

Synthesis of Exceptionally Stable Iron and Ruthenium η^1 -tetrahedro-Tetraphosphorus Complexes: Evidence for a Strong Temperature Dependence of M–P₄ π Back Donation**

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In recent years the coordination chemistry of white phosphorus has been carefully investigated and a plethora of transition metal complexes containing P_x fragments derived from either the degradation (P, P₂, and P₃ ligands) of the P₄ tetrahedron or the reaggregation (up to P₁₂) of fragments thereof have been synthesized and characterized.^[1] Considerable effort has been invested in the synthesis of stable coordination compounds containing the intact P₄ molecule, but in spite of the many attempts and of the existence of an old example, [[N(CH₂CH₂PPh₂)₃]Ni(η^1 -P₄)] (**1**),^[2] it is generally considered more easy to reductively open one,^[3] two,^[4] or three^[5] bonds of the P₄ tetrahedron than to coordinate the P₄ molecule as an intact η^1 -end-on ligand. Only recently, however, η^1 -P₄ compounds have been described either as thermally unstable species, [[P(CH₂CH₂PPh₂)₃]M(η^1 -P₄)]OTf (M = Co (**2**), Rh (**3**); OTf = OSO₂CF₃)^[6] and [M(CO)₃-(PR₃)₂(η^1 -P₄)] (M = W, R = Cy (**4**), iPr (**5**); M = Mo, R = Cy (**6**)),^[7] or as a slightly air-sensitive solid, [[MeC(CH₂PPh₂)₂]Re(CO)₂(η^1 -P₄)]Y (Y = OTf, BPh₄ (**7**)).^[8] In all of these compounds, which were characterized by either X-ray diffraction (**1**, **4**) or ³¹P NMR spectroscopy (**2**–**7**), the P₄ molecule is bonded to the organometallic fragment through a lone pair of electrons on one of the phosphorus atoms. Beautiful examples of thermally unstable side-on P₄ complexes have recently been reported.^[9]

We report here on the synthesis and the chemical-physical characterization of a family of novel η^1 -tetrahedro-tetraphosphorus complexes of iron and ruthenium of formula [Cp*M(L)₂(η^1 -P₄)]Y (L = phosphane or diphosphane ligand; M = Fe, Ru) which exhibit an exceptional stability in comparison to the few known η^1 -P₄ derivatives as well as to the free phosphorus molecule. Some preliminary data illustrating the electronic structure and reactivity of the new tetraphosphorus complexes are also provided.

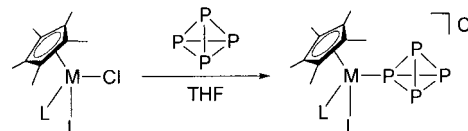
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Reaction of [Cp*M(L)₂]Cl (Cp* = η^5 -C₅Me₅; M = Fe,^[10] L₂ = Ph₂PCH₂CH₂PPh₂; M = Ru,^[11] L = PEt₃, L₂ = Ph₂PCH₂CH₂PPh₂) with one equivalent of P₄ in THF at room temperature under a nitrogen atmosphere leads to removal of chloride and coordination of the P₄ molecule through one lone pair of electrons on phosphorus (Scheme 1). Addition of



Scheme 1. Synthesis of the P₄-transition metal complexes **8**–**10**. **8**: M = Fe, L = 1/2 dppe; **9**: M = Ru, L = PEt₃; **10**: M = Ru, L = 1/2 dppe; dppe = Ph₂PCH₂CH₂PPh₂.

ethanol/*n*-hexane (1:2 v/v) and slow concentration of the resulting solution under a brisk current of nitrogen affords reddish purple (M = Fe) or orange (M = Ru) microcrystalline solids of formula [Cp*M(L)₂(η^1 -P₄)]Cl (M = Fe, L₂ = Ph₂PCH₂CH₂PPh₂ (**8**-Cl); M = Ru, L = PEt₃ (**9**-Cl), L₂ = Ph₂PCH₂CH₂PPh₂ (**10**-Cl)) in excellent yields (> 80 %). Metathesis with NH₄PF₆, NaBPh₄, or NaBAR₄ (Ar = B(CF₃)₃C₆H₂) yields the corresponding hexafluorophosphate or tetraarylborate salts, respectively. Complexes **8**–**10** are thermally and air stable in the solid state, and dissolve in most common organic solvents. The iron derivative slowly decomposes in halogenated hydrocarbons to give back the chloride adduct, while the ruthenium salts are readily crystallized from dichloromethane/ethanol mixtures without decomposition even under aerobic conditions.

The coordination of the intact P₄ molecule as a *tetrahedro*- η^1 -P₄ ligand has been ascertained by X-ray diffraction analysis on crystals of **8**-BPh₄ grown by slow diffusion of *n*-pentane into a saturated solution of the complex in THF.^[12] The X-ray analysis reveals the expected η^1 -coordination of the tetraphosphorus ligand (Figure 1) with the iron atom Fe1 coordinated in a roughly octahedral arrangement by the two dppe P-donor atoms and the Cp* ring occupying three contiguous sites of the coordination polyhedron.

The Fe–P_{apical} distance is 2.1621(7) Å and is considerably shorter than the Fe–P distances in the related complexes prepared by Scherer et al., namely *exo,exo*-butterfly complex [(C₅H₂tBu₃)(CO)Fe]₂(μ , $\eta^{1:1}$ -P₄)] (*d*_{Fe–P_{av}} = 2.3516 Å)^[13] and the diiron species [(C₅H₃tBu₂)Fe](μ , $\eta^{4:1}$ -P₄)[Fe(CO)(C₅H₃-tBu₂)]^[14] in which the *exo*-cyclic Fe– η^1 -P₄ separation (2.211(1) Å) is still slightly longer than in **8**-BPh₄. The bond lengths within the P₄ molecule are slightly dissimilar; the basal P–P separation ranges between 2.2033(11) and 2.2363(11) Å and hence is longer than the *d*_{P_{apical}–P_{basal}} distances which vary from 2.1589(10) to 2.1664(10) Å. This type of deformation of the coordinated tetraphosphorus ligand is opposite to that found in **1** (*d*_{P_{basal}–P_{basal}} = 2.20(3) Å; *d*_{P_{apical}–P_{basal}} = 2.09(3) Å),^[2] but parallels the values reported by Scheer for the tungsten derivative **4** (av *d*_{P_{basal}–P_{basal}} = 2.190 Å; av *d*_{P_{apical}–P_{basal}} = 2.172 Å).^[7] The P₄ tetrahedron in the latter compound is less compressed than that in **8**, probably reflecting the differences in the distribution of the overall electron density in the two

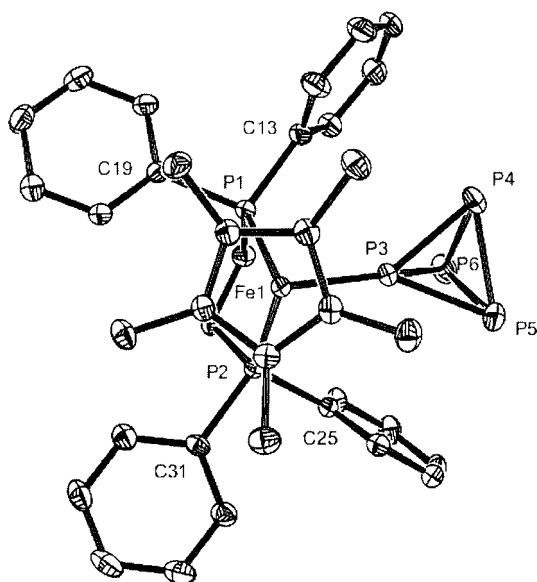


Figure 1. Structure of the complex cation in **8**-BPh₄ (ORTEP drawing). Selected bond lengths [Å] and angles [°]: Fe-P1 2.2343(7), Fe-P2 2.2502(7), Fe-P3 2.1621(7), P3-P4 2.1664(10), P3-P5 2.1615(10), P3-P6 2.1589(10), P4-P6 2.2112(12), P4-P5 2.2363(11), P5-P6 2.2033(11), Fe-Cp*_{centroid} 1.758(2); P3-Fe-P1 88.62(3), P3-Fe-P2 93.02(3), P1-Fe-P2 85.41(3).

isoelectronic d⁶ complexes (W⁰ vs. Fe^{II}) and the cationic charge of **8**.^[15]

The ⁵⁷Fe Mössbauer spectra recorded in the temperature window between 77 and 350 K exhibit *QS* parameters typical for [Cp*Fe(dppe)(L)]Y complexes containing an η¹-coordinated L ligand, but quite large isomeric shifts ranging from 0.31 to 0.40 mm s⁻¹. In the rich family of [Cp*Fe(dppe)] complexes, δ values from ⁵⁷Fe Mössbauer spectra generally fall in the range between 0.15 and 0.30 mm s⁻¹ and increase when the electron-releasing properties of L decrease. It is also noteworthy that for **8**-BPh₄ the δ parameter depends on the temperature; this is rather unusual for iron piano-stool complexes. The decrease of δ with temperature suggests that the electron density at the metal center increases with temperature. Accordingly, the π back donation could be weaker at high temperature.

The P₄ molecule remains firmly coordinated to the metal center in solution; the complexes **8–10** exhibit a temperature-invariant first-order A₂MX₃ pattern in the ³¹P NMR spectra. The four naked phosphorus atoms form the MX₃ part of the spectrum with the three nonmetalated atoms exhibiting a doublet at δ ~ -484 roughly independent of the metal and the ancillary phosphane ligand(s). In contrast, the unique P atom of the P₄ unit coordinated to the metal (P_M) features a quartet of triplets shifted downfield with respect to the signal for free P₄ (δ = -526.9). Remarkably, the iron complex displays the largest coordination chemical shift (δ_M = -299.54) suggesting a considerable perturbation of the electronic density in the P₄ tetrahedron and pointing to a strong π back donation from the metal to the P₄ ligand.

Consistent with this intriguing view of the electronic structure of **8**, variable-temperature ³¹P{¹H} NMR measurements show that the high-field P_M multiplet experiences a quite surprising temperature dependence moving steadily

from δ = -289.22 at -80 °C to -303.01 at 40 °C (Δ = δ_{313K} - δ_{193K} = 13.79). Neither the P_X (Δ = 2.74) nor the dppe (Δ = 1.24) doublets exhibit such unusual temperature dependence of the chemical shift.^[16]

The reactivity of the robust *tetrahedro*-tetraphosphorus complexes described here is under scrutiny. Preliminary data indicate that once coordinated to the metal center the P₄ molecule is extremely resistant to oxidants, such as *meta*-chloroperbenzoic acid, H₂O₂, or O₂, and nucleophiles, such as water and alcohols, but still endowed with reactivity towards electrophilic transition metal moieties. Thus, bimetallic clusters incorporating a bridging P₄ ligand may be readily synthesized. As an example the heterobimetallic complexes [Cp*Fe(dppe)(μ,η^{1:1}-P₄){Re(CO)₂[MeC(CH₂PPh₂)₃]}(BPh₄)₂, [Cp*Ru(PEt₃)₂(μ,η^{1:1}-P₄){Re(CO)₂[MeC(CH₂PPh₂)₃]}(BPh₄)₂ and [Cp*Ru(dppe)(μ,η^{1:1}-P₄){W(CO)₅}]BPh₄ were prepared by treating **8**, **9**, and **10** in THF with [[MeC(CH₂PPh₂)₃]-Re(CO)₂(OTf)] and [W(CO)₅(thf)], respectively.^[17] Remarkably, the reaction of **10** with iodine is straightforward and produces four equivalents of PI₃ at room temperature. One molecule of PI₃ is efficiently scavenged by the metal fragment affording the very rare PI₃ metal complex [Cp*Ru(dppe)-(PI₃)]BPh₄.^[18]

Experimental Section

General procedure for the synthesis of complexes **8–10**: A solution of [Cp*M(L₂)Cl] (M = Fe, L₂ = Ph₂PCH₂CH₂PPh₂; M = Ru, L = PEt₃, L₂ = Ph₂PCH₂CH₂PPh₂) (0.50 mmol) in THF (20 mL) was treated at 25 °C with a small excess of white phosphorus (0.08 g, 0.64 mmol) under nitrogen. Addition of ethanol/*n*-hexane (10 mL, 1:2 v/v) and slow concentration of the resulting solution under a current of nitrogen gave purple (**8**) or orange (**9**, **10**) microcrystals of the η¹-P₄ complexes [Cp*M(L₂)(η¹-P₄)]Cl (M = Fe, L₂ = Ph₂PCH₂CH₂PPh₂) (**8**-Cl); M = Ru, L = PEt₃ (**9**-Cl), L₂ = Ph₂PCH₂CH₂PPh₂ (**10**-Cl)) in yields higher than 80%. The solid complexes were filtered under nitrogen and washed twice with ethanol (2 × 3 mL) and light petroleum ether (2 × 5 mL). Metathesis with NaBPh₄ in THF/EtOH afforded the corresponding tetraphenylborate salts.

8-BPh₄: Purple crystals, yield 80%; ³¹P{¹H} NMR (81.01 MHz, [D₆]acetone, 20 °C, H₃PO₄, A₂MX₃ pattern): δ_A = 87.49, δ_M = -299.54, δ_X = -482.12, J(P_A,P_M) = 39.1, J(P_A,P_X) ~ 0, J(P_M,P_X) = 228.9 Hz; ¹H NMR (200.13 MHz, CD₂Cl₂, TMS): δ = 1.49 (br d, J(H,P_M) = 1.8 Hz, 15 H; C₅(CH₃)₅); MS (FAB +, *o*-nitrophenyl *n*-octylether): *m/z* (%): [M⁺], 713 (4), [M⁺ - P₄], 589 (100); elemental analysis calcd (%) for C₆₀H₅₉BFeP₆: C 69.79, H 5.76; found: C 69.45, H 5.79.

9-BPh₄: Orange crystals, yield 86%; ³¹P{¹H} NMR (81.01 MHz, CD₂Cl₂, 20 °C, H₃PO₄, A₂MX₃ pattern): δ_A = 20.97, δ_M = -332.05, δ_X = -480.96, J(P_A,P_M) = 55.3, J(P_A,P_X) ~ 0, J(P_M,P_X) = 228.9 Hz; ¹H NMR (200.13 MHz, CD₂Cl₂, TMS): δ = 1.61 (dt, J(H,P_M) = 5.1, J(H,P_A) = 1.5 Hz, 15 H; C₅(CH₃)₅); ¹³C{¹H} NMR (50.32 MHz, CD₂Cl₂, 20 °C, TMS): δ = 9.95 (s; P(CH₂CH₃)₃), 11.23 (s; C₅(CH₃)₅), 22.20 (td, J(C,P_A) = 13.3, J(C,P_M) = 5 Hz, P(CH₂CH₃)₃), 96.90 (s; C₅(CH₃)₅); elemental analysis calcd (%) for C₄₆H₆₅BP₆Ru: C 60.33, H 7.15; found: C 60.03, H 7.33.

10-BPh₄: Orange crystals, yield 90%; ³¹P{¹H} NMR (81.01 MHz, CD₂Cl₂, 20 °C, H₃PO₄, A₂MX₃ pattern): δ_A = 70.44, δ_M = -308.46, δ_X = -490.29, J(P_A,P_M) = 44.1, J(P_A,P_X) ~ 0, J(P_M,P_X) = 233.5 Hz; ¹H NMR (200.13 MHz, CD₂Cl₂, TMS): δ = 1.53 (dt, J(H,P_M) = 5.0, J(H,P_A) = 1.9 Hz, 15 H; C₅(CH₃)₅); ¹³C{¹H} NMR (50.32 MHz, CD₂Cl₂, 20 °C, TMS): δ = 10.54 (s; C₅(CH₃)₅), 22.50 (vt, J(C,P_A) = 22.3 Hz, CH₂), 97.13 (s; C₅(CH₃)₅); MS (FAB +, *o*-NPOE): *m/z* (%): [M⁺] 759 (13), [M⁺ - P₄] 635 (100); elemental analysis calcd (%) for C₆₀H₅₉BP₆Ru: C 66.86, H 5.52; found: C 66.67, H 5.38.

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A Dual Channel Fluorescence Chemosensor for Anions Involving Intermolecular Excited State Proton Transfer**

Kihang Choi and Andrew D. Hamilton*

Effective fluorescence chemosensors must convert molecular recognition into changes in fluorescence that are both highly sensitive and easy to detect. A key issue in sensor design is the connection of substrate binding in a recognition domain to photophysical changes in a fluorophore with optimal sensitivity.^[1] In recent years there has been great interest in anion recognition and sensing, because of their importance in biological and environmental settings.^[2] Many fluorescence anion sensors utilizing competitive binding,^[3] photo-induced electron transfer,^[4] metal-to-ligand charge transfer,^[5] and excimer/exiplex formation^[6] mechanisms have been developed. Surprisingly, the strategy of linking a fluorophore with emission from an internal charge transfer (CT) excited state to an ion-binding domain, while widely used for cation sensing, has been rarely exploited for anion sensing.^[1a, 7] Anion binding close to the fluorophore could lead to the stabilization of positive charge developed in the fluorophore excited state and to the opening of another fluorescence emission channel through intermolecular excited state proton transfer (ESPT)^[8] (Figure 1). Herein we report the preparation of anion sensors using this strategy and show that one of them can function as a dual-channel sensor system.

As the anion-binding domain we used macrocycle **1** which can bind certain anions strongly and selectively through hydrogen bonding to the three amide NH groups.^[9] In a first design, we attached covalently a fluorophore onto the periphery of **1**. 4-Trifluoromethyl-7-aminocoumarin, which possesses an excited state where negative charge is transferred from the nitrogen atom to the coumarin ring,^[10] was connected to the monocarboxy derivative of **1** to give **2** (Boc = *tert*-butoxycarbonyl).^[11, 12] This fluorophore-appended macrocycle showed modest changes in the intensity of its fluorescence emission upon addition of different anions. The binding constants were determined by fluorescence titration and showed high selectivity for tetrahedral anions such as H₂PO₄⁻ (Table 1), which mirrors the properties of **1**. Although this high selectivity (especially for phosphate over chloride) is desirable for sensing applications,^[2a, c] the changes in emission intensity and wavelength (+2 nm for H₂PO₄⁻) induced by anion binding were small. It appears that the negative charge on the bound anion is not effectively positioned to interact with the increasing positive charge on the nitrogen atom of the fluorophore, and has little effect on the excited-state energy.^[13]

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