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Oxidative degradation of the ascorbate anion in the presence of platinum and palladium. Formation and structures of platinum and palladium oxalate complexes

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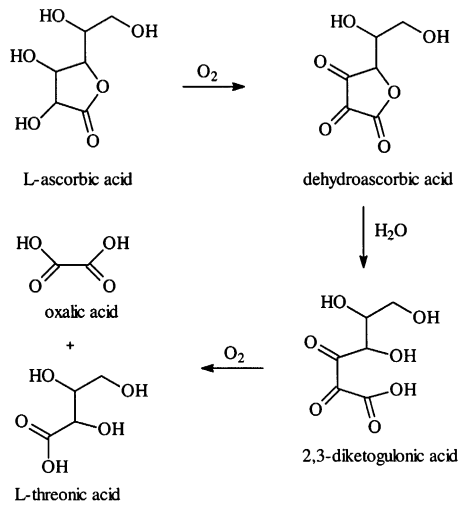
Abstract

The reactions of $[Pt(NO_3)_2(dppm)]$ (dppm = bis(diphenylphosphino)methane) and *cis*-$[Pt(NO_3)_2(PEt_3)_2]$ with sodium ascorbate are described. Complexes containing *O*,*O*-coordinated ascorbate ligands are formed initially, but on standing further oxidation and cleavage of the ligand occur to produce the corresponding oxalate complexes. The reactions were monitored by NMR spectroscopy, and reactions of $[Pt(NO_3)_2(dppm)]$ with oxalic acid or calcium threonate also produced $[Pt(C_2O_4)(dppm)]$. Reactions of $[PtMe(Me_2CO)(dppe)]^+$ or $[PdMe(Me_2CO)(P\frown P)]^+$ ($P\frown P$ = dppe, dppp) with sodium ascorbate result in cleavage of the M–C bond and oxidation of ascorbate to again produce metal oxalate derivatives. The solid state structures of $[Pt(C_2O_4)(dppm)]\cdot Me_2CO$, $[Pd(C_2O_4)(dppe)]\cdot H_2O$ and $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2\cdot 2Me_2CO$, determined by X-ray crystallography, are described.

Keywords: Oxidative degradation; Platinum; Palladium; Oxalates

1. Introduction

The oxidation of vitamin C (L-ascorbic acid) to oxalic acid in aqueous solution is known to be catalyzed by metal ions [1]. This process is believed to involve oxidation of ascorbic acid to dehydroascorbic acid, followed by hydrolysis that leads to opening of the lactone ring to produce 2,3-diketogulonic acid. Cleavage and further oxidation produce oxalic acid and L-threonic acid (Scheme 1) [1,2]. Martell and Khan performed pioneering work on the catalytic effects of iron(III) and copper(II), and their chelate complexes, on the oxidation of ascorbic acid [3,4]. The rate-determining step in their proposed mechanism involves electron transfer from the ascorbate monoanion ($HAsc^-$) to the metal ion. The authors stated that unless the metal ion has a stable lower valence form, it will not participate in the electron transfer scheme and will thus not function as a catalyst [3]. Since then, other studies



Scheme 1. Oxidation and hydrolysis of L-ascorbic acid.

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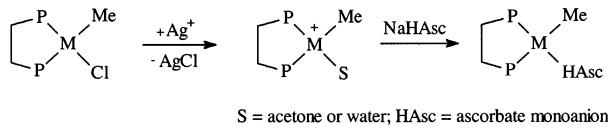
have shown that the reaction of ascorbic acid with dioxygen in aqueous pyridine is catalyzed by cobalt(II), nickel(II), manganese(II) and zinc(II) [4–6]. In all these cases the role of the metal ion in the process is not a redox function, but it serves to increase the rate of radical formation. The proposed mechanism involves the formation of monomeric metal–dioxygen complexes. The dimeric μ-peroxo ruthenium ascorbate complex $[Ru_2Cl_2(HAsc)_2(OH_2)_2(\mu\text{-}O_2)]$ was proposed as an intermediate in the catalytic oxidation of ascorbic acid by ruthenium(III) [7]. All these studies have focused on the kinetic aspects of the oxidation of ascorbic acid to dehydroascorbic acid, but not on the fate of the latter. There are few data in the literature on the further degradation of ascorbic acid to oxalic acid in the presence of metal ions.

Recently, studies of reactions between L-ascorbic acid and cobalt(II) and gadolinium(III) in aqueous solution have shown that the metal ascorbate complexes that are formed initially slowly decompose to generate oxalate complexes, which precipitate from solution [8]. We have recently reported the synthesis and characterization of a series of diamine- and diphosphine-platinum ascorbate complexes [9]. In the diphosphine case, species of the type $[Pt(Asc\text{-}O^2,O^3)(P\frown P)]\cdot H_2O$ ($P\frown P$ = dppm, dppe, dppp) were formed, whereas a number of complexes were identified for the diamine derivatives. These included $[Pt(Asc\text{-}O^2,O^3)(N\frown N)]$, monodentate ascorbate species of the form $[Pt(Asc\text{-}O^2)_2(N\frown N)]$, and the thermodynamically stable $[Pt(Asc\text{-}C^2,O^3)(N\frown N)]$ [9]. Whereas the dppe and dppp ascorbate derivatives proved to be stable towards further reaction, the dppm complex slowly underwent oxidative degradation to the corresponding oxalate complex. This paper describes our attempts to determine the nature of this process. Oxalate complexes of the type $[M(C_2O_4)L_2]$ (M = Pd, Pt; L = tertiary phosphine or L_2 = diphosphine) are well known, and have been prepared previously from reaction of the corresponding carbonates with oxalic acid [10–12], or by treatment of $[MCl_2L_2]$ with $Ag_2C_2O_4$ [13,14].

We have also attempted to synthesize and isolate monodentate ascorbate complexes. In addition to their implication in the reactions of the diamineplatinum species mentioned above [9], monodentate ascorbate species have been implicated as intermediates in the reduction of diamineplatinum(IV) complexes used in chemotherapy [15]. We reasoned that an appropriate approach to the synthesis of monodentate ascorbate complexes would be to block three of the four coordination sites of the square planar palladium(II) or platinum(II) center to prevent the formation of ascorbate chelates. (Platinum(IV) species used in chemotherapy are generally believed to be reduced to the divalent form prior to binding to DNA.) We chose to use the platinum and palladium diphosphine complexes



S = acetone or water; HAsc = ascorbate monoanion

Scheme 2. Outline for the synthesis of monodentate ascorbate complexes.

$[MClMeL_2]$ (M = Pt or Pd, L_2 = dppe or dppp) as precursors, these having the advantage of possessing strong M–P and M–C bonds, as well as being easily prepared. Our aim was to prepare monodentate ascorbate complexes of the type $[MMe(HAsc)L_2]$ (M = Pt or Pd; L_2 = dppe or dppp) from the precursor complexes $[MClMeL_2]$ as outlined in Scheme 2. Treatment of these complexes with 1 equiv. of $AgBF_4$ in acetone solution would produce cationic species with a weakly coordinated solvent molecule, which could be easily replaced by ascorbate on treatment of the cationic intermediate with sodium ascorbate.

2. Results and discussion

2.1. Reactions of *cis*-$[Pt(NO_3)_2(PEt_3)_2]$ and $[Pt(NO_3)_2(dppm)]$ with sodium ascorbate

We have previously reported the preparation and characterization of platinum(II) ascorbate complexes containing diamine or diphosphine ligands [9]. The ascorbate groups in the diamine complexes were initially coordinated through O^2 and O^3, but the complexes isomerized slowly to the more thermodynamically stable C,O-chelates. In contrast, the diphosphine compounds were isolated as the O,O-bound chelates, $[Pt(Asc\text{-}O^2,O^3)(P\frown P)]\cdot H_2O$ ($P\frown P$ = dppe, dppp), but attempts to crystallize these from a variety of solvents were unsuccessful. Crystallization from solvents such as $CHCl_3$ or CH_2Cl_2 resulted in cleavage of the ascorbate moiety and production of the dichloroplatinum(II) complexes $[PtCl_2(P\frown P)]$. Crystallization from other solvents was also complicated by the susceptibility of the complexes to oxidation [9]. We have also found that reaction of the monodentate phosphine complex *cis*-$[Pt(NO_3)_2(PEt_3)_2]$ with sodium ascorbate results in formation of the ascorbate chelate $[Pt(Asc\text{-}O^2,O^3)(PEt_3)_2]$, as determined by $^{31}P\{^1H\}$ NMR analysis of the reaction mixture ($\delta(P)$ 5.6 d, $^2J_{PP}$ = 22 Hz, $^1J_{Pt-P}$ = 3300 Hz; 6.2 d, $^2J_{PP}$ = 22 Hz, $^1J_{Pt-P}$ = 3472 Hz). Elemental analysis of the product obtained from this reaction, however, indicated that partial oxidation to the corresponding oxalate complex, $[Pt(C_2O_4)(PEt_3)_2]$, had occurred (the analytical data were consistent with a 1:2 mixture of the ascorbate and oxalate complexes).

The reaction between [Pt(NO_3)$_2$(dppm)] and sodium ascorbate in the presence of air also produced the oxalate complex [Pt(C_2O_4)(dppm)]. This reaction was monitored by NMR spectroscopy over a period of 48 h. The $^{31}P\{^1H\}$ NMR spectrum of the reaction mixture of [Pt(NO_3)$_2$(dppm)] and sodium ascorbate in wet acetone immediately after mixing revealed the presence of two species (Fig. 1). Two overlapping signals were observed at -61.7 ppm ($^1J_{Pt-P} = 2962$ and 3009 Hz) due to [Pt(Asc-O^2,O^3)(dppm)], while a single peak at -66.0 ppm ($^1J_{Pt-P} = 3401$ Hz) was due to unreacted [Pt(NO_3)$_2$(dppm)]. As the reaction proceeded, the peak at -66.0 ppm disappeared and resonances due to two new species were observed. The pair of doublets centered at -58.0 ppm ($^2J_{PP} = 81$ Hz) was due to an unsymmetrical species with a chelating dppm ligand, and the singlet at -63.5 ppm ($^1J_{PtP} = 3085$ Hz) was due to [Pt(C_2O_4)(dppm)]. After 27 h the peak due to the ascorbate complex had diminished, whereas the signal due to the oxalate complex had increased in intensity. After 48 h the ascorbate complex had been converted completely to the oxalate complex, and the peaks due to the unsymmetrical intermediate had disappeared. Crystals of [Pt(C_2O_4)(dppm)]·Me_2CO separated from the reaction mixture upon standing.

We have also carried out reactions of [Pt(NO_3)$_2$-(dppm)] with calcium threonate and with oxalic acid, and [Pt(C_2O_4)(dppm)] was formed in each case. When [Pt(NO_3)$_2$(dppm)] was treated with 1 equiv. of calcium threonate, complete conversion to the oxalate complex was apparent after 21 h. The reaction between [Pt(NO_3)$_2$(dppm)] and oxalic acid in a water–acetone mixture was 50% complete after 5 h, and [Pt(C_2O_4)-(dppm)] was again formed quantitatively after 21 h. If threonate and/or oxalate ions were produced by cleavage of dehydroascorbic acid during the course of the reaction of [Pt(NO_3)$_2$(dppm)] with ascorbate ion, they could certainly account for the formation of [Pt(C_2O_4)(dppm)]. Oxidation of dehydroascorbic acid itself was slow, however, compared with the reactions of the platinum complexes. When a solution of dehydroascorbic acid in wet acetone was allowed to stand at ambient temperature, virtually no reaction occurred over a period of 7 days. Thus, uncatalyzed degradation of dehydroascorbic acid is too slow to account for the formation of [Pt(C_2O_4)(dppm)], and some continued interaction of the ligand with platinum appears likely to account for the oxidation of ascorbate.

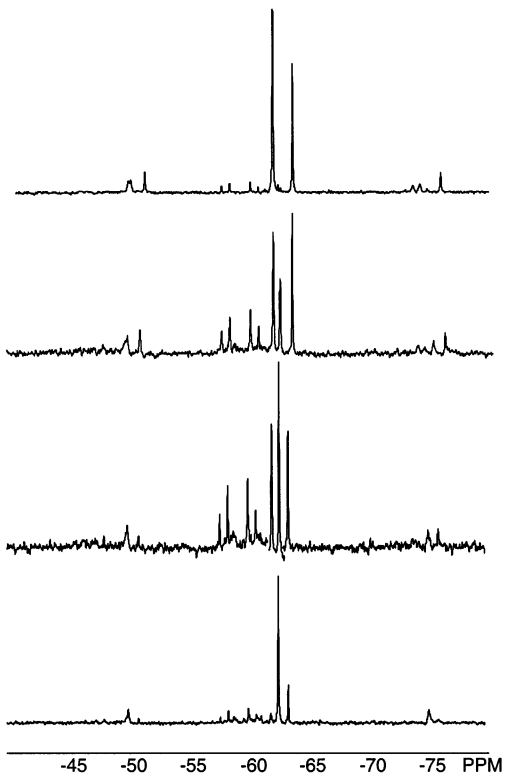


Fig. 1. $^{31}P\{^1H\}$ NMR spectra of reaction mixtures of [Pt(NO_3)$_2$(dppm)] and sodium ascorbate in acetone-d_6 solution after 2 h (top), 21 h, 27 h and 48 h.

2.2. Reactions of methylplatinum and methylpalladium complexes with sodium ascorbate

The nitrate complex [Pt(NO_3)Me(dppe)] ($\delta(P)$ 35.4, $^1J_{PtP} = 4538$ Hz; $\delta(P)$ 50.6, $^1J_{PtP} = 1792$ Hz) was prepared by treatment of [PtClMe(dppe)] with 1 equiv. of $AgNO_3$ in CH_2Cl_2–MeOH solution, followed by filtration and evaporation of the solvents. In acetone-d_6 solution, the nitrate was displaced by solvent, resulting in a modest change in the ^{31}P NMR parameters ($\delta(P)$ 34.6, $^1J_{PtP} = 3914$ Hz; $\delta(P)$ 50.5, $^1J_{PtP} = 1724$ Hz). The reaction between [Pt(NO_3)Me(dppe)] and sodium ascorbate produced a mixture of products. The major species was believed to be the monodentate ascorbate complex [Pt(HAsc-O^3)Me(dppe)] ($\delta(P)$ 36.4, $^1J_{PtP} = 4436$ Hz; $\delta(P)$ 50.8, $^1J_{PtP} = 1844$ Hz), whereas the minor product exhibited two signals at 30.9 and 32.9 ppm which were assigned to the chelate complex [Pt(Asc-O^2,O^3)(dppe)] [9]. The reaction was slow and oxidative degradation of the complexes occurred on standing in solution, so it was not possible to separate the products.

In order to increase the reaction rates, we turned our attention to the corresponding palladium complexes. Treatment of [PdClMe(dppe)] with 1 equiv. of $AgBF_4$ in acetone solution produced the cationic complex [PdMe(Me_2CO)(dppe)]$^+$. After filtration, the $^{31}P\{^1H\}$ NMR spectrum of the filtrate consisted of a doublet at 62.6 ppm ($^2J_{PP} = 25$ Hz) due to the P atom *trans* to Me, and a broad doublet at 38.6 ppm ($^2J_{PP} = 25$ Hz) due to the P atom *trans* to acetone. The broadness of the latter signal is likely to be due to rapid, reversible dissociation of solvent molecules in solution. This assignment is consistent with that for the analogous platinum complex described above, where the signal due to the P

atom *trans* to Me was observed at higher frequency than that *trans* to acetone.

An acetone solution of $[PdMe(Me_2CO)(dppe)]BF_4$ was treated with a solution of sodium ascorbate in D_2O, and the reaction was monitored by $^{31}P\{^1H\}$ NMR spectroscopy. During the course of the reaction several unidentified intermediates were formed, but after 60 h the oxalate complex $[Pd(C_2O_4)(dppe)]$ was produced almost quantitatively. The first new species to be formed may have been the monodentate ascorbate complex, [Pd(HAsc-O^3)Me(dppe)], but we were unable to isolate this or any of the other intermediates. Instead, crystals of the oxalate complex $[Pd(C_2O_4)(dppe)]\cdot H_2O$ separated from an aliquot of the reaction mixture when it was allowed to stand in an NMR tube. The solid state structure of the oxalate complex was determined by X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum of this complex recorded in $CDCl_3$ solution contained a single peak at 58.0 ppm. Another aliquot of the reaction mixture produced crystals of a dinuclear oxalate-bridged complex $[Pd_2(\mu\text{-}C_2O_4)(dppe)_2][BF_4]_2$, whose $^{31}P\{^1H\}$ NMR spectrum in $CDCl_3$ solution consisted of a singlet at 70.3 ppm.

In a manner similar to that for the dppe case, [PdClMe(dppp)] was converted to $[PdMe(Me_2CO)(dppp)]BF_4$ by treatment with $AgBF_4$ in acetone solution. After removal of the precipitate of AgCl, the pale yellow filtrate was treated with a solution of sodium ascorbate in D_2O, and a green solution was obtained. Again, several unidentified complexes were detected by $^{31}P\{^1H\}$ NMR spectroscopy, in addition to the signals due to the starting material. Crystals of the oxalate-bridged dimer $[Pd_2(\mu\text{-}C_2O_4)_2(dppp)_2][BF_4]_2$ separated from an aliquot of the reaction mixture in an NMR tube. The structure of the dimer was determined by X-ray crystallography. The $^{31}P\{^1H\}$ NMR spectrum of $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2$ in $CDCl_3$ solution showed a singlet at 19.8 ppm. Evaporation of the reaction mixture after 48 h produced a yellow solid, which was identified by elemental analysis as $[Pd(C_2O_4)(dppp)]\cdot 2H_2O$. The $^{31}P\{^1H\}$ NMR spectrum of this complex dissolved in $CDCl_3$ solution consisted of a singlet at 15.7 ppm.

The methyl group present originally in $[PdClMe(P^{\frown}P)]$ ($P^{\frown}P$ = dppe or dppp) was lost during the course of the reaction with $AgBF_4$ and NaHAsc. Some HBF_4 may be formed (since a small amount of water would be present in the acetone, then D_2O was added deliberately), which could cleave the Pd–C bond to produce $[Pd(OH_2)_2(P^{\frown}P)]^{2+}$. Oxidative degradation of ascorbate to oxalate is likely to occur in the coordination sphere of palladium by a mechanism similar to that operating in the platinum case described earlier. Then, depending on the palladium/oxalate ratio, either the monomeric oxalate complex or the oxalate-bridged dimer would be formed. With a deficiency of oxalate, the dimeric derivative would be favored, whereas with excess oxalate $[Pd(C_2O_4)(P^{\frown}P)]$ would be the major product. Indeed, treatment of the dinuclear oxalate complexes $[Pd_2(\mu\text{-}C_2O_4)(P^{\frown}P)_2][BF_4]_2$ with excess $K_2C_2O_4$ resulted in bridge cleavage and formation of the mononuclear complexes.

2.3. Crystal structure of $[Pt(C_2O_4)(dppm)]\cdot Me_2CO$

Crystals of $[Pt(C_2O_4)(dppm)]\cdot Me_2CO$ were isolated by slow evaporation of the mixture obtained from the reaction of $[Pt(NO_3)_2(dppm)]$ with sodium ascorbate in acetone solution. The molecular structure of the complex is shown in Fig. 2. Selected bond distances and angles are listed in Table 1. The coordination geometry around platinum is planar, the sum of the angles about the metal being 360.05°, but the presence of two strained rings results in two smaller and two larger angles. The O1–Pt–O2 angle of 81.42(10)° is similar to the corresponding angle of 81.4(3)° in $[Pt(C_2O_4)(PMe_3)_2]$ [16]. The small P1–Pt–P2 angle of

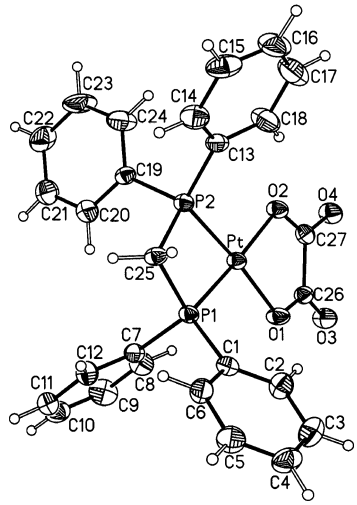


Fig. 2. The molecular structure of $[Pt(C_2O_4)(dppm)]$. The acetone molecule has been omitted for clarity.

Table 1
Selected bond distances (Å) and angles (°) for $[Pt(C_2O_4)(dppm)]\cdot Me_2CO$

Bond distances		*Bond angles*	
Pt–O1	2.073(3)	O1–Pt–O2	81.42(10)
Pt–O2	2.075(3)	O1–Pt–P1	102.30(8)
Pt–P1	2.2170(9)	O2–Pt–P2	102.84(8)
Pt–P2	2.2232(10)	P1–Pt–P2	73.49(4)
O2–C27	1.295(5)	P1–C25–P2	91.81(16)
O1–C26	1.302(5)	O3–C26–O1	124.8(3)
O3–C26	1.215(5)	O4–C27–O2	124.3(4)
O4–C27	1.219(5)	O1–C26–C2	115.5(3)
C26–C27	1.571(5)	O2–C27–C1	116.3(3)
		O3–C26–C2	119.7(3)
		O4–C27–C1	119.4(3)

73.49(4)° in the present case is due to the strained four-membered chelate ring. The larger P1–Pt–O1 and P2–Pt–O2 angles of 102.30(8) and 102.84(8)° compensate for these angles being reduced from 90°. The P–Pt–O angles are substantially larger than the mean P–Pt–O angles of 90.7° in $[Pt(C_2O_4)(PMe_3)_2]$ [16] and 95.8° in $[Pt(C_2O_4)(dcpe)]\cdot MeCN$ [17]. The mean Pt–O distance of 2.074 Å is similar to those in $[Pt(C_2O_4)(PMe_3)_2]$ (2.065 Å) and $[Pt(C_2O_4)(dcpe)]\cdot MeCN$ (2.063 Å). As expected, the coordinated C–O distances of 1.295(5) and 1.302(5) Å are longer than the uncoordinated C–O distances of 1.219(5) and 1.215(5) Å, where the latter are formally double bonds. The coordinated C–O distances are similar to the corresponding distances of 1.30(1) Å in $[Pt(C_2O_4)(PMe_3)_2]$ [16] and 1.29(1) Å in $[Pt(C_2O_4)(dcpe)]\cdot MeCN$ [17]. Intermolecular hydrogen bonding occurs between the uncoordinated oxygen atom O3 of the oxalate ligand and two hydrogen atoms on the phenyl groups of another molecule. The O3···H21 distance is 2.554 Å and the O3–H21–C21 angle is 167.8°, while the O3···H4 distance is 2.488 Å and the O3–H4–C4 angle is 160.4°. There is also hydrogen bonding between the oxygen atom of the acetone molecule and one of the methylene hydrogen atoms of a dppm ligand. The O1S···H25 distance is 2.342 Å and the O1S–H25–C25 angle is 131.8°.

2.4. Crystal structure of $[Pd(C_2O_4)(dppe)]\cdot H_2O$

Crystals of $[Pd(C_2O_4)(dppe)]\cdot H_2O$ were obtained by slow evaporation of an acetone solution of the product obtained from the reaction of $[PdMe(Me_2CO)(dppe)]$-BF_4 with sodium ascorbate. The molecular structure of $[Pd(C_2O_4)(dppe)]\cdot H_2O$ is shown in Fig. 3. Selected bond distances and angles are listed in Table 2. The coordination geometry around palladium is perfectly planar as in the platinum case above, the sum of the angles around palladium being 360.01°. Here P(1)–Pd–P(2), O(1)–Pd–O(2), O(1)–Pd–P(2) and O(2)–Pd–P(2) angles are 84.52(5), 81.78(12), 99.26(9) and 94.45(10)°, respectively. The mean Pd–O and Pd–P distances of 2.061(3) and 2.229(13) Å agree well with the corresponding distances in $[Pd(C_2O_4)(PEt_3)_2]$ [18]. The C–O distances in the oxalate ligand are also similar to those in $[Pd(C_2O_4)(PEt_3)_2]$. As above, the coordinated C–O distances of 1.282(5) Å and 1.294(5) Å are longer than the uncoordinated C–O distances of 1.212(5) and 1.214(5) Å. Intermolecular hydrogen bonding occurs in this case between the hydrogens of the water molecule and the uncoordinated oxygen atoms of two different molecules of $[Pd(C_2O_4)(dppe)]$. The O(5S)–H(5A)···O(3) angle is 173.1°, while the H(5A)···O(3) distance is 2.060 Å. The O(5S)–H(5B)···O(3) angle is 159.0° while the H(5B)···O(4′) distance is 2.031Å. The H···O distances of 2.031 and 2.060 Å, as well as the near linear O–H···O angles are indicative of strong hydrogen bonding interactions.

2.5. Crystal structure of $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2\cdot 2Me_2CO$

The molecular structure of the cation in $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2\cdot 2Me_2CO$ is shown in Fig. 4. The molecule is a dinuclear oxalate-bridged complex with a center of inversion located at the midpoint of the C–C bond of the bridging oxalate ligand. The only other structure of a dinuclear oxalate-bridged palladium complex is that of $[(Bu_2S)(Ph)Pd(\mu\text{-}C_2O_4)Pd(Ph)(SBu_2)]$ [19]. The simple binuclear geometry involving symmetric, in-plane bridging with a single oxalate ion binding through two oxygen atoms to each of two metal centers has been observed in the chemistry of nickel(II), iron(II), manganese(II), cobalt(II), zinc(II) and copper(II) [20–28]. Table 3 lists some selected bond distances and angles for one half of the $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2]^{2+}$ cation. The planar oxalate bridge ensures that the two coordination planes around palladium are also co-planar with a Pd–Pd distance of 5.416 Å. This is in contrast to the μ-hydroxo dimer $[Pd_2(\mu\text{-}OH)_2(dppp)_2][BF_4]_2$ where the dihedral angle between the

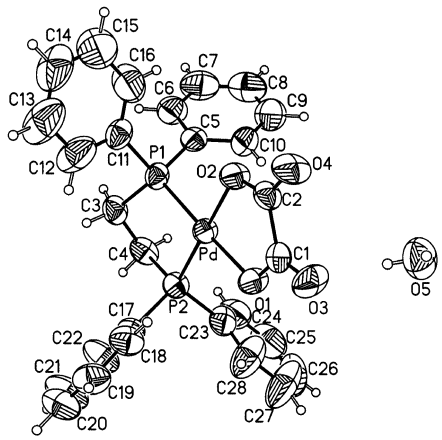


Fig. 3. Molecular structure of $[Pd(C_2O_4)(dppe)]\cdot H_2O$.

Table 2
Selected bond distances (Å) and angles (°) for $[Pd(C_2O_4)(dppe)]\cdot H_2O$

Bond distances		*Bond angles*	
Pd–O(1)	2.068(3)	O(1)–Pd–O(2)	81.78(12)
Pd–O(2)	2.053(3)	O(1)–Pd–P(2)	99.26(9)
Pd–P(1)	2.2217(13)	O(2)–Pd–P(2)	94.45(10)
Pd–P(2)	2.2357(13)	P(1)–Pd–P(2)	84.52(5)
O(2)–C(2)	1.282(5)	O(3)–C–O(1)	123.8(5)
O(1)–C(1)	1.294(5)	O(4)–C–O(2)	124.8(5)
O(3)–C(1)	1.212(5)	O(1)–C(1)–C(2)	116.1(4)
O(4)–C(2)	1.214(5)	O(2)–C(2)–C(1)	116.3(4)
C(1)–C(2)	1.561(7)	O(3)–C(1)–C(2)	120.1(4)
		O(4)–C(2)–C(1)	118.9(5)

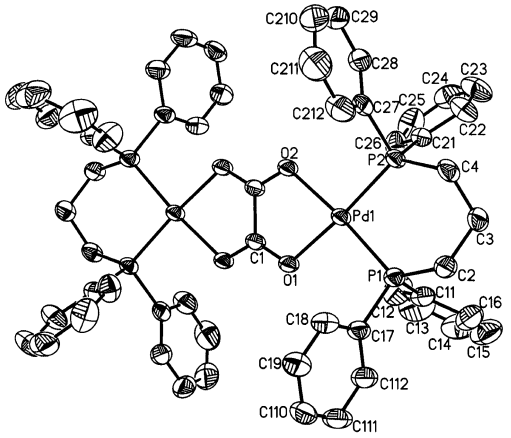


Fig. 4. Molecular structure of the $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2]^{2+}$ cation. The BF_4^- ions and acetone molecules have been omitted for clarity.

Table 3
Selected bond distances (Å) and angles (°) for the $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2]^{2+}$ cation

Bond distances		*Bond angles*	
Pd(1)–O(1)	2.1022(16)	O(1)–Pd(1)–O(2)	80.68(6)
Pd(1)–O(2)	2.0993(17)	O(1)–Pd(1)–P(1)	93.31(5)
Pd(1)–P(1)	2.2280(7)	O(2)–Pd(1)–P(2)	93.10(5)
Pd(1)–P(2)	2.2239(6)	P(1)–Pd(1)–P(2)	92.85(3)
O(1)–C(1)	1.257(3)	C(1)–O(1)–Pd(1)	111.56(15)
O(2)–C(1) # 1	1.255(3)	C(1) # 1–O(2)–Pd(1)	111.61(15)
C(1)–C(1) # 1	1.548(5)	O(2) # 1–C(1)–O(1)	124.4(2)
		O(2) # 1–C(1)–C(1) # 1	118.0(3)
		O(1) # 1–C(1)–C(1) # 1	117.7(3)

two coordination planes is 33.3(8)° with a shorter Pd–Pd distance of 3.098(2) Å [29]. In $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2]^{2+}$ the O(1)–Pd(1)–O(2), O(1)–Pd(1)–P(1), P(1)–Pd(1)–P(2) and O(2)–Pd(1)–P(2) angles are 80.68(6)°, 93.31(3)°, 82.85(3)° and 93.10(5)°, respectively, and the sum of the angles around palladium is 359.94°. The mean Pd–O distance is slightly longer than the corresponding distances in $[Pd(C_2O_4)(dppe)]$ and $[Pd(C_2O_4)(PEt_3)_2]$ [18]. In the bridging oxalate ligand the C–O distances are nearly identical (1.255(3) and 1.257(3) Å), as expected because the negative charge is delocalized over the four C–O bonds. Similar features were observed in the structure of $[(Bu_2S)(Ph)Pd(\mu\text{-}C_2O_4)Pd(Ph)(SBu_2)]$ [19] with C–O distances of 1.253(3) and 1.247(3) Å.

3. Summary

The reactions of $[Pt(NO_3)_2(P^{\frown}P)]$ ($P^{\frown}P$ = dppm, dppe, dppp) or *cis*-$[Pt(NO_3)_2(PEt_3)_2]$ with sodium ascorbate produce the ascorbate complexes [Pt(Asc-O^2,O^3)($P^{\frown}P$)] or [Pt(Asc-O^2,O^3)$(PEt_3)_2$]. The dppe and dppp derivatives are stable in solution, but the dppm and PEt_3 compounds undergo degradation of the ascorbate ligands to produce the corresponding oxalates, and the solid state structure of $[Pt(C_2O_4)(dppm)]\cdot Me_2CO$ has been determined by X-ray crystallography. The available evidence suggests that oxidative cleavage of the ascorbate probably occurs within the coordination sphere of the metal. Such coordination and oxidative cleavage of ascorbate represents one possible fate of platinum compounds used in cancer therapy. In the palladium systems, the initially formed monodentate ascorbate complexes [PdMe(HAsc-O^3)($P^{\frown}P$)] undergo Pd–C bond cleavage and oxidation of the ascorbate ligand to again produce oxalate complexes, which may be isolated as monomeric or dimeric derivatives $[Pd(C_2O_4)(P^{\frown}P)]$ or $[Pd_2(\mu\text{-}C_2O_4)(P^{\frown}P)_2]^{2+}$. Further studies on the mechanism of oxidative degradation of ascorbate ligands in the presence of metal ions are in progress.

4. Experimental

Silver nitrate, sodium ascorbate and calcium threonate were purchased from Aldrich. $[Pt(NO_3)_2(dppm)]$ and [PdClMe(cod)] were prepared as described previously [9,30]. NMR spectra were recorded on a Varian Unity plus 300 spectrometer at 300.0 MHz for ^1H and 121.4 MHz for ^{31}P, respectively. ^1H chemical shifts were measured relative to the residual solvent signal, while ^{31}P chemical shifts were measured relative to external H_3PO_4.

4.1. Preparation of *cis*-$[Pt(NO_3)_2(PEt_3)_2]$

An aqueous solution (5 ml) of silver nitrate (0.34 g, 2.0 mmol) was added to a suspension of $[PtCl_2(PEt_3)_2]$ (0.50 g, 1.0 mmol) in acetone (40 ml) in a flask protected from light. The reaction mixture was stirred at room temperature (r.t.) for 24 h. After removing the AgCl by filtration through Celite, the filtrate was evaporated to dryness to leave a yellow solid (0.40 g, 72%). *Anal.* Calc. for $C_{12}H_{30}N_2O_6P_2Pt$: C, 25.95; H, 5.44; N, 5.04. Found: C, 26.00; H, 5.49, N, 4.96%. $^{31}P\{^1H\}$ NMR (acetone-d_6): $\delta(P)$ 7.3 (s, $^1J_{PtP} = 3730$ Hz).

4.2. Reaction of *cis*-$[Pt(NO_3)_2(PEt_3)_2]$ with sodium ascorbate

$[Pt(NO_3)_2(PEt_3)_2]$ (0.28 g, 0.50 mmol) in acetone (10 ml) was added dropwise to a solution of sodium ascorbate (0.20 g, 1.0 mmol) at r.t. under dinitrogen. After 20 h, the $^{31}P\{^1H\}$ NMR spectrum of an aliquot taken from the reaction mixture showed two doublets at $\delta(P)$ 5.61 ($^2J_{PP} = 22$ Hz, $^1J_{PtP} = 3300$ Hz) and 6.17 ($^2J_{PP} = 22$ Hz, $^1J_{PtP} = 3472$ Hz), due to [Pt(Asc-O^2,O^3)$(PEt_3)_2$].

The solvent was removed in vacuo to produce a yellow crystalline solid (0.10 g, 33%). ^{1}H NMR (acetone-d_6): $\delta(H)$ 1.16 (12H, t, CH_3), 3.22 (18H, m, CH_2), 3.64 (2H, m, *H*6, *H*6'), 3.89 (1H, t, $^3J_{HH} = 6$ Hz, *H*5), 4.29 (1H, d, $^3J_{HH} = 6$ Hz, *H*4). ^{31}P{^{1}H} NMR (acetone-d_6): $\delta(P)$ 5.6 (d, $^2J_{PP} = 22$ Hz, $^1J_{PtP} = 3300$ Hz), 6.2 (d, $^2J_{PP} = 22$ Hz, $^1J_{PtP} = 3472$ Hz).

4.3. Reaction of [Pt(NO$_3$)$_2$(dppm)] with sodium ascorbate

A mixture of [Pt(NO$_3$)$_2$(dppm)] (0.39 g, 0.5 mmol) and sodium ascorbate (0.20 g, 1.0 mmol) in acetone (20 ml) was stirred at r.t. in the presence of air. The reaction was monitored by NMR spectroscopy over a period of 48 h. After 60 h, a cream-colored precipitate was formed, which was collected by filtration and identified as [Pt(C$_2$O$_4$)(dppm)]. ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta(P)$ −63.5 (s, $^1J_{PtP} = 3087$ Hz). Crystals of [Pt(C$_2$O$_4$)(dppm)]·Me$_2$CO were obtained by slow evaporation of an acetone solution.

4.4. Reaction of [Pt(NO$_3$)$_2$(dppm)] with calcium threonate

A solution of calcium threonate (0.083 g, 0.25 mmol) in D$_2$O (10 ml) was added dropwise to a solution of [Pt(NO$_3$)$_2$(dppm)] (0.193 g, 0.25 mmol) in acetone (20 ml) under an atmosphere of dinitrogen. The reaction mixture was stirred at r.t. for 21 h. An aliquot of the reaction mixture was transferred to a NMR tube and analyzed by ^{31}P{^{1}H} NMR spectroscopy. It exhibited a single resonance at −64.0 ppm ($^1J_{PtP} = 3040$ Hz).

4.5. Reaction of [Pt(NO$_3$)$_2$(dppm)] with oxalic acid

A mixture of [Pt(NO$_3$)$_2$(dppm)] (0.39 g, 0.5 mmol) in acetone (20 ml) and oxalic acid (0.045g, 0.5 mmol) in water (5 ml) was stirred at r.t. After 5 h a white solid was collected by filtration (0.10 g, 50%). ^{31}P{^{1}H} NMR (acetone-d_6): $\delta(P)$ −63.5 (s, $^1J_{PtP} = 3040$ Hz).

4.6. Preparation of [PdClMe(dppe)]

A CH_2Cl_2 solution (20 ml) of dppe (0.80 g, 2.0 mmol) was added dropwise to a stirred CH_2Cl_2 solution (40 ml) of [PdClMe(cod)] (0.53 g, 2.0 mmol) under dinitrogen at r.t. After 1.5 h the solvent was removed under reduced pressure, and the resulting off-white solid was washed with ether and dried in vacuo (0.95 g, 86%). ^{1}H NMR (CDCl$_3$): $\delta(H)$ 0.79 (dd, $^3J_{PH} = 7$, 3 Hz, 3H, CH_3), 2.37 (m, 4H, CH_2), 7.40–7.65 (m, 20H, C$_6H_5$). ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta(P)$ 31.5 (d, $^2J_{PP} = 24$ Hz), 59.2 (d, $^2J_{PP} = 24$ Hz). ^{31}P{^{1}H} NMR (acetone-d_6): $\delta(P)$ 32.5 (d, $^2J_{PP} = 25$ Hz), 60.7 (d, $^2J_{PP} = 25$ Hz).

4.7. Preparation of [PdMe(Me$_2$CO)(dppe)]BF$_4$

A solution of AgBF$_4$ (0.25 g, 1.32 mmol) in acetone (20 ml) was added to a stirred solution of [PdClMe(dppe)] (0.56 g, 1.0 mmol) in acetone (20 ml) under dinitrogen in the absence of light. The color of the solution changed from yellow to a milky white due to formation of AgCl. After 3 h the now brown reaction mixture was filtered through Celite and the yellow filtrate was reduced to 10 ml. The ^{31}P{^{1}H} NMR spectrum of the filtrate (acetone-d_6 added) exhibited resonances at 62.5 (d, $^2J_{PP} = 25$ Hz) and 39.0 ppm (br).

4.8. Formation of [Pd(C$_2$O$_4$)(dppe)]·H$_2$O and [Pd$_2$(μ-C$_2$O$_4$)(dppe)$_2$][BF$_4$]$_2$

A solution of sodium ascorbate (0.20 g, 1.0 mmol) in D$_2$O (1 ml) was added under N$_2$ to the yellow filtrate of [PdMe(Me$_2$CO)(dppe)]BF$_4$ formed above. The solution darkened immediately, but turned yellow again after 30 min. ^{31}P NMR (acetone-d_6): $\delta(P)$ 63.3 (d, $^2J_{PP} = 25$ Hz), 61.1 (d, $^2J_{PP} = 25$ Hz). Yellow crystals of [Pd(C$_2$O$_4$)(dppe)]·H$_2$O suitable for X-ray diffraction formed in the NMR tube after 3 days. ^{1}H NMR (CDCl$_3$): $\delta(H)$ 2.66 (d, 4H, $^2J_{PH} = 20$ Hz, CH_2), 7.48–7.85 (m, 20H, C$_6H_5$). A second yellow solid was isolated after 60 h by removing the solvent in vacuo. ^{31}P{^{1}H} NMR (CDCl$_3$): $\delta(P)$ 58.0 (s). Crystals of [Pd$_2$(μ-C$_2$O$_4$)(dppe)$_2$][BF$_4$]$_2$ separated from this solution on standing in the NMR tube.

4.9. Reaction of [PdMe(Me$_2$CO)(dppe)]BF$_4$ with dehydroascorbic acid

Silver tetrafluoroborate (0.01 g, 0.05 mmol) was added to a solution of [PdClMe(dppe)] (0.028 g, 0.05 mmol) in acetone (20 ml), and the mixture was allowed to stir for 2 h in the dark at r.t. It was filtered through Celite to remove the precipitate of AgCl, and the pale yellow filtrate was placed under dinitrogen. A solution of dehydroascorbic acid (0.009 g, 0.05 mmol) in water (5 ml) was added dropwise. An aliquot of the resulting dark yellow reaction mixture was taken and transferred to an NMR tube containing a few drops of acetone-d_6. ^{31}P{^{1}H} NMR: $\delta(P)$ 34.2 (d, $^2J_{PP} = 25$ Hz), 58.0 (s), 62.5 (d, $^2J_{PP} = 25$ Hz).

4.10. Reaction of [PdMe(Me$_2$CO)(dppe)]BF$_4$ with calcium threonate

A solution of [PdMe(Me$_2$CO)(dppe)]BF$_4$ was prepared as above, and a solution of calcium threonate (0.017 g, 0.06 mmol) in water (15 ml) was added dropwise while stirring under dinitrogen. An aliquot of the dark yellow reaction mixture was taken and transferred to an NMR tube containing a few drops of

acetone-d_6. $^{31}P\{^1H\}$ NMR: $\delta(P)$ 34.2 (d, $^2J_{PP} = 25$ Hz), 58.0 (s), 62.5 (d, $^2J_{PP} = 25$ Hz).

4.11. Reaction of $[PdMe(Me_2CO)(dppe)]BF_4$ with oxalic acid

A solution of $[PdMe(Me_2CO)(dppe)]BF_4$ was prepared as above, and excess oxalic acid in water (15 ml) was added dropwise. An aliquot of the dark yellow reaction mixture was taken after 2 h and transferred to an NMR tube containing a few drops of acetone-d_6. $^{31}P\{^1H\}$ NMR: $\delta(P)$ 58.0 (s).

4.12. Preparation of $[Pd_2(\mu\text{-}C_2O_4)(dppe)_2][BF_4]_2\cdot 2H_2O$

A solution of $AgBF_4$ (0.13 g, 0.50 mmol) in acetone (15 ml) was added to a solution of [PdClMe(dppe)] (0.28 g, 0.50 mmol) in CH_2Cl_2 (15 ml), and the reaction mixture was stirred in the dark for 2 h at r.t. The solution was filtered through Celite to remove the white precipitate of AgCl. Anhydrous oxalic acid (0.045 g, 0.50 mmol) was added to the yellow filtrate and the solution was stirred for 1 h at room temperature. A yellow precipitate formed which was collected by filtration (0.177 g, 50%). *Anal.* Calc. for $C_{54}H_{52}B_2F_8O_6P_4Pd_2$: C, 49.60; H, 3.98. Found: C, 49.71; H, 3.83%. IR (Nujol): ν(CO) 1608 cm^{-1}. ^1H NMR (CD_3OD): $\delta(H)$ 2.92 (d, 8H, $^2J_{PH} = 24$ Hz, CH_2), 7.70 (m, 40H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 70.9 (s).

4.13. Conversion of $[Pd_2(\mu\text{-}C_2O_4)(dppe)_2][BF_4]_2$ to $[Pd(C_2O_4)(dppe)]$

A solution of $[Pd_2(\mu\text{-}C_2O_4)(dppe)_2][BF_4]_2$ in acetone-d_6 (1 ml) was placed in an NMR tube. Excess $K_2C_2O_4$ in D_2O (1 ml) was added and the NMR spectrum of the reaction mixture was recorded. The peak originally observed at 72.5 ppm disappeared, and a new resonance was found at 62.5 ppm (s).

4.14. Preparation of [PdClMe(dppp)]

A solution of dppp (0.82 g, 2.0 mmol) in CH_2Cl_2 (20 ml) was added dropwise to a stirred CH_2Cl_2 solution (40 ml) of [PdClMe(cod)] (0.53 g, 2.0 mmol) under dinitrogen at r.t. After 1.5 h the solvent was removed and the resulting white solid was washed with ether and dried in vacuo (1.14 g, 100%). ^1H NMR ($CDCl_3$): $\delta(H)$ 0.74 (dd, $^3J_{PH} = 7$, 3 Hz, 3H, CH_3), 2.32 (m, 4H, CH_2), 3.44 (m, 2H, CH_2), 7.30–7.60 (m, 20H, C_6H_5). $^{31}P\{^1H\}$ NMR ($CDCl_3$): $\delta(P)$ 6.8 (d, $^2J_{PP} = 51$ Hz), 27.0 (d, $^2J_{PP} = 51$ Hz).

4.15. Preparation of $[PdMe(Me_2CO)(dppp)]BF_4$

A mixture of [PdClMe(dppp)] (0.28 g, 0.51 mmol) and $AgBF_4$ (0.097 g, 0.51 mmol) in acetone (30 ml) was stirred in the dark for 3 h. The precipitate of AgCl was removed by filtration through Celite, and the filtrate was placed under N_2. ^{31}P NMR (acetone-d_6 added): $\delta(P)$ −3.7 (d, $^2J_{PP} = 51$ Hz), 30.7 (d, $^2J_{PP} = 51$ Hz).

Table 4
Crystal data and structure refinement for $[Pt(C_2O_4)(dppm)]\cdot Me_2CO$, $[Pd(C_2O_4)(dppe)]\cdot H_2O$ and $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2\cdot 2Me_2CO$

	$[Pt(C_2O_4)(dppm)]\cdot Me_2CO$	$[Pd(C_2O_4)(dppe)]\cdot H_2O$	$[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2\cdot 2Me_2CO$
Crystal size (mm^3)	$0.34\times0.21\times0.04$	$0.38\times0.38\times0.33$	$0.34\times0.26\times0.04$
Crystal system	triclinic	orthorhombic	triclinic
Space group, Z	$P\bar{1}$, 2	*Pbca*, 8	$P\bar{1}$, 2
Unit cell parameters			
a (Å)	9.9717(11)	14.7148(3)	10.4624(1)
b (Å)	11.0885(12)	18.8486(3)	12.7079(2)
c (Å)	13.6966(15)	19.6469(3)	14.4698(2)
α (°)	76.749(7)	90	110.083(1)
β (°)	85.525(7)	90	102.728(1)
γ (°)	76.231(7)	90	106.447(1)
V (Å^3)	1431.3(3)	5449.13(16)	1621.67(4)
Density (g cm^{-3}) (calculated)	1.683	1.489	1.449
Temperature (K)	180(2)	298(2)	213(2)
Absorption coefficient (mm^{-1})	5.051	0.834	0.724
Range (°)	1.94–26.46	2.04–25.00	1.85–26.40
Reflections collected	24382	99394	29734
Independent reflections (R_{int})	5863 (0.045)	4806 (0.12)	6614 (0.05)
Least-squares parameters	343	333	381
$R(F)$, $R_w(F^2)$ ($F^2 > 2.0\sigma(F^2)$)	0.0240, 0.0652	0.0572, 0.1010	0.0323, 0.0685
$R(F)$, $R_w(F^2)$ (all data)	0.0273, 0.0704	0.1003, 0.1142	0.0481, 0.0740
$S(F^2)$	1.142	1.102	1.021

4.16. Reaction of $[PdMe(Me_2CO)(dppp)]BF_4$ with sodium ascorbate

A solution of sodium ascorbate (0.20 g, 1.0 mmol) in D_2O (1 ml) was added to the above filtrate while stirring under dinitrogen. Crystals of $[Pd_2(\mu\text{-}C_2O_4)(dppp)_2][BF_4]_2\cdot 2Me_2CO$ suitable for X-ray diffraction were obtained by slow evaporation of the reaction mixture. IR (Nujol): ν(CO) 1604 cm^{-1}. ^1H NMR (acetone-d_6): $\delta(H)$ 2.97 (m, 8H, CH_2), 3.30 (t, $^3J_{HH} = 5$ Hz, 4H, CH_2), 7.50–7.80 (m, 40H, C_6H_5). $^{31}P\{^1H\}$ NMR (acetone-d_6): $\delta(P)$ 19.8 (s). Evaporation of the solvent after 48 h produced a yellow solid identified as $[Pd(C_2O_4)(dppp)]\cdot 2H_2O$ (0.02g, 7%). *Anal*. Calc. for $C_{29}H_{30}O_6P_2Pd$: C 54.17; H, 4.66. Found: C, 54.48; H, 4.67%.

4.17. X-ray crystallography

Preliminary examination and data collection were performed using a Bruker SMART CCD detector system single crystal X-ray diffractometer, as described elsewhere [31]. Structure solution and refinement were carried out using the SHELXTL-PLUS (5.03) software package [32]. Crystal data and structure refinement parameters are given in Table 4.

5. Supplementary material

Crystallographic data have been deposited with the Cambridge Crystallographic Data Centre, CCDC nos. 158293, 158294 and 158295. 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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