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Mono- and dinuclear tetraphosphabutadiene ferrate anions⁺

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Reduction of $[Cp^{Ar}Fe(\mu-Br)]_2$ (1, $Cp^{Ar} = C_5(C_6H_4-4-Et)_5)$ by potassium napthalenide, followed by the addition of white phosphorus, affords $[K(18-c-6)\{Cp^{Ar}Fe(\eta^4-P_4)\}]$ (2, 18-c-6 = [18]crown-6), which features a planar cyclo- P_4^{-2-} ligand. The related diiron complex $[Na_2(THF)_5(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)]$ (3) was obtained by reducing 1 with sodium amalgam in the presence of P₄. Protonation of 3 affords $[Na(THF)_3][(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)(H)]$ (4), while the reaction of 3 with trimethylchlorosilane gives the nortricyclane compound $P_7(SiMe_3)_3$ as the main product.

While numerous transition metal polyphosphido complexes are reported in the literature, pentaphosphaferrocenes play a pivotal role as phosphorus analogues of the ubiquitous ferrocene molecule and their chemistry has been investigated extensively.1 other Among applications, pentaphosphaferrocenes were used as constituents of 1D and 2D polymers and spherical fullerene-like supramolecules.²⁻⁶ Strikingly, anionic tetraphosphido complexes $[Cp^{R}Fe(\eta^{4}-cy$ clo-P₄)]⁻, which are isoelectronic with pentaphosphaferrocene, are elusive. Cesium and potassium salts of the 6π aromatic $(cyclo-P_4)^{2-}$ dianion were synthesized and characterized by Korber.⁷ Early transition metal complexes [Cp*M(CO)₂(cyclo- P_4] (M = Nb, Ta) and [{(P_2N_2)Zr}₂(cyclo- P_4)] (P_2N_2 = PhP-(CH₂SiMe₂NSiMe₂CH₂)₂PPh) were reported by Fryzuk and Scherer.^{8–10} Driess, Scheer and our group synthesized dinuclear cobalt and iron complexes with a planar cyclo-P₄ middledeck.¹¹⁻¹⁷ Related dinuclear cyclopentadienyl iron complexes bridging tetraphosphabutadiene of and tetraphoshabicyclo[1.1.0]butane-1,3-diyl ligands were also

Scheer and co-workers (2017):





this work: (cyclo)tetraphosphido ferrate anions



 $\label{eq:Figure 1. Selected neutral and anionic polyphosphide complexes, $$ Cp' = C_5H_2-1,2,4-tBu_3, $ Ar = C_6H_4-4-Et, 18-c-6 = [18] crown-6. $$$

described.^{18–22} Complexes **A**–**C** (Figure 1) reported by Scheer in 2017 are particularly noteworthy, because they are very rare examples of mononuclear complexes with cyclo- $P_4^{2^-}$ units.^{23,24} In 2011, we reported that the reaction of P_4 with an anionic "Cp*Fe⁻" source [K(18-c-6){Cp*Fe(η^4 -napthalene)}] (Cp* = C₅Me₅; 18-c-6 = [18]crown-6) produces a mixture of polyphosphide anions including [K₂(18-c-6)₂{Cp*Fe(η^4 -P₇)}] and [[K(18-c-6)(thf)_x][(Cp*Fe)₃(cyclo-P₃)₂] (x = 0 - 2) as major products.²⁵ Hoping that steric bulk might afford the targeted [Cp^RFe(cyclo-P₄)]⁻ anion, we turned to the sterically more demanding pentaarylcyclopentadienyl ligand C₅(C₆H₄-4-Et)₅ (Cp^{Ar}).²⁶⁻²⁸ As a result of these investigations, we have obtained

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⁺ Dedicated to Philip P. Power on the occasion of his 65th birthday.

Electronic Supplementary Information (ESI) available: [details of any supplementary information available should be included here]. See DOI: 10.1039/x0xx00000x



Scheme 1. Synthesis and molecular structure of **2** ($C_{10}H_8$ = naphthalene). The H atoms and ethyl group on the aryl rings are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and bond angles (°): Fe1–Cp^{Ar}(centroid) 1.6751(7), Fe1–P4(centroid) 1.7532(4), Fe1–P1 2.3247(6), Fe1–P2 2.3315(6), Fe1–P3 2.3221(5), Fe1–P4 2.3303(5), P1–P2 2.1633(7), P2–P3 2.1722(6), P3–P4 2.1656 (7), P1–P4 2.1558(6), K…P1 3.6742(5), K1…P2 3.5701(5), K1…P3 3.4490(5), K1…P4 3.5431(5); Cp^{Ar}(centroid)–Fe1–P4(centroid) 178.1(1); P1–P2–P3 89.77(2), P2–P3–P4 89.81(3), P3–P4–P1 90.13(2), P4–P1–P2 90.29(3), P1–P2–P3–P4 torsion angle 0.45, angle between Cp^{Ar} and the P₄ plane 1.79(6).

mono- and dinuclear tetraphosphabutadiene complexes. Here, we describe the synthesis and characterization of $[K(18-c-6){Cp^{Ar}Fe(\eta^4-cyclo-P_4)}]$ (2) and $[Na_2(THF)_5][(Cp^{Ar}Fe)_2-(\mu,\eta^{4:4}-P_4)]$ (3). Moreover, we report the results of an initial reactivity study of **3** with Et₃N·HCl and Me₃SiCl, which has led to $[Na(THF)_3][(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)(H)]$ (4) and the nortricyclane compound P₇(SiMe₃)₃ (5).

The reaction of $[Cp^{Ar}Fe(\mu-Br)]_2$ (1)²⁸ with potassium napthalenide (four equiv.) in THF, followed by the addition of P₄ (two equiv.), affords the desired $[Cp^{Ar}Fe(\eta^4-cyclo-P_4)]]^$ anion as the main phosphorus-containing product as evidenced by a ³¹P NMR singlet at 112.2 ppm observed in the crude reaction mixture. Overreduction of 1 is apparent in the ¹H NMR spectrum (formation of Cp^{Ar}K). Nevertheless, olive green [K(18-c-6){Cp^{Ar}Fe(η^4 -P₄)}] (2) can be isolated as a pure crystalline solid in low yield (4%) when [18]crown-6 (two equiv. referring to 1) is added to the reaction(Scheme 1).‡

Crystals suitable of **2** for single-crystal XRD were obtained from DME. The molecular structure (Scheme 2) shows an η^4 -coordinated P_4 square. The P–P bond lengths (2.1558(6) – 2.1722(6) Å) suggest a delocalized structure similar to that in **A–C**^{23,24} (Figure 1) and [K₂([18]-crown-6)₂(P₄)] (P–P 2.160(2)–2.172 (2) Å).^{7b} The ¹H and ¹³C{¹H} NMR spectra are in agreement with the crystallographically determined structure, displaying one set of signals for the Cp^{Ar} ligand. A sharp ³¹P{¹H} NMR singlet is observed for **2** at 114.1 ppm in THF-*d*₈, which compares to chemical shift of 322.8 ppm for [K₂([18]-crown-6)₂(cyclo-P₄)] and 175.2 ppm for cobalt complex [Cp'Co(η^4 -cyclo-P₄)] (**A**, Figure 1).^{7,13}

The molecular structure of **2** was reproduced by a DFT optimization of the truncated model $[(C_5Ph_5)Fe(\eta^4-cy-clo-P_4)]^-(2')$ at the B3LYP/def2-TZVP level.^{29,30} An analysis of the frontier Kohn-Sham molecular orbitals suggests a d⁶ configuration for iron. The HOMO and HOMO-1 are P-centered MOs, while the HOMO-2, HOMO-3 and HOMO-4 have large contributions from Fe d orbitals (Figure 2, see also

Figure S20 in the ESI). A shoulder at 405 nm_{ie} ($\epsilon_{Article}$ 2800 L·mol⁻¹·cm⁻¹) and a DOI: 10.1039/C7DT04641C



weak absorption at 653 nm ($\epsilon = 550 \text{ L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) were observed in the UV-vis spectrum (THF, Figure S4, ESI). According to TDDFT calculations, these bands can assigned to transitions from the cyclo-P₄²⁻-based HOMO to Cp-based as well as metal-based virtual orbitals.‡

Attempting to improve the synthesis of **2**, we investigated the reduction of **1** with an excess of Na/Hg in the presence of P_4 .

However, this reaction affords the diiron compound $[Na_2(THF)_5\{(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)\}]$ (**3**, Scheme 2) instead.‡ Crystalline **3** is highly air sensitive and slowly decomposes to $[Na(THF)_3\{(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)(H)\}]$ (**4**, vide infra) and other products in THF solution.‡ **3** can nonetheless be isolated as a dark brown-red solid in moderate yield (up to 67%) by crystallization from THF/diethyl ether. **3** is likely formed in a stepwise process via neutral $[(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)]^{21}$ and the putative monoanionic complex $Na[(Cp^{Ar}Fe)_2(\mu,\eta^{4:4}-P_4)]$.

Single-crystal XRD on a crystal obtained from THF/diethyl ether revealed a centrosymmetric dimer, where two P₂ dumbbells are sandwiched between two Cp^{Ar}Fe units (Scheme 2). P1–P2 (2.0782(17) Å) and P3–P4 (2.0778(17) Å) of the planar *cisoid*-P₄ moiety are slightly shorter than in the known neutral analogue $[(Cp^{Ar'}Fe)_2(\mu, \eta^{4:4}-P_4)]$ (Cp^{Ar'} = C₅(C₆H₄-4-*n*Bu)₅, P1–P2 2.100(2) Å, P3–P4 2.098(2) Å).²² The P2…P3 bond distance of 2.635(2) Å is long, indicating a weak interaction between the P₂ moieties similar to the weak P…P bond in kite-like distorted



Scheme 2. Synthesis and molecular structure of **3**. The H atoms and ethyl group on the aryl rings are omitted for clarity. Thermal ellipsoids are drawn at the 35% probability level. Selected bond distances (Å) and bond angles (°):Fe1–Cp^{Ar}(centroid) 1.706(1), Fe1–P₄(centroid) 1.641(1), Fe1···Fe1′ 3.281(1), Fe1–P1 2.3575(9), Fe1–P2

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2.3626(9), Fe1–P3 2.3463(9), Fe1–P4 2.3390(9), P1–P2 2.0782(17), P2–P3 2.5246(16), P3–P4 2.0778(17), P1–P4 2.779(2), Na1–P1 4.073(2), Na1–P2 3.003(2), Na2–P3 2.931(2), Na2–P4 2.997(2); Cp^{Ar}(centroid)–Fe1–P₄(centroid) 176.1(1); P1–P2–P3–P4 torsion angle 0.





[(Cp'Fe)₂(μ -P₄)] reported by Walter and co-workers.²¹ Unlike neutral [($Cp^{Ar'}Fe$)₂(μ , $\eta^{4:4}$ -P₄)], **3** gives rise to a single ³¹P{¹H} NMR signal at ambient temperature. This signal is slightly broad ($\Delta v_{1/2}$ = 12 Hz) at 300 K and broadens upon cooling to 193 K ($\Delta v_{1/2}$ = 123 Hz, Figure S8).§ Different from $[(Cp^{Ar'}Fe)_2(\mu,\eta^{4:4}-P_4)],$ а decoalescence is not observed.Protonation of with 3 Et₃N·HCl affords $[Na(THF)_{3}{(Cp^{Ar}Fe)_{2}(\mu,\eta^{4:4}-P_{4})(H)}]$ (4, Scheme 3) in 44% yield. ¹H NMR spectra of the crude product show paramagnetically shifted ¹H NMR resonances of a by-product, presumably the oxidized compound Na[($Cp^{Ar}Fe$)₂(μ -P₄)], in addition to the signals of the major product 4. Both species have a similar solubility, rendering their complete separation difficult.§§ 3 also converts to 4 by reaction with traces of water present in the solvent, and $[H(Et_2O)]BAr^F$ (BAr^F = B[C₆H₃-3,5-(CF₃)₂]₄).³¹

Crystals of **4** gave low intensities in the single-crystal X-ray diffraction experiment. Nevertheless, the atom connectivity could be firmly established, and we could refine the disorder of the non-solvent parts of the structure.[‡] The ³¹P(¹H} NMR spectrum reveals an A₂M₂ spin system (pseudo-triplets, $J_{P,P} = 52$ Hz, Figure S12, ESI) at room temperature in THF- d_8 . The two multiplets form the A₂M₂ part of an A₂M₂X spin system in the proton-coupled ³¹P NMR spectrum (Figures 5 and S13, ESI). A simulation converged with $J_{P,H}$ coupling constants of 32 Hz



Figure 3. Proton-coupled ^{31}P NMR spectrum of 4 in THF-d₈ at 300 K, The phosphorus-decoupled $^{1}\text{H}\{^{31}\text{P}\}$ NMR signal of the Fe-H unit is shown in the inset 039/C7DT04641C

and 27 Hz.³² The phosphorus-decoupled ¹H{³¹P} NMR spectrum displays a singlet at –7.25 ppm (Figure S11, ESI), which shows the typical high-field shift for a hydride ligand. A seven-line multiplet forming the X-part of the A_2M_2X spin system is observed in the phosphorus-coupled ¹H NMR spectrum (Figures 5 and S10, ESI).

The NMR spectra of **4** are highly temperature dependent, indicating fluxional behaviour.[‡] Upon cooling to 193 K, the ${}^{31}P{}^{1}H{}$ NMR signals decoalesce to four broad signals (ABCD spin system, Figure S14, ESI). This indicates that the H atom apparently is highly mobile.

DFT calculations performed on the truncated model [Na{CpFe}₂(μ , η ^{4:4}-P₄)(H)] ^{29,30} hint at a plausible mechanism for this fluxional behaviour. Two simultaneous dynamic processes may be involved: i) fluctuation of the hydrogen atom between the P-atoms; ii) fluctuation of P-atoms similar to that observed in the related neutral complexes $[(Cp^{R}Fe)_{2}(\mu,\eta^{4:4}-P_{4})]$ reported previously by Scherer and Scheer. ^{18–22} DFT optimizations gave two minimum structures 4A and 4B (Figure 4), which are in agreement with the unsymmetric ABCD spin system observed by ³¹P{¹H} NMR at 193 K. In both isomers, the hydride ligand bridges the Fe center and one P atom. 4A and 4B are separated merely by 3 kcal mol⁻¹ and are connected by the transition state **4TS** (+4.6 kcal mol^{-1} with respect to **4A**). In the structure of 4TS, the hydrogen atom is located at the midpoint between the two P atoms and the Fe atom (Figure 4). Optimizations of other conceivable isomers converged to either 4A or 4B in all cases (Figure S22, ESI). The averaging of the ³¹P NMR signals at room temperature is thus easily explained by the migration of the H atom between the phosphorus atoms (see Figure S23, ESI).³⁴

The reaction of **3** with an excess of Me₃SiCl gives P₇(SiMe₃)₃ (**5**),³⁵ P(SiMe₃)₃ (**6**)³⁶ and PH(SiMe₃)₂ (**7**)³⁷ in a 10 : 1 : 1 ratio (Scheme 3). This presents a proof-of-principle that the phosphorus fragment can be liberated by a suitable electrophile. The fate of the "Cp^{Ar}Fe" moiety is unknown. **5** – **7** are commonly prepared by alkali metal reduction of white or red phosphorus and subsequent addition of Me₃SiCl.^{35–37}

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In summary, P_4 activation by an in-situ generated naphthalene iron complex resulted in the tetraphosphacyclobutadiene ferrate anion [K(18-c-6){Cp^{Ar}Fe(η^4 -P₄)}] (2) with a terminal, planar *cyclo*-P₄²⁻ ligand. This complex is a rare mononuclear ferrate anion obtained directly from P₄. §§§ The high tendency of such species to form dinuclear structures is evident from the synthesis of [Na₂(THF)₅][(Cp^{Ar}Fe)₂(μ , $\eta^{4:4}$ -P₄)] (3), which was obtained under modified reactions conditions and using sodium amalgam. The P₄ fragment in **3** remains intact upon protonation, while the reaction with trimethylchlorosilane leads to uncoordinated P₇ and P₁ species. The latter reaction shows that the polyphosphido ligands can be released from the metal center by suitable electrophiles, which may open up new prospects for P₄ functionalization using anionic metalates. Further studies in this direction are underway.

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Notes and references

‡ See the electronic supplementary information for details on the synthesis and characterization of **2–7**.

§The low temperature ${}^{31}P{}^{1}H$ NMR spectrum of **3** at 193 K shows an additional minor resonance at -111.5 ppm slightly upfield from the dominant resonance. This minor signal might presumably arise from a bonding isomer of 3.³⁸

§§ The isolated product **4** may still contain unknown byproducts, which include a paramagnetic complex that gives rise to broad ¹H NMR signals at 6.57 and 2.57 ppm. In this case, the compound can be purified further by recrystallization from THF/*n*-hexane and THF/diethyl ether.

S While this manuscript was under review, Mézailles and coworkers reported the preparation of a terminal cyclo-P₄ iron complex stabilised by a tridentate phosphane ligand. 39

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Anionic tetraphosphido complexes are accessible by reacting white phosphorus with low-valent cyclopentadienyliron species prepared by alkali metal reduction (Ar = C_6H_4 -4-Et, 18-c-6 = [18]crown-6).