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Reaction of $[(PPh_3)_3RuCl_2]$ with white phosphorus: synthesis of the first Ru^{II} complex featuring a *tetrahedro*-tetraphosphorus ligand

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The title reaction affords slightly air- and light-sensitive $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(PPh_3)_2(\eta^1\text{-}P_4)]$, which belongs to a very rare family of soluble *tetrahedro*-tetraphosphorus complexes and represents the first ruthenium species of this type.

White phosphorus, which exhibits an unique structure formed by tetrahedral P_4 molecules, is the principal material used for the industrial preparation of organophosphorus compounds. These compounds are of commercial interest and are produced in megaton amounts as fertilizers, pesticides, detergents, additives for lubricants in polymers, metal extractants in nuclear industry, flame retardants for plastic materials *etc.*[1]

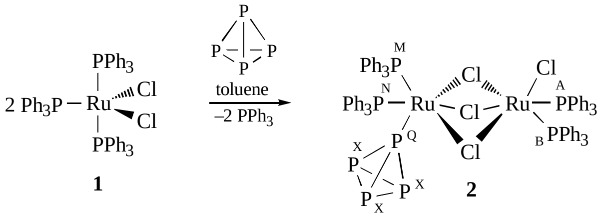
Presently, the industrial use of white phosphorus is based on the preliminary transformation of P_4 to PCl_3 by a reaction with chlorine. The chlorination step causes serious environmental problems due to the emission of large amounts of HCl into the atmosphere. For this reason, it is environmentally important to develop a cleaner process for the preparation of organophosphorus derivatives with comparable or reduced costs. An interesting alternative to the current technology may be catalytic activation and functionalisation of P_4 by transition metal complexes.[2] To successfully accomplish this goal, a deeper knowledge of the co-ordination chemistry of the P_4 molecule with transition metals is required.

One of the most largely employed homogeneous catalyst is $[(PPh_3)_3RuCl_2]$ **1**.[3] Therefore, we believed that this ruthenium derivative and related complexes can also be useful materials to study the catalytic functionalisation of white phosphorus. Despite the vast literature concerning P_4 as a source of P_x ligands in transition metal complexes,[4] the reaction of P_4 with **1** was not yet studied, and the number of ruthenium complexes featuring polyphosphorus units is also very limited.[5]

Here, we report on our preliminary studies in the reaction of white phosphorus with **1**, which, to the best of our knowledge, leads to the synthesis of the first ruthenium complex supporting an intact P_4 ligand.[6]

When a solution of white phosphorus in dry and deoxygenated toluene is added to one equivalent of **1** dissolved in the same solvent, a dark brown solution forms within 15 min on standing at room temperature.† From this solution, reddish-brown microcrystals of binuclear ruthenium species $[(PPh_3)_2ClRu(\mu\text{-}Cl)_3Ru(PPh_3)_2(\eta^1\text{-}P_4)]$ **2** are obtained after layering with *n*-hexane. Release of two equivalents of PPh_3 into the solution (^{31}P NMR detected) accompanies the formation of the binuclear complex. Changing the ratio between **1** and P_4 does not modify the course of the reaction, and even when a tenfold excess of white phosphorus is used only **2** forms.

Solutions of **2** in organic solvents are unstable (air- and light-sensitive). A slow decomposition takes place, even under nitrogen, at room temperature to afford a brown precipitate, which is almost insoluble in all common organic solvents and cannot be further characterised. However, once generated from **1** and P_4, the stability of **2** in toluene at room temperature is enough to allow the characterization of **2** by variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy and then to propose a reliable structure for this unusual complex in solution.



The $^{31}P\{^1H\}$ NMR spectrum of **2** (Figure 1) displays a temperature-dependent $ABMNQX_3$ spin system with a strong coupling between the nuclei Q and X ($^1J_{QX}$ = 230.7 Hz, T = –30 °C) and less intense couplings between the other P nuclei. An analysis of both coupling constants and chemical shifts suggests that the P_4 molecule is η^1-coordinated to one ruthenium atom, with *cis*-disposed PPh_3 ligands. The signals due to the naked phosphorus atoms, P_Q and P_X, are practically temperature invariant in the temperature range examined (from –80 to 40 °C), indicating that the P_4 molecule coordinated to Ru is freely rotating in solution. The two P resonances originating from the P_4 ligand appear at very high fields (δ_Q –320.61, δ_X –472.43) and exhibit a large 'coordination-chemical shift', [$\Delta = \delta_{P_{coord}} - \delta_{P_4\,free}$], in comparison with the free P_4 molecule by approximately 53 (P_X) and 205 ppm (P_Q), respectively. The Δ value experienced by P_Q atom indicates that the Ru-bonded P atom is electronically perturbed upon coordination. Noticeably, the low-field shift of the P_Q atom in **2** is larger than that observed for the corresponding metal-coordinated P atoms in the other two known complexes featuring a *tetrahedro*-P_4 ligand. Thus, $[(triphos)Re(CO)_2(\eta^1\text{-}P_4)]^+$ shows a coordinated P atom at –390.5 ppm (Δ = 136.4 ppm) [triphos = $MeC(CH_2PPh_2)_3$],[6(*c*)] while in the tungsten complex $[(CO)_3(PPh_3)W(\eta^1\text{-}P_4)]$, the metal-coordinated P atom resonates at –422.0 ppm (Δ = 104.9 ppm).[6(*b*)] The high Δ value for P_Q in **2** suggests that the coordinated P_4 ligand should exhibit an enhanced reactivity towards nucleophiles with respect to the free molecule and then makes such a species amenable to testing as a promoter of alcohol phosphorylation reactions. The theoretical modelling of the catalytic oxidative phosphorylation of methanol with white phosphorus indicates that the formation of an η^1-P_4 complex is a necessary prerequisite to accomplish the P–O bond-forming step.[7]

The binuclear structure of **2** was confirmed by computer simulation of the eight-nuclei spin system.‡ The proposed struc-

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† *Synthesis of* **2**: an excess of white phosphorus (0.13 g, 1.09 mmol) was added to a stirred solution of **1** (0.96 g, 1.0 mmol) in dry toluene (10 ml) under nitrogen. After 20 min, the dark brown solution was layered with *n*-hexane (10 ml) and cooled at 0 °C. The reddish-brown microcrystals of **2** were separated by filtration under nitrogen, washed with *n*-hexane and dried in a brisk stream of nitrogen. Yield 40%. $^{31}P\{^1H\}$ NMR (–30 °C, [$^2H_8$]toluene, 81.01 MHz, reference 85% H_3PO_4), $ABMNQX_3$ spin system: δ_A 51.83, δ_B 47.54, δ_M 40.15, δ_N 39.69, δ_Q –320.61, δ_X –472.43, ($^1J_{QX}$ = 230.7 Hz, $^2J_{MQ}$ = 41.2 Hz, $^2J_{AB}$ = 37.8 Hz, $^2J_{NQ}$ = 29.0 Hz, $^2J_{MN}$ = 27.5 Hz, $^4J_{BQ}$ = 5.6 Hz). The assignment of the phosphorus network has been confirmed by the $^{31}P,^{31}P$-COSY 2D-NMR spectrum. Found (%): C, 56.43; H, 4.16; Cl, 9.02; P, 16.84. Calc. for $C_{72}H_{60}Cl_4P_8Ru_2$ (%): C, 57.01; H, 3.99; Cl, 9.35; P, 16.33.

‡ The computer simulation of the $^{31}P\{^1H\}$ NMR spectrum was carried out with the SCANDAL program, developed by A. Vacca (University of Florence, Italy) and J. A. Ramirez (University of Valencia, Spain). The initial choices of shifts and coupling constants were refined by iterative least-squares calculations using the experimental digitised spectrum. The final parameters gave a satisfactory fit between experimental and calculated spectra, the agreement factor being less than 1% in all cases.

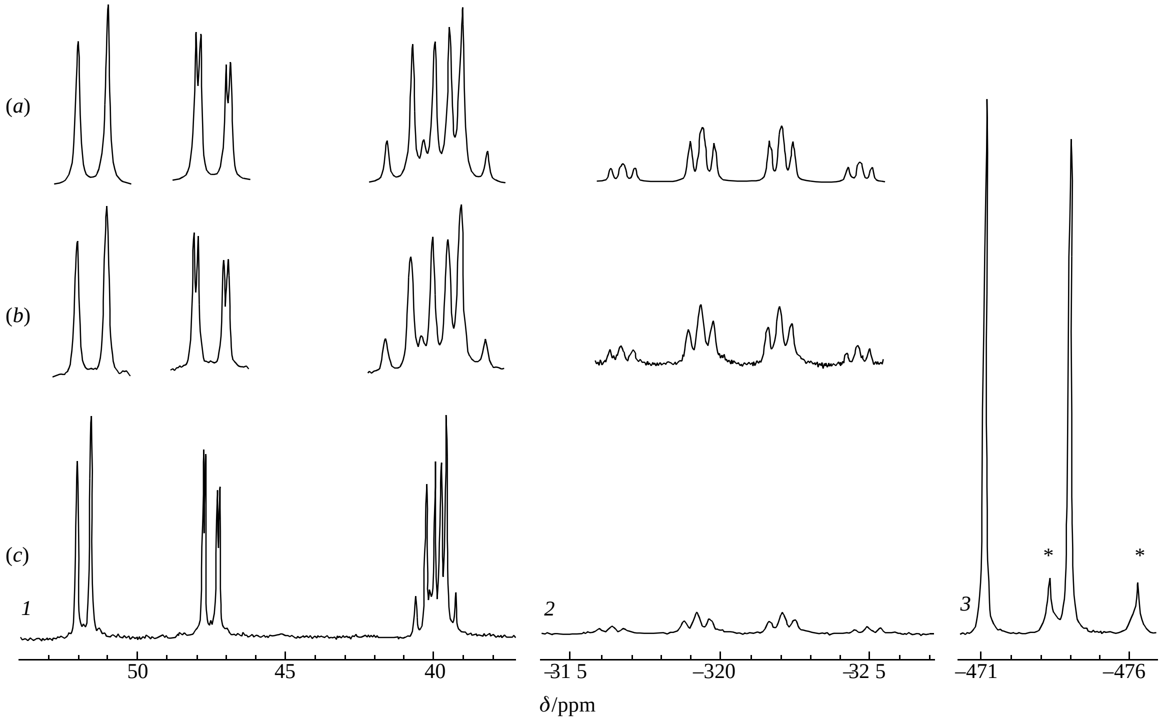

Figure 1 (*a*) Computed and (*b*), (*c*) experimental $^{31}P\{^1H\}$ NMR spectra of **2** in [$^2H_8$]toluene at –30 °C. ABMNQX_3 system; *1* refers to the PPh_3 resonances (AB and MN components), *2* and *3* denote the resonances due to the ruthenium-coordinated P atom (Q) and the three equivalent basal (X_3) P nuclei of the P_4 ligand, respectively. Signals of a secondary product, likely an isomer of **2**, are indicated by asterisks.

ture entails a binuclear system with two ruthenium atoms experiencing different coordination environments imposed by the presence of the unique P_4 ligand. The ruthenium atom bearing the *tetrahedro*-P_4 ligand is at the centre of an octahedron with the coordination polyhedron completed by three bridging chlorides and two *cis* PPh_3 ligands forming the strongly perturbed second-order MN part of the experimental splitting pattern. The remaining metal atom, more far away from the P_4 molecule, is also hexacoordinate by two *cis* phosphines, which form a slightly perturbed AB spin system at relatively lower fields, and by four chloride ligands, three of which are in bridging positions. The long-range coupling between P_B and P_Q ($^4J_{QB}$ = 5.6 Hz) agrees with the proposed binuclear structure. Binuclear complexes are ubiquitous among Ru^{II}-phosphine complexes,[8] and among them a number of asymmetric face-sharing bioctahedral complexes with three bridging halides have also been reported.[9]

Although variable-temperature $^{31}P\{^1H\}$ NMR spectroscopy and 2D-exchange spectroscopy (at 20 °C) do not indicate any intermetallic exchange between the two pairs of PPh_3, a dynamic process scrambling the two phosphines coordinated to each metallic site (intrametallic exchange) takes place slightly over –15 °C. However, the fast-exchange limit of the spectrum could not be reached as extensive decomposition of **2** occurs just over room temperature to form an intractable brown precipitate.

Studies are in progress in our laboratories aimed at either extending the number of *tetrahedro*-P_4 complexes to other ruthenium precursors or investigating the reactivity of the Ru-coordinated P_4 ligand. Studies on the latter topic are important because ruthenium complexes can cause the catalytic conversion of white phosphorus and organic substrates to organophosphorus derivatives.[10]

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