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

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The monoalkynylphosphine complexes *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)(tht)] (R = Ph **1a**, Tol **1b**, *t*Bu **1c**, tht = tetrahydrothiophene) have been prepared by bridge splitting [{Pt(C_6F_5)$_2$(μ-tht)}$_2$] or by displacement of only one tht ligand from *cis*-[Pt(C_6F_5)$_2$(tht)$_2$] with $PPh_2C{\equiv}CR$. Complexes **1** react with *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] to give binuclear derivatives [(C_6F_5)$_2$Pt(μ-tht)(μ-1κP:2η^2-$PPh_2C{\equiv}CR$)Pt(C_6F_5)$_2$] (R = Ph **2a**, Tol **2b**, *t*Bu **2c**), containing a mixed tht/$PPh_2C{\equiv}CR$ bridging system. In contrast, treatment of **1** with [Pt(η^2-C_2H_4)(PPh_3)$_2$] affords mixed-valence Pt(II)−Pt(0) complexes [{(C_6F_5)$_2$(tht)Pt(μ-1κP:2η^2-$PPh_2C{\equiv}CR$)}Pt(PPh_3)$_2$] (R = Ph **3a**, Tol **3b**) stabilized by only one κP:η^2 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(C_6F_5)$_2$($PPh_2C{\equiv}CR$)$_2$] and *cis*-[Pt($C{\equiv}CR'$)$_2$($PPh_2C{\equiv}CR$)$_2$] (M = Pt, Pd; R = Ph, Tol; R′= Ph, *t*Bu) with 1 or 2 equiv of [Pt(η^2-C_2H_4)(PPh_3)$_2$] yield the corresponding mixed-valence binuclear complexes *cis*-[{(C_6F_5)$_2$M($PPh_2C{\equiv}CR$)(μ-1κP:2η^2-$PPh_2C{\equiv}CR$)}Pt(PPh_3)$_2$] (M = Pt, R = Ph **4a**, Tol **4b**; M = Pd, R = Ph **5a**, Tol **5b**) and *cis*-[{($C{\equiv}CR'$)$_2$Pt($PPh_2C{\equiv}CR$)(μ-1κP:2η^2-$PPh_2C{\equiv}CR$)}Pt(PPh_3)$_2$] (R′ = Ph, R = Ph **6a**, Tol **6b**; R′ = *t*Bu, R = Ph **7a**, Tol **7b**), bearing only one $PPh_2C{\equiv}CR$ η^2-coordinated to a Pt(0)(PPh_3)$_2$ fragment.

Introduction

Alkynyldiphenylphosphines $PPh_2C{\equiv}CR$ 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 phosphido (PPh_2) and alkynide ($C{\equiv}CR$) 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 η^2-alkyne complexes of zerovalent

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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 $[\{M(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CF_3)L\}_2]$ (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 $[M(\eta^2\text{-}C_2H_4)(dcpe)]$ (dcpe: 1,2-bis(dicyclohexylphosphino)ethane) and $PPh_2C{\equiv}CMe$[2c,d] results in the formation of the monomeric η^2-alkynylphosphine $[M(\eta^2\text{-}PPh_2C{\equiv}CMe)(dcpe)]$ 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≡CR′) and examining their reactivity toward the solvento 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 $(\mu\text{-}Cl)_2$ (when R = *t*Bu) or mixed μ-Cl/μ-$PPh_2C{\equiv}CR$ (when R = Ph) binuclear complexes,[6] only homo- and heterobimetallic double alkynyl bridged $(\mu\text{-}C{\equiv}CR)_2$ complexes were formed by using *cis*-$[Pt(C{\equiv}CR')_2(PPh_2C{\equiv}CR)_2]$ as precursors.[7] Several unusual symmetrical $[\{(PPh_2C{\equiv}C\mathit{t}Bu)_2Pt(\mu_3\text{-}\eta^2\text{-}C{\equiv}CPh)_2\}\{M(C_6F_5)_2\}_2]$ and $[\{Pt(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CPh)_2(\mu\text{-}\eta^2\text{-}C{\equiv}C\mathit{t}Bu)_2\}\{Pt(C_6F_5)_2\}_2]$ trimetallic species were also prepared when these *cis*-bis(alkynyl)bis(alkynyldiphenylphosphine) 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 $PPh_2C{\equiv}C\mathit{t}Bu$ 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($\eta^2$-alkyne) adducts $[(C_6F_5)_2M\{\mu\text{-}\kappa PP{:}\eta^2\text{-}(PPh_2C{\equiv}CR)_2\}Pt(C_6F_5)_2]$ 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 and characterization of novel P-coordinated monoalkynylphosphine complexes *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(tht)]$ (R = Ph, Tol, *t*Bu) and examine their reactivity toward *cis*-$[Pt(C_6F_5)_2(thf)_2]$ and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$. 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≡CR′ (R′ = Ph, *t*Bu; R = Ph, Tol)] with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$.

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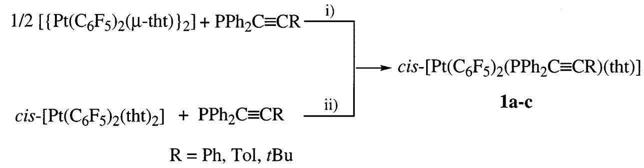
Scheme 1



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**), *t*Bu[8b] (**c**)]. These complexes are isolated as white, air-stable solids by bridge splitting the tetrahydrothiophene-bridged binuclear complex $[\{Pt(C_6F_5)_2(\mu\text{-}tht)\}_2]$ 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 ν(C≡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-α-CH_2 36.8−36.9/2.83−2.89; β-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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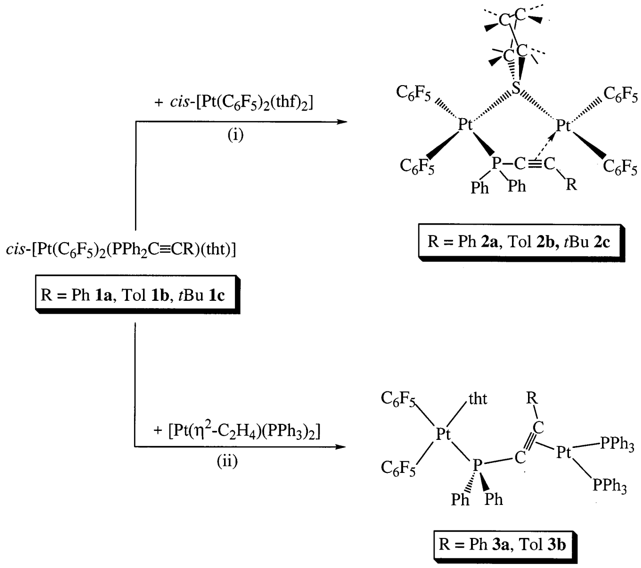
Scheme 2



The reactivity of complexes **1** toward the Pt(II) and Pt(0) substrates,, *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] and [Pt(η^2-C_2H_4)(PPh_3)$_2$], respectively, has been examined and the results of these reactions are summarized in Scheme 2. Treatment of *cis*-[Pt(C_6F_5)$_2$($PPh_2C{\equiv}CR$)(tht)] (R = Ph **1a**, Tol **1b**, *t*Bu **1c**) with 1 equiv of *cis*-[Pt(C_6F_5)$_2$(thf)$_2$] at room temperature in CH_2Cl_2 immediately gives the binuclear heterobridged [(C_6F_5)$_2$Pt(μ-tht)(μ-1κP:2η^2-$PPh_2C{\equiv}CR$)Pt(C_6F_5)$_2$] (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-$PPh_2C{\equiv}CR$) 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 ^{1}H NMR spectra, which show, at room temperature, two different signals for both the α-CH_2 (δ 3.82−3.18) and β-CH_2 [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 ^{19}F NMR spectra at room temperature confirm the presence of four rigid nonequivalent C_6F_5 groups (four *para*-fluorine triplets and AA′MXX′ spin systems), and the ^{31}P{^{1}H} 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-μ:η^2-$PPh_2C{\equiv}CR$ 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]

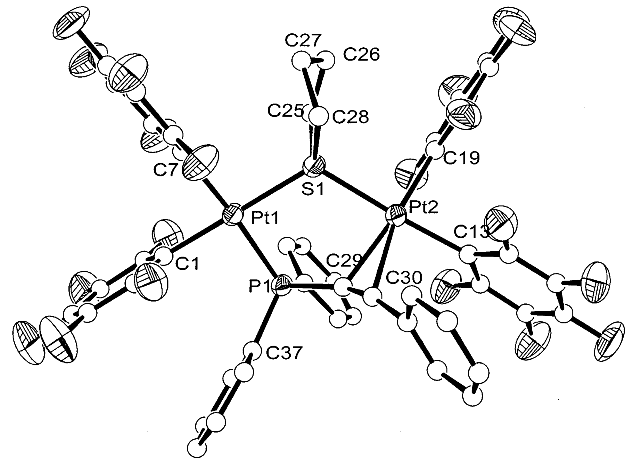


Figure 1. Molecular structure of [(C_6F_5)$_2$Pt(μ-tht)(μ-1κP:2η^2-$PPh_2C{\equiv}CPh$)Pt(C_6F_5)$_2$], **2a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) [(C_6F_5)$_2$Pt(μ-tht)(μ-1κP:2η^2-$PPh_2C{\equiv}CPh$)Pt(C_6F_5)$_2$] (2a·0.5C_6H_{14})

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(C_6F_5)$_2$" 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:η^2-$PPh_2C{\equiv}CR$)(μ-X) are very scarce. As far as we know, the only examples characterized by X-ray diffraction are the recently described dinuclear derivatives [(C_6F_5)$_2$Pt(μ-Cl)(μ-1κP:2η^2-$PPh_2C{\equiv}CPh$)PtCl($PPh_2C{\equiv}CPh$)],[6] obtained by the reaction of *cis*-[PtCl$_2$($PPh_2C{\equiv}CPh$)$_2$] with *cis*-[Pt(C_6F_5)$_2$(thf)$_2$], the trinuclear complex [{*cis*-Pt(μ-κP:η^2-$PPh_2C{\equiv}CPh$)$_2$(μ-η^1:η^2-$PPh_2C{\equiv}CtBu$)$_2$}-{Pt(C_6F_5)$_2$}$_2$],[7] in which two terminal "*cis*-Pt(C_6F_5)$_2$" moieties are linked to a central platinum atom through both alkynyl units (μ-η^2) and both alkynylphosphine ligands (μ-κP:η^2), and the d^6−d^8 species [($PPh_2C{\equiv}CPh$)-Cp*Ru(μ-Cl)(μ-κP:η^2-$PPh_2C{\equiv}CPh$)Pt(C_6F_5)$_2$].[11] In addition, several X-ray-characterized examples of platinum complexes with tht bridging ligands are known, in particular (NBu_4)$_2$[*trans*-PtCl$_2${(μ-tht)Pt(C_6F_5)$_3$}$_2$][12] (tht monobridge), (NBu_4)[Pt_2Ag(μ-tht)$_2$(C_6F_5)$_6$][13] (tht mono-

(12) Usón, R.; Forniés, J.; Tomás, M.; Ara, I. *J. Chem. Soc., Dalton Trans.* **1989**, 1011.

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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 μ-tht/μ-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 μ-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 phosphinoalkynes, 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 $cis\text{-}[Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(tht)]$ **1a** and **1b** react in acetone with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ to give, in moderate yields, the novel $[\{(C_6F_5)_2(tht)Pt(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CR)\}Pt(PPh_3)_2]$ (R = Ph **3a**, Tol **3b**) complexes (Scheme 2, ii), stabilized by only one $\kappa P{:}\eta^2$-$PPh_2C{\equiv}CR$ 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 $PPh_2C{\equiv}C\mathit{t}Bu$ 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 $cis\text{-}[Pt(C_6X_5)_2L_2]$ (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 formation is remarkable, as binuclear Pt(I)−Pt(I) derivatives or more simple Pt(II)−Pt(II) phosphide/alkynide species could have been also obtained by simple P−C(alkyne) bond cleavage.[4]

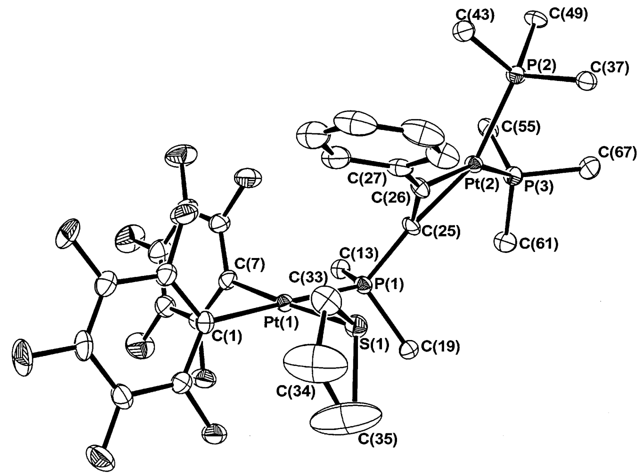

Figure 2. View of the molecular structure of $[\{(C_6F_5)_2(tht)Pt(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CPh)\}Pt(PPh_3)_2]$, **3a**. Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity, and the phenyl groups bound to the phosphorus atoms are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

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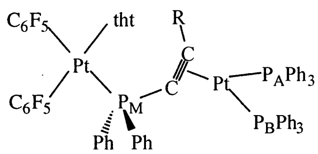
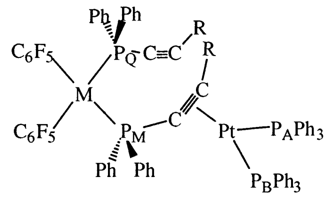
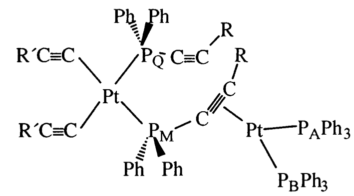
Table 2. $^{31}P\{^1H\}$ NMR Data at 20 °C for Complexes 3−7 (δ in ppm, *J* in Hz, $^1J_{Pt-P}$ in brackets)



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′= *t*Bu; R = Ph **7a**, Tol **7b**

compound	δ P_A	δ P_B	δ P_M	δ P_Q	$^2J_{PA-PB}$	$^3J_{PA-PM}$	$^3J_{PB-PM}$	$^2J_{PM-PQ}$
3a[a]	24.84 (s, br)	24.38 (s, br)	−16.00 (s, br)					
	[3493]	[3643]	[2386]					
3b[a]	24.85 (s, br)		−15.70 (s, br)					
	[3480]	[3638]	[2391]					
4a[a]	25.64	24.26	−8.54	−14.28	27.9	20.3	17.7	
	[3492]	[3674]	[2428]	[2315]				
4b[b]	25.72	24.74	−8.93	−15.30	27.9	29.7	27.6	
	[3474]	[3685]	[2462]	[2337]				
5a[b]	25.79	24.09	−3.94	−7.75	27.2	27.5	23.1	
	[3488]	[3685]						
5b[b]	25.81	24.34	−4.19	−7.97	27.6	27.6	19.7	
	[3470]	[3687]						
6a[b]	24.90		1.94	−10.3	*c*	*c*	*c*	*c*
	[3535]	[3737]	[2381]	[2325]	*c*	*c*	*c*	
6b[a]	25.00		0.04	−10.36				18.8
	[3645]		*c*	[2338]				
7a[a]	24.33	25.30	5.11	−10.56	26.8	45.7	28.4	18.6
	[3770]	[3460]	[2418]	[2292]				
7b[b]	25.40		4.88	−10.73	*c*	*c*	*c*	*c*
	[≈3443]	[≈3648]	[2426]	[2284]				

[a] In $CDCl_3$. [b] In CD_3COCD_3. [c] It cannot be calculated.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for $[\{(C_6F_5)_2(tht)Pt(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CPh)\}Pt(PPh_3)_2]$ ($3a\cdot CH_2Cl_2$)

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 PPh_2 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 ($PPh_2C{\equiv}CPh$ δ −33.53; $PPh_2C{\equiv}CTol$ −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 CH_2Cl_2 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 $PPh_2C{\equiv}CPh$ ligand to the $Pt(PPh_3)_2$ fragment. The Pt(2) center displays a close to planar trigonal coordination, typical of metal (d^{10})−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 PPh_2 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* C_6F_5 groups, to the phosphorus atom of the bridging $PPh_2C{\equiv}CPh$ 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*-$[MX_2(PPh_2C{\equiv}CR)_2]$ (X = C_6F_5, M = Pt, Pd; X = C≡CR′, M = Pt) toward the solvento tetrahydrothiophene Pt(II) complex

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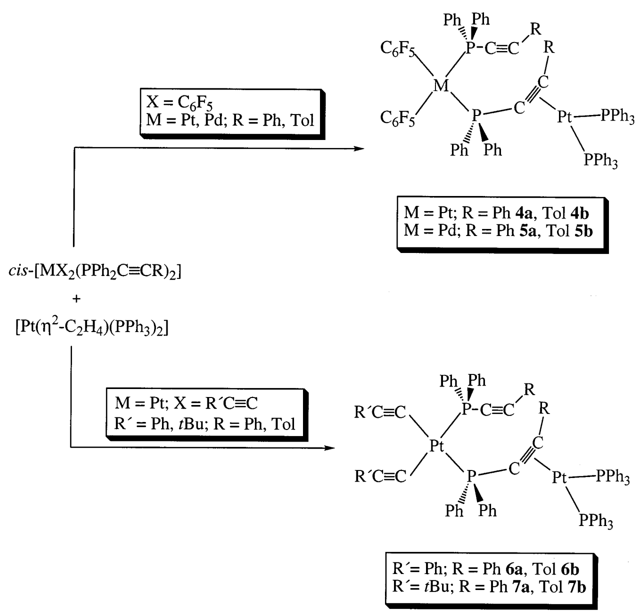
Scheme 3



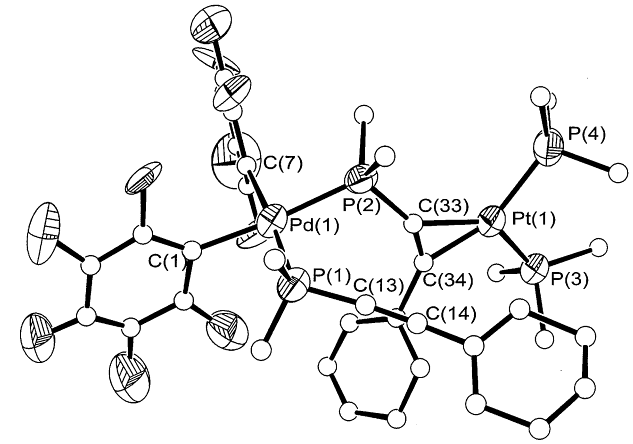


Figure 3. Schematic view of the preliminary X-ray diffraction study of **5a** showing the connectivity of the atoms. For the sake of clarity, the phenyl groups bound to the phosphorus atoms are represented by their *ipso*-carbons only.

cis-[$Pt(C_6F_5)_2(thf)_2$]. The reactions of *cis*-[$M(C{\equiv}CR')_2$-($PPh_2C{\equiv}CR)_2$] with 1 equiv of the solvento complex lead to binuclear derivatives stabilized by alkynyl bridging ligands [{$(PPh_2C{\equiv}CR)_2Pt(\mu\text{-}C{\equiv}CR')_2$}$Pt(C_6F_5)_2$],[7] indicating that alkynyl groups possess a higher η^2-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 $Pt{-}C_6F_5$ bond, are the only final species when the solvento complex *cis*-[$Pt(C_6F_5)_2$-($thf)_2$] reacts with *cis*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CR)_2$] (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*-[$M(C_6F_5)_2(PPh_2C{\equiv}CR)_2$] (M = Pt, Pd; R = Ph, Tol) and *cis*-[$Pt(C{\equiv}CR')_2(PPh_2C{\equiv}CR)_2$] (R = Ph, Tol; R′= Ph, *t*Bu), toward [$Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$]. Following a procedure similar to that used for complexes **3**, the reactions of the ethylene Pt(0) derivative [$Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$] 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*-[{$(C_6F_5)_2M(PPh_2C{\equiv}CR)(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CR)$}$Pt(PPh_3)_2$] (M = Pt, R = Ph **4a**, Tol **4b**; M = Pd, R = Ph **5a**, Tol **5b**) and *cis*-[{$(C{\equiv}CR')_2Pt(PPh_2C{\equiv}CR)$-($\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CR)$}$Pt(PPh_3)_2$] (R′ = Ph, R = Ph **6a**, Tol **6b**; R′ = *t*Bu, R = Ph **7a**, Tol **7b**), respectively, with a $Pt(PPh_3)_2$ 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*-[$M(C_6F_5)_2(thf)_2$] form exclusively double alkynide bridged systems. This difference can be explained in terms of a stronger π-acceptor ability of the $-PC{\equiv}CR$ unit, which favors coordination to the relatively electron rich Pt(0). Recent theoretical calculations have shown that P-complexation of these ligands reduces the $\pi^*C{\equiv}C$ occupancy.[1d] This fact, which is related to the higher $\nu(C{\equiv}C)$ 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 ($\Delta\delta$ for [$Pt(C{\equiv}CR')_2(PPh_2C{\equiv}CR)_2$] 26.03−27.4) will also increase the electronegativity of P and raise the preference of the acetylenic $M{-}PC{\equiv}CR$ 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 $Pt(PPh_3)_2$ 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 η^2-alkyne interaction. Similar reactions were attempted between *cis*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CtBu)_2$] or *cis*-[$Pt(C{\equiv}CR')_2(PPh_2C{\equiv}CtBu)_2$] (R′ = Ph, Tol) and [$Pt(\eta^2\text{-}C_2H_4)$-($PPh_3)_2$], but in all cases, the Pt(II) precursors remained unreacted in solution, even after longer reaction times, confirming again the lower η^2-bonding capability of $PPh_2C{\equiv}CtBu$ ligands. We also noted that attempts to involve both $PPh_2C{\equiv}CR$ groups in η^2-coordination failed. Thus, treatment of *cis*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CTol)_2$] or *cis*-[$Pt(C{\equiv}CR')_2(PPh_2C{\equiv}CPh)_2$] with 2 molar equiv of [Pt-($\eta^2\text{-}C_2H_4)(PPh_3)_2$] 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, ^{19}F, $^{31}P\{^1H\}$, and $^{13}C\{^1H\}$ 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-($C_6F_5)_2(PPh_2C{\equiv}CPh)_2$", which acts as a monoacetylenic

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ligand toward the low-valent metal in the $Pt(PPh_3)_2$ 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**) ν(C≡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 $PPh_2C{\equiv}CR$ (2173−2177 cm^{-1}) or alkynide (2121 **6a**, 2123 cm^{-1} **6b**) ligands. The most relevant feature of the room-temperature ^{1}H 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*-butylalkynyde complexes **7**. Complexes **4** and **5**, containing C_6F_5 groups, display at −50 °C a ^{19}F NMR pattern characteristic of a rigid molecule (two different sets of resonances due to rigid C_6F_5 rings with nonequivalent 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 C_6F_5 groups around their Pt−C bonds. The ^{31}P{^{1}H} NMR data (20 °C) for these complexes (**4**−**7**) are shown in Table 2. All complexes display an ABMQ splitting pattern with the corresponding ^{195}Pt satellites, and from the analysis of the ABM part of the spectrum, δP_A, δP_B, δP_M, $^2J_{PA-PB}$, $^3J_{PA-PM}$, and $^3J_{PB-PM}$ 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 PPh_2 end on the basis of the larger $^3J_{PM-P}$ 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 ($^2J_{PM-PQ}$ 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 C_6F_5 *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 ^{13}C 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 $PPh_2C{\equiv}CTol$ ligands resonate close to those seen in the precursor (δ 78.5, $^1J_{P-C}$ 99.2 Hz, C_α; 106.2 br C_β vs 79.1 C_α and 108.3 C_β in [$Pt(C_6F_5)_2(PPh_2C{\equiv}CTol)_2$]), and a signal observed at δ 153.1 (d, J_{P-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 $PPh_2C{\equiv}CPh$) occur at positions similar

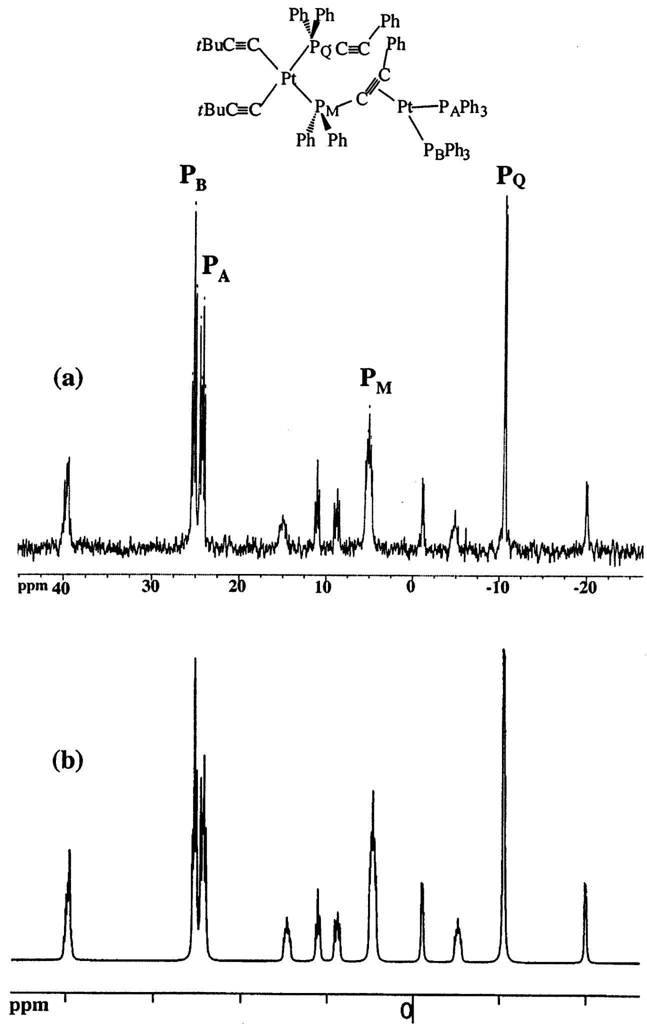

Figure 4. Real (a) and simulated (b) ^{31}P{^{1}H} NMR spectra of **7a**.

to those observed in the starting material (see Experimental Section for details), but the alkynyl carbons of the alkynyl bridging κP:η^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*-[$Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(tht)$] **1**, and investigate their reactivity toward *cis*-[$Pt(C_6F_5)_2(thf)_2$] and [$Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$]. We have shown that while complexes **1** react with the solvento derivatives *cis*-[$Pt(C_6F_5)_2(thf)_2$] to give the first reported examples of hetero (μ-tht)/(μ-κP:η^2-$PPh_2C{\equiv}CR$) bridged diplatinum(II) complexes, the reaction with the ethylene platinum(0) complex results in the formation of the single μ-κP:η^2-$PPh_2C{\equiv}CR$ bridged mixed-valence Pt(II)−Pt(0) complexes accessible through η^2-alkyne complexation of the $Pt(PPh_3)_2$ unit. By comparison, the reactivity of [$Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2$] toward several *cis*-bis(alkynylphosphine) *cis*-[$MX_2(PPh_2C{\equiv}CR)_2$] (X = C_6F_5, 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

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for **1**. These complexes have been shown to bind only one $Pt(PPh_3)_2$ unit, leading to related M(II)−Pt(0) homo (**4**, **6**, **7**) and hetero (Pd−Pt **5**) binuclear complexes stabilized by a κP:η^2-$PPh_2C{\equiv}CR$ 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 $PPh_2C{\equiv}CR$ ligand indicates that the acetylenic unit on these molecules exhibits a stronger η^2-bonding capability toward Pt(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 $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ confirms previous observations that indicate the absence or very low η^2-bonding capability of these bulky molecules. The successful synthesis of complex $[(C_6F_5)_2Pt(\mu\text{-tht})(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}C\mathit{t}Bu)Pt(C_6F_5)_2]$, **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. $PPh_2C{\equiv}CR$ (R = Ph,[20] Tol,[1k] *t*Bu[20]), *cis*-$[Pt(C_6F_5)_2(tht)_2]$,[21] $[\{Pt(\mu\text{-tht})(C_6F_5)_2\}_2]$,[22] *cis*-$[Pt(C_6F_5)_2(thf)_2]$,[23] *cis*-$[Pt(C{\equiv}CR)_2COD]$ (R = Ph,[24] *t*Bu[25]), *cis*-$[M(C_6F_5)_2(PPh_2C{\equiv}CR)_2]$ (M = Pt, Pd; R = Ph,[8a] Tol[8b]), and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$[26] were prepared according to literature methods. The synthesis of *cis*-$[Pt(C{\equiv}CR)_2(PPh_2C{\equiv}CTol)_2]$ (R = Ph, *t*Bu) was similar to that described for *cis*-$[Pt(C{\equiv}CR)_2(PPh_2C{\equiv}CPh)_2]$.[7]

Synthesis of *cis*-$[Pt(C{\equiv}CR)_2(PPh_2C{\equiv}CTol)_2]$ (R = Ph, *t*Bu). A solution of *cis*-$[Pt(C{\equiv}CPh)_2(COD)]$ (0.590 g, 1.167 mmol) in CH_2Cl_2 (20 mL) was treated at room temperature with $PPh_2C{\equiv}CTol$ (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, *cis*-$[Pt(C{\equiv}CPh)_2(PPh_2C{\equiv}CTol)_2]$ (0.606 g, 52% yield).

cis-$[Pt(C{\equiv}C\mathit{t}Bu)_2(PPh_2C{\equiv}CTol)_2]$ was prepared similarly using *cis*-$[Pt(C{\equiv}C\mathit{t}Bu)_2(COD)]$ (0.500 g, 1.07 mmol) and $PPh_2C{\equiv}CTol$ (0.645 g, 2.148 mmol) (0.472 g, 46% yield).

Data for *cis*-$[Pt(C{\equiv}CPh)_2(PPh_2C{\equiv}CTol)_2]$. Anal. Calcd for $C_{58}H_{44}P_2Pt$: C, 69.80; H, 4.44. Found: C, 69.51; H, 4.49. MS (ES+ ionized with Ag^+): *m/z* 1196 $[M + Ag + Tol]^+$ 35%; 1106 $[M + Ag + H]^+$ 10%; 896 $[Pt(C_2Ph)(PPh_2C_2Tol)_2]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2172 (vs), 2123 (s). ^1H NMR ($CDCl_3$, 20 °C): δ 7.87 (s, br, 8H); 7.28 (m, 14H); 6.95 (m, 16H) CH, Ph, Tol; 2.33 (s, CH_3). ^{13}C NMR ($CDCl_3$, 20 °C): δ 139.9 (s, C^4, Tol); 133.4 ("t", J_{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, Tol); 127.9 ("t", J_{C-P} = 5.8, *m*-C, PPh_2); 126.8 (s, CH, Tol); 124.8 (s, Ph); 117.6 (s, C^1, Tol); 109.2 (*A*XX′ five line pattern, $^3J_{C-Ptrans} + {}^3J_{C-Pcis}$ = 36.4, Pt satellites not observed, ≡C_βPh); 108.3 (*A*XX′, $^2J_{C-P} + {}^4J_{C-P}$ = 15.4, ≡C_βTol); 101.7 (AXX′, dd, $^2J_{C-Ptrans} + {}^2J_{C-Pcis}$ = 178.1, Pt−C_α≡); 80.1 (AXX′, d, $^1J_{C-P} + {}^3J_{C-P}$ = 103.9, −PC_α≡); 21.4 (s, CH_3). ^{31}P NMR ($CDCl_3$, 20 °C): δ −6.39 (s, $^1J_{Pt-P}$ = 2347).

Data for *cis*-$[Pt(C{\equiv}C\mathit{t}Bu)_2(PPh_2C{\equiv}CTol)_2]$. Anal. Calcd for $C_{54}H_{52}P_2Pt$: C, 67.70; H, 5.47. Found: C, 67.46; H, 5.42. MS (ES+ ionized with Ag^+): *m/z* 1065 $[M + Ag]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2173 (vs). ^1H NMR ($CDCl_3$, 20 °C): δ 7.86 (m, 8H); 7.27 (m, 12H) Ph; 6.93 (AB, J_{H-H} = 7.8, δ_A 6.96, δ_B 6.90, C_6H_4); 2.32 (s, CH_3); 0.92 (s, *t*Bu). ^{13}C NMR ($CDCl_3$, 20 °C): δ 139.6 (s, C^4, Tol); 133.5 ("t", J_{C-P} = 6.3, *o*-C, PPh_2); 131.7 (s, *p*-C, PPh_2); 131.6 (AXX′ four lines, $^1J_{C-P} + {}^3J_{C-P}$ = 54.8, *i*-C, PPh_2); 129.8 (s, CH, Tol); 128.5 (s, CH, Tol); 127.6 ("t", J_{C-P} = 5.8, *m*-C, PPh_2); 117.9 (s, C^1, Tol); 116.9 (*A*XX′ five line pattern, $^3J_{C-Ptrans} + {}^3J_{C-Pcis}$ = 35.9, ≡C_β*t*Bu); 107.6 (*A*XX′, $^2J_{C-P} + {}^4J_{C-P}$ = 14.8, ≡C_βTol); 84.8 (AXX′, dd, $^2J_{C-Ptrans} + {}^2J_{C-Pcis}$ = 180.1, Pt−C_α≡); 80.9 (AXX′, d, $^1J_{C-P} + {}^3J_{C-P}$ = 100.0, P−C_α≡); 31.5, 31.4 (s, −C(CH_3)$_3$); 28.6 (s, $^3J_{Pt-C}$ = 21.5, −CMe$_3$); 21.4, 21.3 (s, CH_3). ^{31}P NMR ($CDCl_3$, 20 °C): δ −6.19 (s, $^1J_{Pt-P}$ = 2319).

Synthesis of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CR)(tht)]$ (R = Ph 1a, Tol 1b, *t*Bu[8b] 1c). Method a. A solution of $PPh_2C{\equiv}CPh$ (0.101 g, 0.354 mmol) in CH_2Cl_2 (20 mL) was treated with *cis*-$[Pt(C_6F_5)_2(tht)_2]$ (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 $[\{Pt(C_6F_5)_2(\mu\text{-tht})\}_2]$ (0.185 g, 0.150 mmol) in CH_2Cl_2 (10 mL) was added $PPh_2C{\equiv}CPh$ (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: $PPh_2C{\equiv}CTol$ (0.106 g, 0.354 mmol) and *cis*-$[Pt(C_6F_5)_2(tht)_2]$ (0.250 g, 0.354 mmol) (5 h of stirring) (0.253 g, 78% yield) or $[\{Pt(C_6F_5)_2(\mu\text{-tht})\}_2]$ (0.182 g, 0.147 mmol) and $PPh_2C{\equiv}CTol$ (0.088 g, 0.295 mmol) (0.230 g, 85% yield).

The synthesis of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}C\mathit{t}Bu)(tht)]$, **1c**, using method a has been previously described.[8b] **1c** can be also obtained following method b: $[\{Pt(C_6F_5)_2(\mu\text{-tht})\}_2]$ (0.178 g, 0.144 mmol) and $PPh_2C{\equiv}C\mathit{t}Bu$ (0.077 g, 0.288 mmol) (0.173 g, 68% yield).

Data for 1a. Anal. Calcd for $C_{36}H_{23}F_{10}PPtS$: 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}): $\nu(C{\equiv}C)$ 2179 (vs); $\nu(C_6F_5)_{X-sens}$ 803 (vs), 786 (s). ^1H NMR ($CDCl_3$, 20 °C): δ 7.73−7.41 (m, 15H, Ph); 2.89 (s, 4H, α-CH_2, tht), 1.71 (s, 4H, β-CH_2, tht). ^{13}C NMR ($CDCl_3$, 20 °C): δ 146.7−136.6 (C_6F_5); 132.4 (d, J_{C-P} = 12.9, *o*-C, PPh_2); 132.0 (s, *o*-C, Ph); 130.9 (d, $^4J_{C-P} \approx 1$, *p*-C, PPh_2); 130.3 (s, *p*-C, Ph); 129.1 (d, $^1J_{C-P}$ = 62, *i*-C, PPh_2); 128.4 (s, *m*-C, Ph); 128.3 (d, J_{C-P} = 11.5, *m*-C, PPh_2); 120.2 (d, $^3J_{C-P} \approx 2.5$, *i*-C, Ph); 108.1 (d, $^2J_{C-P}$ = 14.5, $\equiv C_\beta$Ph); 78.6 (d, $^1J_{C-P}$ = 98, $-PC_\alpha\equiv$); 36.9 (s, br, α-CH_2, tht); 29.6 (s, br, β-CH_2−, tht). ^{19}F NMR ($CDCl_3$, 20 °C): δ −118.2 (m, $^3J_{Pt-o-F} \approx 410$, 290, 4*o*-F); −160.4 (t, 1*p*-F); −162.7 (m, 2*m*-F); −163.1 (t, 1*p*-F); −164.5 (m, 2*m*-F). ^{31}P NMR ($CDCl_3$, 20 °C): δ −5.71 (s, $^1J_{Pt-P}$ = 2470).

Data for 1b. Anal. Calcd for $C_{37}H_{25}F_{10}PPtS$: 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 $[Pt(PPh_2C_2Tol)(tht)]^+$ 80%; 495 $[Pt(PPh_2C_2Tol)]^+$ 85%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2171 (vs); $\nu(C_6F_5)_{X-sens}$ 812 (s), 800 (s). ^1H NMR ($CDCl_3$, 20 °C): δ 7.73 (dd, *o*-H, Ph), 7.42 (m, 8H) (CH, Ph, Tol); 7.20 (d, $J_{H-H} \approx 7.6$, 2H, C_6H_4); 2.89 (s, 4H, α-CH_2, tht); 2.40 (s, 3H, CH_3); 1.70 (s, 4H, β-CH_2, tht). ^{13}C NMR ($CDCl_3$, 20 °C): δ 147.9−135.0 (C_6F_5); 140.9 (s, C^4, Tol); 132.4 (d, J_{C-P} = 12.8, *o*-C, PPh_2); 131.9 (s, CH, Tol); 130.8 (d, $^4J_{C-P} \approx 1$, *p*-C, PPh_2); 129.2 (s, CH, Tol); 129.25 (d, $^1J_{C-P}$ = 62.0, *i*-C, PPh_2); 128.2 (d, J_{C-P} = 11.5, *m*-C, PPh_2); 117.1 (d, $^3J_{C-P} \approx 2.5$, C^1, Tol); 108.6 (d, $^2J_{C-P}$ = 15.0, $\equiv C_\beta$Tol); C_α should appear as a doublet, but one of the peaks overlaps with the $CDCl_3$ signal (≈77.83, $^1J_{C-P} \approx 100$); 36.9 (s, α-CH_2, tht), 29.5 (s, β-CH_2, tht); 21.4 (s, CH_3, Tol). ^{19}F NMR ($CDCl_3$, 20 °C): δ −118.2 (m, $^3J_{Pt-o-F} \approx 390$, 330, 4*o*-F); −160.4 (t, 1*p*-F); −162.8 (m, 2*m*-F); −163.2 (t, 1*p*-F); −164.5 (m, 2*m*-F). ^{31}P NMR ($CDCl_3$, 20 °C): δ −5.87 (s, $^1J_{Pt-P}$ = 2472).

Data for 1c. Analytical, IR, ^1H, ^{31}P, and ^{19}F NMR data for this complex have been reported.[8b] ^{13}C NMR ($CDCl_3$, 20 °C): δ 147.9−135.0 (C_6F_5); 132.2 (d, J_{C-P} = 12.8, *o*-C, PPh_2); 130.6 (d, $^4J_{C-P}$ = 2.4, *p*-C, PPh_2); 129.8 (d, $^1J_{C-P}$ = 62, $^2J_{Pt-C}$ = 24, *i*-C, PPh_2); 128.1 (d, J_{C-P} = 11.5, *m*-C, PPh_2); 119.5 (d, $^2J_{C-P}$ = 13.2, $\equiv C_\beta t$Bu); 68.3 (d, $^1J_{C\alpha-P}$ = 102, $P-C_\alpha\equiv$); 36.8 (d, $^3J_{C-P}$ = 3, α-CH_2, tht); 29.9 (d, $^4J_{C-P}$ = 1.2, $-C(CH_3)_3$); 29.4 (s, β-CH_2, tht); 28.6 (d, $^3J_{C-P}$ = 1.8, $-C$Me$_3$).

Synthesis of $[(C_6F_5)_2Pt(\mu\text{-tht})(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CR)Pt(C_6F_5)_2]$ (R = Ph 2a, Tol 2b, *t*Bu 2c). A general procedure for **2a** is given: a solution of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CPh)(tht)]$, **1a** (0.150 g, 0.166 mmol), in CH_2Cl_2 (20 mL) was treated with *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (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*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CTol)(tht)]$, **1b**, and 0.110 g (0.163 mmol) of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.200 g, 85% yield); 0.141 g (0.160 mmol) of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}C t Bu)(tht)]$, **1c**, and 0.108 g (0.160 mmol) of *cis*-$[Pt(C_6F_5)_2(thf)_2]$ (0.116 g, 52% yield).

Data for 2a. Anal. Calcd for $C_{48}F_{20}H_{23}PPt_2S$: 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 $[M - 2C_6F_5]^+$ 1%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2051 (w), 2006 (m); $\nu(C_6F_5)_{X-sens}$ 805 (s, br). ^1H NMR ($CDCl_3$, 20 °C): δ 7.66 (m, 8H), 7.47 (s, br, 7H) Ph; 3.82 (2H), 3.64 (2H) (s, br, α-CH_2, tht); 1.67 (2H), 1.55 (2H) (s, br, β-CH_2, tht). ^{19}F NMR ($CDCl_3$, 20 °C): δ −117.6 (m, $^3J_{Pt-o-F} \approx 370$, 2*o*-F); −118.3 (m, 2*o*-F); −118.6 (m, 2*o*-F); −119.2 (m, br, $^3J_{Pt-o-F} \approx 340$, 2*o*-F); −156.5 (t, *p*-F); −157.5 (t, *p*-F); −158.9 (t, *p*-F); −160.8 (m, 4*m*-F + *p*-F); −163.2 (m, 4*m*-F). ^{31}P NMR ($CDCl_3$, 20 °C): δ 24.25 (s, $^1J_{Pt-P}$ = 2349).

Data for 2b. Anal. Calcd for $C_{49}F_{20}H_{25}PPt_2S$: 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 $[M - 2C_6F_5 - 1H]^+$ 2%; 829 $[Pt(C_6F_5)_2(PPh_2C_2Tol)]^+$ 5%; 662 $[Pt(C_6F_5)(PPh_2C_2Tol)]^+$ 6%; 583 $[Pt(PPh_2C_2Tol)(tht)]^+$ 10%; 495 $[Pt(PPh_2C_2Tol)]^+$ 8%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2059 (w), 2017 (m); $\nu(C_6F_5)_{X-sens}$ 815 (m), 804 (s). ^1H NMR ($CDCl_3$, 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-CH_2, tht); 2.42 (s, CH_3); 2.17 (2H), 1.66 (2H) (s, br, β-CH_2, tht). ^{19}F NMR ($CDCl_3$, 20 °C): δ −117.6 (m, $^3J_{Pt-o-F}$ = 365, 2*o*-F), −118.3 (m, 2*o*-F); −118.6 (m, 2*o*-F); −119.1 (m, br, $^3J_{Pt-o-F}$ = 335, 2*o*-F); −156.7 (t, *p*-F); −157.6 (t, *p*-F); −159.1 (t, *p*-F); −160.9 (m, 4*m*-F + 1*p*-F); −163.3 (m, 4*m*-F). ^{31}P NMR ($CDCl_3$, 20 °C): δ 24.25 (s, $^1J_{Pt-P}$ = 2359).

Data for 2c. Anal. Calcd for $C_{46}F_{20}H_{27}PPt_2S$: C, 39.10; H, 1.93; S, 2.27. Found: C, 38.75; H, 1.72; S, 2.36. MS (FAB+): *m/z* 1078 $[M - 2C_6F_5]^+$ 12%; 894 $[Pt(PPh_2C_2tBu)_2(C_6F_5)]^+$ 55%; 727 $[Pt(PPh_2C_2tBu)_2]^+$ 87%; 549 $[Pt(PPh_2C_2tBu)(tht)]^+$ 60%; 461 $[Pt(PPh_2C_2tBu)]^+$ 75%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 1982 (m, br); $\nu(C_6F_5)_{X-sens}$ 806 (s, br), 791 (m), 774 (sh). ^1H NMR ($CDCl_3$): δ at 20 °C, 8.05−7.33 (vbr, Ph); 3.77, 3.18 (vbr, α-CH_2, tht); 1.92 (vbr, β-CH_2, tht); 1.38 (s, 9H, *t*Bu); 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-CH_2, tht); 2.08 (s, br, 2H, β-CH_2, tht), the other signal corresponding to β-CH_2 protons could be overlapped with the signal of *t*Bu group at δ 1.36. ^{19}F NMR ($CDCl_3$): δ at 20 °C, −117.7 (s, br, 2*o*-F), −118.2 (s, br, 4*o*-F); −118.5 (s, br, 2*o*-F); −156.6 (t, *p*-F); −157.5 (t, *p*-F); −157.9 (t, *p*-F); −161.0 [overlapping of dt (1*p*-F and a broad signal due to 3*m*-F)]; −161.5 (m, br, 1*m*-F); −162.6 (m, 2*m*-F); −163.2 (m, br, 1*m*-F); −163.5 (m, br, 1*m*-F); at −50 °C, −116.5 (m, $^3J_{Pt-o-F} \approx 360$, 1*o*-F); −117.8 (m, $^3J_{Pt-o-F} \approx 360$, 1*o*-F); −118.2 (m, 1*o*-F); −118.5 (m, 2*o*-F); −119.3 (m, 2*o*-F); −120.3 (m, $^3J_{Pt-o-F} \approx 310$, 1*o*-F); −156.2 (t, 1*p*-F); −156.9 (t, 1*p*-F); −157.4 (t, 1*p*-F); −160.2 (m, 3*m*-F); −160.5 (t, 1*p*-F); −160.9 (m, 1*m*-F); −161.8 (m, 1*m*-F); −162.2 (m, 1*m*-F); −162.8 (m, 1*m*-F); −163.1 (m, 1*m*-F). ^{31}P NM*R* ($CDCl_3$, 20 °C): δ 22.09 (s, $^1J_{Pt-P}$ = 2332).

Synthesis of $[\{(C_6F_5)_2(tht)Pt(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CR)\}Pt(PPh_3)_2]$ (R = Ph 3a, Tol 3b). To a solution of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CPh)(tht)]$ (0.141 g, 0.156 mmol) in acetone (30 mL) was added 0.117 g (0.156 mmol) of $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$, and the mixture was stirred at room temperature for 2 h. The resulting colorless solution was filtered through Celite under N_2 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*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CTol)(tht)]$ (0.146 g, 0.159 mmol) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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 $C_{72}F_{10}H_{53}P_3Pt_2S$: C, 53.27; H, 3.29; S, 1.97. Found: C, 53.42; H, 3.56; S, 1.50. MS (FAB+): *m/z* 1359 $[M - PPh_3 - 1H]^+$ 11%; 719 $[Pt(PPh_3)_2]^+$ 100%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 1715 (s); $\nu(C_6F_5)_{X-sens}$ 801 (m), 782 (m). ^1H NMR ($CDCl_3$, 20 °C): δ 7.55 (m), 7.47−6.75 (45H) Ph; 1.99 (br, 4H, α-CH_2, tht); 1.14 (br, 4H, β-CH_2, tht). ^{13}C NMR ($CDCl_3$, −50 °C): δ 148−137 (C_6F_5); 135.3−126.3 (Ph), 31.4 (α-CH_2, tht); 29.5 (β-CH_2, tht). Signals due to C_α and C_β are not observed. ^{19}F NMR ($CDCl_3$, 20 °C): δ −117.4 (m, $^3J_{Pt-o-F}$ = 280, 2*o*-F); −118.0 (m, $^3J_{Pt-o-F}$ = 430, 2*o*-F); −161.8 (t, 1*p*-F); −163.5 (m, 2*m*-F); −165.3 (m, 1*p*-F + 2*m*-F).

Data for 3b. Anal. Calcd for $C_{73}F_{10}H_{55}P_3Pt_2S$: C, 53.55; H, 3.38; S, 1.96. Found: C, 53.78; H, 3.56; S, 1.27. MS (FAB+): *m/z* 1380 $[M - tht - C_6F_5 - 1H]^+$ 4.2%; 757 $[Pt(PPh_3)(PPh_2C_2Tol)]^+$ 10%; 719 $[Pt(PPh_3)_2]^+$ 100%. IR (cm^{-1}): $\nu(C{\equiv}C)$ 1714 (s, br); $\nu(C_6F_5)_{X-sens}$ 800 (m), 793 (m). ^1H NMR ($CDCl_3$, 20 °C): δ 7.53 (m, 6H); 7.23−6.65 (m, 38H) (CH, Ph, Tol); 2.12 (s, CH_3); 1.98 (br, 4H, α-CH_2, tht); 1.16 (br, 4H, β-CH_2, tht). ^{19}F NMR ($CDCl_3$, 20 °C): δ −117.4 (m, $^3J_{Pt-o-F}$ = 329, 2*o*-F); −118.0 (m, $^3J_{Pt-o-F}$ = 425, 2*o*-F); −161.9 (t, 1*p*-F); −163.6 (m, 2*m*-F); −165.3 (m, 1*p*-F + 2*m*-F).

Synthesis of *cis*-$[\{(C_6F_5)_2M(PPh_2C{\equiv}CR)(\mu\text{-}1\kappa P{:}2\eta^2\text{-}PPh_2C{\equiv}CR)\}Pt(PPh_3)_2]$ (M = Pt, R = Ph 4a, Tol 4b; M = Pd, R = Ph 5a, Tol 5b). Synthesis of 4a. A solution of *cis*-

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$[Pt(C_6F_5)_2(PPh_2C{\equiv}CPh)_2]$ (0.166 g, 0.151 mmol) in 10 mL of acetone was treated with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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 CH_3COCH_3.

Synthesis of 4b. A solution of *cis*-$[Pt(C_6F_5)_2(PPh_2C{\equiv}CTol)_2]$ (0.188 g, 0.167 mmol) in 30 mL of acetone was treated with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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*-$[Pd(C_6F_5)_2(PPh_2C{\equiv}CPh)_2]$ (0.167 g, 0.165 mmol) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (0.148 g, 0.198 mmol) (0.188 g, 66% yield). **5b**: *cis*-$[Pd(C_6F_5)_2(PPh_2C{\equiv}CTol)_2]$ (0.175 g, 0.168 mmol) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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 $Pt(PPh_3)_2$ fragment, yielding solids that contained higher amounts of the corresponding mononuclear starting derivatives.

Data for 4a·CH₃COCH₃. Anal. Calcd for $C_{88}F_{10}H_{60}P_4Pt_2.C_3H_6O$: C, 58.15; H, 3.54. Found: C, 58.19; H, 3.24. MS (FAB+): *m/z* peak molecular not observed; 718 $[Pt(PPh_3)_2 - 1H]^+$ 53%. IR (cm^{-1}): ν(C≡C) 2177 (s), 1756 (vs); $\nu(C_6F_5)_{X-sens}$ 792 (m), 778 (m); a medium band at 1716 cm^{-1} probably due to CH_3COCH_3 is also observed. ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.58−6.57 (m, 60H, Ph). ^{19}F NMR ($CDCl_3$): δ at −50 °C, −113.4 (s, br, 1*o*-F); −113.8 (s, br, $^3J_{Pt-o-F} \approx 360$, 1*o*-F); −116.5 (s, br, $^3J_{Pt-o-F} = 302$, 1*o*-F); −119.5 (s, br, 1*o*-F); −162.4 (t, 1*p*-F); −163.2 (m, 1*m*-F); −163.8 (m, 1*p*-F, 1*m*-F); −164.3 (m, 1*m*-F); −164.8 (m, 1*m*-F); at 20 °C, −115.4 (vbr, *o*-F); −163.3 (t, 1*p*-F); −164.3 (t, 1*p*-F); −164.6 (m, br, 4*m*-F).

Data for 4b. Anal. Calcd for $C_{90}F_{10}H_{64}P_4Pt_2$: 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 $[M + Ag - PPh_3]^+$ 18%; 1656 $[M + Ag - PPh_2C_2Tol]^+$ 36%. IR (cm^{-1}): ν(C≡C) 2177 (s), 1691 (m); $\nu(C_6F_5)_{X-sens}$ 791 (m), 778 (m). ^{1}H NMR (CD_3COCD_3, 20 °C): δ 7.61−6.72 (58H, Ph); 2.50, 2.20 (s, CH_3). ^{13}C NMR (CD_3COCD_3, −50 °C): δ 153.1 (d, $J_{P-C} = 57$ Hz, C$_\alpha$ or C$_B$, η^2-C≡CTol); 146.4−137.4 (C_6F_5); 140.4 (s, C^4, Tol); 135.6−126.5 (aromatics); 117.73, 117.70 (s, C^1, Tol); 106.2 (br, C$_\beta$, ≡C$_\beta$Tol); 78.5 ($J_{C-P} = 99.2$, C$_\alpha$, −PC$_\alpha$≡); 20.7, 20.5 (s, *C*H$_3$). ^{19}F NMR (CD_3COCD_3): δ at −50 °C, −112.4 (s, br, $^3J_{Pt-o-F} \approx 285$, 2*o*-F); −115.0 (s, br, $^3J_{Pt-o-F} \approx 310$, 1*o*-F); −117.5 (br, 1*o*-F); −162.8 (t, 1*p*-F); −163.3 (br, 1*m*-F); −163.8 (br, 1*m*-F); −164.2 (t, 1*p*-F); −164.7 (m, br, 2*m*-F); at 20 °C, −113.5, −114.8 (vbr, *o*-F); −163.9 (t, 1*p*-F); −164.9 (m, 1*p*-F, *m*-F).

Data for 5a. Anal. Calcd for $C_{88}F_{10}H_{60}P_4PdPt$: C, 61.00; H, 3.49. Found: C, 61.11; H, 3.59. MS (FAB+): *m/z* 1446 $[M - PPh_2C_2Ph]^+$ 13%; 719 $[Pt(PPh_3)_2]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2174 (s), 1753 (s), 1716 (sh); $\nu(C_6F_5)_{X-sens}$ 778 (m). ^{1}H NMR (CD_3COCD_3, 20 °C): 7.70−6.76 (60H, Ph). ^{19}F NMR (CD_3COCD_3): δ at −50 °C, −109.4 (m, 2*o*-F); −112.4 (s, 1*o*-F); −115.3 (s, br, 1*o*-F); −162.0 (t, 1*p*-F); −162.3 (m, 1*m*-F); −163.3 (m, 1*m*-F); −163.4 (t, 1*p*-F); −164.0 (m, 2*m*-F); at 20 °C, −110.9 (vbr); −112.4 (vbr) *o*-F; −163.0 (t, 1*p*-F); −163.4 (vbr, *m*-F); −164.0 (m, 1*p*-F); −164.3 (vbr, *m*-F).

Data for 5b. Anal. Calcd for $C_{90}F_{10}H_{64}P_4PdPt$: C, 61.39; H, 3.66. Found: C, 61.85; H, 3.92. MS (ES+ ionized with Ag$^+$): 1869 $[M + Ag]^+$ 3%; 1593 $[M - C_6F_5]^+$ 38%; 1292 $[M - C_6F_5 - PPh_2C_2Tol]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2176 (s), 1746 (sh), 1712 (m); $\nu(C_6F_5)_{X-sens}$ 776 (m, br). ^{1}H NMR (CD_3COCD_3): δ 7.57−6.74 (58H, Ph); 2.51, 2.22 (s, CH_3). ^{19}F NMR (CD_3COCD_3): δ at −50 °C, −109.7 (m, 2*o*-F); −112.1 (s, br, 1*o*-F); −114.8 (s, br, 1*o*-F); −162.0 (t, 1*p*-F); −162.45 (br, 1*m*-F); −163.15 (br, 1*m*-F); −163.35 (t, 1*p*-F); −164.0 (m, 2*m*-F); at 20 °C, −110.8 (s, br, 2*o*-F); −112.2 (vbr, 2*o*-F); −163.0 (t, 1*p*-F); −163.9 (br, 2*m*-F); −164.0 (t, 1*p*-F); −164.4 (m, 2*m*-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*-$[Pt(C{\equiv}CPh)_2(PPh_2C{\equiv}CPh)_2]$ (0.159 g, 0.164 mmol) in acetone (20 mL) was treated with $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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*-$[Pt(C{\equiv}CPh)_2(PPh_2C{\equiv}CTol)_2]$ (0.159 g, 0.160 mmol) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (0.143 g, 0.192 mmol) (0.205 g, 75% yield), or *cis*-$[Pt(C{\equiv}C\textit{t}Bu)_2(PPh_2C{\equiv}CTol)_2]$ (0.168 g, 0.175 mmol) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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*-$[Pt(C{\equiv}C\textit{t}Bu)_2(PPh_2C{\equiv}CPh)_2]$ (0.162 g, 0.174 mmol) and $[Pt(\eta^2\text{-}C_2H_4)(PPh_3)_2]$ (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 $C_{92}H_{70}P_4Pt_2$: C, 65.16; H, 4.12. Found: C, 64.76; H, 4.50. MS (FAB+): *m/z* 1689 $[M]^+$ 3%; 1427 $[M - PPh_3]^+$ 28%; 1325 $[M - PPh_3 - C_2Ph]^+$ 20%; 1224 $[M - PPh_3 - 2(C_2Ph)]^+$ 57%; 1123 $[M - PPh_3 - 3(C_2Ph)]^+$ 17%; 719 $[Pt(PPh_3)_2]^+$ 80%. IR (cm^{-1}): ν(C≡C) 2174 (m), 2121 (m), 1743 (sh), 1705 (m, br). ^{1}H NMR (CD_3COCD_3): δ 7.10 (m, 70H, Ph).

Data for 6b. Anal. Calcd for $C_{94}H_{74}P_4Pt_2$: C, 65.73; H, 4.34. Found: C, 66.08; H, 4.65. MS (FAB+): (%) 1215 $[M - 2(C_2Ph) - PPh_2C_2Tol + 1H]^+$ 24%; 719 $[Pt(PPh_3)_2]^+$ 67%. IR (cm^{-1}): ν(C≡C) 2173 (m), 2123 (m), 1760 (sh), 1715 (m). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.87−6.28 (68 H, Ph); 2.29, 2.07 (s, C*H*$_3$).

Data for 7a. Anal. Calcd for $C_{88}H_{78}P_4Pt_2$: C, 64.07; H, 4.77. Found: C, 63.98; H, 4.64. MS (FAB+): *m/z* 1647 $[M - 2H]^+$ 2%; 1386 $[M - PPh_3]^+$ 3%; 1306 $[M - PPh_3 - C_2\textit{t}Bu + 1H]^+$ 3.5%; 1224 $[M - PPh_3 - 2(C_2\textit{t}Bu)]^+$ 10%; 1123 $[M - PPh_3 - 2(C_2\textit{t}Bu) - C_2Ph]^+$ 10%; 1022 $[M - PPh_3 - 2(C_2\textit{t}Bu) - 2(C_2Ph)]^+$ 10%; 719 $[Pt(PPh_3)_2]^+$ 75%. IR (cm^{-1}): ν(C≡C) 2175 (m), 1748 (sh), 1705 (m, br). ^{1}H NMR ($CDCl_3$, 20 °C): δ 7.96, 7.49−6.34, 6.13 (br, 60 H, Ph); 1.16, 1.10 (s, 9H, *t*Bu). ^{13}C NMR (CD_3COCD_3): δ at −50 °C, 136.3−126.1, 123.6 (s), 120.98 (s) (phenyl resonances); 115.0 (dd, $^2J_{C-Ptrans}/^2J_{C-Pcis} \approx 240/33$, Pt−C$_\alpha$); 106.6 (d, $^2J_{C-P} = 11.9$, ≡C$_\beta$Ph); 87.0 (pst, $J_{C-P} \approx 18.4$, ≡C$_\beta$*t*Bu); 81.0 (dm, $^1J_{C-P} \approx 85$, −PC$_\alpha$≡); 32.2, 31.5 (s, −C(*C*H$_3$)$_3$); 29.0, 28.8 (s, −*C*Me$_3$).

Data for 7b. Anal. Calcd for $C_{90}H_{82}P_4Pt_2$: C, 64.43; H, 4.93. Found: C, 64.40; H, 4.57. MS (FAB+): *m/z* 1678 $[M + 1H]^+$ 5%; 1416 $[M - PPh_3 + 2H]^+$ 11%; 1335 $[M - PPh_3 - C_2\textit{t}Bu + 2H]^+$ 12%; 1254 $[M - PPh_3 - 2C_2\textit{t}Bu + 2H]^+$ 26%; 1138 $[M - PPh_3 - 2C_2\textit{t}Bu - C_2Tol + 1H]^+$ 19%; 719 $[Pt(PPh_3)_2]^+$ 100%. IR (cm^{-1}): ν(C≡C) 2174 (m), 1751 (sh), 1713 (m, br). ^{1}H NMR (CD_3COCD_3, 20 °C): δ 7.90−6.30 (m, 58H, Ph); 2.30, 2.26 (s, CH_3); 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 CH_2Cl_2 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 F^2. All non-

(27) Otwinowski, Z.; Minor, W. *Methods Enzymol.* **1996**, *276*A, 307.

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Table 4. Crystal Data and Structure Refinement for 2a·0.5C_6H_{14} and 3a·CH_2Cl_2

	2a·0.5C_6H_{14}	**3a**·CH_2Cl_2
empirical formula	$C_{48}F_{20}H_{23}PPt_2S \cdot C_3H_7$	$C_{72}F_{10}H_{53}P_3Pt_2S \cdot CH_2Cl_2$
fw	1475.96	1708.22
temperature (K)	293(2)	150(1)
cryst syst, space group	triclinic, $P\bar{1}$	triclinic, $P\bar{1}$
unit cell dimens, *a* (Å)	12.4059(2)	12.5657(1)
b (Å)	13.3668(2)	14.0831(2)
c (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)
Z, D_{calcd} (Mg/m^3)	2, 2.021	2, 1.772
abs coeff (mm^{-1})	5.953	4.629
F(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 F^2	1.261	1.371
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0309$, $wR_2 = 0.0707$	$R_1 = 0.0318$, $wR_2 = 0.0770$
R indices (all data)	$R_1 = 0.0460$, $wR_2 = 0.0748$	$R_1 = 0.0400$, $wR_2 = 0.0800$
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/Å^3 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 CH_2Cl_2. Some crystallographic details are shown in Table 4.

(28) Sheldrick, G. M. *SHELX-97, a program for the refinement of crystal structures*; University of Göttingen: Germany, 1997.

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Supporting Information Available: Further details of the structure determination of **2a**·0.5C_6H_{14} and **3a**·CH_2Cl_2, 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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