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Platinum(II) phosphonate complexes derived from *endo*-8-camphanylphosphonic acid

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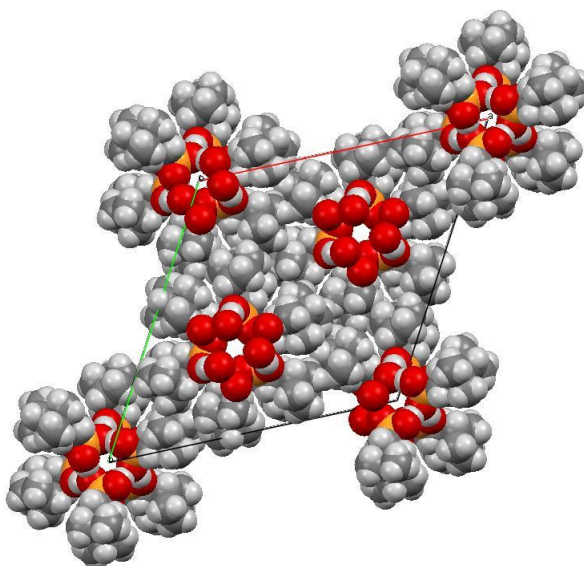
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Synopsis

Reactions of *cis*-[PtCl₂L₂] [L = PPh₃, PMe₂Ph or L₂ = Ph₂P(CH₂)₂PPh₂] with *endo*-8-camphanylphosphonic acid (CamPO₃H₂) and Ag₂O gave platinum(II) phosphonate complexes [Pt(O₃PCam)L₂], which were studied in detail by NMR spectroscopy. The structure of [Pt(O₃PCam)(PPh₃)₂]·2CHCl₃ shows that the bulky camphanyl group is directed into a pocket formed by the Pt and the two PPh₃ ligands, because of the preference of the O₃P-CH₂ group to have a staggered conformation. This observation is supported by theoretical calculations. The X-ray structure of camPO₃H₂ was also determined and shows hydrogen-bonded hexamers assembled to form a structure comprising hydrophilic channels surrounded by a sheath of hydrophobic camphanyl groups.

Graphic:



Abstract

The reactions of *cis*-[PtCl₂L₂] [L = PPh₃, PMe₂Ph or L₂ = Ph₂P(CH₂)₂PPh₂ (dppe)] with *endo*-8-camphanylphosphonic acid (CamPO₃H₂) and Ag₂O in refluxing dichloromethane gave platinum(II) phosphonate complexes [Pt(O₃PCam)L₂]. The X-ray crystal structure of [Pt(O₃PCam)(PPh₃)₂]·2CHCl₃ shows that the bulky camphanyl group, rather than being directed away from the platinum, is instead directed into a pocket formed by the Pt and the two PPh₃ ligands. This allows the O₃P-CH₂ group to have a preferred staggered conformation. The complexes were studied in detail by NMR spectroscopy, which demonstrates non-fluxional behaviour for the sterically bulky PPh₃ and dppe derivatives, which contain inequivalent phosphine ligands in their ³¹P NMR spectra. These findings are backed up by theoretical calculations on the PPh₃ and PPhMe₂ derivatives, which show respectively high and low energy barriers to rotation of the camphanyl group in the PPh₃ and PPhMe₂ complexes. The X-ray crystal structure of CamPO₃H₂ is also reported, and consists of hydrogen-bonded hexameric aggregates, which assemble to form a columnar structure containing hydrophilic phosphonic acid channels surrounded by a sheath of bulky, hydrophobic camphanyl groups.

Keywords: Platinum; Phosphonic acid; Phosphonate complexes; X-ray crystal structure; NMR spectroscopy; Theoretical calculations

Introduction

Previously we reported the synthesis of *endo*-8-camphanylphosphonic acid [CamP(O)(OH)₂] **1** by the oxidation of the corresponding phosphinic acid [CamPH(O)(OH)].[1,2] Such organophosphorus acids are of potential interest for their coordination chemistry, with the camphanyl group providing a readily-incorporated, bulky, chiral, and hydrophobic group. However, since the discovery of CamP(O)(OH)₂, relatively few studies have utilised this phosphonic acid. The methyl ester CamP(O)(OMe)₂, formed by methylation of CamP(O)(OH)₂ with CH₂N₂, forms a complex with uranyl nitrate, UO₂(NO₃)₂(CamP(O)(OMe)₂)₂. [2] CamP(O)(OH)₂ has also been utilised in the synthesis of a variety of iron(III) phosphonate clusters. For example, reaction of CamP(O)(OH)₂ with the oxo-bridged iron-carboxylate aggregate [Fe₃(μ₃-O)(^tBuCO₂)₆(H₂O)₃]Cl and pyridine (py) yielded the tetranuclear iron-phosphonate aggregate [Fe₄(μ₃-O)(^tBuCO₂)₄(CamPO₃)₃(py)₄] [3] while the same reaction in the absence of pyridine yielded nonanuclear [Fe₉O₄(^tBuCO₂)₁₃(CamPO₃)₃].[4] An even larger dodecanuclear aggregate [Fe₁₂(μ₂-O)₄(μ₃-O)₄(PhCO₂)₁₄)(CamPO₃H)₆] was prepared by reaction of [Fe₃(μ₃-O)(PhCO₂)₆(H₂O)₃]Cl with CamP(O)(OH)₂ in the presence of Et₃N.[5] In these compounds, the bulky camphanyl group contributes to a substantial hydrocarbon sheath around the inorganic core of the aggregate. This structural motif was also seen in the polymeric calcium salt of the corresponding phosphinic acid, CamPH(O)(OH), which has a columnar structure comprising a hydrophilic, inorganic core surrounded by a sheath of camphanyl groups.[6]

In this paper we report the synthesis and characterisation of some platinum(II) phosphine complexes of CamP(O)(OH)₂. To date, relatively few platinum(II) complexes containing bidentate chelating phosphonate ligands have been reported. A series of platinum(II)-phosphine complexes [Pt(O₃PR)₂L₂] derived from PhP(O)(OH)₂ and

MeP(O)(OH)₂ were prepared by reaction of *cis*-[PtCl₂L₂] [L = e.g. PPh₃, PMePh₂ or L₂ = Ph₂P(CH₂)_nPPh₂ (n = 2, 3, 4)] with the phosphonic acid in refluxing dichloromethane in the presence of silver(I) oxide as a base and halide-abstracting reagent.[7] The same methodology has been extended to analogous ferrocenyl-phosphonate complexes [Pt{O₃P(CH₂)_nFc}(PPh₃)₂] (Fc = Fe(C₅H₄)(C₅H₅); n = 0, 1, 2) and Fe{C₅H₄PO₃Pt(PPh₃)₂}₂ [8] and to the fluorinated derivatives [Pt(O₃PCH₂CH₂R_f)(PPh₃)₂] (R_f = n-C₄F₉ or n-C₆F₁₃) and [Pt(O₃PC₆H₄R)(PPh₃)₂] (R = *p*-F, *p*-CF₃ or *p-n*-C₆F₁₃).[9] More widely, platinum(II) complexes with phosphonate ligands have attracted some interest for their biological activity,[10,11] though there are very few studies in contrast to related complexes containing phosphate ligands, because of the significance of the latter to the interactions of platinum-based anticancer drugs with DNA.[12,13,14,15]

Results and discussion

X-Ray structure of 8-camphanylphosphonic acid, CamP(O)(OH)₂ **1**

The camphanylphosphonic acid CamP(O)(OH)₂ used in this study was prepared by oxidation of the corresponding phosphinic acid CamPH(O)(OH), itself prepared in high yield by the radical-catalysed addition of hypophosphorous acid to camphene.[2] During attempts to prepare a strontium salt of CamP(O)(OH)₂ by reaction of strontium nitrate with CamP(O)(OH)₂ and urea in methanol/water, colourless hexagonal crystals of CamP(O)(OH)₂ were obtained. In light of the interest in metal-phosphonate derivatives of this compound, the X-ray structure of CamP(O)(OH)₂ was determined to investigate how the bulky hydrophobic camphanyl groups might influence the hydrogen bond-directed structure. The molecular structure together with the atom numbering scheme are shown in Figure 1, and selected bond lengths and angles are given in Table 1. The P-CH₂ bond distance in **1** [1.762(8) Å] is similar,

but slightly shorter, than other methylene-phosphonic acids reported in the literature, such as $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$ [1.805(1) Å],[16] $(\text{HO})_2\text{P}(\text{O})\text{CH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$ [1.7858(5) Å],[17] and $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$ [1.787(2) Å].[18] The P=O double bond length of **1** [1.511(5) Å] is comparable to those in the same phosphonic acids, which are 1.513(1), 1.5016(4), and 1.505(1) Å respectively.

The structure of **1** is comprised of hydrogen-bonded hexamers, packed about the three-fold axis. Three molecules are linked in a ring by O(3)-H(03)···O(2) interactions between adjacent molecules, then these trimers are linked together by six O(1)-H(01)···O(2) interactions to form the hexameric unit which contains a central cavity formed by the P=O and P-OH groups, surrounded by the camphanyl groups, Figure 2. The $\text{CamP}(\text{O})(\text{OH})_2$ hexamers then stack upon each other to give a discontinuous hydrophilic central core surrounded by the bulky hydrophobic camphanyl groups, as shown in Figure 3.

Structural studies on other phosphonic acids with organic substituents of modest steric bulk, such as $\text{FcCH}_2\text{P}(\text{O})(\text{OH})_2$, [16] $\text{Me}_3\text{SiCH}_2\text{CH}_2\text{P}(\text{O})(\text{OH})_2$, [18] *p*- $\text{CH}_3\text{C}_6\text{H}_4\text{C}(\text{O})\text{CH}_2\text{CH}_2\text{PO}_3\text{H}_2$, [19] *o*- $\text{FC}_6\text{H}_4\text{CH}_2\text{PO}_3\text{H}_2$, [20] and 2,4,6-*i*-Pr₃C₆H₂PO₃H₂ [21] indicate that a layered structure (containing $\text{RPO}_3\text{H}_2 \cdots \text{H}_2\text{O}_3\text{PR}$) is a common structural feature. However, for phosphonic acids containing bulky groups, a small number of cage structures have been reported. Thus, ^tBuPO₃H₂, when crystallised from CDCl₃, has (like CamPO_3H_2 **1**) a hexameric cage structure,[22] while 4-^tBu-2,6-Mes₂-C₆H₂PO₃H₂ (Mes = 2,4,6-trimethylphenyl) crystallises as a monohydrate in the form of a hydrogen-bonded tetramer.[23] In these structures of bulky phosphonic acids, and also in the structure of the calcium salt of $\text{CamPH}(\text{O})(\text{OH})$, [6] there is a hydrophilic core surrounded by a hydrophobic organic sheath, which maximises separation of the hydrophilic inorganic part from the hydrophobic organic part. This suggests that further studies into the chemistry of metal-

phosphonate derivatives of camphene-derived organophosphorus acids are worthy of investigation for the possibility of generating interesting structures.

Synthesis of platinum(II)-phosphine complexes derived from **1**

The general synthetic route to the 8-camphanylphosphonic acid-derived Pt(II) complexes **2**, **3** and **4** involves the reaction of an excess of silver(I) oxide with equimolar quantities of the platinum dichloride complexes *cis*-[PtCl₂L₂] [L = PPh₃, PPhMe₂; L₂ = dppe (1,2-bis(diphenylphosphino)ethane)] and phosphonic acid **1**. The reaction proceeds in dichloromethane at reflux, with complete reaction (as determined by ³¹P NMR) typically occurring within a 36 h period. Upon completion, the unreacted silver oxide and silver chloride (a byproduct of the reaction) are simply removed by filtration.

Platinacycles **2** and **4** are readily purified by recrystallisation from chloroform/petroleum spirit while the purification of platinacycle **3** was achieved by washing the crude product with acetone. Synthesised in moderate yield, the crystalline platinacycles **2**, **3** and **4** are stable both in air and in organic solvents such as dichloromethane and methanol.

The attempted synthesis of the analogous 1,5-cyclo-octadiene (cod) complex [Pt(O₃PCam)(cod)] was unsuccessful; the reaction of equimolar amounts of **1** and [PtCl₂(cod)] with excess Ag₂O in refluxing dichloromethane afforded a large number of products from ³¹P NMR spectroscopy, and no further investigations were carried out.

NMR spectroscopic characterisation

The ³¹P{¹H} NMR data of the platinum-phosphonate complexes **2** and **4**, Table 2, are more complicated than the analogous methyl- and phenyl-phosphonate complexes [Pt(O₃PR)L₂] (R = Me or Ph; L = PPh₃ or L₂ = dppe) that have been previously reported.[7]

In the methyl- and phenyl-phosphonates the phosphine phosphorus atoms are equivalent, giving a single peak with $^1J_{PtP}$ coupling. In contrast, the donor phosphorus atoms (P_x and P_y , refer Table 2) of the camphanyl analogues **2** and **4** are inequivalent, coupling to each other to produce two doublets in the $^{31}P\{^1H\}$ NMR spectra. These doublets are further split by $^1J_{PtP}$ and $^3J_{PP}$ coupling. The inequivalence of the phosphine phosphorus atoms of **2** and **4** is also reflected in the difference in the one-bond Pt- P_x and Pt- P_y coupling constants which, for example, are 3732 and 3843 Hz for the PPh_3 complex **2**. The inequivalence of the phosphine ligand environments of **2** and **4** is proposed to arise from the steric restriction produced by replacement of a less bulky methyl or phenyl group by the sterically bulky camphanyl group. This steric restriction prevents the free rotation of the camphanyl group, which results in the phosphine ligands becoming inequivalent. This is supported by NOE studies of complex **2**, as well as theoretical studies (*vide infra*).

In contrast, the $^{31}P\{^1H\}$ NMR spectrum of the $PPhMe_2$ complex **3** shows a singlet for the phosphine ligands (with $^3J_{PP}$ coupling to the phosphonate phosphorus) indicating that even though the bulky camphanyl group is present, the donor phosphine environments are equivalent. In this case, it is proposed that the decreased steric bulk of the $PPhMe_2$ ligand permits free rotation to occur, making the phosphine ligands equivalent. Both a bulky group on the phosphonate ligand (camphanyl) and bulky phosphine ligands are required to produce the steric interactions that result in inequivalence of the phosphine donors.

The magnitudes of the $^1J_{PtP}$ coupling constants, which lie between 3654 and 3843 Hz, are comparable with those of the methyl- and phenyl-phosphonate analogues,[7] and are consistent with phosphine ligands *trans* to low *trans*-influence oxygen donor groups.[24] Thus, $[Pt(O_3PMe)(PPh_3)_2]$ has $^1J_{PtP}$ 3848 Hz, and the phenyl-phosphonate analogue $[Pt(O_3PPh)(PPh_3)_2]$ has $^1J_{PtP}$ 3877 Hz.

The phosphonate phosphorus P_z appears as a distinctive triplet-like pattern between δ 53.2 (**3**) and 58.4 (**4**). It is worth noting that the expected multiplicity for P_z , a doublet of doublet pattern, was not observed. The simplification of this doublet of doublet pattern to an observed triplet-like pattern occurs as the result of the P_z - P_x and P_z - P_y couplings being approximately equal. $[\text{Pt}(\text{O}_3\text{PPh})(\text{PPh}_3)_2]$ is reported to have a $^2J_{\text{PtP}}$ coupling constant of 27 Hz;^[7] this is not consistent with other $^2J_{\text{PtP}}$ coupling constants in this type of complex and is therefore assumed to be an error.

One- and two-dimensional NMR studies were carried out to fully assign the ^1H and ^{13}C NMR spectra of complex **2**, discussed below. The camphanyl regions of the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of **3** and **4** were similar to those of **2**, and were assigned by comparison. Tables 3 and 4 summarise the ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR spectra of the platinum complexes, and Scheme 1 gives the atom labelling scheme.

The $^{13}\text{C}\{^1\text{H}\}$ NMR spectrum of the camphanyl region of **2** comprised ten resonances, consisting of two methyl, three methine, four methylene and a quaternary resonance. The methylene signal (δ 27.9) which exhibited a large one-bond carbon to phosphorus coupling (J 121.9 Hz) is assigned to C_8 . The other three methylene signals (δ 20.1, 24.8 and 37.1) belonging to C_5 , C_6 and C_7 respectively are assigned by comparison with those chemical shifts obtained for 8-camphanylphosphonic acid **1** (δ 21.0, 25.6 and 37.8 respectively). The methine signal (δ 49.0), which does not couple to phosphorus, is assigned to C_1 as $^4J_{\text{PC}}$ coupling is not observed. The other two methine signals (δ 46.1 and 42.5) belonging to C_3 and C_4 respectively, exhibiting two and three bond P-C coupling (J 3.4 Hz and 3.3 Hz respectively), are assigned by comparison with those chemical shifts obtained for **1** (δ 46.0, d, J 3.9 and δ 43.5, J 3.6 respectively). The assignment of quaternary carbon C_2 (δ 37.5) which is coupled to phosphorus (J 13.1 Hz) is confirmed by its absence in the DEPT experiment.

Due to the complexity of the aryl region of **2** the signals (δ 131.5-124.4) belonging to the phenyl rings of the triphenylphosphines were not assigned.

In the ^{13}C - ^1H correlated NMR spectrum of **2** the cross peaks relating to the camphanyl carbon signals identified all proton resonances relating to the camphanyl moiety. Identification of many of the resonances in the ^1H NMR spectrum was possible by examination of H_4 crosspeaks in the COSY45 spectrum. Consequently, resonances belonging to H_4 (δ 2.58), H_3 (δ 1.96), $\text{H}_{8'/8''}$ (δ 1.60, 1.54), $\text{H}_{7''}$ (δ 1.68), $\text{H}_{5''}$ (δ 1.26), and $\text{H}_{7'}$ (δ 1.05) were readily identified. Remaining structural ambiguities were resolved by NOE difference spectroscopy. Particularly diagnostic are the NOE's observed from Me' to $\text{H}_{7''}$ and to H_3 [but not significantly from Me' to $\text{H}_{8'/8''}$] indicating that $\text{H}_{7''}$ and H_3 are on the same side of the molecule, confirming the *endo* disposition of the $-\text{CH}_2\text{PO}_3$ group. Other NOEs of significance are those of H_4 to $\text{H}_{5'}$ (but not to $\text{H}_{5''}$), $\text{H}_{7'}$ to $\text{H}_{6'}$ (but not $\text{H}_{6''}$) and H_3 to $\text{H}_{7''}$ (but not $\text{H}_{7'}$). The remainder of the NOE data, along with the COSY spectrum, gave the complete spectral assignment.

Interestingly, significant NOEs between H_3 or H_4 of the camphanyl and the *ortho*-phenyl protons (δ 7.49-7.37) of the triphenylphosphine ligand of **2** were observed. Although at first glance these NOEs seem unlikely, construction of a molecular model of **2** reveals the close proximity of the triphenylphosphine ligand protons to the camphanyl protons H_3 and H_4 , and therefore the possibility of an enhancement. Further NOE studies of the three phenyl regions (δ 7.49-7.37, 7.36-7.28 and 7.25-7.13 signals present in ratios of 2:1:2) indicate that the phenyl protons at δ 7.49 to 7.37 are the *ortho* protons. That is, the irradiation of the *meta* protons (δ 7.25 to 7.13) results in an enhancement of both the *ortho* (δ 7.49-7.37) and *para* (δ 7.36-7.28) proton resonances whereas irradiation of the *ortho* proton (δ 7.49-7.37) gives an enhanced *meta* (δ 7.36-7.28) proton signal along with an enhancement of the camphanyl H_4 signal.

X-Ray structure of [Pt(O₃PCam)(PPh₃)₂] · 2·2CHCl₃

In order to determine if there are any structural features that might render the PPh₃ groups of complex **2** inequivalent (*vide supra*), an X-ray structure determination was carried out. Crystals of the di-chloroform solvate were obtained from CHCl₃-hexane. The structure of the complex is shown in Figure 4, with the atom numbering scheme. Selected bond lengths and angles are given in Table 5.

The complex crystallises as the di-chloroform solvate, both of which form H-bonds to the P=O oxygen atom. The camphanyl group showed some fluxionality with elongated ellipsoids [especially C(9) and C(10)], as shown in Figure 4. The platinum centre is slightly distorted from a square-planar geometry, with an angle of 9.0° between the P(2)-Pt(1)-P(3) and O(1)-Pt(1)-O(2) planes. A similar angle of 9.1° was observed in [Pt(O₃PCH₂Fc)(PPh₃)₂] [8] (CSD refcode ODASUH), but the other six crystallographically characterised examples of platinum(II) phosphonates are more regular, for example [Pt(O₃PPh)(PPh₃)₂] (CSD refcode SOYMIC), where the corresponding angle is only 2.2°. [7] Other bond parameters for **2** are ordinary, and remarkably constant for all 8 known examples of structurally characterised platinum(II) phosphonates, with P-O 1.56-1.58 Å, P=O 1.475-1.496 Å, O-P-O 100-102°, and O-Pt-O 71-72°.

It is noteworthy that the bulky camphanyl group is directed into a ‘pocket’ formed by the two triphenylphosphine ligands and the platinum atom. Rotation about the P-CH₂ bond would orient the camphanyl group away from the platinum, but at the expense of eclipsing the CH₂ C-H bonds with the P-O bonds, and the camphanyl PCH₂-C bond with the P=O bond, which would be unfavourable. Instead, the complex adopts the observed staggered conformation. Because of the asymmetric nature of the camphanyl group, the two PPh₃ ligands are inequivalent; restricted fluxionality of the system maintains this inequivalence in solution, as observed in the ³¹P{¹H} NMR spectrum of the complex. It is worth noting that

[Pt(O₃PCH₂Fc)(PPh₃)₂] [8] has a similar arrangement of the CH₂Fc group, which also points into the Pt(PPh₃)₂ pocket, but because of a plane of symmetry in this system, the PPh₃ groups remain equivalent.

Theoretical studies

In order to quantitatively rationalise the different NMR spectroscopic behaviour of the PPh₃ and PPhMe₂ complexes theoretical calculations were carried out. Figure 5 shows the density functional theory potential energy curves for rotation of the camphanyl group in complexes **2** and **3**. Both compounds exhibit three distinct maxima and three distinct minima corresponding to the hydrogen atoms of the CH₂ group being either eclipsed or staggered relative to the adjacent P=O and P-O groups. We find that the energetic barrier for rotation of the camphanyl group in **3** is low, with the three maxima just 9-13 kJ mol⁻¹ higher than the global minimum. Additional steric interactions due to the bulky PPh₃ ligands in **2** greatly increase the energetic barrier for rotation of the camphanyl group, to 55 kJ mol⁻¹. This much higher energetic barrier will greatly reduce the rate at which the camphanyl group rotates in **2** compared to **3** and thus supports the NMR and X-ray crystallographic observations.

Experimental

Camphanylphosphonic acid **1** was prepared as described previously.[2] Silver(I) oxide was used as supplied from BDH. The complexes *cis*-[PtCl₂(PPh₃)₂], *cis*-[PtCl₂(PPhMe₂)₂] and [PtCl₂(dppe)] were prepared by reaction of [PtCl₂(cod)] [25] (cod = 1,5-cyclo-octadiene) with the stoichiometric amount of the phosphine in dichloromethane, followed by precipitation of the product with petroleum spirits (b.p. 40-60 °C).[26,27]

^1H (300.13 MHz) and $^{13}\text{C}\{^1\text{H}\}$ (75.47 MHz) NMR spectra were recorded on a Bruker AC300P spectrometer in CDCl_3 (unless otherwise specified), with chemical shifts relative to $\text{CD}(\text{H})\text{Cl}_3$ (δ ^1H 7.26 and ^{13}C 77.06). Scheme 1 shows the atom numbering scheme used in NMR assignments. NOE difference spectra were measured on a solution that had not been degassed and were acquired with an irradiation time of 3s, typically achieving 50 to 60% saturation of the irradiated multiplet. Each multiplet was recorded in cycles of 16 scans for long term averaging. COSY45 NMR spectra were acquired with 1K increments in the F2 dimension, 256 increments zero filled to 512 increments in the F1 dimension and 32 scans per increment. After transformation the data matrix was symmetrised. ^{13}C - ^1H correlation spectra were acquired with 1K increments in F2 and 128 increments zero filled to 1K increments in F1 with 32 or 128 scans per increment. $^{31}\text{P}\{^1\text{H}\}$ NMR spectra were recorded on a JEOL FX90Q spectrometer (36.23 MHz) in CHCl_3 solution. Chemical shifts are externally referenced to 85% H_3PO_4 (δ 0.0) and a glass capillary used to provide a lock signal.

Elemental microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, NZ. Melting points were recorded on a Reichert hot-stage apparatus and are uncorrected. ESI mass spectra were recorded in methanol solution on a Bruker MicrOTOF instrument that was calibrated using a solution of sodium formate; a capillary exit voltage of 120V was used).

Synthesis of $[\text{Pt}(\text{O}_3\text{PCam})(\text{PPh}_3)_2]$ **2**

8-Camphanylphosphonic acid **1** (0.06 g, 0.27 mmol), *cis*- $[\text{PtCl}_2(\text{PPh}_3)_2]$ (0.21 g, 0.27 mmol) and an excess of silver(I) oxide (0.17 g, 0.73 mmol) were added in succession to dichloromethane (30 mL). After refluxing and stirring for 36 h the insoluble silver salts were removed by filtration and the yellow solution evaporated to dryness under reduced pressure. Recrystallisation of the yellow oil from chloroform/petroleum spirits gave **2** as a colourless

needle-like crystalline solid that was dried under vacuum (0.15 g, 60%), m.p. 224-225 °C. Found: C 58.18; H 5.12%. $C_{46}H_{47}PtP_3O_3$ requires C 59.04; H 5.06%. ESI MS (positive ion); $[M+H]^+$ m/z 936.2933 (calculated for $C_{46}H_{48}O_3P_3Pt$ m/z 936.2463; $[M+Na]^+$ m/z 958.2741 (calculated for $C_{46}H_{47}NaO_3P_3Pt$ m/z 958.2741).

Synthesis of $[Pt(O_3PCam)(PPhMe_2)_2]$ **3**

Complex **3** was prepared by the method for **2**, starting from *cis*- $[PtCl_2(PPhMe_2)_2]$. Purification of the crude reaction mixture was achieved by removing the solvent under vacuum and washing the resulting yellow solid with acetone (0.5 mL) to remove impurities, to give a white crystalline solid of **3** (yield 67%). M.p. 233-234 °C. Found C, 45.35; H, 5.97%. $C_{26}H_{39}PtP_3O_3$ requires C, 45.40; H, 5.72%.

Synthesis of $[Pt(O_3PCam)(dppe)]$ **4**

Complex **4** was prepared by the method described for **2**, starting from $[PtCl_2(dppe)]$. Purification of **4** was achieved by the recrystallisation of the crude reaction mixture, a yellow oil, from chloroform/petroleum spirit at room temperature to give colourless needle-like crystals of **4** in 70% yield. M.p. >140 °C (decomp.).

Theoretical calculations

The geometries of complexes **2** and **3** were optimised using the B3LYP density functional method with the 6-311+G(d,p) basis set for the H, C, O and P atoms and the cc-pVTZ basis set and effective core potential for the Pt atoms. The initial geometry for optimisation of **2** was taken from the corresponding X-ray crystal structure. The crystal structure of **3** has not yet been determined, hence the initial geometry was inferred using the orientation of the camphanyl group in **2** and the $Pt(PMe_2Ph)_2$ framework from other

comparable crystal structures of Pt(PMe₂Ph)₂ complexes.[28,29,30] The potential energy curve for rotation of the camphanyl group in **2** and **3** (Figure 5) was calculated by displacing the O-P-C-C dihedral angle from -180° to +180° in 10° increments with all other geometric parameters fixed at their optimised values. All density functional theory calculations were completed using Gaussian 09, Revision A.01.[31]

X-ray crystal structure of 8-camphanylphosphonic acid 1

Cell parameters and intensity data were collected at 163 K on a Nicolet R3 four-circle diffractometer with monochromatic Mo-K_α X-rays. No absorption correction was deemed necessary because of the low μ value. The structure was solved by direct methods and refinement (on F_o^2) included all non-hydrogen atoms anisotropic and with C-bonded hydrogen atoms in calculated positions. The H atom on O(1) was located and included with fixed coordinates, while that on O(3) was included in a calculated position on the O(3)····O(2)' vector.

Crystal and refinement data: C₁₀H₁₉O₃P, M 218.22, trigonal, space group R-3, $a = b = 27.012(5)$, $c = 8.041(4)$ Å, $U = 5081(3)$ Å³. D_c 1.284 g cm⁻³ for $Z = 18$. $F(000)$ 2124, $\mu(\text{Mo-K}\alpha) = 0.22$ mm⁻¹. Total data 1522, unique 1193 (R_{int} 0.0945), θ_{max} 45°, R_1 0.0842 ($I > 2\sigma(I)$), wR_2 0.1985 (all data), GoF 0.916, Δe +0.62/-0.41 e Å⁻³. The same space group has been reported previously for this compound,[4] though details of the structure have not been published.

X-ray crystal structure of [Pt(O₃PCam)(PPh₃)₂] 2·2CHCl₃

Crystals of the complex were obtained by crystallisation from a chloroform-hexane solution at room temperature. Cell parameters and intensity data were collected at 93(2) K on

a Bruker APEX II CCD diffractometer with monochromatic Mo-K α X-rays. The structure was solved and processed normally (refinement by full-matrix least-squares on F^2 as a dichloroform solvate).

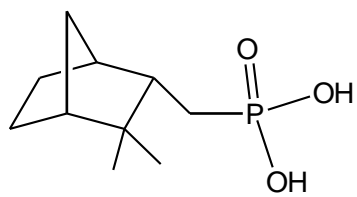
Crystal and refinement data: C₄₈H₄₉Cl₆O₃P₃Pt, M 1174.57, monoclinic, space group P 2(1)/n, $a = 12.7670(2)$, $b = 18.2748(3)$, $c = 20.8727(5)$ Å, $\beta = 92.183(1)^\circ$, $U = 4866.37(16)$ Å³. D_c 1.603 g cm⁻³ for $Z = 4$. $F(000)$ 2344, $\mu(\text{Mo-K}\alpha) = 3.352$ mm⁻¹. Total data 62474, unique 11614 (R_{int} 0.0484), R_1 0.0318 ($I > 2\sigma(I)$), wR_2 0.0780 (all data), GoF 1.025, Δe +1.306 and -1.281 e Å⁻³.

Supplementary data

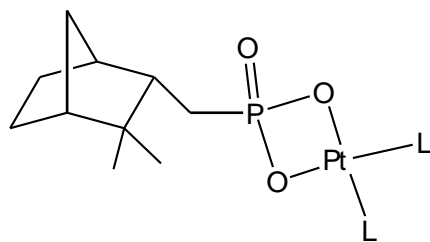
CCDC 787904 (**1**) and 787903 (**2**) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

Acknowledgements

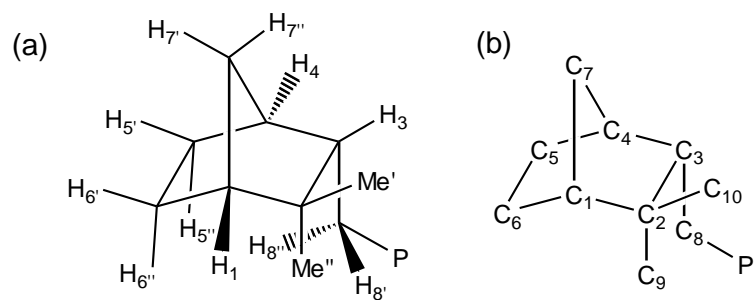
We thank the University of Waikato for financial support of this work, and Tania Groutso (University of Auckland) for the collection of the data set of **2**. Robert Appleby is thanked for preparation of camphanylphosphonic acid.



1



- 2;** L = PPh₃
- 3;** L = PPhMe₂
- 4;** L₂ = Ph₂PCH₂CH₂PPh₂ (dppe)

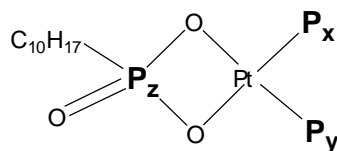


Scheme 1 NMR atom labelling schemes (a) hydrogen atoms; (b) carbon atoms

Table 1 Bond lengths (Å) and selected bond angles (°) for 8-camphanylphosphonic acid **1**.
Estimated standard deviations are in parentheses.

P(1)-O(2)	1.511(5)	P(1)-O(1)	1.534(6)
P(1)-O(3)	1.548(6)	P(1)-C(8)	1.762(8)
C(1)-C(6)	1.521(11)	C(1)-C(7)	1.521(12)
C(1)-C(2)	1.555(11)	C(2)-C(8)	1.532(10)
C(2)-C(3)	1.576(11)	C(3)-C(4)	1.520(12)
C(3)-C(10)	1.522(12)	C(3)-C(9)	1.541(11)
C(4)-C(5)	1.529(12)	C(4)-C(7)	1.547(12)
C(5)-C(6)	1.538(12)		
O(1)-P(1)-C(8)	106.4(3)	O(2)-P(1)-C(8)	112.2(3)
O(3)-P(1)-C(8)	104.0(4)	O(1)-P(1)-O(2)	111.2(3)
O(1)-P(1)-O(3)	110.8(3)	O(2)-P(1)-O(3)	111.9(3)

Table 2 $^{31}\text{P}\{^1\text{H}\}$ NMR data for the platinum-phosphonate complexes **2**, **3** and **4**, together with the atom labelling scheme



	P_x δ	P_y δ	P_z δ	$^1\text{JP}_x\text{-Pt}$ Hz	$^1\text{JP}_y\text{-Pt}$ Hz	$^2\text{JP}_x\text{-P}_y$ Hz	$^2\text{JP}_z\text{-Pt}$ Hz	$^3\text{JP}_x/\text{P}_y\text{-P}_z$ Hz
2	5.4 dd	7.5 dd	55.3 t	3732	3843	26	117	7
3	-20.9 d	-20.9 d	53.2 t	3654	3654	0	100	4
4	30.5 dd	31.0 dd	58.4 t	3730	3701	20	102	7

Table 3 ^1H NMR data[¶] for the platinum-phosphonate complexes **2**, **3** and **4**, together with data for camphanylphosphonic acid **1**

Compound	CamP(O)(OH) ₂ 1 [†]	[Pt(O ₃ PCam)(PPh ₃) ₂] 2	[Pt(O ₃ PCam)(PPhMe ₂) ₂] 3	[Pt(O ₃ PCam)(dppe)] 4
Solvent	CD ₃ OD	CDCl ₃	CDCl ₃	CDCl ₃
H ₄	2.38 (br, s)	2.58 (br, s)	2.75 (br, s)	2.49 (br, s)
H ₃	1.82 (m)	1.96 (br, m)	2.01 (br, m)	1.84 (br, m)
H ₁	1.77 (br, s)	1.69 (br, s)	1.74 (br, s)	1.56 (br, s)
H _{8',8''}	1.72 (m*)	1.60 (d, ² J 12.2)	1.61 (d, ² J 11.7)	1.66 (br, s*)
	1.65 (m)	1.54 (br, m)	1.59 (br, m)	1.61 (br, m)
H _{7''}	1.66 (m)	1.68 (br, s*)	1.67 (d, ² J 13.0)	1.35 (d, ² J 10.6)
H _{6''}	1.60 (m)	1.47 (s)	1.56 (s)	1.39 (s)
H _{6'}	1.32 (m)	1.10 (s)	1.21 (s)	1.04 (s)
H _{7'}	1.20 (dt, ² J 9.7, ³ J 1.7)	1.05 (d, ² J 9.8)	1.15 (d, ² J 11.1)	0.84 (d, ² J 10.6)
H _{5''}	1.44 (m)	1.26 (m)	1.49 (br, m)	1.28 (br, m)
H _{5'}	1.34 (m)	0.83 (br, m)	1.22 (br, m)	0.87 (br, m)
Me [?]	0.98 (s)	0.95 (s)	1.01 (s)	0.84 (s)
Me [?]	0.83 (s)	0.71 (s)	0.81 (s)	0.70 (s)
Ph	-	7.80-7.30 (m)	7.37-7.28 (m)	7.95-7.20 (m)

[¶] Refer Scheme 1 for atom numbering scheme; Coupling constants J in Hz [†] From reference 2; * Multiplicity not discernible

Table 4 $^{13}\text{C}\{^1\text{H}\}$ NMR data[¶] for the platinum-phosphonate complexes **2**, **3** and **4**, together with data for camphanylphosphonic acid **1**

Compound	CamP(O)(OH) ₂ 1 [†]	[Pt(O ₃ PCam)(PPh ₃) ₂] 2	[Pt(O ₃ PCam)(PPhMe ₂) ₂] 3	[Pt(O ₃ PCam)(dppe)] 4
Solvent	CD ₃ OD	CDCl ₃	CDCl ₃	CDCl ₃
C ₅	21.0	20.1	20.5	20.2
C ₉ (Me ^{''})	22.3	22.0	22.2	22.1
C ₆	25.6	24.8	24.8	24.7
C ₈	25.2 (¹ JPC 138.3)	27.9 (¹ JPC 121.9)	28.6 (¹ JPC 122.0)	28.0 (¹ JPC 121.3)
C ₁₀ (Me')	32.3	32.4	32.3	32.2
C ₇	37.8	37.1	37.0	37.1
C ₂	38.3 (³ JPC 14.1)	37.5 (³ JPC 13.1)	37.6 (³ JPC 13.0)	37.5 (³ JPC 13.9)
C ₄	43.5 (³ JPC 3.6)	42.5 (³ JPC 3.3)	42.8 (³ JPC 3.2)	42.0 (³ JPC 3.0)
C ₃	46.0 (² JPC 3.9)	46.1 (² JPC 3.4)	46.4 (² JPC 3.1)	46.2 (² JPC 3.2)
C ₁	50.1 (⁴ JPC 3.9)	49.0*	49.0*	48.8*

[¶] Refer Scheme 1 for atom numbering scheme. Excluding aromatic resonances between *ca.* δ 128 and 132, and alkyl groups of PPhMe₂ and dppe. Coupling constants J in Hz

[†] From reference 2

* ⁴JPC coupling not discernible

Table 5 Selected bond lengths (Å) and selected bond angles (°) for [Pt(O₃PCam)(PPh₃)₂]
2·2CHCl₃. Estimated standard deviations are in parentheses.

Pt(1)-O(1)	2.084(2)	Pt(1)-O(2)	2.088(2)
Pt(1)-P(3)	2.2316(10)	Pt(1)-P(2)	2.2423(12)
Pt(1)···P(1)	2.6825(11)	P(1)-O(3)	1.490(3)
P(1)-O(2)	1.575(3)	P(1)-O(1)	1.580(3)
P(1)-C(1)	1.811(4)		
O(1)-Pt(1)-O(2)	71.58(9)	O(1)-Pt(1)-P(3)	168.30(7)
O(2)-Pt(1)-P(3)	98.80(7)	O(1)-Pt(1)-P(2)	93.27(7)
O(2)-Pt(1)-P(2)	163.52(7)	P(3)-Pt(1)-P(2)	96.96(4)
O(3)-P(1)-O(2)	115.20(14)	O(3)-P(1)-O(1)	114.27(14)
O(2)-P(1)-O(1)	101.32(13)	O(3)-P(1)-C(1)	108.39(17)
O(2)-P(1)-C(1)	107.70(16)	O(1)-P(1)-C(1)	109.62(16)

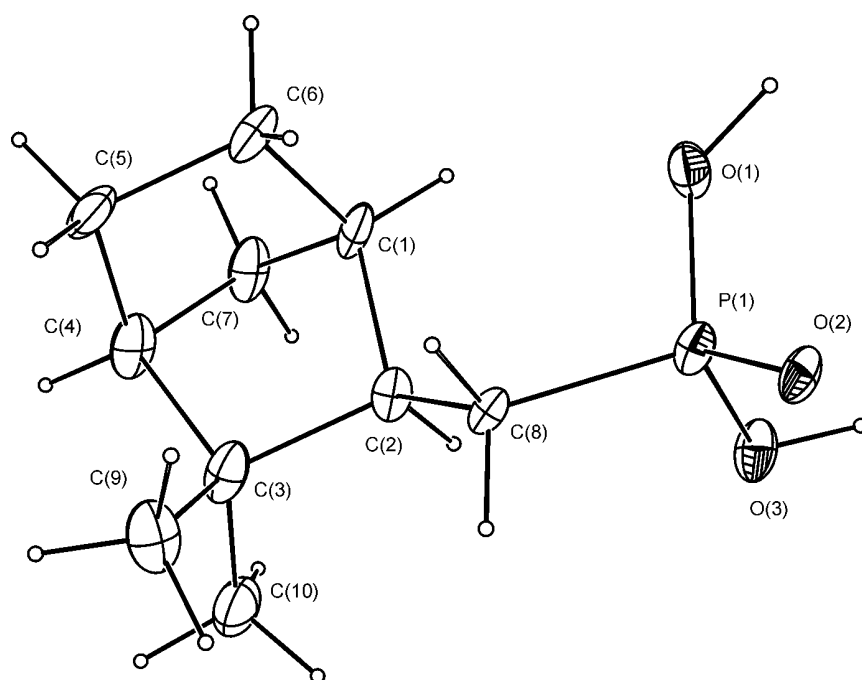


Figure 1 Molecular structure of 8-camphanylphosphonic acid **1**, showing the atom numbering scheme. Thermal ellipsoids are shown at the 50% probability level.

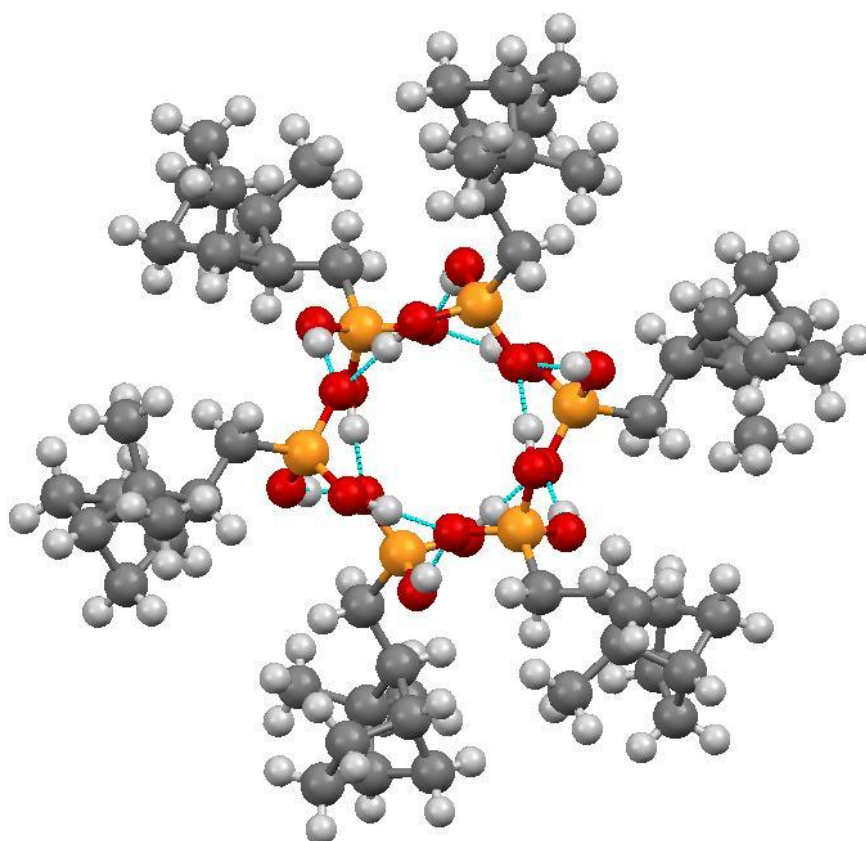


Figure 2 The hydrogen-bonded hexameric core of 8-camphanylphosphonic acid **1**, showing the presence of a central cavity and a hydrophobic camphanyl exterior

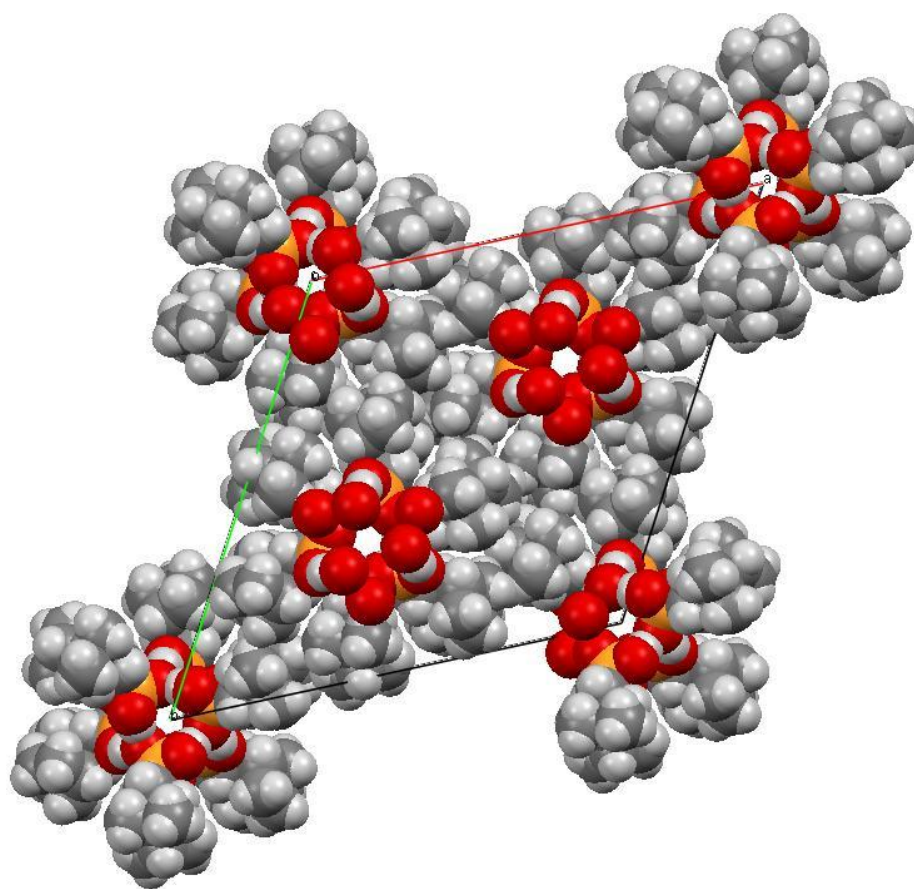


Figure 3 Space-filling representation showing the unit cell packing of the hexameric hydrogen-bonded assemblies of CamP(O)(OH)₂ **1**, with hydrophilic channels running parallel to the crystallographic *c* axis.

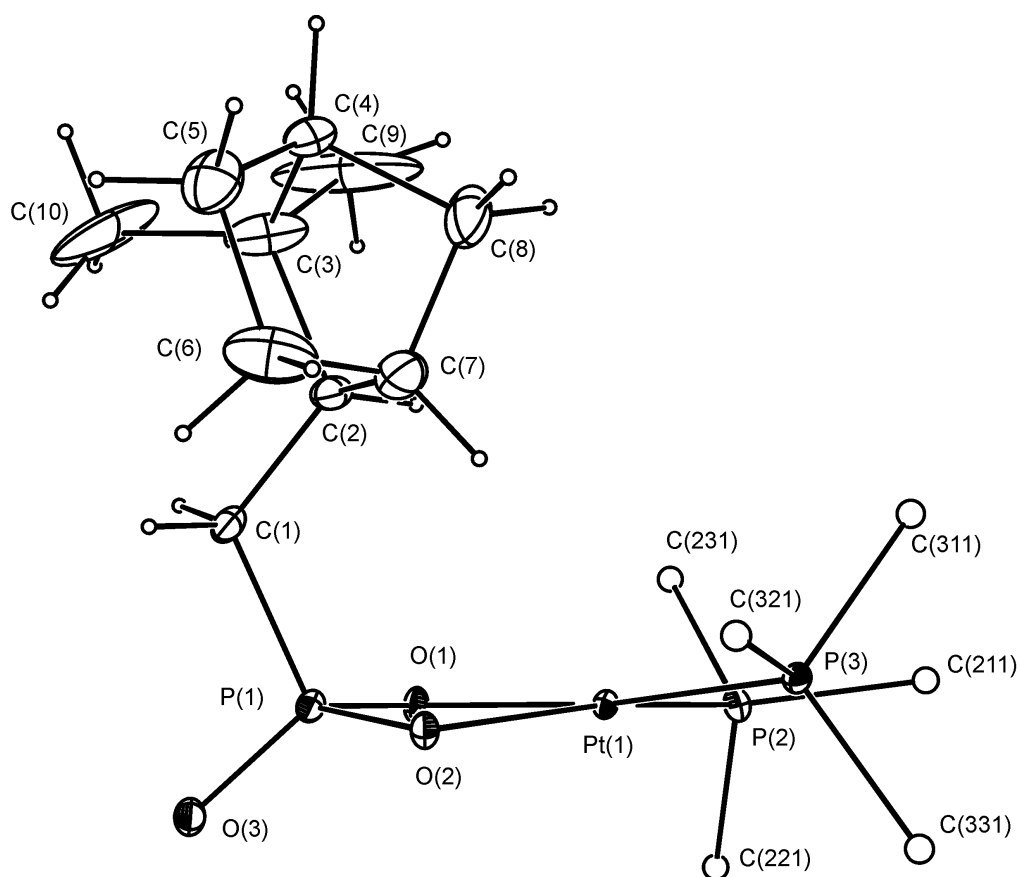


Figure 4 Molecular structure of $[\text{Pt}(\text{O}_3\text{PCam})(\text{PPh}_3)_2] \cdot 2 \cdot 2\text{CHCl}_3$, showing the atom numbering scheme; thermal ellipsoids are at the 50% probability level, chloroform solvate molecules are not shown, and *ipso* carbon atoms of the PPh_3 ligands are shown as small circles

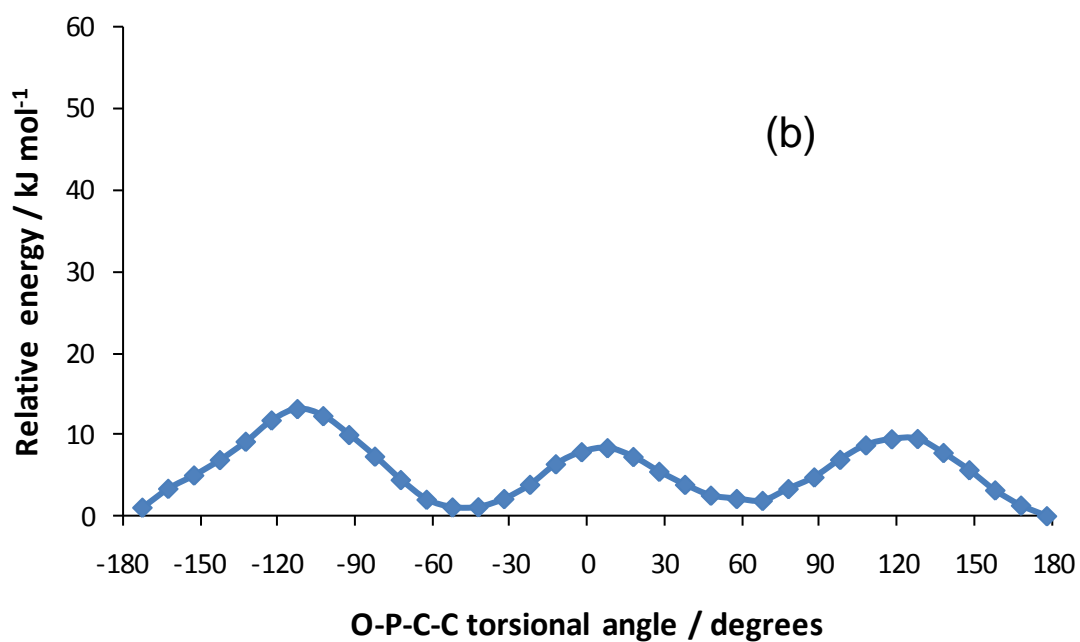
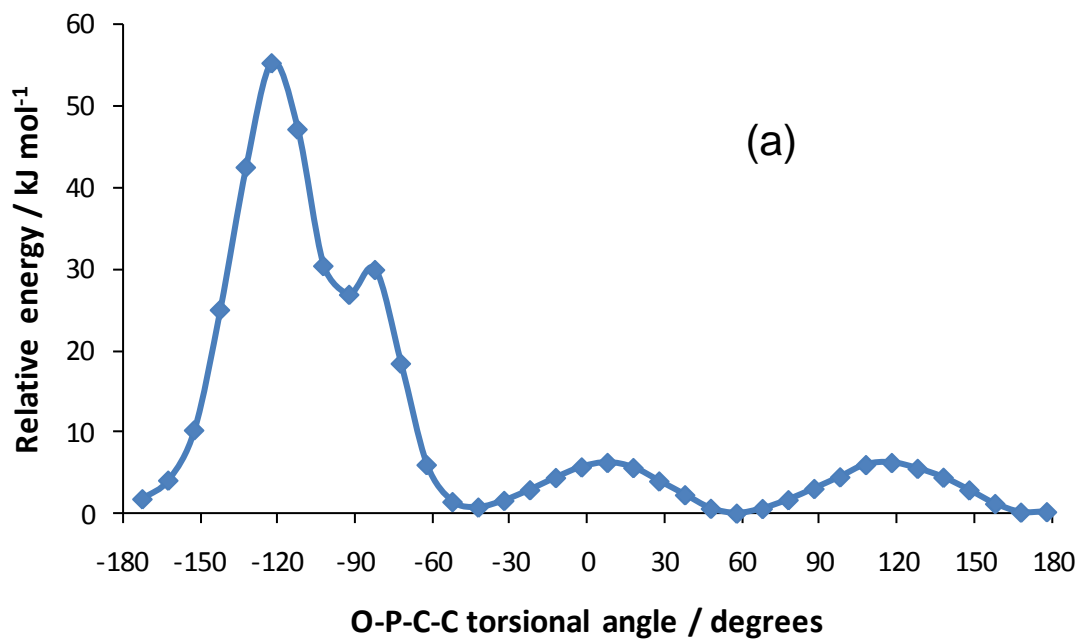


Figure 5 B3LYP/6-311+G(d,p) potential energy curves for rotation of the camphanyl group about the O-P-C-C torsional angle in (a) $[\text{Pt}(\text{O}_3\text{PCam})(\text{PPh}_3)_2]$ **2** and (b) $[\text{Pt}(\text{O}_3\text{PCam})(\text{PPhMe}_2)_2]$ **3**

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