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Article

Getting a Clue to the Hydrolytic Activation of White Phosphorus: The Generation and Stabilization of $P(OH)_2PHPHPH(OH)$ at Ruthenium Centers

Pierluigi Barbaro,[†] Massimo Di Vaira,[‡] Maurizio Peruzzini,[†] Stefano Seniori Costantini,[‡] and Piero Stoppioni*,[‡]

ICCOM CNR, via Madonna del Piano, 10, 50019, Sesto Fiorentino, Firenze, Italy, and
Dipartimento di Chimica, Università di Firenze, via della Lastruccia, 3,
50019 Sesto Fiorentino, Firenze, Italy

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The bimetallic compound $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)][CF_3SO_3]_2$, in which the tetrahedral P_4 is bound to two $CpRu(PPh_3)_2$ fragments, slowly reacts under mild conditions with a moderate excess of water (1:20) to yield a mixture of compounds. Among the hydrolysis products, the new, remarkably stable complexes $[\{CpRu(PPh_3)\}\{CpRu(PPh_3)_2\}\{\mu^{1,4:3},\eta^{2:1}\text{-}P(OH)_2PHPHPH(OH)\}](CF_3SO_3)_2$ (**2**) and $[\{CpRu(PPh_3)_2\}\{CpRu(PPh_3)\{P(OH)_3\}\}(\mu,\eta^{1:1}\text{-}P_2H_4)](CF_3SO_3)_2$ (**3**) have been isolated. In the former, the previously unknown 1,1,4-tris(hydroxy)tetraphosphane molecule, $P(OH)_2PHPHPH(OH)$, is 1,4- and, respectively, 3-coordinated to the $CpRu(PPh_3)$ and the $CpRu(PPh_3)_2$ moieties; in the latter, the diphosphane P_2H_4 is stabilized through coordination to two different metal fragments. All of the compounds were characterized by elemental analyses and IR and NMR spectroscopy. The crystal structure of **2** was determined by X-ray analysis. The formation of the hydroxytetraphosphane, containing the tetraphosphorus entity, provides a clue to the hydrolytic activation of the P_4 molecule.

Introduction

The activation and functionalization of small, readily available molecules represent important processes for the advancement of knowledge on chemical reactivity which, in addition, may open the way to many industrial applications. This is particularly important at the present time, when more and more stringent European legislation requires that local industries devote increasing attention to the environmental impact of any newly implemented processes.

A huge number of studies have focused on the activation of simple molecules, either largely available in nature, such as CH_4,[1] CO_2,[2] and N_2,[3] or easily produced in industrial plants, such as H_2[4] or NH_3.[5] Very often, transition metal reagents are employed to carry out these processes, with the final aim of developing a true catalytic cycle that directly converts the feedstock species into valuable chemical products.

A simple, small molecule that has received comparatively less attention is elemental white phosphorus, which only recently has become the target of controlled metal-mediated activation.[6,7] P_4 is indeed readily available and provides the key entry to many aspects of phosphorus chemistry. Moreover, it represents the basis for the preparation of the myriad organophosphorus compounds, which are among the chemical specialties with the largest worldwide production.[8] Organophosphorus compounds are synthesized commercially from P_4, which, upon oxidation with chlorine to PCl_3 or PCl_5, is straightforwardly transformed into the target products.

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* To whom correspondence should be addressed. Fax: (+39)0554573385: E-mail: piero.stoppioni@unifi.it.

[†] ICCOM CNR.

[‡] Università di Firenze.

(1) (a) Jones, W. D. *Acc. Chem. Res.* **2003**, *36*, 140–146. (b) Crabtree, R. H. *Chem. Rev.* **1995**, *95*, 987–1007.

(2) Castro-Rodriguez, I.; Meyer, K. *Chem. Commun.* **2006**, 1353–1368.

(3) (a) Fryzuk, M. D.; Kozak, C. M.; Bowdridge, M. R.; Patrick, B. O.; Rettig, S. J. *J. Am. Chem. Soc.* **2002**, *124*, 8389–8397. (b) Fryzuk, M. D.; Johson, S. A. *Coord. Chem. Rev.* **2000**, *200−202*, 379–409.

(4) Heinekey, D. M.; Lledós, A.; Lluch, J. M. *Chem. Soc. Rev.* **2004**, *33*, 175–182.

(5) Kol, M.; Schrock, R. R.; Kempe, R.; Davis, W. M. *J. Am. Chem. Soc.* **1994**, *116*, 4382–4390.

(6) Peruzzini, M.; Gonsalvi, L.; Romerosa, A. *Chem. Soc. Rev.* **2005**, *34*, 1038–1047.

(7) (a) Peruzzini, M.; Abdreimova, R. R.; Budnikova, Y.; Romerosa, A.; Scherer, O. J.; Sitzmann, H. *J. Organomet. Chem.* **2004**, *689*, 4319–4331. (b) Ehses, M.; Romerosa, A.; Peruzzini, M. *Top. Curr. Chem.* **2002**, *220*, 108–140. (c) Cummins, C. C. *Angew. Chem., Int. Ed.* **2006**, *45*, 862–870.

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Recently, the activation of white phosphorus has been accomplished with either heterocyclic carbenes[9] or highly nucleophilic main group compounds.[10] These studies have disclosed new opportunities in this area, allowing achievement of the partial degradation of the molecule and its functionalization via the insertion of organic fragments into assembled polyphosphorus units, without the involvement of any transition metal. The use of readily available reagents, effective for the direct incorporation of phosphorus atoms from P_4 into inorganic or organic molecules, would be more profitable, and this goal may be pursued through mild metal-catalyzed reactions that, avoiding hazardous processes, may furthermore provide an environmental benefit. Achieving the coordination of the intact tetrahedral molecule of white phosphorus and studying its reactivity is mandatory for this purpose.

Previous work from our group has highlighted the utility of the Cp^RRuL_2 platform ($Cp^R = C_5H_5$, C_5Me_5; L = phosphane) to coordinate the intact P_4 molecule, yielding stable mononuclear[11] or dinuclear[12] cationic complexes $[\{Cp^RRuL_2\}_n(\eta^1\text{-}P_4)]Y_n$ ($n = 1, 2$; Y = PF_6, CF_3SO_3). Furthermore, these mono- or bimetallic compounds, which may be easily obtained in gram amounts, have been found to be useful for investigating the reactivity of the coordinated P_4 under mild reaction conditions. Unexpectedly, the reactivity of the coordinated tetraphosphorus molecule in the ruthenium cyclopentadienyl derivatives is spectacularly modified with respect to that of the free molecule. An interesting feature in this respect is the straightforward reactivity toward water of the coordinated P_4 molecule, which readily undergoes disproportionation at room temperature.[11b,c,12] By studying the hydrolysis of the bimetallic $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)][CF_3SO_3]_2$ (**1**) compound, which contains the doubly metallated P_4 bridging ligand, intriguing features have appeared.[12] Remarkably, both the nature of the products and the time needed to complete the hydrolysis are strongly affected by the relative amounts of the complex and water. Thus, the addition of 100 equiv of water to 1 equiv of **1** in THF hydrolyzes the coordinated P_4 ligand in a few hours, yielding a mixture of diphosphane, P_2H_4, and phosphorus oxoacids, H_3PO_2 and H_3PO_3. While the diphosphane molecule is stabilized through end-on/end-on coordination to two $CpRu(PPh_3)_2$ fragments,[12] the oxo derivatives are obtained as either free molecules or as ligands P-coordinated to ruthenium after their tautomerization to the pyramidal species, $PH(OH)_2$ and $P(OH)_3$.[13] In contrast to this chemistry, quick quenching of the hydrolyzed THF solution of the dinuclear derivative **1**, carried out using a large excess of water, affords selectively phosphorous acid, H_3PO_3, and a bimetallic compound containing the unprecedented 1-hydroxytriphosphane molecule, stabilized as a bridging ligand between two $CpRu(PPh_3)_2$ fragments.[14]

Herein, we report a further breakthrough in this type of reactivity, showing that the reaction of the doubly coordinated P_4 may be significantly slowed down by reducing the amount of water and that, among the several products which are formed by hydrolysis under these conditions, the previously unknown 1,1,4-tris(hydroxy)tetraphosphane, $P(OH)_2$-PHPHPH(OH), is generated. The formation of this intriguing molecule, which is stabilized through coordination to two nonequivalent {CpRu} platforms, besides its intrinsic interest, provides an important clue to the understanding of the initial steps of the coordinated P_4 hydrolytic degradation.

Results and Discussion

Compound **1** in THF is completely hydrolyzed within 6 days in the presence of 20 equiv of water. Reactions carried out on different batches are reproducible with respect to both the amount and nature of the products obtained. The $^{31}P\{^1H\}$ NMR spectrum of the solid obtained after workup (see Experimental Section) shows the presence of a mixture of several compounds. The two most abundant species are identified as $[\{CpRu(PPh_3)\}\{CpRu(PPh_3)_2\}\{\mu^{1,4:3},\eta^{2:1}\text{-}P(OH)_2\text{-}PHPHPH(OH)\}]^{2+}$ (**2**) and $[\{CpRu(PPh_3)_2\}\{CpRu(PPh_3)\text{-}\{P(OH)_3\}\}(\mu,\eta^{1:1}\text{-}P_2H_4)]^{2+}$ (**3**), Scheme 1; their fractional amounts (35% and 30%, respectively) have been estimated with reference to the four P atoms of the educt species **1** by careful integration of the ^{31}P NMR resonances. The remaining minor species are the known complex cations $[CpRu(PPh_3)_2\{PH(OH)_2\}]^+$ (**4**),[13] $[CpRu(PPh_3)_2\{P(OH)_3\}]^+$ (**5**),[13] $[CpRu(PPh_3)_2(PH_3)]^+$ (**6**),[11b] $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_2H_4)]^{2+}$ (**7**),[12] and the free phosphorous acid, H_3PO_3, which were identified by comparing the ^{31}P NMR spectrum of the reaction mixture originating from the hydrolysis of **1** with those of pure samples.[11b,12] Notably, the 1-hydroxytriphosphane complex $[\{CpRu(PPh_3)_2\}_2\{\mu^{1:3},\eta^{1:1}\text{-}PH(OH)PHPH_2\}]^{2+}$ (**8**), previously obtained in the presence of excess water,[14] has never been detected among the hydrolysis products of **1** obtained by the present procedure. The new complexes **2** and **3** were separated as yellow solids from the reaction mixture by careful selective precipitation. Both compounds are air-stable in the solid state and soluble in common organic solvents such as acetone, dichloromethane, and chloroform,

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(8) (a) Corbridge, D. E. C. Phosphorus. An Outline of its Chemistry, Biochemistry and Technology. In *Studies in Inorganic Chemistry*, 5th ed.; Elsevier: New York, 1995; Vol. *20*. (b) Emsley, J. *The 13th Element: The Sordid Tale of Murder, Fire, and Phosphorus*; Wiley: New York, 2002.

(9) (a) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *Angew. Chem., Int. Ed.* **2007**, *119*, 7052–7055. (b) Masuda, J. D.; Schoeller, W. W.; Donnadieu, B.; Bertrand, G. *J. Am. Chem. Soc.* **2007**, *129*, 14180–14181.

(10) (a) Xiong, Y.; Yao, S.; Brym, M.; Driess, M. *Angew. Chem., Int. Ed.* **2007**, *46*, 4511–4513. (b) Fox, A. R.; Wright, R. J.; Rivard, E.; Power, P. P. *Angew. Chem., Int. Ed.* **2005**, *44*, 7729–7733. (c) Kraus, F.; Aschenbrenner, J. C.; Korber, N. *Angew. Chem., Int. Ed.* **2003**, *42*, 4030–4033. (d) Chan, W. T. K.; García, F.; Hopkins, A. D.; Martin, L. C.; McPartlin, M.; Wright, D. S. *Angew. Chem., Int. Ed.* **2007**, *46*, 3084–3086. (e) Peng, Y.; Fan, H.; Zhu, H.; Roesky, H.; Magull, J.; Hughes, C. *Angew. Chem., Int. Ed.* **2004**, *43*, 3443–3445.

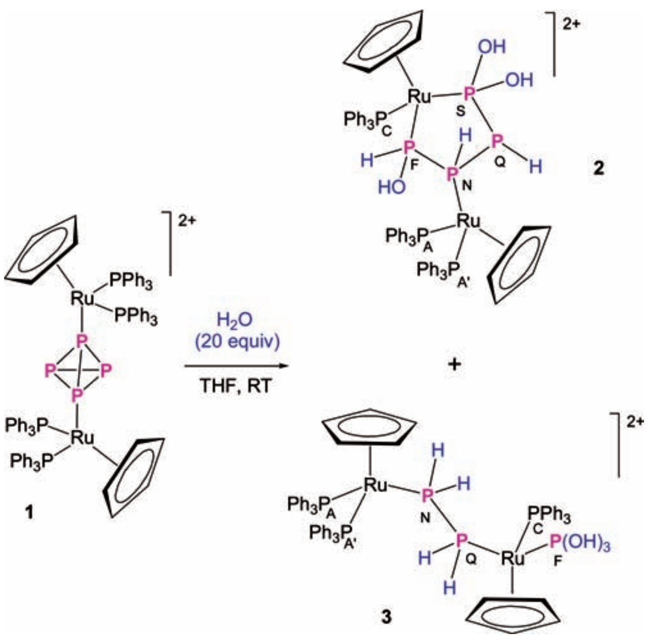
(11) (a) de los Rios, I.; Hamon, J.-R.; Hamon, P.; Lapinte, C.; Toupet, L.; Romerosa, A.; Peruzzini, M. *Angew. Chem., Int. Ed.* **2001**, *40*, 3910–3912. (b) Di Vaira, M.; Frediani, P.; Seniori Costantini, S.; Peruzzini, M.; Stoppioni, P. *Dalton Trans.* **2005**, *2234*, 2236. (c) Di Vaira, M.; Peruzzini, M.; Seniori Costantini, S.; Stoppioni, P. *J. Organomet. Chem.* **2006**, *691*, 3931–3937.

(12) Barbaro, P.; Di Vaira, M.; Seniori Costantini, S.; Peruzzini, M.; Stoppioni, P. *Chem.—Eur. J.* **2007**, *13*, 6682–6690.

(13) Akbayeva, D. N.; Di Vaira, M.; Seniori Costantini, S.; Peruzzini, M.; Stoppioni, P. *Dalton Trans.* **2006**, 389–395.

(14) Barbaro, P.; Di Vaira, M.; Seniori Costantini, S.; Peruzzini, M.; Stoppioni, P. *Angew. Chem., Int. Ed.* **2008**, *47*, 4425–4427.

Scheme 1



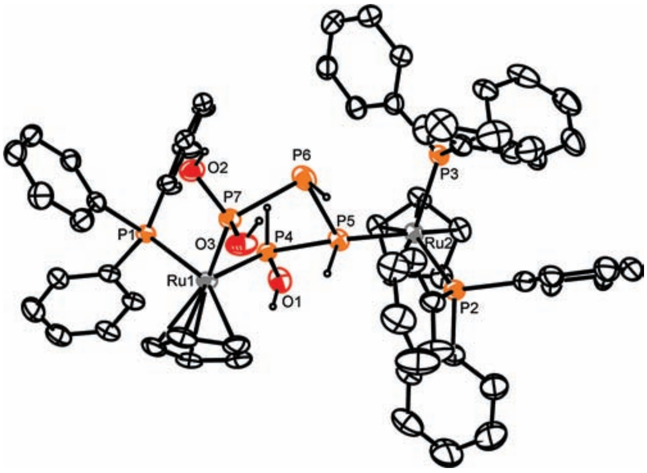


Figure 1. A view of the cation in the structure of **2**, with 30% probability ellipsoids. Hydrogen atoms of the phenyl and cyclopentadienyl rings are not shown for clarity.

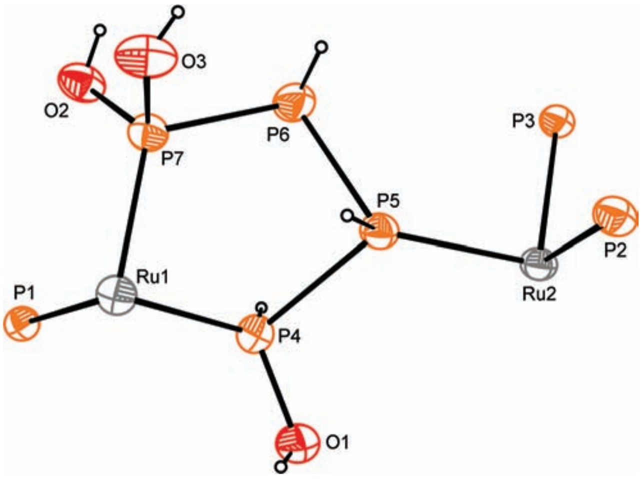


Figure 2. The core of the cation in the structure of **2**, with 30% probability ellipsoids. Selected bond lengths (Å) and angles (deg): Ru1−P4 2.240(1), Ru1−P7 2.235(1), Ru2−P5 2.300(1), P4−P5 2.232(2), P5−P6 2.244(2), P6−P7 2.226(2), P4−O1 1.598(4), P7−O2 1.585(4), P7−O3 1.579(4), P4−Ru1−P7 88.45(5), Ru1−P4−P5 109.04(7), P4−P5−P6 92.10(7), P5−P6−P7 97.65(7), P6−P7−Ru1 116.92(7).

but they are insoluble in diethyl ether and *n*-hexane. Recrystallization of **2** from acetone and *n*-hexane afforded yellow crystals suitable for X-ray diffraction, while attempts to grow single crystals of **3** were unsuccessful.

An overall view of the dimetal cation in the structure of **2** is shown in Figure 1, and its core is presented in Figure 2. The P(OH)$_2$PHPHPH(OH) unit is coordinated with its two hydroxylated ends to the metal atom bearing only one triphenylphosphane coligand, and it bonds the other metal atom, coordinated by both triphenylphosphanes of the original CpRu(PPh$_3$)$_2$ fragment, through one of the central atoms of the tetraphosphorus chain. The 2.312(1) Å Ru1−P1 bond distance, formed by the triphenylphosphane to the former metal atom (Figure 2), is 0.040 Å smaller than the 2.352 Å mean of the Ru2−P2 and Ru2−P3 distances formed by the two PPh$_3$ ligands with the other metal atom. On the other hand, the latter distances are in line with those previously found, for analogous bond types, in the dimetal cations containing the PH(OH)PHPH$_2$[14] and P_2H_4[12] units (2.345 and 2.360 Å, respectively, mean values). As far as the coordinating bonds formed by the P(OH)$_2$PHPHPH(OH) unit in **2** are concerned, the Ru1−P4 and Ru1−P7 bonds to Ru1 are, again, shorter (by 0.062 Å, in the mean) than the single Ru2−P5 bond formed with Ru2. Possibly, the overall shorter Ru−P distances around Ru1 are due to the lower steric requirements of one PPh$_3$ ligand, compared to those of the two triphenylphosphanes linked to Ru2 (there were two coordinating PPh$_3$ ligands also in the other,[12,14] abovementioned, cations). The three P−P distances in the P(OH)$_2$PHPHPH(OH) unit, spanning the 2.226−2.244 Å range, are rather closely grouped, the longest one being formed by the two central, nonhydroxylated, P atoms. The five-membered ring formed by the four atoms of the tetraphosphane unit and Ru1 is in the envelope conformation, with the P4, P6, P7, and Ru1 atoms lying in a plane (P7 deviates most from the plane, by 0.121(1) Å), whereas P5 is significantly displaced from it. The hinge angle between the above plane and that passing through the P5, P4, and P6 atoms is 124.3(1)°.

In keeping with the X-ray structural analysis, the $^{31}P\{^1H\}$ spectrum of **2** shows a second-order AA′CFNQS spin system, in which A, A′, and C are the triphenylphosphane P atoms and F, N, Q, and S are the phosphorus atoms of the bridging 1,1,4-tris(hydroxy)tetraphosphane; the labels of the P atoms are sketched in Scheme 1. The NMR parameters of **2** were obtained by computer simulation of the experimental spectrum (Figure 3). The chemical shifts of the phosphane P atoms of the CpRu(PPh$_3$)$_2$ fragment (P_A, $P_{A'}$) are in the range observed for [CpRu(PPh$_3$)$_2$(L)]$^+$ complexes,[11−15] while the signal of the phosphane P atom of the CpRu(PPh$_3$) moiety (P_C) is appreciably downfield-shifted (δ 56.5). The NMR resonances of the tetraphosphane chain in the P(OH)$_2$PHPHPH(OH) bridging ligand exhibit chemical shifts span-

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(15) Rüba, E.; Simanko, W.; Mauthner, K.; Soldouzi, K. M.; Slugovc, C.; Mereiter, K.; Schmid, R. *Organometallics* **1999**, *18*, 3843–3850.

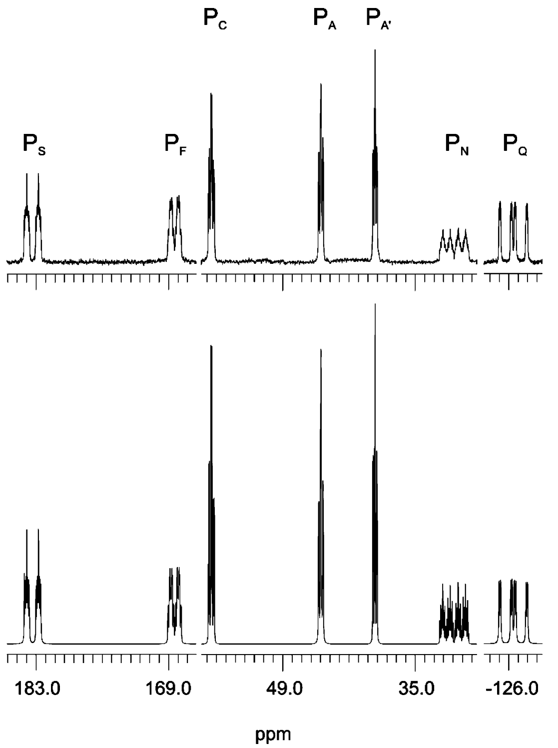

Figure 3. Computed (bottom) and experimental (top) $^{31}P\{^1H\}$ NMR spectra of **2**.

ning a range of more than 300 ppm, with the signals of the oxygenated P atoms (P_F, P_S) falling at the low-field end of the range (δ_F 168.4, δ_S 183.4) and the multiplet of the nonmetallated P−H phosphorus (P_Q) at the high-field end (δ_Q −126.5). The signal of the metallated P−H atom (P_N), at ca. 31 ppm, shows a coordination chemical shift of about 160 ppm with respect to P_Q. In the ^1H NMR spectrum, the hydrogens bound to P_F, P_N, and P_Q yield broad multiplets (δ_F 5.80, δ_N 3.61, δ_Q 1.40) with H−P coupling constants that are in the range observed for 1-hydroxytriphosphane.[14]

The 1,1,4-tris(hydroxy)tetraphosphane molecule, stabilized in **2** by $\mu^{1,4:3},\eta^{2:1}$-coordination to two {CpRu} moieties, is particularly intriguing as it represents an additional member of the practically unknown family of polyhydroxyphosphanes, that is, compounds of general formula $P_nH_{[(n+2)-m]}(OH)_m$ ($m \leq n + 2$),[16] which may be formally related to the slightly more investigated, but still elusive, family of polyphosphorus hydrides (P_nH_{n+2}),[17] by substitution of OH groups for one or more H atoms of the hydrides. The latter linear phosphanes are formally isoelectronic with the corresponding alkanes but are quite reactive, undergoing exothermic decomposition through disproportionation, even at low temperatures. Remarkably, no compound formed by their reaction with oxygen has been fully characterized, as they spontaneously ignite, yielding, as the final product, phosphoric acid.

The $[\{CpRu(PPh_3)_2\}\{CpRu(PPh_3)(P(OH)_3)\}(\mu,\eta^{1:1}\text{-}P_2H_4)][CF_3SO_2]_2$ formula and the structure of **3** have been assigned on the basis of elemental analysis and ^1H and ^{31}P NMR data, the latter being obtained through computer simulation of the experimental spectrum. The dinuclear complex cation contains the diphosphane, P_2H_4, molecule bridging two nonequivalent ruthenium moieties, namely, $CpRu(PPh_3)_2$ and $CpRu(PPh_3)(P(OH)_3$. The latter is likely formed by substitution of a molecule of phosphorous acid, coordinating through the P lone pair as a result of $H_3PO_3 \leftrightarrow P(OH)_3$ tautomerization,[13] for one of the triphenylphosphane ligands of the parent compound **1**. Such substitution, certainly promoted by the well-known mobility of a PPh_3 ligand in the $CpRu(PPh_3)_2$ moiety, has been observed also for the compounds $[CpRu(PPh_3)_2\{PR(OH)_2\}]CF_3SO_3$ [R = H (**4**), OH (**5**)], which undergo replacement of a coordinated triphenylphosphane molecule under mild conditions by a $PR(OH)_2$ species (H_3PO_2 or H_3PO_3 tautomer).[13] In the ^{31}P NMR spectra of these compounds, the signal of the remaining phosphane is downfield-shifted with respect to that of the parent $CpRu(PPh_3)_2$ fragment.[13] An analogous downfield shift is observed for the PPh_3 ligand of the $CpRu(PPh_3)\{P(OH)_3\}$ fragment in **5**. Thus, the ^{31}P NMR spectrum of **3** exhibits a second-order AA′CFNQ spin system (labels as in Scheme 1) in which AA′ and C are the triphenylphosphane P atoms, F is the phosphorus atom of the coordinated $P(OH)_3$ ligand, and N and Q are the nonequivalent P atoms of the bridging diphosphane. The resonances of the $CpRu(PPh_3)_2$ triphenylphosphane P atoms (P_A and $P_{A'}$) occur at the expected frequencies, and the low-field shift of the P_C multiplet of the $CpRu(PPh_3)(P(OH)_3)$ moiety is comparable to that of the P_C atom in **2** where the $CpRu(PPh_3)$ fragment is bound to the hydroxylated P_S and P_F atoms. The $P(OH)_3$ ligand exhibits a shift analogous to that observed for **5**. Finally, the two nonequivalent P_2H_4 atoms (P_N and P_Q) yield two distinct multiplets whose chemical shifts are slightly downfield with respect to that exhibited by the P_2H_4 molecule symmetrically bound to two $CpRu(PPh_3)_2$ units in **7**.[12] In the ^1H NMR spectrum, the hydrogens bound to P_N and P_Q yield broad multiplets (δ 5.22, 4.61, 4.48, and 4.04) with H−P coupling constants that are in the range observed for **7**.[14] The two cyclopentadienyls yield two resonances (δ 4.89 and 4.80), as expected for two nonequivalent metal fragments. Therefore, although the structure of **3** could not be authenticated by crystallographic methods, there is strong evidence for the present assignment, based on the analysis of the $^{31}P\{^1H\}$, ^{31}P NMR, and ^1H spectra and the comparison with the NMR parameters of **7**. In view of the existence of a small amount of compound **7** among the minor products of the present hydrolysis process, it may be assumed that **3** is formed from **7** by substitution of the $P(OH)_3$ molecule for a phosphane ligand.

The numerous species containing up to four phosphorus atoms, that is, PH_3,[11b,c] $PH(OH)_2$,[12,13] $P(OH)_3$,[12,13] P_2H_4,[12] $PH_2PHPH(OH)$,[14] and the present $P(OH)_2PHPHPH(OH)$, obtained by the various processes of hydrolysis of **1** and stabilized by coordination to one or two metal moieties, may be assumed as thermodynamic sinks along the degradation pathway of the dimetallated P_4 ligand. Their number suggests

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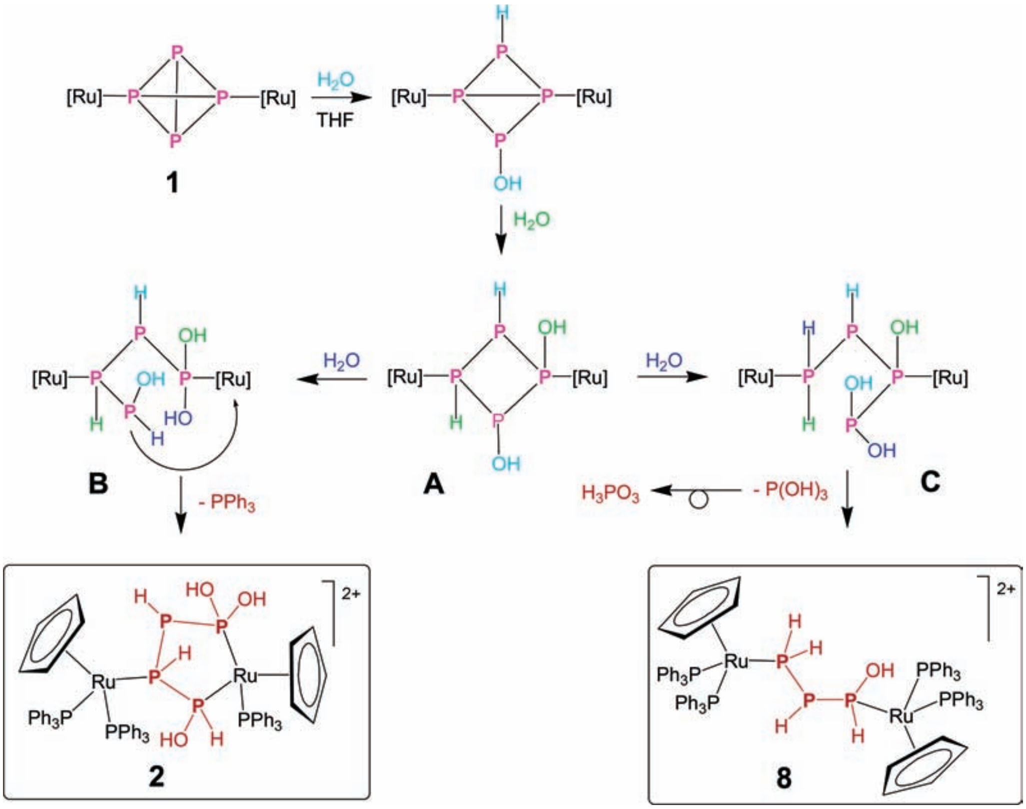
(16) To the best of our knowledge, no free polyhydroxophosphane $P_nH_{[(n+2)-m]}(OH)_m$ with $n > 1$ is known. The tris(hydroxy)phosphane PH(OH)PHPH$_2$, stabilized as the μ,η^1,η^1-ligand, has been reported in $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}PH(OH)PHPH_2)]CF_3SO_3$ (ref 14).

(17) Baudler, M.; Glinka, K. *Chem. Rev.* **1994**, *94*, 1273–1297.

Scheme 2



that several routes may be activated during the hydrolysis of **1**, depending on the reaction conditions, particularly the amount of added water.

Therefore, although no rigorous and comprehensive mechanistic picture of the hydrolysis of the dimetallated P_4 in **1** may be proposed in the absence of an in-depth kinetic study and of a reliable energetic profile of the reaction, possibly backed up by theoretical modeling of the process, it seems nevertheless to be possible to trace some hypotheses about the initial steps of the process, particularly those leading to the formation of compound **2**, which is the main focus of the present paper. Indeed, the $P(OH)_2PHPHPH(OH)$ formula suggests that the species sandwiched in **2** may result from the addition of three water molecules to P_4 without complete disruption of the cage. A trivial assignment of oxidation numbers shows that a disproportionate reshuffle occurs, yielding the oxidation numbers +2, −1, −1, and 0 for the four P atoms of the molecule, in the above order. A pictorial description of a possible route for the stepwise addition of three water molecules to **1**, with the cleavage of three P−P bonds, however *without total disruption of the diruthenium−tetraphosphorus assembly*, is shown in Scheme 2. Whatever the detailed order of addition, one may assume that the first two water molecules add across the P−P bond connecting the pair of unmetallated P atoms and that connecting the metallated pair, yielding the (undetected) species 1,2-(dihydroxy)tetraphosphacyclobutane (**A**) 1,3-dicoordinated to two $\{CpRu(PPh_3)_2\}$ moieties. Then, in order that the formation of the 1,1,4-tris(hydroxy)tetraphosphane found in **2** is rationalized, the addition of the third water molecule to **A** should take place with complete 1,4-regioselectivity, resulting in the intermediate **B**. From this point on, the process would be straightforward and the formation of **2** would be brought about by coordination of the pending PH(OH) end of the opened tetraphosphane to the ruthenium center already coordinated by the distal $P(OH)_2$ end, with associated decoordination of a triphenylphosphane ligand. By contrast, the alternative addition of the third water molecule across the 3,4-P−P bond in **A** yields, after passing through **C** and the addition of a fourth water molecule, the triphosphorus chain featuring the 1-hydroxytriphosphane, $PH(OH)PHPH_2$, ligand, which has been characterized in the complex $[\{CpRu(PPh_3)_2\}_2\{\mu^{1:3},\eta^{1:1}\text{-}PH_2PHPH(OH)\}]^{2+}$ (**8**).[14] One equivalent of $P(OH)_3$ accompanies the formation of **8**, which, once released in the reaction medium, retrotautomerizes to the more stable oxyacid form, H_3PO_3.[13,14]

The progressive addition of three or four water molecules, besides being controlled by the electronic properties of the coordinated P_4 molecule and ensuing species, is clearly affected by the reaction conditions. In our hands, the hydrolysis of the doubly metallated molecule is in fact specific in the presence of a large amount of water, going with almost complete regioselectivity to the formation of **8**,[14] with no detectable amount of the tetraphosphane species found in **2**.

Experimental Section

All reactions and manipulations were performed under an atmosphere of dry, oxygen-free argon. The solvents were purified according to standard procedures. ^1H, ^{19}F, and ^{31}P NMR spectra were run on Bruker Avance 400 DRX spectrometers, equipped with variable-temperature control units accurate to ±0.1 °C. ^{19}F and ^{31}P chemical shifts are relative to external $CFCl_3$ and to 85% H_3PO_4, respectively. ^{1}H 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 (Hz) of **2** and **3** and were obtained from 1D ^{31}P{^{1}H}, ^{1}H, and ^{1}H{^{31}P} NMR spectra with the aid of computer simulation using the *gNMR* program.[18] ^{19}F NMR spectra of compounds **2** and **3** yielded a singlet at −75.5 ppm for the triflate anion. Nujol mull infrared spectra were run on a Perkin-Elmer Spectrum BX FT-IR spectrometer with samples between NaCl discs. Microanalyses were carried out at the Microanalytical Laboratory of the Department of Chemistry of the University of Firenze. [{CpRu(PPh$_3$)$_2$}$_2$(μ,$\eta^{1:1}$-P$_4$)][CF$_3$SO$_3$]$_2$ (**1**) was prepared according to the literature method.[12]

Hydrolysis of 1. A 20-fold excess of water (0.21 mL, ca. 12 mmol) was added to a Schlenk flask charged with [{CpRu(PPh$_3$)$_2$}$_2$(μ,$\eta^{1:1}$-P$_4$)](CF$_3$SO$_3$)$_2$ (**1**) (1.08 g, 0.60 mmol) and THF (120 mL), and the resulting solution was stirred at room temperature. The parent compound **1**, as observed by carrying out the ^{31}P NMR spectrum on small aliquots of the solution, is completely hydrolyzed after 6 days. The solvent was then removed under reduced pressure to yield an orange solid.

[{CpRu(PPh$_3$)}{CpRu(PPh$_3$)$_2$}{$\mu^{1,4:3}$,$\eta^{2:1}$-P(OH)$_2$PHPHPH(OH)}][CF$_3$SO$_3$]$_2$ (2). The crude hydrolyzed mixture, obtained as described above, was dissolved in acetone (30 mL), and *n*-hexane was added up to saturation (ca. 5 mL). The resulting solution separated within two days yielding yellow crystals, which were collected on a glass frit, washed with a 1:1 acetone/*n*-hexane mixture (20 mL), and dried. Yield: 40 mg, 0.025 mmol, 4%. Elem anal. (%) calcd for $C_{66}H_{61}F_6O_9P_7Ru_2S_2$ (1595.2): C, 49.7; H, 3.9; P, 13.6. Found: C, 49.2; H, 4.0; P, 13.3. IR (NaCl, cm^{-1}): ν(O−H) 3058 (br); ν(P−H) 2307 (br). ^{31}P{^{1}H} NMR (161.89 MHz, CD$_2$Cl$_2$, 0 °C) δ 183.4 (m, P$_S$, ^1J(P$_S$−P$_Q$) 199.5, ^2J(P$_S$−P$_C$) 42.0, ^2J(P$_S$−P$_F$) 28.0, ^2J(P$_S$−P$_N$) 15.0, 1P), 168.4 (m, P$_F$, ^2J(P$_F$−P$_C$) 40.0, ^1J(P$_F$−P$_N$) 126.0, ^2J(P$_F$−P$_Q$) 25.0, ^3J(P$_F$−P$_{A'}$) 8.0, ^1J(P$_F$−H) 391.0, 1P), 56.5 (m, P$_C$, ^3J(P$_C$−P$_N$) 16.0, 1P), 45.0 (m, P$_A$, ^2J(P$_A$−P$_{A'}$) 33.0, ^2J(P$_A$−P$_N$) 39.0, ^3J(P$_A$−P$_Q$) 7.0, 1P), 39.3 (m, P$_{A'}$, ^2J(P$_{A'}$−P$_N$) 35.0, 1P), 30.9 (m, P$_N$, ^1J(P$_N$−P$_Q$) 263.0, ^1J(P$_N$−H) 365, 1P), −126.5 (m, P$_Q$, ^1J(P$_N$−H) 195.0, 1P). ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$, 0 °C): δ 7.70−6.90 (m, 45H, C$_6$H$_5$), 5.80 (brm, 1H, HP$_F$), 4.88 (s, 5H, C$_5$H$_5$), 4.86 (s, 5H, C$_5$H$_5$), 3.61 (brm, 1H, HP$_N$), 1.40 (brm, 1H, HP$_Q$).

[{CpRu(PPh$_3$)$_2$}{CpRu(PPh$_3$)(P(OH)$_3$)}{μ,$\eta^{1:1}$-P$_2$H$_4$}][CF$_3$SO$_3$]$_2$ (3). After the separation of **2**, the yellow solution was carefully concentrated to half volume under argon to yield a yellow precipitate which was separated from the solution. The solvent of the solution was removed at reduced pressure. The remaining solid was dissolved in the minimum amount of CH$_2$Cl$_2$, and *n*-hexane was added. The yellow solid which separated overnight was collected on a glass frit, washed with *n*-hexane, and dried. Yield: 50 mg 0.032 mmol, 5%. Elem anal. (%) calcd for $C_{66}H_{62}F_6O_9P_6Ru_2S_2$ (1565.2): C, 50.6; H, 4.0; P, 11.9. Found: C, 49.9; H, 4.3; P, 11.5. IR (NaCl, cm^{-1}): ν(O−H) 3055 (br); ν(P−H) 2322 (br). ^{31}P{^{1}H} NMR (161.89 MHz, CD$_2$Cl$_2$, 0 °C): δ 134.3 (m, P$_F$, ^2J(P$_F$−P$_C$) 54.5, ^2J(P$_F$−P$_Q$) 72.5, ^3J(P$_F$−P$_M$) 4.0, 1P), 50.9 (m, P$_C$, ^2J(P$_C$−P$_Q$) 38.0, ^3J(P$_C$−P$_M$) 16.5, 1P), 41.7 (m, P$_A$, ^2J(P$_A$−P$_{A'}$) 29.5, ^3J(P$_A$−P$_Q$) 7.0, ^2J(P$_A$−P$_M$) 45.0, 1P), 40.8 (m, P$_{A'}$, ^3J(P$_{A'}$−P$_Q$) 7.0, ^2J(P$_{A'}$−P$_M$) 44.0, 1P), −54.1 (m, P$_Q$, ^1J(P$_Q$−P$_M$) 64.0, ^1J(P$_Q$−H) 353.0, 1P), −55.8 (m, P$_M$, ^1J(P$_M$−H) 350.0). ^{1}H NMR (400.13 MHz, CD$_2$Cl$_2$, 0 °C): δ 7.70−6.90 (m, 45H, C$_6$H$_5$), 5.22 (brm, 1H, HP$_N$), 4.89 (s, 5H, C$_5$H$_5$), 4.81 (s, 5H, C$_5$H$_5$), 4.61 (brm, 1H, HP$_Q$), 4.48 (brm, 1H, HP$_N$), 4.04 (brm, 1H, HP$_Q$).

Table 1. Crystal Data, Data Collection, and Structure Refinement Parameters for **2**[a]

empirical formula	$C_{66}H_{61}F_6O_9P_7Ru_2S_2$
fw (g mol^{-1})	1595.20
temp (K)	130(2)
cryst system	monoclinic
space group	$P2_1/c$
a (Å)	14.493(1)
b (Å)	18.021(1)
c (Å)	26.931(1)
β (deg)	91.635(6)
V (Å^3)	7030.9(8)
Z	4
ρ_{calcd} (g cm^{-3})	1.507
μ (mm^{-1})	6.133
reflns collected	123158
independent reflns	13824 (R_{int} = 0.0692)
obsd reflns [$I > 2\sigma(I)$]	9600
data/restraints/params	13824/86/928
final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0508$, $wR_2 = 0.1328$
R indices (all data)	$R_1 = 0.0780$, $wR_2 = 0.1586$
goodness-of-fit on F^2	1.042
largest difference peak and hole/e Å^{-3}	1.412 and −0.829 e Å^{-3}

[a] CCDC reference number 000000. For crystallographic data in CIF or other electronic format see the Supporting Information.

Crystallography. X-ray diffraction data for **2** were collected at 130 K on an Oxford Diffraction Xcalibur PX Ultra CCD diffractometer, using Cu Kα radiation (λ = 1.5418 Å). Crystal data and the main data collection and structure refinement parameters are given in Table 1. Lattice constants were obtained from the setting angles of 33 910 reflections in the θ range 3.9−72.1°. Intensity data were corrected for absorption by a multiscan procedure (max/min transmission factor values: 1.000/0.650).[19] The structure was solved by direct methods, with SIR-97,[20] and was refined by full-matrix least-squares on F^2 values, with SHELXL-97.[21] The asymmetric unit contains one dimetal cation and two triflate anions, one of which, disorderly arranged, was refined as consisting of two complementary fractions, imposing similarity restraints on geometries. In the final cycles, all non-hydrogen atoms, including those of the disordered anion, were assigned anisotropic temperature factors. Hydrogen atoms were in calculated positions, riding, except for those bound to phosphorus or oxygen atoms, whose positions, identified on ΔF Fourier maps, were allowed to refine, with some restraints on distances; the hydrogen temperature factors were linked to the equivalent isotropic thermal parameters of the respective carrier atoms, according to the expression $U_H = 1.2U_{C,P}^{eq}$, or $U_H = 1.5U_O^{eq}$ for the hydroxyl hydrogens. Although large voids are present in the structure, possibly due to the irregular shape of the rather large cation, no chemically significant residual density was found in those regions, the highest ΔF peaks lying instead in proximity of the heavy atom positions. Programs used in the crystallographic calculations included PARST,[22] the WinGX package,[23] and ORTEP.[24]

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Supporting Information Available: Crystallographic data for **2** in CIF format. This material is available free of charge via the Internet at http://pubs.acs.org.

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(18) Budzelaar, P. H. M.; *gNMR V4.0*, Cherwell Scientific Publishing: Oxford, England, 1995−1997.

(19) *ABSPACK* routine in the *CrysAlisPro* package: *CrysAlisPro*; Oxford Diffraction Ltd.: Abingdon, Oxfordshire, England, 2006.

(20) Altomare, A.; Burla, M. C.; Camalli, M.; Cascarano, G.; Giacovazzo, C.; Guagliardi, A.; Moliterni, A. G.; Polidori, G.; Spagna, R. *J. Appl. Crystallogr.* **1999**, *32*, 115–119.

(21) Sheldrick, G. M. *Shelxl97*; University of Göttingen: Göttingen, Germany, 1997.

(22) Nardelli, M. *J. Appl. Crystallogr.* **1995**, *28*, 659.

(23) Farrugia, L. J. *J. Appl. Crystallogr.* **1999**, *32*, 837–838.

(24) Farrugia, L. J. *J. Appl. Crystallogr.* **1997**, *30*, 565.