Angewandte
Chemie

DOI: 10.1002/anie.200800723

Phosphorus Activation

Controlling the Activation of White Phosphorus: Formation of Phosphorous Acid and Ruthenium-Coordinated 1-Hydroxytriphosphane by Hydrolysis of Doubly Metalated P_4

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Dedicated to Professor Jan Reedijk

The reactivity of white phosphorus with transition-metal compounds is a mature field of inorganic and organometallic chemistry that has been extensively investigated in the past few decades. Research in this field has led to the synthesis of an amazing variety of transition-metal complexes containing P_n units originating from either the coupling or the degradation of the cage molecule(s) as well as from the recombination of smaller fragments into polyatomic aggregates.[1] These compounds often contain species with unique geometric and electronic properties which, apart from exhibiting a rich and intriguing chemistry,[1–3] have found interest either as building blocks for the construction of networks of mono- and polydimensional inorganic structures[4] or as phosphorus-transfer agents towards inorganic and organic molecules.[5] The recent activation of white phosphorus with either heterocyclic carbenes[6] or highly nucleophilic main group compounds[1–3,7] has led to new opportunities in this area, especially by allowing the partial degradation of the molecule and its functionalization by insertion of organic fragments into the assembled polyphosphorus units without the involvement of a transition metal.[2a,3e,5]

Previous work from our group has highlighted the utility of $\{Cp^RRuL_2\}$ moieties ($Cp^R = C_5H_5$, C_5Me_5; L = phosphane) for coordinating the intact P_4 molecule in reactions that yield stable mono-[8] or dinuclear[9] cationic complexes $[\{Cp^RRuL_2\}_n(\eta^1\text{-}P_4)]^{n+}$ ($n = 1, 2$). Furthermore, these mono- or bimetallic compounds, which are easily obtained in gram amounts, have proved to be useful for investigating the reactivity of coordinated P_4 under mild conditions. For example, we have found that the reactivity of the coordinated P_4 molecule in the cyclopentadienyl derivatives is spectacularly modified with respect to that of the free molecule as it readily undergoes quantitative disproportionation with water at room temperature.[8b,9] Thus, addition of excess water (100 equivalents) to one equivalent of $[CpRuL_2(\eta^1\text{-}P_4)](CF_3SO_3)$ (**1**) or $[\{CpRuL_2\}_2(\mu,\eta^{1:1}\text{-}P_4)](CF_3SO_3)_2$ (**2**) in THF hydrolyzes the coordinated P_4 ligand in a few hours to yield a mixture of phosphine (PH_3), diphosphane (P_2H_4), and the phosphorus oxyacids H_3PO_2 and H_3PO_3 in ratios that depend strongly on the hapticity of the P_4 molecule (η^1 vs. $\mu,\eta^{1:1}$). The hydrogenated molecules are stabilized by coordination to $\{CpRu(PPh_3)_2\}$ fragment(s),[8b,c,9] whereas the oxo derivatives are obtained as either free molecules or coordinate to ruthenium after tautomerization to the pyramidal species $PH(OH)_2$ and $P(OH)_3$, respectively.[10] The above products, which contain one or two phosphorus atoms from the parent P_4 molecule, are clearly the thermodynamic sinks in the degradation of P_4, which appears to follow aspecific pathways.

Herein we report further breakthroughs in this reaction and show that the reactivity of coordinated P_4 is a modular process which, surprisingly, is strongly dependent on the amount of water used for the hydrolysis reaction. In particular, we demonstrate that rapid quenching of the hydrolysis of the dinuclear derivative **2** with a large excess of water affords only phosphorous acid (H_3PO_3) and a new bimetallic compound containing the previously unknown 1-hydroxytriphosphane molecule, which is stabilized as a bridging ligand between two $\{CpRu(PPh_3)_2\}$ fragments (Scheme 1). The formation of this molecule, besides its intrinsic interest due to the fact that it has never been observed previously either in the free state or as a ligand, gives important hints regarding the initial step of the hydrolytic degradation of coordinated P_4 and pinpoints the existence of a selective disproportionation of P_4 that differs from its well-known alkaline hydrolysis, which gives only PH_3 and hypophosphorous acid (H_3PO_2).

The addition of 500 equivalents of water to one equivalent of **2** in THF is a simple process that leads to the formation of one equivalent of H_3PO_3 and one equivalent of the new complex $[\{CpRu(PPh_3)_2\}_2\{\mu^{1:3},\eta^{1:1}\text{-}PH(OH)PHPH_2\}](CF_3SO_3)_2$ (**3**) within a few minutes (^{31}P NMR monitoring). Work-up of this solution gave **3** in excellent yield, and recrystallization from $CHCl_3$/*n*-hexane provided yellow crystals suitable for X-ray analysis.

The diruthenium cation in **3** contains the previously unknown molecule $PH(OH)PHPH_2$, which bridges two $\{CpRu(PPh_3)_2\}$ moieties through the phosphorus atoms of the PH(OH) and PH_2 end-groups. These two groups are affected by twofold positional disorder in the solid-state

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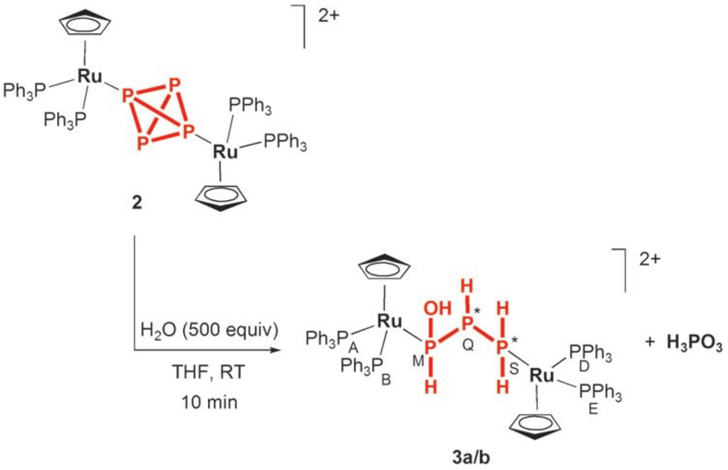

Scheme 1.

structure of **3** since the dimetal cation possesses overall crystallographic mirror symmetry about a plane intersecting the central P atom of the bridging group. Moreover, the position of the hydroxyl oxygen is further split due to co-crystallization of the two diastereoisomers in different ratios. The geometry of one of these diastereoisomers, with the bridging unit arranged according to one of the mirror-related orientations attained in the structure, is shown in Figure 1. Further details of the structure determination procedure can be found in the Supporting Information.

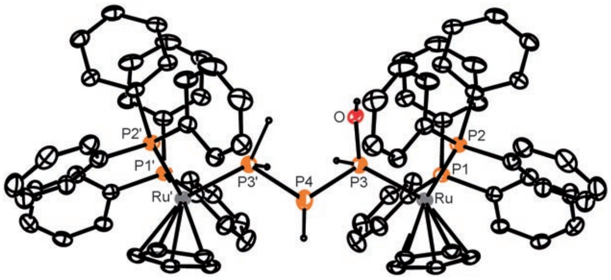

Figure 1. A view of the geometry of the more abundant diastereoisomer of the dimetal cation in the structure of **3** (30% probability thermal ellipsoids). Only one of the mirror-related orientations of the bridging PH(OH)PHPH$_2$ moiety present in the structure is shown. Primed atoms are related to the corresponding unprimed ones by a mirror plane. The hydrogen atoms of the phenyl groups have been omitted for clarity. Selected bond lengths [Å] and angles [°]: Ru–P1 2.348(1), Ru–P2 2.341(1), Ru–P3 2.266(1), P3–P4 2.197(2), P3–O 1.53(1); P1-Ru-P2 100.39(4), P1-Ru-P3 92.89(4), P2-Ru-P3 91.93(4), Ru-P3-P4 115.10(6), P3-P4-P3′ 100.7(1), Ru-P3-P4-P3′ 163.88(6).

The ^{31}P{^{1}H} NMR spectrum of **3** in CD_2Cl_2 (Figure 2) confirms that the solid-state structure is maintained in solution and substantiates the presence of two diastereoisomers in an approximate ratio of 83% (**3a**) to 17% (**3b**). The ^{31}P{^{1}H} NMR spectrum of each diastereoisomer consists of a second-order ABDEMQS spin system (see Scheme 1 for atom labeling). The resonances of the triphosphane phosphorus atoms in these two diastereoisomers exhibit identical patterns and only slightly different chemical shifts (see Experimental Section). The most significant difference concerns the central PH phosphorus atom of the P_3 chain, whose resonance at $\delta = -97.4$ ppm in **3a** is shifted about 20 ppm upfield in **3b** ($\delta = -115.1$ ppm). Inspection of the coupling constants obtained by computer simulation of the ^{31}P{^{1}H} NMR spectra of each diastereoisomer shows the expected high values for $^{1}J_{P,P}$ (approx. 230–250 Hz) and indicates that only the two-bond coupling between the terminal P-atoms of the triphosphane ligand ($^{2}J_{PH(OH),PH_2}$) is markedly different for the two diastereoisomers (47.3 Hz in **3b** and 7.5 Hz in **3a**). This situation likely reflects the different arrangements of the triphosphane substituents in the two species.

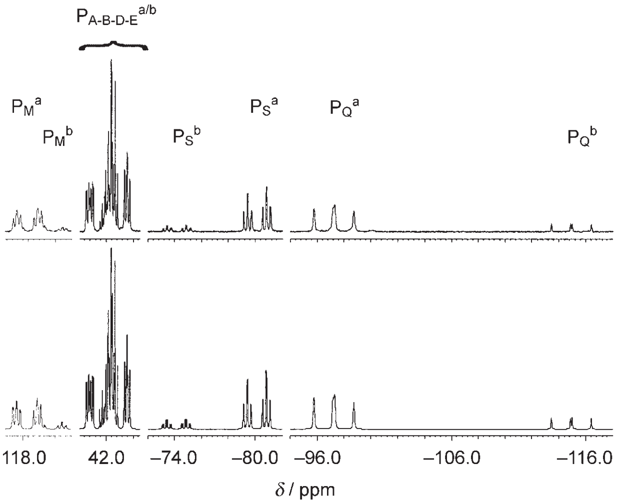

Figure 2. Experimental (top; 161.89 MHz, CD_2Cl_2, 0 °C) and computed (bottom) ^{31}P{^{1}H} NMR spectrum of **3**.

Complex **3** is a yellow microcrystalline material that is stable in the solid state, where it can be manipulated in air without decomposition. Solutions of **3** in halogenated hydrocarbons are stable under an inert atmosphere. The coordinatively stabilized 1-hydroxytriphosphane molecule in **3** belongs to the family of polyphosphane oxides, which are practically unknown as free molecules. To our knowledge, the only report of a compound with the same P_3H_5O formula as that of the present bridging ligand has been provided by Baudler and co-workers, who detected this molecule in the mass spectrum of the volatile products of calcium phosphide hydrolysis.[11]

A relevant feature of the reaction leading to **3** is the complete absence of H_3PO_2 from the reaction products, whereas one equivalent of H_3PO_3 is formed. This finding is mechanistically important as it points to the occurrence of a stoichiometric process in which four molecules of water formally add to the bridging P_4 ligand of **2**. This addition favors a disproportionative redox process where three electrons are removed from the same P-atom of the tetraphosphorus tetrahedron, which is consequently oxidized to H_3PO_3. These three electrons are unequally redistributed among the remaining three P atoms of the P_4 molecule in the simultaneous reduction step of the disproportionation. This process leads to formation of the chain of the 1-hydroxytriphosphane ligand $[P^0H(OH)P^IHP^{II}H_2]$, which is eventually stabilized by double $\mu^{1:3},\eta^{1:1}$-coordination to ruthenium. The reaction transforming **2** into **3** does not therefore resemble the well-known caustic phosphorus hydrolysis that occurs in an alkaline medium, where PH_3 and three equivalents of H_3PO_2 are generated by disproportionation of white phosphorus in a process that consumes six molecules of water. Rather, this reaction should be considered as an alternative hydrolytic disproportionation pathway and not a preliminary step in the conventional P_4 alkaline hydrolysis. In keeping with this latter observation, solutions of **3** in THF do not undergo further hydrolysis when treated with water, irrespective of the amount of water added and the reaction time. It should also be noted that the different reaction pathway followed in the presence of smaller amounts of water (100 equivalents) reaches completion in two hours.

We hope that this peculiar reactivity of coordinated P_4, which contributes to shed more light onto the degradation of P_4 in water, can be exploited in a number of transformations involving organic reagents. Studies are in progress in our laboratories to achieve this goal.

Experimental Section

Preparation of **3**: Distilled water (4.50 mL, 250 mmol) was added to a red THF solution (100 mL) of $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)](CF_3SO_3)_2$ (**2**; 902 mg, 0.50 mmol).[9] The solution was stirred at room temperature in a closed system for 10 min and then the solvent was quickly removed under reduced pressure to yield an orange solid. This solid was dissolved in $CHCl_3$ (20 mL) and the solution extracted with water (2 × 20 mL). The ^1H-decoupled and ^1H-coupled ^{31}P NMR spectra of this aqueous solution showed resonances identical to those of pure H_3PO_3 in the same solvent. The organic phase was dried with Na_2SO_4 and compound **3** was obtained by removing the solvent under reduced pressure (830 mg, 0.46 mmol; yield: 93%). Crystals suitable for X-ray analysis were grown from $CHCl_3$ and *n*-hexane. Elemental analysis (%) calcd for $C_{84}H_{75}F_6O_7P_7Ru_2S_2$ (1793.6): C 56.3, H 4.2, P 12.1; found: C 55.9, H 4.3, P 11.9. IR (NaCl): $\tilde{\nu} = 3055$ (br; ν(O-H)), 2289 (s; ν(P-H)), 2243 cm^{-1} (s; ν(P-H)) $^{31}P\{^1H\}$ NMR (161.89 MHz, CD_2Cl_2, 0 °C): Major diastereoisomer: $\delta = 117.7$ (P_M, $J_{M,Q} = 250.6$, $J_{M,A} = 49.6$, $J_{M,B} = 37.2$, $J_{M,S} = 7.5$ Hz), 43.3 (P_A, $J_{A,B} = 28.6$ Hz), 41.8 (P_D, $J_{D,E} = 29.9$ Hz), 41.5 (P_E), 40.5 (P_B), −80.0 (P_S, $J_{S,D} = 45.0$, $J_{S,E} = 45.0$ Hz), −97.4 ppm (P_Q, $J_{Q,S} = 229.2$, $J_{Q,A} = 9.4$, $J_{Q,B} = 6.2$, $J_{Q,D} = 6.0$ Hz). Minor diastereoisomer: $\delta = 116.4$ (P_M, $J_{M,Q} = 251.7$, $J_{M,S} = 47.3$, $J_{M,A} = 47.8$, $J_{M,B} = 12.4$ Hz), 42.3 (P_A, $J_{A,B} = 28.7$ Hz), 42.1 (P_D, $J_{D,E} = 29.9$ Hz), 41.7 (P_E), 41.6 (P_B), −73.8 (P_S, $J_{S,D} = 47.3$, $J_{S,E} = 14.0$ Hz), −115.1 ppm (P_Q, $J_{Q,S} = 230.7$, $J_{Q,D} = 5.0$, $J_{Q,E} = 2.0$ Hz). Selected ^1H NMR spectroscopic data (400.13 MHz, CD_2Cl_2, 0 °C): Major diastereoisomer: $\delta = 6.34$ (H-P_M, $^1J_{H,P} = 393.2$ Hz), 5.33 (H-P_s, $^1J_{H,P} = 352.5$ Hz), 4.23 (H-P_Q, $^1J_{H,P} = 201.1$ Hz), 3.75 ppm (H-P_S, $^1J_{H,P} = 352.5$, $J = 9.5$, $J = 23.1$ Hz). Minor diastereoisomer: $\delta = 7.31$ (H-P_M, $^1J_{H,P} = 375.4$ Hz), 4.73 (H-P_S, $^1J_{H,P} = 350.5$ Hz), 4.30 (H-P_s, $^1J_{H,P} = 350.5$ Hz), 3.44 ppm (H-P_Q, $^1J_{H,P} = 199.8$ Hz)

Received: February 13, 2008

Keywords: hydrolysis · phosphanes · phosphorus · ruthenium

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