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The first water-soluble tetraphosphorus ruthenium complex. Synthesis, characterization and kinetic study of its hydrolysis

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ABSTRACT

Reaction of the water-soluble complex [CpRu(TPPMS)$_2$Cl] (**1**) [TPPMS = sodium salt of *m*-monosulfonated triphenylphosphine, $Ph_2P(m\text{-}C_6H_4SO_3Na)$] with 1 equiv of white phosphorus in the presence of $TlPF_6$ or $AgBF_4$ as chloride scavengers, yielded the stable hydrosoluble complexes [CpRu(TPPMS)$_2$(η^1-P_4)]X (**2**) (X = PF_6, BF_4). Addition of water to DMF solutions of **2** causes hydrolysis ovf coordinated P_4 giving as main products complexes [CpRu(TPPMS)$_2$(PH_3)]X (**3**) (X = PF_6, BF_4) together with hydrogen and phosphorous acid, H_3PO_3. The new complexes have been characterized by ^1H and ^{31}P NMR spectroscopy in solution. Kinetic data and activation parameters of the hydrolysis process are reported.

1. Introduction

The reactivity of white phosphorus, P_4, towards different transition metal complexes has been widely developed during the last decades [1–3]. Coordination of white phosphorus to a transition metal crucially changes the reactivity of the P–P bonds of the P_4 tetrahedron resulting in its activation. The following opening of white phosphorus cage leads to a variety of P_n units that may be stabilized in the coordination sphere of transition metal complexes. The understanding of the factors ruling the selective activation of the P_n units is of high interest, mostly because it could help to develop a chlorine-free method for the preparation of useful phosphorus compounds directly from white phosphorus [4].

Recently, it was found that some 16-electron ruthenium complexes may coordinate the intact P_4 molecule forming mono- and bimetallic compounds in good yields [5–7]. The high stability and availability of these complexes have allowed investigating the reactivity of coordinated P_4 towards a variety of different organic and inorganic reagents. The obtained results are particularly intriguing and show that the P_4 molecule in the monometallic [CpRu(PPh$_3$)$_2$(η^1-P_4)]X (X = PF_6, OTf) and [CpRu(dppe)(η^1-P_4)] PF_6 complexes readily undergoes disproportionation with water under mild conditions leading to the corresponding complex bearing phosphine as ligand and free oxygenated phosphorus compounds [6a,b]. On the other hand, working with a bimetallic ruthenium complex, [{CpRu(PPh$_3$)$_2$}$_2$(μ,$\eta^{1:1}$-P_4)](CF_3SO_3)$_2$ and varying the excess of water, formation of H_3PO_3 and polyphosphorus compounds containing P–H and P-OH groups bridging the two metal centres were observed [7].

However, only few examples are mentioned in the literature [6,7] concerning the investigation of the reactivity of white phosphorus towards water-soluble ruthenium complexes. The use of such complexes would help for the extraction of white phosphorus residues from aqueous environments and decrease the danger of P_4 dispersed in water, as it would not be harmful once coordinated to a metal centre. A beautiful example comes from the group of Nitschke [8], who recently demonstrated that P_4 can be sequestered by a self-assembled tetrahedral capsule, which is formed in water by organic hydrophilic linkers and iron(II) ions. Within this system, P_4 becomes water-soluble and air-stable for indefinite time. In addition, the cage has the advantage to release P_4 at will. On the other hand, water-soluble ruthenium complexes such as **1** have been already successfully used to trap highly unstable phosphorus species such as phosphine oxide, H_3PO, generated by electrochemical activation of white phosphorus carried out in water/ethanol mixture [9].

Our interest in this field also resides in the possibility to extract P_4 from an organic solvent (immiscible with water) to an aqueous phase as a possible way to clean organic waste from phosphorus

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residues and to study the relative stability of white phosphorus in water once it is coordinated to a metal. In this study, we present the synthesis of the first water-soluble η^1-P_4 complex obtained by reaction of white phosphorus with the ruthenium precursor [CpRu(TPPMS)$_2$Cl] (**1**). Moreover, the hydrolysis of the corresponding η^1-P_4 derivative has been examined by NMR and the kinetic constant together with activation parameters have been calculated.

2. Results and discussion

2.1. Synthesis and characterization of the complexes

The reaction of [CpRu(TPPMS)$_2$Cl] (**1**) with 1 equiv of white phosphorus in the presence of $TlPF_6$ in DMF or $AgBF_4$ in THF as chloride scavengers leads to the formation of new complexes [CpRu(TPPMS)$_2$(η^1-P_4)]X, where X = PF_6 (**2a**), BF_4 (**2b**), bearing an intact white phosphorus tetrahedron η^1-coordinated to the ruthenium centre (Scheme 1). DMF is the best solvent to perform this reaction due to the very low solubility of the starting complex **1** in organic solvents. On the other hand, reaction of **1** with $AgBF_4$ was run in THF due to the reactivity of the silver cations towards the formyl group of DMF.

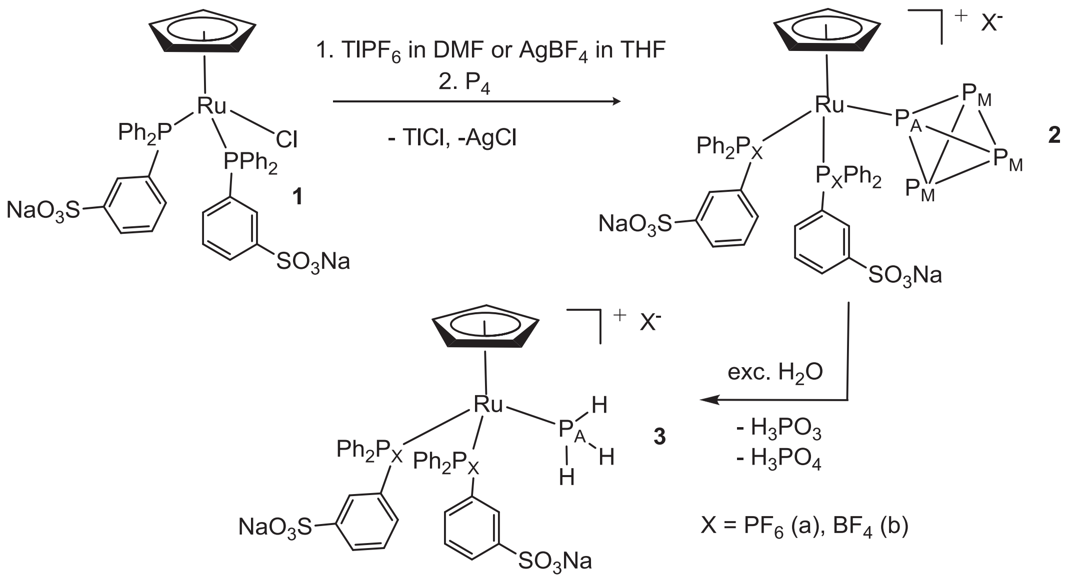
^{31}P NMR spectra of complex **2** exhibits an AM_3X_2 spin system in which A ($\delta = -345.7$ ppm, $^1J_{P(A)P(M)} = 238.9$ Hz, $^2J_{P(A)P(x)} = 63.9$ Hz) denotes the phosphorus atom of P_4 η^1-bound to the metal centre, M ($\delta = -487.1$ ppm, $^1J_{P(A)P(M)} = 238.9$ Hz) corresponds to three uncoordinated phosphorus atoms of P_4 tetrahedron, and X ($\delta = 39.4$ ppm, $^2J_{P(A)P(x)} = 63.9$ Hz) is the phosphorus atom of TPPMS. As a result, P_A is split into a quartet by three P_M phosphorus atoms and each line of quartet is split into a triplet by two equivalent P_x phosphorus atoms affording the quartet of triplets (Fig. 1).

Complex **2** is insoluble in several low polar organic solvents (THF, CH_2Cl_2) while it dissolves in water as well as in other polar solvents like CH_3OH and DMF where it is stable under an inert atmosphere. It reacts with water either when dissolved in the neat solvents or when H_2O is added to a solution of **2** in DMF or CH_3OH. The choice of solvent is relevant for the final result. Using MeOH and adding a 100-fold excess of water with respect to **2**, the main products of hydrolysis are the oxyacids H_3PO_3 (31%), H_3PO_4 (31%) and the phosphine complex [CpRu(TPPMS)$_2$(PH_3)]PF_6 (**3**) (24%), the latter identified by independent synthesis [9]. The dimethyl phosphite ester, OP(H)(OCH_3)$_2$ (14%), likely obtained by reaction of the formed acid with the solvent, was also present and was identified by ^{31}P NMR [10]. Running the test in neat water, rapid decomposition of the starting complex **2** occurs via decoordination of P_4 and H_3PO_3 and H_3PO_4 were observed to form exclusively. The synthon [CpRu(TPPMS)$_2$]$^+$ coordinates a water molecule giving a very broad signal at *ca.* +42 ppm, indicating the formation of [CpRu(TPPMS)$_2$(H_2O)]$^+$ confirmed by independent synthesis [11].

When complex **2** is dissolved in DMF and treated with 10 equiv of H_2O, the main product of hydrolysis is [CpRu(TPPMS)$_2$(PH_3)]$^+$ (**3**), which is slowly formed together with H_3PO_3 and some H_3PO_4 (Scheme 2) whose amount never exceeds 10%. H_3PO_4 is always formed in smaller amounts with respect to H_3PO_3 and its formation may be likely due to a secondary reaction affecting phosphorus acid in the presence of the ruthenium moiety. The overall process, which at first glance could be considered as a disproportionation of ruthenium-coordinated P_4, takes one day at $T = 25$ °C in NMR tube scale without stirring. Remarkably, no trace of free hypophosphorous acid, H_3PO_2, was observed for the hydrolysis reaction which markedly contrasts with the well known caustic disproportionation reaction of white phosphorus taking place in alkaline conditions [6c–e].

However, and in contrast with the *prima facie* evidence, the existence of a more complicated and unspecific pathway follows from the observation that dihydrogen is also released from the hydrolysis as confirmed by running the reaction in DMF-d_7, and recording the ^{1}H NMR spectrum where a singlet at 4.8 ppm confirms the formation of H_2. The experimental evidence for the formation of hydrogen together with that of phosphorus oxyacids indicates that more than one hydrolytic decomposition pathways may be operative.

The ^{31}P{^{1}H} NMR spectrum of complex **3** exhibits an AX_2 spin system (Fig. 2), where the doublet at 45.1 ppm corresponds to two equivalent P_x atoms of TPPMS coupled with P_A atom of coordinated phosphine P_AH_3 ($^2J_{P(A)P(x)} = 51.0$ Hz); the triplet at -112.9 ppm is attributed to P_A atom split in turn by coupling with two P atoms ($^2J_{P(A)P(x)} = 51.0$ Hz). The latter signal becomes a quartet of triplets ($\delta = -112.9$ ppm, $^1J_{PH} = 358.7$ Hz, $^2J_{P(A)P(N)} = 51.0$ Hz) in the proton-coupled ^{31}P NMR spectrum due to the coupling with three hydrogen atoms (Fig. 2, inset). Additionally, the formation of both



Scheme 1. Synthesis of **2** and subsequent hydrolytic disproportionation carried out at RT in THF.

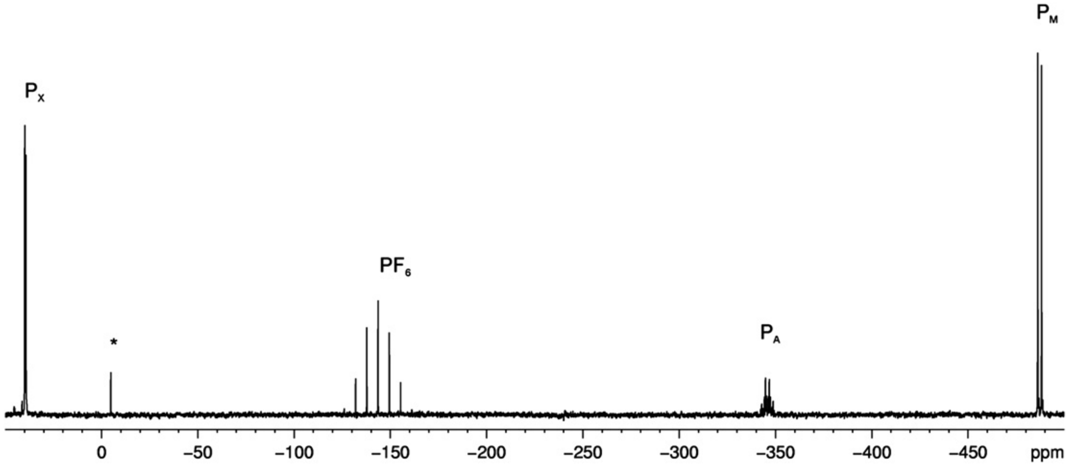


Fig. 1. $^{31}P\{^1H\}$ NMR spectrum of $[CpRu(TPPMS)_2(\eta^1\text{-}P_4)]PF_6$ in DMF solution (C_6D_6 external reference in Evans tube, 20 °C, 121.49 MHz; the singlet at −5 ppm indicated by a star corresponds to PPh_3 used as an internal standard).

phosphorous acid (H_3PO_3) and phosphoric acid (H_3PO_4) is observed in the reaction mixture according to ^{31}P NMR data ($\delta = 2.7$ ppm, d, $^1J_{PH} = 667.0$ Hz; $\delta = 0.9$ ppm, s, respectively).

*2.2. Kinetic of the hydrolysis reaction of complex **2** with water*

The kinetic of hydrolysis of **2a** was investigated at RT in DMF by ^{31}P NMR spectroscopy using PPh_3 as internal standard (Fig. 3). DMF was chosen due to the high solubility of **2** in this solvent. Moreover, and at variance with THF, no insoluble residue separated out during the reaction.

The disappearance of $[CpRu(TPPMS)_2(\eta^1\text{-}P_4)]^+$ follows a kinetic law that can be reduced to pseudo-first order relative to complex **2**. The pseudo-first order rate constant, k_{obs} at 25 °C, was evaluated by least-squares fitting of the concentration-time profiles and calculated from the gradient of the plot shown in Fig. 3 giving $k_{obs} = 0.119$ (h^{-1}). Correspondingly, the second-order rate constant k_2 can be obtained from equation $k_2 = k_{obs}/[A]_0$ where $[A]_0$ is the molar concentration of water (which is the reagent used in excess) so $k_2 = 0.386$ ($M^{-1}\,h^{-1}$). The half-life time of **2** is therefore $t_{1/2} = 1/k_2[A]_0 = 8.39$ (h). The hydrolysis of **2** is complete in 18 h working at 25 °C. The following Scheme 3 shows the percentage of each component in the final reaction mixture, carrying out the reaction at 25 °C and 35 °C respectively. The percentage relative to molecular hydrogen could not be determined since the quantitative measurement was performed by ^{31}P NMR.

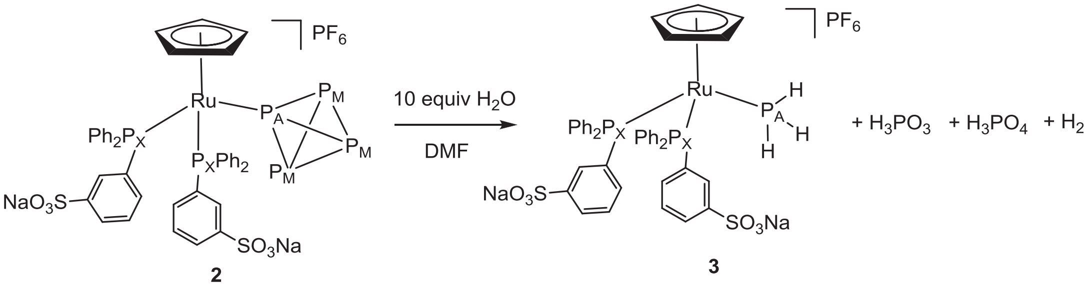
By repeating the test at slightly higher temperature, 35 °C, it was observed that the hydrolysis reaction is faster and the secondary reaction of P_4 de-coordination from **2** becomes more important as shown in Scheme 4 [12]. This causes the coordinatively unsaturated fragment $[CpRu(TPPMS)_2]^+$ to coordinate free H_3PO_2 and H_3PO_3 giving complexes $[CpRu(TPPMS)_2\{PH(OH)_2\}]^+$ (**4**) and $[CpRu(TPPMS)_2\{P(OH)_3\}]^+$ (**5**) which are present in the final mixture. Complex **4** has been reported by us elsewhere [9] and complex **5** was identified by independent synthesis, see Experimental section.

The tests were repeated in the temperature range from 9 to 25 °C. The values of k_2 ($M^{-1}\,h^{-1}$) at different temperatures are shown in Table 1. The corresponding Eyring plot shown in Fig. 4, gave the activation parameters for the hydrolysis of **2** to **3**, corresponding to $\Delta H^{\neq} = +17.5 \pm 0.5\ \mathrm{kJ\,mol^{-1}}$ and $\Delta S^{\neq} = -262.0 \pm 1\ \mathrm{J\,mol^{-1}\,K^{-1}}$, hence $\Delta G^{\neq} = +95.6 \pm 0.5\ \mathrm{kJ\,mol^{-1}}$ at 298 K.

The large negative value for the activation entropy is consistent with an associative reaction mechanism where nucleophilic attack of three molecules of water on the $\eta^1\text{-}P_4$ moiety causes the P—P bond cleavage and the formation of three P—OH and three P—H bonds as already hypothesized by us [7c] for a dimetallated P_4 unit in the presence of an excess of water. Addition of water to **2** gives therefore **3** and H_3PO_3 in 1:1 ratio. This ratio remains constant during the hydrolysis from the beginning until its completion and is independent from the temperature at which the experiment is carried out, going from 9 °C to 35 °C. The whole amount (in mmol) of formed H_3PO_3 is due to free H_3PO_3 plus the amount of free H_3PO_4, (which is likely formed by an independent mechanism from the oxidation of phosphorous acid) and the amount of complex **5** containing the pyramidal tautomer $P(OH)_3$.

3. Conclusions

The 16-electron ruthenium fragment $[CpRu(TPPMS)_2]^+$ reacts with white phosphorus leading to the formation of a water-soluble species $[CpRu(TPPMS)_2(\eta^1\text{-}P_4)]X$ (**2**) ($X = PF_6, BF_4$) with the intact P_4 molecule coordinated to Ru. The mild hydrolysis of **2** in the presence



Scheme 2. Hydrolysis of coordinated P_4 in **2** carried out in the range 9–25 °C in DMF.

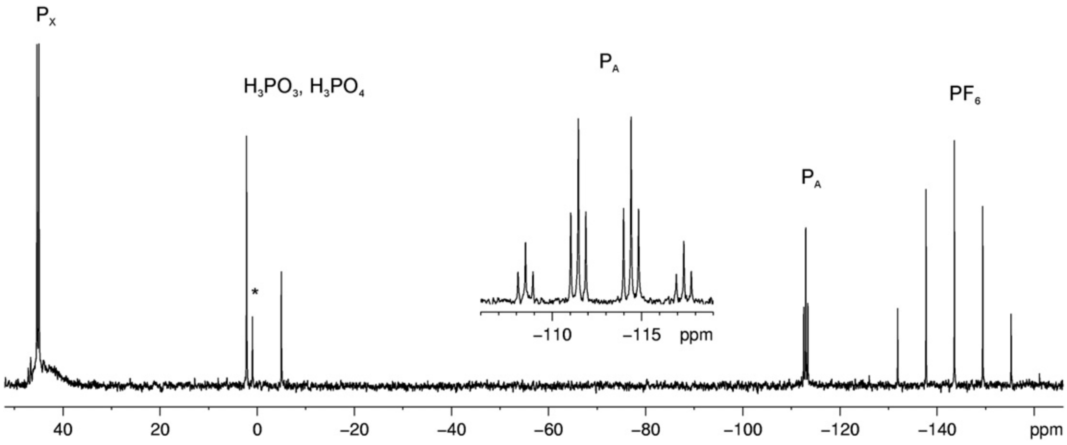


Fig. 2. $^{31}P\{^1H\}$ NMR spectrum of **3a** in DMF. The inset shows the signal of the ruthenium-coordinated phosphine P_A atom in the decoupling off ^{31}P NMR spectrum. Both spectra were registered in DMF, the singlet at −5 ppm indicated by a star corresponds to PPh_3 used as an internal standard (C_6D_6 external reference in Evans tube, 20 °C, 121.49 MHz).

of a known excess of water carried out at $T = 25$ °C or lower, leads to the cleavage of P—P bonds in the coordinated P_4 tetrahedron and results in the formation of $[CpRu(TPPMS)_2(PH_3)]X$ (**3**) ($X = PF_6$, BF_4), free phosphorus acid, H_3PO_3, hydrogen and phosphoric acid H_3PO_4, as final products. When the hydrolysis is carried out at 35 °C or at higher temperature, dissociation of P_4 from **2** also occurs, generating in solution the highly reactive fragment $[CpRu(TPPMS)_2]^+$, that can coordinate free H_3PO_2 and H_3PO_3 affording the corresponding hydroxyphosphine complexes $[CpRu(TPPMS)_2\{PH(OH)_2\}]X$ (**4**) and $[CpRu(TPPMS)_2\{P(OH)_3\}]X$ (**5**) ($X = PF_6$, BF_4). The final reaction mixture contains free H_3PO_3, free H_3PO_4 and free P_4 in addition to **3**, **4** and **5**. Noticeably, free H_3PO_2 has never been observed throughout the experiment; it is present in small quantity (less than 10%) as dihydroxyphosphine ligand coordinated to ruthenium following its tautomerization to $HP(OH)_2$ [13]. The kinetics of hydrolysis of the coordinated P_4 unit was studied by $^{31}P\{^1H\}$ NMR in the temperature range 9–35 °C giving $\Delta G^{\neq} = +95.6\ \mathrm{kJ\,mol^{-1}}$ at 298 K. The high negative value of the activation entropy, $\Delta S^{\neq} = -262.0 \pm 1\ \mathrm{J\,mol^{-1}\,K^{-1}}$ points to an associative mechanism where the nucleophilic attack of water on the η^1-P_4 moiety takes place in the transition state. Unfortunately no intermediates have been detected by low temperature NMR spectroscopy. A theoretical modelling of the reaction will be undertaken to validate the suggested associative mechanism of the hydrolysis.

4. Experimental section

4.1. General remarks and synthesis

All experiments were carried out under dry nitrogen using standard Schlenk techniques. The solvents were purified according to standard procedures [14]. THF was distilled over Na/benzophenone. DMF was dried by calcium hydride, distilled (3 times) in vacuum and stored under nitrogen on molecular sieves 4 Å. White phosphorus was purified by recrystallization from DMF. The resulting phosphorus was melted (50 °C) in DMF and rolled into beads while stirring with a magnetic bar and then cooling. White phosphorus was stored under a protective nitrogen atmosphere in a flask filled with water in a dark place and was washed sequentially in ethanol, acetone and diethyl ether prior to use.

^1H and ^{31}P NMR spectra were recorded with a Bruker Avance 400 and Bruker Avance 300 spectrometers. ^{31}P chemical shifts are relative to external 85% H_3PO_4 and ^1H chemical shifts are relative to tetramethylsilane as external reference and were calibrated against the residual solvent resonance. Downfield values are reported as positive, coupling constants are in hertz.

Infrared spectra were recorded with a Perkin–Elmer Spectrum BX FT-IR spectrophotometer in KBr disks. Microanalyses were carried out at the high-temperature element CHNS-O analyser

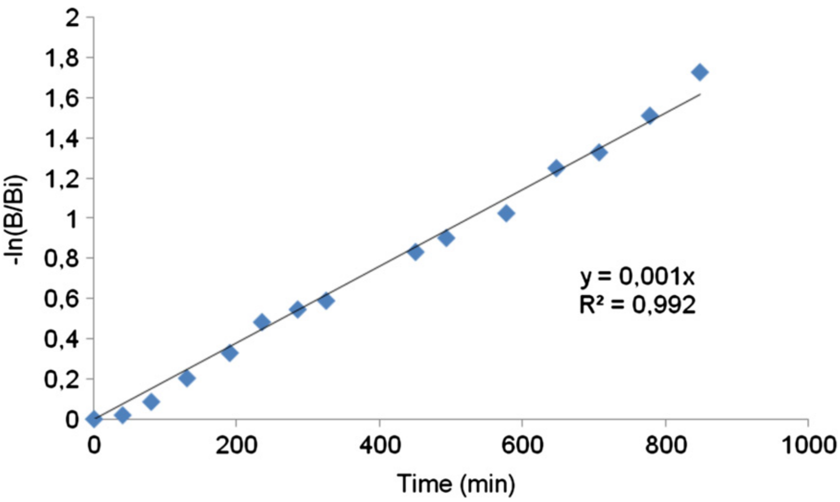
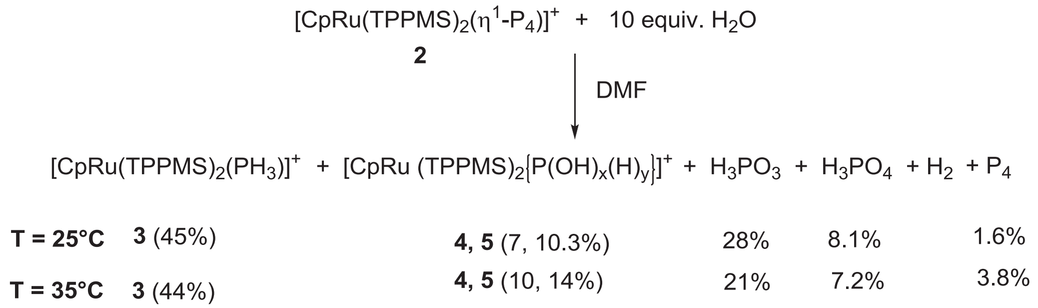
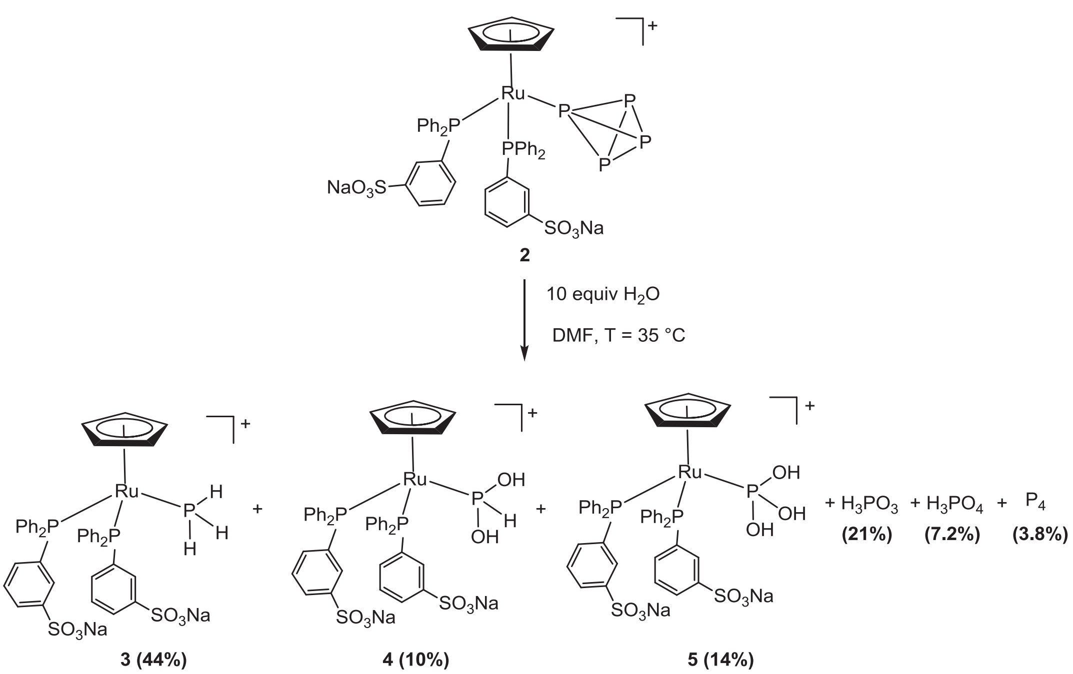


Fig. 3. Plot of $[-\ln(B/B_i)]$ *vs.* time, where B is the molar concentration of **2a** at reaction time $t = 0$; B_i is the molar concentration of **2a** during the hydrolysis measured by integration of the $^{31}P\{^1H\}$ NMR resonance with respect to a known amount of PPh_3 dissolved in C_6D_6 inside the Evans tube. The graph refers to the reaction carried out in DMF at $T = 25$ °C.



Scheme 3.



Scheme 4. Hydrolysis of **2** carried out at $T = 35$ °C in DMF.

EuroEA3028-HT-OM from EUROVECTOR. TPPMS [15] and [CpRu(TPPMS)$_2$Cl] [16] were prepared according to the literature. TlPF$_6$ (Strem Chemicals), AgBF$_4$ (Aldrich) and H$_3$PO$_3$ were used as received from commercial suppliers.

4.1.1. *Synthesis of [CpRu(TPPMS)$_2$(η^1-P$_4$)]PF$_6$ (**2a**)*

[CpRu(TPPMS)$_2$Cl] (60.0 mg, 0.0644 mmol, 1.0 equiv) was dissolved in 10 mL of DMF and TlPF$_6$ (22.6 mg, 0.0644 mmol, 1.0 equiv) was added as a solid under vigorous stirring [17]. After stirring for 3 h at RT, the white fine microcrystalline precipitate of TlCl was separated out by filtration under nitrogen leaving a pale-yellow solution. A 0.0785 M solution of P$_4$ (0.98 mL, 0.0773 mmol, 1.2 equiv) in THF was added to the filtrate via a syringe. After stirring for 30 min at RT, the colour changed from yellow to orange. The solvent was evaporated to dryness and the reddish orange residue was washed with diethyl ether (2 × 3 mL) before being dried under vacuum. Yield: 63.7 mg, 85%. Anal. Calcd for **2a**, $C_{41}H_{33}F_6Na_2O_6P_7RuS_2$ ($M_w = 1163.68$): C 42.32, H 2.86, P 18.63, S 5.51. Found: C 42.21, H 2.98, P 18.54, S 5.39.

^{1}H NMR (300.13 MHz, DMF-d_7, 20 °C): 5.6 (s, 5H, Cp), 7.5–7.7 (m, 6H, aromatic), 7.9–8.1 (m, 20 H, aromatic), 8.5 (m, 2H, aromatic). ^{31}P{^{1}H} NMR (121.49 MHz, DMF-d_7, 20 °C): A$_2$MX$_3$ spin system, $\delta = 39.4$ (d, $^2J_{PP} = 63.9$ Hz, 2P, P$_A$ (TPPMS)), −143.6 (septet, $^1J_{PF} = 709.7$ Hz, PF$_6$), −345.7 (qt, $^1J_{PP} = 238.9$ Hz, $^2J_{PP} = 63.9$ Hz, 1P, P$_{M(P4)}$), −487.1 (d, $^1J_{PP} = 238.9$ Hz, 3P, P$_{X(P4)}$).

IR (KBr): ν_{SO3} 1196 (vs), ν_{PF6} 832 (s) cm^{-1}.

Table 1
Second-order rate constants k_2 (M^{-1} h^{-1}), pseudo-first order rate constant k_{obs} (s^{-1}) and Gibbs activation free energies at different temperatures (K) for the hydrolysis of **2** to **3**.

Temperature (K)	k_2 (M^{-1} h^{-1})	10^3 k_{obs} (s^{-1})	$\Delta G^{\neq}$ (kJ mol^{-1})
298	0.386	0.0331	95.6
293	0.342	0.0223	94.3
287	0.284	0.0208	92.7
282	0.246	0.0169	91.4

4.1.2. *Synthesis of [CpRu(TPPMS)$_2$(η^1-P$_4$)]BF$_4$ (**2b**)*

[CpRu(TPPMS)$_2$Cl] (30.0 mg, 0.032 mmol, 1.0 equiv) was dissolved in 10 ml of THF and AgBF$_4$ (6.2 mg, 0.032 mmol, 1.0 equiv) was added as a solid under vigorous stirring. After stirring for 4 h at RT, the white fine microcrystalline precipitate of AgCl was filtered out under nitrogen leaving a yellow solution. Then 0.43 ml of a THF solution 0.112 M in P$_4$ (0.048 mmol, 1.5 equiv) was added to the filtrate via a syringe. After stirring for 30 min at RT, the colour of the

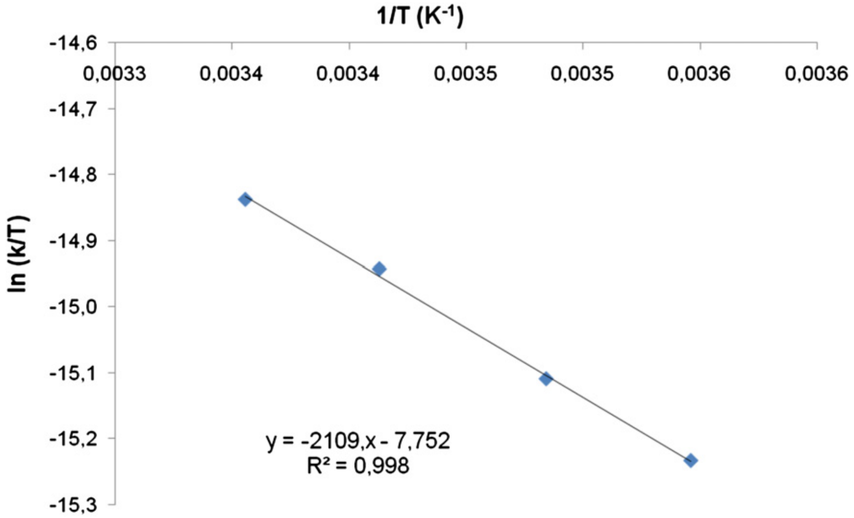


Fig. 4. Eyring plot for the hydrolysis of **2** in DMF.

reaction mixture changed from pale-yellow to orange. The solvent was evaporated to dryness and the orange-red residue was washed with diethyl ether (2 × 3 mL) before being dried under vacuum. The solvent was evaporated to dryness and the residue was then dissolved in dry DMF in order to remove AgCl. After filtration through cannula the solvent was evaporated from the filtrate and the product was dried in vacuum. Yield 26.2 mg, 74%. Anal. Calcd for **2b**, $C_{41}H_{33}BF_4Na_2O_6P_6RuS_2$ ($M_w = 1105.52$): C 44.54, H 3.01, P 16.81, S 5.80. Found: C 44.25, H 3.18, P 16.69, S 5.79.

The complexes **2a** and **2b** exhibit identical NMR spectra excepting the signals of the counter ion PF_6^- in **2a**.

*4.1.3. Synthesis of [CpRu(TPPMS)$_2$(PH$_3$)]PF$_6$ (**3a**)*

To a solution of [CpRu(TPPMS)$_2$(η^1-P$_4$)]PF$_6$ (200.0 mg, 0.172 mmol, 1.0 equiv) in DMF, degassed water (28.0 µL, 1.556 mmol, 10.0 equiv) was added and the resulting mixture was stirred for 12 h at RT. Addition of diethyl ether caused the precipitation of the product that was separated by filtration with cannula. The yellow solid was washed with diethyl ether (2 × 5 mL) before being dried under vacuum. Yield: 88.1 mg, 48%. Anal. Calcd for **3a**, $C_{41}H_{36}F_6Na_2O_6P_4RuS_2$ ($M_w = 1073.79$): C 45.86, H 3.38, P 11.54, S 5.97. Found: C 45.52, H 3.48, P 11.20, S 5.79.

^{1}H NMR (300.13 MHz, DMF-d_7, 20 °C): $\delta = 5.1$ (dt, $^1J_{PH} = 358.7$ Hz, $^3J_{PH} = 5.5$ Hz, 3H, PH$_3$), 5.5 (s, 5H, Cp), 7.5–7.7 (m, 6 H, aromatic), 7.9–8.2 (m, 20 H, aromatic), 8.5 (m, 2H, aromatic). ^{31}P {^{1}H} NMR (121.49 MHz, DMF-d_7, 20 °C): $\delta = 45.1$ (d, $^2J_{PP} = 51.0$ Hz, 2P, TPPMS), −112.9 (t, $^2J_{PP} = 51.0$ Hz, 1P, PH$_3$), −143.6 (septet, $^1J_{PF} = 709.6$ Hz, PF$_6$); ^{31}P NMR (121.49 MHz, DMF-d_7, 20 °C): $\delta = 45.1$ (br d, $^2J_{PP} = 51.0$ Hz, 2P, TPPMS), −112.9 (qt, $^1J_{PH} = 358.7$ Hz, $^2J_{PP} = 51.0$ Hz, 1P, PH$_3$), −143.6 (septet, $^1J_{PF} = 709.6$ Hz, PF$_6$); ESI-MS: $C_{41}H_{36}O_6P_3RuS_2$ (mass of the complex anion, without 2 Na$^+$), M^-/z: 883.0 (molecular peak), 848.9 ($M^-/z - PH_3$) (fragment derived from loss of PH$_3$).

*4.1.4. Synthesis of [CpRu(TPPMS)$_2$(PH$_3$)]BF$_4$ (**3b**)*

Complex [CpRu(TPPMS)$_2$(PH$_3$)]BF$_4$ was prepared from [CpRu(TPPMS)$_2$(η^1-P$_4$)]BF$_4$ following a procedure similar to that of **3a**. Yield: 86.8 mg, 50%. Anal. Calcd for **3b**, $C_{41}H_{36}BF_4Na_2O_6P_3RuS_2$ ($M_w = 1015.63$): C 48.49, H 3.57, P 9.15, S 6.31. Found: C 48.34, H 3.68, P 9.08, S 6.22.

The complex cations of **3a** and **3b** exhibit identical NMR and IR spectra apart for the counter anions. ESI-MS: $C_{41}H_{36}O_6P_3RuS_2$ (mass of the complex anion, without 2 Na$^+$), M^-/z: 883.0 (molecular peak), 848.9 ($M^-/z - PH_3$) (fragment derived from loss of PH$_3$).

*4.1.5. Synthesis of [CpRu(TPPMS)$_2${P(OH)$_3$}]PF$_6$ (**4**)*

[CpRu(TPPMS)$_2$Cl] (15.0 mg, 0.0161 mmol, 1.0 equiv) was dissolved in 0.5 mL of DMF, TlPF$_6$ (5.6 mg, 0.0161 mmol, 1.0 equiv) and H$_3$PO$_3$ (1.32 mg, 1.0 equiv) were added. After 3 h at RT, the white fine microcrystalline precipitate of TlCl separated out from the solution and the surnatant was taken off by syringe. The solvent was evaporated to dryness and the residue was dissolved in DMF-d_7, for NMR characterization.

^{1}H NMR (300.13 MHz, CD$_3$OD, 20 °C): $\delta = 4.8$ (Cp, s, 5 H), 7.0–7.5 (m, 24 H, aromatic), 8.0–8.2 (m, 4 H, aromatic).

^{31}P{^{1}H} NMR (121.49 MHz, CD$_3$OD, 20 °C): $\delta = 131.1$ (t, $^2J_{PP} = 63.9$ Hz, 1P, P(OH)$_3$), 46.2 (d, $^2J_{PP} = 63.9$ Hz, 2P, TPPMS), −143.5 (septet, $^1J_{PF} = 709.6$ Hz, 1P, PF$_6$). The proton-coupled ^{31}P NMR spectrum shows invariant signals, confirming the absence of any P–H bonds.

4.2. Kinetic study

*4.2.1. Kinetic measurements for the hydrolysis of **2a***

Degassed water (2.0 µL, 0.111 mmol, 10 equiv) was added to an NMR Evans tube (C$_6$D$_6$) containing 12.9 mg (0.011 mmol, 1 equiv) of complex **2a** dissolved in 0.45 mL of DMF. The resulting solution was monitored by ^{31}P NMR spectroscopy until complete disappearance of **2a**. The main products formed during hydrolysis exhibited resonances assigned to H$_3$PO$_3$, H$_3$PO$_4$ and [CpRu(TPPMS)$_2$(PH$_3$)]PF$_6$ (**3a**). The relative concentration of each species in the reaction mixture was determined by integration of the corresponding signals in the ^{31}P{^{1}H} NMR spectra, referenced to a known amount of PPh$_3$ dissolved in C$_6$D$_6$ and used as an internal reference.

Activation parameters were extracted by ln *k*/*T* *vs.* 1/*T* plot according to equation (1).

$$\ln\left(\frac{k}{T}\right) = -\frac{\Delta H^{\neq}}{R\cdot T} + \frac{\Delta S^{\neq}}{R} + \ln(Kb/h) \tag{1}$$

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[10] Dimethyl phosphite ester gives a singlet at $\delta = 12.8$ ppm, which becomes in the proton-coupled ^{31}P a doublet of multiplets, having $^1J_{PH} = 701.3$ Hz and $^3J_{PH} = 12.4$ Hz.

[11] [CpRu(TPPMS)$_2$Cl] (**1**) was dissolved in cold water and an equimolar amount of solid TlPF$_6$ was added. After stirring 2 h at RT, white precipitate was formed and ^{31}P NMR of the surnatant showed a broad signal at *ca.* 42 ppm.

[12] Similar behavior has been observed when the hydrolysis of [HRu(dppm)$_2$(η^1-P$_4$)]$^+$ (dppm = *bis*-diphenylphosphinomethane) was carried out at 35 °C or higher temperature, P$_4$ was released from the complex and the unsaturated fragment [HRu(dppm)$_2$]$^+$ reacted with phosphorous acid H$_3$PO$_3$ formed in the reaction mixture. M. Peruzzini, V. Mirabello, M. Caporali, L. Gonsalvi, unpublished results.

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[17] The same reaction has been carried out using NH$_4$PF$_6$ (10.5 mg, 0.0644 mmol) as chloride scavenger.