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Hydrolytic disproportionation of coordinated white phosphorus in [CpRu(dppe)(η^1-P_4)]PF_6 [dppe = 1,2-bis(diphenylphosphino)ethane]

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Abstract

The reaction of [CpRu(dppe)Cl] (**1**), dppe = 1,2-bis(diphenylphosphino)ethane, with one equivalent of P_4 in the presence of $TlPF_6$ affords the stable complex [CpRu(dppe)(η^1-P_4)]PF_6 (**2**) which contains the tetrahedral P_4 molecule η^1-bound to the metal. The tetraphosphorus ligand readily reacts with water upon mixing acetone or THF solutions of the complex with excess water. The complexes [CpRu(dppe)(PH_3)]PF_6 (**5**) and [CpRu(dppe){$P(OH)_3$}]PF_6 (**6**), identified among the hydrolysis products, contain the PH_3 molecule and, respectively, the unstable $P(OH)_3$ tautomer of the phosphorous acid bound to the CpRu(dppe) fragment. In CH_2Cl_2 the coordinated $P(OH)_3$ molecule in **6** easily yields the compound [CpRu(dppe){$PF(OH)_2$}]PF_2O_2 (**8**), via hydrolysis of the hexafluorophosphate anion and F/OH substitution in the coordinated $P(OH)_3$ molecule. All the compounds have been characterized by elemental analyses and NMR measurements. The crystal structures of **2** and **8** have been determined by X-ray diffraction methods.

Keywords: Ruthenium cyclopentadienyl complexes; Bidendate ligands; White phosphorus coordination; White phosphorus disproportionation; Crystal structures

1. Introduction

We have recently found that white phosphorus readily binds to the $CpRu(PPh_3)_2$ fragment yielding the compounds [$CpRu(PPh_3)_2$(η^1-P_4)]Y (Y = PF_6, CF_3SO_3) (**3**), which contain the P_4 tetrahedral molecule η^1 coordinated to the metal [1]. Such complexes, at variance with the few unstable P_4 compounds previously described [2–5], possess good stability being then suitable for investigating the reactivity of the coordinated P_4 molecule and comparing the chemistry of the coordinated cage with that of the free molecule. This topic deserves particular interest in view of the central role played in the synthesis of organophosphorus derivatives by the P_4 molecule [6,7], which is generally activated only in harsh conditions [8]. Solutions of [$CpRu(PPh_3)_2$(η^1-P_4)]Y (Y = PF_6, CF_3SO_3) (**3**) undergo hydrolysis in exceedingly mild conditions to yield quantitatively PH_3, which remains coordinated to the metal in the complexes [$CpRu(PPh_3)_2(PH_3)$]Y (Y = PF_6, CF_3SO_3), in addition to phosphorous acid and oxygenated compounds [1]. The [$CpRu(PPh_3)_2Cl$] complex is known to promote and/or catalyze a number of conversions and to allow the rapid assembly of complex molecules with high selectivity [9]. Such reactions are highly affected by the nature of the two phosphorus donors; for example, the use of a bidentate ligand such as dppe [dppe = 1,2-bis(diphenylphosphino)ethane], instead of triphenylphosphine, prevents the condensation of allylic alcohols and terminal alkynes, presumably due to the reluctance of the dppe ligand to dissociate from the ruthenium center [10]. With the aim to obtain more information on the coordinating properties of the P_4 cage and on the remarkable reactivity of the coordinated species, we have investigated the behaviour of the molecule in the presence of [CpRu(dppe)Cl] (**1**) thus probing the effect of a chelating diphosphine in the hydrolysis of coordinated white phosphorus.

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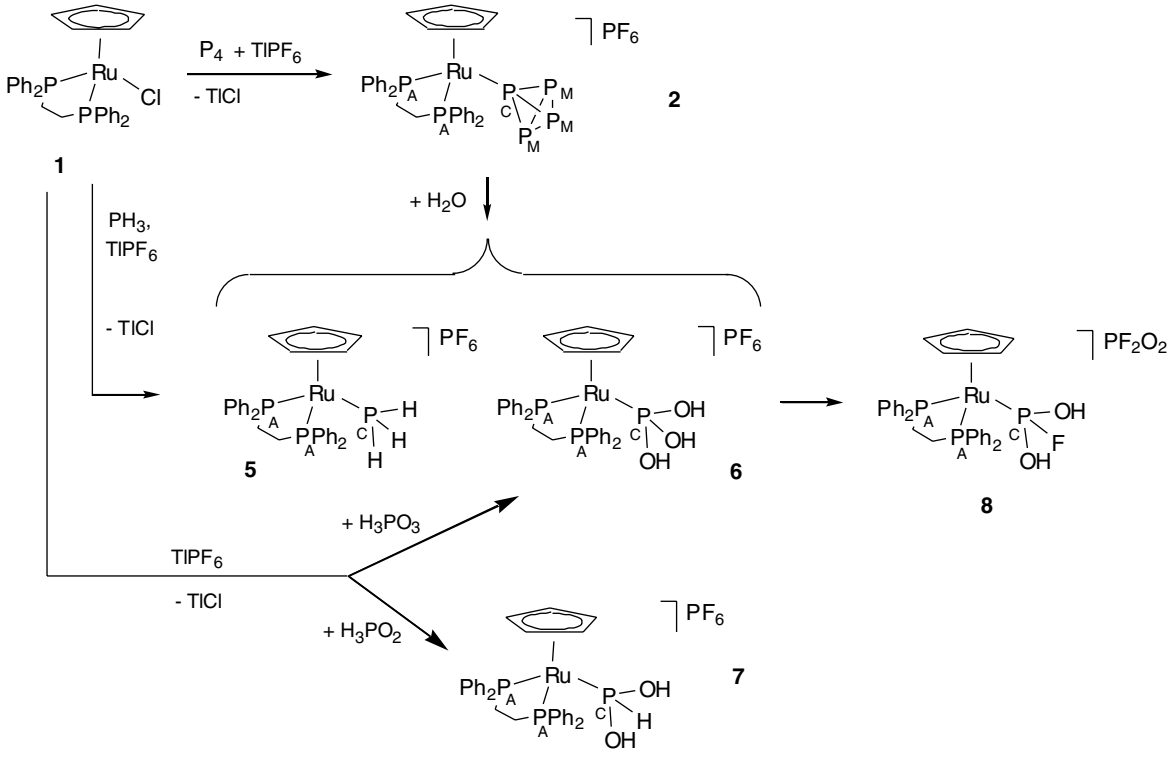
2. Results and discussion

The reaction of the dppe ruthenium complex [CpRu(dppe)Cl] (**1**) with the P_4 molecule, in the presence of $TlPF_6$ or $AgCF_3SO_3$, differs from that of the bis-triphenylphosphine $[CpRu(PPh_3)_2Cl]$ complex, which yields readily and quantitatively the compounds $[CpRu(PPh_3)_2(\eta^1\text{-}P_4)]Y$ (Y = PF_6 or CF_3SO_3) (**3**), irrespectively of the halide scavenger used [1]. In the case of **1**, while $AgCF_3SO_3$ leads predominantly to the reduction of the silver ion by white phosphorus, $TlPF_6$, whose cation has no oxidizing properties, slowly brings about precipitation of TlCl and coordination of the P_4 molecule, yielding $[CpRu(dppe)(\eta^1\text{-}P_4)]PF_6$ (**2**) within a few days (Scheme 1). Such behaviour is attributed to reduced mobility of the chloride ion in [CpRu(dppe)Cl], with respect to $[CpRu(PPh_3)_2Cl]$. Compound **2** exhibits a good stability and in this regard it behaves as the related $[CpRu(PPh_3)_2(\eta^1\text{-}P_4)]Y$ (**3**) [1] and $[Cp^*Ru(dppe)(\eta^1\text{-}P_4)]BPh_4$ (**4**) [11] derivatives. The P_4 molecule is firmly coordinated to the metal in solution, yielding a temperature-invariant first-order A_2CM_3 spin pattern in the ^{31}P NMR spectrum. The four phosphorus atoms of the cage yield the CM_3 part of the resonances with the metal-coordinated P_C atom featuring a quartet of triplets (Table 1) due to the coupling to P_M and P_A, respectively, significantly downfield shifted with respect to the signal of the free P_4, while the three naked P atoms yield a doublet. The chemical shift of the naked P_M phosphorus atoms is relatively close to that exhibited by the P atoms in corresponding position in the compounds **3** and **4**.

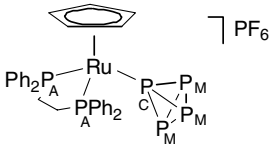
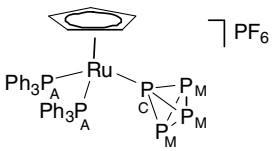
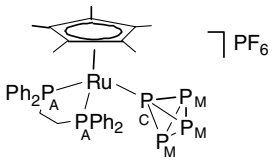
The X-ray structure of the complex cation in **2** is shown in Fig. 1 and values of selected bond distances and angles are given in Table 2. The P–Ru–P angle formed by the phosphine donor atoms is considerably smaller, by 21.4°, than that formed by the triphenylphosphine donors in **3**, due to the restraint set by the chelate ligand in the present compound **2**. The Ru–P(dppe) distances in **2** are 0.06 Å shorter than the Ru–P(PPh_3) distances in **3**, whereas the value of the Ru–P(P_4) distance is only 0.01 Å smaller for **2**, the latter difference being possibly due to different temperatures of data collection for the two structures. The P_4 geometry in **2** is that of a trigonal pyramid (as it was in **3**), with basal bonds 0.04 Å longer, in the mean, than the P–P bonds formed by the coordinating P atom. The mean values of P–P bonds of both types are 0.02 Å smaller in **2** than in **3**.

When a solution of **2** in acetone or THF is treated with excess water (1:100), hydrolysis of the P_4 ligand completes at room temperature within 2 h. The reaction, carried out on different batches in NMR tubes, is reproducible both regarding the nature and the amount of the various products obtained; among these, the new complexes $[CpRu(dppe)(PH_3)]PF_6$ (**5**) and $[CpRu(dppe)\{P(OH)_3\}]PF_6$ (**6**), as well as phosphorous acid have been unambiguously identified. Compound **5** and H_3PO_3 occur in ca. 50% yield with respect to the P_4 derivative **2**, while **6** forms in lower amount (ca. 10% based on **2**). The PH_3 molecule in **5** and the otherwise unstable $P(OH)_3$ tautomer of the phosphorous acid, H_3PO_3, in **6** are bound to the CpRu(dppe) fragment. The two complexes have been characterized by



Scheme 1.

Table 1
^{31}P NMR data of the ruthenium complexes with the intact P_4[a]

		δ P_A	δ P_C	δ P_M
	**2**	75.1 (d, $^2J(P_A–P_C) = 52.0$ Hz)	−328.8 (tq, $^1J(P_C–P_M) = 238.5$ Hz)	−495.5 (d)
	**3**	39.0 (d, $^2J(P_A–P_C) = 64.0$ Hz)	−348.2 (tq, $^1J(P_C–P_M) = 235.0$ Hz)	−487.0 (d)
	**4**	70.4 (d, $^2J(P_A–P_C) = 44.0$ Hz)	−308.5 (tq, $^1J(P_C–P_M) = 233.5$ Hz)	−490.3 (d)

[a] NMR data in $(CD_3)_2CO$ solution; chemical shifts are in ppm with respect to H_3PO_4 as external standard. White phosphorus yields a singlet at −526.9 ppm.

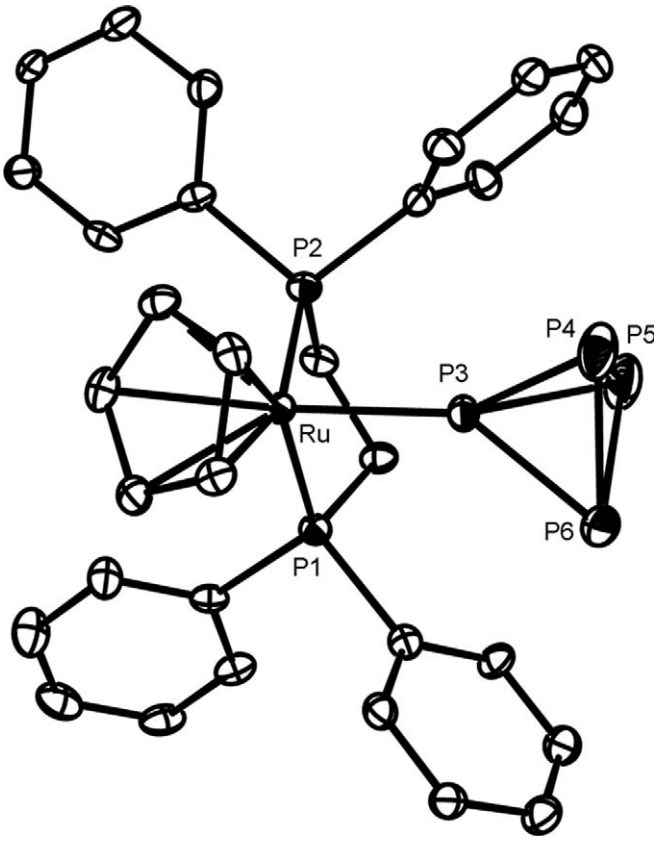


Fig. 1. A view of the cation in the structure of [CpRu(dppe)(η^1-P_4)]PF_6 (**2**). Thermal ellipsoids are shown at the 30% probability level and hydrogen atoms are not shown for clarity.

comparing the ^1H and ^{31}P NMR data of the hydrolyzed samples with those of the complexes that have been independently synthesized (see below). Likewise, the presence of free phosphorous acid has been ascertained by considering the ^{31}P shift of solutions containing the pure acid; in this regard the ^1H coupled ^{31}P spectrum of H_3PO_3 and those of the complexes **5** and **6** have been particularly useful to detect the possible presence of hydrogens directly bound to phosphorus, since these exhibit multiplets characterized by typically large P–H coupling constants [12,13]. The residual fractions of the P_4 cage and of the CpRu(dppe) fragment yield a variety of compounds which have not been yet characterized.

Table 2
Selected bond lengths (Å) and bond angles (°) for [CpRu(dppe)(η^1-P_4)]PF_6 (**2**)

Ru–P(1)	2.303(1)	P(3)–P(6)	2.147(2)
Ru–P(2)	2.306(1)	P(4)–P(5)	2.181(3)
Ru–P(3)	2.254(1)	P(4)–P(6)	2.201(2)
P(3)–P(4)	2.139(2)	P(5)–P(6)	2.181(2)
P(3)–P(5)	2.148(2)	Ru–C(Cp)	2.189–2.242
P(1)–Ru–P(2)	83.16(4)	P(2)–Ru–P(3)	93.17(5)
P(1)–Ru–P(3)	87.55(5)		

Some comments seem to be appropriate about the easy hydrolysis of the coordinated P_4 molecule undergone by **2** and **3**, which is intriguing, in view of the well known stability of white phosphorus in water. Also interesting is the different behaviour of the compounds [CpRu(PPh_3)$_2$(η^1-P_4)]Y (**3**), which easily react with water [1], and [Cp*Ru(dppe)(η^1-P_4)]Y, which are indefinitely stable in the same conditions [11]. Such a dichotomy might suggest that hydrolysis of **3** is favoured by the presence of the monodentate triphenylphosphine, that is known to detache easily from [CpRu(PPh_3)$_2$Cl] [14,15], while dissociation is less likely for the chelate ligand in the dppe complexes [9]. However, the hydrolysis undergone by **2** seems to rule out a dissociative mechanism that would involve coordination by a water molecule replacing the phosphine. Rather, comparisons between the crystal structures of the Cp derivatives **2** and

3 [1] and that of the Cp^* iron complex $[Cp^*Fe(dppe)(\eta^1\text{-}P_4)](BPh_4)$ [11] (as well as comparisons with the optimized geometries, from quantum mechanical calculations, of the models of Cp^* ruthenium complexes corresponding to **2** and **3** – these are reported with the Supplementary material) suggest that the higher bulkiness of Cp^* compared to Cp limits access by the water molecules to the metal coordination sphere. In an attempt to get a clue about the puzzling hydrolysis mechanism, calculations have been performed on models in which the region of the $Ru(\eta^1\text{-}P_4)$ moiety in **3** was probed by an approaching water molecule. Possible paths seem to involve, in the first stage, the close approach of the water molecule to the region of the $Ru–P(P_4)$ bond (which, however, implies crossing a very high energy barrier). If that is accomplished, a metal hydride is formed by dissociation of the water molecule, with a P_4 phosphorus atom still semicoordinated; simultaneously, a P–P bond of the cage opens, due to attack on a "basal" phosphorus by the OH fragment from the water molecule.

As a check on the nature of one of the hydrolysis products, the compound $[CpRu(dppe)(PH_3)]PF_6$ (**5**) has been independently synthesized by reaction of **1** in THF with gaseous PH_3 in the presence of $TlPF_6$. The complex, which adds to the small group of metal PH_3 derivatives [1,16–22], is quite stable under an inert atmosphere and the PH_3 molecule remains firmly coordinated to the metal in solution, yielding a first-order A_2C spin pattern in the ^{31}P NMR spectrum; the lower field doublet is assigned to the phosphorus atoms (P_A) of the dppe ligand and the higher field triplet to the phosphine atom (P_C). The latter signal turns into a quartet of triplets in the $^{31}P–^{1}H$ coupled spectrum, the observed value of ^1J(P–H) (360.0 Hz) being in the range of those found for the $[CpRu(PPh_3)_2(PH_3)]Y$ complexes ($Y = PF_6$, CF_3SO_3) [1] and for tetracoordinated P–H systems [12]. The hydrogens directly bound to phosphorus yield in the ^1H NMR spectrum a doublet of triplets (δ 4.41 ppm), characterized by the large $^1J(H–P_C)$ coupling mentioned above and a weak $^3J(H–P_A)$ one (2.0 Hz). With the aim to ascertain the nature of the complexes containing oxygenated phosphorus ligand(s), which are formed in the hydrolysis, the complexes $[CpRu(dppe)\{P(OH)_3\}]PF_6$ (**6**) and $[CpRu(dppe)\{HP(OH)_2\}]PF_6$ (**7**), have been synthesized in high yields by reacting **1** with the stoichiometric amount of the appropriate acid of phosphorus (H_3PO_2 or H_3PO_3) in water (50%), in the presence of the stoichiometric amount of $TlPF_6$. The yellow compounds are stable under an inert atmosphere and are soluble in common organic solvents; compound **6** dissolved in CH_2Cl_2 decomposes in ca. 1 day (see later). The ^{31}P NMR spectra of the cations in **6** and **7** exhibit an A_2C pattern with the lower field triplet assigned to the phosphorus atom (P_C) of the acid (hypophosphorous or phosphorous) and the higher field doublet to the dppe atoms (P_A). The triplet of the hypophosphorous derivative **7** is doubled in the $^{31}P–H$ coupled spectrum, showing that only one hydrogen is bound to the P atom; the observed value of ^1J(P–H) (418.0 Hz) is similar to that found for $[CpRu(PPh_3)_2\{HP(OH)_2\}]Y$ complexes [23]. The hydrogen directly bound to phosphorus yields a doublet of triplets (δ 7.45 ppm) in the ^1H NMR spectrum, characterized by the above strong $^1J(H–P_C)$ coupling and a weak $^3J(H–P_A)$ one (2.0 Hz). On the other hand, no coupling is observed for the coordinated H_3PO_3, clearly showing that no hydrogen is bound to the P_C atom in that case. Such NMR data, which parallel those of the compounds $[CpRu(PPh_3)_2\{P(OH)_3\}]PF_6$ and $[CpRu(PPh_3)_2\{HP(OH)_2\}]PF_6$ [23], whose structures have been determined by X-ray analyses, allow to assess unambiguously that the unstable tautomers $P(OH)_3$ and $HP(OH)_2$ of the hypophosphorous and phosphorous acids are stabilized by coordination through their P atom to the ruthenium of the CpRu(dppe) fragment. The stabilization of the pyramidal tautomers of the two acids, which are known to occur predominantly with the tetrahedral structure [24–28], confirms the preference by the soft metal center of the cationic $CpRu(L)_2$ fragment ($L = PPh_3$, 1/2dppe) for the P atom of the acid molecule. Such coordination mode had been observed only in two compounds [13,29,30], before the above-mentioned report [23].

Compound **6** dissolved in CH_2Cl_2 decomposes within 24 h to yield a complex of formula $[CpRu(dppe)\{P(F)(OH)_2\}]PF_2O_2$ (**8**), which is stable under an inert atmosphere and is soluble in common organic solvents. The $^{31}P\{^1H\}$ NMR spectrum of the cation exhibits an A_2CX ($X = ^{19}F$) pattern with a doublet, assigned to the dppe phosphorus atoms, and a lower field doublet of triplets. The latter resonances exhibit a large coupling (1137 Hz), which is typical for a P–F group, and a small one due to the coupling with the dppe phosphorus donors. The ^{31}P and ^{19}F NMR spectra exhibit also the resonances due to the $PF_2O_2^-$ anion [31]. The behaviour of the coordinated $P(OH)_3$ in the present dppe derivative **6** parallels that of the same ligand in the $[CpRu(PPh_3)_2\{P(OH)_3\}]PF_6$ compound (**9**) [23], which yields the $[CpRu(PPh_3)_2\{P(F)(OH)_2\}]PF_2O_2$ product (**10**) by decomposition [23], showing that the hexafluorophosphate hydrolysis leads to substitution of an OH of the coordinated $P(OH)_3$ ligand by a fluorine atom, to yield the $PF(OH)_2$ species which is the tautomer of the extremely unstable monofluorophosphorous acid, HPFO(OH), detected only in small amounts in the reactions of HPF_2O [32].

The structure of **8** has been determined by X-ray diffraction. A view of the $[CpRu(dppe)(PF(OH)_2)]^+$ complex cation is shown in Fig. 2 and values of selected bond distances and angles are given in Table 3. The Ru–P distances formed by the phosphine donors, slightly shorter than in **2**, are ca. 0.07 Å shorter than the distances formed by the PPh_3 phosphorus atoms in **10** [23], while the distance to the metal formed by the $PF(OH)_2$ phosphorus in **8** is only 0.014 Å shorter than in **10**. The value of the P–Ru–P angle formed by the dppe ligand in **8** is closely similar to that found for **2** and is 18.7° smaller than the angle formed by the triphenylphosphine P atoms in **10**. In the $PF(OH)_2$ ligand of **8**, apparently less affected by disorder than the analogous group in **10**, the atomic site considered to be 100% F forms

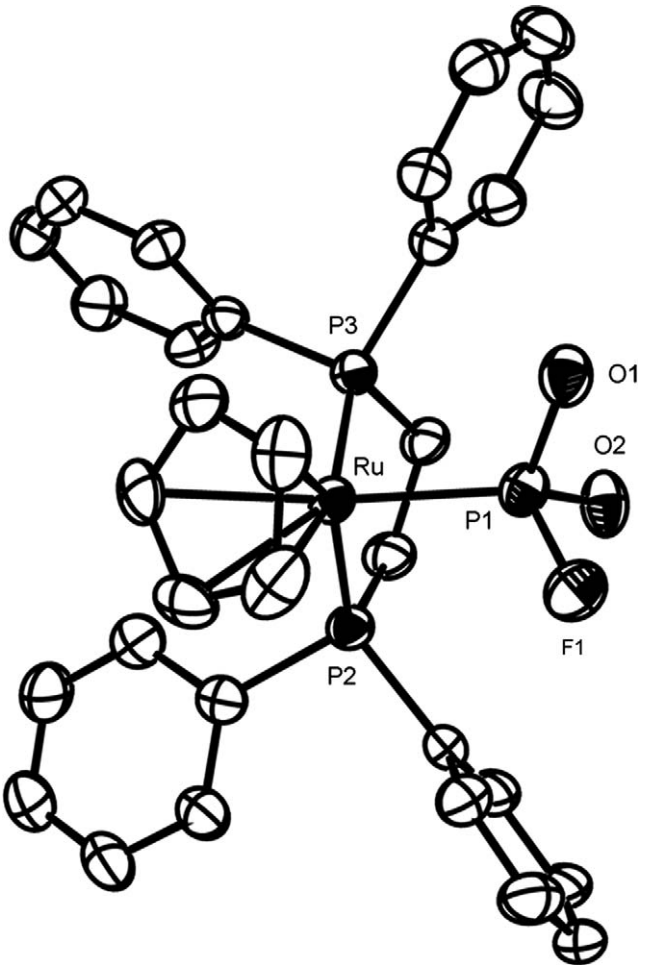


Fig. 2. A view of the cation in the structure of [CpRu(dppe){P-F(OH)$_2$}]PF_2O_2 (**8**), with 30% probability ellipsoids.

Table 3
Selected bond lengths (Å) and bond angles (°) for [CpRu(dppe){P-F(OH)$_2$}]PF_2O_2 (**8**)

Ru–P(1)	2.228(2)	P(3)–O(1)	1.567(4)
Ru–P(2)	2.289(2)	P(3)–O(2)	1.564(4)
Ru–P(3)	2.286(1)	P(3)–O(3)	1.576(3)
O(1)···O(4)[a]	2.623(6)	Ru–C(Cp)	2.226–2.248
O(2)···O(3)[a]	2.601(6)		
P(2)–Ru–P(3)	83.52(5)	P(1)–Ru–P(3)	89.08(5)
P(1)–Ru–P(2)	94.24(5)		

[a] Sites O(3) and O(4), belonging to the $PF_2O_2^-$ anion, were both assigned 2/3 O and 1/3 F population parameters.

with the other two (oxygen) sites F–P–O angles which are 7.4° smaller, in the mean, than the O–P–O angle.

3. Experimental

3.1. General

All reactions and manipulations were performed under an atmosphere of dry oxygen-free argon. The solvents were purified according to standard procedures [33]. The ^{1}H, ^{19}F and ^{31}P NMR spectra were measured on a Varian Gemini g300bb spectrometer operating at 300 MHz (^{1}H), 282.28 MHz (^{19}F) and 121.46 MHz (^{31}P). Chemical shifts are relative to tetramethylsilane (^{1}H), to $CFCl_3$ (^{19}F) and to H_3PO_4 85% (^{31}P) as external standards at 0.00 ppm; coupling constants are given in Hertz. Microanalyses were done by the Microanalytical Laboratory of the Department of Chemistry of the University of Firenze. [CpRu(dppe)Cl] (**1**) was prepared according to the literature method [34]. H_3PO_2 and H_3PO_3 water solutions and the ligand dppe (Aldrich) were used as received.

3.2. Synthesis of the complexes

3.2.1. [CpRu(dppe)(η^1-P_4)]$PF_6 \cdot CH_2Cl_2$ (**2**)

A suspension of [CpRu(dppe)Cl] (**1**) (300 mg, 0.50 mmol) and of $TlPF_6$ (175 mg, 0.50 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and THF (20 cm^3) was slowly added at room temperature to a solution of white phosphorus (87 mg, 0.70 mmol) dissolved in THF (20 cm^3). The resulting slurry was stirred at room temperature for 5 days; the precipitated TlCl was filtered off and the solvent evaporated under reduced pressure. The orange solid was washed twice with toluene (5 cm^3), dried under vacuum and recrystallized from CH_2Cl_2–hexane. Yield: 300 mg (65%). Anal. Calc. for $C_{32}H_{31}Cl_2F_6P_7Ru$: C, 41.85; H, 3.41. Found: C, 41.75; H, 3.50%. ^{1}H NMR [δ, $(CD_3)_2CO$, 20 °C]: 7.80–7.20 (20H, m, Ph), 5.43 (5H, s, Cp), 2.86 (4H, mbr, CH_2). ^{31}P{^{1}H} NMR: 75.1 (2P, d, $^2J(P_A–P_C) = 52.0$, P_A), −143.1 (1P, sept, $^1J(P–F) = 709.5$, PF_6), −328.8 (1P, tq, $^1J(P_C–P_M) = 238.0$, P_C), −495.5 (3P, d, P_M).

3.2.2. [CpRu(dppe)(PH_3)]PF_6 (**5**)

PH_3 was gently bubbled for 10 min through a solution of [CpRu(dppe)Cl] (**1**) (300 mg, 0.50 mmol) and of $TlPF_6$ (175 mg, 0.50 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and THF (20 cm^3). Afterwards the reaction flask was isolated and stirred at room temperature for 20 h; the precipitated TlCl was filtered off and yellow microcrystals of **5** were obtained by evaporating the solvent under reduced pressure. The solid was recrystallized from CH_2Cl_2–hexane. Yield: 250 mg (68%). Anal. Calc. for $C_{31}H_{32}F_6P_4Ru$: C, 50.07; H, 4.34. Found: C, 49.83; H, 4.40%. ^{1}H NMR [δ, $(CD_3)_2CO$, 20 °C]: 7.80–7.20 (20H, m, Ph), 4.87 (5H, s, Cp), 4.41 (3H, dt, $^1J(H–P_C) = 360.0$, $^3J(H–P_A) = 2.0$, PH_3), 2.86 (4H, mbr, CH_2). ^{31}P{^{1}H} NMR: 80.1 (2P, d, $^2J(P_A–P_C) = 41.0$, P_A), −105.4 (1P, t, P_C), −143.1 (1P, sept, $^1J(P–F) = 709.0$, PF_6).

3.2.3. [CpRu(dppe){$P(OH)_3$}](PF_6) (**6**)

To a solution of [CpRu(dppe)Cl] (**1**) (300 mg, 0.50 mmol) and of $TlPF_6$ (175 mg, 0.50 mmol) in a mixture of CH_2Cl_2 (20 cm^3) and THF (20 cm^3) was added at room temperature one equivalent of H_3PO_3 (50% water solution). The resulting slurry was stirred at room temperature for 4 h; in the meantime the orange colour of the solution faded to light yellow. The precipitated TlCl was

filtered off and the solvent evaporated under reduced pressure. The solid was washed twice with ether (5 cm^3) and recrystallized from CH_2Cl_2–hexane. Yield: 330 mg (83%). Anal. Calc. for $C_{31}H_{32}F_6O_3P_4Ru$: C, 47.04; H, 4.08. Found: C, 46.80; H, 4.15%. ^1H NMR [δ, $(CD_3)_2CO$, 20 °C]: 7.90–7.20 (20H, m, Ph), 5.21 (5H, s, Cp), 2.91 (4H, mbr, CH_2). $^{31}P\{^1H\}$ NMR: 138.1 (1P, t, $^2J(P_C–P_A) = 59.0$, P_C), 82.9 (2P, d, P_A), −143.1 (1P, sept, $^1J(P–F) = 709.0$, PF_6).

3.2.4. [CpRu(dppe){HP(OH)$_2$}]PF$_6$ (7)

The light yellow compound has been obtained through the same procedure as the phosphorous acid derivative **6** by adding to a solution of **1** and the chloride scavenger the stoichiometric amount of H_3PO_2 in 50% water solution. Yield: 85%. Anal. Calc. for $C_{31}H_{32}F_6O_2P_4Ru$: C, 48.00; H, 4.16. Found: C, 47.75; H, 4.25%. ^1H NMR [δ, $(CD_3)_2CO$, 20 °C]: 7.45 (1H, dt, $^1J(H–P_C) = 418.0$, $^3J(H–P_A) = 2.0$, $HP(OH)_2$), 7.80–7.20 (20H, m, Ph), 5.03 (5H, s, Cp), 2.75 (4H, mbr, CH_2). $^{31}P\{^1H\}$ NMR: 146,1 (1P, t, $^2J(P_C–P_A) = 53.0$, P_F), 83.1 (2P, d, P_A), −143.1 (1P, sept, $^1J(P–F) = 709.0$, PF_6).

3.2.5. [CpRu(dppe){PF(OH)$_2$}]PF$_2$O$_2$ (8)

[CpRu(dppe)$(P(OH)_3)$]PF_6 (**6**) (240 mg, 0.3 mmol) was dissolved in CH_2Cl_2 (20 cm^3) and the solution was left at room temperature for 20 h. The yellow complex was obtained by adding hexane (20 cm^3). Yield: 95 mg (42%). Anal. Calc. for $C_{31}H_{31}F_3O_4P_4Ru$: C, 49.67; H, 4.17. Found: C, 49.45; H, 4.21%. ^1H NMR (δ, $CDCl_3$, 20 °C): 7.70–7.10 (20H, m, Ph), 4.98 (5H, s, Cp), 2.73 (4H, m, CH_2). $^{31}P\{^1H\}$ NMR: 141,9 (1P, dt, $^1J(P_C–F) = 1137.5$, $^2J(P_C–P_A) = 63$, P_C), 83.1 (2P, d, P_A), −13.8 (1P, t, $^1J(P–F) = 961.1$, PF_2O_2). ^{19}F NMR: 3.1 (1F, d, $^1J(F–P_C) = 1138.1$, $PF(OH)_2$), −83.1 (2F, d, $^1J(F–P) = 962.5$, PF_2O_2).

3.3. X-ray crystallography of [CpRu(dppe)(η^1-P$_4$)]PF$_6$ (2) and [CpRu(dppe){PF(OH)$_2$}]PF$_2$O$_2$ (8)

X-ray diffraction data for **2**, as dichloromethane solvate, and **8** were collected on an Oxford Diffraction Xcalibur 3 CCD diffractometer, using Mo Kα radiation ($\lambda = 0.71069$ Å). Crystal data and the main data collection and structure refinement parameters are given in Table 4. Lattice constants were obtained from the setting angles of 3990 (**2**) and 6268 (**8**) reflections in the θ range 3–16°. Both intensity data sets were corrected for absorption by a multi-scan procedure [35]. The structures were solved by direct methods, with SIR-97 [36], and were refined by full-matrix least-squares on F^2 values [37]. All non-hydrogen atoms were refined anisotropically. All hydrogens bound to carbons were placed in idealized positions, each riding on the respective carrier atom, with its temperature factor linked to the overall U of the latter. The absolute structure, in view of the acentric space group of **2**, could be assigned on the basis of Flack's test [−0.05(3) parameter value, for the chosen enantiomer] [38]. In the structure of **8** the oxygen atoms of the $PF(OH)_2$ group were identified on the basis of the hydrogen bonds formed with sites of the anion (and in view of the slightly shorter P–O distances than the P–F one). The positional parameters of the $PF(OH)_2$ hydrogen atoms were refined with the O–H distances restrained to a unique value ($U_H = 1.5U_O^{eq}$). In the tetrahedral $PF_2O_2^-$ anion of **8** one of the peripheral sites, which formed (i) a distance to phosphorus distinctly longer (by 0.10 Å) than those formed by the other sites and (ii) angles at phosphorus with the other three sites smaller than the tetrahedral value, was considered to be occupied only by fluorine, consistently with the literature data [39]. The second fluorine atom in the anion was considered to be equally distributed among the other three sites. Programs used in the crystallographic calculations included PARST [40] and ORTEP [41].

Table 4
Crystal data and structure refinement parameters for compounds [CpRu(dppe)(η^1-P$_4$)]PF$_6$ (**2**) and [CpRu(dppe)(PF(OH)$_2$)](PF$_2$O$_2$) (**8**)

Compound	**2**	**8**
Formula	$C_{32}H_{31}Cl_2F_6P_7Ru$	$C_{31}H_{31}F_3O_4P_4Ru$
Formula weight	918.33	749.51
Crystal system	Orthorhombic	Orthorhombic
Space group	$Pbc2_1$[a]	$Pbca$
a (Å)	12.837(1)	16.077(2)
b (Å)	14.773(1)	18.707(2)
c (Å)	19.263(1)	20.920(2)
α (°)	90	90
β (°)	90	90
γ (°)	90	90
V (Å^3)	3653.1(5)	6292(1)
Z	4	8
Crystal size (mm)	0.15 × 0.20 × 0.40	0.06 × 0.40 × 0.60
μ(Mo Kα) (mm^{-1})	0.938	0.755
T (K)	150(2)	293(2)
Reflection collected	35173	60821
Independent reflections (R_{int})	7385 (0.0613)	6400 (0.0454)
Number of parameters (restraints)	433 (1)	395
R_1, wR_2 [$I > 2\sigma(I)$]	0.0351, 0.0742	0.0677, 0.1759
R_1, wR_2 (all data)	0.0652, 0.0743	0.0987, 0.1946
Goodness-of-fit	0.882	1.060

[a] Alternative setting of $Pca2_1$, No. 29.

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Appendix A. Supplementary material

CCDC reference numbers 602500 and 602501 contain the supplementary crystallographic data for **2** and **8**, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via

www.ccdc.cam.ac.uk/data_request/cif. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.jorganchem.2006.05.049.

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