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Synthesis, characterization and crystal structure of [Pt(Me)(dppe){η^1-CH(PPh_3)(COOEt)}]BF_4. An example of overcrowded molecule and correlated properties

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Abstract

The complex [Pt(Me)(dppe){η^1-CH(PPh_3)(COOEt)}]BF_4 has been synthesized and characterized spectroscopically and structurally. It crystallizes in the space group $P2_1/n$, with lattice constants $a = 14.525(3)$ Å, $b = 14.931(3)$ Å, $c = 21.921(4)$ Å, $\beta = 103.47(3)°$. The X-ray analysis revealed a particularly overcrowded molecular structure containing high stereochemical constraints. The structural features account for specific chemical and physical properties of this compound, thus representing an interesting example of applied crystallography. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Crystal structures; Platinum; Metal complexes; Phosphorus ylides

1. Introduction

Complexes of transition metals with phosphorus ylides [1] play an important role in organometallic chemistry [2]. Of particular interest is the organometallic chemistry of carbonyl-stabilized phoshorus ylides, which can be used in the air and give rise to metal–C(ylide) or metal–O(ylide) coordination [2d] or chelating systems that, in some cases, have been revealed to be important olefin oligomerization catalysts [3].

Continuing our studies on Pt(II) and Pd(II) complexes with carbonyl-stabilized phosphorus ylides [4], we have recently taken into consideration the organometallic chemistry of a particular stabilized ylide, ketenylidenetriphenylphosphorane, $Ph_3PC{=}C{=}O$, a cumulene ylide that has shown to be an easy-to-use synthon in the attainment of metal-substituted ketenes of the type $L_nM(PPh_3)C{=}C{=}O$ (Chart 1) [5].

As a part of this ongoing research we have synthesized complexes [Pt(Me)(L–L){η^1-C(PPh_3)CO}]BF_4, **1a**, **1b** [L–L = 1,2-bis(diphenylphosphino)ethane (dppe) (**a**), 1,5-cyclooctadiene (cod) (**b**)], according to Reaction 1.

Both of the compounds **1a** and **1b** have been characterized and the corresponding results will be reported elsewhere. For a deeper investigation into the molecular structure of **1a**, an X-ray analysis was attempted on single crystals, which accidentally formed in the mother liquors of the synthesis reaction consisting of an acetone–ethyl ether mixture.

The structural data showed, to our disappointment, that the complex had a quite different chemical composition [Pt(Me)(dppe){η^1-CH(PPh_3)(COOEt)}]BF_4, **2**, (Chart 2). This complex could only form from the reaction of **1a** with ethanol, which was most likely present as an impurity in the solvents we have used.

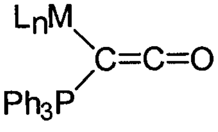

Chart 1.

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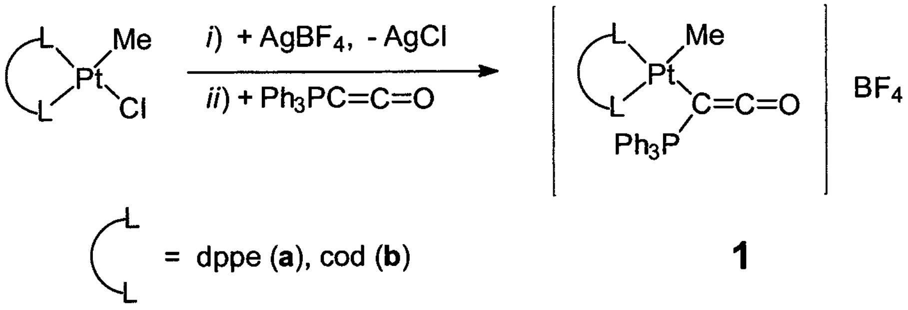
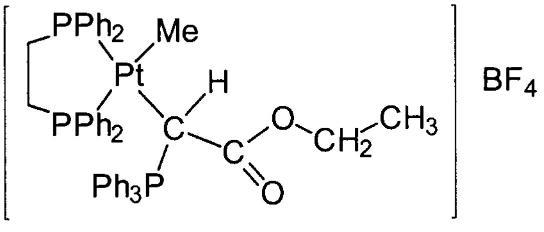


1

(1)



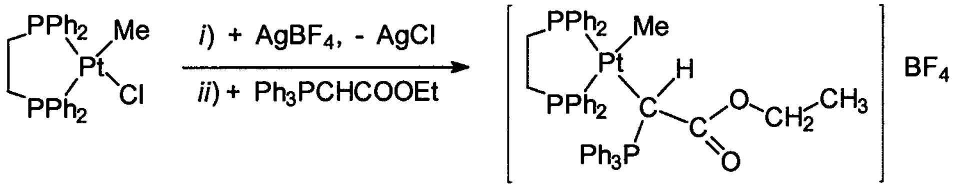
2

Chart 2.

However, compound **2**, in spite of its apparent irrelevance in relation to our aims, was revealed to exhibit rather interesting properties from a crystallochemical point of view, which prompted us to prepare it purposely for a thorough characterization. Here we report the synthesis, physico-chemical characterization and crystal structure of **2**.

2. Results and discussion

We first attempted to obtain compound **2** by treating complex **1a** with ethanol, without success [6]. Instead, we succeeded in the synthesis of **2** by direct reaction of [Pt(Cl)Me(dppe)] with carboethoxymethylenetriphenylphosphorane, $Ph_3PCHCOOEt$, according to Reaction 2.



2

(2)

Compound **2** thus obtained has been fully characterized by elemental analysis, IR and ^{1}H-, ^{31}P- and ^{13}C-NMR spectroscopy and ESI mass spectrum.

The IR spectrum showed a strong C=O band at 1695 cm^{-1} in agreement with the literature IR data for the carbonyl stretching of M–C(ylide) complexes [7]. The ^{31}P{^{1}H}-NMR data, confirmed the coordination of the carboethoxymethylenetriphenylphosphorane to Pt(II) through the ylidic carbon, on the basis of the phosphonium chemical shift at 27.44 ppm, which is about 9 ppm downfield from that observed for the free ylide, and from the phosphorus–platinum coupling constant value (71.5 Hz) [4]. In the ^{1}H-NMR spectrum the methyne proton generated a doublet of doublet of doublets at 4.61 ppm, flanked by ^{195}Pt satellites ($^2J_{PtH} = 90.8$ Hz), due to the coupling with phosphonium and with both the *cis* and *trans* inequivalent phosphorus atoms of the diphosphine ligand. The presence of a platinum-bonded methyl group was indicated by a doublet of doublets at 0.18 ppm, flanked by ^{195}Pt satellites, whereas the ethyl CH_3 gave rise to a triplet at 1.06 ppm. The signal of $–O–CH_2–$ showed a complex pattern corresponding to an AB system, confirmed through a simulation experiment (Fig. 1), indicating the inequivalence of the two methylene protons. The signals resulting from $–CH_2–CH_2–$ spanned quite a wide range, consisting of two complex systems centered at 2.8 and 1.6 ppm, respectively.

^{13}C{^{1}H}-NMR spectrum was in agreement with the suggested coordination mode through the ylidic carbon. Signals attributable to CO (172.57 ppm), CH (27.60 ppm), $Pt–CH_3$ (1.62 ppm), $–O–CH_2–$ (61.07 ppm) and $–O–CH_2–CH_3$ (15.04 ppm) were observed, along with the complex pattern arising from the phenyl groups. Signals due to $–CH_2–CH_2–$ were present as two distinct doublets of doublets at 28.23 and 20.20 ppm, mirroring the quite large difference between these two methylene groups observed in the ^{1}H-NMR spectrum.

Positive-ion ESI mass spectrum of **2** in CH_3CN showed several fragments including that corresponding

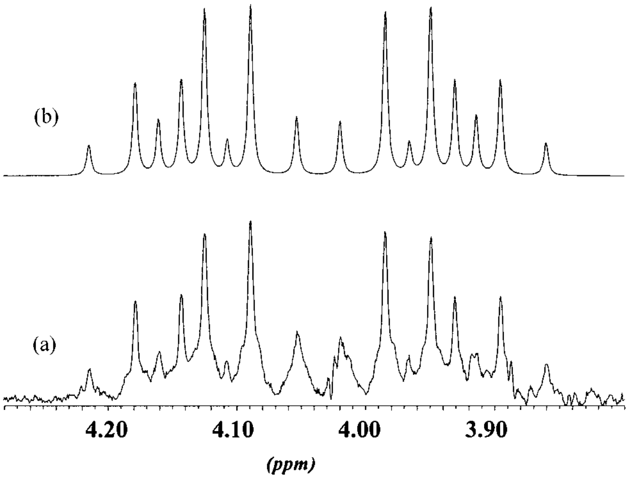


Fig. 1. Experimental (a) and simulated (b) ^{1}H-NMR spectrum relative to the –O–CH$_A$H$_B$– fragment.

to the molecular ion [Pt(Me)(dppe){η^1-CH(PPh$_3$)-(COOEt)}], [M]$^+$, centered at *m*/*z* 957. The higher isotopic cluster in the spectrum was that centered at *m*/*z* 608, corresponding to [Pt(Me)(dppe)]$^+$ and arising from [M]$^+$ through the loss of Ph$_3$PCHCOOEt. A signal at *m*/*z* 349, corresponding to the protonated ylide, [Ph$_3$PCH$_2$COOEt]$^+$ was also present. Other signals were observed at *m*/*z* 626 [Pt(Me)(dppe) + H$_2$O]$^+$, 649 [Pt(Me)(dppe) + CH$_3$CN]$^+$ and 911 [M − CH$_3$CH$_2$OH]$^+$.

An ms/ms experiment performed on the [M]$^+$ ions yielded the same isotopic clusters as those present in the main spectrum. These features are particularly interesting, since ESI is a 'soft' ionization method that usually allows observation of the molecular ions with little or no fragmentation. The fact that the most intense signal in the spectrum corresponded to a fragment resulting from the loss of the σ-bonded ylide could be an indication that this ligand is weakly bonded and that M$^+$ is relatively unstable.

All these data confirmed the chemical structure of **2** and excluded any isomeric constitution, for example, the coordination of the ylide to Pt through oxygen.

However we were unable to obtain crystals of **2** prepared in this manner for a further confirmation through an X-ray analysis. This circumstance, together with the apparent impossibility of obtaining **2** through direct treatment of **1a** with ethanol and the ESI MS results appeared to be ascribable to the molecular and crystal structure itself of the complex **2**.

Our belief was supported by the results of the X-ray analysis of the crystals of **2** accidentally formed during

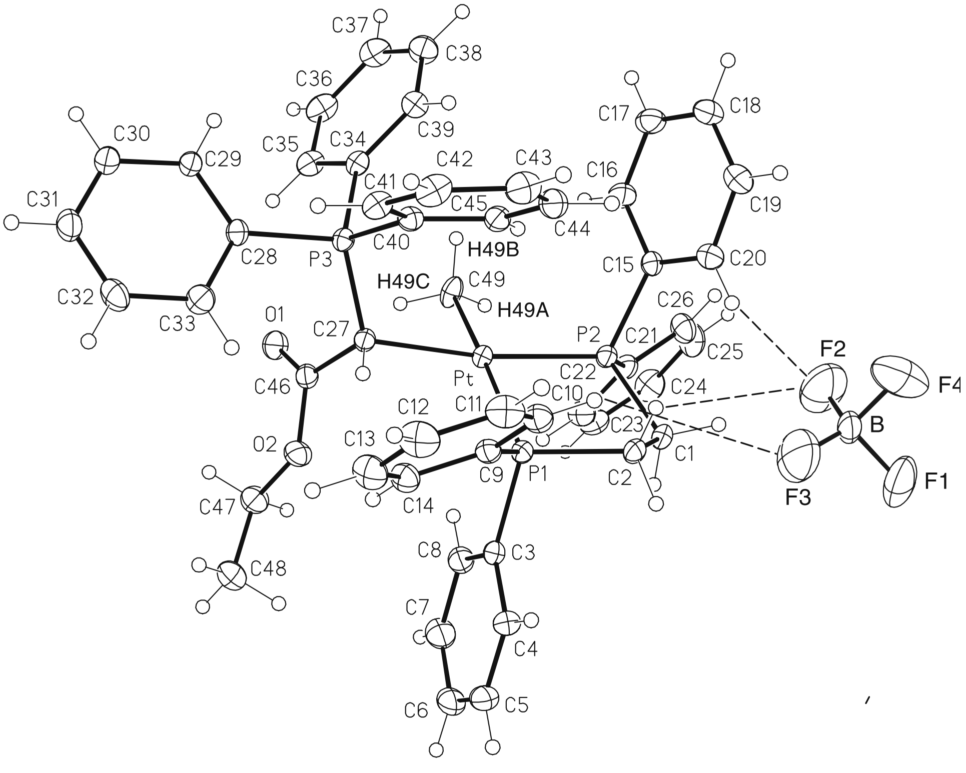


Fig. 2. ORTEP view of **2** (thermal ellipsoids at 50% probability level). Selected geometrical parameters are: bond distances (Å): Pt–C(27) 2.162(7), Pt–C(49) 2.103(7), Pt–P(1) 2.307(2), Pt–P(2) 2.226(2); bond angles (°): C(27)–Pt–C(49) 91.3(3), C(27)–Pt–P(1) 93.8(2), P(1)–Pt–P(2) 86.1(1), P(2)–Pt–C(49) 90.5(2); torsion angles (°): C(33)–C(28)–P(3)–C(27) 35.0(7), C(35)–C(34)–P(3)–C(27) 66.0(7), C(45)–C(40)–P(3)–C(27) 64.3(7), C(27)–C(46)–O(2)–C(47) − 170.6(7), C(46)–O(2)–C(47)–C(48) − 163.1(7), P(2)–C(1)–C(2)–P(1) 46.3(6); non-bonded distances (Å) between atoms of the phenyl rings C(40) → C(45) and C(9) → C(14): C(10)···C(45) 3.65(1), C(10)···C(44) 3.42(1), C(12)···C(42) 3.81(2), C(11)···C(42) 3.52(1), C(11)···C(43) 3.462(1), C(12)···C(42) 3.81(2).

Table 1
Some relevant short intramolecular contact distances and angles present in **1**

X···H–C (X = O, C)	X···C (Å)	X···H (Å)	X···H–C (°)
O(1)···H(35)–C(35)	3.20(1)	2.51(1)	132
O(1)···H(49C)–C(49)	3.28(1)	2.65(1)	141
C(16)···H(45)–C(45)	3.98(1)	3.12(1)	155
C(15)···H(45)–C(45)	3.84(1)	3.00(1)	150
C(16)···H(49B)–C(49)	3.50(1)	3.04(1)	111
C(19)···H(44)–C(44)	3.88(2)	3.09(1)	144
C(21)···H(49A)–C(49)	3.44(1)	2.74(1)	132
C(22)···H(49A)–C(49)	3.52(1)	2.73(1)	140
C(34)···H(49B)–C(49)	3.27(1)	2.66(1)	121
C(35)···H(49B)–C(49)	3.39(1)	2.88(1)	114
C(35)···H(49C)–C(49)	3.39(1)	3.04(1)	103
C(36)···H(49B)–C(49)	3.96(1)	3.31(1)	127
C(1)···H(49B)–C(49)	3.79(1)	2.96(1)	146

Table 2
A few crucial contact distances (Å) involving the C(49)'s methyl protons in the assumed conformation (a) and in the alternative limit orientation as obtained by a rotation of 60° (b)

Atom···atom	a	b
H(49A)···C(16)	3.46	2.76
H(49B)···C(34)	2.67	2.46
H(49B)···C(35)	2.88	2.43
H(49B)···C(36)	3.31	3.10
H(49A)···H(16)	2.72	1.98
H(49B)···C(39)	2.96	3.16
O(1)···H(49C)	2.48	3.19

-mthe synthesis of **1a** (vide supra) that are reported and discussed here [8].

The molecular structure of [Pt(Me)(dppe){η^1-CH(PPh_3)(COOEt)}]BF_4 is shown in Fig. 2, with atom labeling. Some geometrical parameters are also reported.

The main features of this molecule are normal: the coordination about Pt is square planar without any appreciable deviation from a regular geometry; the PPh_3 group shows the usual propeller conformation [9]; the ester group assumes the most stable full extended conformation; the phenyl groups C(40) → C(45) and C(9) → C(14) face each other at graphite distances controlled by attractive dispersion forces. However the most important feature of the structure is the presence of a number of intramolecular contact distances which could give rise either to weak bonding interactions or to repulsive van der Waals interactions.

Most of these distances are reported in Table 1, and will be discussed separately.

The distances O(1)···H(35) 2.51(1) Å, O(1)···H(49C) 2.48(1) Å, or O(1)···C(35) 3.20(1) Å, O(1)···C(49) 3.28(1) Å, fall unequivocally in the range of the now generally accepted classical hydrogen bonding of the type C–H···X (X acceptor = O, N) [10], even though only the angle O(1)···H(49*C*)–C(49) 141(1)° fits for this assumption [11]. Thus we can attribute to these distances a significant role in the stabilization of the molecular conformation of the cation.

The distances between the hydrogen atoms of the platinum bonded methyl group and atoms of the phenyl rings deserve special comments, in particular H(49B)···C(35) 2.89(1) Å, H(49B)···C(34) 2.67(1) Å, H(49B)···C(39) 2.96(1) Å, H(49A)···C(21) 2.74(1) Å, H(49A)···C(22) 2.73(1) Å and H(49B)···C(21) 3.06(1) Å. The methyl protons have been localized at idealized positions assuming C–H distances of 0.96 Å, sp^3 geometry and the orientation of the methyl group as suggested by electron density residuals in the difference Fourier syntheses. The intramolecular non-bonded distances arising from different orientations of the methyl protons would be expected to be almost unchanged or much shorter, as has been tested by suitable calculations (see for example Table 2). Thus we ascribe to the assumed hydrogen coordinates a high degree of confidence.

A few of these non-bonded distances could be considered as possible π-hydrogen bonding of the type C–H···C(π) [12]. Actually C–H units in analogous situations have been proved to operate as hydrogen-bond donors [13]. The most severe criticism of this bonding interaction concerns the geometrical features present in these structures. This kind of bonding is directional in nature and aims for linearity, and the involved hydrogen atoms should be nearly equidistant from all the atoms belonging to the π-system, in the present case the phenyl groups [12]. In this structure the first require-

Table 3
Possible CH···F hydrogen bonds

CH in *xyz*	C···F (Å)	H···F (Å)	C–H···F (°)	Equivalent position of F
C(2)H(2A)	C(2)···F(2) 3.31(2)	H(2A)···F(2) 2.59(1)	C(2)H(2A)···F(2) 131(1)	*x*, *y*, *z*
C(10)H(10)	C(10)···F(3) 3.50(2)	H(10)···F(3) 2.72(1)	C(10)H(10)···F(3) 143 (1)	*x*, *y*, *z*
C(20)H(20)	C(20)···F(2) 3.72(2)	H(20)···F(2) 2.57(1)	C(20)H(20)···F(2) 152 (1)	*x*, *y*, *z*
C(18)H(18)	C(18)···F(1) 3.35(2)	H(18)···F(1) 2.48(1)	C(18)H(18)···F(1) 156(1)	$-0.5-x$, $-0.5+y$, $-0.5-z$
C(23)H(23)	C(23)···F(3) 3.52	H(23)···F(3) 2.62(1)	C(23)H(23)···F(3) 159(1)	$0.5-x$, $-0.5+y$, $-0.5-z$
C(37)H(37)	C(37)···F(1) 3.40(1)	H(37)···F(1) 2.57(1)	C(37)H(37)···F(1) 150(1)	*x*, $1-y$, *z*
C(31)H(31)	C(31)···F(1) 3.64(1)	H(37)···F(1) 2.71(1)	C(37)H(37)···F(1) 173(1)	$0.5+x$, $0.5-y$, $0.5+z$

ment is not always satisfied whilst the second is absolutely absent in spite of the quite short distances observed between methyl protons and some phenyl carbon atoms (Table 3).

Thus, we consider the contact distances reported in Table 2 as repulsive ones [14].

The above-mentioned observations furnish a picture of a quite overcrowded molecule, probably lacking any degree of conformational freedom, which is likely to exhibit the same structure both in the solid state and in solution.

Under the assumption that complex **1a** has almost the same molecular structure as **2**, a noticeable stereochemical hindrance can be imagined for an attack of ethanol at the ketenyl group, which is tightly enclosed and screened in a sort of molecular hollow, thus preventing the direct formation of **2** from **1a**. As noted earlier **2** was formed from **1a** just serendipitously, maybe in the presence of some impurity which acted as a catalyst.

Moreover, a similar problem also seems to be present in the crystallization process of the whole complex. An inspection of the packing features reveals the presence of weak forces involved in the lattice stabilization of this ionic complex. The Coulomb energy which falls off with the ionic separation [15], is here certainly very poor on account of the centre-to-centre distances between anions and cations in the range of 6.3–6.8 Å. In fact, the lattice stabilization seems to be mainly due to the weak hydrogen bonds BF···HC between units at x, y, z; $x, 1-y, z$; $-0.5-x, -0.5+y, -0.5-z$; $0.5-x, -0.5+y, -0.5-z$ (see Table 3) which are characterized by reliable H···F distances of ca. 2.4–2.7 Å and C–H···F angles of ca. 130–160°, producing a self-assembled three-dimensional molecular network [16].

3. Conclusions

In this work we have reported the synthesis and characterization of $[Pt(Me)(dppe)\{\eta^1\text{-}CH(PPh_3)(COOEt)\}]BF_4$. Spectroscopic data are in agreement with a square planar coordination around Pt atom and the ESI mass spectrum of this complex suggests a relative instability of the cation $[Pt(Me)(dppe)\{\eta^1\text{-}CH(PPh_3)(COOEt)\}]^+$. The X-ray structural analysis of serendipitously obtained crystals of **2** indicates the presence of several molecular constraints due mainly to van der Waals repulsive interactions which are only weakly counterbalanced by intramolecular hydrogen bonds and London dispersion forces. No stabilizing π-hydrogen bonds can be surmised as the complex lacks the usual geometrical requirements. The overcrowding of the cationic moiety accounts for the relatively weak bonding of the ylide fragment to Pt.

4. Experimental

All reactions and manipulations were carried out under an atmosphere of dry Ar using standard Schlenk techniques. Solvents were dried by conventional methods and distilled under Ar before use. [Pt(Me)Cl(dppe)] [17] and $Ph_3PCHCOOEt$ [18] were synthesized according to literature methods. IR spectra were recorded on a Perkin–Elmer 983 spectrophotometer. ^{1}H-, ^{13}C- and ^{31}P-NMR spectra were recorded at 298 K on a Bruker AC 200 spectrometer. Chemical shifts are reported in ppm (δ) relative to Me_4Si (^{1}H and ^{13}C) and external 85% H_3PO_4 (^{31}P). Electrospray Ionization (ESI) mass spectra of **2** were recorded on a LCQ (Finnigan MAT) instrument. Elemental analyses were provided by the Microanalysis Laboratory of the Chimica Inorganica, Metallorganica e Analitica (CIMA) department, University of Padua.

4.1. Synthesis of compound 2

A 0.65 M acetone solution of $AgBF_4$ (0.55 ml, 0.36 mmol) was added dropwise to a stirred solution of [Pt(Me)Cl(dppe)] (0.212 g, 0.33 mmol) in CH_2Cl_2 (30 ml). After 1 h the reaction mixture was filtered to remove solid AgCl and the obtained solution was treated with $Ph_3PCHCOOEt$ (0.115 g, 0.33 mmol) in CH_2Cl_2 (10 ml). After 2 h the solution was concentrated to a small volume (5 ml) and on addition of Et_2O a white solid precipitated. This solid was filtered off, washed with Et_2O and dried under vacuum. Yield: 0.282 g (82%).

2: m.p. 187–189°C (dec.). Anal. Found: C, 55.79, H, 4.56. Calc. for $C_{49}H_{48}O_2BF_4P_3Pt$: C, 56.39; H, 4.64%. IR (Nujol, cm^{-1}) 1695. ^{1}H-NMR ($CDCl_3$, 200 MHz, TMS): $\delta = 7.90$–7.05 (m, 35H, Ph), 4.61 (ddd, $^2J_{P(y)H} = 10.14$, $^3J_{PH} = 8.30$, $^3J_{PH} = 7.77$, $^2J_{PtH} = 90.8$ Hz, 1H, CH), 4.13 (m, $^2J_{HH} = 10.78$, $^3J_{HH} = 7.10$, 1H, O–CH_AH$_B$), 3.94 (m, $^2J_{HH} = 10.78$, $^3J_{HH} = 7.10$, 1H, O–CH$_A$$H_B$), 3.2–2.4, 1.8–1.4 (m, 4H, CH_2CH_2), 1.06 (t, $^3J_{HH} = 7.10$ Hz, 3H, CH_3), 0.18 (dd, $^3J_{PH} = 6.98$, $^3J_{PH} = 5.03$, $^2J_{PtH} = 62.1$ Hz, 3H, Pt–CH_3). ^{31}P{^{1}H}-NMR ($CDCl_3$, 80 MHz, 85% H_3PO_4): $\delta = 49.24$ (d, $^2J_{PP} = 8.18$, $^1J_{PtP} = 1705$ Hz), 42.22 (d, $^2J_{PP} = 7.77$, $^1J_{PtP} = 3097$ Hz), 27.44 (dd, $^2J_{PP} = 8.18$, $^2J_{PP} = 7.77$, $^2J_{PtP} = 71.5$ Hz). ^{13}C{^{1}H}-NMR ($CDCl_3$, 50 MHz, TMS): $\delta = 172.57$ (d, $^2J_{PC} = 4.97$, $^2J_{PtC} = 42.7$ Hz, CO), 135.7–121.6 (m, Ph), 61.07 (s, O–CH_2), 28.23 (dd, $^1J_{PC} = 33.13$, $^2J_{PC} = 7.80$ Hz, CH$_2$CH$_2$), 20.60 (dd, $^1J_{PC} = 73.29$, $^2J_{PC} = 49.92$ Hz, CH$_2$$CH_2$), 27.60 (dd, $^1J_{PC} = 38.06$, $^2J_{PC} = 15{,}77$ Hz, CH), 15.04 (s, CH_3), 1.62 (d, $^2J_{PC} = 82.71$, $^1J_{PtC} = 534.7$ Hz, Pt–CH_3). ESI MS (CH_3CN): 957 $[Pt(Me)(dppe)(Ph_3PCHCOOEt)]^+$, $[M]^+$, 911 $[M-CH_3CH_2OH]^+$, 649 $[Pt(Me)(dppe)+CH_3CN]^+$, 626 $[Pt(Me)(dppe)+H_2O]^+$, 608 $[Pt(Me)(dppe)]^+$, 349 $[Ph_3PCH_2COOEt]^+$.

4.2. Crystal structure determination

Crystal data for $C_{49}H_{48}O_2BF_4P_3Pt$, **2**: MW = 1043.68 monoclinic, space group $P2_1/n$, $a = 14.525(3)$, $b = 14.931(3)$, $c = 21.921(4)$ Å, $\beta = 103.47(3)°$; $V = 4623(2)$ Å^3; $Z = 4$, $D_{calc} = 1.50$ g cm^{-3}; $F(000) = 2088$; $\lambda(\text{Mo–K}_\alpha) = 0.71073$ Å; $\mu = 31.93$ cm^{-1}, $T = 293(2)$ K. A prismatic colorless crystal of dimensions 0.24 × 0.30 × 0.32 mm was centered on a four-circle Philips PW1100 (Febo System) [19] diffractometer operating in θ–2θ scan mode with graphite-monochromated Mo–K$_\alpha$, following standard procedures. There were no significant fluctuations of intensities other than those expected from Poisson statistics. The intensity data were corrected for Lorentz–polarization effects and for absorption, as described by North et al. [20].

The structure was solved by heavy atoms methods [21]. Refinement was carried out by full-matrix least-squares; the function minimized was $\Sigma w(F_o^2 - F_c^2)^2$, with weighting scheme $w = 1/[s^2(F_o^2) + 23.17P]$, where $P = \max(F_o^2 + 2F_c^2)/3$. All non-hydrogen atoms were refined with anisotropic thermal parameters. The H-atoms were placed in calculated positions with fixed, isotropic thermal parameters ($1.2U_{eq}$ of the parent carbon atom). For a total of 543 parameters, $wR' = [\Sigma w(F_o^2 - F_c^2)^2 \Sigma w(F_o^2)^2]^{1/2} = 0.121$, $S = 1.34$, and conventional $R = 0.057$, based on the F values of 9853 reflections having $F_o^2 = 2\sigma(F_o^2)$.

Structure refinement and final geometrical calculations were carried out with SHELXL-97 [22] and PARST [23] programs, drawings were produced using ORTEP II [24].

5. Supplementary material

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC no. 15688 for compound **2**. Copies of this information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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