Dalton
www.rsc.org/dalton

Easy hydrolysis of white phosphorus coordinated to ruthenium

Massimo Di Vaira,[a] Piero Frediani,[b] Stefano Seniori Costantini,[a] Maurizio Peruzzini[c] and Piero Stoppioni*[a]

[a] *Dipartimento di Chimica, Università di Firenze, via della Lastruccia n. 3, 50019, Sesto Fiorentino, Firenze, Italy. E-mail: piero.stoppioni@unifi.it*
[b] *Dipartimento di Chimica Organica "Ugo Schiff", Università di Firenze, via della Lastruccia n. 13, 50019, Sesto Fiorentino, Firenze, Italy. E-mail: piero.frediani@unifi.it*
[c] *ICCOM CNR, Via Madonna del Piano, snc, 50019, Sesto Fiorentino, Firenze, Italy. E-mail: mperuzzini@iccom.cnr.it*

Received 6th April 2005, Accepted 19th May 2005
First published as an Advance Article on the web 31st May 2005

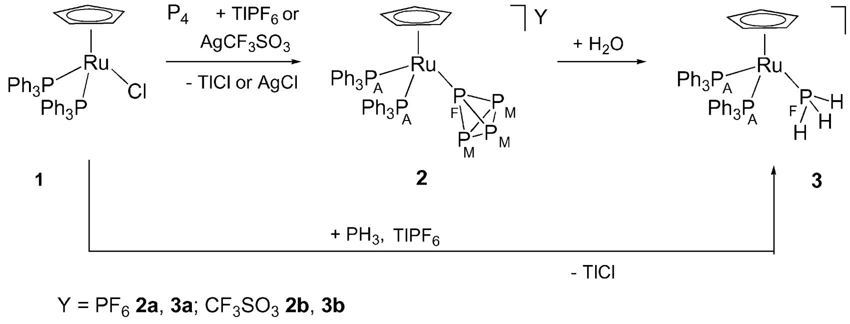
The P_4 molecule bound to ruthenium as an η^1-ligand in $[CpRu(PPh_3)_2(\eta^1\text{-}P_4)]Y$ (Y = PF_6, CF_3SO_3) undergoes an easy reaction with water in exceedingly mild conditions to yield PH_3, which remains coordinated to the $[CpRu(PPh_3)_2]$ fragment, and oxygenated derivatives.

In recent years the chemistry of white phosphorus in the presence of transition-metal fragments has been widely investigated and many compounds containing P_x units originating either from the degradation of the P_4 tetrahedron or reaggregation of fragments thereof have been synthesized and characterized.[1] The compounds, besides having unique geometric and electronic properties,[2] have also been found to be useful building blocks for networks of inorganic coordination compounds.[3] Previous studies have shown that it is easier to cleave bond(s) of the cage than attaining coordination by the intact P_4 molecule.[2,4] Indeed, until some years ago, only a few compounds, thermally unstable and difficult to handle, containing the intact molecule had been described.[5,6] Accordingly, the reactivity of the coordinated molecule had not been investigated. Recently rhenium,[7] iron[8] and ruthenium[8] complexes containing the intact P_4 molecule bound to the metal have been described. These *tetrahedro*-tetraphosphorus complexes are readily obtained and possess stability and solubility properties that make them suitable as starting materials for investigating the reactivity of the coordinated P_4 molecule and comparing the chemistry of the coordinated ligand with the free, highly reactive, molecule. Such a topic is of particular interest in view of the central role of the P_4 molecule in the synthesis of organophosphorus derivatives.[9] The P_4 allotrope, which is activated only in harsh conditions,[10] is in fact the starting material for the production of a large variety of organophosphorus compounds which rival the chemistry of carbon in terms of complexity and applications.[9]

Herein, we describe the synthesis and characterization of new tetraphosphorus complexes $[CpRu(PPh_3)_2(\eta^1\text{-}P_4)]Y$ (Y = PF_6 **2a**, CF_3SO_3 **2b**) and report on the *astonishing hydrolysis* of the coordinated tetraphosphorus molecule, which takes place under exceedingly mild conditions to yield one equivalent of the phosphine complexes $[CpRu(PPh_3)_2(PH_3)]Y$ (Y = PF_6 **3a**, CF_3SO_3 **3b**).

Reaction of $[CpRu(PPh_3)_2Cl]$ (**1**) under argon in CH_2Cl_2–THF with one equivalent of P_4 in the presence of chloride scavengers ($TlPF_6$ or $AgCF_3SO_3$), leads to precipitation of TlCl or AgCl and coordination of the P_4 molecule (Scheme 1) to yield the orange $[CpRu(PPh_3)_2(\eta^1\text{-}P_4)]Y$ complexes in excellent yield (>95%).† The compounds exhibit an exceptional stability in comparison to the few known η^1-P_4 derivatives[5,6] as well as to the free phosphorus molecule and, in this regard, they behave as the related Cp* analogous derivatives.[8] The P_4 molecule remains firmly coordinated to the metal in solution yielding a temperature-invariant and anion independent first-order A_2FM_3 spin pattern in the ^{31}P NMR spectra. The four phosphorus atoms of the cage yield the FM_3 part of the spectrum with the P_F atom coordinated to the metal featuring a quartet of triplets, due to the coupling to P_M and P_A, respectively, significantly shifted downfield with respect to the signal of the free P_4 (δ −526.9 ppm); the three naked P atoms yield a doublet at −487.0 ppm. The chemical shift of the naked P_M atoms is similar to that shown by $[Cp^*Ru(dppe)(\eta^1\text{-}P_4)]BPh_4$, whereas the signal of the coordinated phosphorus (δ −348.2) is shifted at lower frequency with respect to that of the Cp* derivative (δ −308.46).[8] The X-ray structure of the complex cation in **2a** is shown in Fig. 1.‡ The P–P distances formed by the coordinating phosphorus atom are consistently shorter by an average of 0.043 Å than those among the distal P atoms, similarly to what has been found for the $[Cp^*Fe(dppe)(\eta^1\text{-}P_4)]^+$ cation[8] and, to a lesser extent, for the $[W(CO)_3(PCy_3)_2(\eta^1\text{-}P_4)]$ complex.[6]

When a solution of **2a** or **2b** in acetone or THF is treated with excess water (1 : 100), unexpected hydrolysis of the P_4 ligand occurs at room temperature, affording $[CpRu(PPh_3)_2(PH_3)]Y$ (Y = PF_6 **3a**, CF_3SO_3 **3b**) in substantially quantitative ruthenium yield within 1 h.§ The reaction, intriguing in view of the well known stability of elemental phosphorus in water, is promoted by subtle changes in the properties of the metal fragment from those of $[Cp^*Ru(dppe)(\eta^1\text{-}P_4)]PF_6$, whose solutions are indefinitely stable at room temperature in the presence of water.[8]



Scheme 1

DOI: 10.1039/b504795a

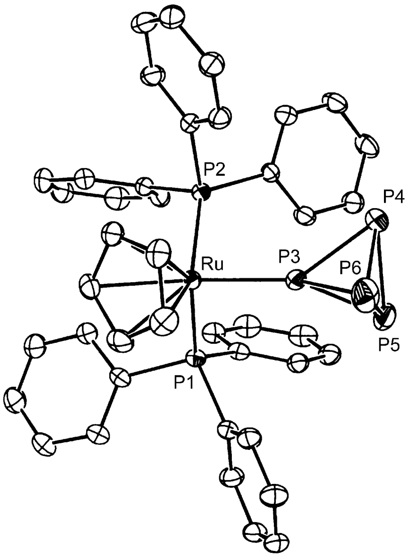


Fig. 1 View of the [CpRu(PPh$_3$)$_2$(η^1-P$_4$)]$^+$ cation in **2a**. In this and the following ORTEP diagram thermal ellipsoids are at the 20% probability level and hydrogen atoms are not shown for clarity. Selected bond lengths (Å) and angles (°): Ru–P1 2.364(1), Ru–P2 2.360(1), Ru–P3 2.269(2), P3–P4 2.154(2), P3–P5 2.145(2), P3–P6 2.141(2), P4–P5 2.180(2), P4–P6 2.200(3), P5–P6 2.189(3); P1–Ru–P2 104.54(4), P1–Ru–P3 94.70(5), P2–Ru–P3 90.10(5).

The single P-atom hydrogenation leading to **3a** and **3b** is accompanied (as revealed by NMR in solution) by formation of H$_3$PO$_3$ (*ca.* 100% with respect to **3a** or **3b**), while the rest of the P$_4$ atoms yield a red solid of difficult characterization, featuring a broad ^{31}P NMR resonance at *ca.* 43 ppm in CD$_2$Cl$_2$. The nature of this solid, which contains hydrogen, phosphorus and oxygen in a *ca.* 1 : 1 : 2.5 ratio, according to XPS and elemental analysis, has not been clarified by mass spectrometry and variable-temperature 1D- and 2D-NMR measurements. The strict similarity in reactivity of **2a** and **2b** rules out any involvement of the anion in the hydrolysis. Complexes **3a** and **3b** represent rare examples of metal PH$_3$ derivatives.[11–17] A view of the complex cation [CpRu(PPh$_3$)$_2$(PH$_3$)]$^+$, which was authenticated by X-ray diffraction analysis,‡ is reported in Fig. 2. The 2.283(1) Å Ru–P(PH$_3$) distance in **3a** is at the low end of the 2.25–2.49 Å range of values found for distances formed by the PH$_3$ ligand with various metal atoms. The P–H distance in **3a** of 1.27(2) Å is at the short end of the range of P–H distances recently reported (1.3–1.5 Å).[15–17]

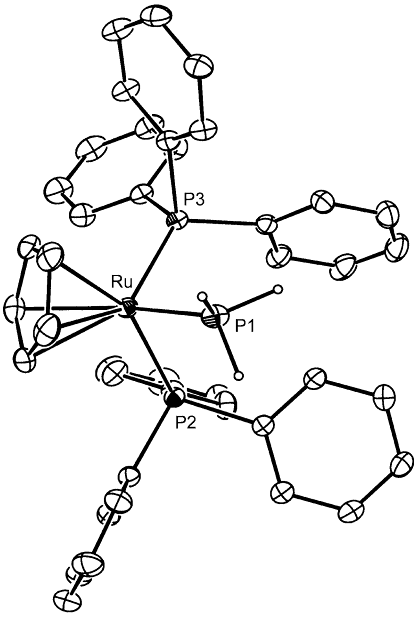


Fig. 2 Structure of the [CpRu(PPh$_3$)$_2$(PH$_3$)]$^+$ cation in **3a**. Selected bond lengths (Å) and angles (°): Ru–P1 2.283(1), Ru–P2 2.357(1), Ru–P3 2.335(1), P1–H 1.27(2); P1–Ru–P2 90.53(3), P1–Ru–P3 95.43(3), P2–Ru–P3 100.59(3), H–P1–H 94(2).

Complex **3a** may be independently synthesized in almost quantitative yield by reaction of **1** in THF with gaseous PH$_3$ in the presence of TlPF$_6$.¶

Studies are in progress to highlight the reaction mechanism, the nature of the red solid accompanying the formation of **3a** and **3b**, and the scope of this surprising reaction, by extending the reactivity studies of **2a** and **2b** towards other nucleophiles. In this respect, preliminary tests confirm that methanol and other simple reagents may also easily react with coordinated P$_4$, thus paving the way to still unexplored paths of phosphorus chemistry.

Notes and references

† A solution of [CpRu(PPh$_3$)$_2$Cl] (**1**) (2.00 g, 2.75 mmol) and TlPF$_6$ (960 mg, 2.75 mmol) in a mixture of CH$_2$Cl$_2$ (90 cm^3) and THF (140 cm^3) was added at room temperature to a solution of white phosphorus (380 mg, 3.07 mmol) in THF (30 cm^3) under argon. The resulting slurry was stirred at room temperature for 4 h; the precipitated TlCl was filtered off and [CpRu(PPh$_3$)$_2$(η^1-P$_4$)]PF$_6$ **2a** was obtained as orange microcrystals by evaporating the solvent under reduced pressure (2.50 g, 95%). The solid was recrystallized from CH$_2$Cl$_2$–hexane (Found: C 51.3; H, 3.8. C$_{41}$H$_{35}$F$_6$P$_7$Ru requires C 51.3; H 3.7%). **2b** was obtained through the same procedure as **2a** using AgCF$_3$SO$_3$ as chloride scavenger (Found: C 52.1; H, 3.9. C$_{42}$H$_{35}$F$_3$O$_3$P$_6$RuS requires C 52.3; H 3.7%). δ_P (121.5 MHz, (CD$_3$)$_2$CO, 25 °C, 85% H$_3$PO$_4$; complex cation A$_2$FM$_3$ pattern) 39.0 (2P, d, ^2J(P$_A$P$_F$) 64 Hz, P$_A$), −348.2 (1P, tq, ^1J(P$_F$P$_M$) 235 Hz, P$_F$), −487.0 (3P, d, P$_M$), −143.10 (1P, sept, ^1J(PF) 714 Hz, PF$_6$, only for **2a**). δ_H (300.0 MHz, (CD$_3$)$_2$CO, 25 °C, TMS) 7.60–7.10 (30H, m, Ph), 5.04 (5H, s, Cp).

‡ *Crystal data*: **2a**: C$_{41}$H$_{35}$F$_6$P$_7$Ru, M = 959.55, monoclinic, space group $P2_1/c$, a = 11.611(5), b = 14.619(4), c = 24.489(5) Å, β = 94.95(3)°, U = 4141(2) Å^3, Z = 4, T = 293 K, μ(Mo-Kα) = 0.706 mm^{-1}. 28874 reflections collected, 11949 unique, 6783 ($I > 2\sigma_I$), R_{int} = 0.033. Final residual was R_1 = 0.067 for data with $I > 2\sigma_I$ and wR_2 = 0.203 for all data. **3a**: C$_{41}$H$_{38}$F$_6$P$_4$Ru, M = 869.66, monoclinic, space group $P2_1/c$, a = 10.107(1), b = 18.603(2), c = 20.228(3) Å, β = 95.95(3)°, U = 3782.8(8) Å^3, Z = 4, T = 293 K, μ(Mo-Kα) = 0.643 mm^{-1}. 31410 reflections collected, 12180 unique, 8354 ($I > 2\sigma_I$), R_{int} = 0.024. PH$_3$ H atom positions refined with one constraint. Final residual was R_1 = 0.055 for data with $I > 2\sigma_I$ and wR_2 = 0.173 for all data. CCDC reference numbers 262402 (**2a**) and 262404 (**3a**). See http://www.rsc.org/suppdata/dt/b5/b504795a/ for crystallographic data in CIF or other electronic format.

§ Distilled water (1.08 g, 60 mmol) was added to a solution of [CpRu(PPh$_3$)$_2$(η^1-P$_4$)]PF$_6$ **2a** (576 mg, 0.60 mmol) in THF or acetone (50 cm^3) and the solution was stirred at room temperature for 2 h under argon. The solvent was removed under reduced pressure and the remaining red solid was extracted twice with acetone (2 × 5 cm^3) leaving a reddish solid. [CpRu(PPh$_3$)$_2$(PH$_3$)]PF$_6$ **3a** was obtained as a yellowish solid by concentrating the acetone solution. The crude **3a** was recrystallized from CH$_2$Cl$_2$–hexane (420 mg, 80%) (Found: C 56.5; H, 4.5. C$_{41}$H$_{38}$F$_6$P$_4$Ru requires C 56.6; H 4.4%). **3b** was obtained through the same workup as **3a** (Found: C 57.5; H, 4.6. C$_{42}$H$_{38}$F$_3$O$_3$P$_3$RuS requires C 57.7; H 4.4%). δ_P (121.4 MHz, (CD$_3$)$_2$CO, 25 °C, H$_3$PO$_4$; complex cation A$_2$F pattern) 44.7 (2P, d, ^2J(P$_A$P$_F$) 51 Hz, P$_A$), −113.2 (1P, t, P$_F$), −143.1 (1P, sept, ^1J(PF) 714 Hz, PF$_6$, only for **3a**). δ_P (121.5 MHz, (CD$_3$)$_2$CO, 25 °C, 85% H$_3$PO$_4$; hydrogen coupled, complex cation A$_2$FX$_3$ pattern) 44.8 (2P, d, ^2J(P$_A$P$_F$) 51 Hz, P$_A$), −113.1 (1P, qt, ^1J(P$_F$H) 358, P$_F$), −143.1 (1P, sept, ^1J(PF) 714 Hz, PF$_6$, only for **2a**). δ_H (300.0 MHz, (CD$_3$)$_2$CO, 25 °C, TMS) 7.46–7.10 (30H, m, Ph), 4.91 (5H, s, Cp), 4.52 (3H, dt, ^1J(HP$_F$) 357 Hz, ^3J(HP$_A$) 6 Hz, PH$_3$). The red solid (60 mg) yields a 1 : 1 : 2.5 ratio between hydrogen, phosphorus and oxygen (XPS and elemental analysis). δ_P (121.4 MHz, CD$_2$Cl$_2$, 25 °C, 85 % H$_3$PO$_4$) broad band centered at 43.0.

¶ PH$_3$ was gently bubbled for 5 min through a solution of [CpRu(PPh$_3$)$_2$Cl] (730 mg, 1.00 mmol) and TlPF$_6$ (350 mg, 1.00 mmol) in a mixture of CH$_2$Cl$_2$ (20 cm^3) and THF (30 cm^3). The resulting slurry was stirred at room temperature for 1 h; the precipitated TlCl was filtered off and yellow microcrystals of **3a** were obtained by evaporating the solvent under reduced pressure. The solid was recrystallized from CH$_2$Cl$_2$–hexane (850 mg, 98%).

1 K. H. Whitmire, *Adv. Organomet. Chem.*, 1998, **42**, 2; O. J. Scherer, *Acc. Chem. Res.*, 1999, **32**, 751; M. Peruzzini, I. de los Rios,

A. Romerosa and F. Vizza, *Eur. J. Inorg. Chem.*, 2001, 593; M. P. Ehses, A. Romerosa and M. Peruzzini, *Top. Curr. Chem.*, 2001, **220**, 107.

2 E. Urnėžius, W. W. Brennessel, C. J. Cramer, J. E. Ellis and P. von Ragué Schleyer, *Science*, 2002, **295**, 832, and references therein.

3 J. Bai, A. V. Virovets and M. Scheer, *Science*, 2003, **300**, 781; J. Bai, A. V. Virovets and M. Scheer, *Angew. Chem., Int. Ed.*, 2002, **41**, 1737; J. Bai, E. Leiner and M. Scheer, *Angew. Chem., Int. Ed.*, 2002, **41**, 783.

4 A. P. Ginsberg and W. E. Lindsell, *J. Am. Chem. Soc.*, 1971, **93**, 2082; O. J. Scherer, M. Swarowsky and G. Wolmershäuser, *Organometallics*, 1989, **8**, 841; F. Cecconi, C. A. Ghilardi, S. Midollini and A. Orlandini, *Inorg. Chem.*, 1986, **25**, 1766.

5 P. Dapporto, S. Midollini and L. Sacconi, *Angew. Chem., Int. Ed. Engl.*, 1979, **18**, 469; P. Dapporto, L. Sacconi and P. Stoppioni, *Inorg. Chem.*, 1981, **20**, 3834; M. Di Vaira, M. P. Ehses, M. Peruzzini and P. Stoppioni, *Eur. J. Inorg. Chem.*, 2000, 2193.

6 T. Gröer, G. Baum and M. Scheer, *Organometallics*, 1998, **17**, 5916.

7 M. Peruzzini, L. Marvelli, A. Romerosa, R. Rossi, F. Vizza and F. Zanobini, *Eur. J. Inorg. Chem.*, 1999, 931.

8 I. de los Rios, J.-R. Hamon, P. Hamon, C. Lapinte, L. Toupet, A. Romerosa and M. Peruzzini, *Angew. Chem., Int. Ed.*, 2001, **40**, 3910.

9 D. E. C. Corbridge, *Phosphorus, an Outline of its Chemistry Biochemistry and Technology*, Elsevier, Amsterdam, 5th edn., 1995; K. B. Dillon, F. Mathey and J. F. Nixon, *Phosphorus: the Carbon Copy*, Wiley, Chichester, 1998.

10 L. Maier, *Top. Curr. Chem.*, 1971, **19**, 95 (*Eur. Pat.*, WO9943612, 1999).

11 G. Huttner and S. Schelle, *J. Cryst. Mol. Struct.*, 1971, **1**, 69.

12 G. Huttner and S. Schelle, *J. Organomet. Chem.*, 1973, **47**, 383.

13 J. Bould, P. Brint, X. L. R. Fontaine, J. D. Kennedy and M. Thornton-Pett, *J. Chem. Soc., Chem. Commun.*, 1989, 1763.

14 A. J. Deeming, S. Doherty, J. E. Marshall, J. L. Powell and A. M. Senior, *J. Chem. Soc., Dalton Trans.*, 1993, 1093.

15 R. P. Hughes, J. M. Smith, C. D. Incarvito, K.-C. Lam, B. Rhatigan and A. L. Rheingold, *Organometallics*, 2002, **21**, 2136.

16 G. Frenking, K. Wichmann, N. Frohlich, J. Grobe, W. Golla, D. Le Van, B. Krebs and M. Lage, *Organometallics*, 2002, **21**, 2921.

17 U. Vogel and M. Scheer, *Z. Anorg. Allg. Chem.*, 2001, **627**, 1593.