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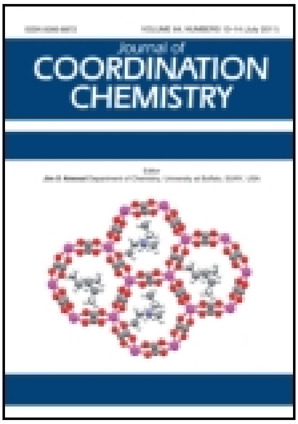

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Synthesis and characterization of a platinum(II) complex of camphenylphosphonic acid

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Synthesis and characterization of a platinum(II) complex of camphenylphosphonic acid

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Camphenylphosphonic acid RPO_3H_2, prepared by the literature reaction of PCl_5 with camphene, has been characterized by a single-crystal X-ray diffraction study. The compound crystallizes with a double chain structure formed by connected eight-membered hydrogen-bonded rings. Reaction of RPO_3H_2 with *cis*-$[PtCl_2(PPh_3)_2]$ and excess silver(I) oxide in refluxing dichloromethane gives the platinum(II) phosphonate complex $[Pt\{O_3PR\}(PPh_3)_2]$. $^{31}P\{^1H\}$ NMR spectroscopic characterization of $[Pt\{O_3PR\}(PPh_3)_2]$ shows that the two PPh_3 ligands are inequivalent due to asymmetry of the camphenyl group. An X-ray diffraction study on the platinum complex shows that the PC–H bond is directed toward the four-membered ring, resulting in the terpene group pointing away from the ring, in contrast to the previously reported structure of the saturated camphanylphosphonate complex. The differences are discussed in terms of steric interactions involving the phosphonate ligands.

Keywords: Phosphonic acids; Phosphonate complexes; Terpenes; Platinum complexes; X-ray structure determinations

1. Introduction

Terpenes are attractive starting materials for synthesis of new ligands, due to their ease of availability, organic solubility, and chirality. Terpene-derived phosphonic acids have attracted some interest, such as recent syntheses of *endo*-bornylphosphonic acid and *exo*-β-fenchylphosphonic acid [1]. We are interested in utilizing camphene as an inexpensive terpene in the synthesis of new organophosphorus compounds and metal complexes thereof, and have reported the synthesis of *endo*-8-camphanyl-phosphinic and -phosphonic acids [2–4]. The latter has attracted some interest for its coordination chemistry as a bulky phosphonate ligand in high nuclearity iron aggregates [5–7]. 8-Camphanylphosphonic acid ($camPO_3H_2$) (**1**) (scheme 1) also reacts with platinum(II) phosphine complexes *cis*-$[PtCl_2L_2]$ [$L = PPh_3$, PMe_2Ph; $L_2 = Ph_2P(CH_2)_2PPh_2$] in the presence of excess silver(I) oxide to give platinum(II) phosphonate complexes $[Pt(O_3Pcam)L_2]$ (**2**) [8]. NMR spectroscopic investigation of these complexes showed ligand-dependent behavior; in the case of the PPh_3 and $Ph_2P(CH_2)_2PPh_2$ complexes

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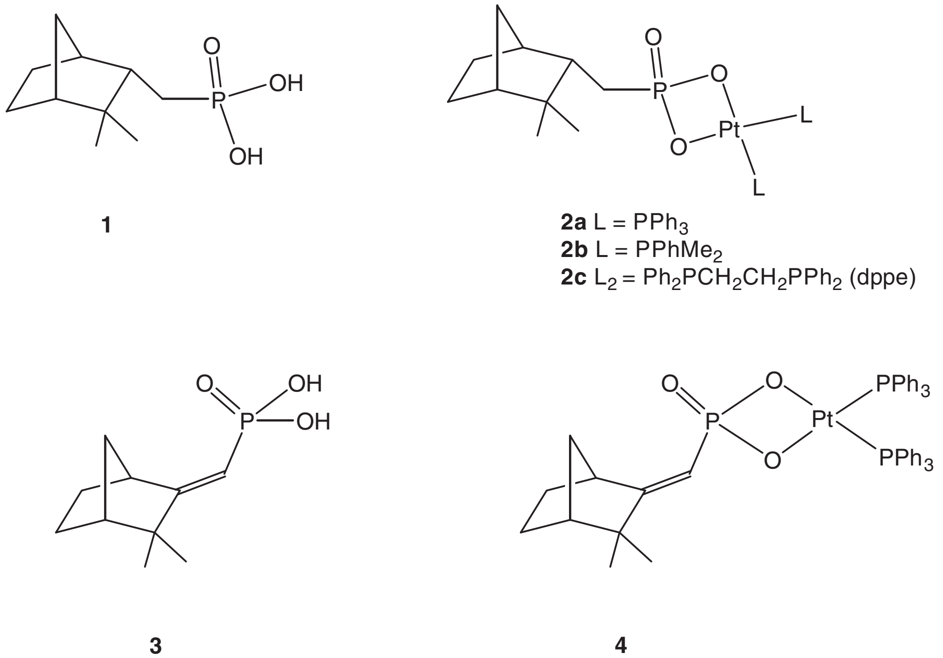


1

2a L = PPh_3
2b L = $PPhMe_2$
2c $L_2 = Ph_2PCH_2CH_2PPh_2$ (dppe)

3

4

Scheme 1. Structures of camphene-derived compounds reported herein.

(but not the PMe_2Ph complex **2b**) the phosphine ligands were inequivalent at room temperature due to restricted rotation of the camphanyl group, which was supported by theoretical calculations.

In this contribution, we report the corresponding chemistry of a related unsaturated organophosphorus acid, camphenylphosphonic acid (**3**). This has been known for some time from studies by Marsh and Gardner [9] and subsequently by Chavane [10] but despite its simple synthesis from inexpensive precursors (PCl_5 and camphene) it appears to have not been subsequently investigated.

2. Results and discussion

Racemic camphenylphosphonic acid (**3**) was prepared by a slightly modified procedure of that previously reported by Chavane [10]. The compound is only sparingly soluble in dichloromethane and chloroform, and was crystallized from ethanol (in which it is quite soluble) forming colorless crystals that were pure by ^{31}P NMR spectroscopy (δ 12.3 in alkaline D_2O). The compound was also characterized by ESI mass spectrometry (in methanol solution) and displayed considerable aggregation in both positive- and negative-ion modes. As expected, and as observed for other phosphonic acids [11, 12], RPO_3H_2 (**3**) gave an $[M - H]^-$ ion at m/z 215.080 (calculated m/z 215.083). However, a series of higher mass aggregate ions $[nRPO_3H_2 - H]^-$ at m/z 431.134 ($n = 2$), 647.213 ($n = 3$), 863.298 ($n = 4$), 1079.390 ($n = 5$), and 1295.488 ($n = 6$) were observed, as shown

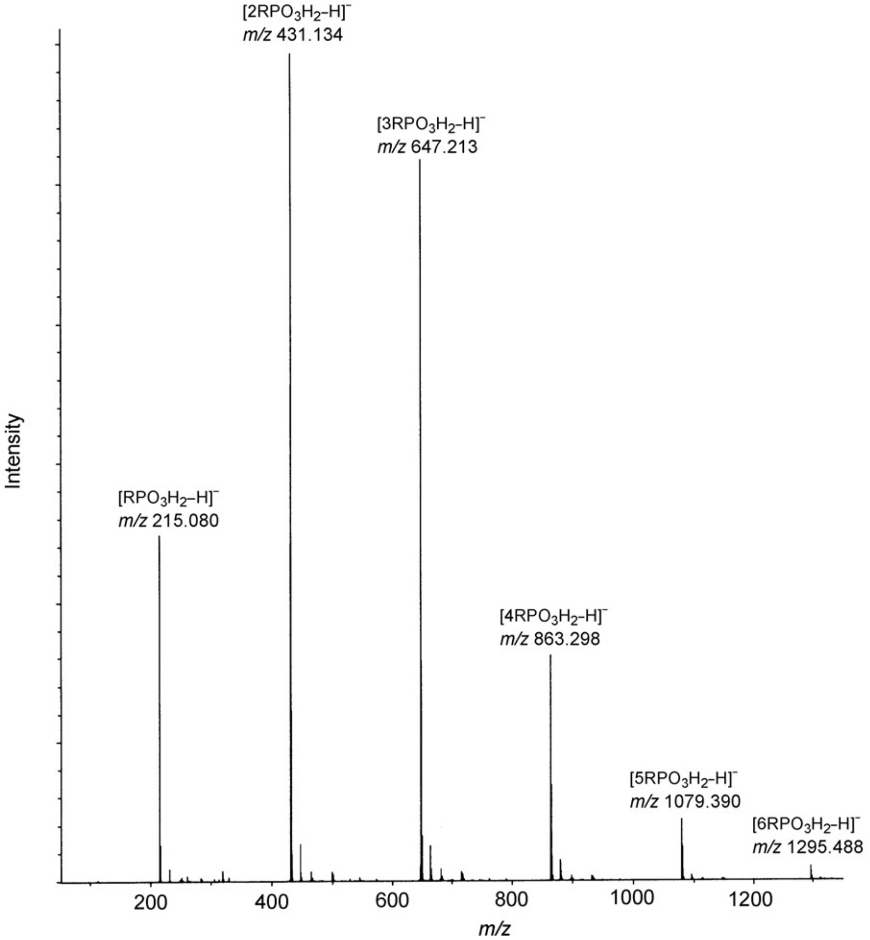


Figure 1. Negative-ion ESI mass spectrum of camphenylphosphonic acid RPO_3H_2 (**3**) in methanol, showing the formation of aggregate ions $[nRPO_3H_2 - H]^-$.

in figure 1. In positive-ion mode aggregation also occurred, but to a lesser extent; the base peak was $[RPO_3H_2 + H]^+$ (observed m/z 217.103, calculated m/z 217.099), together with aggregate ions $[nRPO_3H_2 + H]^+$ at m/z 433.198 ($n = 2$), 649.294 ($n = 3$), and 865.388 ($n = 4$). Additional ions due to aggregation with adventitious alkali metal cations was also seen, for example with the observation of $[RPO_3H_2 + Na]^+$ (m/z 239.086) and $[RPO_3H_2 + K]^+$ (m/z 255.059). The extensive aggregation observed in the ESI MS analysis is consistent with the aggregation of the compound found in the solid state (*vide infra*).

Previously, we reported the X-ray structure of camphanylphosphonic acid (**1**) and found it to have an interesting hydrogen-bonded hexameric structure as a result of the steric bulk of the camphanyl groups. The structure of the unsaturated camphenyl analog **3** was therefore determined for comparative purposes. The molecular structure is shown in figure 2 together with the atom-numbering scheme, while bond lengths and angles are given in table 1. The H-bonding network generates a puckered double

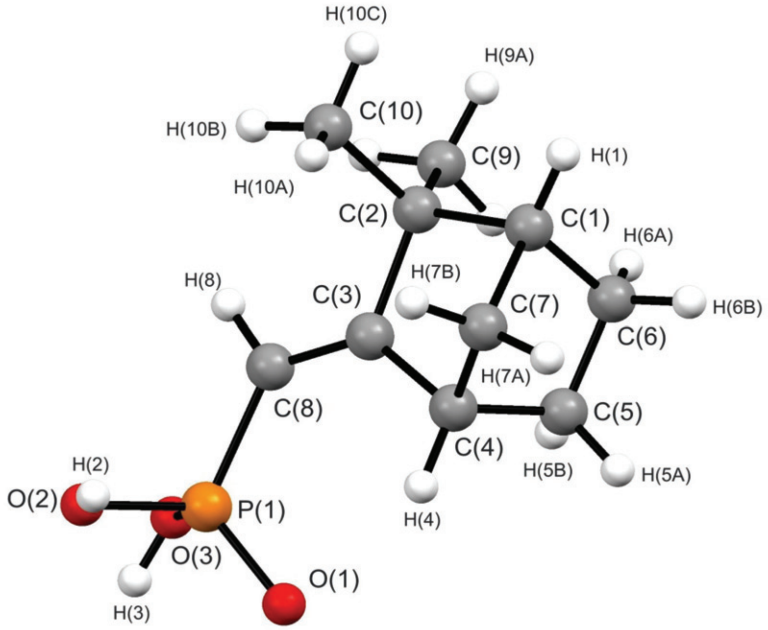


Figure 2. Molecular structure of camphenylphosphonic acid (**3**) showing the atom-numbering scheme.

chain parallel to the *b*-axis with the P = O acting as a H-bond acceptor from two P–O–H groups from adjacent molecules, generating linked eight-membered rings (table 1 and figure 3). The dimer units are similar to those commonly formed by carboxylic acids [13, 14]. The basic eight-membered ring motif is common for phosphonic acids [1, 15–22] and also for arsonic acids $RAsO_3H_2$ [23–29], although the way these are further linked together varies a lot. Even for those with the same linked structures as found for **3**, the chains can vary from very puckered (e.g. in *p*-$MeOC_6H_4PO_3H_2$ CSD refcode AFUWAZ [15]) to quite flat (e.g. $C_6H_{11}PO_3H_2$ CSD refcode UFEGER [19]).

Reaction of *cis*-[$PtCl_2(PPh_3)_2$] with slightly more than 1 mole equivalent of RPO_3H_2 (**3**) and a large excess of silver(I) oxide (as a halide-abstracting reagent and base) in refluxing dichloromethane for 48 h, followed by filtration to remove silver salts and precipitation of the product yielded a pinkish solid identified as [$Pt(O_3PR)(PPh_3)_2$] (**4**). Crystallization by vapor diffusion of diethyl ether into a dichloromethane solution of the complex at room temperature produced colorless crystals suitable for an X-ray diffraction study. The molecular structure of the compound is shown in figure 4 together with the atom-numbering scheme, while selected bond lengths and angles are given in table 2. The structure confirms the compound as a complex of camphenylphosphonic acid, coordinated as a dianion, forming a four-membered Pt–O–P(O)–O ring system. The complex crystallizes with one molecule of diethyl ether in the crystal; however, elemental microanalytical data on the crystals used for the crystallographic study were not satisfactory for either the unsolvated complex or its ether solvate. The complex did, however, appear pure by ^{31}P NMR spectroscopy.

Table 1. Bond lengths (Å) and angles (°), and hydrogen-bond details, for **3** with estimated standard deviations in parentheses.

P(1)–O(1)	1.485(4)	P(1)–O(3)	1.561(4)
P(1)–O(2)	1.565(4)	P(1)–C(8)	1.757(6)
C(1)–C(6)	1.422(11)	C(1)–C(2)	1.570(9)
C(1)–C(7)	1.643(11)	C(2)–C(9)	1.522(9)
C(2)–C(10)	1.531(9)	C(2)–C(3)	1.538(8)
C(3)–C(8)	1.321(8)	C(3)–C(4)	1.488(9)
C(4)–C(5)	1.403(11)	C(4)–C(7)	1.569(11)
C(5)–C(6)	1.396(12)		
O(1)–P(1)–O(3)	112.9(3)	O(1)–P(1)–O(2)	112.4(2)
O(3)–P(1)–O(2)	103.7(2)	O(1)–P(1)–C(8)	114.9(2)
O(3)–P(1)–C(8)	104.0(3)	O(2)–P(1)–C(8)	108.1(2)
C(6)–C(1)–C(2)	107.0(8)	C(6)–C(1)–C(7)	97.7(6)
C(2)–C(1)–C(7)	103.2(5)	C(9)–C(2)–C(10)	108.6(6)
C(9)–C(2)–C(3)	110.7(6)	C(10)–C(2)–C(3)	111.6(5)
C(9)–C(2)–C(1)	116.8(6)	C(10)–C(2)–C(1)	109.3(6)
C(3)–C(2)–C(1)	99.7(5)	C(8)–C(3)–C(4)	130.3(6)
C(8)–C(3)–C(2)	123.2(5)	C(4)–C(3)–C(2)	106.4(5)
C(5)–C(4)–C(3)	107.3(8)	C(5)–C(4)–C(7)	102.0(6)
C(3)–C(4)–C(7)	104.1(6)	C(6)–C(5)–C(4)	105.6(8)
C(5)–C(6)–C(1)	108.5(8)	C(4)–C(7)–C(1)	87.7(5)
C(3)–C(8)–P(1)	127.9(5)		

Hydrogen-bonding parameters:
(1) O(2)–H: 0.84 Å; H···O(1)$^{(a)}$: 1.85 Å; O(2)···O(1): 2.66(1) Å; O(2)–H···O(1): 161°.
(2) O(3)–H: 0.84 Å; H···O(1)$^{(b)}$: 1.85 Å; O(3)···O(1): 2.60(1) Å; O(3)–H···O(1): 148°.
Symmetry operations: $^{(a)}-x,\ y-½,\ -z+½$; $^{(b)}-x,\ y+½,\ -z+½$.

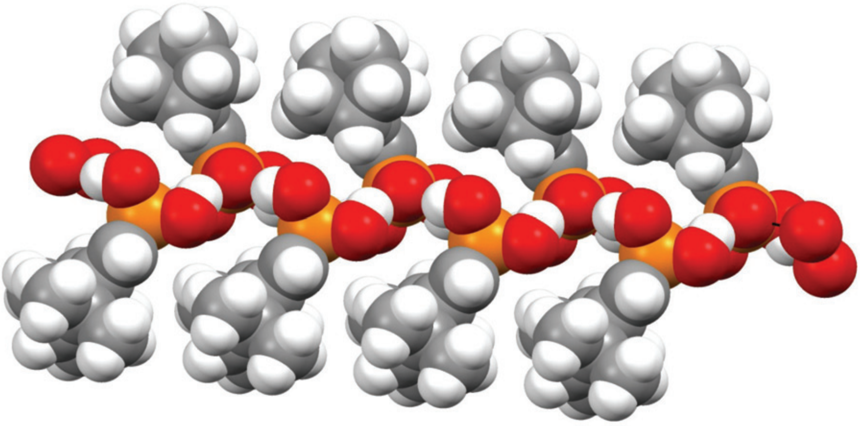


Figure 3. Space filling diagram of camphenylphosphonic acid **3** showing the formation of a ladder structure formed by hydrogen-bonded eight-membered rings.

The complex has many similarities with the previously reported complex of the saturated analog, camphanylphosphonic acid (**2a**). The platinum–oxygen distances of **4** [Pt(1)–O(1) 2.079(6) and Pt(1)–O(2) 2.061(6) Å] are comparable to those in **2a** [2.084(2) and 2.088(2) Å]. The four-membered ring of **4** is slightly puckered, with a dihedral angle between the O(1)–Pt(1)–O(2) and O(1)–P(3)–O(2) planes of 13.5(6)°, the direction of this puckering being toward the camphenyl group (making it adopt a slightly more axial

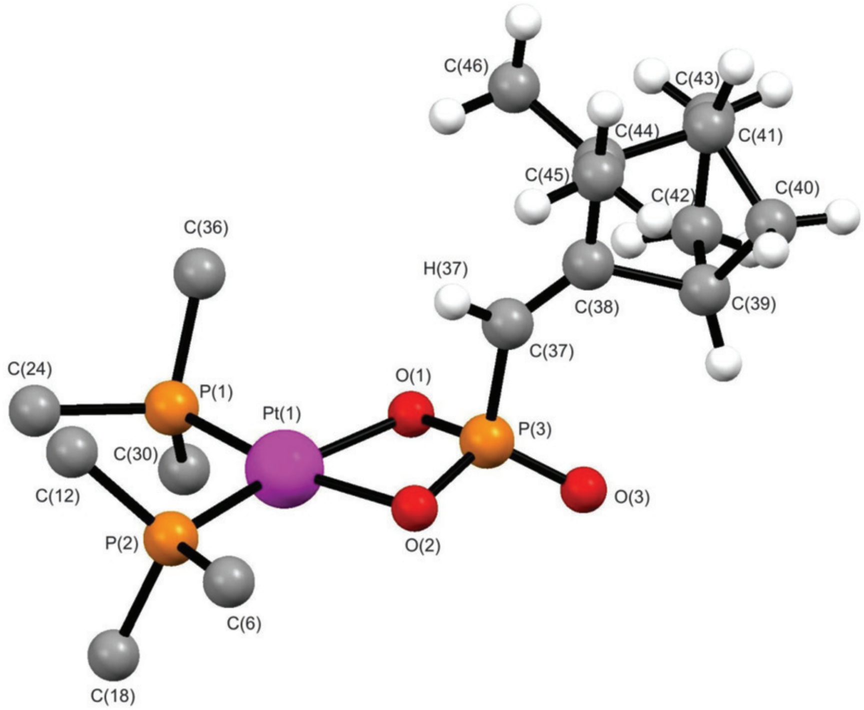


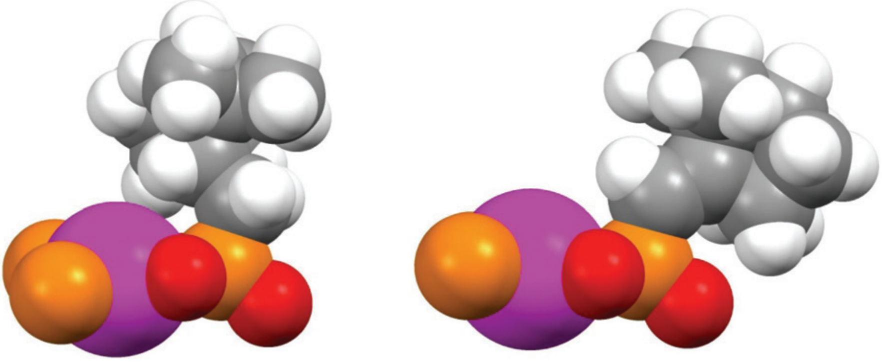
Figure 4. Molecular structure of [Pt(O_3PR)(PPh_3)$_2$] (**4**) (R = camphenyl) showing the atom-numbering scheme; only *ipso* carbons of the triphenylphosphines are shown for clarity.

Table 2. Selected bond lengths (Å) and angles (°) for [Pt{O_3PR}(PPh_3)$_2$] (**4**) with estimated standard deviations in parentheses.

Pt(1)–O(2)	2.061(6)	Pt(1)–O(1)	2.079(6)
Pt(1)–P(2)	2.228(2)	Pt(1)–P(1)	2.248(2)
P(3)–O(3)	1.472(7)	P(3)–O(1)	1.565(7)
P(3)–O(2)	1.587(7)	P(3)–C(37)	1.800(11)
C(37)–C(38)	1.310(15)		
O(2)–Pt(1)–O(1)	71.5(3)	O(2)–Pt(1)–P(2)	97.5(2)
O(1)–Pt(1)–P(2)	169.0(2)	O(2)–Pt(1)–P(1)	165.5(2)
O(1)–Pt(1)–P(1)	94.0(2)	P(2)–Pt(1)–P(1)	96.98(9)
O(3)–P(3)–O(1)	115.7(4)	O(3)–P(3)–O(2)	115.7(4)
O(1)–P(3)–O(2)	100.2(4)	O(3)–P(3)–C(37)	112.4(4)
O(1)–P(3)–C(37)	105.8(5)	O(2)–P(3)–C(37)	105.9(4)
P(3)–O(1)–Pt(1)	93.3(3)	P(3)–O(2)–Pt(1)	93.4(3)
C(38)–C(37)–P(3)	129.1(8)		

position on the four-membered ring). The corresponding dihedral angle in **2a** is 10.0(1)°.

The key difference between **4** and its saturated camphanyl analog **2a** lies in the orientation of the terpene group with respect to the platinum coordination plane, as shown in figure 5. In **2a**, the two C–H bonds of the P–CH_2 group are directed away from the platinum, resulting in the camphanyl group adopting a position (in a pocket



2 **4**

Figure 5. Molecular structures of the cores of the complexes [Pt(O_3PR)(PPh_3)$_2$] (**2**, R = camphanyl; **4**, R = camphenyl) along the O ··· O vector, showing the disposition of the terpene group relative to the four-membered Pt–O–P(O)–O rings.

formed by the PPh_3 ligands) above the four-membered Pt–O–P(O)–O ring. This conformation is preferred in order to eliminate eclipsing of the C–H and P–O bonds. In contrast, in **4**, the C–H bond of the P–CH group points toward the four-membered ring, approximately bisecting the O(1)–P(3)–O(2) angle (the H(37)–C(37)–P(3)–O(3) torsion angle is 159(1)°). This allows the camphenyl group to adopt a position directed away from the four-membered ring, thus minimizing steric interactions with the bulky PPh_3 ligands, even though the C(37)–C(38) and P(3)–O(3) bonds are almost eclipsed [torsion angle 19(1)°]. Thus the simple change from a saturated CH_2 group in **2a** to an unsaturated CH group in **4** has a considerable effect on the overall preferred conformation of the complexes in the solid state.

The camphenyl group of **4** is oriented in such as way that there is partial symmetry about the (vertical) plane containing Pt(1), P(3), O(3), C(37), H(37), C(38), C(39), and C(44). The two methyl groups C(45) and C(46) are approximately symmetrically disposed about this plane, but the symmetry is broken by the remainder of the terpene skeleton. One bridge contains a single carbon, C(40), while on the other side of the plane, the bridge contains two carbon atoms, C(42) and C(43). This asymmetry accounts for the inequivalence in the PPh_3 environments (at δ 11.5 and 6.7) observed in the $^{31}P\{^1H\}$ NMR spectrum of **4**, which showed two doublets of doublets (with $^2J(PP)$ coupling of 25 Hz), as well as a smaller $^3J(PP)$ coupling to the phosphonate phosphorus of 6 Hz. The two triphenylphosphines also show $^1J(PtP)$ couplings of 3863 and 3845 Hz, values which are typical for phosphine ligands *trans* to low *trans*-influence O-donor ligands [8]. The phosphonate phosphorus is a characteristic triplet resonance at δ 40.3 [$^3J(PP)$ 6 Hz] due to coupling to the two triphenylphosphines, as well as $^2J(PtP)$ coupling of 121 Hz. These ^{31}P NMR parameters are similar to those of **2a** and are consistent with the formation of a metallacyclic platinum–phosphonate complex. The ^1H NMR spectrum of **4** showed complex multiplets for the PPh_3 ligands (between δ 7 and 8), a complex set of resonances due to the camphenyl group (which were not assigned), and a distinctive doublet at δ 5.47 assigned to the P–CH = C proton, with $^2J(PH)$ 13.6 Hz.

In conclusion, camphenylphosphonic acid (**3**) has been characterized by mass spectrometry and a single-crystal X-ray diffraction study. This "forgotten" organophosphorus acid forms an analogous platinum(II)–phosphonate coordination complex to its saturated analog camphanylphosphonic acid, providing a useful alternative. However, the subtle change from a saturated to an unsaturated ligand causes changes in the orientation of the terpene–phosphonate ligand relative to the coordination plane of the complex.

3. Experimental

R-(+)-Camphene (Aldrich), PCl_5 (BDH), and silver(I) oxide (BDH) were used as supplied. *cis*-$[PtCl_2(PPh_3)_2]$ was prepared from $[PtCl_2(cod)]$ [30] and 2 mole equivalents of PPh_3 [31]. Reactions were carried out in dried glassware but without further precautions to exclude air, light, or moisture. Elemental microanalyses were carried out by the Campbell Microanalytical Laboratory, University of Otago, Dunedin, NZ. 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 120 V was used. NMR spectra were recorded in $CDCl_3$ on a Bruker AVIII 400 instrument using Topspin 3.0 software; signals were referenced relative to residual non-deuterated solvent peaks, or external H_3PO_4 (for ^{31}P NMR spectra). GCMS data were recorded on a HP 4789 GC interfaced to a HP 4869B mass selective detector operated in scanning mode. A 25 m HP-1 methyl silicone capillary column (o.d. 0.22 mm) was used.

3.1. *Synthesis and characterization of camphenylphosphonic acid (3)*

Compound **3** was prepared by minor modification of the method reported by Chavane [10] involving reaction of camphene with PCl_5. The resulting white solid was hydrolyzed in water, and after extraction into aqueous base, washing with ether, followed by acidification, a colorless oily solid of the crude product was obtained. The ether-insoluble fraction was recovered to give a crude product of **3** as a colorless crystalline solid; m.p. 162–164°C, lit. 167–169°C [10]. $^{31}P\{^1H\}$ NMR ($D_2O + NaOH$), δ 12.3(s). ESI MS: positive-ion $[RPO_3H_2 + H]^+$, m/z 217.103, calculated m/z 217.099; negative-ion $[RPO_3H_2 - H]^-$, m/z 215.080, calculated m/z 215.083. A wide range of aggregate ions were also observed, as described in section 2. The compound was also characterized by GCMS analysis of its methyl ester $RP(O)(OMe)_2$ (prepared by reaction of **3** with excess ethereal diazomethane [32] for 24 h), which gave an $[M]^+$ ion at m/z 244. ^{13}C (DEPT) NMR, δ 105.3 [d, P–CH, $^1J(PC)$ 193], 47.0 (s, CH), 44.1 [d, CH, $^3J(PC)$ 6], 37.2 (s, CH_2), 28.5 (s, CH_3), 27.7 (s, CH_2), 25.4 (s, CH_3), 23.4 (s, CH_2).

3.2. *Synthesis and characterization of $[Pt(O_3PR)(PPh_3)_2]$ (4)*

cis-$[PtCl_2(PPh_3)_2]$ (400 mg, 0.506 mmol) and camphenylphosphonic acid (**3**) (113 mg, 0.523 mmol) with silver(I) oxide (0.5 g, excess) were refluxed in dichloromethane (40 mL) for 48 h. The solution was filtered (glass fiber filter paper) to remove insoluble silver salts giving a pale brown solution. The volume was reduced to 20 mL on a rotary evaporator and petroleum spirits (b.p. 40–60°C) added until the solution turned cloudy,

Table 3. Crystal, collection, and refinement data for the X-ray structure determinations of camphenylphosphonic acid (**3**) and its platinum bis(triphenylphosphine) complex (**4**).

Compound	**3**	**4**
Empirical formula	$C_{10}H_{17}O_3P$	$C_{50}H_{55}O_4P_3Pt$
Formula weight	216.21	1007.94
Temperature (K)	158(2)	94(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
Unit cell dimensions (Å, °)		
a	12.146(8)	10.7557(5)
b	6.049(3)	12.6577(6)
c	14.724(10)	18.6339(10)
α	90	73.436(3)
β	90.03(2)	74.456(3)
γ	90	69.595(3)
Volume (Å^3), Z	1081.7(12), 4	2238.52(19), 2
Calculated density (g cm^{-3})	1.328	1.495
Absorption coefficient (mm^{-1})	0.234	3.285
F(000)	464	1020
Crystal size (mm^3)	0.45 × 0.25 × 0.16	0.22 × 0.20 × 0.10
Reflections collected/unique	2844/1424 [$R_{\text{int}} = 0.0949$]	49,908/10,701 [$R_{\text{int}} = 0.0917$]
Absorption correction	Empirical	Multiscan
Max. and min. transmission	0.4106 and 0.3401	0.7347 and 0.5318
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	1424/48/129	10,701/0/518
Goodness-of-fit on F^2	0.811	1.122
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0597$, $wR_2 = 0.1278$	$R_1 = 0.0763$, $wR_2 = 0.1824$
R indices (all data)	$R_1 = 0.1187$, $wR_2 = 0.1444$	$R_1 = 0.0952$, $wR_2 = 0.1925$
Largest difference peak and hole (e Å^{-3})	0.581 and −0.329	6.897 and −3.101

and allowed to crystallize, assisted by slow evaporation of the solvents. The resulting light pink-brown crystals were filtered, washed with petroleum spirits (10 mL) and dried under vacuum to give **4** (310 mg, 66%). Purification was achieved by slow vapor diffusion of diethyl ether into a filtered dichloromethane solution of the complex at room temperature, giving colorless crystals suitable for an X-ray diffraction study. Found: C 56.86; H 5.08. $C_{46}H_{45}O_3P_3Pt$ (**4**) requires C 59.14; H 4.86%; **4** · Et_2O requires 59.56, H 5.50%. $^{31}P\{^1H\}$ NMR, δ 40.3 [t, RPO_3, $^3J(PP)$ 6, $^2J(PtP)$ 121], 11.5 [dd, PPh_3, $^2J(PP)$ 25, $^3J(PP)$ 6, $^1J(PtP)$ 3863], 6.7 [dd, PPh_3, $^2J(PP)$ 25, $^3J(PP)$ 6, $^1J(PtP)$ 3845].

3.3. *X-ray structure determinations*

Colorless rods of **3** were obtained from ethanol; a fragment of one crystal was selected for the study; crystals of **4** were obtained from dichloromethane-diethyl ether. X-ray data were collected on a Siemens P4 four-circle diffractometer for **3** and on a Bruker Apex II CCD for **4**. For both structures the organic group showed partial disorder resulting in large prolate thermal ellipsoids, with one carbon [C(47)] for **4** being treated isotropically to prevent it becoming non-positive definite. All other non-hydrogen atoms were assigned anisotropic factors and hydrogen atoms were placed in calculated positions. The structures were solved and refined (on F_o^2) using the SHELX-97 programs [33, 34] operating under WinGX [35]. Crystal and refinement data are summarized in table 3.

Supplementary material

CCDC No. 835387 (**3**) and 835388 (**4**) contain the supplementary crystallographic data for this article. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre, *via* www.ccdc.cam.ac.uk/data_request/cif.

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