

Synthesis and characterisation of new binuclear complexes containing a relatively strong Pt to Hg donor bond. Molecular structure of complex [Pt(C[^]P)(μ-O₂CCH₃)₂Hg(O₂CCH₃)]

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Received 27th June 2003, Accepted 4th September 2003

First published as an Advance Article on the web 18th September 2003

[{Pt(C[^]P)(μ-O₂CCH₃)₂}]₂ (**1A**) (C[^]P = CH₂-C₆H₄-P(*o*-tolyl)₂-κC,P) reacts with Hg(O₂CCH₃)₂ and [{Pt(C[^]P)(μ-O₂CCF₃)₂}]₂ (**1B**) reacts with Hg(O₂CCF₃)₂ in a 1 : 2 molar ratio to afford the neutral complexes [Pt(C[^]P)(μ-O₂CCH₃)₂Hg(O₂CCH₃)] (**2**) and [Pt(C[^]P)(μ-O₂CCF₃)₂Hg(O₂CCF₃)] (**3**) respectively. They also react with equimolar amounts of HgX₂ (X = Cl, Br, I) to give mixtures of the corresponding neutral complexes [Pt(C[^]P)(μ-O₂CR)₂HgX] (R = CH₃, X = Cl **4**, Br **5**, I **6**; R = CF₃, X = Cl **7**, Br **8**, I **9**) and [{Pt(C[^]P)(μ-X)]₂ (X = Cl, Br, I). Complexes **4–6** could be isolated from the mixtures as pure samples but complexes **7–9** could not. Complexes [Pt(C[^]P)(μ-O₂CR)₂HgX] (R = CH₃, X = Cl **4**, Br **5**, I **6**; R = CF₃, X = Cl **7**, Br **8**, I **9**) can also be prepared by treatment of the carboxylate derivatives [Pt(C[^]P)(μ-O₂CR)₂Hg(O₂CR)] (R = CH₃ **2**, CF₃ **3**) with methanol solutions of HX (X = Cl, Br, I) in 1 : 1 molar ratio, this being the only way to obtain pure samples of complexes **7–9**. The study of the molecular structure of **2** by X-ray diffraction reveals the existence of a very strong Pt to Hg donor bond (Pt–Hg = 2.6131(6) Å). The NMR data of **2** are in agreement with its observed structure in the solid state. The similarity of the NMR data of all complexes leads us to propose the same structure for all of them, which seems to be retained in solution at room temperature.

Introduction

It is well known that electron rich platinum(II) complexes can react with mercury(II) compounds HgX₂ (X = halide or carboxylate) to give heterodimetallic complexes. These compounds can be classified as: a) adducts containing Pt to Hg donor bonds^{1–7} with both metal centres in an oxidation state of 2 and b) products of oxidative addition containing a Pt–Hg covalent bond,^{8–11} which can be important as reaction intermediates.

Well-characterised compounds with higher nuclearity (Pt₂Hg) have also been reported by Puddephatt *et al.* These complexes, [PtMe₂X(HgX)(^tbu₂bpy){PtMe₂(^tbu₂bpy)}] (X = Br, CF₃COO; ^tbu₂bpy = 4,4'-di-*tert*-butyl-2,2'-bipyridyl) are unsymmetric, containing both covalent and donor–acceptor Pt–Hg bonds within the same molecule.¹¹

We have previously described the synthesis of neutral Pt^{II} complexes [Pt(C[^]P)(L[^]L)] [C[^]P = CH₂-C₆H₄-P(*o*-tolyl)₂-κC,P; L[^]L = S₂CNMe₂, S₂COEt, acac-*O,O'*] and demonstrated their ability to form heteronuclear compounds containing Pt–Hg bonds when they are reacted with Hg^{II} salts (HgX₂, X = Br, I, CH₃COO, CF₃COO). These reactions proceed differently depending on the nature of the chelate ligand L[^]L and especially on the nature of X.

In some cases, the oxidative addition of HgX₂ (X = CH₃COO, CF₃COO) to Pt^{II} takes place yielding Pt^{IV} compounds which contain covalent Pt–Hg bonds;¹⁰ and in others, adducts containing unsupported Pt^{II}–Hg donor–acceptor bonds are formed.^{4,5} In most cases, the chelate ligands bonded to platinum (C[^]P and L[^]L) remain unchanged, but in reactions of [Pt(C[^]P)(acac-*O,O'*)] with Hg(O₂CR)₂ (R = CH₃, CF₃), the acac[−] ligand is substituted by the carboxylate groups from the coordination sphere of the platinum centre, and is also deprotonated by a second equivalent of Hg(O₂CR)₂ (R = CH₃, CF₃).⁴ In the resulting compounds containing the fragment “Pt(C[^]P)(μ-O₂CR)₂Hg”, the Pt–Hg interaction has been described as a Lewis acid–base type showing a Pt–Hg bond length (*ca.* 2.65 Å)

which is clearly shorter than those observed in many of this kind of complex, *i.e.*, the Pt–Hg interaction consists of a very strong Pt to Hg dative bond with both metals in a formal oxidation state of 2.

Given that it was considered that the marked stability of the fragments “Pt(C[^]P)(μ-O₂CR)₂Hg” (R = CH₃, CF₃), due to the strong Pt to Hg bond, could be the driving force behind these reactions, we decided to prepare new compounds containing the same heterodimetallic fragments. Two synthetic routes have allowed us to obtain new mixed Pt–Hg heterodinuclear complexes. Their synthesis and structural characterisation are reported in this paper.

Results and discussion

Synthesis and characterisation of complex [{Pt(C[^]P)(μ-O₂CCF₃)₂}]₂ (**1B**)

The dinuclear complex [{Pt(C[^]P)(μ-O₂CCF₃)₂}]₂ (**1B**) (C[^]P = CH₂-C₆H₄-P(*o*-tolyl)₂-κC,P) was prepared in the same way as complex [{Pt(C[^]P)(μ-O₂CCH₃)₂}]₂ (**1A**),¹² by addition of sodium trifluoroacetate (NaO₂CCF₃) to a solution containing [Pt(C[^]P)(THF)₂]₂ClO₄, generated *in situ*. As in compound **1A**, the ³¹P{¹H}, ¹H and ¹⁹F NMR spectra of complex **1B** in CDCl₃ at low temperature (223 K) show the signals expected for only one fragment “Pt(C[^]P)(μ-O₂CCF₃)” (Table 1, and Experimental section). We thus consider that both dinuclear complexes **1A** and **1B** exhibit a *trans* configuration (Scheme 1) like the palladium derivative [{Pd(C[^]P)(μ-O₂CCH₃)₂}]₂ previously described by Herrmann.¹³

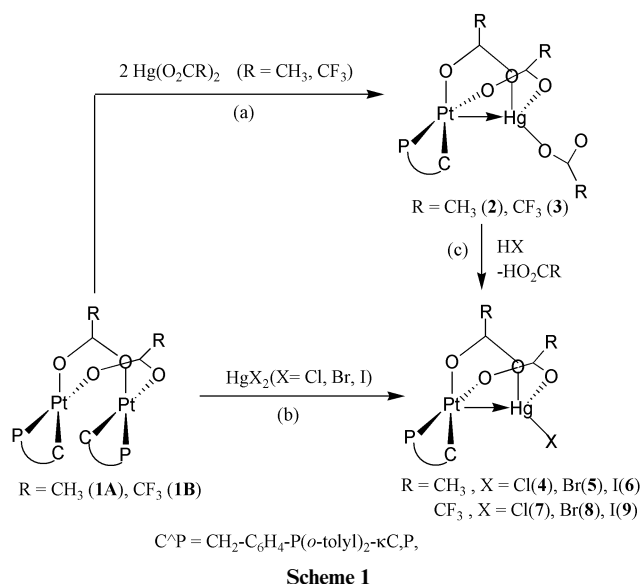
Synthesis and characterisation of complexes [Pt(C[^]P)(μ-O₂CR)₂HgX] (R = CH₃, X = O₂CCH₃ **2**, Cl **4**, Br **5**, I **6**; R = CF₃, X = O₂CCF₃ **3**, Cl **7**, Br **8**, I **9**)

The reactions of complex [{Pt(C[^]P)(μ-O₂CCH₃)₂}]₂ (**1A**) with Hg(O₂CCH₃)₂ and [{Pt(C[^]P)(μ-O₂CCF₃)₂}]₂ (**1B**) with Hg-

Table 1 ^{31}P $\{^1\text{H}\}$ NMR data for complexes 1–9

Complex	δ_{P}	$J_{\text{Pt-P}}$	$^2J_{\text{Hg-P}}$
$[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\}_2]$ (1A)	8.42	5311	
$[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\}_2]$ (1B)	10.47	5488	
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\text{O}_2\text{CCH}_3)]$ (2)	11.68	3958	130
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{Hg}(\text{O}_2\text{CCF}_3)]$ (3)	12.76	3678	161
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{HgCl}]$ (4)	11.55	3912	118
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{HgBr}]$ (5)	11.19	3960	108
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{HgI}]$ (6)	10.30	4011	98
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{HgCl}]$ (7)	12.67	3686	148
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{HgBr}]$ (8)	11.86	3740	143
$[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{HgI}]$ (9)	10.63	3834	126

$\text{C}^{\wedge}\text{P} = \text{CH}_2\text{-C}_6\text{H}_4\text{-P}(o\text{-tolyl})_2\text{-}\kappa\text{C,P}$; δ (ppm), J (Hz), CDCl_3 , $T = 293$ K.



$(\text{O}_2\text{CCF}_3)_2$ in a 1 : 2 molar ratio, afforded the neutral complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\text{O}_2\text{CCH}_3)]$ (**2**) and $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{Hg}(\text{O}_2\text{CCF}_3)]$ (**3**) respectively (Scheme 1a). Complexes **2** and **3** were isolated as pure samples in good yield.

Complexes $[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CR})_2\}_2]$ ($\text{C}^{\wedge}\text{P} = \text{CH}_2\text{-C}_6\text{H}_4\text{-P}(o\text{-tolyl})_2\text{-}\kappa\text{C,P}$, $\text{R} = \text{CH}_3$ **1A**, CF_3 **1B**) also react with an equimolar amount of HgX_2 ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in CH_2Cl_2 or CHCl_3 , to afford mixtures of the corresponding neutral complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CR})_2\text{HgX}]$ ($\text{R} = \text{CH}_3$, $\text{X} = \text{Cl}$ **4**, Br **5**, I **6**; $\text{R} = \text{CF}_3$, $\text{X} = \text{Cl}$ **7**, Br **8**, I **9**) and $[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-X})\}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) (Scheme 1b).

These reactions proceed with the asymmetric breaking of the “ $\text{Pt}_2(\mu\text{-O}_2\text{CR})_2$ ” system. The way these reactions take place indicates a great stability of the “ $\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CR})_2\text{Hg}$ ” unit, which is probably due to the formation of a relatively strong Pt to Hg donor bond. When the starting material is $[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\}_2]$ (**1A**), it is possible to separate the two components of the mixtures by evaporation of the solvent to dryness and addition of diethyl ether to the residue. Complexes $[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-X})\}_2]$ ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) remain insoluble and complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{HgX}]$ ($\text{X} = \text{Cl}$ **4**, Br **5**, I **6**) can be isolated from the ether solutions as pure samples in a good yield. However, when the starting material is $[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\}_2]$ (**1B**), although the reactions proceed in the same way the separation of the two components of each mixture is not possible and complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{HgX}]$ ($\text{X} = \text{Cl}$ **7**, Br **8**, I **9**) can not be obtained from their reaction mixtures.

Complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CR})_2\text{HgX}]$ ($\text{R} = \text{CH}_3$, $\text{X} = \text{Cl}$ **4**, Br **5**, I **6**; $\text{R} = \text{CF}_3$, $\text{X} = \text{Cl}$ **7**, Br **8**, I **9**) can be also prepared by treatment of $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CR})_2\text{Hg}(\text{O}_2\text{CR})]$ ($\text{R} = \text{CH}_3$ **2**, CF_3 **3**) with methanol solutions of HX ($\text{X} = \text{Cl}, \text{Br}, \text{I}$) in a 1 : 1 molar ratio (Scheme 1c).

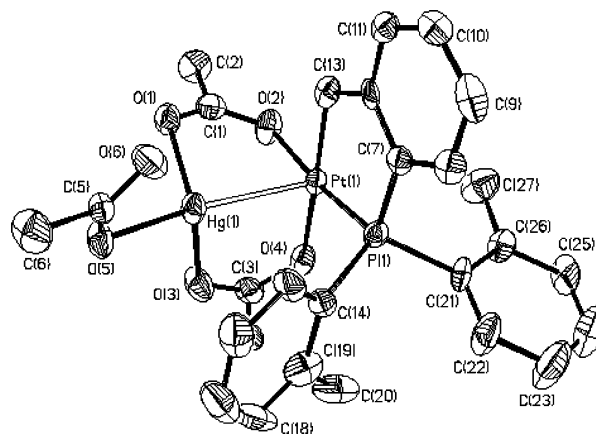
Table 2 Selected bond distances (\AA) and angles ($^\circ$) for complex **2**

$\text{Pt}(1)\text{-Hg}(1)$	2.6131(6)	$\text{Pt}(1)\text{-C}(13)$	2.039(10)
$\text{Pt}(1)\text{-O}(2)$	2.066(7)	$\text{Hg}(1)\text{-O}(1)$	2.404(7)
$\text{Pt}(1)\text{-O}(4)$	2.131(8)	$\text{Hg}(1)\text{-O}(3)$	2.350(8)
$\text{Pt}(1)\text{-P}(1)$	2.224(3)	$\text{Hg}(1)\text{-O}(5)$	2.107(7)
$\text{C}(13)\text{-Pt}(1)\text{-P}(1)$	85.2(3)	$\text{O}(3)\text{-Hg}(1)\text{-O}(5)$	104.6(3)
$\text{P}(1)\text{-Pt}(1)\text{-O}(4)$	101.1(2)	$\text{Pt}(1)\text{-Hg}(1)\text{-O}(3)$	81.1(2)
$\text{O}(4)\text{-Pt}(1)\text{-O}(2)$	85.3(4)	$\text{Pt}(1)\text{-Hg}(1)\text{-O}(1)$	80.8(2)
$\text{O}(2)\text{-Pt}(1)\text{-C}(13)$	88.3(4)	$\text{Pt}(1)\text{-Hg}(1)\text{-O}(5)$	166.4(2)
$\text{O}(5)\text{-Hg}(1)\text{-O}(1)$	111.1(3)	$\text{O}(1)\text{-Hg}(1)\text{-O}(3)$	91.0(3)

Complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{HgX}]$ ($\text{X} = \text{Cl}$ **4**, Br **5**, I **6**) can therefore be obtained in two ways; however for complexes $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{HgX}]$ ($\text{X} = \text{Cl}$ **7**, Br **8**, I **9**) the second procedure is the only one capable of affording pure samples.

Compounds **2–9** have been characterised by elemental analysis (see Experimental section) and common spectroscopic methods (FTIR, ^{31}P , ^1H and ^{13}C NMR). The similar spectroscopic data obtained for these complexes would suggest a similar structure. This structure, shown in Scheme 1, is in agreement with that observed in the X-ray study on complex **2**.

A drawing of the structure of complex **2** appears in Fig. 1. Selected bond distances and angles are listed in Table 2. It is a dinuclear platinum and mercury compound with both atoms connected by a metal–metal bond supported by two acetate bridging ligands. The five-coordinated Pt atom is located at the centre of the base of a distorted square pyramid with the Hg atom in the apical position. The angle between the Pt–Hg vector and the perpendicular to the best Pt basal plane [$\text{Pt}(1)$, $\text{C}(13)$, $\text{P}(1)$, $\text{O}(2)$, $\text{O}(4)$] is only 3.41° .¹⁴ The base of the pyramid is almost square-planar. Angles around the Pt between *cis* ligands deviate from the theoretical value (90°), especially the angle $\text{P}(1)\text{-Pt}(1)\text{-O}(4)$, [$101.1(2)^\circ$]. The $\text{Pt}\text{-P}$,^{5,15} $\text{Pt}\text{-C}$,¹⁵ and $\text{Pt}\text{-O}$,^{8,9,16} bond lengths are similar to those found in other complexes containing the same kind of ligands. The $\text{Pt}\text{-O}$ bond lengths [$\text{Pt}(1)\text{-O}(2) = 2.066(7)$ \AA , $\text{Pt}(1)\text{-O}(4) = 2.131(8)$ \AA] show the higher *trans* influence of C with respect to P.^{16,17}

**Fig. 1** Structure of complex $[\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\text{O}_2\text{CCH}_3)]$ (**2**).

The geometry around the Pt atom is similar to that observed in other complexes for which the Pt–Hg interaction has been described as a Lewis acid–base type.^{1–7,18,19} However, as in complex $[\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\mu\text{-}3\text{-acac}2\text{-}\kappa\text{C}^3, \text{O})\text{Hg}(\text{O}_2\text{CCH}_3\text{-}\kappa\text{O})\}_2]$,⁴ containing the same bimetallic fragment “ $\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}$ ”, the $\text{Pt}(1)\text{-Hg}(1)$ bond distance [2.6131(6) \AA] is clearly shorter than those observed in these kinds of complexes. As far as we know, only the complex $[\text{PtMe}_2(\text{OOCFF}_3)(\text{HgOOCFF}_3)(\text{bu}_2\text{bpy})\{\text{PtMe}_2(\text{bu}_2\text{bpy})\}]$ ¹¹ contains a Pt to Hg donor bond with a similar intermetallic distance (2.628 \AA). The Pt–Hg bond distance observed in complex **2** is similar to those observed in many complexes in which the Pt and Hg centres are covalently bonded such as $[(\text{PPh}_3)_2(\text{C}_6\text{Cl}_3\text{H}_2)\text{-Pt-Hg-(C}_6\text{Cl}_3\text{-H}_2)]$ [$\text{Pt-Hg} = 2.637(1)$ \AA],²⁰ $[(\text{PPh}_3)_2\{\text{Ge}(\text{CF}_3)_3\}\text{-Pt-Hg-}\{\text{Ge}$

(CF₃)₃] [Pt–Hg = 2.666 Å]²¹ [(PPh₃)₂{Sn(C₆F₅)₃}–Pt–Hg–{Ge(C₆F₅)₃}] [Pt–Hg = 2.618 Å],²² [{Pt(PR₂CH₂CH₂PR₂–κP,P)(CNC₆H₃Me₂)₂Hg}] [R = Ph, Pt–Hg = 2.615 Å].²³ These facts suggest that the Pt–Hg interaction is most probably a very strong Pt to Hg dative bond with both metals in a formal oxidation state of 2. Although the acetate groups bridge Pt(1) and Hg(1), they do not seem to be responsible for the short Pt–Hg distance given the numerous binuclear transition metal complexes with a double carboxylate bridge showing non-bonded intermetallic separations (*ca.* 3 Å).^{24,25} The two bridging acetate groups are asymmetrically bonded, with the Pt–O bond lengths [Pt(1)–O(2) = 2.066(7) Å, Pt(1)–O(4) = 2.131(8) Å] shorter than the Hg–O ones [Hg(1)–O(1) = 2.404(7) Å, Hg(1)–O(3) = 2.350(8) Å]. The two Pt(1)(μ-O₂CCH₃)Hg(1) fragments show distortions from planarity. The best least-squares planes calculated for these fragments are perpendicular to each other (interplanar angle, 94.41°), and they are also nearly perpendicular to the basal plane, with angles between the basal plane and the best least-squares planes calculated for the fragments Pt(1), O(2), C(1), O(1), Hg(1) and Pt(1), O(4), C(3), O(3), Hg(1) of 92.31° and 87.27° respectively.¹⁴

Hg(1) has a very distorted tetrahedral environment, with bond angles around Hg(1) ranging from 80.8(2)° to 166.4(2)°; this big distortion may be due to the existence of two bridging acetate groups perpendicular to each other which make the angles Pt(1)–Hg(1)–O(1) [80.8(2)°] and Pt(1)–Hg(1)–O(3) [81.1(2)°] rather acute and, in both cases, similar to those found in [(2-Me₂NCH₂-C₆H₄)₂(MeCO₂)PtHg(O₂CMe)] [80.4(2)°].^{8,9}

The ³¹P{¹H} NMR spectra of compounds **2–9** at room temperature are very significant. They show, in each case, only one singlet flanked by the corresponding ¹⁹⁵Pt and ¹⁹⁹Hg satellites (Table 1). The frequencies of these signals and the ¹⁹⁵Pt–P and ¹⁹⁹Hg–P coupling constants are very similar for all of them. The observation of ¹⁹⁹Hg–P coupling suggests the existence of a strong Pt–Hg bond, which is retained in solution, since in other Pt^{II}–Hg adducts containing an unsupported Pt to Hg donor bond such as [{Pt(C^ΛP)(L^ΛL)HgX(μ-X)}₂] (L^ΛL = S₂CNMe₂, S₂COEt, acac-O,O'; X = Br, I), ¹⁹⁹Hg–P coupling has never been observed.^{4,5} The values of ²J_{Hg–P} are in agreement with the *cis* disposition of both atoms around the platinum centre.^{23,26}

In our experience, with platinum(II) complexes containing the same C^ΛP group we have observed a decrease in the values of ¹J(¹⁹⁵Pt–³¹P) when they react with a Lewis acid such as HgX₂ or Ag to form a Pt to M (M = Hg^{II}, Ag^I) donor bond. A similar effect in the values of the ¹J(¹⁹⁵Pt–³¹P) coupling constants was observed by other authors on adding Ag⁺, as Lewis acid, to the hydride complexes *trans*-[PtH(C₆X₅)(PR₃)₂] (X = F, Cl; R = Me, Et; X = H, R = Et).²⁷ In addition, comparing related compounds of the type [{Pt(C^ΛP)(L^ΛL)HgX(μ-X)}₂] (L^ΛL = S₂CNMe₂, S₂COEt, acac-O,O'; X = Br, I), we observed that as the electronegativity of the halide bonded to mercury increases (I < Br), the ¹J(¹⁹⁵Pt–³¹P) coupling constant becomes smaller. Once again, comparing the ³¹P{¹H} NMR data of related compounds, amongst them, **4–6** (or **7–9**) we observed a relationship between the electronegativity of the halogen and the ¹J(¹⁹⁵Pt–³¹P) and ²J(¹⁹⁹Hg–³¹P) coupling constants values; in these complexes as the electronegativity of the halide bonded to mercury increases (I < Br < Cl), the ¹J(¹⁹⁵Pt–³¹P) and the ²J(¹⁹⁹Hg–³¹P) becomes lower and higher respectively (Table 1).

The ¹H (for complexes **2–9**) and ¹⁹F (for complexes **3, 7–9**) NMR spectra at room temperature can be also interpreted in terms of the proposed geometry. The correct assignment of the CH₃ signals in complexes [Pt(C^ΛP)(μ-O₂CCH₃)₂HgX] (X = O₂CCH₃, **2** Cl **4**, Br **5**, I **6**) was carried out by ROESY experiments.

In all complexes (**2–9**) the C^ΛP group gave the signals expected for the different kind of hydrogen atoms: a) several downfield multiplets due to the aromatic protons, b) a multiplet close to 4 ppm due to the methylenic group which appears as an AB system with ²J_{H–H} close to 17 Hz. The high frequency of this

signal is common in complexes containing the Pt(C^ΛP) metalacycle in which the platinum centre is involved in a Pt→M (M = Ag, Hg) donor bond;^{4,5,10,12} and c) two singlets due to the CH₃ (*o*-tolyl) groups about 2 and 3 ppm, showing their inequivalence. The signal around 3.0 ppm is assigned to the methyl group located in close proximity to the d_{z²} orbital of platinum, due to the paramagnetic anisotropy of the metal atom, in accordance with the literature.^{28–31} All the acetate (or trifluoroacetate) ligands contained in each complex are inequivalent and each one gives its corresponding signal (see Experimental section).

The ¹³C{¹H} NMR spectra of complexes **2–9** show the expected signals for the different kinds of carbons of the C^ΛP and carboxylate groups (see Experimental section). The correct assignment of the methyl carbon signals was carried out with the aid of HMQC experiments.

The aromatic carbon atoms of the C^ΛP group give several multiplets between 125 and 160 ppm. The methylenic carbon (Pt–CH₂) gives a singlet between 15 and 20 ppm, flanked by the ¹⁹⁵Pt satellites with a ¹J_{Pt–C} close to 650 Hz. The methyl carbon atoms of the inequivalent *o*-tolyl groups show two doublets close to 25 ppm. The values of ³J_{P–C} are different from each other. The signal which appears at lower field (*ca.* 26 ppm) can be assigned to the methyl carbon located in close proximity to the d_{z²} orbital of platinum due to the paramagnetic anisotropy of the metal atom.^{28–31}

The carboxylate groups contained in each complex are inequivalent. Each one shows two signals; the highfield one, due to CH₃ or CF₃, which appears in the trifluoroacetate derivatives as a quartet of very low intensity, which prevents it from being completely analysed.

Conclusion

In conclusion, complexes with the stoichiometry [Pt(C^ΛP)(μ-O₂CR)₂HgX] (R = CH₃, X = O₂CCH₃, Cl, Br, I; R = CF₃, X = O₂CCF₃, Cl, Br, I) have been prepared. They exhibit a relatively strong Pt to Hg donor bond with both metals in a formal oxidation state of 2. The strength of this metal–metal bond becomes apparent in the short Pt–Hg distance observed in the X-ray structure of compound **2** (Pt–Hg = 2.6131(6) Å). It is also evident in solution, since ¹⁹⁹Hg–³¹P coupling has been observed. This coupling had been never observed in other complexes containing the same kind of metal–metal bond.

Experimental

General procedures and materials

Elemental analyses were performed on a Perkin-Elmer 240-B microanalyzer. IR spectra were recorded on a Perkin-Elmer 599 spectrophotometer (Nujol mulls between polyethylene plates in the range 200–4000 cm⁻¹). NMR spectra were recorded on a Varian Unity-300 or a Bruker ARX-300 spectrometers using the standard references. Hg(O₂CCH₃)₂, Hg(O₂CCF₃)₂ were purchased from Aldrich. Complexes [{Pt(CH₂-C₆H₄-P(*o*-tolyl)₂-κC,P)(μ-O₂CCH₃)₂] (**1A**)¹² and [{Pt(CH₂-C₆H₄-P(*o*-tolyl)₂-κC,P)(μ-Cl)]₂¹⁵ were prepared as described elsewhere.

Synthesis

[Pt(C^ΛP)(μ-O₂CCF₃)₂] (**1B**). [{Pt(C^ΛP)(μ-Cl)]₂ (1.45 g, 1.35 mmol) and AgClO₄ (0.56 g, 2.70 mmol) were suspended in THF (50 mL) and allowed to react for 4 h at room temperature in the dark. The AgCl that formed was filtered off through Celite and the resulting solution concentrated to *ca.* 3 mL. Methanol (20 mL) and NaO₂CCF₃ (0.37 g, 2.70 mmol) were added and the mixture was stirred at room temperature for 40 min. The solid was filtered and recrystallized from CH₂Cl₂/n-pentane to give a yellow solid, **1B** (0.94 g, 57%) (Found: C,

45.38; H, 3.06. $C_{46}F_6H_{40}O_4P_2Pt_2$ requires C, 45.18; H, 3.30%; $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1673vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 223 K): $\delta = 2.05$ (s, 3H, Me C^{^A}P), 2.41(d, 1H, $^2J_{\text{H-H}} = 16$ Hz, CH_2 C^{^A}P), 3.08 (d, 1H, $^2J_{\text{H-H}} = 16$ Hz, CH_2 C^{^A}P), 3.12 (s, 3H, Me C^{^A}P), 6.3–7.5 (m, C_6H_4 , C^{^A}P); ^{19}F : $\delta = -74.45$.

[Pt(C^{^A}P)(μ -O₂CCH₃)₂Hg(O₂CCH₃)] (2). To a solution of [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\}_2$] (**1A**) (0.6180 g, 0.554 mmol) in 45 mL of CHCl_3 $\text{Hg}(\text{O}_2\text{CCH}_3)_2$ (0.3532 g, 1.108 mmol) was added and the mixture was stirred at room temperature for 6 h. The resulting yellow solution was filtered through Celite and then evaporated to dryness. Addition of diethyl ether (20 mL) to the residue yielded a yellow solid, **2** (0.81 g, 83%) (Found: C, 37.38; H, 3.28. $\text{C}_{27}\text{H}_{26}\text{HgO}_6\text{P}_2$ requires C, 37.01; H, 3.34%; $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1558vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 1.82$ (s, 3H, Me, terminal acetate), 1.90 (s, 3H, Me, bridging acetate), 2.06 (s, 6H, Me bridging acetate, Me C^{^A}P), 2.97 (s, 3H, Me C^{^A}P), 3.99 (ν_{A}), 4.22 (ν_{B}) ($^2J_{\text{H-H}} = 16$ Hz, CH_2 C^{^A}P), 6.8–7.6 (m, C_6H_4 , C^{^A}P); ^{13}C : $\delta = 16.10$ (s, CH_2 C^{^A}P, $J_{\text{Pt-C}} = 662$ Hz), 19.24 (s, Me, terminal acetate), 22.20 (d, $^3J_{\text{P-C}} = 6$ Hz, Me C^{^A}P), 23.11 (d, $^4J_{\text{P-C}} = 6$ Hz, Me, bridging acetate *trans* to P), 24.13 (s, Me, bridging acetate *trans* to C), 25.35 (d, $^3J_{\text{P-C}} = 10$ Hz, Me C^{^A}P), 125–160 (m, C_6H_4 , C^{^A}P), 176.02 (s, COO, terminal acetate), 178.71 (d, $^3J_{\text{P-C}} = 4$ Hz, COO, bridging acetate *trans* to P), 179.17 (s, COO, bridging acetate *trans* to C).

[Pt(C^{^A}P)(μ -O₂CCF₃)₂Hg(O₂CCF₃)] (3). To a solution of [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\}_2$] (**1B**) (0.4486 g, 0.367 mmol) in 25 mL of CH_2Cl_2 $\text{Hg}(\text{O}_2\text{CCF}_3)_2$ (0.3129 g, 0.734 mmol) was added and the mixture was reacted at room temperature for 45 min. The resulting yellow solution was then evaporated to dryness. Addition of n-pentane (20 mL) to the residue rendered a yellow solid, **3** (0.66 g, 87%) (Found C, 31.09; H, 2.20. $\text{C}_{27}\text{F}_9\text{H}_{20}\text{HgO}_6\text{P}_2$ requires C, 31.24; H, 1.94%; $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1667vs, 1699vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 2.02$ (s, 3H, Me C^{^A}P), 2.97 (s, 3H, Me C^{^A}P), 4.38 (ν_{A}), 4.50 (ν_{B}) ($^2J_{\text{H-H}} = 17$ Hz, CH_2 C^{^A}P), 6.8–7.7 (m, C_6H_4 , C^{^A}P); ^{19}F : $\delta = -72.24$ (s, terminal O_2CCF_3), -73.48 (s, bridging O_2CCF_3), -74.00 (s, bridging O_2CCF_3); ^{13}C : $\delta = 19.04$ (s, CH_2 C^{^A}P, $J_{\text{Pt-C}} = 606$ Hz), 22.87 (d, $^3J_{\text{P-C}} = 6$ Hz, Me C^{^A}P), 26.48 (d, $^3J_{\text{P-C}} = 8$ Hz, Me C^{^A}P), 116.09 (q, $J_{\text{F-C}} = 284$ Hz, CF_3), 116.96 (q, $J_{\text{F-C}} = 287$ Hz, CF_3), 117.63 (q, $J_{\text{F-C}} = 287$ Hz, CF_3), 125–155 (m, C_6H_4 , C^{^A}P), 161.37 (q, COO, $^2J_{\text{F-C}} = 39$ Hz), 163.59 (q, COO, $^2J_{\text{F-C}} = 40$ Hz), 163.80 (q, COO, $^2J_{\text{F-C}} = 38$ Hz).

[Pt(C^{^A}P)(μ -O₂CCH₃)₂HgCl] (4). *Method A.* A mixture of [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\}_2$] (**1A**) (0.2653 g, 0.238 mmol) and HgCl_2 (0.0646 g, 0.238 mmol) was allowed to react in CH_2Cl_2 (20 mL) at room temperature for 45 min. The resulting solution was evaporated to dryness and diethyl ether (30 mL) added to the residue. The insoluble [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-Cl})\}_2$] was removed by filtration and the solution evaporated to dryness. The addition of n-pentane to the residue gave **4** as a pale yellow solid (0.132 g, 65%) (Found: C, 35.45; H, 3.13. $\text{C}_{25}\text{ClH}_{26}\text{HgO}_4\text{P}_2$ requires C, 35.22; H, 3.07%; $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1549vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 1.91$ (s, 3H, Me, bridging acetate), 2.03 (s, 3H, Me C^{^A}P), 2.05 (s, 3H, Me, bridging acetate), 3.00 (s, 3H, Me C^{^A}P), 4.04 (ν_{A}), 4.12 (ν_{B}) ($^2J_{\text{H-H}} = 18$ Hz, CH_2 C^{^A}P), 6.8–7.6 (m, C_6H_4 , C^{^A}P); ^{13}C : $\delta = 16.00$ (s, CH_2 C^{^A}P, $J_{\text{Pt-C}} = 664$ Hz), 22.29 (d, $^3J_{\text{P-C}} = 7$ Hz, Me C^{^A}P), 23.16 (d, $^4J_{\text{P-C}} = 7$ Hz, Me, bridging acetate *trans* to P), 24.00 (s, Me, bridging acetate *trans* to C), 25.77 (d, $^3J_{\text{P-C}} = 10$ Hz, Me C^{^A}P), 125–160 (m, C_6H_4 , C^{^A}P), 178.66 (d, $^3J_{\text{P-C}} = 4$ Hz, COO, bridging acetate *trans* to P), 179.20 (s, COO, bridging acetate *trans* to C).

Method B. To a solution of [$\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\text{O}_2\text{CCH}_3)$] (**2**) (0.1544 g, 0.176 mmol) in CH_2Cl_2 (15 mL) 0.176 mmol of HCl (solution 0.241 M in methanol) was added. After 15 min the yellow solution was evaporated to dryness and n-pentane (20 mL) added to the residue to give **4** as a pale yellow solid (0.107 g, 71%).

[Pt(C^{^A}P)(μ -O₂CCH₃)₂HgBr] (5). This compound was prepared in the same way as **4**.

Method A. [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\}_2$] (**1A**) (0.2139 g, 0.192 mmol), HgBr_2 (0.0691 g, 0.192 mmol) in CHCl_3 (30 mL). Compound **5** was recrystallised from cold Et_2O (-5°C) and n-pentane (0.0395 g, 23%) (Found: C, 33.37; H, 2.73. $\text{BrC}_{25}\text{H}_{26}\text{HgO}_4\text{P}_2$ requires C, 33.47; H, 2.92%; $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1558vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 1.91$ (s, 3H, bridging acetate), 2.03 (s, 3H, Me C^{^A}P), 2.06 (s, 3H, bridging acetate), 3.00 (s, 3H, Me C^{^A}P), 4.00 (ν_{A}), 4.12 (ν_{B}) ($^2J_{\text{H-H}} = 17$ Hz, CH_2 C^{^A}P), 6.6–7.6 (m, C_6H_4 , C^{^A}P); ^{13}C : $\delta = 15.56$ (s, CH_2 C^{^A}P, $J_{\text{Pt-C}} = 668$ Hz), 22.21 (s, Me C^{^A}P), 23.30 (s, Me, bridging acetate *trans* to P), 24.00 (s, Me, bridging acetate *trans* to C), 25.82 (s, Me C^{^A}P), 125–160 (m, C_6H_4 , C^{^A}P), 178.74 (s, COO, bridging acetate *trans* to P), 179.25 (s, COO, bridging acetate *trans* to C).

Method B. To a solution of [$\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\text{O}_2\text{CCH}_3)$] (**2**) (0.20 g, 0.228 mmol) in CH_2Cl_2 (15 mL) 0.26 mmol of HBr (solution 0.0883 M in methanol) were added. After 15 min the yellow solution was filtered through Celite, evaporated to dryness and diethyl ether (25 mL) added to the residue. The ether solution was evaporated to dryness. Addition of n-pentane to the residue gave **5** as a pale yellow solid (0.045 g, 21%).

[Pt(C^{^A}P)(μ -O₂CCH₃)₂HgI] (6). *Method A.* A mixture of [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\}_2$] (**1A**) (0.220 g, 0.197 mmol) and HgI_2 (0.0896 g, 0.197 mmol) was allowed to react in CHCl_3 (20 mL) at room temperature for 45 min. The resulting solution was evaporated to dryness and diethyl ether (15 mL) added to the residue. The insoluble [$\{\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-I})\}_2$] was removed by filtration and the solution evaporated to ca. 5 mL. The precipitated solid was identified as **6** (0.105 g, 56%) (Found: C, 31.58; H, 2.85. $\text{C}_{25}\text{H}_{26}\text{HgIO}_4\text{P}_2$ requires C, 31.81; H, 2.77%). $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1548vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 1.92$ (s, 3H, bridging acetate), 2.04 (s, 3H, Me C^{^A}P), 2.06 (s, 3H, bridging acetate), 3.01 (s, 3H, Me C^{^A}P), 3.93 (ν_{A}), 4.10 (ν_{B}) ($^2J_{\text{H-H}} = 17$ Hz, CH_2 C^{^A}P), 6.8–7.6 (m, C_6H_4 , C^{^A}P); ^{13}C : $\delta = 14.73$ (s, CH_2 C^{^A}P, $J_{\text{Pt-C}} = 664$ Hz), 22.07 (d, $^3J_{\text{P-C}} = 6$ Hz, Me C^{^A}P), 23.35 (d, $^4J_{\text{P-C}} = 7$ Hz, Me, acetate *trans* to P), 23.98 (s, Me, bridging acetate *trans* to C), 25.72 (d, $^3J_{\text{P-C}} = 12$ Hz, Me C^{^A}P), 125–160 (m, C_6H_4 , C^{^A}P), 178.63 (d, $^3J_{\text{P-C}} = 4$ Hz, COO, bridging acetate *trans* to P), 179.24 (s, COO, bridging acetate *trans* to C).

Method B. Compound **6** was prepared in the same way as **4**. [$\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCH}_3)_2\text{Hg}(\text{O}_2\text{CCH}_3)$] (**2**) (0.1503 g, 0.171 mmol), HI (0.3 mL, solution 0.7 M in methanol). Yield: 0.05 g, 27%.

[Pt(C^{^A}P)(μ -O₂CCF₃)₂HgCl] (7). To a solution of [$\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{Hg}(\text{O}_2\text{CCF}_3)$] (**3**) (0.1431 g, 0.138 mmol) in CH_2Cl_2 (15 mL) 0.138 mmol of HCl (solution 0.241 M in methanol) were added. After 20 min the yellow solution was evaporated to dryness and n-pentane (20 mL) added to the residue to give **7** as a yellow solid (0.076 g, 55%) (Found: C, 31.70; H, 2.16. $\text{C}_{25}\text{ClF}_6\text{H}_{20}\text{HgO}_4\text{P}_2$ requires C, 31.26; H, 2.10%; $\bar{\nu}_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1659vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 2.00$ (s, 3H, Me C^{^A}P), 3.00 (s, 3H, Me C^{^A}P), 4.35 (s, 1H, $^2J_{\text{Pt-H}} = 116$ Hz), 4.35 (s, 1H, $^2J_{\text{Pt-H}} = 150$ Hz), 6.8–7.8 (m, C_6H_4 , C^{^A}P); ^{19}F : $\delta = -73.67$ (s), -74.12 (s); ^{13}C : $\delta = 17.57$ (s, CH_2 C^{^A}P, $J_{\text{Pt-C}} = 627$ Hz), 22.39 (d, $^3J_{\text{P-C}} = 6$ Hz, Me C^{^A}P), 26.66 (s, Me C^{^A}P), 125–155 (m, C_6H_4 , C^{^A}P).

[Pt(C^{^A}P)(μ -O₂CCF₃)₂HgBr] (8). To a solution of [$\text{Pt}(\text{C}^{\wedge}\text{P})(\mu\text{-O}_2\text{CCF}_3)_2\text{Hg}(\text{O}_2\text{CCF}_3)$] (**3**) (0.1520 g, 0.146 mmol) in CH_2Cl_2 (15 mL) 0.146 mmol of HBr (solution 0.088 M in methanol) were added. After 20 min the yellow solution was evaporated to dryness and n-pentane (20 mL) added to the residue to give **8** as a yellow solid (0.066 g, 45%) (Found: C, 30.11; H, 1.99. $\text{BrC}_{25}\text{F}_6\text{H}_{20}\text{HgO}_4\text{P}_2$ requires C, 29.88; H,

2.00%; $\nu_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1661 vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 2.00$ (s, 3H, Me C^{^P}), 3.00 (s, 3H, Me C^{^P}), 4.33 (s, 1H, CH₂ C^{^P}, $^2J_{\text{Pt-H}} = 117$ Hz), 4.33 (s, 1H, CH₂ C^{^P}, $^2J_{\text{Pt-H}} = 150$ Hz), 6.8–7.8 (m, C₆H₄, C^{^P}); ^{19}F : $\delta = -73.70$ (s), -74.15 (s); ^{13}C : $\delta = 16.94$ (s, CH₂ C^{^P}, $J_{\text{Pt-C}} = 638$ Hz), 22.40 (d, $^3J_{\text{P-C}} = 6$ Hz, Me C^{^P}), 26.61 (s, Me C^{^P}), 125–155 (m, C₆H₄, C^{^P}).

[Pt(C^{^P})(μ -O₂CCF₃)₂HgI] (9). To a solution of [Pt(C^{^P})(μ -O₂CCF₃)₂Hg(O₂CCF₃)] (3) (0.161 g, 0.155 mmol) at 0 °C in CH₂Cl₂ (15 mL) 0.175 mmol of HI (solution 0.7 M in methanol) were added. After 5 min a red solid appeared and it was removed by filtration. Evaporation of the resulting solution to dryness and addition of n-pentane (20 mL) to the residue gave **9** as a yellow solid (0.066 g, 37%) (Found: C, 28.67; H, 2.69. C₂₅F₆H₂₀HgIO₄PPt requires C, 28.54; H, 1.92%); $\nu_{\max}/\text{cm}^{-1}$ ($\nu_{\text{asym}}\text{COO}$) 1657 vs (Nujol); $^1\text{H NMR}$ (300 MHz, CDCl_3 , 293 K): $\delta = 2.00$ (s, 3H, Me C^{^P}), 3.00 (s, 3H, Me C^{^P}), 4.22 (ν_A), 4.32 (ν_B) (CH₂ C^{^P}, $^2J_{\text{H-H}} = 17$ Hz), 6.8–7.6 (m, C₆H₄, C^{^P}); ^{19}F : $\delta = -73.85$ (s), -74.26 (s); ^{13}C : $\delta = 15.84$ (s, CH₂ C^{^P}, $J_{\text{Pt-C}} = 651$ Hz), 22.10 (s, Me C^{^P}), 26.40 (s, Me C^{^P}), 125–155 (m, C₆H₄, C^{^P}).

Crystal structure determination

A pale yellow crystal of complex **2** covered with a viscous oil was transferred to the cold stream of the low temperature device of an automated four circle Siemens P4 diffractometer. Cell constants were calculated from 90 well centered reflections with 2θ angles ranging from 24 to 25°. Data were collected at 173 K by the ω - 2θ method. Three check reflections measured at regular intervals showed no significant loss of intensity through the course of data collection. An empirical absorption correction based on ψ scans was applied, with maximum and minimum transmission factors being 0.902 and 0.641. The structure was solved by the Patterson method. All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were added at calculated positions and assigned isotropic displacement parameters equal to 1.2 or 1.5 times the U_{iso} value of their respective parent carbon atoms. There are some peaks of electron density higher than 1 e \AA^{-3} in the final map. All of them are located very close to the heavy atoms and have no chemical significance. All calculations were carried out using the SHELXL-93 program.³²

Crystal data. C₂₇H₂₉HgO₆PtP, $M = 876.15$, monoclinic, space group $P2_1/c$, $a = 15.579(1)$, $b = 12.105(1)$, $c = 14.832(1)$ Å, $\beta = 93.50(1)^\circ$, $U = 2791.9(3)$ Å³, $T = 173(2)$ K, $Z = 4$, $\mu(\text{Mo-K}\alpha) = 10.593\text{ mm}^{-1}$, reflections collected: 6760, unique: 4880 ($R_{\text{int}} = 0.031$), observed [$I > 2\sigma(I)$]: 3681. The final $R(F)$ was 0.0432 (observed data) and $wR(F^2)$ was 0.1070 (all data).

CCDC reference number 213988.

See <http://www.rsc.org/suppdata/dt/b3/b307375k/> for crystallographic data in CIF or other electronic format.

Acknowledgements

Funding from the Spanish Ministry of Science and Technology, Directorate General for Research (Project BQU2002-03997-CO2-02 PGE, FEDER) is gratefully acknowledged.

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