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Triple-decker sandwich complexes with a bent *cyclo*-P₅ middle-deck†

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New types of triple-decker complexes with an organo-substituted P₅ middle-deck were synthesized by the reaction of [Cp*Fe(η⁴-P₅R)][−] (1a: R = CH₂SiMe₃; 1b: R = NMe₂) with halogeno-bridged transition metal dimers [Cp'''MX]₂ (M = Cr, Fe, Co, Ni; X = Cl, Br). By oxidation of [(Cp*Fe)(Cp'''Co)(μ,η^{4:3}-P₅CH₂SiMe₃)] 2a with [Cp₂Fe][PF₆], the cationic complex [(Cp*Fe)(Cp'''Co)(μ,η^{5:4}-P₅CH₂SiMe₃)]⁺ was isolated. The electronic structure of the synthesized complexes was elucidated by DFT calculations.

Ferrocene is one of the most frequently used organometallic reagents in chemistry, with very broad applications.^{1–3} This 65 year old molecule^{4,5} does not only show a fascinating chemistry in redox processes but particularly as a starting material for subsequent reactions. Its ability to be metalated^{6,7} or to undergo Friedel–Craft reactions^{8,9} renders it a valuable starting material in organometallic synthesis. The isolobal analogue of ferrocene is pentaphosphaferrocene and its Cp* derivative [Cp*Fe(η⁵-P₅)] (**I**) was first discovered in 1987.¹⁰ The majority of reactivity studies of **I** is dedicated to the coordination chemistry towards Lewis acidic coordination moieties, forming 1D and 2D coordination polymers^{11–15} or spherical supramolecular clusters.^{16–20} In cothermolysis or cophotolysis reactions with organometallic reagents, fragmentations and deformations of the *cyclo*-P₅ ring of **I** occur.^{21–24} A new direction for the reactivity of pentaphosphaferrocene opened up when **I** was used in redox processes^{25–27} and especially when it was converted by nucleophiles.²⁸ In the latter case, a selective

functionalization of the P₅ ring in **I** was achieved. As a result, monoanionic complexes of the type [Cp*Fe(η⁴-P₅R)][−] (R = CH₂SiMe₃, NMe₂, PH₂) were isolated, leading to new perspectives in the chemistry of **I**. These monoanionic complexes raised the question, whether reacting them with electrophiles leads to a reformation of the initial *cyclo*-P₅ ring (by the retention of the former substitution), or if a rearrangement takes place to give products with novel structures. Moreover, so far only few triple-decker complexes exhibiting a *cyclo*-P₅ middle deck are known. Starting from P₄ in thermolysis reactions, the compounds [(Cp^{BIG}Mn)₂(μ,η^{5:5}-P₅)] (Cp^{BIG} = C₅(4-*n*BuC₆H₄)₅) and [(Cp^RCr)₂(μ,η^{5:5}-P₅)] (Cp^R = Cp, Cp*) are obtained.^{29–31} Starting from **I**, some cationic triple-decker compounds [(Cp*M)(Cp^RM')(η^{5:5}-P₅)]⁺ (M, M' = Fe, Ru; Cp^R = Cp, Cp*), containing group 8 elements, have been reported.^{32,33} Furthermore, mixed-metal lanthanide-iron compounds with a *cyclo*-P₅ middle-deck²⁶ and triple-decker complexes consisting of **I** and a [M(CO)₃] fragment (M = Cr, Mo, W) are known.³⁴ Herein, we report the synthesis of the first neutral complexes with a functionalized P₅ middle-deck under mild conditions. By using different transition metal halides [Cp'''MX]₂ (M = Cr, Fe, Co, Ni; X = Cl, Br), a broad variety of different triple-decker complexes are easily accessible. Their bonding situation has been investigated by quantum chemical computations.

The reaction of **1a/1b** with the transition metal dimers [Cp'''MX]₂ (M = Cr, Fe, Co, Ni; X = Cl, Br) leads to the triple-decker complexes **2–5**, containing the whole 3d element series from Cp'''Cr to Cp'''Ni decks (Scheme 1). Unfortunately, despite several efforts, we were not able to synthesize the missing manganese containing triple-decker complex in this series.³⁵ Whereas the compounds **3–5** are diamagnetic, the obtained cobalt/iron triple-decker **2a/2b** are paramagnetic. The EPR spectra of **2a** and **2b** in toluene at 77 K show an isotropic signal for both compounds, centred at *g*_{iso} = 2.069 and 2.076, respectively, with no hyperfine coupling. The determination of the effective magnetic moment of **2a** and **2b** in solution by the Evans method results in one unpaired electron (**2a**: μ_{eff} = 2.14 μ_B; **2b**: μ_{eff} = 1.83 μ_B). As DFT calculations on the B3LYP/def2-SVP level of theory show, the single-occupied molecular orbitals (SOMO) of **2a** and **2b** are very similar, indicating

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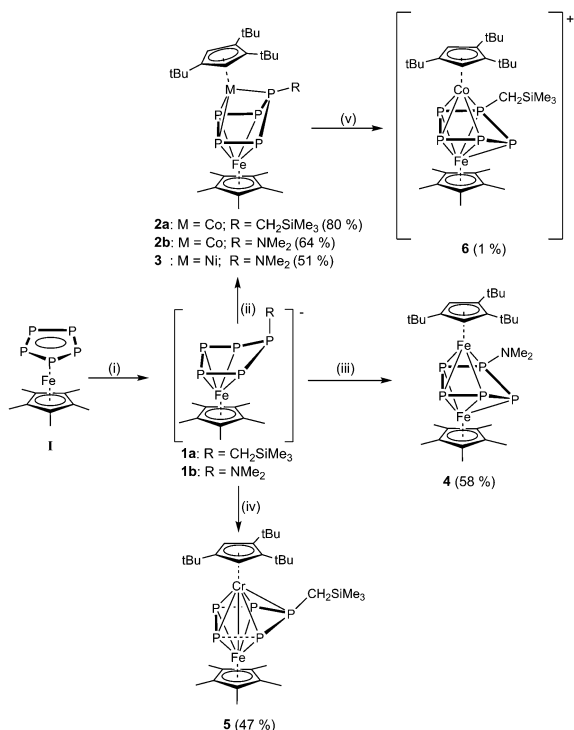
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Scheme 1 Reactions of **1**: (i) LiCH₂SiMe₃ in Et₂O or LiNMe₂ in THF, r.t.; reaction of **1a**: (ii) [Cp'''CoCl]₂ in THF, r.t., (iv) [Cp'''CrCl]₂ in THF, r.t.; reaction of **1b**: (iii) [Cp'''CoCl]₂ or [Cp'''NiBr]₂ in THF, r.t., (iii) [Cp'''FeBr]₂ in THF, r.t.; reaction of **2a**: (v) [Cp₂Fe][PF₆] in THF, r.t. –50 °C → r.t. Yields in parentheses.

the minor influence of the substituent of the *cyclo*-P₅ ring on the features of the SOMO (Fig. 1).³⁶ All SOMOs are delocalized, but the analysis of the spin density reveals that the metal centre bonded to the Cp''' ligand exhibits the highest spin density. The calculated atomic spin densities of **2a/2b** show that the Co atom possesses the highest positive spin density (about 62%), followed by the Fe atom (about 19%).

The ³¹P NMR spectrum of the diamagnetic nickel/iron triple-decker complex **3** shows an AXX'ZZ' spin system, with one triplet of triplets centered at 40.6 ppm and two multiplets centered at –30.29 and –53.9 ppm. For the iron/iron triple-decker complex **4**, the ¹H NMR spectrum shows only sharp signals. However, in contrast to the triple-decker complex **3**, in

the ³¹P NMR spectrum of **4** one sharp signal at 73.8 ppm, one broad signal at –131.1 ppm and one very broad signal at –150.8 ppm are observed at room temperature. By cooling down the sample to 193 K, five broad signals in a 1:1:1:1:1 integral ratio are monitored in the ³¹P NMR spectrum, centered at 65.8, 42.2, –104.5, –195.0 and –344.9 ppm, revealing a dynamic behavior of the P₅ ring. In this process, the phosphorus atoms adjacent to the substituted P atom coordinate alternately to the Cp*Fe fragment, and the Cp'''Fe fragment slips over the middle-deck. At 193 K, the signals of the Cp''' ligand in the ¹H NMR spectrum of **4** become very broad, showing that the free rotation of the cyclopentadienyl ligand is slowed down.

When **1a** is reacted with [Cp'''CrCl]₂, the ³¹P NMR spectrum of the reaction solution shows a broad doublet of doublets at 281.1, one broad doublet at 9.5 ppm and a triplet of triplets at –66.7 ppm for the chromium/iron triple-decker complex **5**. Also, one set of signals of an unidentified byproduct is observed (in about 13%), but **5** can be isolated and purified further by recrystallization. By cooling down the sample of **5** in the ³¹P NMR spectrum at 253 K, the signals become sharp and a fine structure is determined.³⁶ The simulation of this spectrum reveals unusual coupling constants: the ¹J_{P-P} coupling (P2–P3) between the P₂ dumbbell and the P₃ allylic moiety is remarkably small (22.65 Hz). This is consistent with the corresponding elongated P–P distance (*vide infra*). The ²J_{P-P} coupling (P1–P3) is comparably large with a value of about 100 Hz. Usually the absolute value of a ¹J_{P-P} coupling is significantly higher compared to a ²J_{P-P} coupling, as it is observed in **3** or the starting materials **1a/1b**. This unusual behaviour may originate from the orbital interaction between the phosphorus atoms *via* the metal centres (as it is seen in the HOMO–3,³⁶ which has contributions from the atomic orbitals of the P1, Cr and Fe atom, respectively, and the orbital of the P3–P4 unit).

Compounds **2–5** could all be characterized by X-ray structure analysis. The triple-decker complexes **2a**, **2b** and **3** exhibit a similar structural motif, in which the P₅ ligand adopts a η⁴:η³-coordination mode (Fig. 2). Compared to **1a/1b**, in **2a/2b** and **3** the enveloped conformation of the P₅ unit becomes more distinct, with three of the five phosphorus atoms (P1, P3, P4; labeling according to Fig. 2) coordinating to the Cp''' metal fragment. The phosphorus atom, which does not lie in the η⁴-P₄ plane, still bears the organic rest. In **1a/1b**, all P–P bonds

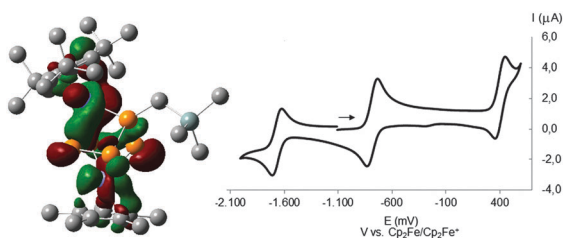


Fig. 1 Left: Isosurface of the single-occupied molecular orbitals (SOMO) in **2a** calculated on the B3LYP/def2-SVP level of theory. Hydrogens are omitted for clarity. Right: Cyclic voltammogram of **2a** recorded at a platinum disc electrode in CH₂Cl₂ at 100 mV s^{–1} and referenced against fc/fc⁺; supporting electrolyte [Bu₄N][PF₆] (0.1 mol L^{–1}).

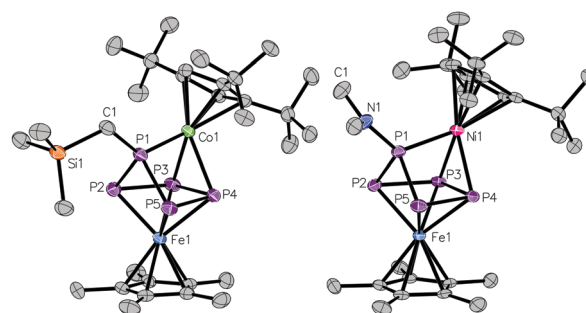


Fig. 2 Molecular structure of **2a** (left) and **3** (right). Ellipsoids are drawn at 50% probability level. H atoms bonded to carbon are omitted for clarity.

of the P_5 ring exhibit double bond character. In the triple-decker sandwich complex **2a** the P–P bond lengths range from 2.1771(7) Å to 2.3530(7) Å. Compounds **2b** and **3** show similar values (**2b**: 2.1569(8)–2.4132(8) Å; **3**: 2.1620(7)–2.4739(7) Å). Particularly noticeable is the rather long P3–P4 bond in the backbone of the P_5 ring of **2a**, **2b** and **3** (in **2a**: 2.3530(7) Å; **2b**: 2.4132(8) Å; **3**: 2.4738(7) Å). The corresponding Wiberg bond index (WBI) values for these bonds are 0.70, 0.67 and 0.51 for **2a**, **2b**, and **3**, respectively.

The elongation of this P–P bond, by going from **2a** to **3**, is in line with the increased electron density in the P_5 moiety (compound **2a** features a CH_2SiMe_3 group exhibiting a +I effect; compound **2b** features an NMe_2 group exhibiting a +M effect; compound **3** contains one additional electron due to the exchange of the cobalt with a nickel atom). Furthermore in **2b** and **3**, the NMe_2 group is planarly arranged with the sum of the angles around the nitrogen atom of 360° (in **2a**: 359.99° ; in **3**: 359.96°), and the N–P bond possesses double bond character (**2b**: 1.665(2); **3**: 1.671(2) Å), reflecting the donating character of the NMe_2 group in these compounds. The WBI values for the Co1–P1 bond order in **2b** (0.76) are similar to **2a** (0.75) upon introduction of the more electronegative NMe_2 substituent on the P1 atom. The Mulliken charges in **2a** and **2b** are akin.³⁶

By comparing **2a**, **2b** and **3** with the iron/iron complex **4**, the conformation of the P_5 ring changes (Fig. 3). Due to a distortion of the phosphorus ring, the Fe2–P5 bond (2.6313(5) Å) is prolonged (remaining Fe–P bond lengths in **4**: 2.1362(5)–2.4690(5) Å, Fig. 3), thus the coordination mode of the P_5 ligand is best described as $\eta^4:\eta^4$. Furthermore, the enveloped P_5 ring of **4** is bent towards the Cp^*Fe fragment – instead towards the $Cp'''M$ fragment, as observed in the triple-decker sandwich complexes **2a,b**. The phosphorus atom, which bears the dimethylamine rest, lies within a distorted η^4-P_4 plane. In comparison to **2a**, **2b** and **3**, the P2–P3 (2.3587(6) Å) and P4–P5 (2.3187(6) Å) bonds are considerably longer in **4** and the P3–P4 bond exhibits double bond character in **4** (2.1054(6) Å).

If the P_5 moiety coordinates to the electron deficient $Cp'''Cr$ metal fragment in **5**, a significant structural change of the initial *cyclo*- P_5 ring is found. The original *cylco*- P_5 ring of **5** is broken into a P_2 dumbbell (P3–P4: 2.1040(7) Å; labeling according to Fig. 3) and a P_3 fragment (P1–P5: 2.1549(6) Å; P1–P2: 2.1558(7) Å), while a Fe–Cr bond (2.6252(4) Å) is formed. The small WBI of the P2–P3

and P4–P5 distances (0.22 each) also reflect the P_2/P_3 separation of the former P_5 ring. Compared to the Cr–Fe bond length in $[CpFe(CO)_2Cr(CO)_3Cp]$ (2.901(1) Å)³⁷ or in $[(CpCr)(CpFe)(\eta^{4:4}\text{-oct})]$ (oct = cyclooctatetraene), (2.7261(8) Å),³⁸ the metal–metal bond in **5** is shortened. The WBI for the Cr–Fe bond equals 0.47, which is considerably larger in comparison to the M–M WBI of the previously discussed triple-decker compounds **2a–3** (0.12–0.13).

The iron/nickel and iron/iron containing complexes **3** and **4** are stable and formally only differ by one electron in comparison to the iron/cobalt containing triple-decker complexes **2a/2b**. Therefore, the electrochemical properties of **2a/2b** were investigated. The cyclic voltammogram of **2a** in CH_2Cl_2 shows two oxidations and one reduction (Fig. 1). The first oxidation occurs at a half potential of -0.79 V and exhibits a reversible character ($i_{p(\text{reverse})}/i_{p(\text{forward})} = 0.82$).³⁹ The second oxidation at 0.39 V is considered irreversible. At -1.67 V, a reversible reduction is observed ($i_{p(\text{reverse})}/i_{p(\text{forward})} = 0.98$). The cyclic voltammogram of **2b** exhibits similar features,³⁶ with one reversible oxidation at -0.88 V ($i_{p(\text{reverse})}/i_{p(\text{forward})} = 0.98$) and a following irreversible one at 0.39 V.³⁹ A reversible reduction is observed at -1.61 V ($i_{p(\text{reverse})}/i_{p(\text{forward})} = 0.97$).

Based on these studies, we chose the oxidizing agents $[Cp_2Fe][PF_6]$ for the chemical oxidization of **2a**, which has a half potential of -0.59 V against fc/fc^+ in MeCN.⁴⁰ Contrary to the expectation that $[(Cp^*Fe)(Cp'''Co)(\mu, \eta^{4:3}\text{-}P_5CH_2SiMe_3)]^+$ (**6**) should be diamagnetic in analogy to **4**, in the ^{31}P NMR spectrum of the reaction solution of **2a** with $[Cp_2Fe][PF_6]$ only signals of low intensity for some minor impurities could be determined, as well as a septet centered at -140.4 ppm for the $[PF_6]^-$ ion. DFT calculations show that the triplet state of the cation of **[6]**⁺ in the gas phase is by 16.7 kJ mol^{−1} lower in energy than the singlet state. A few single crystals of **[6][PF_6]** were obtained from a Et_2O solution (Scheme 1). The X-ray structure analysis reveals that **[6]**⁺ is not just isoelectronic to the triple-decker complex $[(Cp^*Fe)(Cp'''Fe)(\mu, \eta^{4:4}\text{-}P_5NMe_2)]$ (**4**), but that **2a** undergoes a structural rearrangement during the oxidation, resulting in **[6]**⁺ to be isostructural to **4** (Fig. 4). The phosphorus atom, which bears the organic rest and was out of the η^4-P_4 plane in **2a**, interchanges hereby the position with an unsubstituted phosphorus atom from the η^4-P_4 plane. Unfortunately, we did not succeed in isolating any reduced products of **2a** or **2b**, by using K or KH as reducing agents despite many attempts.

In summary, we showed a subsequent chemistry of the anionic functionalized pentaphosphaferrocenes, by reacting

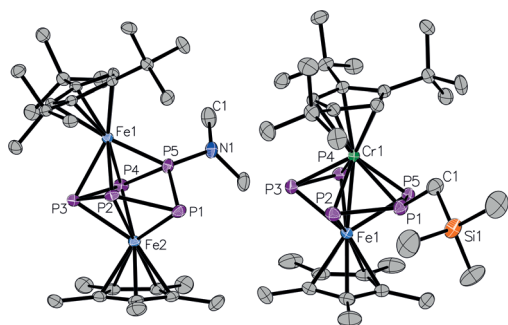


Fig. 3 Molecular structure of **4** (left) and **5** (right). Ellipsoids are drawn at 50% probability level. H atoms bonded to carbon are omitted for clarity.

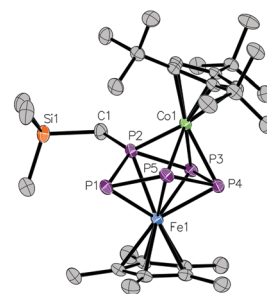


Fig. 4 Molecular structure of cationic part of **[6][PF_6]**. Ellipsoids are drawn at 50% probability level. H atoms bonded to carbon are omitted for clarity.



them with transition metal halide dimers. That way, several unique neutral triple-decker sandwich complexes with unprecedented functionalized *cyclo*-P₅ middle-decks were obtained. The integrity of the initial *cyclo*-P₅ middle-deck depends strongly on the electronic situation of the coordinating metal fragments, which leads from a structural rearrangement of the enveloped P₅ moiety in **2a/2b**, **3** and **4** to a complete fragmentation of the P₅ ring, as seen for [(Cp*Fe)(Cp'''Cr)(μ,η^{4:5}-P₅CH₂SiMe₃)] (**5**). In addition, the triple-decker complexes **2a** and **2b** show interesting electrochemical properties and a change of conformation of the P₅ moiety is observed upon oxidation. The successful salt elimination of the anionic pentaphosphaferrocene derivatives opens new avenues for the chemistry of pentaphosphaferrocene. Further functionalization of the P₅ ring should now be possible, which will lead to transfer reactions of the P₅ moiety or to the isolation of uncoordinated organo-substituted phosphorus derivatives.

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