Polyphosphorus Compounds

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Iodine Activation of Coordinated White Phosphorus: Formation and Transformation of 1,3-Dihydride-2-iodidecyclotetraphosphane**

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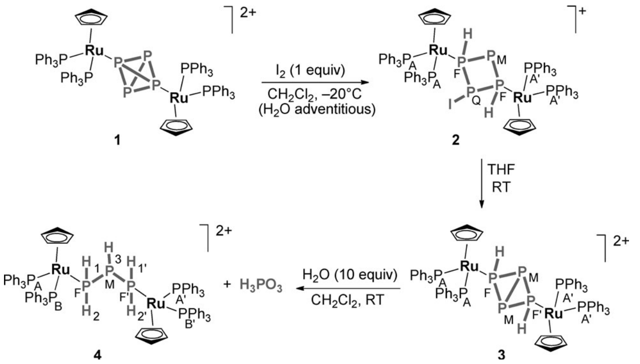
A great number of studies have recently focused on the controlled activation of white phosphorus (P_4) aimed at converting this reactive molecule into valuable organophosphorus compounds through stoichiometric or catalytic reactions. Until now, the activation of P_4 has been achieved by using heterocyclic carbenes,[1] highly nucleophilic main group compounds,[2] or early- and late-transition-metal/ligand fragments.[3] The reactivity patterns provided by the latter class of compounds is particularly intriguing in view of the well-known ability of metal complexes to promote catalytic processes[4] and to support a variety of P_4 transformations, eventually resulting in a myriad of P_n topologies.[3,5]

The intact P_4 molecule may be bound to one[6] or two metal fragments[7] and previous work from our group has shown that, once coordinated, its reactivity is spectacularly modified with respect to the free molecule. Worth recalling is the straightforward reactivity of the coordinated P_4 molecule toward water, thus promoting an easy disproportionation of the tetraphosphorus array at room temperature.[6a,7,9] Remarkably, several compounds have been isolated during the stepwise hydrolytic disassembly of coordinated P_4 by tuning the relative amounts of the reagent complex and water. Thus, compounds that contain one phosphorus atom (PH_3, H_3PO/PH_2OH, $PH(OH)_2/H_3PO_2$, and $P(OH)_3/H_3PO_3$)[6a,8,9] as well as polyphosphorus molecules (P_2H_4,[7] P_3H_4OH,[10] and $P_4H_3(OH)_3$[11]) may be generated and characterized; polyphosphorus products, which are all stabilized through coordination to two metal fragments, are either extremely unstable or even unknown as free molecules.[12]

Herein, we report a so far unknown reactivity of white phosphorus coordinated to two $CpRu(PPh_3)_2$ moieties and show that I_2 adds nucleophilically to the P_4 bridge in dinuclear $[\{CpRu(PPh_3)_2\}_2(\mu,\eta^{1:1}\text{-}P_4)](OTf)_2$ (**1**, $OTf = OSO_2CF_3$) to afford, in the presence of traces of water, the monocation $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2I)]^+$ (**2**, Scheme 1), which contains the unprecedented 1,3-dihydride-2-iodidecyclotetraphosphane anion. Iodide is easily dissociated from compound **2** to give the so far elusive 1,3-dihydride-2,4-bicyclotetraphosphane[1,1,0] (P_4H_2), which is also stabilized through coordination to two ruthenium centers in $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2)](OTf)_2$ (**3**). The doubly coordinated P_4H_2 molecule is still reactive toward water and easily adds three water molecules to give quantitatively the triphosphane (P_3H_5) together with one molecule of phosphorous acid (H_3PO_3). The intriguing triphosphane molecule is stabilized as a bridging ligand in the compound $[\{CpRu(PPh_3)_2\}_2\{\mu^{1:3},\eta^{1:1}\text{-}PH_2PHPH_2\}](OTf)_2$ (**4**).



Scheme 1. Formation of 1,3-dihydride-2-iodidecyclotetraphosphane (**2**) and transformation to **3** and **4**.

Compound **1** reacts rapidly with one equivalent of iodine at −20 °C in CH_2Cl_2 to give a dark-brown solid, which contains the $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2I)]^+$ cation (**2**), circa 50 % with respect to **1** according to $^{31}P\{^1H\}$ NMR monitoring (elemental analysis, NMR, and IR data in the Supporting Information). Although the separation of **2** from the starting material was not trivial, purification including fractional crystallization (see Experimental Section) gave a crystalline material, which was identified as dimetallic $\{[CpRu(PPh_3)_2]_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2I)]\}I_{0.5}(OTf)_{0.5}\cdot 3.2\,CH_2Cl_2$ by single-crystal X-ray diffraction analysis.[13] In the crystal of **2**, the charge of the monocation $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2I)]^+$ (Figure 1) is counterbalanced by triflate and iodide anions (50 % each), and the lattice also contains co-crystallized CH_2Cl_2 solvent molecules.

The diruthenium assembly in **2** stabilizes the previously unknown $P_4H_2I^-$ anion (folding angle 130.1(2)°), which bridges two $CpRu(PPh_3)_2$ moieties through the hydrogenated phosphorus atoms; the anion assumes a chair-type conformation with the iodine atom positioned *trans* with respect to both ruthenium atoms and the naked P6 atom (Figure 1). The P–I bond distance is within the range that is usually observed.[14] The solid-state structure of **2** is maintained in CD_2Cl_2

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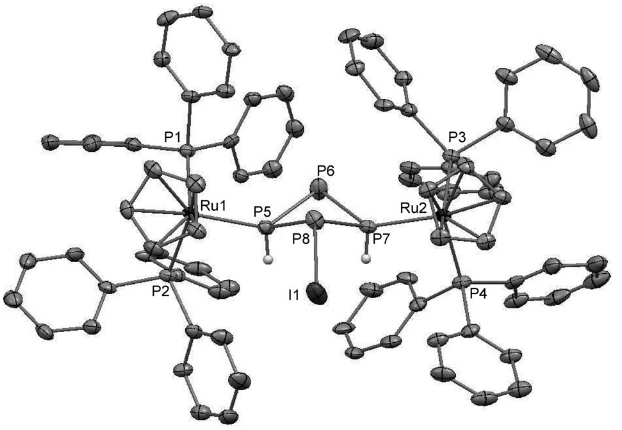

Figure 1. Geometry of the dimetallic cationic complex in **2** with 30% probability thermal ellipsoids. Hydrogen atoms of the ancillary PPh_3 and Cp ligands are omitted for clarity. Selected bond lengths [Å]: Ru1–P1 2.369(2), Ru1–P2 2.347(2), Ru1–P5 2.259(3), Ru2–P3 2.349(2), Ru2–P4 2.358(2), Ru2–P7 2.261(3), P5–P6 2.224(4), P5–P8 2.238(4), P6–P7 2.218(4), P7–P8 2.208(4), P8–I1 2.474(3), P5···P7 2.977(8), P6···P8 2.996(4).

solution, as confirmed by the $^{31}P\{^1H\}$ NMR spectrum, which shows four broad resonances centred at $\delta = 40.0$, 16.3, -5.0, and -49.5 ppm (integration 4:2:1:1), which do not resolve on lowering the temperature to -90°C. While the low-field signal is typical of $CpRu(PPh_3)_2$ phosphines,[6–11] the remaining three sets of resonances are assigned to the tetraphosphorus $P_4H_2I^-$ unit. The lower-field signal (br ddt, $^1J_{P\text{-}P} = 152$ Hz, $^1J_{P\text{-}P} = 160$ Hz and $^2J_{P\text{-}P} = 45$ Hz), which doubles in the ^{1}H-coupled spectrum ($^1J_{P\text{-}H}$ 185 Hz), may be safely assigned to the hydrogenated phosphorus atoms. The remaining resonances appear as a large singlet and a broad triplet ($^1J_{P\text{-}P} = 150.0$ Hz), and are ascribed to the substituted and the naked P-atoms of the $P_4H_2I^-$ unit, respectively. The formation of **2** also takes place when the reaction is run in dry CD_2Cl_2, thus ruling out the solvent as source of hydrogen atoms, which is accordingly provided by adventitious water. CD_2Cl_2 with traces of D_2O affords the perdeuterated analogue [D_2]-**2**, thus supporting this hypothesis.

In polar solvents, iodide is dissociated from complex **2** to give the new complex $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2)](OTf)_2$ (**3**), which shows a $^{31}P\{^1H\}$ NMR splitting pattern that fully correlates with the simulated $A_2A'_2FF'M_2$ spin system (Figure 2). The two PH phosphorus atoms of the P_4H_2 molecule exhibit chemical shifts ($\delta_{PF} = 11.4$ ppm) in the region typical for coordinated PH groups of PH(OH)PHPH-$P(OH)_2$,[11] while the two uncoordinated P atoms appear at high field ($\delta_{PM} = -297.3$ ppm).[2a,15]

Despite numerous attempts, crystallization of **3** never gave a pure compound, but provided a solid solution of $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2)](OTf)_2$ (**3**) and $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_3H_5)](OTf)_2$ (**4**, see below) in variable ratios; in the crystal that was found more useful for X-ray analysis, the two species are in a molar ratio of 1:2 (Figure 3). The most significant difference between the two cations consists in the bidentate ligand tethering the two $CpRu(PPh_3)_2$ fragments, that is, 1,3-dihydride-2,4-cyclotetraphosphane[1,1,0] (P_4H_2) in **3** and triphosphane (P_3H_5) in **4** (see below). The 1,3-dihydride-2,4-bicyclotetraphosphane[1.1.0] molecule is coordinated to the two $CpRu(PPh_3)_2$ units through the hydrogenated phosphorus atoms (Figure 3). The coordination geometry is very similar to that of the parent $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4)]^{2+}$ cation.[7] The cyclic P_4H_2 molecule shows a butterfly arrangement, with the angle between the P triangles being 100.3(2)° and a P–P separation between the uncoordinated P atoms of 2.312(6) Å, which is longer than those reported for the few bicyclotetraphosphane species described until now.[15]

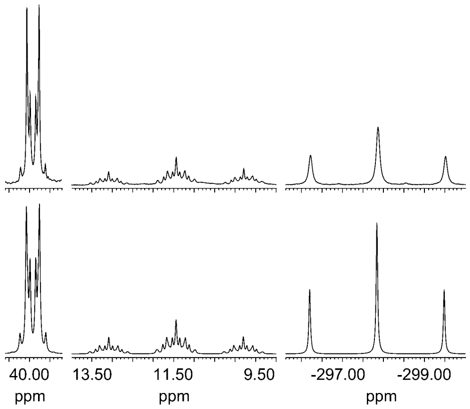

Figure 2. Experimental (top; 161.89 MHz, CD_2Cl_2, 0°C) and computed (bottom) $^{31}P\{^1H\}$ NMR spectrum of **3**.

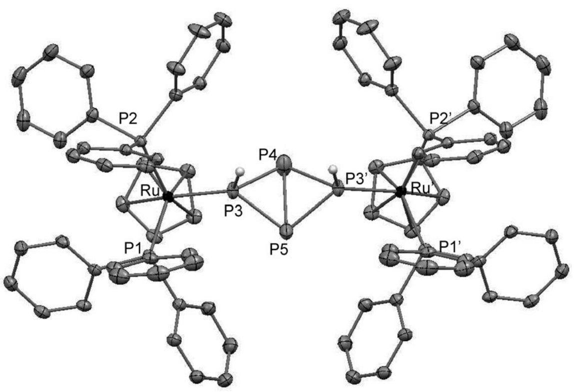

Figure 3. Geometry of the dimetallic cationic complex in **3** in the crystal structure of the solid solution of $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_4H_2)](OTf)_2$ (**3**) and $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_3H_5)](OTf)_2$ (**4**) in a molar ratio of 1:2 with 30% probability thermal ellipsoids. Primed atoms are related to the corresponding unprimed ones by a mirror plane. Hydrogen atoms of phenyl groups and Cp ligands are omitted for clarity. Selected bond lengths [Å]: Ru–P1 2.3404(8), Ru–P2 2.3411(8), Ru–P3 2.2731(8), P3–P4 2.163(2), P3–P5 2.121(3), P4–P5 2.312(6), P3···P3′ 3.322(1).

Generally, these sparse examples of P_4R_2 molecules contain bulky substituents that sterically protect the bicyclotetraphosphane core. Alkaline salts[16a] and rhodium complexes[16b,c] of the anion HP_4^- were described, but the neutral tetraphosphorus dihydride P_4H_2 has only been observed by mass spectrometry.[12,17]

Although sandwiched between two $CpRu(PPh_3)_2$ moieties, the coordinated P_4H_2 molecule is quite reactive and solutions of **3** in the presence of a small amount of water undergo hydrolytic disproportionation within a few minutes (^{31}P NMR monitoring) to give quantitatively complex $[\{CpRu(PPh_3)_2\}_2(\mu^{1:3},\eta^{1:1}\text{-}P_3H_5)](OTf)_2$ (**4**) and phosphorous acid (H_3PO_3; Scheme 1). Workup of the solution and crystallization from $CHCl_3/C_6H_6$ provided **4** as yellow crystals, suitable for X-ray analysis, which shows a fully hydrogenated triphosphane molecule (P_3H_5) bridging the two metal ends (Figure 4).

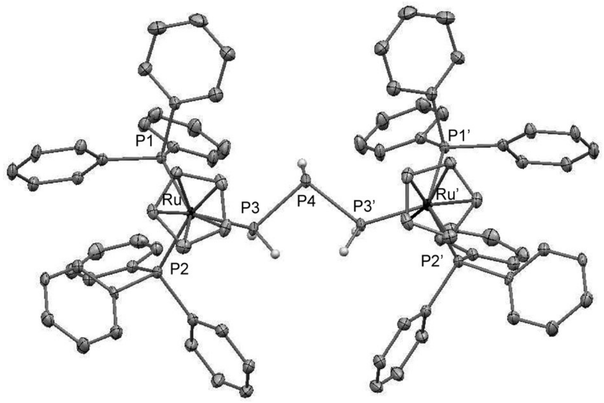

Figure 4. Geometry of the dimetallic cationic complex in **4** with 30% probability thermal ellipsoids. Primed atoms are related to the corresponding unprimed ones by a mirror plane. Hydrogen atoms of phenyl and cyclopentadienyl groups are omitted for clarity. Selected bond lengths [Å]: Ru–P1 2.354(1), Ru–P2 2.341(1), Ru–P3 2.275(1), P3–P4 2.197(2).

The previously unknown PH_2PHPH_2 molecule shows P–P bond lengths ($d_{P\text{-}P} = 2.22(2)$ Å)[14] typical for P–P single bonds in an acyclic phosphorus chain, while the P3-P4-P3′ angle (99.18(5)°) is near the lower end of the 90°–120° range found for bond angles in acyclic phosphorus chains.[7,10,11] The ^{31}P{^{1}H} NMR spectrum of **4** (Figure 5), which fully correlates with a simulated ABA′B′FF′M spin system (Scheme 1 for atom labelling), confirms that the solid-state structure is maintained in solution. Inconsistent with the standard hydrolysis of **1**, the hydrolytic degradation of the P_4 tetrahedron mediated by iodine does not include the formation of hydroxypolyphosphane species,[18] thus suggesting that a different hydrolytic mechanism might be operative.

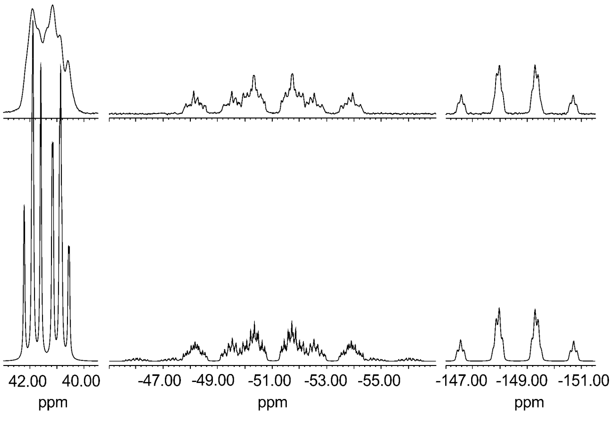

Figure 5. Experimental (top; 161.89 MHz, CD_2Cl_2, 0 °C) and computed (bottom) ^{31}P{^{1}H} NMR spectrum of **4**.

In conclusion, we have shown that the nucleophilic addition of I_2 to dicationic compound **1** activates the coordinated P_4 molecule, which easily undergoes hydrogenation from adventitious water without disruption of the P_4 frame. This result and the following reactions of the $P_4H_2I^-$ derivative, resulting in the high-yielding generation of the so far elusive P_4H_2 and P_3H_5 molecules, highlight the significance of a stable metal coordination of P_4 to bring about controlled transformations of the phosphorus molecule. The scope of this approach was further extended by the interception and characterization of new polyphosphane molecules, such as P_4H_2 and P_3H_5, which are practically unknown in the free state. Although most of the current research in the area of white phosphorus is driven by the tantalizing possibility to catalytically assemble P–C bonds from P_4, there is no doubt that the metal-mediated conversion of white phosphorus into valuable hydrogenated polyphosphanes (P_xH_y) is also an intriguing process, both from a fundamental viewpoint and with regard to possible synthetic applications related to the direct functionalization of P–H bonds. The presented chemistry, although still in its infancy, may open intriguing perspectives in this regard.

Experimental Section

2: I_2 (127 mg, 0.50 mmol) in CH_2Cl_2 (10 mL) was added to a solution of **1** (902 mg, 0.50 mmol) in CH_2Cl_2 (30 mL) at −20 °C. The solution was stirred for 10 min, then the solvent was quickly removed under reduced pressure to give a brown solid, which was recrystallized from CH_2Cl_2/*n*-hexane to give product **2** in 50% yield (450 mg).

3: **2** (450 mg, 0.25 mmol) was dissolved in a solution of NaOTf (50 mg, 0.30 mmol) in THF (30 mL) and the mixture was stirred for 30 min, during which time pure compound **3** precipitated as a yellow solid in 70% yield (310 mg).

4: A few drops of water were added to a stirred solution of **3** (310 mg, 0.17 mmol) in CH_2Cl_2 (30 mL), the slurry was stirred at room temperature for 15 min before the solvent was removed under reduced pressure to give **4** as a yellow solid in 93% yield (370 mg). Crystals suitable for X-ray analysis were grown from $CHCl_3/C_6H_6$.

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