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Platinum(0) Complexes with Alkynylphosphane Ligands

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The reactivity of the Pt^0 derivative [Pt$_2$(dba)$_3$] (dba = *trans*,*trans*-dibenzylideneacetone) towards PPh$_2$C≡CR [R = Ph, tolyl (Tol), C$_5$H$_4$N-2] and PPh$_2$C≡CPPh$_2$ (dppa) has been explored. Treatment of [Pt$_2$(dba)$_3$] with PPh$_2$C≡CR (8 equiv.) in THF gave the tetrahedral complexes [Pt(PPh$_2$C≡CR)$_4$] [R = Ph (**1**), Tol (**3**), C$_5$H$_4$N-2 (**5**)], whereas reactions with a molar ratio of 1:4 afforded the binuclear derivatives [{Pt(PPh$_2$C≡CR)(μ-κ*P*:η^2-PPh$_2$C≡CR)}$_2$] [R = Ph (**2**), Tol (**4**) X-ray, C$_5$H$_4$N-2 (**6**)], which were shown to be generated through the mononuclear complexes **1**, **3** and **5** as intermediate species. An analogous reaction using 4 equiv. of PPh$_2$C≡CPPh$_2$ afforded [Pt$_2$(PPh$_2$C≡CPPh$_2$)$_2$(μ-κ^2*PP*′-PPh$_2$C≡CPPh$_2$)$_3$] (**7**), in which two "Pt(PPh$_2$C≡CPPh$_2$)" fragments are joined through three bridging dppa ligands (μ-κ^2*PP*′-PPh$_2$C≡CPPh$_2$). Attempts to crystallize **7** at –30 °C afforded crystals of [Pt$_2${PPh$_2$C≡CP(O)Ph$_2$}$_2$(μ-κ^2*PP*′-PPh$_2$C≡CPPh$_2$)$_3$] (**8**) by oxidation of the free end of the terminal dppa ligands. The compound was characterized by X-ray diffraction.

Introduction

Alkynylphosphanes PR$_{3-n}$(C≡CR′)$_n$ are polyfunctional ligands that show versatile behaviour in coordination chemistry.[1,2] Although P coordination is commonly kinetically favoured,[3–13] they can act as a bridging ligand through the phosphorus and the triple bond.[3,4,7,8,10–12,14–16] Only a few examples are known in which alkyne coordination is favoured, usually with metals in low oxidation states.[17–19] As expected, linear bis(phosphane)poly-ine [PPh$_2$(C≡C)$_n$PPh$_2$] ligands have been demonstrated to offer higher coordination and to generate on occasion chains, rings or polymers.[14,20–24]

Furthermore, alkynylphosphanes have shown an interesting reactivity in transition-metal chemistry including (i) insertion into reactive M–H or M–C bonds;[5,6,8,25–29] (ii) intramolecular coupling reactions;[5,6,8,14,21,23,30–32] (iii) P–C(alkyne) bond cleavage processes to afford alkynyl (C≡C) and phosphide (PPh$_2$) fragments,[15,33–37] which are often involved in subsequent coupling or insertion reactions;[38–40] and (iv) activation of the uncoordinated alkyne function upon simple P coordination toward electrophilic or nucleophilic attacks.[9,17,18,41–43]

In this area we have described several homo- and heterometallic Pt^{II} derivatives that contain (μ-PPh$_2$C≡CR)(μ-X) [X = Cl,[3,11,12] C≡CR′,[4] C≡C–C$_6$H$_4$–C≡CPh,[10] tetrahydrothiophene (tht),[7,44] *o*-C$_6$H$_4$E$_2$ (E = O, S)[8]], (μ-PPh$_2$C≡CFc)$_2$[45] or (μ-dppa)$_n$ (n = 1, 2)[46,47] bridging systems. In addition, we have reported several mixed-valence Pt^{II}–Pt^0 complexes stabilized by one (μ-PPh$_2$C≡CR) [R = Ph, tolyl (Tol), C$_6$H$_4$C≡CPh] bridging alkynylphosphane,[44] and we have also demonstrated an efficient and easy sequential insertion of two PPh$_2$C≡CR (R = Ph, Tol) ligands into the robust Pt–C$_6$F$_5$ bond.[5,6,8]

Despite the coordinative possibilities of these ligands, only a few examples are known in which alkynylphosphane ligands are coordinated to Pt^0 centres,[18,44,48–50] and those that have been structurally characterized are particularly scarce.[18,44,49] It is therefore of interest to investigate platinum(0) complexes that contain alkynylphosphane (PPh$_2$C≡CR) and bis(diphenylphosphanyl)acetylene (PPh$_2$C≡CPPh$_2$) ligands.

Results and Discussion

To investigate the behaviour of alkynylphosphane ligands with Pt^0, the reactions of the precursor [Pt$_2$(dba)$_3$] with PPh$_2$C≡CR (R = Ph, Tol, C$_5$H$_4$N-2) were explored (Scheme 1). Treatment of [Pt$_2$(dba)$_3$] in tetrahydrofuran at room temperature with the corresponding PPh$_2$C≡CR ligand in 1:8 molar ratio over 2 h led to the formation of the Pt^0 derivatives [Pt(PPh$_2$C≡CR)$_4$] [R = Ph (**1**), Tol (**3**), C$_5$H$_4$N-2 (**5**)] (Scheme 1, i), which were isolated as yellow solids after usual workup. In the cases of **1** and **3**, the solids obtained were impure, with small traces of the free PPh$_2$C≡CR and the binuclear derivatives [{Pt(PPh$_2$C≡CR)(μ-κ*P*:η^2-PPh$_2$C≡CR)}$_2$] [R = Ph (**2**), Tol (**4**)], as observed by ^{31}P{^{1}H} NMR spectroscopy, so they had to be recrystallized from THF/*n*-hexane. Longer periods of reaction times increased the formation of the binuclear derivatives **2** or **4**. It should be noted that the related complex

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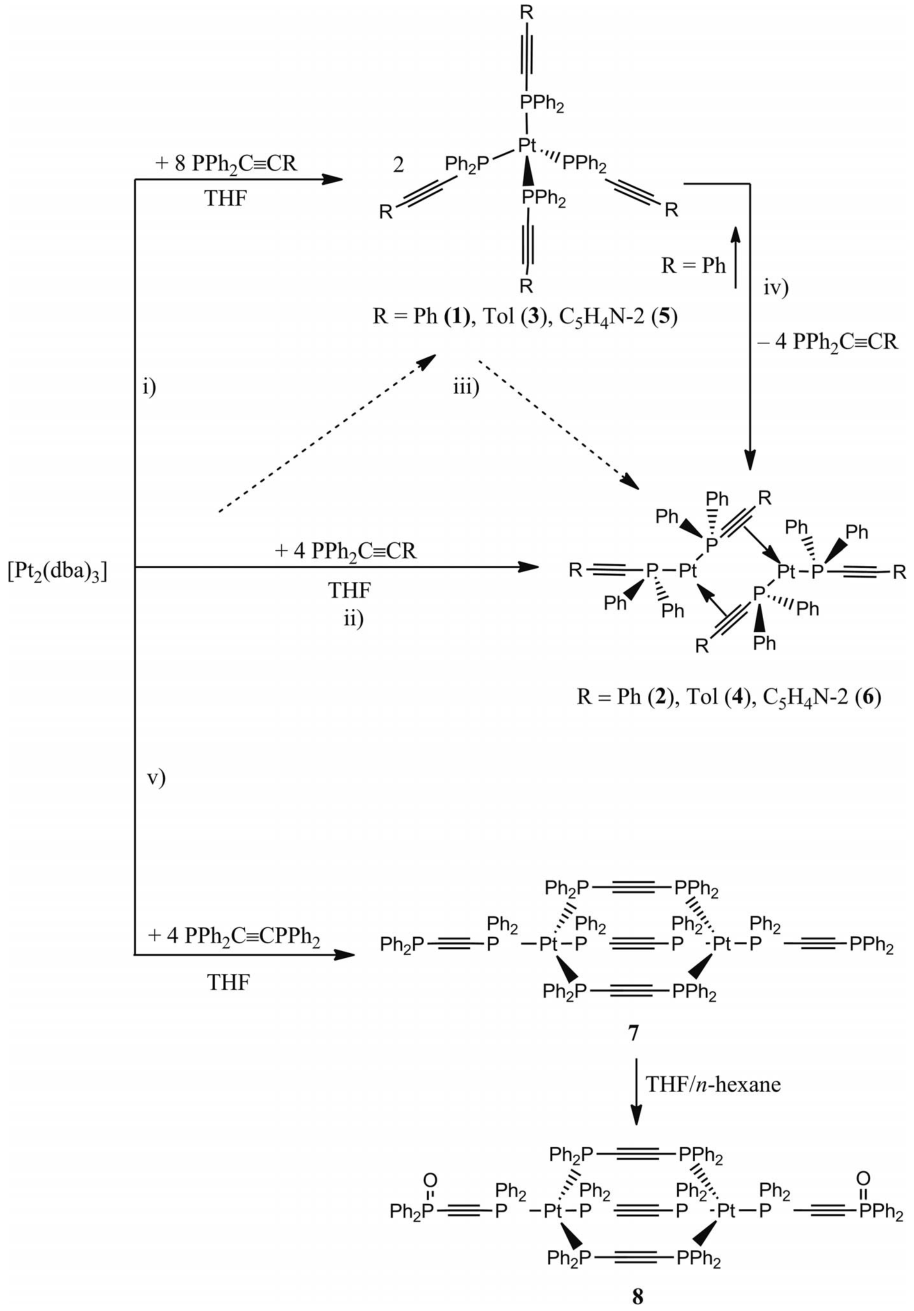

Scheme 1. Synthetic pathways for the synthesis of complexes **1**–**8**.

[Pt(PPh$_2$C≡CCH$_3$)$_4$] has been previously reported,[50] the nature of which was established by spectroscopic evidence (IR, ^{1}H NMR and UV/Vis).

With the aim of obtaining the binuclear derivatives **2**, **4** and **6**, the reactions between [Pt$_2$(dba)$_3$] and PPh$_2$C≡CR were carried out in THF at room temperature in a 1:4 molar ratio, thereby affording [{Pt(PPh$_2$C≡CR)(μ-κ*P*:η^2-PPh$_2$C≡CR)}$_2$] [R = Ph (**2**), Tol (**4**), C$_5$H$_4$N-2 (**6**)] (Scheme 1, ii) as pure solids. Control by ^{31}P{^{1}H} NMR spectroscopy (CDCl$_3$) of the reaction that led to **4** in THF revealed that the formation of the binuclear products takes place through the mononuclear [Pt(PPh$_2$C≡CR)$_4$] derivatives (Scheme 1, iii). Thus, after the addition of phosphane (ca. 1 min), complex **3** was initially formed and was the only product observed together with a small amount of PPh$_2$(O)-C≡CTol (always present). Over time, the signals due to **3** decreased, whereas those of **4** gradually increased and after 6 h; **4** and **3** were present in an approximate ratio of 3:1 (**4**:**3**). After 24 h, **3** had disappeared and **4** was the only platinum-containing product in the reaction medium. This result clearly indicates that the tetracoordinate complexes seem to be the kinetic initially formed products, which gradually evolve into the thermodynamic more stable tricoordinate diplatinum derivatives. In fact, pyridin(alkynyl)phosphane **5** evolved into a mixture of **6** and free phosphane by stirring the complex in toluene over four days (Scheme 1,

iv) and the tolyl derivative **3** needed 6 h in toluene heated under reflux conditions to give the binuclear **4** together with free phosphane. However, once complex **1** was isolated, its conversion to the binuclear derivative **2** was not complete (even in toluene at reflux) and a mixture of **2**/**1**/$PPh_2C{\equiv}CPh$ was always present. In fact, monitoring the reaction between pure binuclear derivative **2** and $PPh_2C{\equiv}CPh$ (4 equiv.) in THF by $^{31}P\{^1H\}$ NMR spectroscopy in $CDCl_3$ established that a mixture of **2**/**1**/$PPh_2C{\equiv}CPh$ was always observed, thereby indicating a possible equilibrium in solution.

We note that the formation of η^2-alkyne bimetallic complexes was irreversible (**4**, **6**) or clearly a majority (**2**), thus indicating that the Pt^0 centre has a remarkable preference for the π-donor acetylenic density of *P*-bonded alkynylphosphanes. This behaviour is in agreement with previous results in binuclear Pt^{II}–Pt^0 systems that contain μ-κP:$\eta^2$$PPh_2C{\equiv}CR$ bridging ligands, in which the Pt^{II} centre has been shown to have a clear preference for P coordination,[44] whereas the alkyne $PC{\equiv}CR$ unit favours coordination to the relatively electron-rich Pt^0 centre. In the context of this work, we note that related $[\{M(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CCF_3)L\}_2]$ (M = Pt, Pd; **L** = $PPh_2C{\equiv}CCF_3$, PPh_3) derivatives were isolated by Carty et al. in 1974 from the reduction of *cis*-$[MCl_2(PPh_2C{\equiv}CCF_3)_2]$ with $NaBH_4$ in THF and the structure of $[\{Pd(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CCF_3)\text{-}PPh_3\}_2]$ was confirmed by X-ray diffraction.[49]

Attempts to carry out a complete X-ray diffraction study of the mononuclear complexes **1**, **3** or **5** were unsuccessful. The poor quality of all crystals obtained prevented their satisfactory refinement. However, the connectivity was unequivocally established on a crystal of **5**, thereby confirming the presence of four alkynylphosphanes coordinated to the Pt^0 centre. Evidence of the tetrahedral coordination of four alkynylphosphanes in solution is mainly derived from their $^{195}Pt\{^1H\}$ NMR spectra, which show a quintet due to coupling to four phosphorus (δ = –4601 to –4606 ppm), with a coupling constant ^1J(Pt,P) of 3942 to 3956 Hz (Figure 1) in the typical range of Pt^0 phosphane complexes[51] and the $^{31}P\{^1H\}$ NMR spectra, which exhibit a singlet resonance (δ = –17.7 to –18.6 ppm) flanked by platinum satellites. The downfield shift in relation to the $PPh_2C{\equiv}CR$ free ligands [$\Delta\delta$ = 14.8 (**1**), 14.5 (**3**), 15.7 ppm (**5**)] confirms the P coordination to the Pt^0 centre. The MALDI-TOF(+) mass spectra show the peaks that correspond to $[Pt(PPh_2C{\equiv}CR)_3]^+$ fragments as parent peaks and in the IR spectra the most remarkable absorption is one ν(C≡C) band in the range 2160–2164 cm^{-1}, which is typical of *P*-coordinated $PPh_2C{\equiv}CR$ ligands.

The bimetallic formulation with the double-bridged $(\mu\text{-}PPh_2C{\equiv}CR)_2$ of complexes **2**, **4** and **6** is consistent with their analytical and spectroscopic data and it has been confirmed by an X-ray diffraction study on complex **4**. The MALDI-TOF(+) mass spectra exhibit the corresponding molecular peak and those due to the fragment $[Pt_2(PPh_2C{\equiv}CR)_3]^+$. The IR spectra of **2**, **4** and **6** confirm the presence of bridging and terminal alkynylphosphane ligands. Thus, they exhibit one high-frequency absorption (2167–2178 cm^{-1}) located at slightly higher frequencies than those of mononuclear derivatives **1**, **3**, **5** (2160–2164 cm^{-1}), which is assigned to the terminal *P*-coordinated $PPh_2C{\equiv}CR$, and a low-frequency band (1717–1756 cm^{-1}), which appears with a shoulder, attributed to the alkynylphosphane bridging group. The remarkable lowering of this latter νC≡C frequency in relation to free phosphanes is consistent with that expected for an η^2-coordination to the Pt^0 centre.[44,52,53] The most relevant feature of the ^1H NMR spectra is the presence of two different methyl signals in the tolyl derivative **4**. All binuclear complexes (**2**, **4** and **6**) display in the $^{31}P\{^1H\}$ NMR spectra the expected AA′XX′ splitting pattern with the corresponding ^{195}Pt satellites. From the analysis of the spectra obtained (two pseudotriplets located at δ = –5.78 to –7.22 and at 4.06 to 8.10 ppm), it is only possible to obtain the value of the *N* parameter [$N = {}^2J(P^A,P^X{}_{cis}) + {}^3J(P^A,P^{X'}{}_{trans})$ = 79.3–79.6 Hz]. It is worth noting that both signals appear remarkably downfield-shifted with regard to that of the corresponding precursors **1**, **3** and **5**, thus suggesting the occurrence of more robust Pt–P bonds in the tricoordinate platinum units. In each complex the most deshielded signal (δ = 4.06 to 8.10 ppm), with $^1J(P^A,Pt)$ coupling constants in the range 3764–3834 Hz, is tentatively attributed to the alkynylphosphane bridging ligands, whereas the low-frequency resonance [δ = –7.22 to –5.78 ppm; $^1J(P^X,Pt)$ = 3523–3643 Hz] is assigned to the terminal *P*-coordinated alkynylphosphanes. This assignment is in agreement with previous observations in heterobridged d^8–Pt^{II} [d^8 = Pt^{II}, Pd^{II}][3,4,8,10] and d^6–Pt^{II} [d^6 = Rh^{III}, Ir^{III}, Ru^{II}][11,12] and mixed-valence Pt^{II}–Pt^0 complexes[7,44] that contain terminal and bridging alkynylphosphane ligands in which the phosphorus resonance of the bridging ligands is systematically found notably deshielded in relation to the terminal one. The $^{195}Pt\{^1H\}$ NMR spectra

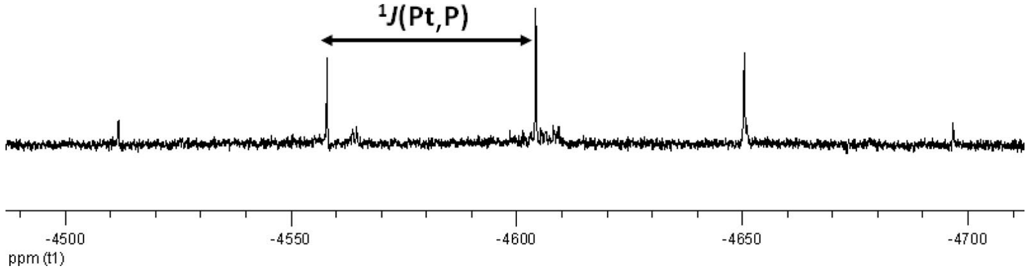

Figure 1. $^{195}Pt\{^1H\}$ NMR spectrum of $[Pt(PPh_2C{\equiv}CTol)_4]$ (**3**) in $CDCl_3$ at 298 K.

show the expected platinum resonance as a well-resolved dddd centred in the range δ = –4614 to –4590 ppm, which is very close to the resonance found for the mononuclear precursors. The analysis of these signals as first-order spin systems allowed us to obtain the long range two- and four-bond platinum–phosphorus coupling constants [^2J(Pt,P$^{A'}$) = 56–75 Hz; ^4J(Pt,P$^{X'}$) = 24–26 Hz].

Table 1. Selected distances [Å] and angles [°] of **4**.

Pt1–C10	2.039(6)	P1–C1	1.778(7)
Pt1–C11	2.068(7)	P2–C10	1.767(7)
Pt1–P3	2.2447(16)	P3–C19	1.784(8)
Pt1–P1	2.272(2)	P4–C28	1.785(8)
Pt2–C1	2.026(6)	C1–C2	1.305(9)
Pt2–C2	2.068(7)	C10–C11	1.290(9)
Pt2–P4	2.2472(16)	C19–C20	1.187(10)
Pt2–P2	2.278(2)	C28–C29	1.181(10)
C11–Pt1–P3	114.5(2)	C19–P3–Pt1	121.1(2)
C10–Pt1–P1	102.0(2)	C28–P4–Pt2	119.6(3)
C11–Pt1–P1	138.1(2)	C2–C1–P1	152.2(6)
P3–Pt1–P1	107.37(6)	C1–C2–C3	142.2(6)
C2–Pt2–P4	116.9(2)	C11–C10–P2	152.9(6)
C1–Pt2–P2	102.1(2)	C10–C11–C12	144.5(7)
C2–Pt2–P2	139.0(2)	C20–C19–P3	179.3(7)
P4–Pt2–P2	103.94(7)	C19–C20–C21	179.3(9)
C1–P1–Pt1	109.6(2)	C29–C28–P4	178.4(7)
C10–P2–Pt2	110.2(2)	C28–C29–C30	176.6(8)

The structure of **4** is shown in Figure 2 and relevant bond lengths and angles are summarized in Table 1. The structure consists of two "Pt(PPh$_2$C≡CTol)" moieties connected by two alkynylphosphane ligands (Pt···Pt 4.267 Å), which are coordinated by acting as μ-κ*P*:η^2 bridging ligands. The central octanuclear Pt$_2$P$_2$C$_4$ core is bent, with the dihedral angle formed by the best platinum coordination planes being 57.91°. The geometry around the Pt centres is approximately trigonal planar, which is typical of metal(d^{10})–alkyne complexes.[18,44,53–55] The dihedral angles between the planes P1–Pt1–P3 and C10–Pt1–C11 is 9.7(4)° and between P2–Pt2–P4 and C1–Pt2–C2 is 5.6(4)°. The torsion angles P1–C1–C2–C3 and P2–C10–C11–C12 are 7.97 and 0.66°, respectively.

The η^2-platinum(0)–acetylenic linkage is asymmetric with the Pt–C$_\alpha$ distances [2.026(6), 2.039(6) Å] being slightly shorter than the corresponding Pt–C$_\beta$ bond lengths [2.068(7) Å]. As expected, the η^2-complexed C≡C bond lengths [1.305(9) and 1.290(9) Å] are considerably longer than the uncoordinated alkynyl lengths [1.187(10), 1.181(10) Å] and comparable to those found in the mixed-valence Pt^{II}–Pt^0 complexes [Pt(C$_6$F$_5$)$_2$(tht)(μ-PPh$_2$C≡CR)-Pt(PPh$_3$)$_2$] [R = Ph[44] 1.302(5) Å; R = C$_6$H$_4$–C≡CPh,[7] 1.303(7) Å]. The bridging P–C$_\alpha$–C$_\beta$–C$_\gamma$ skeleton shows a marked deviation from linearity [P–C$_\alpha$–C$_\beta$ 152.2(6), 152.9(6)°; C$_\alpha$–C$_\beta$–C$_\gamma$ 142.2(6), 144.5(7)°] relative to the

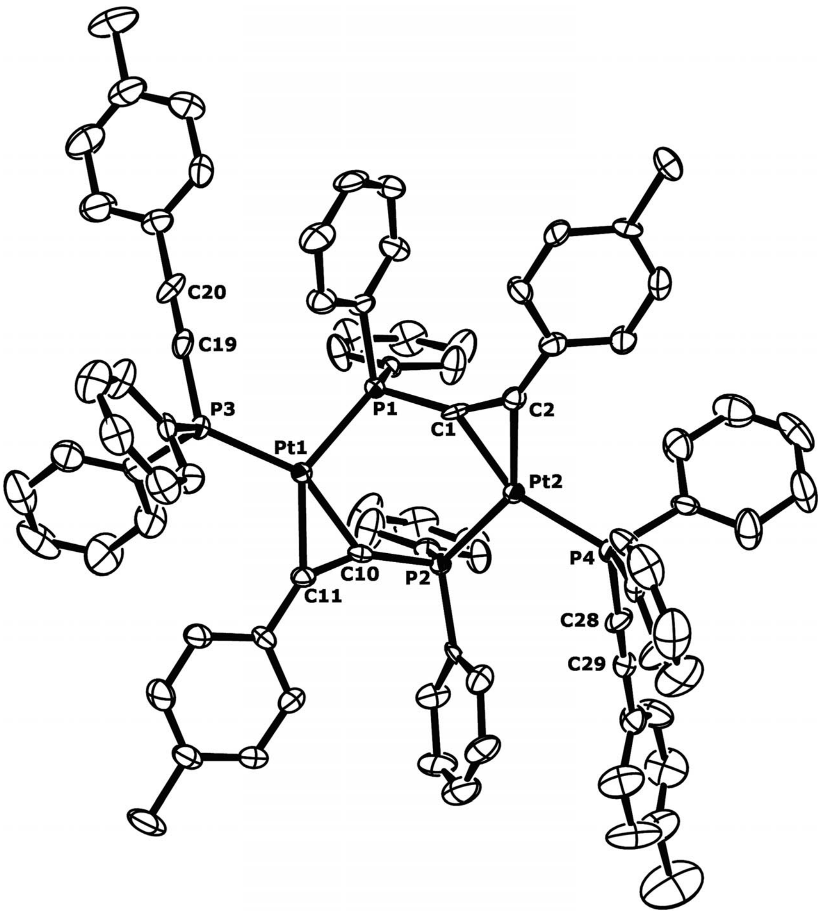

Figure 2. Molecular structure of [{Pt(PPh$_2$C≡CTol)(μ-κ*P*:η^2-PPh$_2$C≡CTol)}$_2$] (**4**).

angles at C_α and C_β observed on the terminal P–C_α–C_β–C_γ units [P–C_α–C_β 178.4(7), 179.3(7)°; C_α–C_β–C_γ 176.6(8), 179.3(9)°]. Both facts are consistent with a remarkable backbonding from Pt^0 centres into the π* orbitals of the bridging ligands, thereby affording some metallacyclopropene character to the bonding. The Pt–P bridging bond lengths [2.272(2), 2.278(2) Å] are slightly longer than the corresponding Pt–P terminal bond lengths [2.2447(16), 2.2472(16) Å]. However, the P–C(acetylenic) distances are almost identical [1.778(7), 1.767(7) Å (bridging); 1.784(8), 1.785(8) Å (terminal)].

In this context, we decided to examine the reactivity of $[Pt_2(dba)_3]$ toward the potentially trifunctional ligand bis(diphenylphosphanyl)acetylene, $PPh_2C{\equiv}CPPh_2$ (dppa). It is worth mentioning that zerovalent platinum–dppa derivatives have been investigated in the past. Thus, King et al. reported that the reaction of $K_2[PtCl_4]$ with $PPh_2C{\equiv}CPPh_2$ (excess amount) in $EtOH/H_2O$ under reflux conditions in the presence of $NaBH_4$ gave a yellow solid of $[Pt(PPh_2C{\equiv}CPPh_2)_2]$,[48] for which a mononuclear formulation with a linear κ-*P* two-coordination was proposed on the basis of IR spectroscopy. A binuclear platinum(0) complex $[\{Pt(PPh_3)_2(PPh_2C{\equiv}CPPh_2)\}_2]$ with a typical tetrahedral Pt^0 environment and P coordination for the dppa ligand has also been reported,[50] but it was only characterized by spectroscopic means (IR, ^1H NMR and UV/Vis).

Following a procedure similar to that used for binuclear complexes **2**, **4** and **6**, treatment of $[Pt_2(dba)_3]$ with $PPh_2C{\equiv}CPPh_2$ (1:4) (Scheme 1, v) in THF resulted in the formation of a yellow solid (**7**), the IR spectra of which exhibit a band at 2007 cm^{-1} close the band at 2002 cm^{-1} that was reported by King for $[Pt(dppa)_2]$, thereby suggesting that both complexes are the same. This complex **7** was formulated as the binuclear neutral derivative $[Pt_2(PPh_2C{\equiv}CPPh_2)_2(\mu\text{-}\kappa^2PP'\text{-}PPh_2C{\equiv}CPPh_2)_3]$, in which two "$Pt(PPh_2C{\equiv}CPPh_2)$" fragments are attached through a system of three dppa bridging ligands ($\mu\text{-}\kappa^2PP'\text{-}PPh_2C{\equiv}CPPh_2$). This formulation, mainly based on spectroscopic (mass spectrometry and NMR) data, is in accordance with the typical tetrahedral coordination of Pt^0 and with its easy evolution into the related complex **8**. Compound **7** is moderately stable in the solid state, but upon standing in solution, evolves, even at low temperature, toward the oxidized product $[Pt_2\{PPh_2C{\equiv}CP(O)Ph_2\}_2(\mu\text{-}\kappa^2PP'\text{-}PPh_2C{\equiv}CPPh_2)_3]$ (**8**). In fact, attempts to crystallize complex **7** at –30 °C in THF/*n*-hexane afforded crystals of **8**.

The crystal structure of complex **8** is shown in Figure 3, with selected bond lengths and angles in Table 2. The structure consists of two bis(diphenylphosphanyl)acetylene oxide platinum fragments "$[Pt\{PPh_2C{\equiv}CP(O)Ph_2\}]$" bridged by three dppa ligands. The platinum(0) centres show a distorted tetrahedral environment with P–Pt–P in the central bridging core that lies in the range 99.91(4)–109.22(4)° and P(7)/(9)–Pt–$P_{(dppa)}$ in the range 111.76(3)–118.95(3)°. The Pt–P–$C_{acetylene(dppa)}$ angles deviate slightly from the ideal tetrahedral [112.39(13)–114.01(13)°]. The three dppa bridges display P–C≡C angles that range from 175.0 to 177.3(4)°, whereas in the terminal dppa oxide these angles

Table 2. Selected distances [Å] and angles [°] of **8**·1.5THF.

Pt1–P7	2.2643(10)	C1–C2	1.201(6)
Pt1–P3	2.2940(9)	C3–C4	1.201(5)
Pt1–P1	2.3034(10)	C5–C6	1.213(6)
Pt1–P5	2.3073(10)	C7–C8	1.205(6)
Pt2–P9	2.2731(10)	C9–C10	1.207(6)
Pt2–P4	2.3065(10)	P8–O1	1.370(6)
Pt2–P6	2.3178(10)	P10–O2	1.418(5)
Pt2–P2	2.3180(11)		
P7–Pt1–P3	112.08(2)	C5–P5–Pt1	113.14(13)
P7–Pt1–P1	117.11(2)	C6–P6–Pt2	114.01(13)
P3–Pt1–P1	104.32(3)	C2–C1–P1	177.0(4)
P7–Pt1–P5	113.69(3)	C1–C2–P2	176.0(4)
P3–Pt1–P5	107.28(3)	C4–C3–P3	176.9(4)
P1–Pt1–P5	101.24(3)	C3–C4–P4	177.3(4)
P9–Pt2–P4	111.74(3)	C6–C5–P5	175.0(4)
P9–Pt2–P6	118.93(3)	C5–C6–P6	176.1(4)
P4–Pt2–P6	103.63(4)	C8–C7–P7	171.9(4)
P9–Pt2–P2	112.39(3)	C7–C8–P8	170.1(5)
P4–Pt2–P2	109.22(4)	C10–C9–P9	174.6(4)
P6–Pt2–P2	99.91(4)	C9–C10–P10	177.8(5)
C1–P1–Pt1	112.39(13)	C7–P7–Pt1	117.17(14)
C2–P2–Pt2	113.87(14)	O1–P8–C8	114.6(3)
C3–P3–Pt1	113.86(13)	C9–P9–Pt2	117.06(14)
C4–P4–Pt2	113.08(13)	O2–P10–C10	116.7(2)

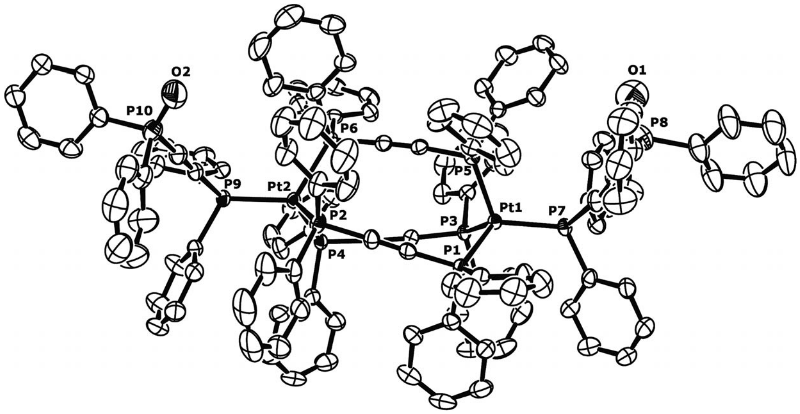

Figure 3. Molecular structure of $[Pt_2\{PPh_2C{\equiv}CP(O)Ph_2\}_2(\mu\text{-}\kappa^2PP'\text{-}PPh_2C{\equiv}CPPh_2)_3]$·1.5THF (**8**·1.5THF).

range from 170.1(5) to 177.8(5)°. The C≡C bond lengths [1.201(5)–1.213(6) Å] are similar to the uncoordinated C≡C distance in **4**. The P–O [1.370(6), 1.418(5) Å] bond lengths and the O–P–C angles [114.6(3), 117.17(14)°] are in the range of those observed in terminal alkynylphosphane oxides.[8,18,56]

The helical twist for the $Pt_2(dppa)_3$ skeleton about the Pt···Pt axis is 27.5°, taken as the average of the torsion angles P5–Pt1–Pt2–P6 28.9°, P1–Pt1–Pt2–P2 30.1° and P3–Pt1–Pt2–P4 23.6°. We note that the related tris(dppa) d^{10} derivatives, $[Ni_2(CO)_2(dppa)_3]$,[57] $[Cu_2(dppa)_3(CH_3CN)_2][BF_4]_2$,[58] $[Cu_2(dppa)_3(O_3SCF_3)_2]$,[58] $[Cu_2(X)_2(dppa)_3]$ (X = TeBu, $SSiMe_3$),[59,60] $[Ag_2(dppa)_3(BF_4)_2]$,[61] $[Au_2(dppa)_3Cl_2]$[62]; and d^6 derivatives, $[Mo_2(CO)_6(dppa)_3]$[63] and $[W_2(CO)_6(dppa)_3]$,[64] are also helical. This arrangement leaves the terminal diphenylphosphane acetylene oxide fragments in a *transoidal* disposition, with a torsion angle between the two terminal acetylene vectors C9–C10 and C8–C7 of 51.23°.

The IR spectrum of **7** exhibits a characteristic ν(C≡C) medium absorption at 2107 cm^{-1}, whereas **8** also displays a ν(C≡C) signal at similar frequencies (2109 cm^{-1}), together with a new band in the P=O stretching region (1211 cm^{-1}), in accordance with the presence of the partially oxidized bis(diphenylphosphane)acetylene $PPh_2C{\equiv}CP(O)Ph_2$ ligands. The $^{31}P\{^1H\}$ NMR spectrum of **7** (Figure 4) displays a first-order AX_3 pattern (δ_A = –7.6 ppm, δ_X = –21.4 ppm, J_{AX} = 64 Hz) with well-resolved platinum satellites for the bridging P–(dppa) signal [$J(Pt,P^X)$ = 3692 Hz], attributed to the coordinated phosphorus atoms and a high-field singlet (δ = –31.6 ppm), which appears close to that seen in free dppa, due to the uncoordinated phosphorus of terminal dppa. The $^{195}Pt\{^1H\}$ NMR spectrum of **7** shows a doublet of quartet of small doublets centred at δ = –4471 ppm, the analysis of which as a first-order spin system allows us to calculate not only the $^1J(Pt,P^X)$ (3692 Hz), but also $^1J(Pt,P^A)$ (4594 Hz) and $^4J(Pt,P_{free})$ (30 Hz) that are not resolved in the corresponding phosphorus spectrum. As expected, in the $^{31}P\{^1H\}$ NMR spectrum of **8**, the oxidized phosphorus resonance appears notably deshielded in relation to that in complex **7** (δ = 6.6 ppm for **8** versus δ = –31.6 ppm for **7**), whereas the signals that correspond to P^A and P^X atoms are slightly affected [P^A, δ = –7.52 ppm (q); P^X, δ = –21.23 ppm (d); $^2J(P^A,P^X)$ = 65 Hz].

Although unexpected, the formation of an alkynylphosphane oxide complex starting from the corresponding alkynylphosphane ligand has been previously reported. Of interest for this work are, for example, $[\{(\eta^5\text{-}C_5H_5)Ni\}_2\{PPh_2(O)C{\equiv}CCF_3\}]$, which was obtained as one byproduct in the reaction of $[(\eta^5\text{-}C_5H_5)_2Ni]$ with $PPh_2C{\equiv}CCF_3$;[56] $[Pt\{\eta^2\text{-}PPh_2(O)C{\equiv}CMe\}(dcpe)]$ [dcpe = 1,2-bis(dicyclohexylphosphino)ethane], which was obtained by air oxidation of $[Pt(\eta^2\text{-}PPh_2C{\equiv}CMe)(dcpe)]$;[18] or $[(C_6F_5)_2Pt\{\mu\text{-}\kappa O{:}\eta^2\text{-}PPh_2(O)C{\equiv}CPh\}]_2$,[8] which was obtained as a subproduct in the reaction between $[Ir(cod)(PPh_2C{\equiv}CPh)_2](ClO_4)$ [cod = 1,5-cyclooctadiene] and $[cis\text{-}Pt(C_6F_5)_2(thf)_2]$.

In conclusion, we have shown that the formation of the binuclear derivatives, stabilized by a double alkynylphosphane bridging system, $[\{Pt(PPh_2C{\equiv}CR)(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CR)\}_2]$ [R = Ph (**2**), Tol (**4**), C_5H_4N-2 (**6**)] with trigonal planar Pt^0 centres, takes place through the formation of the tetrahedral mononuclear derivatives $[Pt(PPh_2C{\equiv}CR)_4]$ [R = Ph (**1**), Tol (**3**), C_5H_4N-2 (**5**)]. It is also possible to generate binuclear derivatives **7** and **8**, in which two PtL [**L** = $PPh_2C{\equiv}CPPh_2$ or $PPh_2C{\equiv}CP(O)Ph_2$] apical fragments are bridged by three ($\mu\text{-}\kappa^2 PP'\text{-}PPh_2C{\equiv}CPPh_2$) bridging ligands to form a helical twisted cage.

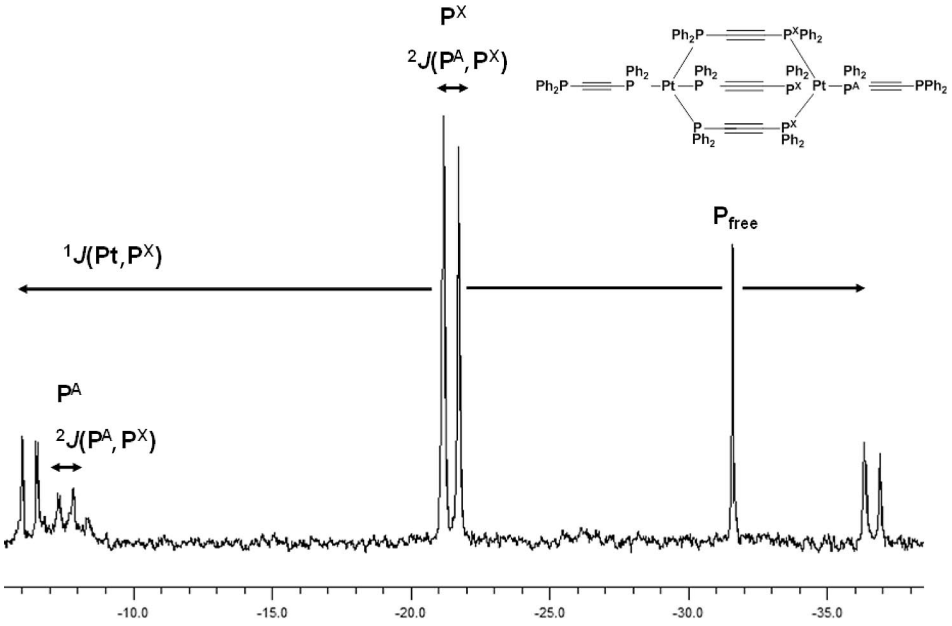

Figure 4. $^{31}P\{^1H\}$ NMR spectra of **7**.

Experimental Section

General Remarks: All reactions were carried out under an Ar atmosphere using Schlenk tube techniques. Solvents were obtained with a solvent purification system (M-BRAUN MB SPS-800). IR spectra were recorded with a FTIR Nicolet Nexus spectrometer as Nujol mulls between polyethylene sheets and NMR spectra were recorded with either a Bruker ARX 300 or a Bruker Avance 400 spectrometer. Chemical shifts are reported in ppm relative to external standards ($SiMe_4$, 85% H_3PO_4 and $Na_2[PtCl_6]$) and coupling constants in Hz. Elemental analyses were carried out with a Perkin–Elmer 2400 CHNS/O microanalyzer and MALDI-TOF spectra with a Microflex MALDI-TOF Bruker spectrometer operating in the linear and reflector modes using dithranol as matrix. Starting materials $[Pt_2(dba)_3]$,[65] $PPh_2C{\equiv}CPh$, $PPh_2C{\equiv}CTol$, and $PPh_2C{\equiv}C\text{-}C_5H_4N\text{-}2$ were prepared as described previously.[66,67] $PPh_2C{\equiv}CPPh_2$ (Aldrich) was used as supplied.

$[Pt(PPh_2C{\equiv}CPh)_4]$ (1): A purple solution of $[Pt_2(dba)_3]$ (0.200 g, 0.183 mmol) in THF (30 mL) was treated with $PPh_2C{\equiv}CPh$ (0.420 g, 1.467 mmol) (1:8 molar ratio) and the mixture was stirred to give a yellow solution in 30 min. After 1.5 h of stirring, the solution was concentrated to approximately 5 mL. Addition of cold MeOH (10 mL) afforded a yellow solid (0.213 g, 43% yield), which was collected by filtration and washed with cold MeOH (2 mL). The $^{31}P\{^1H\}$ NMR spectrum was assigned to **1**, with small traces of free phosphane ($PPh_2C{\equiv}CPh$) and **2**. Recrystallization from THF/*n*-hexane gave **1** as a pure solid. $C_{80}H_{60}P_4Pt$ (1340.34): calcd. C 71.69, H 4.51; found C 72.06, H 4.31. IR: $\tilde{\nu} = \nu(C{\equiv}C)$ 2160 (m) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1054 $[Pt(PPh_2C{\equiv}CPh)_3]^+$ (100). ^1H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 7.42 (m, 18 H, Ph), 7.35 (m, 6 H, Ph), 7.18 [d, J(H–H) = 4 Hz, 14 H, Ph], 7.06 [t, J(H–H) = 8 Hz, 8 H, Ph], 6.92 [t, J(H–H) = 8 Hz, 14 H, Ph] ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 20 °C): δ = –18.5 [s, ^1J(Pt,P) = 3954 Hz] ppm. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = –4606 [quintet, ^1J(Pt,P) = 3954 Hz] ppm.

$[\{Pt(PPh_2C{\equiv}CPh)(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CPh)\}_2]$ (2): $PPh_2C{\equiv}CPh$ (0.100 g, 0.366 mmol) (1:4 molar ratio) was added to a solution of $[Pt_2(dba)_3]$ (0.100 g, 0.092 mmol) in THF (30 mL). The initially purple solution slowly changed to orange (2 h) and then to yellow after 8 h of stirring. Evaporation to a small volume (5 mL) and the addition of cold MeOH (10 mL) afforded **2** as a yellow solid (0.120 g, 85% yield). $C_{80}H_{60}P_4Pt_2$ (1535.43): calcd. C 62.58, H 3.94; found C 62.94, H 4.09. IR: $\tilde{\nu} = \nu(C{\equiv}C)_{terminal}$ 2167 (m); $\nu(C{\equiv}C)_{bridge}$ 1741 (m), 1722 (sh) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1534 $[M - H]^+$ (38), 1248 $[Pt_2(PPh_2C{\equiv}CPh)_3]^+$ (100). ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.67 (m, 10 H, Ph), 7.42 (m, 6 H, Ph), 7.35 (m, 2 H, Ph), 7.19 (m, 20 H, Ph), 7.03 (m, 6 H, Ph), 6.85 (m, 8 H, Ph), 6.71 [t, J(H–H) = 7 Hz, 4 H, Ph], 6.56 [d, J(H–H) = 7 Hz, 4 H, Ph] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta_{AA'}$ = 4.11; $\delta_{XX'}$ = –6.25 ppm; $N = J_{AX} + J_{AX'}$ = 79.3 Hz, $^1J(Pt,P^A)$ = 3814 Hz, $^1J(Pt,P^X)$ = 3523 Hz. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = –4609 [dddd, $^1J(Pt,P^A)$ = 3814 Hz, $^1J(Pt,P^X)$ = 3523 Hz, $^2J(Pt,P^{A'})$ = 71 Hz, $^4J(Pt,P^{X'})$ = 24 Hz] ppm.

$[Pt(PPh_2C{\equiv}CTol)_4]$ (3): A purple solution of $[Pt_2(dba)_3]$ (0.200 g, 0.183 mmol) in THF (30 mL) was treated with $PPh_2C{\equiv}CTol$ (0.440 g, 1.467 mmol) (1:8 molar ratio), and the mixture was stirred for 2 h. The resulting yellow solution was evaporated to a small volume (5 mL). Addition of cold MeOH (10 mL) caused the separation of a yellow solid (0.238 g, 47% yield), which was shown to be **3**, with small traces of free phosphane ($PPh_2C{\equiv}CTol$) and **4**. Recrystallization from THF/*n*-hexane gave **3** as a pure solid. $C_{84}H_{68}P_4Pt$ (1396.45): calcd. C 72.25, H 4.91; found C 71.65, H 4.74. IR: $\tilde{\nu} = \nu(C{\equiv}C)$ 2164 (m) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1096 $[Pt(PPh_2C{\equiv}CTol)_3]^+$ (100). ^1H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 7.40 (m, 16 H, *o*-Ph), 7.05 [AB system: δ_A = 7.09, δ_B = 6.99, J(A–B) = 8 Hz, 16 H, C_6H_4], 7.04 [t, J(H–H) = 7 Hz, 8 H, *p*-Ph], 6.91 [t, J(H–H) = 7 Hz, 16 H, *m*-Ph], 2.34 (s, 12 H, $C_6H_4\text{–}CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 20 °C): δ = –18.6 [s, ^1J(Pt,P) = 3957 Hz] ppm. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = –4604 [quintet, ^1J(Pt,P) = 3956 Hz] ppm.

$[\{Pt(PPh_2C{\equiv}CTol)(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CTol)\}_2]$ (4): Complex **4** was prepared as a yellow solid (0.123 g, 84% yield) by following a similar procedure to that of **2**, using $[Pt_2(dba)_3]$ (0.100 g, 0.092 mmol) and $PPh_2C{\equiv}CTol$ (0.109 g, 0.366 mmol) (1:4 molar ratio). $C_{84}H_{68}P_4Pt_2$ (1591.54): calcd. C 63.39, H 4.31; found C 63.56, H 4.51. IR: $\tilde{\nu} = \nu(C{\equiv}C)_{terminal}$ 2168 (m); $\nu(C{\equiv}C)_{bridge}$ 1743 (sh), 1717 (m) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1590 $[M - H]^+$ (29), 1290 $[Pt_2(PPh_2C{\equiv}CTol)_3]^+$ (100). ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.69 (m, 14 H, Ph), 7.42 (m, 6 H, Ph), 7.20 (m, 18 H, Ph), 7.03–6.85 (14 H, Ph), 6.46 [AB system: δ_A 6.50, δ_B = 6.41, J(A–B) = 6 Hz, 4 H, C_6H_4], 2.31 (s, 6 H, $C_6H_4\text{–}CH_3$), 2.09 (s, 6 H, $C_6H_4\text{–}CH_3$) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 20 °C): $\delta_{AA'}$ = 4.06; $\delta_{XX'}$ = –5.78 ppm, $N = J_{AX} + J_{AX'}$ = 79.4 Hz, $^1J(Pt,P^A)$ = 3834 Hz, $^1J(Pt,P^X)$ = 3536 Hz. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = –4614 [dddd, $^1J(Pt,P^A)$ = 3834 Hz, $^1J(Pt,P^X)$ 3536 Hz, $^2J(Pt,P^{A'})$ 75 Hz, $^4J(Pt,P^{X'})$ 26 Hz] ppm.

$[Pt(PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2)_4]$ (5): A purple solution of $[Pt_2(dba)_3]$ (0.200 g, 0.183 mmol) in THF (30 mL) was treated with $PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2$ (0.421 g, 1.467 mmol) (1:8 molar ratio). After 2 h of stirring, the yellow solution obtained was evaporated to a small volume (5 mL) and cold MeOH (10 mL) was added to give **5** as an orange solid (0.245 g, 50% yield). $C_{76}H_{56}N_4P_4Pt$ (1344.29): calcd. C 67.90, H 4.20, N 4.17; found C 67.57, H 4.34, N 3.82. IR: $\tilde{\nu} = \nu(C{\equiv}C)$ 2163 (m) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1057 $[Pt(PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2)_3]^+$ (100). ^1H NMR (400.1 MHz, $CDCl_3$, 20 °C): δ = 8.52 (m, 4 H, H^6), 7.46 (m, 18 H), 7.35 (m, 4 H), 7.12 (m, 8 H), 7.02 (m, 8 H), 6.94 [t, J(H–H) = 7.2 Hz, 14 H] (aromatics) ppm. $^{31}P\{^1H\}$ NMR (162.0 MHz, $CDCl_3$, 20 °C): δ = –17.7 [s, ^1J(Pt,P) = 3942 Hz] ppm. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = –4601 [quintet, ^1J(Pt,P) = 3943 Hz] ppm.

$[\{Pt(PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2)(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2)\}_2]$ (6): Method A: Complex **6** was prepared as a yellow solid (0.070 g, 50% yield) by following a similar procedure to that of **2**, using $[Pt_2(dba)_3]$ (0.100 g, 0.092 mmol) and $PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2$ (0.105 g, 0.366 mmol) (1:4 molar ratio). Method B: A yellow solution of **5** (0.100 g, 0.074 mmol) in toluene (30 mL) was stirred for 4 d, and a yellow solid was gradually generated. The final product **6** was collected by filtration, washed with toluene (2 mL) and *n*-hexane (2 mL) and dried (0.030 g, 41% yield). $C_{76}H_{56}N_4P_4Pt_2$ (1539.38): calcd. C 59.30, H 3.67, N 3.64; found C 58.81, H 3.67, N 3.62. IR: $\tilde{\nu} = \nu(C{\equiv}C)_{terminal}$ 2178 (m); $\nu(C{\equiv}C)_{bridge}$ 1756 (sh), 1717 (m) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1538 $[M - H]^+$ (100), 1251 $[Pt_2(PPh_2C{\equiv}C\text{–}C_5H_4N\text{-}2)_3]^+$ (71). ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 8.50 (m, 2 H, $H^6{}_t$), 8.24 (m, 2 H, $H^6{}_\mu$), 7.87 (m, 8 H), 7.35 (m, 10 H), 7.16 (m, 4 H), 6.82 (m, 12 H) (aromatics), 6.45 [d, J(H–H) = 7.6 Hz, 2 H, H^3] ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): $\delta_{AA'}$ = 8.10, $\delta_{XX'}$ = –7.22 ppm; $N = J_{AX} + J_{AX'}$ 79.6, $^1J(Pt,P^A)$ = 3764 Hz, $^1J(Pt,P^X)$ = 3643 Hz. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = – 4590 [dddd, $^1J(Pt,P^A)$ = 3764 Hz, $^1J(Pt,P^X)$ = 3643 Hz, $^2J(Pt,P^{A'})$ = 56 Hz, $^4J(Pt,P^{X'})$ = 24 Hz] ppm.

$[Pt_2(PPh_2C{\equiv}CPPh_2)_2(\mu\text{-}\kappa^2PP'\text{–}PPh_2C{\equiv}CPPh_2)_3]$ (7): A purple solution of $[Pt_2(dba)_3]$ (0.100 g, 0.095 mmol) in THF (30 mL) was treated with $PPh_2C{\equiv}CPPh_2$ (0.144 g, 0.366 mmol) and the mixture stirred for 2 h. The resulting yellow solution was evaporated to a small volume (5 mL). Addition of cold MeOH (10 mL) gave **7** as a yellow solid (0.150 g, 69 % yield). $C_{130}H_{100}P_{10}Pt_2$ (2362.14): calcd. C 66.10, H 4.27; found C 66.12, H 4.23. IR: $\tilde{\nu}$ = ν(C≡C) 2107 (m) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1572 $[Pt_2(PPh_2C{\equiv}CPPh_2)_3]^+$ (100), 1967 $[Pt_2(PPh_2C{\equiv}CPPh_2)_4]^+$ (40). ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.55 (pt, 8 H, Ph), 7.24 (m, 8 H, Ph), 7.17 (m, 32 H, Ph), 7.07 (m, 4 H, Ph), 7.00 (m, 12 H, Ph), 6.92 (m, 12 H, Ph), 6.72 (m, 24 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): = AX_3 system δ_{PA} = –7.6 [q, $^2J(P^A,P^X)$ = 64 Hz, 1 P], δ_{PX} –21.4 [d, $^2J(P^X,P^A)$ = 64 Hz, $^1J(Pt,P^X)$ = 3692 Hz, 3 P], –31.6 (s, 1 P) ppm. $^{195}Pt\{^1H\}$ NMR (85.62 MHz, $CDCl_3$, 20 °C): δ = –4471 [dqd, $^1J(Pt,P^A)$ = 4594 Hz, $^1J(Pt,P^X)$ = 3692 Hz, $^4J(Pt,P_{free})$ = 30 Hz] ppm.

Crystals of $[Pt_2\{PPh_2C{\equiv}CP(O)Ph_2\}_2(\mu\text{-}\kappa^2PP'\text{–}PPh_2C{\equiv}CPPh_2)_3]$ (8): Yellow crystals of **8** were grown by slow diffusion of *n*-hexane into a concentrated solution of **7** in THF at –30 °C. $C_{130}H_{100}O_2P_{10}Pt_2$ (2394.14): calcd. C 65.22, H 4.21; found C 64.85, H 4.22. IR: $\tilde{\nu}$ = ν(C≡C) 2108 (m); ν(P=O) 1211 (s) cm^{-1}. MALDI-TOF(+): *m*/*z* (%) = 1572 $[Pt_2(PPh_2C{\equiv}CPPh_2)_3]^+$ (100), 1983 $[Pt_2(PPh_2C{\equiv}CPPh_2)_3\{PPh_2C{\equiv}CP(O)Ph_2\}]^+$ (50). ^1H NMR (300.1 MHz, $CDCl_3$, 20 °C): δ = 7.63 (m, 8 H, Ph), 7.42 (m, 4 H, Ph), 7.14 (m, 40 H, Ph), 7.00 (m, 12 H, Ph), 6.92 (m, 8 H, Ph), 6.72 (m, 28 H, Ph) ppm. $^{31}P\{^1H\}$ NMR (121.5 MHz, $CDCl_3$, 20 °C): δ = 6.56 (s, 1 P), AX_3 system δ_{PA} = –7.52 [q, $^2J(P^A,P^X)$ = 65 Hz, 1 P], δ_{PX} = –21.23 [d, $^2J(P^A,P^X)$ = 65 Hz, $^1J(Pt,P^X)$ = 3673 Hz, 3 P] ppm.

X-ray Crystallography: Table 3 reports details of the structural analysis of **4** and **8**. Pale yellow crystals of **4** were obtained by slow diffusion at –30 °C of *n*-hexane into a solution of **4** in CH_2Cl_2, whereas yellow crystals of **8** were obtained by slow diffusion at –30 °C of *n*-hexane into a solution of complex **7** in THF, and 1.5 molecules of THF were found in the asymmetric unit of **8**. X-ray intensity data were collected with graphite-monochromated Mo-K_α radiation. Data collection was performed with a Nonius κCCD area-detector diffractometer, and the images were processed with the DENZO and SCALEPACK suite of programs.[68] The absorption corrections were carried out using multiscan[69] with the WINGX program suite.[70] The structures were solved by Patterson Methods using SHELXS-97[71] (**4**) or direct and Patterson methods using SIR2004[72] (**8**), and refined by full-matrix least-squares cycles on F^2 with SHELXL-97.[71] All non-hydrogen atoms were assigned anisotropic displacement parameters. All the hydrogen atoms were constrained to idealized geometries by fixing isotropic displacement parameters to 1.2 times the U_{iso} value of their attached carbon atom for the aromatic and 1.5 times for the methyl groups. For complex **4**, inspection of the structure with PLATON[73] showed the possibility of the presence of symmetry planes, therbey suggesting three new possible space groups ($P2_1am$, $Pma2$, $Pmam$). All attempts to resolve the structure in any of them were unsuccessful. Several restraints have been used to model the THF molecules in **8**. Finally, the structures show some residual peaks greater than 1 eA^{-3} in the vicinity of the platinum atoms (**4**) or the crystallization solvent (**8**), but with no chemical meaning.

CCDC-871278 (for **4**) and -871279 (for **8**·1.5THF) contain 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.

Table 3. Crystallographic data for **4** and **8**·1.5THF.

	4	**8**·1.5THF
Empirical formula	$C_{84}H_{68}P_4Pt_2$	$C_{138.5}\ H_{112}O_7P_{10}Pt_2$
M_r	1591.44	2588.32
T [K]	173(1)	173(1)
λ [Å]	0.71073	0.71073
Crystal system	orthorhombic	monoclinic
Space group	$P2_12_12_1$	$P2_1/n$
a [Å]	18.1764(3)	13.1666(2)
b [Å]	19.1815(3)	28.5794(5)
c [Å]	19.8367(4)	32.5787(5)
α [°]	90	90
β [°]	90	99.4900(10)
γ [°]	90	90
V [Å^3]	6916.1(2)	12091.4(3)
Z	4	4
$D_{calcd.}$ [Mg m^{-3}]	1.528	1.374
ε [mm^{-1}]	4.179	2.496
$F(000)$	3152	5048
Crystal size [mm^3]	0.2 × 0.175 × 0.175	0.40 × 0.25 × 0.20
2θ range [°]	1.52 to 26.37	2.67 to 26.37
Index ranges	$-22 \leq h \leq 16$ $-17 \leq k \leq 23$ $-16 \leq l \leq 24$	$-16 \leq h \leq 16$ $-35 \leq k \leq 35$ $-40 \leq l \leq 40$
Reflections collected	25803	162035
Independent reflections	13645 [R(int) = 0.0447]	24615 [R(int) = 0.0765]
Data / restraints / parameters	13645 / 0/811	24615 / 12 / 1384
Goodness of fit on F^2[a]	1.017	1.044
Final R indices [$I > 2\sigma(I)$][a]	$R1$ = 0.0397, $wR2$ = 0.0694	$R1$ = 0.0339, $wR2$ = 0.0909
R indices (all data)	$R1$ = 0.0660, $wR2$ = 0.0783	$R1$ = 0.0441, $wR2$ = 0.0975
Largest diff. peak and hole [e Å^{-3}]	1.031 and –0.873	1.784 and –0.856

[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 = $\{\Sigma[w(F_o^2 - F_c^2)^2]/(N_{obsd.} - N_{param.})\}^{1/2}$; $w = [\sigma^2(F_o^2) + (g_1P)^2 + g_2P]^{-1}$; $P = [\max(F_o^2;0) + 2F_c^2]/3$.

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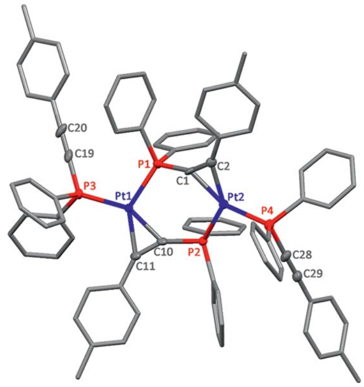
Alkynylphosphane Ligands

Tetrahedral Pt^0 complexes $[Pt(PPh_2C{\equiv}CR)_4]$, which evolve into binuclear derivatives $[\{Pt(PPh_2C{\equiv}CR)(\mu\text{-}\kappa P{:}\eta^2\text{-}PPh_2C{\equiv}CR)\}_2]$ [R = Ph, tolyl, C_5H_4N-2], and binuclear compounds stabilized by a $(\mu\text{-}PPh_2\text{-}C{\equiv}CPPh_2)_3$ triply bridging system have been prepared and fully characterized.



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Platinum(0) Complexes with Alkynylphosphane Ligands

Keywords: Platinum / Bridging ligands / Phosphane ligands / Homometallic complexes / Alkynes