

Ethynyltolan Platinum Complexes with (Arylalkynyl)phosphane Ligands

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The ethynyltolan mononuclear complexes *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(PPh₂C≡CR)₂] [R = tol (**2**), C₆H₄C≡CPh (**3**)], which contain (arylalkynyl)phosphane ligands, were prepared, and the X-ray molecular structure of **2** was determined. The reaction of **2** and **3** with *cis*-[Pt(C₆F₅)₂(thf)₂] (thf = tetrahydrofuran) in the appropriate molar ratio gave the dinuclear platinum derivatives *cis*-[{Pt(PPh₂C≡CR)₂(μ-η¹:η²-C^α,C^β-C≡CC₆H₄C≡CPh)₂]Pt(C₆F₅)₂] [R = tol (**4**), C₆H₄C≡CPh

(**5**)] and the trinuclear derivatives [{Pt(μ-η¹:η²-C^α,C^β-C≡CC₆H₄C≡CPh)₂(μ-1κP:2η²-C^α,C^β-PPh₂C≡CR)₂]Pt(C₆F₅)₂] [R = tol (**6**), C₆H₄C≡CPh (**7**)], which are stabilized by a double ethynyltolan bridging system or a mixed ethynyltolan/alkynylphosphane bridging system, respectively.

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Introduction

The ability of alkynylphosphanes (PPh₂C≡CR) to bind several metal centres through single P-complexation and/or π-coordination has been well documented.^[1–16] Furthermore, these ligands have revealed an interesting reactivity in transition-metal chemistry, such as insertion into reactive M–H or M–C bonds,^[17–25] intramolecular coupling reactions^[10,26–29] or P–C bond cleavage to afford alkynide (C≡CR) and phosphide (PPh₂) fragments,^[6,12,30–35] which are often involved in subsequent coupling or insertion reactions.^[36–39] In addition, simple P-coordination of alkynylphosphanes polarizes the electron density of the alkyne function by concentrating it on the C^α atom, which favours its interaction with electrophilic and nucleophilic substrates such as water,^[40,41] ethanol,^[42,43] HX,^[44–46] PPh₂H^[47] or amines.^[7,48] PPh₂C≡C–X–C≡CR ligands are able to offer higher coordination and reactivity possibilities due to the extension of the delocalised π-system. However, they have only been used as precursors of polymetallic complexes^[10,15,49–52] and in P–C bond activation or intramolecular coupling reactions^[51,53–55] on a few occasions.

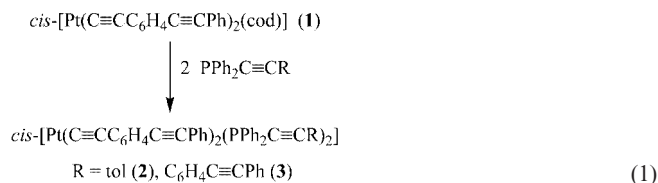
With the aim of exploring the η²-bonding capability of two P-coordinated diphenylphosphane ligands towards a second metal centre as a way of inducing alkyne coupling, we have previously studied the reactivity of *cis*-[MX₂(PPh₂C≡CR)₂] (M = Pd, Pt; X = Cl,^[2] C₆F₅,^[4,8,11] C≡CR';^[3] R = Ph, tol, *t*Bu; R' = Ph, *t*Bu) towards the solvate complex *cis*-[Pt(C₆F₅)₂(thf)₂] (thf = tetrahydrofuran). When X is a C₆F₅ group with a low tendency to

form bridges, the η²-alkyne adducts [{Pt(C₆F₅)₂(μ-κP:η²-PPh₂C≡CR)₂] {Pt(C₆F₅)₂} (R = Ph, tol), which are generated at low temperature, evolve through an unexpectedly easy sequential insertion of both PPh₂C≡CR molecules into a Pt–C₆F₅ bond to form unusual μ-2,3-bis(diphenylphosphanyl)-1,3-butadien-1-yl dinuclear complexes.^[4,8] However, when X is a group with a greater tendency to act as a bridging ligand (X = Cl, C≡CR') these groups compete with the η²-bonding capacity of the PPh₂C≡CR group to coordinate the “Pt(C₆F₅)₂” fragment and only poly-metallic species with X or mixed X/PPh₂C≡CR bridging systems are obtained.^[2,3] In particular, several homo- and heterodimetallic complexes stabilized by double alkynyl bridging systems, such as *cis*-[{Pt(PPh₂C≡CR)₂(μ-η¹:η²-C≡CR')₂]Pt(C₆F₅)₂], and unusual symmetrical *cis*-[{Pt(PPh₂C≡C*t*Bu)₂(μ₃-η²-C≡CPh)₂] {Pt(C₆F₅)₂}₂] and *cis*-[{Pt(μ-κP:η²-PPh₂C≡CR)₂(μ-η²-C≡C*t*Bu)₂] {Pt(C₆F₅)₂}₂] trimetallic species, have been isolated with the mononuclear alkynylplatinum complexes *cis*-[Pt(C≡CR')₂(PPh₂C≡CR)₂] (R', R = Ph, *t*Bu) using 1:1 or 1:2 molar ratios, respectively, thereby indicating the following order of bonding capability: C≡CR' > P-bonded PPh₂C≡CR and C≡CPh > C≡C*t*Bu fragments.^[3] As an extension of this work to ethynyltolan systems {when referring to ethynyltolan as ligand, its deprotonated anion [(phenylethynyl)phenyl]ethynide is meant}, we report here the preparation and characterisation of the neutral complexes *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(PPh₂C≡CR)₂] [R = tol (**2**), C₆H₄C≡CPh (**3**)], which are stabilized by (arylalkynyl)phosphanes. Furthermore, to gain more insight into the synthetic possibilities of the ethynyltolan and (arylalkynyl)phosphane ligands, especially a comparison of the reactivity of inner and outer alkynyl functions, we have investigated the reactivity of these complexes towards *cis*-[Pt(C₆F₅)₂(thf)₂].

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Results and Discussion

The precursor derivative *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(cod)] (**1**) was obtained using a similar procedure to that used for related *cis*-[Pt(C≡CR)₂(cod)] (R = Ph,^[56] *t*Bu^[57]) derivatives. Thus, the reaction of an ethanolic suspension of [PtCl₂(cod)] at low temperature (−30 °C) with HC≡CC₆H₄C≡CPh (2 equiv.) in a solution of NaOEt (3.7 equiv.), prepared “in situ” from a solution of Na in absolute EtOH, yielded **1** as a white solid in low yield (32%). Treatment of **1** with 2 equiv. of the appropriate (arylalkynyl)phosphane (PPh₂C≡Ctol, PPh₂C≡CC₆H₄C≡CPh) easily led to the displacement of the cod ligand and afforded the disubstituted products *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(PPh₂C≡CR)₂] [R = tol (**2**), C₆H₄C≡CPh (**3**); Equation (1)]. These complexes were isolated as orange-brown solids, and their spectroscopic data (see Experimental Section) unequivocally confirmed the P-coordination mode of the PPh₂C≡CR ligands.



The IR spectra of **2** and **3** show two strong $\nu(\text{C}\equiv\text{C})$ bands: the high-frequency band [2171 cm^{−1} (**2**, **3**)] located at slightly higher wavenumbers than that in the corresponding free (arylalkynyl)phosphane is attributed to the $\nu(\text{C}\equiv\text{C})$ stretch of the phosphane ligands, whereas the low-frequency band [2121 (**2**) and 2120 cm^{−1} (**3**)] is assigned to the inner C^α≡C^β fragment of the ethynyltolan ligand. According to this assignment, the precursor derivative *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(cod)] (**1**) shows a medium-intensity band at 2119 cm^{−1}. All complexes **1–3** also show a very weak high-frequency band (2214 cm^{−1}), assigned to the outer C⁵≡C⁶ alkyne group of the ethynyltolan ligand [see the Experimental Section (Figure 3) for the labelling scheme]. The phosphorus resonance in complexes **2** and **3** appears as a singlet that is shifted downfield with respect to the corresponding free ligands [δ = −6.53 (**2**) and −6.27 ppm (**3**) vs. −33.42 (PPh₂C≡Ctol) and −33.27 ppm (PPh₂C≡CC₆H₄C≡CPh)], with platinum coupling constants [2350 (**2**) and 2343 Hz (**3**)] comparable to those reported for mononuclear complexes having a tertiary phosphane group *trans* to a terminal alkyne group.^[3,58] The ¹³C{¹H} NMR spectra are particularly significant. The acetylenic carbon resonances for the (arylalkynyl)phosphane ligands of both complexes can clearly be seen and their assignment is mainly based on the $J_{\text{C,P}}$ coupling constants observed and also by comparison with the corresponding signals in the starting precursor **1** [δ = 96.9 (C^α), 107.8 (C^β), 90.1, 89.4 (C^{5,6}) ppm; see Figure 3 for assignments]. The alkynylphosphane C^{α'} resonances are found as an apparent doublet at lower frequencies than those of the C^{β'} atoms, which are found as the A part of an AXX' sys-

tem [C^{α'}: δ = 80.1 (**2**) and 82.7 ppm (**3**); C^{β'}: δ = 108.6 (**2**) and 107.4 ppm (**3**)]. The coupling constants [$^1J_{\text{C}\alpha',\text{P}}$ + $^3J_{\text{C}\alpha',\text{P}}$] [103.4 (**2**) and 100.2 Hz (**3**)] and [$^2J_{\text{C}\beta',\text{P}}$ + $^4J_{\text{C}\beta',\text{P}}$] [15.1 (**2**) and 14.8 Hz (**3**)] could also be calculated. The C^α and C^β alkynyl resonances also appear as the A part of an AXX' system, with C^α [δ = 105.2 (**2**) and 104.5 ppm (**3**)] appearing as a doublet of doublets [$^2J_{\text{C}\alpha,\text{Ptrans}}$ + $^2J_{\text{C}\alpha,\text{Pcis}}$] = 155.1 (**2**) and 156.2 Hz (**3**) and C^β as a three-line pattern [δ = 109.3 ($^3J_{\text{C}\beta,\text{Ptrans}}$ + $^3J_{\text{C}\beta,\text{Pcis}}$) = 37.6 Hz; **2**) and 109.4 ($^3J_{\text{C}\beta,\text{Ptrans}}$ + $^3J_{\text{C}\beta,\text{Pcis}}$) = 36.4 Hz; **3**) ppm]. The acetylene carbon atoms of the outer fragments [C⁵/C⁶ (**2**) and C^{5,5'}/C^{6,6'} (**3**)] appear as sharp singlets [δ = 89.9, 89.4 (**2**) and 92.2, 89.8, 89.4, 88.3 ppm (**3**)] and were assigned by comparison to these signals in the precursor derivative [δ = 90.1, 89.4 ppm (**1**)]. The alkynylphosphane C^{α'} resonances are shifted upfield in both complexes with respect to those of free PPh₂C≡CR, whereas the C^{β'} carbon resonances are very close to those of the free ligands [$\delta(\text{C}\alpha'/\text{C}\beta')$ = 84.6/107.9 (PPh₂C≡Ctol), 89.2/107.4 (PPh₂C≡CC₆H₄C≡CPh) ppm]. As a consequence, the resulting chemical shift difference (Δ = $\delta\text{C}\beta' - \delta\text{C}\alpha'$), which can be related to the triple-bond polarisation,^[9,13,59,60] is similar in both complexes [Δ = 28.5 (**2**) and 24.7 ppm (**3**)].

An X-ray diffraction study confirmed that **2** (Figure 1) is a slightly distorted square-planar Pt^{II} complex formed by two mutually *cis*-arranged ethynyltolan (C≡CC₆H₄C≡CPh) and (tolylethynyl)phosphane (PPh₂C≡Ctol) ligands. Selected bond lengths and angles are given in Table 1 and crystallographic data in the Experimental Section. Chemically equivalent Pt–C [2.017(4), 2.007(4) Å] and C≡C {1.196(6) and 1.204(6) Å [(tolylethynyl)phosphane groups]; 1.185(6), 1.198(6) and 1.194(6), 1.195(6) Å (ethynyltolan ligands)} bond lengths are identical within experimental error, while the Pt–P bond lengths differ only slightly [2.2792(11), 2.2919(11) Å]. The inner Pt–C^α–C^β/C^α–C^β–C(C₆H₄) [171.9(4)/176.9(5), 173.0(4)/176.5(5)°] and outer acetylenic fragments C(C₆H₄)–C⁵–C⁶/C⁵–C⁶–C(Ph) [175.5(5)/176.9(5), 178.8(6)/177.0(6)°] of the ethynyltolan ligands and the alkynyl moiety in the phosphane fragments P–C^{α'}–C^{β'}/C^{α'}–C^{β'}–C(C₆H₄) [171.2(4)/175.7(5), 173.6(4)/177.6(5)°] do not deviate significantly from linearity. These values are unexceptional and similar to those found in other X-ray crystallographically characterised mononuclear P-coordinated alkynylphosphane^[8,10,14,15,26,27,61,62] or σ -alkynylplatinum^[63–78] complexes. The C₆H₄ group and the phenyl rings on each ethynyltolan ligand are nearly coplanar [dihedral angles: 2.89(15) and 10.81(17)°], which suggests strong π -delocalisation. However, both ethynyltolan ligands are essentially perpendicular to each other [92.18(17), 91.16(20)°]. The two PPh₂C≡Ctol units in this complex exhibit a *cisoidal* arrangement with a dihedral angle between the planes formed by both equivalent Pt–P–C^α atoms [Pt(1)–P(1)–C(33) and Pt(1)–P(2)–C(54)] of 51.90(15)°, which leads to a separation between both α -carbon atoms of only 3.1169(72) Å. Carty et al. have suggested a relationship between the ease of intramolecular coupling of the uncoordinated alkyne triple bonds in P-coordinated alkynylphosphane ligands and the proximity of the α -car-

bon atoms of the proximal alkyne units (less than 3.4 Å, twice the van der Waals radius of the carbon atom).^[27] In fact, we have recently shown that compounds *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)₂] (R = Ph, tol) with “crossed” linear alkynyl moieties and a C^α–C^α separation of 3.20(2) Å (Ph) or 3.34(2) Å (tol) evolve thermally into naphthalene-based bis(diphenylphosphane) complexes^[62] *cis*-[Pt(C₆F₅)₂-{C₁₀H₅-1-Ph-2,3-κPP'(PPh₂)₂}] and *cis*-[Pt(C₆F₅)₂{7-CH₃-C₁₀H₄-1-tol-2,3-κPP'(PPh₂)₂}] by intramolecular [2+2+2] coupling of two adjacent PPh₂C≡CR ligands, in a similar manner to that previously observed by Carty et al. for related dichloridoplatinum(II) derivatives.^[27] Similar naphthalene species can also be generated starting from the diynyl systems *cis*-[Pt(C₆F₅)₂(PPh₂C≡CC₆H₄C≡CR)₂] (R = Ph, *t*Bu), but only by photolysis. In contrast, photolysis of the monoalkynyl complexes *cis*-[Pt(C₆F₅)₂(PPh₂C≡CR)₂] (R = Ph, tol) proceeds with parallel formation of naphthalene species and the new chelating diphosphane complexes *cis*-[Pt(C₆F₅)₂{PPh₂C(Ph)=C(R)PPh(C≡CR)}] (R = Ph, tol).^[62] However, in contrast to this behaviour, complex **2**, which exhibits a very short separation between the alkynyl fragments, shows no evidence of coupling either under thermal (4 h at about 225 °C) or photochemical conditions (irradiation of a toluene solution for 90 min at room temperature using a 400-W Hg lamp).

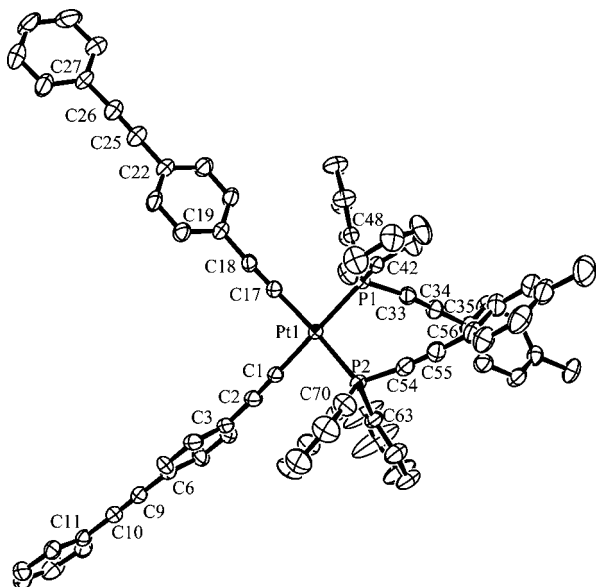


Figure 1. Molecular structure of *cis*-[Pt(C≡CC₆H₄C≡CPh)₂-(PPh₂C≡Ctol)₂] (**2**). Ellipsoids are drawn at the 50% probability level. Hydrogen atoms have been omitted for clarity.

To compare the coordination possibilities of the ethynylnol ligand and the alkyne function of the P-coordinated (arylalkynyl)phosphane ligands, we studied the reactions of **2** and **3** with *cis*-[Pt(C₆F₅)₂(thf)₂]. The results are shown in Scheme 1. Treatment of *cis*-[Pt(C≡CC₆H₄C≡CPh)₂-(PPh₂C≡CR)₂] [R = tol (**2**), C₆H₄C≡CPh (**3**)] with 1 equiv. of *cis*-[Pt(C₆F₅)₂(thf)₂] in CH₂Cl₂ at room temperature afforded the corresponding dinuclear derivatives *cis*-[Pt(PPh₂C≡CR)₂(μ-η¹:η²-C^α,C^β-C≡CC₆H₄C≡CPh)₂]Pt-

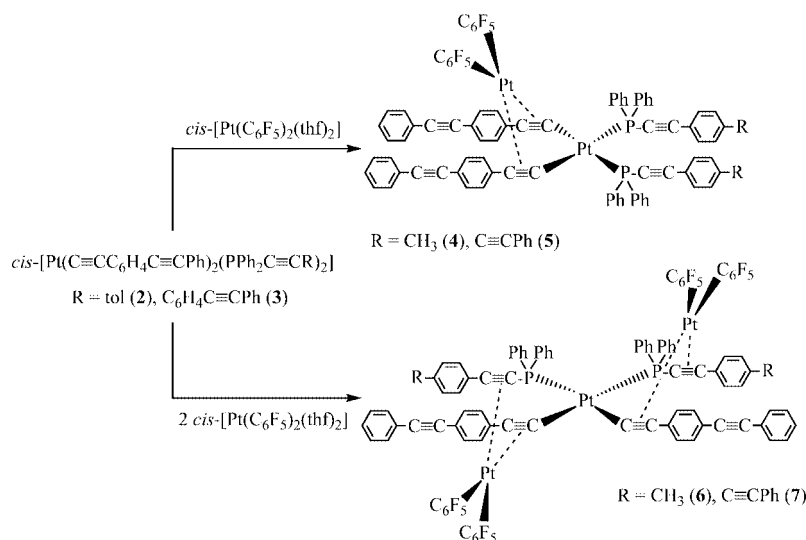
Table 1. Selected bond lengths [Å] and angles [°] for *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(PPh₂C≡Ctol)₂]-C₆H₆ (**2**·C₆H₆).

Pt(1)–C(1)	2.017(4)	C(1)–C(2)	1.185(6)
Pt(1)–C(17)	2.007(4)	C(9)–C(10)	1.198(6)
Pt(1)–P(1)	2.2792(11)	C(17)–C(18)	1.194(6)
Pt(1)–P(2)	2.2919(11)	C(25)–C(26)	1.195(6)
P(1)–C(33)	1.759(5)	C(33)–C(34)	1.196(6)
P(2)–C(54)	1.764(5)	C(54)–C(55)	1.204(6)
C(1)–Pt(1)–C(17)	89.55(17)	Pt(1)–C(17)–C(18)	173.0(4)
C(1)–Pt(1)–P(2)	88.36(12)	C(17)–C(18)–C(19)	176.5(5)
C(17)–Pt(1)–P(1)	88.34(12)	C(22)–C(25)–C(26)	178.8(6)
P(1)–Pt(1)–P(2)	95.30(4)	C(25)–C(26)–C(27)	177.0(6)
Pt(1)–C(1)–C(2)	171.9(4)	P(1)–C(33)–C(34)	171.2(4)
C(1)–C(2)–C(3)	176.9(5)	C(33)–C(34)–C(35)	175.7(5)
C(6)–C(9)–C(10)	175.5(5)	P(2)–C(54)–C(55)	173.6(4)
C(9)–C(10)–C(11)	176.9(5)	C(54)–C(55)–C(56)	177.6(5)

(C₆F₅)₂] [R = tol (**4**), C₆H₄C≡CPh (**5**)] by η²-complexation of the “*cis*-Pt(C₆F₅)₂” fragment with both [*para*-(*para*-phenylethynyl)phenyl]alkynyl ligands. This result was not unexpected and confirms previous observations of the stronger preference of the hard Pt^{II} centre towards platinaalkynyl entities rather than alkynylphosphane groups.^[3,11] However, similar reactions of **2** and **3** with 2 equiv. of *cis*-[Pt(C₆F₅)₂-(thf)₂] in CH₂Cl₂ yielded the trinuclear derivatives *cis*-[{Pt(μ-η¹:η²-C^α,C^β-C≡CC₆H₄C≡CPh)₂(μ-1κP:2η²-C^α,C^β-PPh₂C≡CR)₂}]₂[Pt(C₆F₅)₂]₂] [R = tol (**6**), C₆H₄C≡CPh (**7**)] in which the mononuclear precursors act as symmetrical mixed bis(*cis*-η²:κP:η²)-chelating tetrahapto ligands of the two “*cis*-Pt(C₆F₅)₂” units by binding through both an ethynylnol group (μ-η²-C≡CC₆H₄C≡CPh) and the alkyne function of the corresponding (arylethynyl)phosphane ligand (μ-κP:η², inner for **7**).

Although all attempts to obtain crystals of complexes **4**–**7** have proved fruitless so far, their spectroscopic data (see Experimental Section) are in accordance with the formulation shown in Scheme 1. Thus, complexes **4** and **5** show one strong ν(C≡C) absorption at 2173 (**4**) and 2172 cm^{−1} (**5**), which confirms that the alkynyl units of the PPh₂C≡CR ligands remain uncoordinated. The expected ν(C≡C) absorptions at lower frequencies, assignable to the bridging Pt(μ-C≡CR)₂Pt entity, are not observed, although this structural feature has been found previously in other alkynyl-bridged complexes.^[57] However, both complexes show an additional very weak ν(C≡C) absorption (2216 cm^{−1}) that is clearly due to the outer C⁵≡C⁶ alkyne entity of these bridging alkynyl groups. The trinuclear derivatives **6** and **7** show two high-frequency bands [one sharp at 2174 (**6**) and 2173 cm^{−1} (**7**) and one very weak at 2214 (**6**) and 2216 cm^{−1} (**7**)] corresponding to uncoordinated alkyne units and weak bands [2019 (**6**) and 2020, 1991 cm^{−1} (**7**)] assignable to the ν(C≡C) moiety of the η²-coordinated groups.

The equivalent phosphorus atoms of the terminal alkynylphosphane ligands in the dinuclear derivatives **4** and **5** appear in the ³¹P{¹H} NMR spectra at lower frequencies [δ = −11.20 (**4**) and −10.88 ppm (**5**)] than those in the precursors [δ = −6.53 (**2**) and −6.27 ppm (**3**)]. This high-field shift is similar to that previously observed for related dinuclear



Scheme 1. Synthesis of complexes 4–7.

derivatives $\text{cis-[Pt(PPh}_2\text{C}\equiv\text{CR)}_2(\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{CR}')_2]\text{Pt(C}_6\text{F}_5)_2]$ ^[3] and, therefore, is in keeping with the η^2 -coordination of the “ $\text{cis-Pt(C}_6\text{F}_5)_2$ ” fragment to the ethynyltolan ligands. The magnitude of $^1J_{\text{P,Pt}}$ [2682 (4) and 2677 Hz (5)] is slightly larger than that in the corresponding mononuclear derivatives with terminal ethynyltolan groups [2350 (2) and 2343 Hz (3)] due to the smaller *trans* influence of the bridging ethynyltolan ligands. In accordance with the presence of bridging four-electron (arylalkynyl)phosphane ($\mu\text{-}\kappa\text{P}:\eta^2$) ligands in trinuclear complexes 6 and 7, both complexes show a considerable downfield shift of the phosphorus resonance [$\delta = 0.19$ (6) and 0.43 ppm (7)] with respect to those observed in the mononuclear precursors [$\delta = -6.53$ (2) and -6.27 ppm (3)] and even the dinuclear derivatives, in which the $\text{PPh}_2\text{C}\equiv\text{CR}$ molecules act only as P-donor ligands [$\delta = -11.20$ (4) and -10.88 ppm (5)]. The platinum-phosphorus coupling constants [2514 (6) and 2516 Hz (7)] are slightly larger than those observed for the starting precursors [2350 (2) and 2343 Hz (3)] but somewhat smaller than those of the dinuclear complexes [2682 Hz (4) and 2677 Hz (5)]. It should be noted that the reaction of $\text{cis-[Pt(C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh)}_2(\text{PPh}_2\text{C}\equiv\text{CR})_2]$ [$\text{R} = \text{tol}$ (2), $\text{C}_6\text{H}_4\text{C}\equiv\text{CPh}$ (3)] with 2 equiv. of $\text{cis-[Pt(C}_6\text{F}_5)_2(\text{thf})_2]$ could have taken place with formation of $\text{cis-[Pt(PPh}_2\text{C}\equiv\text{CR)}_2(\mu_3\text{-}\eta^2\text{-C}^\alpha, \text{C}^\beta\text{-C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh)}_2]\text{[Pt(C}_6\text{F}_5)_2]_2}$, where the phosphane ligands act as terminal groups and both ethynyltolan fragments act as five-electron $\mu_3\text{-}\eta^2$ bridging ligands. However, the chemical shift and coupling constant found in the related trinuclear complex $\text{cis-[Pt(PPh}_2\text{C}\equiv\text{C}t\text{Bu)}_2(\mu_3\text{-}\eta^2\text{-C}\equiv\text{CPh)}_2]\text{[Pt(C}_6\text{F}_5)_2]_2}$ [$\delta = -20.55$ ppm ($^1J_{\text{P,Pt}} = 3008$ Hz)]^[3] are clearly different to those observed in the trinuclear derivatives 6 and 7, with the latter being very close to those found in the symmetric isomers $\text{cis-[Pt(}\mu\text{-}\eta^1\text{:}\eta^2\text{-C}\equiv\text{C}t\text{Bu)}_2(\mu\text{-}\kappa\text{P}:\eta^2\text{-PPh}_2\text{C}\equiv\text{CR)}_2]\text{[Pt(C}_6\text{F}_5)_2]_2}$ [$\delta = 0.67$ to -1.96 ppm ($^1J_{\text{P,Pt}} = 2488\text{--}2501$ Hz)]^[3]. These results indicate that, while the phenylethynyl groups in $[\text{Pt}](\text{C}\equiv\text{CPh})_2$ derivatives use both orthogonal π -acetylenic bonds in the formation of $[\text{Pt}](\mu_3\text{-}$

$\eta^2\text{-C}\equiv\text{CPh})_2]\text{[Pt(C}_6\text{F}_5)_2]_2$, the related ethynyltolan fragments in $[\text{Pt}](\text{C}\equiv\text{CC}_6\text{H}_4\text{C}\equiv\text{CPh})_2$ precursors 2, 3 only employ one in the formation of complexes 6 and 7, thereby suggesting the lower bonding capability of these latter groups.

The variable-temperature ^{19}F NMR spectra of dinuclear complexes 4 and 5 indicate a temperature dependence of the spectral pattern. To illustrate this, the temperature dependence of the ^{19}F NMR spectrum of 5 in CDCl_3 is shown in Figure 2. As can be observed, the limiting low-temperature spectrum is compatible with a static structure. This pattern of five distinct signals (1:1:1:1:1) confirms that both C_6F_5 groups are rigid on the NMR timescale and equivalent. Upon raising the temperature, the two *o*-F doublets and the two *m*-F multiplets coalesce (above 273 K for *o*-F and 268 K for *m*-F) to only one *o*-F doublet and one *m*-F multiplet resonance. The approximate calculated activation energy is similar for the *ortho*-fluorine ($\Delta G^\ddagger_{273\text{K}} = 50.01$ kJ mol^{−1}) and for the *meta*-fluorine atoms ($\Delta G^\ddagger_{268\text{K}} = 50.63$ kJ mol^{−1}). The equivalence of the *o*-F atoms (and the *m*-F ones as well) at high temperature can be explained either by assuming a rapid rotation of the C_6F_5 groups around the Pt–C bonds, as previously suggested in other systems with “ $\text{cis-Pt(C}_6\text{F}_5)_2$ ” fragments,^[79–83] or by a fast intramolecular exchange of the “ $\text{cis-Pt(C}_6\text{F}_5)_2$ ” unit below and above the platinum coordination plane. This second possibility has been suggested in related derivatives^[3,57,84] stabilized by a double alkynyl bridging system and assumes the existence of a formal inversion of the PtC_4Pt central skeleton, which could take place via intermediate species with one or two $\mu\text{-}\eta^1$ -bonded alkynyl ligands.^[85] However, we note that in these complexes (4, 5) an exchange mechanism involving the inner alkynyl moieties of the (arylalkynyl)phosphane ligands cannot be discarded. The trinuclear derivatives 6 and 7 show a pattern that is consistent with two inequivalent C_6F_5 rings in which both halves are equivalent at room temperature. The two *ortho*-fluorine resonances are broad at this temperature but, unfortunately,

their extremely low stability in solution, even at low temperature, has prevented us from obtaining the corresponding clean variable-temperature ^{19}F NMR spectra.

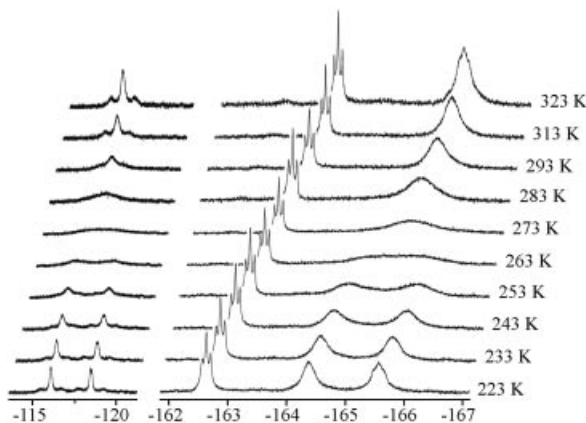


Figure 2. Variable-temperature ^{19}F NMR spectra (chemical shifts in ppm) of *cis*-[Pt(PPh₂C≡CC₆H₄C≡CPh)₂(μ-η¹:η²-C^α,C^β-C≡CC₆H₄C≡CPh)₂]Pt(C₆F₅)₂ (**5**) in CDCl₃.

Conclusion

We have reported the formation of novel (μ-C≡CC₆H₄C≡CPh)₂ (**4**, **5**) and mixed [μ-(C≡CC₆H₄C≡CPh)/μ-(PPh₂C≡CR)] (**6**, **7**) bridging di- and triplatinum complexes. In particular, the synthesis of **6** and **7**, which are stabilized by a mixed bridging system, from **2** and **3** with 2 equiv. of *cis*-[Pt(C₆F₅)₂(thf)₂] instead of the isomeric *cis*-[Pt(PPh₂C≡CR)₂(μ₃-η²-C^α,C^β-C≡CC₆H₄C≡CPh)₂]{Pt(C₆F₅)₂}₂ is remarkable. We have previously shown^[3] that C≡CPh groups are able to act as five-electron donors (μ₃-η²-C^α,C^β-C≡CPh) towards “*cis*-[Pt(C₆F₅)₂]⁺”, thus suggesting that these groups present a stronger η² capability than the more unsaturated C≡CC₆H₄C≡CPh ligands.

Experimental Section

General Remarks: All reactions were carried out under N₂ using dried solvents purified by known procedures and distilled prior to use. IR spectra were recorded with a Perkin–Elmer FT-IR 1000 spectrometer as Nujol mulls between polyethylene sheets and NMR spectra were recorded with a Bruker ARX 300 spectrometer. Chemical shifts are reported in ppm relative to external standards (SiMe₄, CFCl₃ and 85% H₃PO₄). Elemental analyses were carried out with a Perkin–Elmer 2400 CHNS/O microanalyzer and mass spectra were recorded with a VG Autospec spectrometer (FAB⁺) or a Microflex MALDI-TOF Bruker spectrometer operating in the linear and reflector modes using dithranol as the matrix. HC≡CC₆H₄C≡CPh,^[86] PPh₂C≡Ctol,^[87] PPh₂C≡CC₆H₄C≡CPh^[13] and *cis*-[Pt(C₆F₅)(thf)₂]^[88] were prepared according to published procedures. Figure 3 shows the labelling scheme for the carbon atoms in the ethynyltolan ligand and in the (ethynyltolan)diphenylphosphane ligand.

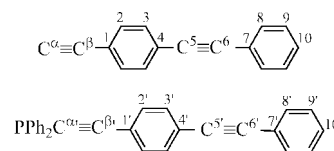


Figure 3. Labelling scheme for the carbon atoms in the ethynyltolan and (ethynyltolan)diphenylphosphane ligand.

Synthesis of *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(cod)] (1**):** A freshly prepared mixture of HC≡CC₆H₄C≡CPh (432 mg, 2.138 mmol) and sodium ethoxide (prepared from 84 mg of sodium and 20 mL of ethanol) was added dropwise, with constant stirring, to a suspension of [PtCl₂(cod)] (400 mg, 1.069 mmol) in deoxygenated ethanol (10 mL) at −30 °C. After stirring at low temperature for 1 h, the resulting white solid was filtered and washed with successive portions of water (2 × 5 mL) and acetone (2 × 5 mL). Yield: 242 mg (32%). C₄₀H₃₀Pt (705.8): calcd. C 68.07, H 4.28; found C 68.42, H 3.98. IR (Nujol): $\tilde{\nu}$ = 2214 (vw), 2119 (m) (C≡C) cm^{−1}. ^1H NMR (300.1 MHz, CDCl₃, 20 °C): δ = 7.50 (m), 7.38 (m), 7.32 (m) (18 H, C₆H₄, Ph), 5.70 (s, $J_{\text{Pt,H}}$ = 43 Hz, 4 H, =CH, cod), 2.58 (s, 8 H, CH₂, cod) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl₃, 20 °C): δ = 131.5 (s), 131.2 (s), 130.8 (s), 128.0 (s, C^{2,3,8,9}), 127.9 (d, J = 16 Hz, C¹⁰), 126.2 (s), 123.1 (s), 120.8 (s, C^{1,4,7}), 107.8 (s, $^2J_{\text{C,Pt}}$ ≈ 370 Hz, C^β), 104.3 (s, $J_{\text{C,Pt}}$ = 80 Hz, =CH, cod), 96.9 (s, C^α), 90.1 (s), 89.4 (s, C^{5,6}) ppm. ES (+, ionized with Na⁺) MS: m/z (%) = 727 (38) [M^+ + Na − H].

Synthesis of *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(PPh₂C≡Ctol)₂] (2**):** PPh₂C≡Ctol (189 mg, 0.630 mmol) was added to a solution of *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(cod)] (**1**; 222 mg, 0.315 mmol) in CH₂Cl₂ (10 mL) to give an orange solution. After stirring for 1 h, the resulting solution was concentrated to a small volume, and addition of ethanol (5 mL) gave **2** as an orange-brown solid. Yield: 220 mg (58%). C₇₄H₅₂P₂Pt (1198.27): calcd. C 74.18, H 4.37; found C 73.83, H 3.98. IR (Nujol): $\tilde{\nu}$ = 2214 (w), 2171 (s), 2121 (s) (C≡C) cm^{−1}. ^1H NMR (300.1 MHz, CDCl₃, 20 °C): δ = 7.83 (m, 8 H), 7.46 (m, 6 H), 7.28 (m) (16 H, aromatics), 7.20 (d, $J_{\text{H,H}}$ = 8.05 Hz, 4 H, C₆H₄), 6.97 (d, $J_{\text{H,H}}$ = 7.65 Hz, 4 H, C₆H₄), 6.88 (d, $J_{\text{H,H}}$ = 7.87 Hz, 4 H, C₆H₄), 6.84 (d, $J_{\text{H,H}}$ = 7.95 Hz, 4 H, C₆H₄), 2.33 (s, 6 H, CH₃) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl₃, 20 °C): δ = 140.0 (s, C⁴, tol), 133.3 (AXX', $^{1+3}J_{\text{C,P}}$ = 12.6 Hz, *o*-C, PPh₂), 131.7 (s), 131.2 (s), 130.2 (s), 128.5 (s), 127.9 (s), 128.0–127.8, 127.5, 123.4 (s), 119.4 (s), 117.6 (s) (aromatics), 109.3 (AXX', $^3J_{\text{C,Ptrans}}$ + $^3J_{\text{C,Pcis}}$ = 37.6 Hz, C^β, =C^βC₆H₄C≡CPh), 108.6 (AXX', $^2J_{\text{C,P}}$ + $^4J_{\text{C,P}}$ = 15.1 Hz, C^{β'}, =C^{β'}tol), 105.2 (dd, AXX', $^2J_{\text{C,Ptrans}}$ + $^2J_{\text{C,Pcis}}$ = 155.1 Hz, C^α, C^{α'}), 89.9 (s), 89.4 (s, C^{5,6}), 80.1 (d, AXX', $^1J_{\text{C,P}}$ + $^3J_{\text{C,P}}$ = 103.4 Hz, C^{α'}, PC^{α'}=), 21.3 (s, CH₃) ppm. $^{31}\text{P}\{^1\text{H}\}$ NMR (121.5 MHz, CDCl₃, 20 °C): δ = −6.53 (s, $^1J_{\text{P,Pt}}$ = 2350 Hz) ppm. FAB(+) MS: m/z (%) = 1198 (8) [M^+].

Synthesis of *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(PPh₂C≡CC₆H₄C≡CPh)₂] (3**):** Complex **3** was synthesised as an orange product according to a procedure similar to **2** but with *cis*-[Pt(C≡CC₆H₄C≡CPh)₂(cod)] (**1**; 186 mg, 0.265 mmol) and PPh₂C≡CC₆H₄C≡CPh (204 mg, 0.528 mmol). Yield: 227 mg (63%). C₈₈H₅₆P₂Pt (1370.4): calcd. C 77.12, H 4.12; found C 76.92, H 3.80. IR (Nujol): $\tilde{\nu}$ = 2214 (w), 2171 (m), 2120 (s) (C≡C) cm^{−1}. ^1H NMR (300.1 MHz, CDCl₃, 20 °C): δ = 7.85 (m, 8 H), 7.51 (m, 12 H), 7.39–7.19 (m) (28 H, aromatics), 6.93 (d, $J_{\text{H,H}}$ = 8.05 Hz, 4 H, C₆H₄), 6.84 (d, $J_{\text{H,H}}$ = 8.05 Hz, 4 H, C₆H₄) ppm. $^{13}\text{C}\{^1\text{H}\}$ NMR (75.5 MHz, CDCl₃, 20 °C): δ = 133.4 (AXX', $^{1+3}J_{\text{C,P}}$ = 12.4 Hz, *o*-C, PPh₂), 131.7 (s), 131.4 (s), 131.24 (s), 131.2 (s), 131.0 (s), 130.5 (s), 130.3 (s, *p*-C, PPh₂), 128.2 (s), 128.11 (d, J = 64 Hz, *i*-C, PPh₂), 128.1 (s), 128.0 (s), 127.99 (s), 124.7 (s), 123.3 (s), 122.3 (s), 119.9 (s), 119.4 (s)

(aromatics), 109.4 (AXX' , three-line pattern, $^3J_{C,P,trans} + ^3J_{C,P,cis} = 36.4$ Hz, $C^{\beta} = C^{\beta}C_6H_4C \equiv CPh$), 107.4 (AXX' , $^2J_{C,P} + ^4J_{C,P} = 14.8$ Hz, $C^{\beta'} = C^{\beta'}C_6H_4C \equiv CPh$), 104.5 (dd, AXX' , $^2J_{C,P,trans} + ^2J_{C,P,cis} = 156.2$ Hz, C^{α} , $C^{\alpha} \equiv$), 92.2 (s), 89.8 (s), 89.4 (s), 88.3 ($C^{5,5',6,6'}$), 82.7 (d, AXX' , $^1J_{C,P} + ^3J_{C,P} = 100.2$ Hz, $C^{\alpha'}$, $PC^{\alpha'} \equiv$) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = -6.27$ (s, $^1J_{P,Pt} = 2343$ Hz) ppm. MALDI-TOF(+) MS: m/z (%) = 1355 (100) [$M^+ - CH_3$], 967 (80) [$Pt(PPh_2C \equiv CC_6H_4C \equiv CPh)_2^+$].

Synthesis of cis -[Pt($PPh_2C \equiv Ctol$) $_2(\mu-\eta^1:\eta^2-C^{\alpha},C^{\beta}-C \equiv CC_6H_4C \equiv CPh)_2$]Pt(C_6F_5) $_2$] (4): cis -[Pt(C_6F_5) $_2$ (thf) $_2$] (59 mg, 0.088 mmol) was added to an orange solution of cis -[Pt($C \equiv CC_6H_4C \equiv CPh$) $_2$ ($PPh_2C \equiv Ctol$) $_2$] (2; 105 mg, 0.088 mmol) in CH_2Cl_2 (15 mL). After stirring at room temperature for 1 h, the solvent was evaporated to leave a small volume, and n -hexane (8 mL) was added to precipitate 4 as a brown solid. Yield: 117 mg (77%). $C_{86}H_{52}F_{10}P_2Pt_2$ (1727.5): calcd. C 59.80, H 3.03; found C 59.97, H 2.65. IR (Nujol): $\tilde{\nu} = 2216$ (vw), 2173 (vs) ($C \equiv C$); 804 (s), 794 (s) (C_6F_5) $_{X-sensitive}$ cm^{-1} . 1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.88$ (m, 8 H, Ph), 7.50 (m, 6 H), 7.34 (m, 20 H), 7.01 (m, 8 H, C_6H_4), 6.84 (d, $J_{H,H} = 7.8$ Hz, 4 H, C_6H_4), 2.36 (s, 6 H, CH_3) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -117.2$ (br. s, 4 F, o -F), -163.5 (t, 2 F, p -F), -165.6 (br. s, 4 F, m -F) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, -30 °C): $\delta = -116.1$ (m, $^3J_{Pt,o-F} \approx 340$ Hz, 2 F, o -F), -118.4 (m, $^3J_{Pt,o-F} \approx 430$ Hz, 2 F, o -F), -162.9 (t, 2 F, p -F), -164.6 (br. m, 2 F, m -F), -165.8 (br. m, 2 F, m -F) ppm. Signal coalescence: o -F (approx. 268 K), m -F (approx. 263 K); $\Delta G^\ddagger \approx 49.2$ kJ mol $^{-1}$. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = -11.20$ (s, $^1J_{P,Pt} = 2682$ Hz) ppm. FAB(+) MS: m/z (%) = 794 (55) [$Pt(PPh_2C \equiv Ctol)_2^+ - H$].

Synthesis of cis -[Pt($PPh_2C \equiv CC_6H_4C \equiv CPh$) $_2(\mu-\eta^1:\eta^2-C^{\alpha},C^{\beta}-C \equiv CC_6H_4C \equiv CPh)_2$]Pt(C_6F_5) $_2$] (5): Complex 5 was prepared as a brown solid in a similar way to 4 starting from cis -[Pt($C \equiv CC_6H_4C \equiv CPh$) $_2$ ($PPh_2C \equiv CC_6H_4C \equiv CPh$) $_2$] (3; 112 mg, 0.082 mmol) and cis -[Pt(C_6F_5) $_2$ (thf) $_2$] (55 mg, 0.082 mmol), and was recrystallised from $CH_2Cl_2/iPrOH$. Yield: 52 mg (43%). $C_{100}H_{56}F_{10}P_2Pt_2$ (1899.6): calcd. C 63.23, H 2.97; found C 63.12, H 2.61. IR (Nujol): $\tilde{\nu} = 2216$ (w), 2172 (s) ($C \equiv C$); 804 (m), 794 (m) (C_6F_5) $_{X-sensitive}$ cm^{-1} . 1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.90$ (m, 8 H, Ph), 7.51–7.21 (m, 40 H, Ph), 7.00 (d, $J_{H,H} = 8.0$ Hz, 4 H, C_6H_4), 6.85 (d, $J_{H,H} = 8$ Hz, 4 H, C_6H_4) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -117.1$ (br. s, 4 F, o -F), -163.4 (t, 2 F, p -F), -165.6 (br. s, 4 F, m -F) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, -50 °C): $\delta = -116.1$ (m, $^3J_{Pt,o-F} \approx 340$ Hz, 2 F, o -F), -118.5 (m, $^3J_{Pt,o-F} \approx 425$ Hz, 2 F, o -F), -162.6 (t, 2 F, p -F), -164.4 (m, 2 F, m -F), -165.6 (m, 2 F, m -F) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, $+50$ °C): $\delta = -116.9$ (m, $^3J_{Pt,o-F} = 405$ Hz, 4 F, o -F), -163.7 (t, 2 F, p -F), -165.8 (br. m, 4 F, m -F) ppm. Signal coalescence: o -F (273 K), m -F (approx. 268 K); $\Delta G^\ddagger \approx 50.01$ (o -F), 50.63 kJ mol $^{-1}$ (m -F). $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = -10.88$ (s, $^1J_{P,Pt} = 2677$ Hz) ppm. MALDI-TOF(+) MS: m/z (%) = 1168 (27) [$Pt(C \equiv CC_6H_4C \equiv CPh)(PPh_2C \equiv CC_6H_4C \equiv CPh)_2^+$], 983 (50) [$Pt(C \equiv CC_6H_4C \equiv CPh)_2(PPh_2C \equiv CC_6H_4C \equiv CPh)^+$], 965 (90) [$Pt(PPh_2C \equiv CC_6H_4C \equiv CPh)_2^+ - 2 H$] $^+$, 765 (100) [$Pt(PPh_2C \equiv CC_6H_4C \equiv CPh)(PPh_2) - H$].

Synthesis of cis -[Pt($\mu-\eta^1:\eta^2-C^{\alpha},C^{\beta}-C \equiv CC_6H_4C \equiv CPh$) $_2(\mu-1kP:2\eta^2-C^{\alpha},C^{\beta}-PPh_2C \equiv Ctol)_2$]Pt(C_6F_5) $_2$] (6): A solution of cis -[Pt($C \equiv CC_6H_4C \equiv CPh$) $_2$ ($PPh_2C \equiv Ctol$) $_2$] (2; 104 mg, 0.087 mmol) in CH_2Cl_2 (15 mL) was treated at room temperature with cis -[Pt(C_6F_5) $_2$ (thf) $_2$] (135 mg, 0.200 mmol; molar ratio 1:2.3). After stirring for 1 h, the solvent was removed in vacuo and the addition of n -hexane (5 mL) caused the precipitation of 6 as a brown solid. Yield: 170 mg (86%). $C_{98}H_{52}F_{20}P_2Pt_3$ (2256.7): calcd. C 52.16, H 2.32; found C 51.78, H 2.01. IR (Nujol): $\tilde{\nu} = 2214$ (vw), 2174 (s),

2019 (w) ($C \equiv C$); 804 (m), 795 (m) (C_6F_5) $_{X-sensitive}$ cm^{-1} . 1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.51$ –7.02 (m, 46 H, aromatics), 2.36 (s, 6 H, CH_3) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -116.6$ (br. s, 4 F, o -F), -117.2 (br. s, 4 F, o -F), -160.6 (t, 2 F, p -F), -161.1 (t, 2 F, p -F), -164.1 (br. m, 8 F, m -F) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 0.19$ (s, $^1J_{P,Pt} = 2514$ Hz) ppm. MALDI-TOF(+) MS: m/z (%) = 1728 (18) [$M^+ - Pt(C_6F_5)_2$], 1296 (50) [$Pt(C \equiv CC_6H_4C \equiv CPh)(PPh_2C \equiv Ctol)_3^+ - H$], 996 (60) [$Pt(C \equiv CC_6H_4C \equiv CPh)(PPh_2C \equiv Ctol)_2^+ - H$].

Synthesis of cis -[Pt($\mu-\eta^1:\eta^2-C^{\alpha},C^{\beta}-C \equiv CC_6H_4C \equiv CPh$) $_2(\mu-1kP:2\eta^2-C^{\alpha},C^{\beta}-PPh_2C \equiv CC_6H_4C \equiv CPh)_2$]Pt(C_6F_5) $_2$] (7): Complex 7 was prepared as a brown solid according to a procedure similar to that for compound 6 starting from cis -[Pt($C \equiv CC_6H_4C \equiv CPh$) $_2$ ($PPh_2C \equiv CC_6H_4C \equiv CPh$) $_2$] (3; 70 mg, 0.051 mmol) and cis -[Pt(C_6F_5) $_2$ (thf) $_2$] (79 mg, 0.117 mmol). Yield: 131 mg (65%). $C_{112}H_{56}F_{20}P_2Pt_3$ (2428.9): calcd. C 55.39, H 2.32; found C 55.72, H 2.61. IR (Nujol): $\tilde{\nu} = 2216$ (w), 2173 (s), 2020 (w), 1991 (w) ($C \equiv C$); 805 (m), 796 (m) (C_6F_5) $_{X-sensitive}$ cm^{-1} . 1H NMR (300.1 MHz, $CDCl_3$, 20 °C): $\delta = 7.53$ –7.17 (m, 56 H, aromatics) ppm. ^{19}F NMR (282.4 MHz, $CDCl_3$, 20 °C): $\delta = -116.5$ (br. s, 4 F, o -F), -117.2 (br. s, 4 F, o -F), -160.2 (t, 2 F, p -F), -160.6 (t, 2 F, p -F), -163.7 (br. m, 4 F, m -F), -164.0 (br. m, 4 F, m -F) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta = 0.43$ (s, $^1J_{P,Pt} = 2516$ Hz) ppm. MALDI-TOF(+) MS: m/z (%) = 1899 (28) [$M^+ - Pt(C_6F_5)_2$], 1731 (50) [$M^+ - Pt(C_6F_5)_2 - C_6F_5 - H$], 1369 (54) [$M^+ - 2 Pt(C_6F_5)_2 - H$], 1151 (57) [$Pt(C_6F_5)(C \equiv CC_6H_4C \equiv CPh)_2(PPh_2C \equiv CC_6H_4C \equiv CPh)^+ + H$], 967 (64) [$Pt(PPh_2C \equiv CC_6H_4C \equiv CPh)_2^+$], 766 (25) [$Pt(PPh_2C \equiv CC_6H_4C \equiv CPh)(PPh_2)^+$].

X-ray Crystallography: A summary of crystal data, data collection and refinement parameters for the structural analysis is given in Table 2. Crystals of complex 2 were obtained at room temperature by slow diffusion of n -hexane into a solution of the compound in benzene. One molecule of benzene was found in the asymmetric

Table 2. Crystal data and structure refinement parameters for 2· C_6H_6 .

Empirical formula	$C_{74}H_{52}P_2Pt \cdot C_6H_6$
Formula mass	1276.29
Temperature [K]	173(1)
Wavelength [Å]	0.71073
Crystal system	triclinic
Space group	$P\bar{1}$
Crystal dimensions [mm]	0.20 × 0.20 × 0.05
a [Å]	15.1950(2)
b [Å]	15.2180(2)
c [Å]	16.2740(2)
α [°]	92.0880(10)
β [°]	116.7850(10)
γ [°]	103.1010(10)
V [Å 3]	3230.12(7)
D_{calcd} [Mg m $^{-3}$]	1.312
Z	2
μ (Mo–K α) [mm $^{-1}$]	2.265
$F(000)$	1292
θ range [°]	1.54–27.92
$T_{min/max}$	0.895 and 0.800
No. of reflns. measd.	52252
No. of obsd. reflns.	15294 [$R(int) = 0.0678$]
Goodness of fit on $F^2[a]$	1.010
Final R indices [$I > 2\sigma(I)$] $^{[a]}$	$R1 = 0.0488$, $wR2 = 0.0976$
R indices (all data)	$R1 = 0.0784$, $wR2 = 0.1068$

[a] $R1 = \Sigma(|F_o| - |F_c|)/\Sigma|F_o|$; $wR2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma wF_o^2]^{1/2}$; goodness of fit = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obs} - N_{param})\}^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$, where $P = [\max(F_o^2; 0) + 2F_c^2]/3$.

unit. This molecule of benzene was found to be disordered over two positions with two consecutive carbon atoms, C(75) and C(80), in the same position and was modelled adequately. The disordered sets of atoms were refined with a partial occupancy of 0.50 each. Data for $2 \cdot \text{C}_6\text{H}_6$ were collected at low temperature (173 K) with a Nonius κ -CCD area-detector diffractometer, using graphite-monochromated Mo-K_α radiation. Data were processed using the DENZO and SCALEPACK suite of programs.^[89] The absorption correction was performed using SORTAV.^[90] The structure was 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 idealised geometries by fixing isotropic displacement parameters at 1.2-times the U_{iso} value of their attached carbon atom for the phenyl hydrogen atoms and 1.5-times for the methyl groups. There are peaks of electron density higher than $1 \text{ e } \text{\AA}^{-3}$ in the final map, but they are located very close to the platinum atoms or in the vicinity of the solvent and have no chemical meaning. CCDC-634038 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request.cif.

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