Di- and trinuclear phosphido-bridged platinum complexes. Crystal structures of [Pt{CH₂=CHC(O)OMe}(PPh₃)₂], *trans*-[Pt₂(μ -PPh₂)₂I₂(PPh₃)₂] and *cis*,*cis*-[Pt₃(μ -I)₂(μ -PPh₂)₂Cl_{0.5}I_{1.5}(PPh₃)₂][†][‡]

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Received 23rd January 2009, Accepted 14th April 2009 First published as an Advance Article on the web 12th May 2009 DOI: 10.1039/b901563a

The readily available Pt(0) methyl acrylate complex [Pt{CH₂=CHC(O)OMe}(PPh₃)₂] (2) allows access to the known, mixed-valence trinuclear cluster [Pt₃(μ -PPh₂)₃Ph(PPh₃)₂] (3) in 64% yield. Oxidation of 3 with 2 equivalents of I₂ afforded the new trinuclear complex [Pt₃(μ -I)₂(μ -PPh₂)₂I₂(PPh₃)₂] (4) whose molecular structure is similar to that of the related compound of empirical formula [Pt₃(μ -I)₂(μ -PPh₂)₂Cl_{0.5}I_{1.5}(PPh₃)₂] (5) which has been generated by oxidation of 3 with successively 1 equivalent of I₂ and 1 equivalent of C₆H₃ICl₂. In these complexes, the four halogen atoms lie on the same side of the almost aligned platinum atoms and the nearly square-planar coordination planes of the metal atoms adopt a "japanese screen", chair-like conformation. The reaction of the dinuclear, metal-metal bonded Pt(I)-Pt(I) complex [Pt₂(μ -PPh₂)₂(PPh₃)₂] with one equivalent of I₂ afforded the Pt(II) complex [Pt₂(μ -PPh₂)₂I₂(PPh₃)₂] (6). The molecular structures of complexes 2·CH₂Cl₂, [Pt₃(μ -I)₂(μ -PPh₂)₂(I_{1.3}Cl_{0.7})(PPh₃)₂][Pt₃(μ -I)₂(μ -PPh₂)₂(I_{1.7}Cl_{0.3})(PPh₃)₂]·C₆H₅Cl·3CH₂Cl₂ (5A·5B·C₆H₅Cl·3CH₂Cl₂) and 6 have been established by single crystal X-ray diffraction studies.

Introduction

Thermolysis of triphenylphosphine Pt(0) complexes, such as $[Pt(PPh_3)_n]^{1,2}$ or $[Pt(C_2H_4)(PPh_3)_2]^{3,4}$ has long been known to produce red solutions which contain d^9-d^9 metal-metal bonded dinuclear complexes, such as [Pt₂(µ-PPh₂)₂(PPh₃)₂]^{1,3,4} and [Pt₂(µ $o-C_6H_4PPh_2)(\mu-PPh_2)(PPh_3)_2$,^{2,5} and the triangular cluster [Pt₃(μ -PPh₂)₃Ph(PPh₃)₂] (3)¹⁻⁴ in poor to medium yield. The latter, mixedvalence $[2 \times Pt(I) + Pt(II)]$ cluster has the remarkable property of displaying different isomeric solid-state structures depending on the solvent used for its crystallization.^{1,3,4,6} This translates in considerable variations of the separation between the formally Pt(I) centres, which ranges from $3.074(4)^{3,4}$ to 3.630(1) Å.¹ Polynuclear phosphido complexes of platinum continue to attract considerable attention because of their diversified structures and rich chemistry,7 including redox aspects.8 The reactivity of 3 has been examined towards oxidation, which was shown to induce reductive coupling of PPh2 and phenyl groups,9 and towards various silanes and siloxanes which afforded the first platinum clusters containing a direct Pt-Si bond.¹⁰ However, the limited yields of its preparation have prevented extensive studies of this cluster. Herein we describe a new and improved synthesis of cluster 3 by thermolysis of the Pt(0) methyl acrylate complex $[Pt{CH₂=CHC(O)OMe}(PPh_3)_2] (2) and report further studies on its oxidation and that of [Pt₂(µ-PPh_2)_2(PPh_3)_2] with halogens, which afforded new di- and trinuclear Pt(II) complexes.$

Results and discussion

Synthesis of $[Pt{CH_2=CHC(O)OMe}(PPh_3)_2]$ (2) and its transformation into $[Pt_3(\mu-PPh_2)_3Ph(PPh_3)_2]$ (3)

The transformations leading to 3 are summarized in Scheme 1.



Refluxing a suspension of the Pt(0) complex $[Pt(C_2H_4)(PPh_3)_2]$ (1) in acetone with an excess of methyl acrylate for 24 h afforded $[Pt{CH_2=CHC(O)OMe}(PPh_3)_2]$ (2) in high yield. This and analogous Pt(0) olefin complexes have been prepared similarly.^{11,12} The ³¹P{¹H} NMR spectrum of 2 contains signals at δ 30.85

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[‡] Electronic supplementary information (ESI) available: ORTEP plots of the crystal structures and views of the crystal packing in **5A**-**5B**. CCDC reference numbers 71938–71940. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/b901563a

Pt–P1	2.2659(9)	P1-Pt-P2	106.00(4)
Pt-P2	2.2903(11)	P1-Pt-C37	105.82(10)
Pt-C37	2.099(3)	P2-Pt-C38	108.41(8)
Pt-C38	2.128(3)	C37-Pt-C38	39.76(12)
C37–C38	1.438(4)	C38-C39-O1	110.6(3)
C38–C39	1.466(4)	C38-C39-O2	126.3(3)
C39–O1	1.347(4)	C39-O1-C40	116.0(3)
C39–O2	1.214(4)	O2-C39-O1	123.0(3)
O1–C40	1.450(4)	Pt-C38-C39	112.3(2)

and 31.9 ppm, typical of an AB system, attributed to the two chemically different phosphorus atoms, with a ${}^{2}J(P-P)$ coupling of 42 Hz consistent with their mutual *cis* relationship and flanked by ${}^{195}Pt$ satellites with ${}^{1}J(Pt-P)$ couplings of 4056 and 3559 Hz, respectively. These data are consistent with those found for this and related [Pt(olefin)(PPh_3)_2] complexes.^{11–13}

An X-ray diffraction study was performed on a single crystal of **2** obtained from a CH_2Cl_2 solution layered with pentane. Its molecular structure is shown in Fig. 1 and selected bond lengths and angles are given in Table 1. A molecule of CH_2Cl_2 crystallizes in the unit cell for each molecule of complex.

Fig. 1 ORTEP view of 2 in $2 \cdot CH_2CI_2$ with partial labelling scheme. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms and solvent molecules are omitted for clarity.

When considering the mid-point of the C=C double bond of the π -bonded CH₂=CHC(O)OMe ligand, the Pt atom has a Y-shape, planar coordination geometry, being further surrounded by two PPh₃ ligands. This is as expected for a 16e Pt(0)L₃-type complex. The coordination geometry around the Pt atom is almost planar, the angle between the PtC₂ and PtP₂ planes being 3.4(2)°. The C=C double bond of the methyl acrylate ligand is linked to the Pt atom in a slightly asymmetric manner: Pt-C37 = 2.099(3) and Pt-C38 = 2.128(3) Å. The longer platinum-phosphorus bond [Pt-P2 = 2.2903(11) Å] is in *trans* position with respect to the CH₂ group and the shorter one [Pt-P1 = 2.2659(9) Å] is *trans* to the carbon atom bearing the carboxylate group, which has a weaker *trans*-influence than the CH₂ group. Consistently, the higher ${}^{1}J(Pt-P)$ value is assigned to P(1) and a ${}^{1}H/{}^{31}P$ NMR 2D experiment showed that P2, which has the smaller ${}^{1}J(Pt-P)$ value, is coupled to two different protons. This leads to the following assignment of the ${}^{31}P{}^{1}H$ NMR signals: P(1) at 30.85 ppm and P(2) at 31.9 ppm. The methyl acrylate mean plane containing C38, C39, O1 and O2 makes an angle of 79.37(13)° with respect to the Pt coordination plane. All these data are consistent with those found in the structures of related bis(phosphine) Pt(0) alkene complexes.^{11,12,14}

Whereas $[Pt(C_2H_4)(PPh_3)_2]$ (1) is thermally transformed into Pt₂ and Pt₃ complexes already in boiling acetone, refluxing an acetone solution of 2 for 3 days did not lead to any transformation, indicating the stability of this complex. However, refluxing a toluene solution of 2 for 5 h afforded the cluster $[Pt_3(\mu PPh_2$ ₃Ph(PPh₃)₂] (3), which has been isolated in an improved yield of 64% and characterized by ${}^{31}P{}^{1}H{}$ NMR spectroscopy.³ According to ${}^{31}P{}^{1}H$ NMR spectroscopy, the mother liquor of 3 contained only the precursor 2. Further heating of this solution for 12 h afforded the familiar red solution which contains diand trinuclear Pt complexes, from which 3 has been previously isolated.^{2,3} Since in an independent reaction, we did not observe any transformation of pure 3 when it was heated in toluene for a few hours, we believe that the dinuclear complexes formed result directly from 2. A detailed mechanism explaining the simultaneous presence of di- and trinuclear complexes starting from various bis(triphenylphosphine)platinum(0) complexes is still lacking but it is most likely that the temperature at which the coordinatively unsaturated $Pt(PPh_3)_2$ fragment is generated from the 16e complex [Pt(PPh₃)₂(olefin)] plays a critical role.

A comparison of our results with those obtained by Bennett *et al.*² concerning the yields of the complexes $[Pt_2(\mu - o-C_6H_4PPh_2)(\mu-PPh_2)(PPh_3)_2]$ and **3** after different times of thermolysis of $[Pt(C_2H_4)(PPh_3)_2]$ suggested that formation of this dinuclear complex results from *in situ* transformation of **3**. However, heating an equimolar mixture of **3**, $[Pt(C_2H_4)(PPh_3)_2]$ and PPh₃ for 3 h did not afford any dinuclear complex (see Experimental section), although thermolysis of $[Pt(C_2H_4)(PPh_3)_2]$ alone does, which confirms the importance of generating *in situ* the coordinatively unsaturated 14e fragment Pt(PPh_3)_2.

Synthesis and characterization of cis,cis,cis- $[Pt_3(\mu-I)_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (4) and molecular structure of cis,cis,cis- $[Pt_3(\mu-I)_2(\mu-PPh_2)_2(I_{1,3}Cl_{0,7})(PPh_3)_2][Pt_3(\mu-I)_2(\mu-PPh_2)_2(I_{1,7}Cl_{0,3})(PPh_3)_2]$ ·C₆H₅Cl·3CH₂Cl₂ (5A·5B·C₆H₅Cl·3CH₂Cl₂)

The reactivity of cluster **3** towards the electrophiles I_2 or H^+ has been studied and found to induce in the former case a reductive coupling reaction between a PPh₂ group and the phenyl ligand, while retaining in the cationic product $[Pt_3(\mu-I)(\mu-PPh_2)_2(PPh_3)_3]^+$ the trinuclear nature of the original cluster.⁹ Since the two electron oxidation of **3** by one equivalent of I_2 did not alter the oxidation states of the Pt atoms [2 Pt(I) + 1 Pt(II)], it should still be possible to oxidize it further with a second equivalent of I_2 and we have now found that two equivalents of I_2 transform **3** into the new complex $[Pt_3(\mu-I)_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (**4**) which forms a yellow, air-stable powder, poorly soluble in organic solvents (Scheme 2).

Despite the low solubility of this complex, its ${}^{31}P{}^{1}H$ NMR spectrum could be recorded and it contains two singlets of equal intensities, at 12.2 and -75.0 ppm, with one and two sets of 195 Pt satellites resulting from the ${}^{1}J(Pt-P)$ coupling constants,





respectively. The former signal corresponds to terminal phosphines with ${}^{1}J(Pt-P) = 4402$ Hz and the latter to the phosphido groups bridging two different Pt atoms, with ${}^{1}J(Pt-P) = 3320$ and 2639 Hz. There is no significant P–P coupling between these signals, which indicates that these nuclei are in mutual *cis* positions. Therefore, the structure of complex **4** is expected to contain the following fragment:



The other substituents of the Pt atoms are the iodine atoms and the complete ligand arrangement should be as shown in Scheme 2.

Suitable crystals of **4** for X-ray diffraction could not be obtained. However, a closely related complex was obtained when the oxidation reaction was performed by using one equivalent I_2

Table 2 Selected bond distances (Å) and angles (°) for 5A in \cdot 5B·C₆H₅Cl·3CH₂Cl₂

Pt1–I1	2.659(2)	I1–Pt1–I3	88.93(7)
Pt1–I3	2.602(2)	I3-Pt1-P1	88.08(11)
Pt1–P1	2.235(4)	P1-Pt1-P2	103.48(14)
Pt1–P2	2.284(4)	I1-Pt1-P2	82.53(10)
Pt2–I1	2.6694(15)	I1-Pt2-I2	90.02(5)
Pt2–I2	2.6896(19)	I1-Pt2-P2	82.86(10)
Pt2–P2	2.254(4)	P2-Pt2-P3	106.12(12)
Pt2–P3	2.265(3)	I2-Pt2-P3	83.11(9)
Pt3–I2	2.6773(18)	I2-Pt3-P3	83.36(9)
Pt3–X1	2.417(3)	I2-Pt3-X1	85.62(9)
Pt3–P3	2.267(4)	X1-Pt3-P4	90.94(12)
Pt3–P4	2.241(3)	P3-Pt3-P4	101.82(12)
		Pt1–I1–Pt2	78.75(5)
		Pt2-I2-Pt3	74.96(5)
		Pt1-P2-Pt2	96.31(14)
		Pt2-P3-Pt3	92.20(13)

followed by one equivalent of PhICl₂, and complete conversion of 3 to a new compound occurred. These reactions were performed with the original objective, which was not fulfilled (see below), to monitor the oxidation steps by sequential introduction of first iodide and then chloride ions as "tags", the reverse sequence being likely to give rise to anion metathesis of chlorides by iodides. Crystals of the product suitable for X-ray diffraction were obtained and an ORTEP view is shown in Fig. 2 and selected bond distances and angles are given in Table 2. The asymmetric unit contains two different molecules, 5A and 5B, whose main difference resides in the occupancy factor of the terminal halogen atoms (iodine or chlorine) of one site (see Fig. 2). A terminal halide position in 5A is occupied at 30% by iodine and at 70% by chlorine, while in 5B it is occupied at 70% by iodine and at 30% by chlorine (see ESI[‡]). The asymmetric unit contains also one molecule of chlorobenzene and three molecules of dichloromethane. This confers on this complex in the crystal the formula $[Pt_3(\mu I)_{2}(\mu-PPh_{2})_{2}(I_{1.3}Cl_{0.7})(PPh_{3})_{2}][Pt_{3}(\mu-I)_{2}(\mu-PPh_{2})_{2}(I_{1.7}Cl_{0.3})(PPh_{3})_{2}]\cdot$ $C_6H_5Cl \cdot 3CH_2Cl_2$ (5A \cdot 5B $\cdot C_6H_5Cl \cdot 3CH_2Cl_2$).



Fig. 2 ORTEP view of the core atoms of **5A** in **5A** \cdot **5B** \cdot $C_6H_3Cl_3CH_2Cl_2$ with partial labelling scheme. Only the ipso carbon atoms of the phenyl groups are shown. The position of the Pt(3)-bound halide in **5A** is occupied at 30% by iodine and at 70% by chlorine, while in **5B** it is occupied at 70% by iodine and at 30% by chlorine. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms and solvent molecules are omitted for clarity.

Table 2 contains a selection of bond distances and angles for molecule **5A** only, since the data for molecule **5B** are very similar (for details see corresponding cif file[‡]). Each molecule contains three, almost aligned and nearly square-planar Pt atoms, without direct metal-metal bonding (Pt1–Pt2 = 3.380(1) and Pt2–Pt3 = 3.265(1) Å in **5A**). The corresponding Pt–Pt distances in **5B**, Pt4–Pt5 = 3.516(1) and Pt5–Pt6 = 3.425(1) Å, present the largest differences between bond lengths in **5A** and **5B**. Each external Pt atom bears a PPh₃ and a halide ligand, both in terminal positions, while the inner Pt2 is connected to Pt1 and Pt3 by two μ -PPh₂ groups and two bridging iodo ligands. All the halides lie on the same side of the triplatinum line, and the phosphorus ligands on the opposite side (Fig. 3), which results in a *cis* arrangement for each Pt atom.



Fig. 3 View of the core atoms of 5A in $(5A \cdot 5B \cdot C_6H_5Cl_3CH_2Cl_2)$ emphasizing the nearly coplanar arrangement of the atoms Pt1, Pt2, Pt3, I2, I3, P2 and P4 (orange plane) and Pt1, Pt2, Pt3, I1, I/Cl, P1 and P3 (blue plane), respectively.

The ligands around each Pt atom are almost coplanar, but the coordination geometry of these metal atoms is not a regular square, the angles around them vary from about 81° to more than 106°. The mean-values for the angles in molecules **5A** and **5B** are the following: P–Pt–P = 102.8°, I–Pt–I = 89.3° and I–Pt–P = 83° for the angles at the Pt atoms, and Pt–P–Pt = 96.5°, Pt–I–Pt = 79° for those at the bridging atoms. All these bond lengths and angles have values similar to those found in analogous complexes.^{5,9,15–17}

The Pt–I distances being longer than the Pt–P distances and the PPh₂ groups being sterically more demanding than an iodine atom, explains why the P–Pt–P angles at Pt are larger than the I–Pt–I angles and also why the Pt–P–Pt angles are larger than the Pt–I–Pt ones.

The overall structure of complexes **5A** and **5B** is not flat. The coordination planes of two consecutive Pt atoms in each molecule

form a roof-angle of about 132° , which gives a "japanese screen"type arrangement to the skeleton of **5A** and **5B** (Fig. 4).



Fig. 4 "Japanese screen"-type arrangement formed by the three consecutive square planes around the Pt(II) centres in 5A.

Few trinuclear Pd or Pt complexes consisting of bridgeconnected square-planar units have been published^{7a,7c,7c,7e,8a,17,18} and examples of both chair and boat conformations have been identified by X-ray diffraction.¹⁸ The sequence of edge-sharing square-planes in **5A** forms a chair-type arrangement. In all the platinum complexes containing four halogens and two phosphido bridges, the halogens lie on the same side of the metal atoms and the phosphides on the other side, as in **5**. The number of anionic ligands (4 halides and 2 phosphido groups) in **5** confirms the oxidation of the two Pt(I) centres of **3** into Pt(II) in **4** and **5**, in agreement with the absence of any Pt–Pt bond and the coordination geometry around each metal atom.

The reaction of **3** with one equivalent of I_2 followed by one equivalent of PhICl₂ as oxidants was expected to form a mixed dichloro, diiodo triplatinum complex. However, the isolation of compound **5** reveals that 4 electron oxidation occurs with redistribution reactions between the halogen atoms. The ³¹P{¹H} NMR spectrum of this reaction mixture shows various signals from 12 to 17 ppm in the range of terminal PPh₃ ligands and from -60 to -70 ppm for phosphido groups bridging Pt atoms not linked by metal-metal bonds. These signals could be attributed to different trinuclear complexes, with different Cl/I ratios.

Synthesis and molecular structure of $[Pt_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (6)

For comparison, iodine oxidation was also applied to the dinuclear complex $[Pt_2(\mu-PPh_2)_2(PPh_3)_2]^{1,3,4}$ which contains a Pt–Pt bond



Scheme 3

Table 3 Selected bond distances (Å) and angles (°) for $[Pt_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (6)

6536(16)	P1-Pt-P1'	75.30(7)
3221(16)	P1–Pt–I	94.19(5)
3374(17)	P1'-Pt-P2	100.58(7)
2688(19)	P2–Pt–I	91.18(5)
	Pt-P1-Pt'	103.49(7)
	5536(16) 3221(16) 3374(17) 2688(19)	5536(16) P1–Pt–P1' 3221(16) P1–Pt–I 3374(17) P1'–Pt–P2 2688(19) P2–Pt–I Pt–P1–Pt'

bridged by two PPh₂ groups. This compound reacted with one equivalent I_2 in a tetrahydrofuran solution, to yield [Pt₂(μ -PPh_2)_2I_2(PPh_3)_2] (6) in spectroscopic quantitative yield (Scheme 3).

Recrystallization from a mixture of CH_2Cl_2 and pentane afforded pale yellow crystals of a new complex, whose molecular structure was solved by X-ray diffraction (Table 3 and Fig. 5).

Complex 6 is constituted by two Pt atoms bridged by two phosphido groups, each Pt bearing in addition a PPh₃group and an iodide ligand in terminal, mutually *cis* positions, in such a way that the PPh₃, and the iodide ligands, are anti to each other. The Pt₂P₄I₂ skeleton has C_2 symmetry with the twofold axis perpendicular to the Pt, Pt', P1, P1' mean plane and intersecting the middle of the Pt–Pt' axis. The ligands around the platinum atoms are almost coplanar, but the angles between them are irregular, in particular P1–Pt–P1' = 75.30(7)° and P1'–Pt–P2 = 100.58(7)° are far from 90°. In addition, the angle at the phosphido bridge, Pt–P1–Pt' = 103.49(7)°, is larger than those found in **5**. As a consequence, the non-bonding Pt–Pt' distance, 3.605(1) Å, is in the range of the largest Pt–Pt distance in **5**. This accounts for the rupture of the Pt(I)–Pt(I) bond in $[Pt_2(\mu-PPh_2)_2(PPh_3)_2]$ upon oxidation with I_2 to give Pt(II) centres in **6**. All the geometrical data for this complex are consistent with those found in similar complexes.^{4,5,15,16} The coordination planes of the platinum atoms make a roof-angle of 164.4°.

The ³¹P{¹H} NMR spectrum of complex **6** belongs to a AA'MM'XX' spin system in which A represents the ³¹P nuclei of the phosphines, M that of the phosphido bridges and X the ¹⁹⁵Pt nuclei. For the AA'MM' subsystem, six lines appear for each of the AA' and the MM' parts. Simulation of these signals gave the following values: ²*J*(P–P) = 378.4, 199.5 and 7.7 Hz between P1 and P2, P1 and P1', and P1' and P2, respectively, and ⁴*J*(P2–P2') = -9.4 Hz. These values are consistent with those determined for similar complexes.¹⁹ In addition, the signals of the phosphine ligands at δ 21.6 and of the phosphido groups at δ –164.4 show pseudo first order ¹⁹⁵Pt satellite signals: a doublet with ¹*J*(Pt–P) = 2165 Hz and two doublets with ¹*J*(Pt–P) = 2384 and 1870 Hz, respectively.

In conclusion, we have described here an improved synthesis of the mixed-valence platinum cluster $[Pt_3(\mu-PPh_2)_3Ph(PPh_3)_2]$ starting from $[Pt_{CH_2}=CHC(O)OMe_{PPh_3}]$ (2) and found that its controlled oxidation afforded the trinuclear complex *cis,cis,cis*- $[Pt_3(\mu-I)_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (4). The dinuclear Pt(II) complex *trans*- $[Pt_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (6) was obtained by oxidation with I₂ of the dinuclear, metal–metal bonded Pt(I) complex $[Pt_2(\mu-PPh_2)_2(PPh_3)_2]$. The crystal structures of 2·CH₂Cl₂, *cis,cis*, *cis*- $[Pt_3(\mu-I)_2(\mu-PPh_2)_2Cl_{0.5}I_{1.5}(PPh_3)_2]$ ·0.5C₆H₅Cl·1.5CH₂Cl₂ (5·0. 5C₆H₅Cl·1.5CH₂Cl₂), which is similar to 4, and 6 unambiguously established the structural details and revealed in the case of



Fig. 5 ORTEP view of **6** with partial labelling scheme. Only the ipso carbon atoms of the corresponding phenyl groups are shown. The ellipsoids enclose 50% of the electronic density. Hydrogen atoms are omitted for clarity. Equivalent position': -x + 1, y, -z + 1/2.

5 an unusual "japanese screen"-type chair arrangement of the skeleton.

Experimental

General

All manipulations were performed under nitrogen using standard Schlenk techniques. The solvents employed were distilled from appropriate drying agents prior to use. NMR spectra were recorded on a Bruker AM 300 instrument, phosphorus chemical shifts (in ppm) were referenced to 85% H₃PO₄ in H₂O. All coupling constants are in Hz. IR spectra were recorded in the 4000–400 cm⁻¹ range on a Bruker IFS66 FT spectrophotometer. [Pt(C₂H₄)(PPh₃)₂] was prepared according to a published procedure.²⁰ The complex [Pt₂(µ-PPh₂)₂(PPh₃)₂] was isolated from the red mixtures obtained by thermolysis of [Pt(C₂H₄)(PPh₃)₂] in acetone.¹ Methyl acrylate was purchased from Aldrich and used without further purification.

Syntheses

 $[Pt{CH_2=CHC(O)OMe}(PPh_3)_2] \cdot CH_2Cl_2$ (2·CH_2Cl_2). To a solution of $[Pt(C_2H_4)(PPh_3)_2]$ (1.00 g, 1.34 mmol) in acetone (30 mL) was added a large excess (1.2 mL) of CH_2=CHC(O)OMe. The solution was refluxed for 24 h and the solvent was evaporated under reduced pressure. The residue was washed with diethylether, dried under vacuum and recrystallized from a mixture of CH_2Cl_2 and pentane. Colourless crystals suitable for X-ray measurements were grown at room temperature after a few days. The mother liquor was again evaporated to dryness under vacuum, and recrystallization of the residue from CH_2Cl_2/pentane afforded a

second crop of crystals. Yield: 0.90 g (1.00 mmol, 75%). Anal. Calcd for $C_{41}H_{38}P_2Cl_2O_2Pt$: C, 55.29; H, 4.30. Found: C, 54.97; H, 4.35. ³¹P{¹H} NMR (CD₂Cl₂): δ 30.85 (¹*J*(Pt–P) = 4056 Hz, ²*J*(P–P) = 50 Hz), 31.9 (¹*J*(Pt–P) = 3559 Hz), ²*J*(P–P) = 42 Hz).

[Pt₃(μ-PPh₂)₃Ph(PPh₃)₂]·2CH₂Cl₂ (3·2CH₂Cl₂). A toluene solution (30 mL) of [Pt{CH₂=CHC(O)OMe}(PPh₃)₂]·CH₂Cl₂ (0.60 g, 0.67 mmol) was heated under reflux for 5 h. The red solution was evaporated to dryness under vacuum. Recrystallization from a mixture of CH₂Cl₂ and pentane at room temperature afforded dark red crystals of 3·2CH₂Cl₂.⁴ Yield: 0.30 g (64% based on Pt).

Attempt of transformation of $[Pt_3(\mu-PPh_2)_3Ph(PPh_3)_2]$ (3) into $[Pt_2(\mu-o-C_6H_4PPh_2)(\mu-PPh_2)(PPh_3)_2]$. A mixture of $[Pt_3(\mu-PPh_2)_3Ph(PPh_3)_2] \cdot 2CH_2Cl_2$ (0.191 g, 0.10 mmol), $[Pt(C_2H_4) \cdot (PPh_3)_2]$ (0.075 g, 0.10 mmol) and PPh_3 (0.026 g, 0.10 mmol) in 50 mL acetone was refluxed for 3 h and then cooled to room temperature. The precipitated cluster $[Pt_3(\mu-PPh_2)_3Ph(PPh_3)_2]$ (0.174 g, 0.10 mmol) was filtered and dried *in vacuo*. Evaporation to dryness of the orange filtrate afforded a yellow solid (0.110 g). Its ³¹P{¹H} NMR spectrum in C₆D₆ showed a peak at 26.3 ppm (OPPh_3) and various signals in the range of terminal phosphines: $\delta 8.3$ (s, ¹J(Pt-P) = 3631 Hz), 11.8 (d, ¹J(Pt-P) = 3592 Hz, J(P-P) = 20 Hz), 12.7 (d, ¹J(Pt-P) = 20 Hz), 13.9 (d, ¹J(Pt-P) = 3497 Hz, ²J(P-P) = 20 Hz).

 $Cis, cis, cis, cis-[Pt_3(\mu-I)_2(\mu-PPh_2)_2I_2(PPh_3)_2]$ (4). To a solution of $[Pt_3(\mu-PPh_2)_3Ph(PPh_3)_2]\cdot 2CH_2CI_2$ (0.096 g, 0.05 mmol) in 10 mL of THF was added I₂ (0.026 g, 0.10 mmol) and the red solution rapidly darkened with formation of a yellow precipitate. After the reaction mixture was stirred for 1 h at room temperature, the

	$2 \cdot CH_2Cl_2$	$\textbf{5A}\textbf{\cdot}\textbf{5B}\textbf{\cdot}\textbf{C}_{6}\textbf{H}_{5}\textbf{C}\textbf{l}\textbf{\cdot}\textbf{3}\textbf{C}\textbf{H}_{2}\textbf{C}\textbf{l}_{2}$	6
Formula	$C_{40}H_{36}O_{2}P_{2}Pt,CH_{2}Cl_{2}$	$C_{129}H_{111}Cl_8I_7P_8Pt_6$	$C_{60}H_{50}I_{2}P_{4}Pt_{2}$
FW [g mol ⁻¹]	890.64	4251.38	1538.86
Crystal system	Monoclinic	Triclinic	Monoclinic
Space group	$P2_1/n$ (No. 14)	<i>P</i> -1 (No. 2)	C2/c (No. 15)
a [Å]	12.160(2)	17.028(2)	17.684(5)
<i>b</i> [Å]	14.283(2)	18.333(2)	18.541(5)
c [Å]	21.322(2)	22.087(2)	17.775(5)
	90	82.66(5)	90
β[°]	90.27(5)	74.61(5)	111.15(5)
γ[°]	90	81.38(5)	90
$V[Å^3]$	3703.2(9)	6544.6(21)	5435(3)
Z	4	2	4
$D(\text{calc}) [\text{g cm}^{-3}]$	1.597	2.157	1.880
μ (Mo-K α) [mm ⁻¹]	4.054	8.348	6.433
<i>F</i> (000)	1768	3960	2928
Crystal size [mm ³]	$0.08 \times 0.10 \times 0.13$	$0.10 \times 0.08 \times 0.08$	0.04 imes 0.06 imes 0.08
Temperature (K)	173	173	173
Mo-Kα radiation [Å]	0.71070	0.71070	0.71070
θ Min–max [°]	2.38, 30.04	1.13, 27.88	1.65, 30.01
Data set	-17:17; 0:20; 0:30	-21:22; -23:24; 0:29	-24:23;-26:23;-24:24
Tot., uniq. data, R(int)	10820, 10819, 0.000	31118, 31118, 0.000	22342, 7915, 0.053
Observed data $[I > 2.0 \sigma(I)]$	7538	20399	6526
$N_{\rm ref}, N_{\rm par}$	10819, 433	31118, 1378	7915, 307
R, wR^2, S	0.0283, 0.0803, 0.98	0.0768, 0.2310, 1.149	0.0462,0.1187, 1.185
w (with $P = (F_o^2 + 2F_c^2)/3$	$1/[\sigma^2(F_o^2) + (0.0192P)^2 + 0.3996P]$	$1/[\sigma^2(F_o^2) + (0.1391P)^2 + 28.3253P]$	$1/[\sigma^2(F_o^2) + (0.0522P)^2]$
Max. and av. shift/error	0.00, 0.00	0.02, 0.00	0.00, 0.00
Min. and max. resd. dens. [e Å ⁻³]	-2.09, 1.608	-6.132, 4.000	-2.94, 1.02

precipitate was filtered and washed with toluene. Attempts to grow crystals suitable for X-ray analysis failed. Yield: 0.061 g, 60%. Anal. Calcd for $C_{60}H_{50}I_4P_4Pt_3$: C, 36.25; H, 2.54. Found: C, 36.81; H, 3.07. ³¹P{¹H} NMR (CH₂Cl₂/CD₂Cl₂): δ 12.1 (PPh₃, ¹*J*(P–Pt) = 4402 Hz), -75.0 (µ-PPh₂, ¹*J*(P–Pt) = 3320 and 2639 Hz).

Cis,cis,cis-[Pt₃(μ -I)₂(μ -PPh₂)₂Cl_{0.5}I_{1.5}(PPh₃)₂] (5). To a solution of [Pt₃(μ -PPh₂)₃Ph(PPh₃)₂]-2CH₂Cl₂ (0.192 g, 0.10 mmol) in 40 mL of CH₂Cl₂ was added I₂ (0.026 g, 0.10 mmol). After the mixture was stirred for 1 h, the brown solution became slowly orange and then PhICl₂ (0.030 g, 0.11 mmol) was added. After further stirring for 1 h, pentane was added to the mixture, affording a yellow precipitate. The latter was recrystallized from a mixture of toluene and pentane to yield a yellow precipitate which was again recrystallized from a mixture of chlorobenzene and pentane, at room temperature, to give yellow crystals suitable for X-ray analysis corresponding to [Pt₃(μ -I)₂(μ -PPh₂)₂(I_{1.3}Cl_{0.7})(PPh₃)₂][Pt₃(μ -I)₂(μ -PPh₂)₂·(I_{1.7}Cl_{0.3})(PPh₃)₂]·C₆H₅Cl·3CH₂Cl₂ (5A·5B·C₆H₅Cl·3CH₂Cl₂).

Trans-[Pt₂(μ-PPh₂)₂I₂(PPh₃)₂] (6). To a solution of [Pt₂(μ-PPh₂)₂(PPh₃)₂] (0.026 g, 0.02 mmol) in 15 ml of THF was added I₂ (0.005 g, 0.02 mmol). The mixture changed colour rapidly from red to pale yellow. The solution was stirred for 1 h at room temperature, evaporated to dryness and the residue washed with diethyl ether before it was recrystallized from a mixture of CH₂Cl₂ and diethyl ether. Yellow crystals suitable for X-ray analysis deposited slowly over 3 days at room temperature. Yield: 0.025 g, 80%. Anal. Calcd for C₆₀H₅₀Pt₂I₂P₄: C, 46.83; H, 3.27. Found: C, 47.12; H, 3.02. ³¹P{¹H} NMR (CH₂Cl₂/CD₂Cl₂): δ 21.6 (PPh₃, ¹J(P-Pt) = 2165 Hz), -164.4 (μ-PPh₂, ¹J(P-Pt) = 2384 and 1870 Hz).

Single crystal X-ray diffraction analysis of $2 \cdot CH_2Cl_2$, (5A \cdot 5B $\cdot C_6H_5Cl$ \cdot 3CH $_2Cl_2$) and 6

Diffraction data were collected on a Kappa CCD diffractometer using graphite-monochromatized Mo-K α radiation ($\lambda = 0.71073$ Å).²¹ Crystallographic and experimental details are summarized in Table 4. The structures were solved by direct methods (SHELXS-97)²² and refined by full-matrix least-squares procedures (based on F^2 , SHELXL-97) with anisotropic thermal parameters for all the non-hydrogen atoms. The hydrogen atoms were introduced into the geometrically calculated positions (SHELXL-97 procedures) and refined riding on the corresponding parent atoms. The absorption was not corrected (small single crystals, see Table 4).

Acknowledgements

We thank the Centre National de la Recherche Scientifique and the Ministère de la Recherche for support and the Agence Universitaire de la Francophonie for a post-doctoral grant to C. O. We are grateful to Dr Clarisse Huguenard for the NMR simulation using Windaisy software.

References

- 1 N. J. Taylor, P. C. Chieh and A. J. Carty, J. Chem. Soc., Chem. Commun., 1975, 448.
- 2 M. A. Bennett, D. E. Berry, T. Dirnberger, D. C. R. Hockless and E. Wenger, J. Chem. Soc., Dalton Trans., 1998, 2367.
- 3 R. Bender, P. Braunstein, A. Tiripicchio and M. Tiripicchio-Camellini, Angew. Chem., Int. Ed. Engl., 1985, 24, 861.
- 4 R. Bender, P. Braunstein, A. Dedieu, P. D. Ellis, B. Huggins, P. D. Harvey, E. Sappa and A. Tiripicchio, *Inorg. Chem.*, 1996, **35**, 1223.
- 5 R. Bender, S.-E. Bouaoud, P. Braunstein, Y. Dusausoy, N. Merabet, J. Raya and D. Rouag, *J. Chem. Soc., Dalton Trans.*, 1999, 735.
- 6 At least one more isomer of [Pt₃(μ-PPh₂)₃Ph(PPh₃)₂] (**3**) has been characterized: K. Hussong and O. J. Scherer, personal communication, 1985; quoted in ref. 4.
- 7 For recent references, see: (a) P. Mastrorilli, Eur. J. Inorg. Chem., 2008, 4835; (b) A. Albinati, P. Leoni, F. Marchetti, L. Marchetti, M. Pasquali and S. Rizzato, Eur. J. Inorg. Chem., 2008, 4092; (c) J. Forniés, C. Fortuño, S. Ibáñez and A. Martin, Inorg. Chem, 2008, 47, 5978; (d) M. Latronico, F. Polini, V. Gallo, P. Mastrorilli, B. Calmuschi-Cula, U. Englert, N. Re, T. Repo and M. Räisänen, Inorg. Chem., 2008, 47, 9779; (e) P. Mastrorilli, Dalton Trans., 2008, 4555, and references cited therein.
- 8 (a) I. Ara, J. Forniés, C. Fortuño, S. Ibáñez, A. Martin, P. Mastrorilli and V. Gallo, *Inorg. Chem.*, 2008, 47, 9069; (b) C. Cavazza, F. Fabrizi de Biani, T. Funaioli, P. Leoni, F. Marchetti, L. Marchetti and P. Zanello, *Inorg. Chem*, 2009, 48, 1385, and references cited therein.
- 9 C. Archambault, R. Bender, P. Braunstein, A. DeCian and J. Fischer, J. Chem. Soc. Chem. Commun., 1996, 2729.
- 10 R. Bender, P. Braunstein, S.-E. Bouaoud, N. Merabet, D. Rouag, P. Zanello and M. Fontani, *New J. Chem.*, 1999, 23, 1045.
- 11 P. A. Chaloner, S. E. Davies and P. B. Hitchcock, *Polyhedron*, 1996, 16, 765.
- 12 P. A. Chaloner, S. E. Davies and P. B. Hitchcock, J. Organomet. Chem., 1997, 527, 145.
- 13 (a) F. Caruso, M. Camalli, G. Pellizer, F. Asaro and M. Lenarda, *Inorg. Chim. Acta*, 1991, **181**, 167; (b) G. Pellizer, M. Graziani, M. Lenarda and B. T. Heaton, *Polyhedron*, 1983, **2**, 657.
- 14 M. E. Jason and J. A. McGinnety, *Inorg. Chem.*, 1975, 14, 3025; R. B. Osborne, H. C. Lewis and J. A. Ibers, *J. Organomet. Chem*, 1981, 208, 125; H. Choi, J. W. Hershberger, A. R. Pinhas and D. M. Ho, *Organometallics*, 1991, 10, 2930.
- 15 N. M. Boag, K. Mohan Rao and N. J. Terrill, Acta Crystallogr., Sect. C, 1991, C47, 1064.
- 16 L. Manojlovic Muir and K. W. Muir, Croat. Chim. Acta, 1984, 57, 587.
- 17 (a) E. Alonso, J. M. Casas, J. Forniés, C. Fortuno, A. Martin, A. G. Orpen, C. A. Tsipis and A. C. Tsipis, *Organometallics*, 2001, **20**, 5571; (b) M. Itazaki, Y. Nishihara and K. Osakada, *Organometallics*, 2004, **23**, 1610.
- 18 H. Brunner, S. Dormeier, I. Grau and M. Zabel, *Eur. J. Inorg. Chem.*, 2002, 2603.
- 19 C. Eaborn, K. J. Odell and A. Pidcock, J. Organomet. Chem., 1979, 170, 105.
- 20 U. Nagel, Chem. Ber., 1982, 115, 1998.
- 21 Kappa CCD Operation Manual, Nonius BV, Delft, The Netherlands, 1997.
- 22 G. M. Sheldrick, SHELX97, Program for the refinement of crystal structures, University of Göttingen, Göttingen, Germany, 1997.