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(η⁵-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(η⁵-P₅)₂CH₂SiMe₃)] 2a with [Cp⁺Fe][PF₆]−, the cationic complex [(Cp⁺Fe)(Cp⁺Co(η⁵-P₅)₂CH₂SiMe₃)]⁺ 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 molecule4,5 does not only show a fascinating chemistry in redox processes but particularly as a starting material for subsequent reactions. Its ability to be metalated6,7 or to undergo Friedel–Craft reactions8,9 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 polymers11–15 or spherical supramolecular clusters.16–20 In coethersynthesis 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 processes25–27 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(η⁵-P₅R)]− (R = CH₂SiMe₃, NMe₂, PH₃) 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 P₅ in thermolysis reactions, the compounds [(Cp⁺Mn₂)(η⁵-P₅)] (Cp⁺ = C₅H₅, C₅Me₅) and [(Cp⁺Cr)₂(η⁵-P₅)] (Cp⁺ = Cp, Cp*) are obtained.29–31 Starting from I, some cationic triple-decker compounds [(Cp⁺M)(Cp⁺M')(η⁵-P₅)]²⁺ (M, M' = Fe, Ru; Cp⁺ = 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)₅] fragment (M = Cr, Mo,W) are known.34–36 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 Cr to Ni triple-decker complexes 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 giso = 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: μeff = 2.14 μB; 2b: μeff = 1.83 μB). 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).⁶⁶ All SOMOs are delocalized, but the analysis of the spin density reveals that the metal centre bonded to the Cp⁷/⁺ 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 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 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 Cp⁷/Fe fragment, and the Cp³/Fe fragment slips over the middle-deck. At 193 K, the signals of the Cp⁷/⁺ 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 [Cp⁷/⁺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.⁶⁶ The simulation of this spectrum reveals unusual coupling constants: the ³P–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 ³P–P coupling (P1–P3) is comparably large with a value of about 100 Hz. Usually the absolute value of a ³P–P coupling is significantly higher compared to a ³P–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–3,⁶⁶ 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:η₄ coordination mode (Fig. 2). Compared to 1a/1b, in 2a/2b and 3 the enveloped configuration 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 Cp⁷/⁺ metal fragment. The phosphorus atom, which does not lie in the η₄-P₅ plane, still bears the organic rest. In 1a/1b, all P–P bonds

**Scheme 1** Reactions of I: (i) LiCH₂SiMe₃ in Et₂O or LiNMe₂ in THF, r.t.; reaction of 1a: (ii) [Cp⁷/⁺CoCl]₂ in THF, r.t.; (iv) [Cp⁷/⁺NiCl]₂ in THF, r.t.; (v) [Cp₂Fe][PF₆] in THF, r.t.; reaction of 1b: (ii) [Cp⁷/⁺CoCl]₂ or [Cp⁷/⁺NiBr]₂ in THF, r.t.; (iii) [Cp⁷/⁺FeBr]₂ in THF, r.t.; reaction of 2a: (v) [Cp₂Fe][PF₆] in THF, r.t. −50 °C → r.t. Yields in parentheses.

**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 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 P₃ 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 +1 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 CoI–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.46

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:η⁴. Furthermore, the enveloped P₅ ring of 4 is bent towards the Cp²Fe fragment – instead towards the Cp²/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:P₃ 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 Cp⁴³/Cr metal fragment in 5, a significant structural change of the initial cyclo-P₃ ring is found. The original cyclo-P₃ ring of 5 is broken into a P₂ dumbbell (P3–P4: 2.1040(7) Å; labeling according to Fig. 3) and a P₁ 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 P₃/P₅ separation of the former P₅ ring. Compared to the Cr–Fe bond length in [CpFe(CO)₃Cr(CO)₃] (2.901(1) Å)57 or in [CpCr(CpFe)[η⁴-oct]] (oct = cyclooctatetraene), (2.7261(8) Å),18 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 (ip(reverse)/ip(forward) = 0.82).39 The second oxidation at 0.39 V is considered irreversible. At −1.67 V, a reversible reduction is observed (ip(reverse)/ip(forward) = 0.98). The cyclic voltammogram of 2b exhibits similar features,46 with one reversible oxidation at −0.88 V (ip(reverse)/ip(forward) = 0.98) and a following irreversible one at 0.39 V.39 A reversible reduction is observed at −1.61 V (ip(reverse)/ip(forward) = 0.97).

Based on these studies, we chose the oxidizing agents [Cp₂Fe][PF₆] for the chemical oxidation of 2a, which has a half potential of −0.59 V against fc/fc⁺ in MeCN.40 Contrary to the expectation that [[Cp²Fe][Cp⁴³Co][η⁴-oct]CH₂SiMe₃]⁺ [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 a Et₂O solution (Scheme 1). The X-ray structure analysis reveals that 6⁺ is not just isoelectronic to the triple-decker complex [[Cp²Fe][Cp⁴³Fe][η⁴:η⁴-P₃NMe₂]]⁻ [4], but that 2a undergoes a structural rearrangement during the oxidation, resulting in 6⁺ to be isoelectronic 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

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·[PF₆]. 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,η₅-Si₅CH₂SiMe₅]] (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 pentaphosphaferradene 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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Notes and references

35 Although a reaction of 2a with [Cp″′MnI]₂ 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.