Facile Single or Double C−H Bond Activation on η^2-Platinum-Complexed Acetylenes by Interaction with [*cis*-PtR_2S_2] and [*cis*-$PtR_2(CO)S$] ($R = C_6F_5$, S = Thf)

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The μ-hydride μ-acetylide [*cis*,*cis*-$(PPh_3)_2Pt(\mu\text{-}H)(\mu\text{-}1\kappa C^{\alpha}{:}\eta^2\text{-}C{\equiv}CPh)Pt(C_6F_5)_2$] (**1b**) and the μ-vinylidene [*cis*,*cis*-$(CO)(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2$] (**2**) have been prepared by reaction of the η^2-phenylacetylene Pt(0) complex $[Pt(\eta^2\text{-}HC{\equiv}CPh)(PPh_3)_2]$ as the starting material with the disolvated [*cis*-PtR_2S_2] and the monosolvated [*cis*-$PtR_2(CO)S$] ($R = C_6F_5$, S = tetrahydrofuran) complexes, respectively. Extension of these reactions to the μ-$\eta^2{:}\eta^2$-bis(alkyne)diplatinum(0) precursor $[\{Pt(PPh_3)_2\}_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}(1,4\text{-}HC{\equiv}C)_2C_6H_4\}]$ and 2 equiv of the corresponding solvated complexes affords the bis(μ-hydride) μ-diethynylbenzene [{*cis*,*cis*-$(PPh_3)_2Pt(\mu\text{-}H)Pt(C_6F_5)_2\}_2\{\mu\text{-}1\kappa C^{\alpha}{:}4\kappa C^{\alpha'}{:}\eta^2{:}\eta^2\text{-}(1,4\text{-}C{\equiv}C)_2C_6H_4\}$] (**4b**) and the bis($\mu$-vinylidene) [{*cis*,*cis*-$(CO)(C_6F_5)_2PtPt(PPh_3)_2\}_2\{\mu_4\text{-}1\kappa C^{\alpha}{:}2\kappa C^{\alpha}{:}3\kappa C^{\alpha'}{:}4\kappa C^{\alpha'}\text{-}(1,4\text{-}C{=}CH)_2C_6H_4\}$] (**3**) tetranuclear derivatives. The preparation of the isomeric [{*trans*-$(PPh_3)(C_6F_5)Pt(\mu\text{-}H)Pt(C_6F_5)(PPh_3)\}_2\{\mu\text{-}1\kappa C^{\alpha}{:}4\kappa C^{\alpha}{:}\eta^2{:}\eta^2\text{-}(1,4\text{-}C{\equiv}C)_2C_6H_4\}$] (**4a**) was achieved by reaction of [{*trans*-$PtH(PPh_3)_2\}_2\{\mu\text{-}1\kappa C^{\alpha}{:}2\,\kappa C^{\alpha'}\text{-}(1,4\text{-}C{\equiv}C)_2C_6H_4\}$] with 2 equiv of [*cis*-PtR_2S_2]. Single-crystal X-ray structural determinations of **1b**, **2**, **3**, and **4b** are reported.

Introduction

The activation of C−H bonds in alkynes induced by transition metals is one of the most active fields of research in organometallic chemistry, due to its involvement in several fundamental steps in catalytic cycles, in carbon−carbon bond forming processes, and in materials science. A great deal of attention has been paid to the transformation in which hydride/acetylide and vinylidene groups are generated, due to their wide chemical potential, this being the subject of extensive reviews.[1−10] On the other hand, all of these carbon-rich species also provide valuable synthons for building higher organometallic architectures, such as polymers or π-conjugated polymetallic synthons, which are of interest due to their potential applications in the emerging field of molecular-scale electronic devices.[11−18] In this area, great progress has been made in the preparation of homo- and heterobimetallic complexes containing π-conjugated hydrocarbon bridges.[7,19−29] In contrast, only a few studies have reported clusters or

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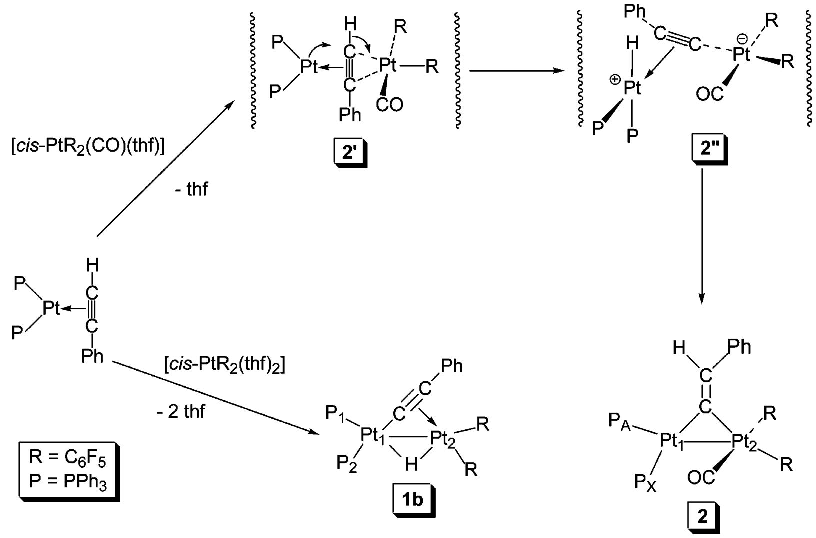
Scheme 1



polynuclear entities at the termini of the unsaturated backbone.[7,30−39]

Transition-metal complexes having a vacant coordinating site or bearing weakly coordinating ligands are known to have a very rich chemistry and have frequently been employed to promote C−H bond activation.[40−45] In the context of our investigations on the reactivity of the di- and monosolvated species [*cis*-PtR_2S_2][21,46] and [*cis*-$PtR_2(CO)S$][47−49] (R = C_6F_5, S = tetrahydrofuran), we described, some time ago, the preparation of the hydride species [{*trans*-$Pt(C_6F_5)(PPh_3)\}_2(\mu\text{-}H)(\mu\text{-}C{\equiv}CPh)$][50] (**1a**) and the unexpected vinylidene diplatinum complex [*cis,cis*-$(CO)(C_6F_5)_2Pt(\mu\text{-}C{=}CHPh)Pt(PPh_3)_2$][49] (**2**), by reaction of these solvated species with the hydride−acetylide mononuclear complex [*trans*-$PtH(C{\equiv}CPh)(PPh_3)_2$]. Pursuing our studies aimed at exploiting the potential reactivity of these solvated species, [*cis*-$PtR_2(CO)S$] and [*cis*-PtR_2S_2], and as a continuation of this work, we were interested to find out whether similar products could be obtained by starting with the isomeric low-valent [$Pt(\eta^2\text{-}HC{\equiv}CPh)(PPh_3)_2$] complex.

In this paper we report an entry to μ-hydride μ-acetylide and μ-vinylidene species, based on an unexpectedly easy C−H activation of η^2-alkynes coordinated to Pt(0), by interaction with [*cis*-$PtR_2(CO)S$] and [*cis*-PtR_2S_2].

Results and Discussion

As is shown in Scheme 1, the reaction of [$Pt(\eta^2\text{-}HC{\equiv}CPh)(PPh_3)_2$] with [*cis*-$PtR_2(CO)S$] causes a rapid rearrangement of the terminal acetylene to a bridging vinylidene group, giving the previously reported complex [*cis,cis*-$Pt(C_6F_5)_2(CO)(\mu\text{-}1\kappa C^{\alpha}{:}2\kappa C^{\alpha}\text{-}C{=}CHPh)Pt(PPh_3)_2$][49] (**2**) in quantitative yield. When the reaction is monitored by NMR spectroscopy at very low temperature (−95 °C) in CD_2Cl_2, it is observed that the formation of **2** is immediate (within seconds) and complete. The NMR spectrum of the solution shows the presence of a single isomer, the one seen by X-ray diffraction structure, indicating that the reaction is *stereoselective*. Although the isomerization of η^2-coordinated terminal alkynes to terminal vinylidene (M=C=CHR) is a well-known process,[1−9] similar rearrangements to yield bridging vinylidene complexes are rare. Previously reported methods to form dinuclear μ-vinylidene complexes include (a) direct reaction of mononuclear vinylidene compounds with unsaturated metal fragments,[51−53] (b) reaction of terminal alkynes or *gem*-dihaloolefins with a dimetallic complex,[54−62] (c) addition of an anionic alkynyl complex to unsaturated hydrocarbons of cationic complexes,[63] (d) addition of an electro-

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phile to a bridging acetylide ligand,[64,65] and, in relation to (d), (e) metal-mediated nucleophilic and electrophilic hydrocarbyl fragment migrations to the β-carbon of an alkynyl bridging group.[66,67] In the case of platinum, Lukehart et al. also reported the synthesis of several bridging vinylidene complexes by *regioselective* addition of the Pt−H bond of [*trans*-PtH(PEt$_3$)$_2$(acetone)]$^+$ across the C≡C triple bond of terminal alkynyl ligands.[68,69] In this context, the reaction pathway leading to complex **2** is a different and easy entry to these types of complexes. Previous theoretical studies concerning the transformation of an acetylene to a vinylidene ligand at a dimetallic site show that the direct and concerted intraligand 1,2-hydrogen shift (η^2-alkyne to μ-vinylidene) is energetically unlike and suggests that this isomerization process seems more plausible via an acetylide−hydride intermediate.[70,71] In this respect, the direct transfer of a metal−hydrogen bond to the β-carbon of an adjacent alkynyl ligand in reactions leading to μ-vinylidene complexes has been recently reported.[66,67] In accordance with this, although we have no evidence of the intermediacy of any hydride−acetylide complex in our system, we suggest that the formation of **2** probably takes place via the dinuclear zwitterionic derivative **2″**, followed by a fast hydride transfer to the β-carbon. We assume that the interaction of the carbonyl solvate with the precursor generates the initial, and probably asymmetric, η^2-bridging acetylene adduct **2′**, which rapidly rearranges via migration of the low-valent fragment to the C−H bond. Interestingly, we have also observed that complex **2** is easily formed even in the solid state only by a prolonged stirring (~12 h) of a solid mixture of [Pt(η^2-HC≡CPh)(PPh$_3$)$_2$] and [*cis*-PtR$_2$(CO)S] at room temperature. The initially white mixture turned orange, and the final solid was identified as **2** by means of IR spectroscopy. Monitoring the reaction by IR reveals only the presence of a new intermediate ν(CO) stretch at 2095 cm^{-1} (2121 cm^{-1} for the precursor and 2083 cm^{-1} for **2**) in the course of the reaction, which could be tentatively attributed to the initial adduct **2′**. This finding is interesting, since several surface-catalyzed reactions involving alkynes have been proposed to occur via vinylidene intermediates.[72−74] A solid-state metal−hydride−alkynyl to metal−vinylidene rearrangement has been also previously found with the 16-electron fragment [(PP$_3$)Co]$^+$ (PP$_3$ = P(Ph$_2$CH$_2$PPh$_2$)$_3$].[75]

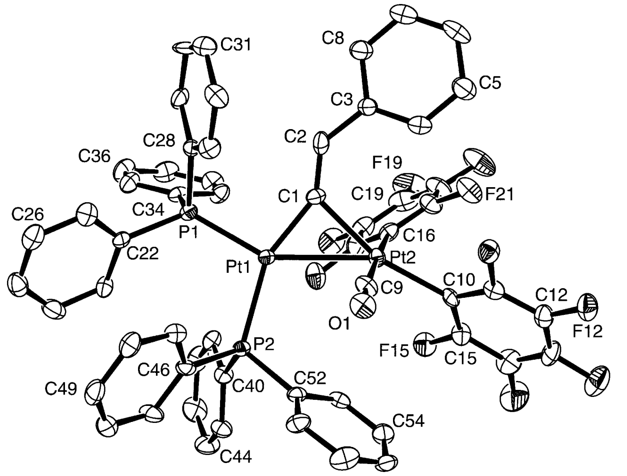

Figure 1. Molecular structure of [*cis,cis*-(OC)(C$_6$F$_5$)$_2$Pt(μ-1κC^α: 2κC^α-C=CHPh)Pt(PPh$_3$)$_2$]·CHCl$_3$·C$_6$H$_{14}$ (**2**·CHCl$_3$·C$_6$H$_{14}$). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for [*cis,cis*-(OC)(C$_6$F$_5$)$_2$Pt(μ-1κC^α: 2κC^α-C=CHPh)Pt(PPh$_3$)$_2$]·CHCl$_3$·C$_6$H$_{14}$ (2·CHCl$_3$·C$_6$H$_{14}$)

Pt(1)−P(1)	2.2415(18)	Pt(1)−P(2)	2.3362(18)	Pt(1)−C(1)	1.934(7)
Pt(1)−Pt(2)	2.7311(4)	Pt(2)−C(1)	2.144(7)	Pt(2)−C(9)	1.924(8)
Pt(2)−C(10)	2.087(7)	Pt(2)−C(16)	2.062(7)	C(1)−C(2)	1.326(10)
C(2)−C(3)	1.459(10)	C(9)−O(1)	1.116(8)		

P(2)−Pt(1)−P(1)	104.81(6)	P(1)−Pt(1)−Pt(2)	149.86(5)
P(2)−Pt(1)−Pt(2)	105.19(4)	C(1)−Pt(1)−P(1)	98.8(2)
C(10)−Pt(2)−Pt(1)	151.75(19)	C(9)−Pt(2)−Pt(1)	79.5(2)
C(10)−Pt(2)−C(1)	163.5(3)	C(16)−Pt(2)−Pt(1)	101.58(19)
C(2)−C(1)−Pt(1)	146.3(6)	Pt(1)−C(1)−Pt(2)	83.9(3)
C(2)−C(1)−Pt(2)	129.2(5)	C(1)−C(2)−C(3)	133.6(7)

The structure of **2** (Figure 1 and Table 1) unambiguously establishes the presence of the bridging vinylidene group, previously confirmed by NMR spectroscopy and reactivity.[49] The vinylidene ligand is asymmetrically located between the metals, with the Pt(2)−C(1) bond (2.144(7) Å) being slightly longer than Pt(1)−C(1) (1.934(7) Å), and its structural parameters compare with those reported for other bimetallic phenylethenylidene-bridged systems.[59,66,68,76,77] The short Pt−Pt distance (2.7311(4) Å), indicative of a metal−metal bond, is close to the values found in related diplatinum complexes.[68,77] If the bridging vinylidene unit is considered as a dianionic ligand, to achieve the necessary 16-electron count at Pt(1), the metal−metal interaction would have to be a dative Pt(1)←Pt(2) bond and the complex would be formally zwitterionic Pt(1)$^+$←Pt(2)$^-$. It should be

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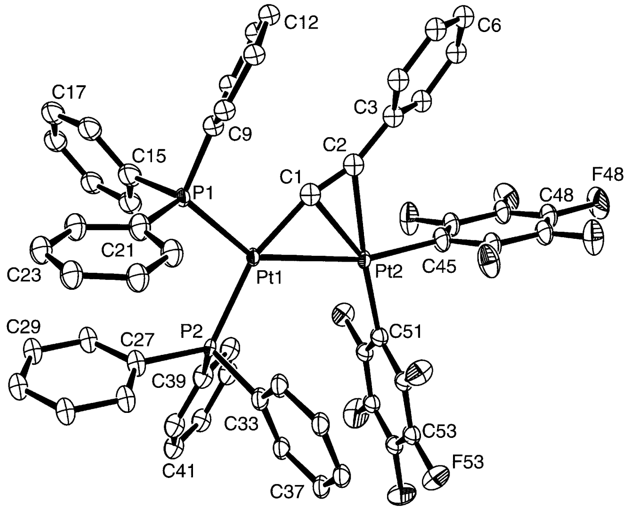

Figure 2. ORTEP view of [*cis,cis*-$(PPh_3)_2Pt(\mu\text{-}H)(\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2\text{-}C{\equiv}CPh)Pt(C_6F_5)_2]\cdot 2CH_2Cl_2$ (**1b**$\cdot 2CH_2Cl_2$). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [*cis,cis*-$(PPh_3)_2Pt(\mu\text{-}H)(\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2\text{-}C{\equiv}CPh)Pt(C_6F_5)_2]\cdot 2CH_2Cl_2$ (1b$\cdot 2CH_2Cl_2$)

Pt(1)–C(1)	1.968(11)	Pt(1)–P(1)	2.288(3)	Pt(1)–P(2)	2.309(3)
Pt(1)–Pt(2)	2.8366(6)	Pt(2)–C(45)	2.033(11)	Pt(2)–C(51)	2.009(10)
Pt(2)–C(1)	2.172(11)	Pt(2)–C(2)	2.326(11)	C(1)–C(2)	1.233(14)

C(1)–Pt(1)–P(1)	94.7(3)	P(1)–Pt(1)–P(2)	102.84(9)
C(1)–Pt(1)–Pt(2)	49.8(3)	P(1)–Pt(1)–Pt(2)	144.56(7)
P(2)–Pt(1)–Pt(2)	112.58(7)	C(45)–Pt(2)–C(51)	85.8(4)
C(45)–Pt(2)–C(1)	120.8(4)	C(45)–Pt(2)–C(2)	89.28(4)
C(45)–Pt(2)–Pt(1)	164.5(3)	C(51)–Pt(2)–Pt(1)	109.7(3)
C(2)–C(1)–Pt(1)	167.0(10)	C(1)–C(2)–C(3)	160.7(12)

noted that the Pt(1) coordination plane forms a dihedral angle of 66.13(14)° with the Pt(2) plane, and this orientation makes the P(1,2)–Pt(1)–Pt(2) angles very different (149.86(5)° for P(1) vs 105.19(4)° for P(2)).

Similarly, treatment of $[Pt(\eta^2\text{-}HC{\equiv}CPh)(PPh_3)_2]$ with the bis(solvated) complex [*cis*-PtR_2S_2] in CH_2Cl_2 immediately results in C–H activation to form, in this case, the μ-hydride μ-acetylide diplatinum asymmetric derivative [*gem*-$(PPh_3)_2Pt(\mu\text{-}H)(\mu\text{-}1\kappa C^{\alpha}\text{:}\eta^2\text{-}C{\equiv}CPh)Pt(C_6F_5)_2$] (**1b**) in good yield. It should be mentioned that an analogous C–H activation was also reported by Stang and co-workers under mild conditions.[78] Complex **1b**, which is stable in solution at room temperature, or even at reflux of acetone for 17 h, isomerizes to the trans isomer **1a** (although with considerable decomposition) by prolonged heating in toluene (2 h). The structure of **1b** (Figure 2, Table 2) reveals that, although the distribution of the PPh_3 and C_6F_5 ligands in this complex is different from that found in the transoidal complex **1a**,[50] the central $Pt_2\text{–}C_{\alpha}\text{–}C_{\beta}\text{-}P_2$ core (roughly planar) is similar in both of the isomers, with the alkynyl ligand σ-bonded to Pt(1) (Pt(1)–C(1) = 1.968(11) Å) and unsymmetrically π-bonded to Pt(2) (Pt(2)–C_{α},C_{β} = 2.172(11), 2.326(11) Å).

The presence of the bridging hydride ligand (not located directly from the Fourier map but confirmed by ^1H NMR spectroscopy) is reflected by the remarkable dissimilarity in the angles around the Pt centers. Thus, the angles P(1)–Pt(1)–Pt(2) (144.56(7)°) and C(45)–Pt(2)–Pt(1) (164.5(3)°) are substantially larger than the corresponding angles P(2)–Pt(1)–Pt(2) (112.58(7)°) and C(51)–Pt(2)–Pt(1) (109.7(3)°). The Pt–Pt distance (2.8366(6) Å) compares to that found in **1a**[50] (2.8159(19) Å) and in other 30e diplatinum hydride species containing mixed μ-H–μ-X bridging systems[79,80] and is in accordance with theoretical calculations which suggest the existence of a through-ring platinum–platinum bonding interaction.[81] The hydride resonance in the ^1H NMR spectrum of **1b** is seen at δ −7.19 as a doublet of doublets ($^2J_{H-P(trans)} = 94.8$ Hz; $^2J_{H-P(cis)} = 13.0$ Hz) with two different sets of ^{195}Pt satellites ($^1J_{Pt(1)-H} = 632.1$, $^1J_{Pt(2)-H} = 450.5$ Hz), in accordance with its bridging nature. The most significant spectroscopic difference between **1a** and **1b** is seen in their $^{31}P\{^1H\}$ NMR spectra. Thus, in agreement with the gem formulation of **1b**, its $^{31}P\{^1H\}$ NMR spectrum displays two sharp doublet resonances ($^2J_{P-P} = 22$ Hz) with the corresponding platinum satellites, contrasting with the singlets pattern seen for **1a**, because the three-bond phosphorus–phosphorus coupling $^3J_{P-P}$ is not resolved.

The C–H bond activation processes can be extended to the binuclear diyne complex $[\{Pt(PPh_3)_2\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}(1,4\text{-}HC{\equiv}C)_2C_6H_4\}]$[82] (Scheme 2). Thus, the reaction of $[\{Pt(PPh_3)_2\}_2\{\mu\text{-}\eta^2\text{:}\eta^2\text{-}(1,4\text{-}HC{\equiv}C)_2C_6H_4\}]$ with 2 equiv of [*cis*-$PtR_2(CO)S$] (Scheme 2, path i) occurs in a similar way, immediately giving (3 min) a dark red solution from which the bis(μ-vinylidene)tetraplatinum compound **3** is isolated as a deep orange solid in high yield (80%). It should be noted that although in recent years an impressive number of organometallic dimers and oligomers, in which a conjugated carbon framework is spanned by a transition-metal center, have been reported,[11–14,16–20,22–25] including bis(vinylidene) compounds,[1,3,4,8,22,26–29] as far as we are aware, this complex **3** is the first species in which an unsaturated delocalized bridge connects two μ-vinylidene termini. Alternatively, this complex can also be obtained, although in very low yield, by treatment of the isomeric dinuclear dihydride derivative [{*trans*-$PtH(PPh_3)_2\}_2\{\mu\text{-}1\kappa C^{\alpha}\text{:}2\ \kappa C^{\alpha'}\text{-}(1,4\text{-}C{\equiv}C)_2C_6H_4\}]$[82] with 2 equiv of [*cis*-$PtR_2(CO)S$] (Scheme 2, path ii). Although the molecular peak was not observed by mass spectrometry, the tetranuclear nature of complex **3** was confirmed by X-ray data. Different dark red-purple crystals of **3**, obtained from $CHCl_3$ or EtOH/hexane, were subjected to several X-ray diffraction studies; although, systematically, the crystals were not of sufficient quality, the connectivity shown in Scheme 2 was unequivocally confirmed, indicating again, as seen by ^1H NMR spectroscopy, that the overall process is *stereoselective*. Thus, its ^1H NMR spectrum shows one vinylidene =CH proton resonance at 5.59 ppm, which appears as a doublet (27.5 Hz) of doublets (7.6 Hz) due to phosphorus coupling (the larger coupling ($^4J_{H-P(X)}$) is attributed to coupling to phosphorus P(X), cis to Pt–Pt, on the basis of decoupling experiments). The $^{31}P\{^1H\}$ spectrum exhibits the expected AX system pattern

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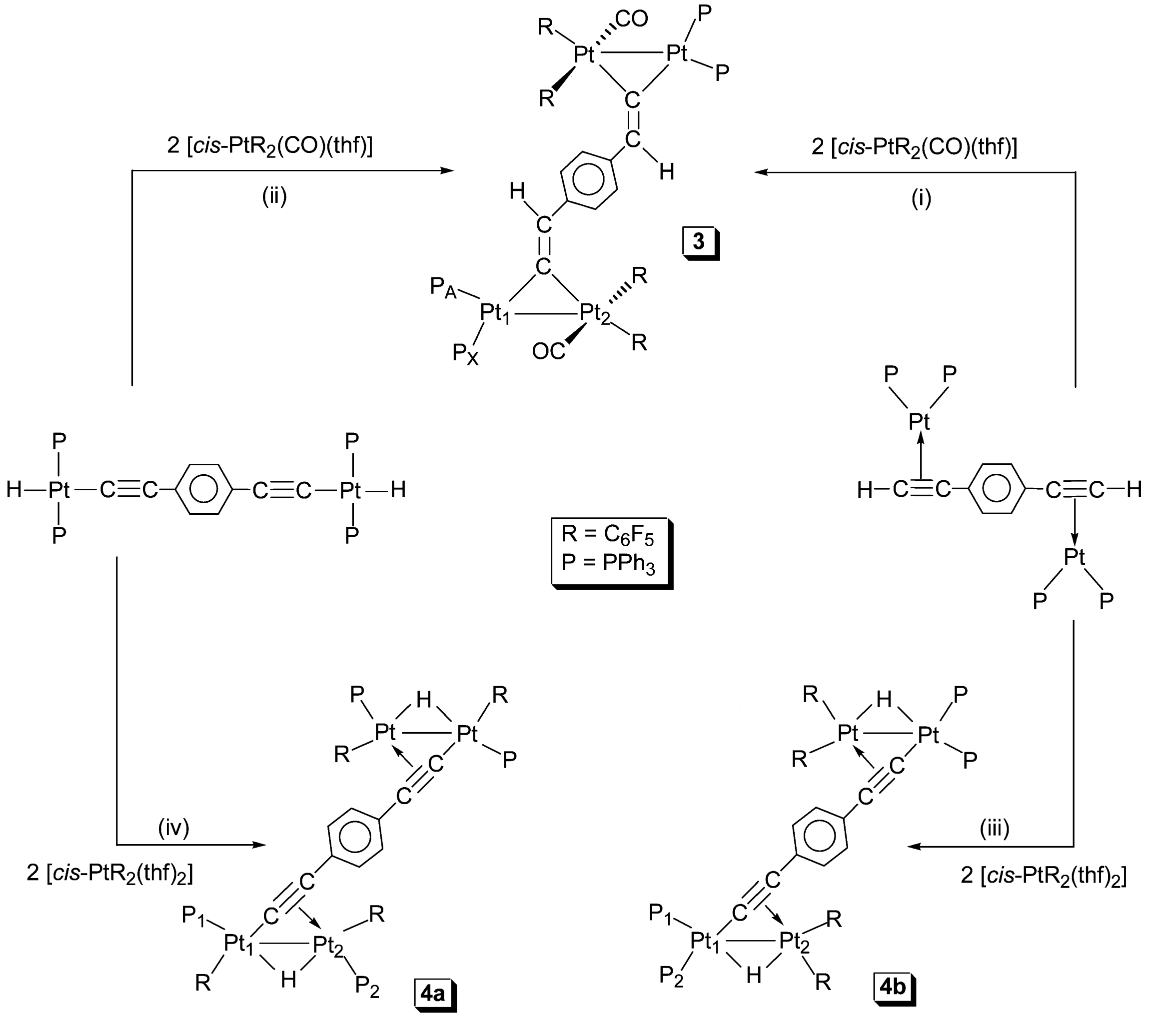
Scheme 2



In CH_2Cl_2, at room temperature: i) 3 min; ii) 24 h; iii) 5 min; iv) 10 min

with platinum satellites, the most deshielded resonance (δ 36.1, doublet, $^2J_{\mathrm{P(A)-P(X)}} = 14.7$ Hz), which shows larger one- and two-bond ^{195}Pt to phosphorus coupling (5538 and 366 Hz), being attributed to the PPh_3 ligand nearly trans to the Pt(2), P(A). The ^{19}F NMR spectrum confirms the presence of two nonequivalent C_6F_5 ligands with different energetic barriers for rotation around the corresponding Pt−C(ipso) bonds (see Experimental Section).

Similarly (see Scheme 2, path iii), when the dinuclear low-valent complex $[\{Pt(PPh_3)_2\}_2\{\mu\text{-}\eta^2{:}\eta^2\text{-}(1,4\text{-}HC{\equiv}C)_2C_6H_4\}]$ reacts with 2 equiv of the disolvated species [*cis*-PtR_2S_2] at room temperature, a double C−H activation takes place, yielding the gem,gem bis(μ-hydride) μ_4-$\sigma{:}\sigma{:}\eta^2{:}\eta^2$-$C_2C_6H_4C_2$ diynyl tetraplatinum complex **4b**, which was isolated as an orange solid in high yield (92%) and characterized by analytical and spectroscopic techniques. Diagnostic for **4b** are the expected upfield hydride resonance (δ −7.19 m, $^2J_{\mathrm{P(trans)-H}} = 92.2$ Hz, $^2J_{\mathrm{P(cis)-H}} = 10.8$ Hz) with two sets of platinum satellites ($^1J_{\mathrm{Pt(1)-H}} \approx 620$ Hz and $^1J_{\mathrm{Pt(2)-H}} \approx 450$ Hz) and also the two close doublet phosphorus resonances ($^2J_{\mathrm{P-P}} = 22.5$ Hz) at 12.6 and 11.1 ppm, with platinum satellite patterns, which are similar to those seen for **1b**.

Interestingly, the corresponding trans,trans bis(μ-hydride) μ_4-$\sigma{:}\sigma{:}\eta^2{:}\eta^2$-$C_2C_6H_4C_2$ tetraplatinum isomer **4a** can be generated by starting from the isomeric dinuclear Pt(II) derivative $[\{trans\text{-}PtH(PPh_3)_2\}_2\{\mu\text{-}1\kappa C^{\alpha}{:}2\kappa C^{\alpha'}\text{-}(1,4\text{-}C{\equiv}C)_2C_6H_4\}]$. As is shown in Scheme 2 (path iv), the reaction of $[\{trans\text{-}PtH(PPh_3)_2\}_2\{\mu\text{-}1\kappa C^{\alpha}{:}2\kappa C^{\alpha'}\text{-}(1,4\text{-}C{\equiv}C)_2C_6H_4\}]$ with 2 equiv of [*cis*-PtR_2S_2] in CH_2Cl_2 affords, after 10 min of stirring at room temperature, an orange solution, from which the tetranuclear bis(μ-hydride) μ_4-$\sigma{:}\sigma{:}\eta^2{:}\eta^2$-$C_2C_6H_4C_2$ isomer **4a** is isolated as an orange solid. Despite the fact that the overall process requires a complex rearrangement of ligands between the platinum centers, the yield is very high (95%). The crystal structure of **4a** (Figure 3, Table 3) confirms the presence of the central unsaturated *p*-diethynylbenzene backbone, which is attached to two identical diplatinum units via the alkynyl groups, σ-bonded to Pt(1) (1.972(7) Å) and asymmetrically η^2-bonded to Pt(2) (Pt(2)−C_α = 2.223(7) Å, Pt(2)−C_β = 2.350(7) Å). The structural details of each of the two essentially planar Pt_2−C_α−C_β−P_2 dimetallic cores, and the Pt(1)−Pt(2) bond distance (2.8260(4) Å), are similar to those observed for the dinuclear isomers **1a** and **1b**. The central ring forms an angle of 83.8(4)° with the planar dimetallic core. The bridging hydride ligands are not located in this study,

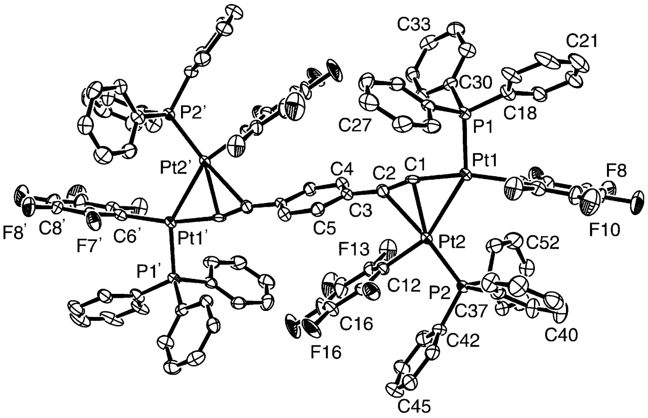


Figure 3. Molecular structure of [{*trans*-$(PPh_3)(C_6F_5)$Pt-(μ-H)Pt$(C_6F_5)(PPh_3)$}$_2${μ-1κC^{α}:4$\kappa C^{\alpha'}$:η^2:η^2-(1,4-C≡C)$_2$-C_6H_4}]·$4CH_2Cl_2$ (**4a**·$4CH_2Cl_2$). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for [{*trans*-$(PPh_3)(C_6F_5)$Pt(μ-H)-Pt$(C_6F_5)(PPh_3)$}$_2${μ-1κC^{α}:4$\kappa C^{\alpha'}$:η^2:η^2-(1,4-C≡C)$_2C_6H_4$}]·$4CH_2Cl_2$ (4a·$4CH_2Cl_2$)

Pt(1)–C(1)	1.972(7)	Pt(1)–C(6)	2.050(7)	Pt(1)–P(1)	2.2566(19)
Pt(1)–Pt(2)	2.8260(4)	Pt(2)–C(12)	2.023(7)	Pt(2)–P(2)	2.2384(19)
Pt(2)–C(1)	2.223(7)	Pt(2)–C(2)	2.350(7)	C(1)–C(2)	1.236(9)

C(1)–Pt(1)–P(1)	96.6(2)	C(6)–Pt(1)–P(1)	96.6(2)
C(1)–Pt(1)–Pt(2)	51.53(19)	C(6)–Pt(1)–Pt(2)	115.21(19)
P(1)–Pt(1)–Pt(2)	148.01(5)	C(12)–Pt(2)–C(1)	113.2(3)
C(12)–Pt(2)–C(2)	82.2(3)	C(12)–Pt(2)–P(2)	90.0(2)
C(12)–Pt(2)–Pt(1)	157.1(2)	P(2)–Pt(2)–Pt(1)	112.91(5)
C(2)–C(1)–Pt(1)	164.2(6)	C(1)–C(2)–C(3)	165.0(8)

but their presence is, again, reflected in the dissimilarity found in the angles around the Pt centers (see Table 3) and confirmed by the proton spectrum, which exhibits a doublet of doublets resonance (δ −7.54; $^2J_{P(trans)-H}$ = 73.7 Hz; $^2J_{P(cis)-H}$ = 14.0 Hz) at a field slightly higher than that seen in **4b** (δ −7.19). The signal is flanked by the corresponding two pairs of ^{195}Pt satellites, the magnitudes of the $^1J_{Pt-H}$ coupling constants ($^1J_{Pt(1)-H}$ ≈ 560 Hz, $^1J_{Pt(2)-H}$ ≈ 515 Hz) being more similar than those found in **4b** (620 and 450 Hz). The ^{19}F,^{13}C{^{1}H}, and ^{31}P{^{1}H} NMR spectra clearly confirm the presence of nonequivalent C_6F_5 and PPh_3 ligands. The most deshielded phosphorus resonance, which exhibits larger short-range ($^1J_{Pt(1)-P(1)}$ = 3826 Hz) and long-range coupling constants ($^2J_{Pt(2)-P(1)}$ = 101 Hz), is assigned to the nucleus P(1), in accordance with the observed open angle P(1)–Pt(1)–Pt(2) of 148.01(5)°, and the low-frequency signal centered at 11.1 ppm ($^1J_{Pt(2)-P(2)}$ = 3587 Hz) is, therefore, assigned to the phosphyne ligand cis to the hydride ligand.

Conclusions

In this paper we report an easy entry to a polymetallic mixed-bridge μ-hydride μ-acetylide system or a μ-vinylidene bridging entity. Rapid single or double activation was observed in mono- or bis(alkyne) complexes, [Pt(η^2-HC≡CPh)$(PPh_3)_2$] and [{Pt$(PPh_3)_2$}$_2${μ-η^2:η^2-(1,4-HC≡C)$_2C_6H_4$}], by interaction with 1 or 2 equiv of the disolvated species [*cis*-PtR_2S_2] (R = C_6F_5, S = thf) to afford the thermodynamically favored dinuclear or tetranuclear isomeric gem μ-hydride μ-acetylide derivatives of Pt(II), **1b** and **4b**. Similar reactions with the platinum carbonyl derivative [*cis*-PtR_2(CO)S], which has only one vacant coordination site, also evolve with single and double C–H activation, yielding, in this case, the diplatinum phenylethenylidene bridging complex [*cis,cis*-(CO)$(C_6F_5)_2$Pt(μ-C=CHPh)Pt$(PPh_3)_2$] (**2**) or the unprecedented bis(μ-vinylidene)tetraplatinum derivative [{*cis, cis*-(CO)$(C_6F_5)_2$PtPt$(PPh_3)_2$}$_2${μ_4-1κC^{α}:2κC^{α}:3$\kappa C^{\alpha'}$:4$\kappa C^{\alpha'}$-(1,4-C=CH)$_2C_6H_4$}] (**3**).

The isomeric tetraplatinum bis(μ-hydride) μ_4-σ:σ:η^2:η^2-$C_2C_6H_4C_2$ complex **4a**, which has a relative trans disposition of the two C_6F_5 and two PPh_3 ligands, is accessible by a process of ligand rearrangement starting from [{*trans*-PtH$(PPh_3)_2$}$_2${μ-1κC^{α}:2 $\kappa C^{\alpha'}$-(1,4-C≡C)$_2C_6H_4$}] and 2 equiv of [*cis*-PtR_2S_2].

It should be noted that **1a** and **4a** and the corresponding **1b** and **4b** are isomers, resulting from the same disolvate precursor [*cis*-PtR_2S_2] and the corresponding isomeric hydride/acetylide of Pt(II) or η^2-complexed acetylene of Pt(0), respectively.

Experimental Section

Experimental techniques, C, H, and N analyses, and IR and NMR spectroscopy were performed as described elsewhere,[83] the temperature of the routine NMR being 293 K. Mass spectra were recorded on a HP-5989B (ES) or a VG Autospec double-focusing (FAB) mass spectrometer.

1,4-Bis(ethynyl)benzene[84] and the complexes [Pt(η^2-HC≡CPh)$(PPh_3)_2$],[85] [{Pt$(PPh_3)_2$}$_2${μ-η^2:η^2-(1,4-HC≡C)$_2C_6H_4$}],[82] [{*trans*-PtH$(PPh_3)_2$}$_2${μ-1κC^{α}:2$\kappa C^{\alpha'}$-(1,4-C≡C)$_2C_6H_4$}],[82] [*cis*-Pt$(C_6F_5)_2$(thf)$_2$],[86] and [*cis*-Pt$(C_6F_5)_2$(CO)(thf)][87] were prepared by literature methods.

Synthesis of [*cis,cis*-$(PPh_3)_2$Pt(μ-H)(μ-1κC$^{\alpha}$:η^2-C≡CPh)-Pt$(C_6F_5)_2$] (1b). A 0.16 g portion (0.24 mmol) of [*cis*-Pt$(C_6F_5)_2$-(thf)$_2$] was added to a CH_2Cl_2 solution (10 mL) of [Pt(η^2-HC≡CPh)$(PPh_3)_2$] (0.20 g, 0.24 mmol), and the mixture was stirred at room temperature for 5 min. The resulting orange solution was evaporated to dryness, and the residue was treated with cold EtOH, yielding **1b** as a beige solid. Yield: 0.20 g (61%). Anal. Calcd for $C_{56}F_{10}H_{36}P_2Pt_2$: C, 49.79; H, 2.69. The complex has a tendency to retain variable amounts of CH_2Cl_2 of crystallization. The best analysis found (C, 48.39; H, 2.81) fits well for $C_{56}F_{10}H_{36}P_2Pt_2\cdot{}^1/_2CH_2Cl_2$: C, 48.70; H, 2.68. MS ES(−): *m/z* 1088 [M − PPh_3]$^-$ (100%). IR (cm^{-1}): ν(C≡C) 2018 (w); $\nu(C_6F_5)_{X-sens}$ 804 (m), 796 (m). ^{1}H NMR ($CDCl_3$, δ (*J*, Hz)): 7.39 (m), 7.22 (m), 7.16 (m) (30 H, Ph, PPh_3); 7.05 (m), 6.93 (m), 6.69 (m) (5 H, Ph, C≡CPh); −7.19 (dd, $^2J_{P(trans)-H}$ = 94.8, $^2J_{P(cis)-H}$ = 13.0, $^1J_{Pt(1)-H}$ = 632.1, $^1J_{Pt(2)-H}$ = 450.5, Pt–μ-H–Pt). ^{19}F NMR ($CDCl_3$, δ): −116.88 (dm, $^3J_{Pt-F}$ ≈ 405, 2*o*-F); −118.78 (d, $^3J_{Pt-F}$ ≈ 455, 2*o*-F); −164.18 (t, 1*p*-F); −164.43 (t, 1*p*-F); −165.29 (m, 2*m*-F); −165.56 (m, 2*m*-F). ^{31}P NMR ($CDCl_3$, δ (*J*, Hz)): 13.2 (d, $^1J_{Pt(1)-P(1)}$ ≈ 3360, $^2J_{Pt(2)-P(1)}$ ≈ 55, $^2J_{P-P}$ ≈ 22, P(1) trans to hydride); 11.5 (d, $^1J_{Pt(1)-P(2)}$ ≈ 2700, $^2J_{Pt(2)-P(2)}$ ≈ 47, $^2J_{P-P}$ ≈ 22, P2 trans to σ-C≡C). The complex is not soluble enough for ^{13}C NMR.

Synthesis of [*cis,cis*-(OC)$(C_6F_5)_2$Pt(μ-1κC^{α}:2κC^{α}-C=CHPh)Pt$(PPh_3)_2$] (2). Method A. A colorless solution of 0.26 g (0.31 mmol) of [Pt(η^2-HC≡CC_6H_5)$(PPh_3)_2$] in 10 mL of CH_2Cl_2 was treated with an equimolecular amount of [*cis*-Pt$(C_6F_5)_2$-(CO)(THF)] (0.20 g, 0.31 mmol), resulting in a immediate color change to deep orange. The mixture was stirred for 3 min and

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Table 4. Crystallographic Data for 1b·$2CH_2Cl_2$, 2·$CHCl_3$·C_6H_{14}, and 4a·$4CH_2Cl_2$

	1b·$2CH_2Cl_2$	**2**·$CHCl_3$·C_6H_{14}	**4a**·$4CH_2Cl_2$
empirical formula	$C_{58}H_{39}Cl_4F_{10}P_2Pt_2$	$C_{64}H_{51}Cl_3F_{10}OP_2Pt_2$	$C_{110}H_{72}Cl_8F_{20}P_4Pt_4$
formula wt	1519.81	1584.52	2961.52
temp (K)	173(1)	123(1)	123(1)
cryst syst	triclinic	triclinic	triclinic
space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
a (Å)	13.5460(3)	13.4490(2)	11.2170(2)
b (Å)	14.0020(2)	14.7380(2)	12.9170(2)
c (Å)	16.1080(4)	17.1680(3)	18.3920(4)
α (deg)	74.1420(10)	68.6360(10)	85.0610(10)
β (deg)	72.5370(10)	80.4930(10)	85.29990(10)
γ (deg)	69.9710(10)	69.8830(10)	89.6960(10)
V (Å^3)	2688.15(11)	2972.63(8)	2645.99(8)
Z	2	2	1
D_{calcd} (Mg/m^3)	1.878	1.770	1.859
abs coeff (mm^{-1})	5.531	4.963	5.616
F(000)	1462	1540	1420
cryst size (mm)	0.25 × 0.15 × 0.10	0.25 × 0.25 × 0.10	0.35 × 0.25 × 0.15
θ range for data collecn (deg)	4.10−25.03	1.27−25.68	1.11−25.68
no. of data/restrains/params	9436/0/403	11 283/8/770	10 027/5/668
goodness of fit on F^2	0.961	1.074	1.075
final *R* indices ($I > 2\sigma(I)$)	R1 = 0.0557, wR2 = 0.1126	R1 = 0.0387, wR2 = 0.1027	R1 = 0.0430, wR2 = 0.1106
R indices (all data)	R1 = 0.1009, wR2 = 0.1273	R1 = 0.0598, wR2 = 0.1269	R1 = 0.0594, wR2 = 0.1247
largest diff peak and hole (e Å^{-3})	2.446 and −1.949	3.231 and −3.064	2.470 and −3.009

evaporated to dryness. Addition of cold *i*-PrOH (~5 mL) to the solid residue yielded **2** as an orange solid. Yield: 89%.

Method B. The synthesis of complex **2** starting from [*trans*-PtH(C≡CPh)$(PPh_3)_2$], as well as its analytical and spectroscopic data (but $^{13}C\{^1H\}$ NMR), has been previously reported by us.[49] ^{13}C NMR ($CDCl_3$, *δ* (*J*, Hz)): 174.0 (s, CO); 148~144 (m, C_6F_5); 137.9 (s, tentatively assigned to =CH); 134.8 (d, *o*-C, $^2J_{C-P} \approx 10$, PPh_3); 134.3 (d, *o*-C, $^2J_{C-P} \approx 12.7$, PPh_3); 132.4 (dm, *i*-C, $^1J_{C-P} = 68$, PPh_3); 131.1 (s, *p*-C, PPh_3); 130.5 (s, *p*-C, PPh_3); 129.2, (s, *o*-C, C_6H_5); 128.3 (m, overlapping of two doublets, *m*-C, PPh_3); 128.1 (s, *m*-C, C_6H_5); 125.8 (s, *p*-C, C_6H_5).

Synthesis of [{*cis,cis*-(CO)$(C_6F_5)_2$PtPt$(PPh_3)_2$}$_2${μ_4-1κC^{α}:2κC^{α}:3$\kappa C^{\alpha'}$:4$\kappa C^{\alpha'}$-(1,4-C=CH)$_2C_6H_4$}] (3). Method A. Complex [{Pt$(PPh_3)_2$}$_2${μ-η^2:η^2-(1,4-HC≡C)$_2C_6H_4$}] (0.12 g, 0.08 mmol) was treated with 0.10 g (0.16 mmol) of [*cis*-Pt$(C_6F_5)_2$(CO)(THF)] in CH_2Cl_2 (10 mL). The resulting red solution was stirred for 3 min and then concentrated under reduced pressure to small volume (1 mL). By addition of *n*-hexane (~15 mL) and cooling for ~12 h (−25 °C), complex **3** precipitates as a red solid. Yield: 80%.

Method B. A solution of [{*trans*-PtH$(PPh_3)_2$}$_2${μ-1κC^{α}:2$\kappa C^{\alpha'}$-(1,4-C≡C)$_2C_6H_4$}] (0.10 g, 0.064 mmol) in CH_2Cl_2 (~15 mL) was treated with 0.08 g (0.128 mmol) of [*cis*-Pt$(C_6F_5)_2$(CO)(THF)], and the mixture was stirred at room temperature for 24 h. Then, the solvent was removed under reduced pressure, and the residue was treated with hexane. The solid was filtered and recrystallized from CH_2Cl_2/hexane. Yield: 20%.

Data for 3. Anal. Calcd for $C_{108}F_{20}H_{66}O_2P_4Pt$: C, 48.40; H, 2.48. Found: C, 47.99; H, 2.16. MS ES(+): *m/z* 1303 [$Pt_2(C_6F_5)_2$(CO)(C=CH)$(PPh_3)_2$ + H]$^+$, 8%; 721 [Pt$(PPh_3)_2$ + 2H]$^+$, 95%. IR (cm^{-1}): ν(CO) 2088 (s); $\nu(C_6F_5)_{X-sens}$ 796 (m), 778 (m). ^1H NMR ($CDCl_3$, *δ* (*J*, Hz)): 7.29 (m), 7.14 (m) (64 H, PPh_3 and C_6H_4); 5.59 (dd, 2H, $^4J_{P-H} = 27.5$ and 7.6; =CH). ^{19}F NMR ($CDCl_3$, *δ*): ≈−109 (br, 2*o*-F); −113.7 (dm, $^3J_{Pt-F} \approx 266$, 4*o*-F, and a broad resonance in the base due to 2*o*-F); the two broad resonances are assigned to *o*-F of C_6F_5 rings trans to Pt(1); −159.8 (t, 2*p*-F); −162.3 (t, 2*p*-F); −163.6 (m, 4*m*-F); −164.7 (v br), −165.9 (v br) (4*m*-F). ^{31}P NMR ($CDCl_3$, *δ* (*J*, Hz)): 36.1 (d, $^1J_{Pt(1)-P(A)} = 5538$, $^2J_{Pt(2)-P(A)} \approx 366$, $^2J_{P-P} = 14.7$, P(A)); 30.8 (d, $^1J_{Pt(1)-P(X)} = 2588$, $^2J_{P-P} = 14.7$, P(X)). ^{13}C NMR ($CDCl_3$, *δ*): 150~140.3 (m, C_6F_5); 134.7 (m, *o*-C, PPh_3); 134.3 (m, *o*-C, PPh_3); 132.4 (dm, *i*-C, PPh_3); 131.1 (m, *p*-C, PPh_3); 130.4 (m, *p*-C, PPh_3); 129.3, (s, C_6H_4); 128.4 (m, *m*-C, PPh_3).

Synthesis of [{*trans*-$(PPh_3)(C_6F_5)$Pt(μ-H)Pt$(C_6F_5)(PPh_3)$}$_2${μ-1κC^{α}:4$\kappa C^{\alpha'}$:η^2:η^2-(1,4-C≡C)$_2C_6H_4$}] (4a). A 0.17 g portion (0.26 mmol) of [*cis*-Pt$(C_6F_5)_2(thf)_2$] was added to a CH_2Cl_2 solution (20 mL) of [{*trans*-PtH$(PPh_3)_2$}$_2${μ-1κC^{α}:2$\kappa C^{\alpha'}$-(1,4-C≡C)$_2C_6H_4$}] (0.20 g, 0.13 mmol), and the mixture was stirred at room temperature for 10 min. The resulting orange solution was evaporated to dryness, and the residue was treated with hexane, yielding **4a** as an orange solid. Yield: 95%. Anal. Calcd for $C_{106}F_{20}H_{66}P_4Pt_4$: C, 48.52; H, 2.54. Found: C, 48.74; H, 1.96. MS FAB(+): *m/z* 2626 [M + 3H]$^+$, 1%; 1056 [$Pt_2H(C_6F_5)_2(PPh_3)_2$]$^+$, 8%; 905 [$Pt_4H(C_{10}H_4)$]$^+$, 15%; 719 [Pt$(PPh_3)_2$]$^+$, 96%; 604 [$Pt_2(PPh)_2$ − 2H]$^+$, 54%; 528 [Pt$(C_6F_5)_2$ − H]$^+$, 31%; 455 [Pt(PPh_3) − 2H]$^+$, 71%; 378 [Pt(PPh_2) − 2H]$^+$, 100%. IR (cm^{-1}): ν(C≡C) 2019 (w); $\nu(C_6F_5)_{X-sens}$ 796 (m br). ^1H NMR ($CDCl_3$, *δ* (*J*, Hz)): 7.54, 7.25 (m, 60 H, Ph, PPh_3); 6.59 (s, 4H, C_6H_4); −7.54 (dd, $^2J_{P(1)-H} = 73.7$, $^2J_{P(2)-H} = 14.0$, $^1J_{Pt(1)-H} \approx 560$, $^1J_{Pt(2)-H} \approx 515$, 2 Pt−$\mu$-H−Pt). ^{19}F NMR ($CDCl_3$, *δ*): −116.19 (dm, $^3J_{Pt-F} \approx 290$, 4*o*-F); −118.49 (d, $^3J_{Pt-F} \approx 350$, 4*o*-F); −162.57 (m, 2*p*-F); −163.89 (m, 4*m*-F); −164.63 (t, 2*p*-F); −165.30 (m, 4*m*-F). ^{31}P NMR ($CDCl_3$, *δ* (*J*, Hz)): 28.8 (s, $^1J_{Pt(1)-P(1)} = 3826$, $^2J_{Pt(2)-P(1)} = 101$, P(1) trans to hydride); 11.1 (s, $^1J_{Pt(2)-P(2)} = 3587$, P(2) trans to C≡C). ^{13}C NMR ($CDCl_3$, *δ* (*J*, Hz)): 148−134 (C_6F_5); 134.1 (d, $^2J_{C-P} = 11.8$, *o*-C, Ph, PPh_3); 133.8 (d, $^2J_{C-P} = 11.1$, *o*-C, Ph, PPh_3); 130.9 (d, $^4J_{C-P} = 2.4$, *p*-C, Ph, PPh_3); 130.8 (d, $^4J_{C-P} = 2.2$, *p*-C, Ph, PPh_3); 130.7 (d, $^1J_{C-P} = 60.8$, *i*-C, Ph, PPh_3); 130.2 (s br, C^2), 129.6 (d, $^1J_{C-P} = 65.0$, $^2J_{Pt-C} = 36.9$, *ipso*-C, Ph, PPh_3); 128.1 (d, $^3J_{C-P} = 7.6$, *m*-C, Ph, PPh_3); 127.9 (d, $^3J_{C-P} = 7.6$, *m*-C, Ph, PPh_3); 124.9 (d, $^4J_{C-P} = 3.6$, $^3J_{Pt-C} = 17.6$, C^1); 108.6 (d, $^2J_{C-P} = 21.1$, C_{α}).

Synthesis of [{*cis,cis*-$(PPh_3)_2$Pt(μ-H)Pt$(C_6F_5)_2$}$_2${μ-1κC^{α}:4$\kappa C^{\alpha'}$:η^2:η^2-(1,4-C≡C)$_2C_6H_4$}] (4b). A 0.15 g portion (0.22 mmol) of [*cis*-Pt$(C_6F_5)_2(thf)_2$] was added to a CH_2Cl_2 solution (10 mL) of [{Pt$(PPh_3)_2$}$_2${μ-η^2:η^2-(1,4-HC≡C)$_2C_6H_4$}] (0.18 g, 0.11 mmol), and the mixture was stirred at room temperature for 5 min. The resulting orange solution was evaporated to dryness, and the residue was treated with cold EtOH, giving **4b** as an orange solid. Yield: 92%. Anal. Calcd for $C_{106}F_{20}H_{66}P_4Pt_4$: C, 48.52; H, 2.54. Found: C, 48.79; H, 2.68. MS ES(+): *m/z* 885 [Pt$(C_6F_5)(PPh_3)_2$] − H]$^+$, 12%; 719 [Pt$(PPh_3)_2$]$^+$, 100%. IR (cm^{-1}): ν(C≡C) 2018 (w); $\nu(C_6F_5)_{X-sens}$ 804 (m), 794 (m). ^1H NMR ($CDCl_3$, *δ* (*J*, Hz)): 7.35, 7.13 (m, 60H, Ph, PPh_3); 6.15 (s, 4H, C_6H_4); −7.19 (dd, $^2J_{P(trans)-H} = 92.2$, $^2J_{P(cis)-H} = 10.8$, $^1J_{Pt(1)-H} \approx 620$, $^1J_{Pt(2)-H} = 450$, 2 Pt−μ-H−Pt). ^{19}F NMR ($CDCl_3$, *δ* (*J*, Hz)): −116.74 (d, $^3J_{Pt-F} \approx 408$, 4*o*-F); −118.46 (dm, $^3J_{Pt-F} \approx 460$, 4*o*-F); −163.10 (t, 2*p*-F); −164.33 (t, 2*p*-F); −164.91 (m, 4*m*-F); −165.17 (m, 4*m*-F). ^{31}P NMR ($CDCl_3$, *δ* (*J*, Hz)): 12.6 (d, $^1J_{Pt(1)-P(1)} = 3372$, $^2J_{Pt(2)-P(1)} = 55$, $^2J_{P-P} = 22.5$, P(1) trans to hydride); 11.1 (d, $^1J_{Pt(1)-P(2)} \approx 2690$, $^2J_{Pt(2)-P(2)} = 40$, $^2J_{P-P} =$

22.5, P(2) trans to C≡C). The complex is not soluble enough for ^{13}C NMR.

X-ray Crystallography. Table 4 reports details of the structural analyses for all complexes. Pale yellow (**1b**), deep red (**2**), or pale orange (**4a**) crystals were obtained by slow diffusion of *n*-hexane into a dichloromethane (**1b** and **4a**; room temperature) or chloroform (**2**; −30 °C) solution of each compound. For complex **2** one molecule of $CHCl_3$ and one of *n*-hexane and for complexes **1b** and **4a** two molecules of CH_2Cl_2 were found in the asymmetric unit. X-ray intensity data were collected with a Nonius κCCD area-detector diffractometer, using graphite-monochromated Mo Kα radiation. Images were processed using the DENZO and SCALEPACK suite of programs,[88] and the absorption correction was performed using XABS2[89] (**2**·$CHCl_3$·C_6H_{14}) or SORTAV[90] (**1b**·$2CH_2Cl_2$, **4a**·$4CH_2Cl_2$). All the structures were solved by Patterson and Fourier methods using the DIRDIF92 program[91] and refined by full-matrix least squares on F^2 with SHELXL-97.[92] All non-hydrogen atoms were assigned anisotropic displacement parameters, and all hydrogen atoms were constrained to idealized geometries fixing isotropic displacement parameters of 1.2 times the U_{iso} value of their attached carbon for the phenyl and vinylidene hydrogens and 1.5 for the methyl groups. For complex **2** one molecule of $CHCl_3$ and one of *n*-hexane and for complex **4a** one molecule of CH_2Cl_2 showed positional disorder and were modelized adequately. For complexes **1b**, **2**, and **4a** some residual peaks greater than 1 e Å^{-3} were observed in the vicinity of the heavy atoms or the disorder solvents, but these had no chemical significance.

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Supporting Information Available: Further details of the structure determinations of **1b**, **2**·$CHCl_3$·C_6H_{14}, and **4a**·$4CH_2Cl_2$, including tables giving atomic coordinates, bond distances and angles, and thermal parameters; crystallographic data are also available as CIF files. This material is available free of charge via the Internet at http://pubs.acs.org.

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