (s, CH₃); 1.16, 1.04 (s, 9H, *t*Bu).

Crystal Structure Determinations for 2a and 3a. Crystals of **2a** and **3a** suitable for X-ray analysis were obtained by slow diffusion of *n*-hexane into a CH₂Cl₂ solution of **2a** or **3a**, respectively. The diffraction measurements were made on a NONIUS Kappa CCD diffractometer, using graphite-monochromated Mo Kα radiation. An empirical absorption correction using SCALEPACK was applied.²⁷ All calculations were carried out using the SHELXL-97 program.²⁸ The structures were solved by direct methods and refined on F². All non-

Table 4. Crystal Data and Structure Refinement for 2a·0.5C₆H₁₄ and 3a·CH₂Cl₂

	2a·0.5C ₆ H ₁₄	3a·CH ₂ Cl ₂
empirical formula	C ₄₈ F ₂₀ H ₂₃ P ₂ S·C ₃ H ₇	C ₇₂ F ₁₀ H ₅₃ P ₃ Pt ₂ S·CH ₂ Cl ₂
fw	1475.96	1708.22
temperature (K)	293(2)	150(1)
cryst syst, space group	triclinic, <i>P</i> $\bar{1}$	triclinic, <i>P</i> $\bar{1}$
unit cell dimens, <i>a</i> (Å)	12.4059(2)	12.5657(1)
<i>b</i> (Å)	13.3668(2)	14.0831(2)
<i>c</i> (Å)	14.7789(3)	20.0108(3)
α (deg)	89.2974(5)	105.4814(7)
β (deg)	84.6206(5)	93.3360(8)
γ (deg)	83.6718(6)	108.2565(6)
volume (Å ³)	2425.08(7)	3201.78(7)
<i>Z</i> , <i>D</i> _{calcd} (Mg/m ³)	2, 2.021	2, 1.772
abs coeff (mm ^{−1})	5.953	4.629
<i>F</i> (000)	1406	1668
θ range for data collection (deg)	4.12 to 26.50	1.73 to 28.06
no. of data/restraints/params	9976/0/659	15251/0/820
goodness-of-fit on <i>F</i> ²	1.261	1.371
final <i>R</i> indices [<i>I</i> > 2 σ (<i>I</i>)]	<i>R</i> ₁ = 0.0309, <i>wR</i> ₂ = 0.0707	<i>R</i> ₁ = 0.0318, <i>wR</i> ₂ = 0.0770
<i>R</i> indices (all data)	<i>R</i> ₁ = 0.0460, <i>wR</i> ₂ = 0.0748	<i>R</i> ₁ = 0.0400, <i>wR</i> ₂ = 0.0800
largest diff peak and hole (e [−] Å ^{−3})	1.390 and −0.816	1.547 and −2.028

hydrogen atoms were located in succeeding difference Fourier syntheses and refined with anisotropic thermal parameters. All hydrogen atoms were constrained to idealized geometries with isotropic displacement parameters equal to 1.2–1.5 times the *U*_{iso} value of their attached carbon. There are peaks of electron density higher than 1 e/Å³ in the final map, but they are located very close to the platinum atoms and have no chemical meaning. Complex **2a** crystallizes with a half molecule of *n*-hexane and **3a** with a molecule of CH₂Cl₂. Some crystallographic details are shown in Table 4.

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Supporting Information Available: Further details of the structure determination of **2a**·0.5C₆H₁₄ and **3a**·CH₂Cl₂, including atomic coordinates, bond distances and angles, and thermal parameters. This material is available free of charge via the Internet at <http://pubs.acs.org>

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