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Reactions of (σ-Alkynyl)platinum Complexes with [Pd(η^3-C_3H_5)Cl]$_2$. Synthesis of Bis(η^2-alkyne)(η^3-allyl)palladium(II) Complexes. Crystal and Molecular Structure of [*cis*-$(PPh_3)_2Pt(\mu$-η^1:η^2-C≡C^{t}Bu)$_2$Pd(η^3-C_3H_5)](ClO_4)

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The σ-bis and tetraalkynyl anions [*cis*-Pt(C_6F_5)$_2$(C≡CR)$_2$]$^{2-}$ and [Pt(C≡CR)$_4$]$^{2-}$ (R = Ph, ^{t}Bu, SiMe$_3$) have been shown to be useful reagents for the formation of bis(μ-alkynyl) complexes via halide displacement reactions. They thus react with {[Pd(η^3-C_3H_5)Cl]$_2$} in a 2:1 molar ratio to form anionic heterobinuclear zwitterionic Q[*cis*-(C_6F_5)$_2$Pt(μ-η^1:η^2-C≡CR)$_2$Pd(η^3-C_3H_5)] (Q = PMePh$_3$, R = Ph; Q = NBu$_4$, R = ^{t}Bu, SiMe$_3$ **1a**−**c**) and (NBu$_4$)[(RC≡C)$_2$Pt(μ-η^1:η^2-C≡CR)$_2$Pd(η^3-C_3H_5)] (R = Ph, ^{t}Bu, SiMe$_3$ **2a**−**c**) complexes. The corresponding trinuclear 1:2 neutral adducts {[Pt(C≡CR)$_4$][Pd(η^3-C_3H_5)]$_2$} (R = Ph, ^{t}Bu, SiMe$_3$ **3a**−**c**) were formed by the addition of 1 equiv of the tetraalkynyl anions to {[Pd(η^3-C_3H_5)Cl]$_2$}. Binuclear derivative analogue [(PPh$_3$)$_2$Pt(μ-η^1:η^2-C≡CR)Pd(η^3-C_3H_5)](ClO$_4$) (R = Ph, ^{t}Bu **4a**,**b**) were produced by the reaction of {[Pd(η^3-C_3H_5)Cl]$_2$} with neutral [*cis*-Pt(PPh$_3$)$_2$(C≡CR)$_2$] (1:2 ratio) in the presence of NaClO$_4$ (excess). The heterobimetallic anionic **1c** (R = SiMe$_3$) and cationic **4b** (R = ^{t}Bu) complexes were characterized by X-ray diffraction. In both, the two bridging alkynyl ligands remained σ bonded to the platinum center and η^2 coordinated to the palladium one.

Introduction

Allylpalladium complexes play a prominent role as potential precursors or intermediates in several palladium-catalyzed organic syntheses.[1] As a result, a large number of allylpalladium compounds have been synthesized, and their reactions with organic substrates have been thoroughly explored.[2] In marked contrast to this, the reactivity of allylpalladium complexes toward other metal derivatives has attracted somewhat less attention.[2a,3] This fact is surprising in view of the established value of bi- and polymetallic species as polyfunctional catalysts.[4]

The bridge-assisted synthetic method has proved to be one of the most flexible routes to heterobimetallic complexes with bridging ligands of all sorts.[4b,c] We[5] and

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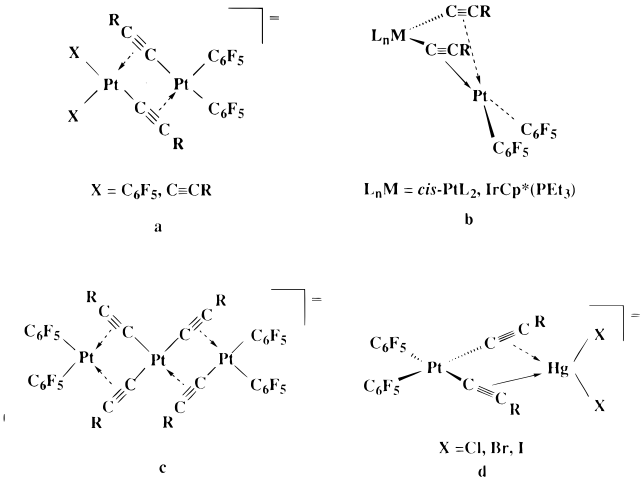
Scheme 1



others[6] have prepared homo and hetero dinuclear doubly alkynyl bridged compounds by reacting σ-bis(alkynyl) complexes with a second complex which has either open coordination sites or other ligands which can be easily displaced by the alkynyl group. More recently bimetallic doubly alkynyl bridged complexes have also been prepared by the cleavage of alkynes and butadiynes induced by metallocene complexes.[7]

We have previously described the preparation of mixed $[cis\text{-Pt}(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ [8] and homoleptic $[\text{Pt}(C{\equiv}CR)_4]^{2-}$ [9] σ-alkynyl anionic species and have shown that they act as monoalkynylating agents in the reaction with the neutral $[cis\text{-M}(C_6F_5)_2(\text{THF})_2]$ (M = Pd, Pt) yielding binuclear complexes[5a,c] (Scheme 1a) in which the metal centers are asymmetric bridged by two alkynyl ligands. Later we were able to show that $[cis\text{-Pt}(C_6F_5)_2(C{\equiv}CPh)_2]^{2-}$ reacts with the solvent complex $[\text{IrCp*}(\text{PEt}_3)(\text{Me}_2\text{CO})_2](\text{ClO}_4)_2$ via a double alkynylation process to yield $[\text{Cp*}(\text{PEt}_3)\text{Ir}(\mu\text{-}\eta^1{:}\eta^2\text{-C}{\equiv}\text{CPh})_2\text{Pt}(C_6F_5)_2]$[5g] in which the alkynyl groups are σ-bonded to the iridium center and π-bonded to the platinum one (Scheme 1b). Although the driving force for these alkynyl transfer processes is not clear, we assume that one of the reasons could be the formation of the less polar end complexes.[5a] Thus, in the reaction of $[cis\text{-M}(C_6F_5)_2(\text{THF})_2]$ and neutral $[cis\text{-PtL}_2(C{\equiv}CR)_2]$ alkynylation was not observed but complexation gave symmetrical doubly alkynyl bridged complexes (Scheme 1b)[5a] and, interestingly, the reaction of the "$cis\text{-Pt}(C_6F_5)_2$" fragment with the binuclear dianionic $[(\text{RC}{\equiv}\text{C})_2\text{Pt}(\mu\text{-}\eta^1{:}\eta^2\text{-}(\text{C}{\equiv}\text{CR})\text{Pt}(C_6F_5)_2\text{-}(\mu\text{-}\eta^1{:}\eta^2\text{-C}{\equiv}\text{CR})]^{2-}$ derivatives gave no alkynylation product but rather π-complexation yielding trimetallic compounds with the simultaneous presence of both symmetrical and unsymmetrical doubly alkynyl bridging systems (Scheme 1c).[5c] In addition the reactions of $[cis\text{-Pt}(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ and $[\text{Pt}(C{\equiv}CR)_4]^{2-}$ with mercury(II) halides gave no alkynylation product but did give 1:1 (Scheme 1d) or 1:2 π-complexes.[5d] It was considered that the anionic nature of these σ bis- and tetraalkynyl complexes should also render them sufficiently nucleophilic to displace halides from other metal centers to form heterometallic alkynyl-bridged complexes. This was indeed the case, and we describe herein the synthesis and properties of new heterometallic (Pt-Pd) bis(μ-alkynyl) complexes that are derived from $[cis\text{-PtX}_2(C{\equiv}CR)_2]^{n-}$ [X = C_6F_5 or C≡CR, $n = 2$; X = PPh_3, $n = 0$] σ-alkynyl derivatives and the (η^3-allyl) palladium chloride dimer. To the best of our knowledge these are the first examples in which the cationic Pd-$(\eta^3\text{-allyl})^+$ unit is attached to η^2-alkyne functions. A preliminary account of this work has been published.[10]

Results and Discussion

The results of reactions starting from $\{[\text{Pd}(\eta^3\text{-}C_3H_5)\text{Cl}]_2\}$ are summarized in Scheme 2. As reported previously[10] homo- and heterobimetallic anionic symmetrical doubly acetylide bridged complexes $(\text{NBu}_4)[cis\text{-}(C_6F_5)_2\text{Pt}(\mu\text{-}\eta^1{:}\eta^2\text{-C}{\equiv}\text{CSiMe}_3)_2\text{M}(C_3H_5)]$ (M = Pt, Pd **1c**) can be easily prepared by reacting $(\text{NBu}_4)_2[cis\text{-Pt}(C_6F_5)_2(\text{C}{\equiv}\text{C-SiMe}_3)_2]$ with $\{[\text{M}(C_3H_5)\text{Cl}]_n\}$ (M = Pt, $n = 4$; M = Pd, $n = 2$) in acetone and in a 4:1 molar ratio for M = Pt or 2:1 for M = Pd. The structure of **1c** was established by X-ray crystallography and revealed that the resulting anion is highly polar, in fact, it is formally zwitterionic, formed by a dianionic "$\{cis\text{-Pt}(C_6F_5)_2(\text{C}{\equiv}\text{CSiMe}_3)_2\}^{2-}$" fragment which acts as a chelating diyne ligand to the cationic "$\{\text{Pd}(\eta^3\text{-}C_3H_5)\}^{+}$" unit. A view of the anion and details of the crystallographic study are available in ref 10 and will not be repeated here. The formation of complexes (**1a**−**c**) is noteworthy since a less-polar anion (with one alkynyl σ-bonded to each metal) could have been expected from an alkynylation process. We found that the analogous heterobinuclear phenyl and *tert*-butyl acetylide species **1a**,**b** can be similarly obtained starting from the corresponding $[cis\text{-Pt}(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ (R = Ph or ^{t}Bu) complexes. However, the same reactions with $\{[\text{Pt}(C_3H_5)\text{Cl}]_4\}$ did not allow the preparation of any stable homobimetallic compounds. Data characterizing the new **1a**,**b** complexes, as well as low temperature NMR data for complex **1c**, are given in the Experimental Section. Thus, the presence of bridging alkynyl ligands can be easily inferred from the observation, in their IR spectra, of a $\nu(\text{C}{\equiv}\text{C})$ absorption (2016 cm^{-1} **1a**; 2015 cm^{-1} **1b**) at lower frequencies than those observed for the mononuclear $[cis\text{-Pt}(C_6F_5)_2(C{\equiv}CR)_2]^{2-}$ [R = Ph 2095, 2082 cm^{-1}; R = ^{t}Bu 2085, 2090(sh) cm^{-1}]

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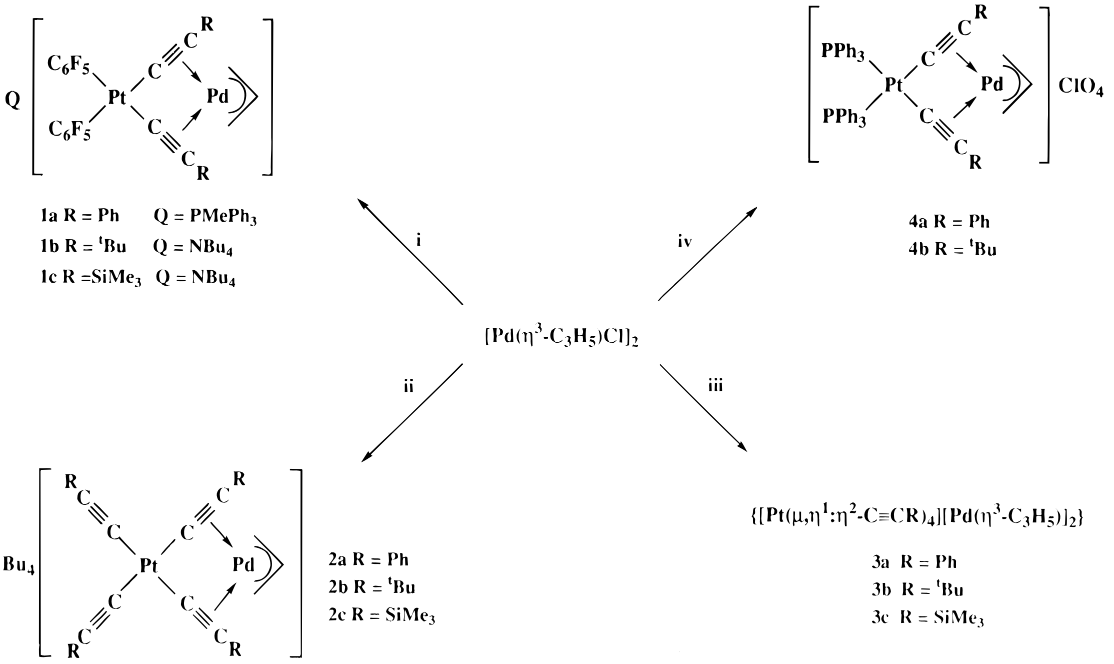
Scheme 2[a]



[a] (i) + 2Q$_2$[*cis*-Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$]; (ii) + 2(NBu$_4$)$_2$[Pt(C≡CR)$_4$]; (iii) + (NBu$_4$)$_2$[Pt(C≡CR)$_4$]; (iv) + 2[*cis*-Pt(C≡CR)$_2$(PPh$_3$)$_2$] + NaClO$_4$ (excess).

precursors and in the range expected for C≡C triple bond side-on coordinated to a transition metal.[5−7] In the ^{1}H NMR spectrum of **1a** the methylene hydrogen atoms of the allyl group give rise to two doublet resonances (δ 3.4 and 4.0) while the methine hydrogen appears as a multiplet at δ 5.5. The two doublet signals are assigned[11] to the anti- and syn-protons (H_{anti} and H_{syn}), respectively, since the doublet separation of the former $J_{anti} = 12.2$ Hz (due to coupling with the central proton) is larger than that of the latter [$J_{syn} = 6.7$ Hz].[11] In the *tert*-butyl acetylide complex **1b**, although the resonances due to syn-protons [δ 4.43 (d); $J_{syn} = 6.5$ Hz] and methine hydrogen [δ 5.3(m)] of the allyl group are clearly visible, the resonance due to the anti-protons overlaps (δ 3.06) with one of the signals which is characteristic of the NBu_4^+ cation. The *tert*-butyl groups of the alkynyl ligands give rise to a singlet resonance at δ 1.15, as expected. We noted that no evidence of allyl group rotamers was detected by recording the ^{1}H NMR spectra of complexes **1a-c** at low temperature (−50 °C, see Experimental Section). Likewise, the ^{13}C{^{1}H} NMR spectra of **1b** and **1c** at low temperature (−50 °C) display two allyl signals (CH and CH$_2$) due to the presence of only one η^3-C$_3$H$_5$ ligand. It has been previously observed[6a,h] that π-complexation of terminal alkynyl ligands to a second metal center results in a downfield shift of the C_α and C_β ^{13}C NMR resonances. It is noteworthy that in the dimeric complexes **1b** and **1c** such deshielding signals are not observed. The alkyne carbon resonances C_α and C_β are observed at δ 80.5 ($^1J_{Pt-C} = 820.2$ Hz) and at δ 106.4 ($^2J_{Pt-C} = 281.7$ Hz) for **1b** and at δ 117.6 and at δ 94.2 for **1c** which are, in fact, slightly shifted to highfield compared to data for the parent complexes (NBu$_4$)$_2$[Pt(C$_6$F$_5$)$_2$(C≡CR)$_2$] [R = ^{t}Bu, δ = 98.2 (C_α, $^1J_{Pt-C} = 1048.2$ Hz) and δ = 110.13 (C_β, $2J_{Pt-C} = 293.4$ Hz); R = SiMe$_3$, δ = 140.7 (C_α, $^1J_{Pt-C} = 997$ Hz) and δ = 104.0 (C_β, $2J_{Pt-C} = 270.7$ Hz)].

The ^{19}F NMR spectra of complexes **1a** and **1b** (and also **1c**)[10] exhibit, at room temperature, a set of three signals only which are those of the *o*-, *p*-, and *m*-fluorine atoms, showing that as expected both C$_6$F$_5$ groups are equivalent. The bent shape of the Pt(acetylide)$_2$Pd core found for complex **1c** should, however, give rise to inequivalence of the *o*-fluorine atoms (and the *m*-fluorine atoms as well) on each C$_6$F$_5$ ligand. The presence of only one type of *o*-F and *m*-F, which appear as sharp resonances, indicates an effective equivalence of these atoms and suggests that the complexes are not rigid in solution. The simplicity of the spectra (at room temperature) can be tentatively explained either by assuming a rapid rotation of C$_6$F$_5$ rings around the Pt-*ipso*-C(C$_6$F$_5$) bonds[12] or a rapid intramolecular exchange of the [Pd(allyl)]$^+$ unit below and above the platinum coordination plane. At −50 °C, the ^{19}F NMR spectra of complexes **1** reveal the same sharp pattern as at room temperature, indicating that the dynamic process is very rapid even at low temperature.

The easy bridge splitting and displacement of the chloride ligands of the (η^3-allyl)palladium dimer allows the synthesis of anionic (Pt−Pd, **2a−c**) or neutral (Pd−Pt−Pd, **3a−c**) tetraalkynyl−allyl compounds by reaction with the corresponding anions [Pt(C≡CR)$_4$]$^{2-}$ at a 1:2 (Scheme 2, ii) or 1:1 (Scheme 2, iii) molar ratio, respectively. The reaction between (NBu$_4$)$_2$[Pt(C≡CR)$_4$]·2H$_2$O (R = ^{t}Bu or SiMe$_3$) and {[Pd(η^3-C$_3$H$_5$)Cl]$_2$} (2:1 molar ratio) in acetone affords deep yellow solutions (slightly dark for R = SiMe$_3$) from which the binuclear anionic derivatives (NBu$_4$)[(C≡CR)$_2$Pt(μ-C≡CR)$_2$Pd(η^3-C$_3$H$_5$)] (R = ^{t}Bu **2b** or SiMe$_3$ **2c**) can be isolated as yellow solids (**2b** 34%, **2c** 85%). However, the analogous

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[11] The assignments of allyl protons resonances in all complexes was made following the usual criteria: (a) Grassi, M.; Meille, S. V.; Musco, A.; Potellini, R.; Sironi, A. *J. Chem. Soc., Dalton Trans.* **1989**, 615 and refs therein. (b) see also ref 2a.

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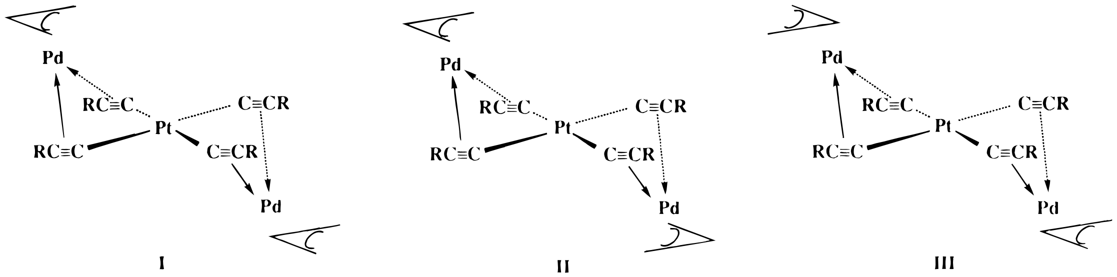
Scheme 3



reactions of $(NBu_4)_2[Pt(C{\equiv}CPh)_4]$ with $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (2:1 molar ratio) lead to a mixture of the analogous anionic derivative **2a** and the corresponding trinuclear neutral compound **3a**. Complex $\{Pt(C{\equiv}CPh)_4[Pd(\eta^3\text{-}C_3H_5)]_2\}$ **3a** (yield 9%) precipitates as a yellow solid during the reaction time, and the evaporation of the filtrate to dryness and subsequent treatment with cold EtOH affords the binuclear anionic complex **2a** although in a very low yield (11%). Complex **3a** precipitates in very high yield (78%) by the addition of 1 equiv of $[Pt(C{\equiv}CPh)]^{2-}$ to $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ in acetone (Scheme 2, iii). Similarly, treatment of $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ with 1 equiv of $[Pt(C{\equiv}CR)_4]^{2-}$ (R = ^{t}Bu, $SiMe_3$) in acetone affords the trinuclear complexes **3b** and **3c**, respectively, in moderate yield (**3b** 60%, **3c** 40%). Complexes **2** and **3** are moderately stable in the solid state, but their solutions (acetone, CH_2Cl_2 or $CHCl_3$) darken in 1 or 2 h. For complexes **2**, no X-ray quality crystals have been obtained, but analytical, conductivity measurements, and spectroscopic data are consistent with structures shown in Scheme 2. Thus, the conductivities of complexes **2** in acetone solutions are those expected for 1:1 electrolytes.[13] The most remarkable feature in the IR spectra of compounds of type **2** is the presence of one (2026 cm^{-1} **2a**; 2020 cm^{-1} **2b**) or two bands (1953 and 1938 cm^{-1} **2c**) which are considerably shifted to lower wavenumbers compared to those of the σ-alkynyl precursor (2075 cm^{-1} R = Ph, 2081cm^{-1} R = ^{t}Bu, 2015 cm^{-1} R = $SiMe_3$) which can be attributed to the $Pt(\mu\text{-}C{\equiv}CR)_2\text{-}Pd$ moiety. Furthermore, they also show additional ν-(C≡C) absorptions at higher frequencies [2098(vs, sh) cm^{-1} **2a**; 2095(s) cm^{-1} **2b**; 2042(vs) and 2027(vs) cm^{-1} **2c**] which is in line with the presence of terminal alkynyl groups.[14] Similar IR patterns have been observed in CH_2Cl_2 solution suggesting that the η^2-alkynyl−Pd interactions remain in this solvent. In contrast, the IR spectra of complexes **3** show only one strong absorption in the region 2023−1954 cm^{-1} (with a shoulder at 1919 cm^{-1} for complex **3c**) indicating that all C≡CR groups are acting as bridging ligands.

The ^1H NMR spectrum of complex **2a** shows the expected resonances for the allyl group (5.46 m, CH; 3.88 d, H_{syn}; 3.28 d, H_{anti}) besides the resonances of the aromatic protons and the NBu_4^+ cation. The ^1H NMR spectra of complexes **2b** and **2c** at room temperature exhibit the expected resonances for one allyl group but only one type of alkynyl ligand (δ 1.17 ^{t}Bu **2b**; 0.05 $SiMe_3$ **2c**), suggesting dynamic behavior that probably involves a rapid “$Pd(\eta^3\text{-allyl})$” unit exchange on the NMR time-scale between bridging and terminal alkynyl groups. A similar phenomenon has been observed previously in the binuclear complexes $(NBu_4)_2[(C_6F_5)_2Pt(\mu\text{-}C{\equiv}CR)_2Pt(C{\equiv}CR)_2]$ (R = ^{t}Bu, $SiMe_3$).[5c] However, while the ^1H NMR spectrum of **2b** remains essentially unchanged in the temperature range (15 °C to −50 °C), the singlet resonance caused by the $SiMe_3$ groups in complex **2c** is split into two different signals (δ 0.05 and 0.002) at −10 °C which is consistent with the presence of terminal and bridging alkynyl ligands according to the structure proposed in Scheme 2. The observed equivalence of terminal and bridging alkynyl ligands at low temperature for complex **2b** could be due to an accidental coincidence of signals. The low temperature (−50 °C) ^{13}C NMR spectra of both complexes (**2b** and **2c**) show, in the high field region, apart from the resonances due to the NBu_4^+ cation, the presence of two magnetically inequivalent *tert*-butyl (δ 32.9, 32.5 $C(CH_3)_3$ and 29.7, 29.0 CMe_3) or trimethylsilyl groups (δ 1.42, 1.37), indicating the presence of terminal and bridging alkynyl ligands. As expected, in the low-field region both complexes reveal, in addition to the singlet resonance due to CH_2 groups of the allyl ligand, five signals which can be attributed to four alkynyl carbon atoms and to the central carbon atom of the $\eta^2\text{-}C_3H_5$ group. The absence of platinum satellites in the alkynyl carbon resonances for **2b** precludes a proper assignment. However, in complex **2c** the C_α and C_β alkynyl carbons appear at δ 130.5 and 119.2 and at δ 106.2 and 93.9, respectively, and are easily assigned since the former show larger coupling constants to ^{195}Pt nuclei (990.3 and 724.2 Hz) than the latter (267 and 244.8 Hz). The downfield resonance (δ 130.5) and the signal at δ 106.2 are tentatively assigned to the C_α and C_β of terminal alkynyl ligands since both the chemical shifts and the $^1J_{Pt-C}$ coupling constant are similar to those observed in the starting material $[Pt(C{\equiv}CSiMe_3)_4]^{2-}$ (δ 140.4, C_α, $^1J_{Pt-C}$ = 924 Hz and δ 104.4, C_β, $^2J_{Pt-C}$ = 250.4 Hz). Assignment of the resonances at 119.2 and 93.9 to the C_α and the C_β of bridging alkynyl ligands is consistent with the slight highfield shifts and the decrease in the magnitude of $^1J_{Pt-C\alpha}$ observed in the dimeric complexes **1b** and **1c**.

For the trinuclear derivatives **3**, unambiguous structural assignment also failed due to the fact the all our attempts to obtain suitable crystals for the X-ray analysis of these complexes were unsuccessful. If it is assumed that the trimetallic species **3** are only 1:2 π-adducts, and if the less favorable situations with the allyl groups located on the same side of the platinum coordination plane are excluded, there should be three isomers for these derivatives, **I**−**III**, shown in Scheme 3.

The room and low temperature ^1H NMR spectra of the *tert*-butyl derivative **3b** exhibit the allyl proton

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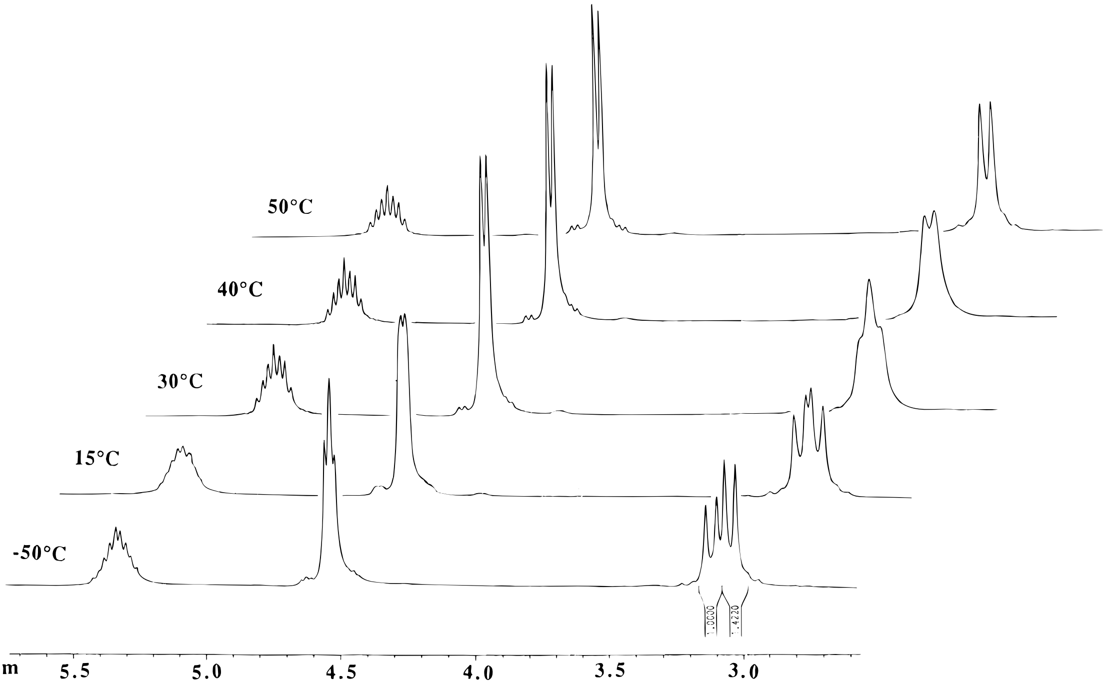

Figure 1. ^1H NMR spectra of complex **3c** at different temperatures (allyl region).

signals of equivalent allyl groups with well separated doublet resonances for the anti (rt δ 2.95) and syn (rt δ 4.46) protons. A singlet at $\delta = 1.16$ in **3b** indicates that at least in solution all alkynyl groups are also equivalent. In the ^{13}C NMR spectrum of **3b** at low temperature (−50 °C) the expected four and two signals due to equivalent alkynyl ($C{\equiv}CCMe_3$) and allyl (CH and CH_2) groups are observed. The C_α (δ 73.4, $^1J_{Pt-C} = 906.5$ Hz) and C_β (δ 107.4, $^2J_{Pt-C} = 297.3$ Hz) carbon resonances are again shifted to highfield compared to those observed in the starting material (δ 98.9, C_α, $^1J_{Pt-C} = 975$ Hz; δ 108.4, C_β, $^2J_{Pt-C} = 279$ Hz). Although the simplicity of the spectra could be attributed to the presence of only one isomer (**II** or **III**), a rapid equilibrium of isomers (including **I**) cannot be excluded.

Thus, the ^1H NMR spectra of complexes **3a** and **3c** (see Figure 1 for complex **3c**) are very similar and temperature dependent. At high temperature (50 °C for **3c**, 30 °C for **3a**) they show, in addition to the methine signal as a multiplet, sharp and well separated doublet resonances only for the anti (δ 3.09 **3c**; δ 3.39 **3a**) and syn (δ 4.54 **3c**; δ 3.93 **3a**) protons showing that both allyl groups are equivalent. The trimethylsilyl groups in **3c** give rise to a sharp singlet (δ 0.14). Both, the anti and syn proton signals broaden (see Figure 1 for complex **3c**) when the system is cooled and finally resolved into a pair of doublets (the two H_{syn} doublets overlap giving an apparent triplet in **3c**) of similar ratio (ca. 1.16:1 for **3a** and 1:1.4 for **3c**), indicating the presence of two magnetically inequivalent allyl groups. For complex **3c**, the signal due to $SiMe_3$ groups is also split at −50 °C into two signals of different intensity but their proximity (δ 0.01 and 0.09) precludes proper integration.

Likewise, the ^{13}C NMR spectrum of **3c** at low temperature (−50 °C) also exhibits the presence of two inequivalent allyl and trimethylsilylalkynyl ligands. The lowfield part of this spectrum showing the alkynyl (C_α and C_β) and methine carbon resonances is given in Figure 2a. Due to the η^2-coordination of the $Me_3SiC{\equiv}C$ units to the palladium center, the alkyne carbon signals in the starting $[Pt(C{\equiv}CSiMe_3)_4]^{2-}$ precursor (Figure 2b) shift highfield, a characteristic which is typical of these heteronuclear platinum−palladium complexes. The more extended low field shift of the C_α resonances in the trimethylsilyl derivatives compared to the *tert*-butylalkynyl complexes, both in the starting precusors and in the **1**−**3** complexes, can be attributed to the β-Si-effect of the $SiMe_3$ group, which produces a partial positivation of the inner C_α carbon atom of the alkynyl ligand.[7c] As can be observed in Figure 2a, the intensity of the signals clearly suggests different ratios for the two magnetically inequivalent allyl and alkynyl ligands, in keeping with the low-temperature proton NMR spec-

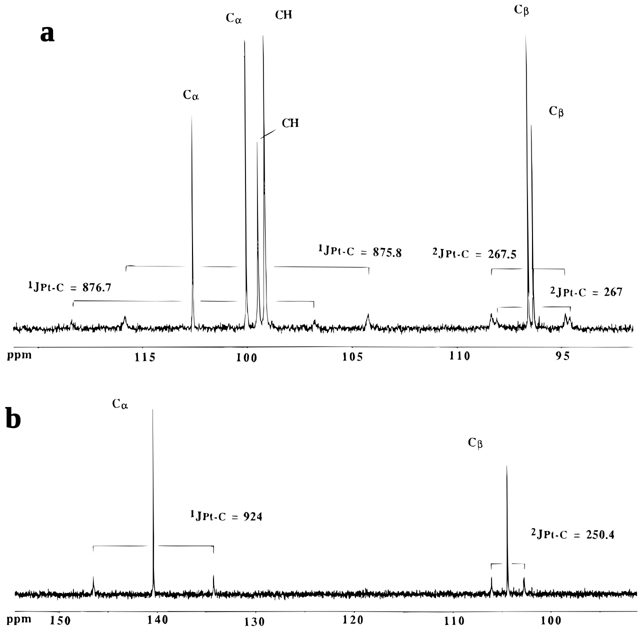

Figure 2. Lowfield region of the ^{13}C NMR spectra of: (a) complex **3c** at −50 °C. (b) $(NBu_4)_2[Pt(C{\equiv}CSiMe_3)_4]{\cdot}2H_2O$ at 15 °C (*J* in Hz).

trum. This fact is not consistent with isomer **I** and could be tentatively attributed to the presence of a mixture of isomers **II** and **III**, whose rate of interconversion is slow at low temperature on the NMR time-scale.

The fluxional behavior of allylpalladium complexes has been thoroughly studied[15] and we have little new to add. There are a number of possible mechanisms for isomerization, including simple π-allyl rotation of the Pd(allyl) units, with or without Pd−alkyne breaking and simultaneous or sequential inversion of the central PtC_4-Pd puckered cores via intermediate species with one or both alkynyl ligands symmetrically (η^1) bridging the two metal centers.[5a,b] Isomerization pathways involving intermolecular reactions via five-coordinated species can also be considered. A η^3-η^1-η^3 movement of the allyl groups at high temperature have to be excluded since no averaging of the syn and anti protons of the allyl groups is observed.

Finally, as a part of this study, the reactions of $\{[Pd(\eta^3\text{-allyl})Cl]_2\}$ with neutral bis-alkynyl platinum derivatives were also examined. Treatment of an acetone solution of the π-allyl palladium chloride dimer with 2 equiv of $[cis\text{-}Pt(C{\equiv}CR)_2(PPh_3)_2]$ (R = Ph, ^{t}Bu) and with an excess of $NaClO_4$ leads to the corresponding cationic heterobimetallic complexes $[cis\text{-}(PPh_3)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CR)\text{-}Pd(\eta^3\text{-}C_3H_5)][ClO_4]$ (R = Ph **4a**; ^{t}Bu **4b**), consistent with Scheme 2 (iv), which were isolated as white (**4a**) and pale yellow (**4b**) solids in good yields. The IR spectrum of **4b** in Nujol mulls shows two weak ν(C≡C) bands at 2040 and 2020 cm^{-1} together with the typical absorption of uncoordinated perchlorate at 1095 and 623 cm^{-1}.[16] Furthermore, consistent with the mutually *cis* disposition of the two PPh_3 ligands,[17] the spectrum shows four bands at 544, 528, 516, and 501 cm^{-1}. Unfortunately, it was not possible to form an emulsion with Nujol for complex **4a**, and the expected absorption due to ν(C≡C) was not observed in CH_2Cl_2 solution.

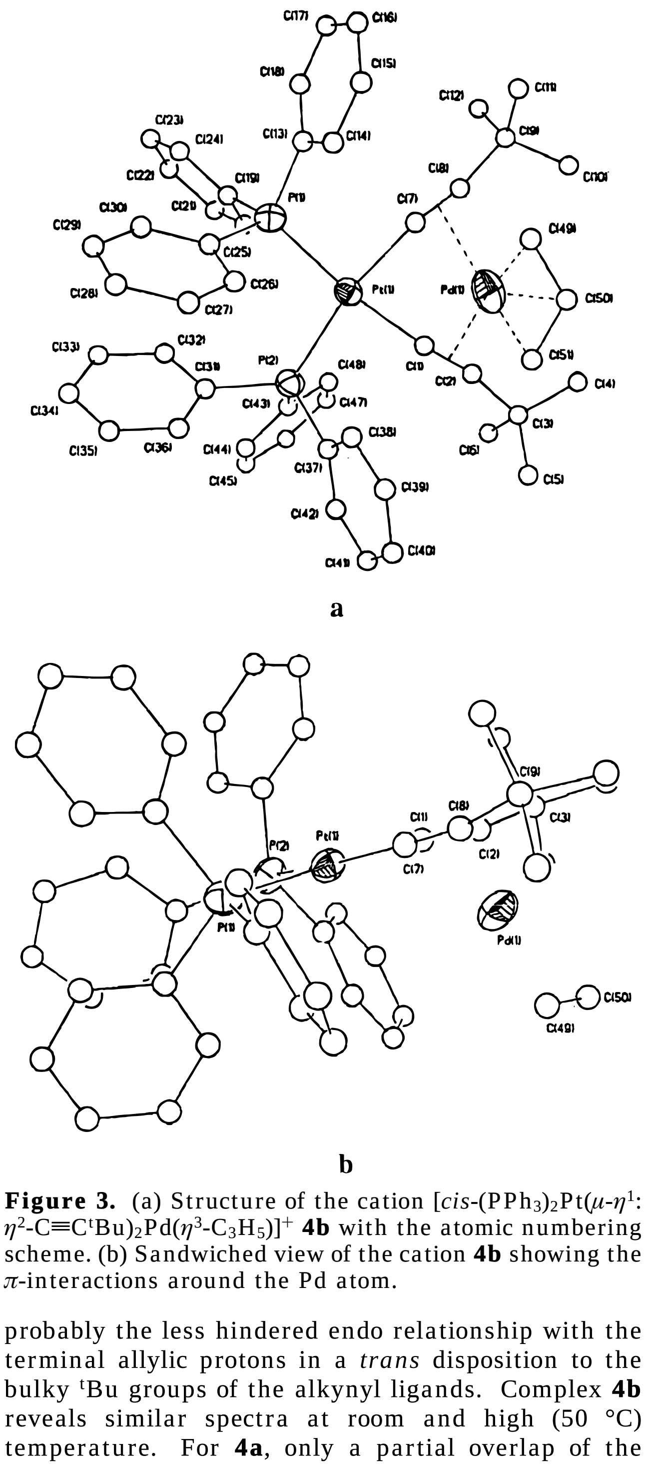

Figure 3. (a) Structure of the cation $[cis\text{-}(PPh_3)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C^tBu)_2Pd(\eta^3\text{-}C_3H_5)]^+$ **4b** with the atomic numbering scheme. (b) Sandwiched view of the cation **4b** showing the π-interactions around the Pd atom.

The low temperature NMR spectra of both complexes are very simple. The ^{31}P NMR spectra show a singlet with platinum satellites in keeping with the *cis* disposition of the PPh_3 ligands, and in the ^{1}H NMR spectra the characteristic signals of only one η^3-allyl moiety, with separated resonances for syn and anti protons, are observed. These spectroscopic data suggest the presence of only one isomer or alternatively that a very fast equilibration between both rotamers (exo and endo) is possible. Complex **4b** crystallizes (see below), adopting probably the less hindered endo relationship with the terminal allylic protons in a *trans* disposition to the bulky ^{t}Bu groups of the alkynyl ligands. Complex **4b** reveals similar spectra at room and high (50 °C) temperature. For **4a**, only a partial overlap of the resonances due to syn and anti protons was observed at room and high temperature. As expected, in the ^{13}C NMR spectra at low temperature (−50 °C) both the C_α (δ 84.7 **4a**; δ 75.6 **4b**) and C_β (δ 102.8 **4a**; δ 112.5 **4b**) alkynyl bridging carbon resonances appear again to be shifted highfield with respect to those observed in the starting complexes $[cis\text{-}Pt(C{\equiv}CR)_2(PPh_3)_2]$ [R = Ph, δ 102.6 (C_α), 109.8 (C_β); R = ^{t}Bu, δ 85.8 (C_α), 117.1 (C_β)]. The structure of **4b** has been determined by X-ray diffraction. A view of the complex cation $[cis\text{-}(PPh_3)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C^tBu)_2Pd(\eta^3\text{-}C_3H_5)]^+$ is given in Figure 3a. Selected bond distances and angles are collected in Table 1. The structure is similar to that of the anion in compound **1c**,[10] in which the Pd(η^3-allyl) unit is coordinated to the bis(alkynyl)platinum fragment through an η^2-side-on coordination of the two alkynyl ligands.

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Table 1. Selected Bond Lengths (Å) and Angles (deg) for 4b

Pt(1)−Pd(1)	3.026 (1)	Pt(1)−P(1)	2.303 (4)
Pt(1)−P(2)	2.305 (3)	Pt(1)−C(1)	2.032 (15)
Pt(1)−C(7)	2.019 (14)	Pd(1)−C(1)	2.245 (14)
Pd(1)−C(2)	2.439 (15)	Pd(1)−C(7)	2.286 (13)
Pd(1)−C(8)	2.487 (15)	Pd(1)−C(49)	2.130 (22)
Pd(1)−C(50)	2.118 (26)	Pd(1)−C(51)	2.159 (22)
C(1)−C(2)	1.213 (22)	C(2)−C(3)	1.467 (26)
C(7)−C(8)	1.187 (20)	C(8)−C(9)	1.496 (23)
C(49)−C(50)	1.396 (48)	C(50)−C(51)	1.366 (39)
Pd(1)−Pt(1)−P(1)	125.2(1)	Pd(1)−Pt(1)−P(2)	122.3(1)
P(1)−Pt(1)−P(2)	101.4(1)	P(2)−Pt(1)−C(1)	86.2(4)
P(1)−Pt(1)−C(7)	91.2(4)	C(1)−Pt(1)−C(7)	81.3(6)
C(1)−Pd(1)−C(7)	71.2(5)	C(2)−Pd(1)−C(8)	108.1(5)
C(7)−Pd(1)−C(49)	105.8(9)	C(8)−Pd(1)−C(49)	91.0(9)
C(1)−Pd(1)−C(51)	108.8(7)	C(2)−Pd(1)−C(51)	92.9(7)
C(49)−Pd(1)−C(51)	67.5(10)	Pt(1)−C(1)−Pd(1)	89.9(5)
Pt(1)−C(1)−C(2)	174.0(13)	C(1)−C(2)−C(3)	165.2(16)
Pt(1)−C(7)−Pd(1)	89.1(5)	Pt(1)−C(7)−C(8)	171.5(12)
C(7)−C(8)−C(9)	167.4(16)	C(49)−C(50)−C(51)	119.2(24)

The most remarkable difference is that the η^2-palladium−alkynide linkages are clearly asymmetric in **4b**, the $\text{Pd}-\text{C}_\alpha$ distances [Pd−C7 2.286(13) Å; Pd−C1 2.245(14) Å] being shorter than the corresponding $\text{Pd}-\text{C}_\beta$ ones [Pd−C8 2.487(15) Å; Pd−C2 2.439(15) Å] and contrasting with the symmetrical η^2-linkages found in the anion **1c** and in $\{[cis\text{-(dppe)Pt}(\mu\text{-C}{\equiv}\text{CR})_2]\text{Pt}(\text{C}_6\text{F}_5)_2\}$.[5a] It should be noted that this type of asymmetry, previously observed in platinum−silver alkynyl compounds,[18] contrast with the asymmetry found in the anion $\{[cis\text{-Pt}(\text{C}_6\text{F}_5)_2(\mu\text{-C}{\equiv}\text{CSiMe}_3)_2]\text{HgBr}_2\}$[5d] with shorter $\text{Hg}-\text{C}_\beta$ than $\text{Hg}-\text{C}_\alpha$ distances. As expected, the distance between the platinum and palladium atoms is slightly shorter in the cation **4b** [3.026(1) Å] than in the binuclear anion **1c** [3.049(2)],[10] but this does not imply a Pt−Pd bonding interaction.

Apart from the above considerations, all the other bond distances and angles in the cation are within the expected range. Thus, the geometry around the palladium atom is similar to that observed in the anion **1c** and in other Pd−allyl complexes.[2a,c,g,3b,11a,15c,g,h,j] In particular, the allyl group is symmetrically bound [Pd−C49 = 2.130(22); Pd−C51 = 2.159(22)] and forms a dihedral angle of 118.44° with the plane defined by the Pd atom and the midpoints of the C≡C triple bonds, close to the typical value found in η^3-allyl Pd and Pt complexes (110°).[2a] The acetylenic fragments are coordinated almost perpendicularly to the palladium coordination plane as would be expected from the geometry of Pd(II)−alkyne: (i) the angles formed by the C≡C triple bonds and the corresponding vectors defined by Pd and the midpoints of the C≡C bonds are 80.5(26)° (C1−C2) and 79.9(21)° (C7−C8) respectively, and (ii) the triple bonds are inclined by 35.9(11)° (C1−C2) and 38.4(11)° (C7−C8) with respect to the normal to the C49PdC51 plane.

On the other hand, in the organometallic platinum fragment "$cis\text{-Pt}(\text{PPh}_3)_2(\text{C}{\equiv}\text{C}^t\text{Bu})_2$", the Pt atom is in a slightly distorted square planar environment [angles ranging from 81.3(6)° (C7−Pt−C8) to 101.4(1)° (P1−Pt−P2)] with similar Pt−P [2.305(3) and 2.303(4) Å] and $\text{Pt}-\text{C}_{(\text{alkynyl})}$ distances [2.019(14) and 2.032(15) Å] to those reported in the literature on related bonds.[5a,g,19]

Finally, the bond lengths and angles of the acetylene skeletons are very similar to those found in the anion **1c**.[10] The $\text{Pt}-\text{C}_\alpha{\equiv}\text{C}_\beta$ fragments are not very distorted [171.5(12)° and 174.0(13)°] in cation **4b**, whereas they are distinctly bent in **1c** (average 167.65(16)°], but the bending-back angles at C_β [167.4(16) and 165.2(16)° in **4b** versus 167.4(17) and 165.5(18)° in **1c**] are practically the same. The C≡C bond lengths in **4b** [1.187(20) Å and 1.213(22) Å] and in **1c** [1.201(25) Å and 1.238(27) Å] are identical within experimental error.

It should be noted that in contrast with other well known heterometallic tweezer like complexes $[\text{M}]\text{-}(\text{C}{\equiv}\text{CR})_2\text{M}'\text{L}_n$ which display almost planar $\text{MC}_4\text{M}'$ cores,[6f−i,k] the palladium atom is not embedded by the bis-alkynyl platinum fragment but sandwiched between the acetylenic fragments and the allyl moiety (see Figure 3b), thus resulting in a central nonplanar PtC7C8C1C2Pd core. A similar structural feature has been found in the anion **1c**,[10] $\{[\text{Pt(dppe)}(\text{C}{\equiv}\text{CPh})_2]\text{Pt}(\text{C}_6\text{F}_5)_2\}$[5a] and $[\text{Cp}^*(\text{PEt}_3)\text{Ir}(\text{C}{\equiv}\text{CPh})_2\text{Pt}(\text{C}_6\text{F}_5)_2]$,[5g] but $\{[cis\text{-Pt}(\mu\text{-C}{\equiv}\text{CSiMe}_3)_2(\text{C}_6\text{F}_5)_2]\text{HgBr}_2\}_2$[5d] displays a planar $\text{Pt}-\text{C}_4-\text{Hg}$ core. Interestingly, in the trinuclear cation $\{[cis\text{-}(\text{PPh}_3)_2\text{Pt}(\mu\text{-C}{\equiv}\text{CPh})_2]_2\text{Ag}\}$ the silver atom is only well embedded by one of the two bis-alkynyl platinum fragments.[5h] It is probable that steric effects are responsible for this structural feature. For square-planar coordination of the monomeric $\text{M}'\text{L}_n$ building block, a tweezer effect of the alkynyl substituents would be more sterically hindered.

Concluding Remarks

Palladium(II) forms a very rich chemistry involving the allyl ligand, and in addition exhibits potential for access to unusual molecules arising from reactions with alkynes. It is generally accepted that the first step in the palladium(II) catalyzed polymerization of alkynes, as well as in the insertion of an alkyne into a Pd−C bond, is the formation of a complex in which the alkyne is η^2-coordinated to the metal center.[20] However, only a few of these proposed alkyne coordination complexes have been reported,[5a,21] and none have been characterized by X-ray diffraction. Due to the analogy of alkynes and metallo acetylides (MC≡CR) and the peculiar ability of the anionic $[\text{PtX}_2(\text{C}{\equiv}\text{CR})_2]^{2-}$ ($\text{X} = \text{C}_6\text{F}_5$ or C≡CR) and neutral $[cis\text{-Pt}(\text{C}{\equiv}\text{CR})_2(\text{PPh}_3)_2]$ substrates to act as chelate metallodiyne ligands, it has been possible to isolate, for the first time, several bis-η^2-alkyne Pd(II) complexes containing the very electrophilic cationic $[\text{Pd(allyl)}]^+$ unit.

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Experimental Section

General Considerations. All the manipulations were carried out under a nitrogen atmosphere. Acetone was treated with $KMnO_4$, distilled, and stored over molecular sieves.

$Q_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CR)_2]$ ($Q = PMePh_3$, $R = Ph$; $Q = NBu_4$, $R = {}^tBu$),[8] $(NBu_4)_2[Pt(C{\equiv}CR)_4]\cdot nH_2O$ ($n = 0$, $R = Ph$;[9] $n = 2$, $R = {}^tBu$,[9] $SiMe_3$[5c]), $[\textit{cis}\text{-}Pt(C{\equiv}CR)_2(PPh_3)_2]$ ($R = Ph$,[22] ${}^tBu$[5a]), and $\{[Pd(\eta3\text{-}C_3H_5)Cl]\}$[23] were prepared by published methods. Proton, ^{13}C, ^{19}F, and ^{31}P NMR spectra were recorded on a Bruker ARX 300 spectrometer. Chemical shifts are reported in ppm relative to external standards (Me_4Si, $CFCl_3$, and 88% H_3PO_4). Infrared spectra were recorded with a Perkin-Elmer 883 spectrometer using Nujol mulls between polyethylene sheets. C, H, and N analyses were carried out with a Perkin-Elmer 240C microanalyzer or a Perkin-Elmer 2400 CHNS/O analyzer. Conductivities were measured in acetone solutions (ca. 5×10^{-4} mol dm^{-3}) using a Phillips 9501/01 conductimeter.

$(PMePh_3)[\textit{cis}\text{-}(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)_2Pd(\eta^3\text{-}C_3H_5)]$ (1a). A stirred suspension of $(PMePh_3)_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CPh)_2]$ (0.23 g, 0.18 mmol) in 15 mL of acetone was treated with 0.0327 g (0.09 mmol) of $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$, and the reaction mixture was stirred at room temperature for 10 min. The resulting deep yellow solution was concentrated to ca. 2 mL, and the slow addition of EtOH (4 mL) gave a yellow microcrystaline solid characterized as compound **1a** (yield 46%). Anal. Calcd for $C_{50}F_{10}H_{33}PPtPd$: C, 51.94; H, 2.87. Found: C, 51.47; H, 2.80. Λ_M: 89 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2016 (s with shoulder); an internal absorption of $PMePh_3^+$ precludes unambiguous assignment of the x-sensitive modes of C_6F_5 groups; three bands at 796 (s), 787 (s), and 775 (s) cm^{-1} are observed. ^1H NMR ($CDCl_3$): at 15°C 7.73, 7.59, 7.19, 7.12 (m, 25H, Ph); 5.52 (m, CH, allyl); 3.98 (d, 2 H_{syn}, $J_{syn} = 6.5$ Hz, allyl); 3.35 (d, 2 H_{anti}, $J_{anti} = 12.2$ Hz, allyl); 3.11 (d, 3H, $^2J_{P-H} = 13$ Hz, $PMePh_3^+$). At −50 °C 7.75 (m), 7.57 (m), 7.13 (d) (25H, Ph); 5.62 (m, CH, allyl); 4.02 (d, 2 H_{syn}, $J_{syn} = 6.25$ Hz, allyl); 3.36 (d, 2 H_{anti}, $J_{anti} = 12.2$ Hz, allyl); 3.09 (d, 3H, $^2J_{P-H} = 13.12$ Hz, $PMePh_3^+$). ^{19}F NMR ($CDCl_3$). At 15 °C −116.03 (d, *o*-F, $^3J_{Pt-o-F} = 399$ Hz); −166.44 (m, *p*-F and *m*-F). At −50 °C −116.1 (dd, *o*-F, $^3J_{Pt-o-F} = 399$ Hz); −165.4 (t, *p*-F); −165.7 (m, *m*-F). Due to the low solubility and stability of **1a** in solution, its ^{13}C NMR spectrum could not be registered.

$(NBu_4)[\textit{cis}\text{-}(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C^tBu)_2Pd(\eta^3\text{-}C_3H_5)]$ (1b). To a pale yellow solution of $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.0233 g, 0.064 mmol) in acetone (10 mL) was added $(NBu_4)_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$ (0.15 g, 0.128 mmol), and the mixture was stirred for 25 min. The resulting deep yellow solution was evaporated to dryness, and treatment of the residue with deoxygenated water afforded **1b** as a yellow solid which was repeatedly washed with deoxygenated water and air-dried (yield 78%). Anal. Calcd for $C_{43}F_{10}H_{59}NPtPd$: C, 47.76; H, 5.50; N, 1.30. Found: C, 47.8; H, 5.40; N, 1.36. Λ_M: 93 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2015 (m); $\nu(C_6F_5)$x-sensitive 788 (s), 778 (s). ^1H NMR ($CDCl_3$): at 15 °C, 5.3 (m, CH, allyl); 4.43 (d, 2 H_{syn}, $J_{syn} = 6.5$ Hz, allyl); 3.06 (m, 10 H, overlapping: 2 H_{anti}, allyl and 8 H, NCH_2-, ^nBu); 1.54 (m, 8H, -CH_2-, ^nBu); 1.31 (m, 8H, -CH_2-, ^nBu); 1.15 (s, 18H, ^tBu); 0.89 (t, 12H, -CH_3, ^nBu). The same pattern was found at −50 °C: 5.3 (m, CH, allyl); 4.45 (d, 2 H_{syn}, $J_{syn} = 4.95$ Hz, allyl); 2.98 (br, 10 H, overlapping: 2 H_{anti}, allyl and 8 H, NCH_2-, ^nBu); 1.47 (br, 8H, -CH_2-, ^nBu); 1.22 (br, 8H, -CH_2-, ^nBu); 1.13 (s, 18H, ^tBu); 0.85 (br, 12H, -CH_3, ^nBu). ^{19}F NMR ($CDCl_3$): at 15 °C −115.0 (dm, *o*-F, $^3J_{Pt-o-F} = 416$ Hz); −167.5 (m, *m*-F); −167.9 (t, *p*-F). The same pattern was found at −50 °C: −115.1 (d, *o*-F, $^3J_{Pt-o-F} = 412$ Hz); −166.8 (m, *m*-F); −167.3 (t, *p*-F). ^{13}C NMR ($CDCl_3$): at −50 °C 149.3 (d), 146.3 (d), 136.8 (m), 133.6 (m) (C_6F_5); 106.4 (s, C_β, -$C_\alpha{\equiv}C_\beta{}^tBu$, $^2J_{Pt-C} = 281.7$ Hz); 106.1 (s, CH, allyl); 80.5 (s, C_α, -$C_\alpha{\equiv}C_\beta{}^tBu$; $^1J_{Pt-C} = 820.2$ Hz); 63.1 (s, -CH_2, allyl); 57.9 (s, N-CH_2-, NBu_4); 32.9 (s, -$C(CH_3)_3$); 29.8 (s, -CMe_3); 23.2 (s, -CH_2-, NBu_4); 19.2 (s, -CH_2-, NBu_4); 13.4 (s, -CH_3, NBu_4).

The ^{13}C NMR spectrum of the starting complex **$(NBu_4)_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}C^tBu)_2]$** in $CDCl_3$ at room temperature (15 °C) was also registered: 149.6 (d), 146.7 (d), 137.6−132.7 (m) (C_6F_5); 110.1 (s, C_β, -$C_\alpha{\equiv}C_\beta{}^tBu$, $^2J_{Pt-C} = 293.4$ Hz); 98.2 (s, C_α, -$C_\alpha{\equiv}C_\beta{}^tBu$; $^1J_{Pt-C} = 1048.2$ Hz); 58.8 (s, N-CH_2-, NBu_4); 33.0 (s, -$C(CH_3)_3$); 29.5 (s, -CMe_3); 24.2 (s, -CH_2-, NBu_4); 19.6 (s, -CH_2-, NBu_4); 13.6(s, -CH_3, NBu_4).

$(NBu_4)[\textit{cis}\text{-}(C_6F_5)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CSiMe_3)_2Pd(\eta^3\text{-}C_3H_5)]$ (1c).[10] ^1H NMR ($CDCl_3$): at −50 °C, 5.28 (m, CH, allyl); 4.48 (d, 2 H_{syn}, $J_{syn} = 5.22$ Hz, allyl); 3.06 (m, 10 H, overlapping: 2 H_{anti}, allyl and 8 H, NCH_2-, ^nBu); 1.49 (br, 8H, -CH_2-, ^nBu); 1.26 (br, 8H, -CH_2-, ^nBu); 0.86 (br, 12H, CH_3, ^nBu); 0.05 (t, 18H, -$SiMe_3$). ^{19}F NMR ($CDCl_3$): at −50 °C: −115.2 (dm, *o*-F, $^3J_{Pt-o-F} = 397$ Hz); −166.4 (m, *m*-F and *p*-F). ^{13}C NMR ($CDCl_3$): at −50 °C 149.1 (m), 146.1 (m), 136.7 (m), 133.8 (m) (C_6F_5); 117.6 (s, C_α, -$C_\alpha{\equiv}C_\beta SiMe_3$); 107.9 (s, CH, allyl); 94.2 (s, C_β, -$C_\alpha{\equiv}C_\beta SiMe_3$); 65.4 (s, -$CH_2$, allyl); 58.1 (s, N-$CH_2$-, NBu_4); 23.4 (s, -CH_2-, NBu_4); 19.3 (s, -CH_2-, NBu_4); 13.5 (s, -CH_3, NBu_4); 1.5 (s, $SiMe_3$).

The ^{13}C NMR spectrum of the starting complex **$(NBu_4)_2[\textit{cis}\text{-}Pt(C_6F_5)_2(C{\equiv}CSiMe_3)_2]$** in $CDCl_3$ at room temperature (15 °C) was also registered: 149.3 (d), 146.4 (d), 137.5 −132.9 (m) (C_6F_5); 140.7 (s, C_α, -$C_\alpha{\equiv}C_\beta SiMe_3$, $^1J_{Pt-C} = 997$ Hz); 104.0 (s, C_β, -$C_\alpha{\equiv}C_\beta SiMe_3$; $^2J_{Pt-C} = 270.7$); 58.6 (s, N-CH_2-, NBu_4); 24.1 (s, -CH_2-, NBu_4); 19.4 (s, -CH_2-, NBu_4); 13.5(s, -CH_3, NBu_4); 2.0 (s, $SiMe_3$).

$(NBu_4)[(C{\equiv}CPh)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}CPh)_2Pd(\eta^3\text{-}C_3H_5)]$ (2a). $(NBu_4)_2[Pt(C{\equiv}CPh)_4]$ (0.2 g, 0.18 mmol) was added to a pale yellow solution of $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.034 g, 0.09 mmol) in 15 mL of acetone. The solution immediately turned deep yellow and in a few minutes (∼2) a yellow solid began to precipitate. After 45 min of stirring at room temperature the yellow solid was separated by filtration and identified as the neutral trinuclear derivative $\{Pt(C{\equiv}CPh)_4[Pd(\eta^3\text{-}C_3H_5)_2\}$ **3a** (yield 9%). Evaporation of the filtrate to dryness and treatment with cold EtOH (∼4 mL) afforded complex **2a** as a yellow solid (yield 11%). Anal. Calcd for $C_{51}H_{61}NPtPd$: C, 61.90; H, 6.21; N, 1.42. Found: C, 61.65; H, 6.61; N, 1.34. Λ_M: 84 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}, in CH_2Cl_2 solution): $\nu(C{\equiv}C)$ 2098 (vs, sh); 2026 (s). ^1H NMR ($CDCl_3$): at 15 °C 7.43, 7.16 (m, 20 H, Ph); 5.46 (m, CH, allyl); 3.88 (d, 2 H_{syn}, $J_{syn} = 6.04$ Hz, allyl); 3.41 (m, 8 H, NCH_2−, ^nBu); 3.28 (d, 2 H_{anti}, $J_{anti} = 12.1$ Hz); 1.54 (m, 8H, -CH_2-, ^nBu); 1.37 (m, 8H, -CH_2-, ^nBu); 0.8 (t, 12H, -CH_3, ^nBu).

$(NBu_4)[(C{\equiv}C^tBu)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C{\equiv}C^tBu)_2Pd(\eta^3\text{-}C_3H_5)]$ (2b). $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.0352 g, 0.096 mmol) was added to a colorless solution of $(NBu_4)_2[Pt(C{\equiv}C^tBu)_4]\cdot 2H_2O$ (0.2 gr, 0.19 mmol) in acetone (30 mL), and the mixture was stirred for 10 min at room temperature. The resulting deep yellow solution was concentrated to small volume (∼5 mL) and cooled overnight to −30 °C, yielding **2b** as a yellow solid which was filtered and washed with cold EtOH (yield 34%). Anal. Calcd for $C_{43}H_{77}NPtPd$: C, 56.78; H, 8.53; N, 1.54. Found: C, 56.2; H, 8.23; N, 1.95. Λ_M: 76 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C{\equiv}C)$ 2095 (s); 2020 (s). IR (cm^{-1}, in CH_2Cl_2 solution): $\nu(C{\equiv}C)$ 2097-(m); 2009(s). ^1H NMR ($CDCl_3$): at 15 °C, 5.23 (m, CH, allyl); 4.37 (d, 2 H_{syn}, $J_{syn} = 6.5$ Hz, allyl); 3.56 (m, 8 H, NCH_2-, ^nBu); 3.08 (d , 2 H_{anti}, $J_{anti} = 12.2$ Hz); 1.66 (m, 8H, -CH_2-, ^nBu); 1.54 (m, 8H, -CH_2-, ^nBu); 1.17 (s, 36 H, ^tBu); 0.99 (t, 12H, -CH_3, ^nBu). At −50 °C: 5.25 (m, CH, allyl); 4.40 (d, 2 H_{syn}, $J_{syn} = 6.1$ Hz, allyl); 3.50 (br, 8 H, NCH_2-, ^nBu); 3.07 (d , 2 H_{anti}, $J_{anti} = 12.1$ Hz); 1.66 (br, 8H, -CH_2-, ^nBu); 1.52 (m br, 8H, -CH_2-, ^nBu); 1.13 (s, 36 H, ^tBu); 0.97 (t, 12H, -CH_3, ^nBu). ^{13}C NMR ($CDCl_3$): at −50 °C 110.2 (s), 107.4 (s), 106.1 (s), 90.3 (s), 84.3 (s) (2C_α, 2C_β, -$C_\alpha{\equiv}C_\beta{}^tBu$; CH, allyl); 63.9 (s, -$CH_2$, allyl); 58.2 (s, N-$CH_2$-, NBu_4); 32.9 (s, -$C(CH_3)_3$); 32.5 (s, -$C(CH_3)_3$); 29.7 (s, -CMe_3); 29.0 (s, -CMe_3); 23.9 (s, -CH_2-, NBu_4); 19.7 (s, -CH_2-, NBu_4); 13.9 (s, -CH_3, NBu_4).

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The ^{13}C NMR spectrum of the starting complex **$(NBu_4)_2[Pt(C\equiv C^tBu)_4]\cdot 2H_2O$** in $CDCl_3$ at room temperature (15 °C) was also registered: 108.4 (s, C_β, $-C_\alpha\equiv C_\beta{}^tBu$, $^2J_{Pt-C} = 279$ Hz); 98.9 (s, C_α, $-C_\alpha\equiv C_\beta{}^tBu$, $^1J_{Pt-C} = 975$ Hz); 58.6 (s, NCH_2-, NBu_4); 32.6 (s, $-C(CH_3)_3$); 28.9 (s, $-CMe_3$); 24.2 (s, $-CH_2$-, NBu_4); 19.5 (s, $-CH_2$-, NBu_4); 13.5 (s, $-CH_3$, NBu_4).

$(NBu_4)[(C\equiv CSiMe_3)_2Pt(\mu\text{-}\eta^1{:}\eta^2\text{-}C\equiv CSiMe_3)_2Pd(\eta^3\text{-}C_3H_5)]$ (2c). To a solution of $(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$ (0.4 gr, 0.36 mmol) in 25 mL of acetone $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.0662 g, 0.18 mmol) was added, and the mixture was stirred for 5 min. The resulting dark solution was treated with charcoal and filtered through kieselguhr. Evaporation of the resulting yellow filtrate to dryness produced **2c** as a yellow solid which was filtered and washed with deoxygenated H_2O (yield 85%). Anal. Calcd for $C_{39}H_{77}Si_4NPtPd$: C, 48.10; H, 7.97; N, 1.44. Found: C, 47.87; H, 7.94; N, 1.51. Λ_M: 82 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C\equiv C)$ 2042 (s); 2027 (vs); 1953 (vs); 1938 (s). IR (cm^{-1}, in CH_2Cl_2 solution): $\nu(C\equiv C)$ 2042 (vs); 2027 (vs); 1952 (vs); 1941 (sh). ^1H NMR ($CDCl_3$): at 15 °C 5.23 (m, CH, allyl); 4.41 (d 2 H_{syn}, $J_{syn} = 6.4$ Hz, allyl); 3.50 (m, 8 H, NCH_2-, ^nBu); 3.01 (d, 2 H_{anti}, $J_{anti} = 12.6$ Hz, allyl); 1.68 (m, 8H, $-CH_2$-, ^nBu); 1.51 (s, 8H, $-CH_2$-, ^nBu); 0.98 (t, 12H, $-CH_3$, ^nBu); 0.05 (s, 36 H, $SiMe_3$). At −10 °C: see text. At −50 °C 5.24 (m, CH, allyl); 4.42 (d 2 H_{syn}, $J_{syn} = 5.9$ Hz, allyl); 3.45 (br, 8 H, NCH_2-, ^nBu); 2.99 (d, 2 H_{anti}, $J_{anti} = 12.2$ Hz, allyl); 1.62 (br, 8H, $-CH_2$-, ^nBu); 1.45 (s, 8H, $-CH_2$-, ^nBu); 0.95 (t br, 12H, $-CH_3$, ^nBu); 0.03 (s, 18 H, $SiMe_3$), 0.002 (s, 18 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): at −50 °C 130.5 (s, $C_{\alpha term.}$, $-C_\alpha\equiv C_\beta SiMe_3$, $^1J_{Pt-C} = 990.3$ Hz); 119.2 (s, $C_{\alpha bridg.}$, $-C_\alpha\equiv C_\beta SiMe_3$, $^1J_{Pt-C} = 724.2$ Hz); 108.2 (s, CH, allyl); 106.2 (s, $C_{\beta term.}$, $-C_\alpha\equiv C_\beta SiMe_3$, $^2J_{Pt-C} = 267$ Hz); 93.9 (s, $C_{\beta bridg.}$, $-C_\alpha\equiv C_\beta SiMe_3$, $^2J_{Pt-C} = 244.8$ Hz); 66.0 (s, $-CH_2$, allyl); 58.2 (s, N-CH_2-, NBu_4); 23.9 (s, $-CH_2$-, NBu_4); 19.6 (s, $-CH_2$-, NBu_4); 14.0 (s, $-CH_3$, NBu_4); 1.42 (s, $SiMe_3$); 1.37 (s, $SiMe_3$).

The ^{13}C NMR spectrum of the starting complex **$(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$** in $CDCl_3$ at room temperature (15 °C) was also registered: 140.4 (s, C_α, $-C_\alpha\equiv C_\beta SiMe_3$, $^1J_{Pt-C} = 924$ Hz); 104.4 (s, C_β, $-C_\alpha\equiv C_\beta SiMe_3$; $^2J_{Pt-C} = 250.4$ Hz); 58.7 (s, N-CH_2-, NBu_4); 24.3 (s, $-CH_2$-, NBu_4); 19.5 (s, $-CH_2$-, NBu_4); 13.7 (s, $-CH_3$, NBu_4); 1.3 (s, $SiMe_3$).

$\{[Pt(\mu\text{-}C\equiv CPh)_4][Pd(\eta^3\text{-}C_3H_5)]_2\}$ (3a). A solution of $(NBu_4)_2[Pt(C\equiv CPh)_4]$ (0.25 g, 0.23 mmol) in 10 mL of acetone was treated with 0.084 g (0.23 mmol) of $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ immediately producing a yellow precipitate (**3a**) which was filtered off and washed with acetone (yield 78%). Anal. Calcd for $C_{38}H_{30}PtPd_2$: C, 51.02; H, 3.38. Found: C, 50.9; H, 3.46. IR (cm^{-1}): $\nu(C\equiv C)$ 2023 (vs). ^1H NMR ($CDCl_3$): at 40 °C 7.55, 7.32 (m, 20 H, Ph); 5.50 (m, 2 H, CH, allyl); 3.93 (d, 4 H_{syn}, $J_{syn} = 6.5$ Hz, allyl); 3.39 (d, 4 H_{anti}, $J_{anti} = 12.1$ Hz). At 30 °C the allyl resonances show a similar sharp pattern. At 15 °C 7.55, 7.31 (m, 20 H, Ph); 5.51 (br hump, 2 H, CH, allyl); 3.93 (br, 4 H_{syn}, allyl); 3.41 (d br, 4 H_{anti}, $J_{anti} = 11.1$ Hz, allyl). At 10 °C the CH and the syn and anti protons resonances remain broad but at 0 °C the central proton appears again as a multiplet and the syn and anti protons split in different signals (ca. 1:1.4 ratio). At −30 °C 7.52, 7.33 (m, 20 H, Ph); 5.45 (m, 2 H, CH, allyl); 3.99 (d, $J_{syn} = 6.4$ Hz), 3.90 (d, $J_{syn} = 6.5$ Hz) [4 H_{syn}, 1:1.16 ratio]; 3.43 (d, $J_{anti} = 12.3$ Hz), 3.41 (d, $J_{anti} = 12.2$ Hz) (4 H_{anti}). At −50 °C 7.52, 7.25 (m, 20 H, Ph); 5.62 (overlapping of two multiplets, 2 H, CH, allyl); 4.02 (d), 3.92 (d) [4 H_{syn}, 1.16:1 ratio, $J_{syn} = 6.3$ Hz]; 3.43 (overlapping of two doublets, 4 H_{anti}, $J_{anti} = 12.2$ Hz, allyl). The ^{13}C NMR spectrum could not be obtained due to the low solubility of the complex.

$\{[Pt(\mu\text{-}C\equiv C^tBu)_4][Pd(\eta^3\text{-}C_3H_5)]_2\}$ (3b). To a stirred suspension of $(NBu_4)_2[Pt(C\equiv C^tBu)_4]\cdot 2H_2O$ (0.3 g, 0.29 mmol) in acetone (10 mL) $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.105 g, 0.29 mmol) was added immediately giving a deep yellow solution. After 10 min of stirring the solution was evaporated to dryness and the resulting residue was treated with deoxygenated water, giving a yellow solid which was filtered and washed with water. The yellow product was dissolved in CH_2Cl_2 (20 mL), dried with $MgSO_4$, and, after filtration, the filtrate was evaporated to dryness. Addition of *n*-hexane to the residue afforded **3b** as a yellow solid (yield 60%). Anal. Calcd for $C_{30}H_{46}PtPd_2$: C, 44.24; H, 5.69. Found: C, 44.64; H, 6.29. IR (cm^{-1}): $\nu(C\equiv C)$ 2016 (vs). ^1H NMR ($CDCl_3$): at 15 °C 5.24 (m, 2H, CH, allyl); 4.46 (d, 4H_{syn}, $J_{syn} = 6.3$ Hz); 2.95 (d, 4H_{anti}, $J_{anti} = 11.1$ Hz), 1.16 (s, ^tBu). The same spectra pattern was observed at −50 °C 5.27 (m, 2H, CH, allyl); 4.47 (d, 4H_{syn}, $J_{syn} = 5.7$ Hz); 2.93 (d, 4H_{anti}, $J_{anti} = 12$ Hz), 1.11 (s, ^tBu). ^{13}C NMR ($CDCl_3$): at −50 °C 107.6 (s, CH, allyl); 107.4 (s, C_β, $-C_\alpha\equiv C_\beta{}^tBu$, $^2J_{Pt-C} = 297.3$ Hz); 73.4 (s, C_α, $-C_\alpha\equiv C_\beta{}^tBu$, $^1J_{Pt-C} = 906.5$ Hz); 65.2 (s, $-CH_2$, allyl); 32.7 (s, $-C(CH_3)_3$); 29.97 (s, $-CMe_3$).

$\{[Pt(\mu\text{-}C\equiv CSiMe_3)_4][Pd(\eta^3\text{-}C_3H_5)]_2\}$ (3c). The synthesis was performed as described for **3b** starting from $(NBu_4)_2[Pt(C\equiv CSiMe_3)_4]\cdot 2H_2O$ (0.2 g, 0.18 mmol) and $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.066 gr, 0.18 mmol) (yield 40%). Anal. Calcd for $C_{26}H_{46}Si_4PtPd_2$: C, 35.53; H, 5.28. Found: C, 35.6; H, 5.4. IR (cm^{-1}): $\nu(C\equiv C)$ 1954 (vs); 1919 (sh). ^1H NMR ($CDCl_3$): at 50 °C 5.34 (m, 2 H, CH, allyl); 4.54 (d , 4 H_{syn}, $J_{syn} = 6.7$ Hz); 3.09 (d, 4 H_{anti}, $J_{anti} = 12.3$ Hz); 0.14 (s, 36 H, $SiMe_3$). At 15 °C 5.32 (m, 2 H, CH, allyl); 4.53 (d br, 4 H_{syn}, $J_{syn} = 4.2$ Hz); 3.12 (d, $J_{anti} = 12.6$ Hz), 3.06 (d, $J_{anti} = 12.5$ Hz) (4 H_{anti}); 0.13 (s, 36 H, $SiMe_3$). At −50 °C 5.32 (m, 2 H, CH, allyl); 4.52 (t br, 4 H_{syn}); 3.11 (d), 3.04 (d) (4 H_{anti}, ca. 1:1.4 ratio, $J_{anti} = 12.3$ Hz); 0.10 (s), 0.09 (s) (36 H, $SiMe_3$). ^{13}C NMR ($CDCl_3$): at −50 °C 112.6 (s, C_α, $-C_\alpha\equiv C_\beta SiMe_3$, $^1J_{Pt-C} = 876.7$ Hz); 110.0 (s, C_α, $-C_\alpha\equiv C_\beta SiMe_3$, $^1J_{Pt-C} = 875.8$ Hz); 109.5 (s, CH, allyl); 109.1 (s, CH, allyl); 96.6 (s, C_β, $-C_\alpha\equiv C_\beta SiMe_3$, $^2J_{Pt-C} = 267.5$ Hz); 96.3 (s, C_β, $-C_\alpha\equiv C_\beta SiMe_3$, $^2J_{Pt-C} = 267$ Hz); 66.8 (s, $-CH_2$, allyl); 66.7 (s, $-CH_2$, allyl); 1.37 (s, $SiMe_3$); 1.26 (s, $SiMe_3$).

[*cis*-$(PPh_3)_2Pt(\mu,\eta^1{:}\eta^2\text{-}C\equiv CR)_2Pd(\eta^3\text{-}C_3H_5)](ClO_4)$ (R = Ph (4a), ^tBu (4b)). A typical preparation (complex **4a**) was as follows: To a solution of $\{[Pd(\eta^3\text{-}C_3H_5)Cl]_2\}$ (0.04 g, 0.11 mmol) in acetone (15 mL) was added [*cis*-$Pt(C\equiv CPh)_2(PPh_3)_2$] (0.2 g, 0.22 mmol). After 5 min of stirring, the reaction mixture was treated with an excess of $NaClO_4$ and stirred for 20 min. The resulting dark mixture was evaporated to dryness and the product extracted with CH_2Cl_2 (15 mL). The dichloromethane solution was treated with charcoal and filtered through kieselguhr. Evaporation of the filtrate to dryness and addition of EtOH yielded **4a** as a white solid (yield 75%). Complex **4b** was prepared as a pale yellow solid in a similar way to **4a** using [*cis*-$Pt(C\equiv C^tBu)_2(PPh_3)_2$] as the starting material (yield 60%).

Data for **4a**: Anal. Calcd for $C_{55}H_{45}P_2ClO_4PtPd$: C, 56.52; H, 3.88. Found: C, 56.28; H, 3.85. Λ_M: 128 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C\equiv C)$ not observed. ^1H NMR ($CDCl_3$): at 15 °C 7.39 (m, 36 H, overlap Ph (PPh_3) with *p*-H and *m*-H ($C\equiv CPh$)]; 6.7 (d, 4H, *o*-H ($C\equiv CPh$), $J_{H-H} = 7.31$ Hz); 5.63 (m, CH, allyl); 3.82 (m overlapping of doublets, 2 H_{anti}, 2 H_{syn}, allyl). A similar pattern was observed at −50 °C 7.34 [m, 36 H, overlap Ph (PPh_3) with *p*-H and *m*-H ($C\equiv CPh$)]; 6.62 (d, 4H, *o*-H ($C\equiv CPh$), $J_{H-H} = 7.2$ Hz); 5.65 (m, CH, allyl); 3.86 (d, 2 H_{anti}, $J_{anti} = 12.2$ Hz, allyl); 3.78 (d 2 H_{syn}, $J_{syn} = 6.14$ Hz, allyl). ^{31}P NMR ($CDCl_3$): at 15 °C 12.7, $^1J_{Pt-P} = 2652$ Hz. At −50 °C 12.7, $^1J_{Pt-P} = 2647$ Hz. ^{13}C NMR ($CDCl_3$): at −50 °C 134.0 (m, Ph, PPh_3, *o*-C); 131.8 (s, Ph), 131.1 (s, Ph); 129.2 (AXX′, $^1J_{C-P} + {}^3J_{C-P'} = 59.7$ Hz, Ph, PPh_3, *ipso*-C); 128.8 (s, Ph); 128.5 (t, $J_{P-C} = 5.3$ Hz, Ph, PPh_3, *m*-C); 128.0 (s, Ph), 123.9 (s, Ph, *ipso*-C); 113.1 (s, CH, allyl); 102.8 (AXX′, C_β, $-C_\alpha\equiv C_\beta Ph$, $^3J_{Ptrans-C} + {}^3J_{Pcis-C} = 30.6$ Hz); 84.7 (dd, C_α, $-C_\alpha\equiv C_\beta Ph$, $^2J_{Ptrans-C} = 134.6$ Hz, $^2J_{Pcis-C} = 18.8$ Hz); 76.5 (s, CH_2, allyl).

Data for **4b**: Anal. Calcd for $C_{51}H_{53}P_2ClO_4PtPd$: C, 54.26; H, 4.73. Found: C, 53.97; H, 4.72. Λ_M: 126 Ω^{-1} cm^2 mol^{-1}. IR (cm^{-1}): $\nu(C\equiv C)$ 2040 (w), 2020 (sh). ^1H NMR ($CDCl_3$): at 15 °C 7.30, 7.23 (m, 30 H, Ph); 5.5 (m, CH, allyl); 4.64 (d 2 H_{syn}, $J_{syn} = 6.2$ Hz, allyl); 3.34 (d 2 H_{anti}, $J_{anti} = 12.3$ Hz, allyl); 0.80 (s, 18 H, ^tBu). ^{31}P NMR ($CDCl_3$): at 15 °C 12.62, $^1J_{Pt-P} = 2671$ Hz. The same spectra patterns were observed at −50 °C. ^1H NMR ($CDCl_3$): 7.30 (m, 30 H, Ph); 5.46 (m, CH, allyl); 4.63 (d 2 H_{syn}, $J_{syn} = 6$ Hz, allyl); 3.35 (d 2 H_{anti}, $J_{anti} = 12.2$ Hz, allyl); 0.77 (s, 18 H, ^tBu). ^{31}P NMR ($CDCl_3$) 12.68, $^1J_{Pt-P}$

= 2659 Hz. ^{13}C NMR (CDCl$_3$): at −50 °C 134.0 (t, $J_{P-C} = 5.4$, Ph, *o*-C); 130.8 (s, Ph, *p*-C), 129.6 (AXX′, $^{1}J_{C-P}+{}^{3}J_{C-P'} = 59$ Hz, Ph, *ipso*-C); 128.3 (t, $J_{P-C} = 5.1$ Hz, Ph, *m*-C); 112.5 (AXX′, C_β, -C_α≡$C_\beta{}^t$Bu, $^{3}J_{Ptrans-C} + {}^{3}J_{Pcis-C} = 29.4$ Hz); 111.0 (s, CH, allyl); 75.6 (dd, C_α, -C_α≡$C_\beta{}^t$Bu, $^{2}J_{Ptrans-C} = 135.1$ Hz, $^{2}J_{Pcis-C} = 19.2$ Hz); 31.5 (s, -C(*C*H$_3$)$_3$); 29.9 (s, -*C*Me$_3$).

[*cis*-Pt(C≡CPh)$_2$(PPh$_3$)$_2$]. ^{13}C NMR (CDCl$_3$): at −50 °C 134.4 (t, *o*-C, $J_{P-C} = 5.6$, Ph, PPh$_3$); 131.3 (s, Ph), 131.4 (AXX′, *ipso*-C, $^{1}J_{C-P} + {}^{3}J_{C-P'} = 55.3$ Hz); 129.7 (s, Ph), 127.5 (t, $J_{P-C} = 5.2$ Hz, Ph, *m*-C); 126.7 (s, Ph, -C≡CPh); 124.6 (s, *ipso*-C,-Ph, -C≡CPh); 109.8 (AXX′, C_β, -C_α≡C_βPh, $^{3}J_{Ptrans-C} + {}^{3}J_{Pcis-C} = 34$ Hz); 102.6 (dd, C_α, -C_α≡C_βPh, $^{2}J_{Ptrans-C} = 149.9$ Hz, $^{2}J_{Pcis-C} = 21$ Hz).

[*cis*-Pt(C≡C^{t}Bu)$_2$(PPh$_3$)$_2$]. ^{13}C NMR (CDCl$_3$): at −50 °C 134.5 (t, *o*-C, $J_{P-C} = 5.6$, Ph); 132.2 (AXX′, $^{1}J_{C-P} + {}^{3}J_{C-P'} = 53.6$ Hz, Ph, *ipso*-C); 129.3 (s, Ph, *p*-C), 127.2 (t, $J_{P-C} = 5.3$ Hz, Ph, *m*-C); 117.1 (AXX′, C_β, -C_α≡$C_\beta{}^t$Bu, $^{3}J_{Ptrans-C} + {}^{3}J_{Pcis-C} = 33.9$ Hz, $^{2}J_{Pt-C} = 305$ Hz); 85.8 (dd, C_α, -C_α≡$C_\beta{}^t$Bu, $^{2}J_{Ptrans-C} = 152$ Hz, $^{2}J_{Pcis-C} = 21$ Hz, $^{1}J_{Pt-C} = 1132.5$ Hz); 31.2 (s, -C(*C*H$_3$)$_3$, $^{4}J_{Pt-C} = 7.7$ Hz); 29.87 (s, -*C*Me$_3$, $^{3}J_{Pt-C} = 21.2$ Hz).

X-ray Crystal Structure Determination of [*cis*-(PPh$_3$)$_2$Pt(μ,η^1:η^2-C≡C^{t}Bu)$_2$Pd(η^3-C$_3$H$_5$)](ClO$_4$) (4b). Suitable crystals of complex **4b** were obtained by slow diffusion of *n*-hexane over a concentrated solution of the complex in CH$_2$Cl$_2$. Diffraction data were collected on a Siemens/STOE-AED2 diffractometer with graphite-monochromated Mo K_α radiation and were corrected for Lorentz and polarization effects. SHELXTL-PLUS[24] crystallographic software package was used. A total of 8175 reflections were collected in the range of 4° < 2θ < 48° (*h*,*k*,*l*: 0 to 24, 0 to 18, −33 to 33) using $\omega-\theta$ scans. Absorption correction was based on ψ-scan solutions (maximum and minimum transmission factors: 0.4840 and 0.3574, respectively). The structure was solved by the Patterson method and refined with all atoms (except for disordered ClO$_4^-$ anion) with anisotropic displacement parameters. Hydrogen atoms were not included in the structural model. The highest peak on the final difference Fourier map corresponds to 0.93 e Å^{-3} (largest hole −1.27 e Å^{-3}).

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Supporting Information Available: Tables of refined cell constants with the most relevant data, anisotropic thermal parameters, atom positional parameters, and complete list of bond lengths and angles for **4b** (8 pages). Ordering information is given on any current masthead page.

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[24] SHELXTL-PLUS, Software Package for the Determination Crystal Structure, Release 4.0, Siemens Analytical X-Ray Instrument, Inc., Madison, WI, 1990.