

New dinuclear platinum(II) complex obtained from thermal degradation of platinum(0)–triphenylphosphine complexes

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Thermolysis of [Pt(PPh₃)₂(C₂H₄)], [Pt(PPh₃)₃] or of various complexes of the type [Pt(PPh₃)₂(alkyne)] in toluene gave the dinuclear platinum(II) complex [(Ph₃P)Pt{μ-C₆H₄(PPh₂)-2}(μ-PPh₂)Pt(PPh₃)] in ca. 60% yield as a consequence of both C–H and P–Ph cleavage of co-ordinated triphenylphosphine. The complex, which has been identified by mass spectrometry, NMR (³¹P, ¹⁹⁵Pt) spectroscopy and single-crystal X-ray diffraction analysis, is probably identical with some of the compounds formulated in the literature either as [Pt₂(PPh₃)₄] or [Pt₂(μ-PPh₂)₂{C₆H₄(PPh₂)-2}]₂. The other product of the reaction is the known trinuclear compound [Pt₃(μ-PPh₂)₃(Ph)(PPh₃)₂].

The nature of the platinum-containing products of thermal or photolytic degradation of bis(triphenylphosphine)platinum complexes has been the subject of many studies, but the conclusions remain confusing and sometimes contradictory, mainly because in early work single-crystal X-ray crystallography and NMR (³¹P, ¹⁹⁵Pt) spectroscopy were not readily available. The most definitive results appear to be those of Taylor, Chieh and Carty.¹ From the deep red solutions obtained by heating [Pt(PPh₃)₄] in benzene under argon or nitrogen they isolated and obtained the crystal structures of an orange-red, dinuclear platinum(II) complex [Pt₂(μ-PPh₂)₂(PPh₃)₂] **1** and an orange trinuclear complex **2**, isolated as a benzene solvate [Pt₃(μ-PPh₂)₃(Ph)(PPh₃)₂·C₆H₆] **2a**. These two complexes evidently arise from P–C bond cleavage of co-ordinated triphenylphosphine. More recently, Braunstein and co-workers^{2,3} reported that **1** and **2** are also formed on heating [Pt(PPh₃)₂(C₂H₄)] in acetone or 2-methoxyethanol and that complex **2** exists in a number of crystalline modifications, depending on the solvent of crystallisation. Two interconvertible forms **2b** and **2c** obtained from toluene–pentane and CH₂Cl₂–pentane, respectively, are structurally different: the former contains a bent chain of metal atoms with two ‘short’ [2.758(3) Å] and a ‘long’ Pt–Pt distance [3.586(2) Å]; the latter contains an isosceles triangle having ‘medium’ separations of 2.956(3), 2.956(3) and 3.074(4) Å. The pattern of Pt–Pt distances in the benzene solvate **2a** [2.785(1), 2.785(1) and 3.630(1) Å] is closer to that of **2b** than of **2c**. Red solids have been obtained from closely related reactions, e.g. thermolysis of [Pt(PPh₃)_n] (n = 3 or 4) under nitrogen,^{4–6} thermolysis of [PtPh₂(PPh₃)₂] *in vacuo*,⁷ irradiation at 334 nm of *trans*-[PtH(R)(PPh₃)₂] (R = CH₂CN, CH₂CH₂CN or CH₂CH₂CH₂CN) in toluene,⁸ and thermal elimination of 1,2,3-triphenylcyclopentadiene from the 1-platinacyclohexa-2,4-diene complex [Pt{CPh=CPh–CPh=CHCH₂}(PPh₃)₂].⁹ The products have been formulated variously as trimers, such as [Pt₃(PPh₃)₆] **3**^{4,6} and [Pt₃(μ-PPh₂)₃{C₆H₄(PPh₂)-2}]₃ **4**,⁷ and tetramers such as [Pt₄(PPh₃)₄]^{4,6} and [Pt₄(μ-PPh₂)₄{C₆H₄(PPh₂)-2}]₄,^{7,9} but it seems likely that complex **2** is formed in these reactions.

The relationship of complex **1** to other products reported to arise from thermal or photolytic decomposition of bis-

(triphenylphosphine)platinum complexes is even less clear. Blake and Nyman¹⁰ reported in a preliminary communication that irradiation of the oxalatoplatinum(II) complex [Pt(C₂O₄)(PPh₃)₂] gives a cream, cyclometallated product [Pt₂(μ-PPh₂)₂{C₆H₄(PPh₂)-2}]₂·0.5C₆H₆ **5**, m.p. 244–248 °C, whereas in the full paper¹¹ what is apparently the same compound, m.p. 248–250 °C, described as lemon-yellow, is formulated [Pt₂(PPh₃)₄] **6**, without reference to the discrepancy. The second formulation has been adopted for similar compounds obtained by irradiation at 280 nm of the bis(azido) complex *cis*-[Pt(N₃)₂(PPh₃)₂] in ethanol or thf¹² and irradiation at 313 nm of *trans*-[PtH(R)(PPh₃)₂] (R = CH₂CN, CH₂CH₂CN or CH₂CH₂CH₂CN) in toluene.⁸ However, irradiation of [Pt(PPh₃)₂(C₂H₄)] in ethanol was reported¹³ to give a white solid whose empirical formula corresponded to that of **5** and which became red on standing or heating. The same empirical formula was assigned to the product of thermal decomposition of [PtPh₂(PPh₃)₂].⁷

In this paper we describe a hitherto unreported dinuclear platinum complex, which we identified initially as a by-product of the thermally induced isomerisation of the cyclohexyne-platinum(0) complex [Pt(PPh₃)₂(C₆H₈)], first to the η¹-cyclohex-1-enyl cycloplatinated complex [Pt{C₆H₄(PPh₂)-2}(C₆H₉)(PPh₃)] and subsequently to the isomeric cyclohex-2-enyl and cyclohex-3-enyl complexes.¹⁴

Results

When a solution of [Pt{C₆H₄(PPh₂)-2}(η¹-C₆H₉)(PPh₃)]¹⁴ in [²H₈]toluene was heated at 120 °C for 3 weeks slow formation of a new compound with a characteristic and complex ³¹P NMR spectrum was observed. Conversion was not complete, however, and the new compound could not be separated from starting material. The same compound was formed more rapidly by heating the ethene complex [Pt(PPh₃)₂(C₂H₄)] in toluene for 4–6 d. It was isolated in ca. 60% yield and identified by elemental analysis and by the appearance of a parent ion peak in the mass spectrum as the dinuclear platinum(II) complex [Pt₂(μ-PPh₂){μ-C₆H₄(PPh₂)-2}(PPh₃)₂] **7**. The other, less soluble, product of this reaction was the known trinuclear complex [Pt₃(μ-PPh₂)₂(μ-Ph)(PPh₃)₂] **2**,^{1–3} which was isolated in ca. 30% yield (Scheme 1). Complex **7** was also obtained under similar conditions from

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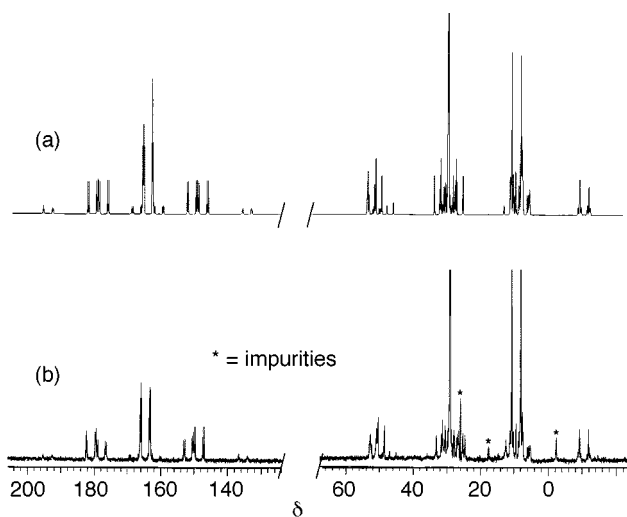
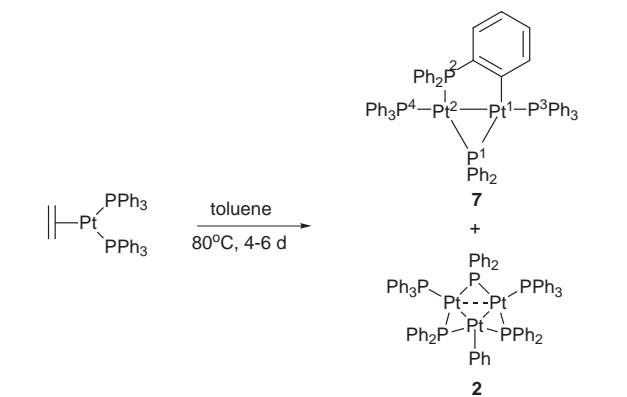


Fig. 1 The $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **7** at 80.98 MHz: (a) simulated, (b) experimental

$[\text{Pt}(\text{PPh}_3)_3]$, though the reaction was slower than for $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$, or from the alkyne complexes $[\text{Pt}(\text{PPh}_3)_2(\text{alkyne})]$ [alkyne = MeC_2Me , $\text{MeC}_2\text{CO}_2\text{Me}$ and C_7H_{10} (cycloheptyne)], together with small amounts of by-products having ^{31}P NMR signals in the region $\delta -50$ to -60 , which may be the corresponding isomeric cycloplatinated complexes analogous to $[\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)]$. On heating in toluene the dimethyl acetylenedicarboxylate complex $[\text{Pt}(\text{PPh}_3)_2(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})]$ undergoes quantitative cyclometallation to give $[\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}\{\eta^1\text{-C}(\text{CO}_2\text{Me})=\text{CHCO}_2\text{Me}\}(\text{PPh}_3)]$, as previously reported,^{15,16} but this compound remained stable to further heating.

The general features of the $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of complex **7** are shown in Fig. 1; impurity peaks at $\delta -2$, $+18$ and $+26$ are marked with an asterisk. Although some of the detail is not clearly reproduced in Fig. 1, it is clear from the complexity of the spectrum that complex **7** must be less symmetrical than $[\text{Pt}_2(\mu\text{-PPh}_2)_2(\text{PPh}_3)_2]$ **1**, the ^{31}P spectrum of which unfortunately has not been reported. There are three main areas of absorption: an approximate doublet of triplets with two pairs of ^{195}Pt satellites at δ_{p} 164.5, two closely spaced multiplets at δ 29.5 and 29.3, and a complex group of peaks in the region of δ 10. On the basis of its chemical shift, the peak at δ 164.5 can be assigned to the phosphorus atom P(1) of a diphenylphosphido group that bridges a platinum–platinum bond.¹⁷ Though there are exceptions, such PPh_2 groups generally have ^{31}P chemical shifts in the range $\delta +50$ to $+300$, e.g. $[(\text{C}_6\text{F}_5)_2\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PPh}_3)]$ (δ_{p} 240.0),¹⁸ $[(\text{Ph}_3\text{P})\text{Pt}(\mu\text{-PPh}_2)(\mu\text{-dppm})\text{Pt}(\text{PPh}_3)]$ (δ_{p} 194.7) (dppm = $\text{Ph}_2\text{PCH}_2\text{PPh}_2$),¹⁹ $[(\text{OC})_4\text{M}(\mu\text{-PPh}_2)_2\text{Pt}(\text{PPh}_3)]$

Table 1 Coupling constants ($^{195}\text{Pt}\text{-}^{31}\text{P}$ and $^{31}\text{P}\text{-}^{31}\text{P}$, in Hz) derived from simulation of $^{31}\text{P}\{-^1\text{H}\}$ NMR spectrum of $[(\text{Ph}_3\text{P})\text{-Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)]$ **7***

$^1J(\text{Pt-P})$	$^2J(\text{Pt-P})$	$^2J(\text{P-P})$	$^3J(\text{P-P})$
Pt(1)P(1) 2117	Pt(1)P(2) -80	P(1)P(2) 213	P(2)P(3) 6
Pt(1)P(3) 3624	Pt(1)P(4) 534	P(1)P(3) 31	P(3)P(4) 152
Pt(2)P(1) 2635	Pt(2)P(3) 227	P(1)P(4) 0	
Pt(2)P(2) 3226		P(2)P(4) 9	
Pt(2)P(4) 3327			

* Atoms numbered as in the diagram of compound **7** (Scheme 1); $^1J(\text{Pt-Pt}) = 1611$ Hz.

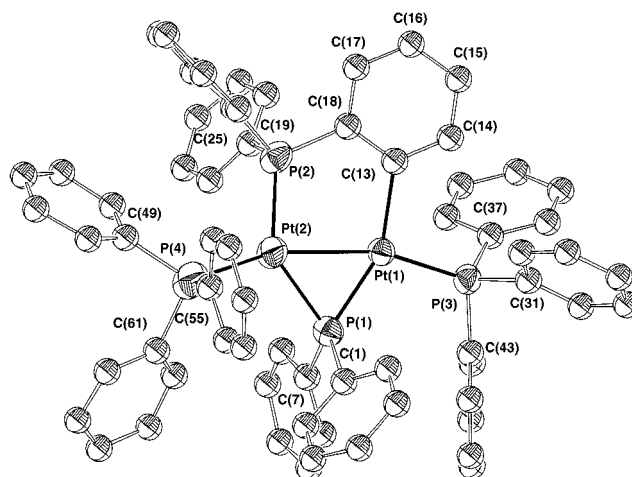


Fig. 2 An ORTEP²⁸ diagram for $[(\text{Ph}_3\text{P})\text{-Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)]$ **7** with atom labelling

$[\text{M} = \text{Cr}, \delta_{\text{p}} 226;$ ²⁰ $\text{M} = \text{Mo}, \delta_{\text{p}} 202;$ ²⁰ $\text{M} = \text{W}, \delta_{\text{p}} 173]$,^{20,21} $[(\eta\text{-C}_5\text{H}_5)(\text{OC})_2\text{Mo}(\mu\text{-PPh}_2)\text{Pt}(\mu\text{-PPh}_2)_2\text{Pt}(\mu\text{-PPh}_2)\text{Mo}(\text{CO})_2(\eta\text{-C}_5\text{H}_5)]$ [δ_{p} (Mo–Pt) 180.8, (Pt–Pt) 254.8],²² and $[(\text{C}_6\text{F}_5)_2\text{-Pt}(\mu\text{-P}^{1,2}\text{Ph}_2)_2\text{Pt}(\mu\text{-P}^3\text{Ph}_2)\text{Pt}(\text{CO})(\mu\text{-P}^4\text{Ph}_2)\text{Pt}(\text{CO})(\text{C}_6\text{F}_5)_2]$ [$\delta_{\text{p}^{1,2}}$ 275.7, 257.2; δ_{p^3} 147.1].²³ In contrast, δ_{p} corresponding to a PPh_2 group bridging a pair of platinum atoms not linked by a metal–metal bond in the last compound is -6.9 .²³ The peaks at δ 29.3 and 29.5 are reasonably ascribed to the phosphorus atoms P(4) and P(3) of inequivalent PPh_3 ligands, which lie along the Pt–Pt axis, and the multiplet at δ 9.5 must belong to the phosphorus atom P(2) of the bridging $\text{C}_6\text{H}_4(\text{PPh}_2)\text{-2}$ group; the corresponding chemical shifts of the closely related, symmetrical platinum(II)–platinum(II) complex $[(\text{Ph}_3\text{P})\text{-Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}_2\text{Pt}(\text{PPh}_3)]$ are δ 25.4 (PPh_3) and -2.6 ($\text{C}_6\text{H}_4\text{PPh}_2$).²⁴ The simulated spectrum based on the assignments is shown in Fig. 1 and the derived Pt–P and P–P coupling constants are listed in Table 1. There is good agreement between the simulated and experimental spectra. The fact that the two-bond coupling constant between Pt(1) and P(2) is negative (-80 Hz) provides supporting evidence for the presence of a metal–metal bond in complex **7**; this criterion has been shown to hold for the extensive series of dinuclear platinum(II) complexes containing bridging dppm ligands.^{25,26}

The ^{195}Pt spectrum of complex **7** confirms the presence of two inequivalent platinum atoms and reproduces the Pt–P coupling constants listed in Table 1, which show no unusual features. The magnitude of the platinum–platinum coupling constant derived from the ^{195}Pt spectrum [$^1J(\text{Pt-Pt})$ 1611 Hz] suggests the presence of a Pt–Pt bond, although the value is at the lower end of the wide range reported for Pt–Pt bonded complexes; there is no correlation between the magnitude of $J(\text{Pt-Pt})$ and Pt–Pt bond length in such compounds.²⁷

A single crystal X-ray study of complex **7** has confirmed the conclusions based on spectroscopic data. The molecular

Table 2 Selected bond distances (Å) and bond angles (°) for $[(\text{Ph}_3\text{P})_2\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}\{\mu\text{-PPh}_2\}\text{Pt}(\text{PPh}_3)]$ **7**

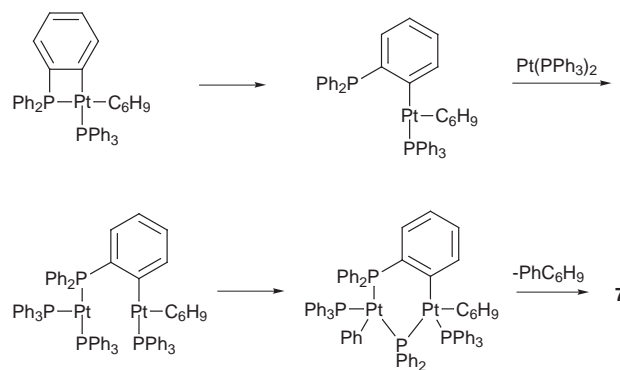
Pt(1)–Pt(2)	2.6549(8)	Pt(1)–P(3)	2.242(3)
Pt(1)–P(1)	2.240(3)	Pt(1)–C(13)	2.123(9)
Pt(2)–P(2)	2.264(4)	Pt(2)–P(1)	2.280(3)
Pt(2)–P(4)	2.291(5)	P(2)–C(18)	1.79(1)
Pt(1)–P(1)–Pt(2)	71.9(1)	Pt(1)–Pt(2)–P(2)	83.23(9)
P(1)–Pt(1)–C(13)	151.7(3)	Pt(2)–Pt(1)–C(13)	97.4(3)
Pt(2)–P(2)–C(18)	115.6(4)	Pt(2)–Pt(1)–P(3)	162.84(8)
Pt(1)–Pt(2)–P(4)	159.7(1)	P(2)–C(18)–C(13)	119.1(7)
P(1)–Pt(2)–P(2)	135.3(1)	Pt(1)–Pt(2)–P(1)	53.35(9)
Pt(2)–Pt(1)–P(1)	54.72(8)	P(2)–Pt(2)–P(4)	115.0(1)
P(1)–Pt(2)–P(4)	109.7(1)	P(3)–Pt(1)–C(13)	99.7(3)
P(1)–Pt(1)–P(3)	108.4(1)		

geometry is shown in Fig. 2 together with atom numbering. Selected interatomic distances and angles are listed in Table 2. The Pt–Pt distance [2.6549(8) Å] is consistent with the presence of a Pt–Pt bond, being greater than those observed in $[(\text{Ph}_3\text{P})_2\text{Pt}\{\mu\text{-PPh}_2\text{C}_6\text{H}_4\text{-2}\}\text{Pt}(\text{PPh}_3)]$ [2.630(1) Å]²⁴ and $[(\text{Ph}_3\text{P})_2\text{Pt}\{\mu\text{-PPh}_2\}\text{Pt}(\text{PPh}_3)]$ **1** [2.604(1) Å].¹ The close approach of the platinum atoms also generates an acute angle of 72° at the phosphorus atom of the bridging PPh₂ group. The Ph₃P–Pt–Pt–PPh₃ axis is distorted considerably from linearity [P(4)–Pt(2)–Pt(1) 160, P(3)–Pt(1)–Pt(2) 163°]. Phosphorus atoms P(2) and P(3) are 0.447 and 0.120 Å, respectively, above the plane defined by Pt(1), Pt(2) and P(1), whereas phosphorus atom P(4) and carbon atom C(13) are both below the plane by 0.474 and 0.182 Å, respectively.

Discussion

Our results add a further piece of information to the puzzle of the degradation of bis(triphenylphosphine)platinum complexes but do not reconcile all the conflicting results. It seems very likely that complex **7** has been isolated by earlier workers, and it is probably identical with the dinuclear compounds **5** or **6** obtained by UV irradiation of $[\text{Pt}(\text{C}_2\text{O}_4)(\text{PPh}_3)_2]$ ^{10,11} or of *cis*- $[\text{Pt}(\text{N}_3)_2(\text{PPh}_3)_2]$.¹² However, the spectroscopic properties of complex **7** do not correspond with those of the solid formulated as $[\text{Pt}_2(\text{PPh}_3)_4]$, which was isolated by UV irradiation at 313 nm of *trans*- $[\text{PtH}(\text{R})(\text{PPh}_3)_2]$ (R = CH₂CN, CH₂CH₂CN or CH₂CH₂CH₂CN);⁸ its mass spectrum was reported to show the parent ion peak at *m/z* 1438 (*cf.* 1362 for **7**) and its ³¹P NMR spectrum to contain complex resonances centred at δ 54. Especially puzzling is our failure to detect or isolate the μ-bis(diphenylphosphido) complex **1** even though this compound has been reported as a product of thermolysis of $[\text{Pt}(\text{PPh}_3)_4]$ in benzene¹ and of $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ in acetone² or 2-methoxyethanol,³ has been structurally characterised,¹ and has been treated with $[\text{AuCl}(\text{PPh}_3)]$ and TIPF₆ to give the structurally characterised cation $[\text{Pt}_2(\mu\text{-PPh}_2)_2\{\text{Au}(\text{PPh}_3)_2(\text{PPh}_3)_2\}]^{2+}$.²⁹ Our attempts to repeat the reactions reported to give the mixture of complexes **1** and **2** invariably gave **7** and **2**, irrespective of the solvent (benzene, toluene, acetone, 2-methoxyethanol, ethanol) and the presence or absence of air; also, prolonged heating of **7**, with or without the presence of PPh₃ or water, did not give **1**, the latter reaction leading to decomposition of the complex. We can only surmise that the conditions required to form **1** are critical, a point that has been emphasised to us by Dr. Braunstein, who has independently identified complex **7**.³⁰ It is also interesting that heating of complex **7** did not give trinuclear **2**, which seems to indicate that presence of platinum(0) fragments is required for the formation of the latter.

At this stage, one can only speculate about the pathway or pathways by which complex **7** is formed. In the case of the precursor $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)]$ a plausible

**Scheme 2**

sequence could be opening of the four-membered ring, addition of a $\text{Pt}(\text{PPh}_3)_2$ fragment to the free phosphine ligand, P–C bond cleavage of co-ordinated PPh₃, and subsequent reductive elimination of the C₆H₉ and C₆H₅ fragments (Scheme 2). A precedent for the first two steps is provided by the comproportionation of $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}]_2$ with $[\text{Pt}(\text{PPh}_3)_2]$ to give the diplatinum(i) complex $[(\text{Ph}_3\text{P})_2\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}_2\text{Pt}(\text{PPh}_3)]$.²⁴ A similar sequence to that in Scheme 2 could occur in the case of the precursors $[\text{Pt}(\text{PPh}_3)_2\text{L}]$ (L = PPh₃, C₂H₄, MeC₂Me or MeC₂CO₂Me) if one assumes that these can undergo an initial, hitherto unobserved orthometallation in addition to, or in competition with, the facile loss of L that is required to generate the $\text{Pt}(\text{PPh}_3)_2$ fragment. In the case of L = MeO₂CC₂CO₂Me orthometallation occurs but the vinyl ligand in the resulting complex $[\text{Pt}\{\text{C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}\{\eta^1\text{-C}(\text{CO}_2\text{Me})=\text{CHCO}_2\text{Me}\}(\text{PPh}_3)]$ must be too firmly bound to allow generation of $[\text{Pt}(\text{PPh}_3)_2]$. Alternatively, the orthometallation may be much faster in this case than the formation of a $\text{Pt}(\text{PPh}_3)_2$ fragment from $[\text{Pt}(\text{PPh}_3)_2(\text{MeO}_2\text{CC}_2\text{CO}_2\text{Me})]$ and no dinuclear species is formed when heating the latter. It is also possible that the electrophilic vinyl fragment present in the orthometallated species prevents the opening of the four-membered ring which is needed for the co-ordination of the $\text{Pt}(\text{PPh}_3)_2$ fragment. Clearly, more experiments are needed to answer these questions and to establish the chemistry of complex **7**.

Experimental

General procedures

All experiments were performed under an inert atmosphere (usually argon) with use of standard Schlenk techniques, and all solvents were dried and degassed prior to use. Infrared spectra were measured in solid KBr or in solution (KBr cells) on Perkin-Elmer 683 or 1800 FT-IR spectrometers, mass spectra by the electron impact (EI) method on a VG Micromass 7070F or a Fisons Instrument VG AutoSpec spectrometer and NMR spectra on Varian XL-200E (¹H at 200 MHz, ³¹P at 80.98 MHz and ¹⁹⁵Pt at 42.83 MHz), Varian Gemini-300 BB (¹H at 300 MHz and ³¹P at 121.4 MHz) and Varian VXR-300 spectrometers (¹H at 300 MHz). The chemical shifts (δ) for ¹H and ¹³C are given in ppm relative to residual signals of the solvent, to external 85% H₃PO₄ for ³¹P and to external K₂PtCl₆ for ¹⁹⁵Pt. The spectra of all nuclei (except ¹H) were ¹H decoupled. Simulations were performed on a program constructed at the University of Victoria by K. R. Dixon based on UAEITR³¹ and NMRPLOT³² and run on an IBM3090 computer. The derived P–P and Pt–P coupling constants for complex **7** are listed in Table 1.

Starting materials

The ethene complex $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ was prepared as described by Nagel.³³ The complexes $[\text{Pt}(\text{PPh}_3)_2(\text{alkyne})]$ (alkyne = MeC₂Me, MeC₂CO₂Me or MeO₂CC₂CO₂Me) were

Table 3 Crystal and structure refinement data for $[(\text{Ph}_3\text{P})\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)]\text{7}$

Chemical formula	$\text{C}_{66}\text{H}_{54}\text{P}_4\text{Pt}_2$
<i>M</i>	1361.23
Crystal system	Monoclinic
Space group	$P2_1/c$ (14)
<i>a</i> /Å	14.345(1)
<i>b</i> /Å	22.311(3)
<i>c</i> /Å	17.459(3)
β /°	97.93(1)
<i>U</i> /Å ³	5534(1)
<i>D</i> _c /g cm ⁻³	1.63
<i>Z</i>	4
<i>T</i> /K	296
$\mu(\text{Cu-K}\alpha)/\text{cm}^{-1}$	108.34
Total reflections	8796
Unique reflections	8488 ($R_{\text{int}} = 0.07$)
Used reflections	6022 [$I > 3\sigma(I)$]
<i>R</i> , <i>R'</i> (used reflections)	0.066, 0.104

prepared by addition of the alkyne to either $[\text{Pt}(\text{PPh}_3)_3]$ or $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$;^{34–36} the cyclohexyne and cycloheptyne analogues were made by treatment of these precursors with 1% sodium amalgam and the appropriate 1,2-dibromocycloalkene.³⁷ The complex $[\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)]$ was made by heating $[\text{Pt}(\text{PPh}_3)_2(\text{C}_6\text{H}_8)]$ as previously described.¹⁴

Preparation of $[(\text{Ph}_3\text{P})\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)]\text{7}$ and $[\text{Pt}_3(\mu\text{-PPh}_2)_3(\text{Ph})(\text{PPh}_3)_2]\text{2}$

A solution of $[\text{Pt}(\text{PPh}_3)_2(\text{C}_2\text{H}_4)]$ (600 mg) in toluene (10 cm³) was heated at 80 °C for 4 d. The trinuclear cluster **2** precipitated as an orange-red microcrystalline powder (141 mg, 30%) when the dark red solution was left overnight at room temperature. It was identified by comparison of its ³¹P and ¹⁹⁵Pt NMR spectra with those reported.^{2,3} The volume of the remaining red solution was reduced by half *in vacuo* and hexane (10 cm³) added with stirring to give a yellow-brown solid. After the solvent had been decanted, the remaining solid was washed with hexane and dried *in vacuo* to give 343 mg of compound **7** (62%). Crystals suitable for X-ray analysis were obtained by layering a toluene solution of **7** with hexane. Similarly, a solution of $[\text{Pt}(\text{PPh}_3)_3]$ (550 mg) in toluene (10 cm³) was heated at 120 °C for 6 d. Separation as described above yielded 101 mg of **2** (32%) and 235 mg of **7** (61%). Compound **7** (Found: C, 58.3; H, 4.05; P, 9.3. $\text{C}_{33}\text{H}_{27}\text{P}_2\text{Pt}$ requires C, 58.3; H, 4.0; P, 9.0%); *m.p.* >250 °C (decomp.); $\tilde{\nu}_{\text{max}}/\text{cm}^{-1}$ (KBr) 3050w, 1585m, 1570w, 1475s, 1430s, 1305m, 1260m, 1180m, 1095s, 1025m, 740s and 690s; δ_{P} (80.98 MHz, C_6D_6) 9.5 [m, P(2)], 29.3 [m, P(4)], 29.5 [m, P(3)] and 164.5 [m, P(1)]; δ_{Pt} (42.83 MHz, C_6D_6) -4848 [m, Pt(2)] and -4351 [m, Pt(1)]; *m/z* 1362 (M^+ , 100), 679 (80) and 603 (74%).

Qualitative NMR experiments

(a) A solution of $[\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\eta^1\text{-C}_6\text{H}_9)(\text{PPh}_3)]$ (40 mg) in $[\text{D}_8]\text{toluene}$ (1.5 cm³) was heated at 120 °C for 3 weeks. Monitoring by ³¹P NMR spectroscopy showed that compound **7** was gradually formed, though starting material remained. (b) Solutions of $[\text{Pt}(\text{PPh}_3)_2(\text{alkyne})]$ (alkyne = MeC₂Me, MeC₂-CO₂Me or C₇H₁₀) in toluene were heated at 120 °C. Monitoring by ³¹P NMR spectroscopy showed that compound **7** was gradually formed, together with traces of the corresponding ortho-metallated complexes. In the case of alkyne = MeC₂Me the trinuclear cluster **2** also appeared after 3 d.

X-Ray crystallography of

$[(\text{Ph}_3\text{P})\text{Pt}\{\mu\text{-C}_6\text{H}_4(\text{PPh}_2)\text{-2}\}(\mu\text{-PPh}_2)\text{Pt}(\text{PPh}_3)]\text{7}$

Selected crystal data, details of data collection, structure anal-

ysis and structure refinement are in Table 3. The structure was solved by direct methods (SIR 92)³⁸ and expanded by use of Fourier techniques (DIRDIF 94).³⁹ Calculations were performed with the TEXSAN program;⁴⁰ final refinement computations were carried out with XTAL 3.4.⁴¹ All non-carbon and -hydrogen atoms were refined anisotropically by full matrix least squares. Carbon atoms were refined isotropically because the rings in two of the phosphine ligands showed large thermal motion. One ring was modelled as disordered over two locations, with half occupancy being assigned to each. Various bond length and angle restraints were imposed on the phenyl rings throughout refinement. Hydrogen atoms were included in calculated positions (C–H 0.95 Å) and held fixed, with common thermal parameter values. Hydrogen atoms on the disordered ring substituent were omitted from the calculations. The largest peaks in final Fourier difference synthesis lie close to the heaviest atoms.

CCDC reference number 186/1016.

See <http://www.rsc.org/suppdata/dt/1998/2367/> for crystallographic files in .cif format.

Acknowledgements

We thank the Alexander von Humboldt Foundation for the award of a Feodor von Lynen Fellowship to Thomas Dirnberger and Mr. Chris Blake for checking the NMR simulations.

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Received 6th April 1998; Paper 8/02586J

