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P_4 Activation

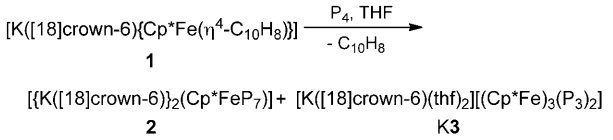
Synthesis of Anionic Iron Polyphosphides by Reaction of White Phosphorus with "Cp*Fe$^-$"**

*Eva-Maria Schnöckelborg, Jan J. Weigand, and Robert Wolf**

The development of new methods for the activation and functionalization of white phosphorus is an important and topical challenge in transition-metal chemistry. The potential of cationic and neutral complexes for P_4 activation has been extensively explored.[1] However, anionic compounds have hardly been considered although the resulting anionic phosphides should offer an attractive reaction chemistry.[2] To our knowledge, the decaphosphatitanocene sandwich $[Ti(P_5)_2]^{2-}$ remains the sole example of an anionic transition-metal polyphosphide that was prepared by the direct reaction of a low-valent transition metalate with P_4.[2a]

Neutral iron polyphosphides are accessible by reacting P_4 with iron carbonyls.[1,3,4] However, these reactions require thermal or photolytic activation and are not very selective. Anionic iron polyphosphides have not been described until very recently.[5] Previously, we synthesized the anionic naphthalene complex [K([18]crown-6){Cp*Fe(η^4-$C_{10}H_8$)}] (**1**, Cp* = C_5Me_5), and we showed that compound **1** behaves as an efficient Cp*Fe$^-$ source in reactions with alkynes.[6] We now show that anionic iron polyphosphides are accessible by reacting **1** with white phosphorus.

The reaction of **1** with P_4 (1:1 ratio in THF; Scheme 1) yielded a dark brown suspension that contained several distinct species featuring different polyphosphorus units according to ^{31}P NMR spectroscopy (Supporting Information, Figure S1).[7] Similar mixtures were obtained when the ratio of the reactants and the reaction conditions were varied. The unambiguous identification of all components proved to be nontrivial owing to their very similar solubilities. Nonetheless, two major products [K{([18]crown-6)}$_2$(Cp*FeP$_7$)] (**2**) and [K([18]crown-6)(thf)$_2$][(Cp*Fe)$_3$(P$_3$)$_2$] (K**3**) could be isolated by fractional crystallization. Compounds **2** and K**3** were structurally characterized by X-ray crystallography and ^{31}P NMR spectroscopy.



Scheme 1. Synthesis of the new polyphosphides **2** and K**3**.

The single-crystal X-ray structure of complex **2** (Figure 1) shows a $(Cp^*FeP_7)^{2-}$ dianion, which features a norbornadiene-like P_7 framework.[5,8,9] Four of the phosphorus atoms are bound to iron (Fe–P4,P5,P6,P7 2.314(1)–2.332(1) Å). These P atoms have comparatively short P–P bond lengths (P4–P5 2.132(2), P6–P7 2.130(1) Å), which indicate partial double-bond character. Similarly short P–P bonds have been observed in iron diphosphene complexes.[10] The apical phosphorus atom P1 also has relatively short P–P bond lengths (P1–P2 2.138(2), P1–P3 2.131(2) Å). This observation may be explained by the delocalization of the negative charge on P1, as previously discussed in other anionic polyphosphides.[11] The remaining P–P distances (P2–P4, P2–P6, P3–P5, P3–P7 2.233(2)–2.251(1) Å) are in the typical range of ordinary single bonds.[13]

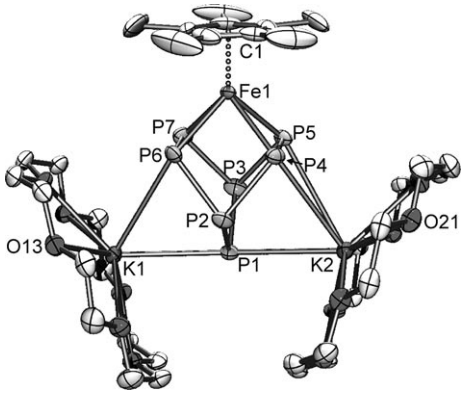


Figure 1. Molecular structure of **2** in the solid state. Ellipsoids are set at 50% probability; H atoms and a THF solvate molecule in the crystal lattice are omitted for clarity.

In agreement with the solid-state structure, the solution ^{31}P{^{1}H} NMR spectrum of **2** features an AA′A″A‴MM′X spin system (Figure 2). The phosphorus atoms P4, P5, P6, and P7, which are coordinated to iron, give rise to the A part of the spectrum at $\delta = -100.7$ ppm. The M part ($\delta = +6.3$ ppm) arises from the bridging atoms P2 and P3, while the X part at $\delta = +151.2$ ppm is due to the apical phosphorus atom P1.[13] A

[*] Dipl.-Chem. E.-M. Schnöckelborg, Dr. J. J. Weigand, Prof. Dr. R. Wolf[+]
Institute of Inorganic and Analytical Chemistry
University of Münster
Corrensstrasse 30, 48149 Münster (Germany)
Fax: (+49) 251-833-6660
E-mail: r.wolf@uni-muenster.de
Homepage: http://www.uni-muenster.de/Chemie.ac/forschung/AK_Wolf.html

[+] Current address: Institute of Inorganic Chemistry
University of Regensburg, 93040 Regensburg (Germany)

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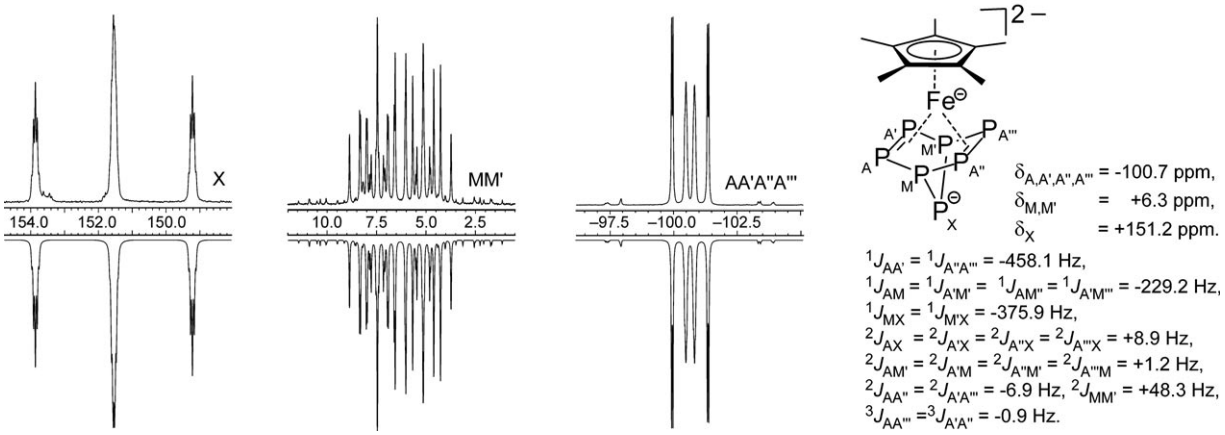

Figure 2. Experimental (upper) and simulated (lower) $^{31}P\{H\}$ NMR spectrum of complex **2** ([D$_8$]THF/[D$_7$]DMF 2:1).

remarkable feature of the ^{31}P NMR spectrum is the $^1J_{P-P}$ coupling constant of −458.1 Hz for the pairs P4/P5 and P6/P7. Such large couplings are usually observed for diphosphene complexes.[10,14] This result is consistent with the proposed norbornadiene-like structure (Figure 2), in which the P4–P5 and P6–P7 bonds should feature partial double-bond character.

X-ray quality crystals of K**3** and [K([18]crown-6)]-[(Cp*Fe)$_3$(P$_3$)$_2$] (K**3**−2THF), which is devoid of THF molecules, were isolated from THF/*n*-hexane (K**3**) and THF/toluene (K**3**−2THF), respectively. The single-crystal X-ray structure of K**3** shows that the [(Cp*Fe)$_3$(P$_3$)$_2$]$^-$ anion (**3**$^-$, Figure 3) is well-separated from the two crystallographically independent [K([18]crown-6)(thf)$_2$]$^+$ cations, which each reside on a crystallographic inversion center.[8] The same anion coordinates to the [K([18]crown-6)]$^+$ cation by a *cyclo*-P$_3$ ligand (K1–P1 3.929(2) Å, K1–P2 3.615(2) Å, K1–P3 3.777(2) Å) in the structure of K**3**−2THF (Supporting Information, Figure S2). The structural parameters of the [(Cp*Fe)$_3$(P$_3$)$_2$]$^-$ anion **3**$^-$ are nearly identical in both structures, and only those of K**3** will subsequently be discussed.

In the anion, two planar P$_3$ rings form a trigonal prism (P1–P4, P2–P5, P3–P6 2.578(3)–2.693(3) Å) that is capped by three Cp*Fe moieties on the rectangular faces. The regular structure of the Fe$_3$P$_6$ core is reminiscent of D_{3h}-symmetric Zintl ions, such as Ge_9^{2-}, Sn_9^{3-}, and Bi_9^{5+}.[15] The P–P bonds within the P$_3$ units (2.306(2)–2.364(3) Å) are significantly longer than the P–P distances in M(*cyclo*-P$_3$) complexes, which typically lie in the range 2.09–2.22 Å.[1a] Iron–iron separations of 3.599(2)–3.646(2) Å indicate that there is no metal–metal bonding. The ^{31}P NMR spectrum of compound **3** in [D$_8$]THF shows a singlet at $\delta = +105.2$ ppm. This unusual low-field ^{31}P NMR shift results from the special bonding environment of the phosphorus atoms, whereas high-field shifts ($\delta < -130$ ppm) are typical for mononuclear M(*cyclo*-P$_3$) complexes.[1,16]

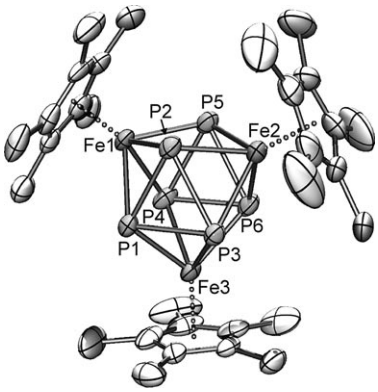

Figure 3. Molecular structure of the [(Cp*Fe)$_3$(P$_3$)$_2$]$^-$-anion **3**$^-$ in the solid state. Ellipsoids are set at 50% probability; H atoms and the [K([18]crown-6)(THF)$_2$]$^+$ cation are omitted for clarity.

The bonding in the cluster anion **3**$^-$ was investigated by quantum-chemical RI-DFT calculations using the program system TURBOMOLE.[7,17–20] Geometry optimization of **3**$^-$ at the BP86/def2-TZVP level gave a good agreement with the experimentally determined structure. A Roby–Davison–Ahlrichs–Heinzmann population analysis provides insight into the bonding situation of **3**$^-$.[21] From this analysis, shared electron numbers (SENs) are obtained, which serve as a measure for the degree of covalent bonding within the cluster. SEN(P–P) values of 0.90–0.93 were calculated for the P–P bonds within the P$_3$ rings. These values correlate with the unusually long intra-ring P–P distances.[22] Furthermore, significant inter-ring SEN(P–P) values were calculated for pairs of P atoms from different P$_3$ rings (SEN(P1–P4) = 0.52, SEN(P2–P5) = 0.52, SEN(P3–P6) = 0.54). These calculated values seem to indicate a weak, covalent bonding interaction between the two P$_3$ rings despite their relatively large separation.

It is interesting to note that the two *cyclo*-P$_3$ ligands show substantial three-center SEN(P–P–P) values (SEN(P1–P2–P3) = 0.29, SEN(P4–P5–P6) = 0.29). P–P–P three-center bonding thus appears to make an important contribution to the bonding in the cluster. These three-center bonds are also apparent in the localized molecular orbitals (LMOs; Figure 4), which are the only P–P bonding LMOs. In contrast, three-center P–Fe–P bonding seems to be less significant (SEN(P–Fe–P) 0.10–0.16).

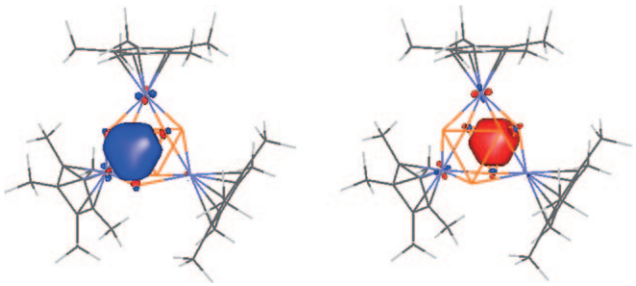

Figure 4. P–P bonding LMOs of the $[(Cp^*Fe)_3(P_3)_2]^-$ anion ($\mathbf{3}^-$).

Using a completely different route, Fenske and co-workers prepared the $[(Cp^*Fe)_3(P_3)_2]^+$ cation ($\mathbf{3}^+$).[23] The molecular structure of $\mathbf{3}^+$, which was determined in the salt $[(Cp^*Fe)_3(P_3)_2][FeCl_3(thf)]$, shows the same connectivity as the anion $\mathbf{3}^-$. However, a closer comparison of both structures reveals significant structural differences (Figure 5). While the

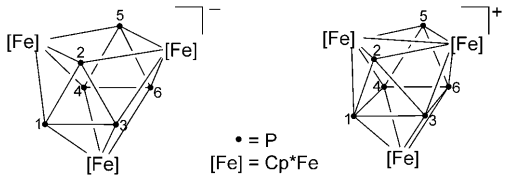

Figure 5. Representations of the structures of $[(Cp^*Fe)_3(P_3)_2]^-$ ($\mathbf{3}^-$, left) and $[(Cp^*Fe)_3(P_3)_2]^+$ ($\mathbf{3}^+$, right).

Fe–Fe and P–P distances of anion $\mathbf{3}^-$ are quite regular, the Fe_3P_6 core of cation $\mathbf{3}^+$ is highly distorted. Thus, the structure of $\mathbf{3}^+$ shows one drastically reduced Fe–Fe contact (2.77 Å) and two substantially longer Fe–Fe distances (3.67 Å and 3.68 Å). Furthermore, the inter-ring P–P distances between the two P_3 rings are markedly different (P1–P4 2.48 Å, P2–P5 4.11 Å, P3–P6 2.49 Å). The ring P–P bond lengths within the *cyclo*-P_3 units (P1–P2 2.268 Å, P1–P3 2.393 Å, P2–P3 2.272 Å) also diverge more strongly than in the anion $\mathbf{3}^-$.

The population analysis of cation $\mathbf{3}^+$, optimized at BP86/def2-TZVP level, confirms the presence of an Fe–Fe bond in the cluster (SEN(Fe–Fe) = 0.25). Similar to the anion $\mathbf{3}^-$, the cation shows significant SEN(P–P–P) values (SEN(P1–P2–P3) = 0.27, SEN(P4–P5–P6) = 0.27), which indicate three-center bonds. The two-center SEN(P–P) values within the P_3 rings are in the range 0.82–0.99. Moreover, the population analysis gave SEN(P–P) values of SEN(P1–P4) = 0.68, SEN(P3–P6) = 0.67, and SEN(P2–P5) = 0.06 between the two P_3 rings. These values show that compared to the anion $\mathbf{3}^-$, the inter-ring bonding in the cation is more strongly localized in the P1–P4 and P3–P6 bonds.

In conclusion, the reaction of the Cp^*Fe^- source **1** with white phosphorus led to remarkable anionic polyphosphido iron complexes under mild conditions. Both P_4 aggregation to a P_7 cage in compound **2** and P_4 degradation to *cyclo*-P_3 units in compound **K3** were observed. Our study demonstrates that the significant yet scarcely utilized synthetic potential of low-valent polyarene metalate anions may open new, promising perspectives for white phosphorus activation and functionalization. Ongoing research in our group aims at an enhanced selectivity of the reaction and reactivity studies of further anionic metalates.

Experimental Section

Synthesis of **2** and **K3**: A solution of **1** (2.983 g, 4.0 mmol) in THF (80 mL) was added to a suspension of P_4 (0.494 g, 4.0 mmol) in THF (40 mL) at −78 °C. The reaction mixture was allowed to warm up to room temperature slowly and was stirred for 12 h. After filtration, the dark brown solution was reduced in volume to 30 mL. Dark brown crystals of **2** (0.187 g, 0.172 mmol, 8 % relative to P_4), which contained one THF solvate molecule per formula unit in the crystal lattice, formed after several days at room temperature. ^{1}H NMR (200.13 MHz, [D$_8$]THF/[D$_7$]DMF 2:1, 300 K): $\delta = 1.6$ (br, 15 H, Cp*), 3.7 ppm (br s, 24 H, [18]crown-6). ^{31}P{^{1}H} NMR (81.01 MHz, [D$_8$]THF/[D$_7$]DMF 2:1, 300 K): AA′A″A‴MM′X spin system; see Figure 2.

The mother liquor that gave the crystals of **2** was further concentrated to 15 mL and layered with *n*-hexane (15 mL). Dark brown crystals of **K3** (1.093 g, 0.906 mmol, 34 % relative to P_4) formed after several days at room temperature. ^{1}H NMR (400.03 MHz, [D$_8$]THF, 300 K): $\delta = 1.7$ (br, 45 H, Cp* of **3**); 3.7 ppm (br s, 24 H, [18]crown-6). ^{31}P{^{1}H} NMR (161.94 MHz, [D$_8$]THF, 300 K): $\delta =$ 105.2 ppm (s, 6 P). The ^{1}H NMR spectrum of the crystals of **K3** showed minor impurities, which could not be removed by further fractional crystallization. Recrystallization of **K3** from THF and toluene (1:1) yielded a few crystals of the THF-free compound **K3**–2 THF, which consisted of the same $[(Cp^*Fe)_3(P_3)_2]^-$ anion $\mathbf{3}^-$ as in **K3** and the $[K([18]crown-6)]^+$ cation (Supporting Information, Figure S2). Further details of the synthesis and characterization of **2** and **K3**, and additional structural data of **K3**–2 THF, can be found in the Supporting Information.

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[8] X-ray data of **2** and K**3** were collected on a Bruker APEXII diffractometer equipped with a rotating anode (graphite monochromator, $\lambda = 0.71073$ Å). The data collection for K**3**–2 THF was performed with a Bruker SMART6000 diffractometer with a rotating anode (Goebel mirror, $\lambda = 1.54178$ Å). The structures were solved by direct methods (SHELXS-97) and refined with SHELXL-97 against F^2 of all reflections.[24] Non-hydrogen atoms were refined with anisotropic displacement parameters. Hydrogen atoms were introduced in calculated positions and refined with a riding model. **2**: $[K([18]crown\text{-}6)]_2[(Cp^*FeP_7)]\cdot THF$ ($C_{38}H_{71}FeK_2O_{13}P_7$), $M_r = 1086.79$; dark brown blocks, $0.09 \times 0.05 \times 0.02$ mm^3; triclinic, $P\bar{1}$; $a = 13.1465(10)$, $b = 13.2719(10)$, $c = 16.4907(12)$ Å; $\alpha = 97.9360(10)$, $\beta = 104.6450(10)$, $\gamma = 104.4960(10)°$; $V = 2632.2(3)$ Å^3; $Z = 2$; $\rho_{calcd} = 1.371$ g cm^{-3}; $\mu = 0.711$ mm^{-1}. 11 603 unique reflections ($R_{int} = 0.0364$). 555 parameters were refined with zero restraints. $R1/wR2$ $[I > 2\sigma(I)]$: 0.0526/0.1245, $R1/wR2$ (all reflections): 0.0821/0.1388. Residual electron density between 0.983 and -0.723 e Å^{-3}. K**3**: $[K([18]crown\text{-}6)(thf)_2][(Cp^*Fe)_3(P_3)_2]$ ($C_{50}H_{85}Fe_3KO_8P_6$), $M_r = 1206.65$; dark brown needles, $0.11 \times 0.05 \times 0.03$ mm^3; monoclinic, $C2/c$; $a = 43.217(3)$, $b = 17.4310(12)$, $c = 15.7036(10)$ Å; $\beta = 90.5870(10)°$; $V = 11\,829.1(13)$ Å^3; $Z = 8$; $\rho_{calcd} = 1.355$ g cm^{-3}; $\mu = 1.006$ mm^{-1}. 13 043 unique reflections ($R_{int} = 0.0663$). 605 parameters were refined using 164 restraints. $R1/wR2$ $[I > 2\sigma(I)]$: 0.1023/0.2466, $R1/wR2$ (all reflections): 0.1117, 0.2509. Residual electron density was found between 1.103 and -1.227 e Å^{-3}. The crown ether and THF molecules of the both crystallographically independent $[K([18]crown\text{-}6)(thf)_2]^+$ cations were heavily disordered. The atoms affected by the disorder were refined over split positions with isotropic temperature factors. Despite the successful refinement, modest final R factors resulted from this disorder. K**3**–2 THF: $C_{42}H_{69}Fe_3KO_6P_6\cdot 0.5\,C_7H_8$, $M_r = 1108.51$; dark brown plates, $0.07 \times 0.06 \times 0.01$ mm^3; monoclinic, $P2_1/n$; $a = 12.1372(2)$, $b = 21.1348(5)$, $c = 20.9586(4)$ Å; $\beta = 102.540(2)°$; $V = 5247.99(18)$ Å^3; $Z = 4$; $\rho_{calcd} = 1.403$ g cm^{-3}; $\mu = 9.348$ mm^{-1}. 5680 crystallographically independent data ($R_{int} = 0.0683$). 529 parameters were refined with 38 restraints. $R1/wR2$ $[I > 2\sigma(I)]$: 0.0516/0.1418, $R1/wR2$ (all reflections): 0.0834, 0.1655. Residual electron density was found between 0.808 and -0.585 e Å^{-3}. The [18]crown-6 molecules showed four disordered carbon atoms and two disordered oxygen atoms that were refined over split positions with isotropic temperature factors. Furthermore, the structure contained a toluene solvate molecule that was severely disordered over a crystallographic inversion center. No satisfactory model for this disorder could be found, and the electron density associated with this solvate molecule was removed from the refinement using the program SQUEEZE (111 electrons/cell in a solvent accessible void of 374.8 Å^3).[25] CCDC 811597 (**2**), CCDC 811598 (K**3**), and CCDC 812447 (K**3**–2 THF) contain the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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