Small-Molecule Activation

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Ferrocene and Pentaphosphaferrocene: A Comparative Study Regarding Redox Chemistry**

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Dedicated to Professor Wolfgang A. Herrmann on the occasion of his 65th birthday

Since its discovery and structural characterization in 1951, ferrocene (Fc) has been a fundamental compound in organometallic chemistry and is still of important synthetic and analytic interest. Apart from its use as a reference redox system (Fc^+/Fc),[1] chiral ferrocene-based ligands are one of the most important classes of auxiliaries in asymmetric homogeneous catalysis,[2] and ferrocene-based polymeric materials have attracted intense interest with their unique physical and chemical features.[3] The isolobal relationship between Cp^- and *cyclo*-P_5^- ligands[4] led to an enlarged understanding of the relations of such compounds, and the discovery of pentaphosphaferrocene can be regarded as a milestone in chemistry.[5] Like ferrocene, the compound $[Cp^*Fe(\eta^5\text{-}P_5)]$ (**1**) was subject of extensive reactivity studies towards organometallic reagents. Similarities are observed in the formation of triple-decker complexes[6,7] or in Cp/*cyclo*-P_5-transfer reactions.[8] Fragmentations and distortions of the *cyclo*-P_5 ring of **1** were found to be significant differences between both compounds.[9,10] Furthermore, the existence of lone pairs at the P atoms opened up an extensive coordination chemistry of the *cyclo*-P_5 unit that led to 1D and 2D polymers[11] and spherical fullerene-like supramolecules.[12]

A view of the HOMO/LUMO orbitals of ferrocene reveals the iron-centered reactivity of ferrocene during oxidation and reduction. In contrast, the HOMOs of the pentaphosphaferrocene show pronounced contributions of the P atoms, whereas for the LUMOs metal contributions are also observed along with P atom portions.[13] Thus, for ferrocene a metal-based redox behavior is found (reversible for oxidation and irreversible for the one- and two-electron reductions accompanied by Cp^- elimination and formation of $CpFe^-$ species[14]), while for pentaphosphaferrocene (**1**) redox reactions will lead to structural changes under participation of P atoms. This was confirmed by Winter et al. by a spectroelectrochemistry study of **1**.[15] They found one irreversible reduction and oxidation to give $19e^-$ and $17e^-$ species that rapidly equilibrate to dimeric products for which structures were proposed. Unfortunately, these products were neither isolated nor spectroscopically completely characterized. Therefore, it was of fundamental interest to approach the open questions of the redox properties and possible structural changes of **1** in a preparative scale. Herein, the high-yield syntheses of the one-electron redox products of **1** are presented, which confirm and clarify the earlier proposed structures. Furthermore, an additional two-electron reduction product was obtained that was not detectable by CV studies. Moreover, first reactivity studies of the resulting reactive species are presented that reveal their high potential for subsequent synthetic purposes.

The chemical reduction of **1** with KH in THF affords the diamagnetic dianion **2** as a dipotassium salt in 86% yield (Scheme 1). The bridging P_{10} ligand in **2** (Figure 1)[14] is best described as two envelope-type η^4-coordinated P_5 units connected by a single P–P bond (P1–P10 2.199(1) Å) that represent a dihydrofulvalene-like ligand. The other P–P bonds are shorter (average 2.1502 Å) but slightly longer than those in **1** (average 2.1202 Å),[11b] which can be attributed to a partial double-bond character. The deviations of the atoms P10 and P1 from the planes defined by the other four P atoms within each envelope are 1.039(1) Å and 1.119(9) Å. Notably, among the three coupling possibilities (that is, C–C, C–P, and P–P), only the latter is realized. Only neutral Rh and Co complexes are known that reveal similar bridging P_{10} ligands.[16] In contrast to **2**, these complexes show pronounced P–P bond alternation within P_5 envelopes, and the larger P–P distances (longest measured: 2.474(2) Å (Co) and 2.624(2) Å (Rh)) even suggest an open-ring structure. Recently, an anionic niobium complex with an envelope-type η^4-P_5 ligand was reported by Cummins et al.[17]

DFT calculations[14] of the dianion of **2** show that the experimental geometry is also retained in the gas phase. This reveals that the conformation of the P_{10} unit is not only a result of crystal packing, but it is the ground-state geometry.

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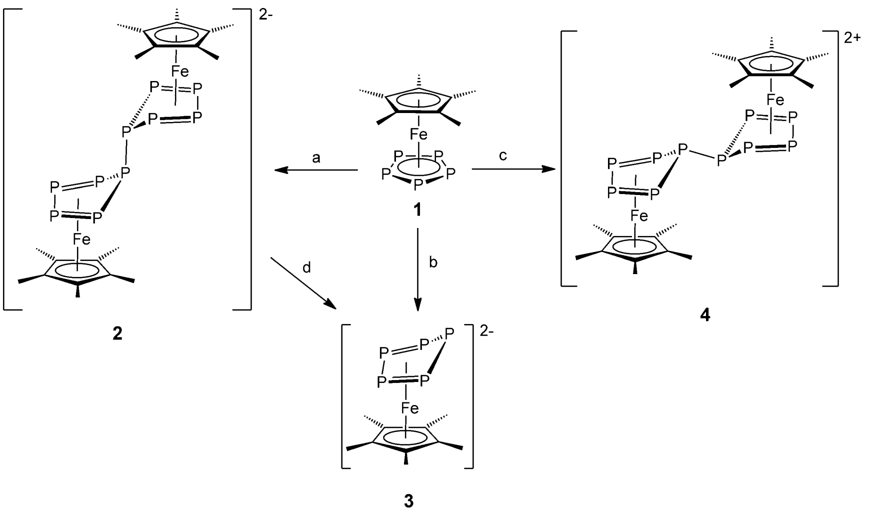
Supporting information for this article (full synthetic and spectroscopic details for **2**–**6**, crystallographic details, and full details and references of the DFT calculations) is available on the WWW under http://dx.doi.org/10.1002/anie.201209329.



Scheme 1. Reactions of **1**: a) KH in THF; b) excess K in DME; c) thianthrenium hexafluoroantimonate in CH_2Cl_2, −35 °C; d) K in DME. The multinuclear spin systems of the products were analyzed by $^{31}P\{^1H\}$ NMR spectroscopy and were simulated accordingly.[14]

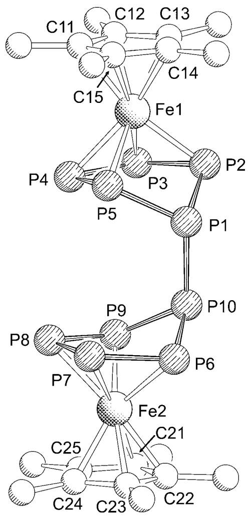


Figure 1. Molecular structure of the dianion of [K(dme)$_2$K(dme)][**2**] (ball-and-stick representation).

The natural charge distribution in **2** shows only a slightly positively charged iron atom (0.13). The four phosphorus atoms coordinating to iron are slightly negatively charged (−0.17 to −0.22), whereas the charge on the out-of-plane phosphorus atoms was calculated to be −0.07.

The reduction of **1** with an excess of K resulted in the formation of the new olive-green dianionic species **3** as a dipotassium salt in 75 % yield (Scheme 1). The dianion **3** can also be obtained by the reaction of the P_{10} dianion **2** with K in 67 % yield. Interestingly **3** was not detected in CV studies of **1**,[15] and our intensive efforts to observe it in CV experiments under different conditions (solvent, supporting electrolyte, temperature) also failed. Only the published results[15] could be reproduced. Interestingly the new complex is able to deprotonate solvents.[14]

In contrast to **2**, compound **3** has a mononuclear structure (Figure 2). Although the P_5 ligand in **3** has a similar envelope-shaped structure, the deviation of the atom P5 from the plane defined by the atoms P1, P2, P3, and P4 is larger (1.231 Å). The distances between P2–P3 (2.133(1) Å), P4–P5 (2.156(1) Å), and P5–P1 (2.153(1) Å) show double-bond character. It is interesting to note that the increase in the $Cp^*_{centroid}$–Fe distances going from **1** (1.535(1) Å)[11b] to **2** (1.696 Å av.) and to **3** (1.729 Å av.) as well as the shortening of the Fe–P bonds lie in the same series: **1** (2.3681 Å av.), **2** (2.3189 Å av.), **3** (2.2910 Å av.). The dianion **3** was found formally in the coordination sphere of Sm complexes.[18] In comparison with those complexes (d(PP) = 2.164(2)–2.228(2) Å), the P–P bond distances in the uncoordinated species **3** are surprisingly similar, which reveals the ionic interaction of the Sm units in such arrangements.

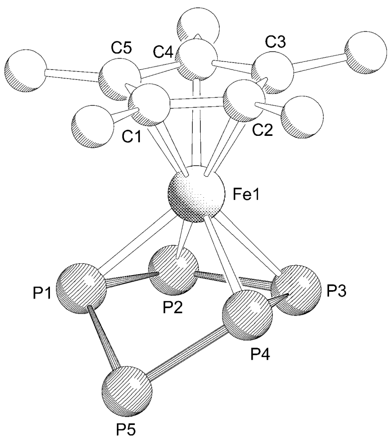


Figure 2. Molecular structure of the dianion of [K(dme)K(dibenzo-[18]crown-6)][**3**] (ball-and-stick representation).

The natural charge distribution in **3** shows a moderately negatively charged phosphorus atoms (−0.25 to −0.30 for the in-plane phosphorus atoms and −0.50 for the out-of-plane phosphorus) and an almost neutral iron atom (0.08).[14]

Finally, the oxidation of **1** was accomplished with the thianthrenium salt, which yielded the dication **4** as a hexafluoroantimonate salt in 45 % yield (Scheme 1). The product appears to be unstable in various solvents and probably decomposes by a nucleophilic degradation path, similar to ferricinium.[19] Like in the case of **2**, the coupling of the resulting $17e^-$ species selectively involves the *cyclo*-P_5 rings. This result agrees with calculations on phosphaferrocenes that indicate that the a_g-type orbitals (HOMO of **1** and other phosphaferrocenes) are devoid of cyclopentadienyl character.[20] The structure of **4** (Figure 3) exhibits a dimeric complex containing a P_{10} ligand which is stereochemically different

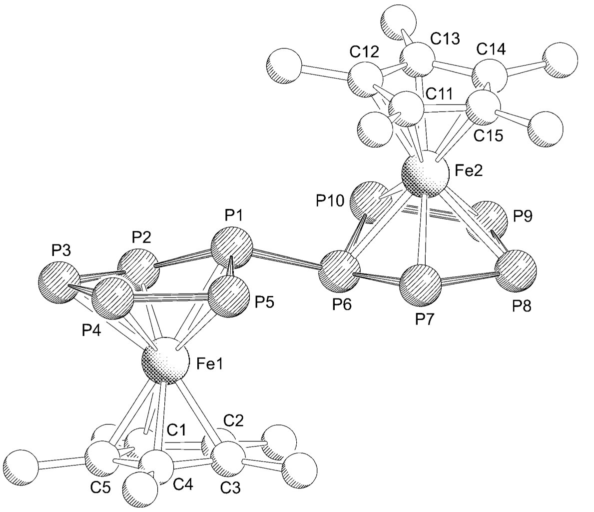


Figure 3. Molecular structure of the dication of [**4**](SbF_6)$_2$ (ball-and-stick representation).

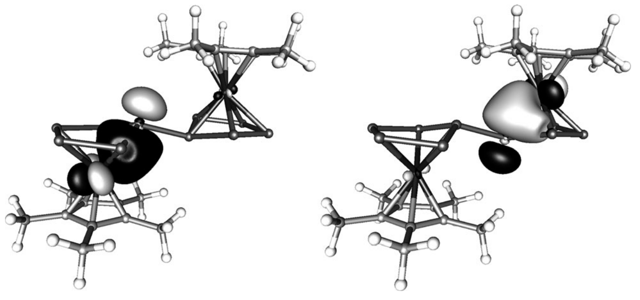


Figure 4. Isosurfaces of the localized molecular orbitals of $[\{Cp^*Fe(\eta^4\text{-}P_5)\}_2]^{2+}$, showing the P1–Fe1 as well as the P6–Fe2 bonding interactions.[14]

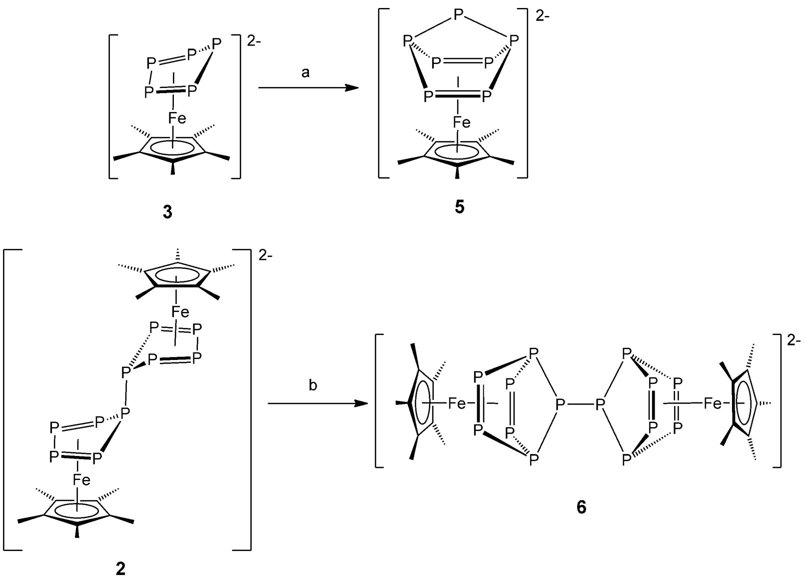
from that of **2**. The single bond P1–P6 (2.199(2) Å) points towards the Cp*Fe moieties in **4**, whereas the similar bond in **2** points away from the Cp*Fe moieties. Even though the atoms P6 and P1 are bent away from the plane defined by the other four P atoms within each envelope (0.573 Å and 0.572 Å), the distances of 2.392(1) Å (Fe1–P1) and 2.386(1) Å (Fe2–P6) clearly indicate bonding interactions. This interaction imposes the *endo* arrangement of the η^5-P_5 rings, which leads to the difference in the stereochemistry of **2** and **4**. The other P–P bonds of **4** exhibit a partial double-bond character (2.1245 Å av.). Although the dication **4** and the dianion **2** are compositionally isomeric, the difference of four electrons leads to several different structural parameters. Thus, the distance $Cp^*_{centroid}$–Fe in **4** (1.7345 Å av.) is slightly longer than in **2** (1.696 Å av.), and the Fe–P bonds show a pronounced alternation: The Fe–P bonds that are closer to the bridging atoms P1 and P6 (2.3089 Å av.) are noticeably shortened in comparison to the others (2.3988 Å av.). Interestingly, the P_{10} unit in the dication **4** deviates less from the planarity than the P_{10} unit in the dianion **2**. This is reminiscent of the difulvene-like nature of the P_{10}^{2+} unit in **4**. In light of the recent success in synthesizing the polyphosphorus cations $[P_4(PPh_3)_2]^{2+}$[21] and $[P_9]^+$,[22] the novel P_{10}^{2+} cation in **4** is a remarkable extension of this field.

DFT calculations on **4** clearly show that there is a bonding interaction between the phosphorus atoms P1 and Fe1 as well as P6 and Fe2. The phosphorus atoms P1 and P6 possess a lone pair of electrons in an orbital that has mainly p character. This orbital interacts with an empty d orbital of Fe, revealing a bonding interaction (Figure 4). Accordingly, the four in-plane P atoms participate with four electrons to the bonding whereas the P atoms P1 and P6 both donate two electrons. Hence, the P_5 unit serves as a six-electron donor and so the 18 valence electron rule is fulfilled. The natural charge distribution in **4** in the singlet spin state shows that the iron atoms (0.06) and the out-of-plane phosphorus atoms (0.04) are almost neutral, whereas the other phosphorus atoms are slightly positively charged (0.09 to 0.13).[14]

The relative stability of the singlet and triplet spin states of **4** was also explored by DFT calculations using different functionals.[14] All functionals favor the singlet spin state, although the difference in energy depends considerably on the applied functional and varies from 0.24 to 54.24 kJ mol^{-1} for the B3LYP and TPSS functional, respectively. Interestingly, the optimized geometry of **4** in the triplet spin state differs considerably from that of **4** in the singlet spin state that was found in the experimental structure.

The products [K(dme)K(dme)$_2$][**2**], K_2[**3**], and [**4**](SbF_6)$_2$ were further characterized by Mössbauer spectroscopy. The spectra show well-resolved doublet resonance lines.[14] The isomer shifts (IS) at 0.46(1), 0.44(1), and 0.45(1) mm s^{-1} for [K(dme)K(dme)$_2$][**2**], K_2[**3**], and [**4**](SbF_6)$_2$ are in the expected range for Fe^{II} $S=0$ moieties and are only slightly smaller in comparison to **1** (0.468(4) mm s^{-1}).[23] The similar IS values for all three compounds are in accordance with the calculated, only slightly charged Fe atoms and can be explained by the subtle interplay of the redox non-innocence of the polyphosphorus ligands and the change of the Fe–P bond lengths (**1**: 2.3681 Å av., **4**: 2.3539 Å av., **2**: 2.3189 Å av., **3**: 2.2910 Å av.) as well as of the Fe–C bond lengths (**1**: 2.109 Å av., **2**: 2.083 Å av., **3**: 2.113 Å av., **4**: 2.119 Å av.). As the quadrupole splitting (QS) is related to the spatial anisotropy of the electron density involved in the iron–ligand interaction, the difference in QS of [K(dme)K(dme)$_2$][**2**], K_2[**3**] and **1** (1.29(1), 1.24(1), and 0.624(1) mm s^{-1}, respectively) is caused by the lower symmetry of the P_{10}^{2-}, P_5^{2-} ligand environment. In contrast to [K(dme)K(dme)$_2$][**2**] and K_2[**3**], the QS for [**4**](SbF_6)$_2$ (0.72(1) mm s^{-1}) is closer to **1**, revealing for [**4**](SbF_6)$_2$ and **1** a more η^5 coordination mode of the five P atoms.

Preliminary reactivity studies of the dianions **2** and **3** towards the activation of white phosphorus were carried out. Starting with **3**, the dianionic species **5** (Scheme 2) with a norbornene-like structural motif of a P_7 unit was obtained. The [K([18]crown-6)] salt of this compound was recently isolated in 8 % yield by the reaction of a Cp*Fe monoanionic species with P_4,[24] but the formation of the dianionic species is not obvious when using this method. However, by starting from **3**, the generation of the dianion **5** is more defined, which is supported by the almost quantitative yield (94 %). Moreover, the reaction of **2** with P_4 affords the dianion **6** that contains a P_{14} moiety in a yield of 52 % (Scheme 2).



Scheme 2. Reactivity of **2** and **3** with P_4. a) P_4 in DME, −70°C; b) P_4 in DME, −40°C.

The structure of $[K(thf)_2K(thf)_{0.66}(dme)_{0.33}]$[**6**] (Figure 5) exhibits a P_{14} ligand, which can be described as two linked norbornadiene-like P_7 cages. The eight P atoms bound to Fe as well as the P–P bonds to the apical atoms P7 and P8 feature relatively short P–P bonds with a partial double-bond character. The observation of relatively short P–P bonds to the apical P atom in **5** can be explained by the delocalization of the negative charge on these atoms. In light of the very similar structural parameters of **5** and **6**, these relatively short P–P bonds must be associated with the delocalization of the overall negative charges. Further support for this statement can be found comparing the structures of **6** with the neutral complex $[\{Ni(PBu_3)_2\}_4P_{14}]$.[25] The remaining P–P distances in **6** (including the coupled P–P bond between both norbornene units) are in the expected range of P–P single bonds. In contrast to **5**,[14] the dianion in the $^{31}P\{^1H\}$ NMR spectrum of **6** features the chemical non-equivalence of the atoms P1, P2, P11, P12 and P3, P4, P13, P14.[14]

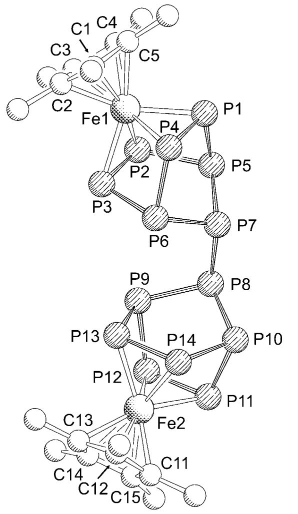


Figure 5. Molecular structure of the dianion of $[K(thf)_2K(thf)_{0.66}(dme)_{0.33}]$[**6**] (ball-and-stick representation).

The results show the large differences in the redox chemistry of pentaphosphaferrocene and ferrocene. Ferrocene mainly features an iron-centered redox behavior with the oxidation of Fe and the reduction under fragmentation and degradation of the metallocene structure. Pentaphosphaferrocene reveals an iron-centered redox behavior that is strongly coupled with the P atoms. This results in the bending of one P atom of the former *cyclo*-P_5 ring. As a consequence, tilted P_5 containing moieties are obtained. The formed radical anionic or cationic species dimerize to yield novel charged P–P coupled P_{10} complexes of iron. The twofold reduction of pentaphosphaferrocene, which could not be observed in CV studies, results in a tilted P_5-containing complex in high yields. In contrast to ferrocene, the initial structure is basically retained after oxidation and reduction. Remarkably, in the dicationic oxidation product **4**, a bond between the out-of-plane P atoms and the Fe nucleus is still present. The novel anionic products are strong nucleophiles and can be used for the activation of small molecules, such as white phosphorus. Hereby, iron complexes with norbornadiene-structured polyphosphorus ligands are obtained including a complex with a P_{14} unit. The high nucleophilicity of the novel dianions turns them into valuable starting materials for further reactivity studies.

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