New types of triple-decker complexes with an organo-substituted $P_5$ middle-deck were synthesized by the reaction of $[\text{Cp}^*\text{Fe}(\eta^5-P_5R)^-]$ ($1a$: $R = \text{CH}_2\text{SiMe}_3$; $1b$: $R = \text{NM}_{2}$) with halo-bridged transition metal dimers $[\text{Cp}^*/\text{MX}]_2$ ($M = \text{Cr, Fe, Co, Ni}; X = \text{Cl, Br}$). By oxidation of $[[\text{Cp}^*\text{Fe}]\text{(Cp}^*/\text{Co})(\eta^1-\text{P}_5\text{CH}_2\text{SiMe}_3)]$ $2a$ with $[\text{Cp}_2\text{Fe}]\text{[PF}_6]$, the cationic complex $[[\text{Cp}^*\text{Fe}]\text{(Cp}^*/\text{Co})(\eta^2-\text{P}_5\text{CH}_2\text{SiMe}_3)]^+$ 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. However, its ability to be metalated or to undergo Friedel–Craft reactions renders it a valuable starting material in organometallic synthesis. The isostructural analogue of ferrocene is pentaphosphaferrocene and its $\text{Cp}^*$ derivative $[\text{Cp}^*\text{Fe}(\eta^5-P_5R)]$ (I) was first discovered in 1987. The majority of reactivity studies of I is dedicated to the coordination chemistry towards Lewis acidic coordination moieties, forming 1D and 2D coordination polymers or spherical supramolecular clusters. In cothermolysis with organometallic reagents, fragmentations and deformations of the cyclo-$P_5$ ring of I occur. A new direction for the reactivity of pentaphosphaferrocene opened up when I was used in redox processes and especially when it was converted by nucleophiles. In the latter case, a selective functionalization of the $P_5$ ring in I was achieved. As a result, monoanionic complexes of the type $[\text{Cp}^*\text{Fe}(\eta^4-P_5R)]^-$ ($R = \text{CH}_2\text{SiMe}_3$, $\text{NM}_{2}$, $\text{PH}_3$) 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-$P_5$ 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-$P_5$ middle deck are known. Starting from $P_4$ in thermal synthesis reactions, the compounds $[[\text{Cp}^*\text{Mn}]_2(\mu\eta^5-P_5)]$ ($\text{Cp}^*\text{Mn} = \text{C}_{5}(4-\text{nBuC}_6\text{H}_4)_5$) and $[[\text{Cp}^*\text{Cr}]_2(\mu\eta^5-P_5)]$ ($\text{Cp}^*\text{Cr} = \text{Cp}, \text{Cp}^*$) are obtained. Starting from I, some cationic triple-decker compounds $[[\text{Cp}^*\text{M}][\text{Cp}^*\text{M}'][\eta^5-P_5]]^+$ ($\text{M, M}' = \text{Fe, Ru}; \text{Cp}^*\text{R} = \text{Cp}, \text{Cp}^*$), containing group 8 elements, have been reported. Furthermore, mixed-metal lanthanide-iron compounds with a cyclo-$P_5$ middle deck are known. Herein, we report the synthesis of the first neutral complexes with a functionalized $P_5$ middle deck under mild conditions. By using different transition metal halides $[\text{Cp}^*/\text{MX}]$ ($M = \text{Cr, Fe, Co, Ni}; X = \text{Cl, Br}$), 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 $[\text{Cp}^*/\text{MX}]_2$ ($M = \text{Cr, Fe, Co, Ni}; X = \text{Cl, Br}$) leads to the triple-decker complexes 2–5, containing the whole 3d element series from $\text{Cr}$ to $\text{Cu}$ and $\text{Ni}$ decks (Scheme 1). Unfortunately, despite several efforts, we were not able to synthesize the missing manganese-containing triple-decker complex in this series. 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 $g_{\text{iso}} = 2.069$ 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 ($2a$: $\mu_{\text{eff}} = 2.14$ $\mu_B$; $2b$: $\mu_{\text{eff}} = 1.83$ $\mu_B$). 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
the minor influence of the substituent of the cyclo-P₅ ring on the features of the SOMO (Fig. 1). All SOMOs are delocalized, but the analysis of the spin density reveals that the metal centre bonded to the Cp^{15} 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 $^{31}$P NMR spectrum of the diamagnetic nickel/iron triple-decker complex 3 shows an AX'X''Z' 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 $^1$H NMR spectrum shows only sharp signals. However, in contrast to the triple-decker complex 3, in the $^{31}$P 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 $^{31}$P NMR spectrum, centered at 65.8, 42.2, −104.5, −195.0 and −344.9 ppm, revealing a dynamic behavior of the P₃ ring. In this process, the phosphorus atoms adjacent to the substituted P atom coordinate alternatingly to the Cp^{15}Fe fragment, and the Cp^{15}Fe fragment slips over the middle-deck. At 193 K, the signals of the Cp^{15} ligand in the $^1$H 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^{15}/CrCl]₀, the $^{31}$P 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 $^{31}$P NMR spectrum at 253 K, the signals become sharp and a fine structure is determined. The simulation of this spectrum reveals unusual coupling constants: the $J_{P-P}$ coupling (P2–P3) between the P₂ dumbbell and the P₃ allicy moiety is remarkably small (22.65 Hz). This is consistent with the corresponding elongated P–P distance (vide infra). The $J_{P-P}$ coupling (P1–P3) is comparably large with a value of about 100 Hz. Usually the absolute value of a $J_{P-P}$ coupling is significantly higher compared to a $J_{P-P}$ 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, 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 P₃ ligand adopts a η₄:η₃-coordination mode (Fig. 2). Compared to 1a/1b, in 2a/2b and 3 the enveloped configuration of the P₃ unit becomes more distinct, with three of the five phosphorus atoms (P₁, P₃, P₄; labeling according to Fig. 2) coordinating to the Cp^{15} metal fragment. The phosphorus atom, which does not lie in the η₄-P₃ plane, still bears the organic rest. In 1a/1b, all P–P bonds...
of the P₅ 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 P₂ 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 P₅ moiety (compound 2a features a CH₃SiMe₃ group exhibiting a +I effect; compound 2b features an NMe₂ group exhibiting +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 NMe₂ 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 NMe₂ 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 NMe₂ substituent on the P₁ atom. The Mulliken charges in 2a and 2b are akin.

By comparing 2a, 2b and 3 with the iron/iron complex 4, the conformation of the P₅ 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 P₅ ligand is best described as η⁴⁺⁺P₅. Furthermore, the enveloped P₅ 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 η⁴⁺⁻P₅ 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 P₅ moiety coordinates to the electron deficient Cp'/M metal fragment in 4, a significant structural change of the initial cyclo-P₂₃ ring is found. The original cyclo-P₂₃ ring of 5 is broken into a P₂ dumbbell (P₃–P₄: 2.1040(7) Å; labeling according to Fig. 3) and a P₃ 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 P₂/P₃ separation of the former P₅ ring. Compared to the Cr–Fe bond length in [CpFe(CO)₅]Cr(CO)₃[Cp] (2.901(1) Å), or in [CpCr(CpFe)[η⁴⁺oct]] (oct = cyclooctatetraene), (2.7261(8) Å), 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 CH₂Cl₂ 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 (½ i(½p(reverse)/½p(forward)) = 0.82). The second oxidation at 0.39 V is considered irreversible. At −1.67 V, a reversible reduction is observed (½ i(½p(reverse)/½p(forward)) = 0.98). The cyclic voltammogram of 2b exhibits similar features,

Based on these studies, we chose the oxidizing agents [Cp₂Fe][PF₆] for the chemical oxidization of 2a, which has a half potential of −0.59 V against Fe/Fe⁺ in MeCN. Contrary to the expectation that [(Cp*Fe)(Cp'/M)μ⁻⁻P₃CH₂SiMe₃][PF₆] (6) should be diamagnetic in analogy to 4, in the 3¹P NMR spectrum of the reaction solution of 2a with [Cp₂Fe][PF₆] only signals of low intensity for some minor impurities could be determined, as well as a septet centered at −140.4 ppm for the [PF₆]⁻⁻ 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][PF₆] were obtained from an Et₂O solution (Scheme 1). The X-ray structure analysis reveals that [6]⁺ is not just isoelectronic to the triple-decker complex [(Cp*Fe)(Cp'/Fe)(μ⁻⁻P₃CH₂SiMe₃)] (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 η¹⁻P₃ plane in 2a, interchanges hereby the position with an unsubstituted phosphorus atom from the η¹⁻P₃ 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...
them with transition metal halide dimers. That way, several unique neutral triple-decker sandwich complexes with unprecedentedly functionalized cyclo-P₃ middle-decks were obtained. The integrity of the initial cyclo-P₃ 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 [[Cp²Fe(Cp²Cr)(μ₆-P₂CH₂SiMe₃)] (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 pentaphosphaferrrocene derivatives opens new avenues for the chemistry of pentaphosphaferrrocene. 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.

The authors thank the Deutsche Forschungsgemeinschaft for funding and Dr M. Walter (Technical University of Braunschweig) for providing [Cp''/MnI].

Notes and references

35 Although a reaction of 2a with [Cp'/MnI] is observed (no signals of 2a or any other compounds are monitored in the ³¹P NMR spectrum of the reaction mixture), no products could be isolated, even after chromatographic work-up.
36 cf. ESI†.
39 Referenced against ferrocene.